



Biannual cycles of organochlorine pesticide enantiomers in arctic air

T. F. Bidleman et al.

Biannual cycles of organochlorine pesticide enantiomers in arctic air suggest changing sources and pathways

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| | |
|--------------------------|--------------|
| Title Page | |
| Abstract | Introduction |
| Conclusions | References |
| Tables | Figures |
| ◀ | ▶ |
| ◀ | ▶ |
| Back | Close |
| Full Screen / Esc | |
| Printer-friendly Version | |
| Interactive Discussion | |



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**Biannual cycles of
organochlorine
pesticide
enantiomers in arctic
air**

T. F. Bidleman et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

Air samples collected during 1994–2000 at the Canadian arctic air monitoring station Alert (82°30' N, 62°20' W) were analyzed by enantiospecific gas chromatography – mass spectrometry for α -hexachlorocyclohexane (α -HCH), *trans*-chlordane (TC) and *cis*-chlordane (CC). Results were expressed as enantiomer fractions (EF = quantities of (+)/[(+)+(–)] enantiomers), where EFs = 0.5, < 0.5 and > 0.5 indicate racemic composition, and preferential depletion of (+) and (–) enantiomers, respectively. Long-term average EFs were close to racemic values for α -HCH (0.504 ± 0.004 , $n = 197$) and CC (0.505 ± 0.004 , $n = 162$), and deviated farther from racemic for TC (0.470 ± 0.013 , $n = 165$). Digital filtration analysis revealed biannual cycles of lower α -HCH EFs in summer-fall and higher EFs in winter-spring. These cycles suggest volatilization of partially degraded α -HCH with EF < 0.5 from open water and advection to Alert during the warm season, and background transport of α -HCH with EF > 0.5 during the cold season. The contribution of sea-volatilized α -HCH was only 11 % at Alert, vs. 32 % at Resolute Bay (74.68° N, 94.90° W) in 1999. EFs of TC also followed biannual cycles of lower and higher values in the warm and cold seasons. These were in phase with low and high cycles of the TC/CC ratio (expressed as $F_{TC} = TC/(TC + CC)$), which suggests greater contribution of microbially “weathered” TC in summer-fall vs. winter-spring. CC was closer to racemic than TC and displayed seasonal cycles only in 1997–1998. EF profiles are likely to change with rising contribution of secondary emission sources, weathering of residues in the environment, and loss of ice cover in the Arctic. Enantiomer-specific analysis could provide added forensic capability to air monitoring programs.

1 Introduction

Production and use of 12 persistent organic pollutants (POPs) were discontinued worldwide in 2001 under the Stockholm Convention. Nine of these were organochlorine

Biannual cycles of organochlorine pesticide enantiomers in arctic air

T. F. Bidleman et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



pesticides (OCPs): aldrin, dieldrin, endrin, chlordane, DDT, heptachlor, hexachlorobenzene, mirex and toxaphene. Three OCPs were added later: hexachlorocyclohexanes (HCHs) and chlordecone in 2009 and endosulfan in 2011 (UNEP, 2014). Some OCPs were already in decline by the 1980s and 1990s through country-specific and regional restrictions and bans; e.g., technical HCH, DDT and toxaphene (Li and Macdonald, 2005; Wong et al., 2005).

Residues of POPs remain in soil (Dalla Valle et al., 2005), vegetation (Dalla Valle et al., 2004) and oceans (Pućko et al., 2013; Stemmler and Lammel, 2009, 2013; Wöhrnschimmel et al., 2012; Xie et al., 2011) as a legacy of 50 or more decades of usage. Emissions from these “secondary sources” buffer atmospheric concentrations in background regions (Cabrerizo et al., 2011; Nizzetto and Perlinger, 2012; Nizzetto et al., 2010; Stemmler and Lammel, 2009; Jantunen et al., 2008; Wöhrnschimmel et al., 2012; Wong et al., 2011). Climate change is expected to increase emissions from both primary and secondary sources (Gouin et al., 2013; Kallenborn et al., 2012a, b; Macdonald et al., 2005; UNEP, 2011), and one consequence is to confound interpretation of temporal trends derived from long-term monitoring data (Kallenborn et al., 2012b; Macdonald et al., 2005). Concentrations of most OCPs in arctic air have fallen over the last two decades (Becker et al., 2012; Hung et al., 2010; Ma et al., 2011), but some have declined more slowly than others or even risen slightly after about 2000. The slowed declines have been attributed to increased volatilization of OCP residues from environmental reservoirs (Becker et al., 2012; Hung et al., 2010; Ma et al., 2011) and linked to rising temperatures and decreasing ice cover (Ma et al., 2011).

Many POPs are chiral, including the OCPs α -HCH (the major constituent of technical HCH) and technical chlordane components *trans*-chlordane (TC) and *cis*-chlordane (CC). Each of these chiral compounds consists of two enantiomers which have the same physicochemical properties. Abiotic transport and transformation processes will not change enantiomer proportions provided they take place in achiral environments. However, enzymes are chiral and enantioselective metabolism of xenobiotics is the “rule rather than the exception” (Hegeman and Laane, 2002). Chiral OCPs were pro-

Biannual cycles of organochlorine pesticide enantiomers in arctic air

T. F. Bidleman et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Biannual cycles of organochlorine pesticide enantiomers in arctic air

T. F. Bidleman et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

duced as racemates (equal proportion of enantiomers), and occurrence of nonracemic residues in soil and water indicates microbial degradation. Enantiospecific analysis of chiral compounds offers unique opportunities in environmental forensics by distinguishing racemic (newly released or protected from microbial attack) and nonracemic (microbially weathered) sources (Bidleman et al., 2012, 2013; Hühnerfuss and Shah, 2009). Volatilization of partially degraded POPs from soil and water carries their distinctive nonracemic enantiomer proportions into the overlying air and such investigations have been recently reviewed (Bidleman et al., 2012, 2013; Ulrich and Falconer, 2011).

Measurements of chiral OCPs in the arctic physical environment have focused one or several sites at a particular time and there have been few investigations of temporal trends. Here we examine the enantiomer proportions of α -HCH, TC and CC in a time series of air samples collected from 1994–2000 at the Alert, Canada monitoring station to gain insight to seasonal changes in sources and transport pathways. This is the largest data set of enantiospecific analytical data for chlordanes at an arctic air monitoring station and the first for α -HCH.

2 Materials and methods

Air samples were collected at Alert, Ellesmere Island, Canada (82°30' N, 62°20' W, 200 m a.s.l.) as part of a monitoring program that has been continuous from 1992 to the present. Sampling and analytical methods have been summarized by Fellin et al. (1996) and Halsall et al. (1998). Archived extracts of polyurethane foam traps, representing gas-phase components, were obtained for chiral analysis from January 1994 through week 34 of 2000. Those from 1994 were composites of four 7-day samples, while individual 7-day samples were available in the other years. Gaps prevented full coverage in any year (Table 1). Enantiomers of α -HCH, TC and CC were determined in the extracts using previously described methods and quality control procedures (Bidleman et al., 2002; Jantunen et al., 2008, 1998; Kurt-Karakus et al., 2005; Wong et al., 2011). Separations were carried out on either Betadex-120 (BDX, 30 m \times 0.25 mm

i.d., 0.25 μm film) or BGB-172 (BGB, 15m × 0.25mm i.d., 0.25 μm film) chiral-phase columns, with detection by electron capture negative ion mass spectrometry. Analytical data were expressed as enantiomer fraction, EF = quantities of (+)/[(+) + (-)] enantiomers. A racemic compound has EF = 0.5, whereas EFs < 0.5 and > 0.5 indicate depletion of (+) and (-) enantiomers, respectively. In some cases, air samples were analyzed on both columns and slight, but significant, biases were noticed. The average $EF_{BGB} = (0.984 \pm 0.022) \cdot EF_{BDX}$ for TC ($p < 0.0001$, $n = 38$), $EF_{BGB} = (1.006 \pm 0.009) \cdot EF_{BDX}$ for CC ($p < 0.04$, $n = 11$) and $EF_{BGB} = (1.010 \pm 0.019) \cdot EF_{BDX}$ for α-HCH ($p < 0.002$, $n = 41$). Since the BGB column was used for most analyses, results from the BDX column were adjusted to the BGB scales.

Time series analysis was conducted by digital filtration (DF) to give best fits for seasonal and long-term trends at 95% confidence (Hung et al., 2002). Air parcel trajectories backwards from Alert were calculated four times each day (00:00, 06:00, 12:00 and 18:00 UTC) at 10 m a.g.l. and going back 72 h over each sampling period (Canadian Meteorological Centre). Ice cover data for the Canadian Archipelago and southern Beaufort Sea were obtained from the Canadian Ice Service (Environment Canada), through the tool IceGraph 2.0 (<http://www.ec.gc.ca/glaces-ice/?lang=En&n=A1A338F4-1&offset=5&toc=show>, accessed 6 July 2014).

3 Results and discussion

OCP concentrations and analysis of seasonal and long-term trends are presented elsewhere (Becker et al., 2008, 2012; Halsall et al., 1998; Hung et al., 2002, 2005, 2010; Su et al., 2008; Wöhrnschimmel et al., 2012). Annual mean air concentrations and EFs of α-HCH, TC and CC from 1994–2000 are summarized in Table 1. The three OCPs declined significantly during this decade, times for 50% concentration decrease between 1993–2001 were 5.0, 4.9 and 6.7 years, respectively (Hung et al., 2010).

ACPD

14, 25027–25050, 2014

Biannual cycles of organochlorine pesticide enantiomers in arctic air

T. F. Bidleman et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



3.1 α -HCH

Emissions of α -HCH from technical HCH peaked in the early 1980s and were greatly reduced by the early 1990s, due largely to bans or restrictions implemented by China, India and the former Soviet Union. By the end of the 1990s arctic air concentrations had dropped to less than 10% of peak values (Li and Macdonald, 2005). A global fate and transport model indicates that secondary emissions of α -HCH from soil and water closely tracked primary emissions throughout technical HCH usage history, and secondary emissions came into dominance in the late 1990s (Wöhrnschimmel et al., 2012).

The mean EF of α -HCH (0.504 ± 0.004 , $n = 197$) over all years (including the partial year 2000) was close to racemic and little interannual variation was found (Table 1). Greater insight is provided by plotting the time series of EFs (Fig. 1a), where DF analysis shows the fitted EF curve often dipping below the long-term mean in summer-fall and rising above the mean in winter-spring. A chart of fractional ice cover in the Archipelago and southern Beaufort Sea is shown in Fig. 1b. Minimum ice cover occurred between weeks 36–39, with the window for 50% ice cover between weeks 29–45. Superimposing these plots (Fig. 1) shows that the EF minima occur during periods of more open water, suggesting α -HCH volatilization from the ocean. Average summer-fall minima and winter-spring maxima EFs from the DF analysis are 0.500 ± 0.003 and 0.507 ± 0.002 ($n = 7$ pairs), and are significantly different at $p = 0.0007$ (paired t test, two sample for means). Sources of air to Alert during the minimum EF periods are shown in Fig. S1 of Supplement as combined 72 h back trajectories from the end of July to mid-October. Air parcels arriving from NE–NW pass over areas of the Arctic Ocean that are mainly ice-covered, while those from the SE–W traverse unfrozen areas of Baffin Bay, the Archipelago and southern Beaufort Sea. The α -HCH in surface water of this region in 1999 was strongly depleted in the (+) enantiomer, with EFs 0.432–0.463, averaging 0.442 ± 0.007 (Bidleman et al., 2007).

**Biannual cycles of
organochlorine
pesticide
enantiomers in arctic
air**

T. F. Bidleman et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Measurements at Resolute Bay (74.68° N, 94.90° W, 67 m a.s.l.) on Cornwallis Island in 1999 found that α -HCH in air was nearly racemic during periods of ice cover and nonracemic after ice breakup. Application of the Harner et al. (2000) source apportionment relationship estimated that seawater volatilization contributed 32 % of the α -HCH in air during the open water period (Jantunen et al., 2008). Similar differences in EFs of α -HCH in air between ice-covered and ice-free periods were found from shipboard measurements in the southern Beaufort Sea (Wong et al., 2011). Alert in the high Arctic appears much less influenced by reemission of nonracemic α -HCH from the ocean. Assuming the mean winter-spring “background” EF = 0.507 and mean summer-fall EF = 0.500 from the fitted DF curves, and the mean EF = 0.442 in seawater of the Archipelago-Beaufort Sea (see above), regional volatilization contributed only 11 % to the α -HCH in air at Alert. EFs of α -HCH at Alert are positively and significantly correlated to ice cover ($p < 0.0005$, $r^2 = 0.061$, Fig. S2a) and α -HCH concentration ($p < 0.005$, $r^2 = 0.042$, Fig. S2b), though in both cases the relationships are weak.

Why are winter-spring EFs at Alert above the racemic value of 0.500? Preferential degradation of (+) α -HCH (EF < 0.5) is common in most Northern Hemisphere aquatic systems, including the Laurentian Great Lakes, arctic wetlands, most of the Arctic Ocean, the North Atlantic and Baltic Sea; while (–) degradation (EF > 0.5) is favored in the Bering-Chukchi seas and parts of the North Sea (reviewed by Bidleman et al., 2012). Mixed degradation, though largely of the (+) enantiomer, was found in the equatorial Indian Ocean (Huang et al., 2013). A compilation of degradation preferences for α -HCH in 270 agricultural and background soils showed that (–) degradation was favored in 50 %, (+) degradation in 20 % and 30 % contained racemic residues, with an overall mean EF of 0.528 ± 0.095 (reviewed by Bidleman et al., 2012, 2013). Regional “footprints” are important in determining the enantiomer composition of α -HCH in air. A 2002 study of α -HCH in passive air samples from across Europe found that proximity to the North Atlantic and Baltic was marked by EFs generally < 0.5, whereas inland samples and those influenced by the Mediterranean tended toward EFs > 0.5. Higher concentrations of α -HCH and EFs > 0.5 were found at eastern European sites

Biannual cycles of organochlorine pesticide enantiomers in arctic air

T. F. Bidleman et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

and suggested old sources with preferential degradation of the (–) enantiomer (Covaci et al., 2010). The situation over the North Pacific is unclear. One study found that the α -HCH in air transported across the North Pacific was racemic above the marine boundary layer and depleted in the (–) enantiomer ($EF > 0.5$) below the boundary layer (Genualdi et al., 2009), while another group reported (+) depletion of α -HCH in sea-level air over the North Pacific and western Arctic ($EF < 0.5$) (Ding et al., 2007). Air samples from coastal stations in eastern and western Canada were influenced by emissions of α -HCH depleted in the (+) or (–) enantiomers, respectively (Shen et al., 2004). The weak correlations in Fig. S2 indicate that processes other than regional volatilization are mainly controlling α -HCH at Alert. In the 1990s, Alert likely received some racemic α -HCH from continued release of technical HCH mixed with air masses containing “recycled” α -HCH with opposite degradation preferences. These resulted in the mean winter-spring background EF of 0.507.

3.2 Chlordanes

All uses of chlordane in the US were cancelled in 1988 and the largest manufacturer stopped world production in 1997 (Ulrich and Falconer, 2011). China continued to produce chlordane until 2003 and usage was phased out by 2008. Between 1994–2000, China produced and domestically consumed about 1800 tons of chlordane, largely for termiticide use (Wang et al., 2013). Thus, both new and old sources of chlordane were contributing to atmospheric levels during the years of this study.

CC in air at Alert was slightly nonracemic, mean $EF = 0.505 \pm 0.004$, $n = 162$. Greater enantioselective degradation was found for TC, mean $EF = 0.470 \pm 0.013$, $n = 165$. EFs in the same ranges were previously reported for TC and CC in smaller sets of air samples (10–23 at each station) from Alert (1993–1996 and 1999), the arctic stations Pallas, Finland (68°58' N, 24°07' E; 1998 and 2001) and Dunai, Russia (74°00' N, 125°00' E; 1994–1995), and Rörvik on the southwest coast of Sweden (57°25' N, 11°56' E; 1998 and 2001) (Bidleman et al., 2002, 2004). TC and CC were racemic in atmospheric deposition samples collected in Sweden, Iceland and Slovakia in 1971–

Biannual cycles of organochlorine pesticide enantiomers in arctic air

T. F. Bidleman et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

1973 (Bidleman et al., 2004). The shift from racemic to non-racemic proportions, especially for TC, suggested a transition toward greater contribution of weathered chlordane sources by the late 1990s. This was corroborated by a time trend of EFs for TC in dated sediments of a remote lake in the Canadian Arctic, which showed increasingly nonracemic compositions from the 1950s into the 1990s (Bidleman et al., 2004; Stern et al., 2005). TC and CC in sediments from US lakes and reservoirs tended to be nonracemic in the upper layers and in suspended sediment, and closer to racemic in deeper layers (Ulrich et al., 2009), again suggesting a shift to secondary sources over time.

10 Trends in EFs of TC in Alert air derived from DF analysis are shown in Fig. 2. A striking feature is the biannual cycling of lower EFs in summer-fall (mean of annual minima = 0.456 ± 0.006) and higher (but still nonracemic) EFs in winter-spring (mean of annual maxima = 0.486 ± 0.006) (Fig. 2a). EFs of CC are more constant and display little seasonality, except in 1997–1998 (Fig. 2b). The EF cycles for TC are in phase with cycles of the TC/CC ratio, expressed as the fraction $F_{TC} = TC/(TC + CC)$ (Fig. 3). F_{TC} in arctic air during all seasons is generally below the compositions of the technical chlordane produced in the US (0.54) (Jantunen et al., 2000) and China (0.43–0.47) (Li et al., 2006), and are thought to indicate weathered chlordane sources (Becker et al., 2012; Hung et al., 2010; Su et al., 2008). A confounding factor is emissions from technical heptachlor which was contaminated with about 18–22 % TC and 2 % CC (NCI, 1977) and boosts the F_{TC} above the technical chlordane composition. Spikes of anomalously high F_{TC} in arctic air have been associated with heptachlor (Becker et al., 2012; Hung et al., 2010; Su et al., 2008). Depletion of TC concentrations and lower F_{TC} in arctic air during summer have been noted since the 1980s (Oehme et al., 1991) and are also seen in temperate latitudes (Hoff et al., 1992). Most explanations have pointed to greater photochemical reactivity of TC and preferential removal from the atmosphere during summer (Becker et al., 2012; Hoff et al., 1992; Oehme, 1991; Su et al., 2008). In support of this hypothesis, the transformation products oxychlordane (OXY) and heptachlor-*exo*-epoxide (HEPX) maximized in arctic air during summer (Su

Biannual cycles of organochlorine pesticide enantiomers in arctic air

T. F. Bidleman et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

et al., 2008), and photolysis products of CC and other cyclodienes have been found in ringed seal (Hühnerfuss and Shah, 2009; Hühnerfuss et al., 2005; Zhu et al., 1995). However, photochemistry may not be the only explanation. Su et al. (2008) examined the temperature dependence of the TC/CC ratio and concluded that thermal effects might account for reduced F_{TC} in summer. This is because the enthalpies of vaporization and octanol-air partitioning are slightly greater for CC than TC, and warmer temperatures in summer could have a greater effect on the vapor-phase concentration of CC.

The similar cycling of F_{TC} and the EF of TC (Fig. 3) suggests that microbial processing plays a role in its transport and fate, but how and where is unclear. Average degradation preferences in > 200 soils worldwide are 56 % (+)TC, 29 % (–)TC, with 15 % of soils containing racemic TC; 22 % (+)CC, 64 % (–)CC, 14 % racemic CC; and average EFs are TC 0.480 ± 0.067 , CC 0.531 ± 0.073 (reviewed by Bidleman et al., 2012, 2013). From these general enantiomer profiles, emissions from soils should be depleted in (+)TC and (–)CC. However, regional variations are apparent; e.g. soils in the midwest USA showed strong preference for (+)TC and (–)CC degradation (Aigner et al., 1998), but both (–)TC and (–)CC were depleted in soils of the Pearl River Delta, China (Li et al., 2006) while mixed enantioselectivity was found in soils of Zhejiang Province, China (Zhang et al., 2012a) and in global background soils (Kurt-Karakus et al., 2005). As for α -HCH, regional footprints of chlordane EFs likely influence air signatures.

The lower EFs of TC in Alert air during summer-fall suggest more active biodegradation in soil and greater contribution of soil emissions during this time, whereas higher EFs in winter-spring indicate less microbially weathered TC, perhaps from outgassing of buildings treated with chlordane termiticides. Only two studies have been made of chiral chlordanes in the air of US private homes, and both reported racemic TC and CC (Jantunen et al., 2000; Leone et al., 2000). Still, transport of nonracemic TC from temperate soils to the Arctic cannot fully explain the trends in Fig. 3. The correlation between EF and F_{TC} is highly significant ($p < 10^{-6}$) because there are a large number

of data points, but the r^2 is only 0.16 (Fig. S3a). Also, enantiospecific degradation of TC to yield an EF of 0.456 (mean of annual minima) would only lower F_{TC} from 0.39 (mean of annual maxima, Fig. 3b) to 0.37, whereas the mean of F_{TC} minima in Fig. 3b is 0.21. Thus, the cycles in EF are indicative, but not the cause, of similar cycles in F_{TC} .

Noting that degradation in soils tends to favor (-)CC and (+)TC (see above), one would expect biannual EF cycles of CC in air to be opposite of those for TC; i.e., higher in the warmer period and lower in the colder period. This pattern is evident in 1997–1998, but little seasonality is seen in other years and deviations from racemic are far less than for TC (Fig. 2b). There is no significant relationship between the EF of CC and F_{TC} (Fig. S3b).

Relationships of EFs to air concentrations and ice cover are shown in Figs. S4 and S5. The EF of TC is positively, but weakly, correlated to air concentration (Fig. S4a, $r^2 = 0.039$, $p = 0.014$). The relationship to ice cover is strongly positive (Fig. S5a, $r^2 = 0.44$, $p < 10^{-20}$), probably because EFs of TC are lower in summer and higher in winter for reasons that are not associated with ice (see above). EFs of CC are not related to air concentration (Fig. S4b) and show a weak negative correlation to ice cover (Fig. S5b, $r^2 = 0.044$, $p = 0.008$). Both chlordanes were racemic in arctic seawater in the mid- to late 1990s (Hoekstra et al., 2003; Jantunen and Bidleman, 1998), and non-racemic chlordanes with preferential depletion of (+)TC and (-)CC were reported in the North Atlantic in 2008 (Zhang et al., 2012b). TC and CC were racemic in air transported across the North Pacific (2003–2006) and at Okinawa (2004) (Genualdi et al., 2009). CC was racemic and (+)TC was depleted in air sampled over the North Atlantic in 2004 (Lohmann et al., 2009), whereas TC was racemic and (-)CC was depleted in 2008 (Zhang et al., 2012b).

Does exchange of chlordanes between arctic soils and air have an influence on enantiomer composition? Regressions of $\ln C_{air}$ vs. $T(K)^{-1}$ at Alert had negative slopes which were significant at $p < 0.001$ for CC and *trans*-nonachlor (TN) (Su et al., 2008), though not for TC, probably because of removal processes which lower its C_{air} in summertime. Such relationships for CC and TN are suggestive of local soil-exchange in-

Biannual cycles of organochlorine pesticide enantiomers in arctic air

T. F. Bidleman et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



fluencing C_{air} (Hoff et al., 1998; Su et al., 2008; Wania et al., 1998). Could chlordanes deposited during winter become enantioselectively degraded in arctic soils in summer and re-emitted?

4 Conclusions

5 Enantiomer compositions of α -HCH, TC and CC give insights to pathways that were influencing Alert in the decade preceding the Stockholm Convention, when these OCPs were in transition from primary to secondary emission sources. Small biannual cycles of higher α -HCH EFs in winter-spring and lower EFs in summer-fall suggest volatilization from open water, though such influence was less at Alert than in the
10 lower Archipelago. Biannual cycles in the EFs of TC were more prominent and suggest different emission sources contributing to atmospheric concentrations in the warm vs. cold seasons. This shift in sources may have contributed to the similar low-high cycles in F_{TC} , although other processes (e.g., photolysis, thermodynamic partitioning effects) cannot be ruled out. Lack of seasonal variation in the EFs of CC is curious and
15 presently cannot be explained. This study provides the first baseline of EFs at an arctic air monitoring station. It is likely that the EF profiles of these and other chiral compounds will continue to change with rising contribution of secondary emission sources, weathering of residues in the environment, and loss of ice cover in the Arctic. Modeling gives insight to the transport and fate processes impacted by climate change, but there
20 are many complexities and uncertainties (Gouin et al., 2013). Modeling and experimentally derived time series through monitoring are recommended as complementary approaches (Gouin et al., 2013; Kallenborn et al., 2012b). Together with signatures of isomers and parent/metabolite compounds, enantiomer-specific analysis could give added diagnostic capability in air monitoring programs.

Biannual cycles of organochlorine pesticide enantiomers in arctic air

T. F. Bidleman et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Biannual cycles of organochlorine pesticide enantiomers in arctic air

T. F. Bidleman et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Biannual cycles of organochlorine pesticide enantiomers in arctic air

T. F. Bidleman et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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Biannual cycles of organochlorine pesticide enantiomers in arctic air

T. F. Bidleman et al.

[Title Page](#)

[Abstract](#)

[Introduction](#)

[Conclusions](#)

[References](#)

[Tables](#)

[Figures](#)

[⏪](#)

[⏩](#)

[◀](#)

[▶](#)

[Back](#)

[Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

[Interactive Discussion](#)



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T. F. Bidleman et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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T. F. Bidleman et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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Biannual cycles of organochlorine pesticide enantiomers in arctic air

T. F. Bidleman et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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**Biannual cycles of
organochlorine
pesticide
enantiomers in arctic
air**

T. F. Bidleman et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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Biannual cycles of organochlorine pesticide enantiomers in arctic air

T. F. Bidleman et al.

Table 1. Annual mean concentrations and enantiomer fractions (EF) of organochlorine pesticides at Alert, Canada.

| Year | α -HCH | | | N ^b | <i>trans</i> -chlordane | | | N ^b | <i>cis</i> -chlordane | | | N ^b |
|-------------------|--|-------------|---------------|----------------|--|-------------|---------------|----------------|--|-------------|---------------|----------------|
| | mean (S.D.) ^a pg m ⁻³ | EF range | mean (S.D.) | | mean (S.D.) ^a pg m ⁻³ | EF range | mean (S.D.) | | mean (S.D.) ^a pg m ⁻³ | EF range | mean (S.D.) | |
| 1994 | 54 (26) | 0.493–0.508 | 0.501 (0.004) | 16 | 0.57 (0.33) | 0.449–0.478 | 0.467 (0.009) | 16 | 1.2 (0.62) | 0.489–0.511 | 0.503 (0.005) | 16 |
| 1995 | 56 (26) | 0.498–0.515 | 0.505 (0.003) | 40 | 1.0 (4.1) | 0.441–0.478 | 0.464 (0.010) | 35 | 0.76 (0.51) | 0.492–0.514 | 0.505 (0.004) | 37 |
| 1996 | 55 (31) | 0.498–0.516 | 0.505 (0.004) | 31 | 0.34 (0.19) | 0.429–0.495 | 0.464 (0.017) | 31 | 0.69 (0.45) | 0.493–0.512 | 0.505 (0.003) | 32 |
| 1997 | 47 (20) | 0.497–0.514 | 0.504 (0.004) | 43 | 0.36 (0.18) | 0.453–0.512 | 0.479 (0.011) | 32 | 0.57 (0.27) | 0.500–0.513 | 0.506 (0.003) | 29 |
| 1998 | 45 (13) | 0.498–0.512 | 0.504 (0.003) | 24 | 0.33 (0.16) | 0.451–0.490 | 0.477 (0.009) | 15 | 0.68 (0.32) | 0.494–0.513 | 0.507 (0.005) | 13 |
| 1999 | 34 (12) | 0.496–0.514 | 0.503 (0.004) | 27 | 0.23 (0.13) | 0.449–0.481 | 0.467 (0.009) | 25 | 0.60 (0.21) | 0.499–0.515 | 0.506 (0.003) | 25 |
| 2000 ^c | 25 (11) | 0.493–0.507 | 0.502 (0.004) | 16 | 0.19 (0.10) | 0.476–0.495 | 0.485 (0.006) | 11 | 0.51 (0.22) | 0.502–0.511 | 0.507 (0.003) | 10 |

^aAnnual mean concentrations from Hung et al., 2010.

^bN refers to number of EF measurements.

^cEF results from weeks 1–34, concentrations for entire year.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Biannual cycles of organochlorine pesticide enantiomers in arctic air

T. F. Bidleman et al.

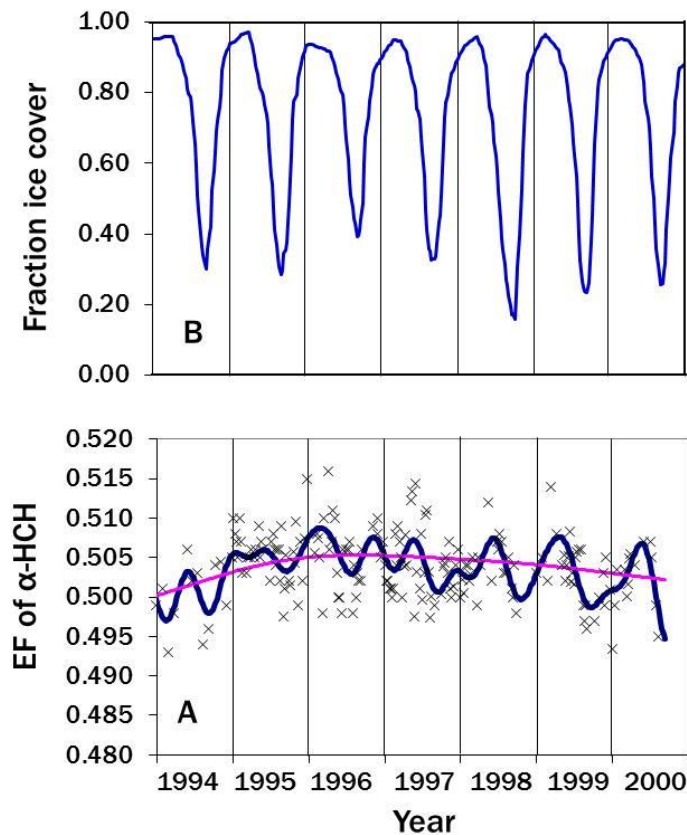


Figure 1. (A) Seasonal (blue) and long-term (pink) trends in the EFs of α -HCH in air at Alert, fitted by digital filtration (DF) analysis (Hung et al., 2002). Experimental points are marked (X). (B) Fractional ice cover in the Canadian Arctic (Canadian Archipelago – southern Beaufort Sea), from IceGraph 2.0 (<http://www.ec.gc.ca/glaces-ice/?lang=En&n=A1A338F4-1&offset=5&toc=show>) (accessed 6 July 2014).

Biannual cycles of organochlorine pesticide enantiomers in arctic air

T. F. Bidleman et al.

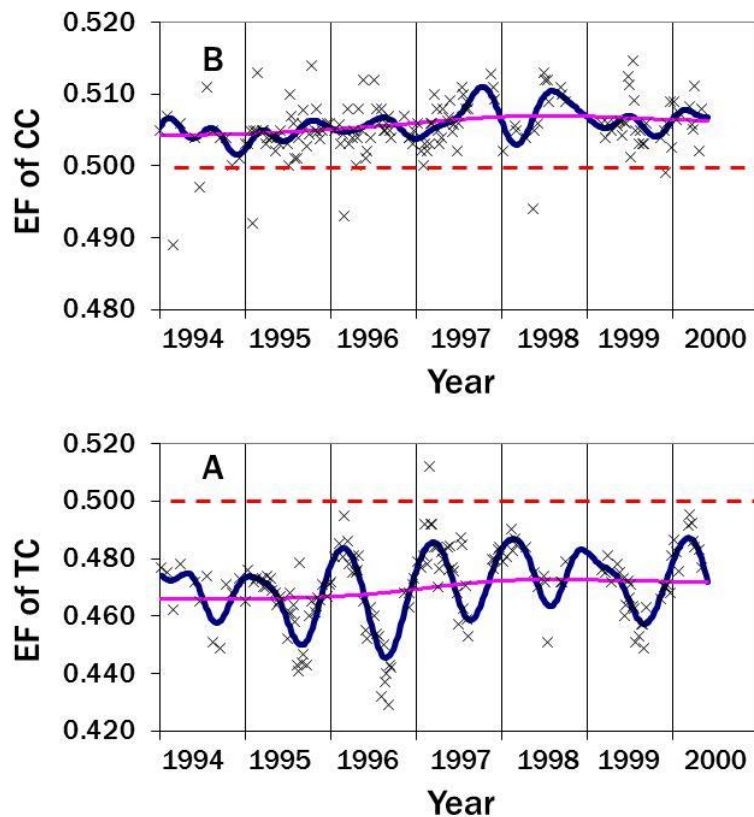


Figure 2. Seasonal (blue) and long-term (pink) trends in EFs of **(A)** *trans*-chlordane (TC) and **(B)** *cis*-chlordane (CC), with experimental points marked (X), as in Fig. 1.

Biannual cycles of organochlorine pesticide enantiomers in arctic air

T. F. Bidleman et al.

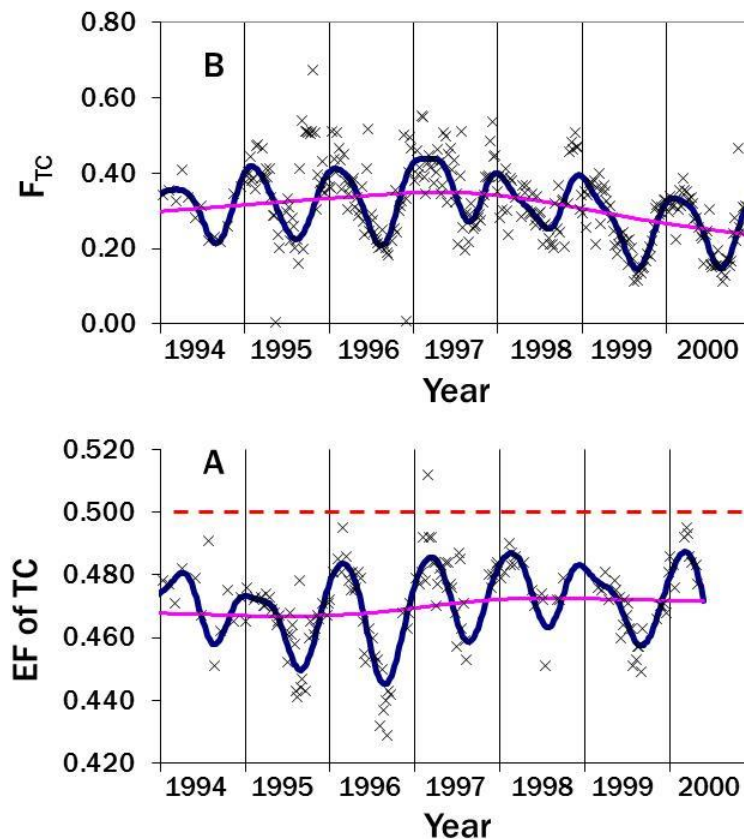


Figure 3. Seasonal (blue) and long-term (pink) trends in **(A)** EFs of TC and **(B)** $F_{TC} = TC/(TC + CC)$ with experimental points marked (X), as in Fig. 1.