RESEARCH ARTICLE

Sedimentary record of polycyclic aromatic hydrocarbons and DDTs in Dianchi Lake, an urban lake in Southwest China

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Abstract Unique time trends of polycyclic aromatic hydrocarbons (PAHs) and dichlorodiphenyltrichloroethanes (DDTs) were found in a dated sediment core from Dianchi Lake (DC), an urban lake in Southwest China. The temporal trend of PAHs in DC was not only different from those in China's coastline and remote lakes of China, but also different from those in more developed countries. Identification of sources suggested that PAHs in DC originated primarily from domestic combustion of coal and biomass. However, a change of source from low- and moderate-temperature combustion to high-temperature combustion processes was observed. Different from those in China's coastline and some developed countries, the temporal trend of DDTs in DC mirrored the historical usage of DDTs in China, with erosion of soils and surface runoff from its drainage area the most likely routes of DDT introduction to the lake. Rapid urbanization and industrialization in its catchment, effective interception of point-source pollution, and changes in sources

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of energy during the last few decades have significantly influenced the vertical profiles of PAHs in DC.

Keyword PAHs . Dichlorodiphenyltrichloroethane . Sediment core . Pesticides . Combustion

Introduction

Dianchi Lake (DC, 24°40′–25°03′N, 102°37′–102°48′E) lies adjacent to the city of Kunming, a metropolis in Yunnan Province, Southwest China (Fig. [1\)](#page-2-0). With a surface area of 306 km² and a drainage area of 2,920 km², it is one of the largest freshwater lakes in China. The lake is approximately 40 km long (north to south) and 12.5 km wide, with an average water depth of 4.7 m (Du et al. [2011\)](#page-7-0). Dianchi Lake receives drainage and effluents from 17 rivers and at least 20 springs and plays an important role for local

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socioeconomic activities. However, rapid urbanization and industrialization in its catchment within the last few decades have resulted in significant contamination and in particular cultural eutrophication of the lake such that it is currently one of the more polluted lakes in China (Fig. S1). Eutrophication of DC has been investigated previously (Du et al. [2011;](#page-7-0) Huang et al. [2007\)](#page-8-0); however, little information about persistent organic pollutants in DC was available.

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in aquatic ecosystems (Fernández et al. [1999;](#page-8-0) Guo et al. [2010;](#page-8-0) Usenko et al. [2007\)](#page-8-0). Due to the direct adverse effects on benthic organisms and continuing sources of substances toxic to wildlife and humans (Kannan et al. [2005\)](#page-8-0), PAHs are still contaminants of concern in sediments (Lang et al. [2008](#page-8-0); Wilcke [2007\)](#page-9-0). Dichlorodiphenyltrichloroethane (DDT) is a common, extensively used organochlorine insecticide used to control vectors of diseases and protect crops to enhance production. To balance potential adverse effects with social benefits of DDT, many countries banned DDT in the 1970s, with China joining them in that ban in the early 1980s (Qiu and Zhu [2010](#page-8-0)). However, technical DDT is still being produced and used in China for some nonagricultural purposes, including export, domestic control of vectors of malaria, and anti-fouling paint for use on marine ships. Measurable concentrations of DDT in various environmental media are still observed in China (Liu et al. [2009](#page-8-0); Qiu et al. [2004;](#page-8-0) Xu et al. [2007\)](#page-9-0). Thus, DDT continues to be of concern in China (Guo et al. [2009](#page-8-0), [2012](#page-8-0); Jiang et al. [2009](#page-8-0)).

Lake sediments are important archives of environmental information, which can act as "geochronometers" of historical deposition of contaminants and general environmental changes over time (Kannan et al. [2005\)](#page-8-0). Historical records of urban lakes, receiving contaminants primarily via wastewater effluents and municipal runoff, might be different from those of sediments in the coastal marine environment or remote lakes. Different routes could have significant effects on the historical records of contaminants in different environmental settings (Macdonald et al. [2000](#page-8-0)). The primary objective of this study was to investigate historical inputs of PAHs and DDTs to DC (a typical urban lake in Southwest China), which emphasizes temporal distributions and the possible changes in sources, as well as to explore the effects of anthropogenic activities on the local environment.

Materials and methods

Sampling

A sediment core was collected from DC, Southwest China, in May 2006. The sampling site (24°50′N, 102°43′E) was near the center part of the lake with water depth of approximately 6 m (Fig. [1\)](#page-2-0). The core was collected by use of a gravity corer and sectioned into 1-cm segments. This core is 55 cm long and only the upper portion of 20 cm was analyzed. Upon collecting, sediments were wrapped in precleaned aluminum foil and transported on ice to the laboratory, where they were stored at −20 °C until further treatment.

Extraction and instrumental analyses

Detailed descriptions of procedures used to extract residues from the sediments have been reported elsewhere (Guo et al. [2010](#page-8-0)). Briefly, an aliquot $(\sim 5$ g dry weight) of freeze-dried, homogenized sample, spiked with PCB-65, PCB-204, and a mixture of deuterated PAHs (naphthalene- d_8 , acenaphthene d_{10} , phenanthrene- d_{10} , chrysene- d_{12} , and perylene- d_{12}) as recovery surrogates, was Soxhlet extracted with a mixture of hexane and acetone (1:1, $v: v$) for 48 h. Approximately 2 g of activated copper was added for desulfurization. Extracts were concentrated and solvent-exchanged into hexane. Cleanup and fractionation were performed on an alumina/silica gel chromatography column. The fraction containing both PAHs and DDTs was eluted by use of 70 ml dichloromethane/hexane (3:7, v:v) and concentrated to 500 μL under a gentle flow of nitrogen. Internal standards, 2-fluorobiphenyl, p-terphenyl- d_{14} , and PCB-82 were added prior to instrumental analysis.

Quantification of both PAHs and DDTs was performed by use of an Agilent 6890 gas chromatograph system that was equipped with an Agilent 5975B mass selective detector operating in selective ion monitoring mode. A DB-5 fused silica capillary column (60 m length \times 0.25 mm i.d. \times 0.25 μm film thickness) was used for chromatographic separation. A splitless injection of 1.0 μ L of sample was conducted with an autosampler. Ultrahigh-purity helium (99.999 %) was employed as the carrier gas at a constant flow rate of 1 ml/min. The injector and detector temperatures were 280 and 300 °C, respectively. Mass spectra were acquired in electron ionization mode with an impact voltage of 70 eV. The GC oven temperature was programmed to increasing from 90 to 180 °C at a rate of 10 °C/min, to 220 ° C at a rate of 2 °C/min, and then to 290 °C at a rate of 8 ° C/min (holds for 30 min). PAHs quantified included naphthalene (NAP), acenaphthylene (ACE), acenaphthene (AC), fluorene (FLU), phenanthrene (PHEN), anthracene (ANT), fluoranthene (FLUO), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHRY), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), indeno(1,2,3-cd)pyrene (INP), dibenzo(ah)anthrathene (DBA), and benzo(ghi)perylene (BghiP). The sum of these PAHs is designated as Σ PAH₁₆. Quantified DDTs included p, p' -DDT and its metabolites, p, p' -DDD and p, p '-DDE. The sum of p, p' -DDT, p, p' -DDD, and p, p' -DDE is designated as DDTs.

Dating of the sediment core

The dating of the sediment core was accomplished based on activity of 137 Cs. In brief, 137 Cs activities were determined using gamma spectrometry on a Canberra S-100 multichannel spectrometer mated to GCW3022 H-P Ge coaxial detector (efficiency, 50 %). The peak in gamma activity at 661.6 KeV was used to determine ¹³⁷Cs activity. Liquid standards were supplied by the Institute of Atomic Energy, Chinese Academy of Sciences (catalog no. 7137 and source no. 586-26-2). Based on the peak $137Cs$ concentration in 1963, an average sedimentation rate of 0.28 cm/a was calculated for intervening time intervals.

Quality control and quality assurance

Method quality control included a procedural blank (solvent), a triplicate spiked blank (standards spiked into solvent), and triplicate spiked matrices (standards spiked into matrices). For PAHs, mean recoveries of surrogates in all samples were 69.9 \pm 16.6 % for naphthalene-d₈, 86.2 \pm 9.4 % for acenaphthene- d_{10} , 90.5 \pm 11.6 % for phenanthrene- d_{10} , 88.7 \pm 12.3 % for chrysene- d_{12} , and 80.6 ± 12.7 % for perylene- d_{12} . Mean recoveries of 16 target PAHs ranged from 75.8±4.9 to 114.3 \pm 8.2 % in triplicate spiked blanks and from 60.8 \pm 1.1 to

120.9±9.1 % in triplicate spiked matrices. For DDTs, recoveries of surrogate in all samples were 66.3 ± 8.8 % for PCB-65 and 75.6±9.5 % for PCB-204. Mean recoveries of three target DDTs ranged from 96.8 ± 7.1 to 105.9 ± 0.6 % in triplicate spiked blanks and from 102.7 ± 6.5 to 117.4 ± 7.2 % in triplicate spiked matrices. Instrument stability was calibrated daily with standard solutions, and daily calibrations were <15 % for all of the target analyses. Only small amounts of PHEN (26.1 \pm 2.0 ng/g dw), NAP (15.8±0.7 ng/g dw), FLU (12.4±0.9 ng/g dw), and FLUO (10.5 \pm 1.1 ng/g dw) were detected in blanks, and these amounts were subtracted from those in samples of sediments. Detection limits were 0.02–0.05 ng/g dry weight for PAHs and 0.05–0.2 ng/g dry weight for DDTs (defined as $S/N > 10$). Results were expressed on a dry weight basis and corrected for surrogate recoveries.

Results and discussion

Temporal trends of PAHs and DDTs in sediment core

The vertical profile of Σ PAH₁₆ and DDTs as a function of depth and predicted year of deposition in the core from DC are schematically shown (Fig. [2](#page-3-0)). Concentrations of contaminants in the sediment core are dependent not only on

Fig. 2 Temporal trends of PAHs and DDTs in sediment core from Dianchi Lake (solid cycle concentrations, open cycle fluxes)

sources of emissions but also on rates of sedimentation and possibly dilution (Fernández et al. [1999](#page-8-0); Lima et al. [2003](#page-8-0)). Because of this, it is more meaningful to assess deposition contaminants based on the depositional flux. Therefore, both concentrations and fluxes of PAHs and DDTs are presented.

High concentrations (479.3 to $4,560.8$ ng/g dw) and the corresponding fluxes (328.8 to 3,128.7 ngcm⁻²year⁻¹) of Σ PAH₁₆ were recorded in sediments from DC. DC is a typical urban lake and receives a large amount of pollutants via riverine and municipal runoff. In addition, DC is a semiclosed lake with a little outlet at its southern end. Water exchange in DC is very limited. The special hydrodynamic characteristics of DC could also help the retention of pollutants in DC. Furthermore, the increasing TOC content in DC sediments (see Fig. S2) could also favor the sequestration of PAHs in sediments and then increase the sedimentary flux of PAHs. Thus, the high fluxes of PAHs in DC are reasonable. Throughout the core, temporal trends of concentrations of Σ PAH₁₆ are characterized by three stages: a slight variation stage in the deeper segments before the 1960s; a sharply increasing stage from segment 12–13 cm to segment 3–4 cm, which corresponds to the period of ~the 1960s to the early 1990s; and a decreasing trend in the most recent sediments, which corresponds to the period of the early 1990s to the present, with a peak value of 4,560.8 ng/g dw in approximately 1994. Among the 16 US EPA-priority PAHs, PHEN was the predominant PAH, followed by FLU and FLUO, accounting for 39.5 \pm 8.6, 12.2 \pm 2.7, and 9.0 \pm 2.3 % of Σ PAH₁₆, respectively (Fig. S3). Alternatively, high molecular weight PAHs (HMW PAHs, sum of BbF, BkF, BaP, DBA, INP, and BghiP) accounted for only 15.0 ± 8.8 % of Σ PAH₁₆. Nevertheless, the relative abundance of HMW PAHs increased significantly from the deeper sediments to the more recent sediments $(5.2 \pm 1.2 \text{ to } 24.2 \pm 1.5 \%)$. The opposite $(75.1 \pm 3.6 \text{ to } 53.9 \pm 1.9 \%)$ was true for low molecular weight PAHs (LMW PAHs, sum of NAP, AC, ACE, FLU, PHEN, and ANT) (Fig. S4).

As for individual PAHs, the vertical profile of PHEN was similar to that of ΣPAH_{16} (Fig. [3\)](#page-4-0), but was clearly different from those for HMW PAHs. Temporal trends of HMW PAHs were similar, characterized by little change in deeper sediments (before 1960s), followed by a rapid increase to the maximum concentration in the early 1990s, and then decreased in the most recent sediments. The lack of change as a function of time for HMW PAHs in deeper sediments could represent historical background concentrations in DC. As regards four-ring PAHs, the vertical profile of CHRY somewhat resembles those of HMW PAHs, but the vertical profile of PRY was different, with an increase in more recent sediments.

Concentrations of DDTs, if detected in sediments, ranged from 0.9 to 53.5 ng/g dw, with corresponding fluxes ranging from 0.75 to 36.6 ngcm⁻²year⁻¹. The pattern of concentrations of DDTs was somewhat similar to that of ΣPAH_{16} . However, differences between the two classes of contaminants were observed. First, DDTs were only detected in the 17–18-cm segment, with a corresponding date of approximately 1944. Second, peak deposition of DDTs was approximately one decade earlier than that of ΣPAH_{16} , with a peak depositional period of ~1983. Concentrations of DDTs increased slightly from the 1940s to the early 1960s, followed by a sharp increase in the early 1980s and a sharp decline in the surface sediment in a zigzag manner. Historical usage of DDT in China began in the early 1950s (Guo et al. [2012\)](#page-8-0). DDT residues found in sediments dating before the 1950s

Fig. 3 Temporal trends of selected individual PAH and PAHs in sediment core (solid cycle concentrations, open cycle fluxes)

Concentrations (ng/g)

could be attributed to migration of DDTs to the deeper sediments. The rapid increase in concentrations of DDTs from the 1960s to the early 1980s corresponds to extensive organochlorine pesticide applications during that period (Hua and Shan [1996](#page-8-0)). To avoid adverse effects on the environment as well as on humans, the Chinese government banned usage of DDT for agricultural purposes in 1983 (Hua and Shan [1996](#page-8-0)), resulting in a rapidly decreasing trend of DDT in the surface sediment after that. A similar trend was also recorded in a sediment core (ZJ-6) from the Pearl River Delta, South China (Zhang et al. [2002\)](#page-9-0).

Comparison of sedimentary records of PAHs and DDTs across China and worldwide

Sedimentary records of PAHs and DDTs across China and worldwide have been reported, and these results have been summarized in Table [1.](#page-5-0) Concentrations of PAHs in sediment cores along China's coastline were generally low, with maximum concentrations usually presented in more recent sediments (Guo et al. [2006](#page-8-0), [2007](#page-8-0); Liu et al. [2005\)](#page-8-0). The same holds true for the pattern of concentrations of PAHs recorded in remote lakes across China (Guo et al. [2010\)](#page-8-0). The ever-increasing PAHs observed in sediment cores along

Table 1 Sedimentary reco PAHs and DDTs across Ch and worldwide

the coastline and in remote lakes across China suggest that emission of PAHs in China continued increasing up through 2006. In urban lakes of China (Guo et al. [2011a,](#page-8-0) [b](#page-8-0)), loading of PAHs was greater than that along the coastline or in remote lakes. Besides, the patterns of down-core PAHs in urban lakes were also different from those of cores from the coastline and remote lakes, with maximum concentrations generally observed in the early 1990s, followed by decreasing concentrations in the more recent sediments. In fact, the environment deterioration has alerted the government's extensive concerns since the early 1980s, especially for those lakes used for drinking water and those lakes adjacent to cities where they are used for recreation. In DC, for example, degradation of water quality, especially eutrophication, started in the early 1970s (Fig. S1). Great efforts, such as sewage interception around the lake, dredging mud from the lake, and ecological restoration, have been undertaken to improve the water quality during the past three decades. Now, environmental deterioration in DC has been effectively curbed, and loading of

a Coastline of China

dDeveloped country

China

contaminants to the lake has been decreased substantially. These efforts also effectively reduced inputs of PAHs into DC, which can clearly be seen in the sedimentary record after approximately 1994.

Sedimentary records of PAHs in China were observed to be elevated until the surface sediment in most cases, which were clearly different from those in more developed countries where PAH concentrations usually peaked in the period 1950s–1980s (Fernández et al. [2000](#page-8-0); Ishitake et al. [2007;](#page-8-0) Lima et al. [2003](#page-8-0); Yim et al. [2005\)](#page-9-0) (Table 1). More developed countries usually finished their industrialization and urbanization before the 1980s. However, China is undergoing a rapid industrialization and urbanization, especially after the "Reform and Open Policy" implemented in 1978. The different patterns in sedimentary record of concentrations of PAHs between China and more developed countries paralleled the different histories of industrialization and urbanization for both areas. However, sedimentary records of PAHs in China's urban lakes cannot properly reflect the Fig. 4 Diagnostic ratios of PAHs in a sediment core from Dianchi Lake

BaA/BaA+CHRY

historical PAH emissions due to point-source pollution being curbed effectively.

Approximate depositional year

Approximate depositional year

ANT/ANT+PHEN

Investigation of sedimentary records of DDTs had previously been conducted primarily in marine sediments along China's coastline (Gong et al. [2007;](#page-8-0) Qiu et al. [2009;](#page-8-0) Wang et al. [2008](#page-8-0); Zhang et al. [2002\)](#page-9-0) (Table [1](#page-5-0)). As with the trends in concentrations of PAHs, despite the Chinese government ban on the agricultural usage of DDT since 1983, concentrations of DDTs in cores from China's coastline have also increased in more recent sediments, expect for a core from the Pearl River Estuary (ZJ-6) in South China (Zhang et al. [2002\)](#page-9-0). However, maximum concentrations of DDTs in cores of sediments along the coastline of China are different from those in DC. The continuously increasing inputs of DDTs into the coastline could be due to successive transportation of DDTs historically utilized on land (Zhang et al. [2002](#page-9-0)). However, another source of DDT could be its continuing use in anti-fouling paint, especially along the coastline, where aquaculture and shipping activities are more intense. Aquaculture and shipping activities have been restricted in DC in recent decades; thus, input of DDTs to DC depended mainly upon erosion of soil and storm runoff within its drainage basin. Thus, it is reasonable that DDTs in sediments of DC have decreased after China's 1983 ban of DDT for agricultural usage.

Overall, sedimentary records of DDTs in DC were not only different from those in China's coastline, but also different from those reported in some developed countries, where DDT concentrations usually peaked in the 1960s to 1970s (Fox et al. [2001](#page-8-0); Götz et al. [2007;](#page-8-0) Venkatesan et al. [1999\)](#page-8-0) (Table [1\)](#page-5-0). However, the peak time of DDT concentration in DC coincided well with China's 1983 ban of DDT for agricultural usage.

Identification of sources of PAHs and DDTs to Dianchi Lake

INP/INP+BghiP

FLUO/FLUO+PYR

Identification of sources of contaminant is of great importance for developing control strategies. Sources of PAHs are sometimes determined by use of diagnostic ratios of PAHs, typically isomers. This method is based on the hypothesis that paired chemicals are diluted to a similar extent and that ratios between their concentrations remain constant en route from sources to receptors (Katsoyiannis et al. [2007](#page-8-0)). Though concerns regarding the limitations of this hypothesis continue to appear in the literature (Galarneau [2008;](#page-8-0) Katsoyiannis et al. [2007;](#page-8-0) Zhang et al. [2005\)](#page-9-0), diagnostic ratios of PAH can still provide some useful information on the source identification

Fig. 5 Down-core variation of DDT/DDE+DDD and DDE/DDD in Dianchi Lake

(Yunker et al. [2002](#page-9-0)). When $R_{\text{ANT/ANT+PHEN}}$ (ratio of ANT/ANT+PHEN) is <0.1 and $R_{Ba\Delta/BaA+CHR}$ is <0.2, the source is generally petrogenic, while when both $R_{\text{INP/INP+}}$ B_{ghiP} and $R_{\text{FLU/FLU+PYR}}$ are greater than 0.5, domestic combustion of coal or biomass is the likely source. If $R_{FLU/FLU+}$ $_{\rm PYR}$ is between 0.4 and 0.5 and $R_{\rm INP/INP+BghiP}$ is between 0.2 and 0.5, combustion of liquid fossil fuel is the likely source. Diagnostic ratios of PAHs in the sediment core from DC are given in Fig. [4](#page-6-0). $R_{\text{ANT/ANT+PHEN}}$ and $R_{\text{BaA/BaA+CHR}}$ in the sediments were 0.13 ± 0.02 (range, 0.09–0.16) and $0.43 \pm$ 0.03 (range, 0.36–0.48), which are indicative of a pyrogenic source of PAHs in DC sediments. Together with $R_{\text{FLUO/FLUO+}}$ $_{\text{PYR}}$ and $R_{\text{INP/INP+BghiP}}$, with the value of 0.60 \pm 0.03 (range, 0.54–0.65) and 0.52 ± 0.05 (range, 0.47–0.62), it can be concluded that input of PAHs in DC originated primarily from domestic combustion of coal and/or biomass. Some additional characteristics of fuel combustion as the source of PAHs were also found in the upper sediments. For example, $R_{\text{INP/INP+}}$ Bghip ratios in the upper sediments were between 0.47 and 0.49 (0.48 ± 0.01) and thus represent some evidence of fuel combustion in recent years.

Relative abundances of PAHs in cores also give useful information on change in sources of PAHs over time. For example, PHEN and FLU, mainly stemming from low- and moderate-temperature combustion of biomass and/or domestic coal (Harrison et al. [1996](#page-8-0); Mai et al. [2003](#page-8-0)), were the dominant compounds throughout the core from DC (Fig. S2). High-temperature combustion, such as industrial combustion of coal, vehicular emission, and gas-fired cooking, produces HMW PAHs (Harrison et al. [1996;](#page-8-0) Mai et al. [2003\)](#page-8-0), but they were only minor components in the core (Fig. S2). The increasing relative abundance of HMW PAHs, along with a decreasing relative abundance of LMW PAHs from the deeper sediments to more recent sediments, suggests a change in sources of PAHs from low- and moderate-temperature combustion processes to high-temperature combustion processes. This coincides well with the results from studies conducted along the coastline and remote lakes in China (Guo et al. [2006](#page-8-0), [2010](#page-8-0)) and the fact that: (1) biomass combustion still contributes a large portion of PAH emissions in China (Qu et al. [2012](#page-8-0)) and (2) industrial coal and oil contribute to the increasing recent energy consumption in China (Xu et al. [2006](#page-9-0)).

DDT is known to degrade to DDE under aerobic conditions and to DDD under anaerobic conditions (Hitch and Day [1992\)](#page-8-0). Therefore, $R_{\text{DDT/DDE+DDD}}$ can be a useful indicator of possible source of DDT. Generally, a ratio of DDT/DDE+DDD greater than 1.0 indicates more recent inputs of DDT. Otherwise, "aged" or "weathered" DDT is suggested. The ratios of DDT/DDE+DDD in the sediment core from DC were much less than 1 (ranged from 0.06 to 0.28, with a mean value of 0.17 ± 0.08), which indicates that DDT input into DC originated from aged DDT. Meanwhile,

the increasing trend of DDT/DDE+DDD to the surface sediment suggests that relatively "new" DDT is continuing to be introduced into DC, though the input rate declined. Ratios of DDE/DDD in the sediment core from DC were also less than 1.0, with values ranging from 0.12 to 0.29 (Fig. [5](#page-6-0)), which suggests that DDT in sediments of DC has degraded to DDD due to the anaerobic conditions. Furthermore, greater values of DDE/DDD in sediments near the top of the core than those in the deeper sediments probably indicate that the input of DDTs after 1983 could come from the erosion of soil in its drainage basin, because DDT weathered on land favors the formation and preservation of DDE, as compared to DDD (Zhang et al. [2002](#page-9-0)).

Conclusions

Concentrations of PAHs and DDTs were analyzed in a sediment core from DC, an urban lake in Southwest China. Concentrations of PAHs and DDTs ranged from 479.3 to 4,560.8 ng/g dw and 0.9 to 53.5 ng/g dw, with peak values at ~1994 and ~1983, respectively. Vertical profiles of PAHs and DDTs in DC were not only different from those in more developed countries, but also different from those in marine sediments along the coastline and in remote lakes of China. PAHs in DC originated mainly from domestic combustion of coal and biomass, with a change in source from low- and moderate-temperature combustion to high-temperature combustion. However, a decreasing trend was observed in the most recent sediments, due to the stricter environmental managements that have been imposed on the urban lake. DDT in DC stemmed primarily from "aged" DDT, and its temporal trend is consistent well with the historical usage of DDT in China, but is different from that in China's coastline, where successive input of DDT historically utilized on land and DDT used in anti-fouling paint is a probability.

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References

Du L-N, Li Y, Chen X-Y, Yang J-X (2011) Effect of eutrophication on molluscan community composition in the Lake Dianchi (China, Yunnan). Limnologica-Ecol Manage Inland Wat 41:213–219

- Fernández P, Vilanova RM, Grimalt JO (1999) Sediment fluxes of polycyclic aromatic hydrocarbons in European high altitude mountain lakes. Environ Sci Technol 33:3716–3722
- Fernández P, Vilanova RM, Martínez C, Appleby P, Grimalt JO (2000) The historical record of atmospheric pyrolytic pollution over Europe registered in the sedimentary PAH from remote mountain lakes. Environ Sci Technol 34:1906–1913
- Fox WM, Connor L, Copplestone D, Johnson MS, Leah RT (2001) The organochlorine contamination history of the Mersey estuary, UK, revealed by analysis of sediment cores from salt marshes. Mar Environ Res 51:213–227
- Götz R, Bauer O-H, Friesel P, Herrmann T, Jantzen E, Kutzke M, Lauer R, Paepke O, Roch K, Rohweder U, Schwartz R, Sievers S, Stachel B (2007) Vertical profile of PCDD/Fs, dioxin-like PCBs, other PCBs, PAHs, chlorobenzenes, DDX, HCHs, organotin compounds and chlorinated ethers in dated sediment/soil cores from flood-plains of the river Elbe, Germany. Chemosphere 67:592–603
- Galarneau E (2008) Source specificity and atmospheric processing of airborne PAHs: implications for source apportionment. Atmos Environ 42:8139–8149
- Gong X, Qi S, Wang Y, Julia EB, Lv C (2007) Historical contamination and sources of organochlorine pesticides in sediment cores from Quanzhou Bay, Southeast China. Mar Pollut Bull 54:1434– 1440
- Guo J-y, Wu F-c, Zhang L, Liao H-q, Zhang R-Y, Li W, Zhao X-L, Chen S-j, Mai B-x (2011a) Screening level of PAHs in sediment core from lake Hongfeng, Southwest China. Arch Environ Contam Toxicol 60:590–596
- Guo J-y, Zhang L, Liao H-q, Tang Z, Zhang S, Wu F-c (2012) Characteristics of DDTs in fish from Lake Taihu: an indicator of continual DDTs input in China. Sci Total Environ 437:196–199
- Guo J, Wu F, Luo X, Liang Z, Liao H, Zhang R, Li W, Zhao X, Chen S, Mai B (2010) Anthropogenic input of polycyclic aromatic hydrocarbons into five lakes in Western China. Environ Pollut 158:2175–2180
- Guo W, Pei Y, Yang Z, Chen H (2011b) Historical changes in polycyclic aromatic hydrocarbons (PAHs) input in Lake Baiyangdian related to regional socio-economic development. J Hazard Mater 187:441–449
- Guo Y, Yu H-Y, Zeng EY (2009) Occurrence, source diagnosis, and biological effect assessment of DDT and its metabolites in various environmental compartments of the Pearl River Delta, South China: a review. Environ Pollut 157:1753–1763
- Guo Z, Lin T, Zhang G, Yang Z, Fang M (2006) High-resolution depositional records of polycyclic aromatic hydrocarbons in the central continental shelf mud of the East China Sea. Environ Sci Technol 40:5304–5311
- Guo Z, Lin T, Zhang G, Zheng M, Zhang Z, Hao Y, Fang M (2007) The sedimentary fluxes of polycyclic aromatic hydrocarbons in the Yangtze River Estuary coastal sea for the past century. Sci Total Environ 386:33–41
- Harrison RM, Smith DJT, Luhana L (1996) Source apportionment of atmospheric polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, UK. Environ Sci Technol 30:825– 832
- Hitch RK, Day HR (1992) Unusual persistence of DDT in some western USA soils. Bull Environ Contam Toxicol 48:259–264
- Hu L, Guo Z, Shi X, Qin Y, Lei K, Zhang G (2011) Temporal trends of aliphatic and polyaromatic hydrocarbons in the Bohai Sea, China: evidence from the sedimentary record. Org Geochem 42:1181–1193
- Hua XM, Shan ZJ (1996) The production and application of pesticides and factor analysis of their pollution in environment in China. Adv Environ Sci 4:33–45 (in Chinese)
- Huang D-B, Bader H-P, Scheidegger R, Schertenleib R, Gujer W (2007) Confronting limitations: new solutions required for urban water management in Kunming City. J Environ Manage 84:49–61
- Ishitake M, Moriwaki H, Katahira K, Yamamoto O, Tsuruho K, Yamazaki H, Yoshikawa S (2007) Vertical profile of polycyclic aromatic hydrocarbons in a sediment core from a reservoir in Osaka City. Environ Geol 52:123–129
- Jiang Y-F, Wang X-T, Jia Y, Wang F, Wu M-H, Sheng G-Y, Fu J-M (2009) Occurrence, distribution and possible sources of organochlorine pesticides in agricultural soil of Shanghai, China. J Hazard Mater 170:989–997
- Kannan K, Johnson-Restrepo B, Yohn SS, Giesy JP, Long DT (2005) Spatial and temporal distribution of polycyclic aromatic hydrocarbons in sediments from Michigan inland lakes. Environ Sci Technol 39:4700–4706
- Katsoyiannis A, Terzi E, Cai Q-Y (2007) On the use of PAH molecular diagnostic ratios in sewage sludge for the understanding of the PAH sources. Is this use appropriate? Chemosphere 69:1337-1339
- Lang C, Tao S, Liu W, Zhang Y, Simonich S (2008) Atmospheric transport and outflow of polycyclic aromatic hydrocarbons from China. Environ Sci Technol 42:5196–5201
- Lima ALC, Eglinton TI, Reddy CM (2003) High-resolution record of pyrogenic polycyclic aromatic hydrocarbon deposition during the 20th century. Environ Sci Technol 37:53–61
- Liu G, Zhang G, Jin Z, Li J (2009) Sedimentary record of hydrophobic organic compounds in relation to regional economic development: a study of Taihu Lake, East China. Environ Pollut 157:2994–3000
- Liu GQ, Zhang G, Li XD, Li J, Peng XZ, Qi SH (2005) Sedimentary record of polycyclic aromatic hydrocarbons in a sediment core from the Pearl River Estuary, South China. Mar Pollut Bull 51:912–921
- Macdonald RW, Barrie LA, Bidleman TF, Diamond ML, Gregor DJ, Semkin RG, Strachan WMJ, Li YF, Wania F, Alaee M, Alexeeva LB, Backus SM, Bailey R, Bewers JM, Gobei C, Halsall CJ, Harner T, Hoff JT, Jantunen LMM, Lockhart WL, Mackay D, Muir DCG, Pudykiewicz J, Reimer KJ, Smith JN, Stern GA, Schroeder WH, Wagemann R, Yunker MB (2000) Contaminants in the Canadian Arctic: 5 years of progress in understanding sources, occurrence and pathways. Sci Total Environ 254:93–234
- Mai BX, Qi SH, Zeng EY, Yang QS, Zhang G, Fu JM, Sheng GY, Peng PA, Wang ZS (2003) Distribution of polycyclic aromatic hydrocarbons in the coastal region off Macao, China: assessment of input sources and transport pathways using compositional analysis. Environ Sci Technol 37:4855–4863
- Qiu X, Zhu T (2010) Using the o, p′-DDT/p, p′-DDT ratio to identify DDT sources in China. Chemosphere 81:1033–1038
- Qiu X, Zhu T, Li J, Pan H, Li Q, Miao G, Gong J (2004) Organochlorine pesticides in the air around the Taihu Lake, China. Environ Sci Technol 38:1368–1374
- Qiu Y-W, Zhang G, Guo L-L, Cheng H-R, Wang W-X, Li X-D, Wai OWH (2009) Current status and historical trends of organochlorine pesticides in the ecosystem of Deep Bay, South China. Estua Coastal Shelf Sci 85:265–272
- Qu C, Li B, Wu H, Giesy JP (2012) Controlling air pollution from straw burning in China calls for efficient recycling. Environ Sci Technol 46:7934–7936
- Usenko S, Landers DH, Appleby PG, Simonich SL (2007) Current and historical deposition of PBDEs, pesticides, PCBs, and PAHs to Rocky Mountain National Park. Environ Sci Technol 41:7235–7241
- Venkatesan MI, Leon RP, Geen AV, Luoma SN (1999) Chlorinated hydrocarbon pesticides and polychlorinated biphenyls in sediment cores from San Francisco Bay. Mar Chem 64:85–97
- Wang Z, Yan W, Chi J, Zhang G (2008) Spatial and vertical distribution of organochlorine pesticides in sediments from Daya Bay, South China. Mar Pollut Bull 56:1578–1585
- Wilcke W (2007) Global patterns of polycyclic aromatic hydrocarbons (PAHs) in soil. Geoderma 141:157–166
- Xu S, Liu W, Tao S (2006) Emission of polycyclic aromatic hydrocarbons in China. Environ Sci Technol 40:702–708
- Xu X, Yang H, Li Q, Yang B, Wang X, Lee FSC (2007) Residues of organochlorine pesticides in near shore waters of LaiZhou Bay and JiaoZhou Bay, Shandong Peninsula, China. Chemosphere 68:126–139
- Yim UH, Hong SH, Shim WJ, Oh JR, Chang M (2005) Spatiotemporal distribution and characteristics of PAHs in sediments from Masan Bay, Korea. Mar Pollut Bull 50:319–326
- Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org Geochem 33:489–515
- Zhang G, Parker A, House A, Mai B, Li X, Kang Y, Wang Z (2002) Sedimentary records of DDT and HCH in the Pearl River Delta, South China. Environ Sci Technol 36:3671–3677
- Zhang XL, Tao S, Liu WX, Yang Y, Zuo Q, Liu SZ (2005) Source diagnostics of polycyclic aromatic hydrocarbons based on species ratios: a multimedia approach. Environ Sci Technol 39:9109–9114