

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
15 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
20 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 7×10^{12} molecules cm^{-2} (~10-20% of the measured BrO VCDs). The retrievals agree well with GOME-2 observations at simultaneous nadir overpasses and ground-based zenith-sky measurements at Harestua, Norway,
25 with mean biases less than $-0.216 \pm 1.13 \times 10^{13}$ molecules cm^{-2} and $0.12 \pm 0.76 \times 10^{13}$ molecules cm^{-2} , respectively. Global distribution and seasonal variation of OMI BrO are generally consistent with previous satellite observations. Global distribution of BrO from OMBRO shows spatial and temporal patterns similar to GOME-2 retrievals. The OMBRO retrievals show enhancement of BrO over U.S. Great Salt Lake. It also shows significant BrO enhancement from the eruption of
30 the Eyjafjallajökull volcano, although the BrO retrievals are affected under high SO_2 loading conditions by the sub-optimum choice of SO_2 cross sections.

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), and since with SCIAMACHY nadir (Kühl *et al.*, 2008) and Global Ozone Monitoring Experiment 2 (GOME-2) measurements (Theys *et al.*, 2011; Toyota *et al.*, 2011). 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 ozone 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 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
5 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 SO₂ abundances in
10 the plume of the Soufrière Hills volcano (Montserrat) by multi-axis DOAS (MAX-DOAS). BrO and SO₂ 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/SO₂ 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
15 (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/SO₂ ratios.

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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
25 algorithm and product history, spectral fitting, AMF calculations, destripping, and fitting 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.

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 km² at direct nadir to about 28×150 km² at the swath edges. The global mode (GM) has 60 ground pixels with a total cross-track swath of 2600 km. There are also spatial and spectral zoom modes with twice finer across-track spatial resolution at nadir. 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.

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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.

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OMI measures ozone and other trace gases, aerosols, clouds, and surface properties. Products developed at the SAO include operational BrO, chlorine dioxide (OCIO), and formaldehyde (H₂CO; González Abad *et al.*, 2015) that are archived at NASA Goddard Earth Sciences (GES) Data and Information Services Center (DISC), and offline (“pre-operational”) ozone profile and tropospheric ozone (O₃) (Liu *et al.*, 2010; Huang *et al.*, 2017, 2018), glyoxal (C₂H₂O₂) (Chan Miller *et al.*, 2014, 2016) and water vapor (H₂O) (Wang *et al.*, 2014, 2016) that are available at

the Aura validation data center (AVDC). All the products except for the ozone 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).

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 radiance and irradiance spectra in OMI GM and RSZM level 1b data product. 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.

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 H₂CO, H₂O and C₂H₂O₂ 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.

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). Unlike the often-used DOAS fitting method (Platt, 1994), radiances are not ratioed to irradiances, logarithms are not taken, and no high-pass filtering is applied.

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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). To improve cross-track stripe correction (Section 3.4) and reduce the noise in the solar irradiance data, the OMI irradiance spectra are composites derived from a principal component analysis of three years of individual 25 OMI irradiance measurements (2005-2007). 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.

Following wavelength correction, an undersampling correction spectrum is computed to partially 30 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 fully-sampled and undersampled representations (Chance *et al.*, 2005).

- 5 Fitting is then performed for all scan lines in the OMI swath granule. In each stage, the fitting is performed individually for the 60 cross-track pixels of a block of 100 OMI across-track swath lines along the flight direction (30 cross-track pixels for the RSZM) according to Eq. (1):

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

- 10 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, α_i , β_j , γ_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. The reference spectra are derived separately for each cross-track position from original high-resolution cross sections convolved with the corresponding OMI slit functions after correcting for the solar
- 15 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
- 25 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.

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 α_i as shown in Eq. 1. Radiances I are then modeled as the this quantity attenuated by absorption from BrO, O₃, NO₂, H₂CO, and SO₂ with coefficients β_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 γ_k after the Beer-Lambert law contribution terms. 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 30°S) 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 (*Polybaseline*) and multiplicative closure polynomials (*PolyScale*), 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 O₄. The spectral region of 343 nm, where O₄ has a small absorption feature, 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 O₄, 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 O₄ 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 O₄ from the fit. It is impossible to quantify O₄ atmospheric content from the absorption feature around 343 nm alone, and its correlation with

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absorption bands of BrO and CH₂O leads to spectral correlations in the course of the non-linear least squares minimization process that are detrimental to the OMI BrO retrievals.

5 3.3 Air mass factors

Due to significant variation in ozone 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.

10 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 SCIMACHY radiances in the shortwave infrared (Buchwitz *et al.*, 2000) and has been demonstrated for total O₃ and SO₂ retrievals from GOME/SCIAMACHY measurements in the ultraviolet (Bracher *et al.*, 2005; 15 Coldewey-Egbers *et al.*, 2005; Weber *et al.*, 2005; Lee *et al.*, 2008).

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% 20 BrO below 15 km, ~10% BrO below 10 km, and ~2% BrO below 5 km. For conditions with enhanced BrO in the lower troposphere, using this profile will overestimate the AMFs and therefore underestimate the BrO VCDs. The AMF profile used can lead to errors up to 50% with variations of albedos and viewing geometry. The mean absolute difference between AMF calculations using the stratospheric profile and the stratospheric-tropospheric profile (Fig. 3, right 25 panel) is 41%. 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%.

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 $AMF = SCD/VCD$.

5 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°, and VZA (Viewing Zenith Angle) = 2.5°). The wavelength-dependence in AMF is visible from the varying differences near BrO absorption peaks and the right wings at different wavelengths. The correlation of the unmodified BrO cross sections with the rest of the fitted
10 molecules is small (typically less than 0.12), except with H₂CO (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 H₂CO under high H₂CO and background BrO conditions similar to De Smedt et al., 2015. In addition, the AMF wavelength dependence increases with the increase of solar and viewing zenith angles and surface
15 albedo, which increases the correlation between modified BrO cross sections and O₃ cross sections. However, the correlation with O₃ becomes noticeable (~0.10) only at SZAs above ~80°.

3.4 Destriping

OMI L1b data exhibit small differences with cross-track position, due to differences in the
20 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. This method, originally developed to mitigate the effect of the South Atlantic Anomaly in SAO
25 OMI BrO, H₂CO, 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 σ 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 processing slow. However, we do it once for a reference scan line, recording the positions of the
30 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.

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 1σ fitting error in parameter i is determined as

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

where ε_{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.

The fitting uncertainties for single measurements of the BrO VCDs typically vary between 4×10^{12} and 7×10^{12} molecules 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.

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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 ozone column, *etc.*) and other sources of VCD uncertainty are not included. We provide here error estimates for these additional error sources.

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 a stratospheric only BrO profile and a stratospheric-tropospheric profile. In this case, we find that the mean absolute difference is 41%. Fig. 4 shows the dependency of the AMFs relative error with respect to wavelength (bottom panel), albedo (middle panel) and VZA (top panel) as a function of the SZA.

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We have investigated the sensitivity of OMI BrO VCD with respect to the retrieval window. We studied four 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). Table 2 summarizes the results of these studies. The current window results in the most stable retrievals with the smallest number of pixels with negative VCD values. The difference in the mean of the VCDs retrieved using the different fitting windows are always smaller than %50.

20 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. To study the impact of the slit function variation we have performed the retrieval using both an online slit function modelled as a Gaussian and the preflight instrument function. The mean difference between these two retrievals is 14% (see Table 3) for orbit number 26564.

To study the impact of the radiative transfer effects of the ozone absorption in our retrieval we have adopted the correction method described by Pukite et al., 2010. We find that between 60 degrees south and 60 degrees north the average difference is smaller than 10% with values around 5 2% near the equator. However, as we move near the poles with solar zenith angles above 60 degrees 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 10 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 15 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 and OMI have different orbits: 20 descending orbit with a local equator crossing time (ECT) of 9:30 am for GOME-2 and afternoon ascending orbit with an ECT of 1:45 pm for OMI. 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 overpasses (SNOs) within 2 minutes between GOME-2 and OMI predicted by NOAA National Calibration Center's SNO prediction tool 25 (<https://ncc.nesdis.noaa.gov/SNOPredictions>). Due to different 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 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 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 O_3 and 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 algorithms and different spatial sampling can also cause some differences. Fig. 7 shows the VCDs monthly averages of GOME2 data (green) to OMBRO (black) from February 2007 to December 2009 where the seasonal variations are clearly seen. GOME2 VCDs show an upward trend that is not seen in OMI retrieved VCDs. Our study shows the mean difference for the whole period is 12%, 10%, 17%, and 10% for Alaska, Southern Pacific, Hudson Bay, and Greenland respectively.

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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 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-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 cm^{-2} (mean relative bias of $3.18 \pm 16.30\%$, with respect to individual Harestua BrO). 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

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of BrO. However, their correlation between GOME-2 BrO and ground-based measurements at Amundsen, U.S. ($r = 0.4$) 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.

4.2 Global distribution of BrO VCDs

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.

Fig. 11 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 cm^{-2}) and maximum values ($\sim 10^{14}$ molecules 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 the winter/spring and smaller in the summer/fall, and the enhancement is more widespread during the spring. In the southern hemisphere, BrO values are larger in southern hemispheric spring and summer (i.e., September and January) and smaller in the winter. 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). 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 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.

5 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.

10 **4.3 Salt lakes and volcanic plumes enhancements of BrO**

Following recent work by Hörmann *et al.* (2016) over the Rann of Kutch we have explored the capability of OMBRO to observe similar enhancements in other salt lakes. Fig. 12 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 15 the Great Salt Lake, BrO enhancement occurs predominantly over the lake bed with enhancements of $\sim 5\text{-}10 \times 10^{12}$ molecules cm^{-2} over background values ($3\text{-}4 \times 10^{13}$ molecules 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 (Figure 3) for the AMF calculation. Second, the OMI derived albedo 20 climatology (Kleipool *et al.* 2008) used in OMBRO has a resolution of 0.5 degrees. 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 25 using OMBRO. 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 4.5×10^{13} molecules cm^{-2} .

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During our analysis of volcanic eruption scenarios, it was discovered that the currently implemented SO₂ molecular absorption cross sections (Vandaele *et al.*, 1994) are a sub-optimum choice (see Fig. 13). Compared to more recent laboratory measurements (Hermans *et al.*, 2009; Vandaele *et al.*, 2009), the original SO₂ cross sections implemented in OMBRO do not extend over the full BrO fitting window and exhibit the wrong behavior longward of 324 nm, overestimating the most recent measurement by up to a factor of 3. As the correlation between BrO and both SO₂ cross sections are very small (-0.03 for the current SO₂ and 0.11 for the latest SO₂ cross sections) over the spectral range of SO₂ cross sections, interference by SO₂ in BrO retrievals is usually not an issue at average atmospheric SO₂ concentrations, but strong volcanic eruptions will render even small SO₂ absorption features past 333 nm significant. Around 334 nm, the Vandaele *et al.* (2009) data show an SO₂ feature that correlates with BrO absorption when SO₂ concentrations are significantly enhanced. As a consequence of this spectral correlation, SO₂ may be partially aliased as BrO, since the implemented SO₂ 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 SO₂ cross sections. The next version of the OMBRO public release will be produced using the updated SO₂ absorption cross sections. Until then, caution is advised when using the OMI BrO product during elevated SO₂ conditions. We recommend to use OMBRO product together with the operational OMI SO₂ product (Li *et al.*, 2013) to flag abnormally high BrO retrievals.

The top panels of Fig. 14 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 8.0×10^{13} are detected in the vicinity of this volcano (e.g., plume extending southeast ward 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 SO₂ as shown from the NASA global SO₂ 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⁻² (not shown). The bottom panels of Fig. 14 show the same BrO retrievals using SO₂ cross sections by

Vandaele et al. (2009). Using the improved SO₂ cross sections increase the BrO over a broader area on both days, supporting that the choice of SO₂ cross sections can affect the BrO retrievals. However, BrO enhancement around the volcano can still clearly be seen with the improved SO₂ cross sections. This suggests that this BrO enhancement is not totally due to aliasing of SO₂ as
5 BrO, but real BrO from the volcanic eruption.

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
10 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 ozone
15 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
20 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
25 employed to reduce the cross-track dependent stripes.

The uncertainties of BrO VCDs included in the data product include only spectral fitting uncertainties, which typically vary between 4 and 7×10^{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
30 vary with cross-track positions, from $\sim 7 \times 10^{12}$ at nadir positions to $\sim 4 \times 10^{12}$ at edge positions. The

use of single stratospheric BrO profile is another source of uncertainty, overestimating AMFs and therefore underestimating BrO VCDs for conditions with enhanced BrO in the lower troposphere. In addition, the used SO₂ cross sections are a sub-optimum choice and can cause errors in the retrievals under high SO₂ concentrations.

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We compared OMI BrO VCDs with BIRA/GOME-2 BrO observations at locations of simultaneous nadir overpasses. 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 cm⁻² (mean relative bias of $-2.6 \pm 22.1\%$). We also compared OMI BrO with ground-based zenith-sky measurements of total
10 BrO at Harestua, Norway. This BrO seasonality in Harestua total BrO is well captured by the OMI BrO and OMI BrO shows a reasonable good agreement with a moderate correlation of 0.46 and a small mean bias of $0.12 \pm 0.76 \times 10^{13}$ molecules cm⁻² (mean relative bias of $3.18 \pm 16.30\%$). The global distribution and seasonal variation of OMI BrO are generally consistent with previous satellite measurements. There are small values in the tropics with no much seasonality, and large
15 values at high latitudes with distinct seasonality. And 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. The retrievals show
20 enhanced BrO of $5-10 \times 10^{12}$ molecules cm⁻² over the U.S. Great Salt Lake and also significant enhancement from the eruption of Eyjafjallajökull volcano despite BrO retrievals under high SO₂ conditions can be affected by the current use of a sub-optimal choice of SO₂ cross sections.

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References

- Abbatt, J. P. D., Thomas, J. L., Abrahamsson, K., Boxe, C., Granfors, A., Jones, A. E., King, M. D., Saiz-Lopez, A., Shepson, P. B., Sodeau, J., Toohey, D. W., Toubin, C., von Glasow, R., Wren, S. N., Yang, X.: Halogen activation via interactions with environmental ice and snow, *Atmos. Chem. Phys.*, 12, 6237–6271, <https://doi.org/10.5194/acp-12-6237-2012>, 2012.
- 5 Acarreta, J.R., De Haan, J.F., and Stammes, P.: Cloud pressure retrieval using the O₂-O₂ absorption band at 477 nm, *J. Geophys. Res.-Atmos.*, 109, <http://dx.doi.org/10.1029/2003JD003915>, 2004.
- Aliwell, S.R., Van Roozendaal, M., Johnston, P.V., Richter, A., Wagner, T., Arlander, D.W., Burrows, J.P., Fish, D.J., Jones, R.L., Tornkvist, K.K., Lambert, J.-C., Pfeilsticker, K., Pundt, I.,
- 10 Analysis for BrO in zenith-sky spectra: An intercomparison exercise for analysis improvement, *J. Geophys. Res.*, 107(D14), doi:10.1029/2001JD000329, 2002.
- Blechschmidt, A.-M., Richter, A., Burrows, J. P., Kaleschke, L., Strong, K., Theys, N., Weber, M., Zhao, X., Zien, A.: An exemplary case of a bromine explosion event linked to cyclone development in the Arctic, *Atmos. Chem. Phys.*, 16, 1773-1788, [https://doi.org/10.5194/acp-16-](https://doi.org/10.5194/acp-16-1773-2016)
- 15 [1773-2016](https://doi.org/10.5194/acp-16-1773-2016), 2016.
- Bobrowski, N., Hönninger, G., Galle, B. and Platt, U.: Detection of bromine monoxide in a volcanic plume, *Nature*, 423, 273-276, 2003.
- Bobrowski, N., von Glasow, R., Aiuppa, A., Inguaggiato, S., Louban, I., Ibrahim, O.W., and Platt, U.: Reactive halogen chemistry in volcanic plumes, *J. Geophys. Res. Atmos.*, 112, D06311, doi:10.1029/2006JD007206, 2007.
- 20 Bobrowski, N., von Glasow, R., Giuffrida, G.B., Tedesco, D., Aiuppa, A., Yalire, M., Arellano, S., Johansson, M., and Galle, B.: Gas emission strength and evolution of the molar ratio of BrO/SO₂ in the plume of Nyiragongo in comparison to Etna, *J. Geophys. Res Atmos.*, 120, 277-291, doi:10.1002/2013JD0 21069, 2015.
- 25 Bracher, A., Lamsal, L.N., Weber, M., Bramstedt, K., Coldewey-Egbers, M., and Burrows, J.P.: Global satellite validation of SCIAMACHY O₃ columns with GOME WFDOAS, *Atmos. Chem. Phys.*, 5, 2357-2368, <https://doi.org/10.5194/acp-5-2357-2005>, 2005.
- Buchwitz, M., Rozanov, V.V., and Burrows, J.P.: A near-infrared optimized DOAS method for the fast global retrieval of atmospheric CH₄, CO, CO₂, H₂O, and N₂O total column amounts from
- 30 SCIAMACHY Envisat-1 nadir radiances, *J. Geophys. Res.*, D105, 15231–15245, 2000.

- Burd, Justine A., Peterson, Peter K., Nghiem, Son V., Perovich, Don K., Simpson, William R.: Snowmelt onset hinders bromine monoxide heterogeneous recycling in the Arctic, *J. Geophys. Res., Atmos.*, 122, 8297-8309, 2017.
- Burrows, J.P. and Chance, K.V.: Scanning Imaging Absorption Spectrometer for Atmospheric
5 Cartography, *Proc. S.P.I.E., Future European and Japanese Remote Sensing Sensors and Programs*, 1490 146-154, 1991.
- Caspar, C. and Chance, K.: GOME wavelength calibration using solar and atmospheric spectra, in: *Third ERS Symposium on Space at the service of our Environment*, edited by: Guyenne, T.-D. and Danesy, D., Vol. 414 of *ESA Special Publication*, p. 609, 1997.
- 10 Chan Miller, C., González Abad, G., Wang, H., Liu, X., Kurosu, T., Jacob, D.J., and Chance, K.: Glyoxal retrieval from the Ozone Monitoring Instrument, *Atmos. Meas. Tech.*, 7, 3891-3907, 2014.
- Chan Miller, C., Jacob, D.J., González Abad, G., and Chance, K.: Hotspot of glyoxal over the Pearl River Delta seen from the OMI satellite instrument: Implications for emissions of aromatic
15 hydrocarbons, *Atmos. Chem. Phys.*, 16, 4631-4639, doi:10.5194/acp-16-4631-2016, 2016.
- Chance, K. and Kurucz, R., An improved high-resolution solar reference spectrum for earth's atmosphere measurements in the ultraviolet, visible, and near infrared, *J. Quant. Spectrosc. Radiat. Transfer*, 111, 1289–1295, doi:10.1016/j.jqsrt.2010.01.036, 2010.
- Chance, K., and Orphal, J.: Revised ultraviolet absorption cross sections of H₂CO for the HITRAN
20 database, *J. Quant. Spectrosc. Radiat. Transfer*, 112, 1509-1510, doi:10.1016/j.jqsrt.2011.02.002, 2011.
- Chance, K., and Kurucz, R.L.: An improved high-resolution solar reference spectrum for Earth's atmosphere measurements in the ultraviolet, visible, and near infrared, *J. Quant. Spectrosc. Radiat. Transfer*, 111, 1289-1295, 2010.
- 25 Chance, K., Kurosu, T.P., and Sioris, C.E.: Undersampling correction for array-detector based satellite spectrometers, *Appl. Opt.*, 44, 1296-1304, 2005.
- Chance, K., Palmer, P.I., Spurr, R.J.D., Martin, R.V., Kurosu, T.P., and Jacob, D. J.: Satellite observations of formaldehyde over North America from GOME, *Geophys. Res. Lett.*, 27, 3461–3464, doi:10.1029/2000GL011857, 2000.
- 30 Chance, K.: Analysis of BrO measurements from the Global Ozone Monitoring Experiment, *Geophys. Res. Lett.*, 25, 3335-3338, 1998.

- Chance, K.: Spectroscopic Measurements of Tropospheric Composition from Satellite Measurements in the Ultraviolet and Visible: Steps Toward Continuous Pollution Monitoring from Space, in “Remote Sensing of the Atmosphere for Environmental Security,” Eds. A. Perrin, N. Ben Sari-Zizi, and J. Demaison, NATO Security through Science Series, ISBN: 1-4020-5089-5, 5 Springer, pp. 1-25, 2006.
- Chance, K.V. and Spurr, R.J.D.: Ring effect studies: Rayleigh scattering, including molecular parameters for rotational Raman scattering, and the Fraunhofer spectrum, *Appl. Opt.*, 36, 5224-5230, doi:10.1364/AO.36.005224, 1997.
- Chance, K.V., Burrows, J.P., and Schneider, W.: Retrieval and molecule sensitivity studies for the 10 Global Ozone Monitoring Experiment and the SCanning Imaging Absorption spectrometer for Atmospheric CHartography, *Proc. S.P.I.E., Remote Sensing of Atmospheric Chemistry*, 1491, 151-165, 1991.
- Choi, S., Wang, Y., Salawitch, R.J., Canty, T., Joiner, J., Zeng, T., Kurosu, T.P., Chance, K., Richter, A., Huey, L.G., Liao, J., Neuman, J.A., Nowak, J.B., Dibb, J.E., Weinheimer, A.J., Diskin, 15 G., Ryerson, T.B., da Silva, A., and Curry, J.: Analysis of satellite-derived Arctic tropospheric BrO columns in conjunction with aircraft measurements during ARCTAS and ARCPAC, *Atmos. Chem. Phys.*, 12, 1255-1285, doi: 10.5194/acp-12-1255-2012, 2012.
- Coldewey-Egbers, M., Weber, M., Lamsal, L.N., de Beek, R., Buchwitz, M., and Burrows, J.P.: Total ozone retrieval from GOME UV spectral data using the weighting function DOAS approach, 20 *Atmos. Chem. Phys.*, 5, 1015-1025, <https://doi.org/10.5194/acp-5-1015-2005>, 2005.
- De Smedt, I., Van Roozendaal, M., Stavrakou, T., Müller, J.- F., Lerot, C., Theys, N., Valks, P., Hao, N., and van der A, R. (2012). Improved retrieval of global tropospheric formaldehyde columns from GOME-2/MetOp-A addressing noise reduction and instrumental degradation issues. *Atmospheric Measurement Techniques*, 5(11):2933–2949.
- 25 De Smedt, I., Stavrakou, T., Hendrick, F., Danckaert, T., Vlemmix, T., Pinardi, G., Theys, N., Lerot, C., Gielen, C., Vigouroux, C., Hermans, C., Fayt, C., Veefkind, P., Müller, J.-F., and Van Roozendaal, M.: Diurnal, seasonal and long-term variations of global formaldehyde columns inferred from combined OMI and GOME-2 observations, *Atmos. Chem. Phys.*, 15, 12519–12545, <https://doi.org/10.5194/acp-15-12519-2015>, 2015.
- 30 Dirksen, R., Dobber, M., Voors, R., and Levelt, P.: Prelaunch characterization of the Ozone Monitoring Instrument transfer function in the spectral domain, *Appl. Opt.*, 45, 3972-3981, 2006.

- Fleischmann, O.C., Hartmann, M., Burrows, J.P., and Orphal, J.: New ultraviolet absorption cross sections of BrO at atmospheric temperatures measured by time-windowing Fourier transform spectroscopy, *J. Photochem. Photobiol. A.*, 168, 117–132, doi:10.1016/j.jphotochem.2004.03.026, 2004.
- 5 González Abad, G., Liu, X., Chance, K., Wang, H., Kurosu, T.P., and Suleiman, R.: Updated Smithsonian Astrophysical Observatory Ozone Monitoring Instrument (SAO OMI) formaldehyde retrieval, *Atmos. Meas. Tech.*, 8, 19-32, doi:10.5194/amt-8-19-2015, 2015.
- Greenblatt, G. D., Orlando, J. J., Burkholder, J. B., and Ravishankara, A. R. (1990). Absorption measurements of oxygen between 330 and 1140 nm. *J. Geophys. Res.*, 95:18577–18582.
- 10 Frieß, U., Sihler, H., Sander, R., Pöhler, D., Yilmaz, S., Platt, U.: The vertical distribution of BrO and aerosols in the Arctic: Measurements by active and passive differential optical absorption spectroscopy, *J. Geophys. Res.*, 116, D00R04, doi: 10.1029/2011JD015938, 2011.
- Hausmann, M., Platt, U.: Spectroscopic measurement of bromine oxide and ozone in the high Arctic during Polar Sunrise Experiment 1992, *J. Geophys. Res.*, D12, 25399-25413, 1994.
- 15 Hebestreit, K., Stutz, J., Rosen, D., Matveiv, V., Peleg, M., Luria, M., Platt, U.: DOAS Measurements of Tropospheric Bromine Oxide in Mid-Latitudes, *Science*, 283, 5398, 55, doi: 10.1126/science.283.5398.55, 1999.
- Hendrick, F., Van Roozendael, M., Chipperfield, M.P., Dorf, M., Goutail, F., Yang, X., Fayt, C., Hermans, C., Pfeilsticker, K., Pommereau, J.-P., Pyle, J.A., Theys, N., and De Mazière, M.
- 20 Retrieval of stratospheric and tropospheric BrO profiles and columns using ground-based zenith-sky DOAS observations at Harestua, 60° N, *Atmos. Chem. Phys.*, 7, 4869-4885, <https://doi.org/10.5194/acp-7-4869-2007>, 2007.
- Hendrick, F., Johnston, P.V., De Mazière, M., Fayt, C., Hermans, C., Kreher, K., Theys, N., Thomas, A., and Van Roozendael, M.: One-decade trend analysis of stratospheric BrO over
- 25 Harestua (60° N) and Lauder (45° S) reveals a decline, *Geophys. Res. Lett.*, 35, L14801, doi:10.1029/2008gl034154, 2008.
- Hendrick, F., Rozanov, A., Johnston, P.V., Bovensmann, H., De Mazière, M., Fayt, C., Hermans, C., Kreher, K., Lotz, W., Sinnhuber, B.-M., Theys, N., Thomas, A., Burrows, J.P., and Van Roozendael, M.: Multi-year comparison of stratospheric BrO vertical profiles retrieved from
- 30 SCIAMACHY limb and ground-based UV-visible measurements, *Atmos. Meas. Tech.*, 2, 273-285, <https://doi.org/10.5194/amt-2-273-2009>, 2009.

- Hermans, C., Vandaele, A.C., and Fally, S.: Fourier transform measurements of SO₂ absorption cross sections: I. Temperature dependence in the 24 000 - 29 000 cm⁻¹ (345-420 nm) region, *J. Quant. Spectrosc. Radiat. Transfer*, 110, 756-765, 2009.
- Hermans, C., Vandaele, A.C., Fally, S., Carleer, M., Colin, R., Coquart, B., Jenouvrier, A., and
5 Merienne, M.-F.: Absorption cross sections of the collision-induced bands of oxygen from the UV to the NIR, NATO Advanced Research Workshop on Weakly Interacting Molecular Pairs: Unconventional Absorbers of Radiation in the Atmosphere, Eds. C. Camy-Peyret and A. Vigasin, Kluwer Academic Publ., NATO Meeting series, ISBN: 1-4020-1596-8, 193-202, 2003.
- Hermans, C., Vandaele, A. C., Carleer, M., Fally, S., Colin, R., Jenouvrier, A., Coquart, B., and
10 Mérienne, M.-F. (1999). Absorption cross-sections of atmospheric constituents: NO₂, O₂, and H₂O. *Environ. Sci. & Pollut. Res.*, 6(3):151–158.
- Holla, R., Schmitt, S., Frieß, U., Pöhler, D., Zingler, J., Corsmeier, U., Platt, U.: Vertical distribution of BrO in the boundary layer at the Dead Sea, *Environ. Chem.*, 10.1071/EN14224, 12, 4, 438-460, 2015.
- 15 Hollwedel, J., Wenig, M., Beirle, S., Kraus, S., Kühl, S., Wilms-Grabe, W., Platt, U., and Wagner, T.: Year-to-year variations of spring time polar tropospheric BrO as seen by GOME, *Adv. Space Res.*, 34, 4, 804-808, 2004.
- Hörmann, C., Sihler, H., Bobrowski, N., Beirle, S., Penning de Vries, M., Platt, U., Wagner, T.: Systematic investigation of bromine monoxide in volcanic plumes from space by using the
20 GOME-2 instrument, *Atmos. Chem. Phys.*, 13, 4749-4781, <https://doi.org/10.5194/acp-13-4749-2013>, 2013.
- Hörmann, C., Sihler, H., Beirle, S., Penning de Vries, M., Platt, U., and Wagner, T.: Seasonal variation of tropospheric bromine monoxide over the Rann of Kutch salt marsh seen from space, *Atmos. Chem. Phys.*, 16, 13015-13034, doi:10.5194/acp-16-13015-2016, 2016.
- 25 Huang, G., Liu, X., Chance, K., Yang, K., Bhartia, P. K., Cai, Z., Allaart, M., Ancellet, G., Calpini, B., Coetzee, G.J.R., Cuevas-Agulló, E., Cupeiro, M., De Backer, H., Dubey, M.K., Fuelberg, H.E., Fujiwara, M., Godin-Beekmann, S., Hall, T.J., Johnson, B., Joseph, E., Kivi, R., Kois, B., Komala, N., König-Langlo, G., Laneve, G., Leblanc, T., Marchand, M., Minschwaner, K.R., Morris, G., Newchurch, M.J., Ogino, S.-Y., Ohkawara, N., Pitters, A.J.M., Posny, F., Querel, R., Scheele, R.,
30 Schmidlin, F.J., Schnell, R.C., Schrems, O., Selkirk, H., Shiotani, M., Skrivánková, P., Stübi, R., Taha, G., Tarasick, D.W., Thompson, A. M., Thouret, V., Tully, M. B., Van Malderen, R., Vömel,

- H., von der Gathen, P., Witte, J.C., and Yela, M.: Validation of 10-year SAO OMI Ozone Profile (PROFOZ) product using ozonesonde observations, *Atmos. Meas. Tech.*, 10, 2455-2475, <https://doi.org/10.5194/amt-10-2455-2017>, 2017.
- Huang, G., Liu, X., Chance, K., Yang, K., and Cai, Z.: Validation of 10-year SAO OMI Ozone Profile (PROFOZ) Product Using Aura MLS Measurements, *Atmos. Meas. Tech.*, 11, 17-32, <https://doi.org/10.5194/amt-11-17-2018>, 2018.
- Kinnison, D., Tilmes, S., Levelt, P.F., Dirksen, R., Dobber, M., Voors, R., and Levelt, P.: Prelaunch characterization of the Ozone Monitoring Instrument transfer function in the spectral domain, *Appl. Opt.*, 45, 3972–3981, doi:10.1364/AO.45.003972, 2006.
- 10 Kleipool, Q.L., Dobber, M.R., de Haan, J.F., and Levelt, P.F.: Earth surface reflectance climatology from 3 years of OMI data, *J. Geophys. Res.*, 113, D18308, doi:10.1029/2008JD010290, 2008.
- Kromminga, H., Voigt, S., Orphal, J., and Burrows, J.P.: The temperature dependence (213–293 K) of the absorption cross-sections of OCIO in the 340–450 nm region measured by Fourier-
15 transform spectroscopy, *J. Photochem. Photobiol. A*, 157, 149-160, 2003.
- Kroon, M., de Haan, J.F., Veeffkind, J.P., Froidevaux, L., Wang, R., Kivi, R., and Hakkarainen, J.J., Validation of operational ozone profiles from the Ozone Monitoring Instrument, *J. Geophys. Res.*, 116, D18305, doi:10.1029/2010JD015100, 2011.
- Kühl, S., Pukite, J., Deutschmann, T., Platt, U., and Wagner, T.: SCIAMACHY limb
20 measurements of NO₂, BrO and OCIO. Retrieval of vertical profiles: algorithm, first results, sensitivity and comparison studies, *Adv. Space Res.*, 42, 1747-1764, 2008.
- Kurosu, T.P., Chance, K., and Sioris, C.E.: Preliminary results for HCHO and BrO from the EOS-Aura Ozone Monitoring Instrument, in *Proc. SPIE 5652, Passive Optical Remote Sensing of the Atmosphere and Clouds IV*, doi: 10.1117/12.578606 2004.
- 25 Lee, C., Richter, A., Weber, M., and Burrows, J.P.: SO₂ Retrieval from SCIAMACHY using the Weighting Function DOAS (WFDOAS) technique: comparison with Standard DOAS retrieval, *Atmos. Chem. Phys.*, 8, 6137–6145, 2008.
- Levelt, P.F., van den Oord, G.H.J., Dobber, M.R., Mälkki, A., Visser, H., de Vries, J., Stammes, P., Lundell, J., and Saari, H.: The Ozone Monitoring Instrument, *IEEE Trans. Geo. Rem. Sens.*,
30 44, 1093-1101, doi:10.1109/TGRS.2006.87233, 2006.

- Li, C., Joiner, J., Krotkov, N. A., and Bhartia, P. K.: A fast and sensitive new satellite SO₂ retrieval algorithm based on principal component analysis: Application to the ozone monitoring instrument, *Geophys. Res. Lett.*, 40, 6314–6318, <https://doi.org/10.1002/2013GL058134>, 2013.
- J. Liao, H. Sihler, L. G. Huey, J. A. Neuman, D. J. Tanner, U. Friess, U. Platt, F. M. Flocke, J. J. Orlando, P. B. Shepson, H. J. Beine, A. J. Weinheimer, S. J. Sjostedt, J. B. Nowak, D. J. Knapp, R. M. Staebler, W. Zheng, R. Sander, S. R. Hall, and K. Ullmann: A comparison of Arctic BrO measurements by chemical ionization mass spectrometry and long path-differential optical absorption spectroscopy, *J. Geophys. Res.-Atmos.*, 116, D00r02, doi:10.1029/2010jd014788, 2011.
- 10 Liao, J., Huey, L. G., Tanner, D. J., Flocke, F. M., Orlando, J. J., Neuman, J. A., Nowak, J. B., Weinheimer, A. J., Hall, S. R., Smith, J. N., Fried, A., Staebler, R. M., Wang, Y., Koo, J.-H., Cantrell, C. A., Weibring, P., Walega, J., Knapp, D. J., Shepson, P. B., Stephens, C. R.: Observations of inorganic bromine (HOBr, BrO, and Br₂) speciation at Barrow, Alaska, in spring 2009, *J. Geophys. Res. Atmos.*, 117, DOI:10.1029/2011JD016641, 2012
- 15 Lindström, P., and Wedin, P.-Å.: Gauss-Newton Based Algorithms for Constrained Nonlinear Least Squares Problems, Tech. Rep. UMINF-901.87, University of Umeå, 1987 (software and report available at <http://plato.asu.edu/sub/nonlsq.html>).
- Liu, X., Bhartia, P.K., Chance, K., Spurr, R.J.D., and Kurosu, T.P.: Ozone profile retrievals from the Ozone Monitoring Instrument, *Atmos. Chem. Phys.* 10, 2521-2537, 2010.
- 20 Malicet, J., Daumont, D., Charbonnier, J., Parisse, C., Chakir, A., and Brion, J.: Ozone UV spectroscopy. II. Absorption cross sections and temperature dependence, *J. Atmos. Chem.*, 21, 263-273, doi:10.1007/BF00696758, 1995.
- Marquardt, D.L.: An algorithm for least-squares estimation of non-linear parameters, *J. Soc. Indust. Appl. Math.* 2, 431-441, 1963.
- 25 Martin, R.V., Sioris, C.E., Chance, K., Ryerson, T.B., Bertram, T.H., Wooldridge, P.J., Cohen, R.C., Neuman, J.A., Swanson, A., and Flocke, F.M.: Evaluation of space-based constraints on global nitrogen oxide emissions with regional aircraft measurements over and downwind of eastern North America, *J. Geophys. Res.*, 111, D15308, doi:10.1029/2005JD006680, 2006.
- Matveev, V., Mordechai, P., Rosen, D., Tov-Alper, D.S., Hebestreit, K., Stutz, J., Platt, U., Blake, D., and Luria, M.: Bromine oxide-ozone interaction over the Dead Sea, *J. Geophys. Res. Atmos.*, 106, 10375-10387, 2001.

- McLinden, C. A., Haley, C. S., and Sioris, C. E., Diurnal effects in limb scatter observations, *J. Geophys. Res.*, 111, D14302, doi:10.1029/2005JD006628, 2006.
- OMI Algorithm Theoretical Basis Document, Volume IV, OMI Trace Gas Algorithms, K. Chance, Ed., ATBD-OMI-04, Version 2.0, 2002.
- 5 Peterson, P. K., Simpson, W. R., and Nghiem, S. V.: Variability of bromine monoxide at Barrow, Alaska, over four halogen activation (March–May) seasons and at two on-ice locations, *J. Geophys. Res.-Atmos.*, 121, 1381–1396, doi:10.1002/2015JD024094, 2016.
- Peterson, Peter K., Simpson, William R., Nghiem, Son V.: Variability of bromine monoxide at Barrow, Alaska, over four halogen activation (March-May) seasons and at two on-ice locations, *J.*
- 10 *Geophys. Res. Atmos.*, 121, 1381-1396, 2016.
- Platt, U.: Differential optical absorption spectroscopy (DOAS), *Chem. Anal. Series*, **127**, 27-83, 1994.
- Platt, U. and Wagner, T.: Satellite mapping of enhanced BrO concentrations in the troposphere, *Nature*, 395, 6701, 486-490, 1998.
- 15 Press, W.H., Flannery, B.P., Teukolsky, S.A., and Vetterling, W.T.: *Numerical Recipes*, ISBN 0-521-30811-9, Cambridge University Press, 1986.
- Richter, A., Begoin, M., Hilboll, A., and Burrows, J.P., An improved NO₂ retrieval for the GOME-2 satellite instrument, *Atmos. Meas. Tech.*, 4, 1147–1159, 2011 doi:10.5194/amt-4-1147-2011.
- 20 Puk, J., Janis, J., Kühl, S., Deutschmann, T., Platt, U., and Wagner, T. (2010). Extending differential optical absorption spectroscopy for limb measurements in the UV. *Atmospheric Measurement Techniques*, 3(3):631–653.
- Richter, A., Wittrock, F., Eisinger, M., and Burrows, J.P., GOME observations of tropospheric BrO in northern hemispheric spring and summer 1997, *Geophys. Res. Lett.*, 25, 14, 2683-2686,
- 25 1998.
- Rodgers, C.D.: *Inverse methods for atmospheric sounding*, World Scientific, 2000.
- Salawitch, R.J., Canty, T., Kurosu, T., Chance, K., Q. Liang A. da Silva S. Pawson J. E. Nielsen J. M. Rodriguez P. K. Bhartia X. Liu L. G. Huey J. Liao R. E. Stickel D. J. Tanner J. E. Dibb W. R. Simpson D. Donohue A. Weinheimer F. Flocke D. Knapp D. Montzka J. A. Neuman
- 30 J. B. Nowak T. B. Ryerson S. Oltmans D. R. Blake E. L. Atlas D. E. Kinnison S. Tilmes L. L. Pan F. Hendrick M. Van Roozendael K. Kreher P. V. Johnston R. S. Gao B. Johnson T. P. Bui

- G. Chen R. B. Pierce J. H. Crawford D. J. Jacob: A new interpretation of total column BrO during Arctic spring, *Geophys. Res. Lett.*, 37, L21805, doi:10.1029/2010GL043798, 2010.
- Salawitch, R.J., Weinstein, D.K., Kovalenko, L.J., Sioris, C.E., Wennberg, P.O., Chance, K., Ko, M.K.W., and McLinden, C.A.: Sensitivity of ozone to bromine in the lower stratosphere, *Geophys. Res. Lett.*, 32, 5, L05811, doi:10.1029/2004GL021504, 2005.
- Schofield, R., Connor, B.J., Kreher, K., Johnston, P.V., and Rodgers, C.D.: The retrieval of profile and chemical information from groundbased UV-visible spectroscopic measurements, *J. Quant. Spectrosc. Radiat. Transfer*, 86, 115 – 131, 2004a.
- Schofield, R., Johnston, P.V., Thomas, A., Kreher, K., Connor, B.J., Wood, S., Shooter, D.,
10 Chipperfield, M P., Richter, A., von Glasow, R., and Rodgers, C.D.: Tropospheric and stratospheric BrO columns over Arrival Heights, Antarctica, 2002, *J. Geophys. Res.*, 111, D22310, doi:10.1029/2005JD007022, 2006.
- Schofield, R., Kreher, K., Connor, B.J., Johnston, P.V., Thomas, A., Shooter, D. Chipperfield, M.P., Rodgers, C.D., and Mount, G.H.: Retrieved tropospheric and stratospheric BrO columns
15 over Lauder, New Zealand, *J. Geophys. Res.*, 109, D14304, doi:10.1029/2003JD00446, 2004b.
- Simpson, W.R., Alvarez-Aviles, L., Douglas, T.A., Sturm, M., and Domine, F.: Halogens in the coastal snow pack near Barrow, Alaska: Evidence for active bromine air-snow chemistry during springtime, *Geophys. Res. Lett.*, 32, L04811, doi:10.1029/2004GL021748, 2005.
- Sihler, H., Platt, U., Beirle, S., Marbach, T., Kühl, S., Dörner, S., Verschaeve, J., Frieß, U., Pöhler,
20 D., Vogel, L., Sander, R., Wagner, T.: Tropospheric BrO column densities in the Arctic derived from satellite: retrieval and comparison to ground-based measurements, *Atmos. Meas. Tech.*, 5, 2779-2807, <https://doi.org/10.5194/amt-5-2779-2012>, 2012.
- Simpson, W. R., von Glasow, R., Riedel, K., Anderson, P., Ariya, P., Bottenheim, J., Burrows, J., Carpenter, L. J., Frieß, U., Goodsite, M. E., Heard, D., Hutterli, M., Jacobi, H.-W., Kaleschke, L.,
25 Neff, B., Plane, J., Platt, U., Richter, A., Roscoe, H., Sander, R., Shepson, P., Sodeau, J., Steffen, A., Wagner, T., Wolff, E.: Halogens and their role in polar boundary-layer ozone depletion, *Atmos. Chem. Phys.*, 7, 4375-4418, <https://doi.org/10.5194/acp-7-4375-2007>, 2007.
- Sioris, C.E., Kovalenko, L.J., McLinden, C.A., Salawitch, R.J., Van Roozendaal, M., Goutail, F., Dorf M., Pfeilsticker, K., Chance, K., von Savigny, C., Liu, X., Kurosu, T.P., Pommereau, J.-P.,
30 Bosch, H., and Frerick, J., Latitudinal and vertical distribution of bromine monoxide in the lower

stratosphere from Scanning Imaging Absorption Spectrometer for Atmospheric Chartography limb scattering measurements, *J. Geophys. Res.*, 111, D14301, doi:10.1029/2005JD006479, 2006.

Slijkhuis, S., von Barga, A., Thomas, W., and Chance, K.: Calculation of undersampling correction spectra for DOAS spectral fitting, in *Proceedings of the European Symposium on Atmospheric Measurements from Space*, 563–569, 1999.

Spurr, R.J.D.: VLIDORT: A linearized pseudo-spherical vector discrete ordinate radiative transfer code for forward model and retrieval studies in multilayer multiple scattering media, *J. Quant. Spectrosc. Radiat. Transfer*, 102, 316–342, doi:10.1016/j.jqsrt.2006.05.005, 2006.

Stutz, J., Ackermann, Ralf, Fast, Jerome D., Barrie, Leonard: Atmospheric reactive chlorine and bromine at the Great Salt Lake, Utah, *Geophys. Res. Lett.*, 29, 18-1, doi: 10.1029/2002GL014812, 2002.

Stutz, J., Thomas, J. L., Hurlock, S. C., Schneider, M., von Glasow, R., Piot, M., Gorham, K., Burkhardt, J. F., Ziemba, L., Dibb, J. E., Lefer, B. L.: Longpath DOAS observations of surface BrO at Summit, Greenland, *Atmos. Chem. Phys.*, 11, 9899–9910, <https://doi.org/10.5194/acp-11-9899-2011>, 2011.

Sun, K., Liu, X., Huang, G., González Abad, G., Cai, Z., Chance, K., and Yang, K. (2017). Deriving the slit functions from omi solar observations and its implications for ozone-profile retrieval. *Atmospheric Measurement Techniques*, 10(10):3677–3695.

Thalman, R. and Volkamer, R. (2013). Temperature dependent absorption cross-sections of O₂–O₂ collision pairs between 340 and 630 nm and at atmospherically relevant pressure. *Physical Chemistry Chemical Physics*, 15(37):15371–15381.

Tas, E., Peleg, M., Matveev, V., Zingler, J., Luria, M.: Frequency and extent of bromine oxide formation over the Dead Sea, *J. Geophys. Res.*, D11304, doi:10.1029/2004JD005665, 2005.

Theys, N., Van Roozendaal, M., Dils, B., Hendrick, F., Hao, N., and De Mazière, M.: First satellite detection of volcanic bromine monoxide emission after the Kasatochi eruption, *Geophys. Res. Lett.*, 36, L03809, doi:10.1029/2008GL036552, 2009.

Theys, N., Van Roozendaal, M., Hendrick, F., Yang, X., De Smedt, I., Richter, A., Begoin, M., Errera, Q., Johnston, P.V., Kreher, K., and De Mazière, M.: Global observations of tropospheric BrO columns using GOME-2 satellite data, *Atmos. Chem. Phys.*, 11, 1791–1811, <https://doi.org/10.5194/acp-11-1791-2011>, 2011.

- K. Toyota, J. C. McConnell, A. Lupu, L. Neary, C. A. McLinden, A. Richter, R. Kwok, K. Semeniuk, J. W. Kaminski, S.-L. Gong, J. Jarosz, M. P. Chipperfield, and C. E. Sioris, *Atmos. Chem. Phys.*, 11, 3949-3979, doi:10.5194/acp-11-3949-2011, 2011.
- Vandaele, A.C., Simon, P.C., Guilmot, J.M., Carleer, M., Colin, R.: SO₂ Absorption Cross Section measurement in the UV using a Fourier Transform Spectrometer. *J. Geophys. Res.*, 99, 25599-25605, 1994.
- Vandaele, A.C., Hermans, C., Simon, P.C., Carleer, M., Colin, R., Fally, S., Mérienne, M.F., Jenouvrier, A., and Coquart, B.: Measurements of the NO₂ absorption cross sections from 42000 cm⁻¹ to 10000 cm⁻¹ (238-1000 nm) at 220 K and 294 K, *J. Quant. Spectrosc. Radiat. Transfer*, 59, 171-184, 1998.
- Vandaele, A.C., Hermans, C., and Fally, S.: Fourier Transform measurements of SO₂ absorption cross sections: II. Temperature dependence in the 29 000 - 44 000 cm⁻¹ (227-345 nm) region, *J. Quant. Spectrosc. Radiat. Transfer*, 110, 2115-2126, 2009.
- Veihelmann, B. and Kleipool, Q.: Reducing Along-Track Stripes in OMI-Level 2 Products, Technical report TN-OMIE-KNMI-785, KNMI, available at http://disc.sci.gsfc.nasa.gov/Aura/data-holdings/OMI/documents/v003/RD08_TN785_i1_Reducing_AlongTrack_Stripes.pdf, 2006.
- von Glasow, R., von Kuhlmann, R., Lawrence, M.G., Platt, U., and Crutzen, P.J.: Impact of reactive bromine chemistry in the troposphere, *Atmos. Chem. Phys.*, 4, 2481-2497, 2004.
- Wang, H., Liu, X., Chance, K., González Abad, G., and Chan Miller, C.: Water vapor retrieval from OMI visible spectra, *Atmos. Meas. Tech.*, 7, 1901-1913, 2014.
- Wang, H., González Abad, G., Liu, X., and Chance, K.: Validation of OMI total column water vapor product, *Atmos. Chem. Phys.*, 16, 11379-11393, doi:10.5194/acp-16-11379-2016, 2016.
- Weber, M., Lamsal, L.N., Coldewey-Egbers, M., Bramstedt, K., and Burrows, J.P.: Pole-to-pole validation of GOME WFDOAS total ozone with groundbased data, *Atmos. Chem. Phys.*, 5, 1341-1355, <https://doi.org/10.5194/acp-5-1341-2005>, 2005.
- Wilmouth, D.M., Hanisco, T.F., Donahue, N.M, and Anderson, J.G.: Fourier transform ultraviolet spectroscopy of the $A^2P_{3/2} \rightarrow X^2P_{3/2}$ transition of BrO, *J. Phys. Chem. A*, 103, 8935-8945, 1999.
- Yung, Y.L., Pinto, J.P., Watson, R.T., and Sander, S. P.: Atmospheric bromine and ozone perturbations in the lower stratosphere, *J. Atmos. Sci.*, 37, 2, 339, 1980.

Zhao, X., Strong, K., Adams, C., Schofield, R., Yang, X., Richter, A., Friess, U., Blechschmidt, A.-M., Koo, J.-H.: A case study of a transported bromine explosion event in the Canadian high arctic, *J. Geophys. Res. Atmos.*, 121, 457-477, doi: 10.1002/2015JD023711, 2015.

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 ₂ CO cross sections | Chance and Orphal, 2011, 300K |
| O ₃ cross sections | Malicet <i>et al.</i> , 1995, 218K, 295K |
| NO ₂ cross sections | Vandaele <i>et al.</i> , 1998, 220K |
| SO ₂ cross sections | Vandaele <i>et al.</i> , 1994, 295K ¹ Hermans <i>et al.</i> , 2009; Vandaele <i>et al.</i> , 2009, 295K ² |
| 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 SO₂ cross sections and will be used in the next version.

Table 2. Error analysis studies.

| Description | Median VCD (Molec. cm ⁻²) | Median uncertainty (Molec. cm ⁻²) | Number of negatives |
|-------------------------------------|--|--|------------------------|
| Operational (V3) | 3.89×10 ¹³ | 7.85×10 ¹² | 1222 |
| 323.0 - 353.5 nm (V2) | 2.69×10 ¹³ | 1.01×10 ¹³ | 4393 |
| 340.0 – 357.5 nm (V1) | 2.48×10 ¹³ | 1.29×10 ¹³ | 9390 |
| 310.0 - 357.5 nm | 1.91×10 ¹³ | 6.83×10 ¹² | 7372 |
| 325.0 - 357.5 nm | 3.10×10 ¹³ | 8.75×10 ¹² | 3107 |
| With O ₂ -O ₂ | 3.57×10 ¹³ | 8.65×10 ¹² | 1265 |
| Online slit function | 5.00×10 ¹³ | 7.92×10 ¹² | 1003 |
| Without common mode | 3.72×10 ¹³ | 1.11×10 ¹³ | 2093 |
| Without HCHO | 2.53×10 ¹³ | 6.93×10 ¹² | 1703 |

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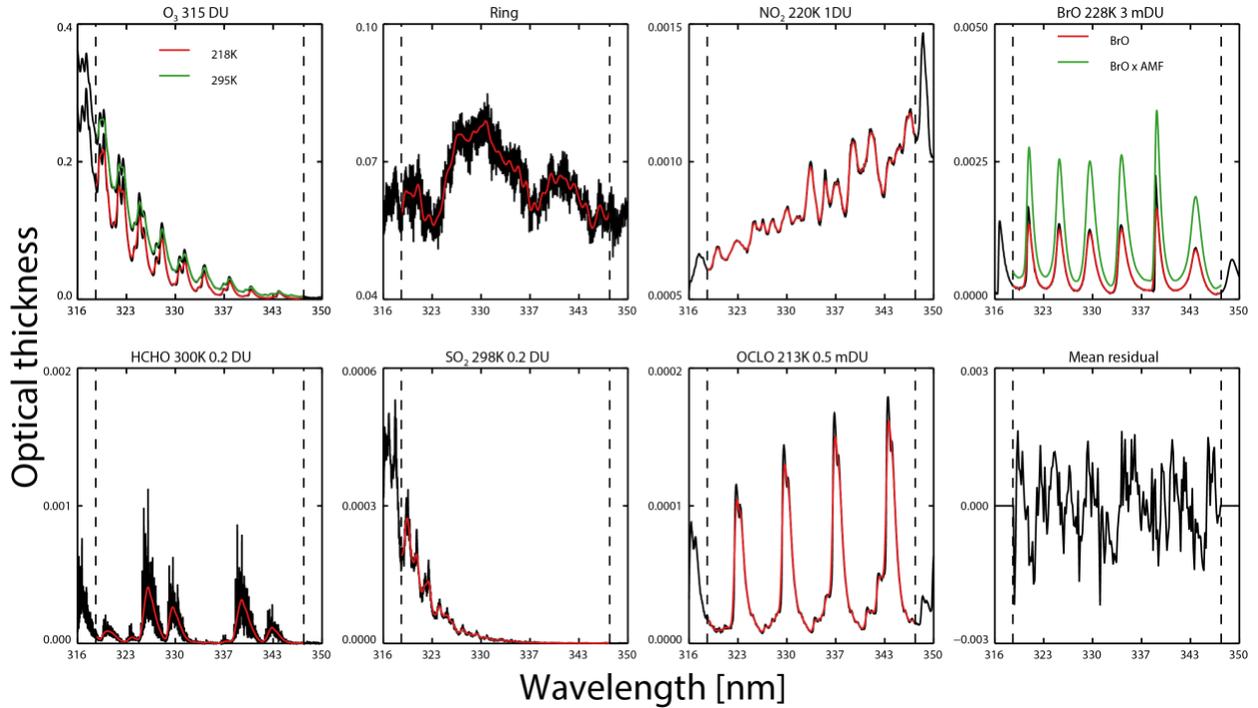
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Table 3. Summary of different errors sources in the BrO vertical column.

| Error source | Type | Parameter uncertainty | Averaged uncertainty on BrO VCD | Evaluation method - reference |
|---|------------|--|--|----------------------------------|
| Measurement noise random | Random | S/N 500 - 1000 | 4-7x10 ¹² molec. cm ⁻² | Error propagation; |
| HCHO | Systematic | Based on literature reported error estimates | 5% | Chance and Orphal, 2011, 300K |
| O ₃ | | | 2% | Malicet et al., 1995, 218K, 295K |
| BrO | | | 8% | Wilmouth et al., 1999, 228K |
| NO ₂ | | | 3% | Vandaele et al., 1998, 220K |
| SO ₂ | | | 5% | Vandaele et al., 1994, 295K |
| OCIO | | | 5% | Kromminga et al., 2003, 213K |
| Ring | | | 5% | Chance and Spurr, 1997 |
| Offset order | Systematic | Vary polynomial order | 10% | Sensitivity analysis |
| Polynomial order | Systematic | Vary polynomial order | 10% | |
| Instrumental slit function and wavelength calibration | Systematic | Preflight and online slit function | 28% | |
| Wavelength interval | Systematic | Varying fitting window | 50% | |

Figures and Figure Captions



- 5 **Figure 1.** Cross sections used in the current operational BrO algorithm except for the SO₂ 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 OMI slit function (which is assumed to be a Gaussian with 0.42nm full width at half maximum. The BrO cross section after multiplication with the wavelength-dependent AMFs used these parameters for the
- 10 **AMF calculation: albedo = 0.05, SZA= 5.0°, and VZA = 2.5°).**

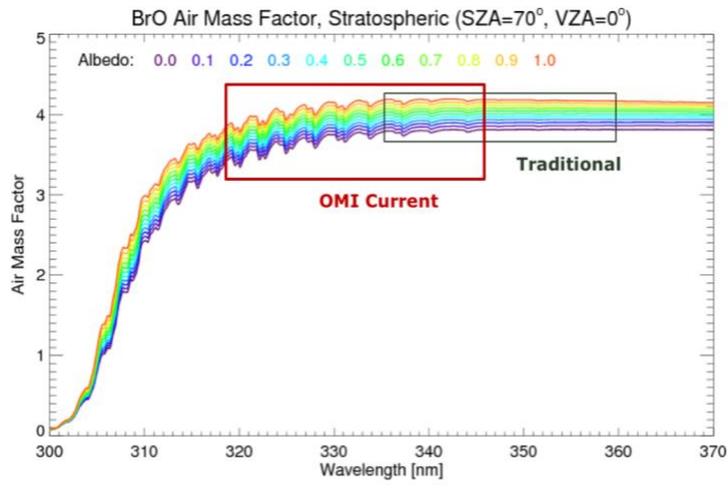


Figure 2. Wavelength- and albedo-dependent air mass factors calculated using a mostly stratospheric fixed BrO profile. The blue box shows the fitting window used in our previous versions, and the red box shows the fitting window used in the current operational algorithm.

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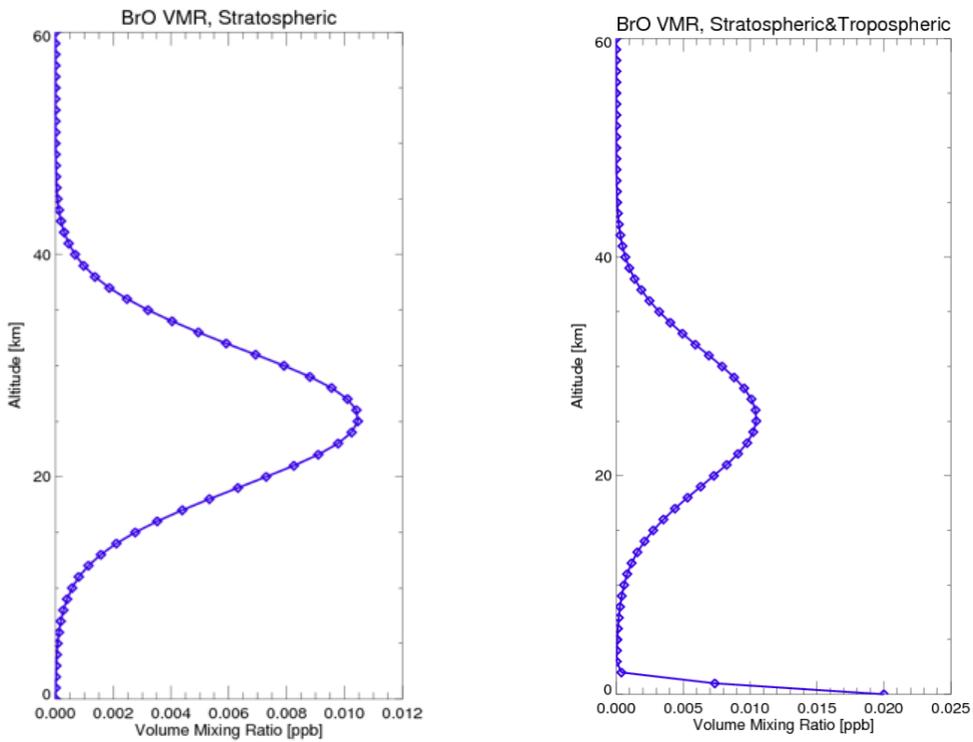


Figure 3. A mostly stratospheric vertical BrO profile used for air mass factors (left panel). Total BrO, BrO < 15 km, BrO < 10 km, and BrO < 5km are 1.55×10^{13} , 5.06×10^{12} , 1.55×10^{12} , and 2.87×10^{11} , respectively. A stratospheric tropospheric vertical BrO profile for air mass factors (right panel) can reduce errors by 50%.

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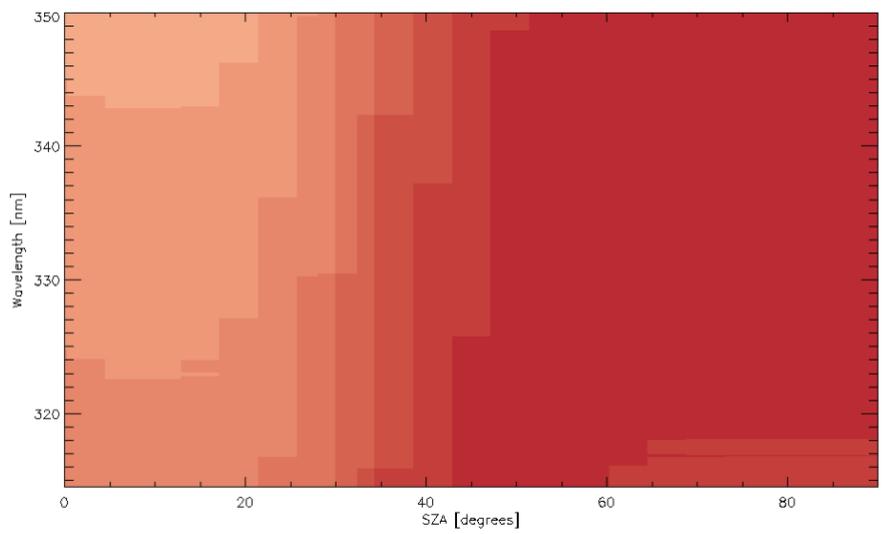
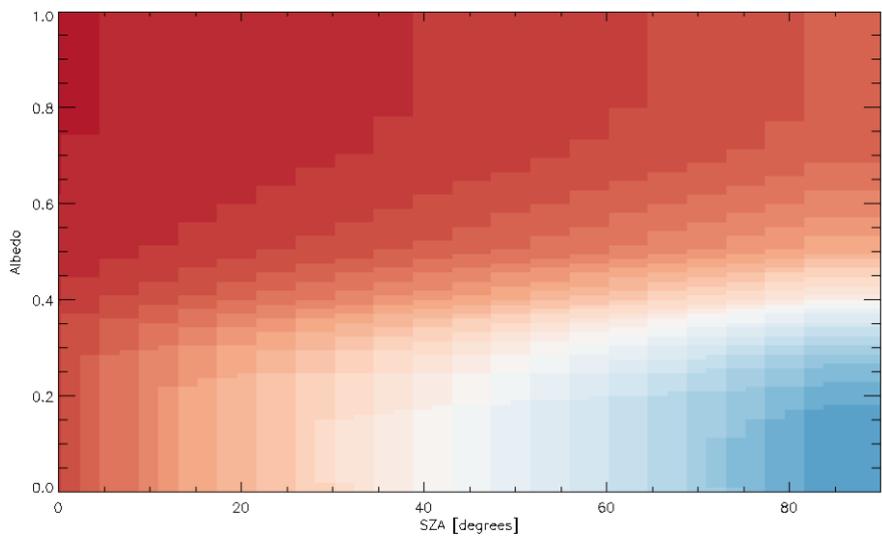
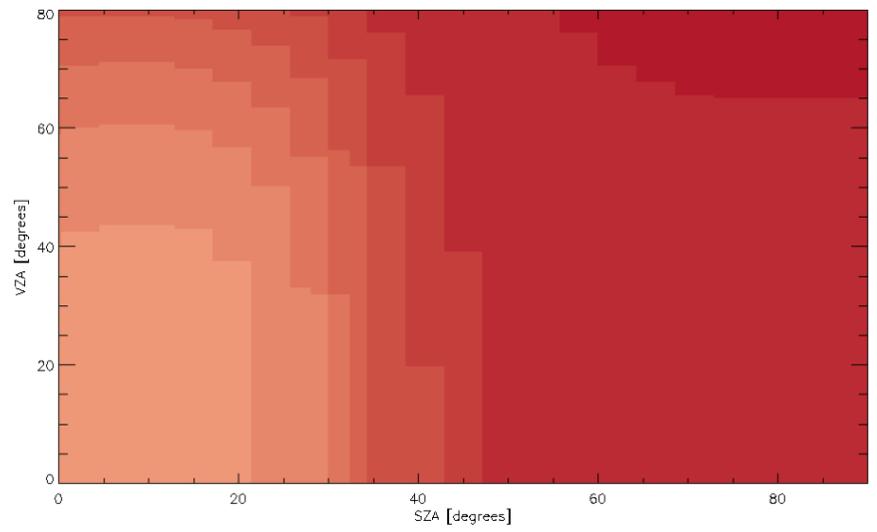


Figure 4. AMFs relative errors as a function of the SZA and the wavelength (bottom panel), albedo (middle panel) and VZA (top panel).

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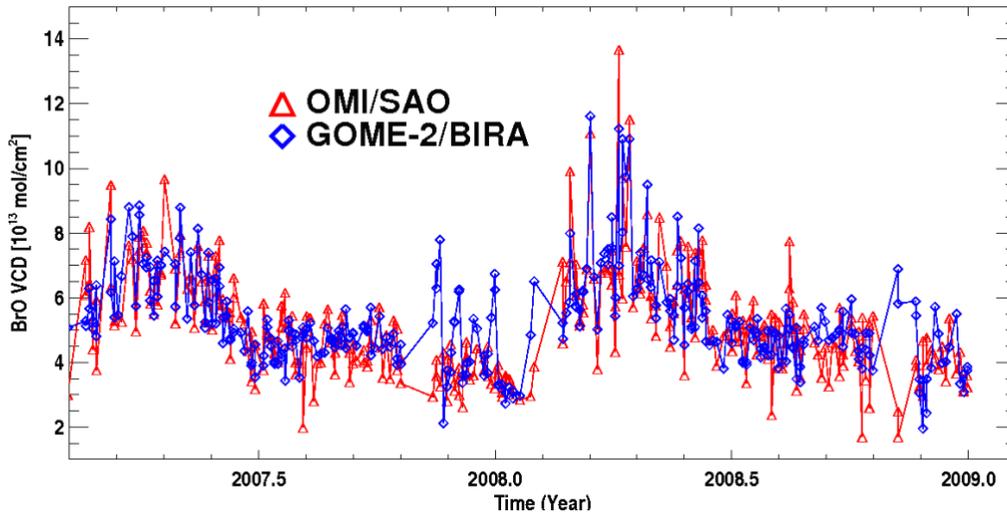


Figure 5. Time series comparison of SAO OMI (red) BrO and BIRA GOME-2 (blue) BrO VCDs from February 2007 to November 2008 using simultaneous nadir overpasses within 2 minutes between OMI and GOME-2 observations.

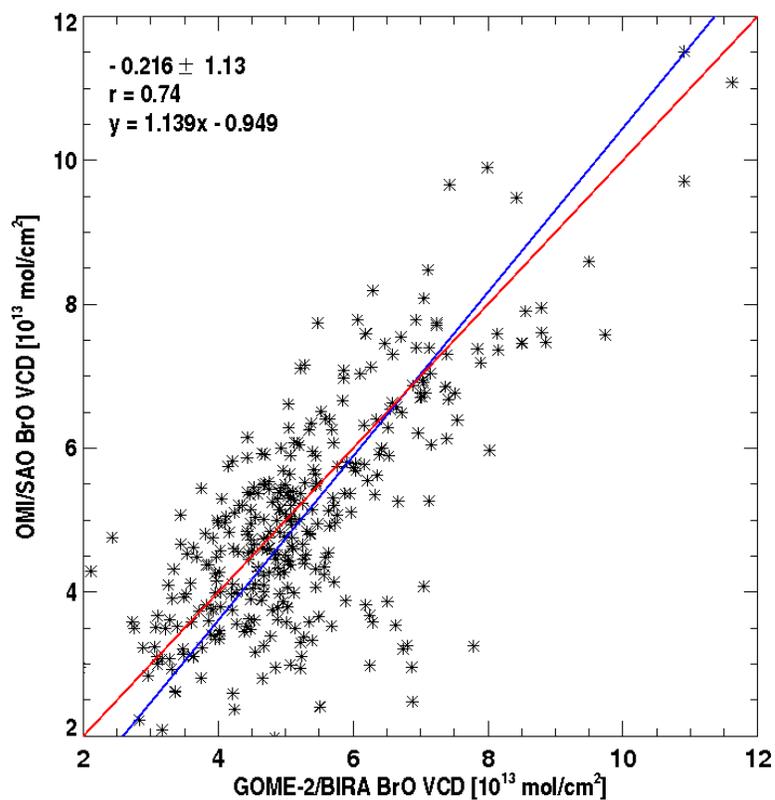


Figure 6. Correlation and orthogonal regression of OMI and GOME-2 BrO for the data shown in Fig. 5. The legends show the mean bias and standard deviation of the differences, correlation, and the orthogonal regression.

5

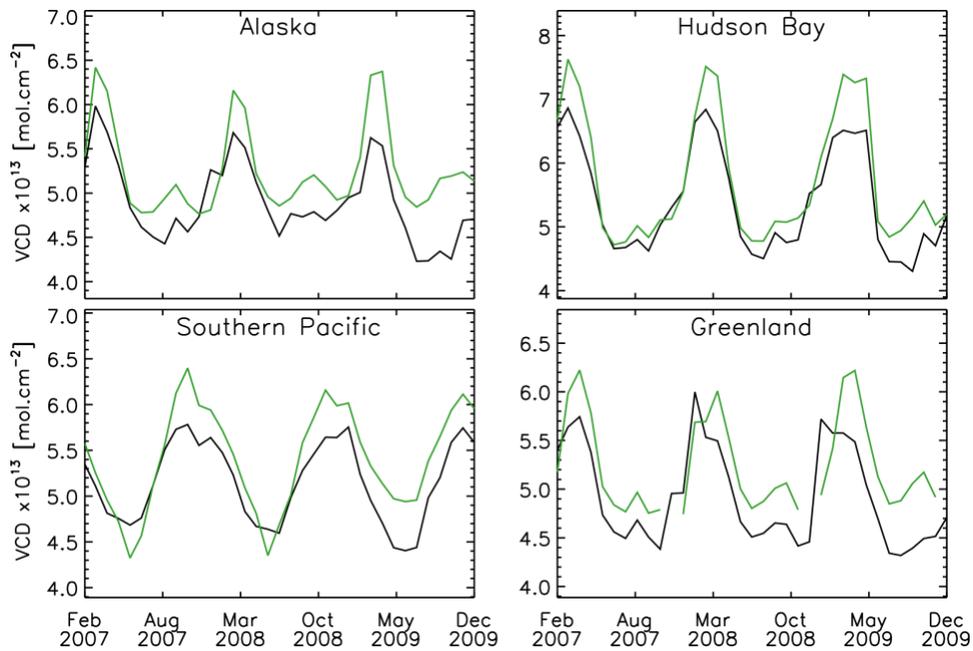
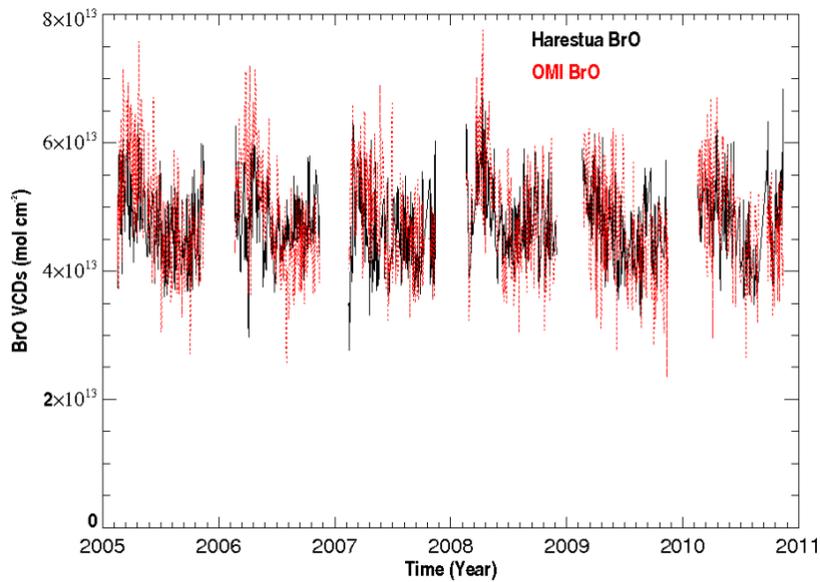


Figure 7. VCD of GOME2 (green) comparison to OMI (black) over four regions from February 2007 to December 2009 for four regions.



5 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.

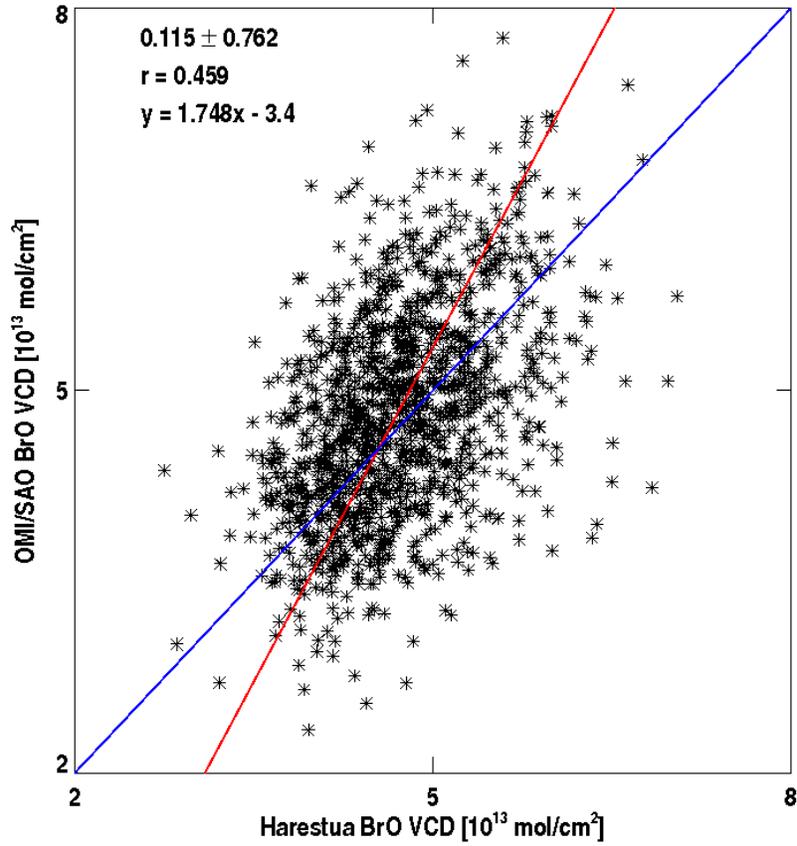


Figure 9. Correlation and orthogonal regression of OMI and Harestua BrO for the data in Fig. 8. The legends show the mean biases and standard deviations of the differences, correlation, and the orthogonal regression.

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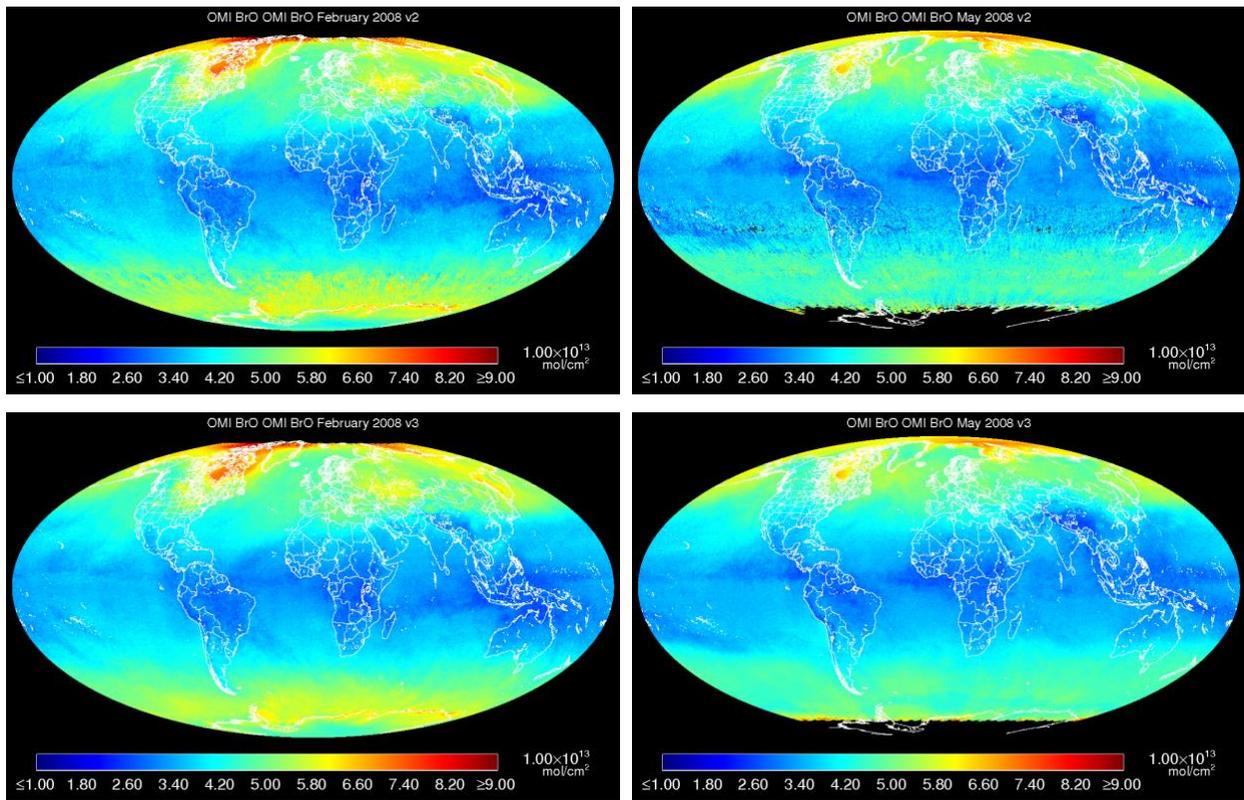


Figure 10. Monthly averages for February and May 2008 for version 3 and version 2.

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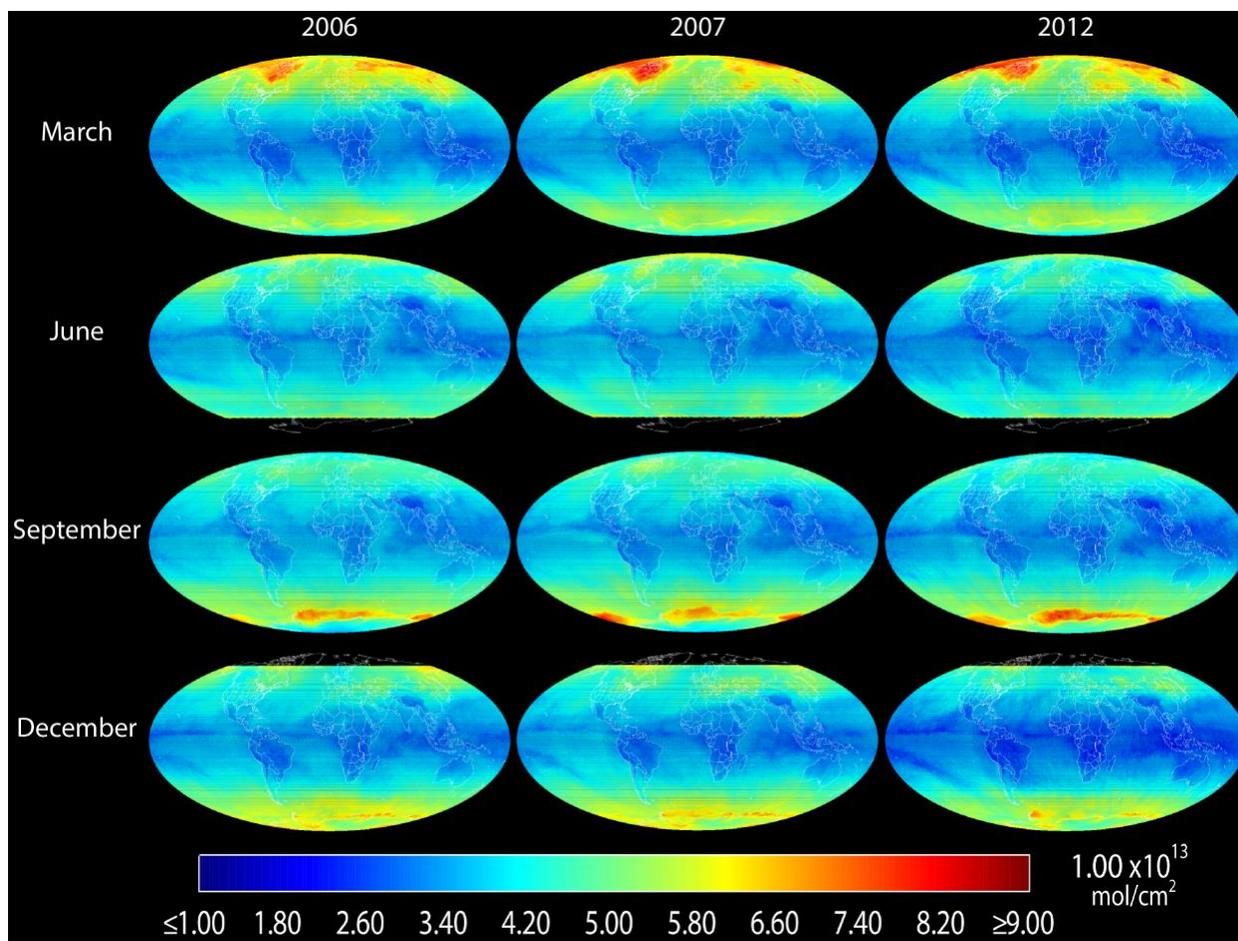


Figure 11. Global distributions of monthly mean BrO VCDs in March, June, September and December (in different rows) of 2006, 2007, and 2012 (different columns). Bromine release “explosions” during the Polar Spring months can be seen clearly.

5

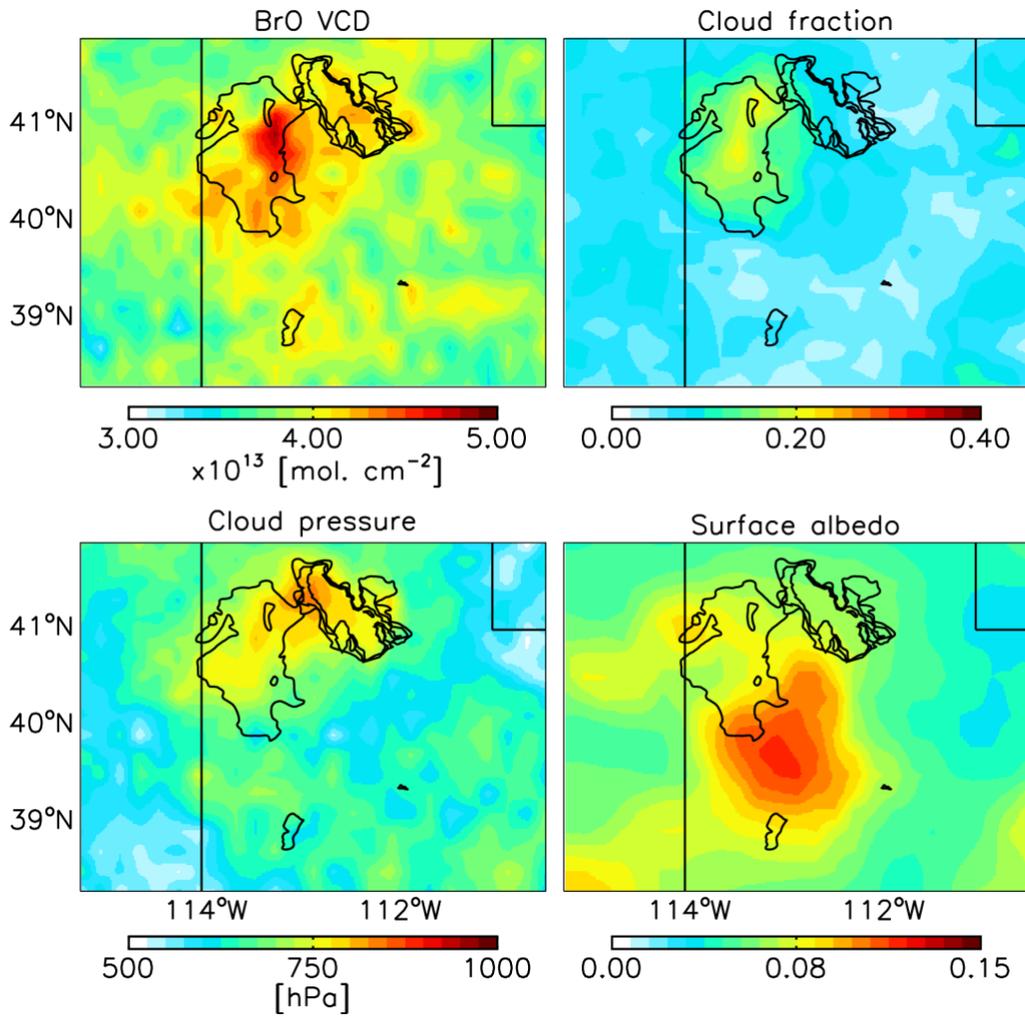


Figure 12. Mean June 2006 BrO VCD over the Great Salt Lake area. Averages have been calculated on a 0.2 x 0.2 degree grid including only pixels with cloud fractions smaller than 0.4.

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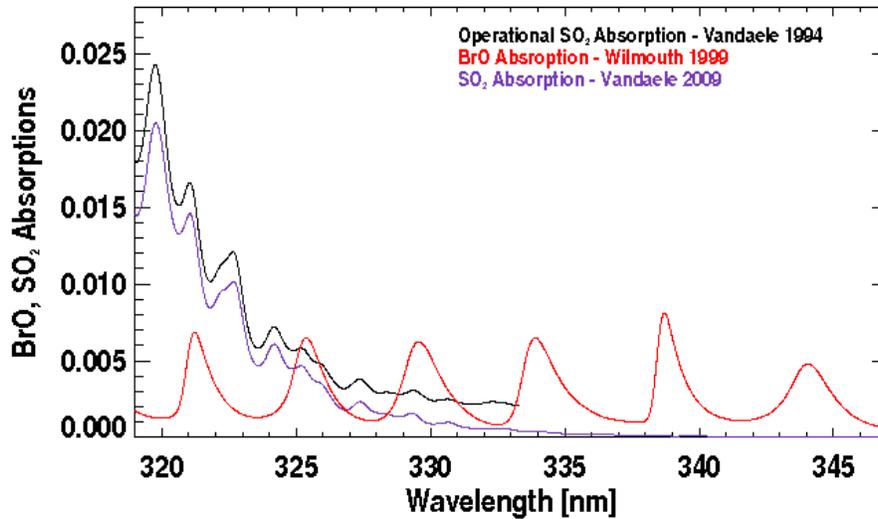


Figure 13. Comparison of BrO absorption (red) and SO₂ absorptions under volcanic scenarios based on cross sections used in the operational algorithm (Vandaele et al., 1994) as shown in black and the recent laboratory cross sections (Vandaele et al., 2009) as shown in purple. For BrO, a SCD of 1.0×10^{14} molecules cm^{-2} is assumed; for SO₂, a SCD of 15 Dobson Units (i.e., 4.03×10^{17} molecules 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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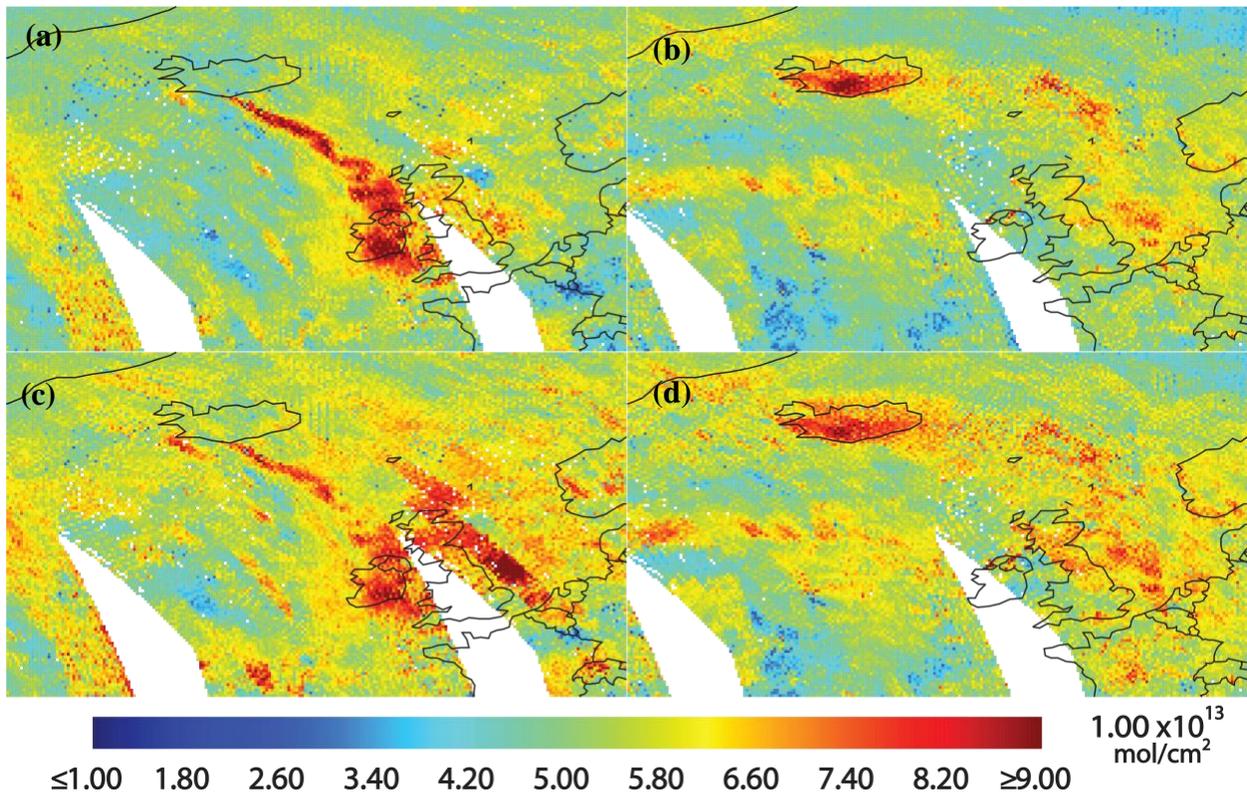


Figure 14. Daily average BrO VCDs from Eyjafjallajökull on May 5 (a) and 17 (b), 2010 produced using the operational SO₂ cross sections and for the same days (c) and (d) using the Vandaele et al. (2009) SO₂ cross sections.

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