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Interactive comment on “Chemistry of the antarctic boundary layer and the interface with snow: an overview of the CHABLIS campaign” by A. E. Jones et al.

A. E. Jones et al.

Received and published: 22 May 2008

We thank the reviewer for some very interesting scientific points raised. We have considered the points and would like to make the following responses:

Comment i) Section 7, which the reviewer refers to, summarises results from CHABLIS papers some of which are already published. The OH and HO₂ results are some of those already published (Bloss et al, 2007). In that paper, Bloss et al conclude: "Elevated levels of NO_x resulting from snowpack photochemistry contributed to HO_x cycling and enhanced levels of OH, however the halogen oxides IO and BrO dominated the CH₃O₂ - HO₂ - OH conversion". We therefore agree with the reviewer that the overview paper had overstated this result, and thank him/her for pointing this out. In

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Interactive Discussion

Discussion Paper



response, we have amended the text to read: "However, CH₃O₂ - HO₂ - OH conversion was dominated by the halogen oxides, IO and BrO...".

Comment ii) We agree with the reviewer that the case here is somewhat overstated, but confirm that a detection limit of 2 pptv does not allow any reasonable constraints to be put on NO₃ chemistry. For example, in their paper exploring DMS measurements during CHABLIS, Read et al (Atmos. Chem. Phys. Discuss., 8, 2657-2694, 2008) consider the various routes whereby DMS might be oxidised during the summer. They used measurements during CHABLIS to constrain the kinetics, and calculated the lifetime of DMS against oxidation by OH, Cl, BrO, IO, O₃. Their calculations show DMS to have a lifetime varying between 22.7 days with respect to OH oxidation to 3.5 days for oxidation by Cl. By contrast, if we use their kinetics (rate constant $1.5 \text{ to } 7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and a mixing ratio of NO₃ of 2 pptv, DMS would have a lifetime varying between 3.4 hours and 44 minutes. This is clearly inconsistent with the other data. Further, box modelling calculations carried out by Alfonso Saiz-Lopez to assess likely mixing ratios of NO₃ at Halley during autumn/winter/spring indicated that NO₃ mixing ratios remained below 0.2 pptv during these time periods. What these assessments suggest is that a much lower detection limit is necessary to constrain NO₃ measurements, even to get a useful upper limit. To adjust the tone in the overview paper, we now say: "The nitrate radical remained below the 2 pptv instrumental detection limit throughout the duration of the campaign. Unfortunately this threshold is too high to explore upper limits to NO₃ chemistry including any role for this oxidant within the boundary layer".

Comment iii) The point we were trying to make in this last paragraph of section 7 was that the CHABLIS data (and by extrapolation, likely, the coastal Antarctic boundary layer) can best be understood by considering both the snow-photochemistry that dominates the plateau region and also the halogen-dominated chemistry of the sea ice zone. Air masses arriving at Halley have an influence from both of these regions, so any interpretation of boundary layer chemistry at Halley must take both into account.

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We agree with the reviewer that there is evidence of halogen chemistry associated with the snowpack/snow photochemistry. However, the likely source of the halogens is sea salt aerosol with origins from the sea ice zone. As far as we are aware, it is still an open question, how far inland from the Antarctic coast such aerosol is active as a halogen source. We are not aware of any evidence for halogen activation in the Antarctic interior. The airflow during CHABLIS was rarely from the deep continental interior, so influence from halogens is conceivable either from the sea ice zone or from snow photochemical sources as outlined above.

In an attempt to clarify this distinction, we have amended the text to read: "Taken as a whole, the CHABLIS campaign clearly reveals that the chemistry of the coastal Antarctic boundary layer can only be understood if we consider both the active snow photochemistry that dominates the continental interior region, and the halogen chemistry that dominates the sea ice zone."

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 5137, 2008.

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