

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

Anonymous Referee #2

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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”.