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Atmospheric
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Interactive comment on “Volatile organic compound ratios as probes of halogen atom chemistry in the Arctic” *by* A. E. Cavender et al.

Anonymous Referee #1

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This papers presents an interesting new method to derive the ratio of [Br]/[Cl] from a combination of measurements of VOCs and modeling. The method is applied to data from the Polar Sunrise Experiment 1995. The authors confirm the range of previous determinations of this ratio and speculate about the reasons for observed large differences in [Br]/[Cl]. They also imply a flux of propanal from the snow pack in order to reconcile their measurements with results from a box model.

Overall this paper is well-written, however I have major concerns about the discussion in section 3.2 and parts of section 3.4 which seems fairly speculative as I will outline below. I suggest to publish the paper only after these concerns have been addressed.

Specific comments:

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p. 11648, l. 11-12: The fact that the [Br]/[Cl] ratio varies greatly during ODEs is nothing new, it has been published by some of the authors of this paper several times already but here in the abstract it sound as if this is a new discovery like the potential flux of propanal. I suggest to reword. The recent review in ACP by Simpson et al. also lists previous determinations of [Br]/[Cl] but this paper is never cited in the current manuscript which might be a good idea to do.

p. 11650, l. 24: Is fossil fuel burning really the only relevant source for these compounds?

section 2.2

Is a box model really appropriate for this study given the likely rather strong vertical gradients of halogen radicals (see Tackett et al 2007; interestingly 3 of the authors of the current manuscript are co-authors of Tackett et al but that paper isn't cited here)? To me it sounds that a one-dimensional (or even higher dimension) model would be the method of choice. Please comment.

p. 11655, l. 27: Strange sentence, please rephrase.

section 3.2:

I have major problems with this section. First the reference to the paper by Apel et al is in my opinion not sufficient as they don't show how equation 2 is actually derived (I tried to do it myself and failed) and also the way the respective equation is written in Apel et al is ambiguous: is [OH] indeed part of the exponent as written in the present manuscript or is it simply multiplied to this term? Second: a key assumption behind using this simple calculation is that oxidant concentrations are constant which might be okay if looking at fast, daytime oxidation as in Apel et al but certainly not if considering timescales of 5-10 days as in the current manuscript. If looking at these longer timescales a proper integration seems to be necessary, rather that using mean oxidant concentrations, to take shifts in the [MEK]/[n-butane] ratio into account that are caused by a competition between Cl and OH which possibly have different diurnal variations. In conclusion I don't know what the ratios derived with equation (2) are actually telling us. Maybe everything becomes clearer when it is explained better but looking at what is written in the text I'd recommend to simply delete section 3.2.

Also on a more technical note: reactions R1 - R5 do not represent a consecutive reaction scheme as stated on line 2 as reactions R2 - R5 are occurring in "parallel", i.e. competing with each other. Only R1 combined with each individual reaction R2, R3, R4, or R5 are consecutive.

p. 11657, l. 19: This section headline suggests that all of the remaining discussion is based on model calculations but as I understand it everything below p. 11659, l. 15 is (at most) "back of the envelope". So I suggest to either rename this section or to split it into two or to delete parts of the second half as explained below.

p. 11658, l. 9-10: What is the [Cl] concentration for the case [Br]/[Cl]=0.?

p. 11659, l. 5 - 10: You argue that propanal might have a strong vertical gradient in the polar boundary layer but in order to calculate its lifetime you assume that both [Br] and [Cl] are constant with height. Again the recent paper by Tackett et al 2007 gives strong indications that there are strong vertical gradients in the halogen radical concentrations which might also imply gradients in HOx species or its partitioning, so again my question is: what does the calculation using equation 3 tell us? I'm not convinced that the flux of propanal estimated from this discussion is any reliable even though I agree that the number calculated with using a constant vertical profile for propanal is very likely an overestimate.

p. 11660, l. 21 - 22: This seems to imply that events 1 - 3 are likely from the end of an ODE. Did I understand this correctly and if so are there other data to support this?

I find most of the discussion of the remainder of section 3.4 very strange. Specifically:

p. 11659, l. 24-29: I don't see how this discussion is consistent with the data from

Simpson et al 2005. They report snow concentrations as a function of distance from the coast and it is not all clear that the distance from the coast is related to the timing of bromine explosion events.

p. 11660, l. 2-3: Again: The data of Simpson et al can't be used for implications about the state of ODE's.

p. 11660, l. 18 - 26: To me this discussion sounds as if you assumed that O3 suddenly drops to very small numbers and that equally suddenly the production of HOBr stops. Both would only happen with an airmass change. The discussion of HOBr sedimentation assumes that HOBr is vertically well-mixed which is unlikely as there are likely strong gradients in at least Br but probably also in BrO. Also by calculating a sedimentation-dominated lifetime you assume that HOBr is inert which clearly isn't the case. Assuming a photolysis frequency of 2e-3 1/s the lifetime is 500 sec, i.e. a lot shorter then the "sedimentation lifetime" of 6h that you calculate. I suggest to delete this section.

p. 11661, l. 3-5: One might imply from these lines that the trajectories for events 1 and 2 are very similar, however when looking at the altitude of the back-trajectories one sees that the air masses for one event originate at the west Greenland coast whereas the other one descends from the plateau. So the airmasses will have encountered very different conditions in the first 36h. Please comment/rephrase.

p. 11661, l. 10/11: How relevant are the relative Henry's coefficients that are derived for liquid solutions for snow and ice??

p. 11662, l. 15-20: Knipping and Dabdub study the marine boundary layer and aqueous sea salt aerosols NOT saline snow packs! One cannot easily apply this to reactions on frozen surfaces.

p. 1662, l. 20: [Cl] might be high in event 4 but a smaller ratio in [Br]/[Cl] as compared to the other events could be explained by exceptionally low [Br] as well.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 11647, 2007.

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