The relationship between enantiomeric fraction and concentration of a-hexachlorocyclohexane in human placentas

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Introduction

Enantiomeric ratios (ERs) and / or enantiomeric fractions (EFs) of chiral pollutants have been used as a versatile tool for process studies[1,2]. They are useful tracers for air-surface (soil-air and water-air) exchange and atmospheric long range transport[3] and for bioaccumulation of persistent organic pollutants along food chain[4]. In this report, we present the deviation of EFs of chiral α-hexachlorocyclohexane in placenta samples from Finland.

Method and materials

The sample collection, preparation, cleanup procedures have been described elsewhere[5]. HRGC *HP5890 (series II)* device was equipped with a capillary chiral column BGB-172 (30 m length and 0.25μm film thickness) for the enantiomers separation. Carrier gas was helium. HRMS *MAT95 (Finnigan)* was used as the detector in a multiple ion detection mode. Limit of detection (LOD) was set as 3 times noise of the analysis. The results with chromatographic peak height above 100 were quantified. (+)-, (-)-Isomers of α-HCH were identified according to the native standard of pure enantiomers (*Dr. Ehrenstorfer GmbH, Germany*). In the first analysis, isotope dilution method was used for the quantification by employing labelled standards (*Cambridge isotope lab, USA and Dr. Ehrenstorfer GmbH*)[5]. Enantiomer ratios (ER) and enantiomer fraction (EF) were calculated according Harner[2]. Statistical analysis and figure plotting was done by Microsoft Excel (*Microsoft, USA*).

Results and Discussion

EF and ER for the racemic mixture should be 0.5 and 1 respectively. 85 placenta samples were investigated for EFs (mean 0.46, SD 0.06). (+)-α-HCH is the more readily degradable enantiomer than (-)-α-HCH in human placenta. α-HCH clearly showed deviation from racemic EF and ER when the total concentration for both enantiomers was lower than ~0.5 ng/g on lipid base.

For humans, we presume that all of the enantioselective residues might result from two possible reasons; one is enantioselective exposure, which means humans are exposed to the enantiomeric sources of pollutant probably enriched along the food chain. The other reason is enantioselective depletion of racemic pollutants by the human body. For chiral pollutants, (1) the major general exposure source of persistent pollutants is food, especially fish and other marine fatty organisms[6], which should not change EF heavily because of their low metabolic capacity in organisms such as molluscs and fish[7]. (2) The people with omnivorous diet are exposed to a mixed set of pollutant sources, which might contain enantiomers close to racemic mixtures. (3) The occupationally exposed individuals are directly exposed to the racemic type of sources. Therefore, we conclude that people face racemic or nearly racemic mixtures of these pollutants. The exposure of the placenta might result either from the pollutant release of the body storage in adipose tissue because of the higher maternal body fat turnover during pregnancy[8,9] or the continuing exposure especially from diet because the pollutants are still present in food[10]. Our data support that humans are exposed to racemic or nearly racemic α-HCH sources, because EFs are 0.5 at higher concentrations of the pollutants. The stable EFs might result from dominant uptake rates of racemic compounds[11]. The EF deviation occurs only if the concentrations are below ~0.5 ng/g in total. This critical concentration should be an important point to conclude about the exposure process, which suggests that the uptake rate becomes less dominant in the exposure process. Also this point might be species- or organ-(tissues) specific according to enzyme selectivity for enantiomers and its activity.

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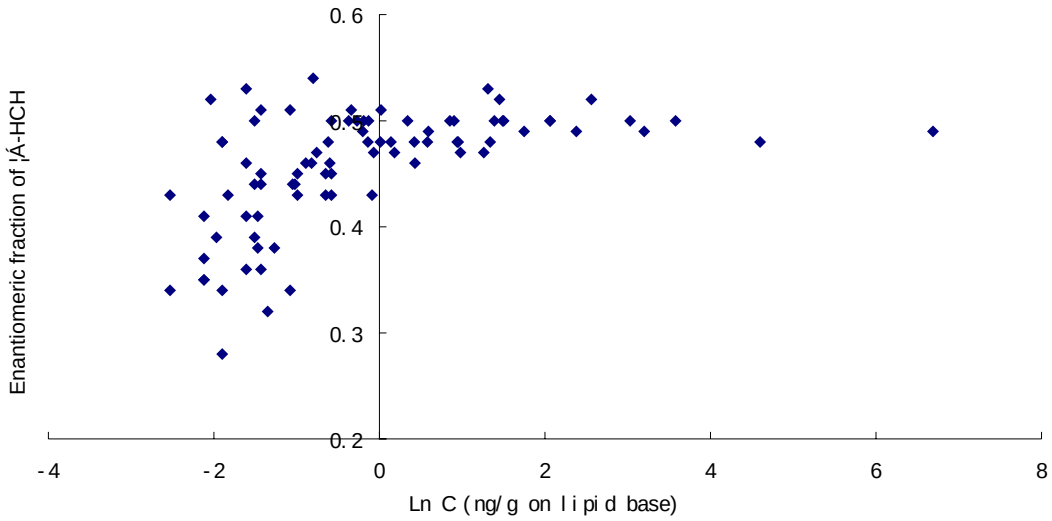

Fig 1. The logarithmic total concentration of α-HCH enantiomers *vs.* their enantiomeric fractions