

## ***Interactive comment on* “The mechanism of halogen liberation in the polar troposphere” by E. Lehrer et al.**

**E. Lehrer et al.**

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First we would like to thank the reviewers for their detailed and constructive comments and questions, which helped us improve the manuscript. Please find our detailed responses to the reviewers' comments below. The original comments by the reviewers are quoted as italics.

### **Response to Reviewer 2:**

We would like to thank reviewer 2 for the detailed review and for identifying several issues in our manuscript related to previous published work. We have taken all comments into account in the revised version of the manuscript. Specifically we apologise for the previous omission of important citations, which we now included in the discus-

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sion section of the updated manuscript.

Response to reviewer 2's specific comments:

1. *A major conclusion of the paper is that with aerosols alone the ozone depletion chemistry (or rather build up of RHS) is too slow, and that the sea ice surface is enough by itself. The conclusion that there is not enough halide in aerosols, and that the source of the halide must be from somewhere other than the aerosol was reported in Impey et al., JGR, 1997. This conclusion was mentioned in the Abstract of that paper.*

Response: The work of Impey et al. 1997 is now cited in the paper specifically quoting the important finding that the aerosol source is not sufficient.

2. *The paper focuses on the importance of recycling via deposition of HOBr to the surface. The importance of this was simulated in the multiphase model of Michalowski et al., JGR, 2000. The fact that deposition to the surface was a necessary feature of ozone depletion events was mentioned in the Abstract of that paper. The main focus of Michalowski et al. was reaction at the surface; in light of that, it seems that that paper would be an essential citation. I note that that paper also simulated a 5 day decay in ozone. It is also important that the Michalowski et al. paper discusses activation on sea salt within the snowpack, since GOME data imply significant BrO over inland Arctic regions. Clearly activation of Br<sub>2</sub> in the snowpack can occur, as discussed in Spicer et al., 2002.*

Response: The important results of the Michalowski et al. 2000 paper are now referenced to, in particular the importance of HOBr transport to the surface and the approximate time scale of O<sub>3</sub> depletion.

3. *It was discussed in Spicer et al., 2002 that there is a problem with the idea that Cl atoms can come only from BrCl, as a simple calculation leads to a Br/Cl ratio much larger than has been inferred from VOC decays. Grannas et al. 2002 noted this problem, and discussed that an artificial Cl<sub>2</sub> source was necessary to simulate Cl atom*

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concentrations.

Response: We included the additional literature (Spicer et al. 2002, Grannas et al. 2002) quoted by reviewer 2 in our discussion of the role of chlorine.

*4. Finally, I would also note that it is inappropriate to say (in the end of section 5.1) "...the observed levels of chlorine atoms in the marine boundary layer are very unlikely due to halogen activation out of sea salt." This sentence implies we are certain about the chemical mechanisms for activation from sea salt. However, this paper leaves out key citations, about alternate mechanisms. Knipping et al., Science, 2000, discuss production of Cl<sub>2</sub> via OH radical reaction with Cl<sup>-</sup>. Since your model does not include condensed phased OH production from photolysis of NO<sub>3</sub><sup>-</sup> and H<sub>2</sub>O<sub>2</sub>, and consider all the reactions of OH, which are certainly not fully known, it is premature to say much about chlorine, definitively, other than that it appears that there is much more chlorine atom concentration than we can account for given our understanding of the chemistry.*

Response: We now state more clearly that our results agree with Fickert et al. (1999) in that chlorine is very unlikely released via HX/HOX heterogeneous reactions from sea salt. We now also cite previous literature (Knipping et al. 2000) concluding that an additional Cl source is needed, but as reviewer 2 noted, our model was not designed to study alternative release mechanisms for chlorine. Therefore we only conclude that higher chlorine levels are not needed in our model to reproduce the bromine catalysed ozone depletion.

Responses to minor comments:

*1. Line 25 on page 3609 should cite Solberg et al., 1996, as that was one of the first and best cases that showed the confinement of the depletion to the stable boundary layer, and the vertical extent of the depletion.*

Response: The reference to Solberg et al. 1996 was added here.

*2. I think some care should be exercised with the last question on page 3619 regarding*

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*the "episodic" nature of the depletion events. I am unsure how much good information there is in the literature to justify (or clarify?) this question. At Alert, the ozone depletion events are very rapid, but this is well known to be related to transport of already depleted air to the site. Are there good citations for the actual rate of ozone depletion, to call them episodic? Or perhaps I misunderstand your intended meaning of the word.*

We clarified this statement by rewording it to read: "What causes the event-like pattern of the occurrence of ozone depletion ?" This modification better expresses that we meant to say "event-like occurrence". Indeed the temporal information on ozone depletion events is limited due the fact that BL ozone can only be measured by ground-based instruments , which cannot easily separate transport and chemical effects in most cases. However satellite observations of BrO suggest an event structure of Br activation and thus likely also O3 loss.

*3. Page 3621 line 19 ?U the text should refer to equation (4), not (3).*

Response: We re-checked all references to equations, tables and figures, and updated the numbering throughout the manuscript.

*4. Section 5.4, line 23 ?U you might clarify this point by adding that there was only a slower buildup of total bromine, and thus a lag in the rapid ozone depletion.*

Response: We included this suggested clarification.

*5. The last sentence in section 5.4 seems to directly contradict the first sentence in the second paragraph of the Conclusions section.*

Response: This is a misunderstanding probably due to poor explanation of cases A-D: In case (B) the main difference to all other cases is that halogen recycling on the aerosol was not allowed, which essentially prevents a bromine explosion. We now include additional explanation to clarify this. The finding that without aerosol recycling there is no efficient bromine release is also stated in the conclusions.

*6. Point 2 of the Conclusions is all discussed in uncited but published literature, but not*

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*the subject of this paper. I don't see why it is included here.*

Response: We agree and deleted this point.

*7. There is no need for both Table 7 and Figure 9; I suggest deleting the Table.*

Response: Table 7 was deleted as suggested.

*8. The first sentence of the final paragraph in the paper is out of place, and should be removed.*

Response: We removed the first sentence of the final paragraph as suggested.

### **Response to Dr. Sander's review:**

We would like to thank Dr. Sander for his detailed review and comments, which resulted in an improved revised version of our manuscript. The introduction has been significantly shortened and more details have been added on the model description.

Response to Dr. Sander's specific comments:

*title of the manuscript is too generic:*

We agree and changed the title. It now reads "A One Dimensional Model Study of the Mechanism of Halogen Liberation and Vertical Transport in the Polar Troposphere"

*The introduction (section 1) is a review of many aspects of polar halogen chemistry.*

We agree and shortened the introduction significantly by deleting less important parts or by summarizing them. The previous section 2 was eliminated and section 3 was completely rewritten to include the essential parts of the previous section 2.

*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  $k_{0liq}$ ? 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?*

We added the required details to the model description and addressed the above questions in the revised version. In particular the values used for  $D$  and  $K(z)$  for each level are now given in new Table 4. The formula for  $v_{t,herm}$  is given in the text. The first and second order reaction coefficients  $k_{liq}^I$  and  $k_{liq}^{II}$  are now also defined as well as the gas phase and liquid phase diffusion coefficients  $D_g$  and  $D_{liq}$ . A complete listing of the chemical reactions is now included as supplemental material.

*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 3617, line 8: We rewrote the statement and now distinguish between mid-latitude and 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".*

Page 3618, line 15: We completely agree with the reviewer. Here it might not have been clear that "it" actually referred to "ozone depletion", not to "Arctic haze". We clarified this by replacing "it" with "polar ozone depletion" in the revised version.

*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 3619, lines 20-22: We modified the sentence accordingly.

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*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 3624, line 20-21: The wording was indeed misleading and we changed it to clarify that a gradient is only expected in the lowest meter. The fact that the gradient is negligible in all layers above is consistent with the field studies which found no detectable gradient.

*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.*

Page 3625, line 22: The main aim of this study was to investigate the role of bromine in boundary layer ozone depletion as well as the influence of vertical mixing. We therefore refrained from further adjusting the chlorine levels.

*Table 2: Are the Henry's law coefficients for HBr and HCl effective values? (their physical solubilities are much lower) If yes, to what pH do they apply?*

Table 2 lists the effective Henry's law coefficients, which were calculated for a pH of 5. This information is now also included in the updated version of the manuscript.

*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 CH<sub>3</sub>Br or CHBr<sub>3</sub>. 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.*

Figure 1: We think that there is only a negligible possibility of confusion, and therefore

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chose not to include an extra item for the products of the Br +VOC reactions. The general picture is still valid, i.e. the products of these reactions ultimately contribute bromide that is available for recycling on aerosols to yield r-Br.

Technical corrections:

page 3621, line 5: The unit of A was corrected.

*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!*

All references were checked and updated in the revised version.

*page 3627, line 1: It is not clear to me how  $[HX]_{aq}$  was calculated. Is this a phase ratio under equilibrium conditions?*

$[HX]_{aq}$  is calculated using  $[HX]_{aq}=[HX]_g \cdot H^*$ ,  $H^*$  being the effective Henry coefficient. We included this explanation in the text.

*Table 2: What is  $k^{II}$ ? Is this the same as  $k^{Iq}$  in the text? If yes, a consistent terminology should be used.*

$k^{II}$  is the second order liquid phase rate constant.  $k_{liq}$  can be  $k^I$  or  $k^{II}$ , depending on if it's a first or second order reaction. Explanations are now added in the caption.

*Figure 8: The figure shows mixing ratios, not concentrations, as stated in the caption.*

We corrected this error in the caption of Figure 8.

*Figure 8: The figure caption does not state which box is shown. Do the plots show the uppermost box?*

The data is indeed from the top box. In order to avoid confusion we clearly state this now in the caption.

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