Responses to: Interactive comment on "Biannual cycles of organochlorine pesticide enantiomers in arctic air suggest changing sources and pathways" by T. F. Bidleman et al.

Reviewer 1, R. Kallenborn

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General comments: Atmospheric samples extracts (presumably in n-hexane/ acetone) from an archive dating back 2 decades (1994 – 2000) where examined and reanalyzed for the here presented study. A well-established enantiomer selective analytical method applying modified cyclodextrin based chiral separators as stationary phase for the capillary gas chromatographic separation.

Especially since results from samples covering such a long time span (between sampling/ extraction and reanalysis(were reported here, the QC strategy to document and control possible changes in enantiomer distribution (EF change) during long-term storage should be documented and described here (I am sure that the authors have considered this aspect, but unfortunately not included in the text).

Response: This is a good point, but it is not feasible to check the effects of storage on possible enantioselective degradation over such a long period. However, we have repeatedly used a standard solution which has been stored for over two decades. The wording added to the manuscript is (page 4, lines 17-21):

"The archived extracts in isooctane were stored at 4 ^{o}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 ^{o}C, for over 20 years and their compositions have remained racemic".

Since the enantiomer selective analysis is a crucial point for the entire study, the chiral separators (complete IUPC name and percentage in the achiral mediating stationary phase) as well as the chosen temperature program and the instrumentation used should be explained in more detail.

Response: More information is now given in Supporting Information (page S2): "Enantiomer separations of α-HCH, TC and CC were carried out on Betadex-120 (BDX, 20% permethylated β-cyclodextrin in SPB-25, 30 m x 0.25 mm i.d., 0.25 µm film, Supelco, Bellefonte, PA, U.S.A.) or BGB-172 (BGB, 20% tert-butyldimethylsilyl-β-cyclodextrin in OV-1701, 15 m x 0.25 mm i.d., 0.25 µm film, BGB Analytik AG, Switzerland), with detection by electron capture negative ion mass spectrometry. Instruments used were a Hewlett-Packard 5890 GC-5989 MS-Engine (Hewlett-Packard, U.S.A.) or Agilent 6890 GC-5973 Mass Selective Detector (MSD). Operating conditions were: injector (splitless, opened after 1 min) 220 ^{o}C, ion source 150°C, quadrupole 100 ^{o}C, helium carrier gas at 40-60 cm s^{-1}, methane reagent gas. Temperature programs were varied according to the analytes and condition of the column. In general, slower ramp times and/or

Statistical significance:
Very small deviations from EF derived from a relatively restricted data set (i.e. P250033/L20:
0.507±0.002 by n = 7 data pairs and more) are evaluated as a significant deviation. Expecting
ultra-low concentration and "peak" identification close to the LOD for most of the values in
combination with a low number of samples for these comparisons, the high confidence provided
here is highly surprising. A (significant) deviation from racemic of 0,007 is implying an method
uncertainty of better than 1.5% for the complete determination method (incl. GC/MS
determination). According to my understanding, different integration settings for the automatic
integration of used quantification software will account for ca. 6-10% of the total uncertainty in
EF determination (dependent on the area/ height of the signals). Therefore a detailed
paragraph on the selected statistical significance criteria, analytical uncertainties, distribution
testing etc. is considered as an important added value for the manuscript in
order allow the interested reader to appreciate the high scientific value of this study.

Response: The comparison in question is of annual mean maxima and minima EFs of α-HCH.
These maxima and minima (now listed in Table 1) were not single points, but were obtained
from digital filtration (DF) fitting of curves to all data points for the year at 95% C.I. The fitted
maxima and minima EFs are listed in Table 1. Means of fitted maxima and minima EFs over the
seven years of the study were compared with a paired t-test and the difference was highly
significant, p=0.0002. So you can see that each year's maximum and minimum EF was derived
from 95% C.I. fits to many data points, and then the means of these were taken over seven
years. The more concise wording in the revised paper is (page 6, lines 4-7):

"Summer-fall minima and winter-spring maxima EFs were obtained from the DF fits to all the
data points at 95% C.I. Seven-year averages of the annual fitted minima and maxima were
0.500 ± 0.003 and 0.508 ± 0.001 (Table 1), and were significantly different at p = 0.0002 (paired
t-test, two sample for means)".

Frequency distributions for the entire data set, summer-fall data, and winter-spring data are now
shown as Figure S6 in Supporting Information, and box-and whisker plots have been added to
the main paper as Figure 1. The following statements are made in the text of the main paper
(page 5, lines 8-17):

"Monthly EFs for all 7 years of data are displayed in Figure 1 as box and whisker plots of arithmetic mean (square), median (horizontal line), $10^{th} - 90^{th}$ percentiles (whiskers), $25^{th}-75^{th}$ percentiles (boxes) and outliers (crosses). EFs of α-HCH are lowest in summer-early fall with a second minimum around January. 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 Supporting Information, Figure S6. 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 the entire data set (p <0.05)".

Detailed Comments: P25032/L3 "EF = quantities of (+)/[(+)+(–)]" The "term" quantities is implying that the amount of the separated enantiomers has been calculated before the EF is determined. Usually, the area ratios derived from the chromatogram directly are used for the EF calculation, please clarify.

Response: "quantities" has been replaced by "peak areas" (page 4, line 9).

P24033/L19 "Average summer-fall minima and winter-spring maxima" Please provide information on average/median concentrations (min/max) underlying these EF values.

Response: In Supporting Information (Figures S2B and S4A,B), we provide plots of EFs vs. concentration for the entire data set. Some of these are significant because of many data points, but the r^2 values are very low (<0.05). This indicates that concentration is not a major factor in controlling EF. Annual mean concentrations and ranges of the analytes are given in Table 1, but we have not associated concentrations with the DF-fitted EFs.

Aspects considered:
1. Does the paper address relevant scientific questions within the scope of ACP? Yes
2. Does the paper present novel concepts, ideas, tools, or data? Yes
3. Are substantial conclusions reached? Yes
4. Are the scientific methods and assumptions valid and clearly outlined? Not completely (revisions/ explanations required)
5. Are the results sufficient to support the interpretations and conclusions? Yes
6. Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)? Yes
7. Do the authors give proper credit to related work and clearly indicate their own new/original contribution? Yes
8. Does the title clearly reflect the contents of the paper? Yes
9. Does the abstract provide a concise and complete summary? Yes
10. Is the overall presentation well structured and clear? Yes
11. Is the language fluent and precise? Yes
12. Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? Yes
13. Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? No
14. Are the number and quality of references appropriate? Yes
15. Is the amount and quality of supplementary material appropriate? Yes

Recommendation: The manuscript is recommended for publication in "Atmospheric Chemistry and physics" after major revisions, for details please see above.

Reviewer 2, Anonymous

Review of "Biannual cycles of organochlorine pesticide enantiomers in arctic air suggest changing sources and pathways"
This is a very interesting work, well written, and the result of an impressive experimental work. To find and describe time trends of EFs with such a small variation can only be achieved if the analytical work is extremely careful, as done in this work. My impression is that this is a nice and important contribution and can be published in Atmospheric Chemistry and physics after the minor-moderate modifications commented below.

Specific comments

Introduction. Line 13. It is possible that the temperature increase associated to climate change can induce an increase of emissions, but this is a complex phenomena with many positive and negative feedbacks. Climate change can also lead to more icefree soils, an increase of vegetation cover, and an increase of surface sequestration of POPs (see Cabrerizo et al. EST 2013). There are other potential feedbacks.

Response: This is a good point, and the text has been modified as follows (page 2, lines 24-30):

"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).

Figures 1-3. Even though not important, usually the A panel is the upper panel, and the B panel is the lower panel, here the opposite is shown. In addition, I would introduce the time trend of concentrations as a third panel in addition to EFs.

Response: A and B now refer to upper and lower panels in the figures. We have not added a third panel of time trends for concentrations, because it is clear from scatter plots in the Supporting Information that concentration is not a controlling variable in determining EFs. Please see our response to a similar comment by Reviewer 1.

Table 1. I suggest to enlarge this table to include either the mean for the summer-fall and winter spring of all parameters for each years, or maybe better the upper and lower limit of the range.

Response: Table 1 has been expanded to include the DF-fitted annual maxima and minima EF values. A set of three stacked "box and whisker" panels (Figure 1) shows the range, 75th and 95th percentiles, mean and median of EF values for the 7-year data set (see response to Reviewer 3).

To correlate with ice cover is ok, but this variable may be related to many others. For example, Stanley et al. J. Marine Systems 2014, shows that years with different ice cover induce different respiration and primary production fluxes. It is possible that different respiration activity from bacteria, could lead to different EFs. I guess that there

are many variables that could be related to ice cover, and that indirectly could affect the remobilization and degradation (EFs) of these chemicals. Some comments could be included in the text. I don't know if there are time series available for bacterial abundance or activity (secondary production) in Arctic seawater, or soils, or snow/ice, but if available, it would be nice to correlate them with the time series of EFs.

Response: Also a good point, and indeed there are spatial variations in EFs of α-HCH in Canadian Archipelago surface water. These variations also show up in air sampled from a ship traversing ice-free waters, but the area covered by air trajectories enroute to Alert was too large for such detail to be observed. The text has been modified to read (page 6, lines 9-18):

"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. 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".

We did not attempt to correlate EFs with bacterial abundance, and do not know if such measurements are available for the years of the study. Water concentration and EF measurements in the Archipelago were only made in 1999 (Bidleman et al., 2007; Jantunen et al., 2008). Also, it is not only bacterial abundance but the type of bacteria that is likely to be important in the enantioselective degradation.

- A small variation of EF are often compared, and statements are made on whether there are differences, but it is not always clear that these statements are supported by statistical tests.

Response: The discussion has been improved; please see our reply to a similar comment by Reviewer 1.

- A 11% contribution from marine volatilization is not a big figure. It is possible that there is volatilization of HCHs in the Canadian Archipelago, but I would say that a small modification of the gas phase EF could be achieved even if there is not a net volatilization, because anyway, even if there is air-water equilibrium, or there is a net deposition, there is always a gross volatilization term of low EF HCH that can modify the atmospheric EF.

Response: This is true! Air that has equilibrated with water will obtain the seawater EF because the ocean is a much larger reservoir. Even if there is net deposition, the air EF will be modified by evasion of some α-HCH from the ocean. This is discussed by Ridal et al., ES&T 1997. The point we are making is that the proportion of ocean-derived α-HCH which reaches Alert is small compared to a situation where air is sampled from shipboard closer to the water (e.g., the Jantunen et al., 2008 and Wong et al., 2011 measurements in the Archipelago).

- Conclusions. It is stated that "It is likely that the EF profiles of these and other chiral compounds will continue to change with rising contribution of secondary emission sources". This is very interesting. Can these temporal trends be commented in the

discussion EFs for CC and TC seem to be increasing over time. This is not clear for a-HCH. Do the authors have the EF from recent years at Alert, or have they been published, so they can be compared?

Response: We have no EF temporal trends beyond this study, but the last sentence in our conclusion indicates that such measurements could be useful. There are documented increases in concentrations of POPs in air within the 2000-2010 decade (Ma et al., 2011; Kallenborn et al., 2012). A thorough analysis of trends from 20 air monitoring stations around the world shows general decline of POPs with increases in only 19 out of 257 time trends (Deguo Kong et al., 2014, added to reference list). However, what is important for EFs is not just the concentrations of POPs, but their sources. Concentrations could be decreasing, but the proportion of secondary emissions increasing, leading to less racemic EFs.

Title. I'm not sure if "biannual" is right here. It means it occurs twice every year, but there just one cycle per year (increase during winter and decrease during summer). So maybe it should be "seasonal" or "annual".

Response: Good point, the first word of the title has been changed to "Annual".

Reviewer 3, Anonymous
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This manuscript present the results from the re-analysis of air sample extracts for selected chiral OC pesticides from the Canadian air toxics sampler at Alert (Canadian Arctic). The resulting time-series of enantiomeric fractions (EFs) of three chiral OCs are presented and discussed for the 7 year period, 1994-2000. This is exactly the sort of use that a sample archive like this should be subjected to, as EFs are not dependent on sample/solvent integrity etc over the storage period. Given the number of samples/data points for each year of study (n=10s in each case), then this gives a statistical robustness to the observed trends, and it's nice to see use of a trend-fitting model like DF applied this dataset. The core of the discussion is related to under-standing the annual variation in EF values, relating seasonal shifts in EFs in arctic air to changes in emissions from secondary sources (soil, water). This is a unique paper and one of a very few to actually report a multi-year time series of EF data. The discussion gives diagnostic insight into contaminant ageing and source type to be affecting the Arctic in the late 1990s. I have no reservations about this manuscript and recommend publication in ACP. The paper is very well written with an excellent narrative style that ends by identifying a clear research need (I'm already looking forward to Part II, 2001-2011!).

Comment: 3.2 Chlordanes (p25038, lines 15-24). In the discussion about TC and CC sources and the role of the temperate ocean, the authors report the preferential depletion of (+)TC and (-) CC in recent water samples (2008) from the N. Atlantic (Zhang et al.2012b). It would be useful if the actual EF values from this study (e.g. mean and range) were reported here, allowing direct comparison to the EF values reported for the Alert air samples in the 1990s. This may help to discount/support the role of northern temperate marine waters as a source of these chemicals to arctic air.

Response: Mean EFs and standard deviations are now included (page 10, lines 18-23).

Suggestion: Is it possible to illustrate EF data for each of the OCs as a box-and-whisker plot? As the n-values are high, plus there doesn't appear to be an underlying multi-year trend in the EFs, then lumping all the annual datasets into 'winter-spring' and 'summerfall' categories would really emphasize the seasonality, perhaps better than a modelled DF trend. Measured outliers could then be investigated. For example, if low value EFs for a-HCH (outliers < 10th percentile) all occurred in July-August (coinciding with ice melt/ice free periods) then this is compelling evidence to suggest a regional arctic seawater signal (akin to the ice-seawater-air work by Wong et al 2011). Ditto, outliers > 90th percentile may be linked to LRT events from afar.

Response: This is a good suggestion, and we have added box-and-whisker plots to the main paper as a new Figure 1. See response to Reviewer 1. This figure has also been reproduced below for purposes of the interactive discussion. There is difficulty relating "outliers to LRT events from afar", because the air trajectories were only run for 72 hours, and most of them did not get out of the arctic region within that time. See Figure S1 of Supporting Information.

Caption for new Figure 1 (see below). 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.