

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 #3

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A significant dataset of OH, HO₂+RO₂ and BrO is presented from Summit in summer and spring. This combination of measurements is fairly unique, and when combined with the unusual nature of the location, with snow emissions of precursors to HO_x formation, this makes for an interesting study. The associated dataset of supporting measurements also includes snow-derived HONO, and also RGM, which it thought to be produced from bromine-related chemistry. BrO measurements are reported using both CIMS and DOAS.

Measurements of OH and HO₂+BrO are compared with model calculations. The model used contains C1 chemistry and is fairly basic, and the inclusion of bromine chemistry

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(and constraining BrO) improves the agreement between OH, HO₂+RO₂ measured and modelled, but significant differences still remain. Correlations between RGM and BrO also provide further evidence that halogen chemistry has an impact at the site (as has been suggested from previous studies at Summit). There is further evidence that the HONO measurements may be higher than the true values.

There are many correlations reported in the paper between model and measurement (R and slope) for a variety of species for different seasons and conditions in the model. It is difficult to draw definite conclusions from the paper due to the large number of these correlations which do cause some confusion. Sometimes the link between a conclusion and the correlation in the data from which it was drawn (which is from an average set of measurements) is not clear.

The subject matter is certainly within scope of ACP, and following some changes, the paper would be suitable for publication.

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.

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?

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?

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.

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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?

Page 12734, line 20, why can HOBr be assumed to be in 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.

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

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.

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

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

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?

Fig 3. The top panel says HO₂, but HO₂+RO₂ is measured.

In the caption to Figure 3, add that the spikes in NO and the responses in OH and HO₂(+RO?) are due to perturbation from the generator, and not natural behaviour.

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

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