



Atmospheric deposition of persistent organic pollutants to the East Rongbuk Glacier in the Himalayas

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ABSTRACT

To assess levels and seasonal trends of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in a high-altitude mountain region, a 2.1 m snowpack sample was collected from the East Rongbuk Glacier at 6572 m a.s.l. on Mt. Everest in September 2005. This snowpack covered a full year period from the fall of 2004 to the summer of 2005 and reflected the major meteorology of the monsoon and non-monsoon seasons. The most abundant compounds detected in the snow samples were γ -hexachlorocyclohexane (γ -HCH) and α -HCH with mean concentrations of 123 pg L^{-1} and 92 pg L^{-1} , respectively. This is the first detection of these compounds in recent snow samples from the Himalayas. Backward air trajectory analysis indicated that the Himalayas could be influenced by the major HCH source regions in both India and China. Among the seven marker PCB congeners (PCB 28, 52, 101, 118, 138, 153, and 180) quantified, PCB 28 and PCB 52 were the only dominant PCB congeners detected, with mean concentrations of 17 pg L^{-1} and 6 pg L^{-1} , respectively. In addition, DDT metabolites, p,p'-DDE and p,p'-DDD were detected in some snow samples and mean concentrations of DDTs were 24 pg L^{-1} . Seasonal differences were observed for α - and γ -HCH concentrations increasing from the non-monsoon season to the monsoon season. Meanwhile, PCB 28 and HCB showed uniform variations with peak concentrations resulting from an effective scavenging by snowfalls between the monsoon and non-monsoon interval. Compared to other high mountain areas, the levels of POPs deposited into the East Rongbuk Glacier were relatively low, resulting from the highest altitude and remoteness from source regions.

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1. Introduction

Persistent organic pollutants (POPs), such as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), are ubiquitous throughout the environment due to their persistence, extensive anthropogenic activities, and the potential for accumulation through the food web. They are subject to long-range atmospheric transport and are deposited in remote areas including polar and high-altitude mountain regions (Daly and Wania, 2005; Wania and Mackay, 1996). The accumulation of POPs in cold regions may be driven by the process of cold condensation promoted by lower temperature and by falling snow as an efficient scavenger (Lei and Wania, 2004). Thus, high-altitude mountain regions as well as the Arctic have received growing interest as receptor regions for long-range transported airborne contaminants (Blais et al., 1998; Fernandez and Grimalt, 2003).

Snow plays an important role in deposition of atmospheric pollutants to the surface environment (Herbert et al., 2006; Lei and

Wania, 2004; Wania et al., 1998). Snow is a major part of the hydrological cycle in cold regions and has a high efficiency at scavenging particles as well as vapor-phase POPs from the atmosphere owing to its large specific surface area (Halsall, 2004). The snowpack therefore serves as a reservoir for various contaminants such as heavy metals and semi-volatile organic compounds (SVOCs). The seasonal snowpack and glacier core are considered an important monitoring matrix because they contain POPs over the long term and may release them during warming seasons or in the future as a result of global warming (Macdonald et al., 2003).

The Himalayas are a massive mountain system separating the Indian subcontinent from the Tibetan Plateau and stretching across six countries: Bhutan, China, India, Nepal, Pakistan, and Afghanistan. The Himalaya mountain system encompasses about 15,000 glaciers which store about 33,000 km^3 of freshwater and serves as a major source of several large perennial rivers (Berthier et al., 2007; Chen et al., 2007). The East Rongbuk Glacier on Mt. Everest, the world's highest peak (a.s.l. 8848 m), is located in southern Tibet. This region is at the boundary of the Indian monsoon-dominated climate and the westerly jet stream-dominated continental climate, showing a strong seasonal variability (Loewen et al., 2007). Since the East Rongbuk Glacier is at very high altitude and under the strong influence of seasonal variation, this region

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is highly favorable for the accumulation of POPs during monsoons. For example, during the southwestern summer Indian monsoon which occurs from June through September, the moisture-laden air mass from the monsoon and local moisture cause snowfall to the glacier. In winter, northeastern winds drive cold and dry continental air through the Tibetan Plateau over the Indian subcontinent (Valsecchi et al., 1999). Long-range atmospheric transport and deposition of POPs and heavy metals to the Himalayan Glaciers is expected to be significantly influenced by these two seasonal monsoon systems (Loewen et al., 2005b). Therefore, studies on POPs in the Himalayas are important.

Although the Himalayas received little attention for POPs monitoring in the past, recently they have received increased attention, with many authors reporting the levels of POPs in the air (Li et al., 2006), soil and grasses (Wang et al., 2007b), spruce needles (Wang et al., 2006), fresh-fallen snow (Wang et al., 2007a), and ice core (Wang et al., 2008a; Wang et al., 2008b) from the Himalayas. In those studies, even though hexachlorocyclohexanes (HCHs) were extensively used in the region, HCHs were detected only in the air and spruce needle samples, not in the ice core or snow. The latter result is rather suspicious, so additional investigation is demanded (Loewen et al., 2005b).

In our previous study, the vertical distribution of trace elements in a series of samples from a snowpack in the East Rongbuk Glacier of Mt. Everest was investigated (Lee et al., 2008). Here we continue this work with an investigation of the distribution of OCPs and PCBs in the same snowpack. The snowpack had a 2.1 m-depth, covering a full year period from the fall of 2004 to the summer of 2005. The samples were analyzed by the isotope dilution method using gas chromatography–high resolution mass spectrometry (GC–HRMS). The objective of this study is to investigate the role of cold trapping and seasonal meteorological changes on the levels and patterns of POPs in a snowpack from the Himalayas.

2. Materials and methods

2.1. Sampling site and methodology

The sampling site and method were precisely described by Lee et al. (2008). In brief, the sampling site (28°01′08″N, 86°57′48″E, 6576 m a.s.l.) was at the northeastern slope of Mt. Everest (Qomolangma) in the Himalayas (Fig. 1). A 2.1-m-depth snowpack was sampled on September 4, 2005. A shallow snow pit was hand-dug with pre-

cleaned plastic shovels by operators wearing full clean room garments and polyethylene gloves. Approximately 10 cm of snow was shaved away from the upwind wall using pre-cleaned low density polyethylene (LDPE) scrapers. A continuous series of 42 snowpack samples were collected from the snow surface to a depth of 2.1 m at 5-cm intervals, by pushing pre-cleaned cylindrical Teflon containers (5 cm in diameter, 35 cm in length) horizontally into the wall of the pit using a pre-cleaned LDPE hammer. The samples were then immediately transferred into pre-cleaned 500 mL LDPE bottles. To minimize contamination from the environment as well as between samples, extreme care was taken during collection, handling, and storage of the samples. For example, the sampling was always conducted from the upwind side of the snow because of potential contamination resulting from human activity. The bottles were packed in double sealed pre-cleaned LDPE bags and were kept frozen until instrumental analysis.

2.2. Extraction and cleanup

The snowpack samples were melted at room temperature inside class 10 clean benches in a class 1000 clean room at the Korea Polar Research Institute (KOPRI). Aliquots were taken for POPs analysis. As each aliquot was quite small, sets of three adjacent samples were combined to increase sample volume for analysis. The volume of the combined samples was approximately 150 mL. The melted snowpack samples were transferred to glass separatory funnels for liquid–liquid extraction. Isotopically labeled standards of 21 OCPs (ES-5349, Cambridge Isotope Labs., USA) and 6 PCBs (P48M-ES, Wellington Labs, Canada) were spiked into the samples as recovery surrogates before extraction. The samples were extracted with 50 mL of dichloromethane three times. The dichloromethane extracts were dried over sodium sulfate (Kanto Chemical Co., Inc., Japan) and then concentrated by a rotary evaporator. Sodium sulfate was cleaned by heating at 450 °C for 24 h before use. Solvents (acetone, dichloromethane, toluene, n-hexane) for cleaning and extraction were purchased from Merck (Darmstadt, Germany).

To reduce laboratory contamination, no further cleanup was conducted using a silica gel or Florisil column because these absorbents can contain some contaminants such as low-chlorinated PCBs. The concentrated extracts were transferred to GC vials using 1 mL of dichloromethane/hexane (1:1 v/v), 2 µL of dodecane (Aldrich, USA) was added as a keeper for volatile compounds, and the mixture subsequently evaporated at room temperature until dry. The vials

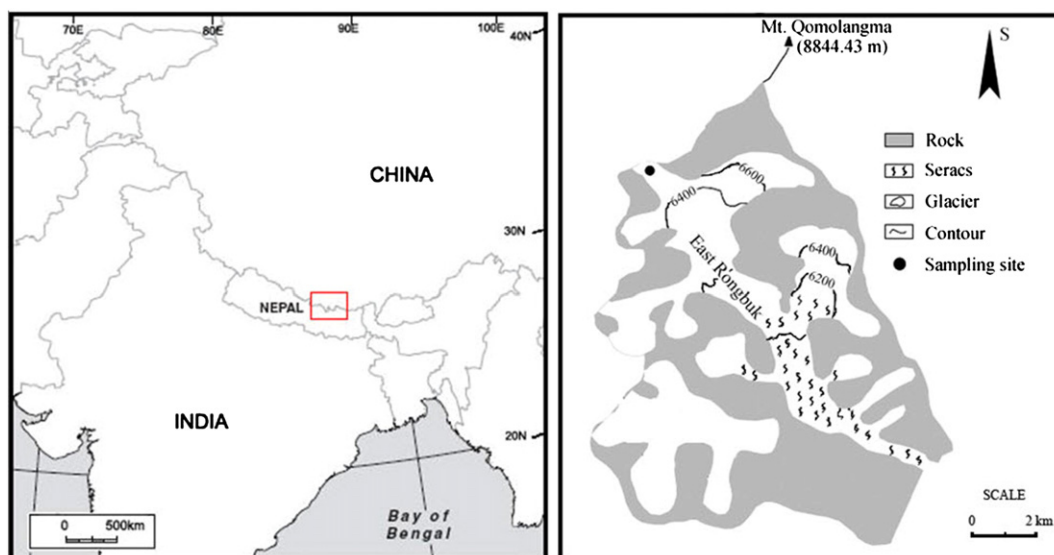


Fig. 1. Location of the snowpack sampling site (28°01′08″N, 86°57′48″E, 6576 m a.s.l.) on the northern slope of Mt. Everest.

were stored at $-20\text{ }^{\circ}\text{C}$ until GC–HRMS analysis. Before analysis, the samples were reconstituted with isotopically labeled standards: 10 μL of EC-5350 ($^{13}\text{C}_{12}$ -PCB 15, $^{13}\text{C}_{12}$ -PCB 70; Cambridge Isotope Labs., USA) and 5 μL of P48M-RS ($^{13}\text{C}_{12}$ -PCB 70, $^{13}\text{C}_{12}$ -PCB 111, $^{13}\text{C}_{12}$ -PCB 170; Wellington Labs, Canada). The final volume was adjusted to 20 μL with nonane (Aldrich, USA).

2.3. GC–HRMS analysis

GC–HRMS measurements were performed on a JMS-800D instrument (JEOL, Japan) interfaced with a 6890N gas chromatography (Agilent Technologies, USA). Measurements were carried out using a 60 m \times 0.25 mm \times 0.25 μm DB-5MS capillary column (Agilent Technologies, USA). The initial column temperature was 100 $^{\circ}\text{C}$ and was held for 1.0 min. The oven temperature was then raised to 220 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C min}^{-1}$ and held for 4 min. It was then increased to 300 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C min}^{-1}$ and held for 5 min. Two separate splitless injections were carried out with an injector temperature of 280 $^{\circ}\text{C}$. The source temperature was 280 $^{\circ}\text{C}$ in the electron impact (EI) mode using ionization energy of 38 eV. All spectra were acquired in the selected ion monitoring (SIM) mode with a resolution of more than 10,000. Mass ions monitored were reported elsewhere (Barr et al., 2003).

2.4. Quality assurance/quality control

The isotope dilution method was used for OCP and PCB determinations. Samples were spiked with ^{13}C -labeled OCP ($^{13}\text{C}_6$ - α -HCH, $^{13}\text{C}_6$ - β -HCH, $^{13}\text{C}_6$ - γ -HCH, $^{13}\text{C}_6$ - δ -HCH, $^{13}\text{C}_6$ -HCB, $^{13}\text{C}_{10}$ -Heptachlor, $^{13}\text{C}_{10}$ -Heptachlor epoxide, $^{13}\text{C}_{12}$ -Aldrin, $^{13}\text{C}_{12}$ -Dieldrin, $^{13}\text{C}_{12}$ -Endrin, $^{13}\text{C}_{10}$ -Oxychlorane, $^{13}\text{C}_{10}$ -trans-Chlordane, $^{13}\text{C}_{10}$ -trans-Nonachlor, $^{13}\text{C}_{10}$ -cis-Nonachlor, $^{13}\text{C}_{12}$ -o,p'-DDE, $^{13}\text{C}_{12}$ -p,p'-DDE, $^{13}\text{C}_{12}$ -o,p'-DDD, $^{13}\text{C}_{12}$ -p,p'-DDD, $^{13}\text{C}_{12}$ -o,p'-DDT, $^{13}\text{C}_{12}$ -p,p'-DDT, and $^{13}\text{C}_{10}$ -Mirex) and ^{13}C -labeled PCB ($^{13}\text{C}_{12}$ -PCB 28, $^{13}\text{C}_{12}$ -PCB 52, $^{13}\text{C}_{12}$ -PCB 101, $^{13}\text{C}_{12}$ -PCB 138, $^{13}\text{C}_{12}$ -PCB 153, and $^{13}\text{C}_{12}$ -PCB 180) internal standards before extraction. The ^{13}C -labeled recovery standards ($^{13}\text{C}_{12}$ -PCB 15, $^{13}\text{C}_{12}$ -PCB 70, $^{13}\text{C}_{12}$ -PCB 111, and $^{13}\text{C}_{12}$ -PCB 170) were spiked before GC–HRMS

analysis. The average recovery of ^{13}C -labeled OCPs ranged from 75 to 125%, and that of ^{13}C -labeled PCBs ranged from 76 to 95%, respectively.

Method blanks ($n=4$) were subject to the same experimental procedures as the real samples. Pre-cleaned bottles were filled with Milli-Q water and kept frozen until analysis to be used as method blanks. OCPs were not detected in method blanks except for HCB. Average blank levels (mean \pm standard deviation) were 16.4 \pm 1.6, 7.0 \pm 0.6, and 1.8 \pm 0.2 pg for HCB, PCB 28, and PCB 52, respectively. Reported values in this study were blank corrected. Limits of detection (LOD) were defined as three times signal-to-noise ratio (S/N) and were calculated for each sample. Average detection limits were 11–104 pg L^{-1} for OCPs and 5–11 pg L^{-1} for PCBs (Table 1).

2.5. Backward air trajectories

In order to assess the origin of air masses arriving at the sampling site, 5-day backward air trajectories for one year between September 2004 and August 2005 were calculated using HYSPLIT 4 (Hybrid Single Particle Lagrangian Integrated Trajectory, Version 4) model (<http://www.arl.noaa.gov/ready/hysplit4.html>). This model was developed by NOAA/ARL (US National Oceanic and Atmospheric Administration/Air Resources Laboratory). Backward air trajectory shows an aerial plan view of the path taken by air parcels at specific altitude. Trajectories at 6500 m above ground were calculated once a day at 00:00 UTC (Coordinated Universal Time). The seasonal (monsoon and non-monsoon) and monthly trajectories are presented in Fig. 2 and Fig. S1 in the supporting information.

3. Results and discussion

3.1. Concentrations of POPs in the East Rongbuk Glacier snowpack

Table 1 presents the concentrations of OCPs and PCBs in the snowpack samples collected in this study. A comparison with POP concentrations in snow and glacier samples collected from other high-altitude mountain areas is provided in Table 2. As shown in these

Table 1
Concentrations (pg L^{-1}) of organochlorine pesticides and polychlorinated biphenyls in the snowpack measured in this study.

Compounds	0–15 cm	~30 cm	~45 cm	~60 cm	~75 cm	~90 cm	~105 cm	~120 cm	~135 cm	~150 cm	~165 cm	~180 cm	~195 cm	~210 cm	DL
α -HCH	130	108	115	105	89	78	105	70	85	87	64	61	125	68	47
β -HCH	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	63
γ -HCH	193	173	164	161	113	111	169	111	78	115	66	ND	185	76	56
δ -HCH	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	57
HCB	30	12	ND	49	58	17	145	33	45	21	22	8	16	13	13
Heptachlor	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	27
Heptachlor Epoxide	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	11
Aldrin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	66
Dieldrin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	46
Endrin	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	104
Oxychlorane	ND	ND	ND	42	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	30
trans-Chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	15
cis-Chlordane	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	17
trans-Nonachlor	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	25
cis-Nonachlor	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20
o,p'-DDE	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	15
p,p'-DDE	ND	ND	ND	13	15	16	20	10	22	17	15	14	ND	15	10
o,p'-DDD	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	20
p,p'-DDD	ND	ND	ND	ND	24	25	22	23	18	24	28	21	ND	ND	16
o,p'-DDT	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	44
p,p'-DDT	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	75
Mirex	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	22
PCB 28	13	4	5	6	28	6	48	26	38	17	9	13	11	11	9
PCB 52	8	2	4	6	5	4	9	12	11	6	3	4	7	ND	11
PCB 101	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10
PCB 118	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	10
PCB 138	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	6
PCB 153	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	5
PCB 180	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	8

DL: average detection limit; ND: not detected.

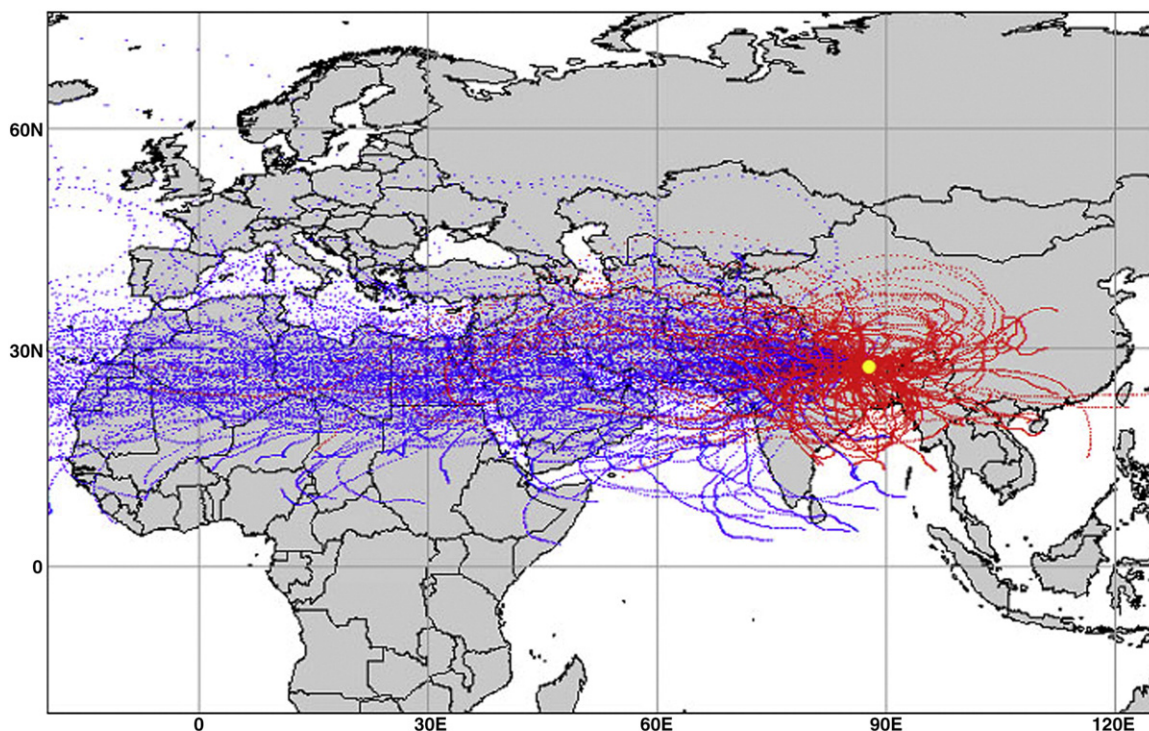


Fig. 2. Five-day backward air trajectories at the sampling site (yellow spot) between September 2004 and August 2005. Red trajectories are for the summer monsoon period, and blue trajectories are for the non-monsoon period. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

tables, more volatile compounds such as α -/ γ -HCHs, PCB 28 and HCB were prevalent in the snowpack, but less volatile compounds such as DDTs and highly chlorinated PCBs were rare. The occurrence of more volatile compounds in the high-altitude mountain region is probably due to long-range atmospheric transport. The following sections discuss the levels and patterns of the relatively volatile compounds, detected in this study.

3.2. Hexachlorocyclohexanes (α - and γ -HCH)

Both α -HCH and γ -HCH were detected in the snow samples collected in this study. The concentrations of α -HCH ranged from 61 to 130 pg L^{-1} with an average of 92 pg L^{-1} , and those of γ -HCH ranged from BDL (below detection limit) to 193 pg L^{-1} with an average of 123 pg L^{-1} . To the best of our knowledge, this is the first study to detect HCHs in recent snow obtained from the Himalaya region. Previous studies detected neither α -HCH nor γ -HCH in firn core samples from Mt. Xixiabangma (Wang et al., 2008b) or in fresh-fallen snow samples from Mt. Everest (Wang et al., 2007a). However, the detection of HCHs in snow from the Himalayas has been expected because this region is close to major HCH source regions in India and

China. HCHs are available in two commercial formulations: one is technical HCH, a mixture of α -HCH (55–80%) and γ -HCH (10–15%), and the other is lindane containing more than 99% γ -HCH. In the past, India and China were the largest consumers of technical HCH, and lindane has been used even after the banning of technical HCHs in these countries (Loewen et al., 2005b; Voldner and Li, 1995). Because of the heavy use of HCHs, high levels of HCHs ranging from 1.4 to 2.9 ng g^{-1} dry weight were observed in spruce needles from the northern slope of the central Himalayas in the Tibetan Plateau in China (Wang et al., 2006). The gaseous concentrations of α -HCH and γ -HCH in air samples collected from the Rongbuk Valley on Mt. Everest were measured in ranges of 8.7–25.9 and 2.6–11.1 pg m^{-3} , respectively in May–June 2002 (Li et al., 2006). Those studies also indicated that the Himalaya mountain region was influenced by both long-range atmospheric transport and cold condensation of HCHs, like other alpine regions (Li et al., 2006; Wang et al., 2006; Yang et al., 2007).

The ratio of α / γ -HCH has been used to identify emission sources and transport of technical HCH versus lindane (Wurl et al., 2006). The α / γ -HCH ratio in technical HCH is around 4–7 (Shen et al., 2004). In this study, γ -HCH was a more abundant isomer; the ratio of α / γ -HCH

Table 2

Average and range of concentrations (pg L^{-1}) of persistent organic pollutants from various mountain areas.

Sampling year	2000	2003	2002	1997	2005	2005	2005
Sampling site	Colle de Lys	Colle de Lys	Punta Indren	Banff	ERG	Dasuopu	ERG
	Alps	Alps	Alps	Rocky	Himalaya	Himalaya	Himalaya
Altitude (m)	4250	4250	3260	1920–2400	5900–6500	6720	6576
Sample type	Firn core	Snow	Snow	Snow	Snow	Firn core	Snowpack
Cover year	1997–2000	2003 July	2002 August	1997 March	2005 April	1998–2005	2004–2005
α -HCH (pg L^{-1})	ND	ND	31 (16–47)	236 (48–430)	ND	ND	92 (61–130)
γ -HCH (pg L^{-1})	435 (84–2343)	88 (11–234)	403 (333–563)	155 (62–280)	ND	ND	123 (ND–193)
HCB (pg L^{-1})	120 (53–168)	3.8 (2.6–5.8)	37 (9.3–95)	12 (3.9–28)	44–72	NA	33 (ND–145)
DDTs (pg L^{-1})	395 (233–646)	1.6 (ND–3.6)	66 (47–96)	21 (ND–61)	401–1560	150–300	24 (ND–43)
PCBs (pg L^{-1})	1175 (585–1944)	91 (16–243)	150 (85–297)	1354 (826–2000)	NA	90–340	16 (3–48)
Reference	Villa et al. (2006)	Finizio et al. (2006)	Herbert et al. (2004)	Lafreniere et al. (2006)	Wang et al. (2007a)	Wang et al. (2008b)	This study

ND: not detected; NA: not available; ERG: East Rongbuk Glacier.

ranged from 0.62 to 1.09 with an average of 0.74 ± 0.15 , suggesting the old usage of technical HCH and the more recent use of lindane in the vicinity of the Himalayas. Lindane has been used as an agricultural pesticide in India and China since 1997 and 1991, respectively (Li et al., 2001; Loewen et al., 2005b; Voldner and Li, 1995). Moreover, γ -HCH has a lower Henry's law constant (H) than α -HCH; e.g., γ -HCH is more water soluble than α -HCH. Thus, α -HCH is more likely to be removed from the snowpack by wind pumping. Wind ventilation was found to result in the rapid loss of α -HCH from the snowpack of the Italian Alps (Herbert et al., 2006). This property may lead to lower α/γ -HCH ratios in a snowpack. Similar α/γ -HCH ratios in snow were observed from European mountains where γ -HCH was a prevalent isomer because of the phasing out of technical HCH and current use of lindane in Europe (Carrera et al., 2001; Finizio et al., 2006; Herbert et al., 2004; Herbert et al., 2006; Villa et al., 2006) and from the Canadian Rocky mountains, ranging from 0.73 to 1.87 (Lafreniere et al., 2006).

3.3. DDT and its metabolites

Extremely low concentrations of DDT metabolites were found in some snow samples. The DDT metabolites detected were p,p'-DDE and p,p'-DDD, while p,p'-DDT and o,p'-DDT were not detected in any samples. The concentrations of DDTs ranged from BDL–43 pg L^{-1} with an average of 24 pg L^{-1} . These levels were comparable with those in alpine snow from the Alps (BDL–3.6 pg L^{-1}) (Herbert et al., 2004) and the Canadian Rocky mountains (BDL–61 pg L^{-1}) (Lafreniere et al., 2006). Even though the Himalaya region is close to DDT sources (Loewen et al., 2005b; Voldner and Li, 1995), very high-altitude sites (>6500 m) may have low concentrations of DDTs (Wang et al., 2006). The concentrations of less volatile compounds such as DDTs and highly chlorinated PCBs were reported to be inversely correlated with elevation because their heavy molecular weights and low volatilities may prevent them from reaching high elevation regions (Blais et al., 1998; Estellano et al., 2008). For instance, soil samples from the central Himalayas over altitudes ranging from 841 to 5450 m showed the highest level of DDTs at 2638 m and a decreasing trend of concentrations with altitude (Loewen et al., 2005a). In the Andes mountain region, air concentrations of DDTs were below detection limits in all samples collected at elevation sites over 2000 m, even though DDTs are currently used in South America (Estellano et al., 2008). The altitude profiles of DDTs in spruce needles from the Himalaya region also reported an inverse correlation with elevation (Wang et al., 2006). In addition, the concentrations of individual DDTs detected in soil were not correlated with elevation, whereas the DDT concentrations in grass samples collected from Mt. Everest with an elevation ranging from 4700 to 5620 m showed a decrease with increasing elevation (Wang et al., 2007b). However, another study detected concentrations of DDTs and metabolites (p,p'-DDD and p,p'-DDT) 15 to 30 times higher than ours in a firn core from the Dasuopu glacier, near our sampling site (Wang et al., 2008b). These conflicting results should be confirmed and carefully considered to assess snow contamination in the Himalayas.

3.4. Polychlorinated biphenyls (PCBs)

Among the 7 marker PCB congeners (PCB 28, 52, 101, 118, 138, 153, 180), only PCB 28 (tri-CB) and PCB 52 (tetra-CB) were detected in most samples. The concentrations of PCB 28 and PCB 52 ranged from 4 to 48 pg L^{-1} with an average of 17 pg L^{-1} and from BDL to 12 pg L^{-1} with an average of 6 pg L^{-1} , respectively. The levels of PCB congeners in our study were comparable with those reported for fresh snow from Punta Indren in the Alps (Herbert et al., 2004) and lower than those in a firn core (Villa et al., 2006) and fresh snow from Colle de Lys in the Alps (Finizio et al., 2006). Meanwhile, Wang et al. (2008b) reported that only PCB 28 was detected in the Himalayan firn core samples with relatively high concentrations ranging from 90 to

340 pg L^{-1} . The total PCB concentrations in this study were much lower than those in other studies because high-chlorinated PCBs were not detected at all.

In general, lighter PCB congeners are more easily transported via the atmosphere mainly in the gas phase, while heavier PCB congeners are mostly associated with particles and tend to deposit to the surface near sources (Wania and Su, 2004). For this reason, both monitoring and simulation studies suggested that the PCB composition shifts toward more volatile congeners with increasing latitudes (Choi et al., 2008; Wania and Su, 2004), i.e., the hypothesis of global fractionation (Wania and Mackay, 1996). The contribution of volatile PCBs can also be expected to increase with elevation in high mountains, which is referred to as "altitudinal fractionation" (Daly and Wania, 2005). In addition, it should be noted that the global emissions of these volatile congeners are much larger than other less volatile congeners, accounting for 53% of the total 7 marker congeners in 2004–2005 (Breivik et al., 2007). The global distribution of PCB emissions (Fig. S2) shows that India emits more PCBs than other surrounding countries, which likely affects the levels of PCBs in the Himalayas.

3.5. Seasonal variations of OCPs and PCBs

Vertical distributions of POPs in a snowpack can reflect variations in deposition, and are significantly influenced by meteorological patterns. The Himalaya region has a strong seasonal variation of meteorological conditions which can significantly affect the transport and the deposition of POPs to this region (Loewen et al., 2005b). Fig. 2 shows daily backward air trajectories for the full one-year period between September 2004 and August 2005 (red: summer monsoon period between June and September, blue: rest of the year). Monthly trajectories are also provided in the supporting information (Fig. S1). As clearly shown in these figures, westerly winds prevail over the non-monsoon seasons. In the non-monsoon seasons, Mt. Everest region was controlled by the westerly winds and influenced by air from the arid and semi-arid regions (Hindman and Upadhyay, 2002). Relative humidity was low with the average of 41.6% in May, increased rapidly in June 2005 (Xie et al., 2006). Many of the 5-day trajectories for these seasons even originated from the Atlantic Ocean, indicating the fast airflow of the jet stream. On the other hand, air masses during the summer monsoon season generally came from India and China, implying increased deposition of POPs to snow. The summer monsoon commenced in June 2005, and impacted on Mt. Everest region, wherefore relative humidity kept high with the average of 86.0% in July. Wind speed was decreased and southerly wind was predominated (Xie et al., 2006).

The snowpack samples had been dated by combining the depth profiles of oxygen isotopes ($\delta^{18}\text{O}$), major ions (Ca^{2+} and SO_4^{2-}) and Al content (as a reference element of the mineral dust), and they showed a very strong difference in concentrations between the monsoon and non-monsoon seasons (Lee et al., 2008). The seasonal distribution of $\delta^{18}\text{O}$ in precipitation is characterized by lower $\delta^{18}\text{O}$ levels during the summer monsoon season and enriched $\delta^{18}\text{O}$ levels during the non-monsoon period (Tian et al., 2003). The $\delta^{18}\text{O}$ values of the snowpack decreased from -10.1 to -23.4% . The more negative values represent the summer monsoon and the less negative values represent the winter time. The concentrations of major ions (Ca^{2+} and SO_4^{2-}) increased in non-monsoon snow, which is consistent with the previous results (Kang et al., 2004). Glacio-chemical studies of snow and ice in the central Himalayas have also reported seasonal differences in major ions related to the influx of mineral dust between monsoon and non-monsoon (Kang et al., 2004). The well-defined $\delta^{18}\text{O}$, Ca^{2+} , SO_4^{2-} and Al concentration profiles (Fig. S3) show the snowpack in this study covered approximately one full year of snow accumulation, from September 2004 to August 2005 (Lee et al., 2008).

Seasonal differences in the snowpack concentrations were observed for both α - and γ -HCH, with similar patterns of variability

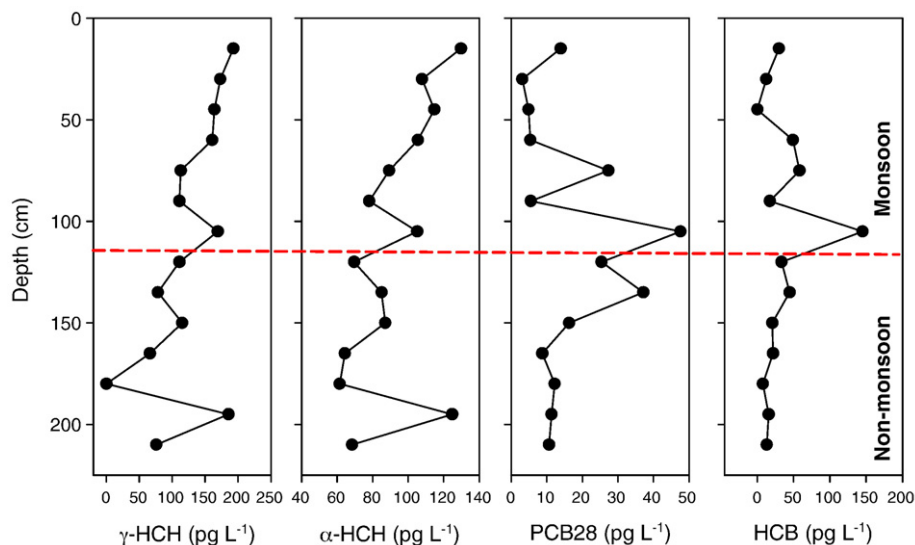


Fig. 3. Depth profiles of α -/ γ -HCH, PCB 28, and HCB concentrations in the snowpack (the dotted line represents the seasonal boundary between monsoon and non-monsoon seasons).

(Fig. 3). The concentrations of HCHs were low during the non-monsoon season (December–April) and increased during the monsoon season (June–September). The *t*-test revealed that significant differences ($p < 0.05$) for both α - and γ -HCH concentrations were found between the monsoon and non-monsoon seasons. This result can be explained by the fact that the sampling site was influenced by air masses transported from the Indian subcontinent and China during the summer monsoon season. The ratio of α / γ -HCH slightly decreased during the summer, suggesting that γ -HCH might be being used, and indeed lindane is currently used as an insecticide both in India and China. As depicted in Fig. 3, distinct concentration peaks of HCHs at the 200 cm depth were correlated with noticeable concentration peaks of Al, Zn, As, Sr, Cd, Sb and Pb at 190–200 cm depth, originating from crustal dust (Lee et al., 2008). It was also reported that the Al concentration exhibited the highest concentration during non-monsoon seasons (Xu et al., 2007).

On the other hand, the variations of PCB 28 and HCB were different from that of HCHs (Fig. 3). The concentrations of PCB 28 and HCB showed uniform variations, but there were peak concentrations at the 105–120 cm depth interval, which is related to monsoon snow deposition (Lee et al., 2008). The relatively small seasonal variability of PCB 28 and HCB could be explained by the facts that the emission sources of these compounds were not quite seasonally dependent and air masses arriving at the sampling site mostly passed over India, which is considered to be the most important source of PCBs near the sampling site (Fig. S2). The peak concentrations of PCB 28 and HCB at the 105–120 cm depth interval (i.e., more deposition) might result from efficient scavenging by falling snow at the beginning of the monsoon season; heavy precipitation was generally recorded in the monsoon season.

4. Conclusion

This study reported the concentrations of OCPs and PCBs in a snowpack from the East Rongbuk Glacier at 6572 m a.s.l. in Mt. Everest. α -HCH and γ -HCH were the major abundant contaminants in the snowpack, indicating that an extremely high-altitude mountain was influenced by long-range atmospheric transport of some pesticides such as lindane currently being used in the vicinity of the Himalayas. In addition, our results suggested that more volatile POPs, such as α -/ γ -HCH, HCB and PCB 28 were prone to undergo atmospheric deposition to snow. Meanwhile, less volatile POPs, such as DDT and highly chlorinated PCBs were not detected in the snow

samples. The influence of seasonal changes in meteorological conditions (monsoon and non-monsoon) on the level of POPs was also assessed. It can be concluded that high precipitation from air masses passing over India and China during the monsoon season increased the levels of POPs in the snow samples.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.scitotenv.2009.09.015](https://doi.org/10.1016/j.scitotenv.2009.09.015).

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