

Response to the Anonymous Referee #2

We would like to thank the reviewer for his/her comments. Listed below are changes made to the manuscript according to the reviewer's comments, and a point-by-point reply to the reviewer's comments. The original comments are shown in italics and responses are given in normal fonts.

This paper examines the step point of the atmospheric concentration of POPs in the Arctic using three statistical analysis. The authors modeled the relative contribution of secondary emission from sea-ice/water on the atmospheric concentration of POPs, to primary emission and degradation. The authors employed long-term monitoring air data from four Arctic stations for their analysis. The paper is well-written but requires improvement on the figures. The paper is suitable for publication pending on the response to the following comments.

General comments:

I think the authors should only show the highlights of the results in the figures instead of everything. For example, Figure 1, 2, 3 and 4 are showing the same results from the step change statistical analysis for the 4 Arctic stations. There are too much information here. Perhaps the authors can just show the significant results and put the rest into the Supplement. The authors should also simplify Figures 5 and 6.

Following the reviewer's suggestion, we have moved Figures 3 and 4 to Supplement (Figs S2 and S3) and combined two subsections 3.1.3 and 3.1.4 to one subsection 3.1.3 Storhofdi and Pallas (line 361 in the revised paper). Further efforts were made to simplify Figs 5 and 6, now Figs 3 and 4 in the revised manuscript by removing the figures for those chemicals showing no statistical significant step changes from Moving T-test and Yamamoto method.

There are very limited data on the concentration of POPs in ice and they may be of high uncertainty. Have you tried running the model with different ice concentration? I see that you have used the measurements from Hansen et al., for α -HCH in ice and snow concentration. Have you considered using recent measurements from Pucko et al. Environ. Sci. Technol., 2010, 44, 9258-9264?

Thanks to the reviewer for providing us Pucko et al's work. Pucko et al's data of monitored α -HCH concentrations in air, ice, and ice brine have been input to the perturbation model to examine potential influence of higher α -HCH concentrations in sea ice and sea ice brine on the fluctuation and temporal trend of this chemical over the Arctic air. Results show that the input higher mean concentrations of α -HCH in sea ice and ice brine (Pucko et al., (2010), compared with the data we used in the present study as presented in Table S1, increases the magnitude of perturbed annual concentrations in air and ice but do not alter their fluctuations and long-term trend

(see new Fig. S7). This suggests again that the changes in temperature dominate the fluctuations of perturbed α -HCH concentrations over the Arctic. Likewise, the perturbed gas-phase air-brine exchange fluxes using Pucko et al.'s data (2010) also exhibited the similar trend and inter-annual fluctuations as the air-ice exchange fluxes, though two time series of the perturbed fluxes differed in magnitude. We have added a new paragraph and discussions for the new result in the revised paper (line 563-578) and a figure (Fig. S7) in the Supplement. Pucko et al.'s manuscript (2010) has been also included in the references of revised paper and Supplement.

Have the authors considered air-brine gas exchange and how would that be affected by climate change?

The reviewer raised an interesting question but we feel that investigation into the association between air-brine gas exchange and climate change is beyond scope of this study. Nevertheless, following the reviewer's comment, we have run the perturbation model using the sampled α -HCH concentrations in air, water, and brine collected by Pucko et al (2010) and compared the results with modeled air-ice exchange fluxes using the data presented in Table S1 of Supplement. It was found that, though the two time series of the perturbed fluxes exhibited the same fluctuation and trend driven by temperatures and sea ice extents, the air-brine exchange fluxes were several orders of magnitude greater than the air-ice fluxes and did not switch from positive to negative as shown in perturbed air-ice flux which turned from positive to negative from 2008 (**Fig. 8**) (line 662-670).

The authors have identified the step points for a number of POPs with the hypothesis that rapid melting of sea ice and rising of temperature is the cause. Does the observed step change coincide with the model results? It is not clearly state in the paper. Maybe the authors can elaborate on this point.

Since the perturbed concentrations discern largely the climate change signals in POPs time series, associated with temperatures and sea ice, it might not be appropriate to compare the step change points in the time series of measured annual mean air concentrations. The latter are driven primarily by emissions and degradation. Nevertheless, the perturbed air concentrations of many PCBs examined in the present study showed the step change in 2001. New Figure S6 in Supplement illustrates the MK-test for perturbed concentration of PCB-28, showing the step change in 2001 which is also the first step change point of monitored PCBs atmospheric concentrations (Tables 1 and 2) and the year when the mean summer temperature and sea ice extent anomalies over the Arctic change their signs (**Fig. 5**). These statements have been added to the revised manuscript (line 554-562) and a new figure (figure S6) has been added to the revised Supplement.

The authors often described the model concentration as "perturbation concentration", which seems awkward. I think it should be called "perturbed concentration" or just

"modeled concentration". It does not sound right when you put two nouns together.

All these were corrected in the revised paper.

Specific comments: p. 1249, line 14, "duo" should be "due"

Thanks for the correction of this typo error.

*Supplement, Reference Hansen et al., "r-HCH" should be "α-HCH"? or "g-HCH"?
Please double check.*

Yes the reviewer is right. It is α -HCH and we have corrected this typo error.