Responses to Referee #1

The authors would like to thank Referee #1 for the detailed reading of our work and his/her insightful comments. Below, we address those comments in a point-by-point basis. Note that, in addition to the draft, we now include a Supplementary Material where the reader is kindly referred to if he/she is interested on particular details on the MAX-DOAS and inversion scheme. Through this Supplementary Material, we not only keep the simplicity of the draft but also provide further insights on the more technical information behind our work. Overall, we consider that our work has improved after both referees comments and suggestions and we are truly grateful for that.

In the following, the Referee Comments are in black and Authors Comments in blue. References to pages and lines of the draft are indicated with "P" and line "L", respectively.

1. General comments

1.1. Documentation of profile inversion and interpretation of the resulting data

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).

For the sake of simplicity for the reader, these DOAS fit statistics have now been included in the Supplementary Material, Sect. 1 (and thus indicated in the draft P5, L23).

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.

Typical Averaging kernels obtained in this work shows that, depending on the extinction condition (scattering and/or absorption) our method is sensible up to an altitude of about approximately 4 km (see Supplementary Material, Sect. 2).
To find out what would be observed by our MAX-DOAS instruments if a layer of aerosols and/or BrO would be placed at high altitudes, we have performed some sensitivity tests (see Supplementary Material, Sect. 3). Results of these simulated scenarios indicate a vertical sensitivity of up 4 km for aerosols and 2.5-3 km for BrO. Thus, figures in this work have been modified to represent our altitude sensitivity. Note that (P1 L29-30 of the initial draft) "and undetectable values above 2 km at both sites" has been deleted. See also responses below.

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 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.
Certainly, each technique has its own benefits but also its own limitations. Thus, the comparison of different techniques usually comes with limitations as well. Indeed, although most of the information retrieved at the surface (i.e., lower layer) with the DOAS observations are mainly influenced by the state of the atmosphere at that layer, in fact they are rarely 100% independent of the state of the atmosphere some the layer(s) just above (e.g., Supplementary Material, Sect. 2). Moreover, the DOAS observations at the instrument's altitude (surface in this case) in fact provide information not only at the instrument location but they integrate information of the atmosphere contained up to several kilometers away of the instrument (depending on the scattering conditions) in the horizontal field of view of the instrument. On the contrary, the ozone observations facilitated in this work do provide information of the amount of O3 present at the very exact instrument's location (in the horizontal and in the vertical) and, unfortunately, there are not in situ measured O3 profiles at both stations on hourly basis. Indeed, any mixture of data obtained by remote and by in situ techniques should be taken with caution. Note that, proceeding as Referee #1 suggests with the DOAS data will only overcome partially the vertical information issue when using in situ and remote sensed data (partial due to the lack of vertical information of the O3 measurements anyway). In addition, there is nothing we can do with to overcome the in situ "punctual" information in the horizontal part compared to the DOAS data. However, given the sort of data (and related limitations) we have, what we can do is acknowledge this sort of limitations in the draft. This is now done on P11, L8-12:
"Note that the estimations provided herein are limited by the information content inherent in the in situ technique measuring near-surface ozone (i.e., information at the exact instrument's location) compared to the DOAS data which integrates information several kilometers away of the instrument (depending on scattering conditions) in the horizontal field of view and also in the vertical (see retrieved averaging kernels in the Supplementary Material).".
Also, the sentence *"Further studies including different sources and sinks of bromine radicals in the Antarctic environment would be needed to confirm these numbers…"* (P10, L22 of the initial draft) is now rephrased as *"Further studies would be needed to confirm these numbers, including investigations on different sources and sinks of bromine…"* (P11, L12-13).
Worth noticing is that, as it was mentioned already on the draft, the calculations presented on Sec. 3.3 are *"approximations"* (P10, L25 of initial draft) and *"simplified scheme"* (P10, L13 of initial draft) and therefore we could only *"estimate"* BrOx (e.g., P9, L19 and L41 or P10 L4 of initial draft). Note that, however, the different approximations involved on our BrOx estimation

seem not far from reality at least at Marambio (P10, L36-38 of initial draft). Moreover, we clearly stated on the draft that *"Further studies including different sources and sinks of bromine radicals in the Antarctic environment would be needed to confirm these numbers"* (P10, L22 of the initial draft) and that *"Additional investigations on the variability and geographical distribution of the bromine source gases throughout the year are suggested to address the bromine pathways in the Antarctic troposphere and their consequences"* (P10, L11-13 of the initial draft) while *"dedicated investigations combining models and collocated observations of e.g. halogenated substances (not only BrO), organic compounds, DMS, NOx, HOx, particles and sea ice properties at different stations, could assist a thorough study of the bromine sources and pathways at Antarctica, their geographical distribution and their projections under a changing environment"* (P11, L31-34 of the initial draft).

1.2. Processing of ancillary data for 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.

The presented work aims at assessing the presence and the seasonal variation of BrOx at the two sites of Antarctica during the sunlit period of 2015. Although surely worth investigating in a forthcoming work, the particular analysis of a given ODE is out of the scope of this paper. Note that such halogens-ODE exercise in polar regions has already being nicely performed in rather recent works (e.g. Thompson et al. 2015 or Halfacre et al. 2014).

Aiming at the aforementioned 2015 description of our work, an overview of the 2015 weather conditions is summarized in Table 3. However, since we understand the Referee's point, the figure of the wind roses (Fig. 5 of the new draft) is now adapted to show the wind directions depending on the wind speeds regimes observed and also referred to throughout the work (low or < 6 m s^{-1}, medium or 6 – 12 m s^{-1} and high wind speeds or > 12 m s^{-1}). Worth noticing is that the 2015 summary presented in the wind rose (Fig. 5, Marambio) is in agreement with the recently publish work of Asmi et al. (2018) focused on site of Marambio and comprising the 2013-2015 period. This agreement is now mentioned in the new draft (P7 L40) and that reference added to the bibliography.

Thus, in the new draft, the paragraph (P7, L23-26 of initial draft)

"Regarding the wind measurements, the speed observed at both stations is shown in Fig. 5, while the wind roses are given in Fig. 6. Observations indicate that, although the higher gusts of wind were quite similar at both stations (~120 km h-1), the mean wind speed at Marambio was in general 50% higher than in Belgrano"

is changed to

"Regarding the wind measurements, the wind rose of the 2015 measurements at each station is shown in Fig. 5 for low, medium and high wind speeds. Note that the information reported for 2015 at Marambio is consistent with the recent publication of Asmi et al. (2018) referred to the

2013-2015 period. The 2015 observations at both stations indicate that, although the higher gusts of wind were quite similar at both stations (~34 m s-1), the median wind speed at Marambio (7.2 m s-1) was in general 50% higher than in Belgrano." (P7 L38-40 to P8 L1).
Worth mentioning is also that, as stated on P9 L28 of the initial draft, the BrOx study presented in Sect. 3.3 is based only on data during low wind conditions (< 6 m s-1). Since, indeed, some exemplary data (under wind speed < 10 m s^{-1}, P8, L10 of the initial draft) of BrO are presented in this work (e.g., Fig. 8 of the new draft), following the referee suggestion, details regarding the wind conditions on the specific days is now added in the new version of the draft (first paragraph of Sec. 3.2).

2. Specific comments

P1 L30: What is a heterogeneous increase? (Exponential) increase by heterogeneous reactions/chemistry?
In the new draft "geographical" is added on P1 L30 and P12 L13.

P3 L11: 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
The work of Hüneke et al. (2017) is based on aircraft-borne observation during different sections of diverse flights. Within that work, the authors include a dive into the Antarctic troposphere (65° S, 21° E) down to an altitude of 4 km. On our work, the study of Hüneke et al (2017) is referred to as one of the few studies *investigating "the presence of tropospheric BrO in the Antarctic region"* (P3 L8-11 of the initial draft). We agree with the referee and the work of Peterson et al (2017) is an interesting study already referred to within our draft. However, the work of Peterson et al (2017) refers to Arctic observations. Since that part of our draft focuses only on Antarctic observations, we consider Hüneke et al (2017) should remain as a relevant reference with regard BrO observations in the Antarctic atmosphere.

P4 L12: Reference missing Bobrowsky(?)/Bobrowski et. al. 2003
The new version of the draft already includes the missing reference in the bibliography.

P5 L14: What does the goal of long term observations entail for parameter selection in detail?
We mean that the parameterization of the radiative transfer model is based on general properties of the Antarctic atmosphere and not particularized for given events (e.g., blowing snow, ODEs…). Indeed, when a study of this kind is limited to a few days, the choice of the parameters determining the vertical retrieval can be performed taking into account the particular conditions of each of those days. However, when long-term observations are used, including a large number of days, the selection of the parameters has to be adequate for a large number of situations too. Thus, the parameterization does not aim not be "optimal" for a particular day but for the whole period.

P5 L23: 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?
As mentioned above, statistics of the dSCD errors are now included in the Supplementary Material. The set of elevation angles was provided in the draft on Table 2 and the time resolution on P4 L29 of the initial draft (i.e., *"every 15 minutes"*).

P5 L23f: a-priori errors: Please elaborate briefly on the idea behind this approach and what _ 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.

We agree with the referee, this point should be clarified and explained in more detail in the manuscript. Reference of Franco et al., (2015) has been replaced by Clémer et al. (2010) and deleted from bibliography and additional details on the profile retrieval are now provided with the following text (P5 L23-32):

"The diagonal elements of the a priori covariance matrix in the inversion was calculated as 100 % of the a priori profile for BrO and based on Clémer et al. (2010) for the aerosol extinction retrieval. Note that, given the large variability of the visibility conditions at Antarctica, the true aerosol profile can strongly differ from the a priori profile. In order to allow the extinction profile retrieval to capture these variations, we followed the method described in Clémer et al. (2010). In this method, the diagonal element of Sa closest to the surface (i.e., Sa (1,1)) is set equal to the squared of a scaling factor (ß) times the maximum partial AOD of the extinction profile obtained in the precedent iteration. In this study, ß has been set to 1. The other diagonal elements decrease linearly with altitude down to 20% of Sa (1,1). Note that, despite not being a statistically Bayesian method, it allows the profiles corresponding to large AOD to differ significantly from the a priori, while the profiles with smaller AOD present lower variations from the a priori."

P5 L25: Why is the correlation length different for aerosols and trace gases?

The correlation length indicates how the particles or gases of one layer interact with their neighbors of the adjacent layers. Prior the study, several tests were performed for aerosols and BrO profile retrievals using three values for the correlation length: 100, 200 and 300 m which are standard for MAX-DOAS retrievals (e.g., Clémer et al. 2010; Frieß et al., 2011). A better agreement between measured and simulated O4 and BrO DSCDs was found when a correlation length of 100 m and 300 m was used for aerosol extinction and BrO profiles, respectively.

P5 L26: 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

To clarify this point, the sentence *"the error of the retrieved profiles provided in this work contains the measurement error and the smoothing error of the retrieval"* (P5, L25-26 of the initial draft) is rephrased to *"the error of the retrieved profiles provided in this work contains the measurement error (experimental dSCDs error) and the smoothing error of the retrieval. The last takes into account that the retrieval is an estimate of the true profile smoothed by the averaging kernel functions."* (P5 L33-36)

P5 L30: 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)

During 2007, in the context of the Arctic Study of Tropospheric Aerosol, Clouds and Radiation (ASTAR) campaign, the sea ice albedo was measured in the Arctic from 310 to 930 nm using a Spectral Modular Airborne Radiation measurement sysTem (SMART-Albedometer). This work is summarized in the PhD thesis of André Ehrlich. Results indicate that in the UV-A spectral range, the sea ice albedo varies from 0.79 up to nearly 1 (see also Prados-Roman et al., 2011). In particular, at 360 nm (wavelength of our interest), the measured sea ice albedo during ASTAR was ~0.82 (Fig. 5.1 of Ehrlich, 2009). This value is in good agreement with the value used on our study and thus it is now mentioned in the new draft (P5, L40-41) and the reference of Ehrlich (2009) added to the bibliography. Furthermore, previously to the work here presented, diverse tests were performed for aerosol extinction and BrO retrievals using surface albedos of 0.8 and

0.9. A better agreement between measured and simulated O4 and BrO DSCDs was obtained when an albedo of 0.8 was used (P5 L30 of the initial draft).

P5 L31: 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?
Note that, by mistake, we wrote "5" instead of "0.5" as the upper limit of AOD (i.e., observations with AOD>0.5 were considered as invalid for profile inversion of BrO). This is corrected in the new draft (P5, L42). Filtering the data in this way, we avoid including data affected by high aerosol loads that could complicate the interpretation of the BrO results. In those situations (high AOD), scattering happens close to the instrument and the dSCDs at different elevation angles can present similar values (i.e., their information content are no longer representative of different layers of the atmosphere). Thus these measurements are not very suitable for vertical profile retrieval.

P5 L32: What are typical DOFs of the data set?
A summary of the degrees of freedom is now provided in the Supplementary Material (Table S1). The reader is now kindly referred to it on P6 L1.

P5 L39: 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?
As remarked by the referee, an ideal a priori should be independent information derived from observations. Unfortunately, observations in the Antarctic atmosphere are not abundant (this is now remarked on P6 L11:
"As a consequence of its logistically-complicated location and to very harsh weather conditions, there are very scare observational data describing the atmosphere at Antarctica".
Regarding our study on the vertical scale, besides the ozone-sondes performed at Belgrano, no other ancillary data are available. The ozone-sonde data have been used to model the pressure, density, temperature and ozone profile of the atmosphere at this station. Thus, we used a usual exponential decreasing function for both a priori profiles (extinction and BrO) and then we performed test varying parameters such as e.g. the correlation length, AOD, surface albedo, etc (just 2 or 3 different values) characterizing the a priori profile and its covariance matrix. Then, we compared the measured and resulting simulated dSCDs (O4 and BrO) to find the values providing the best agreement between both kinds of dSCDs (note that the O4 vertical profile is known in the atmosphere). In fact, this is pretty much the only test we can perform to check if the chosen parameters (a priori profile and covariance) allow to obtain reasonable values of the retrieved profiles.
P6 L36: As mentioned in section 2.2.1...: This is not discussed in 2.2.1 at all (but should be - based on averaging kernels)
"As mentioned in Sect. 2.2.1" is corrected to "As mentioned in Sect. 2.2.2." (referring to P5, L19-20 of the initial draft). See also our responses to General Comments.

P7 L12: 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)
We agree with the referee, unlike at Belgrano, at Marambio there is no complete darkness as already shown by the hours of light at the station (in yellow in Fig. 4 of the draft). However, as

stated in the draft when referring to the DOAS data presented, only DOAS data with SZA < 75° are considered in the work (P4 L40). This is now clarified in the new draft (P7 26-27, P9 L1, P10 L19, L26, L34, and in Figures 3, 4, 6, 7, 10 and 12-14).

P7 L13: What is meant by 'the magnitude and variability of the BrO maximums direct the difference'? What is the maximum referred to? A daily maximum?
"VCD2km" is now added on P7 L28 and L31 and "an absolute" is now added on P7 L29. Thus the sentences result as *"…, the magnitude and variability of the BrO VCD2km maximums direct the difference between both stations, with an absolute maximum BrO VCD2km observed in Marambio being 3.2 times higher than in Belgrano. As can be observed in Fig. 4, it is also worth noticing the clear photolytic activation of BrO in Marambio during austral spring, with levels an order of magnitude higher than the median BrO* VCD_{2km} *values at the station…."*

P8 L4: the VMRs were not 'measured' rather estimated.. The claim of sensitivity up to 6km altitude should be substantiated (see General comments).
In the new draft *"BrO vmr measured"* is changed to *"the BrO vmr retrieved"* (P8 L20) and, accordingly, in the caption of Fig. 10 *"observed"* is changed to *"retrieved"*. Also, "the first 6 kilometres" (P8 L4 of the initial manuscript) is changed to "the lowest kilometers" (P8 L20). See also our responses to the General Comments.

P8 L5: Absence of elevated layers: If this actually can be inferred should be reviewed after assessment of the vertical sensitivity (see General comments)
The sentence (P8 L5-8 of initial draft)
"One characteristic of these BrO observations is that, unlike conclusions of previous Antarctic studies suggesting the presence of reactive bromine above 4 km altitude (e.g., Frieß et al., 2004; Roscoe et al., 2014), during 2015 no elevated plumes of BrO were observed at either of the two Antarctic stations referred to in this work. In fact, during 2015, most of the BrO was confined within the first 2 km of the troposphere (Fig. 8)."
has now been rephrased and moved to (P9 L19-24):
"In previous studies of the Antarctic troposphere (e.g., Frieß et al. 2004 and Roscoe et al. 2014), the presence of uplifted reactive bromine was suggested. While the work of Frieß et al. (2004) remarked the presence of reactive bromine uplifted (> 4 km altitude) due to advection processes, in the work of Roscoe et al. (2014), the authors where able to differentiate between 2 types of BrO vertical profiles: those with only near-surface BrO (centered at 200 m) and those with double peak (centered at 2 km and near-surface). In the work here presented, no uplifted layers (> 2 km) of BrO were detected although, given the limited vertical information content of the MAX-DOAS observations (Supplementary Material), double peak type of BrO profiles cannot be ruled out."
Please, refer also to our responses to the General comments.

P8 L23: 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.
The a priori BrO profiles (and errors) are now included in Fig. 10 (no smoothing) and its caption. Note that the altitude scale now goes up to 3 km. See also our responses to the General Comments.

P8 L41: Whether or not the detection of BrO above 2km can be discussed with the presented data set strongly depends on vertical sensitivity.

Please, see our responses to the General comments.

P8 L41, P9 L1: The inversion error was not clearly defined (see comment p.5 l.25)
As mentioned on our response to comment on P5 L26, this is now clarified in the new draft (P5 L33-36).

P9 L3: 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.
As mentioned on the initial manuscript (P9 L5-8), although the definition of the top of the boundary layer is out of the scope of our work, indeed a threshold between the boundary layer and the free atmosphere needs to be set in order to assess the detection of BrO in the free troposphere. Indeed, (P8 L4-5 of initial draft) *"former studies place the top of the boundary layer in Antarctica between 100 m and 2 km, depending on the boundary layer parametrization and time of the year (e.g., King et al., 2006; Nygård et al., 2013)"*. The definition of the top of the boundary layer is quite a topic by itself and it is usually based on the vertical structure of e.g. its chemical components, temperature, humidity, wind, turbulences, etc. Based on the 10-year climatology of Nygård et al. (2013) investigating the different humidity inversions above given sites (including Marambio but not at Belgrano), the (median) based height of the inversion at Antarctica was located between 0.9 km and 2 km during the non-winter periods (i.e., periods covered in this work). In particular, at Marambio the top of the boundary layer (based on humidity) was at an altitude between 1 and 1.4 km for these periods. Regarding Belgrano, based on monthly averaged temperature profiles obtained from the ozone-sondes at the site, the altitude of the inversion layer (if present) at Belgrano ranged from 1 to 1.5 km (depending on the month), while the lapse rate most of the months suggested a mixing layer height of up to 1 to 2.5 km (depending on the month). Although these data suggest that the top of the boundary layer could vary between 0.9 and 2.5 km depending on the station and time of the year, as the referee remarks, with the data that we have we are not able to define the altitude of the boundary layer at the specific time and dates of our observations. This is now made clear by rephrasing P9 L3-8 of the initial draft
"…the BrO detection limit here provided may be regarded as an upper limit of BrO in the free troposphere since former studies place the top of the boundary layer in Antarctica between 100 m and 2 km, depending on the boundary layer parametrization and time of the year (e.g., King et al., 2006; Nygård et al., 2013). This upper limit of BrO in the free troposphere of Antarctica is consistent with the few previous studies of the vertical distribution of this trace gas in the Arctic and Antarctic regions that set upper limits of BrO in the polar free troposphere of 1.5 and 2 pmol

mol-1, respectively (e.g., Frieß et al., 2011; Prados-Roman et al., 2011; Peterson et al., 2017; Hüneke et al., 2017)."
to:
"…former studies place the top of the boundary layer in Antarctica between 100 m and 2 km, depending on the boundary layer parameterization, station and time of the year (e.g., King et al., 2006; Nygård et al., 2013). Although, Nygård et al., (2013) marked the height of the boundary layer at Marambio between 1 and 1.4 km for the non-winter periods referred to in this work, and the ozone-sondes performed at Belgrano set that height between 1 and 2.5 km at that site (e.g., Parrondo et al., 2014). However, the altitude threshold between the boundary layer and the free troposphere cannot be assessed on the time resolution of our observations. Additional investigations at the two sites would be needed to confirm whether BrO reaches the free troposphere and, given the case, to assess the budget of BrO in the Antarctic free troposphere. Note that previous work on polar environments set BrO below 1.5 and 2 pmol mol^{-1} in the Arctic Arctic and Antarctic free troposphere, respectively (e.g., Frieß et al., 2011; Prados-Roman et al., 2011; Peterson et al., 2017; Hüneke et al., 2017)" (P9 L25-34).
Accordingly, "In fact, in line with previous polar studies, this work sets an upper limit of BrO in the free troposphere of Antarctica of 1 pmol mol-1." (P11 L14-15 of the initial draft) is deleted.
See also our responses to the General Comments with regard the altitude sensitivity of the DOAS data presented.
Worth mentioning is the fact that, in Sect. Sect. 3.1.1., the BrO confined within the first 2 km of the atmosphere (i.e., BrO VCD_{2km}) is the parameter used for comparing the budget of BrO above both stations. Also, the BrOx investigation is based on surface studies. Therefore, our conclusions to these regards are independent of the location of the top of the boundary layer.

P9 L24: 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?
Thank you for noticing that we forgot to write down the value considered for the photolysis rate coefficient of BrO. That value is now stated on P10 L10.
Regarding the BrOx estimation (Eq. (2)), as already mentioned on P10 L13 of the initial draft, the calculations presented are a *"simplified scheme"* and *are "based on conclusions after numerical models and laboratory and campaigned-based observations obtained in the polar regions (mainly the Arctic)"* (P10 L25 of initial draft). We do consider that, as already stated (P10 L38-40 of initial draft), there is a *"need of further investigations for a better understanding of all the processes and key parameters involved in the halogens' pathways in the Antarctic troposphere"* (in the new draft the word *"long-term"* is now added to that sentence, P11 L31). Hence, given the lack of Antarctic literature of many (most) of the required parameters involved in the bromine activation, in Eq. (2) we have used fixed mean values found in literature for polar regions (even if those were from the Arctic region) for all the parameters except for [BrO] and [O3] (where we have used the observations, as already stated on P9 L21-22 of the initial draft).
As for the [HO2] (and [OH]) mentioned by Referee #1, the fixed value used (P9 L20 of initial draft) corresponds to the mean concentration of HO2 (and OH) as observed at the Antarctic station of Halley (e.g., Bloss et al., 2007). In the case of [ClO], the value used (P9 L20 of initial draft) is an average value for Arctic conditions (e.g., Halfacre et al., 2014). We agree with the referee and these sort of details are relevant and should be stated in the text. We have clarified now those details in the new draft (P10 L42).
Worth mentioning is that we consider that (P10 L11-13 of initial draft) *"Additional investigations on the variability and geographical distribution of the bromine source gases throughout the year*

are suggested to address the bromine pathways in the Antarctic troposphere and their consequences". Note that, on P10 L36-39 of the initial draft, we conclude that the kinetic calculations based on Eq (2) are close to reality (i.e., to observations) in the case of Marambio but not in the case of Belgrano. Also, as stated on P11 L31-34 of the initial draft*, "…dedicated investigations combining collocated observations of e.g. halogenated substances (not only BrO), organic compounds, DMS, NOx, HOx, particles and sea ice properties at different stations, could assist a thorough study of the bromine sources and pathways at Antarctica, their geographical distribution and their projections under a changing environment"*. Note that *"models and"* is now added to that sentence (P12 L24) to reinforce the need of model-observation synergies.

P9 L31: What exactly is shown in this figure? Daily averages? maximum values?
The figure shows BrOx (Br + BrO) based on Eq. (2) where [O3] and [BrO] are the observed near-surface BrO and O3 under low wind conditions for the timestamp of the MAX-DOAS measurements. This is now clarified in the draft (P10 L17). Throughout the draft, "near surface" has been changed to "near-surface" (P3 L19, P6 L13, P7 L34 and P8 L6).

P9 L40: What is meant by 'troposphere reactivity'? oxidation capacity?
"tropospheric reactivity" is now changed to "oxidizing capacity" (P10 L28)

P10 L13: 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.
As mentioned throughout the draft (e.g., P3 L8-14 of initial draft), there are very few observational data in the Antarctic environment which forces us to make several assumptions. In this sense, as mentioned above and on P9 L18-41 and P10 L1-11, the BrOx is calculated through Eq. (2) by fixing all the parameters (to values observed in polar regions) except for BrO and O3 (which are the observations).
Later on (P10 L13-24 of the initial draft), those BrO and O3 observations are also used to estimate the lifetime of ozone at each site based on Eq. (1), i.e., assuming that the main O3 depletion is through the bromine-chlorine channel (P10 L37-38 of initial draft) and that the [ClO] is fixed as in Eq. (2) to average Arctic conditions (the later is now included in the new draft, P10 L42). To clarify this even further, *"BrOx regimes"* is now changed to *"BrO and O3 regimes"* (P11 L1).
Since we are aware that these are very simplified approximations and could not be realistic, we do compare (P10 L25-40 of initial draft) *"these observed τO3 with the τO3 estimated above from kinetics"* for given days aiming at evaluating the validity of the simplifications made in our estimations. Note that we extract the *"observed τO3"* from the *"the ozone observations"* (P10 L29 of the initial draft), i.e., form the data shown in Fig. 7 of the initial draft. As stated on P10 L36-38 of the initial draft, *"The resemblance of the observed and calculated τO3 at Marambio suggests that the assumptions made at Marambio's surrounding (e.g., the Br-Cl channel dominates the ozone depletion) is close to reality which seems not to be the case for Belgrano's surroundings"*. Thus, through this exercise we investigate the goodness of our (very simplified) estimations and clearly state that, while the observations at Marambio suggest that the assumptions made at this site are not far from reality, those assumptions are limited in the case of Belgrano's surroundings. Since this observation vs. estimation exercise based on exemplary days have no statistical meaning (this statement is now included in the new draft P11 L28-29, we conclude that there is *a "need of further long-term investigations for a better understanding of all the processes and key parameters involved in the halogens' pathways in the Antarctic troposphere"* (P10 L38-40 of initial draft) *"combining collocated observations of e.g. halogenated*

substances (not only BrO), organic compounds, DMS, NOx, HOx, particles and sea ice properties at different stations" (P11 L32-34 of initial draft). In this regard, we consider that the observation vs. estimation exercise presented is therefore justified and offers some further information of our observations (e.g., at Marambio the dominant ozone chemical loss is driven by the Br-Cl channel while at Belgrano most probably there are more species involved).

P11 L4: 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)
The sentence *"This study reports on the presence and distribution of reactive inorganic bromine (BrOx) in the Antarctic troposphere"* is now changed to *"Based on contemporary ground-based observations performed during 2015 at two Antarctic sites (new sites as far as tropospheric BrO observations is concerned), this study reports on the presence and vertical distribution of reactive inorganic bromine in the low troposphere at the two sites and discusses the geographical distribution of BrOx"* (P11 L35-38).

Table 1: 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.
The periods of the works of Kreher et al. (1997), Saiz-Lopez et al. (2007) and this work are clarified in the new draft (Table 1).

Table 3: days with snowfall: Is this only precipitation (excluding blowing snow)? Information about days with blowing snow would be interesting as well - if available.
The snow fall provided in Table 3 is taken from the 2015 statistics offered by the WMO at each station and are based on surface synoptic observations. This is now clarified in the header of the table. Unfortunately there are no statistics on blowing snow conditions as such. Instead, we can use the wind speed observations threshold of 12 m s^{-1} (e.g., Jones et al. 2009) for blowing snow. In the new draft we have excluded the Fig. 5 (suggested also by Referee #2) and hence the other figures re-numbered. Also, as mentioned on our responses to the General Comments (1.2), we have modified the figure with the wind roses (former Fig. 6) in order to include statistics concerning the wind speed and directions as suggested.

Figures3+4: Please provide errors and detection limits in these plots
For sake of simplicity of the plots, the relative errors of the AOD_{2km} and BrO VCD_{2km} are now provided in the draft (P7 L12 and P7 L25, respectively)

Figure 5: 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.
Figure deleted in the new draft (see our response to Table 3).

Figure 6 (now Figure 5): Additionally, data filtered for the days presented in the profile data would be desirable
This is now shown by the color code (see our response to Table 3).

Figure 7 (now Figure 6): It would be nice to have the reported periods of MAX-DOAS observations marked in these plots.
The periods with MAX-DOAS observations are now indicated (hence the caption adapted).

Figure 8 (now Figure 7): 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.
We appreciate for pointing out these details so we can improve the color plots since, as remarked, they do contain a lot of information. The vertical scales have now been adapted (see our responses to General Comments). Also observations below detection limits are now shown in black and the times when the data are not above the quality filters are now indicated in gray boxes (this is now mentioned in the caption). Indeed, these sort of (often used) contour plots interpolate linearly across rectangles (vertical grid and time stamp). However, we do consider that no relevant information is lost by using these plots. In addition, by showing the plots in this manner (the whole measurement period at each station for AEC and for BrO) it is easier to gain an overview of the measurements at both sites and to gain an insight on the message contained on each plot (e.g., altitude range, temporal range, AEC or BrO variability in time and altitude, periods with no observations due to high SZA, etc.).

Figure 9 (now Figure 8): 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.
Please, refer to our response above. Regarding the timestamp vs. SZA issue the referee realized, unfortunately when drafting the plots of Marambio 25th Sept and Belgrano 11th November, there was a mistake on the decimal day to time conversion for the axes. All the timestamps have been checked for all the plots. Thanks for noticing.

Figure 10: 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
The a priori and error has now been included and no smoothing is applied in the plots. Also, the vertical grid (100 m) is now shown with small ticks (indicated now in the caption).

Figure 11: 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.
In addition to the location of Belgrano and Marambio as new sites regarding ground-based tropospheric BrO observations, this figure also contains information regarding the geographical distribution of BrO. Indeed, as it appears in the caption of the figure *"only the present study provides contemporary observations from different sites"* (i.e., Marambio and Belgrano- making this work particularly relevant). Moreover, through this figure, the reader can easily appreciate the strong difference on BrO between the two new sites and, also, have an overview of the up-to-date maximum values of BrO on the (few) other sites in Antarctica. Even if those other works refer to different years, they also cover the bromine active period and this plot can *"point(ing) once more its heterogeneity with regard to reactive bromine load"* (P8 L38-40 of the initial draft). Thus, we consider this plot is worth keeping.

Figure 12: What is meant by 'depicts the BrOx [...] at each station' Please make clear what is plotted here. Daily averages or maximum values?

The figure shows the BrOx (i.e., BrO + Br), where BrO derives from the observations and Br from Eq. (2). Since that equation depends on O3 (which is also an observation), this parameter is used as color code. The time stamp is that of the BrO measurement. Please refer also to our response to the specific comment to P9 L24.

Technical comments

P2 L 27: added

P4 L3: removed

P4 L31: changed

P5 L14: we consider the referee refers to P4 L14 (changed)

P5 L11: changed

P5 L32: corrected

P6 L19: corrected

P6 L32: added

P8 L33: corrected

P10 L13: corrected

P10 L25 (now P10 L30): corrected

P11 L9 (now P11 L14): corrected

Table 1: corrected

Responses to Referee #2

The authors are grateful for Referee #2's time and constructive comments and the appreciation of our work. In the following, we address his/her comments. Please, note that specific details on the MAX-DOAS and inversion technique has now been included on a Supplementary Material.

The Referee Comments are in black and Authors Comments in blue. References to pages and lines of the draft are indicated with "P" and line "L", respectively.

Specific comments

MAX-DOAS analysis

The authors claim that BrO is not present in significant amounts above 2 km based on their ground-based measurements, where they retrieve BrO vertical profiles from 0-6 km. I am skeptical that ground-based MAX-DOAS measurements can be used to make this claim. For what it is worth, I am skeptical that the prior studies cited could actually observe BrO at those altitudes as well. The information content outside of the lowest elevation angle measurements simply isn't high enough. The authors should present averaging kernels showing that the measurements are sensitive to changes in BrO above 2 km if they are going to make this claim. I also think the presented vertical profiles should also be limited to 2 km unless the averaging kernels show that a higher altitude is merited.

Tests performed with the ratiative transfer confirm the sensitivity of the technique to up to 4 km and 2.5-3 km (aerosols and BrO, respectively). We kindly ask the referee to see the Supplementary Material (Sect. 3) and also our responses to the General Comments 1.1. of Referee #1.

Sea ice conditions between the two sites

I think the author's points about needing to examine the sea ice conditions at both sites and the heterogeneity being potentially linked to sea ice differences is a good one. However, I think simply describing the sea ice around Marambio as seasonal without providing further detail is potentially misleading, as the ice toward the outside edge of the sea ice in the Antarctic is often the oldest sea ice (excluding the "permanently" sea iced sections surrounding Belgrano) (Nghiem et al., 2016). This older sea ice is likely lower salinity than the newer sea ice regions closer to the coast. These differences may impact the overlying snowpack, which is the likely source of the reactive bromine. Of course the proximity of this older ice to open water may also lead to enhanced snow salinity due to sea spray aerosol deposition (e.g. May et al., 2016). In any case, I'd like to see the authors add a more detailed discussion of the sea ice conditions at the two sites.

Indeed, although the mentioned work of Nghiem et al. (2016) states that the "Antarctic sea ice is dominated primarily by first-year sea ice" which is often linked to bromine explosions (e.g., Simpson et al., 2007), dedicated investigations into the link between the properties of the sea ice and the composition of the tropospheric in Antarctica are definitively worth considering (although not easy to undertake from the logistic point of view...).

With regard the data we present in this work, we have now added a new figure (Fig. 9) with closed-up views of the sea ice conditions nearby Belgrano and Marambio on the selected days of Fig. 8 (from end of September to end of November). Note that this new figure does not substitute Fig. 1 since the later provides the reader with a quick overview of the locations of both stations within Antarctica (something missing in this new zoomed in figure). Note that, as stated on the caption of the new figure, "in barely 1 month (25th September - 29th October) the sea ice surrounding Marambio underwent strong transformation, going from medium/highly concentrated sea ice in September and with barely permanent open waters (upper left figure), to pretty much complete open ocean (disappearing all the sea ice beyond 50° W). During the

timeframe of that sea ice transformation, BrO VCD_{2km} peaked at Marambio (Fig. 4). Also, note how the edge of the sea ice nearby Belgrano transforms towards November (e.g., lower right).".

Page1, Line 41: This sentence should have references for these impacts of atmospheric halogens.
As appearing in P2 L4 of the initial draft, the reader is kindly directed to the compendium work of Simpson et al. 2015 on "Tropospheric Halogen Chemistry: Sources, Cycling and Impacts" and the studies referred to in it.

P5 L32: What percentage of the retrievals has a DOF larger than 1?
Details on the DOF are now provided in the Supplementary Material (and indicated on P6 L1 of the new draft).

P5 L40: A summary of the degrees of freedom for the BrO retrievals should be presented here as well.
It is now included in the Supplementary Material.

P6 L39: Can you state the differences in AOD between the two sites more quantitatively?
In the new draft (P7 L14-15) now we add "At Belgrano, 62 % of the AOD_{2km} was lower than 0.05 (12 % between 0.05 and 0.1) compared to 90 % of AOD_{2km} at Marambio that was below 0.05". For clarity, the subscript "2km" has been added to AOD in the vertical axes of Fig. 3 (i.e., AOD_{2km}). Please note that, as mentioned on our draft (P7 L7 of the initial draft), a forthcoming publication will focus on the aerosols observed at the two stations (Gómez-Martín et al. 2018).

P7 L11: 0.8×10^{13} molec cm^{-2} isn't a range as presented. Please clarify, is this a standard deviation?
"range" is changed to "value" on P7 L25 (i.e., 75% of the data BrO VCD2km were < $0.8\cdot10^{13}$ molec cm^{-3})

<u>Suggested figure modifications:</u>

1. Figure 3, 4: I don't really think it is necessary to shade regions without data. It gives the figure a cluttered look.

We appreciate the referee suggestion. However, we do consider that by including the "shades" the reader can have an overview of the amount of data contained in this work at two different sites. Note that by excluding the shaded regions the reader could interpret that we did have MAX-DOAS data throughout the year. We would like to clearly state (not only in the text) that there were periods of time with no MAX-DOAS data (either due to instrumental issues or to SZA > 75°, this now clarified in the caption of both figures and throughout the draft (P7 26-27, P9 L1, P10 L19, L26, L34, and in Figures 3, 4, 6, 7, 10 and 12-14).

2. I think just showing Fig. 6 is sufficient, and the timeseries of wind speed (Fig. 5) isn't really needed.

We agree. In the new draft the Fig. 5 is deleted and the wind roses plots binned by wind speeds so the information is not lots. Please, see our responses to the General Comments (1.2) of Referee #1

3. Fig. 7: Consider plotting both ozone series on the same panel so one can clearly see the differences between the two sites.

Similarly to most of other figures of the work where the information is differentiated between stations (i.e., one plot per station), we'd rather plotting the time series of ozone also in a two panel manner. Moreover, it would be quite complicated to distinguished features when plotting

the O3 time series in one single panel (note the noisy data of Marambio, for instance). Also, please bear in mind that we have now added the time periods with MAX-DOAS observations at each station (making the “one-plot” way even more complicated to understand).

4. Fig. 8,9,10: As I suggest above, the portion above 2 km should be cut unless you can demonstrate that your retrieval is sensitive to the true atmospheric state at higher altitudes.

Referee #2 is kindly referred to the Supplementary Material and to our responses to the General Comments (1.2) of Referee #1.

Relevant changes made in the manuscript

- Figure 5 of the initial draft (Wind speeds) has been deleted.
- Figure 6 of the initial draft (wind roses) have been adapted to show wind speeds rages.
- A new figure has been added (Fig. 9) with details on the sea ice conditions on the exemplary days.
- A Supplementary Material with details on the MAX-DOAS and vertical profile retrievals has been included.
- The vertical scales of the figures showing vertical profiles of aerosol extinction and/or BrO have been adapted to the vertical sensitivity of the MAX-DOAS observations.
- Given the available data, no statement on the altitude of the top of the boundary layer can be done and therefore we cannot conclude whether the BrO detected and shown in this work is in the free troposphere or not.

Reactive bromine in the low troposphere of Antarctica. Estimations at two research sites.

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Abstract.

For decades, reactive halogen species (RHS) have been subject of detailed scientific research due to their influence on the oxidizing capacity of the atmosphere and on the climate. From the RHS, those containing bromine are of particular interest in the polar troposphere as a result of their link to ozone depletion events (ODEs) and to the perturbation of the cycle of e.g. the toxic mercury. Given its remoteness and related limited accessibility compared to the Arctic region, the RHS in the Antarctic troposphere are still poorly characterized. This work presents ground-based observations of tropospheric BrO from two different Antarctic locations: Marambio (64º 13' S, 56º 37' W) and Belgrano II (77º 52' S, 34º 37' W) during the sunlit period of 2015. By means of MAX-DOAS (Multi-axis Differential Optical Absorption Spectroscopy) measurements of BrO performed from the two research sites, the seasonal variation of this reactive trace gas is described along with its vertical and geographical distribution in the Antarctic environment. Results show an overall vertical profile of BrO mixing ratio decreasing with altitude, with a median value of 1.6 pmol mol^{-1} in the lowest layers of the troposphere. Additionally, observations show that the polar sunrise triggers a geographical heterogeneous increase of bromine content in the Antarctic troposphere yielding a maximum BrO at Marambio (26 pmol mol^{-1}), amounting threefold the values observed at Belgrano at dawn. Data presented herein are combined with previous studies and ancillary data to update and expand our knowledge of the geographical and vertical distribution of BrO in the Antarctic troposphere, revealing Marambio as one of the locations with highest BrO reported so far in Antarctica. Furthermore, the observations gathered during 2015 serve as a proxy to investigate the budget of reactive bromine (BrO_x = Br + BrO) and the bromine-mediated ozone loss rate in the Antarctic troposphere.

Eliminado: and undetectable values above 2 km at both sites

1 Introduction

The importance of the halogens (X= Cl, Br, I) in atmospheric chemistry and climate became clear decades ago after observations of these substances were made in the stratosphere and also in the troposphere (e.g., Molina and Rowland, 1974; Farman et al., 1985; Barrie et al., 1988; Oltmans et al., 1989; Fan and Jacob, 1992; Hausmann and Platt, 1994; Solomon, 1999). Indeed, reactive halogen compounds (RHS) are of special interest in the troposphere for limiting the lifetime of species such ozone (O_3), mercury (Hg), dimethyl sulfide (DMS) and organic compounds; for affecting the partitioning of NO_x (NO + NO_2)

and HO_x (OH + HO_2) and, in the case of iodine, for participating in new aerosol formation. As such, the presence and the impact of the tropospheric halogen chemistry have been subject of numerous studies with focus on remote regions and on environments under anthropogenic influence (e.g., Simpson et al., 2015 and references therein). Particular attention has been paid by the scientific community to the role of halogens in the polar regions. Although not unique to these regions, it is in the polar areas where bromine becomes particularly relevant directing the oxidizing capacity of the atmosphere during springtime and causing ozone and mercury depletion events (ODEs and AMDEs, respectively). For details on sources, sinks and historical background, the reader is kindly referred to the compendium works of e.g. Simpson et al. (2007), Steffen et al. (2008), Ariya et al. (2015) and Simpson et al. (2015) and references therein.

Briefly, while the presence of reactive bromine in the global pristine troposphere is primarily due to the photolysis and oxidation of very short-lived bromocarbons emitted from the oceans (e.g., Carpenter and Reimann, 2014), in the polar regions its dominant source is of inorganic origin and is linked to heterogeneous chemistry. Through experimental and modelling studies, it is known that a set of heterogeneous reactions based on acidic substrates comprising hypobromus acid (HOBr) and brominde (Br^-) take place in e.g. sea ice, open leads, brine, frost flowers, snowpacks or sea-salt aerosols (e.g., Fan and Jacob, 1992; Vogt et al., 1996; Platt and Lehrer, 1997; Abbatt et al., 2012; Pratt et al., 2013, Toyota et al., 2014; Simpson et al., 2015, Thompson et al., 2015 and 2017, Custard et al., 2017; Wang and Pratt, 2017). These reactions are summarized as:

$$(HOBr)aq + (H^+)aq + (Br^-)aq \leftrightarrow (Br_2)aq + H_2O \quad (R1)$$

or

$$(HOBr)aq + (H^+)aq + (Cl^-)aq \leftrightarrow (BrCl)aq + H_2O \quad (R2)$$

$$(BrCl)aq + (Br^-)aq \leftrightarrow (Br_2Cl^-)aq \quad (R3)$$

$$(Br_2Cl^-)aq \leftrightarrow (Br_2)aq + (Cl^-)aq \quad (R4)$$

yielding the possibility that molecular bromine (Br_2) transforms from the aqueous (aq) to the gas phase. When this is followed by the photolysis of Br_2 into two bromine atoms, an autocatalytic release of bromine is triggered resulting in an exponential buildup of reactive bromine BrO_x (Br + BrO) in the troposphere and the so-called "Bromine Explosions" events (e.g., Fan and Jacob, 1992; Platt and Lehrer, 1997; Wennberg, 1999; Simpson et al., 2015). These events were firstly observed in the Arctic region by correlating the detection of filterable bromine with ODEs (e.g., Barrie et al., 1988) and, later on, by observing very high amount of BrO (tens of pmol mol^{-1}) in the boundary layer just after the polar sunrise (e.g., Hausmann and Platt, 1994; Tuckermann et al., 1997). Since then, several studies have tried to determine the chemical sources, sinks and pathways of these compounds (e.g., Simpson et al., 2007 and 2015). In particular, the main BrO source reactions involve:

$$Br_2 \xrightarrow{\lambda} 2Br \quad (R5)$$

$$BrCl \xrightarrow{\lambda} Br + Cl \quad (R6)$$

$$Br + O_3 \rightarrow BrO + O_2 \quad (R7)$$

In pristine environments (i.e., very low nitrogen oxide), along with photodissociation (in polar spring $J_{BrO} \sim 3 \cdot 10^{-2}$ s^{-1}, e.g., Thompson et al., 2015), the BrO sink reactions associated with the catalytic ODEs are:

$$BrO + BrO \rightarrow 2Br \quad (R8a)$$

$$\rightarrow Br_2 \quad (R8b)$$

$$BrO + ClO \rightarrow BrCl \quad (R9a)$$

$$\rightarrow Br + Cl \quad (R9b)$$

$$BrO + HO_2 \rightarrow HOBr \quad (R10)$$

$$BrO + OH \rightarrow Br + HO_2 \quad (R11)$$

where R10 represents the main channel for the above mentioned bromine explosions causing ODEs (e.g., Bottenheim et al., 1986; Barrie et al., 1988; Oltmans et al., 1989; Platt and Hönninger, 2003; Simpson al., 2007), where the ozone loss rate is

limited by the BrO self and cross reactions (R8 and R9) and estimated as (e.g, Hausmann and Platt, 1994; Le Bras and Platt, 1995; Platt and Jenssen, 1995; Platt and Lehrer, 1997):

$$-\frac{d[O_3]}{dt} = 2\,(k_{BrO+BrO}\,[BrO]^2 + k_{BrO+ClO}\,[BrO][ClO]) \quad (1)$$

Overall, the attempts from the scientific community to estimate the presence of BrO_x in the Antarctic troposphere initiated 20 years ago with ground-based DOAS measurements of BrO from Arrival Heights (77.8º S, 166.7º E), observations compatible with the presence of 30 pmol mol^{-1} in the first 2 km of the troposphere (Kreher et al., 1997). Due to the complexity of performing measurements in such a hostile and remote environment, very few ground-based scientific works have followed that study (summarised in Table 1). In addition to the sparse ground-based measurements, the presence of tropospheric BrO in the Antarctic region has also been addressed through satellite observations (e.g., Wagner and Platt, 1998; Wagner et al., 2001; Richter et al., 2002; Theys et al., 2011), ship-borne measurements (e.g., Wagner et al., 2007) and, more recently, by airborne DOAS measurements (e.g., Hüneke et al., 2017). In spite of the elapsed years and the efforts of the scientific community, compared to its northern counterpart, the current characterization of BrO_x in the Antarctic troposphere is very poor given the very scarce geographical coverage available with vertical information. Moreover, most of the observations are campaign-based in random years and, hence, the time coverage is also quite limited (see Table 1). The present work aims at improving this geographical, vertical and time coverage by adding two Antarctic sites to those few observing BrO in the Antarctic troposphere. These observations were made by endurable, stable and sensitive DOAS instrumentation built specifically for long-term measurements in hostile environments. Particularly, herein we present the observations performed during 2015 from two stations. The measurement sites and methodologies are introduced in Sect. 2. Section 3 puts forward the results obtained in terms of time series of BrO along with time series of the aerosol optical thickness, near-surface O_3 and meteorology parameters. Then it deepens into the details of the vertical information gained after these observations and assesses the budget and distribution of inorganic reactive bromine in the troposphere of Antarctica. Section 4 summarizes the work.

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2 Observations from two Antarctic stations

During 2015, ground-based spectroscopic measurements were performed from two Antarctic research stations: Marambio and Belgrano II. Details of the measurement sites and methods are provided below, along with ancillary observations.

2.1 Measurement Sites

In 2010, in collaboration with the National Antarctic Direction of Argentina / Argentinian Antarctic Institute (DNA/IAA), INTA deployed a MAX-DOAS (Multi-axis Differential Optical Absorption Spectroscopy, e.g., Platt and Stutz, 2008) instrument at the research base of Belgrano II (77º 52' S, 34º 37' W; 256 m a.s.l,), at the southern end of the Weddell Sea (from now on referred to as "Belgrano"). Later on, in 2015, similar instrumentation was installed in the site of Marambio (64º 13' S, 56º 37' W; 198 m a.s.l.), located on Seymour Island (a small island just east of James Ross Island), in the northern tip of the Antarctic Peninsula. Since then, MAX-DOAS observations have been kept remotely. In 2016, both DOAS stations were accepted as part of the NDACC (Network for the Detection of Atmospheric Composition Change, http://www.ndsc.ncep.noaa.gov/), aiming at long-term atmospheric observations (e.g., De Mazière et al., 2017). Note that, given their location around the Weddell Sea, long-term trace gas observations from these Antarctic sites provide a great opportunity for investigating the troposphere-sea ice interactions in two different scenarios: a station surrounded by seasonal sea ice (Marambio) and another where the perennial (edged) sea ice dominates (Belgrano). Figure 1 shows the locations where INTA has instrumentation deployed in Antarctica and the sea ice concentration (Spreen et al., 2008) surrounding these stations by the end of the austral summer and by mid-winter of the referred year 2015, which was the first year that both instruments operated simultaneously.

2.2 Measuring Method

The spectral measurement technique used for the observations presented in this work was MAX-DOAS, gathering UV/VIS scattered skylight in the sunlit atmosphere. Through this technique, tropospheric vertical profiles of aerosol extinction coefficients (AEC) and BrO volume mixing ratios (vmr) can be inferred. Specific details of the instruments deployment and the spectral analysis and inversion scheme are provided in the following.

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2.2.1 MAX-DOAS instruments

Although in few occasions tropospheric BrO has been measured in remote regions with in situ techniques (e.g., chemical ionization mass spectrometry, Liao et al., 2011), the operational activities in remote and hostile environments renders the DOAS (Differential Optical Absorption Spectroscopy) technique as a very suitable approach given its sensitivity, versatility and instrumental endurance (e.g., Platt and Stutz, 2008). Either with active set-ups (e.g., Long path-DOAS) or with passive ones (e.g., zenith-DOAS, MAX-DOAS, satellite observations), the DOAS technique has been used broadly to research the troposphere in remote environments (e.g., Wagner and Platt, 1998; Bobrowsky et al. 2003; Wagner et al., 2007; Saiz-Lopez et al., 2007a,b; Puentedura, et al. 2012, Prados-Roman et al., 2015; Peterson et al., 2017). In particular, the MAX-DOAS instrumental set-up referred to in this work consists of a telescope scanning the atmosphere at different elevation angles inferring with it vertically-resolved information of the status of the atmosphere regarding aerosols and trace gases (e.g., Hönninger et al., 2004; Wagner et al., 2004). This is indeed an advantage that the MAX-DOAS configuration offers over the standard set-up of the e.g. long path-DOAS and also over in situ instruments (e.g., chemical ionization mass spectrometry, CIMS), whose information is commonly limited to the instrument's altitude. Also, the MAX-DOAS specific ability to characterize the low troposphere overcomes the often limited sensitivity of the satellite observations to the planetary boundary layer.

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The hardware and software of the MAX-DOAS instruments referred to in this work were developed by INTA. For decades, the group has been investigating the atmosphere from different sites of the world by means of the DOAS technique, particularly from polar regions (e.g., Gil et al., 1996; Gil et al., 2008; Yela et al., 2017). The two MAX-DOAS instruments referred to in this study consist of an outdoor unit with a temperate pointing system developed and built at INTA (Figure 2), comprising a stepper motor and a telescope with an 8 cm focal length fused silica lens yielding a field of view of 1º. The sunlight is focused in a quartz fibre bundle which is directed into the indoor unit comprising a temperature-stabilised Czerny-Turner monochromator and a CCD camera fully developed by INTA based on an HAMAMATSU S7031-1008 sensor, kept at -40 ºC ± 0.05 ºC with a temperature control developed and built at INTA. Both instruments operate in off-axis mode scanning the atmosphere from the horizon to the zenith every 15 minutes while the solar zenith angle (SZA) is lower than 85º. For SZA higher than 85º, the telescopes are fixed at zenith position and during the polar night no measurements are performed (i.e., April-August in Marambio and March-September in Belgrano). Further details of the MAX-DOAS instruments installed at Antarctica are provided in Table 2.

2.2.2 Spectral analysis and vertical profile inversion

The spectral analysis of the DOAS observations shown in this work was performed with the INTA's software LANA (e.g., Gil et al., 2008; Peter et al., 2017). The retrieval of BrO was centered in the 335-358 nm spectral range, including the absorption cross-sections of BrO (Fleischmann et al., 2004), O_4 (Thalman and Volkamer, 2013), CH_2O (Meller and Moortgat, 2000), OClO (Kromminga et al., 2003), NO_2 (Vandaele et al., 1998), O_3 (Bogumil et al., 2003) and of a pseudo-Ring spectra (Chance and Spurr, 1997), along with a 5^{th} degree closure term and constant intensity offset. In order to decrease possible instrumental instabilities and to minimize the influence of stratospheric trace gases in the retrieval, the zenith spectrum from each scan was used as a reference. Moreover, only data gathered in off-axis mode with SZA < 75º were used in this work.

Similarly, the O_4 differential slant column densities (dSCDs) were also retrieved (337-370 nm spectral window) in order to invert the vertical profile of the aerosols extinction coefficient (AEC) and therefore to characterize the scattering properties of the atmosphere and the light path of the photons reaching the detector. The reliability of the aerosol vertical information retrieved by MAX-DOAS observations has already been demonstrated under different visibility conditions (e.g., Frieß et al., 2016). This retrieval is based on the concept that the concentration O_4 is known and stable in the atmosphere. Hence, a variation in the O_4 dSCDs is usually related to a change of the optical path, generally due to the presence of aerosols (e.g., Hönninger et al., 2004; Wagner et al., 2004). The inverted AEC vertical profile was then used as input for the linear inversion of the vertical profile of BrO vmr.

In this work, the inversion of the vertical profiles of the AEC and the BrO concentration was based on the Optimal Estimation Method (e.g., Rodgers, 2000). The radiative transfer model (RTM) used was LIDORT (Spurr 2008) and the inversion scheme was BePRO (BIRA, Clémer et al., 2010). The procedure consisted of a two-step approach. First, the AEC were retrieved from the observed O_4 dSCDs through an iterative nonlinear process (e.g., Hendrick et al., 2014; Córdoba-Jabonero et al., 2016). The inferred AEC was then used to invert the targeted BrO profiles.

The RTM input parameters characterising the profile retrievals were carefully chosen for polar conditions and always bearing in mind that the aim is to gain long-term observations in the hostile conditions of Antarctica. For the measurements performed from Marambio station, the pressure (P), temperature (T), O_3 and NO_2 vertical profiles were obtained from standard atmosphere for sub-arctic latitudes (Anderson, 1986). For the observations made from Belgrano, the considered P, T and O_3 profiles were obtained from monthly averaged available ozone-sonde records (from 1999 to 2006, e.g., Parrondo et al., 2014), while the NO_2 profile was taken from the same standard atmosphere. The modelled atmosphere was stratified into layers of 100 m from 0 to 4 km altitude, layers of 1 km from 4 to 6 km (wider grid related to less sensibility at those altitudes) and layers of the same width of those of the standard atmosphere above this altitude. The retrieved profiles were obtained up to an altitude of 6 km. In the inversion scheme, the diagonal elements of the measurement uncertainty covariance matrix were the squared of the dSCDs error after the DOAS fit (1σ). The statistics of the DOAS fit are included in the Supplementary Material. The diagonal elements of the a priori covariance matrix in the inversion was calculated as 100 % of the a priori profile for BrO and based on Clémer et al. (2010) for the aerosol extinction retrieval. Note that, given the large variability of the visibility conditions at Antarctica, the true aerosol profile can strongly differ from the a priori profile. In order to allow the extinction profile retrieval to capture these variations, we followed the method described in Clémer et al. (2010). In this method, the diagonal element of S_a closest to the surface (i.e., $S_a(1,1)$) is set equal to the squared of a scaling factor (ß) times the maximum partial AOD of the extinction profile obtained in the precedent iteration. In this study, ß has been set to 1. The other diagonal elements decrease linearly with altitude down to 20% of $S_a(1,1)$. Note that, despite not being a statistically Bayesian method, it allows the profiles corresponding to large AOD to differ significantly from the a priori, while the profiles with smaller AOD present lower variations from the a priori. The non-diagonal elements were calculated following a Gaussian distribution with a correlation length of 100 m for aerosols and 300 m for trace gases, respectively (e.g., Hendrick et al., 2004). Therefore, the error of the retrieved profiles provided in this work contains the measurement error (experimental dSCDs error) and the smoothing error of the retrieval. The last takes into account that the retrieval is an estimate of the true profile smoothed by the averaging kernel functions.

Given that the measurements in Antarctic stations are frequently affected by blowing snow, the aerosol optical properties were obtained using Henyey-Greenstein phase functions for single scattering albedo SSA = 0.999982 and asymmetry parameter g = 0.89, corresponding to typical values of clean ice crystal (e.g., Frieß et al., 2011). After several tests considering typical snow albedos (between 0.8 – 0.9), the surface albedo was set to 0.8. Note that this value is consistent with observations of the sea ice albedo performed in the UV-A spectral range in the Arctic region (e.g., Ehrlich, 2009). In order to avoid unrealistic values, an upper limit for aerosols optical depth (AOD) was set to 0.5, neglecting therefore all the observations made in such complicated conditions from the light scattering point of view. Also, only retrievals with the degrees of freedom higher than 1

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were taken into consideration. The degrees of freedom of the data set presented in this work are summarized on the Supplementary Material (Table S1).

After the AEC vertical profile was estimated at 360 nm by means of the measured O_4 dSCDs, the aimed BrO vmr vertical profiles were retrieved at 338 nm using the calculated AEC as input of the RTM. In order to properly include the inferred AEC in the retrieval of the BrO vmr profiles, they were calculated at the corresponding wavelength using an Angstrom parameter of 2.2 (e.g., Hegg et al., 2010). An exponential decreasing profile corresponding to AOD = 0.02 was chosen as a priori for the AEC vertical profile. The scale height (SH) of the a priori AEC was set to 0.5 km for Belgrano and to 2 km for Marambio, since these values provided the lower differences between observed and modelled O_4 dSCD for each station. The a priori BrO vertical density corresponded to an exponentially decreasing profile with SH = 1 km and a surface value of ~1.5 pmol mol^{-1}.

2.3 Ancillary Data

As a consequence of its logistically-complicated location and to very harsh weather conditions, there are very scare observational data describing the atmosphere at Antarctica. In order to interpret the aimed bromine results, additionally to the spectra gathered by the MAX-DOAS measurements, near-surface O_3 vmr measured at both stations were also compiled. At both sites, the surface O_3 was measured with ozone analyzers (Thermo Environmental Instrument, Thermo Fisher Scientific, model 49; i.e., TEI49). The operation principle of this in situ instrumentation consists in the attenuation of an ultraviolet light beam (254 nm) by an air sample containing ozone and has a manufactured sensitivity and limit of detection of 1 nmol mol^{-1}. In the case of Marambio station, which contributes to the GAW network (Global Atmosphere Watch, WMO- World Data Centre for Greenhouse Gases WDCGG), the measurements of surface O_3 were carried out by the National Meteorological Service of Argentina (SMN) and can be retrieved from the WMO - World Data Centre for Greenhouse Gases (https://ds.data.jma.go.jp/gmd/wdcgg/). These data from the TEI49 from Marambio is compared every year against the regional standard (WMO, RCC-BsAs, TEI49PS). At the research site of Belgrano, the year-round surface O_3 is measured by INTA since February 2007 (e.g., Jones et al., 2013). At this site, the inlet of the analyzer, protected from rain, snow and dust, is placed 0.85 m above the roof of the base in the cleanest area of the station, being free of pollution from the research site.

Additionally, the weather information was obtained from the observations performed by the SMN at Marambio (WMO station 89055) and by INTA at Belgrano. In the case of Marambio, the weather station is installed in the so-called Scientific Pavilion of the Marambio Antarctic Station together with an Automated Met Station (AMS), which measures the temperature, humidity, precipitation, wind speed and direction besides the atmospheric pressure. The data acquisition system is carried out through a Datalogger Cambell Scientific CR100. In the case of Belgrano, the weather parameters are gathered by a Vaisala weather station installed at the site in 2009. In this case, the weather station is installed on the roof of the base, in a 210 cm mast and it provides wind speed and direction, atmospheric pressure, temperature and relative humidity.

3 Results and Discussions

This section is divided into three main parts. First, it presents the time series of the DOAS measurements and the ancillary observations performed during 2015, offering an overview of the information gathered within the frame of this study. Then, the details and discussion of the retrieved BrO and AEC vertical distributions at the two sites are provided. Finally, the activation of bromine in the Antarctic troposphere during 2015 is investigated along with the reactivity of the Antarctic troposphere with regard to inorganic reactive bromine.

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3.1 Time series

This section presents the observations gathered during 2015 at each station. It first shows the DOAS measurements in terms of aerosol optical depth (AOD) and BrO vertical column densities (VCD). Later on, it shows the results of the ancillary observations (weather parameters and surface ozone).

3.1.1 DOAS observations: BrO VCD_{2km} and AOD_{2km}

Herein, we present the AOD and the BrO VCD measured with the DOAS technique during the sunlit period of 2015. This period lasted for about 8.5 months in Marambio and 7.5 months in Belgrano (Fig. 3 y 4). Due to instrumental issues, there were missing data at the beginning of the year at both stations. Note, however, that the polar sunrise was well covered at both sites and therefore the peak season of the bromine activation (e.g., Simpson et al., 2007).

As mentioned in Sect. 2.2.2, the sensitivity of the MAX-DOAS observations decreases with altitude. Hence, aiming also at comparing both stations, here we refer to the AOD and BrO VCD inferred in the first 2 km of the troposphere at each site (i.e., AOD_{2km} and VCD_{2km}, respectively). Figure 3 shows the AOD_{2km} retrieved at both stations (mean relative error of 40 %). Observations indicate that the aerosol optical thickness of the low troposphere at Belgrano was generally higher than at Marambio. At Belgrano, 62 % of the AOD_{2km} was lower than 0.05 (12 % between 0.05 and 0.1) compared to 90 % of the AOD_{2km} at Marambio that was below 0.05. In addition to this geographical dependence of the AOD, Fig. 3 also suggests that the period with higher aerosol thickness lasted longer in the southernmost station of Belgrano. As seen in the figure, while high AOD were observed at Belgrano during most of the sunlit period, the AOD at Marambio intensified from September until December. The geographical variability of the aerosol load within Antarctica has already been reported (e.g., Savoie et al., 1993; Minikin et al., 1998), although further studies on the distribution of aerosols are needed in order to understand the interannual variability of the different sources (e.g., Giordano et al., 2017). Further insights of the aerosol properties within the Antarctic troposphere during 2015 will be provided in a following work (Gómez-Martín et al., 2018, in preparation).

Regarding the aimed BrO, the pseudo-vertical column densities (VCD_{2km}) are calculated by integrating the BrO concentration obtained within the first 2 km of the troposphere. Results, shown in Fig. 4, indicate that BrO was present in the sunlit Antarctic troposphere at both stations. The median BrO VCD_{2km} values at both sites were quite similar (~ $0.5 \cdot 10^{13}$ molec cm^{-2}, with a mean relative error of 10 %) and 75 % of the observations at both stations fell below a similar value ($0.8 \cdot 10^{13}$ molec cm^{-2}). Also, at both sites, the maximum BrO VCD_{2km} values were observed after the polar sunrise (i.e., SZA < 75° herein) and the BrO levels were undetectable just before the polar sunset (i.e., SZA > 75° herein) and immediately after the polar sunrise. However, the magnitude and variability of the BrO VCD_{2km} maximums direct the difference between both stations, with an absolute maximum BrO VCD_{2km} observed in Marambio being 3.2 times higher than in Belgrano. As can be observed in Fig. 4, it is also worth noticing the clear photolytic activation of BrO in Marambio during austral spring, with levels an order of magnitude higher than the median BrO VCD_{2km} values at the station. Insights on the vertical distribution of BrO and aerosol extinction in the Antarctic troposphere are provided later on in Sect. 3.2.

3.1.2 Ancillary observations: meteorological parameters and surface O_3

Aiming at contextualizing both research stations, this section briefly presents some weather parameters and the near-surface ozone characterising the sites of Marambio and Belgrano during 2015.

Regarding the weather information at each station, the mean observed values of meteorological parameters such temperature (T) and precipitation are provided in Table 3. Overall, observations indicate that Belgrano station sits at a dryer and colder location where, in 2015, temperatures dropped below -40º C. Regarding the wind measurements, the wind rose of the 2015 measurements at each station is shown in Fig. 5 for low, medium and high wind speeds. Note that the information reported for 2015 at Marambio is consistent with the recent publication of Asmi et al. (2018) referred to the 2013-2015 period. The 2015 observations at both stations indicate that, although the higher gusts of wind were quite similar at both stations (~34 m s^{-1}), the

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median wind speed at Marambio (7.2 m s^{-1}) was in general 50% higher than in Belgrano. Concerning the wind direction observed at each station during 2015 (Fig. 5), while the air masses arriving at Marambio had no clear dominant direction, those arriving at Belgrano came usually from the south-south west. Hence, based on the wind rose (Fig. 5), during 2015 Marambio was mostly influenced by air masses coming along the west edge of the Weddell Sea but also from the surrounding Scotia and Amundsen Seas, while the air masses from continental Antarctica dominated the observations performed at Belgrano station. As for the near-surface O_3, the annual variation at both stations showed the seasonal pattern expected in high-latitude stations (Antarctic and sub-Antarctic regions, Fig. 6) and is typical of remote, low NOx environments with O_3 being accumulated during winter (maximum) and destroyed (minimum) during summer. Also, the observed amplitude of the surface O_3 annual cycle at both stations were also characteristic of an Antarctic station (e.g., Helmig et al, 2007, Legrand et al., 2016). While in 2015 the median values of surface O_3 were quite similar at both locations (23 nmol mol^{-1} at Marambio and 24 nmol mol^{-1} at Belgrano), the maximum values reported at Marambio (36.8 nmol mol^{-1}) were about a 10 % higher than those observed at Belgrano station. Regarding the absolute minimum surface O_3 detected, 2015 observations at Marambio indicate ozone depletion events (ODEs) with measurements very close or below instrumental detection limit (1 nmol mol^{-1}), while the minimum surface O_3 detected in Belgrano was not lower than 6 nmol mol^{-1}. This suggests that, compared to Belgrano, Marambio is either as a more photochemically active region or a region more exposed to ozone depleted air masses. Noteworthy is also the high variability of surface ozone observed at Marambio during the polar sunrise as compared to observations at Belgrano station. This behaviour is characteristic of a coastal Antarctic station as reported by e.g. Helmig et al. (2007).

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3.2 Vertical profiles of BrO in the Antarctic troposphere

The time series of BrO vmr retrieved during 2015 in the lowest kilometers of the troposphere of Marambio and Belgrano are provided in Fig. 7, along with the AEC. For clarity, Fig. 8 shows in more detail some examples of the time evolution of BrO as measured at Belgrano and at Marambio and in Fig. 9 the sea ice conditions during those days. The wind speed on those selected days was below 10 m s^{-1}. As can be seen in Fig. 8, the maximum of BrO was located close to the surface although its specific altitude depended on the day, located always below 1 km of altitude. Some days the peak of BrO was located just above the surface (e.g., 11th November in Belgrano or 25th September in Marambio in Fig. 8, both days with winds ≤ 6 m s^{-1}), while in others that BrO maximum was slightly elevated suggesting heterogeneous reactions aloft (e.g., 29th October in Belgrano with wind speed ≤ 2 m s^{-1} or 28th November in Marambio with wind speed 6.5 - 9 m s^{-1}, in Fig. 8). Worth noticing is also the time and seasonal variability of the occurrence of the maximum of BrO vmr. As shown in Fig. 8, on e.g. 29th of October in Belgrano, some days BrO vmr followed the diurnal evolution with a noon maximum predicted by model studies (e.g., Saiz-Lopez et al., 2008) and observations (e.g., Buys et al., 2013) where the BrO formation is linked to the solar irradiance and the photolysis of bromine sources (e.g., Br_2, BrCl). Based on the calm wind conditions observed during that particular day (29th of October), those sources are most probably not far from the station of Belgrano (Fig. 9). On the other hand, e.g. on 28th of November in Marambio (Fig. 8), on other days BrO was present in the low troposphere with a double maximum (morning and evening), characteristic of a late spring behaviour and more related to bromine being recycled e.g. through HOBr (e.g., von Glasow et al., 2002; Pöhler et al., 2010; Liao et al., 2012; Buys et al., 2013). The slightly higher south-easterly winds during those observations on 28th of November at Marambio, points towards bromine sources in the Weddell Sea (Fig. 9). This shown time and altitude dependence of the BrO distribution in the troposphere reinforces the benefits of the sort of instrumentation employed in this work, which offers vertically resolved information and is able to perform long-term observations.

Figure 10 shows a summary of the BrO vmr vertical profiles observed at each station during the sunlit period of 2015. The median BrO vmr in the lowest layers of the troposphere (< 0.5 km) was similar at both stations (~1.6 pmol mol^{-1} above the surface) with 75 % of the BrO data below 2.5 pmol mol^{-1}. However, as shown in Fig. 7, the maximum BrO values observed

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after the polar sunrise (i.e., SZA < 75°) at Marambio (26.0 ± 0.4 pmol mol^{-1}) were over a threefold of those observed after the sun rose at Belgrano (see also Fig. 4). This maximum BrO was detected during austral spring at ~ 200 m of altitude, with a magnitude dependent on the station. This slightly elevated peak of BrO (e.g., Fig. 10) and mentioned also above, has already been foreseen by studies accounting for the vertical gradient of the acidity of the aerosols and/or the effect of convection (e.g., von Glasow et al., 2002; Wagner et al., 2007). Also note that, as shown in Fig. 7, while in Belgrano the maximum BrO observed during October-November (8.1 ± 0.6 pmol mol^{-1}) quadrupled its mean value measured during the rest of the sunlit period, the BrO values observed in Marambio just after the sunrise were over 15 times higher than the BrO mean values at that station. All this suggests that the halogen reactivity at Marambio is considerably stronger than at Belgrano (see also Sect. 3.3). The BrO vmr ranges reported herein (Fig. 10) are comparable to previous tropospheric Artic studies (e.g., Tuckermann et al., 1997; Hönninger and Platt, 2002; Prados-Roman et al., 2011; Liao et al., 2012; Peterson et al., 2017; Simpson et al., 2017) and consistent with the few existing Antarctic measurements (e.g., Table 1). By adding the BrO measurements provided in the frame of this work to the few previous ground-based observations performed at Antarctica from different sites, Fig. 11 depicts an updated map of the maximum values of BrO observed in the lower troposphere of Antarctica, pointing once more its heterogeneity with regard to reactive bromine load. Section 3.3 offers a closer look to this heterogeneity.

Overall, the observations presented in this study indicate that the vertical profile of BrO in the Antarctic troposphere descended with altitude (Fig. 10). Note that, in this work, the detection limit of BrO is regarded as the threshold value above which the inferred BrO is significantly higher than the noise of the inversion. In this case, it is defined as double of the inversion error (Sect. 2.2.2) and corresponds to a mean value of 1 pmol mol^{-1}. In previous studies of the Antarctic troposphere (e.g., Frieß et al. 2004 and Roscoe et al. 2014), the presence of uplifted reactive bromine was suggested. While the work of Frieß et al. (2004) remarked the presence of reactive bromine uplifted (> 4 km altitude) due to advection processes, in the work of Roscoe et al. (2014), the authors where able to differentiate between 2 types of BrO vertical profiles: those with only near-surface BrO (centered at 200 m) and those with double peak (centered at 2 km and near-surface). In the work here presented, no uplifted layers (> 2 km) of BrO were detected although, given the limited vertical information content of the MAX-DOAS observations (Supplementary Material), double peak type of BrO profiles cannot be ruled out. Although the definition of the height of the boundary layer over ice and snow surfaces (e.g., Anderson and Neff, 2008) is out of the scope of this work, former studies place the top of the boundary layer in Antarctica between 100 m and 2 km, depending on the boundary layer parameterization, station and time of the year (e.g., King et al., 2006; Nygård et al., 2013). Nygård et al., (2013) marked the height of the boundary layer at Marambio between 1 and 1.4 km for the non-winter periods of our interest, and the ozone-sondes performed at Belgrano set that height between 1 and 2.5 km at that site (e.g., Parrondo et al., 2014). However, the altitude threshold between the boundary layer and the free troposphere cannot be assessed on the time resolution of our observations. Additional investigations at the two sites would be needed to confirm whether BrO reaches the free troposphere and, given the case, to assess the budget of BrO in the Antarctic free troposphere. Note that previous work on polar environments set BrO below 1.5 and 2 pmol mol^{-1} in the Arctic and Antarctic free troposphere, respectively (e.g., Frieß et al., 2011; Prados-Roman et al., 2011; Peterson et al., 2017; Hüneke et al., 2017).

In addition to the BrO knowledge gained after this work, noteworthy is also the information related to the vertical AEC (Fig. 7, lower panels), sustaining the particularity of the surroundings at each station. In addition to the aforementioned different aerosol optical thickness at both stations (Sect. 3.1.1), there is also a noticeable difference regarding the seasonality and altitude of the maximum AEC at the two sites. While at Marambio the peak of the AEC appeared close to the surface with a clear maximum extinction observed in November, the observations performed from Belgrano suggest that, at this site, the height of the aerosol layer was much more variable than at Marambio, manifesting once more the relevance of vertically resolved observations within the Antarctic troposphere. As mentioned before, the work of Gómez-Martín et al. 2018 (in preparation) will address these issues.

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3.3 BrO_x in Antarctica

In order to investigate the hinted heterogeneity of the Antarctic lower troposphere regarding reactive bromine (BrO_x = Br + BrO), in this section the budget of bromine [Br] is estimated considering steady state of BrO in a pristine atmosphere with virtually no NO (e.g., Zeng at al., 2006), a concentration of ClO of $1.7 \cdot 10^8$ molec cm^{-3} (typical of Arctic conditions, e.g., Halfacre et al., 2014), and concentrations of HO_2 and OH of $2.2 \cdot 10^7$ molec cm^{-3} and $3.9 \cdot 10^5$ molec cm^{-3}, respectively (mean values observed at the Antarctic station of Halley, e.g., Bloss et al., 2007). Hence, [Br] can be estimated from the observed BrO and O_3 concentrations as (e.g., Hausmann and Platt, 1994; Le Bras and Platt, 1995; Zeng et al., 2006; Stephens et al., 2012):

$$[Br] = [BrO] \frac{2\, k_{BrO+BrO}\,[BrO] + k_{BrO+ClO}\,[ClO] + k_{BrO+HO_2}[HO_2] + k_{BrO+OH}\,[OH] + J_{BrO}}{k_{Br+O_3}\,[O_3]} \quad (2)$$

where *J* represents the rate of photolysis ($J_{BrO} = 3.10^{-2}$ s^{-1} for noontime in the polar spring; e.g., Thompson et al. 2015) and *k* the different reaction rates (Table 4). Since the measurements of O_3 were performed near the surface, accordingly only the BrO retrieved in the lowest atmospheric grid (i.e., 100 m) is considered for the calculation of the Br and BrO_x budgets at each site. The possible influence of horizontal advection and blowing snow is limited in the data set by applying an upper limit for the wind speed of 6 m s^{-1}. Note that previous studies pointed 8 m s^{-1} as the wind threshold for blowing snow (e.g., Jones et al., 2009) and others indicated that the steady state approximation is valid for wind speeds lower than the 6 m s^{-1} threshold considered in here (e.g. Liao et al., 2012).

Based on Eq. (2) and observed near-surface BrO and O_3 under low wind conditions (timestamp of the DOAS measurements), Fig. 12 shows the 2015 seasonal evolution of the BrO_x budget at each station and Fig. 13 presents the BrO-Br-BrO_x statistical analysis in the form of box charts at each site (only data for SZA < 75° are considered). Since the kinetic calculations used herein are based on observations performed under low wind conditions, these budgets may be considered as representative of the surroundings of each station. Figure 12 indicates that, in agreement with Peterson et al. (2015), the presence of reactive bromine at both stations do not only correspond to advected bromine-enriched air masses or blowing snow. As expected from previous polar studies (e.g., Simpson et al., 2007 and references therein) and shown in Fig. 12, the maximum bromine-related reactivity of the troposphere at both stations takes place just after the photolysis is triggered with the polar sunrise. As shown in Fig. 12, this maximum reactivity does occur at a medium O_3 regime at both stations (10-25 nmol mol^{-1}). The study of the BrO-Br-BrO_x data (Fig. 13) indicates that, during the sunlit period of 2015, the mean budget of BrO_x at Belgrano (2.0 pmol mol^{-1}) was ~ 17 % higher than at Marambio. However, just after sunrise (i.e., SZA < 75°), the BrO_x budget (and hence the oxidizing capacity) at Marambio triplicated the one at Belgrano (e.g., Fig. 12). Estimated values for atomic bromine radical present in the lowermost troposphere during the sunlit period of 2015 were up to 1.4 pmol mol^{-1} at Belgrano and up to 3.4 pmol mol^{-1} at Marambio (Fig. 13). These ranges are in line with previous model studies for Antarctic latitudes (e.g., von Glasow et al., 2004; Saiz-Lopez et al., 2008) and in the lower limit of Artic model studies (e.g., Thompson et al., 2017).

Overall, these estimations indicate that the BrO_x partitioning was clearly driven by BrO at both sites, indicating that ozone in general was not fully depleted as confirmed by the observations (Sect. 3.1.2). The evolution of the ratio Br to BrO after the polar sunrise (SZA < 75°) is shown in Fig. 14 for each site. The initial Br : BrO after dawn was ~ 0.05 at both stations. Throughout the polar spring, during ODEs, that ratio raised over fourfold at both sites. The baseline of the ratio Br to BrO ratio during the sunlit period could be approximated by an exponential growth with a time constant of about 10 days in Belgrano and 17 days in Marambio (blue line in Fig. 14). Towards summer, that baseline increased up to 0.17 at Belgrano and to 0.10 at Marambio. In the simplified scheme suggested by Eq. (2) and discussed in this section, this Br : BrO increase could be explained by the overall summer decreased of surface O_3 compared to springtime (Fig. 6). Additional investigations on the variability and geographical distribution of the bromine source gases throughout the year are suggested to address the bromine pathways in the Antarctic troposphere and their consequences. Bearing in mind this simplified scheme, based on Eq. (1) and the same fixed concentration of ClO as for Eq. (2) (i.e., to typical values in the Arctic environment), the bromine-mediated

Eliminado: and a concentration of ClO, HO_2 and OH of $1.7 \cdot 10^8$ molec cm^{-3}, $2.2 \cdot 10^7$ molec cm^{-3} and $3.9 \cdot 10^5$ molec cm^{-3}, respectively (e.g., Halfacre et al., 2014; Bloss et al., 2007)

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ozone loss rate can be assessed at each research site for the different BrO and O_3 regimes observed at low wind speed. Similar median BrO values measured during 2015 at both stations (1.6 pmol mol^{-1}) yield similar ozone loss rate of 0.4 nmol mol^{-1} day^{-1} at both sites. During the bromine more active season of October-November at Belgrano (e.g., Fig. 12), this rate speeds up to 2.9 nmol mol^{-1} day^{-1}. During September at Marambio (peak bromine season at that station), the bromine-mediated ozone loss occurs at a much faster rate between 0.7 and 17.4 nmol mol^{-1} day^{-1} (i.e., up to 6 times faster than at Belgrano). Former works have estimated that the bromine driven ozone loss in the polar atmosphere represents 44% of the total O_3 chemical loss (e.g., Liao et al., 2012; Thompson et al., 2017). Therefore, in the sites referred to in this work the shortest (i.e., at highest BrO_x and low wind speed) ozone chemical lifetime τ_{O3} expected is 2.6 days at Belgrano and 0.7 days at Marambio. Note that the estimations provided herein are limited by the information content inherent in the in situ technique measuring near-surface ozone (i.e., information at the exact instrument's location) compared to the DOAS data which integrates information several kilometers away of the instrument (depending on scattering conditions) in the horizontal field of view and also in the vertical (see retrieved averaging kernels in the Supplementary Material). Further studies would be needed to confirm these numbers, including investigations on different sources and sinks of bromine radicals in the Antarctic environment which herein are based on ozone depletion through (only) the BrO-BrO and BrO-ClO channels, dominant however in the polar spring (e.g. Simpson et al., 2007).

All these kinetics approximations are historically based on conclusions from numerical models and laboratory and campaigned-based observations obtained in the polar regions (mainly the Arctic; e.g., Simpson et al., 2007). Nevertheless, the year-round erratic behaviour of the wind speed in Antarctica at each station makes complicated the verification of these estimated (low wind) τ_{O3} with observations. However, the exemplary days provided in Fig. 8 with higher BrO at each station (upper figures) may serve the purpose (low wind speeds). For instance, based on the ozone observations (Fig. 6), the rate of O_3 depletion measured at Marambio (25th September) was 4.1 nmol mol^{-1} h^{-1} and at Belgrano (29th October) it was of 0.58 nmol mol^{-1} h^{-1}. Therefore, as suggested by the above related theoretical calculations, the destruction of surface O_3 during the bromine peak season was indeed much faster at Marambio (7 times faster than in Belgrano). Considering the mean O_3 vmr observed at each station on those days, the observed τ_{O3} at Belgrano was of 1.3 days while at Marambio it was tenfold shorter. Note that, as shown in Fig. 8 (upper figures), on those specific days the BrO load at Marambio was also over an order of magnitude higher than at Belgrano. Comparing these observed τ_{O3} with the τ_{O3} estimated above from kinetics, the measurements show shorter τ_{O3} at both stations (50 % shorter at Belgrano and 18 % shorter at Marambio). Despite the low statistical meaning of this sort of "case study" exercise, the resemblance of the observed and calculated τ_{O3} at Marambio suggests that the assumptions made at Marambio's surrounding (e.g., the Br-Cl channel dominates the ozone depletion) is close to reality which seems not to be the case for Belgrano's surroundings. This reinforces, once more, the need of further long-term investigations for a better understanding of all the processes and key parameters involved in the halogens' pathways in the Antarctic troposphere.

4 Summary and Outlook

As a result of its remoteness and a more complex logistics compared to the Arctic region, the characterization of the Antarctic troposphere with regard to halogen compounds is still very scarce. Based on contemporary ground-based observations performed at two Antarctic sites during 2015 (new sites as far as tropospheric BrO observations is concerned), this study reports on the presence and vertical distribution of reactive inorganic bromine in the low troposphere at the two sites and discusses the geographical distribution of BrO_x. Prior to this study, throughout Antarctica only five sites had reported ground-based observations of BrO in the low troposphere. With the appropriate instrumental set up in the research stations of Belgrano and Marambio, INTA has expanded this net considerably. Moreover, to the authors' knowledge, this is the first study where these bromine observations are reported simultaneously from two Antarctic stations making possible to gain an insight into

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the geographical distribution of reactive bromine in the Antarctic troposphere. Additionally, through the 2015 MAX-DOAS measurements performed at the two sites, this work presents vertically resolved observations of BrO at two different Antarctic stations with a dedicated inversion scheme for inferring the vertical distribution of BrO throughout the Antarctic troposphere. Furthermore, the aerosol extinction and the surface ozone at the two sites are also provided.

Overall, results show the expected seasonal and daytime variation of BrO related to the photolytic activation of reactive bromine triggered by the polar sunrise at the two sites. However, as referred above and unlike some former studies, during the sunlit period of 2015 no elevated plumes of BrO were detected above 2 km. Also, this study reports on the positive detection of BrO in the low troposphere (< 2 km) of Antarctica even under low wind conditions, suggesting that the presence of this trace gas is not only related to horizontal advection and pointing towards surface emissions and vertical mixing. As for the vertical and geographical distribution of BrO in the lower layers of the troposphere, observations indicate a slightly elevated BrO peak at 200 m at both stations, with a maximum value measured at Marambio considerably higher than the observed at Belgrano (26 pmol mol^{-1} vs. 8 pmol mol^{-1}, respectively).

In general, the observations and assessments presented in this work reveal a remarkable geographical heterogeneity of the Antarctic low troposphere with regard the budget of reactive bromine. Beyond blowing snow, the inferred threefold enhancement of BrO_x at Marambio compared to Belgrano after the polar sunrise denotes a geographical heterogeneity also on the bromine sources. Marambio sits on a region surrounded by open waters and seasonal sea ice while the dominant sea ice nearby Belgrano is perennial (Fig. 9). Since bromine explosions are linked to heterogeneous reactions related to e.g. sea ice, open leads and snow surfaces, the type of sea ice and its seasonal evolution around each station may be a good starting point to tackle the bromine sources riddle and to investigate how climate change may affect the budget of BrO_x in the troposphere of Antarctica. Moreover, the geographical distribution of BrO_x and its partitioning addressed in this work also suggests that the reactivity of the troposphere at Marambio is particularly enhanced compared to other Antarctic sites ("hot spot"). Since the presence of BrO_x in the polar atmosphere represents a sink for elemental mercury, this study also reveals the tip of the Antarctic Peninsula (Marambio) as a region for potentially enhanced mercury deposition (bioaccumulation) worth looking into. Also, dedicated investigations combining models and collocated observations of e.g. halogenated substances (not only BrO), organic compounds, DMS, NO_x, HO_x, particles and sea ice properties at different stations, could assist a thorough study of the bromine sources and pathways at Antarctica, their geographical distribution and their projections under a changing environment.

Besides the bromine-related information gained after work, this study also emphasizes the benefits of deploying quality instrumentation in pristine and remote locations able to provide not only surface but also vertically resolved information. It also shows the scientific benefits of maintaining long-term observations despite the efforts related to sustaining research activities in such hostile environment. The data provided by the two ground-based instruments presented herein may, for instance, assist the satellite retrievals to distinguish between tropospheric and stratospheric BrO signal and hence facilitate a more accurate assessment of e.g. stratospheric BrO and ozone trends. Additionally, they could also serve chemistry-climate models for constraining the chemistry behind processes specifically related to polar regions, areas where global models are often weak (particularly in Antarctica).

Data availability. Data are available upon request from the corresponding author.

Competing interests. The authors declare that they have no conflict of interest.

Acknowledgements

Sea ice concentration maps are obtained from the website of the Sea Ice Remote Sensing group of the University of Bremen (https://seaice.uni-bremen.de/start/data-archive/). This work was supported by the Spanish Ministry of Economy and Competitiveness (MINECO) under the projects HELADO (CTM2013-41311-P), VIOLIN (CGL2010-20353) and the Spanish

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Código de campo cambiado

contribution to ORACLE-O3 (POL2006-00382). Authors would also like to acknowledge the work done by the different technicians at the stations of Belgrano and Marambio.

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Table 1. Summary of the published ground-based observations of tropospheric BrO made in Antarctica. Published works of tropospheric BrO observations performed from different Antarctic stations. The time periods of the observations, measurements technique used and maximum BrO reported are also included. The "~" in the maximum BrO reported correspond to estimated values. For details, please refer to respective publication.

Publication	Station	Period of the measurements reported	Measurement technique	BrO vmr (maximum pmol mol^{-1})
Kreher et al. (1997)	Arrival Heights (77.8º S, 166.7º E)	3 months in 1995 (autumn and spring)	Zenith sky DOAS	~30
Frieß et al. (2004)	Neumayer (70.6º S, 8.2º W)	17 days during spring 1999 and 17 days during spring 2000	Zenith sky DOAS	~13
Schofield et al. (2006)	Arrival Heights (77.8º S, 166.7º E)	1 month and 22 days during spring 2002	Zenith sky and Direct Sun DOAS	~13
Saiz-Lopez et al. (2007)	Halley (75.6º S, 26.5º W)	12 months, February 2004-February 2005 (i.e., summer, autumn, winter and spring)	LP-DOAS	20
Buys et al. (2013)	Halley (75.6º S, 26.5º W)	38 days during spring 2007	CIMS	13
Grilli et al. (2013)	Dumont d'Urville (66.7º S, 140º E)	4 days during summer 2011/2012	CEAS	< 2
Roscoe et al. (2014)	Halley (75.6º S, 26.5º W)	2 months and 4 days during spring 2007	MAX-DOAS	~25
Frey et al. (2015)	Dome-C (75.1º S, 123.3º E)	1 month during summer 2011/2012	MAX-DOAS	~2-3
This work	Marambio (64.2º S, 56.6º W)	4.5 months in 2015 (spring, summer and part of autumn)	MAX-DOAS	26.0
This work	Belgrano (77.9º S, 34.6º W)	4.5 months in 2015 (spring, summer and part of autumn)	MAX-DOAS	8.1

Table 2. Details of the MAXDOAS instruments installed in Antarctica. The NEVAII instrument is located in Belgrano research station while the NEVAIII instrument is placed in Marambio.

	Belgrano (NEVA II)	Marambio (NEVA III)
Spectrometer	TRIAX 180	MicroHR
CCD	HAMAMATSU S7031-1008	
Spectral resolution (nm)	0.6	0.5
Azimuth viewing angle (°)	62	116
Elevation angles (°)	2, 3, 5, 10, 15, 30, 60, 90	1, 2, 3, 5, 10, 20, 30, 90

Eliminado: at

Eliminado: Autumn and spring 1995

Eliminado: 4 seasons 2004/2005

Eliminado: 3 seasons 2015 (no winter)

Eliminado: 3 seasons 2015 (no winter)

Table 3. Meteorological parameters (temperature T and snow fall) observed during 2015 at both stations. Data are provided by the World Meteorological Organisation (WMO), the Argentinian Meteorological Centre and INTA's meteorological station (Belgrano). The snow fall is based on surface synoptic observations.

Station	Mean T (ºC)	Maximum T (ºC)	Minimum T (ºC)	Coldest month	Mean T in coldest month (ºC)	Days with snow fall (%)
Marambio	-8.2	17.4	-29.9	September	-16.8	60.8
Belgrano	-13.7	3.0	-43.9	August	-19.7	47.7

Table 4. Rates (*k*) of reactions provided in Sect. 1 and employed in Sect. 3.3. The temperature used for the calculations was T = 262 K, similar to the mean temperature observed during 2015 at each station (Table 3).

Reaction	Rate constant (cm^3 $molec^{-1}$ s^{-1})	Reference
$Br + O_3$	$8.02 \cdot 10^{-13}$	Sander et al. (2006)
BrO + BrO	$3.54 \cdot 10^{-12}$	Sander et al. (2006)
BrO + ClO	$7.83 \cdot 10^{-12}$	Atkinson et al. (2007)
$BrO + HO_2$	$3.03 \cdot 10^{-11}$	Atkinson et al. (2007)
BrO + OH	$4.67 \cdot 10^{-11}$	Atkinson et al. (2007)

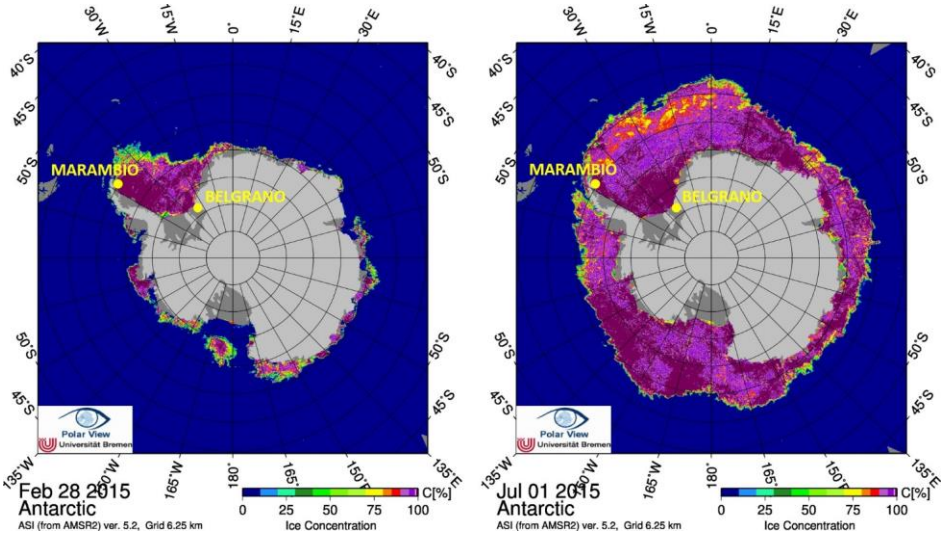

Figure 1: Sea ice concentration surrounding the two Antarctic Stations. The figure shows the sea ice concentration in Antarctica at the end of the austral summer (left) and at mid-winter (right) of 2015. The sea ice maps are downloaded from https://seaice.uni-bremen.de/databrowser/ (Spreen et al., 2008). The two Antarctic stations of Marambio and Belgrano are marked in yellow in both figures. Note the variability of the sea ice mainly nearby Marambio.

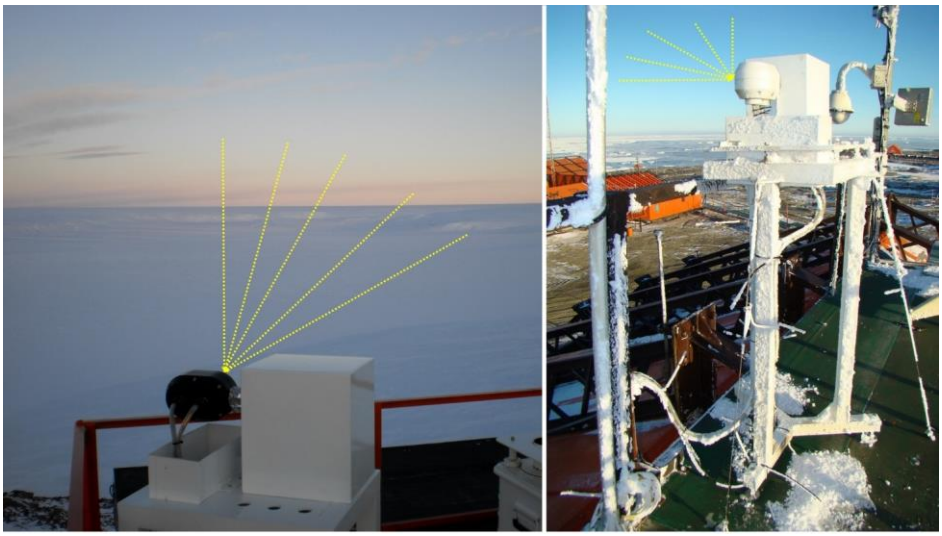

Figure 2: INTA's MAXDOAS instruments mounted in the two Antarctic Stations. The outdoor unit of the MAXDOAS instrument installed in Belgrano is shown in the left figure while the one in Marambio is shown in the right. By scanning the atmosphere at different elevation angles (yellow lines), vertical information of aerosols and trace gases can be retrieved.

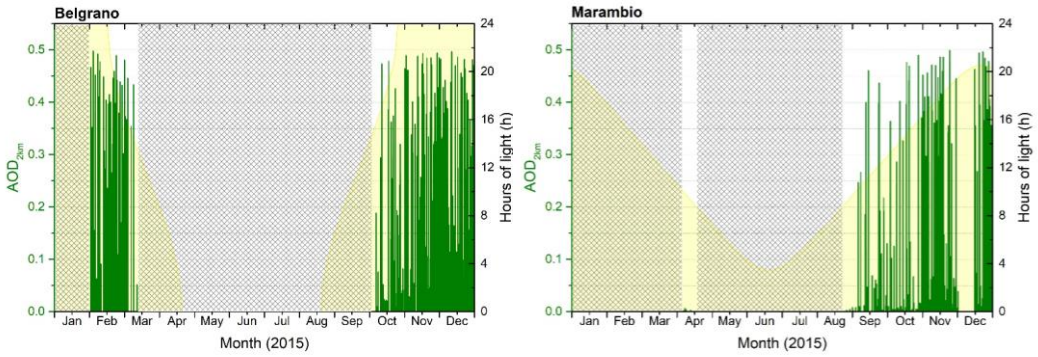

Figure 3: Time series of the aerosol optical depth (AOD) in the first 2 km of the troposphere as observed in Belgrano (left) and in Marambio (right) during 2015. The horizontal scale indicates the time of the year while the left vertical scale shows the AOD. The scale in the right shows the hours of light at each station (shown in yellow in the plots). Note the same scales apply to both figures. Time periods without MAXDOAS observations (i.e., instrumental issues or SZA > 75°) are indicated with shaded areas.

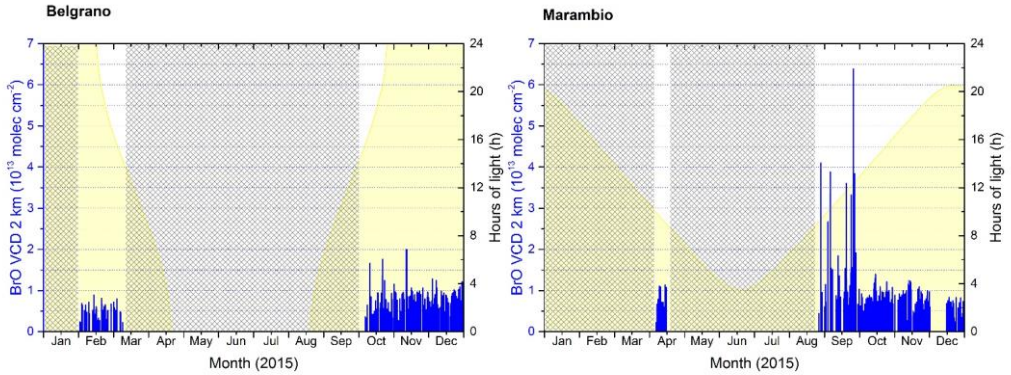

Figure 4: Time series of the BrO vertical column density (VCD) in the first 2 km as observed in Belgrano (left) and in Marambio (right) during 2015. The horizontal scale indicates the time of the year while the left vertical scale shows the BrO VCD. The scale in the right shows the hours of light at each station (shown in yellow in the plots). Note the same scales apply to both figures. Time periods without MAXDOAS observations (i.e., instrumental issues or SZA > 75°) are indicated with shaded areas.

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<*objeto*>**Figure 5: Wind speed at Belgrano (left) and at Marambio (right) during 2015.** The data at Marambio (right figure) derive from the observations performed every 3 h by the Argentinian Weather Service (WMO Station 89055). The data at Belgrano (left figure) are gathered by INTA's weather station place at the site. The Belgrano's raw data (every minute) are shown in grey while the measurement gathered every 3 h in black which is Marambio's data frequency.¶

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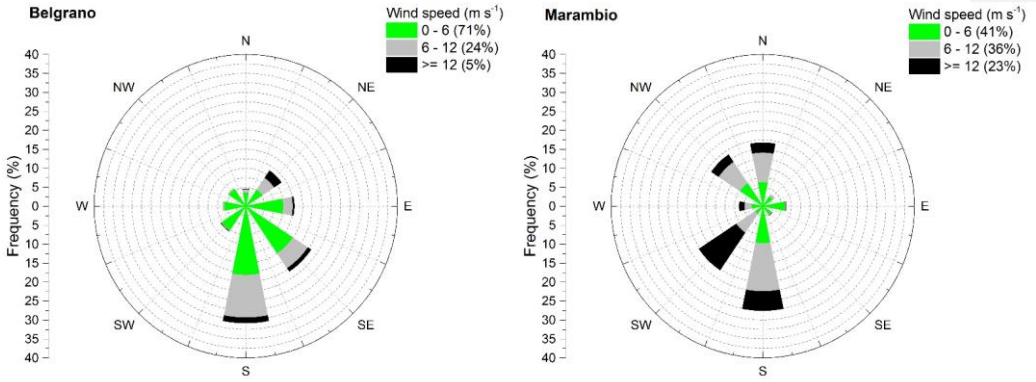

Figure 5: Wind rose at Belgrano (left) and Marambio (right) stations (2015). The vertical scale indicates the frequency count. The Belgrano's data are gathered form INTA's weather station and those at Marambio are provided by the WMO and the Argentinian Weather Service. The colour code in both plots refers to different wind speed regimes: low wind conditions (< 6 m s-1, in green), medium wind conditions (6 - 12 m s^{-1}, in grey) and blowing snow conditions (> 12 m s^{-1}, e.g., Jones et al. 2009, in black). The statistics of each regime at each station during 2015 is indicated in parenthesis.

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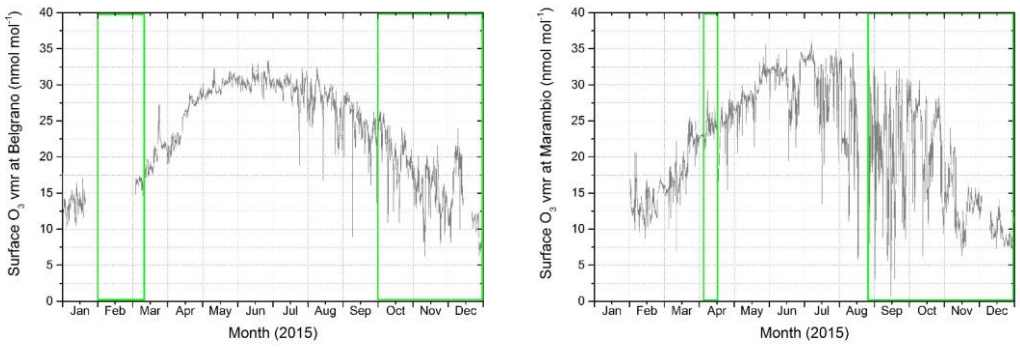

Figure 6: 2015 near-surface ozone observations at Belgrano (left) and Marambio (right) research stations. Note the same vertical scale in both plots. Both data set were gathered by in situ O_3 observations made by INTA (at Belgrano) and by the Argentinian Meteorological Service (at Marambio). The periods with MAX-DOAS data (SZA < 75°) at each station are contained within the green boxes.

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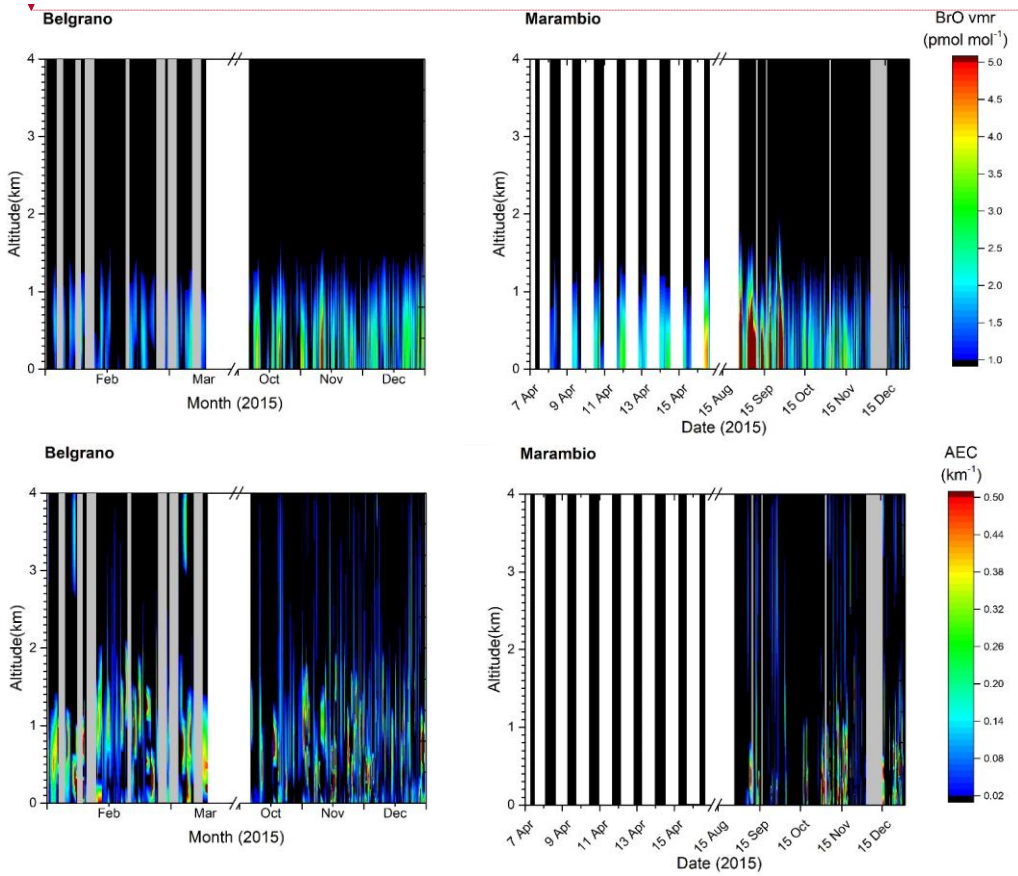

Figure 7: BrO vmr (upper figures) and AEC (lower figures) observed during 2015 in the troposphere of Belgrano (left) and Marambio (right). The vertical scales show the altitude and are forced to be the same for sake of comparison. The horizontal scales indicate the periods of the measurements, which depended on the station. The color code of the upper figures corresponds to the BrO vmr and are forced to be the same for the sake of comparison. The same applies to the color code of the lower figures that indicate the AEC at each station. The BrO vmr higher than 5 pmol mol^{-1} and AEC higher than 0.5 km^{-1} are shown in dark red, while values below detection limit are shown in black. Time periods with no observations (SZA > 75°) are indicated with white areas and those with data below quality filters with grey areas. The vertical grid of the retrieval is indicated with the small ticks in the vertical axis.

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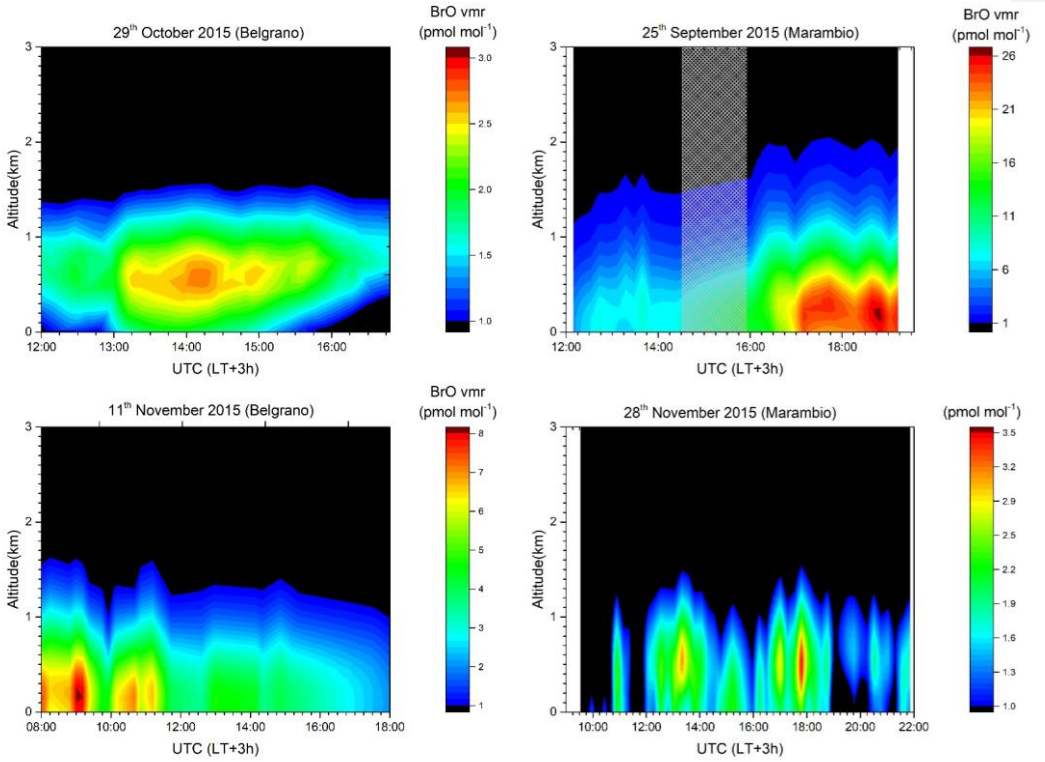

Figure 8: Examples of the daily and vertical evolution of BrO at Belgrano (left) and at Marambio (right). The horizontal scales indicate the time of the day while the vertical scales show the altitude (small ticks indicate the vertical grid of the retrieval). The color code corresponds to the BrO vmr with values below detection limit shown in black. Observations below quality filters are indicated with grey dashed area. Note the different vmr scales of each day.

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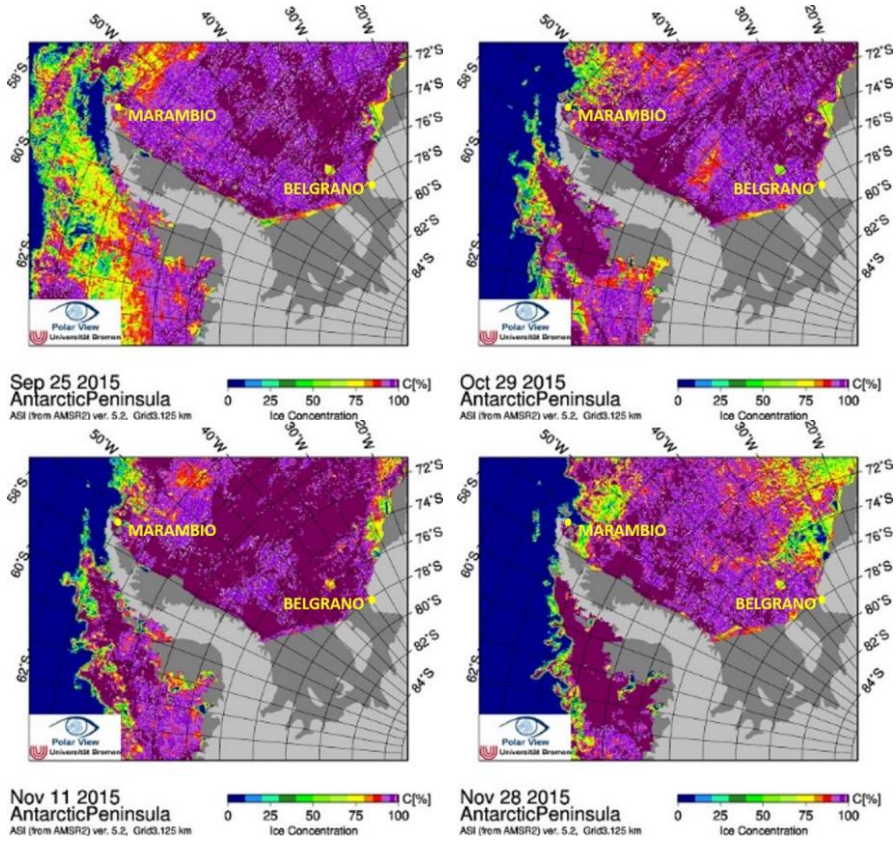

Figure 9: Sea ice conditions around the measurement sites during the exemplary days shown in Fig. 8. The maps of the sea ice concentration are downloaded from https://seaice.uni-bremen.de/databrowser/ (Spreen et al., 2008) and are sorted based on the date. The stations of Marambio and Belgrano are marked in yellow in the figures. As can be seen in the figures, in barely 1 month (25th September - 29th October) the sea ice surrounding Marambio underwent strong transformation, going from medium/highly concentrated sea ice after winter (upper left figure) with barely permanent open waters, to pretty much open ocean (disappearing all the sea ice beyond 50° W). During the timeframe of that sea ice transformation, BrO VCD2km peaked at Marambio (Fig. 4). Also, note how the edge of the sea ice nearby Belgrano transforms towards summer (e.g., lower right).

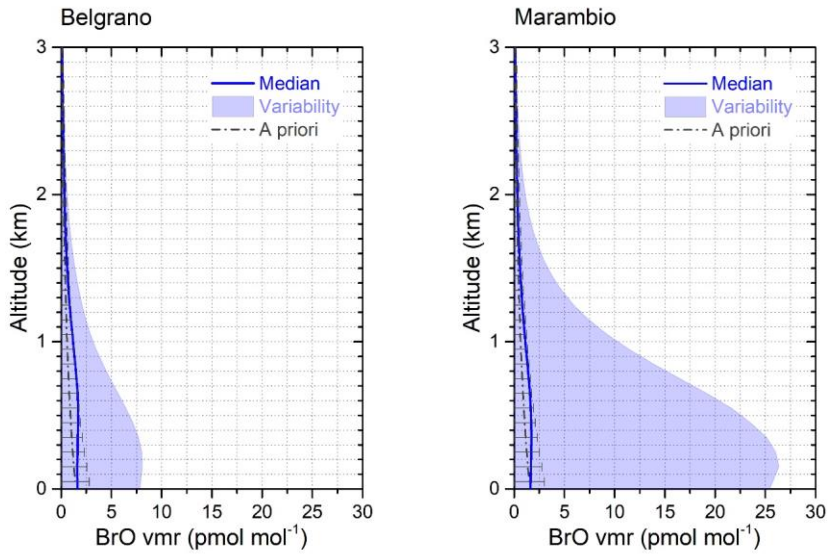

Figure 10: Vertical profile of the BrO volume mixing ratio in the Antarctic troposphere (2015). The observations performed from Belgrano station are shown in the left figure while those performed from Marambio are given in the right one. The median BrO values retrieved are indicated in thick blue lines while the shaded blue areas mark the variability range of BrO vmr throughout the sunlit period (SZA < 75°). The a priori BrO profiles (and error) used in the inversion are shown in dark grey. The vertical grid of the retrieval (100 m) is indicated with the small ticks on the vertical axis. Note the same scales in both plots.

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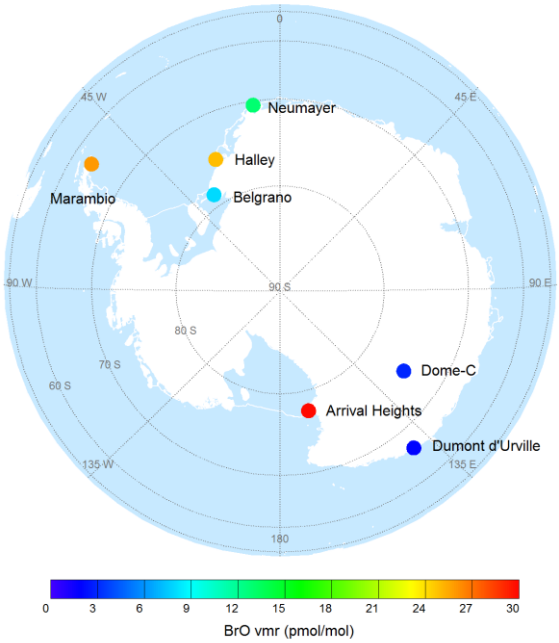

Figure 11: Maximum values of BrO vmr reported in the low troposphere of Antarctica as measured by ground-based observations. The different sites where BrO has been reported in the low troposphere are indicated with a coloured dot. The color code of each dot (station) refers to the maximum BrO vmr reported in literature (Arrival Heights: Kreher et al., 1997; Neumayer: Frieß et al., 2004; Dumont dÚrville: Grilli et al., 2013; Halley: Roscoe et al., 2014; Dome-C: Frey et al., 2015; Marambio and Belgrano: this work). Note that only the present study provides contemporary observations from different sites. Further details are provided on Table 1.

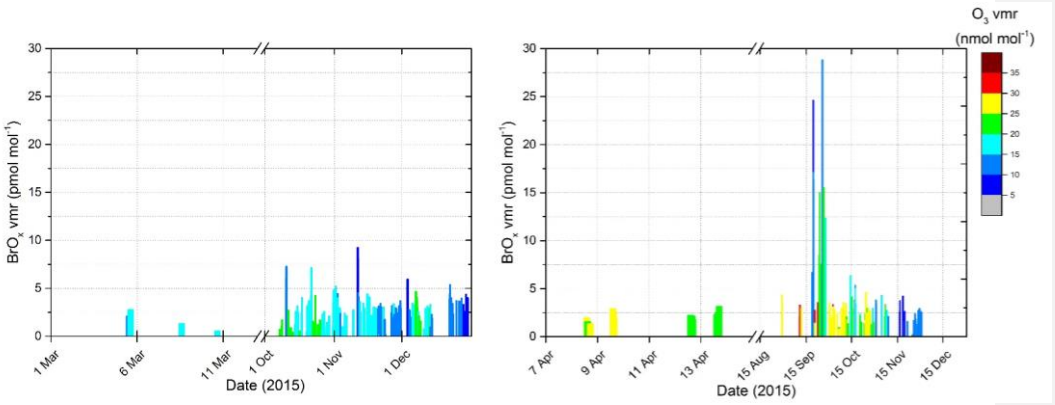

Figure 12: Reactive bromine in the low troposphere of Belgrano (left) and Marambio (right) under different O_3 regimes. The vertical scale depicts the BrO_x (Br+BrO) at each station and the color code refers to the collocated observed O_3 vmr. Note that the vertical scale and the color code apply to both figures. Only observations performed under low wind conditions (< 6 m s^{-1}) and SZA < 75° are included.

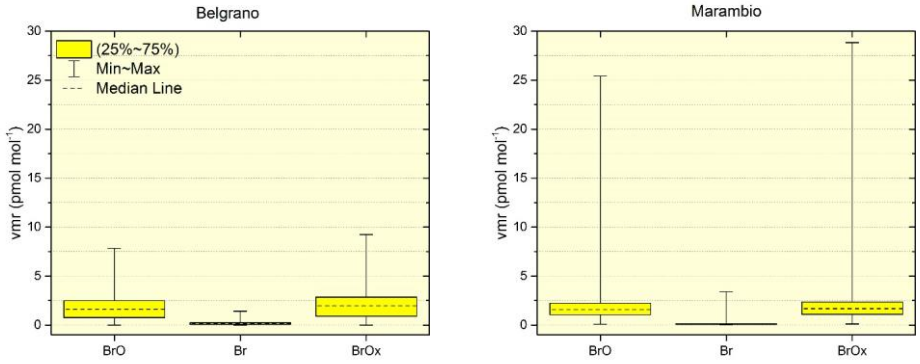

Figure 13: Statistical analysis of the reactive bromine and its partitioning estimated at Belgrano (left) and at Marambio (right) during the sunlit period of 2015. The vertical scale, which is the same in both plots, indicates the range of mixing ratios of BrO, Br and BrO_x at both stations (SZA < 75°). The legend applies to both figures, where the whiskers display the range of the maximum and minimum vmr, the boxes in dark yellow provide the vmr ranges of 25-75 % of the data, while dashed lines depict the median vmr.

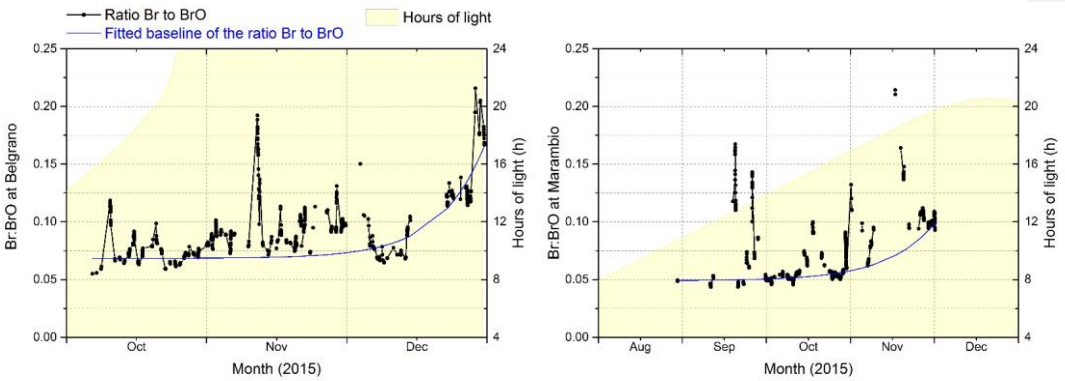

Figure 14: Variability of the ratio Br to BrO after the polar sunrise at Belgrano (left) and Marambio (right). The left axes refer to the Br to BrO ratio (same scales on both plots) with the estimated ratios shown in black and the fitted baseline in blue. The right axes on both plots refer to the hours of light at each station. The horizontal scales indicate the time period. Note that only data observed under low wind conditions and with SZA < 75° are considered.