

Response to Referee #1:

Specific comments:

Was the Palmer Station snow-covered at the time of year for the data reported in Jefferson et al. 1998? This is on the Antarctica peninsula coast in summer.

Palmer Station was not snow-covered at the time of year for the data reported in Jefferson et al. 1998.

Page 12728 Line 16: After “extensive cloud coverage” added “no snow coverage,”

The CIMS was calibrated for OH and HO₂, but reports OH and HO₂+RO₂. How is the sensitivity of the CIMS towards RO₂ known? Is there a calibration with CH₃O₂?

Page 12731 section 2.1 Line 5: after “Tanner et al. (1997).” add “The CIMS was calibrated for OH and HO₂. Because many of the simple RO₂ species (e.g. CH₃O₂) are efficiently converted to HO₂ by this method (Edwards et al., 2003), we assumed that the sensitivities for RO₂ were the same as for HO₂.

At the end of the BrO experimental section (page 12733) mention is made of improvements in the method using the I- ion instead, as there are less interferences. What interferences are there when using the SF₆- ion? How significant are these at this site?

P12733 Line 5 added “The specific candidates for the interference are still not clear.” Because the CIMS detected much higher BrO on 06/20/2008 than LP DOAS and reagent ion SF₆⁻ is reactive with many atmospheric compounds, we suggested that there may be potential interferences using reactive reagent ion SF₆⁻.”

I found the description of the model lacking in some important details. For example, for intermediates that were not measured, rather model calculated, how long did it take for these species to reach a steady-state before being used as input into the constrained model? An example is HCHO which has a reasonably long lifetime.

p. 12734 Line 7 after “10 minute basis” add “A spin-up time of 1000 s was used for model calculations of relatively long-lived species (e.g. H₂O₂ and HCHO).”

What is the impact of just including CH₄ chemistry? Is there a role for larger VOCs, e.g. oxygenated VOCs formed as oxidation products during long-range transport. What is the level of NMHC (this is mentioned as a measurement in Table 1). Is it possible to estimate any impact of other VOCs? Another way of putting this is whether RO₂ is just CH₃O₂?

P. 12734 line 6 after “and NO.” Added “The model only considered CH₄ chemistry because previous studies by Chen et al. (2007) and Sjostedt et al (2007) found that including NMHC decreased OH number densities and increased HO₂+RO₂ number densities less than 10% and that most of the RO₂ is CH₃O₂ at Summit, Greenland. Typical levels of the dominant NMHC species ethane, propane, and butane are 1.0 ppbv, 0.07 ppbv, and 0.04 ppbv, respectively. The NMHC measured in 2007 and 2008 were generally consistent with the measurements in 2003. The average ethane, propane and butane levels were 1.1 ppbv, 0.14 ppbv, 0.03 ppbv, respectively in spring 2007 and 0.9 ppbv, 0.07 ppbv, 0.02 ppbv respectively in summer 2008. Because Summit Greenland is in the middle of Greenland Ice Sheet far away from biogenic and anthropogenic volatile organic carbons (VOCs) sources, we do not expect high levels of oxygenated VOCs reacting with OH at Summit, Greenland. Measurements of larger oxygenated VOCs at Summit, Greenland are needed to validate our assumption.”

Page 12734, line 20, why can HOBr be assumed to be is steady-state? The assumption made by Liao et al (2011b) should be briefly stated. Was a heterogeneous loss for HO₂ included in the model? The recent work of Mao et al shows an important role for this, and the parameterisation used by Mao has a higher uptake at low temperature.

P 12734 Line 20: changed “This assumption was found to be reasonable by Liao et al. (2011b).” to “This assumption is valid because the photolysis lifetime of HOBr is relatively short (~5 minutes) at Summit Greenland in the daytime. The assumption was also found to reasonably predict the observed HOBr at Barrow, AK in Liao et al. (2011b).”

P 12734 Line 21: added “As the photochemical lifetime (= ~2 minute) of HO₂ is much shorter than the lifetime due to heterogeneous loss (= ~150 minute) with a uptake coefficient of 0.1 (Mao et al., 2010), the model did not consider the heterogeneous loss of HO₂.”

Page 12736. Line 5. The ratio of J for the 2007 and 2008 campaigns should be stated to support the statement here.

P12736 Line 5: after “radiative fluxes” added “(J_{O₃}_2007/J_{O₃}_2008= 1 : 1.4)”

Page 12738. Line 4. Is there a reason why the agreement for OH between the model and measurements get worse at high wind speeds? There may be a good reason for not including these data in the averages, but some justification should be given.

P12738 Line 8: added “It is possible that the uncertainty in the instrument calibration increases at high wind speeds (> 8 m s⁻¹) due to turbulent flow in the inlet as suggested in Sjostedt et al. (2007).”

Page 12739, line 8 – what is the interference mentioned here? Is this a known and published interference?

See p12736 Line 19 added: “Following the simple NO_x and HONO lifetime arguments in Chen et al. (2004); NO levels of 12 ppt and HONO levels of 6 ppt would seem to indicate that the soluble nitrite measurement includes species other than HONO.”

P 12739 Line 7-Line 10: changed “As constraining to HONO in the model does not improve the correlation between predictions and observations significantly and the observed HONO may have interference from other compounds, the BM is preferred for comparison to HO_x levels in this environment.”

to “As HO_x predictions from the BM had more data points and the observed HONO in the daytime may have interferences from (Stutz et al., 2010; Sjostedt et al., 2007), the BM is preferred for comparison to HO_x levels in this environment.”

Table 1 – what are typical values of NMHC at this site.

The average ethane, propane and butane levels were 1.1 ppbv, 0.14 ppbv, 0.03 ppbv, respectively in spring 2007 and 0.9 ppbv, 0.07 ppbv, 0.02 ppbv respectively in summer 2008. This was added to the text as described above.

Fig 2. Unless screen was blown up considerably, I found it hard to read the labels on this plot. Could these be increased in size?

The size of the labels in Fig 2 has been increased.

Fig 3. The top panel says HO_2 , but HO_2+RO_2 is measured. In the caption to Figure 3, add that the spikes in NO and the responses in OH and HO_2+RO_2 ? are due to perturbation from the generator, and not natural behaviour.

Fig 3. Caption changed as “An example of elevated OH and depleted $\text{HO}_2 + \text{RO}_2$ at high NO conditions. The spikes in NO and the responses in OH and $\text{HO}_2 + \text{RO}_2$ are due to the measurement site being impacted by the plume of the generator.”

Figure 9, bottom plot, the BrO CIMS and BrO DOAS is quite different at times? Is this discussed in the text?

P 12743 Line 7 added “The BrO levels were near the detection limits of the LP DOAS and CIMS instruments.”

Respond to Referee #2:

p.12728 Strictly, snowpack emits radical precursors; their photolysis or reaction then comprises the HO_x source

p.12728 Line 8: changed “radical sources” into “radical precursors”.

p. 12728 The South Pole NO_x levels reflected both the snowpack source and low boundary layer height

p. 12728 Line 21: changed “...South Pole were due to snowpack emissions that” to “...South Pole were due to low boundary layer height and snowpack emissions that”

p.12730 Br + Hg0 may be the only rapid reaction, but the data / observation of RGM (in isolation) does not establish anything about the *rate* of the Hg oxidation process...

p. 12730 Line 1-2: changed “depleted GEM and elevated RGM may be a signature of active bromine chemistry.” To “elevated RGM may be a signature of active bromine chemistry as RGM is a relatively short lived species (Steffen et al., 2008).”

p.12733 What were the suspected interferences in the CIMS BrO observations – this is not mentioned in the Stutz paper – a correlation plot of the two datasets could be included, and the comparison between the two discussed, as the data presented (e.g. figure 2 around 6/21/08) show quite significant differences between the instruments.

We suspect there might be interferences in the CIMS BrO observation because reagent ion SF₆⁻ used in the campaign is more reactive than I and the CIMS observed higher BrO concentrations than LP DOAS on 06/20/08-06/21/08. The potential interferences in the CIMS BrO observations are still not well known. We did not show a correlation plot of the two BrO datasets because the focus of this paper is the impact of BrO on HO_x partition and most of the time the measurements of BrO were near the detection limit and this topic is discussed in a second Stutz paper.

p.12733 Why not give the LP-DOAS path length as 1.25 km rather than 5/4 km ?

p. 12733 Line 5: change “5/4 (2007/2008) km” to “5 km (in 2007)/ 4 km (in 2008)”.

p.12733 State (very briefly) the Hg monitoring technique, i.e. atomic absorption / fluorescence

p. 12733 Line 18: change “...(FPM).” to “... (FPM) via cold vapor atomic fluorescence”.

p.12734 More details are needed with regard to the modelling: What spin-up time was used for the model calculations, and how did this affect the simulated levels of relatively long-lived species such as H₂O₂ and HCHO. How was the model bromine source implemented – was this a fixed source strength, optimised to replicate the observed BrO – on average ? at noon ? on a particular day ? CIMS or DOAS BrO – what would the effect be of using the other dataset ? What uptake coefficient was used for HOBr loss – were HO₂, BrONO₂ and other potential heterogeneous sinks also included? How did the bromine chemistry affect the NO₂ levels simulated?

p. 12734 Line 7 after “10 minute basis.” add “A spin-up time of 1000 s was used for model calculations of relatively long-lived species (e.g. H₂O₂ and HCHO).”

p. 12734 Line 20 after “(2010b)” add “The box model is constrained by BrO measurements from CIMS and LP DOAS to illustrate the effect of two BrO datasets on HO_x levels. The mass accommodation coefficient of HOBr is assumed to be 0.6 (Wachsmuth et al., 2002).”

p. 23734 Line 21 after “available.” add “The model did not include the heterogeneous sinks of BrONO₂ because the model is constrained to BrO measurements and BrONO₂ does not directly impact the budget of OH and HO₂+RO₂. The impact of BrONO₂ on daytime NO₂ levels is also small due to the low BrO concentrations. Daytime NO₂ levels increased ~5% in 2007 and ~2% in 2008 when the model considered bromine reaction 4 and 5 in the table 2. As the photochemical lifetime (= ~2 minute) of HO₂ is much shorter than the lifetime due to heterogeneous loss (~150 minute) with a uptake coefficient of 0.1 (Mao et al., 2010), the model did not consider the heterogeneous loss of HO₂.”

p.12736 Are these HO₂+RO₂:OH ratios significantly different (e.g. 109 vs 108) – standard deviation would be useful here.

p. 12736 Line 8 change “to OH was 109 : 1 in spring 2007 and 108 : 1 in summer 2008.” to “to OH was 109 : 1 with a standard deviation of 23 in spring 2007 and 108 : 1 with a standard deviation of 37 in summer 2008.”

p.12736 HONO levels: Following the simple NO_x and HONO lifetime arguments in Chen et al. (2004) NO levels of 12 ppt and HONO levels of 6 ppt would seem to indicate that the soluble nitrite measurement includes other species.

p. 12736 Line 19 column 5: add “Following the simple NO_x and HONO lifetime arguments in Chen et al. (2004), NO levels of 12 ppt and HONO levels of 6 ppt would seem to indicate that the soluble nitrite measurement includes species other than HONO.”

p.12736 line 25 Observed in *the* spring 2007 campaign

p. 12736 Line 25: change “in spring” to “in the spring”.

p.12737 RGM vs NO correlation – would this suggest a common origin for both NOx and bromine species - what is the r² value for this correlation – it may be useful to show the plot ?

p. 12737 Line 4-5: The correlation coefficient (R^2) between RGM and NO is 0.19 in 2007 and 0.07 in 2008. We did not expect a high correlation between RGM and NO because that although snow photochemistry probably activates bromine chemistry and produces NO at Summit, the reactions that produce bromine and NO are likely different.

p.12738 Exclusion of HO_x data from high windspeed conditions – what is the effect of this exclusion - What fraction of the total does this amount to, and is there any impact on the correlations – e.g. one might expect the higher windspeed conditions to also have predominantly low photolysis rates and possible lower NO_x levels – is any systematic bias introduced.

p. 12738 Line 8 after “the comparisons.” Add “On average 26% of the HO_x data were excluded and the correlation coefficients were improved (R increase 0.03 on average for BM_model) when HO_x data were filtered at high wind speed conditions. Higher wind speed conditions did not clearly correspond to low photolysis rate or lower NO_x levels. The correlation coefficient (R) between photolysis rate and wind speeds were < 0.1 in 2007 and 2008. The correlation coefficient (R) between predicted NO₂ and wind speeds were -0.35 in 2007 and -0.29 in 2008. There is no clear systematic bias introduced when the HO_x data were filtered at high wind speeds but this filter excluded many of the most scattered points. It is possible that the uncertainty in the CIMS calibration increased at high wind speeds ($> 8 \text{ m s}^{-1}$) due to turbulent flow in the inlet as suggested in Sjostedt et al. (2007).”

p.12738 line 19 The agreement between modelled and observed HO₂+RO₂:OH ratios indicates that the model correctly captures the magnitudes of the fluxes *between* OH and HO₂+RO₂ – less sensitivity to the (combined) source and sink.

P. 12738 Line 14-20 is rewritten as: “The agreement between the predicted and observed HO₂+RO₂ (which is dominated by HO₂) indicates that we have a good understanding of the major sources and sinks of HO₂ which dominants the HO_x family. However, our understanding of the OH sources and sinks is clearly lacking especially during periods of elevated RGM (see section 4.4). The model predicted an average midday HO₂+RO₂ to OH ratio of 121 : 1 in 2007 and 125 : 1 in 2008, consistent with the values predicted by

Chen et al. (2007) using input data from the summit 2003 campaign. The observed average midday HO_2+RO_2 to OH ratios were 109 : 1 in 2007 and 108 : 1 in 2008. The predicted and observed HO_2+RO_2 to OH ratios indicate that a mechanism rolling HO_2 back to OH may be missing, with halogen chemistry a likely prospect.

p.12739 Section 4.1.3 – figure 4 shows slopes of 0.72 and 0.54 for modelled vs observed OH in 2007 and 2008 respectively, while figure 6 (incl. Bromine) shows slopes of 0.78 and 0.56, or 0.72 and 0.50, depending upon the bromine data used. Yet the text reports increases in OH, in all cases, of up to 10 – 12 %. Which is correct ? Is this a consequence of changing intercept in the regression analyses shown in the figures – the intercepts for the fit (and the uncertainty in both intercept and gradient) should be shown in the plots, and discussed in the text.

p. 12739 Section 4.1.3. Changing intercept in the regression analysis also matters and the intercepts are added in the Figures. Line 18: After “observations.” Added “When the model included bromine chemistry and was constrained to CIMS BrO, the intercept increased from 1.12×10^5 molec cm^{-3} to 1.65×10^5 molec cm^{-3} and the slope increased from 0.72 to 0.78 in 2007 and the intercept increased from 8.64×10^5 molec cm^{-3} to 9.23×10^5 molec cm^{-3} and the slope increased from 0.54 to 0.56 in 2008 for OH. When the model included bromine chemistry and was constrained to LPDOAS BrO, the intercepts increased from 1.12×10^5 molec cm^{-3} to 3.20×10^5 molec cm^{-3} and the slope remained the same in 2007 and increased from 8.46×10^5 molec cm^{-3} to 1.15×10^6 molec cm^{-3} and the slope slightly decreased from 0.54 to 0.50 in 2008 for OH. To give a general idea of the difference between predicted OH and HO_2+RO_2 from BM and BM_BrO, the average ratios of OH and HO_2+RO_2 from BM to BM_BrO besides the slopes and intercepts from linear equally weighted bivariate regression are also provided.” The uncertainties in the intercepts and slopes are very small compared to the values of the intercepts and slopes.

p.12740 The air-snow exchange expression is not clear – is this $[\text{H}_2\text{O}_2]$ in the BL or in the snowpack interstitial air – a format of $d[\text{H}_2\text{O}_2]/dt = \dots$ would be clearer.

p. 12740 Line 13-17: changed “For this reason, temperature dependent snow emissions of H_2O_2 , based on net snow-air exchange rate = $A \times \exp(B/\text{Temperature}_{\text{snow}}) - C \times [\text{H}_2\text{O}_2]$ (A , B and C are adjustable constants; temperature is assumed to be ambient temperature instead of snow temperature) (Chen et al., 2007), were added to the BM.”

To “For this reason, temperature dependent snow emissions of H_2O_2 , based on net snow-air exchange rate shown as the following equation, were added to the BM.

$$d[\text{H}_2\text{O}_2]/dt = A \times \exp(B/\text{Temperature}_{\text{snow}}) - C \times [\text{H}_2\text{O}_2] \text{ (molec.cm}^{-3}.\text{s}^{-1} \text{ or ppbv. hr}^{-1}\text{)}$$

A, B and C are adjustable constants. Temperature is assumed to be ambient temperature instead of snow temperature. $[H_2O_2]$ represents ambient H_2O_2 concentration) (Chen et al., 2007)."

p.12741 line 8 Is this an effect of the distribution (across the campaign) of the CIMS BrO measurements favouring the end of the measurement period when HO_x levels were generally higher – I'm not clear that this should affect the average observed:measured ratios, unless there is a trend in these with HO_x levels (which would be worth noting) ?

p. 12741 Line 9: after "campaign." Add "and the increase in HO_x levels in the late period of the 2007 campaign relative to the early period."

p.12741 line 16 which *may* indicate that the box model underestimates the sources of OH – or there may be a change in the sinks or cycling...

p. 12741 Line 16-17 change "decrease." To "decrease or there may be a change in the sinks or cycling."

p.12741 line 18 A little more introduction of this 1-D model result is needed, rather than it just appearing here. What was the vertical gradient of NO across the different inlet heights ? Might this be expected to reduce with windspeed (related to the high wind data exclusion point above) ?

As the 1-D model did not show significant gradients this discussion was deleted.

p.12742 Section 4.5 Figure 9a shows two periods with differing RGM and differing model:measurement HO_x performance, however the LP-DOAS data shown in Figure 2 (a number of points are available each day – not too sparse) seem fairly similar between the two periods (17-19 and 21-22 May) – it would be useful to show these BrO observations on figure 9a.

The measurements of LP DOAS BrO data were added to Figure 9(a).

p. 12742 Line 26-p. 12743 Line 2: changed "Despite evidence that there may be certain levels of BrO present during this period, no BrO measurements from CIMS were available during this time and the BrO measurements from LP DOAS were sparse." to "Up to 5 pptv of BrO were observed by LP DOAS and no CIMS BrO measurements were available during this time. OH predictions from BM_BrO constrained by LP DOAS BrO measurements cannot account for the enhanced OH observed."

Figure 3 – the plot shows HO₂+RO₂, not HO₂

The label and caption in Figure 3 have been changed according to the comment.

Fig 4,5,6,8 please give intercept values, and uncertainties in these and the gradients.

Intercept values are provided in Fig 4, 5, 6, and 8. The uncertainties in the intercept and gradients are very small compared to the values of the slopes and intercept. In fig. 4,5,6,8 the standard errors of the slopes are 10^{-10} to 10^{-8} and the standard errors in the intercepts are 0.1 to 0.2.

Respond to Referee 3:

1) Figure 5 shows the model-measurement correlations for the base model constrained by the observed concentrations of HONO. Comparing this Figure to the model measurement correlations for the base model (Figure 4), it appears that constraining the model to the observed HONO concentrations improves the model measurement agreement for OH for both 2007 and 2008 (Base model slopes for OH of 0.72 and 0.54 for 2007 and 2008, respectively, compared to slopes of 0.92 and 0.72 for the HONO constrained model). However, the discussion in section 4.1.2 states that "constraining HONO in the model does not improve the correlation between predictions and observations Significantly..." It appears that one basis for this conclusion is the fact that constraining the model to the HONO observations "did not improve the ratio of OH to HO₂+ RO₂ relative to the observations." This is not clear from the information presented. This issue should be clarified and addressed in more detail in the revised manuscript, including a presentation of the measured and modeled HO₂ + RO₂:OH ratios.

P 12739 Line 1: After "regressions." Added "The correlation coefficient (R) between predicted and observed HO_x did not improve when the model included HONO source."

Line 4 –Line 10 changed "The predictions of HO_x from the BM HONO were slightly higher than that from the BM. However, inclusion of HONO source in the model did not improve the ratio of OH to HO₂ +RO₂ relative to the observations. As constraining to HONO in the model does not improve the correlation between predictions and observations significantly and the observed HONO may have interference from other compounds, the BM is preferred for comparison to HO_x levels in this environment."

To

“The predictions of both OH and HO₂+RO₂ from the BM HONO were higher than that from the BM as this adds in a HO_x source. However, the ratio of HO₂+RO₂ to OH changed by less than 10% on average. As the HO_x predictions from the BM had more data points, the correlation between predicted and observed HO_x did not improve when HONO was included in the model, and the observed HONO is likely to have interferences (Stutz et al., 2010; Sjostedt et al., 2007), the BM is preferred for comparison to HO_x observations in this work.”

2) Similarly, it is not clear from Figure 6 that inclusion of bromine chemistry significantly improves the model measurement agreement, as the correlation slopes for OH for the base model with CIMS BrO are only slightly better than the base model alone (0.78 and 0.56 versus 0.72 and 0.54 for 2007 and 2008 respectively), while the base model with LPDOAS BrO show slightly worse slopes for OH (0.72 and 0.50). The discussion in section 4.1.3 states that the modeled OH increased 10-12% when including CIMS BrO. Again, the apparent discrepancy between the data shown in the Figure and the discussion needs to be clarified.

Both slopes and intercepts impact the correlation between the observed and modeled HO_x data and the intercepts are also added to the figures.

P 12739 Line 18: after “the CIMS observations” added “When the model included bromine chemistry and was constrained to CIMS BrO, the intercept increased from 1.12×10^5 molec cm⁻³ to 1.65×10^5 molec cm⁻³ and the slope increased from 0.72 to 0.78 in 2007 and the intercept increased from 8.64×10^5 molec cm⁻³ to 9.23×10^5 molec cm⁻³ and the slope increased from 0.54 to 0.56 in 2008 for OH. When the model included bromine chemistry and was constrained to LPDOAS BrO, the intercepts increased from 1.12×10^5 to 3.20×10^5 molec cm⁻³ and the slope remained the same in 2007 and the intercept increased from 8.46×10^5 molec cm⁻³ to 1.15×10^6 molec cm⁻³ and the slope slightly decreased from 0.54 to 0.50 in 2008 for OH. To give a general idea of the difference between predicted OH and HO₂+RO₂ from BM and BM_BrO, the average ratios of OH and HO₂+RO₂ from BM to BM_BrO besides the slopes and intercepts from linear equally weighted bivariate regression are also provided.”

3) One of the main conclusions in the paper is that the reasonable agreement between the measurement and model confirms our understanding of the dominant HO_x sources and sinks, even though the base model appears to significantly underestimate the measured concentrations of OH based on the slopes in Figure 4. The basis for this conclusion is not clear. In section 4.1.1, the authors state that the agreement between the measured and modeled HO₂ + RO₂:OH ratio "indicates that the BM model captures the dominant sources and sinks of HO_x: : :" I would argue that this agreement suggests that the model captures the propagation of radicals rather than the major sources and sinks. The conclusion about the ability of the model to capture the dominant sources and sinks of HO_x may be based on the agreement between the modeled and measured average values shown in Figure 7 (which do agree to within the error of the measurement and the uncertainty in the

model), and perhaps more importantly the significant improvement in the model-measurement agreement when the high RGM periods are excluded (Figure 8). The basis for this conclusion should be clarified in the revised manuscript. The manuscript would also benefit from a brief discussion of the radical budget for the base model, including the rates of radical production and propagation.

We are a little unsure of the reviewers comment. We agree that OH is significantly under predicted which means that we likely don't understand the OH sources and sinks. However, OH is a small component of HO_x which is dominated by HO₂. We do seem to have a reasonable handle on the HO_x budget. For this reason we have added the statement to P 12738 Line 4: "The agreement between the predicted and observed HO₂+RO₂ (which is dominated by HO₂) indicates that we have a good understanding of the major sources and sinks of HO₂ which dominates the HO_x family. However, our understanding of the OH sources and sinks is clearly lacking especially during periods of elevated RGM (see section 4.4)."

4) Minor point – the authors should take care to define the acronyms at the beginning of the manuscript, such as ODE (Ozone Depletion Episode I assume), GEM, RGM, etc.

Revised in the text.