

## Evidence of local emission of organochlorine pesticides in the Tibetan plateau

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### ABSTRACT

Organochlorine pesticides (OCPs) including DDTs, HCHs, chlordanes and hexachlorobenzene (HCB) in the atmosphere of Lhasa, the capital city of Tibet, China, were monitored in an attempt to assess their concentration level and potential sources. Twenty air samples collected at two sites in Lhasa between 6 and 11 August 2006 were analyzed for OCPs. The mean concentrations of  $\alpha$ -,  $\gamma$ -HCHs, HCB, *trans*-chlordane (TC), *cis*-chlordane (CC), *p,p'*-DDE, *p,p'*-DDD, *o,p'*-DDT, and *p,p'*-DDT were 49, 163, 182, 204, 128, 122, 46, 206, and 114  $\text{pg}/\text{m}^3$ , respectively. The relatively low  $\alpha$ -HCH/ $\gamma$ -HCH ratios indicated that lindane is the current source of HCHs in Lhasa. A TC/CC ratio of  $\approx 1.2$  was observed for samples with relatively high chlordane concentrations, suggesting a current local use of technical chlordane. The isomer ratios of DDTs also implied present usages of DDT-containing dicofol and technical DDT in the city. Contrary to other OCPs, HCB displayed higher concentrations during nighttime than daytime, indicative of a dominant contribution from local combustion. We conclude that current use and local emissions may be important sources for OCPs in Lhasa and may contribute to OCP contamination in the environment of the populated agricultural Lhasa River basin.

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### 1. Introduction

Organochlorine pesticides (OCPs) are a group of semi-volatile persistent organic pollutants (POPs) which are subjected to long-range atmospheric transport (LRAT) and can be redistributed globally by the effect of cold condensation. On the grasshopping behavior, POPs follow successive volatilization and deposition steps from warmer areas towards cooler regions. Therefore, the places at high elevation and high latitude with low temperatures were considered to be a condensation region for those long-range transported airborne contaminants (Wania and Mackay, 1993, 1995). Many studies have been conducted in

remote polar and mountain regions not only to evaluate the risk of the POPs to humans and ecosystems, but also to provide the evidence that LRAT of organic contaminants may occur on a global scale (Daly and Wania, 2005; Hung et al., 2002; Shen et al., 2004; Yang et al., 2007).

The Tibetan plateau, also named the “Roof of the World” or the “Third Pole on the Globe” as it is the world’s largest plateau with the highest elevation, located in the eastern Eurasian continent. A large amount of the water vapor coming from the eastern Indian Ocean is deposited or condensed in this region. The plateau is surrounded by many agriculture countries, such as China and India, which have a record of high organochlorine pesticide application in recent history (Li et al., 1998; Li and Macdonald, 2005). It is hypothesized that orographic cold-trapping effect for some OCPs may be particularly pronounced in the Tibetan Plateau. Therefore, several studies conducted in the Tibetan plateau region have been devoted to illustrating the long-range atmospheric transportation (LRAT) and the

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fate of POPs (Cheng et al., 2007; Li et al., 2006; Wang et al., 2006, 2007a,c; Yang et al., 2007). For example, three recent studies showed that the atmospheric transportation 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 south and north-eastern Tibetan Plateau (Cheng et al., 2007; Li et al., 2006; Wang et al., 2007a). The only two reports conducted in the center of the Tibetan Plateau also suggested the LRAT and atmospheric deposition was to be the sources of OCPs in the lake water, sediments and fish (Yang et al., 2007; Zhang et al., 2003). However, all sampling sites in those studies are relatively isolated from densely populated areas, and the conclusions were made based on the fact that Tibet had no record of the OCP application in history (Li et al., 1998). Until now there is no literature about the potential sources and behavior of atmospheric OCPs in densely populated cities in Tibet.

Lhasa, the capital of China's Tibet Autonomous Region, is the political, economic, cultural and transport center of the region. It covers an area of close to 30,000 km<sup>2</sup> and has a population of 400,000. The ancient city of Lhasa is located in plain of the middle reaches of the Lhasa River. The Lhasa River plays an important role in the local economic development. Since the first piece of the wilderness along the Lhasa River was reclaimed to be as BaYi Farm in 1952, large amounts of the land have been used to produce vegetable and meat. Now, with the utilization of the advanced technology supported by the Panam Integrated Rural Development Project (PIRDP) cooperated between the EU and China since 1991, the Lhasa region's vegetation output totaled 132,000 tons in 2006, accounting for about 60% of total consumption in Lhasa city. The increasing trend of agricultural development in Tibet eventually indicates the potential illegal use of organochlorine pesticide for its persistence and effectiveness.

The objectives of this study were to assess the concentrations of OCPs in the atmosphere of Lhasa. And potential sources were investigated based on the compound compositions and diurnal variations. Our result denotes that local emissions rather than long-range air transportation (LRAT) are responsible for most of the organochlorine pesticides in the city.

## 2. Materials and methods

### 2.1. Sampling sites

As shown in Fig. 1, the cities, factories, farm land, and agricultural lands are located along the Lhasa River valley. The most famous agriculture land is situated in the Duilong Deqin County, about 12 km to the west of downtown Lhasa. In this study, two active atmospheric sampling stations were setup on the building roof at about 15 m high. The sampling site WS and ES are located about 6.5 km west and about 6 km east of the Lhasa urban center, respectively.

### 2.2. Sampling method

Sampling was conducted at the same time at the two sampling sites for a consecutive 12 h period during daytime

(7:30 a.m.–7:30 p.m.) and nighttime (7:30 a.m.–7:30 p.m.) from August 6 to August 12, 2006. A total of 20 pairs of samples were collected from the two sampling sites. Air volumes of 252 m<sup>3</sup> were drawn through a Quartz micro-fiber filter (QFF) (Grade GF/A, 20.3 × 25.4 cm, Whatman, Maidstone, England), and subsequently through a 6.5 cm in diameter × 7.5 cm in thickness (a density of 0.030 g cm<sup>-3</sup>) polyurethane foam (PUF) plugs using a high-volume sampler (of the Anderson type) at a flow rate of 0.350 m<sup>3</sup> min<sup>-1</sup>. Prior to sampling, QFFs were baked at 450 °C for 12 h to remove any organic contaminant, and PUF plugs were Soxhlet extracted for 48 h with methanol and then acetone for 24 h, followed by two overnight extractions using dichloromethane (DCM). PUF plugs were dried overnight in a vacuum desiccator and stored in solvent-rinsed glass jars with Teflon lined lids before use. During the sample collection, gloves were worn, and QFFs and PUFs were handled using acetone-rinsed stainless steel tongs. After sampling, loaded QFFs were wrapped with prebaked aluminum foil and sealed with double layers of polyethylene bags. PUFs were placed in solvent-rinsed glass jars with Teflon lined lids, and then transported to the laboratory and stored at -20 °C until extraction. Meteorological data, such as temperature, relative humidity, wind speed/direction, and precipitation were recorded.

### 2.3. Extraction and analysis

Filters and PUFs were spiked with 10 ng of 2,4,5,6-tetrachloro-*m*-xylene (TCmX) and decachlorobiphenyl (PCB-209) as surrogates, and Soxhlet-extracted with dichloromethane for 48 h. Activated copper granules were added to the collection flask to remove elemental sulfur. The extract was concentrated and solvent exchanged to *n*-hexane and purified on an 8 mm i.d. alumina/silica column packed, from the bottom to top, with neutral alumina (6 cm, 3% deactivated), neutral silica gel (10 cm, 3% deactivated), 50% (on a weight basis) sulfuric acid silica (10 cm), and anhydrous sodium sulfate (1 cm). Before use, neutral alumina, neutral silica gel, and anhydrous sodium sulfate were Soxhlet-extracted for 48 h with DCM, and then baked for 12 h in 250, 180, and 450 °C, respectively. The column was eluted with 50 ml of dichloromethane/hexane (1:1) to yield the organochlorine pesticide fraction. The fraction was reduced to a final volume of 25 µL under a gentle stream of nitrogen and solvent exchanged to 25 µL of dodecane containing a known quantity of pentachloronitrobenzene (PCNB) as an internal standard.

OCP analysis was conducted on an Agilent-5975 GC-MSD system with a CP-Sil 8 CB capillary column (50 m, 0.25 mm, 0.25 µm), operating under selected ion monitoring (SIM) mode. Helium was used as the carrier gas at 1.2 mL min<sup>-1</sup> under constant-flow mode. The oven temperature commenced at 60 °C for 1 min and increased to 290 °C (10 min hold time) at a rate of 4 °C min<sup>-1</sup>. Splitless/split injection of a 1 µL sample was performed with a 5 min solvent delay time. Injector temperature was at 250 °C. The inlet degradation of DDT was checked daily and controlled within 15% before field samples were injected and analyzed.

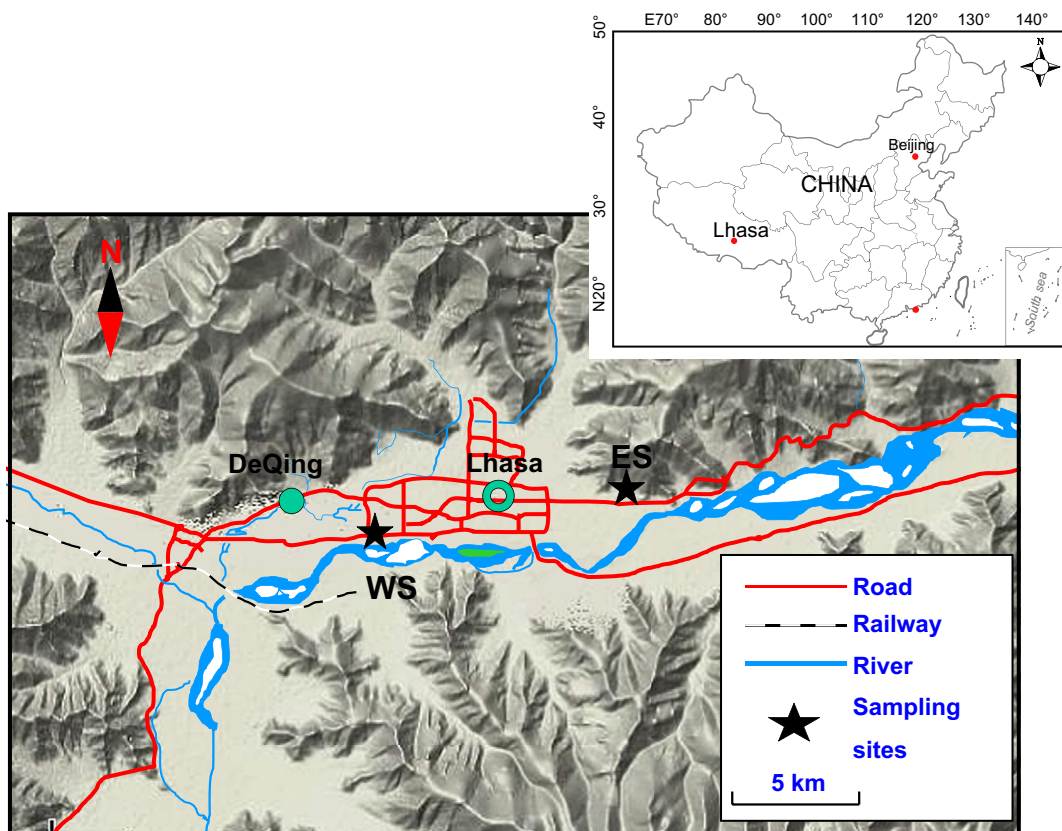


Fig. 1. Map showing the sampling locations in Lhasa, Tibet, China.

#### 2.4. QA/QC

Field blanks were treated like samples and taken through the transportation, deployment, storage, and analytical steps. Four field blanks for each medium (PUF and filter) were deployed at each site. Only low concentrations of TC and CC in PUF were detected in the field blanks. The blank levels were less than 2% of the mass in the samples, and they were appropriately subtracted from the sample concentrations. OCPs level in three solvent blanks was lower than those in the field blanks.

Before the extraction, each media was fortified with 10 ng of recovery standards TCmX and PCB-209. Recoveries for TCmX and PCB-209 were  $72\% \pm 8\%$  and  $91\% \pm 8\%$ , respectively. Data shown in this paper were not corrected for the recoveries.

### 3. Results and discussion

#### 3.1. Concentrations of OCPs in air

The organochlorine pesticides that occurred most frequently in our Lhasa atmospheric samples were HCHs, HCB, chlordane, and DDTs. Table 1 presents the data of the selected gaseous OCPs.

The atmospheric concentrations of  $\alpha$ -HCH at the WS site and ES site ranged from 33 to 89 ( $50 \pm 17$ )  $\text{pg}/\text{m}^3$  and from

30 to 60 ( $47 \pm 11$ )  $\text{pg}/\text{m}^3$ , respectively. The concentrations of  $\gamma$ -HCH ranged from 81 to 259 ( $142 \pm 59$ )  $\text{pg}/\text{m}^3$  and 124 to 272 ( $183 \pm 50$ )  $\text{pg}/\text{m}^3$ , respectively. These levels were comparable to that monitored during the spring time in 2005 at the Waliguan Baseline Observatory, which is located at the edge of the northeastern Tibetan Plateau with an elevation of 3816 m (Cheng et al., 2007), but much higher than that monitored in the Mt. Everest region (Li et al., 2006). Compared with other reported data in the remote area, the  $\alpha$ -HCH concentrations were comparable with those in Arctic, while the  $\gamma$ -HCH concentration was abnormally high (Hung et al., 2005).

It has been widely recognized that HCH in environment is sourced from the two formulations: technical HCH and lindane. Technical HCH typically contains the isomers in the following percentages:  $\alpha$ -HCH, 60–70%;  $\beta$ -HCH, 5–12%;  $\gamma$ -HCH, 10–12%; and  $\delta$ -HCH, 6–10%. Lindane contains >90% of  $\gamma$ -HCH. Given the compositions of the two main HCH pesticides, a high  $\alpha$ -HCH/ $\gamma$ -HCH ratio generally indicates the input of technical HCH while a low ratio indicates a source from lindane. The average  $\alpha$ -HCH/ $\gamma$ -HCH ratio in the atmosphere of Lhasa with  $0.37 \pm 0.07$  and  $0.27 \pm 0.08$  at the WS and ES sites, respectively, was similar to that at the Waliguan Baseline Observatory ( $0.48 \pm 0.27$ ) (Cheng et al., 2007), lower than that of technical HCH, and much lower than that in the Mt. Everest region (2.49) (Li et al., 2006) or in the Arctic (Hung et al., 2005). The large scale

**Table 1**

The concentration data and Clausius–Clapeyron regression results for each pesticide in Lhasa during the sampling period

pg/m <sup>3</sup>	Temp (°C)	$\alpha$ -HCH	$\gamma$ -HCH	HCB	TC	CC	<i>p,p'</i> -DDE	<i>p,p'</i> -DDD	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT
WS site										
Aug 6-N	15.0	41	91	187	231	92	201	74	405	148
Aug 7-D	19.6	89	259	156	545	477	307	97	620	87
Aug 7-N	15.7	35	87	90	57	22	51	27	132	17
Aug 8-D	17.7	70	181	108	256	128	223	70	392	53
Aug 8-N	13.0	40	86	157	85	29	81	38	93	9
Aug 9-D	18.5	56	152	80	139	48	150	67	328	260
Aug 9-N	14.3	47	120	98	119	85	61	29	87	27
Aug 10-D	20.1	46	180	117	270	100	304	142	769	705
Aug 10-N	17.2	33	84	152	65	27	51	29	64	15
Aug 11-D	21.6	44	181	125	228	79	245	117	336	584
Mean		50	142	127	199	109	167	69	322	190
<i>m</i>		-4009	-9869	821	-13070	-13076	-15536	-14591	-18196	-36977
<i>r</i> <sup>2</sup>		0.18	0.61	0.01	0.35	0.21	0.46	0.59	0.44	0.60
<i>P</i>		0.23	0.01	0.79	0.07	0.18	0.03	0.01	0.04	0.01
ES site										
Aug 6-N		42	124	194	49	18	18	6	25	5
Aug 7-D		30	192	48	284	251	162	56	109	147
Aug 7-N		51	152	182	76	63	19	8	40	7
Aug 8-D		60	203	264	292	153	96	23	146	60
Aug 8-N		58	143	383	51	25	36	13	53	8
Aug 9-D		53	196	190	180	51	90	27	110	58
Aug 9-N		53	272	377	440	371	56	17	55	13
Aug 10-D		36	129	102	38	20	113	32	104	46
Aug 10-N		37	164	300	282	222	23	17	43	11
Aug 11-D		56	254	339	395	294	153	32	209	30
Mean		47	183	238	209	147	77	23	89	38
<i>m</i>		2146	-2406	8893	-9288	-10390	-19809	-15984	-16248	-25306
<i>r</i> <sup>2</sup>		0.09	0.08	0.20	0.10	0.08	0.56	0.61	0.61	0.53
<i>p</i>		0.41	0.42	0.20	0.37	0.42	0.01	0.01	0.01	0.02

usage of lindane as an insecticide in most Southeast Asian countries surrounded the Tibetan Plateau could be responsible for those lower ratios (Li et al., 1998).

HCB has several uses in industry and agriculture, and has a long half-life in the atmosphere. Although HCB production has ceased in most countries, it is still being generated inadvertently as a by-product and/or impurity in several chemical processes, such as the manufacture of chlorinated solvents, chlorinated aromatics and pesticides, it is also released to the environment by incomplete combustion, and released from old dumpsites (Barber et al., 2005). The average atmospheric concentration of HCB was  $127 \pm 35$  and  $238 \pm 114$  pg/m<sup>3</sup> at the WS site and ES site in Lhasa during the sampling period, which was much higher than that found in the other remote areas, such as the Arctic (Hung et al., 2005), Mt. Everest (Li et al., 2006), Waliguan Baseline Observatory (Cheng et al., 2007), and other background sites (Barber et al., 2005), and just comparable to the those monitored at other sites in China (Jaward et al., 2005). As Lhasa is a city with only very limited industry, incomplete combustion may be considered as the primary emission source of HCB.

Chlordane used as a termiticide for woods in many parts of the world was detected at high levels where the technical chlordane was sprayed (Bidleman et al., 1998; Murayama et al., 2003). In China, technical chlordane is still being extensively used against termites in buildings, with an estimated amount of over 200 tons/year in recent years (Xu et al., 2004). The most abundant components in the technical mixture are *trans*-chlordane (TC) and *cis*-chlordane

(CC). The concentrations of TC and CC at the WS site ranged from 57 to 545 ( $199 \pm 146$ ) pg/m<sup>3</sup> and from 22 to 477 ( $109 \pm 134$ ) pg/m<sup>3</sup>, at the ES site ranged 38–440 ( $209 \pm 151$ ) pg/m<sup>3</sup> and from 18 to 371 ( $147 \pm 130$ ) pg/m<sup>3</sup>. These values were higher than concentrations reported from other remote sites and comparable to those values detected in other cities such as Guangzhou, Hong Kong and Niigata, Japan (Table 2). Generally, TC was considered to be more susceptible to photodegradation than CC in the environment. Therefore, a TC/CC ratio below the technical formula ratio, which has been reported to be 1.56 (Bidleman et al., 2002), 1.26 (Bailey et al., 2000), and 1.16 (Hung et al., 2005), indicates a more aged source. Fig. 2 displays the TC/CC ratio with the sum of the concentrations of TC and CC at the two studied sites. Lower values (1.13–1.34) of TC/CC ratios in the range of technical chlordane (Hung et al., 2005) were observed in most of the samples with higher TC + CC concentrations, which may indicate fresh use of technical chlordane (Li et al., 2007). However, there is no plausible reason for the high TC/CC ratios ranged from 1.90 to 3.49 (refer to Fig. 2), except for a potential input of chlordane from an unknown source signifying high TC/CC ratios (such as technical heptachlor, which contains 20–22% TC (Bidleman et al., 1998), whereas, there was reported no heptachlor produced and imported in China after 1983) or from the use of technical chlordane with different formulas (Li et al., 2007; Wang et al., 2007b).

The concentrations of DDT and its isomers at Lhasa collected at the two sites are listed in Table 1. The concentrations of *o,p'*-DDT, *p,p'*-DDT, *p,p'*-DDE, and *p,p'*-DDD at the

**Table 2**  
Comparison of OCPs concentrations ( $\text{pg}/\text{m}^3$ ) with those in other places

	$\alpha$ -HCH	$\gamma$ -HCH	HCB	<i>o,p'</i> -DDT	<i>p,p'</i> -DDT	<i>p,p'</i> -DDE	TC	CC
Kinngait (1995) <sup>a</sup>	71.2	9.38	63.4	0.41	0.29	0.49	0.5	0.89
Tagish (1994) <sup>a</sup>	78	13.2	55.1	0.65	0.22	0.71	0.66	1.3
Dunai (1993) <sup>a</sup>	40	9.83	54.7	0.18	0.14	0.36	0.4	0.96
Mt Waliguan <sup>b</sup>	58.4	139	38.4	17.9	4.42	5.12	18.1	22.1
Mt Everest <sup>c</sup>	19.2	7.7	8.9	5.1	3.7	5.1		
Taihu Lake, China <sup>d</sup>	74	46		767	124	212		
Guangzhou, China <sup>e</sup>	139	523		912	718	222	922	1430
Hong Kong, China <sup>e</sup>	46	51		191	358	54	389	380
Niiigata, Japan <sup>f</sup>	103	40			6	5.3	70	61

Years in the parentheses in the table refer to sampling time.

<sup>a</sup> 1993–1995 (Hung et al., 2005).

<sup>b</sup> 2005 (Cheng et al., 2007).

<sup>c</sup> 2002 (Li et al., 2006).

<sup>d</sup> 2002 (Qiu et al., 2004).

<sup>e</sup> 2004 (Li et al., 2007).

<sup>f</sup> 2001 (Murayama et al., 2003).

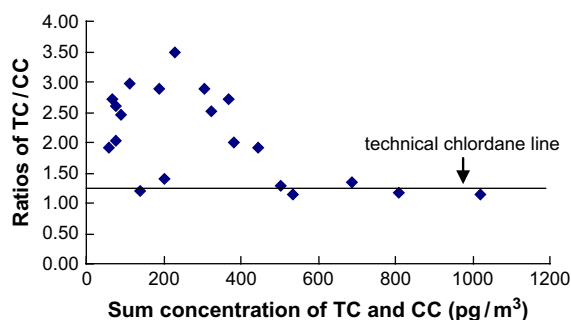
WS site, with the mean values of  $322 \pm 238$ ,  $190 \pm 253$ ,  $167 \pm 102$ ,  $69 \pm 40 \text{ pg}/\text{m}^3$ , respectively, were significantly higher than those at the ES site, with mean values of  $89 \pm 57$ ,  $38 \pm 40$ ,  $77 \pm 55$ ,  $23 \pm 15 \text{ pg}/\text{m}^3$ , respectively, indicating that the WS site was in proximity to the emission source. As showed in Table 2, compared with other DDT air concentration data, DDT and its isomers concentrations at Lhasa in this study were comparable to those in the Taihu Lake and in the Pearl River Delta (Guangzhou and Hong Kong) (Li et al., 2007; Qiu et al., 2004), much higher than those reported in rural or remote places in the world (Table 2).

Both direct application of technical DDT and DDT-containing dicofol may introduce DDT into the environment. As technical DDT contains less *o,p'*-DDT ( $\approx 15\%$ ) than *p,p'*-DDT ( $\approx 85\%$ ), and dicofol has reverse pattern (Qiu et al., 2005), fresh input of DDTs from technical DDT can hence be distinguished from dicofol by lower *o,p'*-DDT/*p,p'*-DDT ratios. The average concentration ratio of *o,p'*-DDT/*p,p'*-DDT in the atmosphere of Lhasa was  $4.24 \pm 2.63$ , suggesting an input of DDT from Dicofol application in Lhasa (Qiu et al., 2005). In the environment, DDT can be microbially transformed to the stable and toxic metabolites DDE and DDD. In general, a small value of the DDT/(DDE + DDD) ratio is indicative of aged (microbially degraded) DDT, and a value much greater than one indicates fresh application. However, this method is not valid when a large amount of dicofol has been used in target areas (Qiu et al., 2005). The

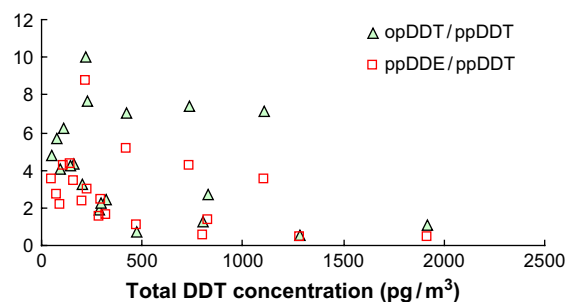
results of the previous study indicated *p,p'*-Cl-DDT was one of the major compounds in dicofol, and it can easily convert to *p,p'*-DDE. Therefore, this conversion of *p,p'*-Cl-DDT to *p,p'*-DDE can lead to a high *p,p'*-DDE/*p,p'*-DDT ratio and could mislead the evaluation of *p,p'*-DDT resident time in the environment. But the low *p,p'*-DDE/*p,p'*-DDT ratio may still indicate the “freshness” of DDT in the environment. The relationship between the total DDT concentrations and the ratios of *o,p'*-DDT/*p,p'*-DDT and *p,p'*-DDE/*p,p'*-DDT were investigated. As shown in Fig. 3, high concentrations of DDT accompanied by both low values for *o,p'*-DDT/*p,p'*-DDT ratios and low values of *p,p'*-DDE/*p,p'*-DDT ratios were found, implying that the technical DDT through illegal use may be present in the Lhasa atmosphere.

### 3.2. Diurnal variation and the possible controlling factors

As illustrated in Fig. 4, except  $\alpha$ -HCH at the ES site that did not exhibit diurnal cycling, most of the OCPs show a clear diurnal cycle. Moreover, there are two different patterns for the diurnal cycle observed for those compounds. The patterns of higher daytime air concentrations exhibited for DDTs, chlordane, and HCH, while the patterns of higher nighttime air concentrations exhibited for HCB. Several factors can vary diurnally, that could potentially affect ambient OCPs concentrations. These include the atmospheric boundary layer height, ongoing



**Fig. 2.** The TC/CC ratio with the sum of the concentrations of TC and CC at the two studied sites.



**Fig. 3.** The *o,p'*-DDT/*p,p'*-DDT and *p,p'*-DDE/*p,p'*-DDT ratios with the total DDT concentrations (Total DDT = *o,p'*-DDT + *p,p'*-DDT + *p,p'*-DDE + *p,p'*-DDD) at the two studied sites.

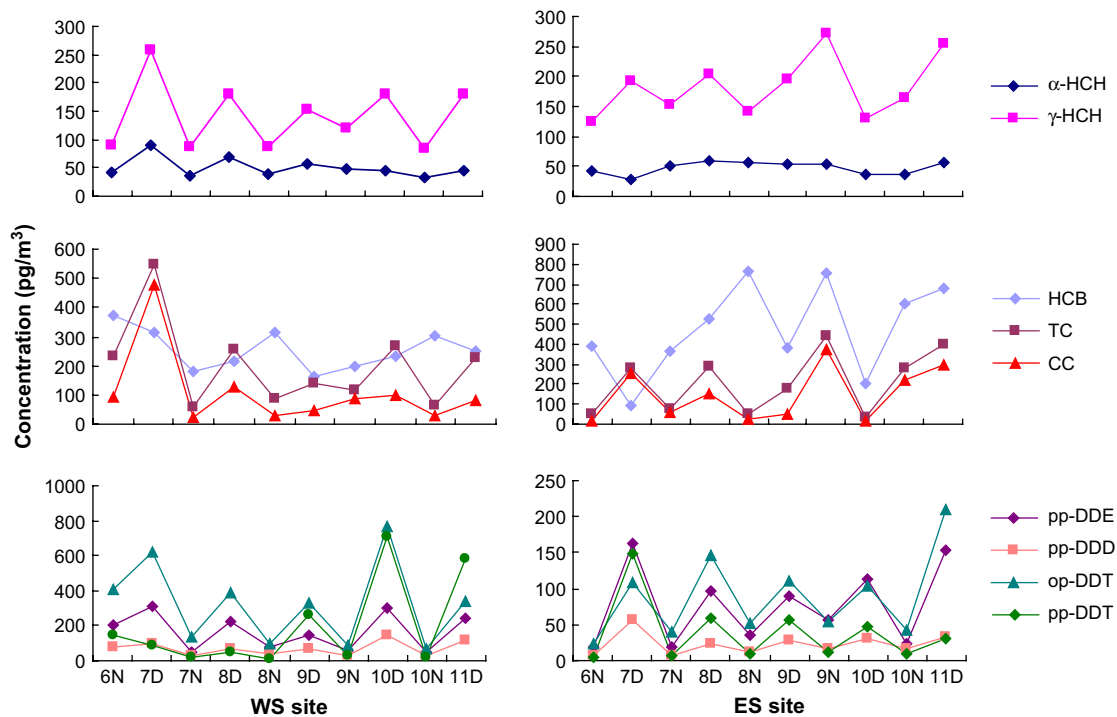


Fig. 4. Diurnal variation of OCPs in Lhasa City.

sources, air and surface soil temperatures, wind direction and wind speed, etc. (MacLeod et al., 2007).

The dependence of semivolatile organic compounds (SOCs) concentration on atmospheric temperature can be described by the Clausius–Clapeyron equation (Bidleman et al., 1998; Cortes et al., 1998; Wania et al., 1998):

$$\ln P = (-\Delta H/R)(1/T) + \text{constant} = m(1/T) + b,$$

where  $P$  is the partial pressure of SOCs in gas-phase (atm),  $\Delta H$  is the enthalpy of vaporization (kJ/mol) and  $T$  is the ambient temperature (K). Inferences can be done using the slope ( $m$ ) and coefficient of determination ( $r^2$ ) with regard to the importance of temperature in controlling the gas-phase ambient concentrations of SOCs and the relative importance of other factors (Lee et al., 2000). Generally steep slopes and high  $r^2$  values indicate that temperature-controlled air-surface cycling and short-term transport influences the ambient gas-phase concentrations (Hoff et al., 1998). Relatively shallow slopes and low  $r^2$  values suggest that other factors (i.e., advection, ongoing sources, wet and dry deposition, atmospheric reactions) and long-range transport influence concentrations (Lee et al., 2000).

The Clausius–Clapeyron regression results and the linear regression coefficient values ( $r^2$ ) of the individual OCPs are given in Table 1. The individual DDT compounds at the both sampling sites tended to be strongly correlated with temperature ( $p < 0.05$ ), showing a  $\ln P$  vs.  $1/T$  slope greater than 14,500. At the both sites, the data reflects the effect of re-volatilization from the surfaces adjacent to the sampling sites. However, much steeper slope and lower  $r^2$  has been found in this study compared to other studies

(Cortes et al., 1998; Li et al., 2007; Yeo et al., 2004), especially for  $p,p'$ -DDT, with the  $m$  values of  $-36,977$  and  $-25,306$  at the WS and ES sites, respectively. This result might be affected by confounding factors (advection and proximity of the sources). During the sampling program, the variation of temperature and wind speed was similar. At night time the temperature and the corresponding wind speed were low while in the daytime the condition was just the reverse (Fig. 5). Therefore, the advection of air from the agriculture regions under the higher ambient temperature during the daytime might enhance the concentration in the receptor site. The impacts of the advection on the diurnal cycling of DDTs at the WS site, which is closer to the agriculture areas (Fig. 1), were more significant. As shown in Fig. 6, the total DDT isomer concentrations and ratios of  $p,p'$ -DDT/ $o,p'$ -DDT and  $p,p'$ -DDT/ $p,p'$ -DDE at the WS sites

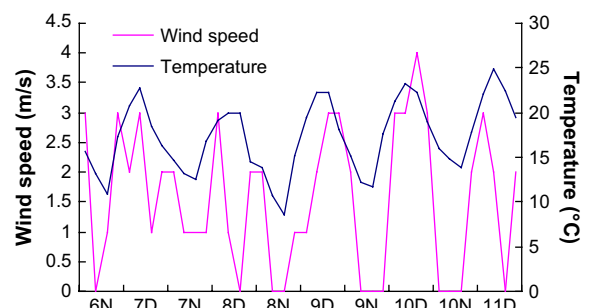


Fig. 5. Diurnal variation of temperature and wind speed.

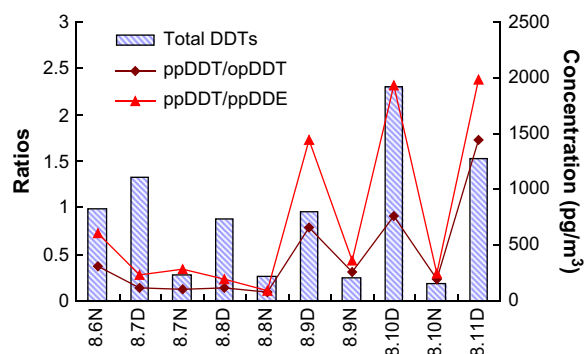


Fig. 6. Diurnal variation of total DDT concentration,  $p,p'$ -DDT/ $o,p'$ -DDT ratios and  $p,p'$ -DDT/ $p,p'$ -DDE ratios at the WS sites.

during the sampling period were plotted as a time-series. Distinguished diurnal patterns were displayed in the DDT isomer concentrations and isomeric ratios of DDTs with the alteration of wind direction and speeds. During the first 2 days, unstable weather influenced the sampling sites with the wind direction changing from east to west. The DDTs followed clear diurnal cycles with the relatively consistent DDTs isomer ratios of more  $o,p'$ -DDT than  $p,p'$ -DDT and more  $p,p'$ -DDE than  $p,p'$ -DDT (from 8.6N to 8.8N). This is consistent with the compositional characteristics of DDTs in dicofol, suggesting the predominant source of DDTs came from dicofol usage (Qiu et al., 2005). Whereas, during the last 3 days (from 8.9D to 8.11D), a stable atmospheric condition was dominant with the strong winds prevailing southwesterly, clearly diurnal cycles were found not only for DDTs concentration but also for the DDTs isomer ratios. When the high speed southwesterly wind was blowing during the daytime period (Fig. 5), the elevated levels of  $p,p'$ -DDT were observed and meanwhile the compositions of DDTs changed to more  $p,p'$ -DDT than  $p,p'$ -DDE and  $o,p'$ -DDT, similar to that of the fresh technical DDT (Fig. 4 and Table 1). Adversely, dicofol-type DDT with more  $o,p'$ -DDT than  $p,p'$ -DDT and more  $p,p'$ -DDE than  $p,p'$ -DDT were observed during night time when the speed of the wind had slowed down.

Gas-phase TC, CC, HCH were negatively correlated with  $1/T$  at the both sites, but there were no significant ( $p > 0.05$ ) or  $r^2$  values were relative lower. This indicated those compound concentrations in the atmosphere at the receptor sites were predominantly driven by the ambient temperature and affected by the advection.

The special behavior of HCB in this study was observed with a negative correlation between the atmospheric concentration and the ambient temperature (Fig. 4). The Clausius–Clapeyron regression results of the flatter slope even positive slope indicates that advection of air or other factors are governing atmospheric concentration levels. HCB might be released to the environment by incomplete combustion (Barber et al., 2005). Therefore, one possible reason may be the enhanced emission of combustion under lower temperature during night time. Besides this, another possible reason might be attributed to the diurnal variation of the boundary layer height (MacLeod et al., 2007).

#### 4. Conclusions

High levels of the atmospheric OCPs concentration were found in the Lhasa region, located in the Tibetan Plateau, especially HCB, TC, CC,  $o,p'$ -DDT, and  $p,p'$ -DDT showing significant local pollution. The potential sources of those pollutants might be due to the combustion and the local usage of chlordane, dicofol and something of the technical DDT. Clearly diurnal variations of the most OCPs concentration were found at the both sampling sites, with higher concentrations during the daytime, and lower concentrations during the night time, while adverse diurnal variability was observed in the HCB concentrations. Compared with the variation in ambient temperature, wind direction and speeds, the diurnal variations for individual OCPs were controlled by different factors. HCB might be determined by the emission source from combustion and the height of the boundary layer.  $\alpha$ -HCH might be controlled by the regional or global concentration levels. Other OCPs were predominantly sourced from the evaporation of the local application those pesticides. As Lhasa River is within the watershed of the Yalung Zangbo River (Yang et al., 2007), it is undoubtedly that the current use and local emissions may be important sources for OCPs in Lhasa and may contribute to OCP contamination in the environment of the populated agricultural Lhasa River basin.

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