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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

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In this manuscript, the author presents results from a 2-D atmospheric transport model for three semivolatile organic chemicals (SVOCs), alpha- and gamma-HCH and HCB. The model covers the northern hemisphere and the troposphere up to an altitude of 12 km and is used to analyze the movement of the SVOCs from the tropics to the Arctic. The manuscript suffers from several shortcomings. First, it is not clear what the overall goal of the work is. In the introduction, the author talks about concepts such as "cold condensation" and "global distillation" but uses these terms in a confusing way, with incorrect interpretation of earlier authors and without coming to a clear research

question (see detailed comments below). In the results section, a wide range of model results (levels and fluxes of the three chemicals at different altitudes and latitudes) is presented, but it is not clear what the most important findings are nor what the innovative contribution of the work is.

Second, there is no real discussion of the model and the underlying assumptions. This includes three aspects that are needed here: a discussion of the model in the light of its conceptual assumptions; a comparison of the model to other models; and a comparison of the model results to field data. In section 4.3, the author compares some of the model results from field data from one single study and only for one of the three compounds (alpha-HCH). However, there are extensive field measurements of all three chemicals and the author needs to include these data. Sources are the monitoring data reported under the European Monitoring and Evaluation Programme, EMEP, see http://tarantula.nilu.no/projects/ccc/index.html, and several studies referring to the EMEP data and/or reporting measurements from individual campaigns; these are for HCHs:

Iwata et al. Distribution of persistent organochlorines in the oceanic air and surface seawater and the role of ocean on their global transport and fate, Environ. Sci. Technol. 1993, 27, 1080-1098

Su et al., Spatial and Seasonal Variations of Hexachlorocyclohexanes (HCHs) and Hexachlorobenzene (HCB) in the Arctic Atmosphere, Environ. Sci. Technol. 2006, 40, 6601-6607 (this paper is referenced by the author but only at one point and in relationship to HCB; but it provides valuable information about HCHs as well)

Ding et al. Atmospheric Hexachlorocyclohexanes in the North Pacific Ocean and the Adjacent Arctic Region: Spatial Patterns, Chiral Signatures, and Sea-Air Exchanges, Environ. Sci. Technol. 2007, 41, 5204-5209

Becker et al. Long-term trends in atmospheric concentrations of a- and g-HCH in the Arctic provide insight into the effects of legislation and climatic fluctuations on contam-

inant levels, Atmospheric Environment 42 (2008) 8225–8233

and for HCB: Barber et al. Hexachlorobenzene in the global environment: Emissions, levels, distribution, trends and processes, Science of the Total Environment 349 (2005) 1-44

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; these include:

Koziol and Pudykiewicz, Global-scale environmental transport of persistent organic pollutants, Chemosphere 2001, 45, 1181-1200

Hansen et al., Modelling atmospheric transport of a-hexachlorocyclohexane in the Northern Hemisphere with a 3-D dynamical model: DEHM-POP. Atmos. Chem. Phys. 2004, 4, 1125-1137

Semeena and Lammel, The significance of the grasshopper effect on the atmospheric distribution of persistent organic substances, Geophys. Res. Lett. 2005, 32, L07804

Semeena and Lammel, Effects of various scenarios of entry of DDT and γ-HCH on the global environmental fate as predicted by a multicompartment chemistry-transport model, Fresenius Environ. Bull. 2003, 12, 925-939.

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 (paramter 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.

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

Specific 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.

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.

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.

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.

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

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

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 authors 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.

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.

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.

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.

p. 460, line 8: “Hoc” should be “Hov”

p. 462, line 12: again, I do not think this is an actual condensation or condensed phase.

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

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.

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

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.

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

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 453, 2010.