Distribution of +/- α-HCH and PCCH Enantiomers in marine Organisms

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The enantiomers of chiral marine pollutants, e.g. α-HCH, β- and γ-PCCH (fig 1) have been resolved by capillary gas chromatography employing modified cyclodextrins as the chiral stationary phase [1].
We have applied a newly developed chiral stationary phase on the base of CP-SIL-5 and β-cyclodextrine (CP-Cyclodex, immobilized, Fa. Chrompack Intern. B. V., Middelburg, The Netherlands) for the determination of the enantiomer ratios of organochlorines in samples of marine mammals.
This capillary column allows temperature programming with detection in the low pg-range using an electron capture detector (fig 2).
The HCH isomers are the most prominent semi-volatile organochlorine compounds present in the northern hemisphere. Therefore, in seals from arctic regions the HCH concentration normally exceeds the HCB content, and the α-HCH contamination always dominates the γ-HCH concentration [2,3].
For α-HCH analyzed in water of the North Sea and the Baltic an enantiomeric [+/-] - ratio not deviating appreciably from 1:1 was established [4,5]. However, first measurements revealed a trend to dominance of (+)-α-HCH over (-)-α-HCH in marine organisms at higher trophic levels [6,7].
This observation was confirmed by investigations of tissues (blubber, brain) of harbour seals from the North Sea and Iceland [8] and other marine mammals (harbour porpoises, grey seals, dolphins) from the Baltic and the North Sea [9]. In blubber of harbour seals from the North Sea and Iceland the [+/-] - ratios of α-HCH varied from 1.21 to 4.47, and in the brain samples the [+/-] - ratios ranged from 7.9 to ∞ [8].
Recently, we analyzed blubber and brain of a hooded seal.
This seal was caught near Jan Mayen in the arctic and taken to a research-station near Murmansk (Kola-peninsula, Russia).

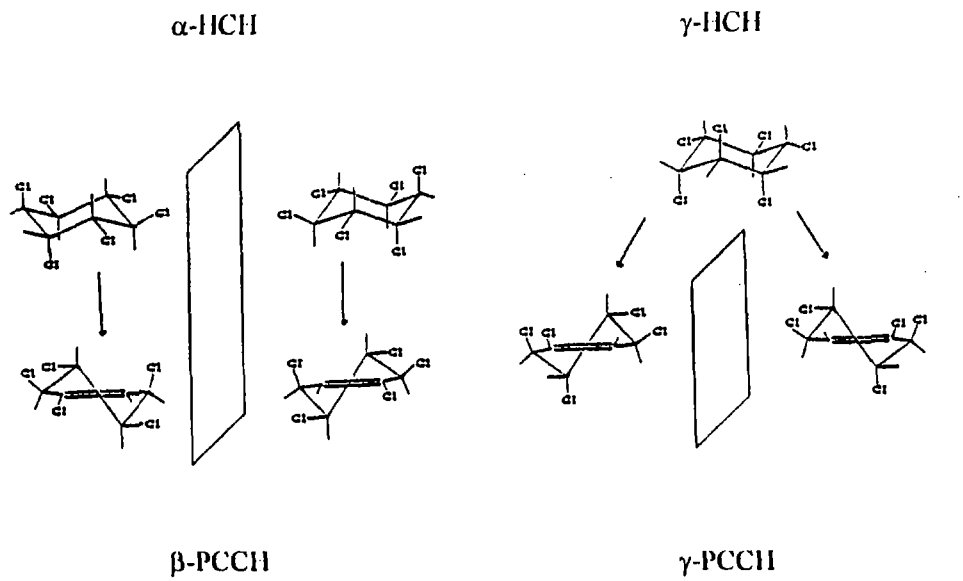

Fig 1: Formation of β- and γ-PCCH from α- and γ-HCH

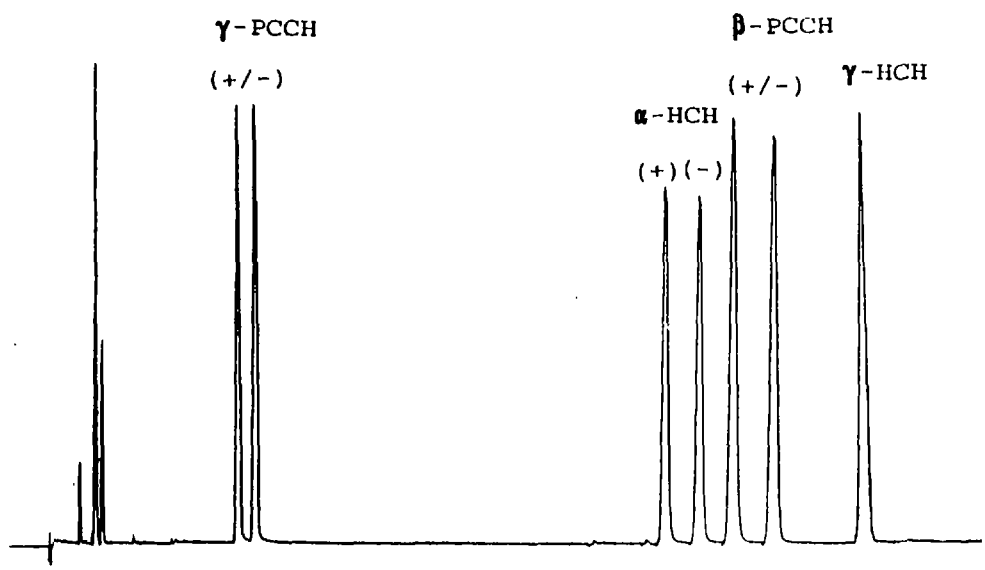

Fig 2: Chromatographic separation of β- and γ-PCCH from α- and γ-HCH on a CP-Cyclodex column (GC conditions: Injector: 200°C; TP: 35 min 150°C, 10°C/ min to 260°C, 30 min 260°C; Detector: ECD, 270°C)

We found in the blubber of the hooded seal a [+/-] - ratio for α-HCH of 0.14, and in the brain tissue higher amounts of both, (+)-α-HCH and (-)-α-HCH. Additionally, the brain contained remarkable concentrations of γ-HCH (Tab. 1).

Tab. 1: HCB and HCH isomers in blubber and brain from a hooded seal from the Murmansk-research station (µg/kg)

	HCB	α-HCH	β-HCH	γ-HCH	(+)-α-HCH	(-)-α-HCH
blubber	58	24	8	14	3	21
brain	4	3	1	80	2	1

These results were surprising. There have been no previous reports of such high concentrations of (-)-α-HCH in the brain of wildlife, and our further investigations of harp seals from the same arctic region (North Norway) resulted in findings, which were in accordance with the literature [3,8,10].
There is a lack of informations about the hooded seal (the Russians have given no anamnesis and no indication about the nature of feed).
It is possible the uptake of high Lindane- contaminated fodder caused the extremely high γ-HCH burden in the brain of the hooded seal, and that the conversion of γ-HCH to α-HCH led to the preferential formation of (-)-α-HCH (fig. 3).

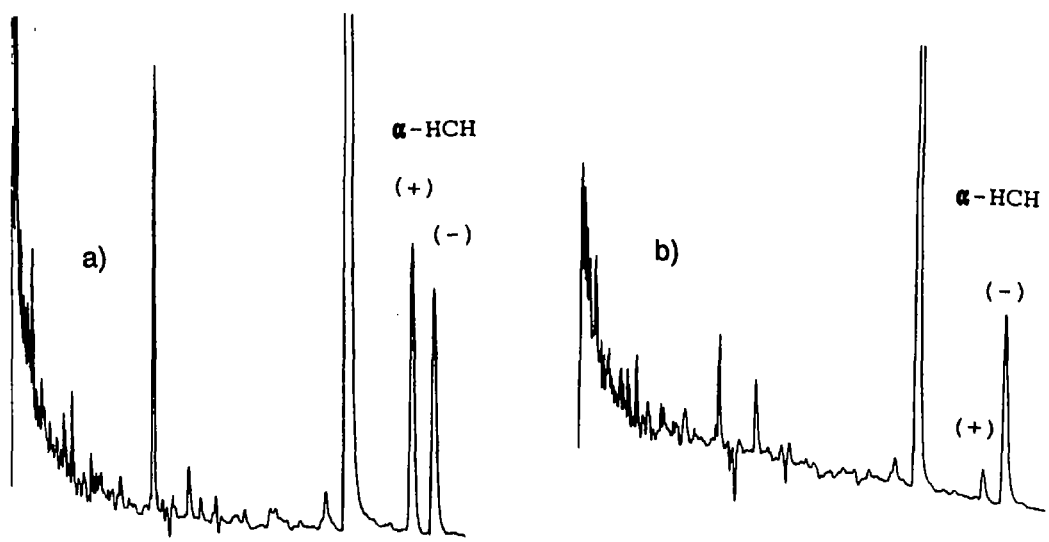

Fig.3: Determination of α-HCH enantiomers in blubber of a) harp seal (North Norway) and b) hooded seal (Murmansk)

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