

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

**A. E. Cavender et al.**

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Anonymous Referee 1:

The authors would like to thank this reviewer for commenting on this manuscript, and appreciate the assistance in making this paper better. Please find our responses to your specific comments below:

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.

We will reword the sentence to say "It is concluded that there must be an additional source of propanal (likely from the snowpack) to correctly simulate the VOC chemistry of the Arctic, and further evidence that the ratio of Br atoms to Cl atoms can vary greatly during ozone depletion events is presented";. In addition, the citation of Simpson et al. 2007 will be included in the appropriate sections of the paper.

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

It is better to say fossil fuel use, which we now say in the revision. These compounds are emitted in automobile exhaust, and they are important evaporative emissions from gasoline, and in the refining of oil. There are no other significant sources.

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.

While a one-dimensional model may have been an appropriate method of analysis, the data presented in this paper and analyzed with the model was only taken at one altitude. Thus, a vertical scale model-measurement comparison and analysis was not possible in this case. It might be much better to do a 3D CTM, but this is beyond the scope of this paper, and not even in existence yet for the Arctic. We have now cited the Tackett et al. paper in the first paragraph of the Introduction.

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

This sentence has been changed to say "The data in this figure imply that ozone depletion can occur with highly varying relative concentrations of Br and Cl atoms."

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

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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 than 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.

First, as discussed in Section 3.2, X is either Cl or OH. Regarding the time scale, we are not trying to exactly simulate the data, but are using this analysis to make the case that it is very likely that chlorine atom chemistry dominates alkane processing during ozone depletion events. We have added a sentence at the end of section 3.2 to clarify this point. We should not present the derivation in the paper, but it can be seen at <http://web.ics.purdue.edu/~acavende/Derivation.jpg>. The derivation shows that the way the equation is written in this manuscript is correct ([X] is part of the exponent).

The first sentence of section 3.2 has been corrected to say "MEK production from n-butane reacting with OH or Cl, and the subsequent removal of MEK by reaction with OH or Cl represents a consecutive reaction scheme. This type of system can be solved mathematically..."

p. 11657, l. 19: This section headline suggests that all of the remaining discussion is

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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.

Thank you for pointing out this mistake - this section has been renamed "Model and measurement comparison".

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

[Cl]=2e4 molec/cm<sup>3</sup> has been added to this sentence

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.

It seems clear to us that our paragraph makes it clear that the calculated flux depends on the "mixing height" estimate, and that this is unknown at this time. We added a sentence to clarify this at the end of that paragraph.

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?

No, our paragraph only discusses that a short ozone depletion event might occur in a way such that there is relatively more Cl- in the surface snow. We have tried to clarify that paragraph accordingly.

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

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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.

We cite Simpson et al. as showing that Br- is enriched as you move inland from the coast, and we cite Toom-Sauntry and Barrie as showing that Br- enrichment occurs to a greater extent as spring progresses. So, for event 4, for which the back trajectory is over the ocean, we believe, as discussed in this section, that it is likely that the Cl-/Br- ratio is larger for the Arctic Ocean surface snow, than it is for inland snowpacks.

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

We cited Simpson et al. to aid in the discussion that ODEs lead to deposition of Br and thus increased probability of Br activation rather than Cl activation, from those snowpacks. This ties in very well to our trajectory analysis on page 11661, which shows that event four has a very different trajectory, consistent with more chlorine activation.

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 than the "sedimentation lifetime" of 6h that you calculate. I suggest to delete this section.

This is a good recommendation, we have done that.

p. 11661, l. 3-5: One might imply from these lines that the trajectories for events 1 and

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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.

This is true, but still, event one is not one that encountered much Arctic Ocean sea ice. This is our main point about the event 4 trajectory.

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

Henry's law coefficients for water are not the same as for ice. However, our statement holds, that the relative Henry's Law coefficients matter for the relative fluxes. We changed the wording to use "ice solubility".

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.

We have replaced "saline snowpacks" with "sea salt particles" in the manuscript. We note that aqueous environments are quite relevant, since this chemistry is very likely to be occurring in a quasi-brine layer, as discussed, for example, in Cho et al., 2002.

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.

This is true. We say that "the high apparent [Cl] during Event 4 could be related to poorly understood snowpack photochemical activation of Cl-", with the key word being "could". We are only offering this as a possibility, we are not excluding any other explanations. It is very clear that we do not know for certain what the operative activation mechanisms are, and that proof awaits us all.

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