

Alpha-HCH Enantiomers Trace Sea-to-Air Gas Exchange During Ice Breakup in the Canadian Archipelago

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Introduction

Technical hexachlorocyclohexane (HCH) was heavily used in Asian countries until it was banned or heavily restricted by China, the former Soviet Union and India between the mid-1980s and 1990¹⁻³. Concentrations of alpha-HCH in arctic air responded quickly to these large-scale usage changes and declined by an order of magnitude from the early 1980s to mid-1990s in steps that closely matched global usage² and emission³ estimates. As a consequence, the direction of net gas exchange in arctic waters went from deposition in the 1980s to air-water equilibrium or volatilization in the mid-1990s⁴⁻⁶. The enantiomers of alpha-HCH are preferentially degraded at different rates in arctic waters and the nonracemic enantiomer signatures have been useful for tracing sea-to-air exchange^{4,5}.

The Tundra Northwest 1999 (TNW-99) expedition covered the eastern Canadian Archipelago in July, traveling from Greenland to Resolute Bay (Cornwallis Island, Nunavut, Canada, 74°N 95°W) and passing through the Davis Strait, Hudson Strait, Foxe Basin and Gulf of Boothia. Air and water samples were collected along this transect, and air sampling continued at Resolute Bay through August 14. The study was done to investigate the spatial variability of alpha- and gamma-HCHs in surface water and air-water gas exchange.

Materials and Methods

Water samples were collected in stainless steel cans using a submersible pump and a polytetrafluoroethylene line surrounded by metal mesh. Water was filtered through a glass fiber filter followed by a 200-mg ENV+ cartridge. Air samples were collected from the bow of the ship and at a land station on Cornwallis Island using a glass fiber filter and polyurethane foam (PUF) cartridge. Filters and adsorbent cartridges were extracted with organic solvents. After cleanup, extracts were blown down with nitrogen and transferred to isooctane to final volumes of ~1 mL for quantitative analysis and ~100 mL for enantiomer analysis. Quantitative determination of the HCHs was done using a 60-m DB-5 column; enantiomer analysis was done on two and sometimes three 30-m chiral columns, which showed different enantiomer elution properties. Instrumentation was an Agilent 6890 GC - 5973 MSD operated in the electron capture negative ion mode (methane gas) and with selected ion monitoring. Recoveries were checked by spiking alpha-HCH-d₆ into the cans of water before filtration and to PUF plugs of air samples before extraction. Recoveries averaged 83 ± 16% for water (N = 16) and 80 ± 15% for air (n = 15). Sampling and analytical details of methods are given in previous publications^{4,5}. Chiral data were expressed as enantiomer fractions, EF = (+)/[(+) + (-)].

Results and Discussion

Concentrations of alpha- and gamma-HCHs in surface water increased from east to west in the Archipelago, from 1.3 and 0.2 ng L⁻¹ in the Davis Strait to 3.5 and 0.4 ng L⁻¹ in Barrow Strait. This is consistent with water transport pathways, in which water from the Beaufort Sea containing high concentrations of HCHs flows out through the Archipelago and becomes diluted with water from Hudson Bay and Baffin Bay which have lower HCH levels^{7,8}. Air concentrations showed no spatial trend. Alpha-HCH concentrations averaged 42 ± 10 pg m⁻³ from the ship and 44 ± 11 pg m⁻³ from the land station on Cornwallis Island. Means for gamma-HCH were 10 ± 2.0 pg m⁻³ from ship and 7.4 ± 2.9 pg m⁻³ from land.

EMV - Chiral Xenobiotics and Natural Halogenated Compounds

The time trends of alpha -HCH concentration and EFs measured on Cornwallis Island are shown in Figure 1. Air concentrations averaged $37 \pm 9.1 \text{ pg m}^{-3}$ from June 7 to July 17, and $53 \pm 5.2 \text{ pg m}^{-3}$ from July 19 to August 14. The difference was significant at $p < 0.001$ and represents a ~40% increase between the two periods. The EFs of alpha-HCH in air were nearly racemic between June 7 – July 17, averaging 0.495 ± 0.004 , underwent a sharp decline to $0.464 - 0.470$ between July 19 – 24, then rose to $0.482 - 0.491$ during July 26 – Aug. 14. The mean EFs were 0.482 ± 0.010 from July 19 – Aug. 14 and 0.487 ± 0.004 from July 26 – Aug. 14. Both were significantly different from the June 7 – July 17 mean at $p < 0.01$.

Results suggest that a specific event was responsible for the increase in nonracemic alpha -HCH in air at Cornwallis Island after July 19. The nonracemic alpha -HCH most likely came from the surface waters of the Archipelago (EF = 0.441–0.457). Water-air fugacity ratios, calculated from air and water concentrations and temperature -dependent Henry's law constants⁶, were 1.4 –2.7, indicating net volatilization. Ice cover maps provided by the Canadian Ice Service showed that the ice near Cornwallis Island broke up during the week of July 19 –26. The change in ice coverage went from 80-90% to "bergy water" (<10% sea ice) during this week. Within two weeks, the ice mass partly reformed, but did not reach the coverage prior to July 19.

Air-sea exchange is an important part of the Arctic Ocean budget for organochlorine pesticides, including HCHs and toxaphene⁷. Currently, extensive ice cover limits the gas exchange loadings of these chemicals, especially in the western Arctic Ocean. Global warming is expected to decrease sea ice, and between 1978-97 the Arctic Ocean lost ice area at a rate of about 3% per decade⁹. The ease of measuring alpha-HCH in air and water, its enantioselective degradation in the Arctic Ocean and the high precision of chiral analysis makes alpha -HCH a useful tracer for investigating the effect of ice cover on air-water gas exchange.

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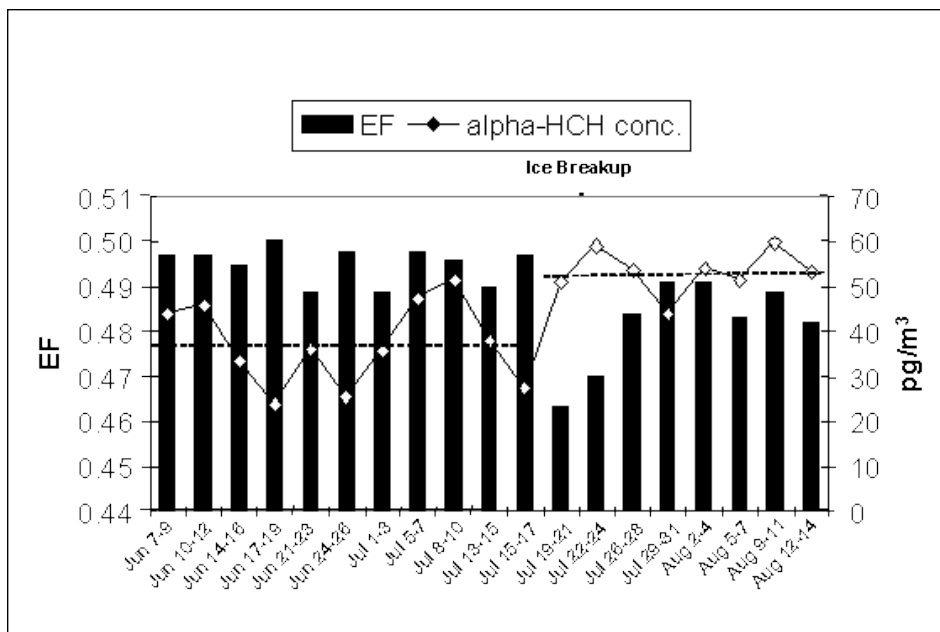


Figure 1. Concentrations (diamonds) and enantiomer fractions (EFs, bars) of alpha-HCH in air sampled at Cornwallis Island during spring-summer, 1999. Dotted lines are mean concentrations of alpha-HCH before and after the beginning of ice breakup (July 19-21).