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Airborne organochlorines in the Canadian High Arctic

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ABSTRACT

In 1984, the Canadian Polar Continental Shelf Project established a research camp on a floating ice island in the Beaufort Sea. The 7 × 4 km island is presently located about 50 km off Ellesmere Island at about 81°N, 100°W. Air samples of 1400–3000 m^3 were collected on the island in August–September 1986 and June 1987, using a filter-solid adsorbent train. Organochlorines in melted snow and Arctic Ocean surface water were preconcentrated using solid adsorbent cartridges. Samples were analyzed by capillary gas chromatography with electron capture detection, and by capillary gas chromatography-mass spectrometry in the negative ion and electron impact modes. Compounds quantified included hexachlorocyclohexanes, hexachlorobenzene, polychlorinated camphenes, chlordane, polychlorinated biphenyls, and DDT compounds (given in order of relative abundance, highest to lowest). Air-sea partitioning of HCH isomers relative to their equilibrium distribution calculated from Henry's Law constants is discussed.

1. Introduction

The Canadian Arctic is a region with low population density and limited sources of local pollution. Despite the archipelagos' remoteness, the Arctic air mass is polluted by anthropogenic emissions in temperate latitudes. Long-range transport of pollutants has been observed since the Arctic haze aerosol was reported in 1956 (Mitchell, 1956). The haze, which consists largely of sulfate, elemental carbon, and other products of fossil fuel combustion and industrial processes, is most dense when the polar air mass has expanded south over the Eurasian and North American continents during December through April. As discussed in a review by Barrie (1986), eastern Europe and Asia are the most likely sources of the aerosol pollution.

Organochlorine (OC) pesticides and industrial chemicals have also been reported in Arctic air. Hexachlorocyclohexanes (HCH), cis-chlordane (CC), hexachlorobenzene (HCB), and polychlorinated biphenyls (PCB) were found in the air at Spitzbergen, Bear Island, Hope Island, and Jan Mayen (Oehme and Ottar, 1984; Pacyna and Oehme, 1988). Airborne components of technical chlordane (cis-, trans-chlordane (CC, TC) and cis-, trans-nonachlor (CN, TN)) were found by Hoff and Chan (1986) at Mould Bay, Northwest Territories, Canada. HCH, dieldrin, and DDT were measured in the snow of east-central Ellesmere Island by McNeely and Gummer (1984).

Atmospheric deposition is a likely source of OC to the Arctic ecosystem. OC pesticides and industrial chemicals (HCB and PCB) have been observed in Arctic marine organisms since the early 1970s (Bowes and Jonkel, 1975). The list of pesticides includes HCH, components of technical chlordane, heptachlor epoxide, polychlorinated camphenes (PCC, e.g., toxaphene), DDT residues, and dieldrin (Norstrom and Muir, 1988). These pollutants quickly move through the few species comprising polar food chains, and they can reach high levels in Arctic animals due to their storage of large amounts of energy rich

substances. Addison and Zinck (1986) observed that PCB have declined more than DDT residues in Arctic seals compared to eastern Canadian seal populations. Their study suggested that DDT input continued for a longer time in the Arctic due to air transport from Asia, where DDT is still heavily used.

A better understanding of OC contaminants in this region is important because of the fragile ecosystem and the native people who rely on marine animals for their food supply. In 1986, Canadian groups from Bedford Institute of Oceanography and Arctic Laboratories initiated an investigation of OC input to and transfer through Arctic food chains (Hargrave et al., 1988). We determined OC pesticides and PCB in air, snow, and surface water in the high Arctic as part of this project.

2. Methods

2.1. Location and dates

The Canadian Polar Continental Shelf Project established a research camp on a tabular iceberg that calved off the Ward Hunt Ice Shelf on the northern shore of Ellesmere Island in 1984. The 7 × 4 km × 45 m thick ice island is presently located off the northwest shore of Axel Heiberg Island (approximately 81°N, 100°W, Fig. 1). The ice island provides a safe sampling platform in a region where shipboard work is not practical due to extensive ice cover. Collections were made at least 2 km from the research camp. Air samples were taken from 25 August to 5 September 1986, and air, snow and seawater samples were taken from 7 June to 15 June 1987. The air temperature during these times was approximately +2 to −10°C

2.2. Collection of samples

2.2.1. Air. Air volumes of 1400–3000 m^3 were pulled through a 20 × 25 cm Gelman AE binderless glass fiber filter (GFF) and two 7.5 cm thick × 7.8 cm diameter polyurethane foam (PUF) plugs at flow rates of 0.6–0.8 m^3/min. Procedures for the cleanup of PUF and filters and sample collection are given elsewhere (Billings and Bidleman, 1983). Electrical power was supplied by gasoline generators operated ~50–100 m downwind of the samplers. After sampling, PUF plugs were placed into metal cans which were sealed with masking tape. GFF were wrapped in solvent-rinsed aluminum foil. Field spikes were prepared by pipetting 1.0 ml of a calibration standard containing 5–25 ng/ml OC

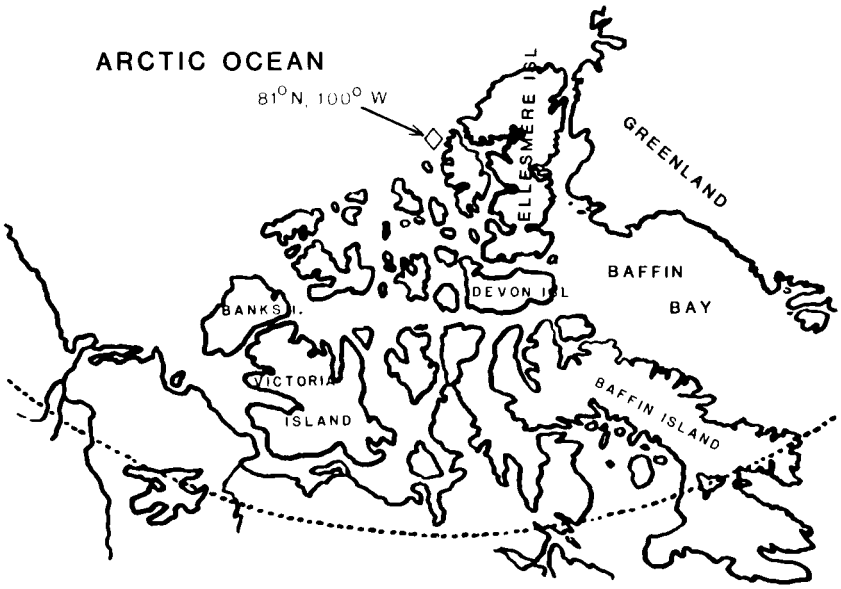

Fig. 1. Location of PCSP Ice Island during August–September 1986 and June 1987 (approximately 81°N, 100°W).

compounds onto several blank PUF plugs. Blank PUF plugs and GFF were carried to and from the field with the samples.

2.2.2. Water and snow. Four seawater samples were taken at a depth of 10 m using a National Bureau of Standards sampler. One sample was taken at 1 m depth by plunging a bottle into a lead of recently exposed water. The salinity was 32 parts-per-thousand and the water temperature was -1.7°C.

Snow was collected by removing the top surface layer (upper 5 cm) into a stainless steel pot, using a solvent-cleaned metal shovel. Two samples were taken prior to a snow event of 12 June 1987; this "older" snow had accumulated before our arrival on 5 June. A snow event sample was taken by scraping the "fresh" snow off the older snow surface. Snow samples were covered and allowed to melt at room temperature ($\sim$20°C) in the laboratory on the ice island.

Melted snow and seawater (2–3 l) were pulled at 0.8–1.3 l/h through a 4.7 cm diameter Gelman AE binderless GFF followed by front and back 500 mg C_8 cartridges (J. T. Baker SPE). This step was done in the laboratory on the ice island and the GFF and cartridges were then shipped in glass jars with polytetrafluoroethylene-lined caps to Columbia for analysis. Before use, the GFF were baked at 400°C for 6 h and stored in solvent-rinsed aluminum foil. C_8 cartridges were extracted with 1:1 ethyl ether/*n*-hexane in a Soxhlet apparatus, dried in a heated vacuum desiccator, and stored in solvent-rinsed glass jars with polytetrafluoroethylene-lined caps. Immediately before sample preconcentration, the cartridges were activated by pulling 3 ml methanol followed by 3 ml distilled H_2O through them. A snow blank was prepared by rinsing the collection pot with $\sim$200 ml distilled water and pulling the water through the sampling system. Two-liter volumes of 10 m depth seawater were spiked with 170 ng each of α-HCH and γ-HCH, and the water was pulled through the collection system. Blank C_8 cartridges and GFF were carried to and from the field with the samples.

2.3. Analytical methods

2.3.1. Extraction and cleanup, air. PUF plugs were extracted in a Soxhlet apparatus with petroleum ether for 8 h. GFF were cut into strips, placed into round-bottom flasks and refluxed with dichloromethane for 8 h. GFF and PUF extracts were concentrated using a rotary evaporator and nitrogen blow-down; filter extracts were transferred into hexane during this step. The samples were split into 2 fractions using a column of silicic acid overlaid with neutral alumina (Keller and Bidleman, 1984; Bidleman et al., 1987). Both fractions were shaken with 18 M sulfuric acid, (except for samples used for dieldrin and endosulfan analysis) isooctane was added, and the fractions were blown down to a final volume for analysis.

2.3.2. Extraction and cleanup, water and snow. The C_8 cartridges were eluted with 3 ml of 1:1 ethyl ether/hexane. Hexane was added to the extracts and the ethyl ether was removed by a nitrogen stream. GFF were cut, placed into a round-bottomed flask and refluxed with acetone for 4 h. GFF extracts were concentrated into hexane by rotary evaporation and nitrogen blow-down. Sample extracts were shaken with 18 M sulfuric acid and δ-HCH was added as an internal standard.

2.4. Gas chromatographic analysis

2.4.1. Electron capture detection. Analyses of air, water, and snow samples were carried out on Varian 3700 and Carlo Erba 4160 instruments with ^{63}Ni electron capture detectors. A 25 m bonded phase (polydimethylsiloxane, 5% phenyl, Hewlett Packard or SGE Corp.) fused silica column was used in both chromatographs. Samples were injected splitless (Grob technique, 1–2 μl volume, 30 s split time) with the column oven at 90°C. After a 1-min hold, the oven was programmed at 5 to 15°C/min to a final temperature of 265°C. Other GC conditions were: carrier gas, hydrogen at 20–40 cm/s; injector 240°C; detector 320°C.

Chromatographic data were collected and processed with a Hewlett-Packard 3390A or Shimadzu Chromatopac CR3A integrator. Air sample components were calculated using peak areas with response factors derived from external standards. PCB were quantified as Aroclor 1242 and Aroclor 1254 using the sum of sample and standard peak areas, and also as the sum of individual PCB congeners. Response factors for the latter were derived from chromatograms of Aroclor standards, using the weight percentages of each congener in Aroclors 1242 and 1254

Table 1. *Ions monitored for GC-MID confirmations*

Negative ion mode	
PCC:	309, 311, 343, 345, 379, 381, 413, 415
Chlordanes and nonachlors:	300, 302, 334, 408, 410, 444
Electron impact mode	
DDE:	246, 248, 316, 318
DDT:	235, 237

reported by Capel et al. (1985). HCH in water and snow samples were quantified by peak areas relative to the δ-HCH internal standard. Pesticide and PCB standards were obtained from the EPA Repository for Pesticides and Industrial Organic Chemicals.

2.4.2. Mass spectrometry. Analyses for chlordane components, PCC, DDE, and DDT were carried out on air samples using a Finnigan 4521C instrument. A 25 m bonded phase (polydimethylsiloxane, 5% phenyl, Hewlett-Packard Corp.) column was used with helium carrier gas. Samples were injected splitless (Grob technique, 2 μl volume, 60 s split time) with the column oven at 90°C. After a 1-min hold, the oven was ramped 15°C/min to 220°C and then at 5°C/min to 300°C. For chlordanes and PCC negative ion mass spectrometry (NIMS) was employed. The ion source was maintained at 130°C and methane at 0.1 torr was used. The mass spectrometer was operated in the multiple ion detection (MID) mode. Ions monitored for chlordanes and PCC (Table 1) were selected from those previously used for NIMS work (Jansson and Wideqvist, 1983; Bidleman et al., 1987). MS confirmation of DDE and DDT was done by electron impact (EIMS) in the MID mode. The ion source was maintained at 150°C and 70 eV. Ions monitored for DDE and DDT are given in Table 1. OC were quantified by comparing sample peak areas to those of external standards or to a mirex internal standard.

3. Results and discussion

3.1. Air

3.1.1. Analytical recovery and breakthrough. PUF plugs that were spiked with an OC calibration standard on the ice island were carried through the same analytical workup as sample plugs. HCB, α-HCH, and γ-HCH had average percent recoveries of 68 ± 3, 69 ± 5, and 72 ± 6 ($n = 4$ for all), respectively. The final values for HCB and HCH were obtained by dividing the quantities found in samples by the average recovery of the field spikes. Analytical recoveries were $\geqslant 82\%$ for OC less volatile than γ-HCH and no correction was made in calculating the final results. Of the compounds collected, pentachlorobenzene (PeCB) and HCB were the only ones that showed breakthrough to the back PUF plugs. PeCB has equal amounts in both traps and no quantitative results could be obtained. HCB showed breakthrough ranging from 27–99% of the front trap values (average = 53%) and HCB results were calculated by summing the quantities on both plugs; for some samples this may represent a lower limit.

3.1.2. GC-ECD air results. Concentrations of OC found on PUF traps for the August 1986 and June 1987 trips are given in Table 2. GFF were analyzed for a few samples (2A, 2B, 7A, and 7B), but none showed detectable residues of the compounds of interest. A comparison of our results to those of others is presented in Table 3.

HCB, α-HCH, and γ-HCH were found in all samples at concentrations similar to values previously reported for the northern hemisphere (Bidleman et al., 1987). Alpha-HCH levels were the highest of all the OC, averaging 546 and 340 pg/m^3 for August 1986 and June 1987 respectively. Average concentrations of γ-HCH for August and June were 31 and 45 pg/m^3. Two types of HCH products are in use throughout the world. In North America and Europe, pure γ-HCH (lindane) is applied almost exclusively, whereas Asia, the Middle East, and Mexico consume large tonnages of technical HCH (FAO, 1978–86). Technical HCH consists of 55–80% α-HCH, 5–14% β-HCH, 8–15% γ-HCH, and minor percentages of other isomers (Metcalf, 1955). The heavy use of technical HCH in the Eastern Hemisphere is probably responsible for the predominance of α-HCH in the northern troposphere (Tanabe et al., 1982). Attesting to this are the extraordinarily high concentrations of HCH (predominately α-HCH), approximately 1000 times above Arctic levels, found in the ambient air of Delhi, India (Kaushik et al., 1987).

The ratios of the mean α-HCH:γ-HCH concentrations were 17.6 for August and 7.6 for

Table 2. *Airborne organochlorines measured at the PCSP Ice Island*[a]

Collection date	Sample	m^3 air	(pg/m^3) HCB	α-HCH	γ-HCH	TC	CC	TN	CN	*p,p'*-DDE	*p,p'*-DDT	PCB light	(Aroclors)[b] heavy	Total	Total PCB (Congeners)	PCC[c]	ENDO I	DIEL
1986																		
25–27 Aug.	1	1344	131	591	27	1.7	3.2	2.0	—	0.2	1.4	6.7	13.0	19.7	19.4	25	9.7	5.0
27–29 Aug.	2A	1449	233	513	33	0.7	2.0	1.2	—	0.2	0.5	8.1	6.3	14.4	18.3	53	6.2	2.7
	2B	1655	199	469	29	1.0	3.0	1.6	—	0.1	0.7	6.7	3.8	10.5	12.9	78	2.7	3.3
29 Aug.–	3A	1738	>190[d]	612	37	1.3	3.7	2.0	0.72	0.2	1.3	8.6	7.5	16.1	14.4	47	8.1	0.1
1 Sept.	3B	2080	217	731	36	1.1	3.6	1.9	0.50	0.1	1.0	9.6	4.3	13.9	14.8	44	6.3	0.5
1–5 Sept.	4A	4208	147	417	24	0.6	1.9	0.9	0.15	<0.1	0.5	7.1	2.1	9.2	9.9	30	8.0	0.3
	4B	4003	209	490	29	1.1	2.4	0.8	0.21	<0.1	0.7	10.0	4.7	14.7	16.0	30	8.5	1.4
	mean		189	546	31	1.1	2.8	1.5	0.40	0.1	0.9	8.1	6.0	14.1	15.1	44	7.1	1.9
1987																		
7–9 June	5	2294	>44[e]	283	41	1.6	2.7	2.1	—	0.5	2.6	9.6	5.4	15.0	9.3	21	1.8	0.2
9–11 June	6A	1738	—	377	45	2.5	4.1	3.2	0.38	—	0.8	—	—	—	—	41	—	—
	6B	1759	155	370	52	2.4	4.9	4.0	0.80	1.0	1.0	16.0	5.5	21.5	17.0	45	—	—
11–13 June	7A	1694	>119[d]	349	53	2.1	3.8	2.8	0.72	3.5	3.2	12.0	6.5	18.5	26.1	38	—	—
	7B	1544	132	302	41	1.9	3.3	5.1	0.76	5.0	1.6	15.5	12.0	27.5	21.7	35	—	—
13–15 June	8	2131	154	358	36	3.4	5.1	4.9	—	4.6	4.3	12.4	6.0	18.4	13.8	34	5.0	1.0
	mean		147	340	45	2.3	4.0	3.7	0.67	2.9	2.3	13.1	7.1	20.2	17.6	36	3.4	0.6

[a] All concentrations based on GC-ECD, except CN which was GC-NIMS.
[b] Light PCB calculated as Aroclor 1242; heavy PCB as Aroclor 1254.
[c] PCC calculated as toxaphene.
[d] HCB breakthrough may have occurred for these samples.
[e] Front trap only.

Table 3. *Comparison of reported OC levels in Arctic air*

	HCB	α-HCH	γ-HCH	ΣHCH	(pg/m³) TC	CC	TN	CN[a]	ΣChlordanes	ΣDDT	PCB[b]
Ice Island, this study											
1986–87											
range	>119–233	283–731	24–53	324–767	0.6–3.4	1.9–5.1	0.8–5.1	0.15–0.8	3.6–13	0.5–8.9	2.1–13
mean	174	451	37	488	1.7	3.4	2.5	0.53	8.0	2.9	6.0
Ice Island[c]											
May–June 1986	73	425	70	495	—	—	—	—	3.6	<1	<2
Aug.–Sept. 1986	63	253	17	270	—	—	—	—	1.9	<1	<1
Spitzbergen[d]											
Fall 1982–83	75–227	407–1416	0.1–6	—	—	0.6–3.2	—	—	—	—	25–75
*W/S 1983–84	29–389	121–787	12–102	—	—	0.6–5.1	—	—	—	—	25–150
Summer 1984	20–201	260–774	24–100	—	—	1.7–5.4	—	—	—	—	—
Bear Island[d]											
Fall 1982–83	78–200	277–1550	0.1–67	—	—	0.5–1.7	—	—	—	—	10–40
W/S 1983	87–201	110–469	23–80	—	—	1.2–1.3	—	—	—	—	10–30
Summer 1984	42–149	38–305	5–41	—	—	0.6–2.1	—	—	—	—	—
Hope Island[e]											
1982–83	100–200	250–1700	<5–75	—	—	1.0–2.0	—	—	—	—	5.0–70
Jan Mayen[e]											
1982–83	50–200	400–1600	<5–50	—	—	0.5–2.0	—	—	—	—	25–300
Mould Bay[f]											
June 1984	—	—	—	—	0.5–1.7	1.1–1.8	1.0–1.5	<0.2–0.4	2.1–3.7	—	—
Bering Sea[g]											
1979	—	—	—	540–1700	—	—	—	—	—	4.0–15	—

[a] GC-NIMS results.
[b] Pentachlorobiphenyl or Aroclor 1254.
[c] Hargrave et al., mean values.
[d] Pacyna and Oehme.
[e] Oehme and Ottar.
[f] Hoff and Chan.
[g] Tanabe and Tatsukawa.
* Winter/Spring.

June. Oehme and Ottar (1984) and Pacyna and Oehme (1988) also found that the α-HCH:γ-HCH ratio in the Norwegian Arctic was lower in the winter–spring than in the summer–fall, and suggested that the proportion of α-HCH is higher in older air masses because of photochemical transformation of γ-HCH to α-HCH. Pollutants are transported into the Arctic from lower latitudes during the winter. During the summer, the polar air mass is relatively stagnant and isolation is most intense, affording the greatest opportunity for photolysis. This simple model might explain the higher proportion of α-HCH in the summer. However the α-HCH:γ-HCH ratio may also be influenced by different rates of atmospheric deposition of the isomers and by transport of HCH from regions where lindane or technical HCH are mainly applied.

The sum of four chlordane components (TC, CC, TN, CN) averaged 5.8 pg/m^3 in August 1986 and 10.7 pg/m^3 in June 1987. The August mean is close to the total of the same four chlordanes at Mould Bay in June 1984 (4.0 pg/m^3) (Hoff and Chan, 1986), but our June mean is nearly three times higher. Average concentrations of CC at the Ice Island (2.8–4.0 pg/m^3) were also higher than those observed in the Norwegian Arctic (0.8–2.8 pg/m^3) (Pacyna and Oehme, 1988).

Ratios of the average chlordane isomer concentrations (R=CC:TN:TC) at the Ice Island were: August $R = 1.0:0.54:0.39$; June $R = 1.0:0.93:0.58$. This order of abundance was also observed by Hoff and Chan (1986) whose mean R in June 1984 = 1.0:0.89:0.56. Technical chlordane has $R = 1.0:0.37:1.26$ (Sovocool et al., 1977). Expectations are for TC to be the dominant isomer in air, since it is the most abundant and volatile of the chlordanes. TC:CC ratios were greater than unity in Columbia, SC (Foreman and Bidleman, 1987), and also in southern Sweden (Bidleman et al., 1987). The reason for the depletion of TC in Arctic air is unknown.

Chlordane and the related pesticide heptachlor have been used in the United States at a total of about 4500 tonnes/year for structural termite control (USEPA, 1983). Since chlordane is not listed separately in the FAO Production Yearbooks, little information is available about its use in other countries. In Japan, about 500 tonnes/year have been used for termite control (Hirose, 1977). Highest reported concentrations of chlordane in ambient air have been in the southern United States, and levels over the North Atlantic increase with proximity to the US (Bidleman et al., 1987).

Concentrations of PCC were similar for both expeditions. Oehme and Stray (1982) identified traces of PCC in the Norwegian Arctic, but PCC were not quantified. No other information is available about the presence of PCC in Arctic air, although PCC have been found in ambient air in the continental United States (Billings and Bidleman, 1983; Rice et al., 1986), over the North Atlantic (Bidleman et al., 1981), and in southern Sweden (Bidleman et al., 1987). Of the identified OC in Arctic air, PCC are third in abundance, a fact that may be important in explaining the PCC residues recently reported in Arctic fish (Norstrom and Muir, 1988).

Toxaphene, a PCC product, was heavily used in the southern United States during the mid 1970s, with a peak consumption of nearly 22,000 tonnes in 1976 (FAO, 1978). Usage declined to 5000 tonnes in 1982 (FAO, 1984), and toxaphene production was halted at the end of that year. Provisions were made for "existing stocks" of toxaphene to be used through 1986 (Federal Register, 1982), but the extent of such use is unknown. Through 1984, toxaphene applications have continued in Mexico at 800–1600 tonnes annually, and use of PCC products at 41–55 tonnes/year has been reported by Poland and Hungary (FAO, 1986). Examination of air trajectories suggested that eastern European sources may have supplied a portion of the PCC found in the atmosphere in southern Sweden (Bidleman et al., 1987). PCC were also found as major OC in rain in the western Mediterranean Sea area (Villeneuve and Cattini, 1986).

Only traces of DDE were found in air on the Ice Island in August 1986 and the average DDT concentration was 0.9 pg/m^3. By comparison, mean DDE and DDT levels for June 1987 were 2.9 pg/m^3 and 2.3 pg/m^3; however, the DDT values may have been inflated by coeluting PCC (Subsection 3.1.3). Dieldrin and endosulfan I were found during both trips; August levels were twice the June levels, although only two June samples were analyzed for these pesticides.

PCB were calculated as Aroclors 1242 (light PCB) or 1254 (heavy PCB) using response factors

derived from the whole Aroclor chromatographic patterns, and also by summing individual PCB congeners. Total PCB derived by these two methods agreed well (Table 2). Mean concentrations of light PCB were similar (8.1 pg/m^3 for August and 13.1 pg/m^3 for June), and the average levels of the heavy PCB were nearly identical (6.0 pg/m^3 for August and 5.9 pg/m^3 for June).

3.1.3. GC-MS air results. Eleven air samples were analyzed for chlordanes and PCC by capillary GC-NIMS. Two chlordanes (TC and CC) and two nonachlors (TN and CN) were clearly identified on front PUF plugs, with only traces on back plugs (Fig. 2) and no detectable chlordanes in blanks. PCC components containing 6–9 chlorines can be seen in the MID chromatograms of Figs. 3 and 4; the most volatile constituents of each homolog are the ones atmospherically transported to the Arctic. No traces of PCC were found on back PUF sample plugs or in blanks.

Chlordanes and PCC in the 11 samples were quantified by GC-ECD against external standards and by GC-NIMS using either external standards or a mirex internal standard. A comparison of the two techniques is given in Table 4. Ratios of quantities found by NIMS and ECD (NIMS/ECD) were calculated for each compound and sample. Average NIMS/ECD ($\pm$one standard deviation) were: TC = 0.55 $\pm$ 0.26, CC = 1.10 $\pm$ 0.53, TN = 0.74 $\pm$ 0.23, PCC = 1.09 $\pm$ 0.57. These ratios are significantly different from 1.00 for TC and TN ($\alpha < 0.01$) but not different for CC and PCC ($\alpha > 0.25$). Perhaps ECD results for TC and TN were slightly inflated by interferences underlying these peaks. However, considering the analytical difficulties at these ultra-trace levels, we feel the agreement between ECD and NIMS results is satisfactory.

Samples of 5, 7B, and 8 were examined by capillary GC-electron impact mass spectrometry in the MID mode for DDE. Samples 5, 7A, 7B, and 8 were checked for DDT. DDE was identified in 7B and 8, both of which showed clear DDE peaks in ECD chromatograms. Estimates of DDE in 7B and 8 by GC-MS were 1.5 and 5.2 pg/m^3 respectively, compared to 5.0 and 4.6 pg/m^3 by GC-ECD. Sample 5 showed only 0.5 pg/m^3 DDE by GC-ECD, and DDE was not found by GC-MS. The DDT content of sample 8 was 2.4 pg/m^3 by GC-MS and 4.3 pg/m^3 by GC-ECD. DDT could not be found by GC-MS in 5

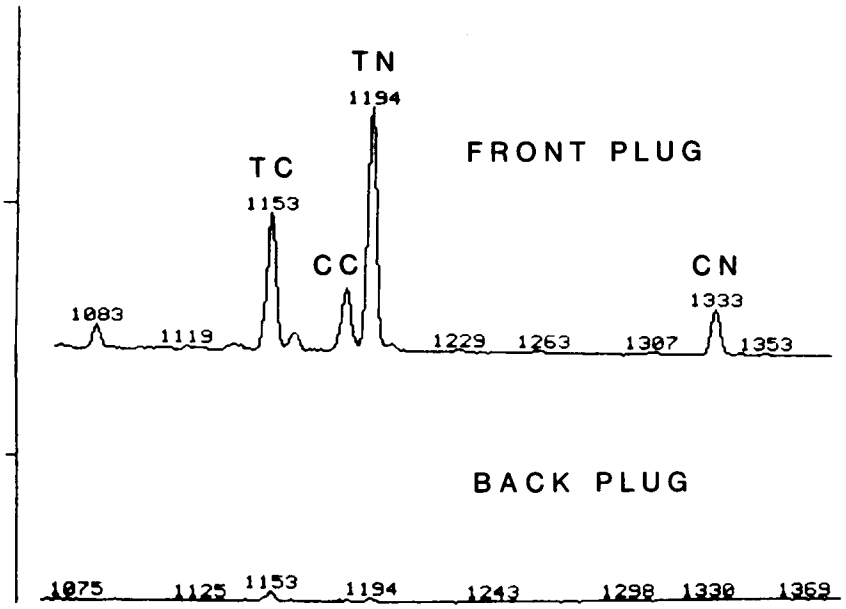

Fig. 2. Reconstructed ion chromatogram of chlordane components in sample 6A. CC appears lower than TC, even though atmospheric levels of CC were higher, because of the different responses of TC and CC for the ions selected.

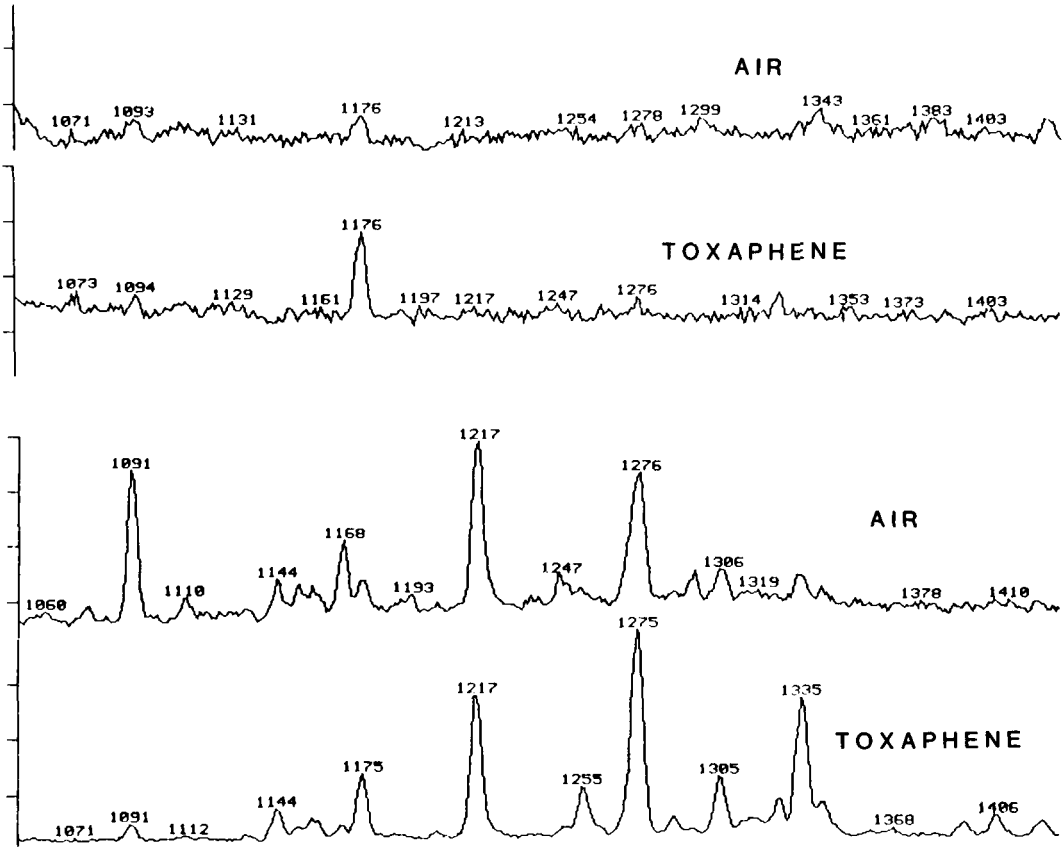

Fig. 3. PCC in sample 6B compared to a toxaphene standard. Top: 6-Cl components, $(M\text{-}Cl)^- = 309, 311$; bottom: 7-Cl components, $(M\text{-}Cl)^- = 343, 345$.

and 7B, even through ECD chromatograms showed a peak at the DDT retention time. Sample 7A contained too much background interference to draw conclusions. Sample 8 had the second highest air volume of the June set, and yielded the most DDT for analysis. Even so, the DDT peak was a small one and DDT in the other samples may have been below the detection limit. Also, the GC-ECD results for DDT may have been fortified by interferences, PCC components being a possibility. Considering that DDT was confirmed in only one sample, the DDT concentrations in Table 2 should be considered upper limits.

These results are the first indications of the presence of DDT compounds in the Canadian Arctic atmosphere. Others have searched without success for DDT and DDE at Arctic stations further east (Oehme and Stray, 1982; Oehme and Ottar, 1984; Pacyna and Oehme, 1988). Tanabe and Tatsukawa (1980) reported total DDT residues averaging 7.6 pg/m^3 over the Bering Sea in 1979. DDE was very low in our samples until the later part of the June expedition, and only the last June sample yielded a confirmed DDT result. It may be that atmospheric input of the DDT group to the Arctic is more variable than for the other OC studied.

3.2. Seawater and snow

3.2.1. Analytical recovery and breakthrough. The mean percent recovery of the HCH from cartridges spiked on the Ice Island was 78.0 ± 8.2 ($n = 2$). The final results for seawater and snow were corrected by dividing the HCH concentrations found by the average recovery of the

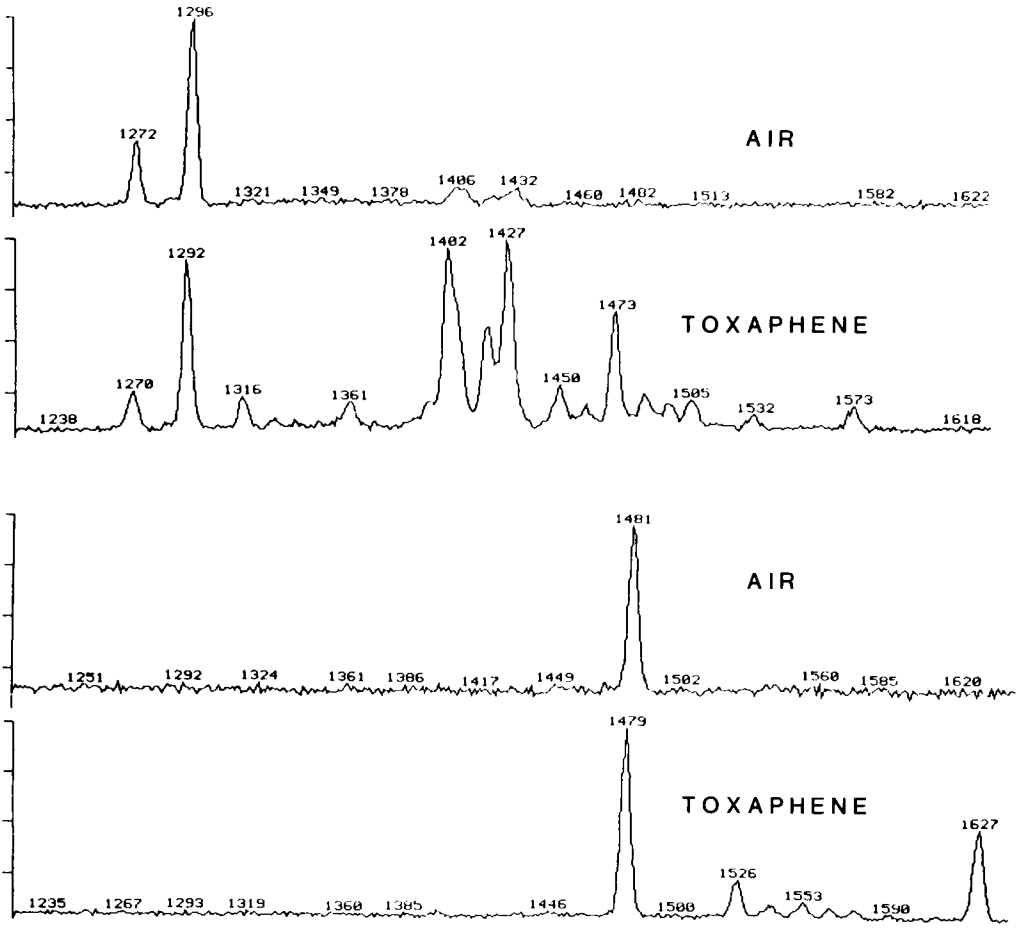

Fig. 4. PCC in sample 6B compared to a toxaphene standard. Top: 8-Cl components, $(M\text{-}Cl)^- = 379, 381$; bottom: 9-Cl components, $(M\text{-}Cl)^- = 413, 415$.

field spikes. No breakthrough to the back cartridge was observed for any of the samples nor were HCH found on GFF.

3.2.2. Water and snow results. Because of the small water volumes sampled, HCH were the only OC detected in seawater (Table 5). Average concentrations over 1–10 m depth were 7.1 ng/l α-HCH and 0.81 ng/l γ-HCH, yielding an α-HCH : γ-HCH ratio of 8.8.

HCH concentrations in the three melted snow samples are also presented in Table 5. The concentrations of α-HCH and γ-HCH in new snow (1.9 and 0.67 ng/l, sample 3) were 6 and 2 times higher than in old snow (means = 0.32 and 0.37 ng/l, samples 1 and 2). The α-HCH : γ-HCH ratio in new snow was 2.8 and 0.86 in old snow. It is not clear why the fresh snow had higher levels of HCH and different isomer ratios than the older snow. Hargrave et al. (1988) found that HCB and HCH levels in Ice Island snow from May 1986 were higher than in August 1986, even though aerial HCB concentrations were about the same. They suggested that HCB deposited in May might have revolatilized later in the summer when temperatures were higher. Perhaps volatilization losses also occur on a shorter time scale as fresh snow ages.

3.3. Air–water equilibrium for HCH

Mean air and water concentrations from the June trip were used to estimate the state of air–water equilibrium for the HCH isomers. The

Table 4. *Comparison of GC-ECD and GC-NIMS analysis of chlordanes and PCC (pg/m³)*

Sample	Method	TC	CC	TN	PCC
1	ECD	1.7	3.2	2.0	25
	NIMS	0.81	2.3	1.1	44
2A	ECD	0.69	2.0	1.2	53
	NIMS	0.76	4.1	1.5	39
2B	ECD	0.97	3.0	1.6	78
	NIMS	0.73	4.1	1.4	45
3A	ECD	1.3	3.7	2.0	47
	NIMS	0.54	7.5	1.8	61
3B	ECD	1.1	3.6	1.9	44
	NIMS	0.29	4.4	1.0	35
4A	ECD	0.57	1.9	0.86	30
	NIMS	0.18	0.93	0.48	14
4B	ECD	1.1	2.4	0.85	30
	NIMS	0.25	1.4	0.45	15
6A	ECD	2.5	4.1	3.2	41
	NIMS	1.1	3.2	2.1	36
6B	ECD	2.4	4.9	3.9	45
	NIMS	1.8	5.3	3.6	99
7A	ECD	2.1	3.8	2.8	38
	NIMS	1.3	3.0	2.3	49
7B	ECD	1.9	3.3	5.1	35
	NIMS	1.3	3.1	2.6	54

Henry's Law constant (H) for the distribution of α-HCH between air and seawater at 23° is 1.1×10^{-5} atm-m³/mol (Atlas et al., 1982). Mackay and Shiu (1981) reviewed the physical properties of γ-HCH and recommended $H = 3.1 \times 10^{-6}$ atm-m³/mol for fresh water at 25°.

Table 5. *Seawater and snow-melt concentrations of HCH*

Collection date (1987)	Sample	Depth	(ng/l) α-HCH	γ-HCH
Water				
9 June	1	10 m	6.4	0.83
9 June	2A	10 m	8.9	1.00
	2B	10 m	6.6	0.72
10 June	3	10 m	7.0	0.61
11 June	4A	10 m	8.1	0.65
	4B	10 m	6.0	0.79
12 June	5	1 m	7.0	1.1
	$\bar{X}$		7.1 ± 1.0	0.81 ± 0.18
Snow		type*		
7 June	1	old	0.34	0.35
9 June	2	old	0.29	0.38
13 June	3	new	1.9	0.67

* See text, Subsection 2.2.2.

Lindane (γ-HCH) is 23% less soluble in 0.5 M sodium chloride than in distilled water (Masterson and Lee, 1972), so the appropriate seawater $H = 3.8 \times 10^{-6}$ atm-m³/mol.

Henry's Law constants for HCH have not been determined at different temperatures, so the values of H at 23–25° were adjusted to −2° by assuming the temperature dependence of H for PCB mixtures. Burkhard et al. (1985) estimated that H for Aroclors 1221 through 1260 decreased by factors of 8–14 between 25° and 0°. We assumed that H decreased by a factor of 11 between 23° and −2° (α-HCH), and a factor of 13 between 25° and −2° (γ-HCH).

Table 6 gives the estimated H at −2°, calculated equilibrium concentrations of HCH in surface water, and actual concentrations. Alpha-HCH appears to be close to equilibrium, but γ-HCH is undersaturated. Whether the difference between the two isomers is real or an artifact of uncertainties in H is unknown. A likely source of error in these calculations is the extrapolation of H to −2°. A better knowledge of H is needed, especially as a function of temperature.

4. Conclusions

Many OC are aerially transported to the high Arctic and become incorporated in the local ecosystem. The PCSP Ice Island provided a clean research station for the collection of air, snow, and water samples for OC analysis. The relative abundance of OC in Arctic air were: α-HCH > HCB > γ-HCH ~ PCC > chlordanes ~ PCB > DDTs. PCC and chlordanes were determined in air samples from both expeditions by GC-ECD and GC-NIMS, with satisfactory agreement between the two techniques. This study has provided the first quantitative information on

Table 6. *Henry's Law constants and air–water partitioning of HCH*

	H (atm-m³/mol[a])	(ng/l) Equilibrium[b]	Actual[c]
α-HCH	1.0×10^{-6}	7.6	7.1
γ-HCH	2.9×10^{-7}	3.4	0.81

[a] H for seawater at −2°.

[b] Calculated from H and June average air concentrations (Table 3).

[c] Average for June surface water (Table 6).

PCC in Arctic air. GC-MS confirmed the presence of DDE, and for the highest-level sample, the presence of DDT. Alpha-HCH and γ-HCH were found in surface seawater and snow during June. The concentration of α-HCH in surface water appeared to be nearly in equilibrium with its concentration in the atmosphere, but γ-HCH was undersaturated. These conclusions are uncertain however, because of possible errors in estimating Henry's Law constants for HCH at the temperature of Arctic waters. Based on limited samples, concentrations of α-HCH in newly fallen snow were higher than in aged snow.

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6. Appendix

CC	cis-chlordane
CN	cis-nonachlor
DDE	*p,p'*-DDE
DDT	*p,p'*-DDT
DIEL	dieldrin
ECD	electron capture detector
EIMS	electron impact mass spectrometry
ENDO I	endosulfan I
GC	gas chromatography
GFF	glass fiber filter
H	Henry's Law constant
HCB	hexachlorobenzene
HCH	hexachlorocyclohexanes
MID	multiple ion detection
n	number of measurements
NIMS	negative ion mass spectrometry
OC	organochlorines
PCB	polychlorinated biphenyls
PCC	polychlorinated camphenes
PSCP	Polar Continental Shelf Project
PeCB	pentachlorobenzene
PUF	polyurethane foam
TC	trans-chlordane
TN	trans-nonachlor

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