Chemosphere 94 (2014) 183–189

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

DDTs and HCHs in sediment cores from the Tibetan Plateau

Hairong Cheng [a], Tian Lin [b,c,*], Gan Zhang [c,d], Guoqing Liu [c,e], Weiling Zhang [c], Shihua Qi [f], Kevin C. Jones [d], Xuewen Zhang [g]

[a] Department of Environmental Engineering, School of Resource and Environmental Sciences, Wuhan University, Wuhan 430079, China
[b] State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China
[c] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[d] Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, UK
[e] Institute of Nuclear Technology, Shenzhen University, Shenzhen 518060, China
[f] Faculty of Environmental Sciences, China University of Geosciences, Wuhan 430074, China
[g] Environmental Monitoring Centre, Environmental Protection Bureau, Xizang (Tibet) Autonomous Region, Lhasa 850000, China

HIGHLIGHTS

- Sediment cores from five critical regions in the Tibetan Plateau were analysed for OCPs.
- The recent increasing trends of OCPs are likely due to the greatest retreat of glaciers.
- The recycling of OCPs in the plateau cryosphere is more sensitive monitor of climate warming.

ARTICLE INFO

Article history:
Received 27 June 2013
Received in revised form 7 September 2013
Accepted 1 October 2013
Available online 31 October 2013

Keywords:
DDTs
HCHs
Sediment core
Time trend
Climate warming
Tibetan Plateau

ABSTRACT

Sediment cores were collected from five critical regions in the Tibetan Plateau and were analysed for OCPs with the objective of examining the time trends and recycling of DDTs and HCHs in the cryogenic area. A concurrent increase of the DDT and HCH concentrations from the late 1980s in Lake Yamzho Yumco, Nam Co and Star Sea were observed. The increasing levels of DDE/DDTs (>0.4) suggested that DDT in the upper layers of the sediment cores may be recycled/"weathered" DDT. Regarding the acceleration of glacier retreat from the 1980s due to global warming, it is suggested that OCPs formerly trapped either in the snow/glacier or in the frozen soil land recently reclaimed in the processes of glacier retreat may have been flushed into the sediment basins. These findings demonstrate the potential impact of global warming on the recycling of POPs in the plateau cryosphere and indicate that the pristine Tibetan Plateau may serve as one of the key probes to the global trend of POPs.

1. Introduction

Persistent organic pollutants (POPs), such as most organochlorine pesticides, are capable of migrating in the atmosphere from warmer places to cooler places. This phenomenon may occur both latitudinally, even at a global scale (Wania and Mackay, 1993) and altitudinally in high mountains (Blais et al., 1998; Carrera et al., 2001; Grimalt et al., 2004; Daly and Wania, 2005). These findings suggest that the cryosphere, i.e., the polar region and cryogenic high mountains, is a significant sink/trap for POPs on the earth (Gregor et al., 1995; Blais et al., 1998; AMAP, 2002b).

As the roof of the world, the Tibetan Plateau encompasses vast cryogenic territory, and many parts of the plateau are considered pristine and minimally contaminated by toxic chemicals. However, many countries and regions around the plateau are current users (for malaria control) and historically important users (agricultural and sanitary usage) of organochlorines. These countries and regions include India (which is/was the world largest consumer of HCH and DDT), Pakistan, Nepal, Thailand and Vietnam, as well as the more developed parts of China. Recent studies showed that the atmospheric transport from the surrounded farm lands was one of the major contributing sources for OCPs in the atmosphere and the fresh snow at the edge of the Tibetan Plateau (Li et al., 2006; Wang et al., 2007). The spruce needle samples along northern slope of central-Himalayas showed that the more volatile OCPs and PAHs positively correlated with altitude (Wang et al., 2006). The mosses and lichen in the southern Himalayas that are directly impacted by the southwestern monsoon exhibited DDT and HCH concentrations were among the highest in the world (Calamari et al., 1991). This finding indicated that the more volatile POPs

* Corresponding author at: State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China.
E-mail address: lintian@vip.gyig.ac.cn (T. Lin).

0045-6535/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.chemosphere.2013.10.012

may also be able to transmit to an altitude up to the middle-upper troposphere, which was recently confirmed by the detection of DDTs and HCB in fresh snow from the East Rongbuk Glacier of Mt. Qomolangma (Wang et al., 2007, 2008).

The Tibetan Plateau has a mean elevation between 4500 m (above the sea level, same below) and 5000 m with isolated mountain massifs of more than 6000–7000 m. Many parts of the plateau are covered by glaciers and snow. The total area of glaciers on the plateau is 104850 km^2, including 40000 km^2 in India and Pakistan and 49873 km^2 in China (WWF, 2005). Since the 1980s, the air temperature has significantly changed on the Tibetan Plateau, which is consistent with global warming. The most recent significant warming period was from the mid-1970s, which was ahead of other places in the world. Due to climate warming, all glaciers, with the exception of several of the larger glaciers on the Tibetan Plateau, have begun shrinking. In the past 40 yrs or more, glaciers have shrunk more than 6606 km^2 on the entire Tibetan Plateau, with the greatest retreat occurring since the mid-1980s and strong retreat being observed since the 1990s. Climate change has shown a great impact on Tibetan lakes (Liu et al., 2009) due to the changing relationship between precipitation, evaporation and the increased water supply from melting glaciers and frozen ground. In addition, climate change also influences the behaviour of pollutants, which impact their cycling in the air, catchments and sediment.

There are few reports on POPs in the environment of the Tibetan Plateau (Fu et al., 2001; Li et al., 2006;Wang et al., 2007; Yang et al., 2007, 2008). In this study, sediment cores were collected from five critical regions on the Tibetan Plateau and were analysed for organochlorine pesticides (OCPs) with the objective of examining their time trend and recycling. In particular, we stress the role of lakes and lake sediment records in remote regions and consider whether recently observed changes in such regions are due to global warming or to other factors.

2. Experimental

2.1. Geographic settings

Lake Yamzho Yumco, Lake Nam Co and Lake Co Ngoin are situated at the southern and central part of the plateau with altitudes of 4500 m, 4800 m and 4700 m, and water areas of 638 km^2, 1962 km^2 and 244 km^2, respectively. Yamzho Yumco is a freshwater lake, and Nam Co and Co Ngoin are saline lakes. The lakes are all fed by glaciers and hence the areas of the lakes change over time. Lake Yamzho Yumco, Lake Nam Co and Lake Co Ngoin are of self-contained watersheds. The Star Sea wetland (or seasonal lake) and the Zoige wetland are situated at the northern and eastern sections of the plateau with altitudes of 4300 m and 3600 m, respectively.

2.2. Sampling

The sampling locations of the sediment cores in the study were positioned with a portable GPS (Garmin Co.), E90°48.3325′/N28°52.4518′ for Lake Yamzho Yumco (water depth 40 m), E91°53.592′/N31°49.993′ for Lake Co Ngoin (water depth 5 m), E90°47.582′/N30°46.913′ for Lake Nam Co (water depth 78 m), E97°20.17′/N35°15.20′ for Star Sea wetland, and E102°30.964′/N32°46.774′ for Zoige wetland (Fig. 1). All of these locations are far away from direct anthropogenic activity. Sediment cores of 15 cm, 10 cm and 9 cm were retrieved with a Kajak gravity corer (KC Denmark Co.) in Lake Yamzho Yumco, Lake Nam Co and Lake Co Ngoin, respectively, and each sample was sectioned onsite at an interval of 0.5 cm. In the Star Sea and Zoige, coring was performed with a soil auger on the frozen wetland. A 12 cm and a 25 cm long core were collected and sectioned at an interval of 2 cm in the Star Sea and 0.5 cm in the Zoige, respectively. In all of the cases, the sediment samples were sealed in aluminium boxes and were stored frozen after returning to the laboratory.

2.3. ^{210}Pb dating

Dating of the sediment cores was conducted by ^{210}Pb dating technology. Details of the procedures were described in the references (Zhang et al., 2002). Briefly, the ^{210}Pb activities in the sediment samples were determined by analysis of the radioactivity of its decay product ^{210}Po, on the assumption that both are at equilibrium. The Po was extracted, purified, and self-plated onto Ag discs at 75–80 °C in 0.5 mol L^{-1} HCl, with ^{209}Po (NIST) used as the yield monitor and tracer in quantification. Counting was performed using a computerised multi-channel a-spectrometer with Au–Si surface barrier detectors. The supported ^{210}Pb was obtained by indirectly determining the α-activity concentration of the supporting parent ^{226}Ra through co-precipitation with $BaSO_4$. In this case, a constant initial ^{210}Pb concentration (CIC) model (McCall et al., 1984) was selected to yield an average sedimentation rate throughout the core.

2.4. Extraction and clean-up

Sediment samples were freeze-dried separately prior to analysis. After large plant fragments were removed with a tweezers, sediments (each 5–10 g) were spiked with 50 ng (5 μL, 10 ppm) of 2,4,5,6-tetrachloro-m-xylene (TCmX) and decachlorobiphenyl (PCB209) as surrogates, and were Soxhlet-extracted with dichloromethane (DCM) for 48 h. Activated copper granules were added to the collection flask to remove elemental sulphur. The extract was concentrated and solvent-exchanged to hexane and further reduced to approximately 5 mL under a gentle nitrogen stream. Before further clean-up, the soil extract was washed with concentrated sulphuric acid. The concentrated extracts were then cleaned up by a chromatograph column packed with 1 g of anhydrous sodium sulphate, 2 g of 1:1 concentrated sulphuric acid/silica gel (middle) and 2 g of silica gel (bottom). OCP was eluted with 20 mL of 3:7 (v/v) DCM/hexane. The effluent was concentrated and solvent-exchanged into hexane on a rotary evaporator and further evaporated to 25 μL (dodecane as 'keeper') under a gentle stream of high purity nitrogen. A known quantity of pentachloronitrobenzene (PCNB) was added as an internal standard prior to instrumental analysis.

2.5. GC-ECD and GC–MS analysis

The OCPs in the sediment core samples (from the lakes) were analysed using a gas chromatograph (Agilent-6890 GC system, Hewlett–Packard, USA) equipped with a ^{63}Ni μ-ECD and a 60 m × 0.25 mm i.d. (0.17 μm film thickness) HP-5MS fused silica capillary column. Helium was used as the carrier gas at 2.5 mL min^{-1} under the constant-flow mode. Helium was filtered through moisture, hydrocarbon, and oxygen filters before entering the GC system. The oven temperature started at 100 °C and increased to 290 °C (10 min hold time) at a rate of 4 °C min^{-1}. The split/splitless injection of a 2 μL sample was performed with a 1 min solvent delay time. The injector and detector temperatures were maintained at 250 °C and 300 °C, respectively. Data were acquired and processed on HP-3365 Chemstation software.

GC–MS analysis was conducted on second batch of samples (from the wetland) using a HP-5972 GC-MSD system (Hewlett–Packard, USA) and operating under the single ion monitoring (SIM) mode. A 30 m × 0.25 mm i.d. (0.25 μm film thickness)

Fig. 1. Map of sampling location in the Tibetan Plateau.

HP-5MS fused silica capillary column was used for the separation. High purity helium was used as the carrier gas at a flow rate of 1.05 mL min^{-1}. The injector and column temperature program was similar to those in the GC-ECD analysis. A 2 μL sample was injected into the split/splitless injector with a 5 min solvent delay. Mass spectra were acquired in the electron impact (EI) mode at 70 eV. Peak confirmation and quantification were performed on a DOS-based HP ChemStation system.

2.6. QA/QC

All chemical standards were purchased from AccuStandard, Inc (New Haven, CT, USA). The instruments were calibrated daily with calibration standards. The GC inlet degradation of DDT (to DDE) was checked daily and controlled within 15%. One method blank and one sample duplicate were analysed along with every batch of 10 field samples. The calculated method detection limits (MDLs) were 0.02–0.06 μg kg^{-1} dw for sediment and 0.03–0.08 μg kg^{-1} dw for soil. Reagent blanks were not observed for DDT and HCH. The percentage recoveries of the surrogate standards were 69 ± 15% for TCmX and 90 ± 5% for PCB209. The data reported were not justified by surrogate recoveries.

3. Results and discussion

3.1. HCH and DDT concentrations

The total HCH (sum of α-, β-, δ-, γ-HCH) concentrations ranged from 1.2 to 9.0 μg kg^{-1}, 0.7 to 2.8 μg kg^{-1}, 0.3 to 1.9 μg kg^{-1}, 0.3 to 0.9 μg kg^{-1} and 0.23 to 20.6 μg kg^{-1} in the core sediments from Lake Yamzho Yumco, Lake Nam Co, Lake Co Ngoin, the Star Sea Wetland and the Zoige Wetland, respectively (Table 1). For the DDTs (sum of p,p′-DDT, p,p′-DDE, p,p′-DDD, o,p′-DDT), the concentrations ranged from 1.0 to 6.3 μg kg^{-1}, 0.4 to 4.1 μg kg^{-1}, 0.67 to 5.9 μg kg^{-1}, 0.2 to 0.4 μg kg^{-1} and 0.60 to 6.2 μg kg^{-1}, respectively. These concentrations are low in comparison to those reported in developed areas of China and India (Mai et al., 2002; Babu Rajendran et al., 2005; Sarkar et al., 2008), reflecting the absence of major pollution sources in these regions. In contrast, the HCH and DDT levels were slightly higher than those observed in European high altitude mountains lakes, such as the Andean Lakes (Borghini et al., 2005), and exhibited similar values to those reported in Canadian lakes (Muir et al., 1995), Lake Baikal (Iwata et al., 1995) and lakes in the Arctic and Antarctic (Loganathan and Kannan, 1994; Muir et al., 1995; Malmquist et al., 2003). These results suggest that the Tibetan Plateau may act as a cold condenser for OCPs due to its dramatic altitudinal gradient and being surrounded by many countries and regions that are current users and historically important users of organochlorines.

3.2. Geographical distribution

As seen in Table 1, the Star Sea wetland had significantly lower mean concentrations of HCHs and DDTs than did the southern lakes. The observed OCP concentrations generally decreased from Lake Yamzho Yumco, to Lake Nam Co, Lake Co Ngoin and the Star Sea Wetland, along a south–north transect on the plateau. In the case of the HCH and DDT fluxes, a similar trend was observed, with higher fluxes in Lake Yamzho Yumco (0.44 ng $cm^{-2}{\cdot}yr^{-1}$ and 0.44 ng $cm^{-2}{\cdot}yr^{-1}$ for DDTs and HCHs, respectively) and much

Table 1
Concentrations and inventories of DDTs and HCHs (μg kg^{-1}) in the sediment cores from the Tibetan plateau.

Location	ΣDDT[a]	ΣHCH[b]	p,p′-DDE/ΣDDT	p,p′-DDE/p,p′-DDT	α-/γ-HCH
	Min–max[c] (mean)	Min–max (mean)	Min–max (mean)	Min–max (mean)	Min–max (mean)
Yamzho Yumco	1.0–6.3 (3.4 ± 1.6[d])	1.2–9.0 (3.4 ± 2.1)	0.15–0.62 (0.34)	0.19–2.3 (0.73)	1.0–3.9 (0.39)
Nam Co	0.4–4.1 (1.8 ± 1.3)	0.7–2.8 (1.5 ± 0.8)	0.03–0.66 (0.31)	0.1–4.6 (1.6)	0.39–0.73 (0.53)
Co Ngoin	0.67–5.9 (1.8 ± 1.5)	0.33–1.9 (0.99 ± 0.51)	0.05–0.96 (0.57)	0.1–2.5 (1.1)	0.3–1.0 (0.66)
Star Sea	0.19–0.38 (0.26 ± 0.07)	0.28–0.90 (0.60 ± 0.27)	0.13–0.85 (0.34)	0.36–0.80 (0.51)	0.05–0.68 (0.30)
Zoige	0.60–6.29 (1.78 ± 1.40)	0.23–20.63 (3.87 ± 5.50)	0.04–0.59 (0.29)	0.52–8.4 (2.8)	–
Average fluxes (ng cm^{-2} yr^{-1})					
Yamzho Yumco	0.44	0.44			
Nam Co	0.31	0.2			
Co Ngoin	0.20	0.10			
Star Sea	0.09	0.22			
Zoige	0.42	0.92			
Inventories (ng cm^{-2}, 1956–2002 and/or 1978–2002)					
Yamzho Yumco	20 (13)[e]	20 (14)			
Nam Co	12 (8)	8 (5)			
Co Ngoin	8 (5)	5 (2)			
Star Sea	(6)	(2)			
Zoige	23 (13)	52 (38)			

[a] ΣDDT: sum of p,p′-DDT, p,p′-DDE, o,p′-DDT and p,p′-DDD.
[b] ΣHCH: sum of α-, β-, δ-, and γ-isomers.
[c] Min = minimum concentration, Max = maximum concentration.
[d] Data in the form of mean ± standard deviation.
[e] Data in parenthesis refer to inventories during 1978–2002.

lower DDT and HCH fluxes in the Star Sea Wetland (0.09 ng cm^{-2}·yr^{-1} and 0.22 ng cm^{-2}·yr^{-1} for DDTs and HCHs, respectively). In a previous study by Yang et al. (2008), the concentrations of HCHs and DDTs in pine needles were found to decrease from the south to the north in the southeast Tibetan Plateau, suggesting important input transported by the warm and humid air flow associated with the Indian Monsoon (see Fig. 1). The accumulation of POPs in high mountains indicates that cold condensation effects are operating on an altitudinal scale, as well as on the latitudinal scale (Davidson et al., 2003; Fernandez and Grimalt, 2003; Wang et al., 2006). However, the four sites in the current study have similar altitudes; therefore, the concentration differences along the altitudinal gradients are negligible. Thus, the geographical distribution of OCPs may possibly reflect the contribution of long-range transport/deposition associated with westerly wind or southwesterly wind.

3.3. Time trends of DDTs and response to climate change

The vertical trends of DDTs in the sediment cores are presented in Fig. 2. Except for Lake Co Ngoin, an increasing trend of DDTs was observed in Lake Yamzho Yumco, Lake Nam Co and the Star Sea Wetland. Unlike those from high latitude lake cores in the Arctic and Antarctic, which, in general, exhibited a later onset of OCPs deposition than the historical global production curve (Muir et al., 1995), the records in the Tibetan lake cores show DDT deposition patterns resembling the production and usage history from the 1960s to 1980s. This finding may be explained by the plateau's proximity to the pollution sources, such as the Indian subcontinent and China, which have experienced heavy use of OCPs, especially HCH and DDT, for agricultural and public health purposes.

Since the global ban on OCP usage in agriculture after the late 1980s, their levels in the low altitude ecosystems have generally dropped (Babu Rajendran et al., 1999; Chen et al., 2000; Monirith et al., 2000). However, there is a recent increasing trend or sharp rebounds of DDTs in the sediment, in contrast to the ice cores, which show a decrease to undetectable levels from the 1980s (Wang et al., 2008). Some studies pointed out that there was no record of the OCP application in history in Tibet (Li et al., 1998; Wang et al., 2005).This means that local emissions of OCPs in the plateau can likely be neglected. The Indian subcontinent and China have experienced heavy use of organochlorine pesticides, such as HCHs and DDT (Santillo et al., 1997; Li et al., 1998). However, the agricultural application of technical DDT was banned in China in 1983 and in India in 1989, and a decreasing trend of DDTs levels are expected, as evidenced by the decreasing trend of DDT observed in the air and green mussels from the east coast of India (Babu Rajendran et al., 1999; Monirith et al., 2000). Although DDT is still used for health services, e.g., in malaria/mosquito control (Santillo et al., 1997), for which there is an exemption under the Stockholm Convention, it is unlikely that the DDT in current use has caused the recent increasing trend or sharp rebounds of DDTs in the Tibetan sediment.

DDT is degraded into DDD under anaerobic conditions and into DDE in aerobic environments (Hitch and Day, 1992). The ratio of DDE/DDTs has been used to identify the possible DDT sources. As shown in Fig. 2, in Lake Yamzho Yumco, the DDE/DDTs ratios fluctuate and increase since the 1980s, and a steady increase of the DDE/DDTs ratio was observed in the Star Sea Wetland, concurrent with the DDT concentration increasing trend. These results suggest that DDTs deposited after the production ban were more likely to be "weathered" DDTs. OCPs can be transported to the cryosphere through airmass, snow and rainfall, and snowfall scavenging is assumed to be the main mechanism, providing a powerful pump for removing contaminants from the atmosphere to the surface (Franz and Eisenreich, 1998). In the past 30 yr or more, due to the climate warming, glaciers have shrunk more than 6606 km^2 on the entire Tibetan Plateau, with the greatest retreat since the mid-1980s. Glacier and snow melt due to climate warming can release archived contaminants accumulated during years of higher fluxes (Blais et al., 1998). According to Blais et al. (2001), in the Antarctic,

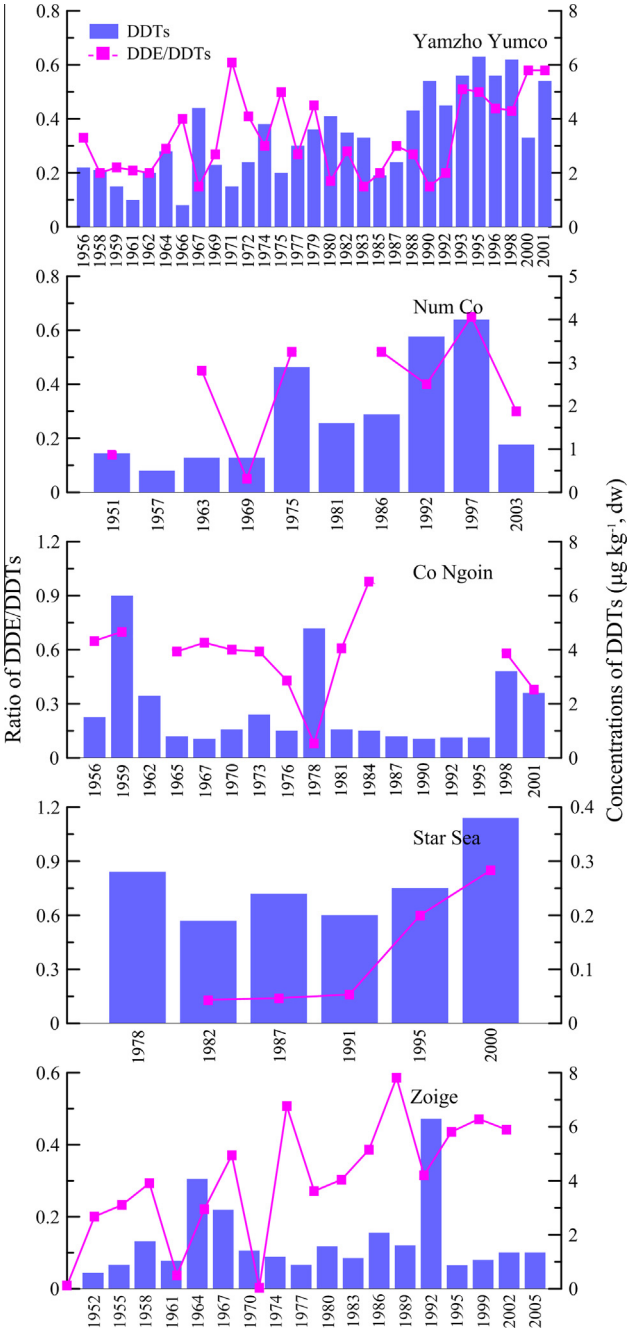

Fig. 2. Historical profiles of DDTs in dated sediment cores from the Tibetan Plateau.

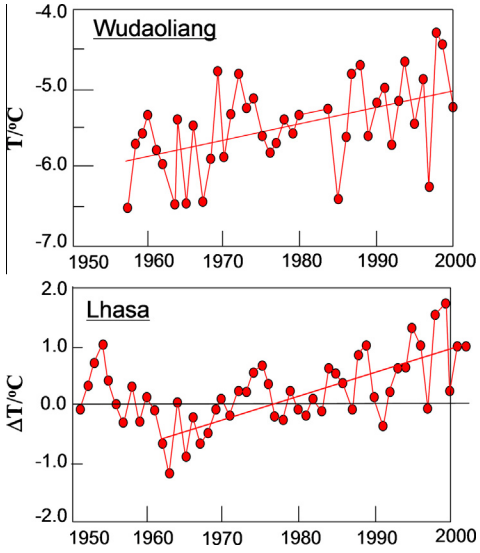

Fig. 3. Temperature trend recorded in the reference sites of Wudaoliang and Lhasa.

approximately 50–97% of the OCPs in the lakes fed by melting glacier water may come from glaciers. A warmer climate is expected to enhance the amount of glacial water discharge into lakes and to deposit more DDTs into lake sediments. Bogdal et al. (2009, 2010) also demonstrated that the release of POPs by glaciers is currently increasing and accounts for the observed increase after the 1990s in the concentrations in lake sediment. The recent increasing trend or sharp rebound of DDT on the Tibetan Plateau lake sediment except the wetland sediment, therefore, is likely due to the accelerated glacier retreat caused by climate warming (Fig. 3), which mobilised the DDTs formerly trapped either in the snow/glacier or in the frozen soil to the sedimentary basins.

Climate warming plays an important role in the water balance of lakes and influences the behaviour and fate of pollutants. There are two significant concerns regarding the glacier/snow melt returning OCPs to lake sediment. Generally, for large glaciers, the melting or ablation often occurs in zones where old ice of the pre-industrial age is emerging (AMAP, 2002a,b). This ice would contain little or no contaminant burden and would act to dilute any contaminants released to aquatic environments (AMAP, 2002a,b). For smaller ice caps, more recent layers of snow and ice might contain higher potential pollutant loads. The impact of increased global temperatures is more significant on the small ice caps than the large glaciers. Thus, in a number of cases, the concentration of OCPs in low flow glacier meltwater times will be higher than in abundant times (AMAP, 2002a,b). Most importantly, as found in Antarctica, the concentrations of DDTs in snow and ice are over 10 times that in lake water (Tanabe et al., 1983), implying an effective DDT cleaning process in lakes. This may suggest that the melting glacier water was to be the source of OCPs in the lake water.

The second concern is the hydrological condition of different lakes. A warmer climate is expected to enhance the amount of glacial water discharge, but the increased temperature increases the evaporation rate. It is indicated that (Shao et al., 2007), in the Qing-Tibetan Plateau, most of the lakes showed negative water balance due to the evaporation driven by increased temperature. Some lakes fed mainly by glacier meltwater, an accelerated retreat of the glaciers in recent times led to an enlargement of the lake areas (Fig. 4) (Shao et al., 2007). With low aqueous solubility and low vapour pressure, organochlorines, DDT in particular, tend to be absorbed by lake sediments and removed from the water column (Eisenreich et al., 1989). For Arctic lakes, they tend to retain only a small fraction of the contaminants received (AMAP, 2002a), and most of the contaminants deposited in the drainage basins are transported across the lake surface in a low density layer under the ice to exit with out-flowing water (AMAP, 2002a). For the four Tibetan lakes in the current study, there is less out-flow, except for the Star Sea Wetland. Nam Co is the largest lake in Tibet; the melted snow and ice of the Nyainqentanglha Mountains form the main water supply of Nam Co. Lake Yamzho Yumco is surrounded by many snow-capped mountains and is fed by numerous small streams; the lake does have an outlet stream at its far western end. For these closed inland lakes, DDT tends to be associated with particles and is removed from the water column and deposited to the sediment whenever the lake shrinks or expands (Fig. 4).

In summary, we suggest that the rise of the temperature may drive more melt-water of glaciers, resulting in an increase of DDT runoff from snow/ice and frozen soil, which is responsible for the

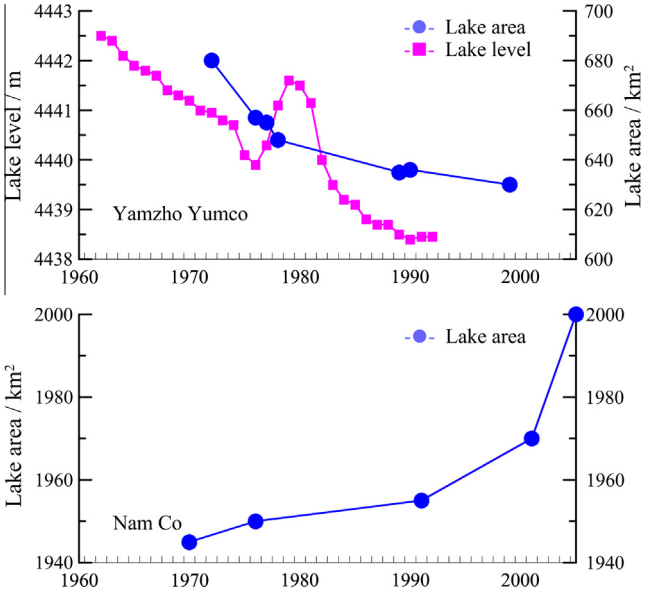

Fig. 4. Lake water level (area) recorded in the Lake Yamzho Yumco and Lake Num Co (Data from the references Yang et al., 2004; Ye et al., 2007; Zhu et al., 2010).

increasing trend of DDT concentrations in the recent sediment. In addition, compared to Arctic lakes, the increasing trend is more obvious in these closed inland lakes in the plateau.

3.4. Time trends of HCHs

The vertical trends of HCHs in the sediment cores are shown in Fig. 5. In Lake Yamzho Yumco, Lake Num Co and the Star Sea Wetland, the HCH concentrations remain relatively constant until the late 1970s, at which point the concentration abruptly reaches the first peak in approximately 1982. After that, the concentration declines to a low level in the mid-1980s and then shows an increasing trend towards the upper layer sediment. In the three lake cores, the HCH concentrations showed a significant decrease around the mid-1980s compared with the vertical trends of the DDTs. Having good water solubility, the HCHs tend to be retained in water, and accumulation in the sediment is determined by both the air–water exchange and the meltwater from glaciers and snow. Thus, the dilution effect or evaporation of melted glacier/snow water had a more significant impact on the HCHs than the DDTs. Similar to the DDTs, the vertical distribution of HCHs reveals an erratic pattern in Lake Co Ngoin, suggesting that there may be other factors affecting the behaviour and fate of HCHs in the lake sediment. In sharp contrast with the DDTs, the sedimentary record of HCHs in the Zoige Wetland was in good agreement with their regional application history in China, where HCH concentrations decreased since the early 1980s. This suggests that the Zoige Wetland was under the influence of HCH usage from China's inland. Due to the lack of catchment area, the HCHs accumulation in the sediment is determined by the direct atmospheric deposition without meltwater from glaciers and snow.

Technical HCH, once the most heavily used pesticide in India with an annual consumption exceeding 6×10^7 kg (Santillo et al., 1997), was banned in 1997, but lindane (γ-HCH) has been used as a replacement since that time. The ratio of α-/γ-HCH has been used to monitor the source and historical use of HCHs and to act as a marker for the atmospheric transport of lindane (Willett et al., 1998). In the core sediments, α-HCH and γ-HCH were the dominant HCH isomers, and the α-/γ-HCH ratios are mostly below 1, which is much lower than that of technical HCH. The lower

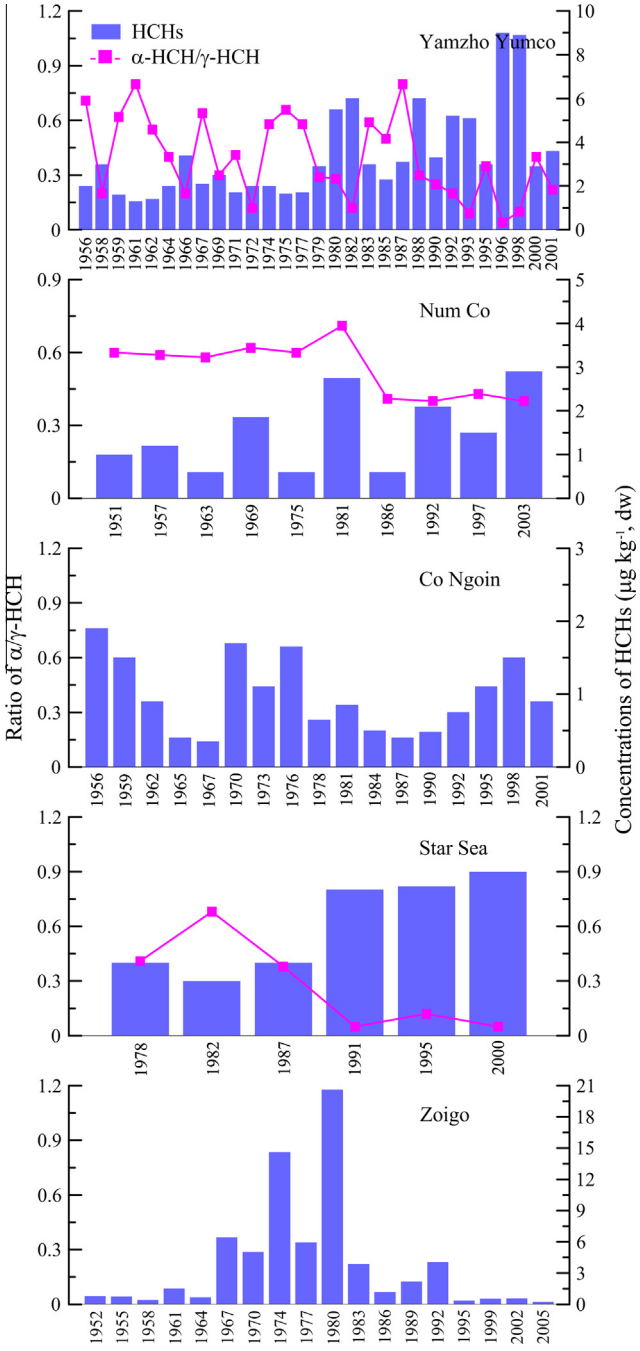

Fig. 5. Historical profiles of HCHs in dated sediment cores from the Tibetan Plateau.

α-/γ-HCH ratios may indicate the preferential degradation of α-HCH or the contribution of recently used lindane.

4. Conclusions

In this study, sediment cores were collected from five critical regions in the Tibetan Plateau and were analysed for DDTs and HCHs with the objective of examining their time trends. Recent increasing trends or sharp rebounds of OCPs in the sediments were observed, most likely due to the retreat of glaciers in response to recent climate warming. In particular, the time trends of OCPs were a more sensitive monitor of climate warming in the closed-basin lakes fed mainly by glacier meltwater. It is different from Arctic lakes that tend to retain only a small fraction of the contaminants they

receive, and most of the contaminants deposited in the drainage basin are transported across the lake surface in a low density layer under the ice to exit with out-flowing water. Lake sediments are considered as the important sink of OCPs released from melting glacier water in the plateau. These findings demonstrated the potential impact of global warming on the recycling of POPs in the plateau's cryosphere.

Acknowledgments

This work was partly financially supported by NSFC (Nos. 41125014 and 40821003). Dr. Gan Zhang wishes to thank the UK Royal Society (RS-NSFC Joint Project) for funding his work in LU.

References

AMAP, 2002a. Influence of Global Climate on Contaminant Pathways Report. Arctic Monitoring and Assessment Programme.

AMAP, 2002b. Persistent Organic Pollutants (POPs) Report. Arctic Monitoring and Assessment Programme.

Babu Rajendran, R., Venugopalan, V.K., Ramesh, R., 1999. Pesticide residues in air from coastal environment, South India. Chemosphere 39, 1699–1706.

Babu Rajendran, R., Imagawa, T., Tao, H., Ramesh, R., 2005. Distribution of PCBs, HCHs and DDTs, and their ecotoxicological implications in Bay of Bengal, India. Environ. Int. 31, 503–512.

Blais, J.M., Schindler, D.W., Muir, D.C.G., Kimpe, L.E., Donald, D.B., Rosenberg, B., 1998. Accumulation of persistent organochlorine compounds in mountains of western Canada. Nature 395, 585–588.

Blais, J. M., Schindler, D. W., Muir, D. C. G., Sharp, M., Donald, D., Lafreniere, M., Braekevelt, E., Strachan, W.M.J., 2001. Melting glaciers are a dominant source of persistent organochlorines to subalpine Bow Lake in Banff National Park, Canada. Ambio 30, pp. 410–415.

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. Environ. Sci. Technol. 43, 8173–8177.

Bogdal, C., Nikolic, D., Luthi, M.P., Schenker, U., Scheringer, M., Hungerbühler, K., 2010. Release of legacy pollutants from melting glaciers: model evidence and conceptual understanding. Environ. Sci. Technol. 44, 4063–4069.

Borghini, F., Grimalt, J.O., Sanchez-Hernandez, J.C., Barra, R., Garcia, C.J., Focardi, S., 2005. Organochlorine compounds in soils and sediments of the mountain Andean Lakes. Environ. Pollut. 136, 253–266.

Calamari, D., Bacci, E., Focardi, S., Gaggi, C., Morosini, M., Vighl, M., 1991. Role of plant biomass in the flobal environmental partitioning of chlorinated hydrocarbons. Environ. Sci. Technol. 25, 1489–1495.

Carrera, G., Fernnandez, P., Vilanova, R.M., Grimalt, J.O., 2001. Persistent organic pollutants in snow from European high mountain areas. Atmos. Environ. 35, 245.

Chen, J.F., Xia, X.M., Ye, X.R., Jin, H.Y., 2000. Marine organic pollution history in the Changjiang Estuary and Zhejiang coastal area-HCHs and DDTs stratigraphical records. Mar. Pollut. Bull. 45, 391–396.

Daly, G.L., Wania, F., 2005. Organic contaminants in mountains. Environ. Sci. Technol. 39, 385–398.

Davidson, D.A., Wilkinson, A.C., Blais, J.M., Kimpe, L.E., Mcdonald, K.M., Schindler, D.W., 2003. Orographic cold-trapping of persistent organic pollutants by vegetation in mountains of western Canada. Environ. Sci. Technol. 37, 209–215.

Eisenreich, S.J., Capel, P.D., Robbins, J.A., Bourbonniere, R., 1989. Accumulation and diagenesis of chlorinated hydrocarbons in lacustrine sediments. Environ. Sci. Technol. 23, 1116–1126.

Fernandez, P., Grimalt, J.O., 2003. On the global distribution of persistent organic pollutants. Chimia 57, 514–521.

Franz, T.P., Eisenreich, S., 1998. Snow scavenging of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in Minnesota. Environ. Sci. Technol. 32, 1771–1778.

Fu, S., Chu, S.G., Xu, X.B., 2001. Organochlorine pesticide residue in soils from Tibet, China. Bull. Environ. Contam. Toxicol. 66, 171–177.

Gregor, D.J., Peters, A.J., Teixeira, C., Jones, N., Spencer, C., 1995. The historical residue trend of PCBs in the Agassiz Ice Cap, Ellesmere Island, Canada. Sci. Total Environ. 160 (161), 117–126.

Grimalt, J.O., Borghini, F., Sanchez-Hernandez, J.C., Barra, R., Torres Garcia, C.J., Focardi, S., 2004. Temperature dependence of the distribution of organochlorine compounds in the mosses of the Andean mountains. Environ. Sci. Technol. 38, 5386–5392.

Hitch, R.K., Day, H.R., 1992. Unusual persistence of DDT in some Western USA soils. Bull. Environ. Contam. Toxicol. 48, 259–264.

Iwata, H., Tanabe, S., Ueda, K., Tatsukawa, R.M., 1995. Persistent organochlorine residues in air, water, sediments, and soils from the Lake Baikal region Russia. Environ. Sci. Technol. 29, 792–801.

Li, Y.F., Cai, D.J., Singh, A., 1998. Technical hexachlorocyclohexane use trends in China and their impact on the environment. Arch. Environ. Contam. Toxicol. 35, 688–697.

Li, J., Zhu, T., Wang, F., Qiu, X.H., Lin, W.L., 2006. Observation of Organochlorine Pesticides in the Air in Mt. Everest Region. Ecotoxicol. Environ. Safety 63, 33–41.

Liu, J., Wang, S., Yu, S., Yang, D., Zhang, L., 2009. Climate warming and growth of high-elevation inland lakes on the Tibetan Plateau. Global Planet. Change 67, 209–217.

Loganathan, B.G., Kannan, K., 1994. Global organochlorine contamination trends: an overview. Ambio 23, 187–191.

Mai, B.X., Fu, J.M., Sheng, G.Y., Kang, Y.H., Lin, Z., Zhang, G., Min, Y.S., Zeng, E.Y., 2002. Chlorinated and polycyclic aromatic hydrocarbons in riverine and estuarine sediments from Pearl River Delta, China. Environ. Pollut. 117, 457–474.

Malmquist, C., Bindler, R., Renberg, I., Van Bavel, B., Karlsson, E., Anderson, N.J., Tysklind, M., 2003. Time trends of selected persistent organic pollutants in lake sediments from Greenland. Environ. Sci. Technol. 37, 4319–4324.

McCall, P.L., Robbins, J.A., Matisoff, G., 1984. 137Cs and210Pb transport and geochronologies in urbanized reservoir with rapidly increasing sedimentation rates. Chem. Geol. 44, 33–65.

Monirith, I., Nakata, H., Watanabe, M., Takahashi, S., Tanabe, S., Seang Tana, T., 2000. Organochlorine contamination in fish and mussels from Cambodia and other Asian countries. In: Tanabe, S. (Ed.), Mussel watch: Marine pollution monitoring in Asian waters. Center for Marine Environmental Studies (CMES), Ehime University, Japan.

Muir, D.C.G., Grift, N.P., Lockhart, W.L., Wilkinson, P., Billeck, B.N., Brunskill, G.J., 1995. Spatial trends and historical profiles of organochlorine pesticides in Arctic lake sediments. Sci. Total Environ. 160 (161), 447–457.

Santillo, D., Johnston, P., Stringer, R., 1997. A catalogue of gross contaminantion: organochlorine production and exposure in India. Pest. News 36, 4–6.

Sarkar, S.K., Bhattacharya, B.D., Bhattacharya, A., Chatterjee, M., Alam, A., Satpathy, K.K., Jonathan, M.P., 2008. Occurrence, distribution and possible sources of organochlorine pesticide residues in tropical coastal environment of India: an overview. Environ. Int. 34, 1062–1071.

Shao, Z.G., Zhu, D.G., Meng, X.G., Zheng, D.X., Qiao, Z.J., Yang, C.B., Han, J.E., Yu, J., Meng, Q.W., Lü, R.P., 2007. Characteristics of the change of major lakes on the Qinghai–Tibet Plateau in the last 25 years. Geol. Bull. China 12, 1633–1645 (in Chinese).

Tanabe, S., Hidaka, H., Tatsukawa, R., 1983. PCBs and chlorinated hydrocarbon pesticides in Antarctic atmosphere and hydrosphere. Chemosphere 12, 277–288.

Wang, T.Y., Lu, Y.L., Zhang, H., Shi, Y.J., 2005. Contamination of persistent organic pollutants (POPs) and relevant management in China. Environ. Int. 31, 813–821.

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. Sci. Total Environ. 372, 193–202.

Wang, F., Zhu, T., Xu, B.Q., Kang, S.C., 2007. Organochlorine pesticides in fresh-fallen snow on East Rongbuk Glacier of Mt. Qomolangma (Everest). Sci. China Series D: Earth Sci. 50, 1097–1102.

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. Atmos. Environ. 42, 6699–6709.

Wania, F., Mackay, D., 1993. Global fractionation and cold condensation of low volatility organochlorine compounds in polar regions. Ambio 22, 10–18.

Willett, K.L., Ulrich, E.M., Hites, R.A., 1998. Differential toxicity and environmental fates of hexachlorocyclohexane isomers. Environ. Sci. Technol. 32, 2197–2207.

WWF, 2005. An overview of glaciers, glacier retreat, and subsequent impacts in Nepal, India and China: Part 3, an overview of glaciers, retreating glaciers, and their impact in the Tibetan Plateau.

Yang, X.D., Wang, S.M., Kamenik, C., Schmidt, R., Shen, J., Zhu, L.P., Li, S.F., 2004. Diatom assemblages and quantitative reconstruction for paleosalinity from a sediment core of Chencuo Lake, southern Tibet. Sci. China Series D Earth Sci. 47, 522–528.

Yang, R., Yao, T., Xu, B., Jiang, G., Xin, X., 2007. Accumulation features of organochlorine pesticides and heavy metals in fish from high mountain lakes and Lhasa River in the Tibetan Plateau. Environ. Int. 33, 151–156.

Yang, R., Yao, T., Xu, B., Jiang, G., Zheng, X., 2008. Distribution of organochlorine pesticides (OCPs) in conifer needles in the southeast Tibetan Plateau. Environ. Pollut. 153, 92–100.

Ye, Q., Zhu, L., Zheng, H., Naruse, R., Zhang, X., Kang, S., 2007. Glacier and lake variations in the Yamzhog Yumco Basin in the last two decades using remote sensing and GIS technologies. J. Glaciol. 53, 673–676.

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.

Zhu, L.P., Xie, M.P., Wu, Y.H., 2010. Quantitative analysis of lake area variations and the influence factors from 1971 to 2004 in the Nam Co Basin of the Tibetan Plateau. Chin. Sci. Bull. 55, 1294–1303.