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Organochlorine pesticides in fresh-fallen snow on East Rongbuk Glacier of Mt. Qomolangma (Everest)

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During a field campaign in April 2005, fresh-fallen snow samples were collected on the East Rongbuk Glacier of the Mt. Qomolangma at four altitudes (6500 m, 6300 m, 6100 m and 5900 m), to study the role of Mt. Qomolangma as "cold-traps" for Persistent Organic Pollutants. From these snow samples collected at the highest-altitude, organochlorine pesticides (OCPs):HCB, *p, p'*-DDT and *p, p'*-DDD were detected, with the concentrations in the ranges of 44—72 pg/L, 401—1560 pg/L, and 20—80 pg/L, respectively. The concentration of *o, p'*-DDT was around the method detection limit. Analysis of backward trajectories showed that the detected compounds came from the north of India, suggesting that DDTs detected in the snow were possibly originated from new emissions in this area. Relationships between the concentrations of OCPs in snow samples and the sampling altitudes were discussed. The altitudes had no obvious effect on HCB concentrations in the fresh-fallen snow, while increases in the concentrations of *p, p'*-DDT and *p, p'*-DDD with increasing altitude were found, which was reversed compared to the trends observed in North America. Three factors likely resulted in this trend: (1) the properties of the target compounds; (2) the low temperatures at high altitudes; and (3) the location of the mountain sampling sites relative to their sources.

Mt. Qomolangma (Everest), Tibet, organochlorine pesticides, snow, long-range transport

Persistent organic pollutants (POPs) are chemically stabile and semi-volatile, which allows them to transport to remote areas far away from their sources. Due to the temperature gradients that exist along latitudes, these compounds tend to condense in the Polar Regions[1,2] and have a latitudinal distribution that is termed "Global Distribution Effect"[3]. High mountains could act as "cold condensers" for POPs due to the temperature gradient that exists when moving from lower to higher altitudes[4]. A common theme throughout the research of POPs in high mountains is the investigation of concentration differences along altitudinal gradients, and the location of the mountain sampling sites relative to the source is obviously an important factor that controls the relationship between the concentration and altitude[5].

The role of snow as an effective scavenger for organic chemicals is well known[6]. Snow may be a valuable medium for monitoring contaminant levels in a region. Until now, the published field studies about POPs in high mountains were all carried out at sites with altitudes lower than 4500 m above sea level (m a.s.l.).

With an average altitude of about 4000 m a.s.l., an area of 2.5 million km^2, and an annual average temperature lower than 0℃[7], the Tibetan Plateau should play an important role as a cold condenser of POPs. It is surrounded by many sources of POPs, including highly populated and rapidly industrializing countries that pesticide usage and industrial pollution are fast increasing.

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Under Asian monsoons and westerly winds, air masses can bring pollutants from the Indian subcontinent and the Eurasian continent to the Tibetan Plateau. Therefore, it is reasonable to believe that the plateau could have an important impact on the global transport of POPs, which has been suggested by limited researches[8,9].

As the summit of the earth, Mt. Qomolangma is considered a pristine region far away from human activities. However, its location at the southern edge of the Tibetan Plateau makes it a possible receptor of POPs transported directly from the Indian subcontinent, where OCPs have been widely used and may still be in use due to their low cost, even though some of them have been banned for use in agriculture[10].

In April 2005, four fresh-fallen snow samples were collected at different altitudes in the Mt. Qomolangma region. This paper reports the concentration of OCPs in the snow and their possible sources. The relationship between their concentrations and altitudes, and possible factors that control this relationship are discussed.

1 Materials and methods

1.1 Sample collection

Snow samples were collected at the East Rongbuk Glacier on the northern slope of Mt. Qomolangma (86°57′E, 28°01′N, Figure 1) in April 2005. Four snow samples were taken from a 2-cm-deep layer of fresh snow (snowfall on April 28) at four altitudes (Sample A: 6500 m，B: 6300 m, C: 6100 m, D: 5900 m). Samples A and B were collected at the surface of the Glacier on April 28, and samples C and D were collected at the seracs on the second day. All the samples were collected within 24 h after the snowfall, using a solvent-cleaned stainless-steel shovel and pre-cleaned gas-tight glass bottle (500 mL, capped with PTFE-coated septa). Special attention was given to collecting only the upper snow layer, to avoid mixing this layer with the older snow below. After collection, snow samples were transported and kept at 0℃ until analysis.

1.2 Extraction

Organochlorine pesticides standards (α-HCH, β-HCH, γ-HCH, HCB, Heptachlor-epoxide, Heptachlor, α-endosulfan, β-endosulfan, Aldrin, Endrin, Dieldrin, *o,p*′-DDT, *p,p*′-DDT, *o,p*′-DDD, *p,p*′-DDD, *o,p*′-DDE, *p,p*′-DDE, *cis*-Chlordane, *trans*-Chlordane) and isotopic standards (α-HCH-D6, *p,p*′-DDE-D8) were purchased from Dr. Ehrenstofer (Germany). No contamination of the target compounds was found in methanol (HPLC Grade, J&K Chemical LTD, USA), which is used as the solvent for standard solution.

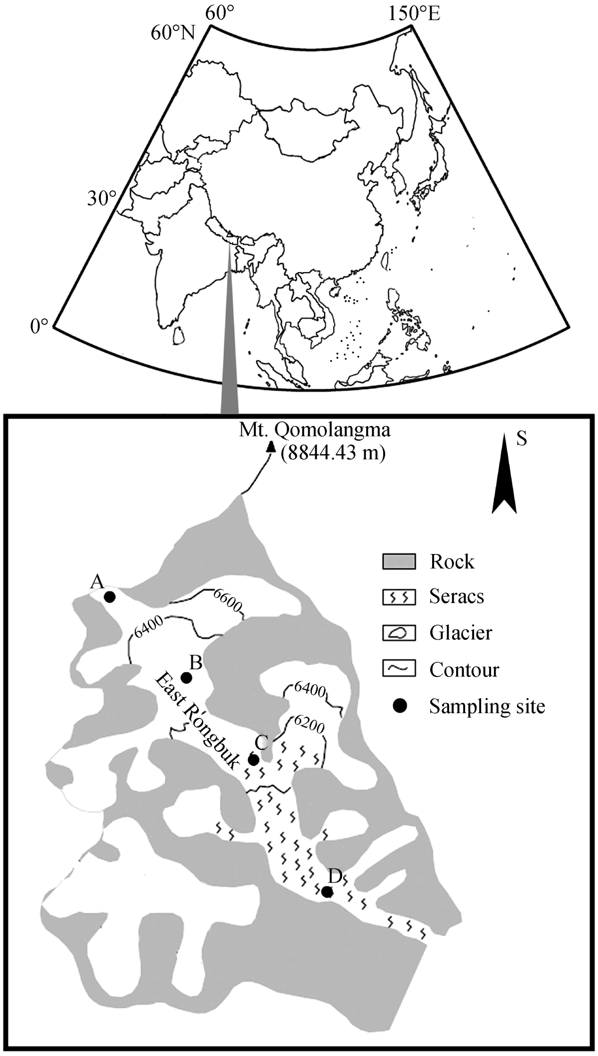

Figure 1 Snow sampling site on the East Rongbuk Glacier, Mt. Qomolangma region.

Headspace Solid-Phase Microextraction (HS-SPME) was chosen for the extraction because of its minimal use of solvent, which also minimizes contamination. This method only requires a small volume of sample, which is convenient because sampling is very difficult under harsh environmental conditions in high mountains. The HS-SPME method has a Method Quantification Limitation (MQL, defined as the concentration of an analyte that produces one peak with a signal-to-noise ratio of 10) lower than direct immersion SPME for OCPs.

The extraction was conducted without separating the particulate and dissolved phases. Because the redistribu-

Table 1 Organochlorine pesticides concentrations in snow and MQL (pg/L)

Chemical	A (6500 m)	B (6300 m)	C (6100 m)	D (5900 m)	MQL
HCB	65	72	44	60	40
p,p′-DDT	1560	1410	401	470	80
p,p′-DDD	80	51	20	21	20
DDD/DDT	0.051	0.036	0.045	0.044	—

N.D. Comp.	HCHs	*p,p*’-DDE	*o,p′*-DDT	*o,p′*-DDD	*o,p′*-DDE	Endosulfans	Chlordanes	Heptachlor
MQL	100—200	80	40	20	30	500	50	100

N. D. Comp.: Compounds that were not detected; MQL: Method Quantification Limitation.

tion of contaminants occurs between the dissolved and particulate phases during the snow melting process, the melt snow does not necessarily reflect the distribution of chemicals in the original snow fractions nor the state of the compounds during their scavenging from the atmosphere[11].

The SPME apparatus (Supelco) consisted of a magnetic stirring and heater unit and a manual reusable syringe assembly with a fiber coating of 65 μm Polydimethyl-Siloxane/Divinylbenzene (PDMS-DVB). A 35 mL aliquot of a melt snow sample was placed into a 40 mL vial capped with PTFE-coated septa. The fiber was lowered into the vial and exposed to the headspace gases above the sample for 60 min at 90℃ with a stirring rate of 900 r/m using a glass stir bar. After extraction, the fiber was thermally desorbed for 4 min into the GC injector at 250℃. Three replicate extractions were conducted for every sample.

1.3 Analysis

Quantitative analysis of organochlorine pesticides was carried out with gas chromatography (Finnigan Trace-GC) mass spectrometry (Finnigan PolarisQ) installed with a DB-5 column (30 m×0.25 mm i.d., 0.25 μm film thickness, J&W).

The GC injector was kept at 250℃ in the split/splitless mode, and high-purity helium ≥99.999% flowed through the column at a constant rate of 1.0 mL/min. The temperature program used to separate all the target compounds is as follows: initial temperature 90℃ (2 min), 25℃/min to 225℃, 0.2℃/min to 227℃, 25℃/min to 260℃ (5 min).

Tandem MS was operated in electron impact mode with the ion source and transferline temperatures set at 250℃ and 280℃, respectively. A damping gas (He, ≥ 99.999%) with a flow rate of 3.0 mL/min was introduced into the ion trap to improve the sensitivity.

The linearity of the method was tested using six aqueous standards with concentrations ranging from 0.1 to 2.0 ng/L. MQL of the HS-SPME-GC-MSMS for some OCPs has been tested and is shown in Table 1.

1.4 Quality assurance and quality control

To determine whether there was contamination during the sample collection, transportation and storage processes, Milli-Q water was used as field blanks at each sampling site and processed along with the samples. Procedural blanks, using Milli-Q water, were also used for quality assurance during extraction and analysis. During the whole analysis procedure, a series of 35 mL 1.0 ng/L aqueous standards solution were extracted and analyzed to monitor instrument variability. The thermal degradation of *p*, *p′*-DDT in the inlet was frequently checked by the injection of *p*, *p′*-DDT standard solution, and the liner will be changed if the degradation ratio is higher than 10%.

During extraction, α-HCH-D6 and *p*, *p′*-DDE-D8 were added to the samples as internal standards to ensure the repeatability of the process. It should be noted that the adding of *p*,*p′*-DDE-D8 could introduce some *p*, *p′*-DDE into the sample, so the results of *p*, *p′*-DDE concentrations in the snow samples might be unreliable and were not discussed in this paper.

2 Results and discussion

2.1 Concentrations in the snow sample

The target compounds of this study included α-, β-, *γ*-HCH; *o*, *p′*-DDT, -DDD, -DDE; *p*, *p′*-DDT, -DDD, -DDE; *α*-, *β*-Endosulfans; *cis*-, *trans*-Chlordane; Heptachlor, Heptachlor-epoxide. In the four samples, only three OCPs were detected: HCB (44—72 pg/L), *p*, *p′*-DDT (401—1560 pg/L), *p*, *p′*-DDD (20—80 pg/L). The concentration of *o*, *p′*-DDT and all of the other target compounds were either around or below the MQL (Table 1).

The HCB concentrations in this study were slightly higher than those observed in European mountains, such as Colle Del Lys, Jori, Gossenkolle, Staroiesnianske, and Redo (2000—4250 m a.s.l., 2.6—37 pg/L)[12−14]. Yet DDT concentrations in this study were much higher than those measured in the above mentioned European mountains (1.6—330 pg/L). This difference may be attributed to differences in geographical location and sampling time[13].

To investigate the transport path of the air mass to each sampling location, backward trajectories were calculated using the hybid single-particle lagrangian integrated trajectory model[15] and the NOAA meteorological data downloaded from ftp://www.arl.noaa.gov/pub/archives/fnl. To represent trajectories within the boundary layer and in the free troposphere, the trajectory end points were set at 500 m and 3500 m above the sampling site A. The noon time (12:00 local standard time) of the snow falling day (April 28) was set as the start time of a 120-h backward trajectory calculation. From Figure 2, one can see that during the sampling period, the air mass with end point 500 m above sampling site came from the northern part of India, while the air mass with end point 3500 m above sampling site originated from Afghanistan, passed Pakistan, north of India, Nepal and northward to the Mt. Qomolangma.

Historically, there has been a large amount of DDT used in India[16]. DDTs were banned for use in agriculture in 1989 and were only permitted for public health reasons, but still 7500—10000 metric tons of DDTs are used in India each year[10,17]. High concentrations of DDT residues were measured in the Ganges[18] and Yamuna Rivers[10]. Relatively high DDTs concentrations were detected in air samples in the Qomolangma region, with India being the probable source[8]. In our study, relatively high *p,p'*-DDT concentrations were found in snow samples with very low DDD/DDT ratio (about 0.05), indicating the contribution of "new" sources in India. Consistent low DDD/DDT ratios were found in all the four snow samples, suggesting that the DDTs in the four samples came from the same source.

Currently no report about observed atmospheric concentration of HCB in India is available. According to the model results of EMEP [19], the typical HCB air concentrations in India were above 80 pg/m^3, which is higher than those in Eastern Europe (30 — 80 pg/m^3) and Northern and Southern Europe (10—30 pg/m^3). This is in accordance with the snow results that HCB concentrations were slightly higher in Mt. Qomolangma than in some of the European mountains.

From the above discussion one can see that "Condensation Effect" in the high mountain regions makes it possible to gain information about the surrounding environment of the sampling locations. Thus the POPs measured can give an indirect reflection of the pollution status of the source regions.

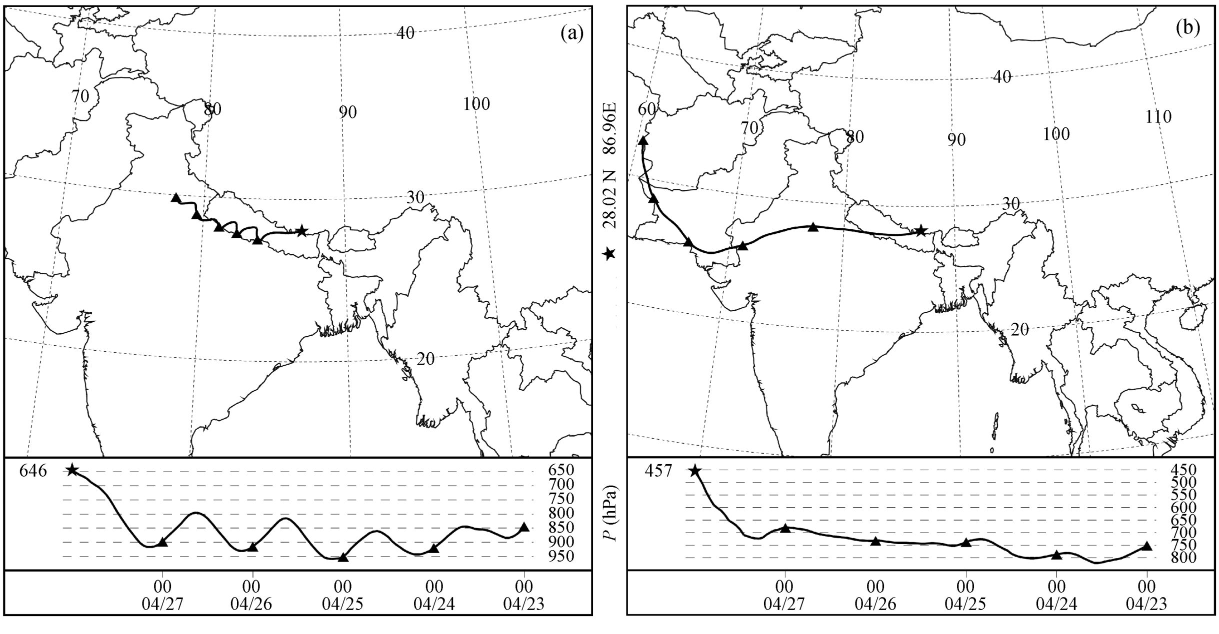

Figure 2 120-h backward trajectories of air mass reaching the sampling site A, with end points 500 m (a) and 3500 m (b) above the surface of site A.

2.2 Concentration differences along altitudinal gradients

A common theme throughout the research of organic contamination in mountains is the investigation of concentration changes along altitudinal gradients. Studies of POPs in air[20,21] and snow[4] in North America showed an increased tendency of concentration with altitude for the more volatile SOCs (e.g., HCB, HCHs, lighter PCBs, PAHs, etc.), but not for the less volatile ones (e.g., DDTs, heavier PCBs, PAHs, etc.).

Table 1 shows the HCB concentration in the fresh-fallen snow does not change with altitude, while the concentrations of p, p'-DDT and p, p'-DDD were increasing with altitude. This trend was reversed to the trends in North America[4]. Three factors likely lead to this result: 1) the properties of the target compounds; 2) the low temperatures at high altitudes; and 3) the location of the mountain sampling sites relative to their sources.

(1) Because the vapor pressure of HCB at 25℃ ($10^{-0.78}$ Pa) is much higher than that of p, p'-DDT($10^{-3.17}$ Pa) and p, p'-DDD($10^{-3.01}$ Pa), these compounds can be used to represent volatile and non-volatile POPs[22]. According to the modeled result of Beyer et al.[23], the overall environmental persistence and characteristic travel distance in air for HCB and p, p'-DDT were 1.1×10^5 km and 800 km, respectively. The deposition rate of POPs is an important factor that controls their characteristic travel distance, and is defined as a function of the air-water partition coefficient K_{AW} and the octanol-air partition coefficient K_{OA}, both of which are functions of temperature[24]. As a result, the deposition rate of DDTs is larger than that of HCB.

(2) During the sampling period, at site A (6500 m), the average monthly temperature in May was −11.2℃[25]. In the Tibetan Plateau, regions with altitude lower than 7000 ma.s.l. had a temperature decrease of about 0.7—0.8℃ per 100 m altitude increase[26,27]. The sampling sites A and B were in the East Rongbuk Glacier with surface covered by snow and ice, while the surface of sampling sites C and D was seracs and rocks. The daily average temperature at sites C and D should be about 5℃ higher than that of sites A and B. Therefore, the low temperature and the large temperature gradient between sampling sites might contribute to the trends of HCB and DDT concentrations, which are reversed to the observation in North America[4].

(3) According to the back-trajectory analysis, air masses coming from the south side of the Himalayas arrived at the top of East Rongbuk Glacier, went northward and then continued downward to lower altitude. As a result, it can be considered that the target compounds were traveling from higher altitude to lower altitude. DDTs, because of their high deposition rate, mostly deposited in the region of the East Rongbuk Glacier. This area has a low ambient temperature, and after deposition, only a small amount of the DDTs were available to deposit at the seracs at lower altitude. Therefore, the concentration of DDTs in fresh-fallen snow was higher at sites A and B than those at sites C and D. In contrast, HCB, which has a lower deposition rate and can travel a longer distance than DDT, showed no significant difference in concentration at all four sampling sites. This is consistent with the report about the atmospheric OCPs concentrations at the different altitudes at Alpine Glacier[14], where DDTs were more concentrated at higher altitudes (4300 m) than at lower altitudes (3200 m, 1600 m). Back-trajectories evaluated during the sampling period confirmed the transport of air masses from France southward to the Alpine Glacier. This result implies that the relationship between altitude and concentration in the Mt. Qomolangma region depends on the location of the mountain sampling sites relative to their sources.

Based on the observation of the changes in OCP concentrations in Arctic fresh-fallen snow, Herbert et al.[28] found the volatilization half-life for HCB and DDTs is longer than 24 h. In our study, the sampling time for all of the 4 sampling locations was within 24 h of the fresh snowfall, so it can be assumed that volatilization was not an issue resulting in concentration differences.

In summary, the properties of the target compounds, the low temperature at high altitudes and the location of the mountain sampling sites relative to their sources are controlling factors that caused the trend of POPs concentrations different from those found in North American mountains. This study also confirms that POPs with high long-range transport potential, such as HCB, can condense at Polar Regions. In contrast, DDTs tend to deposit at mountains at low or middle latitudes, close to their source regions.

3 Conclusions

To our knowledge, this is the first report about POPs concentrations in snow samples at such high altitude. HCB, p,p'-DDT and p,p'-DDD were detected in the fresh-fallen snow. Back-trajectory analysis showed that these compounds came from the north of India, which gives evidence that the low-mid-latitude high mountains could act as cold condensers of POPs. Discussion of the relationship between concentration and altitude showed the importance of mountain sampling locations relative to their sources.

No HCHs were detected in this study, even though they have been widely used in India historically[29] and currently. Apparently, one snow-fall event can only provide limited information about the POPs of this region, it is necessary to conduct long-term continuous observations. The harsh environmental conditions in high mountains make it nearly impossible to collect continuous samples. Hence passive air samplers could play an important role in measuring POPs concentrations in the air of high mountains. In May 2005, we extracted a 24-m-long ice core at the East Rongbuk Glacier, and have installed five pairs of Passive Air Samplers at five altitudes (6500 m, 6300 m, 5800 m, 5200 m and 4200 m) in the Mt. Qomolangma region for one year sampling period. The analysis of these samples will help us to better understand how India affects the Mt. Qomolangma Region as a source of OCPs.

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1 Macdonald R W, Barrie L A, Bidleman T F, et al. Contaminants in the Canadian Arctic: 5 years of progress in understanding sources, occurrence, and pathways. Sci Total Environ, 2000, 254: 93—234

2 Dickhut R M, Cincinelli A, Cochran M, et al. Atmospheric concentrations and air-water flux of organochlorine pesticides along the Western Antarctic Peninsula. Environ Sci Technol, 2005, 39: 465—470

3 Wania F, Mackay D. Tracking the distribution of persistent organic pollutant. Environ Sci Technol, 1996, 30: 390A—396A

4 Blais J M, Schindler D W, Muir D C G, et al. Accumulation of persistent organochlorine compounds in mountains of western Canada. Nature, 1998, 395: 585—588

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

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

7 Shi Y F, et al. eds. Glaciers and Environment in China: Present, Past and Future (in Chinese). Beijing: Science Press, 2000

8 Li J, Zhu T, Wang F, et al. Observation of organochlorine pesticides in the air of the Mt. Everest region. Ecotox Environ Saf, 2006, 63: 33—41

9 Malanichev A, Shatalov V, Vulykh N, et al. Modeling of POP hemispheric Transport, EMAP MSC-E/CCC Technical Report 8/2002, Moscow. 2002

10 Singh R P. Comparison of organochlorine pesticide level in soil and groundwater of Agra, India. Bull Environ Contam Toxicol, 2001, 67: 126—132

11 Wania F, Mackay D, Hoff J T. The importance of snow scavenging of polychlorinated biphenyl and polycyclic aromatic hydrocarbon vapors. Environ Sci Technol, 1999, 33: 195—197

12 Carrera G, Fernandez P, Vilanova R M, et al. Persistent organic pollutants in snow from European high mountain areas. Atmos Environ, 2001, 35: 245—254

13 Herbert B M J, Halsall C J, Fitzpatrick L, et al. Use and validation of novel snow samplers for hydrophobic, semi-volatile organic compounds. Chemosphere, 2004, 56: 227—235

14 Finizio A, Villa S, Raffaele F, et al. Variation of POP concentrations in fresh-fallen snow and air on an Alpine glacier (Monte Rosa). Ecotox Environ Saf, 2006, 63: 25—32

15 Draxler R R, Hess G D. An overview of the Hysplit_4 modeling system for trajectories, dispersion and deposition. Aust Meteorol Mag, 1998, 47: 295—308

16 Li Y F, Macdonald R W. Sources and pathways of selected organochlorine pesticides to the Arctic and the effect of pathway divergence on HCH trends in biota: a review. Sci Total Environ, 2005, 342: 87—106

17 Pandit G G, Rao A M, Jha S K, et al. Monitoring of organochlorine pesticide residues in the Indian marine environment. Chemosphere, 2001, 44: 301—305

18 Kumari A, Sinha, R K, Gopal K. Concentration of Organochlorine Pesticide Residues in Ganga Water in Bihar, India. Environ. Ecol, 2001, 19: 351—356

19 EMEP. Persistent organic pollutant in the Environment. Status Report, 2005/03

20 Shen L, Wania F, Lei Y D, et al. Hexachlorocyclo-hexanes in the North American Atmosphere. Environ Sci Technol, 2004, 38: 965—975

21 Shen L, Wania F, Lei Y D, et al. Atmospheric distribution and long-range transport behavior of organochlorine pesticides in North America. Environ Sci Technol, 2005, 39: 409—420

22 Shen L, Wania F. Compilation, evaluation and selection of physical-chemical property data for organochlorine pesticides. J Chem Eng Data, 2005, 50: 742—768

23 Beyer A, Mackay D, Matthies M, et al. Assessing long-range transport potential of persistent organic pollutants. Environ Sci Technol, 2000, 34: 699—703

24 Beyer A, Wania F, Gouin T, et al. Temperature dependence of the characteristic travel distance. Environ Sci Technol, 2003, 37: 766—771

25 Xie A H, Qin D H, Ren J W, et al. Features of meteorological elements at Mt. Everest 6523 m from May 1 to July 22 in 2005, Annual Report of Key Laboratory of Cryosphere and Environment (in Chinese), 2005, 11: 225—231

26 Team of Integrated Scientific Expedition to Tibetan Plateau From Chinese Academy of Sciences. Report on Scientific expedition to Mt. Qomolangma Area: 1975 Meteorology and Environment (in Chinese). Beijing: Science Press, 1980

27 Team of Integrated Scientific Expedition to Tibetan Plateau from Chinese Academy of Sciences, Report on Scientific Expedition to Mt. Qomolangma Area: 1966—1968 Meteorology and Environment (in Chinese). Beijing: Science Press, 1975

28 Herbert B M J, Halsall C J, Villa S, et al. Rapid changes in PCB and OC pesticide concentrations in Arctic snow. Environ Sci Technol, 2005, 39: 2998—3005

29 Li Y F, Global technical hexachlorocyclohexane usage and its contamination consequences in the environment: from 1948 to 1997. Sci Total Environ, 1999, 232: 121—158