Enantiomeric Ratios of α-Hexachlorocyclohexane (HCH) in Water from the Great Slave Lake, NWT.

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Abstract:
Concentrations of HCHs along with enantiomeric ratios of α-HCH were measured in three different basins of the Great Slave Lake along with the major outflow Mackenzie River. Atmospheric flux estimates indicated that the Great Slave Lake was a sink for HCHs. An enantiomeric ratio of 1.0 was observed for air at Snare Rapids, however E/R between 0.42 to 0.60 were observed in the Great Slave Lake.

Introduction:
Technical HCH (hexachlorocyclohexane) is one of the most widely used organochlorine insecticides in the world, with a cumulative production estimated at several million tons. HCHs are among the more volatile organochlorine pesticides and are dispersed in both freshwater and oceans around the world. In the Arctic, HCHs have become the most abundant organochlorine pesticide in both air and water. Long Range Atmospheric Transport (LRTAP) has been identified as a major source of pollutants into the Arctic. Great Slave Lake, is Canada's fourth largest body of freshwater, it is located in the south central Canadian Arctic (latitude 61-63° N and longitude 109-119° W). Great Slave Lake in turn feeds into the Mackenzie River, Canada's largest river flowing to the Arctic Ocean. Unlike most Arctic lakes which are glacially fed, Great Slave Lake receives a large input of water from the Slave River. The Slave River originates in Alberta, where there is substantial industrial activity and development is taking place. Due to the high surface to volume ratio, Great Slave Lake has the potential to act as a large catchment for atmospheric contamination. Abiotic degradation of HCHs via hydrolysis and photolysis is non-sterioselective, while microbial degradation exhibits a preferential degradation of (+) α-HCH. Enantiomeric ratios of α-HCH (E/R=(+)α-HCH/(-)α-HCH) in water samples were determined in various locations in the Great Slave Lake along with the Slave River input and the output to Mackenzie River.
In this study air, precipitation, water, and suspended sediments samples were collected from three basins of Great Slave Lake along with samples from the Slave and Mackenzie rivers.

Experimental Methods:
a) Field Sampling:
An Alfa-Laval continuous flow centrifuge (4L/min) was used to collect suspended solids from water samples. Water from the outflow of the continuous flow centrifuge was collected in

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5x20 L stainless steel containers and transferred to Yellowknife for extraction. At Northern Analytical Laboratory, water samples were spiked with a field spike (PCB 70, 1,3,5 tribromobenzene) and extracted into dichloromethane using GLVE . The extracts were then shipped to NWRI for further clean-up and fractionation.

A high volume air sampler (General Metal works' model GPS1 adapted for PUF) and an MIC rain collectors were installed at Snare Rapids about 150 km north of Yellowknife. The sampling rate was about 400 L/min and each sample was collected for twenty four hours. A total of 12 air samples (PUF and filter) and one rain sample were collected from this location.

b) Analytical Methodology:

Dichloromethane extracts were dried by passing the samples over anhydrous Na_2SO_4 in an Alihn funnel. The sample volume was reduced to 5 mL by rotary evaporator at 30 °C. The sample was solvent exchanged with hexane and base washed with 0.1M K_2CO_3. The extract was then dried by passing though anhydrous Na_2SO_4. The sample was spiked with PCB 65 and perthane followed by volume reduction to 2mL with a rotary evaporator. The concentrate was applied to 10g of 100% activated 60-mesh silica gel. Four fractions were collected; first with 80 mL of hexane, followed by 85 ml of 35% (v/v) dichloromethane in hexane; the third fraction was eluted with 85 mL of 60% dichloromethane in hexane, and the last fraction consisted of 50 mL of dichloromethane followed by 50 mL of methanol. Each fraction was spiked with 65 ng of octachloronaphthalene and the volumes were reduced to approximately 5 mL with a rotary evaporator. The concentrates were solvent exchanged with isoctane and reduced to a final volume of 1 mL. The extracts were then transferred to vials and stored at 4 °C until analysis.

In the laboratory both plugs and filters were spiked with 10 ng of 1,3,5 tribromobenzene and octachloronaphthalene. PUF plugs were soxhlet extracted using 500 mL of pesticide grade hexane, and the organic portion of the GFF filters were soxhlet extracted with 100 mL of dichloromethane. The extracts were dried by passing the samples through anhydrous Na_2SO_4 in an Alihn funnel. The sample volume was reduced to 5 mL by rotary evaporation at 30 °C. The samples were solvent exchanged with hexane. The extracts were again dried by passing though anhydrous Na_2SO_4, followed by volume reduction to 2 mL under a stream of nitrogen. The extracts were cleaned up and fractionated in the same way as water sample.

Rain columns were extracted with 200 mL of methanol followed by 250 mL of dichloromethane from the rain column. The extract was then washed with 200 mL of 3% NaCl. Subsequently the extract was dried with anhydrous Na_2SO_4 and fractionated on 10g of 100% activated 60-mesh silica gel. Two fractions were collected; the first with 50 mL of hexane, followed by 50 mL of 50% (v/v) dichloromethane and hexane. Volumes of each fraction were reduced and solvent exchanged with isoctane to a final volume of 1 mL. The extracts were then transferred to GC vials with Teflon lined septa and stored at 4 °C until analysis.

Chiral HCHs analysis conditions were; sample introductions were performed using a CTC A2000SE into a Varian 3400 CX gas chromatograph equipped with SPI injector. Injector conditions were as follow: initial temperature 120 °C held for 2min raised to 280 at 300 °C /min held for 35 min. Analytical separations were performed using a 30m x 0.25mm i.d. GammaDex (Supelco), column temperature was at 110 °C held for 2 min raised to 180 at 15 °C /min held for 1 min raised to 285 at 2 °C /min and held for 10 min. The column was connected to the ion source of the MS via a Los Gatos transfer line held at 200°C by GC auxiliary electronics. ECNIMS was performed on a Finnigan 4500 quadrupole mass spectrometer equipped with Teknevent data system. Methane was used as moderating gas and PFB (FC-43) was used as

calibration gas. The MS was operated in selected Ion Monitoring (SIM) mode; monitoring m/e 253,255,257 corresponding to M- Cl ions produced by HCHs in a single window.

Results and Discussions:

HCHs were the major organochlorine contaminant in air and water. Concentrations of HCHs along with atmospheric flux ,α/γ, and E/R are presented in Table 1. Atmospheric flux estimates for HCHs were between -0.007 and 0.042 ng/m^{2}day, indicating that the Great Slave Lake is a sink for HCHs. East Arm and Yellowknife Bay have a similar α/γ' ratio to air indicating a mainly atmospheric source. On the other hand West Arm, Fort Providence, and Mackenzie River have a higher ratio indicating influence of other sources such as the Slave River. The Slave River is the main tributary to the Great Slave Lake and on average accounts for 87% of the total water inflow to the Lake.

Enantiomeric ratios of α-HCH were also presented figure 1. E/R =1.0 was observed for air samples collected during this period at Snare Rapids, which corresponds to the ratio of unmetabolized α-HCH. The E/R value for the rain sample collected from this period was 1.15 based on one sample only. Snow samples collected in this area had E/R values of 1.0. In Great Slave Lake E/Rs varied from 0.42 in the East Arm to 0.61 for Mackenzie River. Backus et. al.[1] reported E/R = 0.57 for the Mackenzie River at Tsiiggehtchic. The deepest point in the Great Slave is located in the East Arm. The concentrations for major ions in East Arm is much lower than the rest of the lake. The majority of the inflow and outflow take place in the southern portion of the lake between the Slave River located at the southeast end of the Great Slave Lake and Mackenzie River located at the southwest end of the lake. As a result there is a small exchange of water between East Arm located in the northeast end of the Great Slave Lake and the rest of the lake. This indicates long residence time for water and hence low E/R values. Similar results were also observed in Yukon River Basin[2]. Similarly Atlin Lake the deepest lake in this system had the lowest E/R value in the Yukon River Basin.

Acknowledgments:

Table 1. Concentration of α and γ-HCH (ng/L), along with atmospheric flux (ng/m^{2}day), α/γ, and E/R ratios.

Location	[α-HCH]	[γ-HCH]	α/γ	Flux (α-HCH)	Flux (γ-HCH)	E/R
Air	7.2x10^{-5}	2.0x10^{-5}	3.6			1.01
Rain	3.4	4.5	0.78			1.15
Yellowknife Bay	0.4	0.2	2.7	-0.017	-0.034	0.63
East Arm	0.2	0.4	4.8	-0.017	-0.008	0.42
Great Salve	0.2	0.5	0.4	-0.017	0.009	0.67
Fort Simpson	0.08	0.09	0.9	-0.007	-0.021	0.62
Mackenzie R.	0.5	0.4	0.8	-0.042	-0.034	0.67

Figure 1. E/R ratios of α–HCH in the Great Slave Lake.

Sampling Location
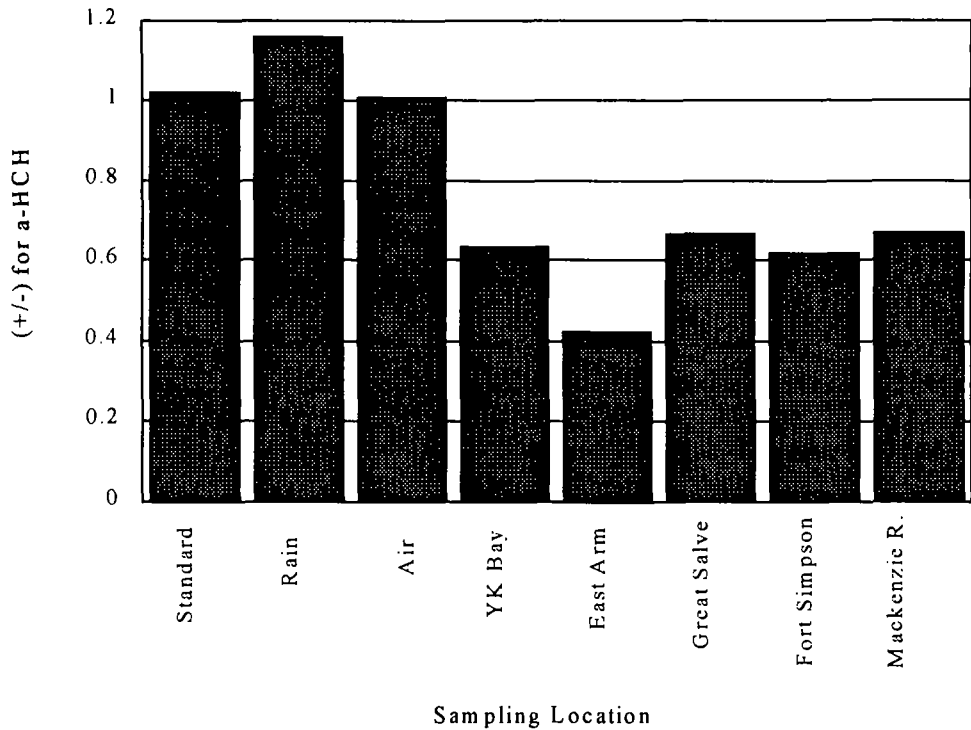
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