

Hexachlorocyclohexanes and Endosulfans in Urban, Rural, and High Altitude Air Samples in the Fraser Valley, British Columbia: Evidence for Trans-Pacific Transport

TOM HARNER,^{*,†} MAHIBA SHOEIB,[†]
MELISSA KOZMA,[‡]
FRANK A. P. C. GOBAS,[‡] AND
SHAO MENG LI[†]

*Meteorological Service of Canada, Environment Canada,
4905 Dufferin Street, Toronto, Ontario, Canada M3H 5T4, and
School of Resource and Environmental Management,
Simon Fraser University, Burnaby,
British Columbia, Canada V5A 1S6*

High-volume air samples collected over the period Aug. 14–30, 2001, in the Lower Fraser Valley, BC, Canada, were used to assess urban/rural differences of organochlorine pesticides (OCPs) for ground level samples and to attempt to directly measure events of trans-Pacific inputs through the mid-troposphere. Hexachlorocyclohexanes (α - and γ -isomers; 2–25 pg m⁻³) and endosulfan1 and -2 (5–150 pg m⁻³) were detected in all ground level samples. Seven air samples were collected during mid-troposphere flights (~4400 m altitude) over the Lower Fraser Valley. These flights occurred concurrently with ground level sampling. Trajectory analysis identified three events of substantial mid-troposphere, trans-Pacific flow where 10-day back trajectories stemmed from potential source regions in Asia. These events were also characterized by higher air concentrations of α -HCH at 4400 m as compared to the ground level stations. This represents the first event-based, aircraft measurement of advection inputs of OCPs in the mid-troposphere of the west coast of North America.

Introduction

Many organochlorine pesticides (OCPs) are persistent, toxic, and bioaccumulative compounds that are capable of long-range atmospheric transport. Knowledge of this behavior has led to their regulation over the past several decades. The ratification of recent international protocols on persistent organic pollutants (POPs) through the UN-ECE (United Nations Economic Commission for Europe) and UNEP (United Nations Environment Program) further establishes these control measures.

Despite the significantly reduced use of OCPs over the past few decades, they continue to contaminate the environment and accumulate in the food chain. Examples include legacy OCPs such as α -HCH (hexachlorocyclohexane), chlordanes, DDTs, and dieldrin as well as modern OCPs such as

lindane (γ -HCH) and endosulfan. These chemicals are routinely detected in the remote arctic atmosphere (1) where they are ultimately deposited and accumulated in food chains (2). Long-term air monitoring studies in the arctic and the Great Lakes indicate that these chemicals are declining relatively slowly with half-lives generally between 5 and 10 years (1). Control measures on OCPs have occurred more slowly in Asian countries (Russia, China, India) (3, 4). Transport of contaminated air from these regions across the Pacific Ocean has been implicated as an important pathway for the delivery of these chemicals across the Canadian west coast and arctic regions (5–7). Lichota et al. (8) recently showed that endangered Vancouver Island Marmots are heavily contaminated with legacy OCPs, with the largest body burdens observed for α -HCH. They argue that this can largely be attributed to atmospheric processes and inputs from trans-Pacific flow.

In an effort to better identify sources of OCPs on the west coast of Canada, an air sampling campaign was conducted. Air samples were collected at an urban site in east Vancouver, a rural site in the Fraser Valley agricultural region, and in the upper boundary layer at an elevation of ~4400 m during flights of the Convair aircraft. Previous studies have shown that trans-Pacific flow occurs in this region of the troposphere (5). Other investigations have identified the Fraser Valley as a potential source of OCPs to the atmosphere. High soil residues of OCPs (9) and their emission to the atmosphere (10) have been reported. The current study was part of the larger "Pacific 2001" field campaign to investigate the atmospheric chemistry of ozone, fine particles, and trace gases and to explore air toxics in the lower Fraser Valley, BC.

Materials and Methods

Sample Collection. Fifteen, 12 h air samples were collected at two sites, one urban and one rural, to compare ground-based concentrations of OCPs in the Fraser Valley, BC, during August 2001. The urban site was situated in Slocan Park, a mixed residential/light industrial area in east Vancouver. The rural site was in an agricultural region just south of Langley, approximately 30 km southeast of Vancouver. Over the same period, eight air samples were collected in the mid-troposphere above the lower Fraser Valley (approximately 4400 m) during flights of a Convair aircraft (Figure 1). Sample dates, volumes, and meteorological data are given in Table 1.

Ground-based high-volume air samples were collected at a rate of approximately 0.4 m³ min⁻¹ using a sampling train consisting of two glass fiber filters (GFFs, 20 cm × 25 cm) for collecting the particle phase followed by two polyurethane foam (PUF) plugs (80 mm diam × 75 mm, PacWill Environmental, Stoney Creek, ON) for trapping gas-phase chemicals. Aboard the Convair (Figure 1), high-volume samples were collected at a rate of 0.3 m³ min⁻¹ using a smaller sampling train consisting of two GFF (110 mm diam) followed by two PUF plugs (110 mm diam × 30 mm).

GFFs were prepared by baking them in an oven at 450 °C overnight and then individually wrapping them in prebaked aluminum foil envelopes and storing them in airtight plastic bags. PUF plugs were prepared by rinsing them profusely with water and then extracting by Soxhlet using acetone (overnight), followed by two overnight extractions using petroleum ether. PUF plugs were dried overnight in a desiccator and stored in solvent-rinsed glass jars with Teflon-lined lids until required. During sample collection/changes, gloves were worn and GFF and PUF were handled using

* Corresponding author phone: (416)739-4837; fax: (416)739-5708; e-mail: tom.harner@ec.gc.ca.

[†] Meteorological Service of Canada.

[‡] Simon Fraser University.

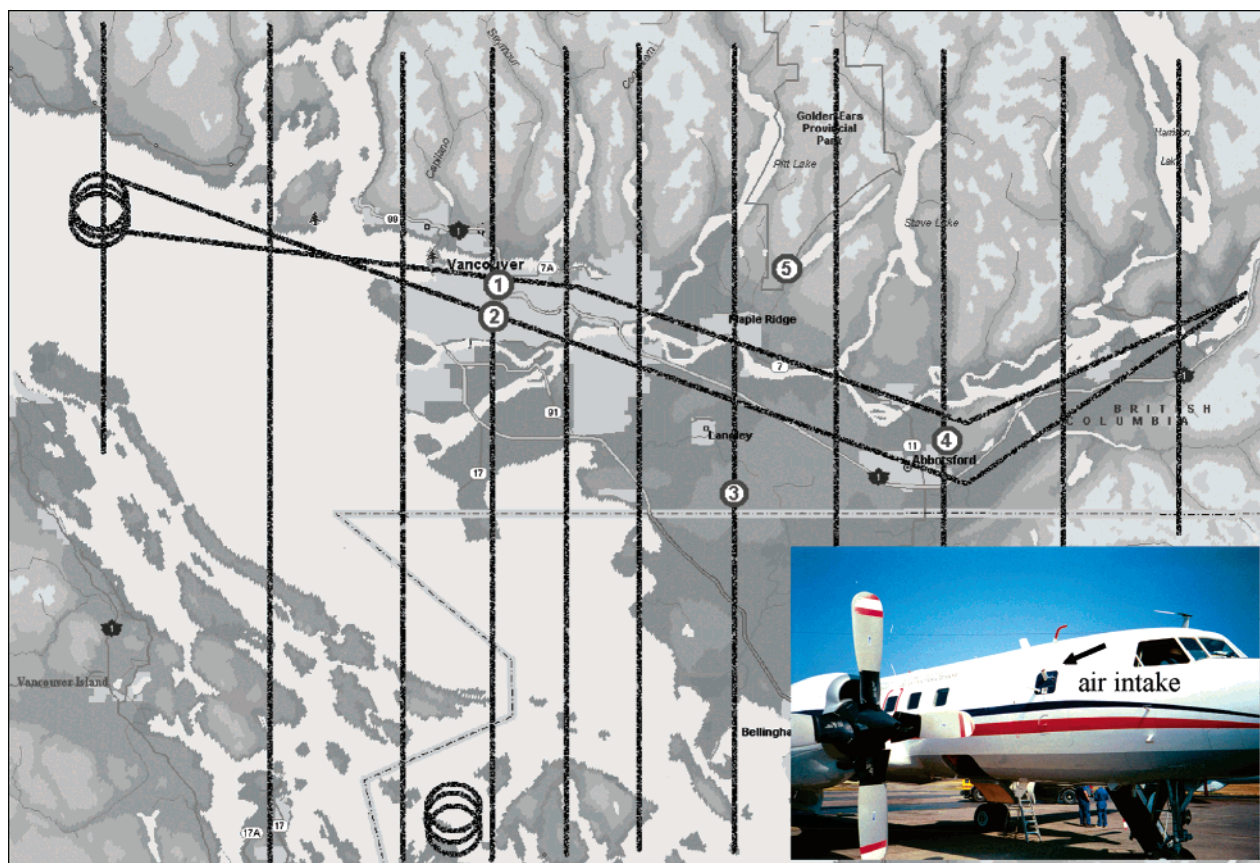


FIGURE 1. Map of Fraser Valley, BC, showing ground-based air sampling locations (1 = Slokan; 3 = Langley), Convair flight tracks, and a figure of Convair aircraft (arrow showing the location of air intake).

TABLE 1. Summary of Meteorological Data and Sampling Information^a

date (Aug 2001)	Langley		Slokan		Convair		
	V _{air} (m ³)	temp (°C)	V _{air} (m ³)	temp (°C)	V _{air} (m ³)	temp (°C)	alt. (m)
A14	434	12–25	423	na	79	–3	4400
A14N	449	12–17	427	na			
15	393	15–26	399	na	62	–2	4400
16	374	13–19	348	15–21			
17	409	13–22	435	14–22			
20	412	11–21	433	13–21	51	–7	4400
21	354	13–17	438	14–16			
25	403	13–22	439	na	67	–4	4300
26	402	14–25	442	na			
26N	457	10–18	464	13–18	59	0	4400
27	402	11–23	436	13–23			
28	418	16–23	440	15–24			
29	433	14–24	437	14–26	63	–1	4400
29N	498	10–14	513	10–17	64	–2	4400

^a V_{air} = air sample volume; alt. = altitude (meters above sea level) of air sample collected from Convair aircraft.; na = data not available.

acetone-rinsed stainless steel tongs. Sample GFF and PUF were kept cold until they were ready for extraction.

Analysis. Prior to their separate extraction, all PUF plugs and GFF were spiked with 9 ng d₆-α-HCH and 9.75 ng of ¹³C heptachlor to check method recoveries. Sample PUF plugs were extracted overnight in a Soxhlet apparatus using petroleum ether. GFFs were extracted using dichloromethane (DCM). Extracts were volume reduced to 1 mL by rotary evaporation and nitrogen blow down and solvent exchanged into isoctane.

All extracts were fractionated on a silicic acid-alumina column to separate OCPs from polychlorinated biphenyls

(PCBs), polychlorinated naphthalenes (PCNs), and other abundant nonpolar compounds that may interfere with the analysis. The column consisted of 3 g of silicic acid (deactivated with 3% water) (Mallinckrodt Baker, Paris, KY), overlaid with 2 g of neutral alumina (deactivated with 6% water) (EM Science Inc., Gibbstown, NJ), and topped with 1 cm anhydrous sodium sulfate. The column was prewashed with 30 mL of dichloromethane and then 50 mL of petroleum ether. The sample was applied and eluted with 50 mL of petroleum ether (fraction 1, containing PCBs and PCNs) and then with 30 mL of DCM (fraction 2, containing OCPs and polycyclic aromatics hydrocarbons, PAHs). Fractions were blown down to about 1 mL under a gentle stream of nitrogen and solvent-exchanged into isoctane.

OCPs were determined by gas chromatography-negative ion mass spectrometry (GC-NIMS) on a Hewlett-Packard 6890 GC-5973 mass spectrometer. Injections (2 μL) were splitless with the split opened after 1 min. The injector was kept at 250 °C. A 60 m DB-5 column (J&W Scientific) with 0.25 mm i.d. and 0.25 μm film thickness was operated with helium carrier gas at a flow of 1.2 mL min^{–1}. The GC oven temperature program was as follows: initial at 90 °C hold for 0.5 min, 15 °C min^{–1} to 160 °C, then 2 °C min^{–1} to 260 °C, hold for 10 min. Methane was used as reagent gas with a flow of 2.2 mL min^{–1}. Transfer line, ion source, and quadrupole temperatures were kept at 275, 150, and 106 °C, respectively.

The 13 OCPs targeted in this study (Table 2) were quantified against a five point calibration curve. Mirex (U.S. Environmental Protection Agency, Research Triangle Park, NC) was used as internal standard to correct for volume difference. The instrument was operated in selective ion mode (SIM) with target/qualifier ions 255/257 for HCHs, 266/268 for heptachlor, 237/239 for heptachlor epoxide, 237/239 for aldrin, 410/408 for *cis*- and *trans*-chlordane, 444/446 for *trans*-

TABLE 2. Summary of Air Concentrations (pg m⁻³) of Selected OCPs at Langley, Slocan, and High Altitude Samples (N = Night Sample)^a

date in Aug. 2001	Langley				Slocan				Convair
	α -HCH	γ -HCH	Endo1	Endo2	α -HCH	γ -HCH	Endo1	Endo2	α -HCH
14	21.0	8.7	11.8	12.7	21.6	18.0	24.9	29.5	1.3
14N	n/a	6.9	33.2	12.9	20.9	15.8	9.3	51.5	
15	20.5	5.6	9.3	14.1	16.4	11.7	10.0	22.6	16.7
16	19.9	4.8	144.1	107.3	24.5	7.2	27.2	31.9	
17	27.3	5.6	52.9	87.0	10.6	4.6	3.0	2.3	
20	22.3	4.6	36.1	30.3	13.3	3.0	4.4	4.6	33.7
21	18.5	6.6	153.8	66.1	13.5	5.0	28.6	18.2	
25	18.3	7.5	16.4	14.0	20.4	5.7	4.0	na	5.1
26	14.1	3.6	54.2	27.8	21.0	10.5	39.4	22.9	
26N	6.2	3.6	16.5	12.1	10.4	5.1	18.9	7.6	17.0
27	1.8	1.6	4.7	24.6	23.8	7.5	26.0	17.4	
28	20.8	6.9	24.7	18.2	11.3	4.0	4.2	3.7	
29	15.1	4.8	3.5	15.0	22.3	4.6	33.7	24.1	60.7
29N	21.9	16.6	47.4	13.7	21.9	13.9	10.6	5.5	28.3
30	na	na	na	na	12.3	5.9	9.4	9.8	

^a LOD values for Langley and Slocan were calculated as the mean of 4 blanks + 3 standard deviation using an average air volume of 450 m³; LOD values were: 2.7, 2.9, 3.2, and 3.1 pg m⁻³ for α -HCH, γ -HCH, Endo1, and Endo2, respectively. For Convair, blanks were below detection, and two-thirds of the instrument detection limit (IDL) was used for blank correction. For α -HCH, this corresponded to 0.002 pg m⁻³, based on an air volume of 50 m⁻³ which was typical for Convair samples (Table 1). All data in Table 2 were blank subtracted but not recovery corrected; na = not available.

nonachlor, 237/239 for dieldrin, 406/408/404 for endosulfan 1 and 2, and 404/406 for Mirex. Surrogate standards containing *d*₆- α -HCH and ¹³C heptachlor epoxide were also determined using GC-NIMS with target/qualifier ions 261/263 and 242/244, respectively.

Results and Discussion

QA/QC. Field blanks were treated like samples and taken through transportation, deployment, storage, and analytical steps. Two field blanks for each medium were deployed at each site, Langley and Slocan, and three blanks were deployed during Convair flights. Levels of OCPs analyzed were below detection in the three Convair blanks. For compounds not detected in blanks, two-thirds of the instrumental detection limit (IDL) was used to blank correct the data. OCPs were detected in field blanks from Langley and Slocan. In these cases, a limit of detection (LOD) was calculated as the average of the 4 field blanks + 3 standard deviations. Data were reported in Table 2 if they exceeded the LOD value. All qualified data were then blank corrected.

Two PUFs were used in the sampling train to evaluate breakthrough of different compounds. No breakthrough was observed for higher molecular weight pesticides. However, the average breakthrough for α - and γ -HCH at Langley and Slocan was 13% and 3%, respectively (*n* = 29). Therefore, data reported in Table 2 represent the sum of these two compounds in both PUFs. No breakthrough was observed during Convair flight samples, probably because of the colder air temperatures and lower sample volumes (Table 1).

Two GFFs were used in the sampling train to collect the particle phase. The second GFF was used to assess the artifact associated with gas-phase chemicals adsorbing to the GFF. In all samples, concentrations of OCPs in the GFF extracts were below the LOD and no data are reported.

Before extraction, each media was fortified with 50 μ L of surrogate recovery standards *d*₆- α -HCH and ¹³C heptachlor epoxide. Recoveries for ¹³C heptachlor epoxide were 72% $\pm$ 20% (*n* = 65). Recoveries for *d*₆- α -HCH were lower with an average of 57% $\pm$ 19% (*n* = 65). Low recoveries for *d*₆- α -HCH are most likely attributed to evaporative losses during concentration of the sample extract. Data shown in Table 2 were not corrected for recovery.

Back-Trajectory Calculations. To investigate trans-Pacific air flow and its contribution to air concentrations of OCPs

in the troposphere, air parcel back trajectories were calculated using the Canadian Meteorological Centre (CMC) Trajectory Model. Ten-day back trajectories were calculated on an hourly basis for the periods covered by the seven Convair flights and concurrent ground-based sampling. Calculations were made at the following heights: 10, 50, and 100 m (representing the atmospheric boundary layer/ground level); and 1000, 2000, 3000, and 4400 m (which coincides with the cruising altitude of the aircraft). Table 3 summarizes trajectory calculations for all heights for the seven sample events.

Comparison of OCPs at Urban and Rural Sites. Table 2 lists air concentrations for OCPs that were above the LOD in more than 50% of the samples. Of the 13 OCPs initially targeted in this study, only α - and γ -HCH and endosulfan1 and endosulfan2 regularly exceeded the LOD (see footnote to Table 2). The chemical classes investigated here exist mainly in the gas phase at ambient temperatures (11) and were only detected on PUF. Figure 2 compares levels and temporal trends of these four OCPs over the study period at the two ground-based sites, Langley (rural) and Slocan (urban).

α - and γ -HCH. Technical HCH is a mixture of several isomers of which α -HCH comprises 60–70% and γ -HCH comprises 10–12% (3). HCH is the dominant OCP detected in arctic air and water (2). As a result of ecosystem health concerns, technical HCH was banned in many countries during the 1970s. In North America, technical HCH use in Mexico continued until 1993. China and the Soviet Union continued to be large consumers of technical HCH until bans on use in the mid-1980s and 1990, respectively. After 1990, usage of HCH continued in India, Vietnam, and isolated parts of the world (3). This continued use coupled with cycling of previously used α -HCH is believed to be the main source of α -HCH to the atmosphere. Large quantities of technical HCH waste (mainly α -, β -, and δ - isomers) resulting from the production of lindane are stored in some European countries, often exposed to the atmosphere (John Vijgen, International HCH and Pesticides Association, Denmark, personal communication). It is not known if such sites are important sources of atmospheric contamination. Because it is fairly volatile (log *K*_{OA} = 7.93) and degrades slowly in the atmosphere (12), α -HCH is easily transported in the atmosphere and attains fairly uniform air concentrations globally (13, 14). Air concentrations of α -HCH derived from a passive

TABLE 3. Summary of 10-day Air Parcel Back Trajectories for Convar Samples

Date (Aug. 2001)	10m	50m	100m	1000m	2000m	3000m	4400m
14							
15							
20							
25							
26N							
29							
29N							

Table 3 legend.

	Trans-Pacific flow	
	None	None of the back trajectories cross international date line.
	Very Weak	At least one trajectory crosses the date line.
	Weak	Most trajectories cross over date line; no trajectories reach Asia.
	Moderate	At least one trajectory reaches Asia.
	Strong	Most trajectories reach Asia.
	Very Strong	All trajectories reach and penetrate Asia.

sampling survey in 2000–2001 (integrated over 1 year) were fairly uniform across Canada (from the west coast to east coast, approximately 20 sites) with the exception of some elevated concentrations on the east coast (15). These high values (approximately twice the average) were attributed to elevated surface ocean water concentrations of α -HCH and contributions from sea–air exchange.

Release of γ -HCH to the environment continues through the use of the commercial product, lindane, which is composed mainly of the active isomer. Usage of γ -HCH in many parts of the world has declined in recent years (16). In North America, the prairie region of Canada has been shown to be a large emission source of γ -HCH (17–19). The results from the passive sampling transect by Shen et al. (15) were consistent and showed elevated γ -HCH air burdens for sites in the prairie region.

Potential sources of α - and γ -HCH to the atmosphere of the Fraser Valley include re-emission from previously

contaminated soils in the region and long-range transport from higher and more recent use regions on the other side of the Pacific Ocean and within Canada. The trans-Pacific transport of HCHs is considered later. Investigations in the Fraser Valley have identified α - and γ -HCH residues in soils (9, 20), and gradient methods and chiral analysis have been used to show that emissions from soils are contributing to air burdens (10). However, the relative contribution of local versus distant sources (e.g., trans-Pacific flow) could not be derived.

During the sampling campaign, air concentrations of α - and γ -HCH were similar at the two sites (Figure 2, Table 2). Concentrations (pg m^{-3}) were 2–25 for α -HCH and 2–18 for γ -HCH. The lack of strong urban–rural differences suggests that the agricultural region was not a dominant contributor to regional air concentrations of HCHs. Clausius–Clapeyron plots of log air concentration versus inverse absolute temperature are often used to differentiate sources for chemicals

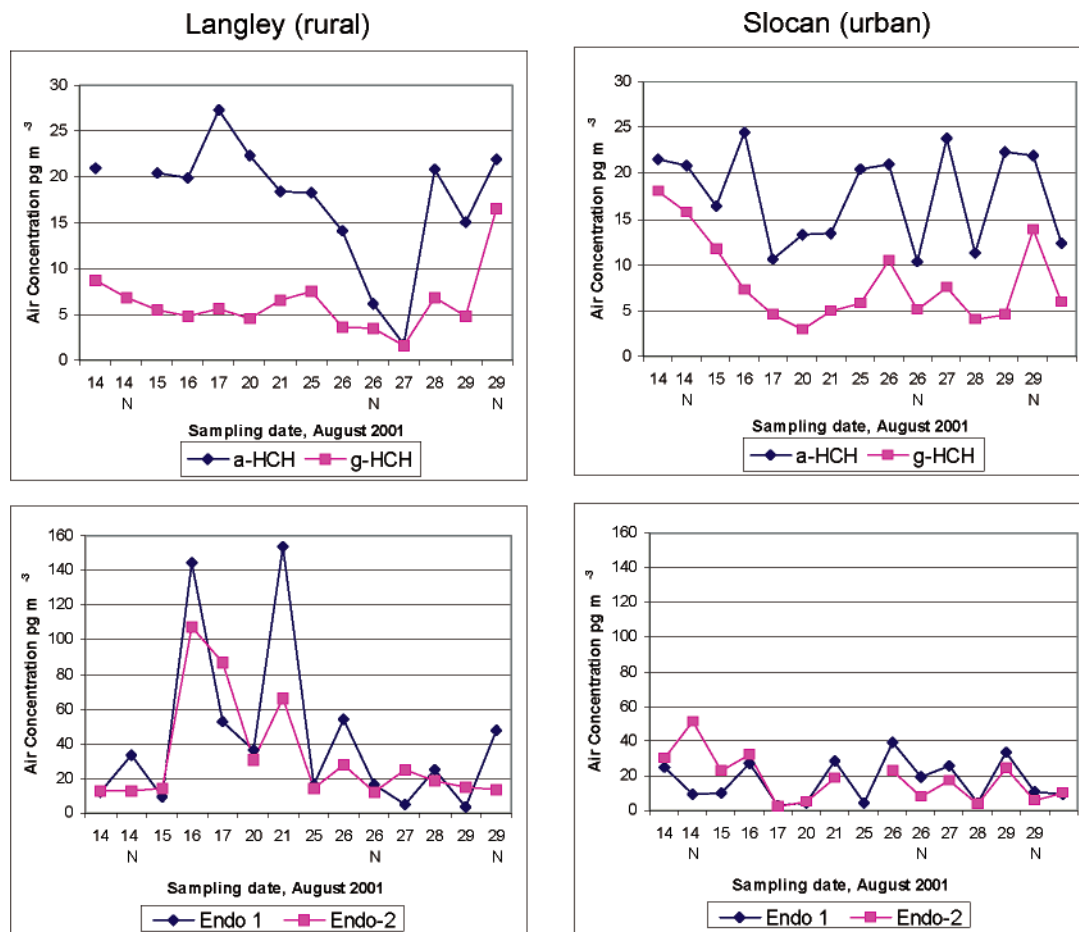


FIGURE 2. Air concentrations of selected POPs at Langley (left panels) and Slocan. N = night sample.

that are observed in air (21). A strong correlation suggests the importance of local emissions, while the lack of a correlation indicates the dominance of input through advection from distant sources. Clausius–Clapeyron plots for the HCHs showed no correlation. However, because of the small temperature difference over the study period (between samples, see Table 1), we feel that a conclusion regarding the importance of local emissions is not warranted.

Endosulfans. Endosulfan has been widely used as an insecticide in agriculture since the mid 1950s. The technical product is a racemic mixture of two isomers, endosulfan 1 and 2. Air sampling conducted under the Northern Contaminants Program (NCP) in the remote Canadian high Arctic at Alert, Nunavut, has revealed endosulfan concentrations in the range 4–6 pg m^{-3} (yearly means) over the period 1993–1999 (22). Endosulfan is widely used throughout North America. Usage of the active ingredient in the U.S. was on the order of 600 000 kg in 2001 on a variety of crops. Hoh and Hites (23) report endosulfan concentrations at four sites in the U.S. with the median concentrations in the range 37–79 pg m^{-3} .

Unlike the HCHs, endosulfans (endosulfan 1 + endosulfan 2) showed higher concentrations at the rural site (Langley) where concentrations for the sum of the two isomers ranged from ~18 to ~82 pg m^{-3} except for an event lasting several days in the middle of the campaign when the concentrations exceeded 250 pg m^{-3} (Figure 2, bottom panels). These higher levels are attributed to local use in the area at the time of sampling. Concentrations were more constant at the urban site (Slocan) and ranged from ~4 to ~62 pg m^{-3} . These concentrations are low as compared to other studies in Canada. For instance, Harner et al. (24) report concentrations in the range 400–800 pg m^{-3} for an urban–rural passive

sampling transect extending north of Toronto. Recent sampling conducted under the Canadian Atmospheric Network for Currently Used Pesticides (CANCUP) shows endosulfan concentrations during the summer of 2003 ranging from a few hundred pg m^{-3} in the Fraser Valley to 10 times higher concentrations (several thousand pg m^{-3}) in Prince Edward Island (25).

Concentrations of endosulfans at Langley and Slocan were also not correlated to temperature. However, as discussed earlier, a Clausius–Clapeyron analysis is not valid for such a small temperature range. Interpretation is also confounded by intermittent application of endosulfan (a currently used pesticide) that typically occurs during the summer in this agricultural region.

Trans-Pacific Transport of OCPs. Trans-Pacific flow of OCPs from Asia has recently been acknowledged as an important pathway for the delivery of OCPs to the west coast of North America and the Arctic (5, 6, 26). Bailey et al. (6) investigated events of unusually high air concentrations at Tagish, Yukon, during 1992–1995 that occurred primarily during the winter. Back-trajectory analysis was used to relate these episodes to trans-Pacific long-range transport from eastern Asia. This relationship was most pronounced for HCHs, chlordanes, and DDT (dichlorodiphenyltrichloroethane). Using a global atmospheric tracer model coupled with soil, cryosphere, and ocean models, Koziol and Pudykiewicz (5) demonstrated that episodes of trans-Pacific flow of HCHs are possible and that when they do occur, they result in higher concentrations in the mid-troposphere (~2000–6000 m) as compared to the surface. They identified the primary source of HCHs, particularly α -HCH, to be emission from soils in previous high usage regions throughout India, China, and parts of southeast Asia (3).

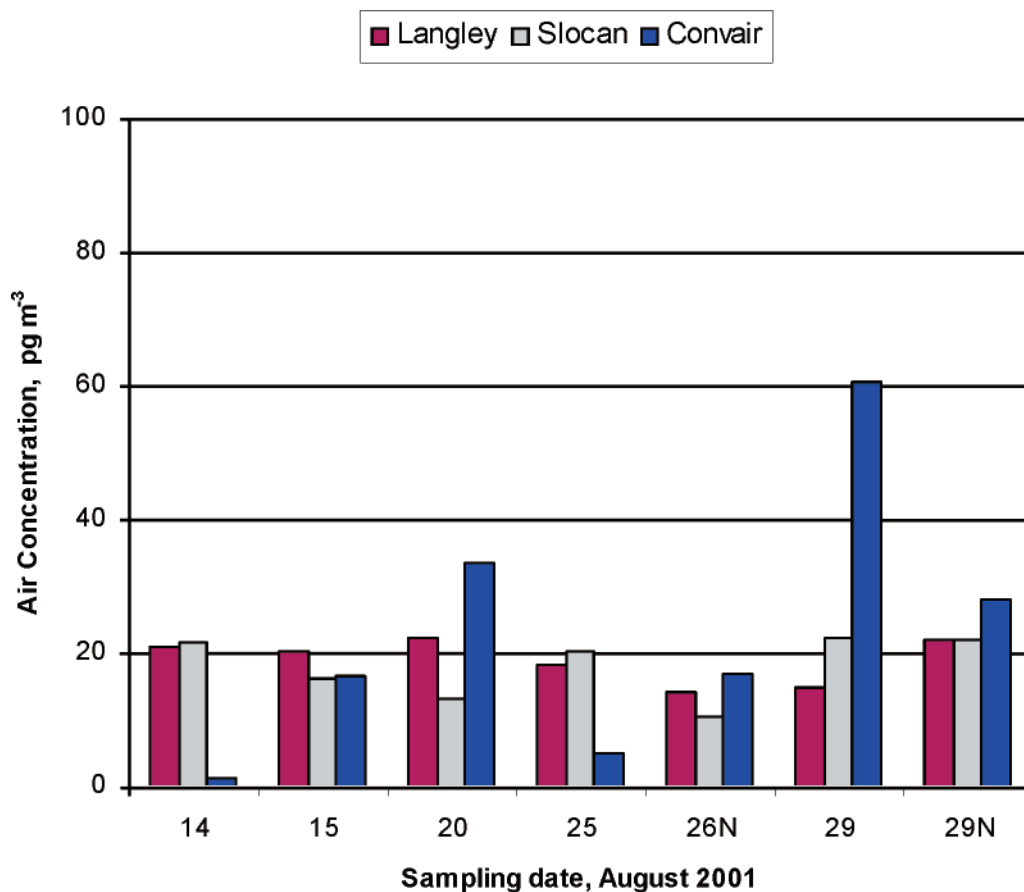


FIGURE 3. Air concentrations of α -HCH at Langley (rural), Slocan (urban), and high altitude samples (4400 m) taken from the Convair aircraft. N = night sample.

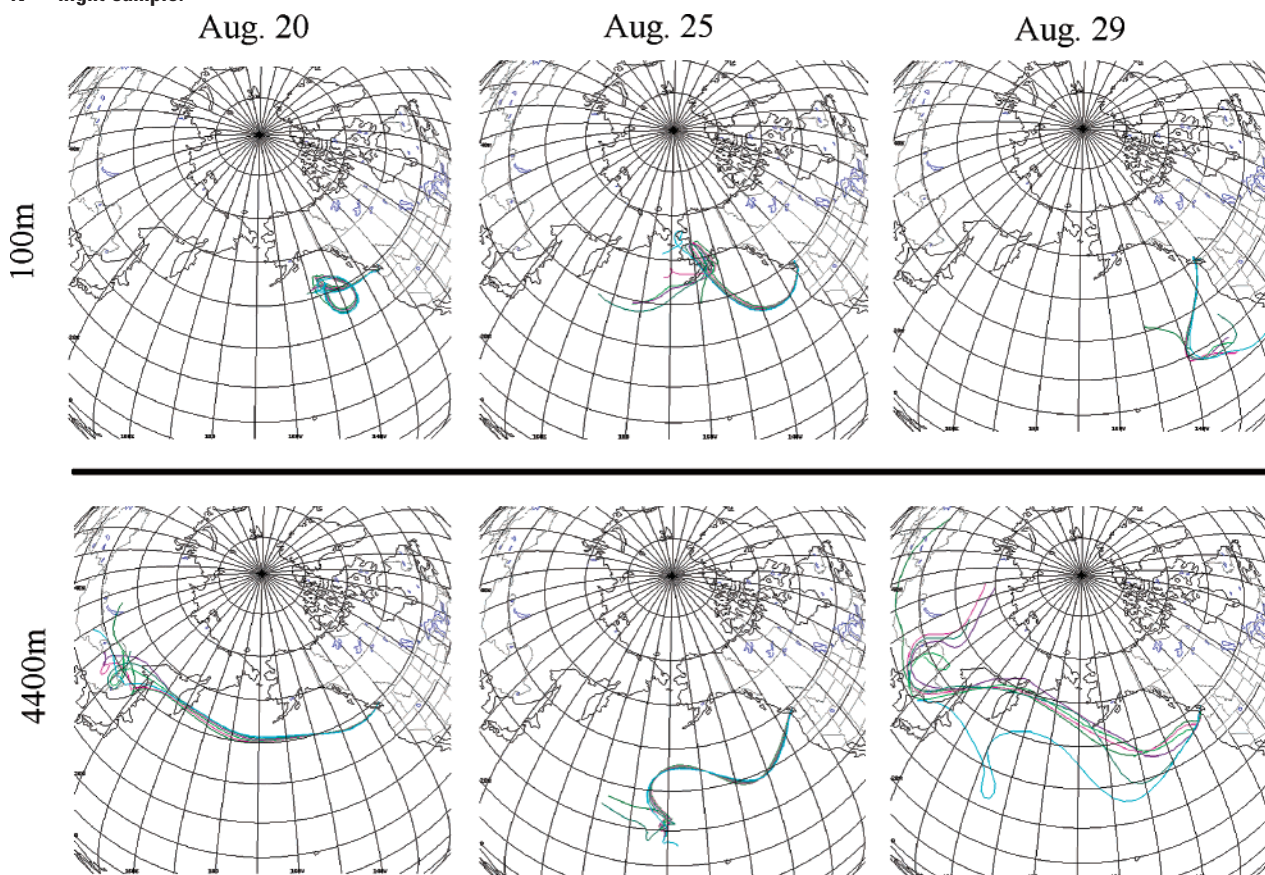


FIGURE 4. 10-day air parcel back trajectories at 4400 and 100 m for three Convair air sample events; Aug. 20 and Aug. 29 exhibit mid-troposphere trans-Pacific flow, while the sample taken on Aug. 25 does not.

The opportunity to collect several concurrent air samples at 4400 m and at two ground level sites during the Pacific 2001 campaign allowed us to directly test the phenomenon suggested by the model. Air concentrations from the Convair flight samples are given in Table 2 and Figure 3. Because of the low sample air volumes that could be obtained during the 3–4 h flights, only α -HCH was consistently above the LOD. It is possible that the nondetection of the higher molecular weight OCPs (chlordanes, DDTs, endosulfan) is due to physical partitioning. Air temperatures in the upper boundary layer were typically several degrees below 0 °C (Table 1). At this temperature, the higher molecular weight OCPs (e.g., chlordanes, DDTs, endosulfans) will begin to partition to particles (11) and experience reduced atmospheric transport.

As can be seen in Figure 3, three of the seven sampling events (Aug. 20, 29, and 29N (night)) showed high α -HCH concentrations (above 20 pg m⁻³) at 4400 m, and these concentrations were higher than the ground-based concentrations at Slocan and Langley. This result is consistent with the profiles predicted by Koziol and Pudykiewicz (5) for trans-Pacific flow events, with higher air concentrations in the mid-troposphere as compared to ground level. For the other four samples (Aug. 14, 15, 25, and 26N), α -HCH concentrations were lower and no enrichment at 4400 m was observed.

Results from 10-day air parcel back trajectories calculated for each sampling period were used to investigate this further. Results confirmed that for the three samples showing enrichment of α -HCH at 4400 m (Aug. 20, 29, and 29N), air trajectories for the mid-troposphere (2000, 3000, and 4400 m) showed moderate to very strong trans-Pacific flow (Table 3) with trajectories that stemmed back to Asia. The trans-Pacific contribution was much weaker for the four samples that did not exhibit enriched α -HCH concentrations at 4400 m (Table 3). The high altitude back trajectories for these samples were not as long and tended to linger over the Pacific Ocean.

To illustrate this further, Figure 4 compares the 10-day back trajectories at 4400 and 100 m for three Convair samples. The Aug. 20 and Aug. 29 events both show strong trans-Pacific flow at 4400 m with enrichment of α -HCH (Figure 3). For the Aug. 25 sample, there is no evidence of trans-Pacific flow with back trajectories at 4400 m stemming back to the mid-Pacific Ocean; no enrichment of α -HCH was observed (Figure 3). Because α -HCH is stable in air (12), its degradation during trans-Pacific events will be minimal and is unlikely to influence observed air concentrations.

It should be noted that the use of air parcel back trajectories is limited especially over a 10-day period where errors of approximately 20% (of the length of the trajectory) can be expected. With this variability in mind, the back trajectories presented here can only be used to represent general regions of air mass origin. For instance, they cannot distinguish a trajectory that passes over northern China versus southern China.

In summary, this study presents the first direct measurements of event-based trans-Pacific flow of α -HCH in the mid-troposphere. This is likely to be an important advection route for other OCPs and other classes of persistent chemicals to North America. These findings also confirm the predictions of a global transport model for HCHs (5). This agreement between model and measured values is important because it adds confidence to the use of such models for predicting pesticide fate and transport on the global scale.

Acknowledgments

We thank Jacinthe Racine of the Canadian Meteorological Center for assistance with back-trajectory analyses; pilots of the Convair aircraft, John Aitken and Tim Leslie; and Walter

Strapp, Kevin Strawbridge, and Marc Lilley for collecting air samples on Convair flights.

Literature Cited

- Hung, H.; Halsall, C. J.; Blanchard, P.; Li, H. H.; Fellin, P.; Stern, G.; Rosenberg, B. Temporal trends of organochlorine pesticides in the Canadian Arctic atmosphere. *Environ. Sci. Technol.* **2002**, *36*, 862–868.
- Macdonald R. W.; et al. Sources, occurrence and pathways of contaminants in the Canadian Arctic: a review. *Sci. Total Environ.* **2000**, *254*, 93–234.
- Li, Y. F.; Scholtz, M. T.; Heyst, B. J. van Global gridded emission inventories of α -hexachlorocyclohexane. *J. Geophys. Res.* **2000**, *105*, 6621–6632.
- Qiu, X.; Zhu, T.; Li, J.; Pan, H.; Li, Q.; Miao, G.; Gong, J. Organochlorine pesticides in the air around the Taihu Lake, China. *Environ. Sci. Technol.* **2004**, *38*, 1368–1374.
- Koziol, A. S.; Pudykiewicz, J. A. Global-scale environmental transport of persistent organic pollutants. *Chemosphere* **2001**, *45*, 1181–1200.
- Bailey, R.; Barrie, L. A.; Halsall, C. J.; Fellin, P.; Muir, D. C. G. Atmospheric organochlorine pesticides in the western Canadian Arctic: Evidence of transpacific transport. *J. Geophys. Res.* **2000**, *105*, 11805–11811.
- Wilkening, K. E.; Barie, L. A.; Engle, M. Trans-Pacific air pollution. *Science* **2000**, *290*, 65–66.
- Lichota, G. B.; McAdie, M.; Ross, P. Endangered Vancouver Island marmots (*Marmota vancouverensis*) sentinels of atmospherically delivered contaminants to British Columbia, Canada. *Environ. Toxicol. Chem.* **2004**, *23*, 402–407.
- Szeto, S. Y.; Price, M. Persistence of pesticide residues in mineral and organic soils in the Fraser Valley of British Columbia. *J. Agric. Food Chem.* **1991**, *39*, 1679–1684.
- Finizio, A.; Bidleman, T. F.; Szeto, S. Y. Emission of chiral pesticides from an agricultural soil in the Fraser Valley, British Columbia. *Chemosphere* **1998**, *36*, 345–355.
- Shoeib, M.; Harner, T. Using measured octanol-air partition coefficients to explain environmental partitioning of organohalogen pesticides. *Environ. Toxicol. Chem.* **2002**, *21*, 984–990.
- Brubaker, W. W.; Hites, R. A. OH reaction kinetics of gas-phase α - and γ -hexachlorocyclohexane and hexachlorobenzene. *Environ. Sci. Technol.* **1998**, *32*, 766–769.
- Wania, F.; Mackay, D. A global distribution model for persistent organic pollutants. *Sci. Total Environ.* **1995**, *160/161*, 211–232.
- Lakaschus, S.; Weber, K.; Wania, F.; Bruhn, R.; Schrems, O. The air-sea equilibrium and time trend of hexachlorocyclohexanes in the Atlantic Ocean between the Arctic and Antarctica. *Environ. Sci. Technol.* **2002**, *36*, 138–145.
- Shen, L.; Wania, F.; Lei, Y. D.; Teixeira, C.; Muir, D. C. G.; Bidleman, T. F. Hexachlorocyclohexanes in the North American atmosphere. *Environ. Sci. Technol.* **2004**, *38*, 965–975.
- Li, Y. F.; Cai, D. J.; Shan, Z. J.; Zhu, Z. L. Gridded usage inventories of technical hexachlorocyclohexane and Lindane for China with 1/6° latitude by 1/4° longitude resolution. *Arch. Environ. Contam. Toxicol.* **2001**, *41*, 261–266.
- Ma, J.; Daggupaty, S.; Harner, T.; Li, Y. Impacts of lindane usage in the Canadian Prairies on the Great Lakes ecosystem. 1. coupled atmospheric transport model and modeled concentrations in air and soil. *Environ. Sci. Technol.* **2003**, *37*, 3774–3781.
- Ma, J.; Daggupaty, S.; Harner, T.; Blanchard, P.; Waite, D. Impacts of lindane usage in the Canadian Prairies on the Great Lakes ecosystem. 2. Modeled fluxes and loadings to the Great Lakes. *Environ. Sci. Technol.* **2004**, *38*, 984–990.
- Li, Y. F.; Struger, J.; Waite, D.; Ma, J. Gridded Canadian usage inventories with 1/6° × 1/4° latitude and longitude resolution. *Atmos. Environ.* **2004**, *38*, 1117–1121.
- Falconer, R. L.; Bidleman, T. F.; Szeto, S. Chiral pesticides in soils of the Fraser Valley, British Columbia. *J. Agric. Food Chem.* **1997**, *45*, 1946–1951.
- Wania, F.; Haugen, J.-E.; Lei, Y. D.; Mackay, D. Temperature dependence of atmospheric concentrations of semivolatile organic compounds. *Environ. Sci. Technol.* **1998**, *32*, 1013–1021.
- Hung, H.; Blanchard, P.; Halsall, C. J.; Bidleman, T. F.; Stern, G. A.; Fellin, P.; Muir, D. C. G.; Barrie, L. A.; Jantunen, L. M.; Helm, P. A.; Ma, J.; Konoplev, A. *Sci. Total Environ.* (in press).
- Hoh, E.; Hites, R. A. Sources of toxaphene and other organochlorine pesticides in North America as determined by air measurement and potential source contribution function analyses. *Environ. Sci. Technol.* **2004**, *38*, 4187–4194.

- (24) Harner, T.; Shoeib, M.; Diamond, M.; Stern, G.; Rosenberg, B. Using passive air samplers to assess urban-rural trends for persistent organic pollutants. 1. polychlorinated biphenyls and organochlorine pesticides. *Environ. Sci. Technol.* **2004**, *38*, 4474–4483.
- (25) Tuduri, L.; Harner, T.; Blanchard, P.; Waite, D.; Belzer, W.; Froude, F.; Murphy, C.; Poissant, L.; Sproull, J. CANCUP: Canadian Atmospheric Network for Currently-Used Pesticides. 11th Annual International Conference on the St. Lawrence River Ecosystem, Cornwall, Ontario, Canada, May 18–19, 2004.
- (26) Killin, R. K.; Simonich, S. L.; Jaffe, D. A.; DeForest, C. L.; Wilson, G. R. Trans-Pacific and regional atmospheric transport of anthropogenic semi-volatile organic compounds to Cheeka Peak Observatory during the spring of 2002. *J. Geophys. Res.* **2004**, *109*, D25S15, doi: 10.1029/2004JD004386.

Received for review August 19, 2004. Revised manuscript received October 19, 2004. Accepted October 26, 2004.

ES048700H