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Removal of α - and γ -Hexachlorocyclohexane and Enantiomers of α -Hexachlorocyclohexane in the Eastern Arctic Ocean

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Atmospheric concentrations of hexachlorocyclohexanes (HCHs) have declined over the last two decades, and the Arctic Ocean is now eliminating HCHs through degradation, volatilization, and advective outflow. Air and water samples were collected on a cruise of the eastern Arctic Ocean in July–September 1996 for HCHs and enantiomers of α -HCH. Mean concentrations of α - and γ -HCH in air were 37 and 17 pg m⁻³. Back trajectories indicated that the concentration and proportion of γ -HCH increased when air parcels passed over Eurasia where lindane (γ -HCH) is currently used. Mean concentrations in surface water (910 pg L⁻¹ α -HCH; 270 pg L⁻¹ γ -HCH) were lower than those in the western Arctic. The enantiomer ratio, ER = (+)- α -HCH / (–)- α -HCH, averaged 0.87 ± 0.06 ($n = 21$) in surface water and decreased with depth. Microbial degradation rates of HCHs were estimated using vertical profiles of ER and concentration, surface water data from 1979 (21), and the “ventilation” age of water at a particular depth (22). Microbial rate constants were 3–10 times greater than those for hydrolysis. Half-lives for (+)- α -HCH, (–)- α -HCH, and γ -HCH were 5.9, 23.1, and 18.8 years, respectively. Water–air fugacity ratios (f_w/f_a) indicated that α -HCH was near steady state, while γ -HCH was undergoing deposition to the ocean. ERs of α -HCH in air (0.95 ± 0.03 , $n = 16$) were slightly less than racemic, showing the contribution of volatilization to the boundary layer.

Introduction

Hexachlorocyclohexanes (HCHs) are the most abundant organochlorine pesticides in the world's oceans, including the Arctic Ocean (1, 2). It has recently been estimated that 5900 t are contained within the surface layer of the Arctic

Ocean (3) thus providing an enormous reservoir for gas exchange with the atmosphere. In the past, technical HCH was the most widely used insecticide in the world and consisted of α -HCH (60–70%), β -HCH (5–12%), γ -HCH (10–15%), and other minor components (1). Today, most industrialized countries use pure γ -HCH, the only component of the mixture which has insecticidal properties.

The presence of HCHs and other persistent organochlorines in the arctic can be attributed to migration through oceanic circulation and transport via the atmosphere. The latter occurs by two mechanisms. The first is episodic, long-range transport (4–6) where chemicals are carried from source regions over great distances in a relatively short period of time, on the order of days. The second is a more gradual process by which chemicals evaporate from warmer regions and become globally fractionated according to their volatility on a south–north transect (1). These are sometimes referred to as “global distillation” and the “grasshopper effects” (7–9). HCHs have a high atmospheric transport potential by these mechanisms due to their high vapor pressure and low octanol–air partition coefficient (K_{OA}), both favoring evaporation from soil. This coupled with their long atmospheric lifetimes with respect to OH radical attack (α -HCH, 120 days; γ -HCH, 96 days) (10) and low Henry's Law constants (air–water partition coefficients) (11) allows them to attain high concentrations in the Arctic Ocean. HCHs in ocean surface water increase along a latitudinal transect from tropical waters to the Arctic Ocean, providing a classical demonstration of the “cold condensation” effect (9).

Decreased usage of technical HCH in the two decades has led to reduced atmospheric burdens of α -HCH (12–15). Recent measurements in the Arctic indicate that α -HCH is now revolatilizing from the western Arctic Ocean and its regional seas (12–15). This reversal is supported by chiral analysis of the α -HCH in air and surface water (15). In the technical mixture α -HCH exists as a racemate (i.e. 1:1 proportion) of two enantiomeric forms which are nonsuperimposable mirror images. Abiotic processes such as hydrolysis and photolysis reactions do not differentiate between these two forms. However, biological systems may preferentially degrade one over the other, resulting in an enantiomeric ratio in surface water different than 1:1. Volatilization from water transfers nonracemic α -HCH to the atmospheric boundary layer allowing the contribution from gas exchange to be distinguished from atmospheric transport of the racemic α -HCH (15, 16).

The Arctic Ocean is in the process of eliminating HCHs. A recent mass balance for HCHs in the upper 200 m concluded that losses are occurring mainly by water outflow, volatilization, and degradation in that order of importance (3). Degradation by basic hydrolysis was estimated to account for 14% of total losses, and the microbial pathway was not considered.

This paper summarizes results from a cruise of the eastern Arctic Ocean in July–September 1996, aboard the Swedish icebreaker Oden. The expedition continued the survey of HCHs in the Arctic Ocean, begun in the Bering–Chukchi seas in 1993 (14) and a 1994 transect from the Chukchi sea, across the polar cap and into the Greenland Sea (2, 15). Concentrations of HCHs in air and water are presented and used to determine the state of air–water gas exchange. Enantiomer ratios of α -HCH are used to estimate the rate of microbial degradation in the water column and “recycling” from surface water to the atmosphere.

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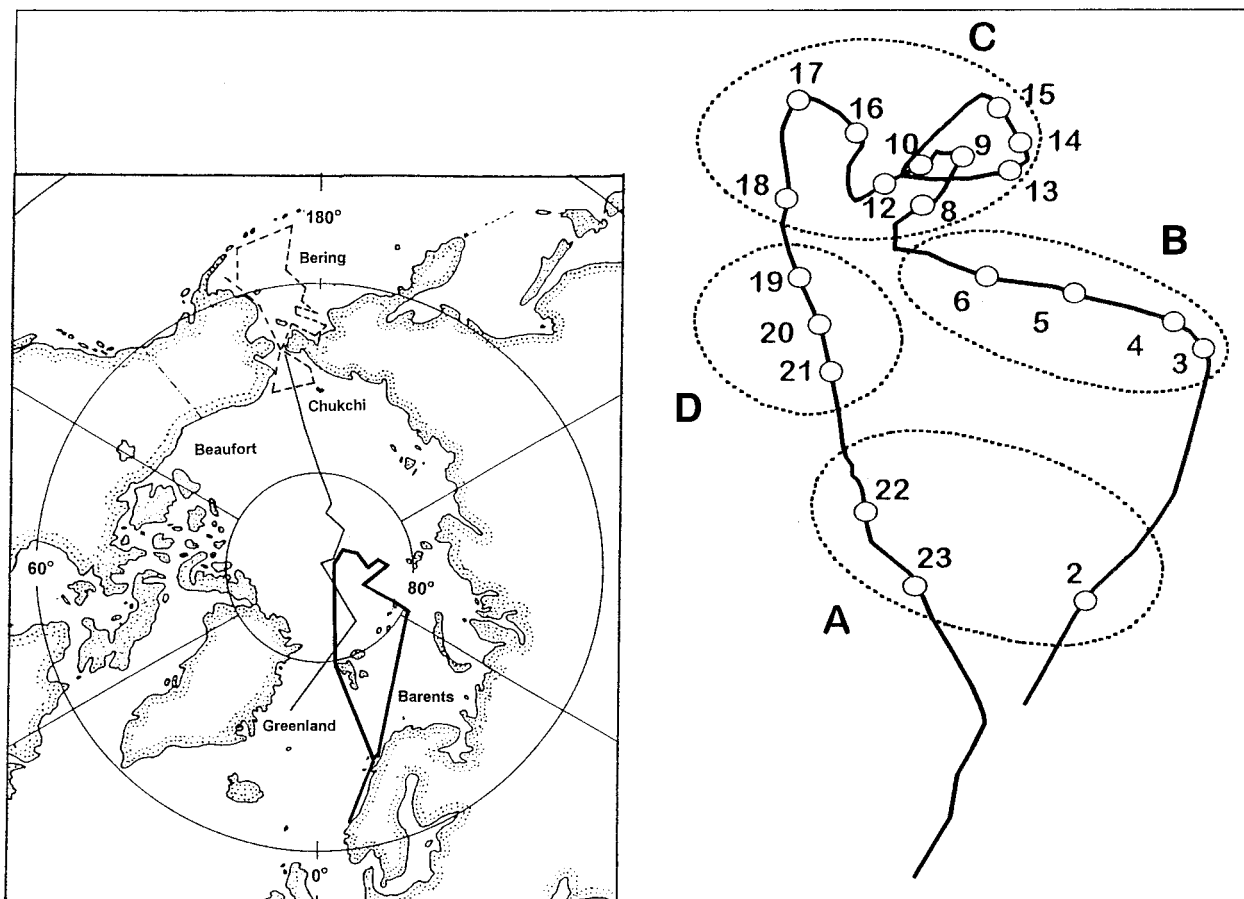


FIGURE 1. Map showing cruise tracks of recent Arctic Ocean research expeditions. Dotted line = Bering-Chukchi sea (BERPAC-93), thin solid line = Arctic Ocean Sections (AOS-94), heavy solid line = ODEN-96. Letters A–D designate station groupings in Table 4.

Experimental Section

Sample Collection. Air and water samples were collected aboard the icebreaker Oden during a three month cruise (Figure 1) of the eastern Arctic Ocean in July–September 1996. Air samples ($n = 34$) were collected using a high volume train consisting of a glass fiber filter (GFF) followed by two polyurethane foam (PUF) plugs (L. A. Rubber Company, Burlington, ON) with flow rates on the order of $0.4 \text{ m}^3 \text{ min}^{-1}$. Prior to use, PUF plugs were washed with water and acetone, Soxhlet extracted with acetone for 24 h followed by petroleum ether for 24 h, and dried in a heated vacuum desiccator. PUF plugs were fortified after sampling by injecting with $500 \mu\text{L}$ of d_6 - α -HCH surrogate standard ($0.0226 \text{ ng } \mu\text{L}^{-1}$, CDN Isotopes, Pointe-Claire, Quebec) in acetone and stored in glass jars having Teflon lined lids at -10°C for the duration of the cruise. Several unused PUF plugs were spiked with α -HCH, γ -HCH, and d_6 - α -HCH to check recoveries. Back PUF plugs were used to determine blank values.

Water samples were collected by submersible pump (surface) or Go-Flo bottle (deep) and transferred to 20 L stainless steel canisters. Each canister was spiked with 1 mL of d_6 - α -HCH recovery standard and shaken thoroughly. The HCHs were extracted onboard the ship by pressurizing the canister to pass the water through glass fiber filters and then through solid-phase extraction cartridges containing 200 mg of Isolute Env+, a hyper-cross-linked styrene-divinylbenzene copolymer (Jones Chromatography, Lakewood, CO). Activation of the cartridges involved eluting with 5 mL of methanol followed by 5 mL of distilled water immediately before use. Teflon tubing (4 mm i.d.) was used for all connections. Used cartridges and filters were wrapped in aluminum foil and stored at $\sim 3^\circ\text{C}$ for the duration of the cruise. Several surface

water samples were spiked with α - and γ -HCH to a final concentration ~ 10 times higher than expected in the water itself and d_6 - α -HCH was also added. Blanks of clean water (deionized water purified with a Milli-Q system and further cleaned by passing through XAD-resin) were spiked with d_6 - α -HCH and treated as samples.

Analysis. PUF plugs were Soxhlet extracted for 24 h with petroleum ether, and the volume was reduced to 2 mL by rotary evaporation and nitrogen blow-down. Extracts were fractionated on a column of 3 g of silicic acid (3% added water) topped with 2 g of neutral alumina (6% water) and ~ 1 g of anhydrous sodium sulfate. The first fraction (F1) was eluted with 30 mL of petroleum ether and the second fraction (F2), which contained the HCHs and most other organochlorine pesticides was eluted with 25 mL of dichloromethane. F2 was transferred into isooctane and reduced to 1 mL by blowing down with a gentle stream on nitrogen. PCB-103 (2,2',4,5',6-pentachlorobiphenyl) was added as internal standard.

Isolute Env+ cartridges were eluted in the laboratory with 15 mL of dichloromethane and transferred to isooctane and reduced to 1 mL. Samples were cleaned on a column of 0.5 g of neutral alumina (6% added water) and eluted with 5 mL of 10% dichloromethane in petroleum ether. Isooctane was again added, the eluate was reduced to 1 mL, and PCB-103 was added.

Air and water sample extracts were quantified by gas chromatography–negative ion mass spectrometry (GC–NIMS) using a Hewlett-Packard 5890 GC–5989B MS. Ions monitored (target, qualifier) in selected ion mode (SIM) were α - and γ -HCH (255, 257) and d_6 - α -HCH (259, 261). Samples qualified if the target/qualifier ratio was within 20% of the

TABLE 1. Sampling Information, Concentrations of HCHs, and Enantiomer Ratios of α -HCH in Air over the Eastern Arctic Ocean

sample	date	lat./long. (initial)	lat/long. (final)	(pg m ⁻³)			ER = (+)/(-)-α-HCH	
				α-HCH	γ-HCH	α/γ	Betadex	BGB
Barents Sea								
air1	96-07-18/19	N71, 8°/E21, 35'	N73, 34°/E24, 60'	26.5	27.8	0.95	0.96	
air2	96-07-19/21	N73, 34°/E25, 1'	N73, 47°/E25, 40'					
air3	96-07-21/22	N73, 52°/E25, 60'	N78, 25°/E56, 10'	20.0	67.8	0.29	0.87	
air4	96-07-22/23	N77, 5°/E41, 15'	N78, 25°/E56, 10'	17.7	36.0	0.49		
air5	96-07-23/24	N78, 25°/E56, 60'	N80, 18°/E65, 43'	11.4	13.3	0.86	0.95	0.94
North East Arctic Ocean								
air6	96-07-24/25	N80, 59°/E67, 42'	N81, 44°/E65, 53'	18.9	7.80	2.42		
air7	96-07-25/26	N81, 46°/E65, 39'	N82, 49°/E65, 39'	25.2	18.5	1.36		
air8	96-07-26/27	N82, 53°/E65, 37'	N83, 50°/E66, 56'	25.3	15.3	1.65	0.95	0.98
air9	96-07-28/29	N84, 48°/E71, 41'	N85, 22°/E71, 41'	24.7	15.1	1.64		
air10	96-07-29/30	N85, 23°/E71, 40'	N85, 34°/E72, 18'	20.1	22.1	0.91	0.90	
air11	96-07-30/01	N85, 40°/E72, 52'	N86, 20°/E74, 15'	30.7	5.9	5.20		
air12	96-08-01/02	N86, 55°/E86, 50'	N87, 3°/E123, 8'	23.2	5.26	4.41		0.95
air13	96-08-03/04	N87, 1°/E129, 50'	N86, 23°/E142, 12'	27.6	17.4	1.59		
air13-2	96-08-23	N87, 9°/E144, 48'	N87, 4°/E142, 17'	36.3	27.6	1.32		
air13-3	96-08-23/24	N87, 4°/E142, 17'	N86, 29°/E130, 6'	38.7	9.34	4.14		
air13-4	96-08-24/25	N86, 29°/E130, 6'	N86, 27°/E130, 57'	38.2	8.56	4.46		1.00
air14	96-08-25/26	N86, 27°/E130, 57'	N85, 26°/E137, 20'	39.0	6.35	6.14		
air15	96-08-29/30	N85, 24°/E152, 17'	N85, 31°/E155, 3'	38.6	19.6	1.97		
air16	96-08-30/31	N85, 31°/E155, 3'	N85, 33°/E156, 35'	40.9	12.8	3.20	0.99	
air17	96-08-31/01	N85, 33°/E156, 37'	N85, 40°/E160, 22'	56.7	15.9	3.57		
air18	96-09-02/03	N86, 57°/E152, 54'	N87, 37°/E146, 47'	46.7	14.7	3.18	0.97	
air19	96-09-03/04	N87, 37°/E146, 47'	N87, 37°/E158, 28'	37.4	13.7	2.73		
air20	96-09-04/05	N87, 37°/E158, 28'	N87, 10°/E169, 13'	45.6	12.2	3.74		
air21	96-09-07/08	N88, 36°/E179, 38'	N88, 52°/E179, 58'	63.7	15.2	4.19		
air22	96-09-08/09	N88, 59°/E179, 59'	N89, 54°/E156, 9'	49.2	18.8	2.62	0.97	0.97
air23	96-09-10/12	N89, 51°/E51, 11	N87, 60°/E23, 19'	52.2	13.1	3.98	0.97	
air24	96-09-12/13	N87, 60°/E23, 19'	N86, 30°/E19, 33'	50.8	12.7	4.00		
air25	96-09-13/14	N86, 25°/E19, 1'	N85, 31°/E12, 30'	28.4	11.3	2.51		
air26	96-09-14/15	N85, 31°/E12, 30'	N85, 33°/E10, 55'	31.6	19.1	1.65		
air27	96-09-15/16	N85, 33°/E10, 55'	N84, 37°/E15, 40'	27.9	9.9	2.82		
air28	96-09-16/17	N84, 33°/E15, 37'	N84, 2°/E11, 18'	32.6	14.3	2.28	0.92	0.94
air29	96-09-17/18	N84, 1°/E11, 11'	N82, 41°/E13, 19'	32.9	16.7	1.97		
air30	96-09-21/22	N78, 15°/E15, 39'	N74, 37°/E14, 34'	40.8	13.1	3.11	0.95	0.98
air31	96-09-22/23	N74, 29°/E14, 37'	N71, 4°/E15, 51'				0.97	
air32	96-09-23/24	N70, 42°/E15, 58'	N67, 29°/E12, 54'	28.4	11.1	2.56	0.97	
air33	96-09-24/25	N67, 29°/E12, 54'	N63, 23°/E6, 19'	43.2	21.5	2.01	0.95	
air34	96-09-25/26	N63, 23°/E6, 18'		68.1	35.6	1.91		

standard value. Analytes were separated on a 30 m DB-5MS column (J&W Scientific) with 0.25-mm i.d. and 0.25 μ m film thickness, operated with helium carrier gas at 40 cm s⁻¹. Injections (1 μ L) were splitless with the split opened after 0.5 min and the injector at 250 °C. The temperature program was 90 °C for 0.5 min, 10 °C min⁻¹ to 160 °C, and 2 °C min⁻¹ to 250 °C. Other operating condition were transfer line 250 °C, ion source 150 °C, quadrupole 100 °C, and methane reagent gas at ~1 Torr.

Chiral analysis of α -HCH was performed by GC-NIMS (SIM mode – ions 255, 257) using two columns: BGB-172 (20% *tert*-butyldimethylsilylated β -cyclodextrin in OV-1701, BGB Analytik AG, Switzerland) and Betadex-120 (20% permethylated β -cyclodextrin in SPB-25, Supelco). Both columns were 30 m \times 0.25 mm diameter and 0.25 μ m film thickness. The first eluting enantiomer was (–)- α -HCH on the BGB-172 and (+) on the Betadex column (15, 16). Temperature programs were (BGB-172) 90 °C, 15 °C min⁻¹ to 140 °C, 1 °C min⁻¹ to 180 °C, hold for 2.0 min, 20 °C min⁻¹ to 240 °C, hold for 5.0 min, and (Betadex-120) 90 °C, 15 °C min⁻¹ to 130 °C, 1 °C min⁻¹ to 190 °C, 20 °C min⁻¹ to 230 °C, hold for 5.0 min. Injections (2 μ L) were splitless with the split opened after 0.5 min. Other GC and MS conditions were as for quantitative analysis.

Results and Discussion

Quality Control. Blank water samples ($n = 3$) and back PUF plugs ($n = 6$) showed no detectable amounts of α - nor γ -HCH by GC-NIMS analysis. Therefore no blank correction was applied. The instrument detection limit (I.D.L.), defined as the lowest quantity of injected standard giving a 2/1 signal/noise value, was 0.2 pg. This corresponded to an air

concentration of ~0.3 pg m⁻³ and a water concentration of ~0.05 ng L⁻¹. All air and water samples were at least an order of magnitude higher in concentration.

Recoveries (as percent) of d_6 - α -HCH was 102.4 \pm 17.8 ($n = 32$) for air sample front PUF plugs and 103.9 \pm 13.7 ($n = 6$) for back PUFs. Spiking tests with PUF plugs and water showed no significant difference in recoveries of d_6 - α -HCH and unlabeled HCHs. Recoveries of d_6 - α -HCH for surface water samples averaged 77.5 \pm 19.7 ($n = 40$). Concentrations of HCHs in air and water were corrected using individual d_6 - α -HCH surrogate recovery values.

In technical mixtures, α -HCH is produced in a 1:1 proportion of its (+)- and (–)-forms. As a validation of the chiral analytical procedure, standard solutions ($n = 3$) containing racemic α -HCH were tested to check that enantiomer ratios, ER = (+)- α -HCH/(–)- α -HCH, were equal to 1.0. ERs determined using the Betadex column were 0.998 \pm 0.008 (ion 255), 0.996 \pm 0.013 (ion 257), and for the BGB column 1.013 \pm 0.002 (ion 255), 1.006 \pm 0.011 (ion 257). ERs for air and water samples are reported using the average for ions 255 and 257. In all samples the ion ratio 255/257 was within 5% of the standard value. Good agreement was obtained between ER values on both columns (Tables 1 and 2). The average percent difference in ERs was 1.9 \pm 1.3% ($n = 5$) for air and 2.1 \pm 1.6% ($n = 11$) for water samples.

Air and Water Concentrations. Concentrations of HCHs in air are summarized in Table 1 and Figure 2. Levels of α -HCH ranged from 11 to 68 (mean 37) pg m⁻³. Li et al. (13) noted that α -HCH in arctic air has declined in response to restrictions of technical HCH usage in Asian countries over the last 15 years. Mean values (pg m⁻³) observed in recent years were 77 at Spitsbergen in 1993 (17), 60 at Alert (NWT

TABLE 2. Concentrations of HCHs and Enantiomer Ratios of α -HCH in Surface and Deep Water of the Eastern Arctic Ocean

station	date	lat./long.	(ng L ⁻¹)		α/γ	ER = (+)/(-)- α -HCH	
			α -HCH	γ -HCH		Betadex	BGB
1a-surface	96-07-15/16	N69,16'/E14, 50'	0.58			0.95	0.93
1b-surface			0.69	0.27	2.52		
1-500m			ND	ND			
2a-surface	96-07-19	N73,29'/E25,15'	0.42	0.14	2.96	0.89	0.91
2b-surface			0.38	0.19	1.98		
2a-180m			0.51	0.20	2.62	0.86	0.89
2b-180m			0.42	0.17	2.40		
3a-surface	96-07-24	N80,30'/E66,50'	0.60	0.18	3.40		0.86
4a-surface	96-07-24	N81,10'/E68,20'	0.72	0.23	3.17	0.83	0.86
4b-surface			0.66	0.21	3.21		
4-255m			0.67	0.14	4.72		
5a-surface	96-07-27	N83,46'/E66,09'	0.82	0.16	5.00		0.80
5b-surface			0.71	0.19	3.80		
5-50m			0.68	0.30	2.27		0.76
5-230m			0.39	0.24	1.62		0.71
5-680m			0.35	0.15	2.39		0.32
6a-surface	96-07-29	N85,34'/E72,15'	0.86	0.26	3.32	0.79	0.80
6b-surface			0.92	0.25	3.64		
6-50m			1.03	0.28	3.61		
6-250m			0.55	0.19	2.87	0.30	0.28
6-1000			0.40	0.19	2.08	0.18	0.16
8a-surface	96-08-02	N87,03'/E129,20'	1.08	0.53	2.04	0.89	
8b-surface			0.77	0.26	2.97		0.92
8-50m			1.27	0.39	3.29		0.83
8-250m			0.54	0.19	2.82		0.41
8-1000m			0.66	0.33	2.04		0.59
9a-surface	96-08-05	N86, 25'/E143,32'	0.87	0.30	2.95	0.91	0.91
9b-surface			0.83	0.26	3.19		
9-220m			0.29	0.16	1.85	0.16	
9-335m			0.33	0.18	1.88	0.24	0.21
9-835m			0.26	0.18	1.45		0.27
10a-surface	96-08-07	N86,21'/E142,56'	1.08	0.30	3.57		0.89
10b-surface			1.05	0.42	2.48		
12a-surface	96-08-17/18	N87,09'/E140,47'	1.16	0.32	3.59		0.90
12b-surface			1.07	0.37	2.85		
12-50m			1.12	0.37	3.04		0.90
12-100m			1.24	0.41	3.01		0.73
12-250m			0.63	0.20	3.10		0.20
13a-surface	96-08-25	N86,27'/E130,26'	0.84	0.31	2.69	0.86	0.91
13b-surface			0.81	0.29	2.83		
14a-surface	96-08-27	N85,24'/E142,50'	0.78	0.27	2.88		0.93
14b-surface			0.74	0.27	2.72		
14-850m			0.38	0.14	2.77		0.54
15a-surface	96-08-31	N85,31'/E156,30'	0.89	0.29	3.04		0.92
15b-surface			0.86	0.31	2.75		
15-850m			0.25	0.13	1.94		0.28
16a-surface	96-09-05	N87,10'/E169,20'	1.29	0.35	3.71	0.87	
16b-surface			1.18	0.33	3.60		
16-850m			0.20	0.11	1.76		0.17
17a-surface	96-09-07	N88,35'/E179,40'	1.59	0.36	4.44	0.79	0.81
17b-surface			1.67	0.34	4.92		
17-850m			0.36	0.15	2.36		0.19
18a-surface	96-09-12	N87,20'/E21,40'	1.16	0.34	3.42	0.88	
18b-surface			1.22	0.30	4.10		
18-300m			0.68	NA	NA		
18-850m			0.30	0.13	2.24		0.19
19a-surface	96-09-14	N85,30'/E12,32'	1.51	0.36	4.18	0.91	0.91
19b-surface			1.58	0.35	4.49		
19-100m			1.56	0.36	4.33	0.81	0.82
19-250m			0.62	0.19	3.31	0.26	0.29
19-850m			0.31	0.13	2.43	0.13	0.11
20a-surface	96-09-17	N84,2'/E11,17'	0.82	0.18	4.53		0.79
20b-surface			0.86	0.20	4.42		
21a-surface	96-09-18	N82,41'/E13,20'	1.16	0.24	4.75	0.73	0.72
21b-surface			1.15	0.27	4.28		
22-surface	96-09-20	N78,57'/E11,20'	0.46	0.13	3.45		0.92
23a-surface	96-09-22	N74,28'/E14,36'	0.32	0.12	2.63		0.90
23b-surface			0.39	0.12	3.18		

Canada) in 1993–1994 (18), 81 on a transarctic cruise in the summer of 1994 (15), and 47 at Lista, southern Norway in 1995 (6). The latter authors noted that α -HCH at Lista has shown a downward trend of 10 pg m⁻³ per year since 1991, thus 37 pg m⁻³ would be predicted for 1996 in excellent agreement with the Oden measurements.

Levels of γ -HCH in eastern arctic air are more variable due to episodic transport of lindane from Europe which becomes superimposed on a background of γ -HCH from

technical HCH usage (6, 17). On the Oden cruise, γ -HCH ranged from 6 to 68 pg m⁻³ and averaged 17 pg m⁻³. To investigate the relationship to source regions, three-dimensional five-day air parcel back-trajectories arriving at the sampling location at a pressure level of 850 and 925 hPa (i.e. ~1.5 and 0.75 km altitude) were determined for all 34 individual air samples (14 combined samples). Trajectories (obtained from the Atmospheric Environment Service) were determined every 6 h resulting in eight trajectories for a 24-h

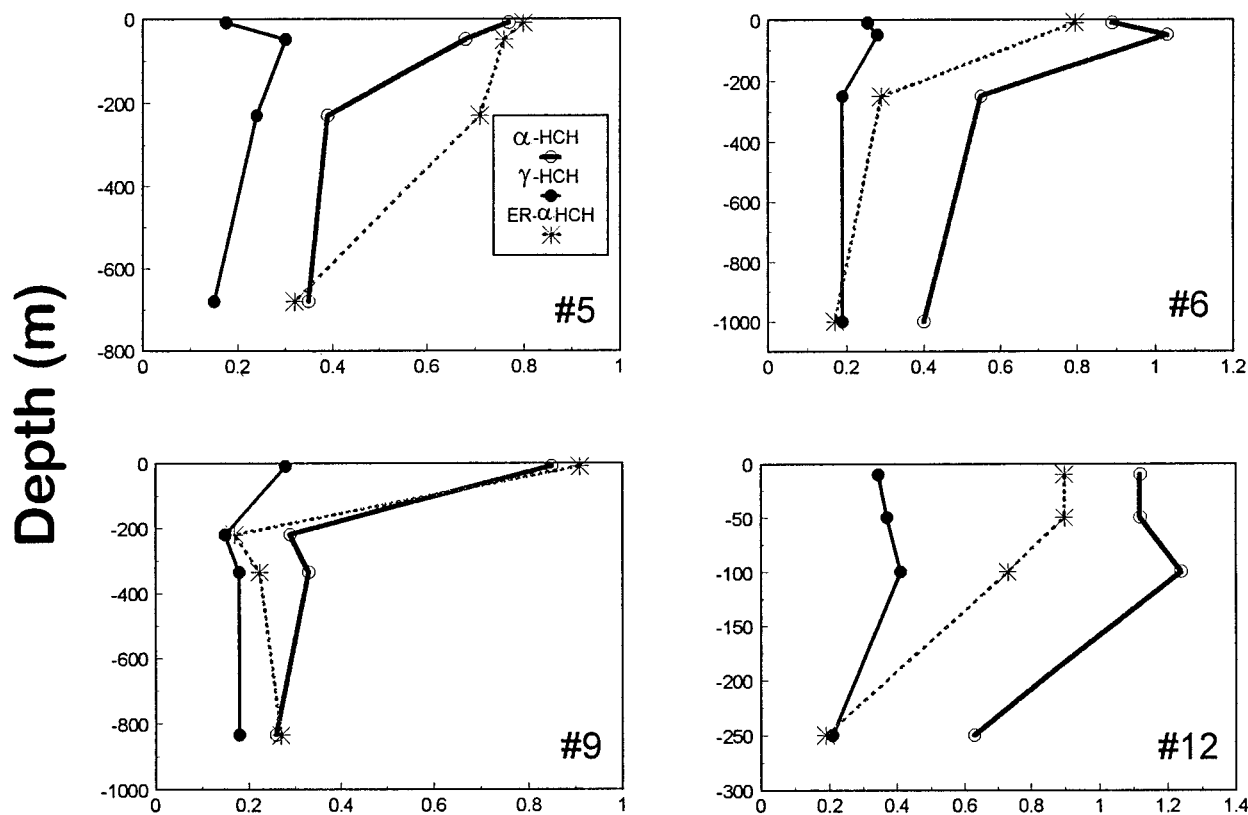


FIGURE 2. Depth profiles for concentration (ng L^{-1}) of α - and γ -HCH in water and α -HCH enantiomer ratio, $\text{ER} = (+)/(-)\text{-}\alpha\text{-HCH}$, in the eastern Arctic Ocean. The horizontal scale is to be used for both concentration and ER values. Refer to Table 2 for sampling locations.

TABLE 3. Estimated Pseudo-First-Order Degradation Rate Constants^a for HCHs in the Eastern Arctic Ocean

	$k_{h\alpha}$	k_{m+}	k_{m-}	$k_{d1} = k_{m+} + k_{h\alpha}$	$k_{d2} = k_{m-} + k_{h\alpha}$
$\alpha\text{-HCH}$ (k , yr^{-1})	0.011	0.117 ± 0.024	0.030 ± 0.029	0.128 ± 0.006	0.041 ± 0.041
(half-life, yr)	63	5.9	23.1	5.4	16.9
	$k_{h\gamma}$	k_m	$k_d = k_m + k_{h\gamma}$		
$\gamma\text{-HCH}$ (k , yr^{-1})	0.0063	0.037 ± 0.020	0.043 ± 0.024		
(half-life, yr)	110	18.8	16.1		

^a $k_d = k_m + k_{h\gamma}$, where subscripts m and h refer to microbial processes and hydrolysis. In the case of α -HCH, (+) and (-) designate the enantiomers.

sample (i.e. four trajectories at two pressure levels). Details are presented elsewhere (19). Higher γ -HCH concentrations and lower α/γ -HCH values were observed for air samples with trajectories that passed over potential lindane source regions. For samples whose trajectories spent $<1\%$ ($n = 16$) of their 5-day history over Eurasia (including the Norwegian and North Sea), $\gamma\text{-HCH} = 13.9 \pm 5.7 \text{ pg m}^{-3}$ and $\alpha/\gamma\text{-HCH} = 3.4 \pm 1.3$. Conversely, when the time spent over Eurasia increased to $>25\%$ ($n = 11$), the resulting values were $\gamma\text{-HCH} = 21.7 \pm 7.4 \text{ pg m}^{-3}$ and $\alpha/\gamma\text{-HCH} = 1.85 \pm 0.80$. Furthermore, for the small set of samples ($n = 5$) which spent the majority of their trajectory time ($>50\%$) over Eurasia, $\gamma\text{-HCH} = 31.0 \pm 22.4 \text{ pg m}^{-3}$ and $\alpha/\gamma\text{-HCH} = 1.70 \pm 0.85$. This is consistent with data by Haugen et al. (6) which shows $\alpha/\gamma\text{-HCH} = 0.5\text{--}2$ at Lista, Norway for samples originating in Eurasian sectors.

Concentrations of HCHs in water are presented in Table 2 and Figure 2. The range and (mean) for surface water were $350\text{--}1630$ (910) pg L^{-1} α -HCH and $120\text{--}400$ (270) pg L^{-1} γ -HCH. These agreed well with measurements by Strachan et al. (20) on the Oden-96 cruise (α -HCH, $870 \pm 330 \text{ ng L}^{-1}$; γ -HCH, $240 \pm 80 \text{ ng L}^{-1}$), who collected and analyzed their samples independently, and also with values reported by Gaul (21) for a 1985 survey of the northeast Atlantic (α -HCH,

$1030 \pm 250 \text{ ng L}^{-1}$; γ -HCH, $220 \pm 80 \text{ ng L}^{-1}$). Both HCHs increased with latitude between $74^\circ\text{--}88^\circ\text{N}$ ($r^2 = 0.58$ and 0.69 for α - and γ -HCH, respectively). Values similar to those on the Oden cruise were found during 1994 in the eastern Arctic Ocean north of Spitsbergen (950 pg L^{-1} α -HCH and 220 pg L^{-1} γ -HCH) and in the Greenland Sea (650 pg L^{-1} α -HCH and 180 pg L^{-1} γ -HCH) (2, 15). Surface concentrations of HCHs in the eastern Arctic Ocean were lower than those in the western Arctic. Averages for α - and γ -HCHs (pg L^{-1}) were 2100 and 455 in the Bering-Chukchi seas in 1993 (14, 15), 2300 and 490 on a 1994 transect across the northern Canada Basin (2, 15), and 4500 and 700 in the Beaufort Sea and Canadian Archipelago in 1986–1993 (3).

Vertical profiles at 11 Oden stations indicated that concentrations at 250–1000 m were $\sim 40\%$ of surface values for α -HCH and $\sim 60\%$ for γ -HCH (Figure 2). Tracer studies in this region (Nansen Basin) indicate that the water masses at 250–1000 m have ages on the order of 12–20 years (22, 23) which coincides with the time of heaviest usage of HCH (13).

Enantiomers of α -HCH in Water. The ERs of α -HCH in surface water ranged from 0.72 to 0.94 and averaged 0.87 ± 0.06 ($n = 21$), indicating selective degradation of (+)- α -HCH.

Mean ERs (\pm s.d.) in the zones identified in Figure 1 and Table 3 were $A = 0.91$ (0.01), $B = 0.83$ (0.03), $C = 0.89$ (0.04), and $D = 0.83$ (0.09). The same metabolic preference and similar ERs were found in the western Arctic Ocean, but (–)- α -HCH was depleted in the Bering and Chukchi seas, which derive from Pacific water (2, 15). Enantioselective breakdown of (+)- α -HCH was greater in subsurface water (Figure 2), with ERs ~ 0.12 – 0.32 (mean = 0.229 ± 0.071) at 250–1000 m, agreeing with results from the western Arctic Ocean and the Greenland Sea (2).

Degradation of HCHs in the Eastern Arctic Ocean.

Removal of HCH from subsurface water occurs by three main mechanisms: biological degradation, hydrolysis, and removal by partitioning to settling particles (sedimentation), with the latter likely to play the least important role (3). An upper limit to the sedimentation rate of α -HCH ($784 \text{ pg m}^{-2} \text{ day}^{-1}$) was estimated from the concentration on particulate matter collected under ice in the Arctic Ocean (2.3 pg mg^{-1}) (24) and the sedimentation rate at the Spitsbergen shelf edge ($341 \text{ mg m}^{-2} \text{ day}^{-1}$) (25, 26), which is the highest reported for the eastern Arctic Ocean. In a 600 m water column with an average concentration of α -HCH = 0.5 ng L^{-1} , the sedimentation rate constant for α -HCH is $9.5 \times 10^{-4} \text{ yr}^{-1}$, corresponding to a half-life >700 yr. Thus hydrolysis and microbial degradation are likely to determine the overall removal rates.

Estimation of the degradation rate due to hydrolysis + microbial processes requires knowledge of initial and final HCH concentrations and time, i.e., the age of the water mass. Tracer studies have determined that the “ventilation age” of the 250–1000 m water in the Nansen Basin of the eastern Arctic Ocean is in the range 12–20 years (22, 23). The ventilation age is the time since the water was at the surface and able to exchange gases with the atmosphere. Over the years this water has subsided, and we assume that there have been no further inputs or losses through atmospheric processes. Levels of α - and γ -HCH were assumed to decrease according to the rates of hydrolysis and microbial action. The initial values can be estimated from the 1979 measurements of Gaul (21), 17 years prior to the Oden expedition, who found $1400 \pm 340 \text{ pg L}^{-1}$ α -HCH and $360 \pm 94 \text{ pg L}^{-1}$ γ -HCH in surface water ($n = 11$) of the Norwegian Sea at 71 – 81°N .

Removal of HCHs from the water column is governed by

$$C = C^0 e^{-(k_d)t} \quad (1)$$

where the overall degradation rate of HCH is the combination of microbial and hydrolysis processes, $k_d = k_m + k_h$. The degradation half-life due to basic hydrolysis in seawater can be estimated from the second-order rate constants at 0°C , $k_b(\alpha\text{-HCH}) = 0.147 \text{ L mol}^{-1} \text{ min}^{-1}$ and $k_b(\gamma\text{-HCH}) = 0.085 \text{ L mol}^{-1} \text{ min}^{-1}$. The pseudo-first-order rate constant ($k_h = k_b a_{\text{OH}}$) at pH = 8 and 0°C ($pK_w = 14.95$) is $k_{h\alpha} = 2.07 \times 10^{-8} \text{ min}^{-1} = 0.011 \text{ yr}^{-1}$ and $k_{h\gamma} = 1.20 \times 10^{-8} \text{ min}^{-1} = 0.0063 \text{ yr}^{-1}$ (27). The resulting hydrolysis half-lives for α - and γ -HCH are 63.6 and 110 years respectively, substantially shorter than the half-life due to sedimentation (~ 700 years).

For γ -HCH, substituting $C_\gamma = 360$ (1979, surface), $C_\gamma = 173$ (1996, 250–1000 m) and $t = 17$ years into eq 1 results in a degradation rate constant $k_d = 0.043 \text{ yr}^{-1}$ (half-life = 16.0 years). Since, $k_{h\gamma} = 0.0063 \text{ yr}^{-1}$, the rate constant due to microbial degradation $k_m = 0.043 - 0.0063 = 0.037 \text{ yr}^{-1}$, which corresponds to a half-life of 18.8 years. Assuming that C_γ and C_γ are the most uncertain terms, a sum of squares of fractional errors approach results in a propagated error of about 54% in k_m ($+0.020 \text{ yr}^{-1}$) with a corresponding half-life of 18.8 ± 10.1 years.

The situation is more complex for α -HCH since microbes are able to distinguish between the (+)- and (–)-enantiomers.

In this case the enantiomers must be treated separately, and the solution requires information about the selectivity (i.e. ER) of the microbial degradation process.

Removal of the two enantiomers can be described by

$$C_{(+)} = C^0_{(+)} e^{-(k_{d1})t} \quad (2)$$

$$C_{(-)} = C^0_{(-)} e^{-(k_{d2})t} \quad (3)$$

where $C^0_{(+)}$ and $C^0_{(-)}$ represent the initial (surface water) concentrations of (+)- and (–)- α -HCH in 1979, and $C_{(+)}$ and $C_{(-)}$ are the respective concentrations 17 years later in subsided water at 250–1000 m depth. We assume that the α -HCH was racemic at the time of input. The pseudo-first-order rate constants k_{d1} and k_{d2} are the sum of microbial and hydrolysis removal rates i.e., $k_{d1} = k_{m+} + k_{h\alpha}$ and $k_{d2} = k_{m-} + k_{h\alpha}$ where k_{m+} and k_{m-} represent microbial degradation rate constants of the (+)- and (–)- α -HCH enantiomers. The overall removal of α -HCH is the sum of eq 2 and 3:

$$C_\alpha = C_{(+)} + C_{(-)} = C^0_{(+)} e^{-(k_{d1})t} + C^0_{(-)} e^{-(k_{d2})t} \quad (4)$$

Assuming $C^0_{(+)} = C^0_{(-)} = 0.5 C^0_\alpha$ (racemic at the time of input), eq 4 can be rewritten as

$$C_\alpha = 0.5 C^0_\alpha (e^{-(k_{d1})t} + e^{-(k_{d2})t}) \quad (5)$$

The values of k_{m+} and k_{m-} are related by eq 6, which corrects a sign error in eq 6 of ref 28:

$$\text{ER} = e^{-[(k_{m+}) - (k_{m-})]t} \quad (6)$$

This can be rearranged to

$$k_{m-} = \ln \text{ER}/t + k_{m+} \quad (7)$$

Combining eq 5–7 and the above definitions for k_{d1} and k_{d2} gives (see Appendix)

$$k_{m+} = (1/t) [\ln(1 + 1/\text{ER}) - \ln C_\alpha/C^0_\alpha - k_{h\alpha}t - 0.693] \quad (8)$$

The average ER value at 250–1000 m was 0.23 ($n = 7$). From Gaul's measurements in 1979 (21) $C^0_\alpha = 1400 \pm 340 \text{ pg L}^{-1}$, and from Oden-1996 (250–1000 m, $n=16$) $C_\alpha = 426 \pm 161 \text{ pg L}^{-1}$. Solving with $t = 17$ years and $k_{h\alpha} = 0.011 \text{ yr}^{-1}$ (from above) gives $k_{m+} = 0.117 \text{ yr}^{-1}$ which corresponds to a half-life of 5.9 years. Substitution into eq 6 gives $k_{m-} = 0.030 \text{ yr}^{-1}$ or a half-life of 22.8 years. As for γ -HCH, the propagated error in k_{m+} and k_{m-} due to uncertainties in ER, C_α and C^0_α is 21%, resulting in overall uncertainties in the half-lives of 1.2 years for (+)- α -HCH and 4.7 years for (–)- α -HCH.

It is important to note that the above estimates are based on assumptions that cannot be easily checked, for instance the assumption that the 17 year-old water at 250–1000 m depth is at the same latitude and longitude as the surface water sampled by Gaul (21) in 1979. This is unlikely due to strong advection in the region. Water from the North Atlantic is transported into the Arctic Ocean through the Fram Strait and by the Norwegian Coastal Current (29), thus the water sampled in 1996 at 250–1000 m depth may have been at the surface at a location further south in 1979. Gaul's 1979 values for surface water at three stations in the North Atlantic between 61 and 70° were $1030 \pm 208 \text{ pg L}^{-1}$ for α -HCH and $290 \pm 17 \text{ pg L}^{-1}$ for γ -HCH, slightly lower than at stations further north (21). It is also possible that a horizontally/vertically moving water mass may be affected by different microbial communities and hence varying HCH degradation rates at different points in time. Regional differences in water

TABLE 4. Gas Exchange of HCHs in the Eastern Arctic Ocean

latitude ^a	temp (K)		C_w , ng m ⁻³		stations	H , Pa m ³ mol ⁻¹		f_w/f_a^b		flux, ^c ng m ⁻² d ⁻¹	
	T_w	T_a	α -HCH	γ -HCH		α -HCH	γ -HCH	α -HCH	γ -HCH	α -HCH	γ -HCH
73–79 A	278	275	405 ± 53	138 ± 24	3	0.159	0.091	0.80	0.32	–3.1	–5.1
80–87 B	272	275	736 ± 123	208 ± 38	4	0.092	0.055	0.84	0.29	–2.5	–5.3
85–88 C	272	270	1030 ± 272	327 ± 41	9	0.092	0.055	1.19	0.47	2.9	–3.9
82–87 D	271	268	1180 ± 288	280 ± 73	4	0.084	0.051	1.26	0.37	3.9	–4.6

^a See Figure 1. ^b A propagated error of approximately 25% has been estimated for the calculation f_w/f_a due to uncertainty in measured air and water concentrations (see Discussion). ^c Positive = volatilization, negative = deposition.

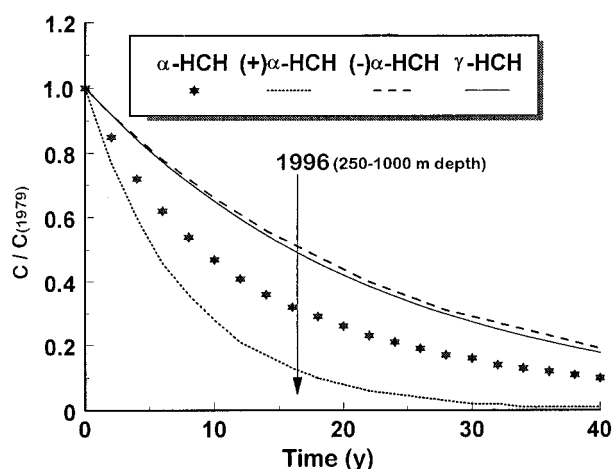


FIGURE 3. Degradation of HCHs in subsurface water of the eastern Arctic Ocean. Plots of eq 1–3 were based on the degradation rate constants in Table 3.

concentrations and ER values were reported by Jantunen and Bidleman (2, 14, 15) for the western Arctic Ocean.

Figure 3 is a plot of eqs 1–3 and summarizes the degradation of HCHs in the eastern Arctic Ocean. Rate constants and half-life estimates are shown in Table 3. The relative removal rate k_{m+}/k_{m-} was 0.117/0.030 = 3.9. This is similar to Buser's result of 2.9 determined from degradation of HCHs in sewage sludge under anaerobic conditions at 25 °C (28). In the sewage sludge experiments γ -HCH degraded faster than either (+)- or (–)- α -HCH. Our calculations for the eastern Arctic Ocean suggest that (+)- α -HCH degrades faster than γ -HCH, by a factor of approximately 3.2, and that the slowest microbial degradation occurs for (–)- α -HCH. This difference may be attributed to types and preferences of the microbial communities and other rate-determining conditions such as temperature and salinity.

In summary, microbial degradation is suggested to be the major removal process of HCHs in the eastern Arctic Ocean and perhaps other water bodies. If air–water exchange with the world oceans is the major loading process of HCHs (12–15), it is conceivable that microbial degradation will indirectly control the long-term fate of HCH globally, both in water and the atmosphere. This is an incentive to better understand and quantify this process.

Air–Water Gas Exchange. Estimates of gas exchange were made in four zones of similar latitudes and concentrations of HCHs in surface water (Figure 1). Mean atmospheric concentrations of 37 pg m⁻³ α -HCH and 17 pg m⁻³ γ -HCH were assumed to be representative of the entire cruise region and also for the atmospheric boundary layer ranging from the sea surface to some indeterminate height. There is likely to be a vertical gradient in HCH concentration over the height of the boundary layer, but we did not attempt to measure it.

Fluxes were calculated using the two film model with fugacity definitions (14, 15) and the Henry's law constants

for artificial seawater as a function of temperature (11). An average windspeed of 5 m s⁻¹ was assumed, corresponding to an air-side mass transfer coefficient (k_g) of 0.005 m s⁻¹ and D_{aw} (86400 k_g/RT) = 0.19 mol m⁻² d⁻¹ Pa⁻¹ for T_w = 272 K. Table 4 summarizes the data, water/air fugacity ratios (f_w/f_a), and fluxes to a unit area of open water. Fugacity ratios of α -HCH ranged from 0.8 to 1.26, close to air–water equilibrium. Net deposition of γ -HCH was indicated by fugacity ratios of 0.29–0.47. By comparison, α -HCH is outgassing from the western Arctic Ocean and the Bering-Chukchi seas, and γ -HCH is close to steady state (14, 15).

It is useful to compare the deviation of f_w/f_a from unity to the error which is propagated in its calculation. Terms with some uncertainty include measured air and water concentrations (C_w and C_a) and the Henry's Law constant (H). Analysis of duplicate surface water samples (Table 2) showed differences of 8.7% ($n=19$) and 14% ($n=18$) for α -HCH and γ -HCH water concentrations. A similar variability is expected for air samples. Thus if we assume an uncertainty of ~10% for C_w and C_a and 20% for H (11), an error of ~25% is propagated in the calculation of f_w/f_a . With this level of uncertainty, we cannot say that f_w/f_a for α -HCH is different from 1.00 in any of the four zones. However, the values for γ -HCH are significantly different from unity.

The range in ERs from air samples was 0.87–1.00, with a mean of 0.95 ± 0.03 ($n=16$). This was significantly different from the racemic ER of an α -HCH standard (1.003 ± 0.011 , $n=6$, pooled Betadex and BGB column results, $p < 0.005$). This suggests that the air sampled from the ship contained a mixture of nonracemic α -HCH from volatilization and racemic α -HCH.

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Appendix—Derivation of Equation 8

Start with the expressions (below) for k_{d1} , k_{d2} , eqs 5 and 7:

$$k_{d1} = k_{m+} + k_{ha}$$

$$k_{d2} = k_{m-} + k_{ha}$$

$$C_a = 0.5 C_a^0 (\exp -k_{d1}t + \exp -k_{d2}t) \quad (5)$$

$$k_{m-} = \ln ER/t + k_{m+} \quad (7)$$

Substitute eq 7 into the expression for k_{d2} :

$$k_{d2} = \ln ER/t + k_{m+} + k_{ha}$$

Substitute this into eq 5:

$$C_{\alpha} = 0.5 C_{\alpha}^{\circ} [\exp -(k_{m+} + k_{ha})t + \exp -(\ln ER/t + k_{m+} + k_{ha})t]$$

$$2C_{\alpha}/C_{\alpha}^{\circ} = (\exp -k_{m+}t)(\exp -k_{ha}t) + (\exp -\ln ER)(\exp -k_{m+}t)(\exp -k_{ha}t)$$

Divide by $\exp -k_{ha}t$

$$(2C_{\alpha}/C_{\alpha}^{\circ})/\exp -k_{ha}t = (\exp -k_{m+}t) + (\exp -\ln ER)(\exp k_{m+}t)$$

Note that $\exp -\ln ER = 1/ER$:

$$(2C_{\alpha}/C_{\alpha}^{\circ})/\exp -k_{ha}t = (\exp -k_{m+}t) + (1/ER)(\exp k_{m+}t) = (\exp -k_{m+}t)(1 + 1/ER)$$

Take the natural logarithm of both sides:

$$0.693 + \ln C_{\alpha}/C_{\alpha}^{\circ} + k_{ha}t = -k_{m+}t + \ln(1 + 1/ER)$$

Solve for k_{m+} :

$$k_{m+} = (1/t)[\ln(1 + 1/ER) - \ln C_{\alpha}/C_{\alpha}^{\circ} - k_{ha}t - 0.693] \quad (8)$$

Literature Cited

- (1) Iwata, H.; Tanabe, S.; Sakai, N.; Tatsukawa, R. *Environ. Sci. Technol.* **1993**, *27*, 1080–1098.
- (2) Jantunen, L. M. M.; Bidleman, T. F. *Arch. Environ. Contam. Toxicol.* **1998**, *35*, 218–228.
- (3) Barrie, L. A.; Macdonald, R.; Bidleman, T.; Diamond, M.; Gregor, D.; Semkin, R.; Strachan, W.; Alae, M.; Backus, S.; Bowers, M.; Gobeil, C.; Halsall, C.; Hoff, J.; Li, A.; Lockhart, L.; Mackay, D.; Muir, D.; Pudykiewicz, J.; Reimer, K.; Smith, J.; Stern, G.; Schroeder, W.; Wagemann, W.; Wania, F.; Yunker, M. Chapter 2 in *Canadian Arctic Contaminants Assessment Report*; Jensen, J., Adair, K., Shearer, R., Eds.; Ministry of Public Works and Government Services, Ottawa, QS-8525-000-EE-A1, Catalog No. R72-260/1997E, ISBN 0-662-25704-9, 1997; pp 25–182.
- (4) Oehme, M.; Ottar, B. *Geophys. Res. Lett.* **1984**, *11*, 1133–1136.
- (5) Oehme, M. *Ambio* **1990**, *20*, 293–297.
- (6) Haugen, J.-E.; Wania, F.; Ritter, N.; Schlabach, M. *Environ. Sci. Technol.* **1998**, *32*, 217–224.
- (7) Goldberg, E. D. *Proc. R. Soc. London B* **1975**, *189*, 277–289.
- (8) Wania, F.; Mackay, D. *Ambio* **1993**, *22*, 10–18.

- (9) Wania, F.; Mackay, D. *Environ. Sci. Technol.* **1996**, *30*, A390–A396.
- (10) Brubaker, W. W., Jr.; Hites, R. A. *Environ. Sci. Technol.* **1998**, *32*, 766–769.
- (11) Kucklick, J. R.; Hinckley, D. A.; Bidleman, T. F. *Marine Chem.* **1991**, *34*, 197–209.
- (12) Bidleman, T. F.; Jantunen, L. M.; Falconer, R. L.; Barrie, L. A.; Fellin, P. *Geophys. Res. Lett.* **1995**, *22*, 219–222.
- (13) Li, Y.-F.; Bidleman, T. F.; Barrie, L. A.; McConnell, L. L. *J. Geophys. Res. Lett.* **1998**, *25*, 39–41.
- (14) Jantunen, L. M.; Bidleman, T. F. *Environ. Sci. Technol.* **1995**, *29*, 1081–1089.
- (15) Jantunen, L. M.; Bidleman, T. F. *J. Geophys. Res.* **1996**, *101*, 28837–28846; corrections *J. Geophys. Res.* **1997**, *102*, 19279–19282.
- (16) Ridal, J. J.; Bidleman, T. F.; Kerman, B. R.; Fox, M.; Strachan, W. M. *J. Environ. Sci. Technol.* **1997**, *31*, 1940–1945.
- (17) Oehme, M.; Haugen, J.-E.; Schlabach, M. *Environ. Sci. Technol.* **1996**, *30*, 2294–2304.
- (18) Halsall, C. J.; Bailey, R.; Stern, G. A.; Barrie, L. A.; Fellin, P.; Muir, D. C. G.; Rovinsky, F. Ya.; Kononov, E. Ya.; Pastukhov, B. *Environ. Pollut.* **1998**, *102*, 51–62.
- (19) Harner, T.; Kylin, H.; Bidleman, T. F.; Halsall, C.; Strachan, W. M. J.; Barrie, L. A.; Fellin, P. *Environ. Sci. Technol.* **1998**, *32*, 3257–3265.
- (20) Strachan, W. M. J.; Teixeira, C. F.; Williamson, M.; Harner, T.; Bidleman, T. F.; Kylin, H. *Organohalogen Compd.* **1998**, *39*, 407–410.
- (21) Gaul, H. *ICES Mar. Sci. Symp.* **1992**, *195*, 110–126.
- (22) Wallace, D. W. R.; Schlosser, P.; Krysell, M.; Bönisch, G. *Deep-Sea Res.* **1992**, *39*, S435–S458.
- (23) Schlosser, P.; Shift, J. H.; Lewis, D.; Pfirman, S. L. *Deep-Sea Res.* **1995**, *42*, 1341–1367.
- (24) Hargrave, B. T.; Harding, G. C.; Wass, W. P.; Erickson, P. E.; Fowler, B. R.; Scott, V. *Arch. Environ. Contam. Toxicol.* **1992**, *22*, 41–54.
- (25) Hebbeln, G.; Wefer, G. *Nature* **1991**, *350*, 409–411.
- (26) Hargrave, B. T.; von Bondungen, B.; Stoffeyn-Egli, P.; Mudie, P. J. *Cont. Shelf Res.* **1994**, *14*, 279–293.
- (27) Ngabe, B.; Bidleman, T. F.; Falconer, R. L. *Environ. Sci. Technol.* **1993**, *27*, 1930–1933.
- (28) Buser, H.-R.; Müller, M. D. *Environ. Sci. Technol.* **1995**, *29*, 664–672.
- (29) Barrie, L. A.; Falck, E.; Gregor, D. J.; Iversen, T.; Loeng, H.; Macdonald, R.; Pfirman, S.; Skotvold, T.; Wartena, E. Chapter 3 In *AMAP Assessment Report*; Gregor, D. J., Loeng, H., Barrie, L. A., Eds.; Arctic Monitoring and Assessment Program, AMAP Secretariat, Oslo, Norway, pp 25–116.

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