INVESTIGATION OF SOURCE APPORTIONMENT FOR α-HCH IN AIR USING ENANTIOSELECTIVE ANALYSIS

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Abstract

Passive air samples deployed throughout Europe were analysed for the enantiomers of α-HCH. When samples were divided according to their proximity to a large water body, Baltic samples had enantiomeric fractions (EFs) < 0.500, showing a consistent excess of the (-) α-HCH enantiomer, while the Mediterranean samples had predominantly EFs > 0.500. Similarly, Atlantic samples had EFs > 0.500 at latitudes < 50 degrees N, whereas at latitudes > 50 degrees N, EFs were largely < 0.500. Inland samples showed a large range in EF values; the highest α-HCH concentrations were racemic, whereas at lower α-HCH concentrations the spread in the EFs increased. Correlations between EFs and concentrations of α-HCH, α-HCH/γ-HCH ratios, latitude and longitude of the sampling locations suggest that enantiomeric analysis is a valuable tool to investigate source apportionment for chiral pollutants.

Introduction

The use of technical HCH, containing approximately 60% α-HCH, 15% β-HCH and 15% γ-HCH, has been reduced substantially in Europe during the 1970s.[1] Lindane, the purified active γ-HCH isomer, has largely replaced technical HCH and is currently used on vegetable and tomato crops in Southern and Eastern European countries.[1] α-HCH is the only isomer in technical HCH that is chiral; when manufactured there are equal amounts of the each enantiomer. Chiral compounds were shown to be degraded enantioselectively in soil and water by microbial activity, resulting in non-racemic residues.[2] Since physical-chemical properties of the two enantiomers are identical, when these non-racemic residues volatilize, their distinctive enantiomer signatures are retained and reflected in the overlying air.[3] The use of enantioselective analysis may help distinguish between transport from current use regions or revolatilization of residues from past applications. The aim of this study was to investigate the suitability of using enantiomeric signatures for source apportionment of α-HCH in European air.

Materials and methods

Air sampling, extraction, and quantitative analysis of HCHs. Air was sampled using passive samplers as previously described.[4] A total of 71 samplers were deployed over a 6 week period during the summer of 2002 across 22 countries (Figure 1). Samples were collected in both urban locations (n = 25) and in rural/remote locations (n = 46). Sample collection, analytical procedures and quality control have been previously described and summarized here.[4] The samplers were spiked with internal standards, extracted with DCM, cleaned-up on a column containing alumina, silica gel, and Na_2SO_4, followed by gel permeation chromatography. The extracts were reduced to a final volume of 25 μl and HCHs were quantified by GC-MS operated in electron capture negative ionization (ECNI) and selected ion monitoring mode.

Enantioselective analysis of α-HCH. The method used has been previously described and validated.[5]. Extracts were fractionated on a silica SPE cartridge (500 mg, 3ml, Supelco), 1st fraction was eluted with hexane and contained PCBs, *p,p'*-DDE and *p,p'*-DDT. The 2nd fraction, containing the other OCPs, including HCHs, was

eluted with 3mL of DCM and further concentrated to 50 µl. A volume of 3 x 5 µl of the extract was injected in solvent vent injection mode and was analysed by GC/ECNI-MS using a 30m x 0.25mm x 0.25 µm Chirasil-Dex column (Chrompack). Both ion source and quadrupole temperatures were 150°C. Three ions (255, 253 and 71) were monitored for α-HCH.

The elution order of the two enantiomers was established using enantioenriched standards (Dr. Ehrenstorfer, Germany). (+) α-HCH eluted as first isomer on the Chirasil-Dex column. The enantiomeric fraction (EF) was calculated as described by Harner et al.:[6]

$$EF = \frac{(+)\alpha HCH}{(+)\alpha HCH + (-)\alpha HCH}$$

To evaluate the accuracy of EF measurements for α-HCH enantiomers, a standard reference material (SRM 1945, whale blubber, NIST) was analysed. EFs for α-HCH enantiomers (0.583 ± 0.004, n=3) compared favourably with the value of 0.574 ± 0.007 (n=5) found by Wong et al.[7]. For α-HCH standards, EFs were 0.499 ± 0.005 (n=9).
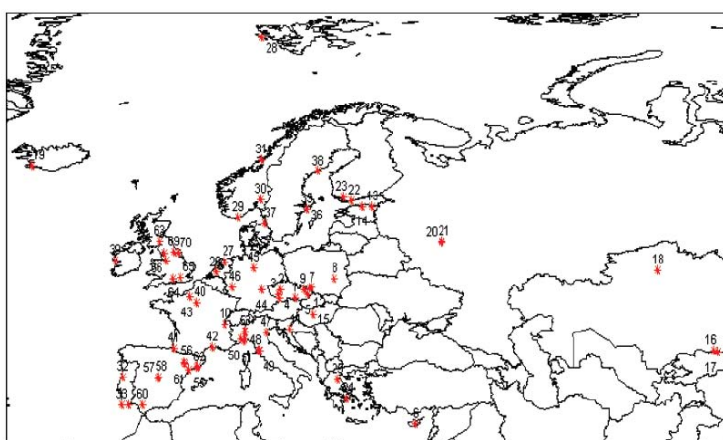

Figure 1. Map showing sampling sites distributed throughout Europe as described by Jaward et al.[4]

Results and discussion

The sample sites were scored according to the water body they are thought to be impacted by or whether they are classed as inland. The following classes were allocated: 1. Inland; 2. Mediterranean; 3. Atlantic; 4. Baltic and the corresponding EFs distributed as shown in Figure 2.
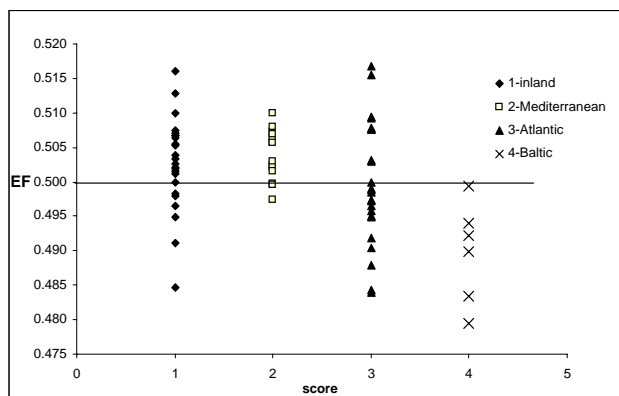

Figure 2. Distribution of EFs in air as a function of their proximity to water body.

The samples impacted by the Mediterranean Sea fell largely above the EF=0.500 line, except for one site (near to Barcelona, Spain). Although this site is right on the coast, the wind rose for the sampling period showed that this site was receiving mainly inland winds (or rather very few winds from the Mediterranean Sea) during the sampling period.

The samples impacted by the Baltic Sea showed a very clear signal, with all EF values being < 0.500 (range 0.479 – 0.499, n = 6). EF values < 0.500 in air samples from the Baltic region have been also reported in the Kattegat Sea by Sundqvist et al.[8] (range EFs: 0.475 – 0.500, n = 9) and in the Southern Baltic Sea by Wiberg et al.[9] (range EFs: 0.454 – 0.493, n = 21). Water samples from the Baltic Sea also showed EF values < 0.500 (range 0.439 - 0.466, n = 23), suggesting that: (i) a large part of the α-HCH measured in the air derives from the volatilisation from water, and (ii) this region shows a preference for depletion of the (+) α-HCH enantiomer. In contrast, samples impacted by the North Sea presented mostly racemic signatures, in accordance with reported EFs in air and water from the same region.[10]

The samples impacted by the Atlantic Ocean showed a large spread of EFs, both below and above 0.500. However, when plotting the EFs for the Atlantic samples versus latitude, we see that at latitudes below 50 degrees N, EFs were largely > 0.500, whereas at latitudes above 50 degrees N, EFs were largely < 0.500 (Figure 3). In the latter category, three sampling sites had EFs > 0.500, for which the discrepancies could not be explained by the wind direction.
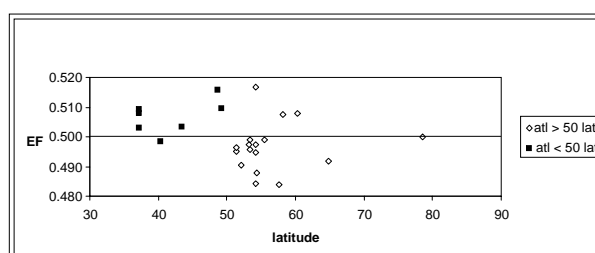

Figure 3. Distribution of EFs in samples impacted by the Atlantic Ocean versus latitude.

Harner et al. found non-racemic patterns (EFs < 0.500) in air from the Eastern Arctic Ocean, similar to the Baltic air samples (Figure 2).[11] This is supported also by EFs for α-HCH measured in air samples collected on a latitudinal transect during an Atlantic cruise.[12] This transect shows that the higher latitude samples (above 40 degrees N) have an EF below 0.5 (water samples at 50-60 degrees N also have an EF<0.5), whereas in the more southern samples, there is no clear trend with respect to enantiomer fractions. However, this probably relates more to the water than latitude; higher concentrations of α-HCH are found in the northern waters, because of water movement and quicker non-selective degradation in the Southern warm waters.

The inland samples also showed a large range of EFs. When plotting the EF values versus α-HCH concentration, we could see that the samples with the highest α-HCH concentration were racemic (EF = 0.500, above 6 ng/sampler) (Figure 4). These sampling sites with higher α-HCH levels resulting from past applications/production of technical HCH or from waste products from lindane production are located mainly in Eastern Europe, e.g. Hungary, Poland, Estonia, Russia and Kazakhstan. The high α-HCH concentrations and racemic EFs in air point to current use of technical HCH mixtures. However, the fact that the α-HCH/γ-HCH ratios are well below 4 points to the parallel use of technical lindane and technical HCH mixtures.[2]
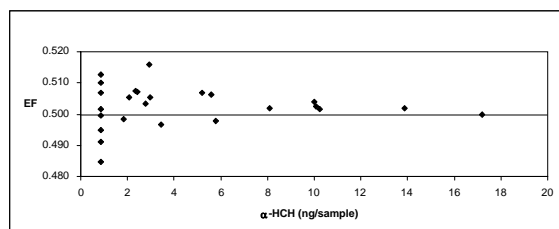

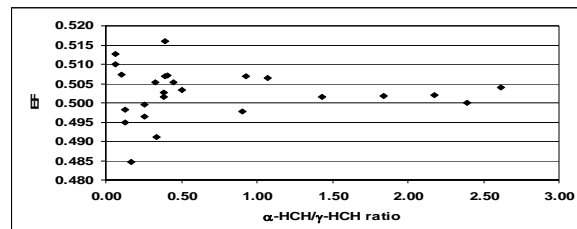Figure 4. Variation of EFs with concentration of α-HCH in inland samples.

Figure 5. Variation of EFs with the ratio α-HCH/γ-HCH in inland samples.

The Eastern European sites also have generally higher ratios α-HCH/γ-HCH (Figure 5). At lower α-HCH concentrations, the spread in the data increased, indicating the presence of a diffuse source of α-HCH, such as volatilization of weathered α-HCH from soil and water. The distribution of α-HCH shown by Figure 4 probably

reflects diffuse emissions from past usage in Europe and limited ongoing usage in the Eastern parts of the continent.[13] Between inland sites, urban sites have generally higher EFs than rural sites, with most of the values being > 0.500. (Figure 6; 1 - urban, 2 - rural). Shen et al. found that (+) α-HCH is enriched in air over continental Canada.[14]

Another interesting trend is how EFs change with distance from the sources of α-HCH. The sites with high α-HCH levels (see previous paragraph) are located at high longitudes, i.e. towards the east. If these sites are considered a source for the α-HCH present in European air, a correlation with longitude emerges for the rural inland sites (but not for the urban samples), after the "source" sites have been removed from the graph. This might be explained by an enhanced degradation of the (+) α-HCH enantiomer as the enantiomers travel further away from the source area (Figure 7).
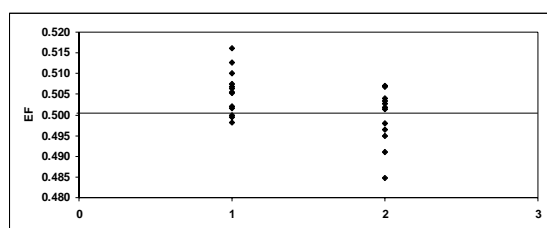

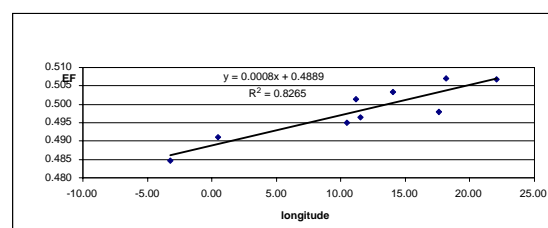Figure 6. Variation of EFs for urban (1) and rural (2) samples.

Figure 7. Variation of EFs in inland rural samples with longitude.

The present study provides further evidence that in the case of α-HCH, the concentration and chiral signature in the air is strongly dependent on the proximity to a water body from where it volatilises and it is impacted to a lesser extent by the volatilisation from soil. While the source of α-HCH is always land-based, it is possible that water bodies act as a "mixing bowl", integrating/averaging the various enantiomeric signatures arriving through a combination of local/regional transport. Because water bodies are large and well-mixed, they will dominate the chiral signature in air for samples close to the water body. Using enantioselective analysis, differences at medium scale (urban vs. rural sites) but also at larger scale (Mediterranean vs. Baltic Sea) are possible to be evidenced. As a consequence, the presence of correlations between EFs and concentrations of α-HCH, α-HCH/γ-HCH ratios, latitude and longitude of the sampling locations makes the use of enantioselective analysis a valuable tool to investigate source apportioning for chiral pollutants.

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