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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Longpath DOAS observations of surface BrO at Summit, Greenland" *by* J. Stutz et al.

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Response to Interactive comment on "Longpath DOAS observations of surface BrO at Summit, Greenland" by Anonymous Referee #2

(Responses are in italics)

The paper is generally well written and reports on a very interesting and surprising dataset which certainly deserves publication in ACP. However, in my opinion, the analysis and discussion in the paper is somewhat incomplete and disappointing, and more work is needed to make this a convincing analysis. This is in part related to the

fact that the model based analysis of the same measurements is presented in several companion papers, leaving little room for interpretation in this manuscript.

The quantitative interpretation of concentrations of atmospheric trace species which are emitted or formed at the surface in a boundary layer of varying stability, such as in the case of BrO over snow, is very challenging without the help of an atmospheric chemistry and transport model. We developed and applied such a model to our data, but decided to present the model and its results in a separate paper by Thomas et al (2011). The interpretation we have provided in this manuscript goes as far as one can go without the use of a model. We have cross-referenced Thomas et al (2011) multiple times in our manuscript, and recommend this manuscript to the reviewer and other readers.

Major Points:

I was surprised not to find any reference to the CIMS measurement of BrO which were also taken during the campaigns. I understand that this is not a comparison paper but the existence of this other data set should be mentioned, and some basic information been given (Are the overall values comparable? Is the variability

comparable? Are the differences between the years comparable? Is the diurnal cycle comparable?). I think this is relevant as the BrO values observed are unexpectedly high and confirmation of the observations by an independent technique adds confidence to the results.

As the reviewer noted we did not intend this manuscript to be an intercomparison paper. A manuscript comparing CIMS and LP-DOAS has already been published (Liao et al. 2011a). Comparison of the data between CIMS and LP-DOAS is also shown in Thomas et al. (2011) and Liao et al (2011b). Maximum levels of BrO are similar be-

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tween the two instruments. There are some differences as both instruments operated near their detection limits. We decided to use the LP-DOAS data for our analysis due to its high specificity towards BrO and the fact that LP-DOAS has been the most widely used method to measure BrO in the atmosphere.

We added the following text to the manuscript to refer to the intercomparison paper and manuscripts that show a comparison of the data: " Measurements of BrO were also performed by Chemical Ionization Mass spectrometry (Liao et al 2011a,b; Thomas et al. 2011). Levels of BrO were similar to those observed by our LP-DOAS system."

The four most striking features of the BrO time series are

– the large difference between the two light paths in 2007

– the large variability of the values over short time periods

– the systematically lower values in 2008

– the difference in diurnal variation between the two years

I think that all these points should be addressed in more detail. Were there instrumental differences between the years other than the improved pointing? Are the results from the shorter path as reliable as those from the longer path? Do the authors think the variability is real, or could this be linked to observational problems?

The reason for the difference between the two light paths in 2007 is not completely clear. Tests during times of good visibility revealed no clear bias above the error of each measurement. Comparisons at times of low visibility, when the shorter light path was exclusively used, could not be performed. It is thus possible, although unlikely, that the lower visibility lead to an instrument bias. There are also reasons why atmospheric BrO levels could be higher during times when the shorter light path was used, i.e. heterogeneous bromine recycling on fog particles and shallow boundary layers that

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enhance bromine levels released from the snow pack. As it is not possible to separate possible instrumental biases from atmospheric phenomena in this case, we do not have a conclusive explanation for the difference in BrO values.

Following the reviewer's suggestion we have expanded the discussion of the difference in BrO mixing ratios on the two different light paths (first paragraph of Section 3).

"In general, BrO mixing ratios measured on the 2 km light path were higher than those measured on the 5 km light path. The reason for the difference between the two light paths in 2007 is unclear. Tests during times of good visibility revealed no clear bias above the error of each measurement. Comparisons at times of low visibility, when the shorter light path was exclusively used, could not be performed. It is thus possible, although unlikely, that the lower visibility lead to an instrument bias. One can also speculate that other reasons could lead to higher atmospheric BrO levels during times of low visibility. The two conditions under which the shorter light path was used were fog and refractive index fluctuations caused by extremely strong surface inversions. In the case of fog events the increased aerosol surface area could lead to a more efficient heterogeneous bromine recycling and thus higher BrO mixing ratios. Similarly, shallow boundary layers could lead to an accumulation of gaseous bromine released from the snow into the lowest meters of the atmosphere and thus to higher BrO levels. Both of these scenarios will be discussed in more detail in Sect. 4. Ultimately we cannot derive a conclusive explanation of the difference in BrO concentrations on the two light path in 2007."

The reviewer is correct that we sometimes saw surprisingly fast changes in BrO levels. One such example is discussed in Section 4.2 where we could clearly attribute the 2 ppt increase in BrO to a change in airmass. During many other occasions we were not able to find a clear explanation for the temporal changes, although airmass changes are obviously a possibility. It should also be noted that there is a certain amount of variability in the data due to the statistical error in the measurements as well as the fact

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that we were often not able to continuously measure due to fog and refractive index fluctuations. Considering this, many of the changes are not as fast as one would think looking just at the figures.

To address this issue in the manuscript we added the following sentences to the first paragraph in section 3:

"The 2007 BrO mixing ratios in Figure 3 sometimes show rapid variations. Part of this variability can be attributed to the statistical errors in the measurements, as shown by the error bars in the figure. Frequent gaps in the data will also lead to discontinuities that appear as fast changes in the mixing ratios. Finally, some of these changes may be attributed to airmass changes or boundary layer venting. An example of a rapid airmass change will be discussed in Sect. 4.2. "

The systematic lower bromine values in 2008 compared to 2007 have also been observed by Dibb et al 2010, who speculated that the lower gas-phase bromine levels are due to lower snow bromide in 2008 compared to 2007. Whether this is a seasonal effect or the difference between the two years is not clear. This topic was discussed in detail in the second paragraph of Section 4.1 in our original manuscript.

The apparent difference in the diurnal profile of BrO is discussed below

The analysis of the diurnal cycle of BrO makes sense as boundary layer depth and photochemistry should both contribute to BrO levels. However, the results are not really conclusive as a) there was no such diurnal cycle in 2007 (assuming that all points shown in Fig. 6 are statistically meaningful), b) the statistical analysis is based on hourly values averaged over several days, and for the same time of the day, photolysis and boundary layer depth can vary, and c) there is a lot of short-term variability in the data which must have other reasons.

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A comparison of figure 6a and 6b shows that the diurnal variation for the times available for both years, i.e. between 10:00 and 21:00 are not that different. The reason why the two curves appear to be different is the missing morning and evening values in 2007. As explained in the manuscript, the reason for the expanded time coverage in 2008 was the use of a laser aiming system that allowed measurements during morning and evening when slow air refractive index variation made it impossible to measure in 2007. Due to the missing morning and evening data we cannot perform the same analysis for the 2007 data as shown in Figure 7 for 2008.

We have revised the second paragraph of Section 4.1 explaining the diurnal behavior in 2007 and 2008 to clarify this point."

"It is difficult to discern a diurnal profile in 2007 due to the lack of morning, evening, and nighttime data, when the operation of the LP-DOAS was not possible. It appears that there is a small decrease in mixing ratios between 12:00 and 18:00 ($\sim$1.5 ppt) compared to the late morning and early evening data ($\sim$1.8ppt). The 2008 data shows a similar behavior in this time period, but at lower absolute BrO levels, as discussed above. In 2008 the use of a laser aiming system allowed data acquisition during a much larger part of the day, thus resulting in better 24h data coverage. The expanded diurnal data in 2008 reveals a much clearer temporal profile of BrO, with a peak in the morning, followed by a general decrease towards 20:00 LT, and another peak around midnight."

Part of the short term variability can be associated with the errors of the measurements, which is one of the reasons to use hourly averages. The other reasons for the variability are variations in atmospheric and snow conditions. The hourly average over well defined meteorological conditions, i.e. air masses in touch with the Greenland ice sheet for 3 or more days, serve to reduce these variations. In addition, averaging allows to extract the more systematic behavior due to boundary layer height and solar radiation.

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We added the following sentence to the first paragraph of Section 4.1. to clarify this point: "Hourly averaging serves to reduce the statistical error of the measurements as well as atmospheric day-to-day variability in the data."

The big question in general is: Where does the bromine come from? The authors try to address this point by looking at time periods with different airmass origin, but do not directly compare the results from these different situations. I would have expected an analysis of how the observed BrO depends on parameters such as wind direction, temperature, wind speed, actinic flux or time of last contact to the open ocean using all the data and not just a subset of hourly averaged values. I'm sure that such an analysis was performed on the measurements, and strongly recommend adding it to the paper.

We agree with the reviewer that the question of the source of bromine is very important. Our study identifies two possible sources. We show that gaseous bromine is released from the snow through in-snow photochemistry (see also Thomas et al 2011 for a more quantitative analysis of this mechanism). While we study this source through a correlation analysis during well-defined meteorological condition, i.e. long residence time over the Greenland ice sheet, it will be active during other times as well. One pathway to produce gas-phase bromine is thus local, and proceeds through snow bromide. The separation of this local source from direct transport of gaseous bromine during other periods, for example through a correlation analysis as suggested by the reviewer, was not possible. The only clear example for direct transport we found in our data-set is one event of elevated BrO which correlates well with other marine tracers. It should also be noted that our results indicate that the transport of bromine to Summit most likely proceeds through dry or wet deposition of bromide. Following a suggestion from Reviewer 1, we have expanded the discussion of transport events from marine areas in Section 5 (see response to reviewer 1).

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I'm not familiar with the "footprint sensitivities" shown in Figs. 4 and 8, and with the little information given in the text, I do not understand what the colours shown represent. Please explain in more detail what is shown and why in some cases there is high values all over the ocean and in others not.

We added the following sentences to explain footprint emission sensitivities more clearly:

"Footprint emission sensitivities provide a source-receptor relationship for air arriving at Summit. They are a measure of the residence time of the air in the retroplume in the lowest 100m of a model grid cell (in units of ns kg -1) (Stohl et al. 2002, Hirdman et al. 2010). Footprint emission sensitivities are thus ideally suited to illustrate contact of airmasses with the surface and potential surface sources during the time before arrival at Summit. The centroid locations are calculated from a cluster analysis of the 60,000 released particles. The location represents the geographic centroid of all the particles."

I'm not convinced that the steady state considerations presented in the conclusions add relevant information. They are not directly linked to the observations reported, are based on very simplified assumptions and much more detailed chemical analysis is presented in other papers of the special issue.

We agree with the reviewer that our pseudo steady state calculation in Section 5 is highly simplified. However, the conclusions are not much different than those from more detailed model calculations. We also believe that it is essential to provide a discussion of the possible impact of our observations with regard to NO_x and HO_x chemistry. This is especially true for our study, which was in large part motivated by the hypothesis that elevated halogen levels could explain previously reported

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disagreement between observed and modeled OH concentrations during previous field experiment at Summit (Sjostedt et al, 2007). The discussion also illustrates that the low levels of BrO can, at times, have an impact for the atmospheric chemistry at Summit. References to the more detailed modeling analysis efforts, for the reader interested in a more accurate analysis, are included in this section.

Minor Points:

P 6711, l 1: The Dibb et al. (2010) paper can hardly have been the motivation for the measurement campaign – it actually reports on results from this campaign.

This is true. We have removed this citation from this part of the text.

P 6715, l5: accompanied with => accompanied by

done

P 6715, l7: varied approximately a factor => varied approximately by a factor

done

P6723, l15: surface => surfaces

done

Fig. 4 and 8: Circles are not visible on standard printout. As far as I can see, they are

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not coloured but grey shaded. Please try to improve on the clarity of this display

We corrected the text and the captions of the figures to reflect the fact that the circles are gray-shaded. We have increase the circle size and letter font in Figures 4 and 8. We will work with the ACP production office to make sure the visibility of the circles is clear in the final version of the manuscript. Please note that, while the data did not change, the color scheme changed slightly in the revised figures.

Fig. 5: remove black line connecting measurement points

done

Fig. 7: Add the year used (2008) to the caption

done

Fig. 8: What is the difference between panels A and B?

Both Panels show the same data. Panel A is included to show the residence of the airmass over the North Atlantic. Panel B is included to show that the air came directly from the Greenland East coast to Summit within one day. We added the following sentence to the caption to clarify this "Both panels show the same data with different spatial resolution."

Fig. 9: Remove black line connecting measurements.

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done

Fig. 9: What are the black line and the green points in the third panel of this figure?

The black line was in the panel by accident. It has been removed. All data points have now the same color.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 6707, 2011.