

A 50-years record of dichloro-diphenyl-trichloroethanes and hexachlorocyclohexanes in lake sediments and penguin droppings on King George Island, Maritime Antarctic

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Abstract: Since the ban on the use of organochlorine pesticides (OCPs) such as dichloro-diphenyl-trichloroethane (DDT) and hexachlorocyclohexane (HCH) in agriculture, their levels have generally dropped. In a number of cases, however, the levels of these OCPs were found to be unchanging or even increasing after the ban. With the aim to unveil the possible causes of these exceptions, we collected two lake cores from King George Island, West Antarctica, and determined their accumulation flux profiles and temporal trends of these OCPs. In the lake core sediments with glacier meltwater input, the accumulation flux of DDT shows an abnormal peak around 1980s in addition to the expected one in 1960s. In the lake core sediments without glacier meltwater input, the accumulation flux of DDT shows a gradual decline trend after the peak in 1960s. This striking difference in the DDT flux profiles between the two lake cores is most likely caused by the regional climate warming and the resulted discharge of the DDT stored in the Antarctic ice cap into the lakes in the Antarctic glacier frontier. Furthermore, to investigate the change of OCPs loadings in the Antarctic coastal ecosystem, we reconstructed the HCH and DDT concentration profiles in penguin droppings and observed a gradual increase for the former and a continuous decrease for the latter during the past 50 years. The increase of HCH seems to be due to the regional warming from the early 1970s and the resulted HCH discharge to the coastal ecosystem by glaciers' meltwater and the illegal use of HCH in the Southern Hemisphere in the recent decade. The different temporal trends of HCH and DDT accumulation rate in the lake core with glacier meltwater input and the aged penguin droppings can be explained by their different water-soluble property.

Keywords: organochlorine pesticides (OCPs); DDT and HCH; lake sediments; penguin droppings; temporal trend; climate warming

Introduction

Organochlorine pesticides (OCPs), such as dichloro-diphenyl-trichloroethane (DDT) and hexachlorocyclohexane (HCH), are well-known environmental contaminants because of their persistent (Hendriksen, 1996; Bidleman, 1999), bio-accumulative capacity (Connell, 1999; Hop, 2002) and global distribution (Wania, 1993; 1996). Over 2.6 and 10 million tons of DDT and HCHs, respectively, have been used widely in agriculture and put a heavy burden on the environment (Voldner, 1995; Li, 1999).

After the first report of DDT in Antarctic penguin tissues by Sladen *et al.* (Sladen, 1966) and in snow by Peterle (Peterle, 1969), most countries banned the use of OCPs in agriculture (Voldner, 1995). To assess the effect of the ban and other environmental regulations, numerous lake sediments have been sampled and examined (Loganathan, 1994; Barra, 2001; Malmquist, 2003). As expected, the OCPs levels in the low-latitude ecosystems have generally dropped. In a number of cases, however, the OCPs levels in the polar or other remote lake sediments were found to be constant or even increasing after the ban (Reviewed, 1994). For example, the OCPs levels in most marine lives from the polar region remained constant or even had a slight increase (Aono, 1997; Macdonald, 2000). These exceptions were usually attributed to the inaccuracies in DDT determination (Muir, 1995) and other obscure factors (Addison, 1986; Norstrom, 1988; Rawn, 2000).

With the aim to unveil the possible causes of the abnormal temporal trends of OCPs in lake sediments (Muir, 1995; Rawn, 2000), we collected two lake cores from King George Island, West Antarctica, with one fed by melting glacier water and the other by annual precipitation.

According to our knowledge, the long-term temporal trends of OCPs in Antarctica are also poorly understood due to the lack of continuous OCPs records in Antarctic lakes except of several OCPs' analysis on wildlife and surface sediments in lakes (Sarkar, 1994; Pu, 1995; Aono, 1997). In this paper, we reported the temporal OCPs profiles in the two lake cores over the past 50 years and their differences and discussed the possible causes.

1 Materials and methods

1.1 Sampling

The research material, named as NR core, 12.5 cm long and 12 cm in diameter, was collected in March 2000 from Niudu Lake about 50 m from the Nelson Ice Cap (62°18' S, 59°03' W), West Antarctica. Niudu Lake was fed by melting glacier water and annual snow during austral summer (December to next year February) (Fig. 1). It has a surface area of 0.04 km², average depth of 0.5 m and maximum depth of 1.0 m. The NR core was sliced at 0.5 cm intervals in clean room into twenty-five subsamples and then stored in solvent-cleaned jars. A comparison core containing penguin droppings, named as AX core, 16 cm long and 12 cm in diameter, was collected from a small pond fed only by annual precipitation in the austral summer of 1999 from Ardley Island (62°13' S, 58°56' W), which is defined as the site of special scientific interest by the Scientific Commission on Antarctic Research (SCAR), in Maxwell Bay (Fig. 1). The AX core was sliced in the field at 2 cm intervals into eight subsamples and then stored in solvent-cleaned jars.

1.2 Organochlorine residue analysis

All subsamples were stored at -24°C prior to organochlorine pesticide analysis. Organochlorine residue in the total 33 freeze-dried and homogenized subsamples were

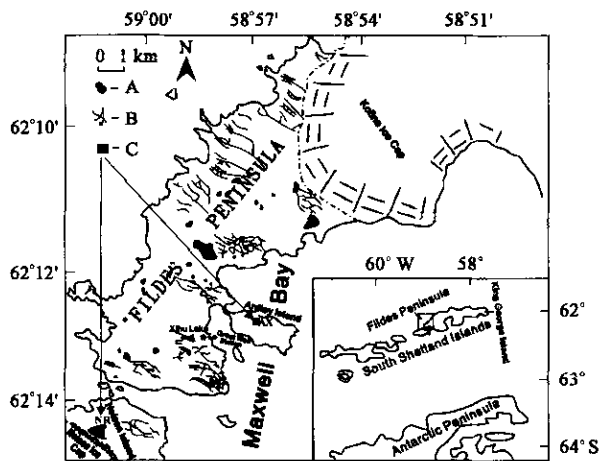


Fig. 1 The sampling sites of the NR lake core near Nelson Ice Cap and the AX lake core in Ardley Island, West Antarctica. Tag (A), (B) and (C) represent lakes, river sand sampling sites (pointed by two arrows) respectively.

performed at Pesticide Residue Analysis Laboratory of China Agricultural University. Sample preparations consisted of extraction and cleanup according to China National Standard (No: GB/T 5009.19—1996). Briefly, 10 ml acetone was added to subsamples of 10 g to extract DDTs (*p*, *p'*-DDT, *p*, *p'*-DDD, *p*, *p'*-DDE and *o*, *p'*-DDT) and HCHs (present α -HCH, β -HCH, γ -HCH and δ -HCH) and then the bottles were shaken for 2 h on a electric shaker at 30 times/min rate. After that, 20 ml petroleum ether was added to extract organochlorines from the acetone solution. Na_2SO_4 solution was then added and the upper clear solution was leached through anhydrous Na_2SO_4 crystal. The filtrate was concentrated into 0.5 ml in pear-shaped bottle using rotary evaporator and then diluted to 5 ml in petroleum ether. The extract was subjected to sulfuric acid clean-up (Barra, 2001). A 2.5 μl aliquot was injected in a HP-4890D GC equipped with a Ni^{63} ECD and HP-35 MS fused silica capillary column (30 m \times 0.25 mm i. d., 0.25 μm film thickness). The carrier gas was nitrogen at 110 kPa. Oven temperature was set and held at 120 $^\circ\text{C}$ for 1 min, then increased to 180 $^\circ\text{C}$ by 18 $^\circ\text{C}/\text{min}$ and held for 5 min, then increased to 230 $^\circ\text{C}$ by 10 $^\circ\text{C}/\text{min}$ and held for 10 min, finally increased to 265 $^\circ\text{C}$ by 20 $^\circ\text{C}/\text{min}$ and held for 30 min. Injector temperature was 270 $^\circ\text{C}$ and detector temperature was 280 $^\circ\text{C}$. A HP-5973 GC-MS was used to identify isomers of DDT and its metabolites and isomers of HCHs in selected samples.

Recovery rates for DDTs and HCHs were determined by spiking pre-cleaned sediments with a mixture of standard solutions of 100 ng/g to be 83.3%—89.8% and 87.1%—89.9% for DDTs and HCHs, respectively. The data are reported here with no correction. Instrument calibrations and quantitations were performed against pure reference standards; daily blank samples were analyzed with each batch of samples and positive peaks were not detectable. Detection limits were 0.02 ng/g dw for all analytes considering the noise-to-signal ratio greater than 3. All samples were performed in duplicate, and the determinations are presented as geometric mean.

1.3 Organic carbon analysis

Total organic carbon (TOC) in the Niudu Lake

sediments is very low at 0.1%—0.3% (Liu, 2004), implying that the NR core is free of significant bio-interfusion. Herein, only the air-dried subsamples of AX core were powdered and homogenized in a clear agate mortar to determine TOC according to the method of Gaudette *et al.* (Gaudette, 1974). Briefly, 10 ml of 1 mol/L $\text{K}_2\text{Cr}_2\text{O}_7$ solution was added to 0.5 g of sediments, then 20 ml of concentrated sulfuric acid was added and the mixture was gently shaken, and left to digest for 30 min. The solution was then diluted to 200 ml with distilled water and 10 ml of phosphoric acid and 0.2 g of NaF were added. Finally, the solution was cooled and titrated with anhydrous ferrous sulfate ammonium.

1.4 Dating

The chronological control of NR and AX cores was based on ^{210}Pb and ^{137}Cs dating techniques. The activities of ^{210}Pb in sediments were determined by γ -ray spectrometer with a solid-state Ge(Li) detector (EG & Gortec Co. LTD) under low background in the shield room. The activity of unsupported ^{210}Pb was calculated by subtracting supported ^{210}Pb as the measures of ^{226}Ra from the total ^{210}Pb activities in the sediments (Table 1). The unsupported ^{210}Pb activities show an overall decrease downward in two cores indicating the lack of reworking after deposition. We calculated the age using CRS model as described by Appleby *et al.* (Appleby, 1995) in the same region assuming a half-life of 22.3 years for ^{210}Pb . To verify the ^{210}Pb dating results, the contents of ^{137}Cs in the sediments were determined. The time mark around 1964 of the maximum ^{137}Cs fallout works well in the AX core, but fails in all NR subsamples because the ^{137}Cs activities are below detection limit. Based upon these two dating techniques, the bottom data of the NR and the AX cores were determined at 1924 and 1946, respectively.

2 Results and discussion

2.1 Sedimentary environments

The sediments in Niudu Lake and AX pond are mainly from aquatic transport via melting snow water in the watershed. The melting glacier, even though discharging a large amount of meltwater, does not seem to be a considerable source for the sediments because the melting glacier river only flows through the iced base.

The OCPs compounds in Niudu Lake and AX pond have more complex sources. For Niudu Lake, they can be from direct atmospheric deposition into its surface and watershed and the supply by melting glacier. The average concentrations of DDTs and HCHs in the NR core are 11.20 and 11.91 ng/g, respectively, much higher than 0.10 ± 0.04 ng/g ($n = 5$) and 0.21 ± 0.10 ng/g ($n = 5$) in the surface weathering soil on King George Island (Pu, 1995). Therefore, the contribution from the direct atmospheric deposition is about 0.9%—1.8% of the OCPs loading in the core; and 98% of the OCPs in the core are likely derived from the annual precipitation in the watershed and the meltwater of Nelson Ice Cap. In fact, according to the researches on the inventories of OCPs in Canada melting glacier-fed lakes (Blais, 2001), melting glacier covers about 50%—97% of the total influx in lakes.

Table 1 Concentrations(ng/g dw) of DDTs and unsupported ^{210}Pb activities(Bq/kg dw) at different depths in the NR and AX cores

Depth, cm		Unsupported ^{210}Pb , Bq/kg		<i>o, p'</i> -DDT		<i>p, p'</i> -DDT		<i>p, p'</i> -DDD		<i>p, p'</i> -DDE		DDTs	
NR	AX	NR	AX	NR	AX	NR	AX	NR	AX	NR	AX	NR	AX
0-0.5	0-2	ND	105.23 ± 24.5	3.95	0.80	12.83	< 0.02	0.99	1.70	10.74	< 0.02	28.51	2.50
0.5-1.0	2-4	80.96 ± 26.50	79.35 ± 25.00	4.32	0.90	8.82	< 0.02	0.89	1.88	6.43	2.49	20.46	5.28
1.0-1.5	4-6	ND	95.15 ± 22.50	1.40	0.60	3.87	< 0.02	0.43	1.35	0.30	2.04	6.00	3.99
1.5-2.0	6-8	40.29 ± 14.50	59.90 ± 24.50	3.04	0.75	11.28	1.96	0.98	1.00	0.54	1.59	15.84	5.30
2.0-2.5	8-10	ND	38.80 ± 15.0*	2.00	1.59	5.78	2.15	0.77	0.56	0.46	0.96	9.00	5.26
2.5-3.0	10-12	ND	49.67 ± 20.00	2.19	3.73	12.35	4.17	0.92	0.72	0.51	1.15	15.97	9.78
3.0-3.5	12-14	ND	44.15 ± 15.50	2.86	1.58	6.79	1.01	0.61	0.43	0.37	0.81	10.62	3.84
3.5-4.0	14-16	64.57 ± 15.50	35.56 ± 15.00	8.00	1.39	44.46	0.53	2.15	0.40	1.17	0.79	55.77	3.11
4.0-4.5		ND		2.95		7.55		0.60		0.40		11.50	
4.5-5.0		ND		2.34		4.26		0.54		0.33		7.47	
5.0-5.5		ND		1.59		8.61		0.71		0.46		11.37	
5.5-6.0		49.93 ± 15.50		11.72		14.03		0.76		0.51		27.01	
6.0-6.5		ND		1.42		4.81		0.48		0.44		7.16	
6.5-7.0		ND		2.66		5.46		0.43		0.41		8.97	
7.0-7.5		ND		4.49		0.00		0.16		0.15		4.81	
7.5-8.0		64.44 ± 20.00		6.08		5.59		0.60		0.37		12.64	
8.0-8.5		ND		0.74		0.73		0.18		0.23		1.87	
8.5-9.0		ND		0.66		1.19		0.21		0.27		2.34	
9.0-9.5		ND		0.79		1.35		0.25		0.30		2.70	
9.5-10		39.72 ± 12.50		1.21		1.37		0.20		0.25		3.03	
10-10.5		ND		1.27		3.20		0.34		0.38		5.18	
10.5-11		ND		0.54		0.88		0.20		0.24		1.86	
11-11.5		ND		0.42		0.95		0.19		0.20		1.76	
11.5-12		36.59 ± 15.00		1.62		2.50		0.34		0.27		4.73	
12-12.5		ND		1.48		1.30		0.34		0.20		3.32	

Note: DDTs = *o, p'*-DDT + *p, p'*-DDT + *p, p'*-DDD + *p, p'*-DDE; * maximum of ^{137}Cs activity; ND: not determined

For AX core, TOC is between 9.95%—10.47% with little variation. The concentrations of five bio-elements: fluorine, selenium, copper, zinc and calcium, for penguin droppings (Sun, 2000; 2001a) are significantly correlated with each other throughout the core ($r^2 > 0.44$, $n = 8$) (unpublished data), confirming that the organic matter is from penguin droppings. Thus, the OCPs compounds in the AX pond sediments can be from direct atmospheric deposition in its surface and watershed and the delivery via penguin droppings. The average concentrations of DDTs and HCHs in the AX sediments amended by penguin droppings are 4.89 and 8.32 ng/g , respectively, much higher than those in the weathering soil (Pu, 1995). The average concentrations of DDTs and HCHs in fresh penguin droppings are also high at 1.49 ± 0.62 and 2.67 ± 0.92 ng/g ($n = 3$, on wet weight basis, ww), respectively. Therefore, penguins, through the bio-magnification by food chain from the beginning of surface seawater (Hop, 2002), delivered a large amount of droppings and OCPs compounds into X pond.

The accumulation of OCP compounds in the NR and AX cores can be affected by atmospheric temperature, watershed area and others. As shown in Fig. 2, there exists a remarkable correlation between the accumulation rates in the NR and AX cores and the station air temperature on King George Island. This suggests that the elevated deposition in these cores is fed by the increasing precipitation associating with climate warming (Thompson, 1999). The sedimentation process became faster during 1970 and 1990 when the atmospheric climate in the Antarctic region turned warmer. The average accumulation rate was approximately $378 \text{ g}/(\text{m}^2 \cdot \text{a})$ from 1924 to 1970; and after that, it increased to $786 \text{ g}/$

$(\text{m}^2 \cdot \text{a})$ in 1990.

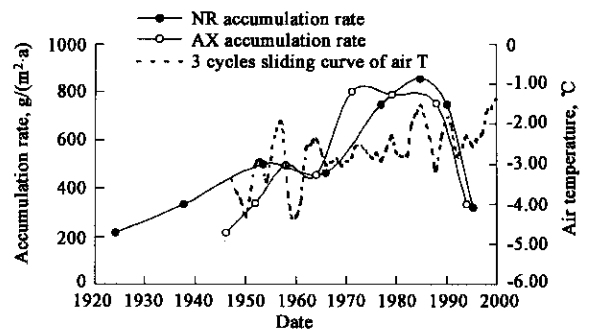


Fig. 2 The accumulation rate in the NR and AX core varied with date and the annual air temperature changes from 1944 to 2000 on Bellingshausen Scientific Station ($62^{\circ}12'S$, $58^{\circ}58'W$)

Data on air temperature from: <http://cdiac.esd.ornl.gov/ndp/ndp032.html>

While watershed area is a major factor, its relative impact on the sediments and the temporal trends of OCPs in Niudu Lake and AX pond is expected to be insignificant. The effect of watershed area on the input of OCPs into lakes is usually measured by focusing factor (Muir, 1995; Van Metre, 1997), defined as the magnification of the accumulation flux of ^{210}Pb in a lake compared with the regional atmospheric flux of ^{210}Pb . The focusing factor of a lake is mainly determined by the ratio of its watershed area to its own surface area. The watershed area and the surface area, thus the focusing factor, of lake and pond have not been remarkably changed for the past 50 years (Muir, 1995).

2.2 DDT in lake sediments

2.2.1 Concentrations of DDT compounds

Table 1 gives the determined DDTs concentrations at

different depths of two cores. The DDT concentrations in the NR core ranges from 6.00 to 55.77 ng/g (average 16.83 ng/g, $n = 14$) from the depth of 0 to 7.0 cm; it is 12.64 ng/g in the 7.5–8.0 cm section. The DDT concentrations in AX core dropped quickly from the first maximum of 9.78 ng/g at 10–12 cm, and then declined continuously to a low level of about 2.50 ng/g in the surface sediments. Throughout the cores, especially in the upper sections, the concentrations of *o,p'*-DDT and *p,p'*-DDT in the NR core are higher than those in the AX core, indicating the former continuous meltwater supply of snow or ice, which is believed to have a high proportion of *o,p'*-DDT and *p,p'*-DDT. Additionally, the percentage of *o,p'*-DDT and *p,p'*-DDT in the total DDTs of the NR core is about 85%, higher than that in the AX core, suggesting a far slower degradation rate in ice cap than in the ice-free area.

2.2.2 Accumulation fluxes of DDT compounds

The accumulation fluxes of DDT, $F(\text{ng}/(\text{m}^2 \cdot \text{a}))$, in the NR and AX cores were calculated according to $F = VC$ (Barra, 2001) and are plotted in Fig. 3. Here V and C stand for the accumulation rate ($\text{g}/(\text{m}^2 \cdot \text{a})$) and the DDT concentration in the subsamples (ng/g), respectively. The DDT flux in the AX core dropped quickly first from the peak value of about 8693 $\text{ng}/(\text{m}^2 \cdot \text{a})$ around 1950s, and then declined continuously to a low level of about 2257 $\text{ng}/(\text{m}^2 \cdot \text{a})$ in the recent decade (Fig. 3). The DDT flux peak appears somewhat earlier than the maximum usage of DDT, likely caused by the errors in ^{210}Pb dating and the insufficient subsampling (at 2 cm intervals). Similar to the observed DDT profiles in air (Macdonald, 2000), snow, ice core (Eisenreich, 1989), and sediments (Van Meter, 1997; 1998; Chen, 1999; Fox, 2001), this remarkable drop of DDT levels in the AX core from mid-1950s is apparently indebted to the global DDT usage ban.

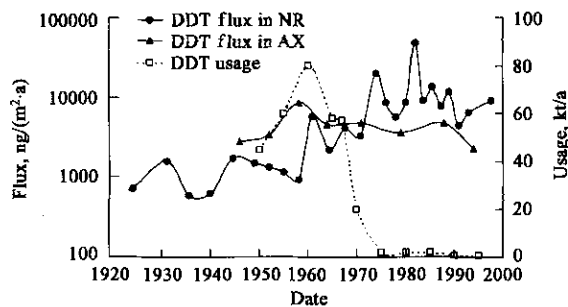


Fig. 3 Flux(dw) profile of DDTs in the NR and AX core and the historical global usage of DDT

Data on DDT usage inventories cited from Voldner and Li, 1995

Strikingly different from the one in the AX core, the DDT flux in the NR core has another and surprising peak around 1980s in addition to the expected one in 1960s (Fig. 3). Especially, the DDT flux between 1970 and 1990 is about 3303–47804 $\text{ng}/(\text{m}^2 \cdot \text{a})$ with an average value of 13650 $\text{ng}/(\text{m}^2 \cdot \text{a})$ ($n = 5$), twice as high as the one in the early 1960s, the period of global maximum usage of DDT (Voldner, 1995).

What caused the unusual difference in the accumulation flux of DDTs between the NR and AX cores? The global distribution models by Wania and Mackay (Wania, 1993) pointed out that DDT was transported to Antarctica mainly via

long-rang atmosphere and deposited in the snow pack. Since the NR and AX cores are from the same area, it is unlikely that they get a different amount of direct atmospheric DDT deposition. Another possible factor, the low cold condensation effect, also can not explain the difference for less volatile DDTs compounds in the same area (Wania, 1993).

According to Blais *et al.* (Blais, 2001), 50%–97% of the organochlorines in the lakes fed by melting glacier water may come from glacier. With low aqueous solubility, low vapor pressure and slow rate of biological and chemical transformation, organochlorines, DDT in particular, tend to be absorbed by lake sediments and removed from the water column (Eisenreich, 1989). In Antarctica, the concentrations of DDTs in snow and ice are over ten times that in lake water (Tanabe, 1983), implying an effective DDT cleaning process in lakes. Furthermore, Sarkar *et al.* (Sarkar, 1994) made a clear observation that the DDTs concentrations in Antarctic lake sediments rose from December to next year February due to the contribution from the seasonal glacier water. A warmer climate is expected to enhance the amount of melting glacier water, discharge and deposit more DDTs into the Niudu Lake sediments. The second peak of the DDT flux around 1980s in the NR core, therefore, is very likely due to the increased melting glacier water and the climate warming since 1970s in this region (<http://cdiac.esd.ornl.gov/epubs/ndp/ndp032/ndp032.html>).

The DDTs flux in the AX core, which is amended by penguin droppings, dropped quickly since 1950s and then kept declining. The absence of the second peak around 1980s in the AX core can be attributed to the fact that AX pond is not close to glacier. Although portion of the meltwater from Nelson and Kolins Ice Cap enters Maxwell Bay in austral summer, most of the DDTs in the meltwater may have been removed before entering Maxwell Bay due to DDTs poor solubility in water (Tanabe, 1983). This also explains the observation that the accumulation flux of DDTs in the NR core is on the whole higher than that in the AX core. Thus, the DDT compounds in AX pond delivered by penguin droppings reflect the burden on surface seawater.

2.2.3 Classification of DDT temporal trends

The expected DDT deposition profile in the AX core and the abnormal one in the NR core are not unique to Antarctica; similar observations have also been reported in high Arctic regions of Canada. The declined DDT loading in the areas free of glacier DDT input has been documented well (Gregor, 1989; Loganathan, 1994). The profiles of DDTs in seven lakes collected from Canada Yukon, as reported by Rawn *et al.* (Rawn, 2001), show that the DDT peaks occurred from the early 1960s to the early 1970s in the lakes without glacier input such as Lake Fox, Watson and Hanson, and that they occurred between 1975 and 1993 in Lake Lindeman, whose watershed is affected by glacier in a proportion of 12%. Furthermore, Muir *et al.* (Muir, 1995) reported DDT concentration peaks between 1980 and 1990, in addition to the expected ones in 1960s, in several Arctic lakes fed by melting glacier water. We summarize these observations in Table 2. Apparently, all exceptional profiles of DDT deposition are associated with the meltwater from either glacier or permanent snow. We therefore propose two

kinds of areas in the globe-with or without the inputs from melting glacier or permanent snow water; and the DDT deposition rate in the former has a ubiquitous increase after

the DDT ban despite lacking of direct atmospheric deposition.

Table 2 Summary of historical DDT deposition profiles on the globe

Area	Location	Material	Fed by melting ice	Peak time	Reference
Nelson Island	62°18'S, 59°03'W	Lake sediment	Yes	1974, 1982	This study
Ardley Island	62°13'S, 58°56'W	Lake sediment	No	1950s	This study
China	30°30'N, 122°30'W	Estuary sediment	No	1962, 1972	Chen, 1999
England	/	Estuary sediment	No	Mid-1960s	Fox, 2001
Coralville Reservoir(USA)	/	Reservoir sediment	No	Later-1960s	Van Metre, 1997
Blackshear Lake etc.(USA)	/	Lake sediment	No	Mid-1960s	Van Metre, 1998
Tampa Bay, Florida	27°N	Bay sediment	No	Mid-1960s	Santschi, 2001
Galveston Bay, USA	29°N	Bay sediment	No	Mid-1960s	Santschi, 2001
Ontario Lake	/	Lake sediment	No	Early-1970s	Eisenreich, 1989
Fox Lake	61°15'N, 135°29'W	Lake sediment	No	Mid-1960s	Rawn, 2001
Lindeman Lake, Canada	59°47'N, 135°03'W	Lake sediment	Yes	1981, 1993	Rawn, 2001
Experimental Lake	49°45'N, 93°47'W	Lake sediment	Yes	1984	Muir, 1995
Hawk Lake	63°38'N, 90°42'W	Lake sediment	Yes	1961, 1985	Muir, 1995
Amitut Lake	75°03'N, 93°48'W	Lake sediment	Yes	1980	Muir, 1995
Far Lake	63°42'N, 90°40'W	Lake sediment	Yes	1970, 1986	Muir, 1995

2.3 HCHs in lake sediments

2.3.1 Concentrations of HCH

The total HCH and its four isomers concentrations at different depths in the NR and AX core are summarized in Table 3. As shown in this table, the HCHs concentrations peak at 173.61 and 7.40 ng/g, respectively, around 6—8

cm and 0—1 cm in the NR core, far higher than those in other sections. The HCHs concentrations in the AX core have a general increment trend, from 3.71 ng/g in 8—16 cm, 12.19 ng/g in 4—6 cm, and then to 26.03 ng/g in 0—2 cm. Because the OCPs in the AX core are mainly from penguin droppings, we will discuss it in more detail.

Table 3 Concentrations (ng/g, dw) of HCHs at different depths in the NR and AX cores

Depth, cm		α -HCH		β -HCH		γ -HCH		δ -HCH		HCHs	
NR	AX	NR	AX	NR	AX	NR	AX	NR	AX	NR	AX
0—0.5	0—2	0.81	3.58	0.07	11.39	4.77	11.1	1.74	< 0.02	7.40	26.0
0.5—1.0	2—4	0.36	1.93	0.04	< 0.02	3.58	5.31	2.00	0.65	5.98	7.89
1.0—1.5	4—6	0.20	2.51	0.02	4.73	1.58	4.96	< 0.02	< 0.02	1.81	12.2
1.5—2.0	6—8	0.27	1.49	0.03	2.06	3.22	0.69	< 0.02	1.40	3.54	5.64
2.0—2.5	8—10	0.28	0.44	0.04	0.20	2.36	2.35	< 0.02	0.38	2.69	3.37
2.5—3.0	10—12	0.29	0.40	0.03	0.26	2.03	3.35	< 0.02	0.44	2.36	4.45
3.0—3.5	12—14	0.31	0.32	0.04	0.25	2.33	1.52	< 0.02	< 0.02	2.69	2.09
3.5—4.0	14—16	0.32	0.61	0.04	0.33	2.62	3.84	< 0.02	0.14	3.00	4.93
4.0—4.5		0.29		0.03		2.11		< 0.02		2.44	
4.5—5.0		0.34		0.03		2.38		< 0.02		2.76	
5.0—5.5		0.40		0.04		2.86		< 0.02		3.31	
5.5—6.0		0.51		0.05		4.54		< 0.02		5.11	
6.0—6.5		0.33		0.08		30.8		0.66		31.9	
6.5—7.0		0.36		0.07		172		0.91		174	
7.0—7.5		0.21		0.04		2.39		0.34		2.97	
7.5—8.0		0.35		0.05		7.13		0.79		8.33	
8.0—8.5		0.22		0.04		3.54		0.20		4.00	
8.5—9.0		0.27		0.05		4.17		0.23		4.72	
9.0—9.5		0.28		0.05		4.34		< 0.02		4.68	
9.5—10		0.25		0.05		4.44		< 0.02		4.74	
10—10.5		0.33		0.06		4.98		< 0.02		5.39	
10.5—11		0.32		0.05		3.92		< 0.02		4.30	
11—11.5		0.30		0.04		3.49		< 0.02		3.84	
11.5—12		0.28		0.04		3.28		< 0.02		3.61	
12—12.5		0.27		0.04		1.98		0.25		2.54	

Note: HCHs = α -HCH + β -HCH + γ -HCH + δ -HCH

In the NR core, the major isomer is γ -HCH and followed by α -HCH > β -HCH > δ -HCH, consistent with the previous observations in Antarctica lakes (Sarkar, 1994); α/γ ratio (α -HCH/ γ -HCH) ranges from 0.02 to 0.17, and 0.17 for the surface 0.5 cm sediments, which was recently deposited. The α/γ ratios in the NR core are comparable with those in a small Chica de San Pedro lake in Chile ranging from 0 to 0.86 (Barra, 2001). Additionally, the α/γ ratio in the surface 0.5 cm sediments is far higher than those in other sections of the NR core, especially the 6—8 cm section with

the maximum concentrations of HCHs. This pattern agrees well with the observation in Chile Lake (Barra, 2001). Therefore, the recent deposition of HCH in the Antarctic region may be from the current legal or illegal use of technical HCH or Lindane in the Southern Hemisphere, especially in South America.

2.3.2 Accumulation fluxes of HCHs

The accumulation fluxes of HCHs (ng/(m²·a)) in the NR core were calculated using the same method as in section 2.2.2 and are plotted in Fig. 4, which shows two peaks

around 1970s and mid-1990s as marked by the arrows. Briefly, the HCHs flux shows a steady increase before 1960s and then abruptly reaches the first peak around 1970s at 14446—78645 $\text{ng}/(\text{m}^2 \cdot \text{a})$, average 46545 $\text{ng}/(\text{m}^2 \cdot \text{a})$ ($n = 2$), corresponding to the period of maximum global usage of HCHs; after that, it declined gradually to a low level of about 1848 $\text{ng}/(\text{m}^2 \cdot \text{a})$ in mid-1980s and then rose to the unexpected second peak at 4500—5569 $\text{ng}/(\text{m}^2 \cdot \text{a})$ in recent decade. The second peak is apparently not consistent with the decline trend of HCH usage (Li, 1999; Loganathan, 1994; Macdonald, 2000). Additionally, different from the DDT pattern, HCH seems not to be significantly affected by climate warming.

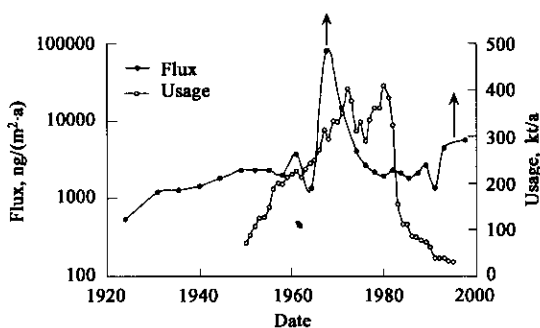


Fig. 4 Comparison of the HCHs flux (dw) recorded in NR core and the historical global HCHs usage

Data on global inventories of HCHs cited from Li, 1999

As seen in Fig. 3 and 4, the temporal trends of HCHs and DDTs accumulation rate in the NR core are quite different. This difference is likely due to their distinct water-soluble property, which are 62.4 $\mu\text{g}/\text{ml}$ and 0.1 $\mu\text{g}/\text{ml}$ at room temperature, respectively. Therefore, DDT compounds in the aquatic basis are removed more easily than HCH by attaching to solid particles of sediments before entering Maxwell Bay. In fact, the study by Tanabe *et al.* (Tanabe, 1982; 1983) indicated that the HCH concentrations in snow and lake water are 4.90 and 0.31 ng/g , respectively, much higher than the DDT concentrations of 0.016 and 0.0013 ng/g . At the same time, the sediments in eight lakes fed by melting glacier from Schirmacher Oasis (between 70°44' S, 11°47' E and 70°46' S, 11°41' E), Antarctica, contain a HCH concentration of 0.0929 ng/g , much lower than the DDT level of 0.8449 ng/g (Sarkar, 1994). Therefore, more HCHs compounds were carried with increasing meltwater into Maxwell Bay and elevated the HCHs flux in the AX core of penguin dropping sediments in the past decades.

Having good water solubility, the HCH accumulation rate in the Niudu Lake, which is near the glacier, thus mainly depends on direct atmospheric deposition. Thus, the atmospheric flux of HCH in King George Island can be estimated as the accumulation flux of HCH in the NR core over the focusing factor of the Niudu Lake, which is 12.8. For the AX pond, far from glacier, the accumulation flux of HCH is determined by both the direct atmospheric deposition and the meltwater from glacier and snow.

2.4 DDTs and HCHs in penguin droppings

2.4.1 Temporal trend of DDT in penguin droppings

The penguins living in Maxwell Bay take DDTs from the surface water, and historical penguin droppings could to some degree record the variations of DDTs in the surface seawater.

For the aim to reconstruct the temporal trend of DDTs concentrations in penguin droppings from the mixtures of penguin droppings and weathering soil in the AX core, we used the method as described in our previous study (Sun, 2001b) on the assumption that the ratio of DDTs concentrations in droppings to weathering soil is constant. The profile of DDTs in penguin droppings over the last 50 years was thereby reconstructed and is plotted in Fig. 5. As seen in this figure, the first peak of DDTs in penguin droppings at 20.52 ng/g (dw) occurs in the later 1950s. After that, the DDT content drops to 11.17 ng/g (dw) and then remains constant around 10.47 ng/g (dw) till the later 1980s, most likely due to the restriction of DDT use in agriculture. This result agrees well with another observation on penguin droppings from Ardley Island in our recent study (unpublished data) that the DDT content decreases to 5.49 ng/g (dw) in the mid-1990s and 2.13 ng/g (dw) at the present time.

2.4.2 Temporal trend of HCH in penguin droppings

We separated and identified the temporal trend of HCHs in penguin droppings from the mixtures of droppings and weathering soil over the last 50 years using the same method and plot it in Fig. 5. As seen in this figure, the HCHs levels in the penguin droppings are 11.53—24.23 ng/g , average 17.30 ng/g ($n = 3$), between ca. 1970 and 1985, the period of maximum global usage. They show a gradual increase in that time period probably due to two reasons. First, climate warming from 1970s has made ice cap and snow pack discharge a considerable ice-stored HCH to Maxwell Bay as inferred from the direct observation in Antarctic Peninsula (Vaughan, 1996). Second, there was an increasing atmospheric deposition from the illegal use of HCH. After that time period, they decrease to approximately 3.82 ng/g (dw) in fresh droppings (unpublished data), most likely due to the restriction on Lindane use from 1998 in Chile (Barra, 2001).

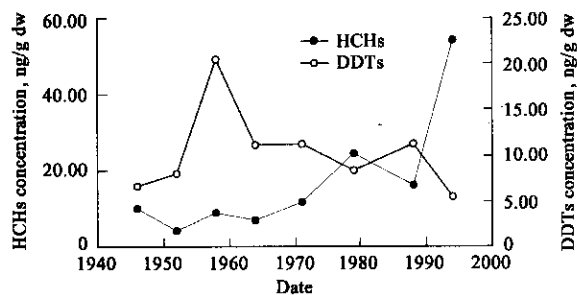


Fig. 5 Concentrations of HCHs and DDTs in penguin droppings in the past 50 years referred from the AX core amended by penguin droppings

It was worthwhile to note that the time trend of DDT in penguin droppings is different from the one of HCH. This is likely due to their distinct water-soluble property as discussed in Section 2.3.2. Consequently, the abrupt discharge of HCHs compounds contained in meltwater might impact coastal ecosystem (such as, penguin, krill) as well as surface seawater in polar region (Tanabe, 1983; Macdonald, 2000). Additionally, the above results agree primarily with a long-term observation by Aono *et al.* (Aono, 1997) that the HCHs levels in Minke whale of the Antarctic oceans is 1.8 ng/g ($n = 20$) in 1988/1989 and 2.7 ng/g ($n = 20$) in 1992/1993

and other observations for the increase of HCHs contents since the early 1970s in Arctic bear, ringed seal and sea birds (Addison, 1986; Norstrom, 1988).

3 Conclusions

In summary, the regional climate warming might have discharged the DDT stored in the Antarctic ice cap, caused abnormal increase of DDT deposition around 1980s in the lakes in the Antarctic glacier frontier. Our results suggested two kinds of temporal trends for the DDT accumulation in lake sediments: associated or not with melting glacier feed; and this rule seems to be applicable to other regions in the globe. Further researching and monitoring programs on the DDT deposition rate in the areas near glaciers will be greatly helpful to test this assumption and understand the impact of climate warming and OCPs on Antarctic ecosystem. The temporal trends of HCHs in penguin droppings agree with other observations and indicate an unexpected pollution due to climate warming and melting glacier influx for the polar coastal ecosystem.

Acknowledgements: The authors are grateful to Professor Yu Hanqing (School of Chemistry Science, University of Science and Technology of China) and our colleague including Professor Xie Zhouqing, Dr. Liu Xiaodong, Dr. Zhu Renbin *et al.* in Institute of Polar Environment for their valuable comments. Thanks for constructive advice are also due to an anonymous reviewer and Professor Kenneth A. Rahn (Center for Atmospheric Chemistry Studies, University of Rhode Island).

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