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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Meteorological controls on the vertical distribution of bromine monoxide in the lower troposphere" *by* P. K. Peterson et al.

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We thank Anonymous Referee #1 for the constructive comments on this manuscript. In our response, we first address the overarching concerns of the reviewer, followed by addressing individual comments. We denote points that that the reviewer raises using bold text followed by our reply. Please also see our replies to Anonymous Referee #2.

Main concerns. 1) MAX-DOAS analysis shown in this study is a two-step approach, where an "ad-hoc" optimal estimation (EO) is used to first retrieve the aerosol extinction coefficient profile and second - BrO profile. The 2nd step depends on the 1st step. Since the authors rightfully criticize applicability of the OE to the 2nd step where DOF is approximately 2 and full profile cannot be

reliably retrieved, the same argument applies to the 1st step (same MAX-DOAS data are used). The authors have to demonstrate that the OE in the first step provide reliable enough profiles for the 2nd step and that the error from the aerosol extinction profile retrieval does not introduce a significant error in LT-VCD BrO analysis. In addition, the retrieved aerosol extinction profile is MAX-DOAS averaging kernel smoothed profile with low sensitivity above 1 km. The forward RT modeling in the second step requires the "true" profile. It will be interesting to see what effect this resolution degradation has on the LT-VCD BrO analysis.

Rather than criticizing the applicability of optimal estimation (OE) in this case, we merely seek to clarify the limitations of profiles retrieved in this manner, as they lend themselves to overinterpretation. The use of a retrieved aerosol particle extinction profile, rather than the true profile, will introduce errors in the resulting BrO profile and these errors should be quantified. One can estimate the errors in BrO retrieval due to uncertainties in the aerosol particle extinction profile by examining the sensitivity of the BrO retrieval to perturbations in the aerosol particle extinction profile. We retrieved BrO profiles from the same BrO dSCD data over an ensemble of varying aerosol particle extinction profiles, and examined the resulting variability in the quantities discussed in this manuscript. We found that the LT-VCD was not heavily influenced by changes in the aerosol profile, with an estimated error of 4.6% (1 Sigma), which is lower than error introduced by uncertainties in the BrO dSCD measurements. The ratio's retrieved $\mathrm{VCD}_{200\mathrm{m}}/\mathrm{LT}-\mathrm{VCD}$ have an estimated error of 4.9% (1 Sigma). Thus, it is reasonable to conclude that our conclusions about the vertical structure of halogen events at Barrow presented in this manuscript are not substantially influenced by errors in aerosol retrieval. We have added a summary of this analysis to the revised manuscript at the end of Section 2.4.

2) Since BrO activation is linked to heterogeneous reactions any dependence on other physical parameters (e.g. temperature) should be done for the same aerosol conditions. Under strong wind conditions it is also important to know the source of air masses brought into the MAX-DOAS instrument field of view. Are there any independent aerosol measurements at the NOAA and/or ARM Barrow facilities that can give information about the dependence of wind speed and aerosols? In general, Arctic climatology is very complicated and decoupling of different meteorological parameters is not straightforward. Please also include information whether there were passing polar lows and/or cyclones.

We agree that decoupling of differing parameters is not straightforward. We examined variations of BrO with temperature and wind speed under similar aerosol loadings and did not find anything that would change or add to the presented analysis. We include Fig. 1 of this response that shows some further analysis. That figure shows the response of BrO to various environmental parameters at various extinction levels is shown in two scatter plots. On the left, the response of BrO to temperature changes in various bins of aerosol particle extinction is shown. These data are split into three bins, low extinction shown in blue x's, moderate extinction, shown in red circles, and high extinction, shown in green diamonds. The right plot is identically structured, showing the relationship between BrO and wind speed. We also examined air mass history, and found that for this field campaign, measured air masses had similar origins and contact with sea ice areas, making it difficult to discuss the influence of air mass history on observed BrO. Please see our response to Reviewer 2, as well as Section 3.3 of the revised manuscript for an expanded discussion of our air mass history analysis. There were some stormy events over the measurement period, but measurements during these periods constitute a small part of the data set. We examined the relationship between BrO and air pressure, but did not find anything that would substantially add to the manuscript.

p. 23954 , l 24. The sensitivity to upper troposphere and lower stratosphere is reduced but still present especially at SZA > 75deg. How do the authors account for it in the analysis at SZA > 75deg?

In our spectral fitting, a near temporally coincident zenith spectrum is used as the reference, which (as the referee notes) removes most of the influence from higher altitudes. In principle, one could use a fixed reference spectrum (e.g. at local solar noon on a clear day) for the fitting, but that choice makes the analysis more dependent on long-term drifts, so we instead take the "local zenith" reference choice. Due to this choice, there is a small influence at SZA $>$ 75 degrees, but for consistency, we do not treat data collected at SZA $>$ 75 degrees differently from other data. To reduce influence from the spectra even closer to twilight, we do not analyze data collected at SZA $>$ 85 degrees. Overall, data collected between 75 and 85 degrees SZA represents only 30% of our data, so the inclusion or exclusion of these data would not change the findings of the manuscript.

p. 23954 Methods, MAX-DOAS measurements: I suggest that all the data presented in this work (IL1, BARC, SIMS, sondes) are described in this section, including description of the measurement locations and azimuthal direction of MAX-DOAS measurements. It will also be helpful to get an idea about the meteorological conditions during the campaign and description of the air masses that are traversed by the measured photons. How do you treat cloudy data?

We have modified the methods section to include all requested information, and added information on the azimuth of the DOAS, as well as modifying Fig. 5 to better show the environmental conditions around the measurement sites, as well as the azimuths of each DOAS instrument. Please see Section 2.5, last paragraph of the revised manuscript. We do not screen for cloudy data other than using the degrees of freedom

based filtering described in section 2.4. Due to the relationship between AOD and aloft DOF shown in the left panel of Fig. 3, it is likely any data with low clouds are excluded as a result of the DOF filtering.

p. 23955 l. 4 How well is the optical bench temperature maintained? Ocean Optics spectrometers tend to have strong temperature dependence of the slit function (resolution).
The standard deviation of the spectrometer temperature is 0.6 degrees. We have included this information in the revised manuscript.

p. 23955, l. 15. Add "transfer" after instrumental

We have made this change.

p. 23955, l. 20 It will be more meaningful to present residual OD RMS as a function of viewing elevation angle. Since DOAS fitting errors are linearly related to the residual OD RMS I suggest including BrO/O4 DOAS fitting errors as a function of elevation angle too.

Please see Table 1 of this response for this information. This table has been included in the supplemental material.

p. 23956, l. 13. What is the a priori covariance matrix? What are the assumptions about the aerosol optical properties? Are you applying any correction factors to the measured dSCD(O4)? Could you estimate BrO 200m-VCD and LT-VCD errors due to aerosol profile error?

The aerosol assumptions are detailed in Frieß et al. (2011).

> "Since the radiative transfer near the surface is frequently affected by blowing snow, the aerosol optical properties are set to values typical for clean ice crystals, with a single scattering albedo of 0.999982 and a Henyey Greenstein phase function with an asymmetry parameter of g = 0.89 [Dominé et al., 2008, and references therein]. The aerosol extinction profile is retrieved in the lowermost 2 km of the atmosphere on a 100 m vertical grid... In each iteration, the a priori error, i.e., the square root of the diagonal elements of the a priori covariance matrix, is set to three times the a priori extinction, while the non-diagonal elements of Sa are set to zero."

We have added a reference to this information in the revised manuscript, page 8, lines 1-3. We have also added detail on the a priori covariance matrix on page 8, lines 8-10 of the revised manuscript. Please see our response to the reviewer's first point for estimations of the error associated with these quantities.

p. 23957, l. 25 How do you define "the layer in which the observer resides" from a MAX-DOAS perspective?
In the case of this study we mean the lowest portion of the boundary layer when the measured photons traverse a path tangent to the ground. We have clarified this point in the text. Please see page 9, lines 18-20 of the revised manuscript.

p. 23959, l. 19, Payne et al (2009) does not "describe how to calculate the BrO averaging kernel for the coarsened grid" the paper applies the method to methane not BrO. Please check your reference or rephrase the sentence. The cutoff 0.7 was used for satellite nadir measurements of methane. While it is likely it is applicable to MAX- DOAS ground-based measurements I would suggest doing some sensitivity studies to confirm this. Payne, V. H., Clough,

S. A., Shephard, M. W., Nassar, R., and Logan, J. A.: Information centered representation of retrievals with limited degrees of freedom for signal: application to methane from the tropospheric emission spectrometer, J. Geophys. Res., 114, D10307, doi:10.1029/2008JD010155, 2009. 23953, 23959

We agree with the reviewer that this wording should be changed. Please see page 11, lines 13-15 of the revised manuscript. Payne et al detail a general method for reducing profiles retrieved via optimal estimation. They then use methane retrievals as an example for the application of this general technique. The application of this technique to BrO is not mentioned in the Payne et al work. We agree that the 0.7 is somewhat arbitrary, we explored multiple values, and found that the conclusions did not change as long as the cutoff was above 0.4, thus we chose to remain consistent with previous work.

p. 23962, l.15 Please replace "observes" for "retrieves". Technically O3 absorption is present in MAX-DOAS data.

We have made this change. We also do fit for O_3, we just do not interpret the retrieved dSCD values because of the complexity of the radiative transfer of ozone and the temperature dependence of the cross section.

p. 23963, l. 25 What do you mean by "large changes in the environment in MAX-DOAS field of view"? Are there any significant differences in elevation, snow cover, landscape, and aerosol types? If there is a significant difference along the line of sight how did you treat it in RT modeling? Please show MAX-DOAS azimuthal direction on Figure 5.

As shown in the revised Fig. 5, the instrument at the BARC building overlooks a large lead which has a convective plume along the line of sight. Since both radiative transfer models are 1D, only changes in the vertical direction are modeled. Thus any reduction in pathlength due to a lead cloud would be modeled as a path-averaged increase in near surface extinction rather than an obstruction in the view direction. This is a potential source of error in the aerosol profile, and resulting BrO profile. We discuss this in Section 3.4 of the revised manuscript. Please see page 17, lines 6-8.

p. 23964, l. 4 Figure 6 gives an impression that a significant number of time coincident observations exist. After closer inspection CIMS data are mainly shown for nighttime when MAX-DOAS instrument did not measure. Why there are so many "holes" in CIMS data?

This CIMS instrument was also used to conduct snow chamber experiments during BROMEX, creating gaps in the time series of ambient BrO. We have pointed this out in the revised manuscript, page 16, lines 18-20.

p. 23964, l. 6 Could you please elaborate why do you claim that the differences in observations at IL1 and BARC explain differences between BARC and CIMS locations. What is the azimuth angle of BARC and IL1 MAX-DOAS observations? Where they pointing towards each other? What were the meteorological conditions at the 3 sites?

Meteorological conditions were similar at the three sites throughout the intercomparison. The azimuth of the DOAS at BARC was 27 degrees east of north, while the azimuth of IL1 was 2 degrees east of north. These azimuths are similar enough that we are confident that any differences do not arise from viewing geometry

differences. However, as show in the revised Fig. 5 of the manuscript, the instrument at BARC overlooks a recurring lead, while the instrument at IL1 does not. Please see our response to Reviewer 2, point number 2, as well as page 17, lines 6-8 of the revised manuscript for additional discussion of this feature.

p. 23965, l. 10 You compare daily averaged MAX-DOAS data with the 15:30 AKSD sonde data. Were the meteorological conditions constant during any particular day? Would the conclusion change if comparison done using time coincident or +/- 1 hr data?

While the meteorological conditions are not constant throughout the day, we feel the comparison of daily averaged LT-VCDs with daily soundings still provides insight into the role of atmospheric stability. We found that the use of temporally coincident data or data off an hour either way did not alter the conclusions.

p. 23965, l. 19. Could you please explain what you mean by "The short diurnal time scales of the temperature gradient.."

We simply mean to point out that the temperature gradient likely varies with a higher frequency than can be observed with twice daily sounding data. We have clarified this point. Please see Page 18. lines 7-10, of the revised manuscript for the modified text.

p. 23965, Since halogen activation is related to heterogeneous reactions it might give more insight if any dependence on temperature is derived from the data bins collected under the same aerosol loading conditions. Since LT-VCD accuracy has a stronger dependence on the aerosol loading than 200m VCD I suggest also including data where only 200m VCD is shown.

While we agree that this is a useful analysis, after performing said analysis, shown in Fig. 1 of this response, we did not find differing behaviour under various aerosol conditions.

p. 23967, l. 29. What is the typical PBL height during the measurement period at this location?

During OASIS, which was conducted at Barrow in 2009 during a similar time frame, PBL heights ranged from less than 100m to over 500m (Boylan et al., 2014).

I am not sure what the authors want to convey by "Therefore, the diurnal pattern of the vertical profile of BrO appears to reflect boundary layer dynamics. The observation of Pöhler et al. (2010) of decreasing surface BrO mixing ratio at higher temperatures could therefore reflect increased vertical mixing of surface sourced BrO that dilutes the surface concentration upon warming rather than being indicative of decreased halogen activation chemistry at higher temperatures." If the source of BrO is located at the ground and shallow PBL is present (< 1000m, probably 400-600 m) convective mixing to the upper layers should not result in in- crease in measured LT-VCD (0 – 2000m). This implies that there is another source of BrO at altitudes > 200 m that is coincident with the potential PBL diurnal evolution. Do you have an independent PBL height estimation to confirm your statement about PBL diurnal evolution? It might be helpful to separate data into "colder" and "warmer" periods to see if the trend persists.

We discuss these issues in detail in our response to Reviewer 2. To address concerns raised by both reviewers, we have expanded our discussion of these observations.

Please see our response to points 4-6 raised by the second reviewer, as well as the last paragraph of section 4.1, which we have substantially revised in response to comments from both reviewers. Regarding the diurnal evolution of the PBL, this is commonly observed in Barrow, although it is less pronounced during periods of heavy inversion (Boylan et al., 2014). We have pointed this out in the revised manuscript.

Role of wind speed (4.2) and Relationship between activation and aerosol particles (4.3) might not be reliably established from LT-VCD or VCD200m/LT-VCD since LT- VCD retrieval is potentially effected by the aerosol retrieval in the 1st step and due to decreased sensitivity of MAX-DOAS at higher AOT.

The reviewer points out the limitations of our data set, which we discuss in section 4.3, page 22, lines 20-24. While the limitations of our data collection at higher AOT complicate interpretation of the role of aerosols and wind speed, Fig. 13 also shows the relationship between BrO and aerosol particle extinction in the near surface layer, where we have the greatest sensitivity. The left panel clearly shows aerosol particle extinction does not depend on wind speed, while there is an increase in BrO with increased aerosol particle extinction, which we pointed out in section 4.3. The conclusions in this paper about the role of blowing snow events and wind speed in general are clearly supported by the near-surface BrO data, in addition to the LT-VCD data. Thus, this data set reliably establishes the role of wind speed and aerosol particles during this field study. We have restructured the discussion of Fig. 13 in Section 4.3 to convey these points more clearly and address the concerns raised by the reviewer.

Figure 5. Please indicate MAX-DOAS azimuthal orientation. In addition, information about snow/ice cover will be valuable

We have modified Fig. 5 to include the requested information.

Figure 7. Please show error bars for both MAX-DOAS and CIMS data

We have modified Fig. 7 to include the requested information.

References

Boylan, P., Helmig, D., Staebler, R., Turnipseed, A., Fairall, C., and Neff, W.: Boundary layer dynamics during the Ocean-Atmosphere-Sea-Ice-Snow (OASIS) 2009 experiment at Barrow, AK, Journal of Geophysical Research: Atmospheres, 119, 2261–2278, 10.1002/2013JD020299, http://doi.wiley.com/10.1002/2013JD020299, 2014.

Frieß U., Sihler, H., Sander, R., Pöhler, D., Yilmaz, S., and Platt, U.: The vertical distribution of BrO and aerosols in the Arctic: Measurements by active and passive differential optical absorption spectroscopy, Journal of Geophysical Research, 116, 10.1029/2011JD015938, http://www.agu.org/pubs/crossref/2011/2011JD015938.shtml, 2011.

Table 1. Errors for MAX-DOAS fitting over all elevation angles.

Elevation Angle	Mean RMS	Mean BrO dSCD Error	Mean O_4 dSCD Error
1 Degree	4.1×10^{-4}	2.0×10^{13} molecules cm^{-2}	5.4×10^{41} molecules^2 cm^{-5}
2 Degree	4.0×10^{-4}	1.9×10^{13} molecules cm^{-2}	5.3×10^{41} molecules^2 cm^{-5}
5 Degree	3.9×10^{-4}	1.9×10^{13} molecules cm^{-2}	5.2×10^{41} molecules^2 cm^{-5}
10 Degree	3.8×10^{-4}	1.8×10^{13} molecules cm^{-2}	5.0×10^{41} molecules^2 cm^{-5}
20 Degree	3.6×10^{-4}	1.7×10^{13} molecules cm^{-2}	4.7×10^{41} molecules^2 cm^{-5}

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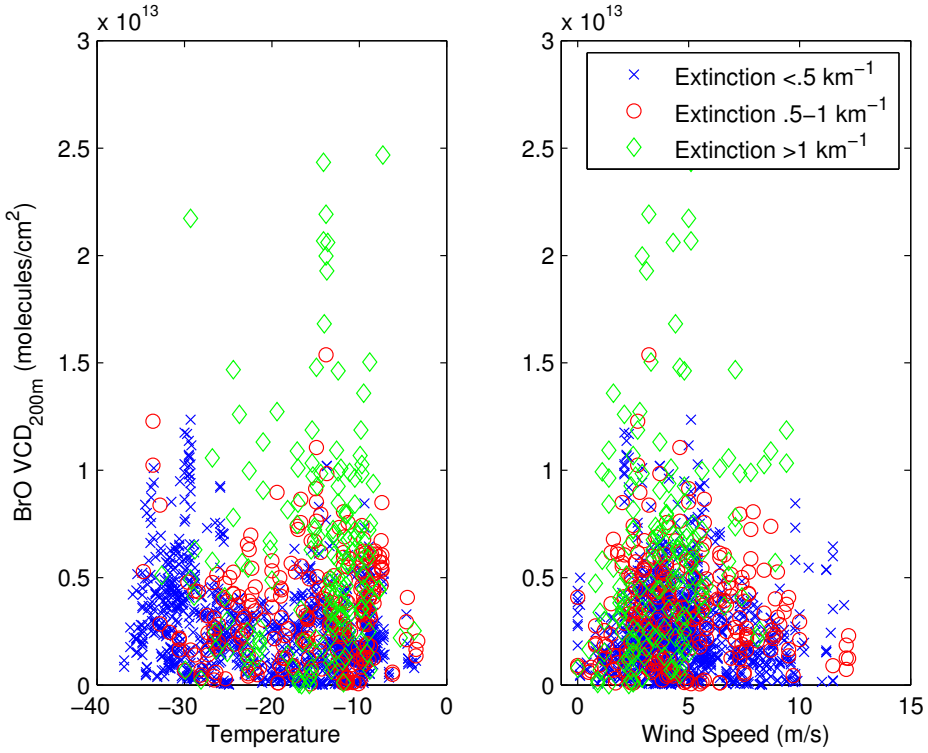

Fig. 1. Response of BrO to environmental parameters