

Interactive comment on “Observations of OH and HO₂ radicals in coastal Antarctica” by W. J. Bloss et al.

W. J. Bloss et al.

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We thank Dr Faloona for his comments on the manuscript. With regard to the general comment regarding the inclusion of the calculations within this paper, our intention was to take the observations a stage further than simply presenting the data timeseries / solar radiation correlations, whilst considering the space constraints of a single (ACP) manuscript. For the model results to be fully justified, we feel that aspects of the model scheme (which, as our data show, has to include an iodine/bromine chemistry module, with associated sensitivity studies of the uncertain photochemical/ kinetic parameters) need a full description, which together with the model results, would make the present manuscript much too long. The steady-state calculations are much more straightforward to present, yet still permit the key features of the radical chemistry, sources and sinks, to be identified. On a point of notation, we prefer to use the term “calculations” to

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refer to the spreadsheet-level analyses included in this manuscript, rather than “model” which we associate (in the atmospheric chemistry context) with forward numerical integration or solution of the differential equations defining the chemical reactions.

Response to specific comments :

-We agree that the steady state assumption does not necessarily require a specific lifetime for the species involved, and have adjusted the manuscript to reflect this.

-The aerosol surface area assumed was estimated from measurements made previously at Halley Bay by Davison et al. (1996) (close - a few km - to the Halley Base site of our measurements, but over the Weddell Sea rather than over the adjacent ice shelf, hence still a rather uncertain quantity). The assumption inherent in the free molecular approximation is that diffusion to the aerosol surface is not rate limiting, i.e. that the aerosol are small. Previous work including our own has shown that this is not the case, and that the error in a coastal marine environment can be a factor of 2 (Bloss et al., 2005) - however given that aerosol surface area is unknown, let alone size distribution, together with uncertainty in the uptake parameters, the free molecular approximation is appropriate. The relative rates of photolysis to heterogeneous loss for HOI range from approximately 200 (midday) to 5 (midnight) with the surface area estimated ($10^{-7} \text{ cm}^2 \text{ cm}^{-3}$), thus the effect of this uncertainty upon calculated OH levels is small during much of the day, but could be significant at higher solar zenith angles.

-The IO measurements were averaged over periods of 20 - 80 minutes depending upon the instrument performance, to achieve adequate signal:noise performance - the details of these measurements have now been reported by Saiz-Lopez et al. (2007), which is reference in the revised manuscript. Only data coincident with the HOx measurements were used to derive equation 5; the correlation coefficient (r^2) for this relationship was 0.72.

-The acetaldehyde value should be interpreted as representing the sum of all (unmeasured) VOCs in assessing the additional OH pseudo-first-order loss rate which would

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be required to replicate the observations, rather than the concentration of that compound alone (although the latter is a possibility). The physical structure of the lower atmosphere over Halley during the CHABLIS campaign has now been presented by Anderson (2007), in which boundary layer heights of ca. 100m during daytime are inferred.

-NO_x lifetime: A more precise statement would be that the apparent NO_x lifetime (approximately 6 hours) is consistent with removal through halogen nitrate photolysis on the estimated aerosol surface area (Bauguitte et al., 2006). We have rephrased this comment in the manuscript.

-OH observed vs. calculated plot, Figure 7: The phrase “reasonably well” refers to scenario 1 rather than scenario 2 - the mean calculated:observed ratios are 0.67, 1.64 and 1.27 for scenarios 1, 2 and 3 respectively.

-The HONO data have been briefly presented in the peer-reviewed literature (Clemitshaw, 2006) and discussed in the context of NO_x / NO_y sources for CHABLIS elsewhere (Jones et al., 2007). The question of the magnitude of HONO production from sunlit snow, and the interpretation of measurements of soluble nitrite in polar regions, is central to quantifying both HO_x and NO_x fluxes to the polar boundary layer, which our boundary layer OH and HO₂ data go some way towards constraining; we feel this issue is a key outcome from our measurements which it is appropriate to discuss here.

-We are wary of including mean IO and BrO statistics in table 1 as the DOAS data for these species over the summer period is highly fragmented (see comments earlier in the paper), while for the other parameters substantial time-series exist; the halogen oxide observations are summarised in section 7, and referenced to the (now published) paper by Saiz-Lopez et al.

-Comments on Table 3 / Figure 6 - We agree the number of significant figures is inappropriate and will amend this. P(OH) does indeed refer to OH production through ozone photolysis i.e. O(1D) + H₂O; we have clarified this in the revised manuscript.

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