Atmos. Chem. Phys. Discuss., 4, S1102–S1105, 2004
www.atmos-chem-phys.org/acpd/4/S1102/

Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

Received and published: 5 July 2004

This paper discusses numerous issues related to the physical and chemical drivers of ozone depletions in the polar boundary layer, and summarizes the state of our knowledge, making use of a 1D model of the photochemistry and vertical scale diffusion. There are a few new things in this paper that make it a quite useful publication, and in particular, the discussion of the importance of the inversion and the lack of downward mixing across the top of the boundary layer, which has not been discussed in detail previously. The paper helps clarify good potential reasons why ozone depletion events are only observed in spring, which is quite important. The paper revolves around several clearly stated important questions, e.g. what are the important sources of reactive bromine, and why does it only occur in spring? I also feel that the presentation of the simulations of the Br2 and HOBr vertical gradients is quite useful, as that result is quite testable through field measurements. This paper is a very comprehensive treatment

of this problem, perhaps more comprehensive than the new information warrants, but it is useful to have all the important issues discussed in one place. With that in mind, the paper has serious flaws that make it, in my judgment, not publishable in its current form. This results from the fact that several of the main conclusions have been published previously, and those publications are not cited or discussed in this paper. If the paper intends to cover all aspects of what we know about the issue of springtime ozone depletion, it ought to put the important previous work in context, and make appropriate reference to previous literature. This should be easily doable in this paper, as the full extent of literature on this subject is still quite manageable.

Specifically, the following citation and discussion omissions have occurred.

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.

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 Br2 in the snowpack can occur, as discussed in Spicer et al., 2002.

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

ACPD

4, S1102–S1105, 2004

Interactive Comment

larger than has been inferred from VOC decays. Grannas et al. 2002 noted this problem, and discussed that an artificial Cl2 source was necessary to simulate Cl atom concentrations.

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 Cl2 via OH radical reaction with Cl-. Since your model does not include condensed phased OH production from photolysis of NO3- and H2O2, 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.

All that said, I think this paper could be much better and publishable. What is new here is that this is the first paper that quantitatively looks at downward mixing of O3 across the top of the boundary layer, and why ozone depletion events are only observed in spring. Much of the added discussion, which is already in the literature, detracts from these new insights. I recommend that this paper is completely rewritten in terms of the real new information, and let students of this literature know about all that has been done.

More minor comments are listed below.

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.

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

ACPD

4, S1102–S1105, 2004

Interactive Comment

tion 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.

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

4. Section 5.4, line 23 Ű 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.

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

6. Point 2 of the Conclusions is all discussed in uncited but published literature, but not the subject of this paper. I don't see why it is included here.

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

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

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