

## Responses to the Associate Editor:

We greatly appreciate the associate editor for his detailed comments. We are confident that by answering them the quality of the manuscript has been greatly improved. In what follows our answers are typed in blue after the associate editor comment (in black). If the text was changed in the manuscript, then the text is typed in bold blue.

For consistency, the following global changes were made:

ozone → O<sub>3</sub>

O<sub>4</sub> → O<sub>2</sub>-O<sub>2</sub>

Figure → Fig.

el at. → *el at.*

degrees → °

### Major Revision

Associate Editor Decision: Reconsider after major revisions (11 Feb 2019) by William R. Simpson

Comments to the Author:

The authors have improved the manuscript and have done supplementary calculations that were requested in the review process, which helps to understand systematic issues related to the OMBRO v3 operational retrieval. These calculations address the issues raised in the review process, but their implications are not yet integrated into the text sufficiently for this manuscript to be acceptable. Therefore, another major revision is necessary to integrate these concepts. No new calculations are being requested, but specific improvements to the text are requested.

It is important for the community to have the OMBRO v3 algorithm described in the literature, and this manuscript does that. It is also important to realize that this is an operational algorithm that should be described and can be improved, and the manuscript describes potential changes to a future version. Lastly, the manuscript needs to give caution to users that will help users to use the product properly.

Yes. We added a paragraph at the end to give caution to the users about these issues and described potential changes in future versions:

**Several important retrieval issues in the current operational algorithm that affect the quantitative use BrO VCDs have been raised in this paper such as the exclusion of O<sub>2</sub>-O<sub>2</sub>, nonoptimal SO<sub>2</sub> cross sections, the neglect of radiative effect of O<sub>3</sub> absorption, and the assumption of stratospheric only BrO profile. The users are advised to pay attention to these issues so that the product can be used properly. Future versions of OMBRO will include updated SO<sub>2</sub> and O<sub>2</sub>-O<sub>2</sub> cross sections, corrections for the radiative transfer effect of the O<sub>3</sub> absorption and reoptimize the spectral fitting windows to mitigate the interferences of other**

trace gases. We will also improve the AMF calculation accounting for clouds and O<sub>3</sub> and will consider the use of model-based climatological BrO profiles. These updates will increase the capabilities of the OMBRO retrieval to quantitatively estimate enhancements over salt lakes and in volcanic plumes.

Main concepts:

1) Although the text now has improved error analysis and caution regarding airmass factor and spectral fitting issues, the abstract and conclusions do not reflect this addition of information. The text now says "To estimate the error associated with the AMFs calculations assuming a stratospheric profile we studied the difference between AMFs calculated using stratospheric only BrO profile and stratospheric-tropospheric profile and found that the mean absolute difference is 41%. Fig. 4 shows the AMF relative error dependency with wavelengths (bottom panel), albedo (middle panel) and VZA (top panel) as a function of the SZA. The AMFs relative errors are greater at high SZAs by about 50% for the case of wavelengths and VZAs." However, the abstract and conclusions do not convey this important issue. The abstract must be modified to indicate the issues with use of a fixed airmass factor.

We have modified the abstract to include text regarding the improved AMF error analysis. The following text has been added to the abstract:

**Additional fitting uncertainties can be caused by the interferences from O<sub>2</sub>-O<sub>2</sub>, and H<sub>2</sub>CO and their correlation with BrO. AMF uncertainties are estimated to be around 10% with the used single stratospheric only BrO profile. However, under conditions of high tropospheric concentrations, AMF errors due to this assumption of profile can be as high as 50%.**

The conclusions are also essentially unaltered and need to reflect the changes made to the full text. The tracked changes mode shows that the major change to the conclusions is removal of a "roadmap" for an improved OMBRO product. That is the wrong direction in which the manuscript should be going. The manuscript should explain that these issues with respect to airmass factor, HCHO, and O<sub>2</sub>-O<sub>2</sub> should be addressed in future retrievals. If the authors don't want to commit to making these changes in the next version (which is a choice), they can simply indicate that these issues are significant and one could consider making these improvements. The conclusions needs to express the way in which these factors affect quantitative use of the OMBRO v3 product VCDs.

We have added/modified the following in the conclusions:

**We have investigated additional fitting uncertainties caused by interferences from O<sub>2</sub>-O<sub>2</sub>, H<sub>2</sub>CO, O<sub>3</sub>, and SO<sub>2</sub>, the impact of the choice of fitting window, the use of common mode, the orders of closure polynomials, and instrument slit functions. Uncertainties in the AMF calculations are estimated at ~10% unless the observation is made over a region with high tropospheric BrO columns. In this case, the use of a single stratospheric BrO profile is another source of uncertainty, overestimating AMFs (up to 50%) and therefore underestimating BrO VCDs.**

We summarize the retrieval issues and bring back and expand on the “roadmap” for the improved of OMBRO product at the end of the conclusion:

Several important retrieval issues in the current operational algorithm that affect the quantitative use BrO VCDs have been raised in this paper such as the exclusion of O<sub>2</sub>-O<sub>2</sub>, nonoptimal SO<sub>2</sub> cross sections, the neglect of radiative effect of O<sub>3</sub> absorption, and the assumption of stratospheric only BrO profile. The users are advised to pay attention to these issues so that the product can be used properly. Future versions of OMBRO will include updated SO<sub>2</sub> and O<sub>2</sub>-O<sub>2</sub> cross sections, corrections for the radiative transfer effect of the O<sub>3</sub> absorption and reoptimize the spectral fitting windows to mitigate the interferences of other trace gases. We will also improve the AMF calculation accounting for clouds and O<sub>3</sub> and will consider the use of model-based climatological BrO profiles. These updates will increase the capabilities of the OMBRO retrieval to quantitatively estimate enhancements over salt lakes and in volcanic plumes.

2) The text on page 8 tries to describe the O<sub>4</sub> absorption as "small", but the response to reviewer version of Figure 1 shows it is larger than BrO.

We have changed the text “O<sub>2</sub>-O<sub>2</sub> has a small absorption feature” to “**O<sub>2</sub>-O<sub>2</sub> has an absorption feature larger than the BrO absorption**”

Additionally, there is the band of O<sub>4</sub> at 328nm, which is about 20% of the strength of the shown 344nm band and is in the spectral fit range. (Lampel et al., 2018 <https://www.atmos-chem-phys.net/18/1671/2018/acp-18-1671-2018.pdf>). Lampel et al. provide an improved cross section to the one shown in the supplement's Figure 1 that includes this second interfering peak. The authors need to show these O<sub>4</sub> cross sections to demonstrate the potential for interference due to O<sub>4</sub>.

The supplement's version of Figure 1 (the one including O<sub>4</sub>, but also with the 328nm peak from Lampel et al.) should be used for the main text. The main text should clearly say that O<sub>4</sub> was excluded from the OMBRO v3 fitting, and that this needs to be considered for future fitting. Cross correlations between O<sub>4</sub> and other spectra should also be re-calculated using the Lampel et al. cross section that includes the 328nm peak. The text tries to say that "It is impossible to quantify O<sub>4</sub>...", but clearly other BrO retrievals do just that, so this text needs to be modified to be accurate. The text can still say the choice made for OMBRO v3 was to exclude it. Presumably the common mode spectrum contains at least some of this information. It also needs to be discussed that future fitting needs to consider O<sub>4</sub> -- it is larger than BrO.

Including the O<sub>4</sub> panel on Figure 1 means not including the mean residual. Please take the RMS of the residual and very clearly state this RMS value. To my eye, that RMS may be  $\sim 10^{-3}$ , which indicates that BrO and O<sub>4</sub> features are marginally larger than the residual, which is typical for these retrievals.

We have updated Fig. 1 to include Lampel *et al.* (2018) O<sub>2</sub>-O<sub>2</sub> cross sections and included the RMS in Fig. 1 captions: **The RMS of the fitting residuals are on the order of  $9 \times 10^{-4}$ , indicating that BrO spectral features are slightly bigger than typical fitting residuals.**

Additionally, we changed “It is impossible” to ‘**It is difficult**’ added the following text to the manuscript:

**Lampel *et al.* (2018) provides spectrally resolved O<sub>2</sub>-O<sub>2</sub> cross sections not only at 343 nm, but also at 328 nm (see Fig. 1) which is about 20% of the absorption at 343 nm and has not been shown in previous O<sub>2</sub>-O<sub>2</sub> cross sections. Future updates to the operational OMBRO algorithm will investigate the effect of including Lampel *et al.* (2018) O<sub>2</sub>-O<sub>2</sub> cross sections on the fitting.**

Comments (referring to revised version page and line numbers):

Page 4, line 9: Text says "spatial and spectral zoom modes", but spectral doesn't seem to be mentioned. I'm not actually sure that these details on the zoom mode or rebinning of the mode are really necessary for this manuscript.

The text “The spatial zoom mode (SZM) is employed every 32 days (Levelt et al., 2006): data from this mode are spatially rebinned to global-mode sampling sizes, known as the rebinned spatial zoom mode. The SZM, like the global mode (GM), has 60 cross-track pixels. These are re-binned to 30 pixels, to form “the rebinned spatial zoom mode” (RSZM) which is equivalent in pixel size to the GM data, but with reduced spatial coverage” was deleted from the manuscript.

We also removed the mention of RSZM in Section 2.2 and changed the text from “retrieved from calibrated radiance and irradiance spectra in OMI GM and RSZM level 1b data product” to “**retrieved from calibrated OMI radiance and irradiance spectra**”

Page 6, line 2: The text indicates that row anomaly flags are carried forward, but is not fully clear on how they are used in the retrieval. Presumably these pixels are not used, in which case the text could just say that.

The following text was added to the manuscript

**“We recommend not to use pixels affected by the row anomaly despite being processed by the retrieval algorithm.”**

Page 6, line 13: The sentence about DOAS does not always reflect modern usage of the method. Since this text is describing the method used for OMBRO, there is no need to discuss DOAS and this sentence should be cut from the text.

The sentence was removed from the text.

Page 6, lines 20-27: This section is not clear. Seemingly two irradiance spectra are being discussed, a high resolution one for wavelength calibration, and one at OMI resolution for analysis using equation 1, presumably IO, and if that is, please be clearer. What is the principal component analysis? Is this irradiance spectrum used as the solar reference for all years after 2007?

Principal component analysis (PCA) is a statistical procedure to derive the empirical orthogonal functions or principal components from individual observations. We performed PCA for each cross-track position separately using three years of individual solar irradiance spectra normalized



to 1 AU Sun-Earth distance. Yes. The first principal component of solar irradiance at each cross-track position is used as the solar reference throughout the entire OMI record.

To make it clear, we modified this sentence as follows and have moved it to the paragraph below Eq. 1:

**To improve cross-track stripe biases (Section 3.4), the OMI daily solar irradiance ( $I_0$ ) is substituted by the first principal component of the solar irradiances measured by OMI between 2005 and 2007 (one for each cross-track position). The principal component derived between 2005 and 2007 is used to process the entire mission.**

And the sentence after this sentence stays at the same place with a small change: “Radiance wavelength calibration is performed for a representative **swath** line of radiance measurements (usually in the middle of the orbit) to determine a common wavelength grid for reference spectra.”

Page 7, lines 5-8: This section talks about "scan lines", "60 cross-track pixels", and "100 across-track swath lines". It seems like the language could be made more clear. Figures in the response to reviewer clearly show the dimensions as "cross track index" and "swath line index" (along flight direction). Please use consistent language or explain how these terms are different.

To make it clearer and use consistent language, “scan lines” was changed to “**swath lines**” and the paragraph was rewritten as:

**To process each OMI orbit it is split into blocks of 100 swath lines. Spectral fitting is then performed for each block by processing the 60 cross-track pixels included in each swath line sequentially before advancing to the next swath line. The spectra are modeled according to Eq. (1):**

Page 7, line 13: Presumably the approximate Gaussian spectral slit function (0.42 nm FWHM) was used for convolution. Please be clear on what was used.

No. The approximate Gaussian slit function with 0.42 nm FWHM is only used for plotting Figs. 1 and 12.

We modified the sentence so now it reads “**for each cross-track position from original high-resolution cross sections convolved with the corresponding pre-launch OMI slit functions (Dirksen et al., 2006)**”

Page 8, lines 4-7: It appears that the index  $j$  is spectral and  $k$  is cross track position on the detector. Making this index naming more clear can help in clarifying some of this text, such as "An initial fit of several hundred pixels per cross-track position determines the common mode spectra (one spectrum per cross-track position, between 30 N and 30S) as the average of the fitting residuals." The word "pixels" is probably along-track position. Are all of the along-track positions between 30N and 30S used, or are "several hundred" used? Please reword to be clearer and to make use of the indices.

Actually, the index  $j$  is not spectral and  $k$  is not cross track position on the detector. Instead, the  $i$ ,  $j$ , and  $k$  indices indicate contributions at different stages of the spectra modelling (before Beer-

Lambert law, Beer-Lambert law and after Beer-Lambert law for  $i, j$ , and  $k$  respectively) as shown in Eq. 1 and the text below.

This section was reworded as:

**For each cross-track position, an initial fit of all the pixels along the track between 30°N and 30°S is performed to determine the common mode spectra, derived as the average of the fitting residuals.**

Please note that while we were reviewing Eq. 1 we discovered that  $j$  is not a subscript of  $\beta$  so the equation was updated so that  $\beta_j$  is  $\beta_j$ .

Page 9, line 20: It should be noted that a fixed profile is also inconsistent with the varying tropopause height (both with latitude and dynamically e.g. Salawitch et al. 2010)

Yes, we added the sentence to the manuscript:

**It should be noted that a fixed profile is inconsistent with the varying tropopause height (both with latitude and dynamically e.g. Salawitch *et al.* 2010) and therefore with the profile shape in the stratosphere, but the impact on the AMF is typically small as the scattering weight does not change much in the stratosphere.**

Page 12, line 19: The percent symbol is mis-placed in what should be 50%.  
Changed %50 to **50%**.

Page 13, line 20: Re-word this sentence to say "GOME-2 has a descending orbit..." instead of the awkward "...for GOME-2" and "...for OMI."

Page 13, line 20 was changed to: **GOME-2 has descending orbit with a local equator crossing time (ECT) of 9:30 am and OMI has ascending orbit with an ECT of 1:45 pm.**

Page 14, line 13: Give these percentages also in molecule / cm<sup>2</sup> units (for consistency with other text).

The percentages have also been added in units of molecule cm<sup>-2</sup>.

That sentence now reads as:

**Our study shows that OMI has negative mean biases of  $0.35 \times 10^{13}$  molecules cm<sup>-2</sup> (12%),  $0.33 \times 10^{13}$  molecules cm<sup>-2</sup> (10%),  $0.25 \times 10^{13}$  molecules cm<sup>-2</sup> (17%), and  $0.30 \times 10^{13}$  molecules cm<sup>-2</sup> (10%) for Alaska, Southern Pacific, Hudson Bay, and Greenland, respectively.**

Page 15, line 2: Amundsen is an Icebreaker that was in the Canadian Arctic Ocean.

The manuscript was changed to:

**made from the Icebreaker Amundsen, in the Canadian Arctic Ocean**

Page 15, line 10: The "number of negative pixels" needs a reference (e.g. out of N total pixels).

The total number of total pixels was added to the manuscript in Table 2 caption. The caption now reads:

**Error analysis studies. For reference, the total number of retrieved pixels not affected by the row anomaly is 58112.**

The first paragraph of Section 4.2 including this sentence was removed. We have addressed reviewer #3 comments regarding the differences between V2 and V3 of the OMBRO in Table 2. The comparison of V2 and V3 in Fig. 10 is not needed and also it does not fit into the current structure of the manuscript.

Page 15, line 13: This says V9 for the new retrieval -- V3?  
Yes, V3. However, the entire paragraph is removed as explained above.

Page 15, line 27: Give months for SH winter for clarity. This whole section is fairly long for a simple concept that the distributions look like other satellite retrieved seasonal BrO patterns.

This paragraph was reworded as:

**The seasonality is different between northern and southern hemispheres. In the northern hemisphere, BrO values are larger in spring (March) with widespread enhancement and smaller in fall (September/December). In the southern hemisphere, BrO values are larger in southern hemispheric spring and summer (i.e., September and December) and smaller in the winter (June).**

Page 16, line 12: The Hörmann et al. (2016) paper indicates that OMI spectra were analyzed, not that the OMBRO product was used. I believe they use OMI data but not OMBRO. Please be clearer.

The OMBRO is used by us in this paper. To clarify, we have modified the sentence to below:  
**“Following recent work by Hörmann et al. (2016) over the Rann of Kutch using OMI BrO retrievals from an independent research product, we have explored the capability of our OMBRO product to observe similar enhancements in other salt lakes”**

Page 16, line 19: Figure 3 is cited, but it should be Figure 3, left panel (the profile that was used), rather than the right panel, which was not used in OMBRO v3, but only for sensitivity studies. (Figure 3) was changed to **(Fig. 3 left panel)**

Page 16, lines 25-29: Do not mention results of this other paper unless you intend to show it here. Specifically, you cannot say "around  $4.5 \times 10^{13}$  molecules  $\text{cm}^{-2}$ " unless you want to show that information here.

The following text was removed from the manuscript: We have done a preliminary analysis of salt water bodies including the Rann of Kutch. Although this work is not fully complete and will be a separate paper, however, we see maximum BrO VCDs appearing during March–May every year from 2004 – 2015 similar to what was reported by Hörmann et al., 2016. The BrO VCDs we see are around  $4.5 \times 10^{13}$  molecules  $\text{cm}^{-2}$ .

Page 17, line 25: The unit "molecules  $\text{cm}^{-2}$ " is missing; add it.  
Added **molecules  $\text{cm}^{-2}$**

Page 18, line 5: Add "potentially" before "real BrO". This point needs study, and you are just showing that the old SO<sub>2</sub> cross sections were bad. It would be a different study to try to quantify the BrO, which you don't attempt here, and would be difficult due to AMF issues.

Added **potentially**

Page 19, line 9: Note here that the SNO observations only occur in certain regions of the globe. Added “(SNOs), which only occur around 75°N and 75°S”

Page 19, line 14: replace "no much" with "little"  
Replaced “no much” with “**little**”

Page 19, line 23: Need to discuss that more work is needed to address AMF and spectral issues with these case studies to turn the qualitative identification of BrO into quantitative measurements of BrO VCD.

A new paragraph was added to the conclusions.

**Future versions of OMBRO will include updated SO<sub>2</sub> and O<sub>2</sub>-O<sub>2</sub> cross sections, corrections for the radiative transfer effect of the O<sub>3</sub> absorption and reoptimize the spectral fitting windows to mitigate the interferences of other trace gases. We will also improve the AMF calculation accounting for clouds and O<sub>3</sub> and consider the use of model-based climatological BrO profiles. These updates will increase the capabilities of the OMBRO retrieval to quantitatively estimate enhancements over salt lakes and in volcanic plumes.**

Page 34, Table 2: For V3 algorithm, list wavelengths for consistency. List the total number of observations so that we can tell what the "number of negatives" is in reference to. To my eye, with O2-O2 looks pretty similar to V3 in terms of median VCD, uncertainty, and number of negatives.

The total number of pixels was added to the captions of Table 2 and wavelength was added to V3. We updated the values of Table 2 since we realized that pixels affected by row anomaly were not filtered out previously. After filtering out row anomaly pixels the median from the fitting including O<sub>2</sub>-O<sub>2</sub> is 12% lower.

Figure 1: The text uses molecules cm<sup>-2</sup> fairly consistency, but this figure lists DU and mDU. I think that all (except O<sub>3</sub>) should be converted to molecules cm<sup>-2</sup>.

Figure 1 has been updated to show the values in units of molecules cm<sup>-2</sup>.

Replace the bottom right panel with the O4 spectrum. Clearly indicate the typical RMS on the figures, so that the vertical scales can be compared to typical RMS.

Figure 1 has been updated and now O4 spectrum from Lampel et al. (2018) is shown in the bottom right panel. Typical RMS is mentioned in the figure caption.

The caption now reads:

**Cross sections used in the current operational BrO algorithm except for the SO<sub>2</sub> cross section at 298 K which is to be used in the next version. The black lines are the original cross sections, the color lines show the cross sections convolved with approximate OMI slit function (which is assumed to be a Gaussian with 0.42nm full width at half maximum). The O<sub>2</sub>-O<sub>2</sub> calculation is based on Lampel *et al.* (2018) cross sections. The BrO cross section after multiplication with the wavelength-dependent AMFs used these parameters for the AMF calculation: albedo = 0.05, SZA = 5.0 °, and VZA = 2.5 °). The RMS of the fitting residuals are on the order of 9x10<sup>-4</sup>, indicating that BrO spectral features are slightly bigger than typical fitting residuals.**

Figure 3: This figure needs to be clear that the left panel is used in OMBRO V3, while the right panel was used for a quick test.

Figure caption was updated to read:

**(Left) A mostly stratospheric vertical BrO profile used for air mass factors calculations in OMBRO V3. Total BrO, BrO < 15 km, BrO < 10 km, and BrO < 5km are  $2.05 \times 10^{13}$ ,  $5.06 \times 10^{12}$ ,  $1.55 \times 10^{12}$ , and  $2.87 \times 10^{11}$ , respectively. (Right) A stratospheric tropospheric vertical BrO profile used to investigate the impact of high tropospheric BrO columns on air mass factors calculations. Total BrO, BrO < 15 km, BrO < 10 km, and BrO < 5km are  $6.99 \times 10^{13}$ ,  $5.45 \times 10^{13}$ ,  $5.10 \times 10^{13}$ , and  $4.97 \times 10^{13}$ , respectively.**

Figure 4: Other places use percent errors, so please change the scale bar to percent.

Figure 4 has been updated so the scale bar is in %.

Figure caption now reads:

**The percentage of relative AMF errors as a function of the SZA and the wavelength (top panel), albedo (middle panel) and VZA (bottom panel) when using the stratospheric only BrO profile (Fig. 3, left panel) in the case there exists a significant tropospheric BrO column as shown in the stratospheric-tropospheric BrO profile (Fig. 3, right panel).**

Figure 5: Note the range of latitudes where these SNOs happen.

The figure caption now reads:

**Time series comparison of SAO OMI (red) BrO and BIRA GOME-2 (blue) BrO VCDs from February 2007 to November 2008 using simultaneous nadir overpasses occurring at high latitudes, around 75° S/N, and within 2 minutes between OMI and GOME-2 observations.**

Figure 6: Put units on the bias and stdev of differences and clarify what they are on the figure.

Figure 9: Same fixes as Figure 6

The units are consistent with those on the x- and y-axis, therefore we think they are not necessary inside the plot where they will contribute to overcrowding the figure. The reporting of the bias, standard, correlation and the orthogonal regression line has been modified to identify each one of them.

Figure 13: Note that the straight lines are borders of the state of Utah, and the curving lines represent the Great Salt Lake (Eastern oval area) and Salt flats (Western oval area).

We assume the editor means Figure 12.

The following was added to the Figure 12 caption (now Figure 11): **The straight lines are borders of the state of Utah, and the curving lines represent the Great Salt Lake (Eastern oval area) and Salt flats (Western oval area).**

Figure 14: Add black boxes outlining each of the four panels, which will make it easier to see that there are four panels.

Black boxes outlining each of the four panels have been added to Figure 14 (now Figure 13).

Additional updates:

To improve the readability of the manuscript and reduce some redundancy we have done some modifications by moving some sentences around without changing the meaning and adding additional text to provide better description of the error analysis.

The AMF errors due to the use of stratospheric only BrO profile are discussed in 2<sup>nd</sup> paragraph of Section 3.3 and 4<sup>th</sup> paragraph of Section 3.5. Now it is discussed only in Section 3.5.

In Section 3.3, it now reads: For conditions with enhanced BrO in the lower troposphere, using this profile will overestimate the AMFs and therefore underestimate the BrO VCDs **as discussed in Section 3.5**.

In the 4<sup>th</sup> paragraph of Section 3.5, it now reads:

**To estimate the AMF error associated with enhanced tropospheric concentrations we have studied the difference between AMFs calculated using the stratospheric only BrO profile and a stratospheric-tropospheric profile as shown in the right panel of Fig. 3. Fig. 4 shows the dependency of the relative AMF difference with respect to wavelength (bottom panel), albedo (middle panel) and VZA (top panel) as a function of the SZA between calculations performed using these two profiles. The use of stratospheric only BrO profile can lead to AMF errors up to 50% depending on albedo and viewing geometry. On average, using the stratospheric only BrO profile overestimates AMF and underestimates VCD by 41%.**

Also, the two paragraphs about retrieval sensitivity analysis have been reorganized:

**We have performed sensitivity analysis of OMI BrO VCD with respect to various retrieval settings using orbit 26564 on 13 July 2009. Table 2 shows the median VCDs, median fitting uncertainties and the number of negative VCD pixels for each configuration. Table 3 summarizes the overall fitting error budget including the random fitting uncertainty, cross sections errors (as reported in the literature), and various retrieval settings. We studied five wavelength windows including the current operational window (319.0-347.5 nm) version 2 window (323.0-353.5 nm), version 1 (340.0-357.5 nm) and two extra windows exploring the impact of extending the window to shorter wavelengths (310.0-357.5 nm) and reducing it by limiting its extension to wavelengths above 325 nm (325.0-357.5). The choice of fitting window can cause significant differences in BrO VCDs of up to 50%. The current window results in the most stable retrievals with the smallest number of pixels with negative VCD values.**

**Including the interference of O<sub>2</sub>-O<sub>2</sub> leads to a decrease of the median VCD by ~12% and an increase of the median fitting uncertainty by ~10% with respect to the operational set up. Excluding H<sub>2</sub>CO from the fitting significantly reduces the retrieved BrO columns by ~37%, given that the strong anticorrelation between both molecules is not taken into account. Fitting the mean residual (common mode) has a small impact in the retrieval results, the**



**median VCD only changes ~3%, but reduces the median fitting uncertainty by ~30% with respect to the exclusion of the common mode. To study the impact of the slit functions we have performed the retrieval using both online slit functions, modelled as a Gaussian, and the preflight instrument slit functions. The median difference between these two retrievals is 27% for orbit number 26564. We have investigated the impacts of the order of scaling and baseline polynomials; it can cause uncertainties of ~10% as shown in Table 3.**

In Section 4.1, the sentence “Due to different orbits, all these SNOs occur at high latitudes around 75°S/N” is changed to **“Given Aura and Metop-A satellite orbits, all these SNOs occur at high latitudes around 75°S/N”.**

We added the following sentence to the 3<sup>rd</sup> paragraph of the conclusion section:  
**Monthly mean OMBRO VCDs during 2007-2009 show negative biases of  $0.25-0.35 \times 10^{13}$  molecules  $\text{cm}^{-2}$  (10-17%) over Alaska, Southern Pacific, Hudson Bay, and Greenland.**

and slightly modified the following:

**The BrO seasonality in Harestua is well captured by the OMI BrO and OMBRO retrieval showing a reasonable good agreement with the ground-based measurements. The correlation between both datasets is of 0.46 and the mean bias  $0.12 \pm 0.76 \times 10^{13}$  molecules  $\text{cm}^{-2}$  (mean relative bias of  $3.18 \pm 16.30\%$ ).**

We added the following sentence to the 4<sup>th</sup> paragraph of the conclusion section:  
**Finally, we have explored the feasibility of detecting enhanced BrO column over salt lakes and in volcanic plumes using OMBRO retrievals. We found enhancement of the BrO with respect to the background levels of  $5-10 \times 10^{12}$  molecules  $\text{cm}^{-2}$  over the U.S. Great Salt Lake.**

As the previous Fig. 10 was removed, the previous figures after that have been updated.

Fig. 11 becomes Fig 10

Fig. 12 becomes Fig 11

Fig. 13 becomes Fig 12

Fig. 14 becomes Fig 13

# OMI total bromine monoxide (OMBRO) data product: Algorithm, retrieval and measurement comparisons

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**Abstract.** This paper presents the retrieval algorithm for the operational Ozone Monitoring Instrument (OMI) total bromine monoxide (BrO) data product (OMBRO) developed at the Smithsonian Astrophysical Observatory (SAO), and shows comparisons with correlative measurements and retrieval results. The algorithm is based on direct nonlinear least squares fitting of radiances from the spectral range 319.0-347.5 nm. Radiances are modeled from the solar irradiance, attenuated by contributions from BrO and interfering gases, and including rotational Raman scattering, additive and multiplicative closure polynomials, correction for Nyquist undersampling, and the average fitting residual spectrum. The retrieval uses albedo and wavelength-dependent air mass factors (AMFs), which have been pre-computed using a single mostly stratospheric BrO profile. The BrO cross sections are multiplied by the wavelength-dependent AMFs before fitting so that the vertical column densities (VCDs) are retrieved directly. The fitting uncertainties of BrO VCDs typically vary between 4 and  $7 \times 10^{12}$  molecules  $\text{cm}^{-2}$  (~10-20% of the measured BrO VCDs). Additional fitting uncertainties can be caused by the interferences from  $\text{O}_2\text{-O}_2$ , and  $\text{H}_2\text{CO}$  and their correlation with BrO. AMF uncertainties are estimated to be around 10% with the used single stratospheric only BrO profile. However, under conditions of high tropospheric concentrations, AMFs errors due to this assumption of profile can be as high as 50%.

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The retrievals agree well with GOME-2 observations at simultaneous nadir overpasses and with ground-based zenith-sky measurements at Harestua, Norway, with mean biases less than  $-0.22 \pm 1.13 \times 10^{13}$  molecules  $\text{cm}^{-2}$  and  $0.12 \pm 0.76 \times 10^{13}$  molecules  $\text{cm}^{-2}$ , respectively. Global distribution and seasonal variation of OMI BrO are generally consistent with previous satellite observations. Finally, we confirm the capacity of OMBRO retrievals to observe enhancements of

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BrO over the U.S. Great Salt Lake despite the current retrieval set up considering a stratospheric profile in the AMF calculations. OMBRO retrievals also show significant BrO enhancements from the eruption of the Eyjafjallajökull volcano, although the BrO retrievals are affected under high SO<sub>2</sub> loading conditions by the sub-optimum choice of SO<sub>2</sub> cross sections.

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## 1 Introduction

Bromine monoxide (BrO) is a halogen oxide, predominantly located in the stratosphere and upper troposphere where, like chlorine monoxide (ClO), it is a catalytic element in the destruction of stratospheric ozone (von Glasow *et al.*, 2004; Salawitch *et al.*, 2005), but with higher efficiency per molecule. Sources of tropospheric BrO include bromine release (“explosions”) during the Polar Spring (Hausmann and Platt, 1994; Hollwedel *et al.*, 2004; Simpson *et al.*, 2007; Begoin *et al.*, 2010; Salawitch *et al.*, 2010; Abbatt, *et al.*, 2012; Blechschmidt *et al.*, 2016), volcanic eruptions (Bobrowski *et al.*, 2003; Chance, 2006; Theys *et al.*, 2009;), salt lakes (Hebestreit, *et al.*, 1999; Hörmann *et al.* 2016) and stratospheric transport (Salawitch *et al.*, 2010). Global BrO measurements from space were first proposed for the Scanning Imaging Absorption Spectrometer for Atmospheric Cartography (SCIAMACHY) instrument (Chance *et al.*, 1991) and were first demonstrated with Global Ozone Monitoring Experiment (GOME-1) measurements (Chance, 1998; Platt and Wagner, 1998; Richter *et al.*, 1998; Hegels *et al.*, 1998), and since with SCIAMACHY nadir (Kühl *et al.*, 2008), Global Ozone Monitoring Experiment 2 (GOME-2) measurements (Theys *et al.*, 2011; Toyota *et al.*, 2011) and TROPOMI (Seo, *et al.*, 2018). Initial observations of BrO by OMI were first reported by Kurosu *et al.* (2004). Polar Spring BrO enhancements are known to be associated with boundary layer O<sub>3</sub> depletion (Hausmann and Platt, 1994; von Glasow *et al.*, 2004; Salawitch *et al.*, 2005; Simpson *et al.*, 2007; Salawitch *et al.*, 2010; Abbatt, *et al.*, 2012). OMI measurements of BrO have been used together with chemical and dynamical modeling to investigate stratospheric versus tropospheric enhancements of atmospheric BrO at high northern latitudes (Salawitch *et al.*, 2010). OMI BrO retrieval using the Differential Optical Absorption Spectroscopy (DOAS) method has been used to study the seasonal variations of tropospheric bromine monoxide over the Rann of Kutch salt marsh (Hörmann *et al.* 2016). The Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) campaign (Choi *et al.*, 2012) found consistency between BrO column densities calculated from

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Chemical Ionization Mass Spectrometer (CIMS) measurements with the tropospheric BrO columns derived from OMI using our operational retrieval algorithm. BrO has been observed from the ground in Harestua, Norway (Hendrick *et al.*, 2007), Lauder, New Zealand (Schofield *et al.*, 2004a, 2004b), Antarctica (Schofield *et al.*, 2006), Utqiagvik (Barrow), Alaska (Liao *et al.*, 2011; Frieß *et al.*, 2011; Liao *et al.*, 2012; Sihler *et al.*, 2012; Peterson *et al.*, 2016), Eureka, Canada (Zhao *et al.*, 2015), Summit, Greenland (Stutz *et al.*, 2011) and the Arctic Ocean (Burd *et al.*, 2017).

Enhancement of BrO in the vicinity of salt lakes like the Dead Sea and the Great Salt Lake have been observed from ground-based measurements (Hebestreit *et al.*, 1999; Matveev *et al.*, 2001; Stutz *et al.*, 2002; Tas *et al.*, 2005; Holla *et al.*, 2015). The active bromine compound release is due to the reaction between atmospheric oxidants with salt reservoirs. Satellite observation of salt lake BrO was first reported over the Great Salt Lake and the Dead Sea from OMI (Chance, 2006; Hörmann *et al.* 2016). Seasonal variations of tropospheric BrO over the Rann of Kutch salt marsh have been observed using OMI from an independent research BrO product (Hörmann *et al.* 2016). Bobrowski *et al.* (2003) made the first ground-based observations of BrO and SO<sub>2</sub> abundances in the plume of the Soufrière Hills volcano (Montserrat) by multi-axis DOAS (MAX-DOAS). BrO and SO<sub>2</sub> abundances as functions of the distance from the source were measured by MAX-DOAS in the volcanic plumes of Mt. Etna in Sicily, Italy and Villarica in Chile (Bobrowski *et al.*, 2007). The BrO/SO<sub>2</sub> ratio in the plume of Nyiragongo and Etna was also studied (Bobrowski *et al.*, 2015). The first volcanic BrO measured from space was from the Ambrym volcano, measured by OMI (Chance, 2006). Theys *et al.* (2009) reported on GOME-2 detection of volcanic BrO emission after the Kasatochi eruption. Hörmann *et al.* (2013) examined GOME-2 observations of BrO slant column densities (SCDs) in the vicinity of volcanic plumes; it showed clear enhancements of BrO in ~1/4 of the volcanos, and revealed large spatial differences in BrO/SO<sub>2</sub> ratios.

The purpose of this paper is to describe the OMI BrO operational algorithm and the data product, compare it with ground-based and other satellite measurements and analyze its spatiotemporal characteristics. This paper is organized as follows: Section 2 describes the OMI instrument and the data product. Section 3 gives a detailed description of the operational algorithm including algorithm and product history, spectral fitting, AMF calculations, destriping, and fitting

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uncertainties. Section 4 presents results and discussion including comparison with GOME-2 and ground-based zenith-sky measurements at Harestua, Norway, global distribution, seasonality, enhanced BrO from the U.S. Great Salt Lake and Iceland’s Eyjafjallajökull volcano. Section 5 concludes this study.

## 5 2 OMI instrument and OMBRO data product

### 2.1 OMI instrument

OMI was launched on the NASA Earth Observing System (EOS) Aura satellite into a sun-synchronous orbit on 15 July 2004. It is a push-broom imaging spectrometer that observes solar backscattered radiation in the visible and ultraviolet from 270-500 nm in three channels (UV1: 270-310 nm, UV2: 310-365 nm, visible: 350-500 nm) at spectral resolution of 0.42-0.63 nm and spatial resolution in the normal (global sampling) mode ranging from 13×24 km<sup>2</sup> at direct nadir to about 28×150 km<sup>2</sup> at the swath edges. The global mode (GM) has 60 ground pixels with a total cross-track swath of 2600 km.

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15 Since June 2007, certain cross-track positions of OMI data have been affected by the row anomaly (<http://projects.knmi.nl/omi/research/product/rowanomaly-background.php>): some loose thermal insulating material likely appeared in front of the instrument’s entrance slit, which can block and scatter the light thus causing errors in level 1b data and subsequently the level 2 retrievals (Kroon *et al.*, 2011). Initially, the row anomaly only affected a few positions and the effect was small. But since January 2009, the anomaly has become more serious, spreading to ~1/3 of the positions and retrievals at those positions are not recommended for scientific use. A flagging field has been introduced in the OMI level 1b data to indicate whether an OMI pixel is affected by this instrument anomaly.

25 OMI measures O<sub>3</sub> and other trace gases, aerosols, clouds, and surface properties. Products developed at the SAO include operational BrO, chlorine dioxide (OCIO), and formaldehyde (H<sub>2</sub>CO; González Abad *et al.*, 2015) that are archived at NASA Goddard Earth Sciences (GES) Data and Information Services Center (DISC), and offline (“pre-operational”) O<sub>3</sub> profile and tropospheric O<sub>3</sub> (Liu *et al.*, 2010; Huang *et al.*, 2017, 2018), glyoxal (C<sub>2</sub>H<sub>2</sub>O<sub>2</sub>) (Chan Miller *et al.*,

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2014, 2016) and water vapor (H<sub>2</sub>O) (Wang *et al.*, 2014, 2016) that are available at the Aura validation data center (AVDC). All the products except for the O<sub>3</sub> profile product are produced using nonlinear least-squares (NLLS) fitting methods based on those previously developed at the SAO for the analysis of measurements from the GOME (now GOME-1) (Chance, 1998; Chance, *et al.*, 2000) and SCIAMACHY instruments (Burrows and Chance, 1991; Chance *et al.*, 1991; Martin *et al.*, 2006).

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## 2.2 OMBRO data product

The current operational BrO product, OMBRO version 3, contains BrO vertical column densities (VCDs), slant column densities (SCDs), effective air mass factors (AMFs) and ancillary information retrieved from calibrated OMI radiance and irradiance spectra. Each BrO product file contains a single orbit of data, from pole to pole, for the sunlit portion of the orbit. The data product from 26 August 2004 through the present is available at GES DISC. Data used in this study cover the period from 1 January 2005 to 31 December 2014.

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## 3 Retrieval algorithm

### 3.1 Algorithm and product history

OMBRO Version 1.0 was released on 1 February 2007, based on a spectral fitting window of 338–357 nm. Version 2.0 was released on 13 April 2008. It included major adjustments for Collection 3 Level 1b data, improved destriping measures, change of the fitting window to 340–357.5 nm, improvements to radiance wavelength calibration, and several improvements for processing near-real-time data. In both Versions 1 and 2, total BrO VCDs were retrieved in two steps: first performing spectral fitting using the basic optical absorption spectroscopy (BOAS) method to derive SCDs from OMI radiance spectra, and then converting from SCDs to VCDs by dividing AMFs. This is similar to current SAO H<sub>2</sub>CO, H<sub>2</sub>O and C<sub>2</sub>H<sub>2</sub>O<sub>2</sub> as mentioned previously. The latest Version 3.0.5, released on 28 April 2011, includes major algorithm changes: the fitting window was moved to 319.0–347.5 nm, and BrO cross sections are multiplied by wavelength-dependent AMFs, which are a function of albedo, before fitting, for a direct retrieval of BrO VCDs. SCDs are similarly retrieved in a separate step by fitting BrO cross sections that have not been multiplied with wavelength-dependent AMFs, and an effective AMF = SCD/VCD is computed. Diagnostic



cloud information from the OMCLDO2 product (Acarreta *et al.*, 2004) was added, and the row-anomaly indicating flags were carried over from the level 1b product. We recommend not to use pixels affected by the row anomaly despite being processed by the retrieval algorithm.

5 The current algorithm is described in detail in the rest of this section, with spectral fitting in Section 3.2, AMF calculation prior to spectral fitting in Section 3.3, post-processing de-stripping to remove cross-track dependent biases in Section 3.4, and fitting uncertainties and error estimates in Section 3.5.

### 3.2 Spectral fitting

10 Most aspects of the algorithm physics for the direct fitting of radiances by the BOAS method were developed previously at SAO for analysis of GOME and SCIAMACHY satellite spectra (Chance, 1998, Chance *et al.*, 2000, OMI, 2002; Martin *et al.*, 2006) and in the various algorithm descriptions of other SAO OMI products (Wang *et al.*, 2014; Chan Miller *et al.*, 2014; Gonzalez Abad *et al.*, 2015).

15 The spectral fitting in the SAO OMI BrO retrieval is based on a Gauss-Newton NLLS fitting procedure, the CERN ELSUNC procedure (Lindström and Wedin, 1987), which provides for bounded NLLS fitting. Processing begins with wavelength calibration for both irradiance and radiance. In each case the wavelength registration for the selected fitting window is determined  
20 independently for each cross-track position by cross-correlation of OMI spectra with a high spectral resolution solar irradiance (Caspar and Chance, 1997; Chance, 1998; Chance and Kurucz, 2010) using the preflight instrument slit functions (Dirksen *et al.*, 2006). Radiance wavelength calibration is performed for a representative swath line of radiance measurements (usually in the middle of the orbit) to determine a common wavelength grid for reference spectra.

25 Following wavelength correction, an undersampling correction spectrum is computed to partially correct for spectral undersampling (lack of Nyquist sampling; Chance, 1998; Slijkhuis *et al.*, 1999; Chance *et al.*, 2005). The calculation of the corrections for the undersampling is accomplished by convolving the preflight slit functions with the high-resolution solar spectrum and differencing its  
30 fully-sampled and undersampled representations (Chance *et al.*, 2005).

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**Moved up [1]:** Radiance wavelength calibration is performed for a representative scan line of radiance measurements (usually in the middle of the orbit) to determine a common wavelength grid for reference spectra.

To process each OMI orbit it is split into blocks of 100 swath lines. Spectral fitting is then performed for each block by processing the 60 cross-track pixels included in each swath line sequentially before advancing to the next swath line. The spectra are modeled as follows:

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$$I = \{(aI_0 + \sum_i \alpha_i A_i) e^{-\sum_j \beta_j B_j} + \sum_k \gamma_k C_k\} Poly_{scale} + Poly_{baseline} \quad (1)$$

where  $I_0$  is the solar irradiance (used in our operational BrO retrieval) or radiance reference measurement,  $I$  is the Earthshine radiance (detected at satellite),  $a$  is albedo,  $\alpha_i$ ,  $\beta_j$ ,  $\gamma_k$ , are the coefficients to the reference spectra of  $A_i$ ,  $B_j$ ,  $C_k$ , (for example, trace gas cross sections, Ring effect, vibrational Raman, undersampling correction, common mode, *etc.*) of model constituents. To

10 improve cross-track stripe biases (Section 3.4), the OMI daily solar irradiance ( $I_0$ ) is substituted by the first principal component of the solar irradiances measured by OMI between 2005 and 2007 (one for each cross-track position). The principal component derived between 2005 and 2007 is used to process the entire mission.

15 The reference spectra are derived separately for each cross-track position from original high-resolution cross sections convolved with the corresponding pre-launch OMI slit functions (Dirksen *et al.*, 2006) after correcting for the solar  $I_0$  effect (Aliwell *et al.*, 2002). Fig. 1 shows the trace gas cross sections and Ring spectra used in the current operational algorithm. The black lines are the original high-resolution reference spectra, and the color lines show the corresponding spectra convolved with OMI slit function, which are used in the fitting.

20 For improved numerical stability, radiances and irradiances are divided by their respective averages over the fitting window, renormalizing them to values of ~1. BrO is fitted in the spectral window 319.0–347.5 nm, within the UV-2 channel of the OMI instrument. The switch from the previous fitting window of 340–357.5 nm to this shorter and wider fitting window is based on extensive sensitivity analysis following the method described by Vogel *et al.*, 2013. This new fitting window aims at reducing the fitting uncertainty by including more BrO spectral structures as shown in Fig. 1 and reducing retrieval noise while preserving the stability of the algorithm. An analysis of the retrieval sensitivity to different windows is included in section 3.5.

30 The rotational Raman scattering (Chance and Spurr, 1997; Chance and Kurucz, 2010) and undersampling correction spectra,  $A_i$ , are first added to the albedo-adjusted solar irradiance  $aI_0$ ,

with coefficients  $\alpha_i$  as shown in Eq. 1. Radiances  $I$  are then modeled as this quantity attenuated by absorption from BrO, O<sub>3</sub>, NO<sub>2</sub>, H<sub>2</sub>CO, and SO<sub>2</sub> with coefficients  $\beta_j$  fitted to the reference spectra  $B_j$  as shown in Eq. 1. A common mode spectrum  $C_k$ , computed on line, is added by fitting coefficient  $\gamma_k$  after the Beer-Lambert law contribution terms. For each cross-track position, an initial fit of all the pixels along the track between 30°N and 30°S is performed to determine the common mode spectra, derived as the average of the fitting residuals. The common mode spectra include any instrument effects that are uncorrelated to molecular scattering and absorption. This is done to reduce the fitting root-mean-square (RMS) residuals, and the overall uncertainties. These are then applied as reference spectra in fitting of the entire orbit. The fitting additionally contains additive ( $Poly_{baseline}$ ) and multiplicative closure polynomials ( $Poly_{scale}$ ), parameters for spectral shift and, potentially, squeeze (not normally used). The operational parameters and the cross sections used are provided in Table 1.

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As part of the development of the OMBRO retrieval algorithm, a significant amount of effort was dedicated to algorithm “tuning”, i.e., the optimization of elements in the retrieval process, including interfering absorbers like O<sub>2</sub>-O<sub>2</sub>. The spectral region of 343 nm, where O<sub>2</sub>-O<sub>2</sub> has an absorption feature larger than the BrO absorption, essentially is impossible to avoid in BrO retrievals: the fitting window would have to either terminate at shorter wavelengths or start past this feature, and both approaches yield to unacceptable low information content for the BrO retrievals to succeed. During the tuning process, we investigated the effects of, among many other things, including or excluding O<sub>2</sub>-O<sub>2</sub>, the use of different spectroscopic data sets (Greenblatt et al., 1990 and Hermans et al., 1999 cross-sections), shorter or longer wavelength windows for the retrieval, and even extending the retrieval window beyond the O<sub>2</sub>-O<sub>2</sub> absorption feature but excluding the approximate wavelength slice of the feature itself. The only approach that provided quantitatively satisfactory results - i.e., stability of the retrieval under a wide range of conditions, minimized correlation with clouds, low fitting uncertainties, consistency of OMI global total column BrO with published results, and low noise in pixel-to-pixel retrievals - was to exclude O<sub>2</sub>-O<sub>2</sub> from the OMBRO V3. It is difficult to quantify O<sub>2</sub>-O<sub>2</sub> atmospheric content from the absorption feature around 343 nm alone, and its correlation with absorption bands of BrO and H<sub>2</sub>CO leads to spectral correlations in the course of the non-linear least squares minimization process that are detrimental to the OMI BrO retrievals. Lampel et al., (2018) provides spectrally resolved O<sub>2</sub>-O<sub>2</sub>

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cross sections not only at 343 nm, but also at 328 nm (see Fig. 1) which is about 20% of the absorption at 343 nm and has not been shown in previous O<sub>2</sub>-O<sub>2</sub> cross sections. Future updates to the operational OMBRO algorithm will investigate the effect of including Lampel *et al.*, (2018) O<sub>2</sub>-O<sub>2</sub> cross sections on the fitting.

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### 3.3 Air mass factors

Due to significant variation in O<sub>3</sub> absorption and Rayleigh scattering in the fitting window AMFs vary with wavelength by 10-15% as shown in Fig. 2. At large solar and viewing zenith angles it is difficult to identify a single representative AMF *ad hoc*. The wavelength dependent AMFs are introduced to take into account for such strong variation within the BrO fitting window. They are applied pre-fit to the BrO cross sections, and the spectral fit retrieves VCDs directly. This direct fitting approach is a major departure from the commonly employed 2-step fitting procedure (OMI, 2002). It was first developed for retrievals of trace gases from SCIAMACHY radiances in the shortwave infrared (Buchwitz *et al.*, 2000) and has been demonstrated for total O<sub>3</sub> and SO<sub>2</sub> retrievals from GOME/SCIAMACHY measurements in the ultraviolet (Bracher *et al.*, 2005; Coldewey-Egbers *et al.*, 2005; Weber *et al.*, 2005; Lee *et al.*, 2008).

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The albedo- and wavelength-dependent AMFs were pre-computed with the Linearized Discrete Ordinate Radiative Transfer code (LIDORT, Spurr, 2006) using a single mostly stratospheric BrO profile (Fig. 3, left panel). The BrO profile, based on the model of Yung *et al.* (1980), has ~30% BrO below 15 km, ~10% BrO below 10 km, and ~2% BrO below 5 km. It should be noted that a fixed profile is inconsistent with the varying tropopause height (both with latitude and dynamically e.g. Salawitch *et al.* 2010) and therefore with the profile shape in the stratosphere, but the impact on the AMF is typically small as the scattering weight does not change much in the stratosphere.

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For conditions with enhanced BrO in the lower troposphere, using this profile will overestimate the AMFs and therefore underestimate the BrO VCDs as discussed in Section 3.5. Surface albedos are based on a geographically varying monthly mean climatology derived from OMI (Kleipool *et al.*, 2008). Although AMFs based on this BrO profile only slightly depend on surface albedo, albedo effects can be significant over highly reflective snow/ice surfaces, reducing VCDs by 5-10%.

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In order to provide the AMF in the data product for consistency with previous versions based on a two-step approach, a second fitting of all OMI spectra is performed with unmodified BrO cross sections, which yields SCDs. An effective AMF can then be computed as  $AMF = SCD/VCD$ .

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The green line in the top right panel of Fig. 1 shows the modified BrO cross section after multiplication with the wavelength-dependent AMF (albedo = 0.05, SZA (Solar Zenith Angle) =  $5.0^\circ$ , and VZA (Viewing Zenith Angle) =  $2.5^\circ$ ). The wavelength-dependence in AMF is visible from the varying differences near BrO absorption peaks and the right wings at different  
10 wavelengths. The correlation of the unmodified BrO cross sections with the rest of the fitted molecules is small (typically less than 0.12), except with  $H_2CO$  (0.43). However, it is safe to assume that in most polar regions with enhanced BrO there are no high concentrations of formaldehyde. It will be worthwhile for future studies to assess the interference of  $H_2CO$  under high  $H_2CO$  and background BrO conditions similar to De Smedt et al., 2015. In addition, the AMF  
15 wavelength dependence increases with the increase of solar and viewing zenith angles and surface albedo, which increases the correlation between modified BrO cross sections and  $O_3$  cross sections. However, the correlation with  $O_3$  becomes noticeable ( $\sim 0.10$ ) only at SZAs above  $\sim 80^\circ$ .

### 3.4 Destriping

20 OMI L1b data exhibit small differences with cross-track position, due to differences in the dead/bad pixel masks (cross-track positions are mapped to physically separate areas on the CCD), dark current correction, and radiometric calibration, which lead to cross-track stripes in Level 2 product (Veihelmann and Kleipool, 2006). Our destriping algorithm employs several methods to reduce cross-track striping of the BrO columns. First, we screen outliers in the fitting residuals.  
25 This method, originally developed to mitigate the effect of the South Atlantic Anomaly in SAO OMI BrO,  $H_2CO$ , and OCIO data products, is now also being employed for GOME-2 (Richter *et al.*, 2011). Screening outliers is done through computing the median,  $r_{med}$ , and the standard deviation  $\sigma$  of residual spectra  $r(\lambda)$  and in subsequent refitting excluding any spectral points for which  $r(\lambda) \geq |r_{med} \pm 3\sigma|$ . This can be done repeatedly for every ground pixel, which makes the  
30 processing slow. However, we do it once for a reference swath line, recording the positions of the

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bad pixels, and excluding them by default in each subsequent fit. Second, after the completion of the spectral fitting process for all ground pixels in the granule, a post-processing cross-track bias correction is performed: an average cross-track pattern is calculated from the along-track averages of all BrO VCDs for each cross-track position within a  $\pm 30^\circ$  latitude band around the equator, to which a low-order polynomial is fitted. The differences between the cross-track pattern and the fitted polynomial is then applied as a cross-track VCD correction (or “smoothing”) factor. The smoothed VCDs are provided in a separate data field, *ColumnAmountDestriped*. Smoothed SCDs are derived in an analogous fashion and are also included in the data product.

### 10 3.5 BrO VCD Error Analysis

Estimated fitting uncertainties are given as  $\sigma_i = \sqrt{C_{ii}}$  where  $C$  is the covariance matrix of the standard errors. This definition is strictly true only when the errors are normally distributed. In the case where the level 1 data product uncertainties are not reliable estimates of the actual uncertainties, spectral data are given unity weight over the fitting window, and the  $1\sigma$  fitting error in parameter  $i$  is determined as

$$\sigma_i = \varepsilon_{rms} \sqrt{\frac{c_{ii} \times npoints}{npoints - nvaried}} \quad (2)$$

where  $\varepsilon_{rms}$  is the root mean square of the fitting residuals,  $npoints$  is the number of points in the fitting window, and  $nvaried$  is the number of parameters varied during the fitting.

20 The fitting uncertainties for single measurements of the BrO VCDs typically vary between  $4 \times 10^{12}$  and  $7 \times 10^{12}$  molecules  $\text{cm}^{-2}$ , consistently throughout the data record. The uncertainties vary with cross-track positions, from  $\sim 7 \times 10^{12}$  at nadir positions to  $\sim 4 \times 10^{12}$  at edge positions due to the increase of photon path length through the stratosphere. Relatively, the VCD uncertainties typically range between 10-20% of individual BrO VCDs, but could be as low as 5% over BrO hotspots. This is roughly 2-3 times worse than what was achieved from GOME-1 data.

The BrO VCD retrieval uncertainties listed in the data product only include random spectral fitting errors. Error sources from AMFs (*i.e.*, BrO climatology), atmospheric composition and state



(pressure/temperature vertical profiles, total  $O_3$  column, etc.) and other sources of VCD uncertainty are not included. We provide here error estimates for these additional error sources.

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Uncertainties in the AMFs, used to convert slant to vertical columns, are estimated to be 10% or less except when there is substantially enhanced tropospheric BrO. Hence the total uncertainties of the BrO vertical columns typically range within 15-30%. To estimate the AMF error associated with enhanced tropospheric concentrations we have studied the difference between AMFs calculated using the stratospheric only BrO profile and a stratospheric-tropospheric profile as shown in the right panel of Fig. 3. Fig. 4 shows the dependency of the relative AMF difference with respect to wavelength (top panel), albedo (middle panel) and VZA (bottom panel) as a function of the SZA between calculations performed using these two profiles. The use of stratospheric only BrO profile can lead to AMF errors up to 50% depending on albedo and viewing geometry. On average, using the stratospheric only BrO profile overestimates AMF and underestimates VCD by 41%.

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We have performed sensitivity analysis of OMI BrO VCD with respect to various retrieval settings using orbit 26564 on 13 July 2009. Table 2 shows the median VCDs, median fitting uncertainties and the number of negative VCD pixels for each configuration. Table 3 summarizes the overall fitting error budget including the random fitting uncertainty, cross sections errors (as reported in the literature), and various retrieval settings. We studied five wavelength windows including the current operational window (319.0-347.5 nm) version 2 window (323.0-353.5 nm), version 1 (340.0-357.5 nm) and two extra windows exploring the impact of extending the window to shorter wavelengths (310.0-357.5 nm) and reducing it by limiting its extension to wavelengths above 325 nm (325.0-357.5). The choice of fitting window can cause significant differences in BrO VCDs of up to 50%. The current window results in the most stable retrievals with the smallest number of pixels with negative VCD values.

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Including the interference of  $O_2-O_2$  leads to a decrease of the median VCD by ~12% and an increase of the median fitting uncertainty by ~10% with respect to the operational set up. Excluding  $H_2CO$  from the fitting significantly reduces the retrieved BrO columns by ~37%, given that the strong anticorrelation between both molecules is not taken into account. Fitting the mean residual

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(common mode) has a small impact in the retrieval results, the median VCD only changes ~3%, but reduces the median fitting uncertainty by ~30% with respect to the exclusion of the common mode. To study the impact of the slit functions, we have performed the retrieval using both online slit functions, modelled as a Gaussian, and the preflight instrument slit functions. The median difference between these two retrievals is 27% for orbit number 26564. We have investigated the impacts of the order of scaling and baseline polynomials; it can cause uncertainties of ~10% as shown in Table 3.

To study the impact of the radiative transfer effects of the O<sub>3</sub> absorption in our retrieval we have adopted the correction method described by Pukite et al., 2010. We find that between 60° south and 60° north the average difference is smaller than 10% with values around 2% near the equator. However, as we move near the poles with solar zenith angles above 60°, the differences start to be bigger arriving to mean values around 30%.

#### 4 Results and discussions

Comparisons of the OMI OMBRO product with GOME-2 satellite retrievals and remote sensing ground based measurements over Harestua, Norway as well as monthly mean averages illustrate the quality of the retrieval on a global scale. On a local scale, recent scientific studies looking at BrO enhancements in volcanic plumes and over salt lakes are pushing the limits of the current OMBRO setups. In the following sections, we provide details of these comparisons (section 4.1) and discuss OMI OMBRO global distribution (section 4.2) and local enhancements over salt lakes and volcanic plumes observations (section 4.3), and their applicability and strategies to correctly use the publicly available OMBRO product.

##### 4.1 Comparisons with GOME-2 and ground-based observations

To assess the quality of the OMBRO product, we first compared OMI BrO VCDs with BIRA/GOME-2 BrO observations (Theys et al., 2011). GOME-2 has descending orbit with a local equator crossing time (ECT) of 9:30 am and OMI has ascending orbit with an ECT of 1:45 pm. To minimize the effects of diurnal variation especially under high SZAs (e.g., McLinden et al., 2006; Sioris et al., 2006) on the comparison, we conduct the comparison using simultaneous nadir

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overpasses (SNOs) within 2 minutes between GOME-2 and OMI predicted by NOAA National Calibration Center's SNO prediction tool (<https://ncc.nesdis.noaa.gov/SNOPredictions>). Given Aura and Metop-A satellite orbits, all these SNOs occur at high latitudes around 75°S/N. Fig. 5 shows the time series of comparison of individual OMI/GOME-2 BrO retrievals from February 5 2007 through November 2008. The temporal variation of BrO at the SNO locations is captured similarly by OMI and GOME-2 BrO. The scatter plot in Fig. 6 quantifies the comparison between OMI and GOME-2 BrO. OMI BrO shows excellent agreement with GOME-2 BrO with a correlation of 0.74, and a mean bias of  $-0.216 \pm 1.13 \times 10^{13}$  molecules  $\text{cm}^{-2}$  (mean relative bias of  $-2.6 \pm 22.1\%$ ). Considering very different retrieval algorithms including different cross sections and BrO profiles, such a good agreement is remarkable. GOME-2 retrievals use the BrO cross sections of Fleischmann *et al.* (2004) while our BrO retrievals use the BrO cross sections of Wilmouth *et al.* (1999). According to the sensitivity studies by Hendrick *et al.* (2009), using the Fleischmann cross section increases BrO by  $\sim 10\%$ . So, accounting for different cross sections, OMI BrO underestimates the GOME-2 BrO by  $\sim 10\%$ . In addition, the GOME-2 algorithm uses a residual technique to estimate tropospheric BrO from measured BrO SCDs by subtracting a dynamic estimate of stratospheric BrO climatology driven by  $\text{O}_3$  and  $\text{NO}_2$  concentrations and by using two different tropospheric BrO profiles depending on surface albedo conditions. This is very different from the approach of using a single BrO profile in the OMI BrO algorithm, and can contribute to some of the BrO differences. Furthermore, additional algorithm uncertainties in both 10 15 20 algorithms and different spatial sampling can also cause some differences. Fig. 7 shows the VCDs monthly averages of GOME-2 data (green) and OMBRO (black) from February 2007 to December 2009 where the seasonal variations are clearly seen. Our study shows that OMI has negative mean biases of  $0.35 \times 10^{13}$  molecules  $\text{cm}^{-2}$  (12%),  $0.33 \times 10^{13}$  molecules  $\text{cm}^{-2}$  (10%),  $0.25 \times 10^{13}$  molecules  $\text{cm}^{-2}$  (17%), and  $0.30 \times 10^{13}$  molecules  $\text{cm}^{-2}$  (10%) for Alaska, Southern Pacific, Hudson Bay, and 25 Greenland, respectively.

We also used ground-based zenith-sky measurements of total column BrO at Harestua, Norway (Hendrick *et al.*, 2007) to estimate the quality of the OMI BrO. We compared daily mean total BrO at Harestua with the mean OMI BrO from individual footprints that contain the location of 30 Harestua site. Fig. 8 shows the time series of the comparison between OMI total BrO and Harestua total BrO from February 2005 through August 2011 with the scatter plot shown in Fig. 9. Ground-

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based BrO shows an obvious seasonality with high values in the winter/spring and low values in the summer/fall. Such seasonality is well captured by OMI BrO. OMI BrO shows a reasonable good agreement with Harestua BrO with a correlation of 0.46 and a mean bias of  $0.12 \pm 0.76 \times 10^{13}$  molecules  $\text{cm}^{-2}$  (mean relative bias of  $3.18 \pm 16.30\%$ , with respect to individual Harestua BrO).

5 Sihler *et al.* (2012) compared GOME-2 BrO to ground-based observations at Utqiagvik (Barrow) finding the correlation to be weaker ( $r = 0.3$ ), likely due to both elevated and shallow surface layers of BrO. However, their correlation between GOME-2 BrO and ground-based measurements made from the Icebreaker Amundsen, in the Canadian Arctic Ocean, ( $r = 0.4$ ) is closer to our correlation here. From the Harestua data, tropospheric BrO typically consists of 15-30% of the total BrO, larger than what we have assumed in the troposphere. The use of a single BrO profile in the OMI BrO algorithm will likely underestimate the actual BrO. Accounting for the uncertainty due to profile shape, OMI BrO will have a larger positive bias relative to Harestua measurements, which can be caused by other algorithm uncertainties and the spatiotemporal differences between OMI and Harestua BrO.

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#### 4.2 Global distribution of BrO VCDs

Fig. 10 presents the global distribution of monthly mean BrO VCDs for selected months (March, June, September, December) showing BrO seasonality for three different years (2006, 2007 and 2012). BrO typically increases with latitude, with minimal values in the tropics ( $\sim 2 \times 10^{13}$  molecules  $\text{cm}^{-2}$ ) and maximum values ( $\sim 10^{14}$  molecules  $\text{cm}^{-2}$ ) around polar regions especially in the northern hemisphere winter/spring. In the tropics, BrO shows little seasonality but at higher latitudes in polar regions, BrO displays evident seasonality. The seasonality is different between northern and southern hemispheres. In the northern hemisphere, BrO values are larger in spring (March) with widespread enhancement and smaller in fall (September/December). In the southern hemisphere, BrO values are larger in southern hemispheric spring and summer (i.e., September and December) and smaller in the winter (June). Such global distribution and seasonal variation are generally consistent with previous satellite measurements (*cf.* Chance, 1998; [http://bro.aeronomie.be/level3\\_monthly.php?cmd=map](http://bro.aeronomie.be/level3_monthly.php?cmd=map)). BrO in the tropics shows consistent zonal distributions with lower values over land and in the intertropical convergence zone. This might be related to the impacts of clouds on the retrievals (e.g. BrO below thick clouds cannot be

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measured, there are uncertainties in the AMF calculation under cloudy conditions) and will be investigated in detail in future studies. The global distribution and seasonal variation are consistent from year to year, but the distributions from different years disclose some interannual variation. For example, BrO values in 2007 are smaller in January but are larger in March compared to those in 2006. Although OMI data since 2009 have been seriously affected by the row anomaly at certain cross-track positions, the monthly mean data derived from good cross-track positions are hardly affected by the row anomaly as shown from the very similar global distribution and seasonality in 2012.

### 4.3 Salt lakes and volcanic plumes enhancements of BrO

10 Following recent work by Hörmann *et al.* (2016) over the Rann of Kutch using OMI BrO retrievals  
15 from an independent research product we have explored the capability of our OMBRO product to  
observe similar enhancements in other salt lakes. Fig. 1 shows monthly averaged OMI BrO over  
the Great Salt Lake for 06/2006, the corresponding surface albedo used in the retrieval, cloud cover  
(assuming a cloud filter of 40%) as well as the cloud pressure. Over the Great Salt Lake, BrO  
20 enhancement occurs predominantly over the lake bed with enhancements of  $\sim 5\text{-}10 \times 10^{12}$  molecules  
 $\text{cm}^{-2}$  over background values ( $3\text{-}4 \times 10^{13}$  molecules  $\text{cm}^{-2}$ ). Despite observing these enhancements,  
the users of OMBRO for these kinds of studies should be aware of three limitations of the current  
retrieval algorithm. First, the BrO columns assume a mostly stratospheric BrO profile (Fig. 3 left  
25 panel) for the AMF calculation. Second, the OMI derived albedo climatology (Kleipool *et al.*  
2008) used in OMBRO has a resolution of  $0.5^\circ$ . At this resolution OMBRO retrievals can have  
biases given the size of OMI pixels and the inherent sub-pixel albedo variability. Finally, high  
albedos inherent to salt lakes surface yield abnormally high cloud fractions and low cloud  
pressures over the salt lakes (Hörmann *et al.*, 2016). All these factors should be considered in  
studies addressing the spatiotemporal distribution of BrO over salt lakes using OMBRO.

25 During our analysis of volcanic eruption scenarios, it was discovered that the currently  
implemented  $\text{SO}_2$  molecular absorption cross sections (Vandaele *et al.*, 1994) are a sub-optimum  
choice (see Fig. 12). Compared to more recent laboratory measurements (Hermans *et al.*, 2009;  
Vandaele *et al.*, 2009), the original  $\text{SO}_2$  cross sections implemented in OMBRO do not extend  
30 over the full BrO fitting window and exhibit the wrong behavior longward of 324 nm,

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overestimating the most recent measurement by up to a factor of 3. As the correlation between BrO and both SO<sub>2</sub> cross sections are very small (-0.03 for the current SO<sub>2</sub> and 0.11 for the latest SO<sub>2</sub> cross sections) over the spectral range of SO<sub>2</sub> cross sections, interference by SO<sub>2</sub> in BrO retrievals is usually not an issue at average atmospheric SO<sub>2</sub> concentrations, but strong volcanic eruptions will render even small SO<sub>2</sub> absorption features past 333 nm significant. Around 334 nm, the Vandaele *et al.* (2009) data show an SO<sub>2</sub> feature that correlates with BrO absorption when SO<sub>2</sub> concentrations are significantly enhanced. As a consequence of this spectral correlation, SO<sub>2</sub> may be partially aliased as BrO, since the implemented SO<sub>2</sub> cross sections cannot account for it. Fig. 13 presents an example from the 2010 Eyjafjallajökull eruption to show that the BrO retrieval can be affected by the choice of SO<sub>2</sub> cross sections. The next version of the OMBRO public release will be produced using the updated SO<sub>2</sub> absorption cross sections. Until then, caution is advised when using the OMI BrO product during elevated SO<sub>2</sub> conditions. We recommend to use OMBRO product together with the operational OMI SO<sub>2</sub> product (Li *et al.*, 2013) to flag abnormally high BrO retrievals.

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The top panels of Fig. 13 show daily average operational BrO VCDs from the eruption of the Eyjafjallajökull volcano on May 5 and 17, 2010, respectively. Enhanced BrO values in excess of  $8.0 \times 10^{13}$  molecules cm<sup>-2</sup> are detected in the vicinity of this volcano (e.g., plume extending southeastward from the volcano on May 5 and, high BrO over Iceland on May 17). Some of these enhanced BrO values correspond to the locations of enhanced SO<sub>2</sub> as shown from the NASA global SO<sub>2</sub> monitoring website (<https://so2.gsfc.nasa.gov/>). This enhancement of BrO is not related to the seasonal variation of BrO as no such BrO enhancement is detected over Eyjafjallajökull during May 5-17, 2011 (a year after the eruption), with BrO values of only up to  $\sim 5.3 \times 10^{13}$  molecules cm<sup>-2</sup> (not shown). The bottom panels of Fig. 13 show the same BrO retrievals using SO<sub>2</sub> cross sections by Vandaele *et al.* (2009). Using the improved SO<sub>2</sub> cross sections increase the BrO over a broader area on both days, supporting that the choice of SO<sub>2</sub> cross sections can affect the BrO retrievals. However, BrO enhancement around the volcano can still clearly be seen with the improved SO<sub>2</sub> cross sections. This suggests that this BrO enhancement is not totally due to aliasing of SO<sub>2</sub> as BrO, but *potentially* real BrO from the volcanic eruption.

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## 5 Conclusions

This paper describes the current operational OMI BrO retrieval algorithm developed at SAO and the corresponding V3 OMI total BrO (OMBRO) product in detail. The OMI BrO retrieval algorithm is based on nonlinear least-squares direct fitting of radiance spectra in the spectral range 319.0-347.5 nm to obtain vertical column densities (VCDs) directly in one step. Compared to previous versions of two-step algorithms, the fitting window was moved to shorter wavelengths and the spectral range was increased to reduce the fitting uncertainty. Because air mass factors (AMFs) vary significantly with wavelengths as a result of significant variation of  $O_3$  absorption, the wavelength and surface albedo dependent AMF, which is precomputed with the Linearized Discrete Ordinate Radiative Transfer (LIDORT) code using a single mostly stratospheric BrO profile, is applied pre-fit to BrO cross sections for direct fitting of VCDs. Prior to the spectral fitting of BrO, wavelength calibration is performed for both irradiance and radiance at each cross-track position and reference spectra are properly prepared at the radiance wavelength grid. Then radiances are modeled from the measured solar irradiance, accounting for rotational Raman scattering, undersampling, attenuation from BrO and interfering gases, and including additive and multiplicative closure polynomials, and the average fitting residual spectrum. To maintain consistency with previous versions, a second fitting of all OMI spectra is performed with unmodified BrO cross sections to derive SCDs and the effective AMFs. Then a destriping step is employed to reduce the cross-track dependent stripes.

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The uncertainties of BrO VCDs included in the data product include only spectral fitting uncertainties, which typically vary between 4 and  $7 \times 10^{12}$  molecules  $cm^{-2}$  (10-20% of BrO VCDs, could be as low as 5% over BrO hotspots), consistent throughout the data record. The uncertainties vary with cross-track positions, from  $\sim 7 \times 10^{12}$  at nadir positions to  $\sim 4 \times 10^{12}$  at edge positions. We have investigated additional fitting uncertainties caused by interferences from  $O_2-O_2$ ,  $H_2CO$ ,  $O_3$ , and  $SO_2$ , the impact of the choice of fitting window, the use of common mode, the orders of closure polynomials, and instrument slit functions. Uncertainties in the AMF calculations are estimated at  $\sim 10\%$  unless the observation is made over a region with high tropospheric BrO columns. In this case, the use of a single stratospheric BrO profile is another source of uncertainty, overestimating AMFs (up to 50%) and therefore underestimating BrO VCDs.

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We compared OMI BrO VCDs with BIRA/GOME-2 BrO observations at locations of simultaneous nadir overpasses (SNOs), which only occur around 75°N and 75°S. OMI BrO shows excellent agreement with GOME-2 BrO with a correlation of 0.74, and a mean bias of  $-0.216 \pm 1.13 \times 10^{13}$  molecules  $\text{cm}^{-2}$  (mean relative bias of  $-2.6 \pm 22.1\%$ ). Monthly mean OMBRO VCDs during 2007-2009 show negative biases of  $0.25-0.35 \times 10^{13}$  molecules  $\text{cm}^{-2}$  (10-17%) over Alaska, Southern Pacific, Hudson Bay, and Greenland, respectively. We also compared OMI BrO with ground-based zenith-sky measurements of total BrO at Harestua, Norway. The BrO seasonality in Harestua is well captured by the OMI BrO and OMBRO retrieval showing a reasonable good agreement with the ground-based measurements. The correlation between both datasets is of 0.46 and the mean bias  $0.12 \pm 0.76 \times 10^{13}$  molecules  $\text{cm}^{-2}$  (mean relative bias of  $3.18 \pm 16.30\%$ ).

The global distribution and seasonal variation of OMBRO are generally consistent with previous satellite measurements. There are small values in the tropics with little seasonality, and large values at high latitudes with distinct seasonality. The seasonality is different between the northern and southern hemisphere, with larger values in the hemispheric winter/spring (spring/summer) and smaller values in summer/fall (winter) for the northern (southern) hemisphere. This spatiotemporal variation is generally consistent from year to year and is hardly affected by the row anomaly, but does show some interannual variation. Finally, we have explored the feasibility of detecting enhanced BrO column over salt lakes and in volcanic plumes using OMBRO retrievals. We found enhancement of the BrO with respect to the background levels of  $5-10 \times 10^{12}$  molecules  $\text{cm}^{-2}$  over the U.S. Great Salt Lake. We also observed a significant enhancement from the eruption of Eyjafjallajökull volcano although BrO retrievals under high  $\text{SO}_2$  conditions can be affected by the current use of a sub-optimal choice of  $\text{SO}_2$  cross sections.

Several important retrieval issues in the current operational algorithm that affect the quantitative use BrO VCDs have been raised in this paper such as the exclusion of  $\text{O}_2\text{-O}_2$  nonoptimal  $\text{SO}_2$  cross sections, the neglect of radiative effect of  $\text{O}_3$  absorption, and the assumption of stratospheric only BrO profile. The users are advised to pay attention to these issues so that the product can be used properly. Future versions of OMBRO will include updated  $\text{SO}_2$  and  $\text{O}_2\text{-O}_2$  cross sections, corrections for the radiative transfer effect of the  $\text{O}_3$  absorption and reoptimize the spectral fitting

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windows to mitigate the interferences of other trace gases. We will also improve the AMF calculation accounting for clouds and O<sub>3</sub> and will consider the use of model-based climatological BrO profiles. These updates will increase the capabilities of the OMBRO retrieval to quantitatively estimate enhancements over salt lakes and in volcanic plumes.

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#### **Acknowledgements**

This study is supported by NASA Atmospheric Composition Program/Aura Science Team (NNX11AE58G) and the Smithsonian Institution. Part of the research was carried out at the Jet  
10 Propulsion Laboratory, California Institute of Technology, under a contract with NASA. The Dutch-Finnish OMI instrument is part of the NASA EOS Aura satellite payload. The OMI project is managed by NIVR and KNMI in the Netherlands. We acknowledge the OMI International Science Team for providing the SAO OMBRO data product used in this study.

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**Table 1. Fitting window and parameters used to derive BrO vertical column densities**

Parameter	Description/value
Fitting window	319.0 - 347.5 nm
Baseline polynomial	4th order
Scaling polynomial	4th order
Instrument slit function	Hyper-parameterization of pre-flight measurements, Dirksen <i>et al.</i> , 2006
Wavelength calibration	Spectral shift (no squeeze)
Solar reference spectrum	Chance and Kurucz, 2010
BrO cross sections	Wilmouth <i>et al.</i> , 1999, 228K
H <sub>2</sub> CO cross sections	Chance and Orphal, 2011, 300K
O <sub>3</sub> cross sections	Malicet <i>et al.</i> , 1995, 218K, 295K
NO <sub>2</sub> cross sections	Vandaele <i>et al.</i> , 1998, 220K
SO <sub>2</sub> cross sections	Vandaele <i>et al.</i> , 1994, 295K <sup>1</sup> Hermans <i>et al.</i> , 2009; Vandaele <i>et al.</i> , 2009, 295K <sup>2</sup>
OCIO cross sections	Kromminga <i>et al.</i> , 2003, 213K
Molecular Ring cross sections	Chance and Spurr, 1997
Undersampling correction	Computed on-line, Chance <i>et al.</i> , 2005
Residual (common mode) spectrum	Computed on-line between 30°N and 30°S

1. Used in the current operational algorithm.
2. Used for testing sensitivity to SO<sub>2</sub> cross sections and will be used in the next version.



**Table 2. Error analysis studies. For reference, the total number of retrieved pixels not affected by the row anomaly is 58112.**

<u>Description</u>	<u>Median VCD</u> (Molec. cm <sup>-2</sup> )	<u>Median uncertainty</u> (Molec. cm <sup>-2</sup> )	<u>Number of</u> <u>negatives</u>
<u>319 - 347.5 nm Op. (V3)</u>	<u>4.02×10<sup>13</sup></u>	<u>7.11×10<sup>12</sup></u>	<u>88</u>
<u>323.0 - 353.5 nm (V2)</u>	<u>2.65×10<sup>13</sup></u>	<u>9.27×10<sup>12</sup></u>	<u>1604</u>
<u>340.0 - 357.5 nm (V1)</u>	<u>2.86×10<sup>13</sup></u>	<u>1.19×10<sup>13</sup></u>	<u>3351</u>
<u>310.0 - 357.5 nm</u>	<u>1.97×10<sup>13</sup></u>	<u>6.18×10<sup>12</sup></u>	<u>2728</u>
<u>325.0 - 357.5 nm</u>	<u>3.16×10<sup>13</sup></u>	<u>8.02×10<sup>12</sup></u>	<u>1416</u>
<u>With O<sub>2</sub>-O<sub>2</sub></u>	<u>3.54×10<sup>13</sup></u>	<u>7.80×10<sup>12</sup></u>	<u>319</u>
<u>Online slit function</u>	<u>5.09×10<sup>13</sup></u>	<u>7.16×10<sup>12</sup></u>	<u>68</u>
<u>Without common mode</u>	<u>3.89×10<sup>13</sup></u>	<u>1.02×10<sup>13</sup></u>	<u>116</u>
<u>Without H<sub>2</sub>CO</u>	<u>2.52×10<sup>13</sup></u>	<u>6.27×10<sup>12</sup></u>	<u>816</u>

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**Table 3. Summary of different errors sources in the BrO vertical column.**

Error source	Type	Parameter uncertainty	Averaged uncertainty on BrO VCD	Evaluation on method reference
Measurement noise random	Random	S/N 500 - 1000	$4-7 \times 10^{12}$ molec. cm <sup>-2</sup>	Error propagation;
H <sub>2</sub> CO	Systematic	Based on literature reported error estimates	5%	Chance and Orphal, 2011, 300K
O <sub>3</sub>			2%	Malicet et al., 1995, 218K, 295K
BrO			8%	Wilmouth et al., 1999, 228K
NO <sub>2</sub>			3%	Vandaele et al., 1998, 220K
SO <sub>2</sub>			5%	Vandaele et al., 1994, 295K
OCIO			5%	Kromminga et al., 2003, 213K
Ring			5%	Chance and Spurr, 1997
Order of baseline polynomial	Systematic	Vary polynomial order	10%	Sensitivity analysis
Order of scaling polynomial	Systematic	Vary polynomial order	10%	
Instrumental slit function and wavelength calibration	Systematic	Preflight and online slit function	27%	
Wavelength interval	Systematic	Varying fitting window	50%	

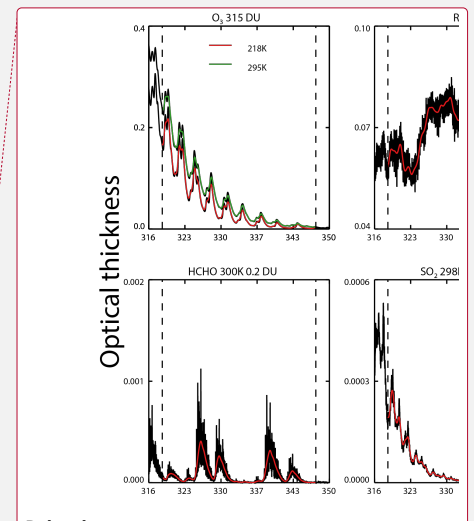
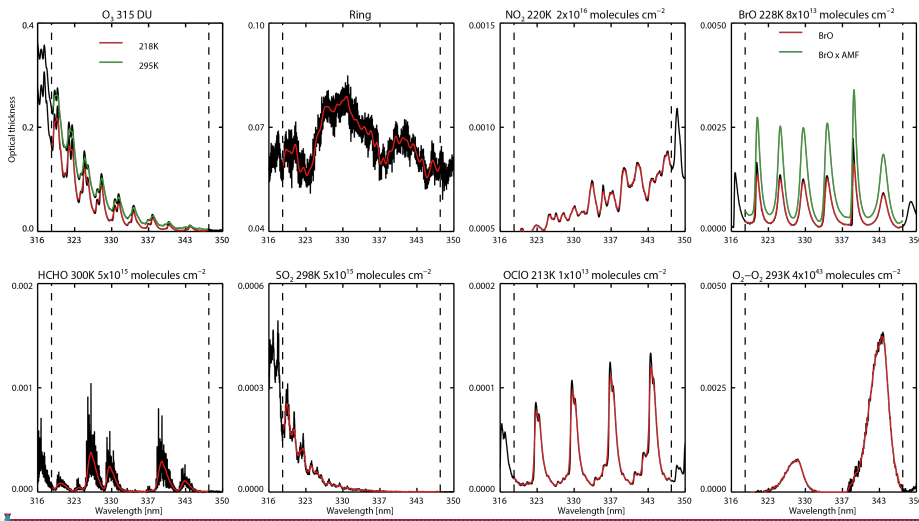
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5 **Figure 1. Cross sections used in the current operational BrO algorithm except for the SO<sub>2</sub> cross section at 298 K which is to be used in the next version. The black lines are the original cross sections, the color lines show the cross sections convolved with approximate OMI slit function (which is assumed to be a Gaussian with 0.42nm full width at half maximum). The O<sub>2</sub>-O<sub>2</sub> calculation is based on Lampel *et al.* (2018) cross sections. The BrO cross section after multiplication with the wavelength-dependent AMFs used these parameters for the AMF calculation: albedo = 0.05, SZA= 5.0°, and VZA = 2.5°. The RMS of the fitting residuals are on the order of 9x10<sup>-4</sup>, indicating that BrO spectral features are slightly bigger than typical fitting residuals.**

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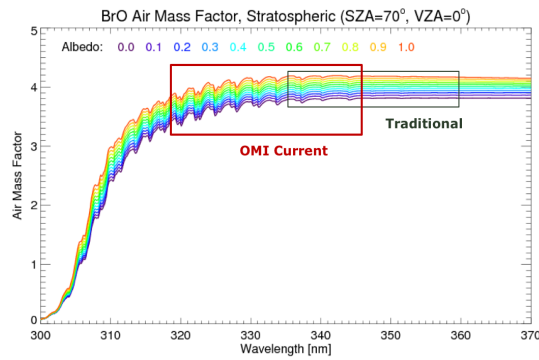


Figure 2. Wavelength- and albedo-dependent air mass factors calculated using a mostly stratospheric fixed BrO profile. The blue box shows the fitting window used in our previous versions, and the red box shows the fitting window used in the current operational algorithm.

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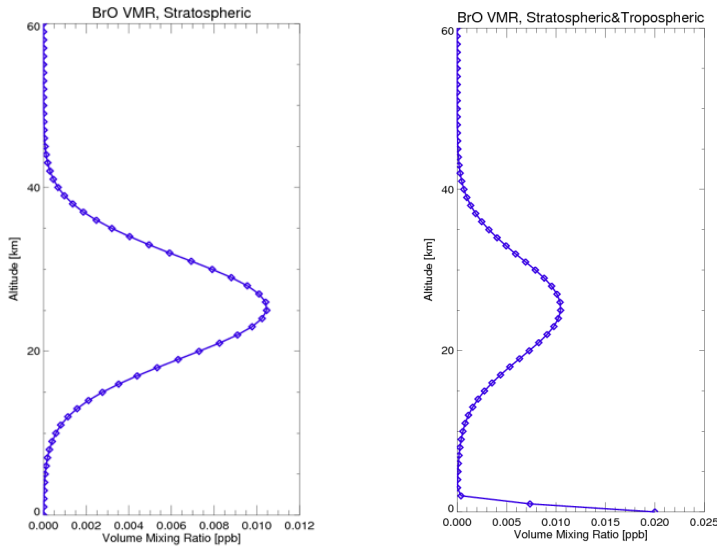
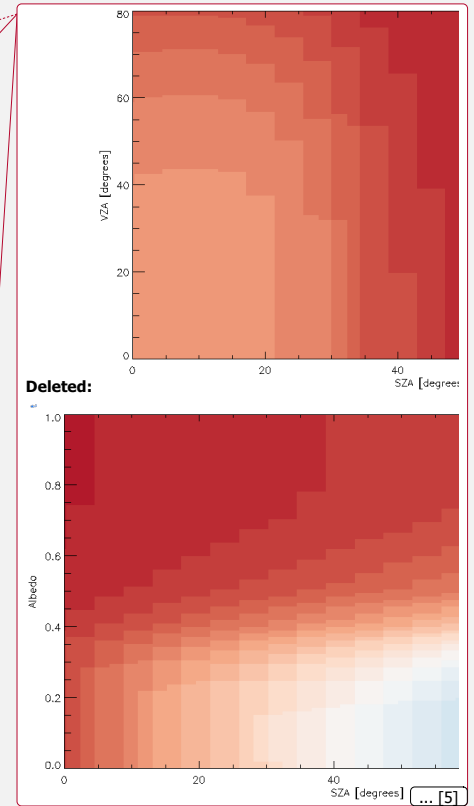
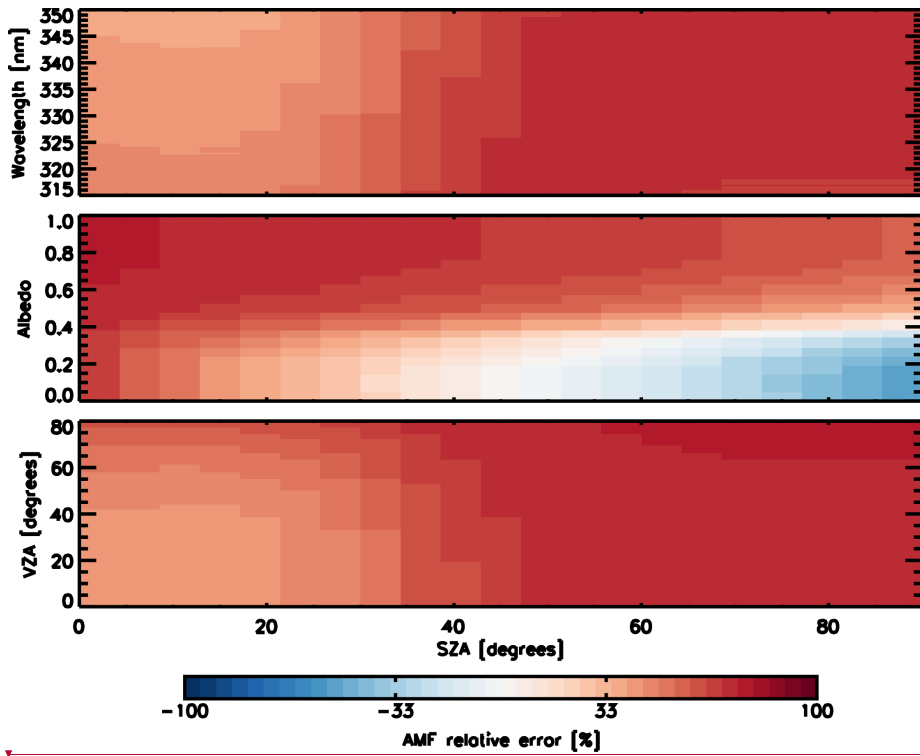


Figure 3. (Left) A mostly stratospheric vertical BrO profile used for air mass factors calculations in OMBRO V3. Total BrO, BrO < 15 km, BrO < 10 km, and BrO < 5km are  $2.05 \times 10^{13}$ ,  $5.06 \times 10^{12}$ ,  $1.55 \times 10^{12}$ , and  $2.87 \times 10^{11}$  molecules  $\text{cm}^{-2}$ , respectively. (Right) A stratospheric tropospheric vertical BrO profile used to investigate the impact of high tropospheric BrO columns on air mass factors calculations. Total BrO, BrO < 15 km, BrO < 10 km, and BrO < 5km are  $6.99 \times 10^{13}$ ,  $5.45 \times 10^{13}$ ,  $5.10 \times 10^{13}$ , and  $4.97 \times 10^{13}$  molecules  $\text{cm}^{-2}$ , respectively.

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Figure 4. The percentage of relative AMF errors as a function of the SZA and the wavelength (top panel), albedo (middle panel) and VZA (bottom panel) when using the stratospheric only BrO profile (Fig. 3, left panel) in the case there exists a significant tropospheric BrO column as shown in the stratospheric-tropospheric BrO profile (Fig. 3, right panel).

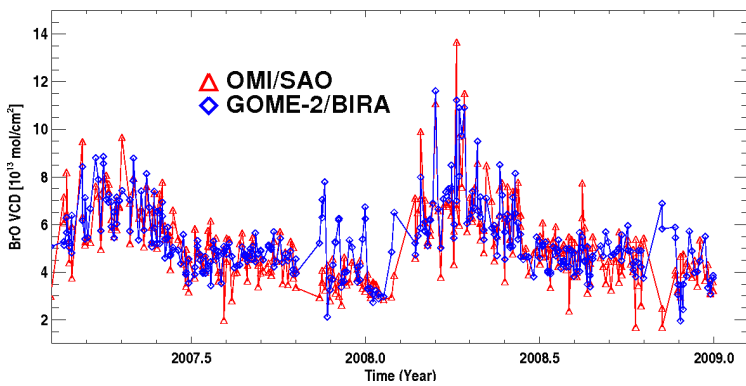


Figure 5. Time series comparison of SAO OMI (red) BrO and BIRA GOME-2 (blue) BrO VCDs from February 2007 to November 2008 using simultaneous nadir overpasses occurring at high latitudes, around 75° S/N, and within 2 minutes between OMI and GOME-2 observations.

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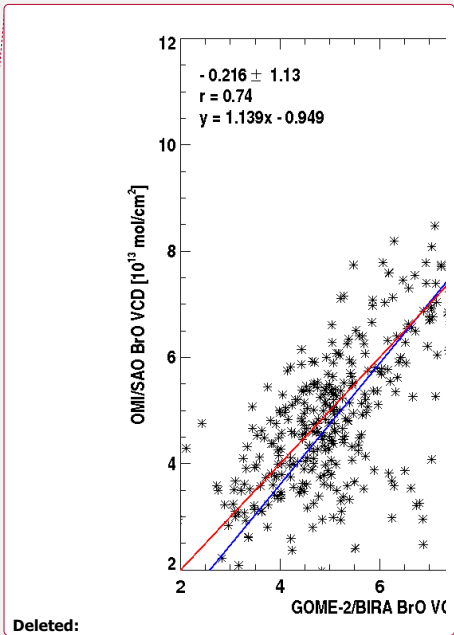
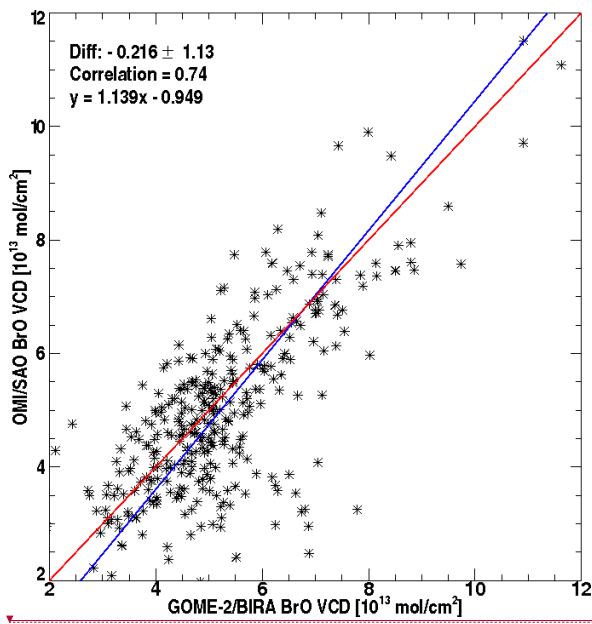
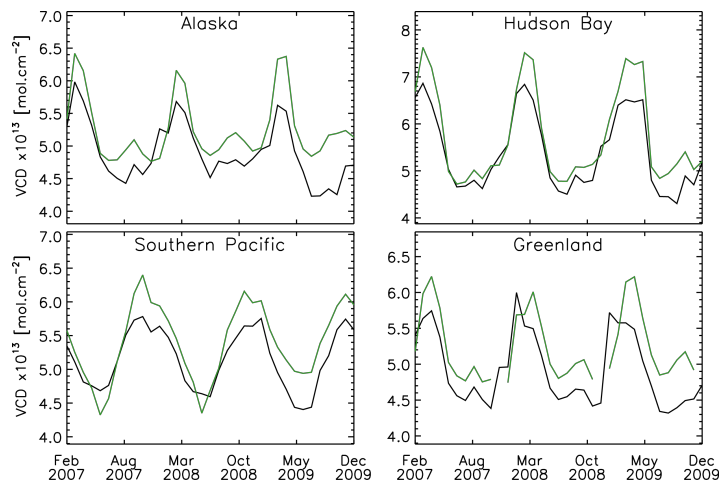
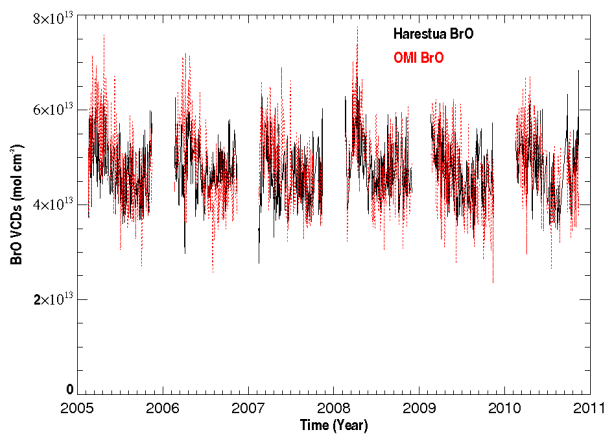


Figure 6. Correlation and orthogonal regression of OMI and GOME-2 BrO for the data shown in Fig. 5. The legends show the mean bias and standard deviation of the differences, correlation, and the orthogonal regression.

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5 **Figure 7. VCD of GOME-2 (green) comparison to OMI (black) over four regions from February 2007 to December 2009 for four regions. Each region is defined by a square with the following latitude/longitude boundaries: Alaska (50°N-70°N/165°W-135°W), Hudson Bay (50°N-65°N/95°W-75°W), Southern Pacific (70°S-50°S/135°E-155°E), and Greenland (60°N-80°N/60°W-15°W).**



10 **Figure 8. Time series comparison of ground-based zenith-sky total BrO (black) at Harestua, Norway and coincident SAO OMI BrO (red) from February 2005 through August 2011.**

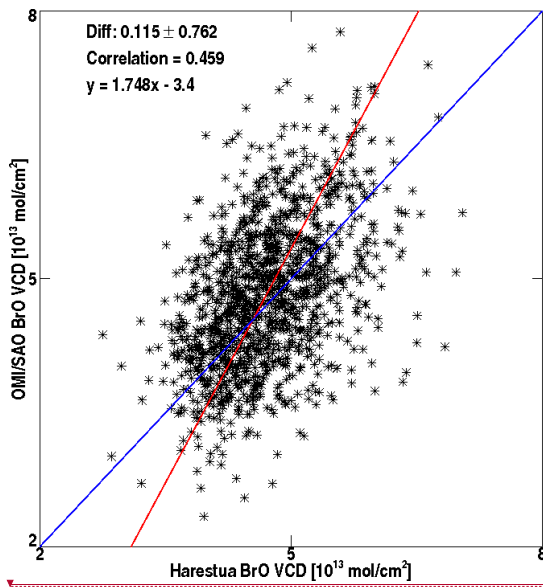
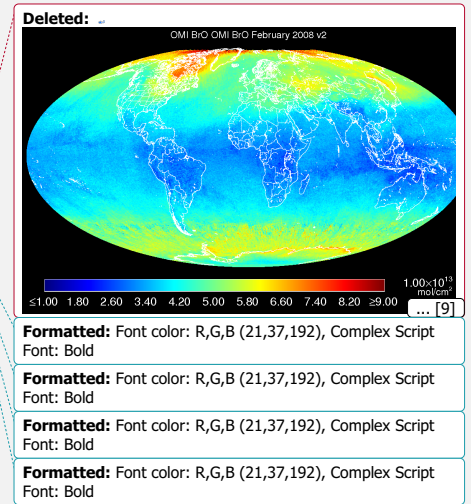
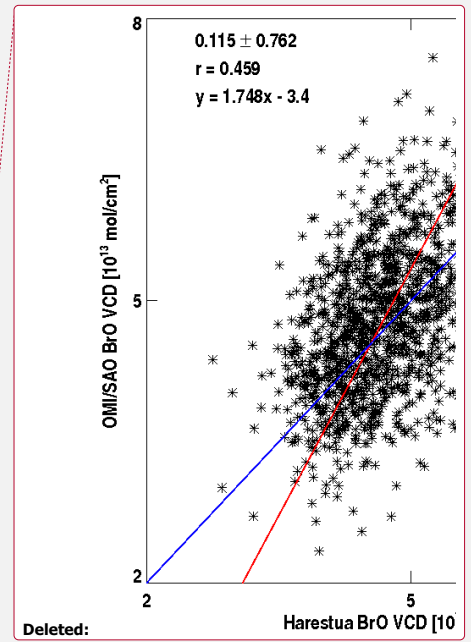


Figure 9. Correlation and orthogonal regression of OMI and Harestua BrO for the data in Fig. 8. The legends show the mean biases and standard deviations of the differences, correlation, and the orthogonal regression.



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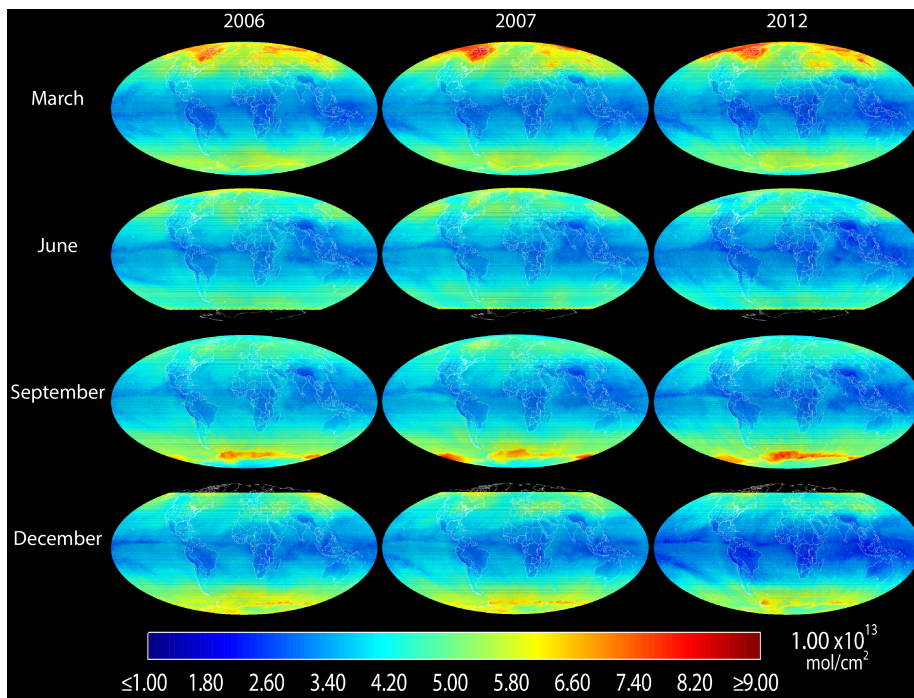


Figure 10. Global distributions of monthly mean BrO VCDs in March, June, September and December (in different rows) of 2006, 2007, and 2012 (different columns). Bromine release “explosions” during the Polar Spring months can be seen clearly.

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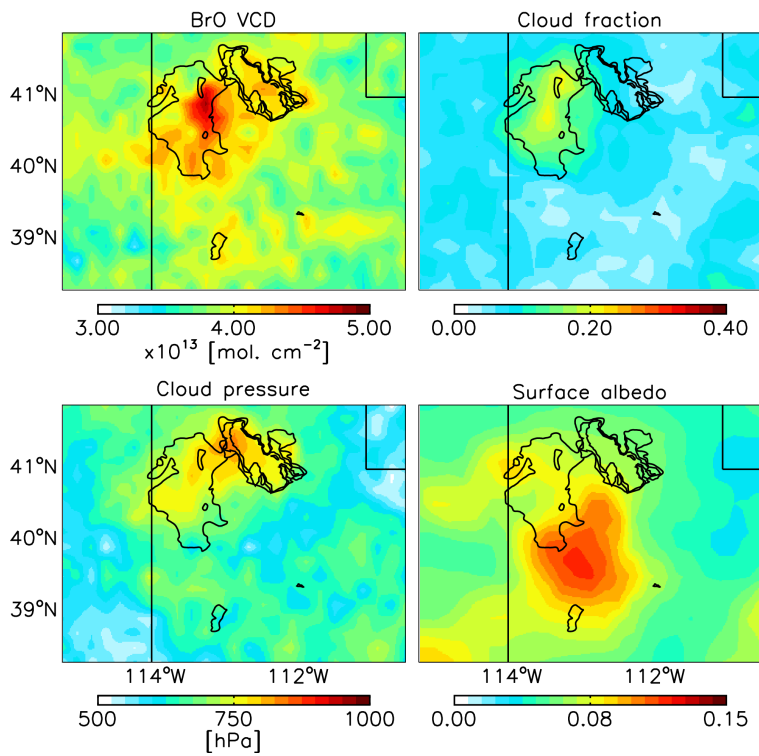
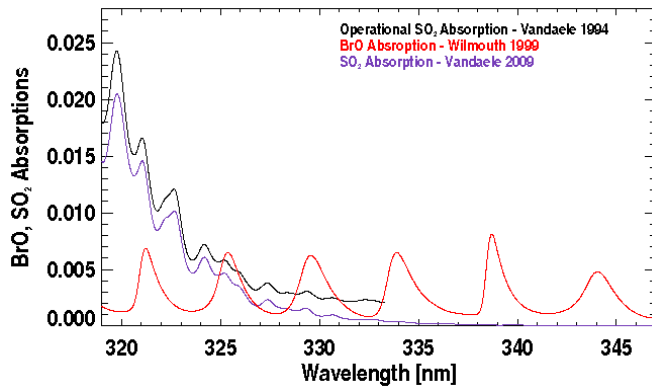


Figure 11. Mean June 2006 BrO VCD over the Great Salt Lake area. Averages have been calculated on a  $0.2^\circ \times 0.2^\circ$  grid including only pixels with cloud fractions smaller than 0.4. The straight lines are borders of the state of Utah, and the curving lines represent the Great Salt Lake (Eastern oval area) and Salt flats (Western oval area).

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Figure 12. Comparison of BrO absorption (red) and SO<sub>2</sub> absorptions under volcanic scenarios based on cross sections used in the operational algorithm (Vandaele et al., 1994) as shown in black and the recent laboratory cross sections (Vandaele et al., 2009) as shown in purple. For BrO, a SCD of  $1.0 \times 10^{14}$  molecules  $\text{cm}^{-2}$  is assumed; for SO<sub>2</sub>, a SCD of 15 Dobson Units (i.e.,  $4.03 \times 10^{17}$  molecules  $\text{cm}^{-2}$ ) is assumed. Cross sections have been convolved with OMI slit function (which is assumed to be a Gaussian with 0.42nm full width at half maximum).

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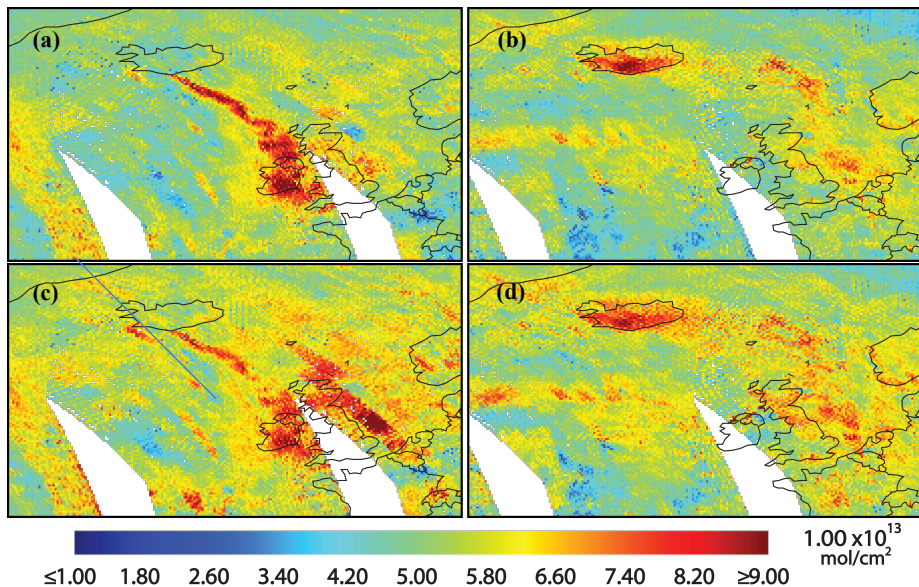
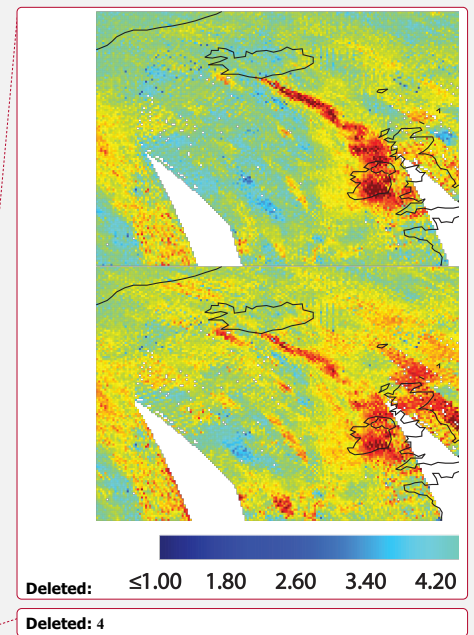


Figure 13. Daily average BrO VCDs from Eyjafjallajökull on May 5 (a) and 17 (b), 2010 produced using the operational SO<sub>2</sub> cross sections and for the same days (c) and (d) using the Vandaele et al. (2009) SO<sub>2</sub> cross sections.

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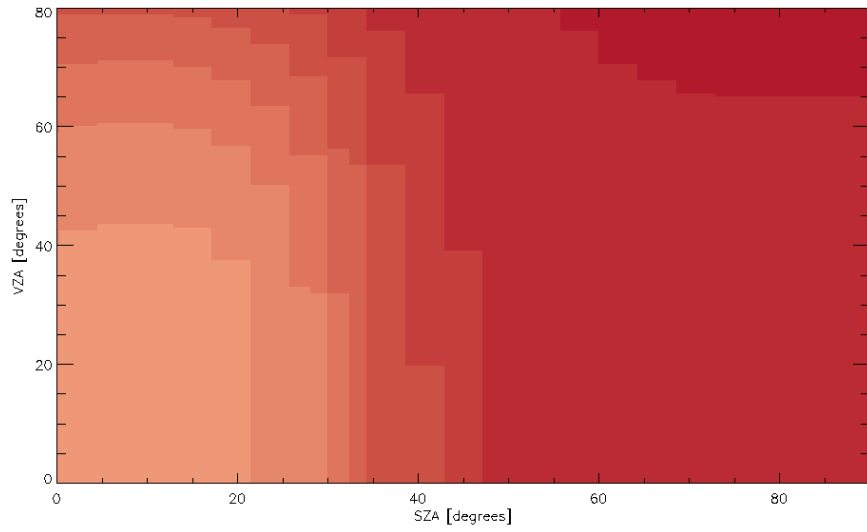


The difference in the mean of the VCDs retrieved using the different fitting windows are always smaller than %50.

Additional sensitivity studies also shown in Table 2 include excluding from the fitting interfering molecules ( $O_4$  and  $CH_2O$ ), using pre-flight measurements of the slit function or calculating them for each orbit, not including the mean residual (common mode) in the spectral fitting, and changing the order of the closure polynomials. In these experiments, everything else is kept the same as in the operational retrieval. In Table 2, we list the median VCDs and the median uncertainties for BrO for 13 July 2009 orbit number 26564 for each one of these retrieval configurations except for the test of the different orders of the closure polynomials. The results of the polynomial sensitivity test are summarized in Table 3.

Table 2 shows the median VCD, median uncertainties and the number of negative pixels for the current operational version (V3), V2, and V1. Fig. 10 shows the monthly mean averages for V3 and V2 for the months of February and May of 2008. The differences on the VCD are about 30% in V3 comparing to V2. In comparison with V2 retrieval, the new retrieval (V9) does not show a large increase in the VCD concentrations, especially at the north polar region. The BrO background concentrations over the Pacific Ocean remain the same between the two versions, however, there are more retrieved VCDs.

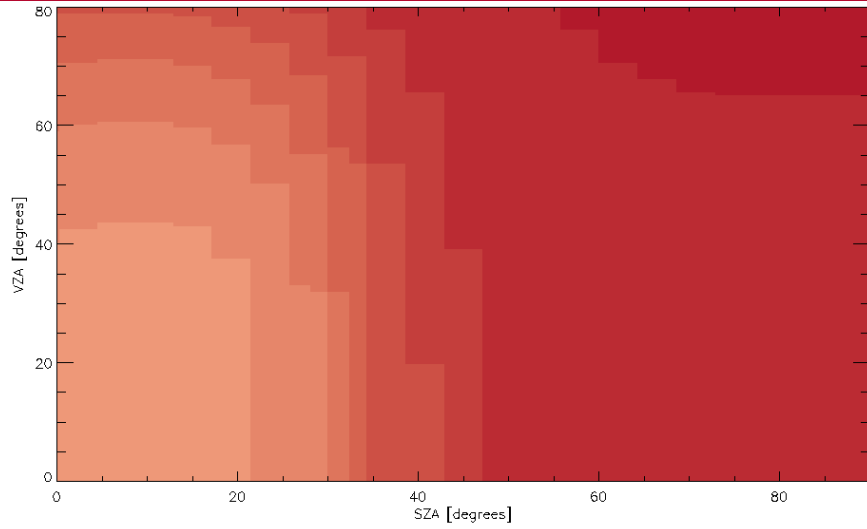
We have done a preliminary analysis of salt water bodies including the Rann of Kutch. Although this work is not fully complete and will be a separate paper, however, we see maximum BrO VCDs appearing during March–May every year from 2004 – 2015 similar to what was reported by Hörmann et al., 2016. The BrO VCDs we see are around  $4.5 \times 10^{13}$  molecules  $cm^{-2}$ .



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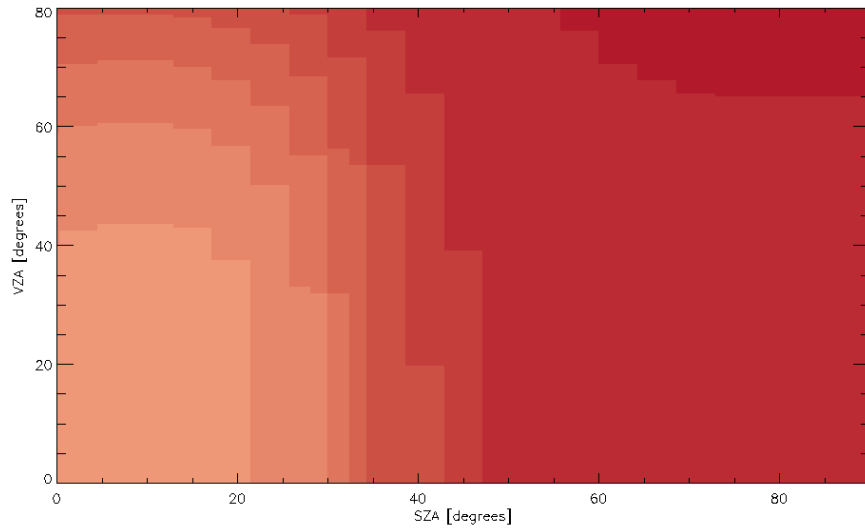
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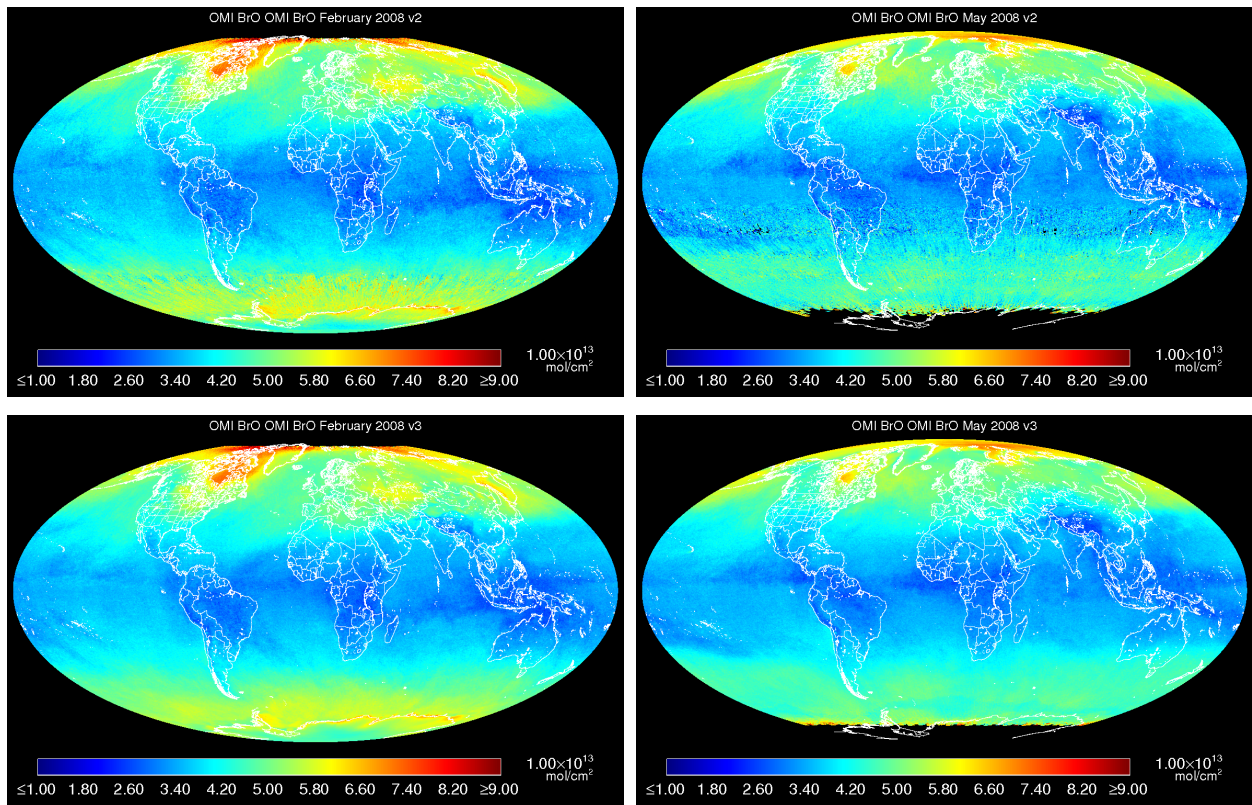


Figure 10. Monthly averages for February and May 2008 for version 3 and version 2.