

Interactive comment on “Atmospheric transport of persistent semi-volatile organic chemicals to the Arctic and cold condensation at the mid-troposphere – Part 1: 2-D modeling in mean atmosphere” by J. Ma

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We appreciate the constructive comments from the anonymous referee. Major revisions were made following the Referee's comments. Our responses to the referee's comments are detailed below.

The referee raised three shortcomings of the manuscript. The first is unclear for what the overall goal of the work is. The referee challenged the concept of “cold condensation” and “global distillation” that we used in the paper.

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Primary motivation of this work was to clarify poleward atmospheric transport and global distillation/cold condensation effect on SVOCs. As we indicated in Introduction, previous interpretation on global distillation (e.g., the UNEP's statements that we cited in Introduction) appeared misleading in the sense of atmospheric transport of SVOCs to the Arctic because the statements suggested that such the poleward long-range transport occurs near the surface. We examined the major pathways of atmospheric transport of SVOCs to the Arctic and cold condensation (winds, temperature, deposition, clouds...) in both mean meridional atmospheric circulation (part 1) and episodic events (part 2, Zhang et al., 2009). To further highlight the objectives in the paper, in the revised paper we wrote “The objectives of the present study are (1) to examine major atmospheric pathways of poleward transport of SVOCs under the mean meridional atmospheric circulation, and (2) to examine the cold trapping of SVOCs in the mid-troposphere over the warm latitudes” (the last paragraph of Introduction). Other changes to highlight the motivation of this work were also made in this section. We agree with the referee that the term of cold condensation might results in confusion. We used this term in the previous version of the manuscript in order to be consistent with the UNEP's statement. We noticed Wania and Westgate's suggestion (2008) for better using “cold trapping” instead of “condensation”. This has been added in the revised first paragraph in Introduction. In the end of this section, we wrote “Although the global distillation / cold condensation terminologies have been used in the UNEP's statements and many studies, in the present study “cold trapping” will be used wherever possible”. So “cold trapping” is used throughout the rest of revised manuscript.

The second shortcoming that the referee indicated was lack of model description and evaluations against other models and measurements. In reality, the non-steady state solution to Eq. (1) was given by 2D version of Canadian Model for Environmental Transport of Organochlorine Pesticides (CanMETOP). The CanMETOP has been extensively used in atmospheric modeling of SVOCs. In the revised paper, The CanMETOP was briefly described. The 3D version of the CanMETOP was also used in the second part (Zhang et al., 2009) of this study. In the second part of the paper, two

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models (MEDIA and CanMETOP) were used to capture episodic atmospheric transport of HCHs to the Arctic. The purpose for application of the two models in this study was, through two models' inter-comparison, to ascertain that the episodic atmospheric transport events can be more faithfully captured and modeled. If the two models, started with the same governing equation for the atmospheric transport but solved with different numerical schemes and parameterizations, can duplicate each other's results, the modeled transport events are more close to a realistic reproduction of the actual transport events, as we stated in the manuscript (Zhang et al., 2009).

Other modeling studies on HCHs provided by the referee have been cited and added in Reference section in the revised manuscript.

The 2D modeling study was mostly designated as a quantitative conceptual examination to the UNEP's statements on global distillation, as we stated in the last paragraph of Introduction of the revised paper. Given that the model results reported in the first part of paper dealt with 2D transport under the mean meridional atmospheric circulation, it is very difficult to compare the model results with other 3D atmospheric models and measurements taken at a signal site, though there are extensive field measurements available, as we stated in the beginning of section 4.3. This was the reason that the modeled results were compared with measured a-HCH in the Arctic because of homogeneous distribution of HCHs in air throughout the Arctic, as we indicated in section 4.3. Nevertheless, from the information provided by the referee, we are happy to know there was another aircraft measurement of SVOCs. By assuming that atmospheric concentration of a-HCH in the free atmosphere was uniformly distributed in the same latitude (note that our results were 2D modeling results under the mean meridional atmosphere circulation and zonally averaged winds and air temperatures), we further compared the modeled a-HCH air concentrations by 2D CanMETOP with this aircraft monitored data. New results have been presented in the revised paper (section 4.3). Results showed a good agreement between modeled and measured concentrations. For g-HCH and HCB, we only input artificial soil residues in tropical region in order to

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examine poleward atmospheric transport cycle (emitted from warm latitudes and deposited to the Arctic) under the mean meridional atmosphere, their results cannot be compared with measurements, as stated in the newly-added last paragraph of section 4.3.

In subsequent responses to the referee, our replies will follow the referee's comments.

Referee comments: In addition, it seems that the model is technically flawed because in eq. 3 on p. 459 only deposition to soil is considered, although the largest part of the deposition flux goes into ocean water, but ocean water is not considered in the model. Furthermore, the heading of section 4.3 should be changed to "model evaluation", because "verification" is a term that is not appropriate in this context; models of open systems can never be verified, as extensively discussed by Oreskes et al. *Science* 1994, 263, 641-646, Verification, Validation and Confirmation of Numerical Models in the Earth Sciences. Finally, there are several other studies using atmospheric transport models and describing the transport of alpha- and gamma-HCH that need to be referenced.

Reply: In the revised paper, we added Eq. (2b) to expand Eq. (2a) (Eq. (2) in the previous version of the paper) to include other air/surface exchange processes (e.g., water surface) by expressing $\bar{A}G$ as the air compartment in contact with several other media. Accordingly, F_s in Eq (3) can be replaced by the fraction of SVOCs transported from air to any underlying surface. Following the suggestion of the referee, "model verification" of section 4.3 has been changed to "model evaluation". The references provided by the referee have been cited in the revised paper.

Referee comments: A third major shortcoming is that the chemical property data used as model input have not been derived from the relevant sources. Degradation of all three compounds in air has been measured by Brubaker and Hites, *Environ. Sci. Technol.* 1998, 32, 766-769 and this study needs to be referenced. Furthermore, it is not clear from what sources the degradation half-lives in soil were taken (parameter

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eta_s in eq. 3; table 1). To my knowledge, the references provided (Schenker (2005) and Xiao (2004)) do not contain degradation half-lives in soil.

Reply: We further checked relevant sources of the chemical property data in Table 1. Brubaker and Hites' paper has been cited in the revised paper. Schenker (2005) and Xiao (2004) were referred to other physical/chemical properties, not for degradation half-lives. Degradation half-lives in soil are referred to Mackay et al (1997) which has been added to References section.

Referee comments: Finally, the language of the manuscript needs improvement; there are many typos and awkward and unclear expressions. Moreover, the manuscript is too long.

Reply: Efforts have been made for improving English. A native English speaker helps to polish English/grammar. Efforts are also made to reduce the size of the paper. In the revised paper, figure 11 and table 2 as well as corresponding texts and equations (11), (12) have been deleted.

Specific comments

Referee comments: p. 455, line 8-10: Goldberg is not represented properly here. He only talks about mobilization of SVOCs from soil and their transfer to ocean water; he is concerned with adverse effects of SVOCs on wildlife in oceans but does not at all talk about the Arctic in the 1975 paper cited here. Goldberg used the term "global distillation" only to point out the mobilization of SVOCs from soils.

Reply: Correspondent text has been removed from the revised manuscript.

Referee comments: p. 455, line 12: it is "cold trapping", not "tripping". These processes are not at all "the similar process" as global distillation introduced by Goldberg, but they describe the complement of the global distillation process, namely the enrichment of SVOCs in the solid and liquid phases of colder environments.

Reply: Thanks for correcting the word. The referee's point on the complement of the
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global distillation process has been added to the revised paper.

Referee comments: p. 455, line 19: the document by Stow (2005) is not an appropriate reference here; first, the document is not anymore available at the URL provided (www.unece.org/env/popsxg/docs/2005/a%20effects%20of%20deposition%2015%2006%2005.pdf), but beyond that, it is not suitable here because there is empirical information about latitudinal fractionation of SVOCs that needs to be referenced here: Meijer et al., Influence of Environmental Variables on the Spatial Distribution of PCBs in Norwegian and U.K. Soils: Implications for Global Cycling, Environ. Sci. Technol. 2002, 36, 2146-2153.

Reply: This reference has been deleted in the text and references list. Instead, Meijer et al's work (2002) provided by the referee has been cited in the revised manuscript.

Referee comments: p. 455, line 28: SVOCs do not at all "condense", i.e. form a liquid or solid phase. They partition into solid or liquid phases such as soil, water or vegetation in colder environments, because their vapor pressure is a strong function of temperature and decreases significantly with decreasing temperature. But this is not a condensation process although the term "cold condensation" is used by some authors. "Cold trapping" avoids this misunderstanding and is more appropriate.

Reply: The referee's point is right! See our previous response. "Cold condensation" has been replaced by "Cold trapping" wherever possible in the revised paper, as indicated in the end of Introduction.

Referee comments: p. 456, lines 3-4: this sentence is awkward and needs to be rewritten.

Reply: The sentence has been removed.

Referee comments: p. 456, line 26: differs from [not with] the Arctic.

Reply: Corrected. Thanks!

Referee comments: p. 457, line 13-14: I disagree – why should the large-scale vertical motion contribute in any way to the cold condensation effect? The cold condensation effect is solely driven by the temperature dependence of the Henry's law constant and the octanol-air partition coefficient of chemicals. If the author means to say that large-scale vertical motion contributes to transport of SVOCs to the Arctic, it should be stated in this way. The term “cold condensation” should be avoided because, as the author's own case shows, it leads to misunderstandings.

Reply: We agree with the referee's comments. The sentence has been deleted in the revised paper.

Referee comments: p. 457, line 27: Wania and Mackay (2000) is not a source for degradation rate constants of these chemicals. The author needs to consult and reference the paper by Brubaker and Hites, Environ. Sci. Technol. 1998, 32, 766-769.

Reply: We have replaced the paper by Wania and Mackay (2000) by Brubaker and Hites' paper which is also listed on references section.

Referee comments: p. 460, line 11-12: “the flux of a persistent substance to the soil – a function of the substance in the soil” - this sentence does not make sense.

Reply: The sentence has been deleted.

Referee comments: p. 460, eq. 3: the term F_s needs to be determined in a similar way for deposition to ocean water or, more precisely, for deposition to soil and ocean water in combination. This would also require a degradation rate constant for ocean water to be included. At this point, the model is technically flawed.

Reply: Done! See our previous responses.

Referee comments: p. 460, line 8: “Hoc” should be “Hov”

Reply: Corrected. Thanks!

Referee comments: p. 462, line 12: again, I do not think this is an actual condensation

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or condensed phase.

Reply: “condensed phase” has been changed to “solid phase” in the revised manuscript.

Referee comments: p. 462, line 18: “1 ton” is not a concentration. This is highly confusing.

Reply: “concentration” has been deleted. It is a unit of soil residue. Thanks for the correction!

Referee comments: p. 463, line 6-7: “Interestingly, the gamma-HCH-laden air sinks only over the Arctic by a strong downward motion – a signature of the downdraft of the Polar cell” – to me, this is not an interesting finding but an obvious fact that is to be expected.

Reply: The word “interestingly” has been deleted.

Referee comments: p. 464, line 6: again, “1 ton” is not a concentration!

Reply: “concentration” is deleted.

Referee comments: p. 465, line 21-22: Wania and Mackay (1993) is not an appropriate reference here, at least not if it is the only reference provided. To demonstrate the homogenous distribution of SVOCs in the Arctic, empirical studies need to be referenced as well.

Reply: Two new references (Pacyna and Oehme, 1988 and Su et al, 2006) on spatial uniform distribution of HCHs and HCBs in the Arctic have been cited in text and References section.

Referee comments: p. 465, line 28: The study by Harner et al. (2005) is NOT the only attempt to measure SVOCs in the mid-troposphere. Another study of this type is that by Knap and Binkley, Chlorinated Organic Compounds in the Troposphere over the Western North Atlantic Ocean Measured by Aircraft, Atmospheric Environment 1991,

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25 A, 1507-1516, and this study should be included and referenced here as well.

Reply: Glad to know this work! The paper has been cited in text and the references section. In particular, the aircraft measured a-HCH data reported in this paper have been used to further compare with 2D modeling results (see previous responses).

Referee comments: p. 478, caption of Figure 1: how was the OH radical concentration in air implemented in the model? This is a spatially variable parameter that is crucial for calculating the environmental fate of airborne chemicals. Wania and Mackay (1996) is not an appropriate reference for OH radical concentrations; the author should use data from Spivakovsky et al., Three-dimensional climatological distribution of tropospheric OH: Update and evaluation. *J. Geophys. Res.* 2000, 105, 8931–8980.

Reply: The OH radical concentration used to compute the degradation rate was averaged over the Northern Hemisphere using values collected by Toose et al (2004) at 17 molecules cm⁻³. This value is higher than Spivakovsky et al's mean value in the Northern Hemisphere (11 molecules cm³). These have been added in the caption of Figure 1. Toose et al (2004) and Spivakovsky et al (2000) have been also cited in Reference section.

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