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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Observations of hydroxyl and peroxy radicals and the impact of BrO at Summit, Greenland in 2007 and 2008" *by* J. Liao et al.

Anonymous Referee #1

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This paper describes observations and analysis of measurements of OH and (HO2 + RO2), performed together with related species notably including BrO at Summit, Greenland during (local) spring 2007 and summer 2008. The paper briefly describes the context of the campaign and measurement methods, followed by a presentation of the OH and HO2+RO2 data itself, and a simple model analysis focussing upon changes in the model performance which result from including bromine reactions. In addition to the direct evidence for the role of bromine obtained from the BrO observations, further indications of halogen ativity follow from the enhanced RGM levels periodically observed. Bromine chemistry is found to improve model-measurement agreement for OH, but significant model underestimates remain.

The paper is suitable in scope and topic for presentation in ACP, and in including direct bromine (and RGM) measurements usefully confirms the hypothesis of halogen activity at Summit, and its impact upon HOx, advanced by the authors in previous work. However in a number of places I feel the manuscript could be more precisely worded, and in a couple of places the text seems at odds with the data presented in the figures. These aspects should be addressed prior to full publication in ACP.

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

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

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.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.

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

p.12733 State (very briefly) the Hg monitoring technique, i.e. atomic absorption / 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.12736 Are these HO2+RO2:OH ratios significantly different (e.g. 109 vs 108) – standard deviation would be useful here.

p.12736 HONO levels: Following the simple NOx 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 25 Observed in *the* spring 2007 campaign

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.12738 Exclusion of HOx 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 NOx levels – is any systematic bias introduced.

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.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.12740 The air-snow exchange expression is not clear – is this [H2O2] in the BL or in

the snowpack interstitial air –a format of d[H2O2]/dt = ... would be clearer.

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 HOx 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 HOx levels (which would be worth noting) ?

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 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) ?

p.12742 Section 4.5 Figure 9a shows two periods with differing RGM and differing model:measurement HOx 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.

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

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

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