



Chiral persistent organic pollutants as tracers of atmospheric sources and fate: review and prospects for investigating climate change influences

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ABSTRACT

Elimination of persistent organic pollutants (POPs) under national and international controls reduces “primary” emissions, but “secondary” emissions continue from residues deposited in soil, water, ice and vegetation during former years of high usage. Secondary sources are expected to dominate in the future, when POPs transport and accumulation will be controlled by air–surface exchange and the biogeochemical cycle of organic carbon. Climate change is likely to affect mobilization of POPs through, e.g., increased temperature, loss of ice cover in polar regions, melting glaciers and changes in soil and water microbiology which affect degradation and transformation. Chiral compounds offer advantages for following transport and fate pathways because of their ability to distinguish racemic (newly released or protected from microbial attack) and nonracemic (microbially altered) sources. Here we explain the rationale for this approach and suggest applications where chiral POPs could aid investigation of climate-mediated exchange and degradation processes. Examples include distinguishing agricultural vs. non-agricultural and recently used vs. residual pesticides, degradation and sequestration processes in soil, historical vs. recent atmospheric deposition, sources in arctic air and influence of ice cover on volatilization.

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1. Introduction

Production and use of persistent organic pollutants (POPs) have been reduced or eliminated under the Stockholm Convention and other regional/national initiatives. In response to curbing “primary” emissions, concentrations of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in arctic air have dropped over two decades with times for 50% reduction of ~3–20 years (Hung et al., 2010). Residues of legacy POPs in arctic biota are also declining at 0.8–8% per year (Riget et al., 2010). Although encouraging, these downward trends are buffered by continuing release of POPs deposited in soil, water, ice and vegetation during former years of high usage (Ruzickova et al., 2008; Stemmler and Lammel, 2009; Li et al., 2010; Nizzetto et al., 2010a; Nizzetto et al., 2010b; Schuster et al., 2011). Such “secondary” emissions are expected to dominate in the future when POPs transport and accumulation will be controlled by air–surface exchange and the biogeochemical cycle of organic carbon (Nizzetto et al., 2010b; UNEP, 2011). Climate change may increase both primary and secondary emissions and thereby confound interpretation of temporal trend records (Macdonald et al., 2005; UNEP, 2011). Air concentrations of some POPs at arctic stations have recently stabilized or even increased. Statistically removing the earlier declining trends reveals rising residual concentrations which are

significantly associated with increased surface air temperature and loss of ice cover, suggesting revolatilization from secondary sources brought about by climate change (Ma et al., 2011). A comprehensive review of climate change influences on the global distribution and fate of POPs has recently been published (Kallenborn et al., 2012).

Chiral compounds offer special advantage for following transport and fate pathways. Enantiomers (see Section 2) have identical vapor pressures, water solubilities and partition coefficients among air, water and octanol. Transport (advection, deposition, and volatilization) and abiotic reactions (photolysis, hydrolysis, OH radical attack) will not change enantiomer proportions for the compounds discussed in this article, provided they take place in achiral environments. However, enzymes are chiral and enantioselective metabolism is the “rule rather than the exception” (Hegeman and Laane, 2002). Many commercial chiral chemicals are racemates (equal proportion of enantiomers). For these, nonracemic residues in the environment indicate microbial degradation in soil and water or enantioselective processes in higher organisms (e.g., absorption, translocation, excretion, preferential membrane transport). Determination of individual enantiomers by chromatography on chiral stationary phases provides the ability to distinguish racemic (newly released or

protected from microbial attack) and nonracemic (microbially weathered) sources.

Here we review enantioselective degradation of chiral OCPs and PCBs in soil and water, and use of enantiomer proportions to infer source contributions and follow environmental fate; e.g., distinguishing agricultural vs. non-agricultural and recently used vs. residual pesticides, degradation and sequestration processes in soil, historical vs. recent atmospheric deposition, sources in arctic air and influence of ice cover on volatilization. We suggest applications of chiral compounds to investigate of processes that are apt to be influenced by climate change.

2. Chiral Chemicals

Many classes of environmental contaminants include chiral compounds: pesticides, PCBs, brominated flame retardants (BFRs), pharmaceuticals and personal care products. Chiral compounds are mirror-image molecules having: (a) an asymmetric atom with four different substituents, e.g., *o,p'*-DDT; (b) steric hindrance which prevents rotation about a bond, leading to an asymmetric structure; e.g., "atropisomeric" PCBs; (c) cyclic POPs which have asymmetric carbons and/or lack a plane of symmetry, e.g., *trans*- and *cis*-chlordane (TC, CC), α -hexachlorocyclohexane (α -HCH). Metabolites are often chiral: *o,p'*-DDD, oxychlordane (OXY), heptachlor *exo*-epoxide (HEPX), atropisomeric PCB methyl sulfones and OH-PCBs. Some "prochiral" compounds are converted to chiral metabolites, e.g. the achiral pesticide lindane (γ -HCH) is metabolized to chiral γ -pentachlorocyclohexene (γ -PCCH (Huhnerfuss et al., 1992). Some compounds have more than one stereogenic feature, leading to multiple pairs of enantiomers. Principles of chirality, analytical methods and environmental applications for chiral POPs and other compounds have been reviewed (Kallenborn and Huhnerfuss, 2001; Berthod, 2006; Vetter and Bester, 2006; Wong, 2006; Garrison, 2006; Eljarrat et al., 2008; Huhnerfuss and Shah, 2009; Lehmler et al., 2010; Perez-Fernandez et al., 2010; Ulrich and Falconer, 2011).

Data from enantioselective analysis are expressed as enantiomer fraction, $EF = (+)/[(+) + (-)]$ or $E_1/(E_1 + E_2)$, where (+) and (-) refer to optical signs (direction of polarized light rotation), and E_1 and E_2 to the order of chromatographic peak elutions (De

Geus et al., 2000; Harner et al., 2000b; Ulrich et al., 2003). Enantiomers are also designated by *R*- and *S*- configurations according to the Cahn-Ingold-Prelog (CIP) rules (Huhnerfuss and Shah, 2009), but there is no relationship between *R*, *S* and optical signs. Sometimes the enantiomer ratio, $ER = (+)/(-)$ or E_1/E_2 , is used, $EF = ER/(ER + 1)$. A racemic compound has $EF = 0.5$ and $ER = 1$. Degradation can be ambivalent; i.e., depletion of either enantiomer, and averaging EFs can misrepresent the true extent of enantioselectivity. Deviation from racemic (DFR), the absolute value of $(0.5 - EF)$ has been suggested to express enantioselectivity regardless of the degradation preference (Harrad et al., 2003; Kurt-Karakus et al., 2005; Jamshidi et al., 2007).

3. Enantioselective Degradation in Soil and Water

3.1. Soil

Chiral POPs undergo enantioselective degradation in soil, resulting in accumulation of nonracemic residues. A survey of chiral PCBs in background soils along a transect from the U.K. to northern Norway found nonracemic residues in 50–88% of the samples (Schuster et al., 2011), and nonracemic TC and CC were reported in >80% of soils globally (Ulrich and Falconer, 2011). Reported EFs of OCPs and PCBs are listed in Supporting Material (SM), Tables S1 and S2. Frequencies of enantiomer depletions for OCPs in agricultural and background soils worldwide are summarized in Figure 1 from reports where such information is given or can be deduced. Dominant depletions are (-) α -HCH, (-)CC, (+)TC, although opposite preferences and racemic residues are also common. Residues of *o,p'*-DDT are almost equally divided among (+) or (-) depletion or racemic. Regional differences are evident; e.g. preferential depletion of (+)TC and (-)CC in soils of the midwestern (Aigner et al., 1998) and southern (Wiberg et al., 2001a) U.S.A. and in Mexico (Wong et al., 2010), but depletion of both (-)TC and (-)CC in soils of the Pearl River Delta, China (Li et al., 2006). In the case of metabolites, depletions of (-)HEPX and (-)OXY may reflect preferential formation of (+) rather than degradation of (-), although the relative importance of the two processes in soils has not been established. Weighted average EFs and pooled standard deviations from merging the individual data sets in Table S1 (see the SM) are: α -HCH 0.528 ± 0.095 , CC 0.531 ± 0.073 , TC 0.480 ± 0.067 and *o,p'*-DDT 0.511 ± 0.064 .

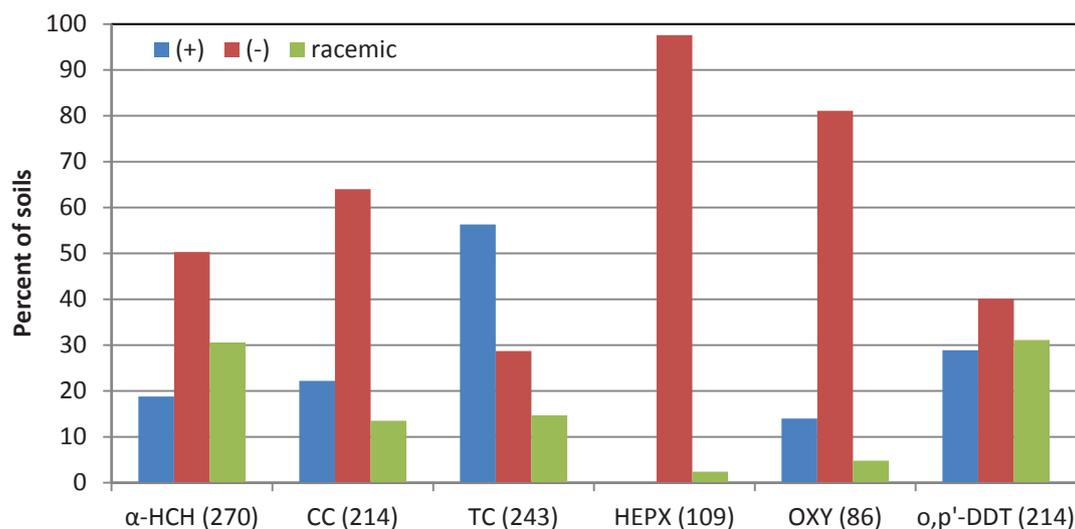


Figure 1. Percent of soils showing depletion of the (+) enantiomer (blue, $EF < 0.5$), depletion of the (-) enantiomer (red, $EF > 0.5$) and containing racemic residues (green, $EF = 0.5$) for α -HCH, *cis*-chlordane (CC), *trans*-chlordane (TC), heptachlor *exo*-epoxide (HEPX), oxychlordane (OXY) and *o,p'*-DDT (number of soils in parentheses), based on reports from the 1990s to the present where such information is given or can be deduced. Data are from: Falconer et al., 1997; Aigner et al., 1998; Finizio et al., 1998; Meijer et al., 2001; Wiberg et al., 2001a; Meijer et al., 2003; Bidleman et al., 2003; Eitzer et al., 2003; Bidleman and Leone, 2004; Kurt-Karakus et al., 2005; Bidleman et al., 2006; Ngabe and Bidleman, 2006; Li et al., 2006; Daly et al., 2007; Kurt-Karakus et al., 2008; Genualdi et al., 2009; Shen et al., 2009; Wong et al., 2009b; Wong et al., 2010; Covaci et al., 2010; Zhang et al., 2011; Ulrich and Falconer, 2011; Zhang et al., 2012b.

Factors influencing enantioselective degradation in soils are not well understood. Several studies have found that EFs or DFRs (see Section 2) were correlated only weakly or not at all with soil organic carbon or organic matter (Kurt–Karakus et al., 2005; Li et al., 2006; Koblizkova et al., 2008; Zhang et al., 2011). DFRs of chiral PCBs in soils have been associated with higher humus and organic nitrogen, soil texture (increased clay vs. sand content), and microbial biomass and its activity (Koblizkova et al., 2008). Zhang et al. (2011) found a weak negative correlation ($r^2 = 0.12$, $p = 0.03$) between the EF of α -HCH and microbial biomass in 38 soils and no correlation with soil texture. Enantioselectivity has been related to soil pH in some studies, but not in others. Soil pH affects carbon and nutrient availability, solubility of metals, and microbial and fungal communities (Rousk et al., 2009). Enantioselective degradation and/or racemization of some chiral fungicides and herbicides is influenced by soil pH (Buser and Muller, 1997; Muller and Buser, 1997; Buser and Muller, 1998; Buerge et al., 2003; Buerge et al., 2006; Li et al., 2011). HEPX, OXY and α -HCH in alpine soils were increasingly nonracemic at higher humus pH, which the authors attributed to more active biodegradation (Shen et al., 2009). However, pH was not a significant factor in explaining EFs of chlordanes, *o,p'*-DDT and α -HCH in Chinese soils (Li et al., 2006; Zhang et al., 2011). The EFs of chiral PCBs 95, 132 and 149 were correlated with pH at a high level of significance ($p = 6 \times 10^{-7}$ to 0.0035) for 101 Swiss soil samples, but r^2 values were low (0.08–0.22) (Bucheli and Brandli, 2006). A strong correlation was found between the EF of PCB 149 and pH in 12 Czech soils ($r^2 = 0.67$, $p = 0.0013$) (Bucheli and Brandli, 2006). Little work has been done to investigate abiotic interactions between soil components and chiral chemicals, but there is evidence for enantioselective sorption of chiral PCBs and the chiral herbicide methyl dichlorprop by humic acid and ash (Oravec et al., 2010).

The average relative standard deviation (RSD) in EFs of TC and CC was 8% in replicate plots spaced one meter apart in grassland and woodland areas (Kurt–Karakus et al., 2007; Kurt–Karakus et al., 2008). EFs of PCBs 95, 136 and 149 varied by 2–4% RSD when sampled repeatedly over several months at urban and suburban sites in Birmingham, U.K. (Jamshidi et al., 2007). The EF of PCB 95 varied by 1.5% RSD over several months at a background site near Birmingham (Desborough and Harrad, 2011). Much greater variability is seen when comparing soils regionally and globally (Kurt–Karakus et al., 2005; Li et al., 2006; Ulrich and Falconer, 2011) (Figure 1) and across land use categories. EF patterns of PCBs 95, 132, 149 and 174 in Swiss soils suggested differences between deciduous and coniferous forest, agriculture and grassland (Bucheli and Brandli, 2006). Such EF variations are larger than analytical (typically 1% or less) and can be attributed to local microbial communities.

Microbial processes in soil degrade POPs, but also lead to sequestering of residues into the soil matrix. These “bound residues” are less degradable and bioaccessible (Gevao et al., 2003; Barruio et al., 2008; Yang et al., 2009). Use of chiral compounds to follow this diagenesis was investigated by Wong and Bidleman (2011) and Wong et al. (2012). Chiral and achiral POPs were spiked into soil and aged for one year. Over that time, portions of the soil were extracted with dichloromethane (DCM) and analyzed. Volatilization potential was determined by passing nitrogen through a soil column and collecting the stripped residues on a sorbent trap. Increased binding to the soil and decreased volatility over time were indicated by a rise in the equilibrium soil–air partition coefficient, $K_{SA} = C_{SOIL}/C_{AIR}$. Spiked α -HCH and chiral BFRs β -1,2,5,6-tetrabromocyclooctane (β -TBCO) and α -1,2-dibromo-4-(1,2-dibromoethyl)cyclohexane (α -tetrabromoethylcyclohexane, α -TBECH) were partially degraded by enantioselective microbial activity, and over the aging period the EF in air deviated increasingly from the EF in DCM extracts of the soil (Figure 2). Results suggest that air stripping accesses the exchangeable, more easily degraded pool of chemical, while DCM extracts both the

exchangeable and less degraded bound pools, resulting in the discrepancy between EF_{AIR} and EF_{SOIL} .

Climate change may impact soil microbial diversity and respiration by altering CO_2 , soil temperature, precipitation patterns and soil moisture, vegetation communities and productivity, and the rate of organic matter decomposition (EEA, 2008; Anderson, 2011). The relative abundance of bacteria and fungi in soil were changed by manipulating CO_2 , temperature and precipitation (Castro et al., 2010), pH (Rousk et al., 2009) and soil frost (Haei et al., 2010; Haei et al., 2011) in experimental plots. Effects of such changes on the diagenesis of chiral compounds are poorly known but evidence suggests that enantioselectivity will be affected. In a pioneering study, Lewis et al. (1999) found that the degradation preferences for enantiomers of the herbicide methyl dichlorprop and the organophosphate insecticide cruformate (Ruelene) were shifted or even reversed by simulated global warming (increasing the soil temperature by 5°C), nutrient amendments or deforestation (conversion from forest to pasture). Analysis of 16S ribosomal RNA indicated changes in microbial populations. The authors surmised that enantioselectivity is controlled by activation of metabolically quiescent microbes or induction of specific enzymes.

3.2. Water

Early reports of enantioselective degradation of α -HCH in the North Sea (Faller et al., 1991) and the Baltic Sea (Huhnerfuss et al., 1992) sparked a new line of research on chiral pollutants in the marine environment. Today, α -HCH is by far the most investigated chiral compound in marine and fresh water. The PCCH degradation products of α -HCH and γ -HCH are also chiral, but are seldom reported (Huhnerfuss et al., 1992; Badea et al., 2011). Observations of nonracemic α -HCH in aquatic systems are compiled in Figure 3, where older data reported as ERs have been converted to EFs. Although measurements span two decades, systematic monitoring of EFs in water bodies has not been done to assess temporal trends. Degradation of (+) α -HCH is favored in most cases, but preferential loss of (–) α -HCH has been found in surface waters of some regions (Figure 3), and in ground water (Law et al., 2004) and dense nonaqueous phase liquids (DNAPL) (Badea et al., 2011) at industrial waste sites. Concentrations of HCHs decrease, and enantioselective degradation of α -HCH increases, with depth in the Arctic Ocean (Jantunen and Bidleman, 1996; Harner et al., 1999; Harner et al., 2000a). Total degradative loss of HCHs in an aquatic system is due to enantioselective and nonenantioselective microbial processes. Hydrolysis is an important removal mechanism in warm temperate waters, but is much slower in cold lakes and polar oceans (Ngabe et al., 1993). Estimated half lives in the eastern Arctic Ocean due to microbial degradation were 5.9, 23 and 18 y for (+) α -HCH, (–) α -HCH and γ -HCH (Harner et al., 1999; Harner et al., 2000a). These rates were included with measured temporal trends in concentration, estimates of advective flows and air–water gas exchange into a mass balance of α -HCH in the western Arctic Ocean, with the result that microbial degradation was the major loss term. The mass balance suggested that α -HCH could be virtually eliminated by 2040, with concentrations dropping from ~1–2 to <0.004–0.006 ng L⁻¹ within this decade (Pucko et al., 2012).

Concentrations and EFs of α -HCH have been reported in the Laurentian Great Lakes between Canada and the U.S.A., small lakes and wetlands in Ontario, Canada, and arctic lakes and wetlands (Law et al., 2001). Racemic α -HCH or preferential degradation of the (+) enantiomer was found in all systems. The low EF extremes were found in cold, oligotrophic lakes and arctic wetlands (Figure 3) and they were related to higher α -HCH concentrations and dissolved inorganic carbon, while more nearly racemic α -HCH was found in mesotrophic and eutrophic systems with higher particulate organic carbon and total phosphorus. Enantioselective

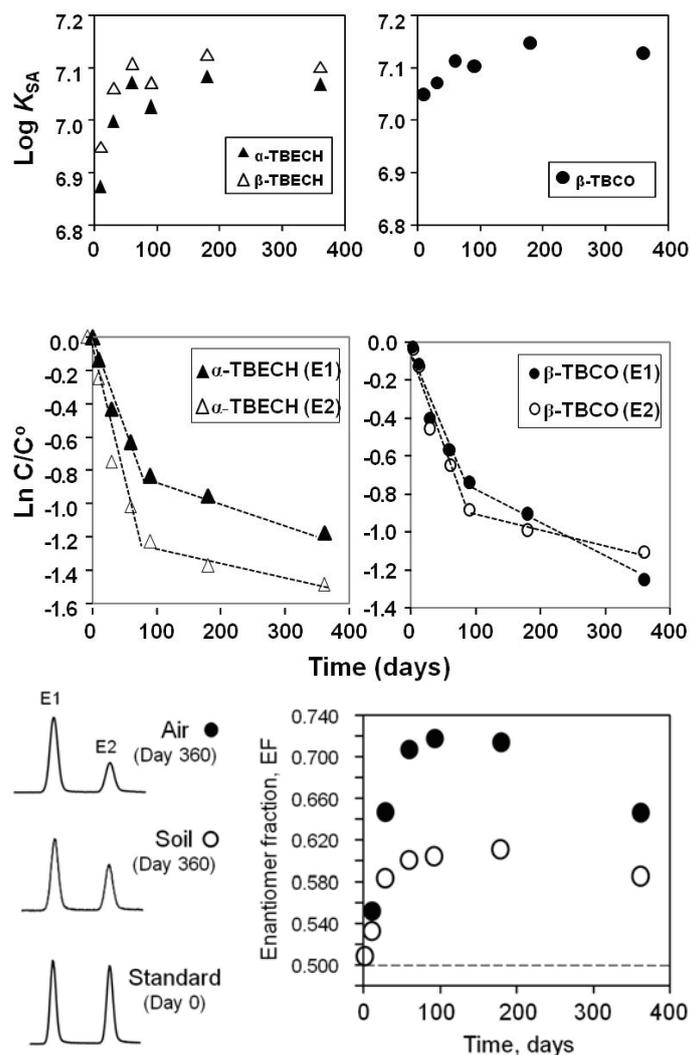


Figure 2. Increase in K_{SA} (top) and biphasic first-order plots of enantioselective degradation (middle) for the chiral brominated flame retardants α -tetrabromoethylcyclohexane (α -TBECH) and β -tetrabromocyclooctane (β -TBCO) in urban soil over 360 days after spiking. Bottom left: Chromatograms of α -TBECH enantiomers in an analytical standard, soil extracted with dichloromethane 360 days after spiking, and air equilibrated with the soil 360 days after spiking. Bottom right: Divergence of EFs of α -TBECH in air and soil with aging time (Wong et al., 2012).

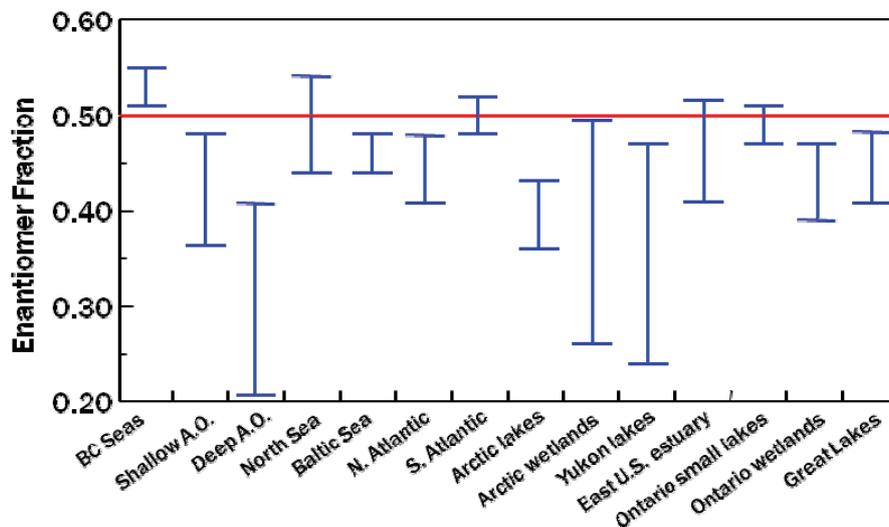


Figure 3. Range of EFs reported for α -HCH in aquatic systems, red line indicates racemic α -HCH ($EF = 0.5$). Data are from: Faller et al., 1991; Falconer et al., 1995; Jantunen and Bidleman, 1996; Ridal et al., 1997; Jantunen and Bidleman, 1998; Harner et al., 1999; Helm et al., 2000; Law et al., 2001; Wiberg et al., 2001b; Padma et al., 2003; Jantunen et al., 2004; Sundqvist et al., 2004; Jantunen et al., 2008a; Jantunen et al., 2008b; Lohmann et al., 2009; Pucko et al., 2010; Pucko et al., 2011; Wong et al., 2011; Zhang et al., 2012b.

degradation was greater (lower EFs) in lakes where α -HCH concentrations became elevated due to past loadings, and long water retention times maximize contact with sediments. Lower EFs occurred in arctic streams during low-flow periods when greater contact would take place with biofilms on rocks and sediment (Falconer et al., 1995; Helm et al., 2000; Law et al., 2001). Non-enantioselective microbial degradation with a half life of 0.6–1.4 y was the main loss process in an arctic lake over winter (Helm et al., 2000).

Padma et al. (2003) found greater enantioselective degradation of (+) α -HCH within the saline part of a temperate estuary with lower bacterial activity than in the upper freshwater reach with higher bacterial activity. Law et al. (2001) surmised that greater enantioselective degradation of α -HCH in oligotrophic systems is due to bacteria that have the ability to survive under low nutrient conditions by inducing multiple enzymes, shifting metabolic pathways, and taking up and using mixed carbon sources. The inverse relationship between enantioselectivity and lake trophic status may be due to the ability of oligotrophic microbes to metabolize or co-metabolize α -HCH whereas eutrophic microbes have ample carbon sources that are more easily metabolized.

Other chiral OCPs in water have been less investigated. TC and CC were racemic in the central Arctic Ocean in 1994 (Jantunen and Bidleman, 1998) and the Beaufort Sea in 1998–2001 (Hoekstra et al., 2003). CC was racemic in the North Atlantic – Greenland Sea in 2004 for most samples (Lohmann et al., 2009), while both TC and CC were nonracemic in 2008 (Zhang et al., 2012a). Depletion of (+)TC was found in the Laurentian Great Lakes Superior, Erie and Ontario. CC was racemic in lakes Superior and Erie and (+)CC was depleted in Lake Ontario (Jantunen et al., 2008a). Enrichment of (+)HEPX was found in the central Arctic Ocean (Jantunen and Bidleman, 1998), the North Atlantic (Lohmann et al., 2009; Zhang et al., 2012a) and the Great Lakes (Jantunen et al., 2008a), while HEPX was racemic in the Beaufort Sea (Hoekstra et al., 2003).

Climate warming is likely to impact algal and microbial communities in aquatic systems through loss of ice cover and consequently increased light intensity, earlier spring phytoplankton blooms, hydrological changes in wetlands which drain into rivers and lakes; and in the ocean by freshening due to lowered salinity (Macdonald et al., 2005). Impacts on enantioselective degradation of α -HCH and other OCPs are difficult to predict, especially since EFs are also apt to change due to decline in primary and rise in secondary emissions. Measurements over the last decade can serve as a baseline from which to assess these changes through future monitoring.

4. Soil–Air and Water–Air Exchange

Because enantiomers have the same physicochemical properties (see Section 2), EFs are not changed when evaporating from soil or water (Bidleman and Falconer, 1999). An example is shown in Figure 4 which shows EFs of racemic *o,p'*-DDT and slightly nonracemic chlordanes volatilizing from an Ontario farm soil during flux studies (Kurt–Karakus et al., 2006). The $EF_{AIR} = EF_{SOIL}$ and is distinguishable from more nonracemic residues in background air. Sampling of air was carried out at 15 cm over agricultural soils in the midwestern U.S. for TC, CC, OXY, HEPX and *o,p'*-DDT (Leone et al., 2001). When their published data for all compounds and sites are considered, EF_{SOIL} and EF_{AIR} are strongly correlated ($r^2=0.88$, $p=10^{-11}$, $n=24$). The EF_{AIR} for *o,p'*-DDT at 40 cm above agricultural soils in the southern U.S. was correlated to EF_{SOIL} ($r^2=0.65$, $p=0.0008$, $n=11$) (Bidleman and Leone, 2004). Close agreement was found between EF_{AIR} and EF_{SOIL} for TC and CC sampled at 3 cm over soil at a farm in the U.K. (Meijer et al., 2003). Studies of TC and CC volatilization at experimental sites in Connecticut, U.S.A. found highest concentrations and $EF_{AIR} = EF_{SOIL}$ at 50 cm, with lower concentrations and greater deviation between EF_{AIR} and EF_{SOIL} at 1.5–2.5 m due to dilution and mixing with chlordanes in background air (Mattina et al., 2002; Eitzer et al., 2003). PCB–95 from primary sources (see Section 5) was racemic in air sampled at 10–130 cm over a grassland site in the U.K., but nonracemic in the soil, air at 3 cm, and grass (Desborough and Harrad, 2011).

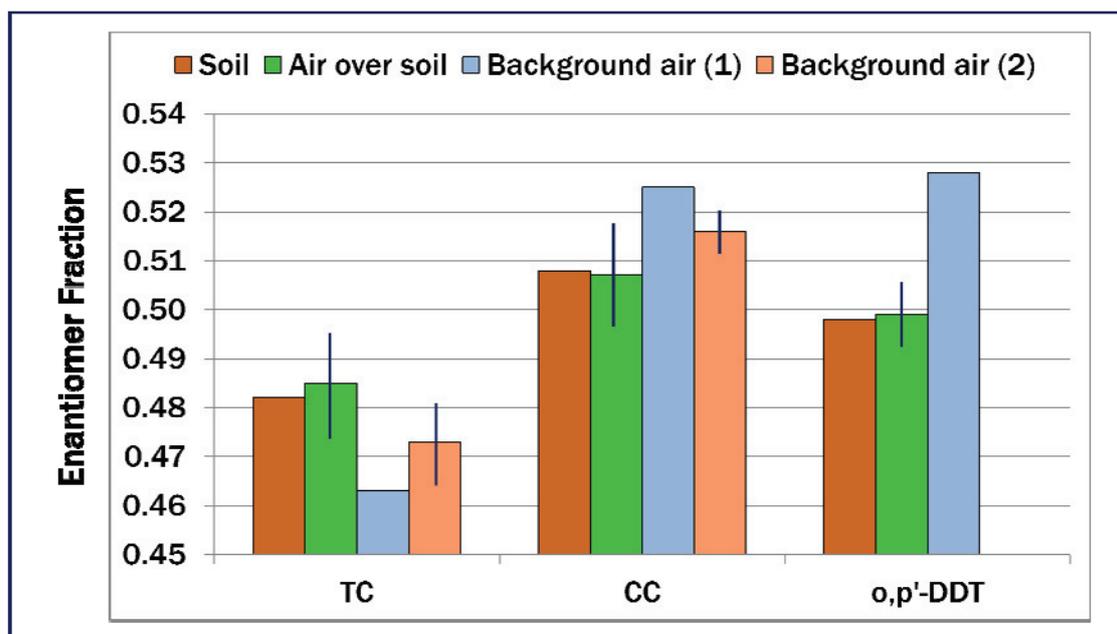


Figure 4. EFs of trans-chlordane (TC), cis-chlordane (CC) and *o,p'*-DDT in agricultural soil from an Ontario farm in 2004–2005 (Kurt–Karakus et al., 2006), multiple air samples collected within 200 cm of the soil surface, single sample of background air (1) from a site 30 km away during this study, and multiple samples of background air (2) from the same site in 2002–2003 (Gouin et al., 2007). Vertical lines are standard deviations where multiple samples were taken. Note close agreement of EFs in soil and air-over-soil, and differences from the background air samples.

Levels of α -HCH in arctic air have declined in step with reduced production and emissions of technical HCH after 1983 (Li and Bidleman, 2003). Consequently, water bodies that were loaded with α -HCH during the peak production in the 1970s – early 1980s became sources to the atmosphere beginning in the early 1990s (Jantunen and Bidleman, 1995; Wania et al., 1999; Pucko et al., 2012). Nonracemic α -HCH has been used to trace volatilization by air sampling over oceans (Jantunen and Bidleman, 1996; Harner et al., 1999; Jantunen et al., 2004; Ding et al., 2007; Jantunen et al., 2008b; Lohmann et al., 2009; Wong et al., 2011; Zhang et al., 2012a) large lakes (Ridal et al., 1997; Jantunen et al., 2008a) and seas (Wiberg et al., 2001b; Sundqvist et al., 2004). EFs in air over these systems varied from nearly racemic when long-range transport dominated to nonracemic upon volatilization from water. Such changes occurred seasonally or spatially in response to water temperature (Ridal et al., 1997; Sundqvist et al., 2004; Jantunen et al., 2008a) and ice cover (Jantunen and Bidleman, 1996; Jantunen et al., 2008b; Wong et al., 2011). Regional influences of these secondary sources are discussed in Section 5.2.

In the Arctic, ice effects are particularly dramatic. On a trans-arctic expedition in 1994, (-) α -HCH was depleted in the Bering-Chukchi seas whereas (+) α -HCH was depleted in the central Arctic Ocean and Greenland Sea. The α -HCH in air over these regions showed the same enantiomer depletions, except over the ice-covered portion of the central Arctic Ocean where α -HCH in air was racemic (Jantunen and Bidleman, 1996). Subsequent investigations in the Canadian Archipelago in 1999 (Jantunen et al., 2008b) and 2007–2008 (Wong et al., 2011) found an abrupt rise in α -HCH air concentrations and an increased proportion of nonracemic α -HCH in air during the spring–summer ice breakup (Figure 5). EFs of α -HCH help to speciate delivery and removal mechanisms from the Arctic Ocean snowpack and ice; e.g. atmospheric deposition which delivers nearly racemic α -HCH vs.

brine intrusion which brings nonracemic α -HCH from seawater upward into the ice and snow cover (Pucko et al., 2011).

5. Regional and Long-Range Transport

5.1. Chlordanes

Soils worldwide contain chlordanes with enantiomer depletion frequencies: (+)TC 56%, (-)TC 29%, (+)CC 22%, (-)CC 64%. Racemic TC and CC were found in 15% and 14% of the soils (Figure 1). Soils around house foundations treated with chlordane for termite control (Eitzer et al., 2001) and air within termiticide-treated homes (Jantunen et al., 2000; Leone et al., 2000) contained racemic TC and CC. Chlordanes in air of rural and background areas of North America tend to be nonracemic with depletion of (+)TC and (-)CC, and closer to racemic in the air of large cities where some termiticide use would be expected (Shen et al., 2004; Gouin et al., 2007; Ulrich and Falconer, 2011). EFs of TC and CC in ambient air of the Laurentian Great Lakes region are intermediate between nonracemic EFs in regional soils and racemic termiticides (Ulrich and Hites, 1998; Bidleman and Falconer, 1999; Gouin et al., 2007), showing the contribution of both source types. Racemic and nonracemic CC were found in the snowpacks of national parks in the western U.S.A., and explained by proximity to either urban or agricultural sources (Genualdi et al., 2011). TC and CC in the air of Mexico were closer to racemic (Wong et al., 2009a) than in the Great Lakes region, while soils in Mexico contained low and nonracemic residues, suggesting that chlordanes in the air of Mexico are derived from sources other than soil emissions (Wong et al., 2010). Nonracemic TC and CC were found in air of Costa Rica (Daly et al., 2007). HEPX in air is nearly always enriched in the (+) enantiomer (Venier and Hites, 2007; Ulrich and Falconer, 2011), and is likely derived from soil emissions (Bidleman et al., 1998).

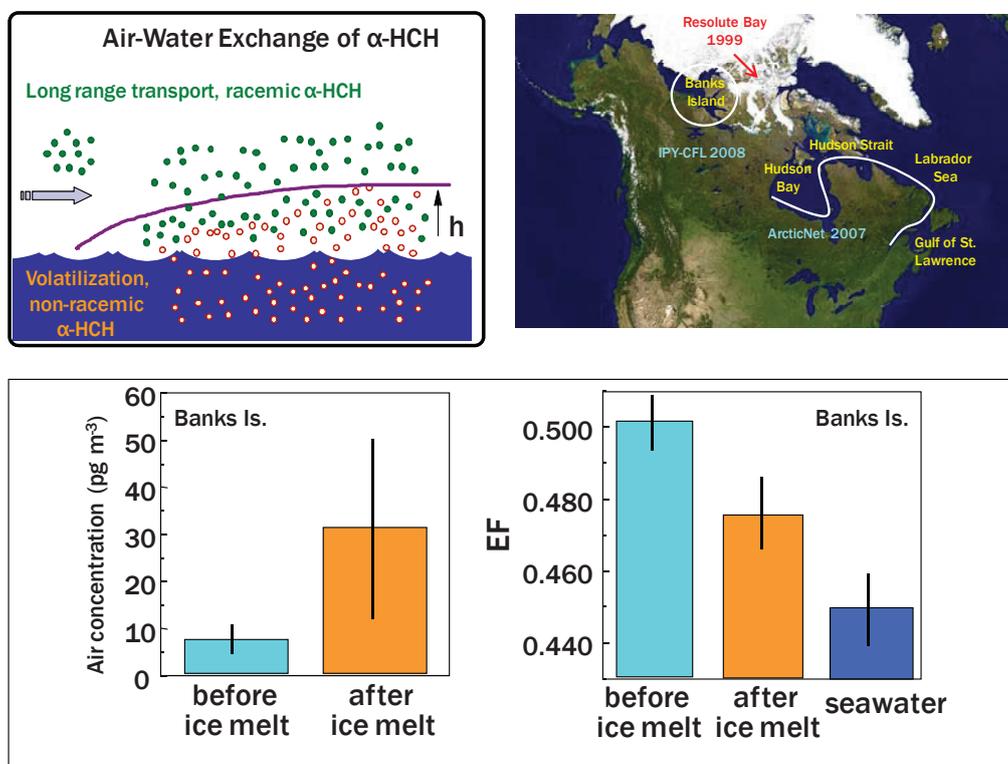


Figure 5. Top left: Sources of α -HCH in the marine boundary layer from long-range transport (racemic) and volatilization from the ocean (nonracemic). Top right: Expeditions in the Canadian Archipelago: Resolute Bay on Tundra Northwest 1999, ArcticNet 2007 and International Polar Year (IPY) – Circumpolar Flaw Lead (CFL) 2008. Bottom left: Increase in air concentrations of α -HCH sampled from shipboard after spring ice breakup at Banks Island (IPY-CFL 2008) and bottom right: switch from racemic α -HCH in air before ice melt (EF = 0.504 ± 0.008) to nonracemic α -HCH (EF = 0.476 ± 0.010) after ice melt, in response to volatilization of nonracemic α -HCH from seawater (EF = 0.457 ± 0.019) (Wong et al., 2011). Similar results were found at Resolute Bay in 1999 (Jantunen et al., 2008b).

TC and CC were racemic in air at Okinawa, Japan in 2004, and ratios of TC/CC were similar to those in technical chlordane. These diagnostics suggest fresh sources or limited biotransformation (Genualdi et al., 2009). The frequency of racemic TC and CC was 50% at 500 m, 89% at 1 249 m, and 92% at 2 763 m at mountain sites in the U.S. Pacific Northwest during 2003–2006, suggesting that chlordanes may be racemic in the free troposphere (Genualdi et al., 2009).

Ground-level air samples collected at the arctic monitoring stations Alert, Canada; Dunai, Russia; and Pallas, Finland, and at the temperate station Rovik on the Swedish west coast during the mid–1990s to 2001 showed depletion of (+)TC, (–)CC, and E1 of chlordane MC5 (Bidleman et al., 2002; Bidleman et al., 2004). In contrast, racemic TC and CC were found in archived samples of atmospheric deposition collected in Sweden, Iceland and Slovakia in 1971–1973 (Bidleman et al., 2004). A sediment core collected in 1999 from a lake on Devon Island (Canadian Arctic) recorded the trend of chlordane deposition (Bidleman et al., 2004; Stern et al., 2005). Depletion of (+)TC was found with EFs closest to racemic in the 1940s – 1950s, decreasing in the 1960s –1970s, and lowest in the 1980s –1990s.

Ulrich et al. (2009) found general depletion of (+)TC and (–)CC in sediments of U.S. lakes, rivers and reservoirs, where sources included soil erosion and atmospheric deposition. In several systems, DFR was greatest in the upper, more recent sediment layers and less at depth, similar to the Devon Island profile. Although diagenesis of deposited chlordanes cannot be ruled out, these studies and an investigation in Long Island Sound, U.S.A. (Li et al., 2007) indicates that enantioselective degradation of TC and CC does not take place in deposited sediments. Otherwise, deviation from racemic would be greater in the deeper sediment layers (Ulrich et al., 2009; Ulrich and Falconer, 2011).

These observations suggest that sources of chlordane have changed over time. Atmospheric transport and soil erosion were dominated by racemic chlordanes in the past and now are influenced to a greater extent by volatilization and erosion of nonracemic residues in soils. Sediment cores from other areas may be useful for inferring recent and historic chlordane deposition from erosion and atmospheric sources.

5.2. α -HCH

Regional patterns of α -HCH in air were examined throughout Europe and over the Atlantic Ocean (Covaci et al., 2010). The proximity to a large water body had a strong influence on EFs which were predominantly: Baltic air <0.5, Mediterranean air >0.5, North Atlantic above 40–50°N <0.5 and lower latitudes >0.5. No clear trend in EFs was seen in air samples from the African coast and South Atlantic. Inland air samples contained racemic α -HCH at higher concentrations and variable EFs at lower concentrations. Urban air tended to have EFs ≥ 0.5 while EFs ≤ 0.5 were found in rural air. Preferential degradation in grassland and woodland soils was largely of (–) α -HCH and EFs increased with higher concentration. Latitude and longitude influences were also evident in the air–soil–grass system. The survey showed that concentrations and EFs in air are controlled by secondary sources from water and soil, in which local microbial populations play a major role, and also by continuing emissions from primary sources; e.g., past production/waste disposal sites in eastern Europe.

Influence of large water bodies on the EFs of α -HCH in air is seen in other studies. Bethan et al. (2001) found that the enantiomer composition of α -HCH in rain collected on the Wadden Sea coast was seasonally dependent, depleted in the (+) enantiomer in late summer – early autumn and closer to racemic in the colder months. Genualdi et al. (2009) sampled air at mountain sites in western U.S. national parks and found that for trans–pacific

events, α -HCH tended to be racemic for transport above and nonracemic for transport below the marine boundary layer. A passive air sampling campaign across North America found that α -HCH was racemic or slightly depleted in the (–) enantiomer in air samples from inland and in the high Arctic where the sea is mainly ice covered (Shen et al., 2004). Higher concentrations and strong depletion of (+) α -HCH were found over the eastern Canadian Archipelago, the eastern Canada seaboard and the north shore of Lake Superior due to volatilization from open water. Depletion of (–) α -HCH was found on the west coast of Canada (Shen et al., 2004), possibly from similar signatures in regional soils (Falconer et al., 1997) or trans–pacific transport (Genualdi et al., 2009).

5.3. DDT compounds

DDT was applied in Mexico for malaria control until 2000, particularly in the southern part of the country, and high levels have been reported in soils of communities where DDT was applied (Herrera–Portugal et al., 2005). Surveys in air (Wong et al., 2009) and nonagricultural soils (Wong et al., 2010) in Mexico found a greater proportion of “fresh” DDT, as indicated by the fraction $F_{DDTE} = p,p'-DDT/(p,p'-DDT + p,p'-DDE)$, in the southern part of the country. The o,p' -DDT in air samples was racemic in some cases or depleted in either enantiomer in others. The DFR was less at more southern latitudes ($r^2 = 0.57$, $p = 0.001$, $n=15$) with higher DDT use ($r^2 = 0.33$, $p = 0.03$, $n=15$). This agrees with the relative “freshness” of DDT in southern Mexico, indicated by the higher F_{DDTE} (see above), or may indicate lack of enantioselective degradation in sites with greater DDT applications. A single study has reported nonracemic o,p' -DDD, in ambient air of Arkansas, U.S.A. (Venier and Hites, 2007), although nonracemic o,p' -DDD was found in soils of the Czech Republic (Koblizkova et al., 2008). DDT has an exemption under the Stockholm Convention when used for vector control in accordance with World Health Organization guidelines (WHO, 2004). DDT residues, particularly o,p' -DDT and o,p' -DDE, are impurities in the pesticide dicofol and contribute to air contamination in the Taihu Lake region of China (Qiu et al., 2004; Qiu et al., 2005; Li et al., 2006). Together with proportions of parent and metabolite compounds, chiral analysis of o,p' -DDT and o,p' -DDD could be useful in speciating DDT sources.

5.4. Chiral PCBs

Chiral PCBs 95, 136 and 149 were racemic in ambient air of the Birmingham, U.K. region, while soil residues were generally nonracemic. Significant differences between air and soil were found at a greater number of sites when comparing DFRs rather than EFs, since the soil EFs varied from above 0.5 to below 0.5 at the sites (Jamshidi et al., 2007). Racemic PCBs in air and nonracemic PCBs in soil were found at other U.K. sites, despite calculations showing that PCB fugacity in soil was higher than in air and net volatilization would be expected (Robson and Harrad, 2004). PCB 95 was racemic in air samples collected 10–130 cm over a grassland site in the U.K., but nonracemic in the soil. However, PCB 95 was nonracemic in air at 3 cm height and in grass (Desborough and Harrad, 2011). Enantioselective degradation of PCBs 95,132, 149 and 174 was found in background soils collected on a transect from the southern U.K. to Norway in 2008, while racemic PCBs 95 and 149 were found in 2006–2008 air samples from along the route (Schuster et al., 2011). A similar application was used to investigate sources of PCBs in the air of the Hudson River estuary (Asher et al., 2007). PCBs 91, 95, 136 and 149 were racemic in air, but nonracemic in water and sediment, suggesting that undegraded local sources dominated PCB input to the air and not volatilization from the estuary. These measurements provide evidence that primary emissions continue to dominate the burden of PCBs in the atmosphere rather than volatilization from soils. The situation is likely to evolve in the future, as primary sources dissipate and secondary sources become dominant.

6. New Direction: Coupling Enantiospecific and Stable Isotope Analyses

Microbial degradation of organic compounds is frequently accompanied by shifts in carbon stable isotope composition which can be followed by compound-specific isotope analysis (CSIA) (Elsner et al., 2005; Hoffstetter et al., 2008). For example, reductive dechlorination of γ -HCH by sulfate-reducing bacteria resulted in ^{13}C enrichment of the residual γ -HCH as the ^{12}C - γ -HCH was preferentially utilized (Badea et al., 2009). Isotopic fractionation occurs mainly during formation or cleavage of chemical bonds and to a much smaller extent during phase transformation processes such as volatilization, sorption or diffusion (Hoffstetter et al., 2008). In this respect, CSIA and enantioselective analyses are complimentary tools for investigating sources, transport and transformation pathways, but they have seldom been coupled. Recently Badea et al. (2011) reported an enantiomer-specific stable isotope carbon analysis (ESIA) to investigate the fate of α -HCH. ESIA was applied to α -HCH degraded in anaerobic laboratory culture of *Clostridium pasteurianum* and naturally in DNAPL below ground at a former chemical plant. Spiked racemic α -HCH was degraded within nine days of laboratory incubation and although residues were enriched in ^{13}C - α -HCH, the degradation process was not enantioselective. The DNAPL samples also showed ^{13}C isotopic fractionation, and for two of three samples this isotopic fractionation was accompanied by shifts in EFs away from racemic. This pioneering study exemplifies the potential of the coupled ESIA technique for probing microbial degradation pathways that may or may not proceed enantioselectively.

7. Chiral Tracers and Climate Change

Nizzetto et al. (2010b) discussed the transition from a primary source controlled world to one dominated by secondary emissions, where POPs accumulate in reservoirs of organic carbon and biogeochemical processes govern their transport and fate. These processes are likely to involve enantioselective degradation in soil and water and exchanges with the atmosphere. Chiral tracers can aid transport and fate investigations in situations where there is enantioselective degradation:

(a) Enantioselective degradation metrics (EFs, DFRs and degradation preference frequencies) reflect the present composition and activity of microbial communities, and these are likely to shift with climate change. Including chiral analysis in long-running atmospheric and aquatic monitoring programs for POPs could reveal large-scale impacts on microbial processing of POPs in soil and water, as well as continuing primary-secondary source transitions. The range of EFs for chiral OCPs (see the SM, Table S1) and PCBs (Table S2) in background soils is much greater than in air, attesting to enantioselective degradation following atmospheric deposition. Re-emission of these deposited POPs will inject a more weathered EF signature into the atmosphere. The present potential for soils and water bodies to influence OCP EFs in air is suggested by their global data base (see the SM, Tables S1 and S2, Figures 1 and 3), though there are likely regional differences in EF “footprints” which have not yet been defined. Such differences are clearly shown for α -HCH in water (Figure 3 and Covaci et al., 2010) and for chlordanes in soil (Section 3.1).

(b) Chiral POPs could be useful for following cycling within forest ecosystem; e.g., volatilization from soil, atmospheric deposition, foliar uptake and release. Climate change is predicted to impact accumulation and release of POPs from the forest canopy (Nizzetto and Perlinger, 2012). Enantioselective transport and/or metabolism of chiral POPs within plant tissues of food crops has been demonstrated for chlordanes (Mattina et al., 2002) and in poplar trees for PCBs (Zhai et al., 2011). It has been argued that global warming may alter uptake and distribution of radionuclides in plants due to changes in soil physicochemical properties,

precipitation and temperature (Dowdall et al., 2008), and these considerations may also apply to organic chemicals.

(c) Revolatilization of POPs from the Arctic Ocean takes place in open water areas, which expand as the ocean loses ice cover seasonally and over the longer term due to climate warming. Chiral tracers are a sensitive indicator of re-emission during ice breakup, as demonstrated for α -HCH (see Section 5), and this concept could be applied to other chiral OCPs and PCBs in the Arctic Ocean and large seasonally frozen lakes.

(d) Melting glaciers release stored POPs into receiving waters (Geisz et al., 2008; Bogdal et al., 2009; Schmid et al., 2011). Sediment cores record the change in chlordane deposition from racemic in the past to nonracemic recently (Section 5). Similarly, snow/ice cores and glacial runoff might be examined for chlordanes and other chiral POPs to determine their diagenetic history.

(e) Microbial processes in soil degrade POPs, but also lead to sequestering of residues into the soil matrix. Chiral compounds show promise for following degradation and changes in volatility during aging of POPs in soil, and migration from exchangeable to bound pools (Section 3.1).

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Supporting Material Available

Reported enantiomer fractions of chiral organochlorine pesticides and metabolites in soil (Table S1), Reported enantiomer fractions of chiral PCBs in soil (Table S2). This information is available free of charge via the Internet at <http://www.atmospolres.com>.

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