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Interactive comment on "Halogens and their role in polar boundary-layer ozone depletion" *by* W. R. Simpson et al.

W. R. Simpson et al.

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The reviewer makes a number of general comments on the manuscript and how we can enhance sections. We appreciate this effort and will act on these comments to improve the manuscript. One point is that the section on models is too short. These sections (observations, models, and laboratory methods) were meant to give very short overviews of these three important areas. As the manuscript was developed, some of the sections grew and models became underrepresented. We will take the reviewers comment and expand the section on models both here and in other sections of the paper.

The reviewer comments on the manuscript not emphasizing the details of chemistry at the interface of ice, specifically in reference to ideas of Finlayson-Pitts and co-workers, i.e. that there is halide oxidation chemistry that occurs in the absence of protons as a reactant. The reviewer seems to be refering to the paper Laskin et al, Science, 2003, 301, 340 - 344, which proposes that hydroxyl radicals can directly oxidize halide atoms at surfaces to produce reactive halogens. We will add reference to this idea at the end of section 3.1.2, where we have already started discussions of the interfacial nature of these reactions and referenced work of Finlayson-Pitts and collaborators. However, we should note that the direct oxidation ideas have been discussed in the context of unfrozen (non-ice) systems and for chlorine atoms rather than bromine, while the conditions of polar halogen activation are different from these warmer aerosol systems. If similar reactions occur for bromide and lead to Br2 or BrCl, it might play a role in initiation of bromine explosions or possibly in the observations of Foster / Spicer et al. of Br2 and BrCl before polar sunrise.

As suggested, section 3.1.7 can be moved to before the preceeding section. We will make this change.

The section on boundary-layer physics and meteorology introduces a reader unfamiliar with boundary layers in polar regions to their particular nature and leads into discussions on how boundary layer structure is related to ozone depletion events and their termination. We feel that some of this discussion is necessary for completeness, but will reduce the introductory paragraphs of this section and refer readers to appropriate references.

The sections on surface fluxes (e.g. HOx and NOx fluxes) are related to the topic through the autocatalytic bromine explosion reactions, as is mentioned in the first sentence of this section. These fluxes greatly affect the near-snow boundary layer chemical composition, and thus are related to bromide oxidation. Above in this review, the reviewer requested that we increase mention of OH oxidation of halides on surfaces as a halogen source. Clearly HOx fluxes influence OH levels near the snow surface and thus are coupled to halogen activation. Additionally, in the bromine explosion mechanism, HO2 is needed to convert BrO to HOBr, and thus HOx is consumed as halogens are activated. Therefore, we feel it important to discuss surface sources of HOx and

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NOx to understand halogen activation.

From the comments of the reviewer, it appears that the structure of the sub-sections of section 3 may be misunderstood. Section 3 (Key environmental processes and their effects on ODEs) has three sub-sections, 3.1, The role of sea ice, 3.2, The role of meteorology and boundary layer physics, and 3.3, The role of surface fluxes and snow photochemistry. It appears from the comments that the reviewer thinks that surface fluxes are under the meteorology and BL physics section. They are not; they are under the surface fluxes section, which is appropriate.

The reviewer asks about the relevance of ODEs. In the paper, we separate this question into the question of the effect inside polar regions, where we state that there are significant and observed effects. The reviewer state their opinion that "ODEs do remain highly episodic, localized events in space and time that may not play a very important role globally". While ODEs got their name from their episodic nature, as observed from coastal locations on the fringe of the ice-pack, satellite images of BrO show that halogen activation is quite routine in the young ice areas. The limited observations on the ice pack indicate that having ozone present is the anomolous situation during polar springtime, not ODEs. Therefore, the polar regions are clearly experiencing ODEs quite often and thus their effects are significant in the polar region. As for export of polar influence to other locations, we have stated that it is unclear how important these effects are. The other effects discussed are polar in nature, but may have global importance. For example, we use polar ice cores to infer the global atmospheric situation, but if they are influenced by particular polar chemistry, we need to understand those influences. We use sulfur oxidation products in ice cores to discuss global aerosol issues, but the presence of halogens in polar regions may influence the ratios of these oxidation products.

References:

Foster, K. L., R. A. Plastridge, J. W. Bottenheim, P. B. Shepson, B. J. Finlayson-Pitts, and C. W. Spicer (2001), The Role of Br2 and BrCl in Surface Ozone Destruction at Polar Sunrise, Science, 291, 471-474.

Laskin, A., D. J. Gaspar, W. Wang, S. W. Hunt, J. P. Cowin, S. D. Colson, and B. J. Finlayson-Pitts (2003), Reactions at Interfaces as a Source of Sulfate Formation in Sea Salt Particles, Science, 301, 340-344.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 4285, 2007.