Differences in Enantioselective Degradation of α-Hexachlorocyclohexane in the Bering-Chukchi Seas and the Arctic Ocean

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1. Introduction

Technical HCH is an insecticidal mixture of 60-70% α-HCH, 5-12% β-HCH, 10-15% γ-HCH, and minor percentages of other isomers which was introduced during World War II and is still in large-scale use today. Canada, the United States and most European countries have eliminated the use of technical HCH in favour of pure γ-HCH (lindane), the active ingredient, but the isomer mixture was heavily used in Asian countries throughout the 1980s[1,2]. HCHs volatilize quickly from source regions[3] and are atmospherically transported to the Arctic where they undergo wet and dry deposition and air-water gas exchange[4].

Of the main isomers in technical HCH, α-HCH is the only one that is chiral. The two enantiomers of α-HCH occur in the technical mixture in a 1:1 ratio (racemic). Enantioselective degradation of α-HCH has been documented in waters of the Canadian Arctic[5,6] and the North Sea[7,8], soils[9,10] and birds, mammals and fish[8,11,12]. In August - September, 1993 water and air samples were collected in the Bering and Chukchi seas on a Russian - U.S. cruise (BERPAC-93)[13]. Samples were again collected on a Canadian - U.S. transect of the Arctic Ocean in July - September 1994 (Arctic Ocean Section, AOS-94). The purpose of these measurements was to investigate the enantioselective degradation of α-HCH and air-sea exchange of α- and γ-HCH. Results of the gas exchange studies have been reported elsewhere[13]. Here we discuss the enantiomeric composition of α-HCH in air and water from the arctic and subarctic regions and potential use of the enantiomers to follow gas exchange.

2. Methods

Water samples of 4-20L were collected at varying depths and passed through a 0.7μm glass fibre filter (GFF) followed by a 1-g or 5-g C_8 bonded silica cartridge (Varian) to concentrate the HCHs. The cartridges and filters were extracted with dichloromethane (DCM). Air samples were collected by drawing 500-1000 m^3 of air through a GFF and polyurethane foam (PUF) plugs, which were extracted with DCM and petroleum spirit, respectively. After being transferred into isooctane, the extracts were cleaned up on a column of alumina followed by treatment with sulphuric or chromic acid. Details of sampling, extraction-cleanup procedures and quantitative analysis by capillary GC with electron capture detection are given elsewhere[13].

Negligible amounts of HCHs were found on water and air filters[13], so enantiomeric analysis was carried out only on extracts of C_8 cartridges and PUF plugs. Enantiomers of α-HCH were determined by capillary GC-negative ion mass spectrometry using a Hewlett-Packard 5890 GC/5989 MS Engine. The two fused silica columns used to separate the enantiomers were Betadex: 20% permethylated β-cyclodextrin in methylphenylpolysiloxane (Supelco, 30 m long, 0.25 mm i.d., 0.25 μm film thickness), and BSCD: 30% tert-butyldimethylsilylated-β-cyclodextrin in methylphenylcyanopropylpolysiloxane (BGB Analytik, Switzerland, 20 m long, 0.25 mm i.d., 0.25 μm film thickness). Samples were injected splitless (2μL, split opened after 1.5 min). The temperature programs were: inject at 90° (1 min), 15-20° min^{-1} to 130-140°, 1.0° min^{-1} to 180-190° (2-20 min), 20° min^{-1} to 230-240° (5-10 min). Other conditions were: helium carrier gas at 50 cm s^{-1}, methane reagent gas at 1.5 Torr, injector temperature 250°, transfer line 250°, ion source 150° and quadrupole 100°. Ions 255 and 257 were monitored. The two columns employed here reverse the elution order of the enantiomers, established using a standard enriched in (-)α-HCH[6]. On BSCD (-)α-HCH elutes first, whereas (+)α-HCH elutes first on Betadex.

3. Results and Discussion

The concentration of α-HCH in the surface water of the Bering and Chukchi seas is 2.0 ng L^{-1} and decreases slowly to 1.5-1.7 ng L^{-1} at 100-300 m[13]. In the upper 60 m of the Beaufort Sea the concentration of α-HCH is 4.5 ng L^{-1}, but drops off rapidly to ~1.0 ng L^{-1} at 200 m[14,15]. We found a reversal in the order of α-HCH enantiomer degradation in the Bering-Chukchi seas compared to the Arctic Ocean. Enantiomer ratios (ER = (+)α-HCH/(-)α-HCH) in Bering and

Chukchi water were ≥1.0 (Fig. 1), indicating selective breakdown of (-)α-HCH, and showed little trend with depth at most stations. In contrast, preferential removal of (+)α-HCH was found in the Beaufort Sea and Canadian Basin where ERs were ≤1.0 in surface water (Fig. 1) and decreased to ≤0.4 at 200-350 m. In some deep samples (+)α-HCH was nearly absent. Reasons for the opposite enantioselectivity in the two oceans are unknown, but different regions of the North Sea also show reversals in the ERs[7]. Loss of (+)α-HCH has been found in the Canadian Archipelago and nearby Amituk Lake[5,6], and (+)α-HCH was degraded faster than (-)α-HCH in sewage sludge[16]. Preferential degradation of (-)α-HCH has been noted in soils from western Canada[9] and Germany[10].

Quantitative measurements of α-HCH show that the water/air fugacity ratio (degree of saturation) is 2.38 in the Bering-Chukchi seas[13] and 1.59 the Canadian Archipelago[5]. This suggests that the net direction of gas exchange is sea-to-air, and that the concentration of α-HCH in the marine boundary layer may be partially controlled by volatilization from surface water. In support of this hypothesis, the ERs in air samples from the open waters of the Bering and Chukchi seas are >1.0, indicating a depletion of (-)α-HCH as for surface water. On AOS-94 the concentration of α-HCH in air dropped from 120-130 pg m^{-3} in the Bering-Chukchi seas to 40-70 pg m^{-3} when traversing the ice-covered Arctic Ocean. The reduction over the ice cap may be due to a dampening of gas exchange. ERs in air over the Arctic Ocean are close to racemic, which would be expected for α-HCH transported from a recent source.

4. References

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Figure 1. α-HCH ERs in Surface Water and Air