**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "On the vertical distribution of boundary layer halogens over coastalAntarctica: implications for O_3, HO_x, NO_x and the Hg lifetime" *by* A. Saiz-Lopez et al.

Anonymous Referee #1

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This paper presents the - to my knowledge - first modeling study of halogen chemistry specific for the Antarctic. It aims at explaining recently measured very high mixing ratios of IO and BrO at Halley station, made by the same group. The authors derive flux strengths for iodine and bromine that are required to reproduce the measured XO mixing ratios in their model. They find that in their model higher iodine oxides have to be taken into account in order to reproduce the observed IO without having a very strong vertical profile. They calculate ozone destruction rates based on the presence of both BrO and IO and estimate the lifetime of mercury under these conditions.

I have a number of comments and questions regarding the setup of the model, its

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formulation and the chemical reactions involved. I assume that this is largely due to a rather brief model description and the omission of a number of details which are, however, required in order to understand the paper. Therefore I suggest to publish the paper only after major revisions.

Major comments

The model and its description

At a number of instances in the text the reader might get the impression that the chemsitry within aerosols is treated in detail, however, only heterogeneous reactions (i.e. at the surface but not in the bulk of the aerosol) is included, this should be stated clearer. The authors speculate about the role of iodine oxides in new particle formation. This would constitute an important loss for iodine oxides, yet it seems to not be included in the model at all. On p. 9398. l. 1 you mention "predictions" of new particle formation - so if you did explicitly include this process in the model, please show nucleation rates and resulting aerosol number concentrations. In summary: Please make clear if this process is included or not and if not then please explain why not. Could you make an estimate, how strongly the concentration of iodine oxides would be affected if the loss due to new particle formation were included?

Equation 1: I don't understand terms 2 and 3 in this equation. The eddy diffusivity is only the first term, so what do the other terms stand for?

According to p. 9390. l. 15-18 the model time step is 2 min and the vertical resolution 1 m. In order to not violate the Courant-Levy criterion vertical velocities can at most be 8.3e-3 m/s. yet at other places in the paper it is stated that the model includes "convective" processes - to me this doesn't fit together and, more importantly, puts all vertical profiles that depend on the vertical profile in question.

Fluxes of what species are prescribed at the surface and what are the source strengths (p. 9391, l. 1-3)?

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Constrained modeling (section 2.2): Even though this is not stated explicitly in the paper I had the impression that NOx is also constrained. If this were the case then you might get problems with the N-mass balance in the model as during the course of the model run about 12 ppt ends up as $XONO_2$. Also: what are the initial concentrations of NO_x?

p. 9392, l. 11: I don't understand what that means or how this is done. Please explain in more detail. Also: how is the diurnal variation determined? Not all species will have the same diurnal variation therefore assumptions like sinusoidal - if something kike this is used - would probably be wrong. Please explain how this is done in the model.

p. 9393, l. 1-2: The deposition velocities for these compounds are not listed in the supplement. How do you calculate/determine them?

p. 9393, l. 11 Is a marine aerosol surface area really appropriate for these conditions?

Iodine chemistry

p. 9395, l. 14 - 17: Many halogen related reactions in the aqueous phase are dependent on acidity. Therefore in aged, acidified sea salt particles the aerosol processing time will be increased not decreased.

p. 9395, l. 19 - 22: Are the rate coefficients of these reactions really kown? I couldn't find them in the listed reference.

Discussion on p. 9397: I feel you should phrase this a bit more cautiously as the chemistry of higher iodine oxides is, to my knowledge, not very well understood and you had to make quite a few assumptions

p. 9397, l. 23-24: In order to show that the chosen photolysis rate is a "lower limit" you should present or at least discuss model runs with lower rates. Also I think, given the uncertainties in the kinetics of higher iodine oxides, it might be useful to present a few model runs where different values for the rate coefficients are chosen.

Source of iodine (p. 9398, l. 8-12): In sea water and therefore also in brine etc the concentration of iodide and iodate is very small, so in order for the sea salt to be a relevant source for it would have to be highly enriched (by a lot more than simple concentration effects). Please expain this a bit better. To me this indicates that the precursors are more likely organic gaseous iodine compounds.

p. 9402, l. 20: You mention the thermal decomposition of I_2O_2 but I couldn't find it in the reaction table in the supplement. Please clarify if it is included in the model or not.

Conclusions: I don't really think that your model can reproduce measured O_3 concentrations including an entrainment term. You have showed elsewhere that high halogen oxide levels are typically present in air masses that have been over the Antarctic continent for days and if you look at O_3 after 2 days on figure 7b the destruction on day 2 is already very strong.

Minor comments

There have been a number of previous modeling studies dealing with ODEs which often have information that is relevant for this paper but which are not cited. This includes: Fan and Jacob 1992, Evans et al. 2003, Michalowksi 2000, Sander et al 1997. The paper of Sander et al is the first paper to consider iodine chemistry in polar regions in detail.

p. 9390, l. 17: Do you really mean "downward convective transport" or rather entrainment?

p. 9390, l. 21: What is a "scale height at the top of the BL"?

p. 9392, l. 19: reference missing in list.

p. 9396, l. 9: Question mark missing.

p. 9396, l. 9-10: What are "enhanced activation mechanisms"?

p. 9399, l. 13-15: These measurements were made at a constant height and therefore

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do not show a rather homogeneous distribution. In one campaign 2 different BrO instruments in situ and DOAS) were used together and showed drastically different BrO concentrations directly above the snow pack and in the DOAS beam (Avallone et al., JGR, 2003). This might be due to release of BrO from or production nearby the snow pack or due to horizontal heterogeneities.

p. 9400, l. 17: Reference to wrong equation.

p. 9400, l. 19-20: Maybe you should also mention that after 48h O_3 has decreased by about 50%.

p. 9401, l. 19-20: The reader might get the impression that you actually calculated the production of NO_x from the photolysis of nitrate in the snowpack, but I assume that you rather simply assumed fluxes of NO_x from the surface, didn't you? Please rephrase.

p. 9402, l. 3-5: I would rather say that you used XO concentrations and XO:X ratios from the model to calculate the lifetime, otherwise the reader might assume that mercury chemistry is included in THAMO as well, which would imply that mercury is acting as a sink for halogens, which, as I understand, is not the case.

p. 9403, l. 1: Are there any mercury measurements available to compare your data with? With these lifetimes there should basically be no Hg^0 present during daytime.

There are many spelling errors in names of cited authors, this includes Hönninger, Frieß, Schönhardt.

Supplement: reference 24 is missing (used in deposition velocities).

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 9385, 2007.

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