Atmos. Chem. Phys. Discuss., 4, S1210–S1213, 2004 www.atmos-chem-phys.org/acpd/4/S1210/ © European Geosciences Union 2004



ACPD

4, S1210-S1213, 2004

Interactive Comment

Interactive comment on "The mechanism of halogen liberation in the polar troposphere" by E. Lehrer et al.

R. Sander (Referee)

sander@mpch-mainz.mpg.de

Received and published: 14 July 2004

1. General comments

Lehrer et al. present a very interesting 1D model study investigating the halogen sources that lead to polar tropospheric ozone destruction events. As far as I know, it is the first model study that addresses surface sources as well as their vertical transport in detail.

Unfortunately, the model description is much too short and many important information are missing. On the other hand, the introductory sections are too long and almost like a review paper. I suggest that the manuscript should be published in ACP after some substantial changes have been made.



2. Specific comments

- I find that the title of the manuscript is too generic. There are no new information regarding the chemical mechanism of the ozone destruction in the paper. A title like "Investigating halogen sources and their vertical transport in the polar troposphere with a 1D model" would be more appropriate.
- The introduction (section 1) is a review of many aspects of polar halogen chemistry. I suggest to restrict the introduction to those topics that are investigated with the 1D model, i.e. focus on the current knowledge about the halogen sources (which is currently in section 3). Section 2 could be completely replaced by a citation of the very good review by Platt and Hönninger (2003).
- The model description in section 4 should be extended. Many details are currently missing: Which values are used for D and K(z) in Eq. (2) at each level? How is v_{therm} in Eq. (4) defined? Is k_{liq} on page 3621, line 10 the same as k'_{liq} ? What is D_g in Eq. (5)? Which values are used in the model? Is D_g identical to D in Eq. (2)? Which chemical reactions are used in the model? A complete listing of the mechanism could be added to the paper as an electronic supplement.
- On page 3617, line 8, referring to the Arctic, Lehrer et al. say that "the well-mixed atmosphere picture used in earlier modelling studies (Sander and Crutzen, 1996; Vogt et al., 1996) cannot be correct". It should be noted, however, that those model studies were done for the mid-latitudes and not for the polar regions.
- page 3618, line 15: My understanding of Arctic haze has been that it is an anthropogenic phenomenon and not a natural. If there is indeed evidence that it is natural, a reference would be useful here. If it is not natural, but a prerequisite for halogen recycling, it should be discussed why bromine explosions also occur in the Antarctic though there is no "Antarctic haze".

ACPD 4, S1210–S1213, 2004

> Interactive Comment

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

- page 3619, lines 20-22: To avoid confusion, it should be noted that Vogt et al. (1996) and Sander and Crutzen (1996) did use FACSIMILE but did not use the 1D-model that is presented here.
- page 3624, line 20-21: Lehrer et al. say that a small concentration gradient was seen by the several field studies as discussed in the introduction. This is in contrast to the text in the introduction where they say: "In particular it could be shown that there is no detectable gradient in the BrO concentration inside the atmospheric boundary layer.".
- page 3625, line 22: The difference between modeled and observed alkane loss is attributed to unrealistically low initial chlorine concentrations. I suggest to perform a sensitivity study with more realistic initial chlorine concentrations to check if this brings the model results closer to the observations.
- Table 2: Are the Henry's law coefficients for HBr and HCI effective values? (their physical solubilities are much lower) If yes, to what pH do they apply?
- Figure 1: The arrow from Br back to Org. Br can lead to confusion. Organic bromine as a halogen source is thought to be mainly CH₃Br or CHBr₃. Reaction of Br with VOCs, as shown in the figure, however, leads to different products, e.g. oxygenated bromine-containing species or even HBr. Thus this pathway is not a true recycling process as the figure may suggest.

3. Technical corrections

• page 3621, line 5: The unit of A is incorrect.

Interactive Comment

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

- page 3621, line 13 and page 3621, line 19 and page 3623, line 8 and page 3626, line 22: References to several equations and tables are incorrect. Please check the numbers here and elsewhere in the text!
- page 3627, line 1: It is not clear to me how $[HX]_{\rm aq}$ was calculated. Is this a phase ratio under equilibrium conditions?
- Table 2: What is k^{II} ? Is this the same as k_{liq} in the text? If yes, a consistent terminology should be used.
- Figure 8: The figure shows mixing ratios, not concentrations, as stated in the caption.
- Figure 8: The figure caption does not state which box is shown. Do the plots show the uppermost box?

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 3607, 2004.

ACPD 4, S1210–S1213, 2004

> Interactive Comment

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper