

**“Coupling of HO<sub>x</sub>, NO<sub>x</sub> and halogen chemistry in the Antarctic boundary layer” by W. J. Bloss *et al.***

**Response to Referee Comments**

We thank the reviewers and editor for their comments on the manuscript. We outline below responses to the points raised, and summarise the changes made to the revised manuscript.

**Reviewer 1**

**Halogen Nitrates.** The key processes calculated to dominate removal for INO<sub>3</sub> and BrNO<sub>3</sub> are heterogeneous loss and dry deposition (ca. 63 and 36 % respectively for INO<sub>3</sub>), however it is important to note that these rates are directly dependent upon our assumed aerosol surface area, reaction probability and boundary layer height – in effect, the uncertainty over their combined magnitude is accounted for in setting the NO<sub>x</sub> source strength to replicate the observed NO. The fate of the halogen nitrates during CHABLIS is also discussed further in Bauguitte *et al.* (2009).

**DOAS IO / BrO data coverage**

The (mutually exclusive) IO and BrO data coverage arises from technical limitations in the DOAS instrument –these molecules primarily absorb at different wavelengths (ca. 400-500 and 300-400 nm respectively), while the instrument coverage only extends over a ca. 25 nm range. During the period of the HO<sub>x</sub> observations, the DOAS system did not have a dedicated operator, and so was run on a single wavelength range (molecule) for blocks of a few days duration (data analysis was not real time). We have modified the manuscript to clarify this.

**Role of chlorine chemistry**

Chlorine reactions could in principle contribute to VOC oxidation and HO<sub>x</sub> radical production, and alter the partitioning of HO<sub>x</sub> and NO<sub>x</sub> species. No measurements of gas-phase chlorine species were made during CHABLIS, but some constraints may be obtained from VOC ratios. Using NMHC measurements obtained during CHABLIS, Read *et al.* (2006) estimated [Cl] from  $1.7 \times 10^3$  -  $3.4 \times 10^4$  cm<sup>-3</sup> during local spring ozone depletion events, and a longer-term (springtime) value of  $2.3 \times 10^3$  cm<sup>-3</sup> (slightly larger than southern hemispheric global average of the order of  $2 \times 10^3$  cm<sup>-3</sup> – Rudolph *et al.*, 1996). These absolute [Cl] levels are uncertain, being dependent upon assumed airmass processing times, and were derived for a different season to the measurements considered in the paper, but may be used to crudely estimate potential Cl chemical impacts. At the higher Cl levels determined during CHABLIS ( $2.3 \times 10^3$  and  $3.4 \times 10^4$  cm<sup>-3</sup>), considering only reaction with CH<sub>4</sub>, Cl-initiated VOC oxidation would correspond to an RO<sub>2</sub> production rates of  $6.3 \times 10^3$  and  $9.6 \times 10^4$  molec cm<sup>-3</sup> s<sup>-1</sup> respectively. These (effectively 24-hour average) values may be compared with (24-hour mean) calculated HO<sub>x</sub> production rates from O(<sup>1</sup>D)+H<sub>2</sub>O and HCHO photolysis of  $9.72 \times 10^4$  and  $1.25 \times 10^5$  molec cm<sup>-3</sup>s<sup>-1</sup> respectively (ACPD manuscript, figure 6b). It is therefore possible that Cl chemistry comprised a measureable contribution to radical production, if the elevated levels observed during Aug-Sept were also present during the summer – but this would worsen the model –

measurement disagreement. An argument against this is that ozone depletion events were not observed during the summer, only during the springtime period - although O<sub>3</sub> loss is thought to be dominated by Br and I chemistry (e.g. Saiz-Lopez *et al.*, 2008) so the presence of Cl cannot be precluded on this basis. The probable main source of chlorine at Halley, sea-salt aerosol, has been found to show a pronounced seasonal cycle which maximises during spring (when Read *et al.* performed their analyses) and minimises in the summer (when the HO<sub>x</sub> observations were made) – Wagenbach *et al.*, 1998 - further indicating that the actual Cl levels present are likely to be significantly lower than the values noted above. The second potential impact of chlorine chemistry arises through perturbations to HO<sub>x</sub> cycling analogous to the IO and BrO reactions discussed. Taking the Cl levels estimated above ( $2.3 \times 10^3$  and  $3.4 \times 10^4$  cm<sup>-3</sup>), and the measured mean O<sub>3</sub> level to derive a ClO production rate, and considering ClO removal by reaction with itself, IO, BrO, HO<sub>2</sub>, NO and NO<sub>2</sub>, steady-state ClO concentrations of  $5.6 \times 10^5$  and  $8.3 \times 10^6$  molecules cm<sup>-3</sup> are obtained (ClO removal found to be dominated by the well-constrained ClO + NO reaction). At a typical peak HO<sub>2</sub> level of 2 nmolmol<sup>-1</sup>, the flux through the HO<sub>2</sub> + ClO reaction is  $3 \times 10^{-4}$  nmolmol<sup>-1</sup> hr<sup>-1</sup> for the higher ClO level, which is approximately a factor of 130 less than the main OH production and HO<sub>2</sub> removal rates (as shown in Figure 6b). It is therefore unlikely that chlorine chemistry is having a significant impact upon either the HO<sub>x</sub> production or partitioning in this environment.

We have amended the manuscript to include an abridged version of this qualitative discussion of chlorine chemistry.

**HO<sub>x</sub> observations** We explicitly discuss potential errors in the HO<sub>x</sub> observations as one of the three potential sources for the model-observation discrepancy in the discussion section of the paper (the others being overestimated sources and missing sinks), but are not able to identify any single specific problem, which would not be expected to also occur in other environments, and where any such issues are not apparent. The instrument performance, as assessed by the calibration factor, was approximately constant over the course of the campaign (shown in Bloss *et al.*, 2007), and no “step changes” in the measured HO<sub>x</sub> levels, or other ancillary parameters, were apparent. With regard to the related point raised by Referee 2 (inlet temperature), the fluorescence cells protruded from a heated enclosure into the ambient air. The temperature of the enclosure was regulated (at ca. 20 °C), so there will have been a gradient towards ambient temperatures through the body of the fluorescence cells, however this would have been a) small in comparison to the adiabatic cooling resulting from expansion of the sampled airstream into the low pressure region (to ca. 220K; Creasey *et al.*, 1997) and b) also present and hence implicitly included during calibration – the calibration source was mounted externally on the ambient system *in situ*). We would not expect any significant heating from absorption of solar radiation, although this was not directly measured.

Recent chamber intercomparisons of OH and HO<sub>2</sub> measurements (Schlosser *et al.*, 2009; Fuchs *et al.*, 2010), between instruments very similar to that used here, have shown good agreement for OH (relative range up to 1.13) but substantial variability for HO<sub>2</sub> (relative range up to 1.45). The latter value is somewhat larger than the

known measurement uncertainty (27 % in the case of the CHABLIS observations; Bloss et al., 2007) would indicate, and may indicate that additional sources of measurement error are present – but would not in isolation account for the model – measurement discrepancy found here. We recognise that application of Occam’s Razor would suggest that the HO<sub>x</sub> measurements are in error, but cannot identify a single likely cause of such a problem, hence have also considered potential explanations for the discrepancy considering the *known* uncertainties within the chemical and physical parameters – additional unknown uncertainties are of course also likely to be present, in both model and measurements. We note that other measurements of HO<sub>x</sub> in similar environments, using different techniques, have also failed to reconcile observations with model simulations.

A further reason we have some degree of confidence in the observations is that further measurements of OH were performed at Halley two years after the CHABLIS campaign, using a different approach (Chemical Ionisation Mass Spectrometry). These data are still unpublished, but the OH levels observed during late Jan / Feb are similar to the OH observations reported here – *i.e.* substantially lower than those modelled (N. Brough, A. Jones, personal communication) – although of course other reactant levels and conditions may also differ.

We have altered the manuscript (discussion section 6.4.3 and conclusions) to incorporate the points above and to more explicitly acknowledge that a possible cause of the discrepancy is of course measurement error, in addition to the other factors discussed.

**Role of iodine in HO<sub>x</sub> cycling.** The manuscript advances one potential mechanism by which iodine reactions may not lead to elevated HO<sub>x</sub> – namely, if the CH<sub>3</sub>O<sub>2</sub> + IO reaction produces “stable” products (HCHO, HI) rather than leading to radical propagation. This would also introduce a further OH sink in the form of HI. In terms of current understanding, we would certainly agree that HOI is well known to form from HO<sub>2</sub> + IO and photolyse to yield OH, but heterogeneous uptake is also a known sink to HOI which will divert some fraction of HO<sub>x</sub> from the gas phase – this is considered in the paper, but is found to be small. It would seem likely that an explanation would lie in the iodine chemistry rather than the analogous bromine processes, as the iodine reactions are both much faster (and levels of IO, BrO are thought to be similar (notwithstanding the measurement limitation noted above). Possible uncertainties in the iodine chemistry are discussed in the manuscript (*Model Conditions and Chemistry*, now re-numbered in line with the Editor’s suggestion).

**Comparison of HO<sub>x</sub> observations with modelled levels.** The table below compares the peak HO<sub>x</sub> levels with the equivalent modelled quantity, and repeats the comparison for the subset of the time period for which IO observations were available (and well reproduced); the model/observed ratio is also given for each case. Uncertainties are one standard deviation. The values reflect the behaviour shown in Figures 2a and 2b; while the modelled:observed ratio shows some improvement for the subset of observations for which IO measurements were available, this reflects the fact that the distribution of these was biased towards the end of the campaign,

where the overall agreement was better (see figure 2). We have included this table and accompanying discussion in the revised manuscript (new Table 3).

Comparison of modelled and observed mean daily maximum OH and HO<sub>2</sub> values.

	OH / 10 <sup>6</sup> cm <sup>-3</sup>	OH M/O	HO <sub>2</sub> / nmolmol <sup>-1</sup>	HO <sub>2</sub> M/O
<i>Whole Timeseries</i>				
Observed	0.98 ± 0.30		1.10 ± 0.33	
Model A	3.75 ± 1.21	3.8	3.12 ± 0.79	2.8
Model C	2.24 ± 0.77	2.3	2.26 ± 0.58	2.1
<i>IO Observations Only</i>				
Observed	0.84 ± 0.22		1.30 ± 0.38	
Model A	2.77 ± 0.51	3.3	2.87 ± 0.49	2.0
Model C	1.70 ± 0.25	2.0	2.31 ± 0.56	1.8

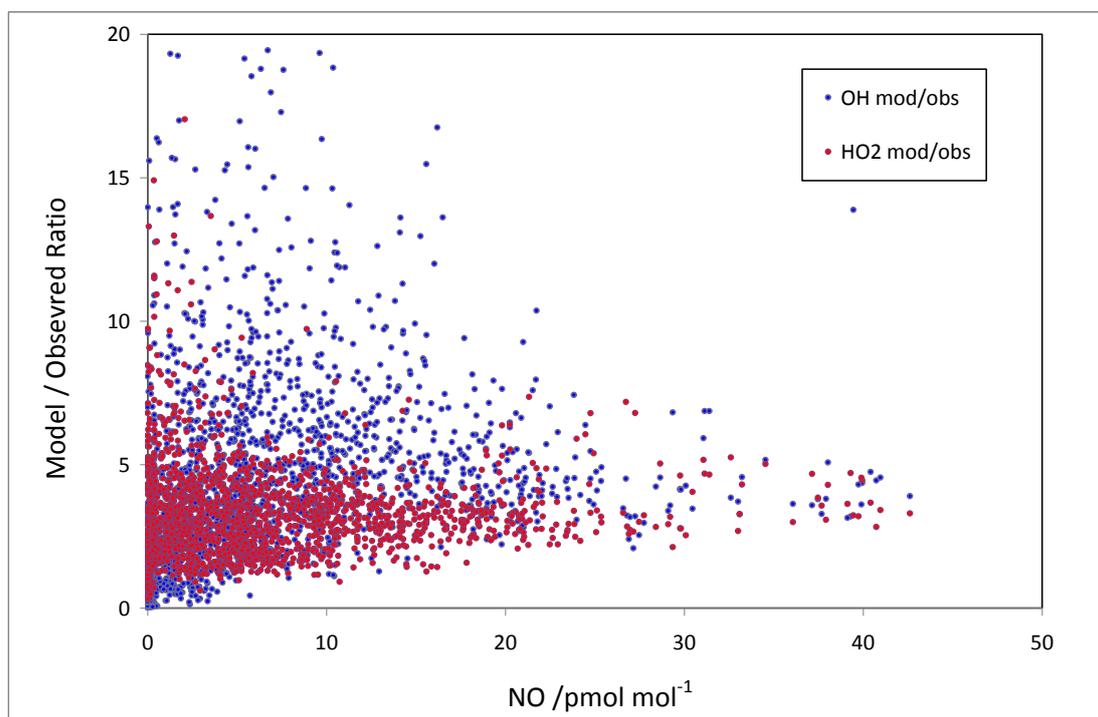
**RO<sub>2</sub> radicals.** RO<sub>2</sub> measurements were attempted during CHABLIS (using the PERCA approach) but unfortunately were not possible due to instrument failure. RO<sub>2</sub> is of course a key reservoir for HO<sub>x</sub>, and would normally be removed by reaction with NO and/or HO<sub>2</sub> (*i.e.* standard chemistry as included in the model); however in this environment we anticipate a shorter lifetime arising from the additional XO sink. Laboratory measurements of the CH<sub>3</sub>O<sub>2</sub> + IO reaction rate constant are not in agreement, and considering the relative abundance of IO and NO, could lead to CH<sub>3</sub>O<sub>2</sub> + IO reaction being three times faster, or ten times slower, than the CH<sub>3</sub>O<sub>2</sub> + NO reaction. The CHABLIS environment is unique in having NO<sub>x</sub> levels lower than most other surface environments outside of the remote MBL, and in also having XO levels one order of magnitude higher than the IO or BrO observed in the open ocean MBL (e.g. Read et al., 2008), so the impacts of the mechanistic uncertainties associated with this chemistry (in particular, the potential for CH<sub>3</sub>O<sub>2</sub> + IO to lead to non-radical product as noted above) are accentuated. In any case, the additional RO<sub>2</sub> sink indicates that the HO<sub>x</sub> is unlikely to reside in RO<sub>2</sub>, but the RO<sub>2</sub> + XO reaction may provide a route to HO<sub>x</sub> loss which would improve the measurement: model comparison. Simultaneous measurement of OH, HO<sub>2</sub>, RO<sub>2</sub> and XO would allow this possibility to be robustly tested in the future.

## Reviewer 2

**NO/NO<sub>2</sub> ratio.** The model (with an optimised NO<sub>x</sub> source strength) describes the IO, BrO and NO/NO<sub>2</sub> ratio well, but overestimates the observed HO<sub>2</sub>. This is in keeping with the relative rates of the reactions controlling the NO<sub>x</sub> ratio: HO<sub>2</sub> + NO is not dominant in this process under the CHABLIS conditions, rather the XO reactions dominate: In terms of NO to NO<sub>2</sub> conversion, 29 % of the flux is calculated to arise from reaction with IO, 23 % with BrO, 19 % with O<sub>3</sub>, 14 % with CH<sub>3</sub>O<sub>2</sub> and 9.5 % with HO<sub>2</sub> (fluxes evaluated at local noon). Over 95 % of the NO<sub>2</sub>-to-NO flux arises from photolysis. Consequently the NO/NO<sub>2</sub> ratio can be well reproduced, despite the HO<sub>2</sub>

overestimate (and reducing HO<sub>x</sub> levels would further reduce their influence upon NO<sub>x</sub>).

**Dependence of the HO<sub>x</sub> model/observed ratio upon NO.** The dependence of the modelled/observed OH and HO<sub>2</sub> ratios (Model A) are shown in the figure below. No trend in either ratio with NO is apparent (in keeping with figure 3d), likely reflecting that NO / NO<sub>2</sub> are not significant direct co-reactants with OH and HO<sub>2</sub> in this environment (the halogens dominating). It is noticeable that the scatter reduces substantially at higher NO levels, probably reflecting that the higher NO<sub>x</sub> and HO<sub>x</sub> levels both occur around local midday, with reduced scatter due to smaller relative measurement (im)precision. We have not included this figure within the revised manuscript, as it largely duplicates the information presented in Figures 3a-d.



**Production of CH<sub>3</sub>O<sub>2</sub>.** Unfortunately no measurements of RO<sub>2</sub> radicals were performed, however as noted above the CH<sub>3</sub>O<sub>2</sub> reaction does not dominate NO<sub>x</sub> partitioning. CH<sub>3</sub>O<sub>2</sub> + HO<sub>2</sub> is calculated to be the dominant HO<sub>x</sub> sink (See Figure 6a), so if the modelled organic peroxy radical levels are underestimated, HO<sub>2</sub> and so OH would be overestimated (as is the case). However, our (admittedly incomplete) understanding of the XO – RO<sub>2</sub> chemistry indicates that we would not expect HO<sub>x</sub> to predominantly reside in the organic peroxy radical pool – see response to reviewer 1, final point, above. We have modified the manuscript (section 6.4.2 and conclusions) to emphasise the potential impact of model underestimates of CH<sub>3</sub>O<sub>2</sub>. Better laboratory understanding of the XO – RO<sub>2</sub> reaction kinetics and products, and field measurements of RO<sub>2</sub> alongside OH and HO<sub>2</sub>, would allow this possibility to be tested.

**Temperature of LIF inlet** – See response to reviewer 1, above.

**Photolysis frequencies instead of rates** – we have modified the manuscript to use this term throughout.

## **Editor Comments**

**Potential Role of Chlorine Chemistry** – See response to reviewer 1, above.

**IONO<sub>2</sub> vs. INO<sub>3</sub>** – we have amended the manuscript to use IONO<sub>2</sub>, BrONO<sub>2</sub> throughout.

**OVOC** – now used consistently throughout

**Section 6.4** – now subdivided as suggested

**LOD** – now defined as Limit of Detection

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