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.

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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^{o}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

lower oven temperatures were used to improve enantiomer resolutions on aged columns. Typical programs were (Kurt-Karakus et al., 2005):

Chlordanes on BDX: 90 °C (1 min), 15 °C min^{-1} to 150 °C, 1 °C min^{-1} to 185 °C (25 min), 20 °C min^{-1} to 225 °C (20 min).

Chlordanes and α-HCH on BGB: 90 °C (1 min), 20 °C min^{-1} to 160 °C, 2 °C min^{-1} to 180 °C (41 min), 25 °C min^{-1} to 225 °C (15 min).

α-HCH on BDX: 90 °C (1 min), 20 °C min^{-1} to 145 °C, 1 °C min^{-1} to 170 °C, 20 °C min^{-1} to 225 °C (15 min).

Chromatographic peaks were integrated manually at each of the two monitored ions. Target/qualifier ion ratios (IRs) for each enantiomer peak were required to fall within the 95% C.I. of IRs for standards, otherwise, the result was rejected (Kurt-Karakus et al., 2005).

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