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

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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 dichlorodiphenyltrichloroethane (ΣDDT) and hexachlorocyclohexane isomers (ΣHCH) were in the range of 0.04-1.61 ng/g and 0.08-1.88 ng/g based on dry weight (dw), while the input fluxes were in the range of 0.3-236 pg/cm^2/yr and 0.7-295 pg/cm^2/yr in the core sediments, respectively. The input fluxes of ΣDDT and ΣHCH generally peaked in sediment layers corresponding to the 1970s-90s 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

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 4,000 meters 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

55 Asian countries for malaria control (Yadav et al. 2015). Previous studies have
56 documented that semi-volatile persistent pollutants released from the surrounding
57 source regions can migrate to TP latitudinally and altitudinally by LRAT (Tao et al.
58 2011; Yang et al. 2010b, 2013).

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

72 Understanding the temporal change of OCPs content in remote region is crucial
73 not only to study the fate and transport of POPs but also to assess the impact of human
74 disturbance and thereafter climate change. Although OCPs were found across the TP in
75 various matrices including air (Li et al., 2006; Wang et al., 2010), soils (Tao et al. 2011,
76 Yuan et al., 2014), 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 towards 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

Geographic 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 m, 4531 m, 4617 m and 2813 m, and water areas of 284 km^2, 61 km^2, 182 km^2, 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 & Su, 1998).

Sediment cores were collected in August 2006 for Lakes Keluke (E96°52.922′/N37°17.165′), Cuo Na (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 cm, 29.5 cm, 43.0 cm and 25 cm 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

121 previous work (Yang et al., 2010a; Yang et al., 2013). Sediment ages and mass
122 sedimentation rates (MSR) were calculated using the constant rate of supply (CRS)
123 model constrained by the relevant ^{137}Cs. The sediment focusing factor (FF), which was
124 used to evaluate the post-depositional horizontal movement of the sediment particles,
125 was calculated as the ratio of the unsupported ^{210}Pb accumulation in a core to that
126 atmospheric ^{210}Pb deposition flux for the region. In this study, lake basin soil was used
127 as proxy measurements for the atmospheric ^{210}Pb flux. The FF values were 0.17, 6.26,
128 5.97 and 0.72 in lakes Peiku, Cuo E, Cuo Na and Keluke, respectively. The MSR varied
129 greatly among the studied lakes with lowest values (0.01~0.05 g cm^2/yr) in the southern
130 lake (Peiku), higher values (0.03~0.20 g cm^2/yr) in the northern lake (Keluke) and
131 highest values (0.09~0.81 g cm^2/yr) in the central lakes (Cuo E and Cuo Na). The
132 unusual increase of MSR in Cuo Na since the 1990s until the 2000s successfully reflects
133 the impact by the Qinghai-Tibet Railway construction (Yang et al., 2010a). The
134 corrected fluxes using FF values in this study were aimed to reduce the overall influence
135 which may cover the environmental factors such as episodes with flood or erosion. Thus,
136 the fluxes could reflect mean basin accumulation rates at a large extent. Detailed
137 information was described in the previous work (Yang et al., 2010a).

138 **Chemical analysis**

139 The OCP standards of α-HCH, β-HCH, γ-HCH, δ-HCH, o,p′-DDE, p,p′-DDE, o,p′-
140 DDD, p,p′-DDD, o,p′- and p,p′-DDT, the surrogate standards polychlorinated biphenyl
141 209 (PCB209) and 2,4,5,6-tetrachloro-m-xylene (TCmX), and the internal standard
142 octachloronaphthalene (OCN) were purchased from Dr. Ehrenstorfer Laboratories
143 (Augsburg, Germany).

144 The solvents n-hexane and dichloromethane used for extraction and cleanup were
145 ultra residue-analytical grade and were purchased from Fisher Scientific (Andover,
146 USA). Silica gel (100-200 mesh, Qingdao Marine Chemical, China) was baked at
147 550°C for 12 h and activated at 180°C for 2 h. Anhydrous sodium sulfate was baked at
148 550°C for 4 h. Copper powder (200 mesh, Sinopharm Chemical Reagent Co. Ltd, China)
149 was activated using hydrochloric acid, then washed twice by distilled water, acetone
150 and dichloromethane, respectively.

151 One gram potions of freeze-dried sediment samples were spiked with surrogates
152 (PCB 209 and TCmX) and extracted using mixed solvents of hexane and
153 dichloromethane (1:1, v/v) by accelerated solvent extraction (Dionex ASE350, U.S.) at
154 a temperature of 150°C and a pressure of 1500 psi. Activated copper powder was added
155 to the extract to remove elemental sulfur. The extracts were concentrated to about 1~2
156 ml by a rotary evaporator. The cleanup was conducted using a glass column packed
157 with 6 g 3% deactivated silica gel, 4 g 2% deactivated alumina and a 2-cm-thickness of
158 anhydrous sodium sulfate from bottom to top. The elution was subsequently conducted
159 using10 ml of hexane and a 50 ml mixture of dichloromethane and hexane (1:1, v/v).
160 The eluate was concentrated to 1~2 ml and was then finally reduced to 0.2 ml in hexane
161 under a gentle stream of pure nitrogen. Quantitative internal standards (20 ng of OCN)
162 were added to the extract before instrumental analysis.

163 The OCPs in the samples were analyzed using a gas chromatograph (Agilent-7890
164 GC, USA) equipped with a ^{63}Ni electron capture detector (micro-ECD). The
165 chromatographic separation was conducted using two capillary columns with different
166 polarity (HP-5 and DB-1701). Both columns were 30 m long and had 0.25 mm i.d. and
167 0.25 μm stationary phase film thickness. The samples were analyzed basically by HP-
168 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°C and 350°C, respectively. One microliter of the extracts was injected in the pulsed splitless 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 ± 8.3% for TCmX and 100 ± 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):

$$Flux_i\ (\mu g/m^2/yr) = C_i \times MSR \times 10/FF$$

$$Inventory\ (ng/cm^2) = \Sigma C_i \rho_i d_i$$

Where C_i is the dry-weight-based concentration in sediment core segment i (ng/g dw), MSR is mass sedimentation rate ($g/cm^2/yr$), 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 ng/g dw, 0.07-1.21 ng/g dw, 0.42-1.61 ng/g dw 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 ng/g dw, 0.08-1.37 ng/g dw, 0.42-1.88 ng/g dw

214 and 0.35-1.15 ng/g dw in the same order as the former lakes. The sediment
215 concentrations of both ΣDDT and ΣHCH measured in this study were higher than those
216 from the Canadian Arctic (Stern et al. 2005), the Antarctic (Klanova et al. 2008) and
217 high altitude lakes from the Southern Himalayas (Guzzella et al. 2011), similar to those
218 from the Norwegian Arctic (Jiao et al. 2009; Evenset et al. 2007), Rocky mountains
219 (Usenko et al. 2007), Andean mountains (Borghini et al. 2005), and the central TP
220 (Zhang et al., 2003; Cheng et al. 2014) but significantly lower than those in European
221 mountains (Grimalt et al. 2004). The elevated concentrations in the TP might be
222 explained by the plateau's proximity to the source regions such as Indian subcontinent
223 and China (Yang et al. 2008). Studies have documented that selected POPs on the TP
224 can be transported from the Indian subcontinent by the southern Asian monsoon (Yang
225 et al. 2008, 2013; Wang et al. 2008).

226 The concentrations of ΣDDT and ΣHCH generally peaked in sediment layers
227 corresponding to the 1970s-90s and in the top sediment layers (Fig. 2). Organic matter
228 usually plays an important role in the distribution and retention of organic contaminants
229 in sediments (Klanova et al., 2008). The core averaged OM content in this study ranged
230 from 48 (Lake Peiku Co) to 200 mg/g (Lake Cuo E), with an average of 117 mg/g.
231 However, no significant correlation between concentration and OM content was
232 observed for all the studied lakes ($P > 0.05$). When concentrations were normalized by
233 OM content, the vertical distribution pattern of HCH and DDT didn't change much (Fig.
234 3), suggesting OM content itself does not cause the significant increase in OCP
235 concentrations in sediment. Thus, OM content played an insignificant role in affecting

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

237 **Input flux and time trends**

238 The input flux of DDT and HCH showed obvious increasing trends for all the studied
239 lakes since the 1950s, when these pesticides were first applied all over the world (Fig.
240 2). The heavy use of OCPs in Indian Subcontinent and China is reflected by the peaks
241 during the 1970s-80s in the input fluxes observed in the lake sediments of this work.

242 However, it is noted that input fluxes of DDT and HCH continued to increase in
243 most of lakes at the top layer sediments (Fig. 2). Since the global ban of DDT and HCH
244 application in agriculture purpose after the late 1980s, their levels in environmental
245 matrices have largely dropped (Li 1999). Although DDT and lindane are still in use in
246 some southern Asian countries, the amount has been greatly reduced in recent years (Li
247 and Macdonald 2005). A recent decreasing trend of OCPs in the air of south India was
248 also evidenced (Rajendran et al. 1999). As expected, deposition fluxes recorded in an
249 ice core from the southern TP were in line with the usage of OCPs in India, which
250 showed a decrease to undetectable levels from the 1980s (Wang et al. 2008). Apparently,
251 the time trends of OCPs in sediment cores observed in this study are quite different
252 from the historical records in Tibetan ice cores in the corresponding recent deposition
253 years. Since there is no official record on the usage of OCPs in this region, the
254 increasing trends of OCPs in top sediment layers implies other local OCP sources may
255 contribute to lake sediments in addition to atmospheric deposition from LRAT sources.

256 The TP and surroundings contain the largest number of glaciers outside the Polar
257 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 temperature in the central TP increased at 0.41°C/yr during the last decade (1997-2006) (Liu et al. 2009). In the past 40 yrs., 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 (Bodal 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 of 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). Amongst, 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 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-90s 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.

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Table1 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
			∑DDT	∑HCH	
Mountain lakes, across TP	2006-07	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	2006-07	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.

Figure legends:

Figure 1 Map showing lake locations.

Figure 2 Temporal trends of concentrations (blue diamonds) and depositional fluxes (red circles) for ΣDDT and ΣHCH in dated sediment cores.

Figure 3 Comparison of temporal trends of OCP concentrations between dry weight basis and OM content basis in Cuo E Lake.

Figure 4 Variations of ratios of α/γ-HCH (A) and o,p′-DDT/p,p′-DDT (B) against deposition year of lake sediments.

Fig. 1 Map showing lake locations.

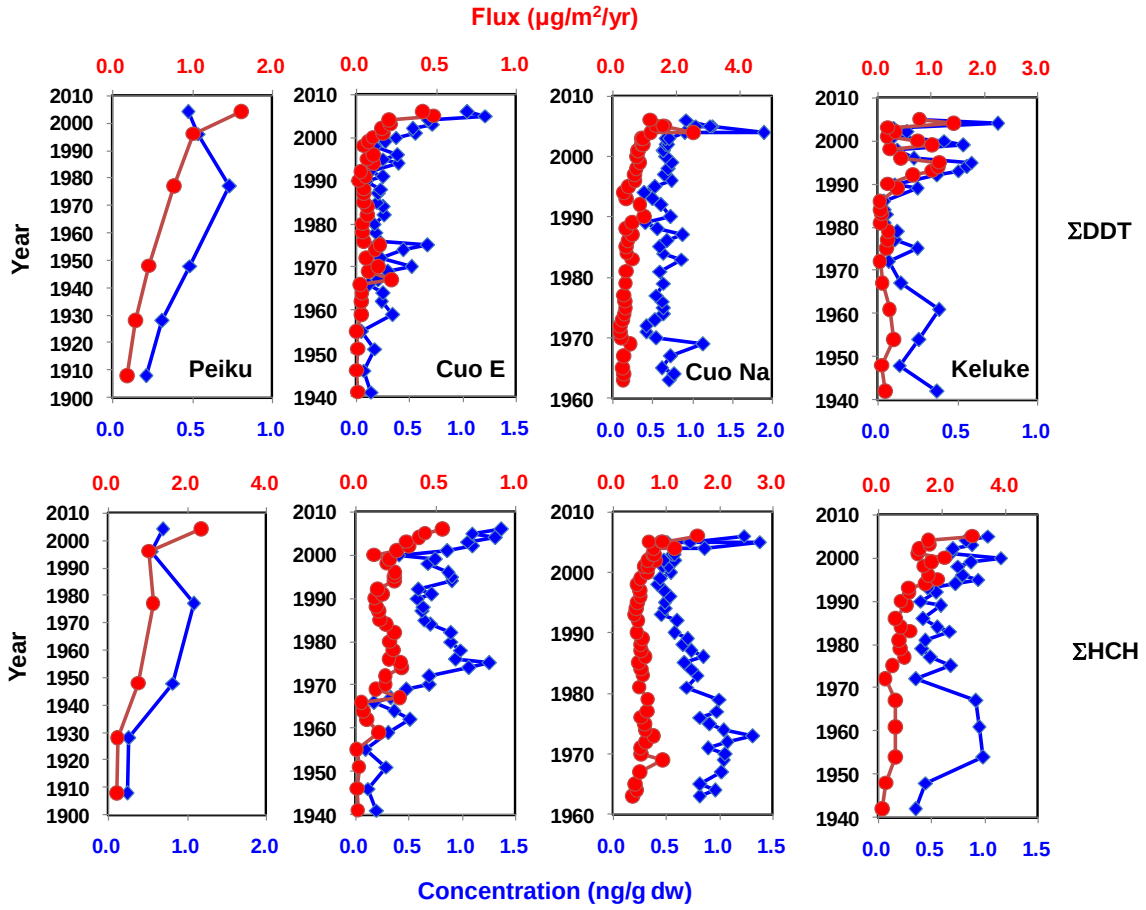


Fig.2 Temporal trends of concentrations (blue diamonds) and depositional fluxes (red circles) for ΣDDT and ΣHCH in dated sediment cores.

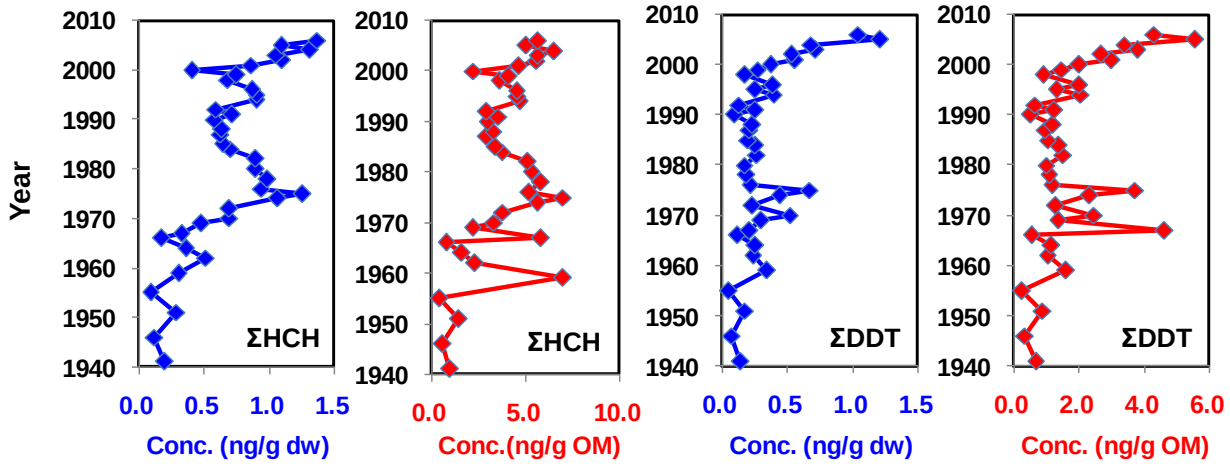
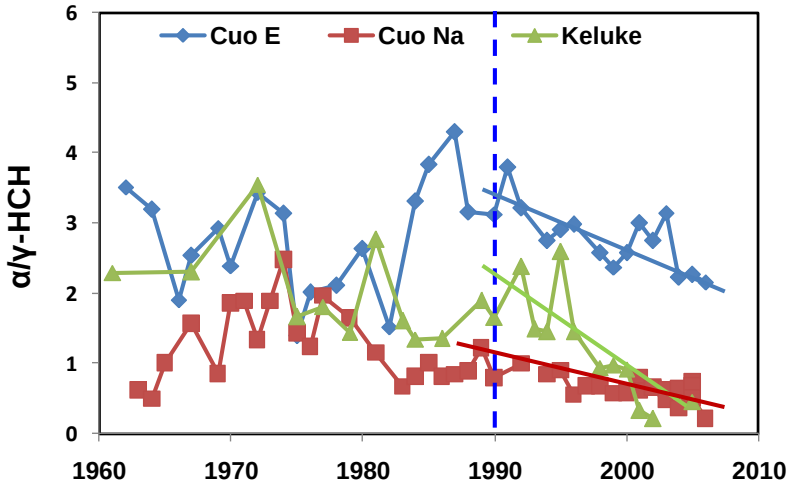
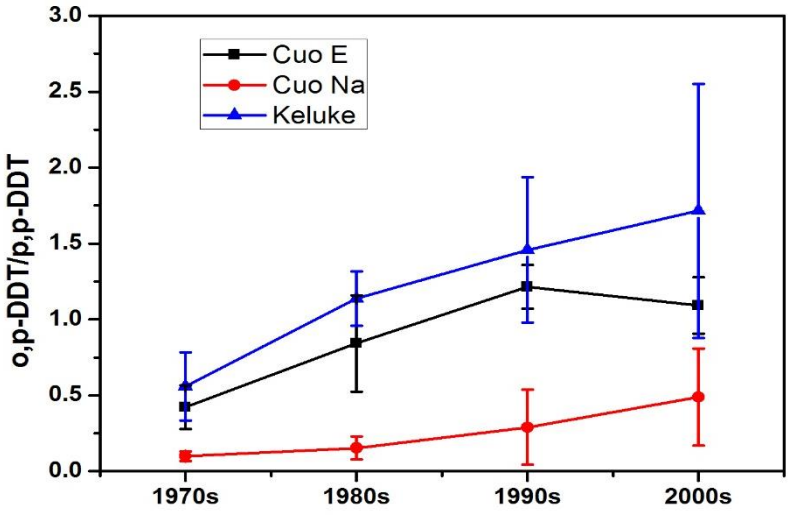


Fig. 3 Comparison of temporal trends of OCP concentrations between dry weight basis and OM content basis in Cuo E Lake.



(A)



(B)

Fig.4 Variations of ratios of α/γ-HCH (A) and o,p′-DDT/p,p′-DDT (B) against deposition year of lake sediments.