Air-Water Gas Exchange of Hexachlorocyclohexanes (HCHs) and the Enantiomers of α-HCH in the Eastern Arctic Ocean

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Introduction

Hexachlorocyclohexanes (HCHs) are the most abundant organochlorine pesticides in the Arctic Ocean (1), delivered by atmospheric transport and ocean currents (2-6). Decreased usage of technical HCH (containing ~70% α-HCH, 15% γ-HCH and other isomers) in the past decade has led to a reduced atmospheric burden of α-HCH (7), and recent measurements in the Bering and Chukchi seas (4) and the western Arctic Ocean (2,3) indicate that α-HCH is now revolatilizing from surface water. This is supported by measurements of the α-HCH enantiomers in air and water from these regions. Volatilization from water transfers non-racemic α-HCH to the overlying air, allowing the contribution from gas exchange to be distinguished from atmospheric transport of the racemic compound (2,3).

HCHs in surface water are not uniformly distributed across the Arctic Ocean. Highest concentrations, ~5-6 ng/L (sum of α- + γ-HCHs), were found in the Beaufort Sea and Canadian Archipelago. Levels in the Bering and Chukchi seas and along a transect across the northern Canada Basin to the pole were ~2-3 ng/L (1-3,5,6), and an average of 1.2 ng/L was reported in the Norwegian Sea south of Spitsbergen (8). This work was done to investigate the occurrence and air-water gas exchange of HCHs and other persistent organic pollutants in the Barents Sea and eastern Arctic Ocean. Air and water samples were collected aboard the Swedish icebreaker Oden during July-September, 1996 (Figure 1) for determination of organochlorine pesticides, PCB congeners and PAHs in water (9), and polychlorinated naphthalenes (PCNs) and coplanar PCBs in air (10). Gas exchange of HCHs and the enantiomer ratios (ER = (+)/(-)) of α-HCH are reported here.

Materials and Methods

Air samples of ~600 m^3 were drawn over 24 h through a glass fibre filter followed by a polyurethane foam (PUF) trap (2,3). Water samples were collected with a submersible pump lowered ~3 m below the water line through aged Tygon tubing into 20-L stainless steel cans. HCHs were extracted from ~15 L of water by pressurizing the cans and filtering the water through 47-mm diameter glass fibre filters followed by 200-mg Isolute Env+ cartridges (Jones Chromatography Co.). The cartridges were activated before use by eluting with 5 mL methanol, then 5 mL distilled water. Samples were fortified with 12-23 ng α-HCH-d_6 recovery surrogate. The water was spiked with α-HCH-d_6, then filtered through ENV+ cartridges. PUF plugs were spiked after air sampling. HCHs were extracted with petroleum ether (PUFs) or dichloromethane (ENV+ cartridges). Since previous investigations have found that HCHs are largely gaseous in air and dissolved in water, filters were not analysed. Sample extracts were reduced into isooctane by rotary evaporation and nitrogen blow-down and cleaned up with neutral alumina (water) or alumina-silicic acid (air) columns and 18M sulphuric acid.

HCHs were determined by capillary GC - negative ion mass on a Hewlett-Packard 5890 GC - 5989B MS Engine, using methane reagent gas. Ions monitored (target,qualifier) were 255,257 for HCHs and 259,261 for α-HCH-d_6. Target/qualifier ratios were within 20% of standard values for quantitative analysis and 10% for enantiomer measurements. Quantitative work was done on a 30-m DB-5 column. Two chiral columns were used for separation of α-HCH enantiomers, Betadex-120 (20% permethylated β-cyclodextrin in SPB-25, Supelco) and BGB-172 (20% tert-butyldimethylsilylated β-cyclodextrin in OV-1701, BGB Analytik AG, Switzerland). All columns were 30 m x 0.25 mm diameter, 0.25 µm film thickness. Further details of sample cleanup and analytical methods are given elsewhere (1-3).

Results and Discussion

Quality Control

Blanks for ENV+ cartridges (n=3) and PUF plugs (n=6) showed no detectable HCHs, and therefore no blank correction was applied. The estimated instrumental detection limit was 0.2 pg, the lowest quantity of HCHs injected which gave a 2:1 signal/noise ratio. Recovery checks were done using undeuterated HCHs to supplement the α-HCH-d_6 surrogate experiments. Average recoveries (± s.d.) for water samples were: α-HCH = 64 ± 13% (n = 5), γ-HCH = 54 ± 8% (n = 5), α-HCH-d_6 = 77 ± 20% (n = 40). Recoveries from PUF plugs were: α-HCH = 67 ± 8% (n = 4), γ-HCH = 84 ± 6% (n = 4), α-HCH-d_6 = 102 ± 18% (n = 32). The enantiomer elution order is reversed on the two chiral columns used here, with (+)α-HCH eluting first on Betadex and second on BGB-172 (1-3). The average percent difference in ER values determined on the two columns was 4.0% for water (n=15) and 1.9% for air (n=5). A racemic α-HCH standard gave ERs = 0.997±0.011 (Betadex) and 1.010±0.006 (BGB-172).

HCHs in Air and Water of the Eastern Arctic

Concentrations of α-HCH in air ranged from 11-68 pg/m^3 (mean = 37 pg/m^3). Li et al. (7) noted that α-HCH in arctic air has declined in response to restrictions of technical HCH usage in Asian countries over the last decade. Mean values observed in recent years were 77 pg/m^3 at Spitsbergen in 1993 (11), 60 pg/m^3 at Alert (NWT Canada) in 1993-94 (12), 81 pg/m^3 on a trans-arctic cruise in the summer of 1994 (2) and 47 pg/m^3 at Lista, southern Norway in 1995 (4). The latter authors noted that α-HCH at Lista has shown a downward trend of 10 pg/m^3 per year since 1991. 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 (4,11). On the Oden cruise, γ-HCH ranged from 6-68 pg/m^3 and averaged 17 pg/m^3.

The range and (mean) concentrations of HCHs in surface water were 350-1630 (910) pg/L α-HCH and 120-400 (270) pg/L γ-HCH. These agreed well with measurements by Strachan et al. (9) on the Oden-96 cruise, who collected and analysed their samples independently, and also with values reported by Gaul (8) for a 1985 survey of the Norwegian Sea. Both HCHs increased with latitude between 74° - 88°N (r^2=0.58 and 0.69 for α- and γ-HCH, respectively). A single station at 69°N near Norway showed elevated levels and was an outlier. Vertical profiles at four stations indicated that concentrations at 600-1000 m were ~50% of surface values for α-HCH and ~75% for γ-HCH.

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 concentrations of 37 pg/m^3 α-HCH and 17 pg/m^3 γ-HCH in air were assumed to be representative of the entire cruise region. Fluxes were calculated using the two-film model with fugacity definitions (2,3) and the Henry's law constants for artificial seawater as a function of temperature (13). An average wind speed of 5 m/s was assumed, corresponding to an air-side mass transfer coefficient (k_g) of 0.005 m/s and D_{aw} (86400 k_g/RT) = 0.19 mol/m^2 d Pa for T_w = 272 K. Table 1 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 0.80-1.26, 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 equilibrium (2,3).

Enantiomers of α-HCH

The ERs of α-HCH in surface water ranged from 0.72-0.94 and averaged 0.87±0.06 (n=21), indicating selective degradation of (+)α-HCH. Mean ERs (± s.d.) in the zones identified in Figure 1 and Table 1 were: A = 0.91 (0.01), B = 0.83 (0.03), C = 0.89 (0.04), 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 (1,2). Enantioselective breakdown of (+)α-HCH was greater in subsurface water, with ERs ~0.2-0.3 at 250-1000 m, agreeing with results from the western Arctic Ocean (1). The range of ERs in air samples was 0.87-1.00, with a mean of 0.95±0.03 (n=16). This suggests that the air sampled from the ship contained a mixture of non-racemic α-HCH from volatilisation and racemic α-HCH transported from continental regions.

Acknowledgements

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Table 1: Gas Exchange of HCHs in the Eastern Arctic Ocean.

	Temp., K		C_w, ng/m^3			H, Pa m^3/mol		f_w/f_a		Flux^b, ng/m^2 d	
Latitude^a	T_w	T_a	α-HCH	γ-HCH	Stations	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) Positive = volatilisation, negative = deposition.

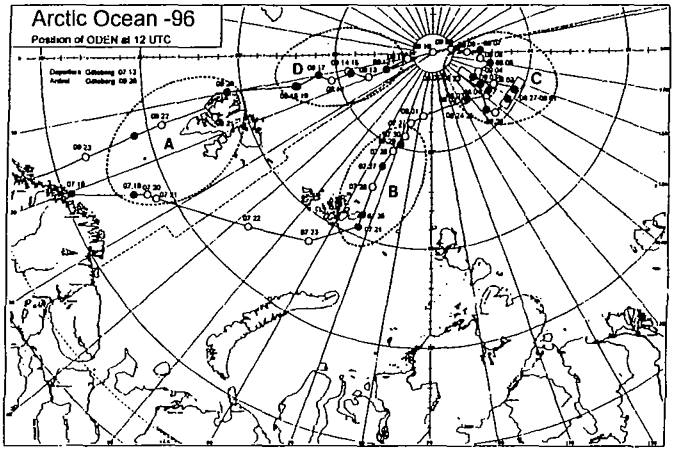

Figure 1. Cruise track of the Oden. Black circles indicate stations where water samples were collected for HCHs. Dotted circles show groupings of stations for gas exchange estimates.