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Interactive comment on "Reactive bromine in the low troposphere of Antarctica. Estimations at two research sites" *by* Cristina Prados-Roman et al.

Anonymous Referee #1

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The paper by Prados-Roman et al. presents observations of reactive bromine in the lower troposphere at two Antarctic research sites from where no data was available until now. This adds to only a handful of Antartic sites where tropospheric bromine chemistry has been investigated so far. Based on MAX-DOAS measurements, they retrieve vertical profiles of aerosol extinction and the BrO radical with an optimal estimation algorithm and complement the results with meteorological observations and surface ozone measurements. Lastly, the amount of reactive bromine at both sites is estimated.

1 General comments

While the observations presented in the paper surely have the potential to add interesting and important insights to our understanding of tropospheric bromine chemistry in polar regions, in particular with the observations of a high activity at Marambio, the site on the Antartic peninsula, I recommend substantial additions to the documentation of the profile retrieval analysis followed by a critical review of its interpretation and the conclusions of the paper before publication.

1.1 Documentation of the profile retrieval process and interpretation of the resulting data

Profile retrieval based on optimal estimation (e.g. Rodgers 2000) as it is used in this publication, is a method to tackle ill-posed inversion problems (in this case the conversion of differential slant columns from MAX-DOAS measurements to vertical profiles of aerosol extinction and trace gases). The problem is ill-posed because the observations alone do not contain enough information to fully determine the state of the atmosphere. Therefore, a-priori information (based on independent knowledge e.g. a climatology) is required for the inversion process. The result of such an inversion is an optimally estimated new state of the atmosphere based on the information contained in the measurements and the a-priori. A meaningful change/update of the a-priori state is only possible, where the instrument is sensitive enough - for the application in this paper both spatially (vertically) and in terms of measurement precision.

Regarding the documentation of the inversion process presented in this paper, the following information should to be added and discussed:

To allow a transparent assessment of the presented profile inversion and to ensure reproducibility and comparability with similar observational data, quantitative information about the quality of the dSCD data should be provided (e.g. a statistic of the DOAS fit error that was used in the inversion as mentioned on page 5 line 23).

To allow an assessment of the aforementioned contribution of the measured data to the retrieved profiles (vs a-priori information) and to judge the vertical sensitivity of the measurements, representative averaging kernels should be presented and absolutely have to be discussed. One of the conclusions of the paper (absence of BrO above 2km) is based on the claim that profiles 'in the first 6km were measured' (page 8 line 4). The vertical sensitivity of inverted MAX-DOAS measurements implied with this is much higher than in publications e.g. by Roscoe et al. (2014), Peterson et al. (2015) or Franco et al. (2015) where comparable sequences of elevation angles and optimal estimation methods were used. The higher vertical sensitivity claimed in this study should be well substantiated or interpretation and conclusions changed. This potentially requires changes to the data presentation as well.

E.g. in the plots of vertical profiles of the entire data set (figure 8) and selected days (figure 9), the presented profiles should be limited to a vertical extent that is based on this analysis and discussion of averaging kernels and the vertical sensitivity. The use of colour map/contour plots should be limited to qualitative discussions (if used at all) as they suggest a higher information content (in terms of vertical resolution - especially when a smoothing between the retrieved layers is used) than can be expected from inverted MAX-DOAS dSCDs and hence could be misleading for readers not familiar with the details of profile retrievals. For quantitative analysis or discussions of the question of elevated layers and export to the free troposphere, profiles based on the information content of the retrieval should be generated. Integrating all layers in the lowermost 2km, as was already done in the analysis in this publication is one, albeit quite conservative solution here. Other publications have produced profiles with vertical layers based on the degrees of freedom (e.g. Roscoe et al. 2014) consisting of two to three layers.

For the comparison with ground-based measurements such as the ozone time series presented here, as well as the estimation of BrOx, again the averaging kernels of the

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Discussion paper

lowermost layers should be considered and all layers with a non-negligible influence on the surface layer results (or at least all layers covered by the width of the averaging kernel corresponding to the lowermost layer) should be integrated rather than just selecting the lowermost layer.

See also suggestions in the Specific Comments section.

1.2 Processing of ancillary data for the interpretation of BrO observations

The ancillary data provided in this study, surface ozone and meteorological observations, are presented in a quite general way and do not provide very specific information that could help the interpretation of the BrO observations. While a description of the general metrological conditions of the two sites and the differences between them (as in table 3) are important, the data provided somewhat lacks a real connection to the observed periods of elevated BrO/ODEs. It would be desirable to have meteorological times series filtered to reflect the periods of profile data presented. For example, it would add important context and improve the quality of this study, if wind directions could be filtered for the periods with elevated BrO as this could provide first insights about the origin of the observed air masses. A correlation of surface ozone and BrO mixing ratios in the lowermost layers of the retrieved profiles could help determine, whether an air mass already depleted in ozone/enriched in BrO was observed or the chemistry happened locally.

2 Specific comments

page 1 line30: What is a heterogeneous increase? (Exponential) increase by heterogeneous reactions/chemistry?

p.3 l.11: Hüneke et al. focuses on upper troposphere lower stratosphere, better example of airborne measurements e.g. Peterson et al. (2017) already cited on p.4 l.13

p.4 l.12: Reference missing Bobrowsky(?)/Bobrowski et. al. 2003

p.5 l.14f: What does the goal of long term observations entail for parameter selection in detail?

p.5 l.23: dSCD errors: Please provide statistics about these errors (mean and std). How many sequences of elevation angles were used for one profile? What is hence the temporal resolution?

p.5 l.23f: a-priori errors: Please elaborate briefly on the idea behind this approach and what β is. This approach means that the statistics of the inversion is no longer Bayesian (in contrast to Rogers 2000). This should be underlined. Was this used for the a-priori of both AECs and BrO and why? Clémer et al. (2010) would be a better citation for the details of this approach.

p.5 l.25: Why is the correlation length different for aerosols and trace gases?

p.5 l.26: A brief explanation what these errors are would improve clarity here. If the combined error is used as 'inversion error' later on (p.8 l.41f/9 l.1), this should be defined here

p.5 l.30: Albedo of 0.8: This value is too low for the UV spectral range. A value of about 0.98 would be more appropriate between 300-400 nm (see Grenfell et al. 1994)

p.5 l.31: AOD limit: How does this limit work exactly? Are retrievals with AOD larger than 5 filtered out afterwards or is there an internal limit? What does that mean for meteorological conditions namely cloud cover? What cloud cover conditions are filtered out by this?

p.5 l.32: What are typical DOFs of the data set?

p.5 l.39: What is meant by 'lower differences'? By definition, the a-priori should be independent information (e.g. from a climatology). This sounds like the O4 dSCDs were used to optimise the a-priori scale heights prior to using them as information independent of the measurements. What could be an explanation for the difference and the very high SH of 2km?

p.6 l.36: As mentioned in section 2.2.1...: This is not discussed in 2.2.1 at all (but should be - based on averaging kernels)

p.7 l.12f: Please make clear which station is referred to. (There is no Polar night at Marambio!) What is meant by 'BrO levels were undetectable just before...and immediately after... '? The data set provided here reports no MAX-DOAS observations within one month from both of these points in time. Does that mean no data or no BrO observations? (compare Fig. 3 and 4)

p.7 l.13: What is meant by 'the magnitude and variability of the BrO maximums direct the difference'? What is the maximum referred to? A daily maximum?

p.8 l.4: the VMRs were not 'measured' rather estimated.. The claim of sensitivity up to 6km altitude should be substantiated (see General comments).

p.8 l.5: Absence of elevated layers: If this actually can be inferred should be reviewed after assessment of the vertical sensitivity (see General comments)

p.8 l.23ff: Discussion of BrO vmr vertical profiles. These profiles should be generated based on information content/the analysis of the averaging kernels (see General comments). The presentation chosen here -without error bars and with a smoothed profile rather than visualising the single layers of the retrieval is misleading for readers not familiar with the details of MAX-DOAS profile inversions. In such a figure, the (typical) a-priori and its errors should be presented as well.

p.8 l.41: Whether or not the detection of BrO above 2km can be discussed with the presented data set strongly depends on vertical sensitivity.

p.8 l.41f/p.9 l.1: The inversion error was not clearly defined (see comment p.5 l.25) p.9 l.3.: BrO in the free troposphere: The absence of BrO and hence an upper limit for BrO in the free troposphere should only be concluded for altitudes where the MAX-DOAS observations are sensitive (based on averaging kernels, see general comments). Based on the data presented, in my opinion, the absence of BrO (above the stated detection limit) in the free troposphere can only be concluded, if one assumes an upper limit of the boundary layer of 1500m or higher because the retrieval quite consistently seems to yield mixing ratios of BrO of at least 1.5 pmol/mol above 1000m altitude (Figure 8 or Belgrano example from 29th October in figure 9). I am not convinced that an altitude of 2000m for the top of the boundary layer is a very regular event in polar regions. Indeed, the two cited publications show e.g. a maximum depth of the convective boundary layer of about 300m for Halley station (King et al. 2006) and give altitudes for the humidity inversion at Marambio of 700m-1300m throughout the year with values of 1000m in spring (Nygard et al 2013). The data as presented here, shows considerable mixing ratios above the detection limit between 700 and 1300m. If the vertical sensitivity at these altitudes is sufficient, discussions about the export of BrO to the free troposphere or the absence thereof should be based on information about the typical depth of the boundary layer at the respective times of the year at the two locations (e.g. the radiosonde data at Belgrano used in the retrieval or -if available- the radiosondes at Marambio used in Nygard et al. 2013) rather than on the stated (quite wide) range of possible altitudes for the top of the boundary layer of 100m to 2km.

p.9 l.24: Estimation of BrOx: Please make the assumptions going into this clearer. I do not understand at all how the observational data feeds into this estimation. Is this an estimation at noon? Was the daily average of BrO and O3 used or the maximum? The rate of BrO photolysis assumed here should be stated. This rate strongly depends on the actinic flux which in turn depends on visibility conditions/cloud cover. How was this treated exactly? What influence does the filtering of total AODs above 5 mean for this? HO2 has a very pronounced daily cycle as well. What justifies the selected, fixed mixing ratio?

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p.9 l.31: What exactly is shown in this figure? Daily averages? maximum values?

p.9 l.40: What is meant by 'troposphere reactivity'? oxidation capacity?

p.10 l.13: This seems a bit circular to me. The O3 measurements were used to calculate BrOx which then is used to estimate the O3 loss rate? Please elaborate your reasoning behind this.

p.11 l.4: I would add 'at two (new) sites' after 'inorganic bromine'. The sentence as it is sounds a bit as if the results apply to the entire Antarctic troposphere while the observations are already quite different for the to sites (as mentioned by the authors later on)

Table1: measurement period column: Please only use months and days here. The use of the term 'season' in an Antartic context is misleading as it could also mean three (summer) seasons. The indicated periods from this study also should rather be 4.5 months than '3 seasons' since the periods from the other publications also only state periods of reported observations and not the entire time when the instruments were deployed.

Table3: days with snowfall: Is this only precipitation (excluding blowing snow)? Information about days with blowing snow would be interesting as well - if available.

Figures3+4: Please provide errors and detection limits in these plots

Figure5: This data is not very helpful. The averaging window could be increased to show wind regimes in different seasons. Alternatively, a histogram of wind speeds would provide more information.

Figure6: Additionally, data filtered for the days presented in the profile data would be desirable

Figure7: It would be nice to have the reported periods of MAX-DOAS observations marked in these plots.

Figure8: These plots are quite small. A blow up or separation of the two periods would benefit the information conveyed by them. The vertical axis should be adapted to the updated vertical sensitivity. Plotting vmr boxes with the size of the retrieval grid (pixels) or aggregated profiles based on averaging kernels rather than using the linear(?) smoothing in the colour map plots would make the nature of the retrieval process and the resulting data clearer. It would also be good to clearly mark periods where data is missing or was filtered out (e.g. based on the AOD limit). For example, it is not clear to me if the periods in the BrO profiles from Marambio in December are missing data or just no BrO at all for half a month.

Figure9: See remarks to Figure 8 regarding smoothing and axis. For the example day from Marambio on September 25th, the data selection should be reviewed. On that day, the SZA limit stated on page 4 of 75 degrees is reached already at 19:25 while the plot shows data until 20:00

Figure10: Dots to indicate the values in the different levels of the retrieval, error bars and a-priori profiles with the respective errors should be added here

Figure11: The location of Belgrano and Marambio is the only new information in this figure. Maximum values are already provided in table 1. As these values are from different years, plotting them in such a manner could be misleading.

Figure12: What is meant by 'depicts the BrOx [...] at each station' Please make clear what is plotted here. Daily averages or maximum values?

3 Technical comments

page 2 line 27: add s: high amounts

p.4 l.3: remove s: aerosol extinction

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p.4 l.31: installed in

p.5 l.14: consists of

p.5 l.11: of a two-step approach

p.5 l.32: taken into consideration

p.6 l.19: installed at the site

p.6 l.32: Herein,

p.8 l.33: considerably stronger

p.10 l.13: this simplified scheme

p.10 l.25: conclusions from

p.11 l.9: performed at the two sites

Table1 - Caption title: observations of tropospheric BrO made in Antarctica

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