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Comment

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

General comments

Although I am not specialist enough to judge on the appropriateness of the chemical schemes used to indirectly infer informations on the halogen content, I have the feeling that some of the assumptions made to provide the link between observed VOCs and the target halogens are somewhat speculative in essence, e.g. the assumed mixing in a 400 m thick boundary layer (precisely shown as being unrealistic in the propanal case), or e.g. in section 3.2 on chlorine, the assumed constant concentration of the key

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oxidants (OH and Cl). In any case, if the main focus in this paper is halogen chemistry, I would have expected to see some more direct comparisons being made with measurements of halogen containing species (e.g. BrO). Were such measurements not available from the Polar Sunrise Experiment? Please comment and justify why only a VOC-based indirect approach to halogen chemistry is feasible here, or refer to existing literature if the link to direct halogen measurements has been made elsewhere and used to demonstrate the suitability of the proposed approach.

Measurements of photolyzable chlorine and bromine were made during this field study by Impey (see Impey et al, 1997). In that paper they calculate and discuss values for [Br]/[Cl], which ranges anywhere from 100-2000. We cite this paper when we discuss the wide range of halogen ratios that have been observed in the past. In addition, the use of VOCs to infer halogen chemistry has occurred very successfully in the past, most notably by Jobson et al., 1994, whom we cite. A problem is that there are no simultaneous measurements of ClO and BrO, and no measurements of the target species, Br and Cl, ever, in the troposphere. So, we are doing the best we can in the context of available data and our admittedly poor state of analytical chemistry!

Specific comments

Pg. 16, and 26: the references to Knipping and Dabdub (2002), Atkinson et al. (1986) and Cadman et al (1976) are not provided in the reference list

We regret this error, and these references have been added.

Pg. 13, l.12-14: The wording "initial slopes" is unclear in this sentence. Looking at the graphs shown in Figure 5, I do not see what is meant by "initial slopes", also the comparison of the model curves with observations suggest that Event 4 would correspond to a [Br]/[Cl] ratio in the range 200-500, instead of the indicated 100-200.

This sentence has been changed to say "Comparing the slopes of the model output with the data at low VOC ratios, the ambient...". When you compare the slopes of Event

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4, $[\text{Br}]/[\text{Cl}]=100$, $[\text{Br}]/[\text{Cl}]=200$ and $[\text{Br}]/[\text{Cl}]=500$ from $[\text{MEK}]/[\text{n-butane}]=0.5$ to 1.0 , the slope for event 4 is right between that of $[\text{Br}]/[\text{Cl}]=100$ and $[\text{Br}]/[\text{Cl}]=200$.

Pg.32, Figure 3: please clearly indicate what represent the solid lines here. Are these simple linear regressions to the measured points, serving as a guide to the eyes?

Thank you for noticing this omission. Yes, these are linear regressions, and that has been corrected in the figure caption.

Pg. 35: the resolution the trajectory maps presented in Figure 6 is too low. It is hardly possible to read the axes legends as well as the tick labels.

This has been resolved.

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

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