**Atmospheric
Chemistry
and Physics
Discussions**

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

M. VAN ROOZENDAEL (Editor)

michelv@oma.be

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Authors: A.E. Cavender, T.A. Biesenthal, J.W. Bottenheim, and P.B. Shepson

Title: Volatile organic compound ratios as probes of halogen atom chemistry in the Arctic

This paper presents an original study where the relative contribution of chlorine and bromine compounds in driving polar ozone depletion events observed during the PSE-1995, is inferred from an analysis of VOC concentration ratios that are used as halogen chemistry indicators. From the comparison between observations and the output from a 0-D model set up with state-of-the-art halogen chemistry, it is concluded that an ad-

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ditional source of proponal must be invoked, which calls for new measurements of this constituent. Results also show that the ratio of Br to Cl atoms may vary considerably, and this observation is made in relation with the history of the observed air masses, and the corresponding extent of halide processing along their trajectory.

The manuscript is well organized and clearly written. Extensive credit is made to the existing literature on the subject, however I noted that three references mentioned in the text are not included in the reference list (see specific comments below).

This paper brings new results of interest for the ACP readership and therefore I recommend its publication in ACP after attention to the points raised 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 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.

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

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.

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?

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.

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

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