

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

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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 = peak areas 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 annual 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

1 with EF >0.5 during the cold season. The contribution of sea-volatilized α -HCH was only
2 11% at Alert, versus 32% at Resolute Bay (74.68°N, 94.90°W) in 1999. EFs of TC also
3 followed annual cycles of lower and higher values in the warm and cold seasons. These were
4 in phase with low and high cycles of the TC/CC ratio (expressed as $FTC = TC/(TC+CC)$),
5 which suggests greater contribution of microbially “weathered” TC in summer-fall versus
6 winter-spring. CC was closer to racemic than TC and displayed seasonal cycles only in 1997-
7 1998. EF profiles are likely to change with rising contribution of secondary emission sources,
8 weathering of residues in the environment, and loss of ice cover in the Arctic. Enantiomer-
9 specific analysis could provide added forensic capability to air monitoring programs.

10

11 **1 Introduction**

12 Production and use of 12 persistent organic pollutants (POPs) were discontinued worldwide in
13 2001 under the Stockholm Convention. Nine of these were organochlorine pesticides (OCPs):
14 aldrin, dieldrin, endrin, chlordane, DDT, heptachlor, hexachlorobenzene, mirex and
15 toxaphene. Three OCPs were added later: hexachlorocyclohexanes (HCHs) and chlordecone
16 in 2009 and endosulfan in 2011 (UNEP, 2014). Some OCPs were already in decline by the
17 1980s and 1990s through country-specific and regional restrictions and bans; e.g., technical
18 HCH, DDT and toxaphene (Li and Macdonald, 2005; Wong et al., 2005).

19 Residues of POPs remain in soil (Dalla Valle et al., 2005), vegetation (Dalla Valle et al.,
20 2004) and oceans (Pućko et al., 2013; Stemmler and Lammel, 2009, 2013; Wöhrnschimmel et
21 al., 2012; Xie et al., 2011) as a legacy of 50 or more decades of usage. Emissions from these
22 “secondary sources” buffer atmospheric concentrations in background regions (Cabrerizo et
23 al., 2011, 2013; Nizzetto and Perlinger, 2012; Nizzetto et al., 2010; Stemmler and Lammel,
24 2009; Jantunen et al., 2008; Wöhrnschimmel et al., 2012; Wong et al., 2011). Climate change
25 is expected to increase emissions from both primary and secondary sources (Gouin et al.,
26 2013; Kallenborn et al., 2012a,b; Macdonald et al., 2005; UNEP 2011), but there are many
27 processes to consider which might shift the emission/deposition balance one way or the other.
28 Increase in temperature, loss of soil organic matter (SOM) due to greater soil respiration, and
29 melting of snow would increase secondary emissions, while increase in vegetation cover and
30 SOM could lead to greater sequestration of POPs (Cabrerizo et al., 2013). One consequence
31 of air-surface exchange processes is to confound interpretation of temporal trends derived
32 from long-term monitoring data (Kallenborn et al., 2012a; Macdonald et al., 2005).

1 Concentrations of most OCPs in arctic air have fallen over the last two decades (Becker et al.,
2 2012; Hung et al., 2010; Ma et al., 2011), but some have declined more slowly than others or
3 even risen slightly after about 2000. The slowed declines have been attributed to increased
4 volatilization of OCP residues from environmental reservoirs (Becker et al., 2012; Hung et
5 al., 2010; Ma et al., 2011) and linked to rising temperatures and decreasing ice cover (Ma et
6 al., 2011).

7 Many POPs are chiral, including the OCPs α -HCH (the major constituent of technical HCH)
8 and technical chlordane components *trans*-chlordane (TC) and *cis*-chlordane (CC). Each of
9 these chiral compounds consists of two enantiomers which have the same physicochemical
10 properties. Abiotic transport and transformation processes will not change enantiomer
11 proportions provided they take place in achiral environments. However, enzymes are chiral
12 and enantioselective metabolism of xenobiotics is the "rule rather than the exception"
13 (Hegeman and Laane, 2002). Chiral OCPs were produced as racemates (equal proportion of
14 enantiomers), and occurrence of nonracemic residues in soil and water indicates microbial
15 degradation. Enantiospecific analysis of chiral compounds offers unique opportunities in
16 environmental forensics by distinguishing racemic (newly released or protected from
17 microbial attack) and nonracemic (microbially weathered) sources (Bidleman et al., 2012,
18 2013; Hühnerfuss and Shah, 2009). Volatilization of partially degraded POPs from soil and
19 water carries their distinctive nonracemic enantiomer proportions into the overlying air and
20 such investigations have been recently reviewed (Bidleman et al., 2012, 2013; Ulrich and
21 Falconer, 2011).

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

28 **2. Materials and methods**

29 Air samples were collected at Alert, Ellesmere Island, Canada (82° 30' N, 62° 20' W, 200
30 m.a.s.l.) as part of a monitoring program that has been continuous from 1992 to the present.
31 Sampling and analytical methods have been summarized by Fellin et al. (1996) and Halsall et
32 al. (1998). Archived extracts of polyurethane foam traps, representing gas-phase components,

1 were obtained for chiral analysis from January 1994 through week 34 of 2000. Those from
2 1994 were composites of four 7-day samples, while individual 7-day samples were available
3 in the other years. Gaps prevented full coverage in any year (Table 1). Enantiomers of α -
4 HCH, TC and CC were determined in the extracts using previously described methods and
5 quality control procedures (Bidleman et al., 2002; Jantunen et al., 2008, 1998; Kurt-Karakus
6 et al., 2005; Wong et al., 2011). Separations were carried out on chiral-phase columns, either
7 Betadex-120 (BDX), or BGB-172 (BGB), with detection by electron capture negative ion
8 mass spectrometry. Details of enantiospecific analysis are given in Supporting Information.
9 Analytical data were expressed as enantiomer fraction, $EF = \text{peak areas of (+)}/[(+) + (-)]$
10 enantiomers. A racemic compound has $EF = 0.5$, whereas $EFs < 0.5$ and > 0.5 indicate
11 depletion of (+) and (-) enantiomers, respectively. In some cases, air samples were analyzed
12 on both columns and slight, but significant, biases were noticed. The average $EF_{BGB} = (0.984$
13 $\pm 0.022) * EF_{BDX}$ for TC ($p < 0.0001$, $n = 38$), $EF_{BGB} = (1.006 \pm 0.009) * EF_{BDX}$ for CC ($p < 0.04$,
14 $n = 11$) and $EF_{BGB} = (1.010 \pm 0.019) * EF_{BDX}$ for α -HCH ($p < 0.002$, $n = 41$). Since the BGB
15 column was used for most analyses, results from the BDX column were adjusted to the BGB
16 scales.

17 The archived extracts in isooctane were stored at 4 °C and the time between archiving and
18 retrieval for these analyses was approximately 10-15 years. It is not feasible to determine
19 whether enantioselective degradation took place over this period. However, we have
20 maintained a standard solution of α -HCH and chlordanes in isooctane, refrigerated at 4 °C, for
21 over 20 years and their compositions have remained racemic.

22 Time series analysis was conducted by digital filtration (DF) to give best fits for seasonal and
23 long-term trends at 95% confidence (Hung et al., 2002; Kong et al., 2014). Air parcel
24 trajectories backwards from Alert were calculated four times each day (0000, 0600, 1200 and
25 1800 UTC) at 10 m above ground level and going back 72 h over each sampling period
26 (Canadian Meteorological Centre). Ice cover data for the Canadian Archipelago and southern
27 Beaufort Sea were obtained from the Canadian Ice Service (Environment Canada), through
28 the tool IceGraph 2.0 (<http://www.ec.gc.ca/glaces-ice/?lang=En&n=A1A338F4-1&offset=5&toc=show>, accessed December 18, 2014).

30

1 **3. Results and discussion**

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

8 Monthly EFs for all 7 years of data are displayed in Figure 1 as box and whisker plots of
9 arithmetic mean (square), median (horizontal line), 10th – 90th percentiles (whiskers), 25th-75th
10 percentiles (boxes) and outliers (crosses). EFs of α -HCH are lowest in summer-early fall. EFs
11 of CC are fairly constant over most of the year, with slightly higher values in July and
12 September, while EFs of TC show a distinct minimum in late summer. Frequency
13 distributions of EFs for all data, summer-fall (June – October) and winter-spring (November –
14 May) are shown in Supporting Information, Figure S6. Distributions were not significantly
15 different from normal for α -HCH in each period ($p > 0.05$, Shapiro-Wilk test). Normal
16 distributions were also indicated for CC and TC in summer-fall ($p > 0.05$), but not for winter-
17 spring nor for the entire data set ($p < 0.05$). The time series of EFs are plotted in Figures 2-4
18 and are discussed by compound below.

19 **3.1. α -HCH**

20 Emissions of α -HCH from technical HCH peaked in the early 1980s and were greatly reduced
21 by the early 1990s, due largely to bans or restrictions implemented by China, India and the
22 former Soviet Union. By the end of the 1990s arctic air concentrations had dropped to less
23 than 10% of peak values (Li and Macdonald, 2005). A global fate and transport model
24 indicates that secondary emissions of α -HCH from soil and water closely tracked primary
25 emissions throughout technical HCH usage history, and secondary emissions came into
26 dominance in the late 1990s (Wöhrnschimmel et al., 2012). The mean EF of α -HCH ($0.504 \pm$
27 0.004 , $n = 197$) over all years (including the partial year 2000) was close to racemic and little
28 interannual variation was found (Table 1). Greater insight is provided by plotting the time
29 series of EFs (Figure 2B), where DF analysis shows the fitted EF curve often dipping below
30 the long-term mean in summer-fall and rising above the mean in winter-spring. A chart of
31 fractional ice cover in the Archipelago and southern Beaufort Sea is shown in Figure 2A.

1 Minimum ice cover occurred between weeks 36-39, with the window for 50% ice cover
2 between weeks 29-45. Superimposing these plots (Figure 2) shows that the EF minima occur
3 during periods of more open water, suggesting α -HCH volatilization from the ocean.
4 Summer-fall minima and winter-spring maxima EFs for each year were obtained from the DF
5 fits to all the annual data points at 95% C.I. Seven-year averages of the annual fitted minima
6 and maxima were 0.500 ± 0.003 and 0.508 ± 0.001 (Table 1), and were significantly different
7 at $p = 0.0002$ (paired t-test, two sample for means). Sources of air to Alert during the
8 minimum EF periods are shown in Figure S1 of Supporting Information as combined 72-h
9 back trajectories from the end of July to mid-October. Air parcels arriving from NE-NW pass
10 over areas of the Arctic Ocean that are mainly ice-covered, while those from the SE-W
11 traverse unfrozen areas of Baffin Bay, the Archipelago and southern Beaufort Sea. The α -
12 HCH in surface water of this region in 1999 was strongly depleted in the (+) enantiomer, with
13 EFs 0.432-0.463, averaging 0.442 ± 0.007 . A strong spatial trend was evident, with lower EFs
14 in the Beaufort Sea – western Archipelago region than in the eastern Archipelago (Bidleman
15 et al., 2007). Shipboard-scale measurements in the Archipelago showed a close correlation
16 between EFs in air and water for ice-free regions (Jantunen et al., 2008); however, the area
17 over which air trajectories passed enroute to Alert was too large and variable to make
18 correlations with regional EF signatures.

19 Measurements at Resolute Bay (74.68°N , 94.90°W , 67 m.a.s.l.) on Cornwallis Island in 1999
20 showed that α -HCH in air was nearly racemic during periods of ice cover and nonracemic
21 after ice breakup. Application of the Harner et al. (2000) source apportionment relationship
22 estimated that seawater volatilization contributed 32% of the α -HCH in air during the open
23 water period (Jantunen et al., 2008). Similar differences in EFs of α -HCH in air between ice-
24 covered and ice-free periods were found from shipboard measurements in the southern
25 Beaufort Sea (Wong et al., 2011). Alert in the high Arctic appears much less influenced by
26 reemission of nonracemic α -HCH from the ocean. Assuming the mean winter-spring
27 “background” EF = 0.507 and mean summer-fall EF = 0.500 from the fitted DF curves, and
28 the mean EF = 0.442 in seawater of the Archipelago-Beaufort Sea (see above), regional
29 volatilization contributed only 11% to the α -HCH in air at Alert. EFs of α -HCH at Alert are
30 positively and significantly correlated to ice cover ($p < 0.0005$, $r^2 = 0.061$, Figure S2A) and α -
31 HCH concentration ($p < 0.005$, $r^2 = 0.042$, Figure S2B), though in both cases the relationships
32 are weak.

1 Why are winter-spring EFs at Alert above the racemic value of 0.500? Preferential
2 degradation of (+) α -HCH (EF <0.5) is common in most Northern Hemisphere aquatic
3 systems, including the Laurentian Great Lakes, arctic wetlands, most of the Arctic Ocean, the
4 North Atlantic and Baltic Sea; while (-) degradation (EF >0.5) is favored in the Bering-
5 Chukchi seas and parts of the North Sea (reviewed by Bidleman et al., 2012). Mixed
6 degradation, though largely of the (+) enantiomer, was found in the equatorial Indian Ocean
7 (Huang et al., 2013). A compilation of degradation preferences for α -HCH in 270 agricultural
8 and background soils showed that (-) degradation was favored in 50%, (+) degradation in
9 20% and 30% contained racemic residues, with an overall mean EF of 0.528 ± 0.095
10 (reviewed by Bidleman et al, 2012, 2013). Regional “footprints” are important in determining
11 the enantiomer composition of α -HCH in air. A 2002 study of α -HCH in passive air samples
12 from across Europe found that proximity to the North Atlantic and Baltic was marked by EFs
13 generally <0.5, whereas inland samples and those influenced by the Mediterranean tended
14 toward EFs >0.5. Higher concentrations of α -HCH and EFs >0.5 were found at eastern
15 European sites and suggested old sources with preferential degradation of the (-) enantiomer
16 (Covaci et al., 2010). The situation over the North Pacific is unclear. One study found that the
17 α -HCH in air transported across the North Pacific was racemic above the marine boundary
18 layer and depleted in the (-) enantiomer (EF >0.5) below the boundary layer (Genualdi et al.,
19 2009), while another group reported (+) depletion of α -HCH in sea-level air over the North
20 Pacific and western Arctic (Ding et al., 2007). Air samples from coastal stations in eastern
21 and western Canada were influenced by emissions of α -HCH depleted in the (+) or (-)
22 enantiomers, respectively (Shen et al., 2004). The weak correlations in Figure S2 indicate that
23 processes other than regional volatilization are mainly controlling α -HCH at Alert. In the
24 1990s, Alert likely received some racemic α -HCH from continued release of technical HCH
25 mixed with air masses containing “recycled” α -HCH with opposite degradation preferences,
26 These resulted in the mean winter-spring background EF of 0.507.

27 **3.2. Chlordanes**

28 All uses of chlordane in the U.S. were cancelled in 1988 and the largest manufacturer stopped
29 world production in 1997 (Ulrich and Falconer, 2011). China continued to produce chlordane
30 until 2003 and usage was phased out by 2008. Between 1994-2000, China produced and
31 domestically consumed about 1800 tons of chlordane, largely for termiticide use (Wang et al.,

1 2013). Thus, both new and old sources of chlordane were contributing to atmospheric levels
2 during the years of this study.

3 CC in air at Alert was slightly nonracemic, mean EF = 0.505 ± 0.004 , n = 162. Greater
4 enantioselective degradation was found for TC, mean EF = 0.470 ± 0.013 , n = 165. EFs in the
5 same ranges were previously reported for TC and CC in smaller sets of air samples (10-23 at
6 each station) from Alert (1993-1996 and 1999), the arctic stations Pallas, Finland (68° 58' N,
7 24°07'E; 1998 and 2001) and Dunai, Russia (74° 00' N, 125°00'E; 1994-1995), and Rörvik
8 on the southwest coast of Sweden (57°25' N, 11°56'E; 1998 and 2001) (Bidleman et al., 2002,
9 2004). TC and CC were racemic in atmospheric deposition samples collected in Sweden,
10 Iceland and Slovakia in 1971-1973 (Bidleman et al., 2004). The shift from racemic to non-
11 racemic proportions, especially for TC, suggested a transition toward greater contribution of
12 weathered chlordane sources by the late 1990s. This was corroborated by a time trend of EFs
13 for TC in dated sediments of a remote lake in the Canadian Arctic, which showed increasingly
14 nonracemic compositions from the 1950s into the 1990s (Bidleman et al., 2004; Stern et al.,
15 2005). TC and CC in sediments from U.S. lakes and reservoirs tended to be nonracemic in the
16 upper layers and in suspended sediment, and closer to racemic in deeper layers (Ulrich et al.,
17 2009), again suggesting a shift to secondary sources over time.

18 Trends in EFs of TC in Alert air derived from DF analysis are shown in Figure 3A. A striking
19 feature is the annual cycling of lower EFs in summer-fall (mean of annual minima = $0.455 \pm$
20 0.007) and higher (but still nonracemic) EFs in winter-spring (mean of annual maxima =
21 0.482 ± 0.005) (Figure 3A). EFs of CC are more constant and display less seasonality, except
22 in 1997-1998 (Figure 3B). The mean of annual minima and maxima EFs for CC are $0.503 \pm$
23 0.001 and 0.508 ± 0.002 (Table 1). The EF cycles for TC (Figure 4A) are in phase with cycles
24 of the TC/CC ratio, expressed as the fraction $F_{TC} = TC/(TC+CC)$ (Figure 4B). F_{TC} in arctic air
25 during all seasons is generally below the compositions of the technical chlordane produced in
26 the U.S. (0.54) (Jantunen et al., 2000) and China (0.43-0.47) (Li et al., 2006), and are thought
27 to indicate weathered chlordane sources (Becker et al., 2012; Hung et al., 2010; Su et al.,
28 2008). A confounding factor is emissions from technical heptachlor which was contaminated
29 with about 18-22% TC and 2% CC (NCI, 1977) and boosts the F_{TC} above the technical
30 chlordane composition. Spikes of anomalously high F_{TC} in arctic air have been associated
31 with heptachlor (Becker et al., 2012; Hung et al., 2010; Su et al., 2008). Depletion of TC
32 concentrations and lower F_{TC} in arctic air during summer have been noted since the 1980s

1 (Oehme et al., 1991) and are also seen in temperate latitudes (Hoff et al., 1992). Most
2 explanations have pointed to greater photochemical reactivity of TC and preferential removal
3 from the atmosphere during summer (Becker et al., 2012; Hoff et al., 1992; Oehme, 1991; Su
4 et al., 2008). In support of this hypothesis, the transformation products oxychlordane (OXY)
5 and heptachlor-*exo*-epoxide (HEPX) maximized in arctic air during summer (Su et al., 2008),
6 and photolysis products of CC and other cyclodienes have been found in ringed seal
7 (Hühnerfuss and Shah, 2009; Hühnerfuss et al., 2005; Zhu et al., 1995). However,
8 photochemistry may not be the only explanation. Su et al. (2008) examined the temperature
9 dependence of the TC/CC ratio and concluded that thermal effects might account for reduced
10 F_{TC} in summer. This is because the enthalpies of vaporization and octanol-air partitioning are
11 slightly greater for CC than TC, and warmer temperatures in summer could have a greater
12 effect on the vapor-phase concentration of CC.

13 The similar cycling of F_{TC} and the EF of TC (Figure 4) suggests that microbial processing
14 plays a role in its transport and fate, but how and where is unclear. Average degradation
15 preferences in soils worldwide are 56% (+)TC, 29% (-)TC, with 15% of soils containing
16 racemic TC; 22% (+)CC, 64% (-)CC, 14% racemic CC; and average EFs are TC
17 0.480 ± 0.067 , CC 0.531 ± 0.073 (reviewed by Bidleman et al., 2012, 2013). From these general
18 enantiomer profiles, emissions from soils should be depleted in (+)TC and (-)CC. However,
19 regional variations are apparent; e.g. soils in the midwest U.S.A. showed strong preference for
20 (+)TC and (-)CC degradation (Aigner et al., 1998), but both (-)TC and (-)CC were depleted
21 in soils of the Pearl River Delta, China (Li et al., 2006) while mixed enantioselectivity was
22 found in soils of Zhejiang Province, China (Zhang et al., 2012a) and in global background
23 soils (Kurt-Karakus et al., 2005). As for α -HCH, regional footprints of chlordane EFs likely
24 influence air signatures.

25 The lower EFs of TC in Alert air during summer-fall suggest more active biodegradation in
26 soil and greater contribution of soil emissions during this time, whereas higher EFs in winter-
27 spring indicate less microbially weathered TC, perhaps from outgassing of buildings treated
28 with chlordane termiticides. Only two studies have been made of chiral chlordanes in the air
29 of U.S. private homes, and both reported racemic TC and CC (Jantunen et al., 2000; Leone et
30 al., 2000). Still, transport of nonracemic TC from temperate soils to the Arctic cannot fully
31 explain the trends in Figure 4. The correlation between EF and F_{TC} is highly significant (p
32 $< 10^{-6}$) because there are a large number of data points, but the r^2 is only 0.16 (Figure S3A).

1 Also, enantiospecific degradation of TC to yield an EF of 0.456 (mean of annual minima)
2 would only lower F_{TC} from 0.39 (mean of annual maxima, Figure 4B) to 0.37, whereas the
3 mean of F_{TC} minima in Figure 4B is 0.21. Thus, the cycles in EF are indicative, but not the
4 cause, of similar cycles in F_{TC} .

5 Noting that degradation in soils tends to favor (-)CC and (+)TC (see above), one would
6 expect biannual EF cycles of CC in air to be opposite of those for TC; i.e., higher in the
7 warmer period and lower in the colder period. This pattern is evident in 1997-1998, but little
8 seasonality is seen in other years and deviations from racemic are far less than for TC (Figure
9 3B). There is no significant relationship between the EF of CC and F_{TC} (Figure S3B).

10 Relationships of EFs to air concentrations and ice cover are shown in Figures S4 and S5. The
11 EF of TC is positively, but weakly, correlated to air concentration (Figure S4A, $r^2 = 0.039$, p
12 $= 0.014$). The relationship to ice cover is strongly positive (Figure S5A, $r^2 = 0.44$, $p < 10^{-20}$),
13 probably because EFs of TC are lower in summer and higher in winter for reasons that are not
14 associated with ice (see above). EFs of CC are not related to air concentration (Figure S4B)
15 and show a weak negative correlation to ice cover (Figure S5B, $r^2 = 0.044$, $p = 0.008$). Both
16 chlordanes were racemic in arctic seawater in the mid- to late 1990s (Hoekstra et al., 2003;
17 Jantunen and Bidleman, 1998), and nonracemic chlordanes with preferential depletion of
18 (+)TC (mean EF = 0.469 ± 0.032) and (-)CC (mean EF = 0.516 ± 0.033) were reported in the
19 North Atlantic in 2008 (Zhang et al., 2012b). TC and CC were racemic in air transported
20 across the North Pacific (2003-2006) and at Okinawa (2004) (Genualdi et al., 2009). CC was
21 racemic and (+)TC (mean EF = 0.470 ± 0.019) was depleted in air sampled over the North
22 Atlantic in 2004 (Lohmann et al., 2009), whereas TC was racemic and (-)CC (mean EF =
23 0.513 ± 0.011) was depleted in 2008 (Zhang et al., 2012b).

24 Does exchange of chlordanes between arctic soils and air have an influence on enantiomer
25 composition? Regressions of $\ln C_{air}$ vs. $1/T(K)$ at Alert had negative slopes which were
26 significant at $p < 0.001$ for CC and *trans*-nonachlor (TN) (Su et al., 2008), though not for TC,
27 probably because of removal processes which lower its C_{air} in summertime. Such
28 relationships for CC and TN are suggestive of local soil-exchange influencing C_{air} (Hoff et al.,
29 1998; Su et al., 2008; Wania et al., 1998). Could chlordanes deposited during winter become
30 enantioselectively degraded in arctic soils in summer and re-emitted?

31

1 **4. Conclusions**

2 Enantiomer compositions of α -HCH, TC and CC give insights to pathways that were
3 influencing Alert in the decade preceding the Stockholm Convention, when these OCPs were
4 in transition from primary to secondary emission sources. Small biannual cycles of higher α -
5 HCH EFs in winter-spring and lower EFs in summer-fall suggest volatilization from open
6 water, though such influence was less at Alert than in the lower Archipelago. Biannual cycles
7 in the EFs of TC were more prominent and suggest different emission sources contributing to
8 atmospheric concentrations in the warm versus cold seasons. This shift in sources may have
9 contributed to the similar low-high cycles in F_{TC} , although other processes (e.g., photolysis,
10 thermodynamic partitioning effects) cannot be ruled out. Lack of seasonal variation in the EFs
11 of CC is curious and presently cannot be explained. This study provides the first baseline of
12 EFs at an arctic air monitoring station. It is likely that the EF profiles of these and other chiral
13 compounds will continue to change with rising contribution of secondary emission sources,
14 weathering of residues in the environment, and loss of ice cover in the Arctic. Modeling gives
15 insight to the transport and fate processes impacted by climate change, but there are many
16 complexities and uncertainties (Gouin et al., 2013). Modeling and experimentally derived
17 time series through monitoring are recommended as complementary approaches (Gouin et al.,
18 2013; Kallenborn et al., 2012a). Together with signatures of isomers and parent/metabolite
19 compounds, enantiomer-specific analysis could give added diagnostic capability in air
20 monitoring programs.

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30

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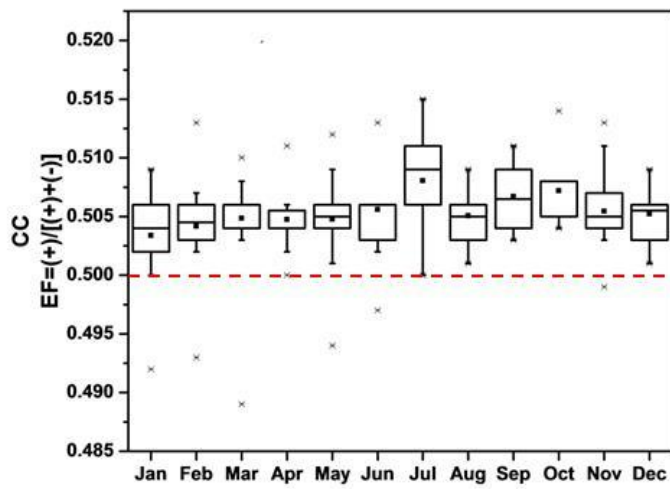
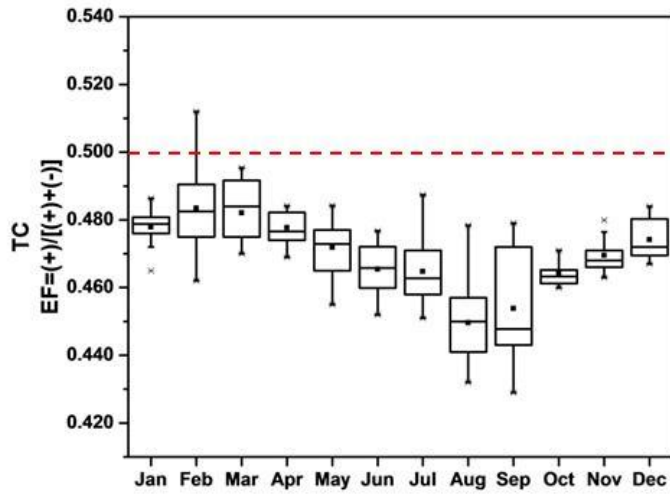
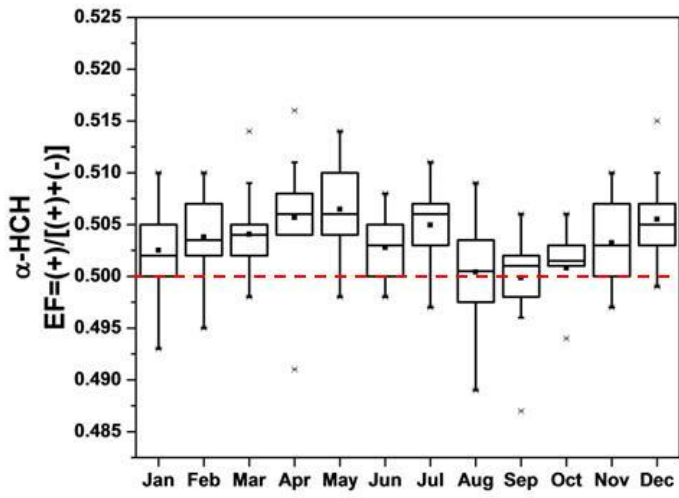
Table 1. Annual mean concentrations and enantiomer fractions (EF) of organochlorine pesticides at Alert, Canada.												
Year	<i>α</i> -HCH				<i>trans</i> -chlordane				<i>cis</i> -chlordane			
	mean (S.D.) ^a pg m ⁻³	range	EF mean (S.D.)	N ^b	mean (S.D.) ^a pg m ⁻³	range	EF mean (S.D.)	N ^b	mean (S.D.) ^a pg m ⁻³	range	EF mean (S.D.)	N ^b
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
Annual minima and maxima EFs, from fitted DF curves												
	<i>α</i> -HCH		<i>trans</i> -chlordane		<i>cis</i> -chlordane							
	minimum	maximum	minimum	maximum	minimum	maximum	minimum	maximum				
1994		0.497	0.505		0.458	0.475		0.502	0.507			
1995		0.503	0.508		0.450	0.478		0.503	0.506			
1996		0.503	0.509		0.445	0.484		0.504	0.507			
1997		0.501	0.507		0.459	0.486		0.504	0.511			
1998		0.500	0.507		0.463	0.487		0.503	0.510			
1999		0.499	0.508		0.457	0.482		0.504	0.507			
2000 ^d		0.495	0.507									
mean		0.500	0.507		0.455	0.482		0.503	0.508			
s.d.		0.003	0.001		0.007	0.005		0.001	0.002			
<p>a) Annual mean concentrations from Hung et al., 2010.</p> <p>b) N refers to number of EF measurements.</p> <p>c) EF results from weeks 1-34, concentrations for entire year.</p> <p>d) Insufficient coverage for the chlordanes to determine their minima and maxima in 2000.</p>												

1 **Figure captions**

- 2 1. Box-and-whisker plots of monthly EFs over all 7 years: arithmetic mean (square),
3 median (horizontal line), 10th – 90th percentiles (whiskers), 25th-75th percentiles
4 (boxes) and outliers (crosses). The dashed red line indicates a racemic composition.
- 5 2. A. Fractional ice cover in the Canadian Arctic (Canadian Archipelago – southern
6 Beaufort Sea), from IceGraph 2.0 ([http://www.ec.gc.ca/glaces-](http://www.ec.gc.ca/glaces-ice/?lang=En&n=A1A338F4-1&offset=5&toc=show)
7 [ice/?lang=En&n=A1A338F4-1&offset=5&toc=show](http://www.ec.gc.ca/glaces-ice/?lang=En&n=A1A338F4-1&offset=5&toc=show)) (accessed July 6, 2014).
8 B. Seasonal (blue) and long-term (pink) trends in the EFs of α -HCH in air at Alert,
9 fitted by digital filtration (DF) analysis (Hung et al., 2002). Experimental points are
10 marked (X).
- 11 3. Seasonal (blue) and long-term (pink) trends in EFs of A. *trans*-chlordane (TC) and
12 B. *cis*-chlordane (CC), with experimental points marked (X), as in Figure 2B.
- 13 4. Seasonal (blue) and long-term (pink) trends in A. EFs of TC and
14 B. $F_{TC} = TC/(TC + CC)$, with experimental points marked (X), as in Figure 2B.

1 Figure 1

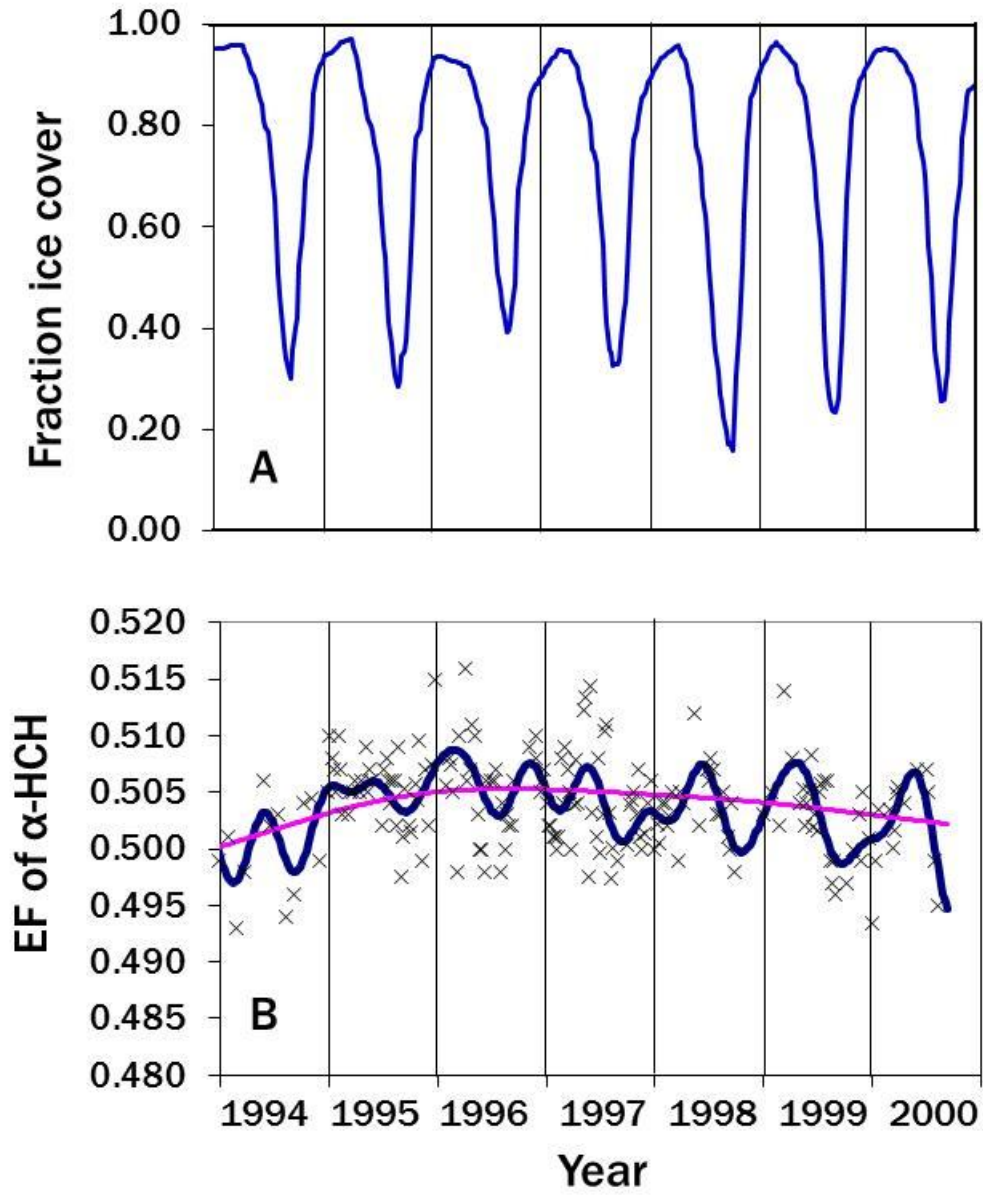
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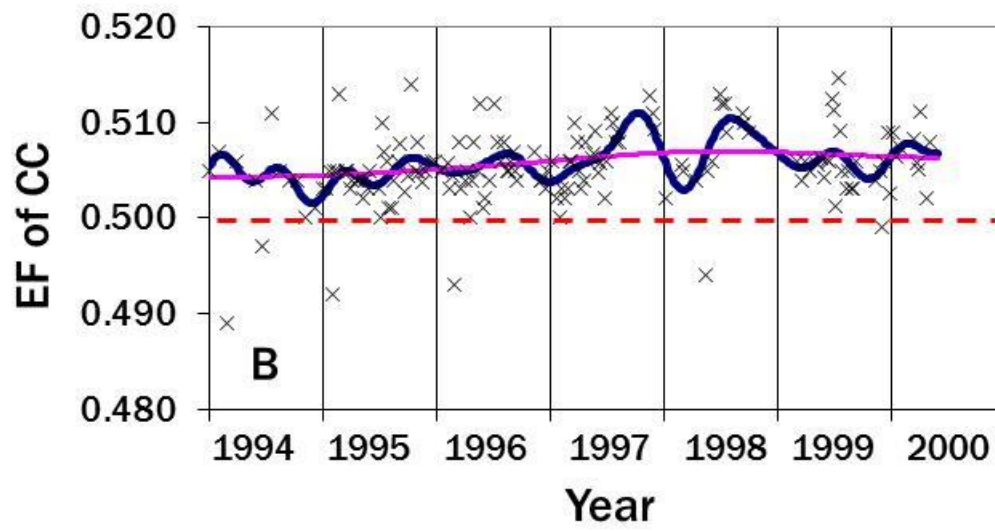
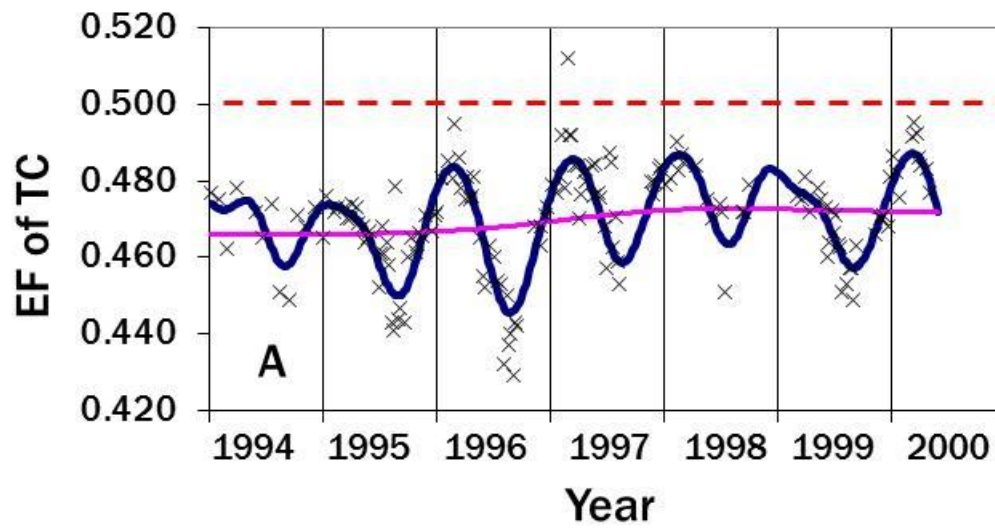
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2 **Figure 2**



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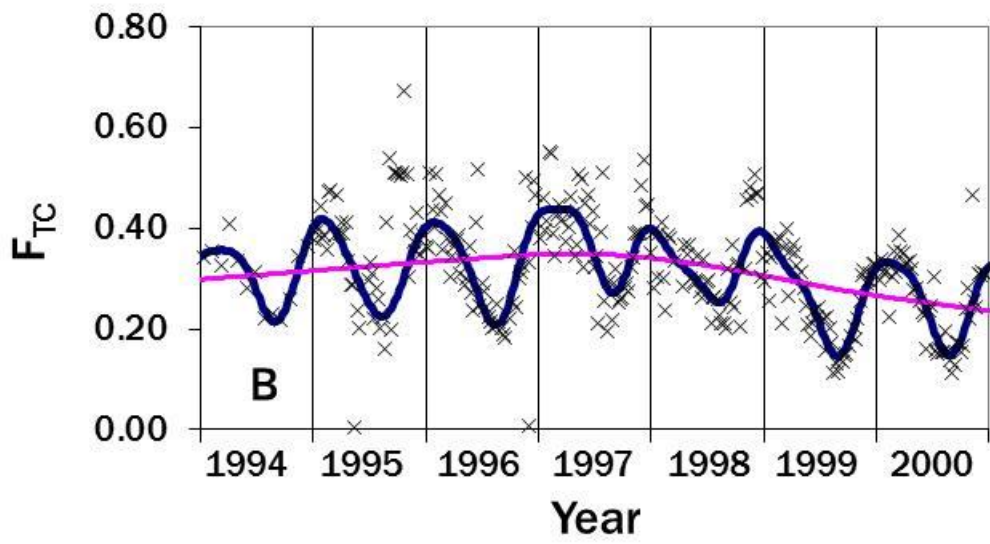
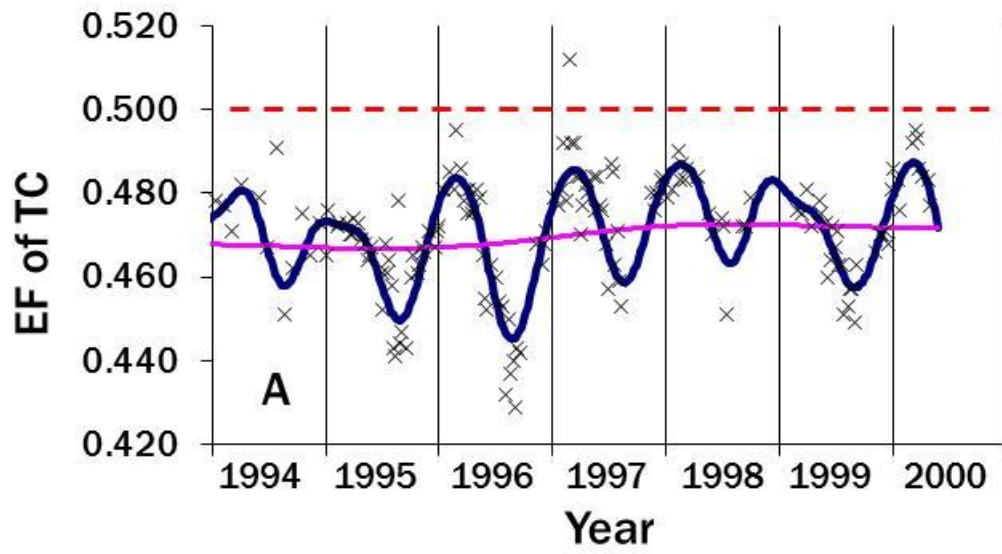
1 Figure 3



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1 **Figure 4**

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