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Historical trends of organochlorine pesticides (OCPs) recorded in sediments across the Tibetan Plateau

Ruiqiang Yang · Ting Xie · Handong Yang · Simon Turner · Guangjian Wu

Abstract Sediment cores from four lakes across the Tibetan Plateau were used as natural archives to study the time trends of organochlorine pesticides (OCPs). The total concentrations of dichlorodiphenyl-trichloroethane (ΣDDT) and hexachlorocyclohexane isomers (ΣHCH) were in the range of 0.04–1.61 and 0.08–1.88 ng/g based on dry weight (dw), while the input fluxes were in the range of 0.3–236 and 0.7–295 pg/cm^2/y in the core sediments, respectively. The input fluxes of ΣDDT and ΣHCH generally peaked in sediment layers corresponding to the 1970s–1990s and peaked in top sediment layers. The ratio of α/γ-HCH decreased in the top layer sediments, implying that the contribution of lindane (pure γ-HCH) has been increasing in recent years. In addition, the ratio of o,p'-DDT/p,p'-DDT increased significantly over the last 15–20 years, suggesting that dicofol (characterized by high ratio of o,p'-DDT/p,p'-DDT about 7.0) has recently become a relatively more important source of DDT compared to technical DDT itself. The time trends of OCPs recorded in lake sediments examined the impact on such remote alpine regions by human activities.

Keywords Sediment core · Alpine lake · DDT · HCH · Historical trend · Tibetan Plateau

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Introduction

Persistent organic pollutants (POPs) are of high concern because they are persistent, toxic, and bioaccumulative in nature. Being semi-volatile, POPs are able to undergo long-range atmospheric transport (LRAT) and distribute globally. Alpine regions play important roles when POPs are transported from lowlands to the high-altitude areas. In recent years, increasing number of studies has revealed that high mountains can act as cold condensers, where cooler temperatures lead to enhanced deposition of selected POPs at high altitude (Daly and Wania 2005).

The Tibetan Plateau (TP), located in Central Asia, is the largest and highest plateau in the world, with an area of 2.5 million square kilometers and an average altitude over 4000 m above sea level (a.s.l.). Most parts of the

TP are remote and inaccessible, which has led to the presumption of its pristine status. However, the TP is located at low latitude, and surrounded by regions with growing air pollution, especially in South and Southeast Asia (Xu et al. 2009). In the past, countries surrounding the TP such as India and China have experienced heavy use of organochlorine pesticides (OCPs) including dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane (HCH). It was reported that about 5×10^5 tonnes of DDT and more than 10^6 tonnes of technical HCH have been applied in India (Li and Macdonald 2005) and about 2.7×10^5 tonnes of DDT as well as 4.5×10^6 tonnes of technical HCH from the 1950s until its ban in 1983 have been used in China (Li et al. 1998). There is growing concern that OCP residues continue to have adverse effect on ecosystems. Moreover, lindane (pure γ-HCH) and DDT are still being used to small extents in tropical and subtropical south Asian countries for malaria control (Yadav et al. 2015). Previous studies have documented that semi-volatile persistent pollutants released from the surrounding source regions can migrate to TP latitudinally and altitudinally by LRAT (Tao et al. 2011; Yang et al. 2010b, 2013).

Lake sediments can serve as ideal archives for exploring the historical human disturbance and climate changes (Bettinetti et al. 2011). Sediments in remote alpine lakes are regarded as sentinels of atmospheric pollution (Guo et al. 2006; Rose and Rippey 2002). The post-depositional sediment mixing in lakes on the TP is relatively limited, and these lakes are minimally disturbed by direct human activities (Fernandez et al. 2000). Thus, the inputs of chemical pollutants to alpine lakes are generally predominated by atmospheric deposition (Juttner et al. 1997). Noticeably, as the world's largest ice storage after the Arctic and Antarctic, glaciers on the TP have shrunk more than 6600 km^2 in the past 40 years or more as a response to climate warming. Climate change has shown a great impact on Tibetan lakes due to the increased water supply from melting glaciers and snow (Liu et al. 2009). It was reported that these changes also have impacts on the recycling of pollutants in lake sediments (Bogdal et al. 2009; Cheng et al. 2014).

Understanding the temporal change of OCPs content in remote region is crucial not only to study the fate and transport of POPs but also to assess the impact of human disturbance and thereafter climate change.

Although OCPs were found across the TP in various matrices including air (Li et al. 2006; Wang et al. 2010), soils (Tao et al. 2011), vegetation (Wang et al. 2006; Yang et al. 2008) and fish (Yang et al. 2007). There are a few studies reported on time trends of OCPs in the TP. Wang et al. (2008) determined that DDT and HCH concentrations in an ice core from the southern TP were significantly influenced by local emissions from India. Cheng et al. (2014) inferred that the meltwater from glaciers was a possible new source for OCP pollution based on analysis of lake sediments in the central TP. Zhang et al. (2003) reported a zigzag increasing trend of DDT and HCH in two sediment cores toward the top layers in the central TP. However, knowledge of the historical trends of environmental contamination by OCPs in the TP is still very limited. In addition, these studies only focused on specific areas of the TP. Therefore, to improve our understanding of the fate and transport of POPs in the TP, the present work was designed with a regional perspective, sediment cores were collected from lakes in three areas along a south-to-north transect (Fig. 1). The time trend and spatial distribution of OCPs across the TP were examined, and gain insights on input sources of the OCPs in the sediments.

Materials and methods

Geographical settings and sampling

In order to study the transport and spatial distribution of OCPs across the TP, four lakes were selected along a south-to-north transect: Peiku Co, Cuo E, Cuo Na and Keluke Lake (Fig. 1), with altitudes of 4595, 4531, 4617 and 2813 m, and water areas of 284, 61, 182, and 57 km^2, respectively. All the lakes are remote and far from urban or agricultural pollution sources. All the lakes are freshwater except for Cuo E, which is brackish with salinity of 892 mg/L in Cl$^-$ (Nie et al. 2013). Peiku Co is a typical tectonic lake at the southern edge of the TP, and precipitation as well as glacier meltwater is the main water supply (Yang et al. 2010a). Cuo E and Cuo Na have developed in broad glaciofluvial basins in the central plateau. Keluke is located in the semi-arid, grassland-steppe climate zones in the northeast TP (Wang and Dou 1998).

Sediment cores were collected in August 2006 for Lakes Keluke (E96°52.922′/N37°17.165′), Cuo Na

Fig. 1 Map showing lake locations

(E91°30.805′/N32°02.921′) and Cuo E (E91°29.087′/N31°25.221′) and 2007 for Lake Peiku (E85°31.015′/N28°48.726′). An HTH gravity sediment corer with an 8.5 cm inner diameter polycarbonate tube was used to collect sediment cores. Cores were collected from the deepest part of the lakes, except for the Peiku Co, where it was taken from a shallower sub-basin. The cores were 24.5, 29.5, 43.0 and 25 in length for lakes Peiku Co, Cuo E, Cuo Na and Keluke, respectively. The cores were sectioned onsite at intervals of 0.5 cm using a stainless steel cutter and a total of 136 samples were obtained. All samples were packed in aluminum foil and were stored at 4 °C in a car refrigerator during transportation, and then they were kept frozen at −20 °C in the laboratory.

Sediment characterization

The samples were analyzed for water content and wet bulk density, from which the dry bulk density was calculated. Organic matter (OM) content of each sample was determined gravimetrically by loss on ignition (LOI) at 550 °C for 4 h.

The sediment was dated using the radionuclides ^{210}Pb and ^{137}Cs by direct gamma assay using an ORTEC HP Ge GWL series well-type coaxial low background intrinsic germanium detector. The detailed

radiometric dating method was described in a previous work (Yang et al. 2010; Yang and Turner 2013). Sediment ages and mass sedimentation rates (MSR) were calculated using the constant rate of supply (CRS) model constrained by the relevant ^{137}Cs. The sediment focusing factor (FF), which was used to evaluate the post-depositional horizontal movement of the sediment particles, was calculated as the ratio of the unsupported ^{210}Pb accumulation in a core to that atmospheric ^{210}Pb deposition flux for the region. In this study, lake basin soil was used as proxy measurements for the atmospheric ^{210}Pb flux. The FF values were 0.17, 6.26, 5.97 and 0.72 in lakes Peiku, Cuo E, Cuo Na and Keluke, respectively. The MSR varied greatly among the studied lakes with lowest values (0.01–0.05 g cm^2/y) in the southern lake (Peiku), higher values (0.03–0.20 g cm^2/y) in the northern lake (Keluke) and highest values (0.09–0.81 g cm^2/y) in the central lakes (Cuo E and Cuo Na). The unusual increase in MSR in Cuo Na since the 1990s until the 2000s successfully reflects the impact by the Qinghai-Tibet Railway construction (Yang et al. 2010a). The corrected fluxes using FF values in this study were aimed to reduce the overall influence which may cover the environmental factors such as episodes with flood or erosion. Thus, the fluxes could reflect mean basin accumulation rates at a large extent. Detailed

information was described in the previous work (Yang et al. 2010a).

Chemical analysis

The OCP standards of α-HCH, β-HCH, γ-HCH, δ-HCH, o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'- and p,p'-DDT, the surrogate standards polychlorinated biphenyl 209 (PCB209) and 2,4,5,6-tetrachloro-m-xylene (TCmX), and the internal standard octachloronaphthalene (OCN) were purchased from Dr. Ehrenstorfer Laboratories (Augsburg, Germany).

The solvents n-hexane and dichloromethane used for extraction and cleanup were ultra residue-analytical grade and were purchased from Fisher Scientific (Andover, USA). Silica gel (100–200 mesh, Qingdao Marine Chemical, China) was baked at 550 °C for 12 h and activated at 180 °C for 2 h. Anhydrous sodium sulfate was baked at 550 °C for 4 h. Copper powder (200 mesh, Sinopharm Chemical Reagent Co. Ltd, China) was activated using hydrochloric acid, then washed twice by distilled water, acetone and dichloromethane, respectively.

One gram potions of freeze-dried sediment samples were spiked with surrogates (PCB 209 and TCmX) and extracted using mixed solvents of hexane and dichloromethane (1:1, v/v) by accelerated solvent extraction (Dionex ASE350, US) at a temperature of 150 °C and a pressure of 1500 psi. Activated copper powder was added to the extract to remove elemental sulfur. The extracts were concentrated to about 1–2 ml by a rotary evaporator. The cleanup was conducted using a glass column packed with 6 g 3% deactivated silica gel, 4 g 2% deactivated alumina and a 2-cm-thickness of anhydrous sodium sulfate from bottom to top. The elution was subsequently conducted using 10 ml of hexane and a 50 ml mixture of dichloromethane and hexane (1:1, v/v). The eluate was concentrated to 1–2 ml and was then finally reduced to 0.2 ml in hexane under a gentle stream of pure nitrogen. Quantitative internal standards (20 ng of OCN) were added to the extract before instrumental analysis.

The OCPs in the samples were analyzed using a gas chromatograph (Agilent-7890 GC, USA) equipped with a [63]Ni electron capture detector (micro-ECD). The chromatographic separation was conducted using two capillary columns with different polarity (HP-5 and DB-1701). Both columns were 30 m long and had 0.25 mm i.d. and 0.25 μm stationary phase film thickness. The samples were analyzed basically by HP-5 column, while further confirmation was conducted by DB-1701 column. Each organochlorine compound is identified on the basis of its occurrence in each of the two specified retention time for the two columns. This facilitated peak recognition when compounds or interferences coeluted on one column. The temperatures of the injector and detector were set at 250 and 350 °C, respectively. One microliter of the extracts was injected in the pulsed split less mode. High-purity helium was used as the carrier gas with a constant flow of 1.2 ml/min, and high-purity nitrogen was used as the make-up gas and controlled at 48.8 ml/min. The oven temperature program was 80 °C, held for 1 min, ramped at 15 °C/min to 140 °C, held for 1 min, and then ramped at 5 °C/min to 230 °C, held for 4 min, and finally ramped at 25 °C/min to 300 °C, and held for 10 min.

Quality control

A procedural blank using anhydrous Na_2SO_4 in place of sediment was analyzed in each batch of 11 sediment samples. The average recoveries of spiked surrogates in all analyzed samples ($N = 136$) were $74 \pm 8.3\%$ for TCmX and $100 \pm 7.6\%$ for PCB209. The concentrations reported in this paper were corrected by the surrogate recoveries. The breakdown of parent DDT was checked daily and the percentage of the breakdown products was less than 10%. One or two segments in each core were analyzed in duplicate, and the average relative percentage differences (RPDs) were in the range of 3.1–28.6%. The method detection limit (MDL) was defined as three times the signal-to-noise ratio (S/N). The MDLs were 0.03, 0.04, 0.01 and 0.06 ng/g dw for α-HCH, β-HCH, γ-HCH and δ-HCH, and 0.05, 0.01, 0.06, 0.04, 0.12 and 0.08 ng/g dw for o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'- and p,p'-DDT, respectively. The instrument performance was routinely checked using quality control standards.

Estimation of chemical flux and inventory

Flux stands for the accumulation rate of the chemical analyte and has been considered as a more meaningful way than concentration to assess pollutant inputs. Inventory is an estimate of the total accumulation of

the pollutants over time per unit area. The two parameters were estimated by the following equations (Perry et al. 2005):

$$\text{Flux}_i \ (\mu g/m^2/y) = C_i \times \text{MSR} \times 10/\text{FF}$$

$$\text{Inventory} \ (ng/cm^2) = \sum C_i \rho_i d_i$$

where C_i is the dry-weight-based concentration in sediment core segment i (ng/g dw), MSR is mass sedimentation rate (g/cm^2/y), and FF is the focusing factor (dimensionless); ρ_i is the dry mass bulk density (g/cm^3), d_i is the thickness of segment i (cm).

Results and discussion

Concentrations

Summary statistics of the concentrations and inventories of OCPs in sediments are shown in Table 1. Concentration comparisons with the results from other remote areas are presented in Table 2. The detailed isomer concentrations of HCH and DDT are shown in Table S1 in the supporting information.

The ΣDDT concentrations (sum of o,p'-DDE, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'- and p,p'-DDT) were in the range of 0.31–0.73, 0.07–1.21, 0.42–1.61 and 0.04–0.75 ng/g dw in the core sediments from Lakes Peiku, Cuo E, Cuo Na and Keluke, respectively. The ΣHCH concentrations (sum of α-, β-, γ- and δ-HCH) were in the range of 0.26–1.08, 0.08–1.37, 0.42–1.88 and 0.35–1.15 ng/g dw in the same order as the former lakes. The sediment concentrations of both ΣDDT and

ΣHCH measured in this study were higher than those from the Canadian Arctic (Stern et al. 2005), the Antarctic (Klanova et al. 2008) and high-altitude lakes from the Southern Himalayas (Guzzella et al. 2011), similar to those from the Norwegian Arctic (Jiao et al. 2009; Evenset et al. 2007), Rocky mountains (Usenko et al. 2007), Andean mountains (Borghini et al. 2005), and the central TP (Zhang et al. 2003; Cheng et al. 2014) but significantly lower than those in European mountains (Grimalt et al. 2004). The elevated concentrations in the TP might be explained by the plateau's proximity to the source regions such as Indian subcontinent and China (Yang et al. 2008). Studies have documented that selected POPs on the TP can be transported from the Indian subcontinent by the southern Asian monsoon (Yang et al. 2008, 2013; Wang et al. 2008).

The concentrations of ΣDDT and ΣHCH generally peaked in sediment layers corresponding to the 1970s–1990s and in the top sediment layers (Fig. 2). Organic matter usually plays an important role in the distribution and retention of organic contaminants in sediments (Klanova et al. 2008). The core averaged OM content in this study ranged from 48 (Lake Peiku Co) to 200 mg/g (Lake Cuo E), with an average of 117 mg/g. However, no significant correlation between concentration and OM content was observed for all the studied lakes ($P > 0.05$). When concentrations were normalized by OM content, the vertical distribution pattern of HCH and DDT did not change much (Fig. 3), suggesting OM content itself does not cause the significant increase in OCP concentrations in sediment. Thus, OM content played an insignificant

Table 1 Concentrations and inventories of ΣDDT and ΣHCH in sediment cores

Lakes	Core concentration range (mean) (ng/g dw)*		Surface concentration (ng/g dw)		Inventories (ng/cm^2)[a]	
	ΣDDT[b]	ΣHCH[c]	ΣDDT	ΣHCH	ΣDDT	ΣHCH
Peiku	0.21–0.73 (0.40)	0.26–1.08 (0.68)	0.48	0.69	0.42	0.61
Cuo E	0.05–1.21 (0.34)	0.08–1.37 (0.75)	1.00	1.37	1.47	3.35
Cuo Na	0.26–1.61 (0.57)	0.46–1.38 (0.77)	0.93	1.23	7.44	7.89
Keluke	0.04–0.75 (0.28)	0.40–1.15 (0.69)	0.28	1.03	0.67	1.63

* Min–max (mean)

[a] Calculated since the 1940s

[b] Sum of p,p'-DDE, o,p'-DDE, p,p'-DDD, o,p'-DDD, p,p'- and o,p'-DDT

[c] Sum of α-, β, γ- and δ-HCH

Table 2 Comparison of OCP concentrations in sediments from remote lakes (ng/g dw)

Locations	Sampling year	Sediment type	Concentration		Reference
			$\sum$DDT	$\sum$HCH	
Mountain lakes, across TP	2006–2007	Core	BDL[a]–2.5[b]	BDL–1.9[c]	This study
Mountain lakes, Central TP	2003	Core	0.4–6.3[d]	0.3–9.0[c]	Cheng et al. ([2014](#))
Andean mountain lakes, Chile	1999	Core	0.019–4.1[f]	0.005–0.23[c]	Borghini et al. ([2005](#))
Rocky Mountain lakes	2003	Core	1.8–9.8[g]	NA[h]	Usenko et al. ([2007](#))
Remote lakes, Norwegian Arctic	2001	Core	1.6–4.0[i]	NA	Evenset et al. ([2007](#))
Remote lakes, Canadian Arctic	1999	Core	BDL–0.20[b]	BDL–0.33[c]	Stern et al. ([2005](#))
Mountain lakes, across TP	2006–2007	Surface	0.28–1.0[b]	0.69–1.4[c]	This study
Southern Himalaya lakes, Nepal	2007	Surface	0.19 ± 0.27[b]	BDL	Guzzella et al. ([2011](#))
James Ross Island, Antarctic	2005	Surface	0.19–1.15[j]	0.14–0.76[c]	Klanova et al. ([2008](#))
Ny-Alesund lakes, Arctic	2005	Surface	0.12–5.9[d]	0.21–7.0[c]	Jiao et al. ([2009](#))
European mountain lakes	2004	Surface	0.27–54[e]	BDL	Grimalt et al. ([2004](#))

[a] *BDL* below the detection limit

[b] Sum of *p,p'*-DDE, *o,p'*-DDE, *p,p'*-DDD, *o,p'*-DDD, *p,p'*- and *o,p'*-DDT

[c] Sum of α-, β-, γ- and δ-HCH

[d] Sum of *p,p'*-DDE, *p,p'*-DDD, *p,p'*- and *o,p'*-DDT

[e] Sum of *p,p'*-DDE, *p,p'*- and *o,p'*-DDT

[f] *p,p'*-DDE

[g] Sum of *p,p'*-DDE and *p,p'*-DDD

[h] *NA* not available

[i] Sum of *p,p'*-DDE, *o,p'*-DDE, *o,p'*-DDD, *p,p'*- and *o,p'*-DDT

[j] Sum of *p,p'*-DDE, *p,p'*- and *o,p'*-DDT

role in affecting the trends of vertical distribution of target compounds in the sediments of these lakes.

Input flux and time trends

The input flux of DDT and HCH showed obvious increasing trends for all the studied lakes since the 1950s, when these pesticides were first applied all over the world (Fig. 2). The heavy use of OCPs in Indian Subcontinent and China is reflected by the peaks during the 1970s–1980s in the input fluxes observed in the lake sediments of this work.

However, it is noted that input fluxes of DDT and HCH continued to increase in most of lakes at the top layer sediments (Fig. 2). Since the global ban of DDT and HCH application in agriculture purpose after the late 1980s, their levels in environmental matrices have largely dropped (Li 1999). Although DDT and lindane are still in use in some southern Asian countries, the amount has been greatly reduced in recent years (Li

and Macdonald 2005). A recent decreasing trend of OCPs in the air of south India was also evidenced (Rajendran et al. 1999). As expected, deposition fluxes recorded in an ice core from the southern TP were in line with the usage of OCPs in India, which showed a decrease to undetectable levels from the 1980s (Wang et al. 2008). Apparently, the time trends of OCPs in sediment cores observed in this study are quite different from the historical records in Tibetan ice cores in the corresponding recent deposition years. Since there is no official record on the usage of OCPs in this region, the increasing trends of OCPs in top sediment layers implies other local OCP sources may contribute to lake sediments in addition to atmospheric deposition from LRAT sources.

The TP and surroundings contain the largest number of glaciers outside the Polar Regions. Climate warming has significant implications for water resources and eco-environment in the TP (Yao et al. 2012). It was reported that the mean annual

Fig. 2 Temporal trends of concentrations (*blue diamonds*) and depositional fluxes (*red circles*) for ΣDDT and ΣHCH in dated sediment cores
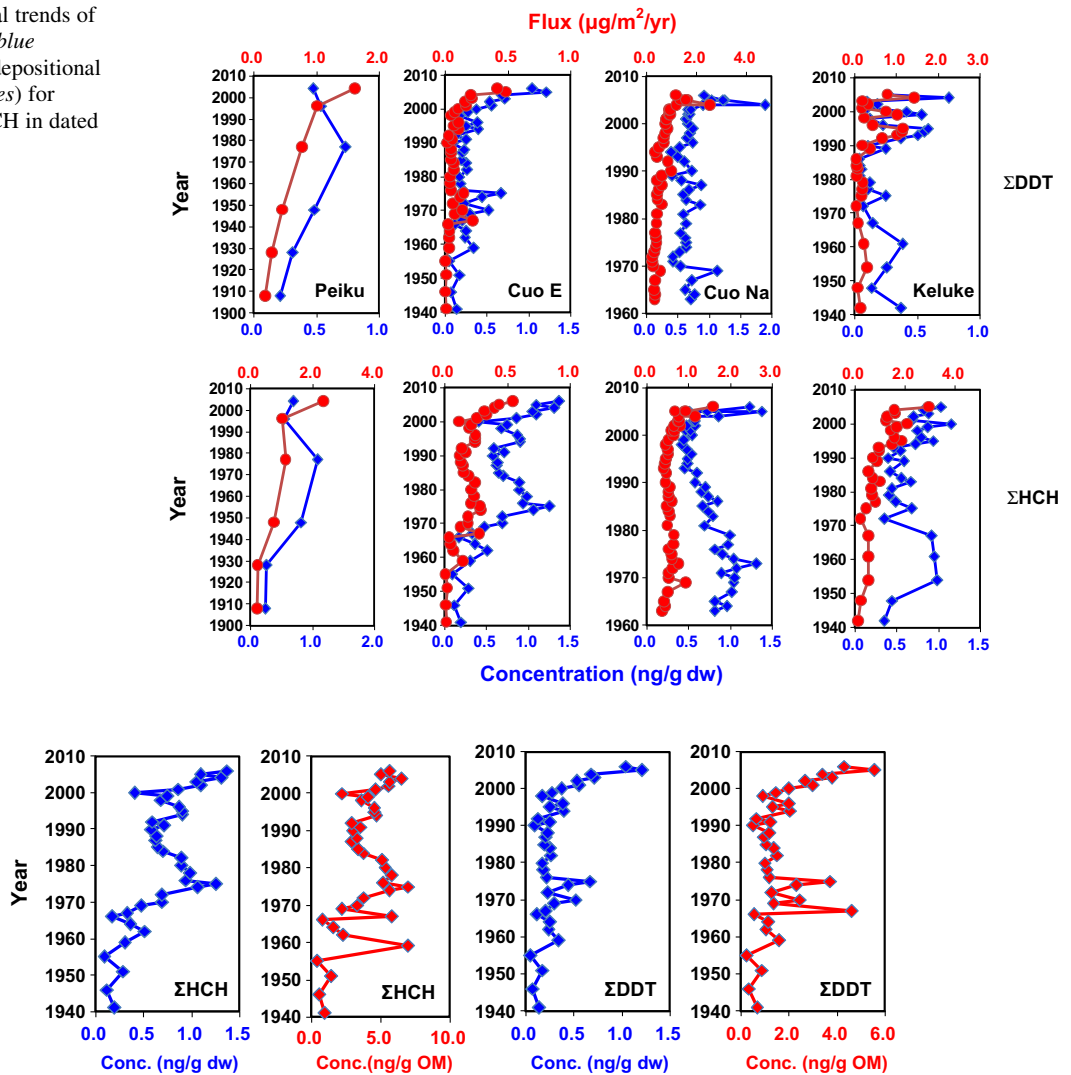
Fig. 3 Comparison of temporal trends of OCP concentrations between dry-weight basis and OM content basis in Cuo E Lake

temperature in the central TP increased at 0.41 °C/y during the last decade (1997–2006) (Liu et al. 2009). In the past 40 years, glaciers have shrunk more than 6600 km^2 on the TP with significant retreat occurring since the mid-1980s and strong retreat being observed since the 1990s (Yang et al. 2015). Considering that meltwater from glaciers or snow to the lake water has become more significant in the TP due to climate warming (Liu et al. 2009), Cheng et al. (2014) suggested that the increasing trend of input flux in the top layers of sediments in the central TP are possibly resulted from the release that OCPs formerly trapped in glaciers or frozen soils in the TP may have been flushed into sedimentary basins. The recent

glacial origin of pollutants released into lakes has been also confirmed by several other studies (Bogdal et al. 2009; Bettinetti et al. 2011; Cheng et al. 2014). The water supply to the studied lakes is influenced to a great extent by meltwater from glaciers or snow (Wang and Dou 1998), as described in the sampling section above. The contribution of glacial origin of OCPs for the recent increase in the top layer sediments in the present work need further study in the future.

Geographical distribution and source assessment

Sources of OCPs to the TP are likely to be significantly affected by the southwest or southeast air mass from

Indian subcontinent (Yang et al. 2013). The geographical distribution of OCP fluxes in lakes along a south-to-north transect is also examined in the present study as follows. In the southern Peiku Co, the temporal resolution is relatively poor due to its low sedimentation rate (Yang et al. 2010a). The input fluxes of ΣDDT and ΣHCH in southern Peiku Co are much higher than in the central Cuo E (Fig. 2). The southern Peiku Co is relatively close to the Indian subcontinent, which is heavily polluted by DDT and HCH. Our previous work also found that concentrations of DDT and HCH in pine needles decreased from the south to the north in the southeast TP, suggesting an important input from the Indian subcontinent by the South Asian monsoon (Yang et al. 2008). However, for the two central lakes, the Cuo Na Lake is unusual that the OCP fluxes are about one-fold higher than those in Cuo E Lake (Fig. 2). Because OCP concentrations are similar between the two lakes, the remarkable increase in OCP fluxes in Cuo Na Lake probably due to local road and railway construction within the catchment, causing OCP-containing soils (0.23 and 0.17 ng/g dw for ΣHCH and ΣDDT, respectively) to be washed into the lake (Xie et al. 2014). This was also in line with the observations that significantly higher sedimentation rate and mercury accumulation rate occurred in Cuo Na Lake (Yang et al. 2010a). There is no general decreasing trend along the south-to-north transects for OCP fluxes. The HCH flux in the northern Keluke Lake is similar to that of the southern Peiku Lake, implying Northern lake basins are significantly influenced by inland OCP sources using air mass back trajectory analysis (Xie et al. 2014). The OCP flux differences between these sites may be related to individual catchment influences, proximity to source areas and to different meteorological conditions across the TP.

Isomer ratio is often used as a probe for sources and transport of OCPs (Willett et al. 1998; Yang et al. 2013). Among, the ratio of α/γ-HCH has been widely used to monitor the source and historical use of HCH (Willett et al. 1998). Technical HCH has an α-/γ-HCH ratio ranging from 3 to 7 (Willett et al. 1998). The averaged α-/γ-HCH ratios in the four lakes of this work ranged from 0.96 to 2.99, significantly lower than the value in technical HCH. In addition, the ratios of α/γ-HCH have generally decreased since around 1990 (Fig. 4a), implying that the contribution of lindane (γ-HCH) has been increasing as a potential
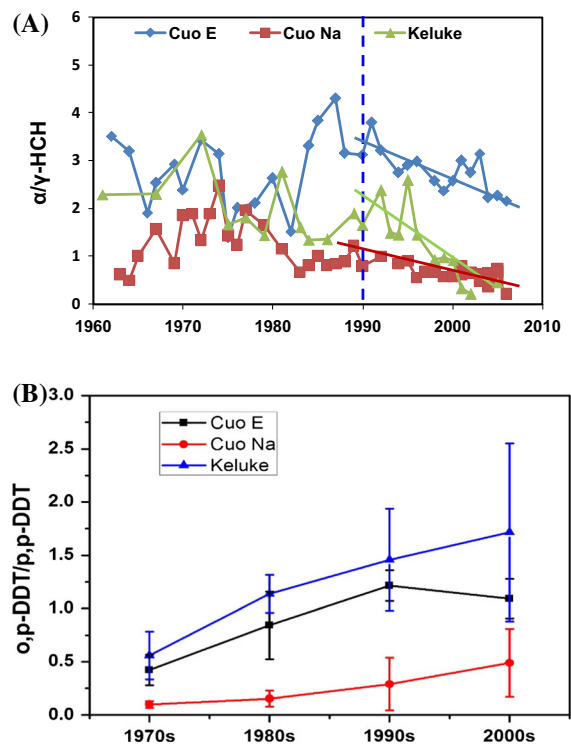
Fig. 4 Variations of ratios of α/γ-HCH (**a**) and o,p′-DDT/p,p′-DDT (**b**) against deposition year of lake sediments

main source in recent years, which is in line with the fact that technical HCH was banned in China in 1983 and in India in 1997, while lindane is still being used in some southern Asian countries (Li and Macdonald 2005).

A high p,p′-DDE/p,p′-DDT ratio usually reflects aged sources, because p,p′-DDT can be degraded to p,p′-DDE and p,p′-DDD. All the averaged ratios of p,p′-DDE/p,p′-DDT in the lakes are larger than 1, with an exception in Cuo Na Lake (0.32), indicating that DDT in the TP are mainly from historical input. However, the averaged ratios of o,p′-DDT/p,p′-DDT in lake sediments ranged from 0.29 to 1.30, which were significantly higher than those in technical DDT (85% p,p′-DDT and 15% o,p′-DDT), suggesting that dicofol, which is characterized by a high ratio of o,p′-DDT/p,p′-DDT (about 7.0) (Qiu et al. 2005), has recently become a relatively more important source of the DDT. Asia is the largest consumer of dicofol and the annual usage in China and India in the year 2000 was 2013 tonnes and 145 tonnes, respectively (Li et al. 2014). In addition, the ratio of o,p′-DDT to the sum of o,p′-DDT and p,p′-DDT has increased significantly in

lake sediments over the last 15–20 years (Fig. 4b), indicating that the contribution of DDT from dicofol may have become more predominant in the current DDT profiles due to the ongoing usage of dicofol in areas surrounding the TP.

Conclusion

This work reveals the time trends of OCP pollution in the TP from retrieved sedimentary records in four remote alpine lakes. The elevated concentrations in sediments in the TP compared to the Polar Regions might be explained by the plateau's proximity to the source regions. The input fluxes of ΣDDT and ΣHCH generally peaked in sediment layers corresponding to the 1970s–1990s when the heavy use of OCPs in surroundings of the TP. Of particular concern is the recent shift in pollution sources of HCHs and DDTs. Isomer ratio analysis (α/γ-HCH and o,p'-DDT/p,p'-DDT) indicated that lindane (pure γ-HCH) and dicofol may have recently become relatively more important sources of HCHs and DDTs. In contrast to recent decline trend that reported in the southern Tibetan ice core, the ongoing increasing trends of OCP fluxes in the top layer sediments should be noticeable. Considering that meltwater from glaciers or snow to the lake water has become more significant in the TP due to climate warming, the influence of climate change on the recycling of contaminants in lake ecosystems of the TP deserves more comprehensive study in the future.

References

Bettinetti, R., Galassi, S., Guilizzoni, P., & Quadroni, S. (2011). Sediment analysis to support the recent glacial origin of DDT pollution in Lake Iseo (Northern Italy). *Chemosphere, 85*(2), 163–169.

Bogdal, C., Schmid, P., Zennegg, M., Anselmetti, F. S., Scheringer, M., & Hungerbuhler, K. (2009). Blast from the past: Melting glaciers as a relevant source for persistent organic pollutants. *Environmental Science and Technology, 43*(21), 8173–8177.

Borghini, F., Grimalt, J. O., Sanchez-Hernandez, J. C., Barra, R., Garcia, C. J. T., & Focardi, S. (2005). Organochlorine compounds in soils and sediments of the mountain Andean Lakes. *Environmental Pollution, 136*(2), 253–266.

Cheng, H. R., Lin, T., Zhang, G., Liu, G. Q., Zhang, W. L., Qi, S. H., et al. (2014). DDTs and HCHs in sediment cores from the Tibetan Plateau. *Chemosphere, 94,* 183–189.

Daly, G. L., & Wania, F. (2005). Organic contaminants in mountains. *Environmental Science and Technology, 39*(2), 385–398.

Evenset, A., Christensen, G. N., Carroll, J., Zaborska, A., Berger, U., Herzke, D., et al. (2007). Historical trends in persistent organic pollutants and metals recorded in sediment from Lake Ellasjoen, Bjornoya, Norwegian Arctic. *Environmental Pollution, 146*(1), 196–205.

Fernandez, P., Vilanova, R. M., Martinez, C., Appleby, P., & Grimalt, J. O. (2000). The historical record of atmospheric pyrolytic pollution over Europe registered in the sedimentary PAH from remote mountain lakes. *Environmental Science and Technology, 34*(10), 1906–1913.

Grimalt, J. O., van Drooge, B. L., Ribes, A., Vilanova, R. M., Fernandez, P., & Appleby, P. (2004). Persistent organochlorine compounds in soils and sediments of European high altitude mountain lakes. *Chemosphere, 54*(10), 1549–1561.

Guo, Z. G., Lin, T., Zhang, G., Yang, Z. S., & Fang, M. (2006). High-resolution depositional records of polycyclic aromatic hydrocarbons in the central continental shelf mud of the East China Sea. *Environmental Science and Technology, 40*(17), 5304–5311.

Guzzella, L., Poma, G., De Paolis, A., Roscioli, C., & Viviano, G. (2011). Organic persistent toxic substances in soils, waters and sediments along an altitudinal gradient at Mt. Sagarmatha, Himalayas, Nepal. *Environmental Pollution, 159*(10), 2552–2564.

Jiao, L. P., Zheng, G. J., Minh, T. B., Richardson, B., Chen, L. Q., Zhang, Y. H., et al. (2009). Persistent toxic substances in remote lake and coastal sediments from Svalbard, Norwegian Arctic: Levels, sources and fluxes. *Environmental Pollution, 157*(4), 1342–1351.

Juttner, I., Henkelmann, B., Schramm, K. W., Steinberg, C. E. W., Winkler, R., & Kettrup, A. (1997). Occurrence of PCDD/F in dated lake sediments of the Black Forest, southwestern Germany. *Environmental Science and Technology, 31*(3), 806–812.

Klanova, J., Matykiewiczova, N., Macka, Z., Prosek, P., Laska, K., & Klan, P. (2008). Persistent organic pollutants in soils and sediments from James ROSS Island, Antarctica. *Environmental Pollution, 152*(2), 416–423.

Li, Y. F. (1999). Global technical hexachlorocyclohexane usage and its contamination consequences in the environment: From 1948 to 1997. *Science of the Total Environment, 232*(3), 121–158.

Li, Y. F., Cai, D. J., & Singh, A. (1998). Technical hexachlorocyclohexane use trends in China and their impact on the environment. *Archives of Environmental Contamination and Toxicology, 35*(4), 688–697.

Li, L., Liu, J. G., & Hu, J. X. (2014). Global inventory, long-range transport and environmental distribution of dicofol. *Environmental Science and Technology, 49*(1), 212–222.

Li, Y. F., & Macdonald, R. W. (2005). Sources and pathways of selected organochlorine pesticides to the Arctic and the effect of pathway divergence on HCH trends in biota: A

review. *Science of the Total Environment, 342*(1–3), 87–106.

Li, J., Zhu, T., Wang, F., Qiu, X. H., & Lin, W. L. (2006). Observation of organochlorine pesticides in the air of the Everest region. *Ecotoxicology Environmental Safety, 63*(1), 33–41.

Liu, J. S., Wang, S. Y., Yu, S. M., Yang, D. Q., & Zhang, L. (2009). Climate warming and growth of high-elevation inland lakes on the Tibetan Plateau. *Global and Planetary Change, 67*(3–4), 209–217.

Nie, Y., Zhang, Y. L., Ding, M. J., Liu, L. S., & Wang, Z. F. (2013). Lake change and its implication in the vicinity of Mt. Qomolangma (Everest), central high Himalayas, 1970–2009. *Environmental Earth Sciences, 68*(1), 251–265.

Perry, E., Norton, S. A., Kamman, N. C., Lorey, P. M., & Driscoll, C. T. (2005). Deconstruction of historic mercury accumulation in lake sediments, northeastern United States. *Ecotoxicology, 14*(1–2), 85–99.

Qiu, X. H., Zhu, T., Yao, B., Hu, J. X., & Hu, S. W. (2005). Contribution of dicofol to the current DDT pollution in China. *Environmental Science and Technology, 39*(12), 4385–4390.

Rajendran, R. B., Venugopalan, V. K., & Ramesh, R. (1999). Pesticide residues in air from coastal environment, south India. *Chemosphere, 39*(10), 1699–1706.

Rose, N. L., & Rippey, B. (2002). The historical record of PAH, PCB, trace metal and fly-ash particle deposition at a remote lake in north-west Scotland. *Environmental Pollution, 117*(1), 121–132.

Stern, G. A., Braekevelt, E., Helm, P. A., Bidleman, T. F., Outridge, P. M., Lockhart, W. L., et al. (2005). Modem and historical fluxes of halogenated organic contaminants to a lake in the Canadian arctic, as determined from annually laminated sediment cores. *Science of the Total Environment, 342*(1–3), 223–243.

Tao, S., Wang, W. T., Liu, W. X., Zuo, Q. A., Wang, X. L., Wang, R., et al. (2011). Polycyclic aromatic hydrocarbons and organochlorine pesticides in surface soils from the Qinghai-Tibetan Plateau. *Journal of Environmental Monitoring, 13*(1), 175–181.

Usenko, S., Landers, D. H., Appleby, P. G., & Simonich, S. L. (2007). Current and historical deposition of PBDEs, pesticides, PCBs, and PAHs to rocky mountain national park. *Environmental Science and Technology, 41*(21), 7235–7241.

Wang, S. M., & Dou, H. S. (1998). *Lakes of China*. Beijing: Science Press.

Wang, X. P., Gong, P., Yao, T. D., & Jones, K. C. (2010). Passive air sampling of organochlorine pesticides, polychlorinated biphenyls, and polybrominated diphenyl ethers across the Tibetan Plateau. *Environmental Science and Technology, 44*(8), 2988–2993.

Wang, X. P., Xu, B. Q., Kang, S. C., Cong, Z. Y., & Yao, T. D. (2008). The historical residue trends of DDT, hexachlorocyclohexanes and polycyclic aromatic hydrocarbons in an ice core from Mt. Everest, central Himalayas, China. *Atmospheric Environment, 42*(27), 6699–6709.

Wang, X. P., Yao, T. D., Cong, Z. Y., Yan, X. L., Kang, S. C., & Zhang, Y. (2006). Gradient distribution of persistent organic contaminants along northern slope of central-Himalayas, China. *Science of the Total Environment, 372*(1), 193–202.

Willett, K. L., Ulrich, E. M., & Hites, R. A. (1998). Differential toxicity and environmental fates of hexachlorocyclohexane isomers. *Environmental Science and Technology, 32*(15), 2197–2207.

Xie, T., Zhang, S. J., & Yang, R. Q. (2014). Contamination levels and source analysis of polycyclic aromatic hydrocarbons and organochlorine pesticides in soils and grasses from lake catchment in the Tibetan Plateau. *Environmental Sciences, 35*(7), 2680–2690 **(in Chinese)**.

Xu, B., Cao, J., Hansen, J., Yao, T., Joswia, D. R., Wang, N., et al. (2009). Black soot and the survival of Tibetan glaciers. *Proceedings of the National Academy of Sciences of the United States of America, 106*(52), 22114–22118.

Yadav, I. C., Devi, N. L., Syed, J. H., Cheng, Z. N., Li, J., Zhang, G., et al. (2015). Current status of persistent organic pesticides residues in air, water, and soil, and their possible effect on neighboring countries: A comprehensive review of India. *Science of the Total Environment, 511*, 123–137.

Yang, H. D., Battarbee, R. W., Turner, S. D., Rose, N. L., Derwent, R. G., Wu, G. J., et al. (2010a). Historical reconstruction of mercury pollution across the Tibetan Plateau using lake sediments. *Environmental Science and Technology, 44*(8), 2918–2924.

Yang, H. D., & Turner, S. D. (2013). Radiometric dating for recent lake sediments on the Tibetan Plateau. *Hydrobiologia, 713*(1), 73–86.

Yang, R. Q., Wang, Y. W., Li, A., Zhang, Q. H., Jing, C. Y., Wang, T., et al. (2010b). Organochlorine pesticides and PCBs in fish from lakes of the Tibetan Plateau and the implications. *Environmental Pollution, 158*(6), 2310–2316.

Yang, S., Xu, B. Q., Cao, J. J., Zender, C. S., & Wang, M. (2015). Climate effect of black carbon aerosol in a Tibetan Plateau glacier. *Atmospheric Environment, 111*, 71–78.

Yang, R. Q., Yao, T. D., Xu, B. Q., Jiang, G. B., & Xin, X. D. (2007). Accumulation features of organochlorine pesticides and heavy metals in fish from high mountain lakes and Lhasa River in the Tibetan Plateau. *Environment International, 33*(2), 151–156.

Yang, R. Q., Yao, T. D., Xu, B. Q., Jiang, G. B., & Zheng, X. Y. (2008). Distribution of organochlorine pesticides (OCPs) in conifer needles in the southeast Tibetan Plateau. *Environmental Pollution, 153*(1), 92–100.

Yang, R. Q., Zhang, S. J., Li, A., Jiang, G. B., & Jing, C. Y. (2013). Altitudinal and spatial signature of persistent organic pollutants in soil, lichen, conifer needles, and bark of the southeast Tibetan Plateau: Implications for sources and environmental cycling. *Environmental Science and Technology, 47*(22), 12736–12743.

Yao, T. D., Thompson, L., Yang, W., Yu, W. S., Gao, Y., Guo, X. J., et al. (2012). Different glacier status with atmospheric circulations in Tibetan Plateau and surroundings. *Nature Climate Change, 2*, 663–667.

Zhang, W. L., Zhang, G., Qi, S. H., & Peng, P. A. (2003). A preliminary study of organochlorine pesticides in water and sediments from two Tibetan lakes. *Geochimica (Beijing), 32*(4), 363–367 **(in Chinese)**.