



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

T. F. Bidleman^{1,2}, L. M. Jantunen², H. Hung³, J. Ma⁴, G. A. Stern⁵, B. Rosenberg⁶, and J. Racine⁷

¹Department of Chemistry, Umeå University, 901 87 Umeå, Sweden

²Air Quality Processes Research Section, Environment Canada, 6248 Eighth Line, Egbert, ON, L0L 1N0, Canada

³Air Quality Processes Research Section, Environment Canada, 4905 Dufferin St., Toronto, ON, M3H 5T4, Canada

⁴Key Laboratory of Western China's Environmental System, Ministry of Education, College of Earth and Environment Sciences, Lanzhou University, Lanzhou, China

⁵Centre for Earth Observation Science, University of Manitoba, 474 Wallace Building, 125 Dysard Road, Winnipeg, MB, R3T 2N2, Canada

⁶Freshwater Institute, Department of Fisheries and Oceans, University of Manitoba, 501 University Crescent, Winnipeg, MB, R3T 2N6, Canada

⁷Air Quality Modelling Application Section, Canadian Meteorological Centre, 2121 Trans-Canada Highway, Dorval, QC, H9P 1J3, Canada

Correspondence to: T. F. Bidleman (terry.bidleman@umu.se)

Received: 9 August 2014 – Published in Atmos. Chem. Phys. Discuss.: 30 September 2014

Revised: 6 January 2015 – Accepted: 6 January 2015 – Published: 9 February 2015

Abstract. Air samples collected during 1994–2000 at the Canadian Arctic air monitoring station Alert (82°30' N, 62°20' W) were analysed 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 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 annual 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 versus 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 pesticides (OCPs): aldrin, dieldrin, endrin, chlordane, DDT, heptachlor, hexachlorobenzene, mirex and toxaphene. Three OCPs were added later: hexachlorocyclohexanes (HCHs) and chlordane 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 (Pučko et al., 2013; Stemmler and Lammel, 2009, 2013; Wöhrnschimmel et al., 2012; Xie et al., 2011) as a legacy of 50 or more years of usage. Emissions from these “secondary sources” buffer atmospheric concentrations in background regions (Cabrerizo et al., 2011, 2013; 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), but there are many processes to consider which might shift the emission/deposition balance one way or the other. Increase in temperature, loss of soil organic matter (SOM) due to greater soil respiration, and melting of snow would increase secondary emissions, while increase in vegetation cover and SOM could lead to greater sequestration of POPs (Cabrerizo et al., 2013). One consequence of air–surface exchange processes is to confound interpretation of temporal trends derived from long-term monitoring data (Kallenborn et al., 2012a; Macdonald et al., 2005). Concentrations of most OCPs in Arctic air have fallen over the last 2 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 produced 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 to 2000 at the Alert, Canada, monitoring station to gain insight into seasonal changes in sources and transport pathways. This is the largest data set of EFs (enantiomer fractions) 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 chiral-phase columns, either β -DEX-120 (BDX), or BGB-172 (BGB), with detection by electron capture negative ion mass spectrometry. Details of enantiospecific analysis are given in the Supplement. Analytical data were expressed as enantiomer fraction, $EF = \text{peak areas of (+)}/[(+)+(-)]$ 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 analysed on both columns and slight, but significant, biases were noticed. The average $EF_{BGB} = (0.984 \pm 0.022) \times EF_{BDX}$ for TC ($p < 0.0001$, $n = 38$), $EF_{BGB} = (1.006 \pm 0.009) \times EF_{BDX}$ for CC ($p < 0.04$, $n = 11$) and $EF_{BGB} = (1.010 \pm 0.019) \times EF_{BDX}$ 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.

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

Time series analysis was conducted by digital filtration (DF) to give best fits for seasonal and long-term trends at

Table 1. (a) Annual mean concentrations and EFs of organochlorine pesticides at Alert, Canada. (b) Annual minima and maxima EFs, from fitted DF curves.

Year	α -HCH				<i>trans</i> -chlordane				<i>cis</i> -chlordane			
	mean (SD) ¹		EF		mean (SD) ¹		EF		mean (SD) ¹		EF	
	pg m ⁻³	range	mean (SD)	N ²	pg m ⁻³	range	mean (SD)	N ²	pg m ⁻³	range	mean (SD)	N ²
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 ³	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

	α -HCH		<i>trans</i> -chlordane		<i>cis</i> -chlordane	
	minimum	maximum	minimum	maximum	minimum	maximum
	1994	0.497	0.505	0.458	0.475	0.502
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 ⁴	0.495	0.507				
mean	0.500	0.507	0.455	0.482	0.503	0.508
SD	0.003	0.001	0.007	0.005	0.001	0.002

¹ Annual mean concentrations from Hung et al. (2010). ² N refers to number of EF measurements. ³ EF results from weeks 1–34, concentrations for entire year.

⁴ Insufficient coverage for the chlordanes to determine their minima and maxima in 2000.

95 % confidence (Hung et al., 2002; Kong et al., 2014). Air parcel trajectories backwards from Alert were calculated four times each day (00:00, 06:00, 12:00 and 18:00 UTC – universal time coordinated) at 10 m above ground level 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 18 December, 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 to 2000 are summarized in Table 1. The three OCPs declined significantly during this decade; the times for a 50 % concentration decrease between 1993 and 2001 were 5.0, 4.9 and 6.7 years, respectively (Hung et al., 2010).

Monthly EFs for all 7 years of data are displayed in Fig. 1 as box and whisker plots of arithmetic mean (square), median (horizontal line), 10th–90th percentiles (whiskers), 25th–75th percentiles (boxes) and outliers (crosses). EFs of α -HCH are lowest in summer–early fall. EFs of CC are fairly constant over most of the year, with slightly higher values

in July and September, while EFs of TC show a distinct minimum in late summer. Frequency distributions of EFs for all data, summer–fall (June–October) and winter–spring (November–May) are shown in Fig. S6 in the Supplement. Distributions were not significantly different from normal for α -HCH in each period ($p > 0.05$, Shapiro–Wilk test). Normal distributions were also indicated for CC and TC in summer–fall ($p > 0.05$), but not for winter–spring nor for the entire data set ($p < 0.05$). The time series of EFs are plotted in Figs. 2–4 and are discussed by compound below.

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. 2b), 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

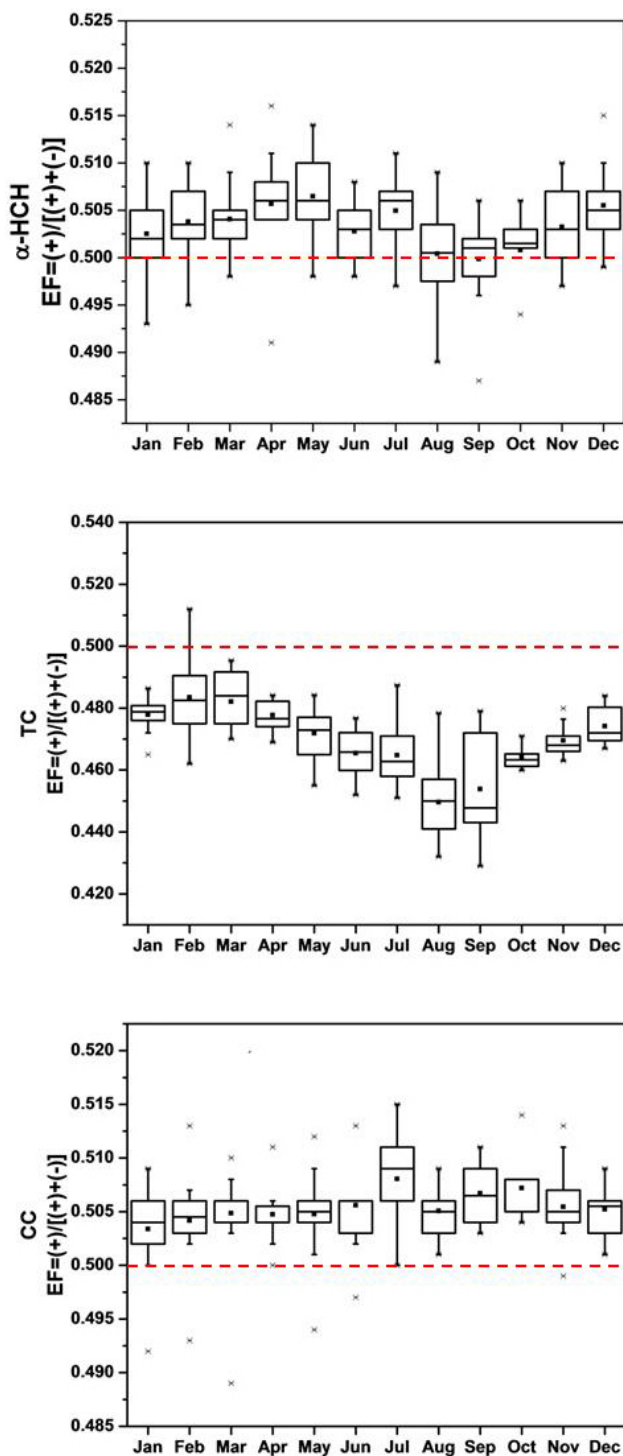


Figure 1. Box and whisker plots of monthly EFs over all 7 years: arithmetic mean (square), median (horizontal line), 10th–90th percentiles (whiskers), 25th–75th percentiles (boxes) and outliers (crosses). The dashed red line indicates a racemic composition.

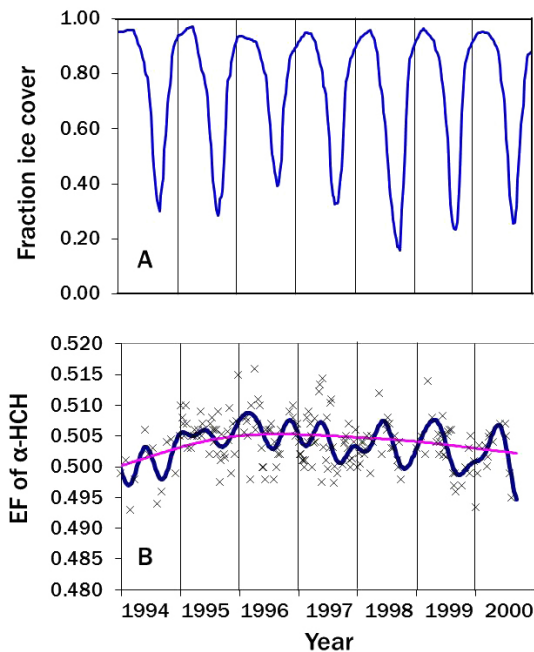


Figure 2. (a) Fractional ice cover in the Canadian Arctic (Canadian Archipelago–southern Beaufort Sea), from IceGraph 2.0 (<http://www.ec.gc.ca/glaces-ice/?lang=En&n=A1A338F4-1&offset=5&toc=show>) (accessed 6 July 2014). (b) Seasonal (blue) and long-term (pink) trends in the EFs of α -HCH in air at Alert, fitted by DF analysis (Hung et al., 2002). Experimental points are marked (X).

fractional ice cover in the archipelago and southern Beaufort Sea is shown in Fig. 2a. Minimum ice cover occurred between weeks 36 and 39, with the window for 50 % ice cover between weeks 29 and 45. Superimposing these plots (Fig. 2) shows that the EF minima occur during periods of more open water, suggesting α -HCH volatilization from the ocean. Summer–fall minima and winter–spring maxima EFs for each year were obtained from the DF fits to all the annual data points at 95 % confidence interval. The 7-year averages of the annual fitted minima and maxima were 0.500 ± 0.003 and 0.507 ± 0.001 (Table 1), and were significantly different at $p = 0.0002$ (paired t test). Sources of air to Alert during the minimum EF periods are shown in Fig. S1 of the Supplement as combined 72 h back trajectories from the end of July to mid-October. Air parcels arriving from the 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 . A strong spatial trend was evident, with lower EFs in the Beaufort Sea – western archipelago region – than in the eastern archipelago (Bidleman et al., 2007). Shipboard-scale measurements in the archipelago showed a close correlation between EFs in air and water for ice-free

regions (Jantunen et al., 2008); however, the area over which air trajectories passed enroute to Alert was too large and variable to make correlations with regional EF signatures.

Measurements at Resolute Bay (74.68° N, 94.90° W, 67 m a.s.l.) on Cornwallis Island in 1999 showed 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 re-emission of nonracemic α -HCH from the ocean. Assuming the mean winter–spring “background” EF = 0.507, 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 favoured 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 favoured 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 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 (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 and 2000, China produced and domestically consumed about 1800 t 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 ± 0.004 , $n = 162$. Greater enantioselective degradation was found for TC; mean EF = 0.470 ± 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), 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 1971–1973 (Bidleman et al., 2004). The shift from racemic to nonracemic 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.

Trends in EFs of TC in Alert air derived from DF analysis are shown in Fig. 3a. A striking feature is the annual cycling of lower EFs in summer–fall (mean of annual minima = 0.455 ± 0.007) and higher (but still nonracemic) EFs in winter–spring (mean of annual maxima = 0.482 ± 0.005) (Fig. 3a). EFs of CC are more constant and display less seasonality, except in 1997–1998 (Fig. 3b). The mean of annual minima and maxima EFs for CC are 0.503 ± 0.001 and 0.508 ± 0.002 (Table 1). The EF cycles for TC (Fig. 4a) are in phase with cycles of the TC/CC ratio, expressed as the

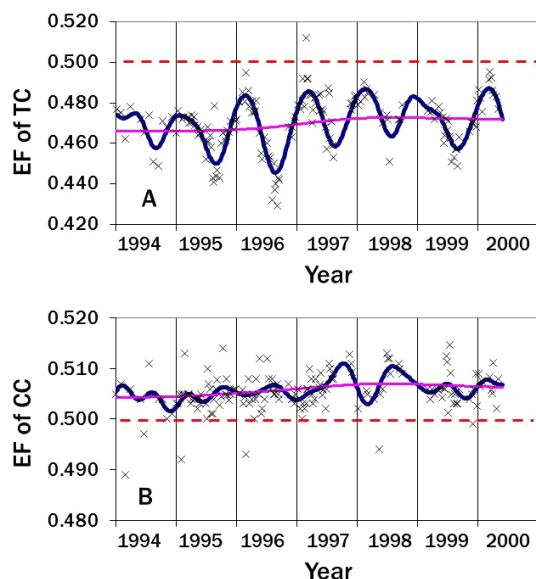


Figure 3. Seasonal (blue) and long-term (pink) trends in EFs of (a) TC and (b) CC, with experimental points marked (X), as in Fig. 2b.

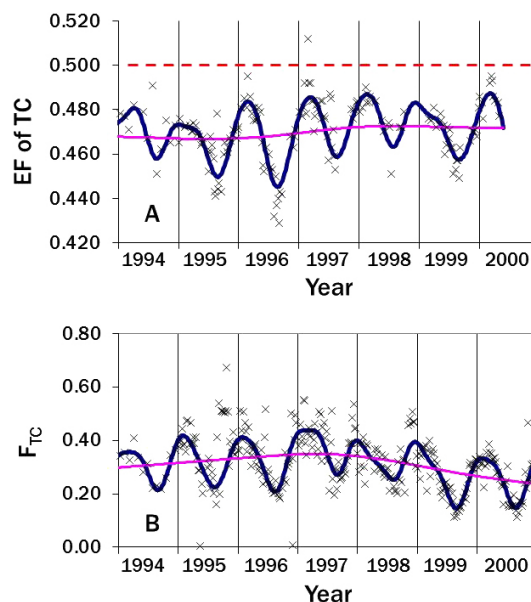


Figure 4. Seasonal (blue) and long-term (pink) trends in (a) EFs of TC and (b) $F_{TC} = TC/(TC+CC)$, with experimental points marked (X), as in Fig. 2b.

fraction $F_{TC} = TC/(TC + CC)$ (Fig. 4b). F_{TC} in Arctic air during all seasons is generally below the compositions of the technical chlordane produced in the USA (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 oxy-chlordane (OXY) and heptachlor *exo*-epoxide (HEPX) maximized in Arctic air during summer (Su et al., 2008), and photolysis products of CC and other cyclodienes were found in ringed seals (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 vapour-phase concentration of CC.

The similar cycling of F_{TC} and the EF of TC (Fig. 4) suggest that microbial processing plays a role in its transport and fate, but how and where is unclear. Average degradation preferences in soils worldwide are 56 % (+)TC, 29 % (–)TC, with 15 % of soils containing racemic TC; 22 % (+)CC, 64 % (–)CC, and 14 % racemic CC; and average EFs are TC 0.480 ± 0.067 , and 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 midwestern 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 the 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. 4. The correlation between EF and F_{TC} is highly significant ($p < 10^{-6}$) because there are a large number of data points;

however, 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. 4b) to 0.37, whereas the mean of F_{TC} minima in Fig. 4b 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 favour (–)CC and (+)TC (see above), one would expect annual 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 less than for TC (Fig. 3b). There is no significant relationship between the EF of CC and F_{TC} (Fig. S3b).

The 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 the 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 nonracemic chlordanes with preferential depletion of (+)TC (mean EF = 0.469 ± 0.032) and (–)CC (mean EF = 0.516 ± 0.033) 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 (mean EF = 0.470 ± 0.019) was depleted in air sampled over the North Atlantic in 2004 (Lohmann et al., 2009), whereas TC was racemic and (–)CC (mean EF = 0.513 ± 0.011) 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 $\ln C_{\text{air}}$ vs. $1/T$ (K) 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 the removal processes which lower its C_{air} in summertime. Such relationships for CC and TN are suggestive of local soil-exchange influencing 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

Enantiomer compositions of α -HCH, TC and CC give insights into 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 annual 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 lower archipelago. Annual cycles in the EFs of TC were more prominent and suggest different emission sources contributing to atmospheric concentrations in the warm versus 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 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. Modelling can provide an insight into the transport and fate processes impacted by climate change; however, there are many complexities and uncertainties (Gouin et al., 2013). Modelling and experimentally derived time series through monitoring are recommended as complementary approaches (Gouin et al., 2013; Kallenborn et al., 2012a). Together with signatures of isomers and parent/metabolite compounds, enantiomer-specific analysis could increase the diagnostic capabilities in air monitoring programs.

The Supplement related to this article is available online at doi:10.5194/acp-15-1411-2015-supplement.

Acknowledgements. T. Bidleman was supported by a Marie Curie Fellowship of the European Community program FP 7 PEOPLE-2009-III, International Incoming Fellowships, project number 252025, and EcoChange, a program of the Swedish Research Council for Environment, Agricultural Sciences and Spatial Planning (Formas). He was granted leave from Environment Canada while this paper was prepared. Air samples from Alert were made available with funding from the Northern Contaminants Program (NCP) (Aboriginal Affairs and Northern Development Canada). We thank the Canadian Forces Station Alert for supporting data collection and Helena Dryfhout-Clark (Environment Canada) for assistance with graphics.

Edited by: R. Ebinghaus

References

- Aigner, E. J., Leone, A. D., and Falconer, R. L.: Concentrations and enantiomeric ratios of organochlorine pesticides in soils of the U.S. cornbelt, *Environ. Sci. Technol.*, 32, 1162–1168, 1998.
- Becker, S., Halsall, C. J., Tych, W., Kallenborn, R., and Su, Y.: Long-term trends in atmospheric concentrations of α - and γ -HCH in the Arctic provide insight into the effects of legislation and climatic fluctuations on contaminant levels, *Atmos. Environ.*, 42, 8225–8233, 2008.
- Becker, S., Halsall, C. J., Tych, W., Kallenborn, R., Schlabach, M., and Manø, S.: Changing sources and environmental factors reduce the rates of decline of organochlorine pesticides in the Arctic atmosphere, *Atmos. Chem. Phys.*, 12, 4033–4044, doi:10.5194/acp-12-4033-2012, 2012.
- Bidleman, T. F., Jantunen, L. M., Helm, P. A., Brorström-Lundén, E., and Juntto, S.: Chlordane enantiomers and temporal trends of chlordane isomers in arctic air, *Environ. Sci. Technol.*, 36, 539–544, 2002.
- Bidleman, T. F., Wong, F., Backe, C., Södergren, A., Brorström-Lundén, E., Helm, P. A., and Stern, G. A.: Chiral signatures of chlordanes indicate changing sources to the atmosphere over the past 30 years, *Atmos. Environ.*, 38, 5963–5970, 2004.
- Bidleman, T. F., Kylin, H., Jantunen, L. M., Helm, P. A., and Macdonald, R. W.: Hexachlorocyclohexanes (HCHs) in the Canadian Archipelago. I. Spatial distribution of α -, β -, and γ -HCHs, *Environ. Sci. Technol.*, 41, 2688–2695, 2007.
- Bidleman, T. F., Jantunen, L. M., Kurt-Karakus, P. B., and Wong, F.: Chiral compounds as tracers of atmospheric sources and fate: review and prospects for investigating climate change influences, *Atmos. Pollut. Res.*, 3, 371–382, 2012.
- Bidleman, T. F., Jantunen, L. M., Kurt-Karakus, P. B., Wong, F., Hung, H., Ma, J., Stern, G. A., and Rosenberg, B.: Chiral chemicals as tracers of atmospheric sources and fate processes in a world of changing climate, in: Wada, Y. (ed.), *Adv. Mass Spectrom.* 19, 199–209, 2013. The Mass Spectrometry Society of Japan.
- Cabrerizo, A., Dachs, J., Jones, K. C., and Barceló, D.: Soil-air exchange controls on background atmospheric concentrations of organochlorine pesticides, *Atmos. Chem. Phys.*, 11, 12799–12811, doi:10.5194/acp-11-12799-2011, 2011.
- Cabrerizo, A., Dachs, J., Barceló, D., and Jones, K. C.: Climatic and biogeochemical controls on the remobilization and reservoirs of persistent organic pollutants in Antarctica, *Environ. Sci. Technol.*, 47, 4299–4306, 2013.
- Covaci, A., Gheorghe, A., Meijer, S., Jaward, F., Jantunen, L., Neels, H., and Jones, K. C.: Investigation of source apportioning for α -HCH using enantioselective analysis, *Environ. Internat.*, 36, 316–322, 2010.
- Dalla Valle, M., Dachs, J., Sweetman, A. J., and Jones, K. C.: Maximum reservoir capacity of vegetation for persistent organic pollutants: Implications for global cycling, *Global Biogeochem. Cy.*, 18, GB4032, doi:10.1029/2004GB002334, 2004.
- Dalla Valle, M., Jurado, E., Dachs, J., Sweetman, A. J., and Jones, K. C.: The maximum reservoir capacity of soils for persistent organic pollutants: implications for global cycling, *Environ. Pollut.*, 134, 153–164, 2005.
- Ding, X., Wang, X.-M., Xie, Z.-Q., Xiang, C.-H., Mai, B.-X., Sun, L.-G., Zheng, M., Sheng, G.-Y., and Fu, J.-M.: Atmospheric hexachlorocyclohexanes in the North Pacific Ocean and the adjacent arctic region: Spatial patterns, chiral signatures, and sea-air exchanges, *Environ. Sci. Technol.*, 41, 5204–5209, 2007.
- Fellin, P., Barrie, L. A., Dougherty, D., Toom, D., Muir, D., Grift, N., Lockhart, L., and Billeck, B.: Air monitoring in the Arctic: Results for selected persistent organic pollutants for 1992, *Environ. Toxicol. Chem.*, 15, 253–261, 1996.
- Genualdi, S. A., Simonich, S. M., Primbs, T. K., Bidleman, T. F., Jantunen, L. M., Ryoo, K.-S., and Zhu, T.: Enantiomeric signatures of organochlorine pesticides in Asian, trans-Pacific, and western U.S. air masses, *Environ. Sci. Technol.*, 43, 2806–2811, 2009.
- Gouin, T., Armitage, J. M., Cousins, I. T., Muir, D. C. G., Ng, C. A., Reid, L., and Tao, S.: Influence of global climate change on chemical fate and bioaccumulation: the role of multimedia models, *Environ. Toxicol. Chem.*, 32, 20–31, 2013.
- Halsall, C. J., Bailey, R., Stern, G. A., Barrie, L. A., Fellin, P., Muir, D. C. G., Billeck, B. N., Lockhart, L., Rovinsky, F. Y., Kononov, E. Y., and Pastukhov, B.: Atmospheric organochlorine pesticides in the western Canadian Arctic: evidence of transpacific transport, *Environ. Pollut.*, 102, 51–62, 1998.
- Harner, T., Wiberg, K., and Norstrom, R. J.: Enantiomer fractions are preferred to enantiomer ratios for describing chiral signatures in environmental analysis, *Environ. Sci. Technol.*, 34, 218–220, 2000.
- Hegeman W. J. M. and Lanne R. W. P. M.: Enantiomeric enrichment of chiral pesticides in the environment, *Rev. Environ. Contam. Toxicol.*, 173, 85–116, 2002.
- Hoekstra, P. F., O'Hara, T. M., Karlsson, H., Solomon, K. R., and Muir, D. C. G.: Enantiomer-specific biomagnifications of α -hexachlorocyclohexane and selected chiral chlordane-related compounds within an arctic marine food web, *Environ. Toxicol. Chem.*, 22, 2482–2491, 2003.
- Hoff, R. M., Muir, D. C. G., and Grift, N. P.: Annual cycle of polychlorinated biphenyls and organohalogen pesticides in air in southern Ontario, *Environ. Sci. Technol.*, 26, 266–275, 1992.
- Hoff, R. M., Brice, K. A., and Halsall, C. J.: Nonlinearity in the slopes of Clausius–Clapeyron plots for SVOCs, *Environ. Sci. Technol.*, 32, 1793–1798, 1998.
- Huang, Y., Xu, Y., Li, J., Xu, W., Zhang, G., Cheng, Z., Liu, J., Wang, Y., and Tian, C.: Organochlorine pesticides in the atmosphere and surface water from the equatorial Indian Ocean: enantiomeric signatures, sources, and fate, *Environ. Sci. Technol.*, 47, 13395–13403, 2013.
- Hühnerfuss, H. and Shah, M. R.: Enantioselective chromatography – A powerful tool for the discrimination of biotic and abiotic transformation processes of chiral environmental pollutants, *J. Chromatogr. A*, 1216, 481–502, 2009.
- Hühnerfuss, H., Bethan, B., and Kallenborn, R.: Syntheses, enantioselective separations of photocyclodienes, and their prevalence in ringed seal liver samples, *Organohalogen Cpd.*, 67, 1356–1359, 2005.
- Hung, H., Halsall, C. J., Blanchard, P., Li, H. H., Fellin, P., Stern, G., and Rosenberg, B.: Temporal trends of organochlorine pesticides in the Canadian Arctic atmosphere, *Environ. Sci. Technol.*, 36, 862–868, 2002.
- Hung, H., Blanchard, P., Halsall, C. J., Bidleman, T. F., Stern, G. A., Fellin, P., Muir, D. G. C., Barrie, L. A., Jantunen, L. M., Helm, P. A., Ma, J., and Konoplev, A.: Temporal and spatial variabilities of atmospheric polychlorinated biphenyls (PCBs), organochlorine

- (OC) pesticides and polycyclic aromatic hydrocarbons (PAHs) in the Canadian Arctic: Results from a decade of monitoring, *Sci. Total Environ.*, 342, 119–144, 2005.
- Hung, H., Kallenborn, R., Breivik, K., Su, Y., Brorström-Lundén, E., Olafsdottir, K., Thorlacius, J. M., Leppänen, S., Bossi, R., Skov, H., Manø, S., Patton, G. W., Stern, G., Sverko, E., and Fellin, P.: Atmospheric monitoring of organic pollutants in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP): 1993–2006, *Sci. Total Environ.*, 408, 2854–2873, 2010.
- Jantunen, L. M., Helm, P. A., Kylin, H., and Bidleman, T. F.: Hexachlorocyclohexanes (HCHs) in the Canadian Archipelago. 2. Air-water gas exchange of α - and γ -HCHs, *Environ. Sci. Technol.*, 42, 465–470, 2008.
- Jantunen, L. M. M. and Bidleman, T. F.: 1998. Organochlorine pesticides and enantiomers of chiral pesticides in Arctic Ocean water, *Arch. Environ. Contam. Toxicol.*, 35, 218–228, 1998.
- Jantunen, L. M. M., Bidleman, T. F., Harner, T., and Parkhurst, W. J.: Toxaphene, chlordane and other organochlorine pesticides in Alabama air, *Environ. Sci. Technol.*, 34, 5097–5105, 2000.
- Kallenborn, R., Reiersen, L.-O., and Olseng, C. D.: Long-term atmospheric monitoring of persistent organic pollutants (POPs) in the Arctic: a versatile tool for regulators and environmental science studies, *Atmos. Pollut. Res.*, 3, 485–493, 2012a.
- Kallenborn, R., Halsall, C., Dellong, M., and Carlsson, P.: The influence of climate change on the global distribution and fate processes of anthropogenic persistent organic pollutants, *J. Environ. Monit.*, 14, 2854–2869, 2012b.
- Kong, D., Macleod, M., Hung, H., and Cousins, I. T.: Statistical analysis of long-term monitoring data for persistent organic pollutants in the atmosphere at 20 monitoring stations broadly indicates declining concentrations, *Environ. Sci. Technol.*, 48, 12492–12499, 2014.
- Kurt-Karakus, P. B., Bidleman, T. F., and Jones, K. C.: Chiral organochlorine pesticide signatures in global background soils, *Environ. Sci. Technol.*, 39, 8671–8677, 2005.
- Leone, A. D., Ulrich, E. M., Bodner, C. E., Falconer, R. L., and Hites, R. A.: Organochlorine pesticide concentrations and enantiomer fractions for chlordane in indoor air from the U.S. cornbelt, *Atmos. Environ.*, 34, 4131–4138, 2000.
- Li, J., Zhang, G., Qi, S., Li, X., and Peng, X.: Concentrations, enantiomeric compositions, and sources of HCH, DDT and chlordane in soils from the Pearl River Delta, South China, *Sci. Total Environ.*, 372, 215–224, 2006.
- Li, Y.-F. and Macdonald, R. W.: Sources and pathways of selected organochlorine pesticides to the Arctic and the effect of pathway divergence on HCH trends in biota: a review, *Sci. Total Environ.*, 342, 87–106, 2005.
- Lohmann, R., Gioia, R., Jones, K. C., Nizzetto, L., Temme, C., Xie, Z., Schulz-Bull, D., Hand, I., Morgan, E., and Jantunen, L.: Organochlorine pesticides and PAHs in the surface water and atmosphere of the North Atlantic and Arctic Ocean, *Environ. Sci. Technol.*, 43, 5633–5639, 2009.
- Ma, J., Hung, H., Tian, C., and Kallenborn, R.: Revolatilization of persistent organic pollutants in the Arctic induced by climate change, *Nature Climate Change*, 1, 256–260, 2011.
- Macdonald, R. W., Harner, T., and Fyfe, J.: Recent climate change in the Arctic and its impact on contaminant pathways and interpretation of temporal trend data, *Sci. Total Environ.*, 342, 5–86, 2005.
- NCI: Bioassay of heptachlor for possible carcinogenicity, National Cancer Institute, Technical Report Series No. 9, NCI-CG-TR-9, U.S. Dept. of Health, Education and Welfare, Bethesda, MD, 1977.
- Nizzetto, L. and Perlinger, J.: Climatic, biological, and land cover controls on the exchange of gas-phase semivolatile chemical pollutants between forest canopies and the atmosphere, *Environ. Sci. Technol.*, 46, 2699–2707, 2012.
- Nizzetto, L., MacLeod, M., Borga, K., Cabrerizo, A., Dachs, J., Di-Guardo, A., Ghirardello, D., Hansen, K. M., Jarvis, A., Lindroth, A., Ludwig, B., Monteith, D., Perlinger, J. A., Scheringer, M., Schwendenmann, L., Semple, K. T., Wick, L. Y., Zhang, G., and Jones, K. C.: Past, present, and future controls on levels of persistent organic pollutants in the global environment, *Environ. Sci. Technol.*, 44, 6526–6531, 2010.
- Oehme, M.: Further evidence for long range air transport of polychlorinated aromatics and pesticides from North America and Eurasia to the Arctic, *Ambio*, 20, 293–297, 1991.
- Pučko, M., Stern, G. A., Macdonald, R. W., Barber, D. G., Rosenberg, B., and Walkusz, W.: When will α -HCH disappear from the western Arctic Ocean?, *J. Mar. Syst.*, 127, 88–100, 2013.
- Shen, L., Wania, F., Lei, Y. D., Teixeira, C., Muir, D. C. G., and Bidleman, T. F.: Hexachlorocyclohexanes in the North American atmosphere, *Environ. Sci. Technol.*, 38, 965–975, 2004.
- Stemmler, I. and Lammel, G.: Cycling of DDT in the global environment 1950–2002: World ocean returns the pollutant, *Geophys. Res. Lett.*, 36, L24602, doi:10.1029/2009GL041340, 2009.
- Stemmler, I. and Lammel, G.: Evidence of the return of past pollution in the ocean: A model study, *Geophys. Res. Lett.*, 40, 1373–1378, doi:10.1002/grl.50248, 2013.
- Stern, G. A., Braekvelt, E., Helm, P. A., Bidleman, T. F., Outridge, P. M., Lockhart, W. L., McNeeley, R., Rosenberg, B., Ikonou, M. G., Tomy, G. T., and Wilkinson, P.: Modern and historical fluxes of halogenated organic contaminants to a lake in the Canadian Arctic, as determined from annually laminated sediment cores, *Sci. Total Environ.*, 342, 223–243, 2005.
- Su, Y., Hung, H., Blanchard, P., Patton, G. W., Kallenborn, R., Konoplev, A., Fellin, P., Li, H., Geen, C., Stern, G., Rosenberg, B., and Barrie, L. A.: A circumpolar perspective of atmospheric organochlorine pesticides (OCPs): Results from six arctic monitoring stations in 2000–2003, *Atmos. Environ.*, 42, 4682–4698, 2008.
- Ulrich, E. M. and Falconer, R. L.: Chiral chlordane components in environmental matrices, in: *Chiral Pesticides: Stereoselectivity and its Consequences*, edited by: Garrison, A. W., Gan, J., and Liu, W., ACS Symposium Series No. 1085, American Chemical Society, Washington, DC, 11–43, 2011.
- Ulrich, E. M., Foreman, W. T., Van Metre, P. C., Wilson, J. T., and Rounds, S. A.: Enantiomer fractions of chlordane components in sediment from U.S. Geological Survey sites in lakes and rivers, *Sci. Total Environ.*, 407, 5884–5893, 2009.
- UNEP: Stockholm Convention, United Nations Environment Programme, Geneva, available at: <http://chm.pops.int/TheConvention/ThePOPs/tabid/673/Default.aspx>, last access: 10 May 2014.

- UNEP/AMAP: Climate Change and POPs: Predicting the Impacts. Report of the UNEP/AMAP Expert Group, Secretariat of the Stockholm Convention, Geneva, 62 pp., 2011.
- Wang, Q., Zhao, L., Fang, X., Xu, J., Li, Y-F., Shi, Y., and Hu, J.: Gridded usage inventories of chlordane in China, *Front. Environ. Sci. Eng.*, 7, 10–18, 2013.
- Wania, F., Haugen, J.-E., Lei, Y. D., and Mackay, D.: Temperature dependence of atmospheric concentrations of semivolatile organic compounds, *Environ. Sci. Technol.*, 32, 1013–1021, 1998.
- Wöhrnschimmel, H., Tay, P., von Waldow, H., Hung, H., Li, Y.-F., MacLeod, M., and Hungerbühler, K.: Comparative assessment of the global fate of α - and β -hexachlorocyclohexane before and after phase-out, *Environ. Sci. Technol.*, 46, 2047–2054, 2012.
- Wong, F., Jantunen, L. M., Pućko, M., Papakyriakou, T., Stern, G. A., and Bidleman, T. F.: Air-water exchange of anthropogenic and natural organohalogen on International Polar Year (IPY) expeditions in the Canadian Arctic, *Environ. Sci. Technol.*, 45, 876–881, 2011.
- Wong, M. H., Leung, A. O. W., Chan, J. K. Y., and Choi, M. P. K.: A review on the usage of POP pesticides in China, with emphasis on DDT loadings in human milk, *Chemosphere*, 60, 740–752, 2005.
- Xie, Z., Koch, B. P., Möller, A., Sturm, R., and Ebinghaus, R.: Transport and fate of hexachlorocyclohexanes in the oceanic air and surface seawater, *Biogeosciences*, 8, 2621–2633, doi:10.5194/bg-8-2621-2011, 2011.
- Zhang, A., Fang, L., Wang, J., Liu, W., Yuan, H., Jantunen, L., and Li, Y-F.: Residues of currently and never used organochlorine pesticides in agricultural soils from Zhejiang Province, China, *J. Agric. Food Chem.*, 60, 2982–2988, 2012a.
- Zhang, L., Bidleman, T. F., Perry, M. J., and Lohmann, R.: The fate of chiral and achiral organochlorine pesticides in the North Atlantic Bloom Experiment, *Environ. Sci. Technol.*, 46, 8106–8114, 2012b.
- Zhu, Z., Norstrom, R. J., Muir, D. C. G., Ferron, L. A., Weber, J.-P., and Dewailly, E.: Persistent cyclodiene compounds in ringed seal blubber, polar bear fat, and human plasma from northern Quebec, Canada: identification and concentrations of photoheptachlor, *Environ. Sci. Technol.*, 29, 267–271, 1995.