

## Air-Water Gas Exchange of Hexachlorocyclohexanes and the Enantiomeric Ratios of $\alpha$ -HCH in the South Atlantic Ocean and Antarctica

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### Introduction

Organochlorine contamination in the Northern Hemisphere has been studied much more extensively than in the Southern Hemisphere but organochlorine residues, including hexachlorocyclohexanes (HCHs), have been found in antarctic air (1,2), water (3), fish, penguins (4) and other birds (5). The global fractionation hypothesis predicts that chemicals released in the temperate and tropical zones will be transported to the colder boreal and polar zones (6), where they will have the tendency to reside for long periods of time. In December 1997 to February 1998, air and water samples were collected in the South Atlantic and Southern Ocean to determine the air-water gas exchange of  $\alpha$ - and  $\gamma$ -HCH and the enantiomer ratios (ER = (+)/(-)) of  $\alpha$ -HCH. Cruise Track: The SA Agulhas left Cape Town, South Africa on November 30, 1997 and proceeded south along 6°E reaching the South African National Antarctic Expedition (SANAE) Base (70°S, 3°E) then returning to Cape Town, February 7, 1998.

### Material and Methods

Water samples of 20-80 L were collected by a submersible pump beneath the ship; the line running from the pump was stainless steel tubing lined with glass. The water was pumped into 40-L stainless steel cans, spiked with surrogate of  $\alpha$ -HCH-*d*<sub>6</sub>, filtered through a glass fibre filter (GFF) and then extracted by two different methods, XAD resin or ENV+ cartridges (Jones Chromatography). In both cases the water was pulled through the adsorbent by a peristaltic pump. The XAD was precleaned by soxhlet extraction in acetone, petroleum ether and dichloromethane, each for 48 h, and stored in chromatographic grade water. The ENV+ cartridges were cleaned with hexane and conditioned with methanol before use. After sampling, the adsorbents were extracted with dichloromethane and the extracts were concentrated by rotary evaporation and nitrogen blowdown into isoctane. The XAD extracts were fractionated on a column of neutral alumina - silicic acid and cleaned up with 18M sulphuric acid. The ENV+ extracts were cleaned up using alumina and sulphuric acid.

Air samples were collected by drawing 700-1500 m<sup>3</sup> of air through a 20x25 cm GFF followed by two polyurethane foam plugs (PUFs, 7.8 cm diameter x 7.5 cm thick). The GFFs were cleaned by baking at 400°C in a muffle furnace, the PUFs were cleaned by soxhlet extraction in acetone and petroleum ether, each for 48 h. After sampling, the PUFs were extracted in petroleum ether for 12 h; the extracts were transferred to isooctane, fractionated on alumina - silicic acid and cleaned up with sulphuric acid. Since previous work has found that HCHs are almost entirely gaseous in air and dissolved in water (7,8), the GFFs were not analysed here.

Clean extracts were transferred to isooctane by nitrogen blow down and analysed using an Hewlett Packard 5890-GC 5989-MS Engine operated in the electron capture negative ion mode. The ions monitored were 255/257 for HCHs and 259/261 for  $\alpha$ -HCH-d<sub>6</sub> (target/qualifier). For quantitative analysis, a DB-5 column was used (30m, J & W) and mirex was added as the internal standard. Two different cyclodextrin chiral columns were used for the enantiomeric analysis: Beta-DEX 325 (20% 2,3-di-O-methyl-6-O-tert-butylidimethylsilyl- $\beta$ -CD in SPB-20, Supelco) and BGB-172 (20% tert-butylidimethylsilylated  $\beta$ -CD in OV-1701, BGB Analytik AG, Switzerland). Details of analytical methods are given in (7,8).

## Results and Discussion

### Quality Control

Two PUFs were spiked with a known amount of HCHs and recoveries were >85%. Checks were also done for XAD and ENV+ by spiking 20-80 L of water with HCHs. Average recoveries were 83±12% (n=5), after subtracting the native amounts in the seawater samples. Yields of the  $\alpha$ -HCH-d<sub>6</sub> surrogate averaged 79±15% (n=14). Blank values for  $\alpha$ - and  $\gamma$ -HCH were 10 pg and 50 pg (water), and 40 pg and 80 pg (air). The enantiomer elution order was confirmed by injecting a solution that was enriched in (+) $\alpha$ -HCH. The two columns used here reversed the elution order of the enantiomers, with (+) $\alpha$ -HCH eluting first on the Beta-DEX 325 and second on BGB-172. Measured ERs of a racemic  $\alpha$ -HCH standard averaged 0.99±0.01 (n=6). The 255/257 ion ratio was required to be within ±5% of the standard for ERs of samples.

### Air and Water Concentrations

Concentrations of HCHs in surface water are averaged by 5° latitude bands in Table 1. The range of  $\alpha$ -HCH (5.5-15.5 pg/L) was small, with no apparent trend from 40-70°S, whereas  $\gamma$ -HCH ranged from 15-185 pg/L with minimal values between 55-59°S and highest concentrations between 65-69°S. By comparison, Iwata et al. (3) found 28 pg/L  $\alpha$ -HCH and 8.2 pg/L  $\gamma$ -HCH in the Southern Ocean on a 1990 expedition.

Atmospheric levels, averaged by the same latitudinal bands, are also given in Table 1. The concentrations of  $\alpha$ -HCH ranged from 0.5-1.7 pg/m<sup>3</sup> and showed no strong trend with latitude although levels dropped slightly between 55-64°S. The trend was markedly different for  $\gamma$ -HCH which ranged from 5-105 pg/m<sup>3</sup> and increased significantly with latitude ( $r^2=0.59$ ). Measurements of HCHs in antarctic air since 1990 are compared in Table 2. Levels of  $\gamma$ -HCH from the Agulhas cruise were similar to those of Larsson et al. (2) but higher than values reported by Bidleman et al. (1) and Iwata et al. (3). Concentrations of  $\alpha$ -HCH were lower than reported by Iwata et al. (3) and closer to those found by Bidleman et al. (1).

Table 1: Average Concentrations  $\pm$  s.d. of HCHs in Air and Water

Latitude (°S)	$\alpha$ -HCH Air pg/m <sup>3</sup>	$\gamma$ -HCH Air pg/m <sup>3</sup>	n	$\alpha$ -HCH Water pg/L	$\gamma$ -HCH Water pg/L	n
40-44	1.2-1.8	4.9-12.9	2	9.4 $\pm$ 4.2	87.3 $\pm$ 83	3
45-49	1.2-1.7	4.0-31.4	2	14 $\pm$ 3.4	78.7 $\pm$ 60.8	6
50-54	0.92 $\pm$ 0.27	18.4 $\pm$ 12.8	7	11 $\pm$ 3	46.5 $\pm$ 42.1	6
55-59	0.68 $\pm$ 0.22	37.1 $\pm$ 20.5	5	8.9 $\pm$ 4.9	28.3 $\pm$ 23.9	5
60-64	0.74 $\pm$ 0.20	28.4 $\pm$ 23.1	5	10.4 $\pm$ 3.5	65.7 $\pm$ 29.2	5
65-69	1.05 $\pm$ 0.26	47.8 $\pm$ 49.9	3	7.5	134.7	1
70	1.31 $\pm$ 0.15	29.0 $\pm$ 15.4	4			

Table 2: Range and (Mean) Concentrations of HCHs in Southern Ocean Air (pg/m<sup>3</sup>)

Year	$\alpha$ -HCH	$\gamma$ -HCH	Reference
1997-1998	0.5-1.5 (1.0)	5-105 (35)	this work
1988-1990	not determined	nd-118 (26)	Larsson et al. (2)
1990	2.7-6.7 (4.0)	1.1-16.9 (3.8)	Bidleman et al. (1)
1989-1990	6.6-40 (26)	7.6-16 (12)	Iwata et al. (3)

### Fugacity Calculations

The net gas exchange direction was estimated from the water/air fugacity ratio, where a fugacity ratio  $>1.0$  implies net volatilization and  $<1.0$  implies deposition. The fugacity ratio was calculated from latitudinally averaged air and water concentrations and the temperature dependent Henry's Law constant (9):

$$f_w/f_a = C_w H / C_a R T_a \quad (1)$$

where  $f_w/f_a$  is the fugacity ratio,  $C_w$  and  $C_a$  are the dissolved concentration in water (pg/m<sup>3</sup>) and vapor-phase concentration in air (pg/m<sup>3</sup>),  $H$  is the Henry's Law constant at the surface water temperature (Pa m<sup>3</sup>/mol),  $R = 8.31$  Pa m<sup>3</sup>/mol K and  $T_a$  (K) is the temperature of the air. Temperatures ranged from 12 to -3 °C (air) and 14 to -1.7 °C (water). The fugacity ratio for  $\alpha$ - and  $\gamma$ -HCH ranged from 0.3-0.9 and 0.07-0.6, respectively. This implies that the net flux is depositional, from air to water. The fugacity ratio was highest in the warmer waters and decreased in the colder waters to the south; this was most dramatic for  $\gamma$ -HCH (Figure 1).

### Enantiomer Ratios of $\alpha$ -HCH

ERs of  $\alpha$ -HCH in the air samples ranged from 0.93-1.07 ( $n=22$ ) and showed a slight trend with latitude (Figure 2). The ERs were  $\geq 1.00$  between 40-54°S and  $\leq 1.00$  from 55-70 °S, indicating a depletion of (-) $\alpha$ -HCH at low latitudes and (+) $\alpha$ -HCH at high latitudes. A similar reversal of the ER was found in the Bering-Chukchi seas region compared to the Arctic Ocean, and was associated with a different degradation preference for the enantiomers in each region (7,8). Interpretation of these results for the Agulhas cruise is pending analysis of the surface water samples for  $\alpha$ -HCH enantiomers.

## Acknowledgments

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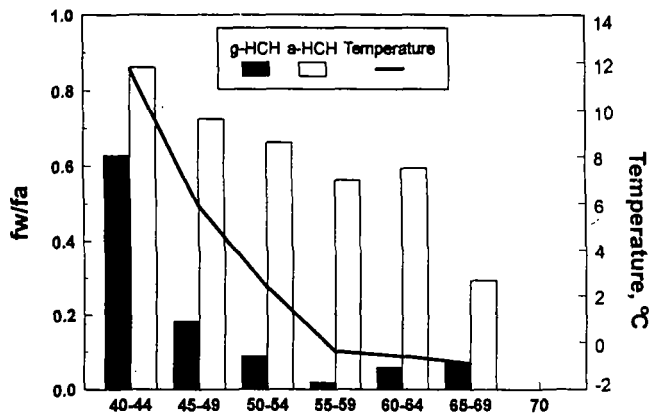


Figure 1: Fugacity ratio of  $\alpha$ - and  $\gamma$ -HCH averaged by 5 degree latitude bands.

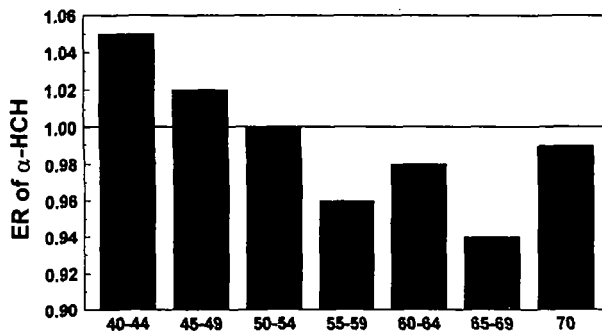


Figure 2: Enantiomeric ratio of  $\alpha$ -HCH in air averaged by 5 degree latitude bands.