

O3M SAF VALIDATION REPORT

Validated products:

| Identifier | Name | Acronym |
|------------|--|-------------|
| O3M-08 | Offline Total BrO | MAG-O-BrO |
| O3M-82 | from GOME-2A&2B | MBG-O-BrO |
| O3M-115 | Reprocessed Total BrO From GOME-2A&2B | MxG-RP1-BrO |

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Reporting period: GOME2/METOP-A January 2007-December 2014

GOME2/MetOP-B January 2013 – December 2014

Input data versions: GOME-2 Level 1B version 5.3 until 17 Jun 2014

GOME2 Level 1B version 6.0 since 17 Jun 2014

Data processor versions: GDP 4.8, UPAS version 1.3.9

Validation report of GOME-2 offline and reprocessed GDP 4.8 BrO total column data for MetOp-A and B

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ACRONYMS AND ABBREVIATIONS

| | |
|-----------|---|
| AMF | Air Mass Factor |
| BIRA-IASB | Belgian Institute for Space Aeronomy |
| BrO | bromine monoxide |
| DLR | German Aerospace Centre |
| DOAS | Differential Optical Absorption Spectroscopy |
| ENVISAT | Environmental Satellite |
| ERS-2 | European Remote Sensing Satellite -2 |
| ESA | European Space Agency |
| EUMETSAT | European Organisation for the Exploitation of Meteorological Satellites |
| FMI | Finnish Meteorological Institute – Arctic Research Centre |
| GB-DOAS | Ground-based DOAS instruments |
| GDP | GOME Data Processor |
| GOME | Global Ozone Monitoring Experiment |
| IMF | Remote Sensing Technology Institute |
| NDACC | Network for the Detection of Atmospheric Composition Change |
| O3M-SAF | Ozone and Atmospheric Chemistry Monitoring Satellite Application Facility |
| OMI | Ozone Monitoring Instrument |
| ROCINN | Retrieval of Cloud Information using Neural Networks |
| SCD | Slant Column Density |
| SCIAMACHY | Scanning Imaging Absorption spectroMeter for Atmospheric CHartography |
| SZA | Solar Zenith Angle |
| TEMIS | Tropospheric Emission Monitoring Internet Service |
| UPAS | Universal Processor for UV/VIS Atmospheric Spectrometers |
| VCD | Vertical Column Density |
| WMO | World Meteorological Organization |

A. INTRODUCTION

A.1. *Scope of this document*

The present document reports on the verification and validation of GOME-2/MetOp-A and GOME-2/MetOp-B offline and reprocessed BrO total column data over the 2007 – 2014 time periods, produced by the GOME Data Processor (GDP) version 4.8 operated at DLR on behalf of EUMETSAT. This report includes verification work performed using the BIRA-IASB scientific retrieval tool synchronized on the GDP settings, as well as comparisons with SCIAMACHY and ground-based measurements. The aim is to investigate whether the GOME-2 BrO total column product fulfill the user requirements in terms of accuracy, as stated in the Product Requirements Document (PRD - Threshold accuracy: 50%; Target accuracy: 30%; Optimal: 15%).

A.2. *Preliminary notes*

The aim of the present document is first to report on the status of the verification of the GOME-2 BrO column against a synchronised scientific algorithm available at BIRA. For this exercise, BrO retrieval settings selected by DLR scientists for GDP version 4.8 are being used. The consistency of this BrO product is then explored by performed various comparisons with existing correlative data sets, including scientific data sets from SCIAMACHY. Ground-based BrO column measurements available for the stations at Harestua in Norway and Lauder in New-Zealand are also used in an attempt to further document the geophysical consistency of the GOME-2 BrO product.

It should be note here that improvements have been made in the BrO column retrieval for both the satellite instruments GOME-2 and SCIAMACHY and for the ground-based DOAS instruments, to resolve the apparent inconsistencies in the GOME-2 retrievals reported in previous validation report for the (Van Roozendaal et al., 2008a). The algorithm improvements for the satellite and ground-based DOAS instruments are described in this document.

Reported validation studies were carried out at the Belgian Institute for Space Aeronomy (IASB-BIRA, Brussels, Belgium) and at DLR Remote Sensing Technology Institute (DLR-IMF, Oberpfaffenhofen, Germany) in the framework of EUMETSAT Satellite Application Facility on Ozone and Atmospheric Chemistry Monitoring (O3M-SAF)

A.3. *Plan of this document*

This document is divided in four main parts, addressing respectively the description of the retrieval settings applied for the BrO product, the verification of this product, comparisons against satellite data and comparisons against ground-based measurements at Harestua and Lauder. This is followed by concluding remarks and perspectives for future work.

A.4. Applicable O3MSAF Documents

- [ATBD] Algorithm Theoretical Basis Document for GOME-2 Total Column Products of Ozone, NO₂, BrO, SO₂, H₂O, HCHO and Cloud Properties (GDP 4.8 for O3M-SAF OTO and NTO), DLR/GOME-2/ATBD/01, Rev. 3/A, Valks, P., et al., March 2015.
- [PUM] Product User Manual for GOME Total Column Products of Ozone, NO₂, BrO, SO₂, H₂O, HCHO and Cloud Properties, DLR/GOME/PUM/01, Rev. 3/A, Valks, P., et. al., 2015.
- [PRD] Product Requirements Document, SAF/O3M/FMI/RQ/PRD/001/Rev. 1.7, D. Hovila, S. Hassinen, D. Loyola, P. Valks, J., S. Kiemle, O. Tuinder, H. Joench-Soerensen, F. Karcher, 2015.

A.5. Technical information

GOME2/Metop-A & GOME2/Metop-B products name **Total BrO column (MAG-O-BrO, MBG-O-BrO, MxG-RP1-BrO)**

Validation reporting period **January 2007 - December 2014**

Level-2 processor version **GDP 4.8, UPAS version 1.3.9**

Input GOME-2/MetOp-A Level-1B data version table

| <i>Start Date</i> | <i>Start Orbit</i> | <i>Level 1B Version</i> |
|-------------------|--------------------|-------------------------|
| Jan., 2007 | 1235 | 5.3 |
| Jun. 17, 2014 | 39748 | 6.0 |

Input GOME-2/MetOp-B Level-1B data version table

| <i>Start Date</i> | <i>Start Orbit</i> | <i>Level 1B Version</i> |
|-------------------|--------------------|-------------------------|
| Jan. 2013 | 1235 | 5.3 |
| Jun. 17, 2014 | 9062 | 6.0 |

B. SETTINGS FOR BRO COLUMN RETRIEVAL FROM GOME-2

B.1. *Experience from ERS-2 GOME and SCIAMACHY*

BrO columns have been retrieved from ERS-2 GOME and ENVISAT SCIAMACHY instruments and settings used for these two instruments are documented in the literature (e.g. Chance, 1998; Richter et al., 1998, 2002, Wagner and Platt, 1998; Van Roozendael et al., 1999, 2002, 2004; De Smedt et al., 2004). For the GOME instrument on ERS-2, BrO slant columns have been commonly derived in the wavelength interval from 344.7 to 359 nm, making use of the characteristic absorption structures of BrO in this region. This interval has been so far considered as optimal for BrO fitting from both satellite and ground-based observations (see e.g. Aliwell et al., 2002; Richter et al., 1998, 1999; Van Roozendael et al., 1998; Wagner and Platt, 1998) since spectral interferences with O₃, O₄, and HCHO are minimised in this region. In the case of SCIAMACHY however different settings had to be adopted, mainly due to the existence of strong polarisation features in the channel 2 of SCIAMACHY that cannot be eliminated by the polarization correction scheme implemented in the Level 0-1 processing. This polarization feature generates spurious interferences with the BrO spectral structures. To get rid of these polarization-related interferences, another fitting interval was adopted for SCIAMACHY displaced at shorter wavelengths in a region less affected by the polarization anomaly but still showing prominent BrO absorption features. It was shown that equally acceptable BrO columns could be retrieved from SCIAMACHY by including two absorption bands (336-347 nm) or three bands (336-351 nm). The SCIAMACHY BrO interval was generally found to produce BrO slant columns in good agreement with GOME (De Smedt et al., 2004; Van Roozendael et al., 2004), although a significant interference with HCHO absorption was noted. SCIAMACHY BrO maps also display systematic negative biases that correlate with orography, possibly due to unresolved spectral interferences with Ring or O₂-O₂.

B.2. *Choice of BrO slant column settings for GOME-2*

In an attempt to define a baseline for GOME-2 processing, the GOME and SCIAMACHY settings have been tested on GOME-2 spectra. As a result of the smaller pixel size of GOME-2 observations (approx. 40x80 km² instead of 40x320 km² for GOME) the noise on the individual GOME-2 BrO measurements was found to be significantly increased in comparison to GOME. On the basis of noise-driven considerations and test retrievals performed at DLR and BIRA, the SCIAMACHY fitting interval using three absorptions bands (336 – 351.5 nm) was believed to represent a good choice for GOME-2 retrieval. In the last validation report, we evaluated a data set generated with the latter settings for the years 2007 and 2008. The outcome of this validation study was that, although the product fulfills some of the user requirements in terms of accuracy, the quality of the GOME-2 product was deceiving. Indeed, the general seasonal variations of the BrO column amount were not physical. In addition, though the mean vertical column levels were generally acceptable for 2007-2008, the effect of the instrumental degradation on the results for the years 2009 and 2010 was very high, leading to a strong overestimation of the total column for this period. For these reasons, improved retrieval settings have been implemented (see below). A data set has been generated for the period 2007-2010, which we now consider for evaluation.

The new BrO DOAS settings have been developed (see details in Theys et al., 2011) with the objective to stabilize the fit as much as possible. An important difference with respect to past settings relies in the choice of the fitting window which has been extended towards shorter wavelengths (332-359 nm) in order to cover five BrO absorption bands. While the BrO values retrieved using both fitting windows are consistent above regions of enhanced tropospheric BrO precursors emissions, the use of this extended wavelength interval leads to an overall reduction of the noise of the slant columns and allows minimizing the impact of several well-known artefacts: a spurious slant column viewing angle dependence, the presence in the measurement maps of cloud structures due to imperfect correction of the Ring effect and a strong interference with formaldehyde absorption over regions heavily polluted or affected by biomass burning or biogenic emission. Moreover, the results show reasonable seasonal variations at all latitudes and are also much less affected by

the degradation of the instrument than past results. In addition to the settings presented in Theys et al. (2011), an equatorial offset correction is applied to the data (Richter et al., 2002). The latter correction enables to correct – to some extent – for the effect of the instrumental degradation on the total BrO column data time series. It consists of a daily correction: the averaged BrO slant column in the tropical latitudinal band of $\pm 5^\circ$ is calculated and subtracted to all slant columns and an equatorial slant column offset of 7.5×10^{13} molec/cm² is added.

As a side note, we have also consistently applied this equatorial correction to SCIAMACHY data (used as correlative data set in this report) and it is interesting to note that, even after almost a decade of operation, the SCIAMACHY instrument provides a BrO data record very stable in time. Applying this equatorial correction to SCIAMACHY BrO data, no sign of zonal vertical column trend is visible anywhere.

The detailed DOAS settings used for GOME-2 BrO slant columns retrieval are given in Table 1.

Table 1. DOAS settings used for GOME-2 BrO slant column verification

| | |
|------------------------------------|--|
| Fitting interval | 332 – 359 nm |
| Sun reference | Sun irradiance from file |
| Wavelength calibration | Wavelength calibration of sun reference optimized by NLLS adjustment on convolved Chance and Spurr solar lines atlas |
| Absorption cross-sections | |
| - BrO | Fleischmann et al., 223°K |
| - NO ₂ | Vandaele (2002), 220°K |
| - Ozone | Brion et al. 1998, convolved at GOME-2 resolution, 228°K + 243°K Use of two additional cross-sections to better take into account O ₃ absorption non-linearity with wavelength (Pukite et al., 2010) |
| - H ₂ CO | Meller & Moortgat et al. 2000 at 298K |
| - OCIO | Bogumil et al., 2003 at 293K |
| - Ring effect | 2 Ring eigenvectors generated using SCIATRAN |
| - Polarization | GOME-2 FM-203 Calibration Key Data, Eta and Zeta |
| Polynomial | 5 rd order (6 parameters) |
| Intensity offset correction | Constant +slope |

In order to convert the retrieved BrO slant columns into vertical columns, Air Mass Factors (AMF) are calculated for each pixel. The AMFs are generated with the LIDORT 3.3 radiative transfer model using pure stratospheric BrO profiles.

Figure 1 presents example of results for the monthly mean for October 2007 (GOME-2A).

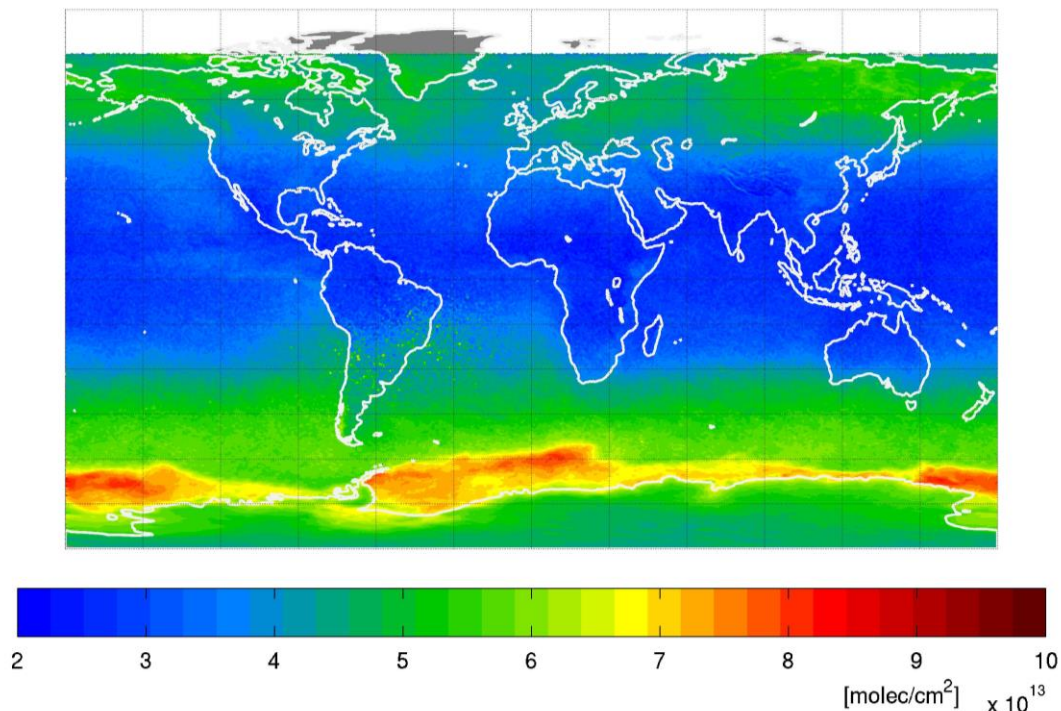


Figure 1. Monthly averaged of GOME-2A BrO vertical columns retrieved for October 2007 (using the baseline settings given in Table 1).

In the following sections the consistency of the GDP 4.8 BrO column product is investigated from the point of view of (1) the verification (i.e. whether BrO retrievals performed with GDP 4.8 are consistent with scientific retrievals performed using same settings), (2) the comparison against another satellite instrument (SCIAMACHY), and (3) the comparison against independent ground-based observations from two stations of the NDACC network.

B.3. Validation data sets

Before presenting any results, it is important to note that the validation of the GOME-2B total BrO column product is difficult because of 1) the scarcity of correlative ground-based measurements and 2) limited quality satellite data sets. The following datasets can be used:

- SCIAMACHY/ENVISAT total BrO columns (De Smedt et al., 2004; Afe et al., 2004; Theys et al., 2011) proved to be of very good quality even a decade long after launch but unfortunately the data record ends on the 8th of April 2012 (after the loss of contact with ENVISAT). Hence SCIAMACHY cannot be used properly to validate GOME-2B total BrO columns.
- GOME-2A is operating in parallel to GOME-2B and the total BrO columns can be compared. However, GOME-2A suffers for many years of a strong instrumental degradation affecting the quality of the total BrO column product. This is illustrated in Figure 2 showing the increase in fitted slant columns, fitting residuals and slant column errors (averaged over the equatorial pacific) as a function of time.

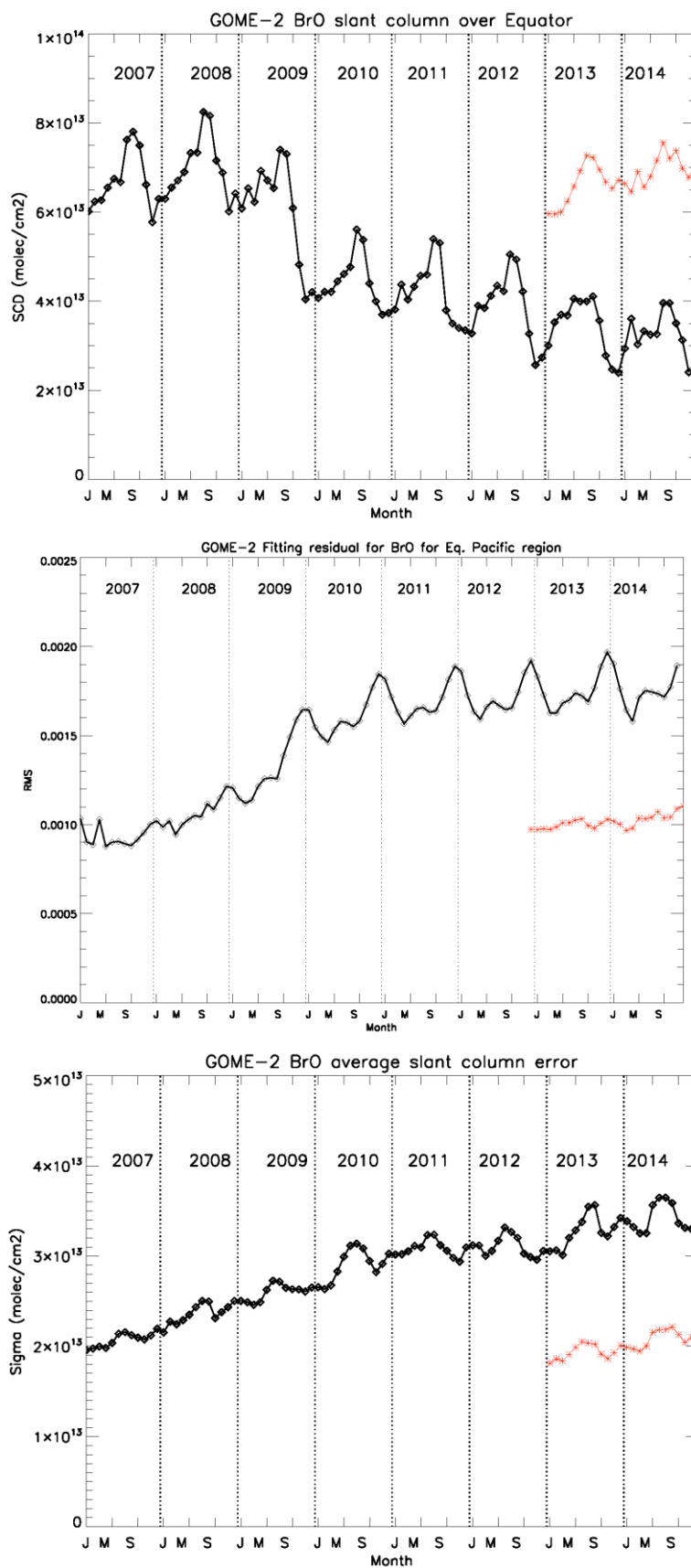


Figure 2. Average BrO slant columns (top), DOAS fitting residuals (middle) and slant column error (bottom) in the equatorial Pacific for GOME-2A (black) and GOME-2B (red).

The instrumental degradation affects not only the residuals and data scatter but also the average slant column values. Therefore we have applied an equatorial slant column offset correction to all datasets (GOME-2A, GOME-2B and SCIAMACHY). Although this correction somehow compensate for the effect of the instrumental degradation, it does so only to some extent and one needs to be cautious in the use of the data. Please note also in Figure 2 that GOME-2B data in Dec. 2012-Jan. 2013 seems to be of similar quality than GOME-2A in early 2007 (beginning of operations).

- Ground-based total BrO columns at Harestua, Norway are available for more than a decade long (Hendrick et al., 2007, 2008, 2009) and will be used. We will also use ground-based data at Lauder but only covers a limited period in the years 2007 and 2008.

C. VERIFICATION OF BRO SLANT COLUMNS

For verification purposes, the retrieval software of BIRA-IASB was synchronised with the GDP 4.8 processor, using a common set of slant column retrieval settings, as documented in Table 1. Comparisons between the two processing systems were performed on a limited set of GOME-2A orbits. Results of these comparisons are illustrated in Figure 3. As can be seen, a good level of agreement was obtained, demonstrating the consistency between the two slant column fitting algorithms. The differences in BrO SCDs retrieved from GDP 4.8 processor and BIRA-IASB software show a small bias of -0.7×10^{12} molec/cm² and a standard deviation of 0.7×10^{13} molec/cm².

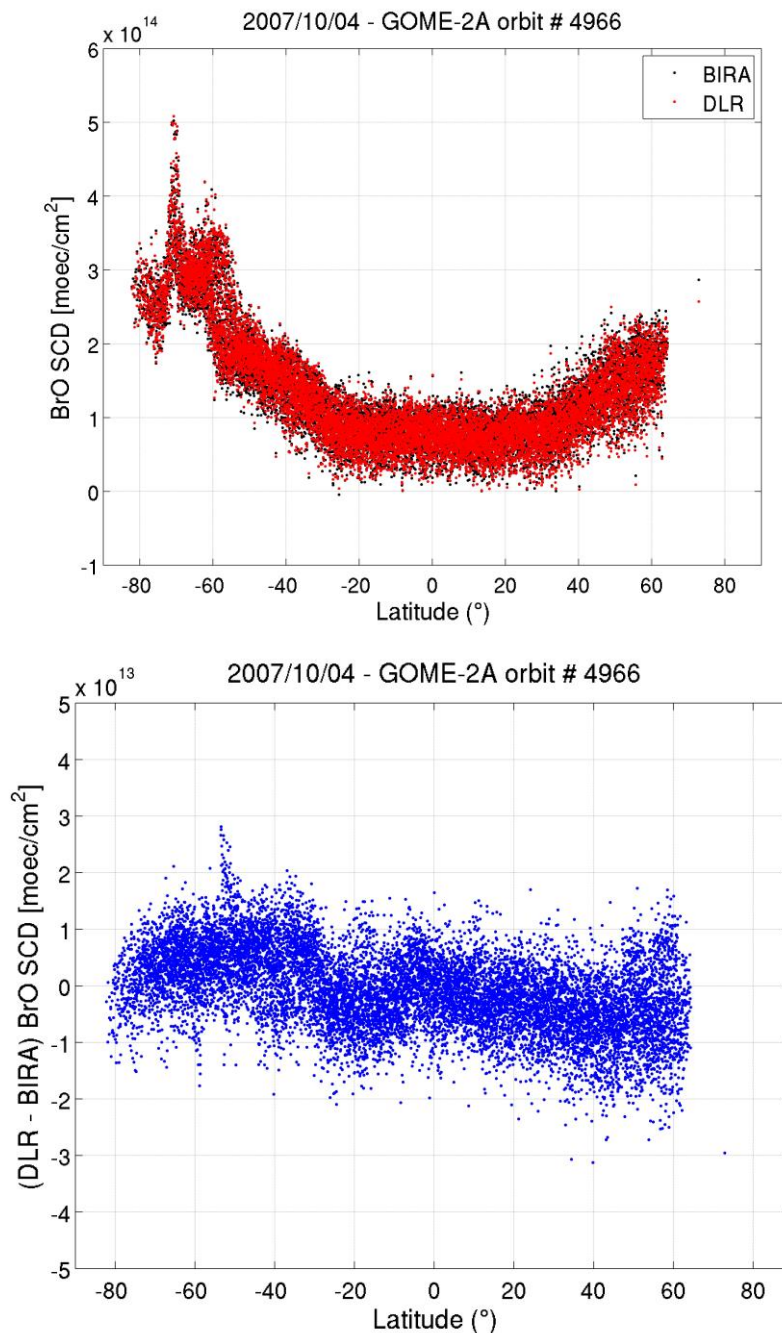


Figure 3. GOME-2A: Comparison of BrO slant columns retrieved from GDP 4.8 and from the BIRA-IASB scientific algorithm. The lower plot corresponds to the difference between GDP 4.8 and BIRA-IASB BrO SCDs. DOAS settings were synchronized according to Table 1.

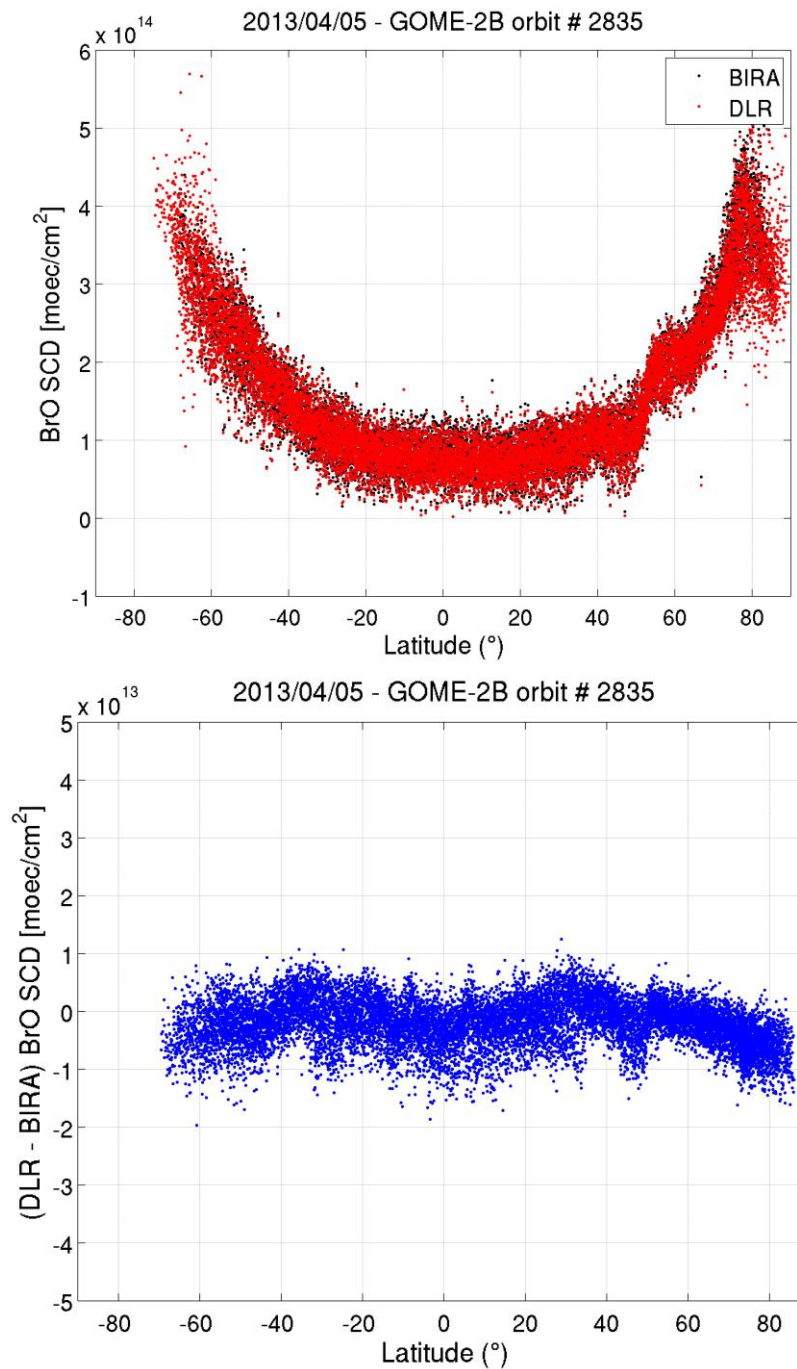


Figure 4. GOME-2B: Comparison of BrO slant columns retrieved from GDP 4.8 and from the BIRA-IASB scientific algorithm. The lower plot corresponds to the difference between GDP 4.8 and BIRA-IASB BrO SCDs. DOAS settings were synchronized according to Table 1.

Figure 4 shows another example of comparison between BrO SCDs from the GDP 4.8 and the BIRA-IASB scientific algorithm for GOME-2B. The agreement is very good. The differences in BrO SCDs retrieved from GDP 4.8 processor and BIRA-IASB software show a small bias of -2×10^{12} molec/cm² and a standard deviation of 0.4×10^{13} molec/cm².

D. COMPARISON AGAINST SATELLITE DATA

BrO slant and vertical column amounts derived from SCIAMACHY instrument have been produced at BIRA-IASB as part of the DUP/DUE TEMIS service (www.temis.nl). This data set has been used here for comparison with GOME-2 retrievals from the GDP 4.8 data set. It should be noted that the SCIAMACHY data set was initially generated using the outdated BrO cross-section from Wahner et al. (1988). This cross-section suffers from inadequate spectral resolution, which results in a systematic overestimation of the BrO slant columns by approximately 20%. Consequently the SCIAMACHY data set has been reprocessed with the BrO cross-section of Fleischmann et al. (2004), the same as used in the GOME-2 retrieval (but convolved at the spectral resolution of SCIAMACHY).

First, we want to illustrate the good geophysical consistency between the different total BrO column products by the mean of monthly averaged maps from GOME-2A, -B and SCIAMACHY. Figures 5 shows the results for April and October 2007 in the Northern and Southern hemispheres, respectively.

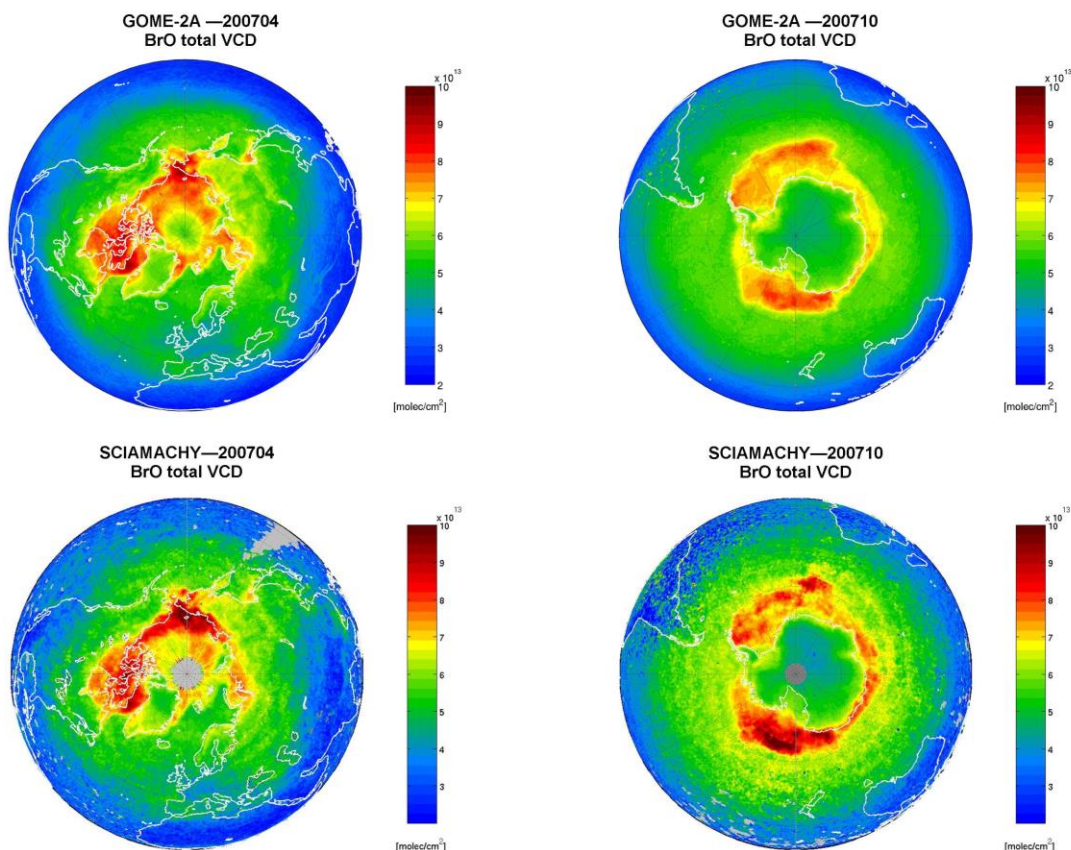


Figure 5. Monthly averages of GOME-2A (top) and SCIAMACHY (bottom) total BrO vertical columns in polar spring (2007) for the Northern Hemisphere (April: left plots) and the Southern Hemisphere (October: right plots). Only data corresponding to solar zenith angles lower than 80° are used.

The results of Figure 5 show that similar BrO VCD spatial patterns are observed for each spring months in both hemispheres. A similar figure as Fig. 5 but comparing GOME-2A and GOME-2B data for 2013 (March and September) is shown in Fig. 6.

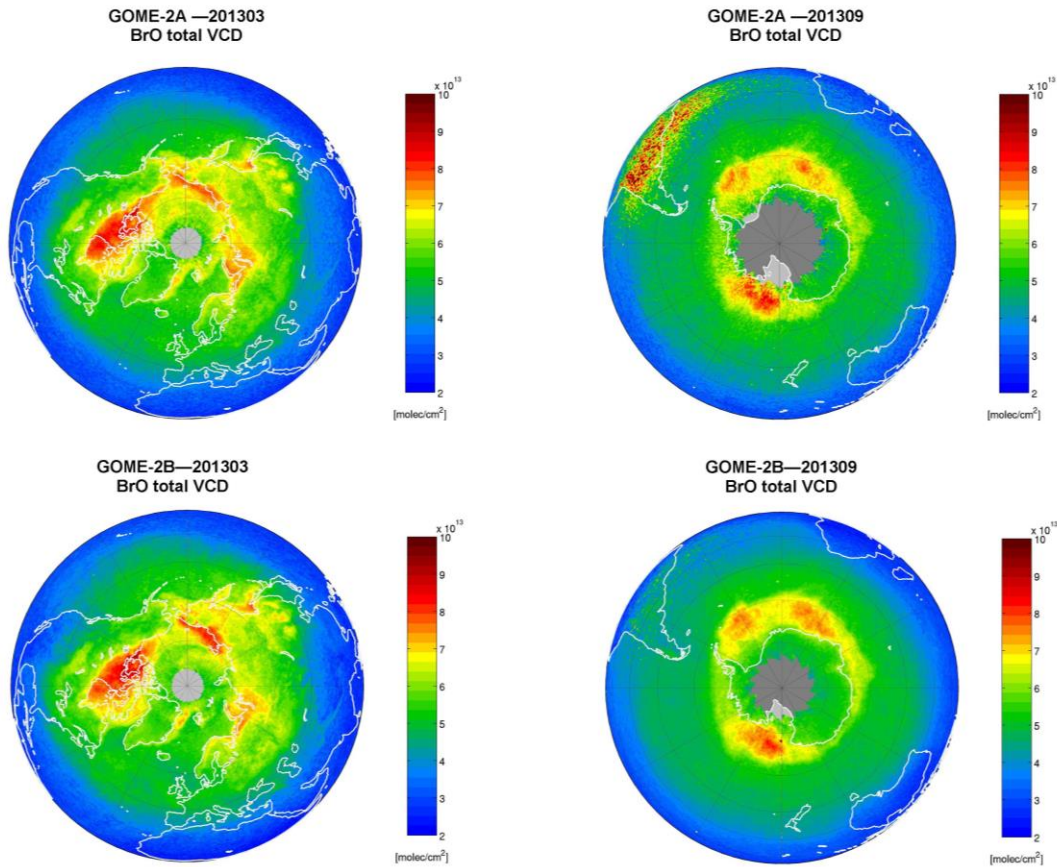


Figure 6. Monthly averages of GOME-2A (top) and GOME-2B (bottom) total BrO vertical columns in polar spring (2013) for the Northern Hemisphere (March: left plots) and the Southern Hemisphere (September: right plots). Only data corresponding to solar zenith angles lower than 80° are used.

As can be seen the results are really close as for the spatial patterns. It suggests also that the GOME-2A BrO product can be used even for recent observations. To further appreciate the stability of the long-term dataset offered by GOME-2A, Figures 7a and 7b presents the GOME-2A results for the 2007-2014 period in both hemispheres (North: April, South: October). Overall, a good coherence is found between the different maps throughout the years. The only time evolving feature is found in South America where the effect of the SAA becomes prominent for the last years.

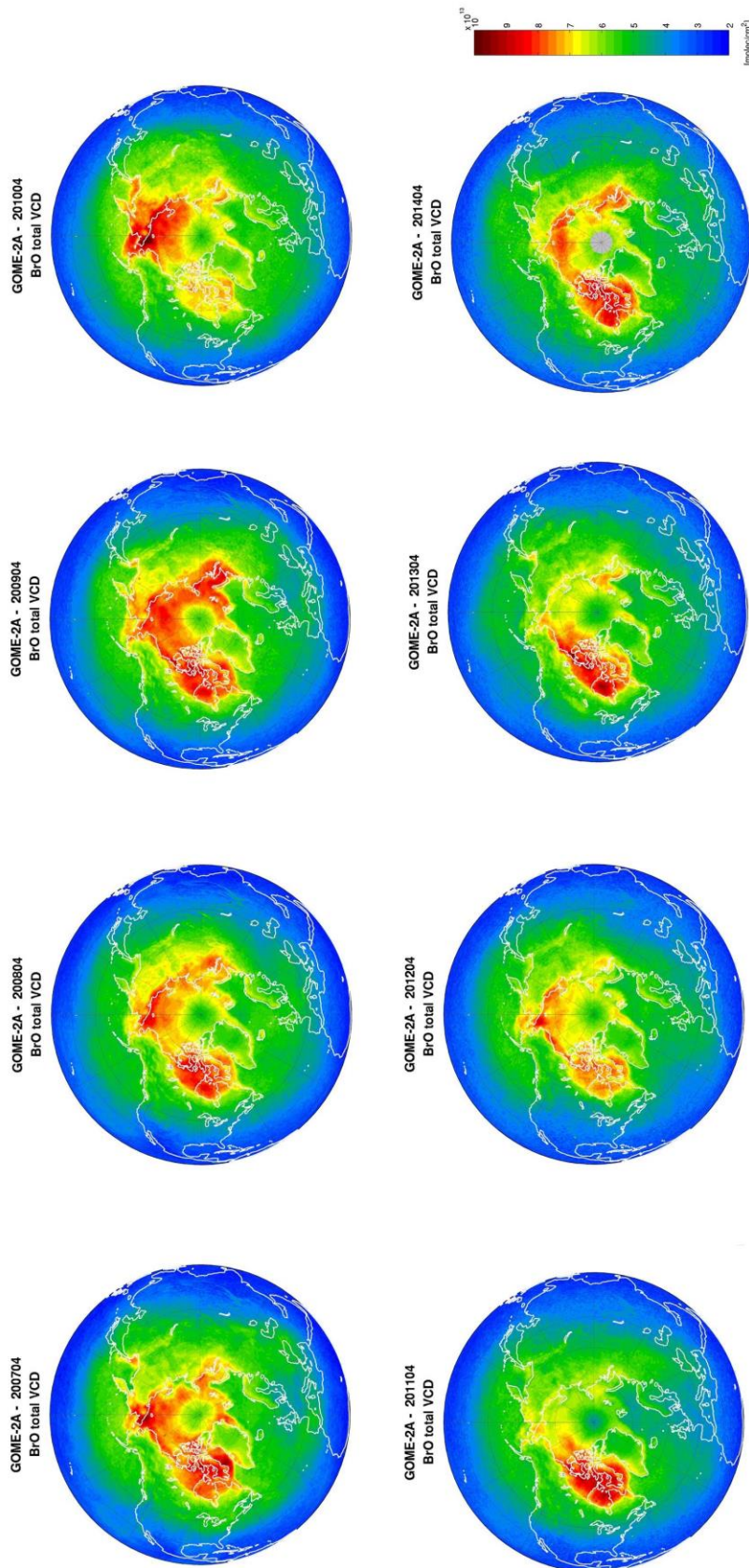


Figure 7a. Monthly averages of GOME-2A total BrO vertical columns in April for 2007-2014 for the Northern Hemisphere. Only data corresponding to solar zenith angles lower than 80° are used.

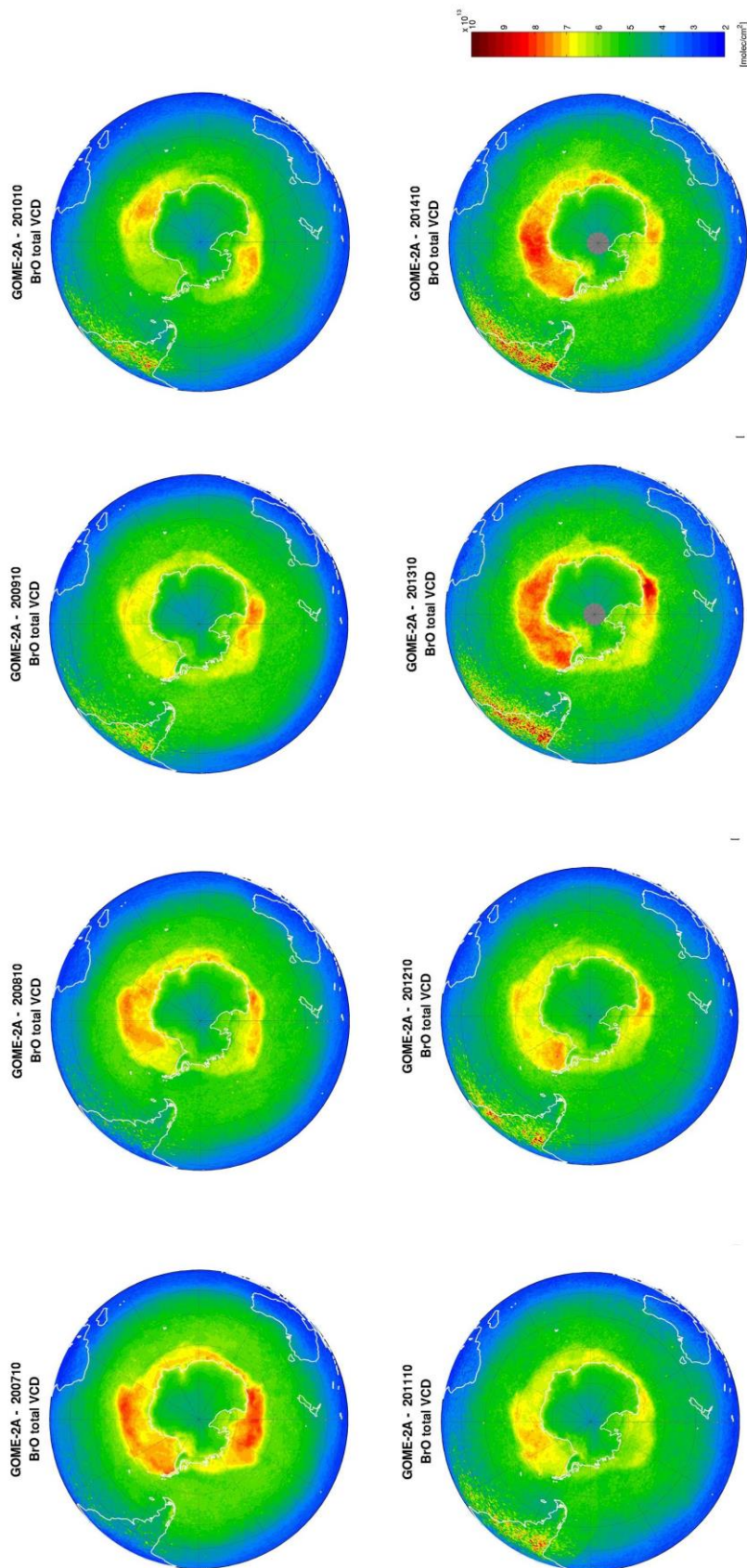


Figure 7b Monthly averages of GOME-2A total BrO vertical columns in October for 2007-2014 for the Southern Hemisphere. Only data corresponding to solar zenith angles lower than 80° are used.

In order to simplify the comparison process within the limited timeframe available for this study, we based our analysis on overpass files for a number of ground-based correlative sites, as detailed in Table 2.

Table 2. List of overpass sites used for the comparison with SCIAMACHY

| Station | Latitude [°] | Longitude [°] | Altitude [m] |
|----------------------|--------------|---------------|--------------|
| Ny_Alesund | 78.92 | 11.92 | 8 |
| Scoresbysund | 70.48 | -21.97 | 17 |
| Sodankyla | 67.37 | 26.65 | 179 |
| Salekhard | 66.67 | 66.67 | 0 |
| Jokioinen | 60.82 | 23.48 | 103 |
| Helsinki | 60.32 | 24.97 | 56 |
| Harestua | 60.20 | 10.80 | 580 |
| St_Petersburg | 59.97 | 30.30 | 60 |
| Zvenigorod | 55.68 | 36.77 | 200 |
| Hamburg | 53.57 | 9.97 | 105 |
| Leicester | 52.62 | -1.12 | 90 |
| De_Bilt | 52.10 | 5.18 | 15 |
| Cabauw | 51.97 | 4.93 | 10 |
| Paris | 48.85 | 2.35 | 50 |
| Verrieres_Le_Buisson | 48.76 | 2.24 | 0 |
| Jungfraujoch | 46.55 | 7.98 | 3450 |
| Haute.Provence | 43.91 | 5.75 | 580 |
| Issyk Kul | 42.62 | 76.97 | 1640 |
| Thessaloniki | 40.63 | 22.96 | 60 |
| XiangHe | 39.75 | 116.96 | 36 |
| GSFC | 38.99 | -76.84 | 102 |
| Table_Mountain | 34.38 | -117.68 | 2200 |
| Sevilleta | 34.35 | -106.88 | 1477 |
| Kanpur | 26.45 | 80.35 | 142 |
| Mussafa | 24.37 | 54.47 | 10 |
| Mukdahan | 16.61 | 104.68 | 166 |
| Djougou | 9.71 | 1.68 | 430 |
| Ilorin | 8.32 | 4.34 | 350 |
| Merida | 8.24 | -71.08 | 4765 |
| Nairobi | -1.32 | 36.92 | 1624 |
| La Reunion | -21.06 | 55.48 | 24 |
| Sao_Paulo | -23.56 | -46.73 | 865 |
| Kerguelen | -49.35 | 70.25 | 2 |
| Dumont_D'Urville | -66.67 | 140.02 | 40 |

GOME-2 and SCIAMACHY BrO columns have been extracted above each site according to measurement periods available from the different data sets. In order to provide a meaningful temporal perspective, time-series of monthly averaged BrO columns have been plotted for comparison over the time period from January 2007 until December 2014. Results from the SCIAMACHY and GOME-2A&B comparisons are represented in Figure 8 for a representative selection of sites.

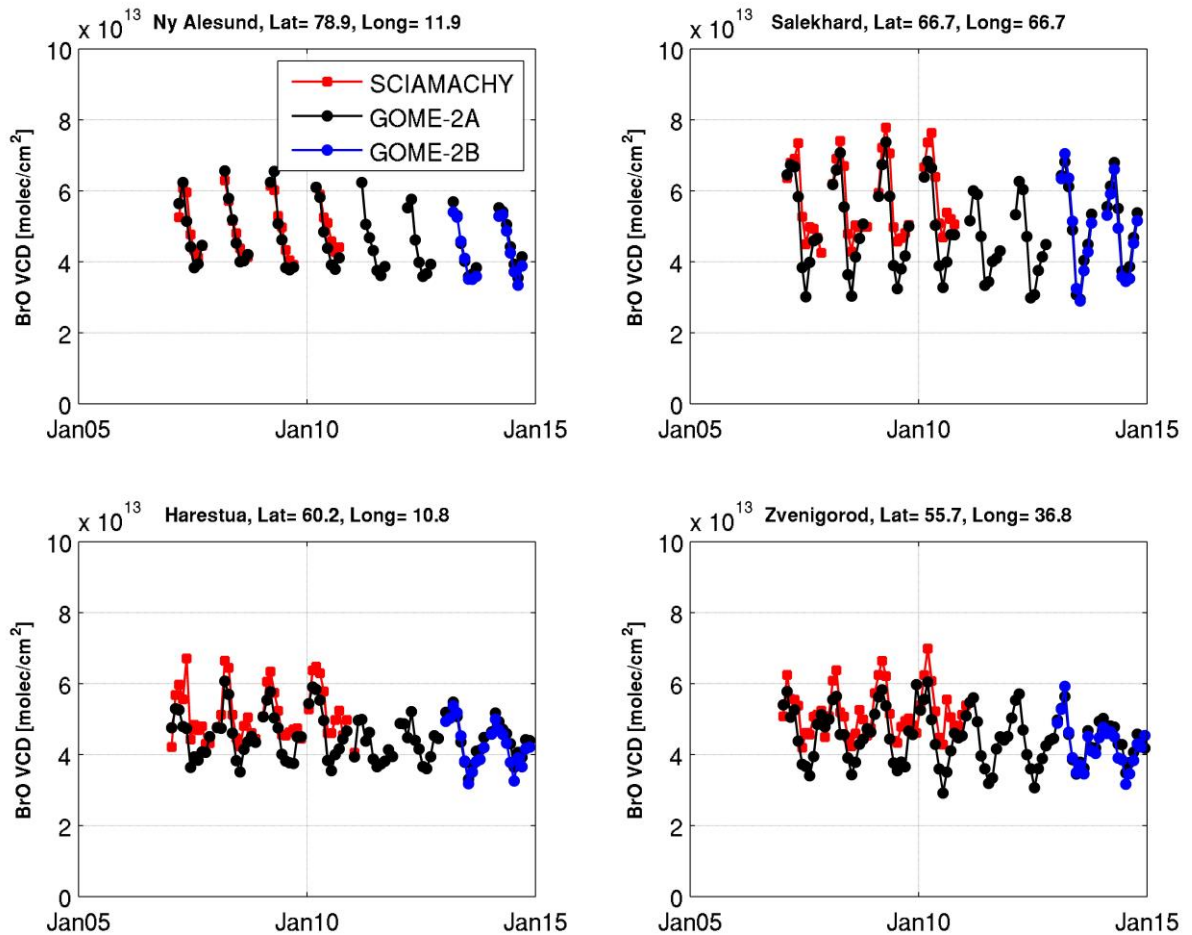


Figure 8. Comparison of time-series of monthly averaged BrO vertical columns retrieved from SCIAMACHY, GOME-2A and GOME-2B over the January 2007- December 2014 period, at a number of ground-based sites.

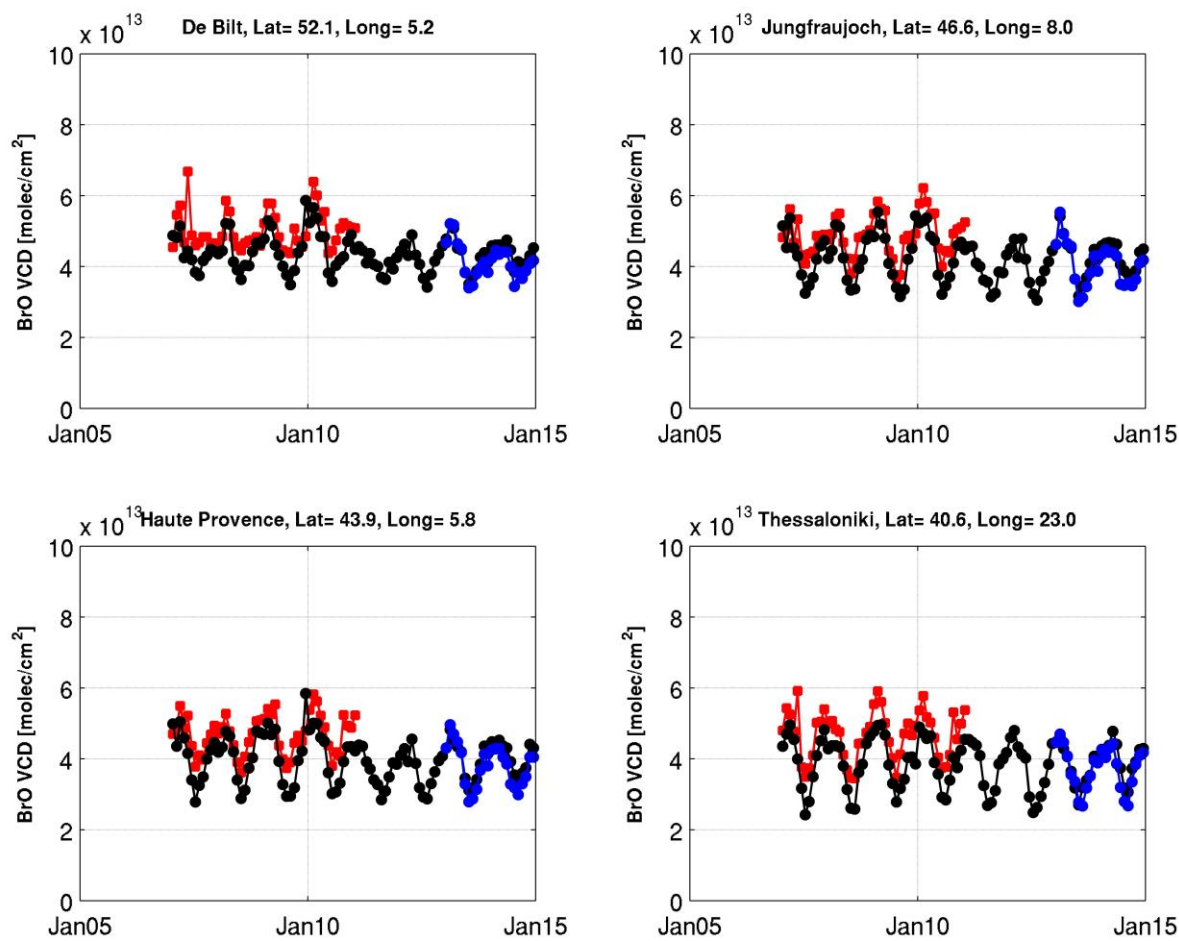


Figure 8. Continued.

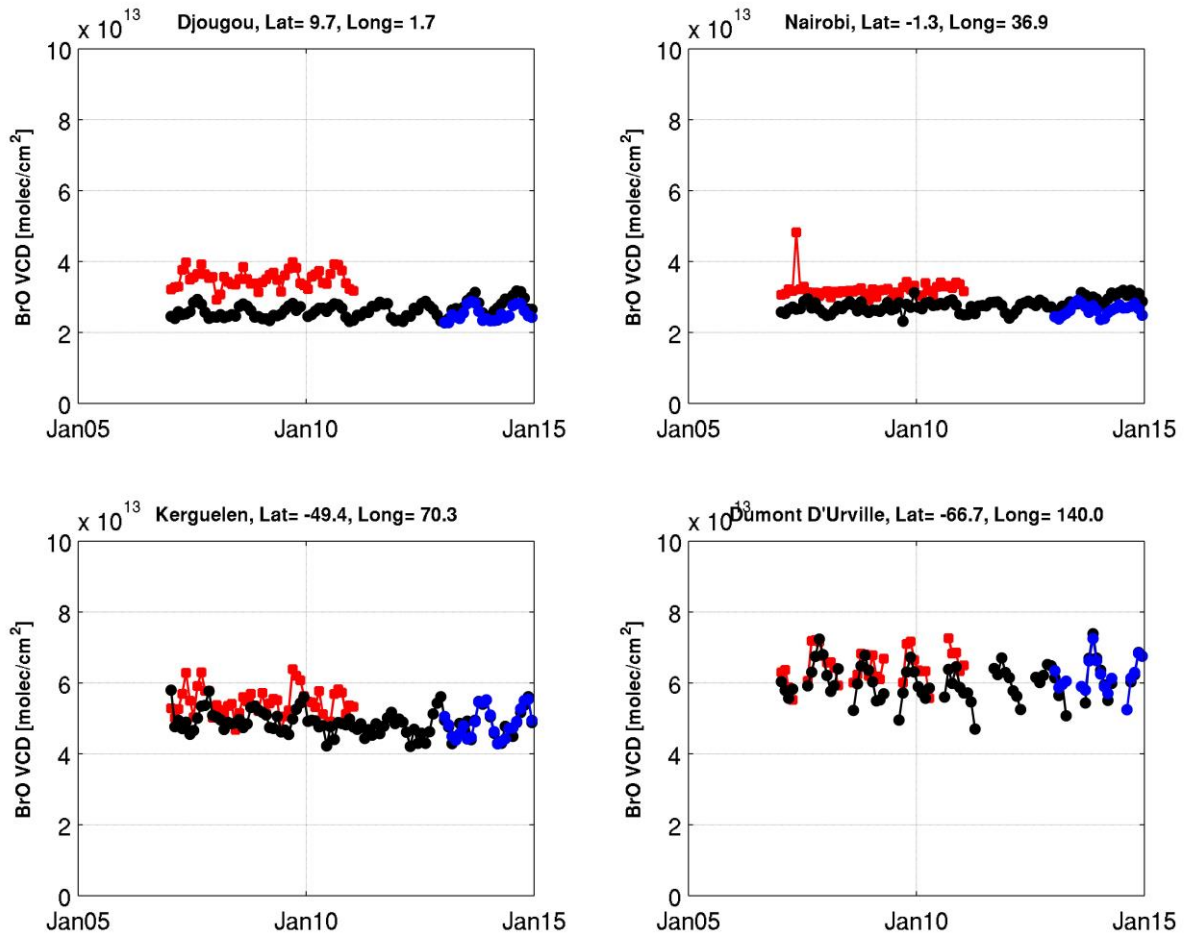


Figure 8. Continued.

In general, the GOME-2A and SCIAMACHY BrO columns for the 2007-2011 period show a fairly good agreement. At all latitudes, the seasonal patterns are well reproduced by both GOME-2A and SCIAMACHY. However, as can be seen in Figure 8, the GOME-2 retrieval generally gives lower BrO columns than the SCIAMACHY data. This tendency is also observed for tropical sites (e.g., Nairobi) and this might look in contradiction with the equatorial offset correction of 7.5×10^{13} molec/cm² that is consistently applied to both satellite data sets. The reason for the lower values of GOME-2A BrO VCDs compared to SCIAMACHY comes from the fact that the equatorial correction is applied to the slant columns but not to the vertical columns. Since GOME-2A has a larger swath than SCIAMACHY, the air mass factors applied to GOME-2A are larger (due to larger viewing angles) and thus the vertical columns are expected to be smaller. We have done the same comparison as in Fig. 8 but limiting the GOME-2A viewing angles to maximum $\pm 31^\circ$ (similar as SCIAMACHY) and the agreement between GOME-2A and SCIAMACHY was found better at all latitudes (not shown) confirming the impact of the equatorial correction. In the next validation exercises, one should probably find another ad-hoc post-processing normalization procedure than the equatorial correction used here (e.g. based on vertical columns rather than slant columns). Although the accuracy of the GOME-2A total BrO column product depends on the equatorial offset used, this is less the case as the solar zenith angles increases. In particular, near the poles where the interesting boundary layer emissions of bromine occur, GOME-2A and SCIAMACHY are quite close. From Fig.8, it can also be seen that the GOME-2A data set is quite stable with time. Indeed the equatorial correction stabilizes the time series and no systematic drift can be identified. Nevertheless, the degradation of the GOME-2A instrument increase the scatter on the GOME-2A total BrO columns and this is - of course - not compensated by the equatorial correction.

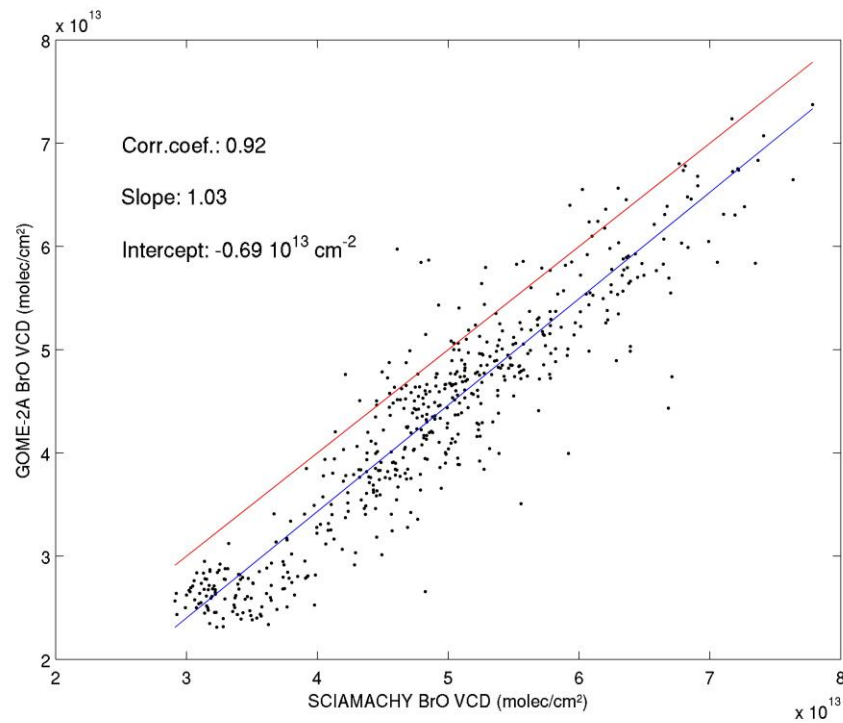


Figure 9. Correlation between BrO VCD retrieved from GOME-2A and SCIAMACHY. The blue line is the linear regression line (slope: 1.03, intercept: -6.9 10¹² molec/cm²; correlation coefficient: 0.92). The red line represents the reference line of slope equal to unity.

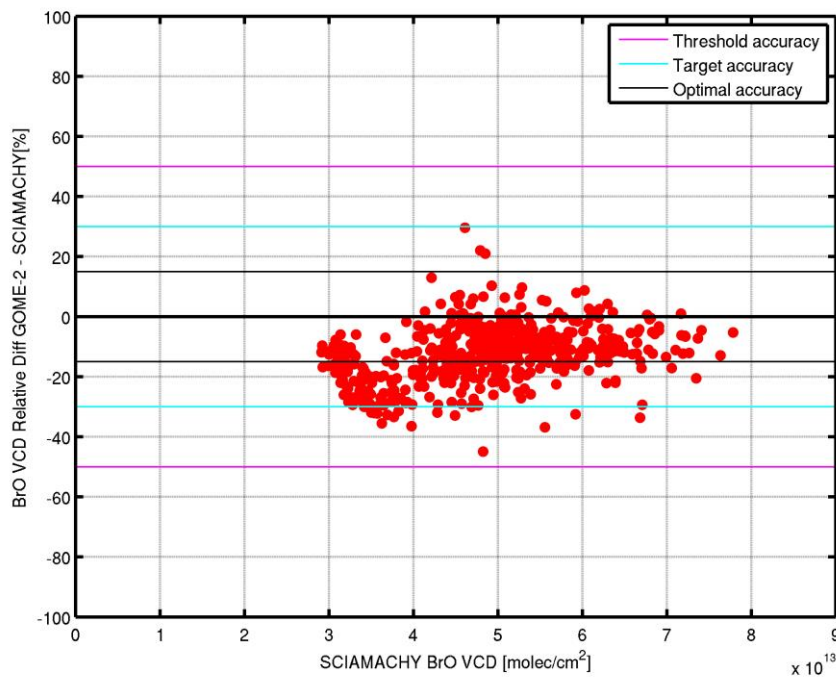


Figure 10. Relative difference in BrO VCD between GOME-2A and SCIAMACHY plotted as a function of SCIAMACHY BrO VCD.

In Figure 9, all coincident monthly average BrO VCD values are compared in a correlation plot (2007-2011). The column-dependency of the differences is more clearly depicted in Figure 10, where relative differences with respect to SCIAMACHY are expressed as a function of the BrO VCD. Note that the relative differences between GOME-2A and SCIAMACHY BrO VCDs are within the PRD threshold, target and optimal accuracies respectively for 100%, 97% and 67% of the 2007-2011 data. Based on these results and on the discussion above on the accuracy of the GOME-2A BrO column product, one can say that SCIAMACHY and GOME-2A agree within their respective uncertainties ($\sim 20\%$). For a majority of cases, the GOME-2A total BrO column product reaches the optimal accuracy as stated in the Product Requirements Document.

Figure 8 also shows an excellent consistency between GOME-2A and GOME-2B results. In Figure 11, both data sets are compared in a scatter plot (similarly as Figure 9) for the period 2013-2014. The correlation coefficient is of 0.98 and the linear regression line is characterized by a slope of 1.06 and an intercept of $-4.4 \cdot 10^{12}$ molec/cm².

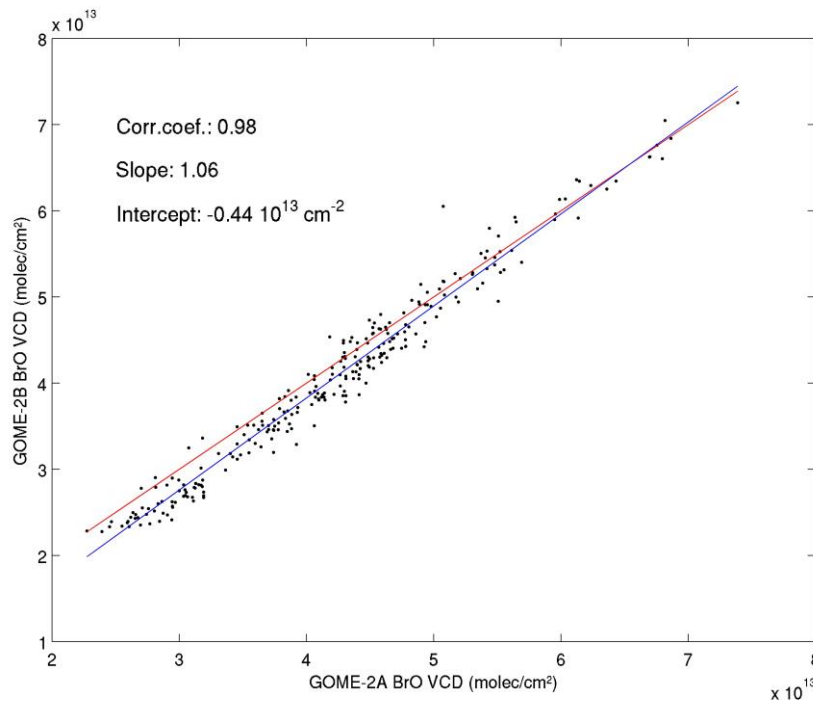


Figure 11. Correlation between BrO VCD retrieved from GOME-2A and GOME-2B. The blue line is the linear regression line (slope: 1.06, intercept: $-4.4 \cdot 10^{12}$ molec/cm²; correlation coefficient: 0.98). The red line represents the reference line of slope equal to unity.

Figure 12 shows additional illustration of the good geophysical consistency of the various total BrO column products for monthly zonal means. The same conclusions as from Figure 8 can be drawn from Figure 12.

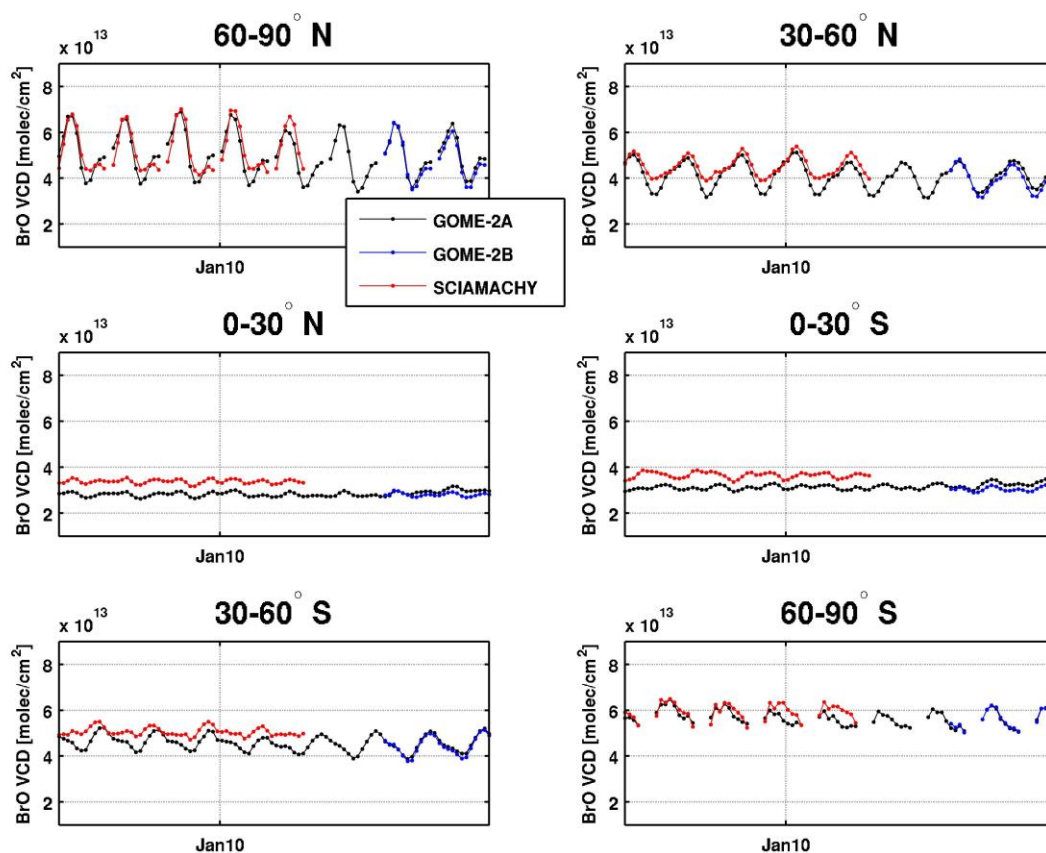


Figure 12. Time-series of total BrO vertical columns from GOME-2A, GOME-2B and SCIAMACHY observations (2007-2014) for different latitudinal bands (monthly zonal averages). Only data corresponding to solar zenith angles lower than 80° are shown.

E. COMPARISON AGAINST GROUND-BASED MEASUREMENTS

Ground-based zenith-sky UV-visible observations have been continuously performed at the NDACC station of Harestua, Norway since 1998 as well as in Lauder, New-Zealand since 1995. The instruments consist of zenith-sky looking grating spectrometers using cooled photodiode-array detectors. Spectral range and resolution are optimised for BrO measurements in the 330–360 nm. Total, stratospheric and tropospheric BrO columns are retrieved from measured slant columns using a profiling algorithm based on the optimal estimation method, as described in Hendrick et al. (2007). The sensitivity of the zenith-sky observations to the tropospheric BrO detection is increased by using for the spectral analysis a fixed reference spectrum corresponding to clear-sky noon summer conditions. The use of a photochemical box-model optimised for bromine chemistry embedded inside the inversion tool allows performing retrievals at any solar zenith angle, therefore allowing for appropriate photochemical matching with satellite observations.

In order to provide an independent reference, BrO total columns derived from latest versions of the ground-based measurements have been compared to GDP 4.8 BrO columns for the period from January 2007 until December 2014 (when available). Since the ground-based retrievals provide both stratospheric and tropospheric contributions of the total BrO column, the satellite VCDs have been tentatively recalculated with AMFs (referred as total AMFs) accounting for this BrO vertical distribution. The GOME-2A columns show a good agreement with ground-based results at Harestua and Lauder, as displayed in Figures 13 and 14.

In Table 3, we estimate the mean and standard deviation of the relative differences (GOME-2A minus ground-based columns). At Harestua, the mean bias ranges between 9% and -14% depending on the year, but remains within the optimal accuracy of 15%. At Lauder, there is a bias of about 20%, i.e. below the target accuracy of 30%. In Figure 15, the GOME-2B results are compared to the ground-based data at Harestua for 2013 and 2014. Again, the mean bias is small, i.e. less than 10% (within the optimal accuracy requirement of 15%) as indicated in Table 3.

Table 3. Mean and standard deviation of the differences (in %) between GOME-2 (A and B) and ground-based BrO observations at Harestua and Lauder.

| | 2007 | 2008 | 2009 | 2010 | 2011 | 2012 | 2013 | 2014 |
|-------------------------------|-------|-------|------|-------|-------|--------|--------|--------|
| Harestua (GOME-2A) | 7±18 | 9±16 | 7±16 | -1±18 | -6±14 | -16±12 | -13±13 | -14±14 |
| Harestua (GOME-2B) | - | - | - | - | - | - | -9±14 | -7±15 |
| Lauder (GOME-2A) | 19±19 | 20±18 | - | - | - | - | - | - |

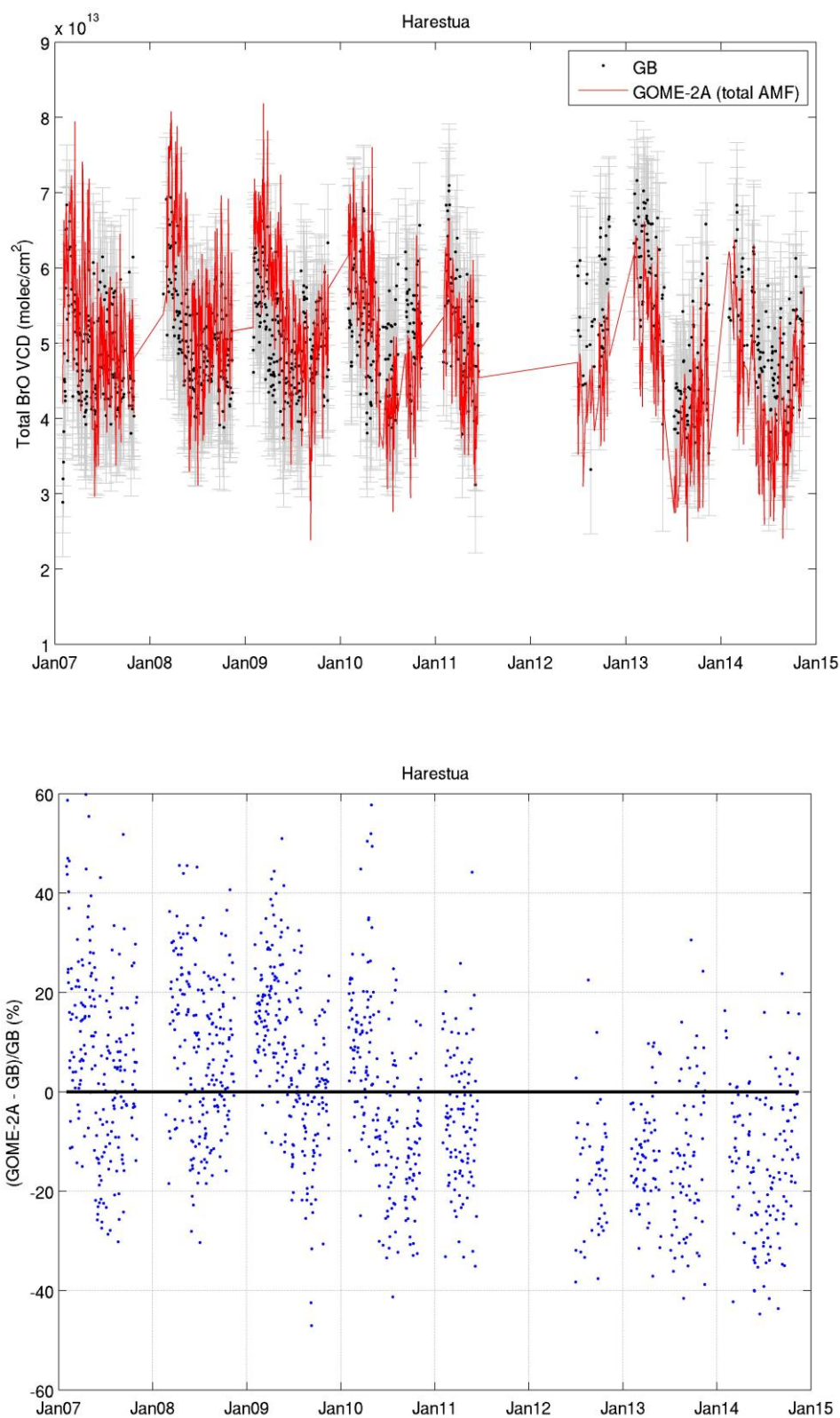


Figure 13. (upper plot) Comparison of BrO total columns retrieved from GOME-2A and ground-based UV-visible measurements at the Harestua station (data originator: F. Hendrick), (lower plot) relative difference between GOME-2A and ground-based BrO columns.

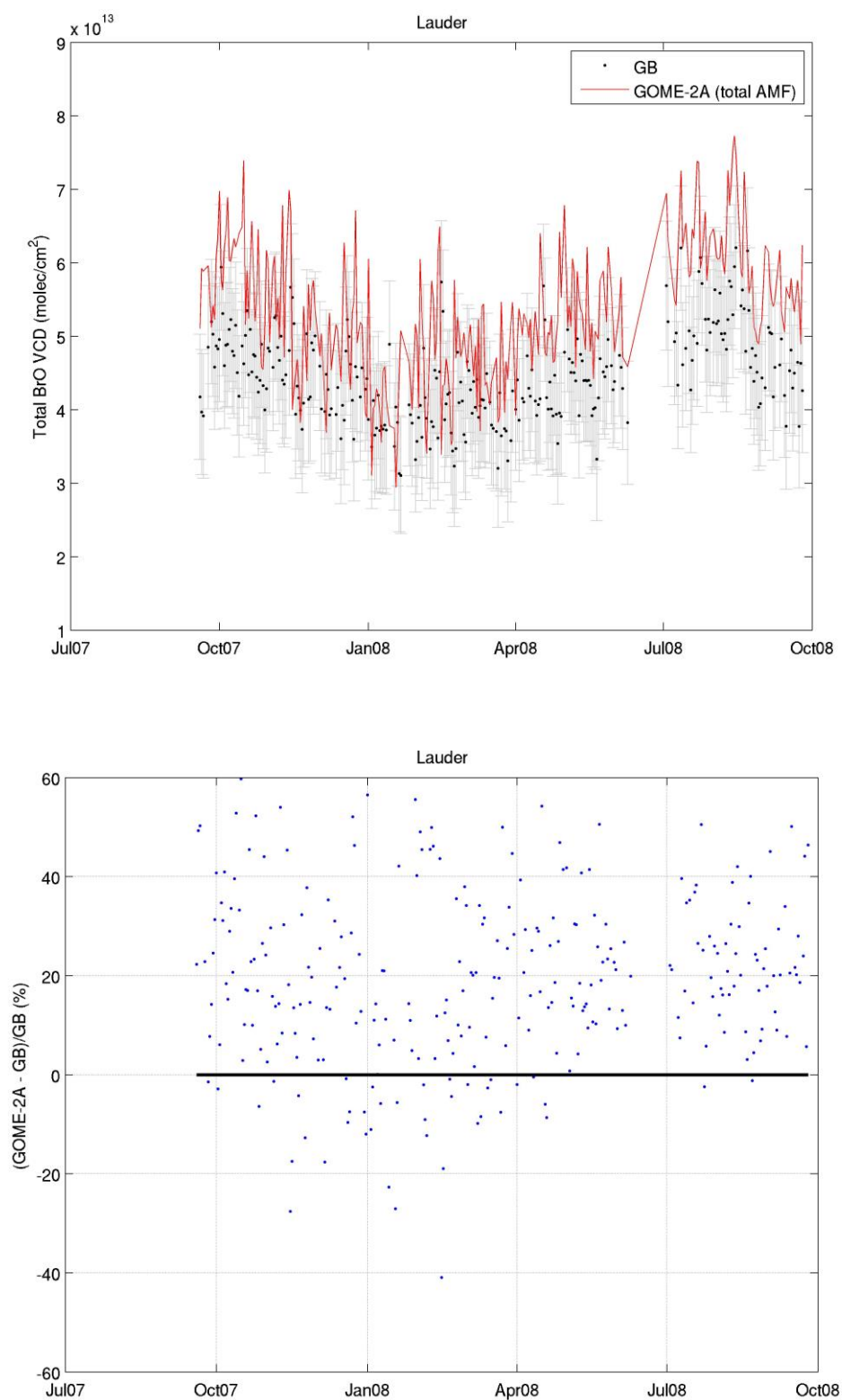


Figure 14. (upper plot) Comparison of BrO total columns retrieved from GOME-2A and ground-based UV-visible measurements at the Lauder station (data originators: P. Johnston and F. Hendrick), (lower plot) relative difference between GOME-2A and ground-based BrO columns.

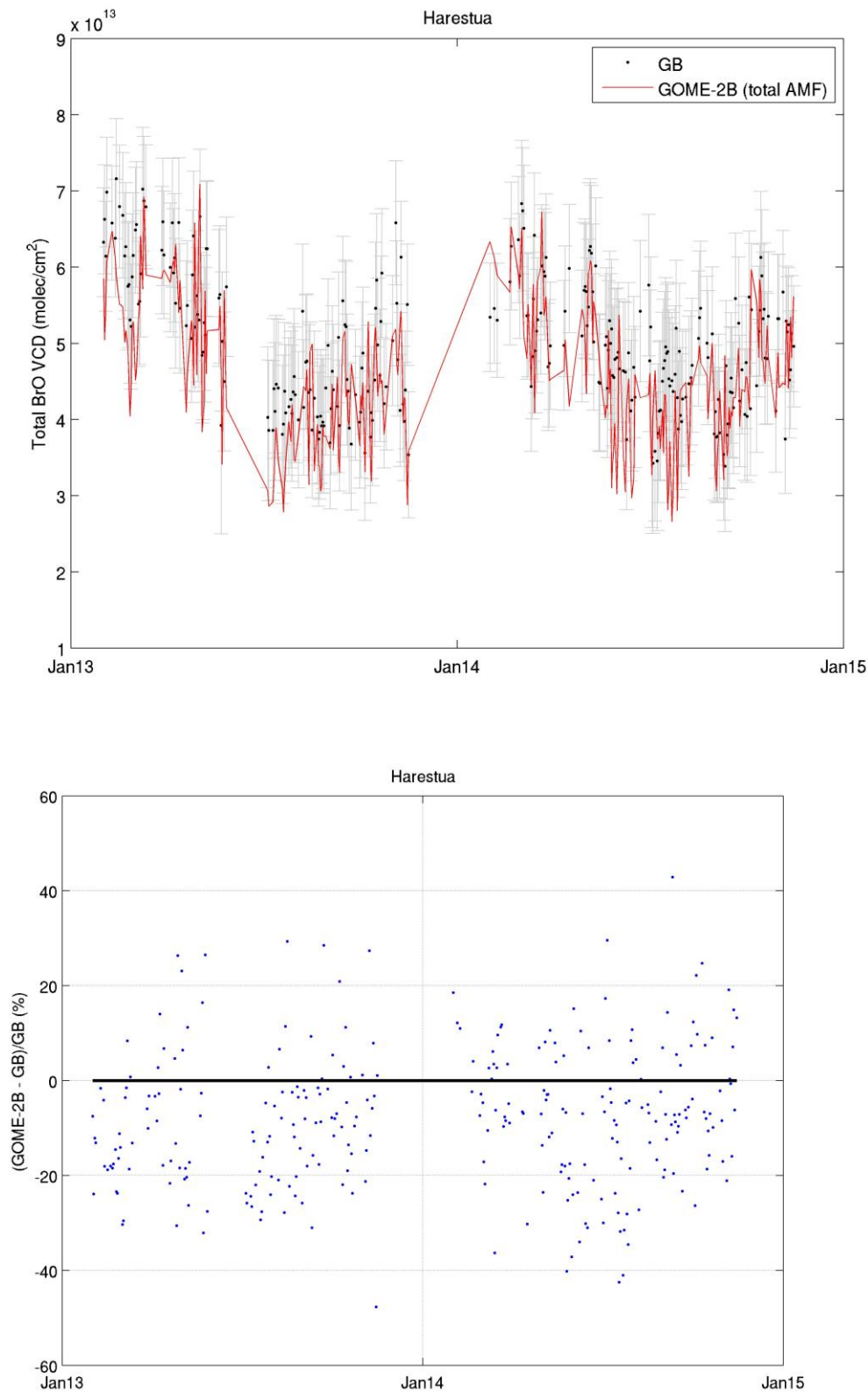


Figure 15. (upper plot) Comparison of BrO total columns retrieved from GOME-2B and ground-based UV-visible measurements at the Harestua station (data originators: F. Hendrick), (lower plot) relative difference between GOME-2B and ground-based BrO columns.

At Harestua, the comparison to ground-based columns with GOME2-A data shows a decreasing trend (despite the earthshine normalization) probably due to instrument degradation. Figure 15 shows also that GOME-2B is lower than the ground-based data since the beginning. At the time of writing, there are several reasons that could explain this behavior:

1. There is a real stratospheric BrO decreasing trend
2. Ground-based data after January 2012 have been empirically corrected in order to take into account of a possible off-set due to instrumental changes after this date. However, the impact of this correction on the trend observed in the difference between GOME-2 and ground-based vertical columns should be further investigated.
3. GOME-2A shows a clear trend (which cannot be explained completely by the actual stratospheric trend). It is likely due to the instrument degradation and that the equatorial offset correction is not sufficient anymore (the trend of the SCDs over the equator is huge, see Figure 2). E.g., the GOME-2A decreasing trend is more apparent for summer when the sensitivity to uncertainties in the equatorial offset correction is the largest. We note that for the strong polar spring BrO emissions the effect should be modest (see e.g. Fig 7)

Further investigations are needed to mitigate this effect, e.g. retrievals including slit function fitting and/or better offset correction. We therefore recommend not to use the current data product for investigating BrO trends.

F. CONCLUSIONS

As part of this validation report, the verification and validation of the GOME-2A&B reprocessed and off-line total BrO products, as produced by the GDP 4.8, have been addressed based on tools available at BIRA-IASB.

GOME-2 BrO vertical columns have been evaluated using (1) scientific retrievals based on the QDOAS tool and (2) comparisons with correlative data sets from SCIAMACHY and from ground-based zenith-sky measurements. A new fitting interval 332-359 nm has been selected as baseline for BrO slant column retrieval in GDP 4.8. As extensively described in Theys et al. (2011), this interval has been found to minimize the impact of several well-known artifacts. Moreover, an additional equatorial offset correction has been applied as was previously applied to other sensors.

For verification purpose, the QDOAS and GDP 4.8 retrieval tools were synchronized until a good level of agreement was found confirming the reliability of the GDP for BrO slant column fitting.

The difference between GOME-2A and SCIAMACHY data show a negligible column-dependent pattern for the 2007-2011 period. The bias is of about -10 % and is found to be rather stable in time. It comes out of the analysis that the equatorial offset correction enables to compensate to a large extend for the instrumental degradation effect on the retrieved total BrO vertical columns (for the mean values; the scatter of the data is of course increasing continuously). The agreement between GOME-2A and -2B results is found excellent and the BrO columns agree within ~5% on average.

Additional comparisons using latest versions of available ground-based DOAS measurements at two stations of the NDACC (Harestua, Norway and Lauder, New Zealand) further consolidate the findings of the SCIAMACHY- GOME-2 comparison with mean bias of the column differences (for 2007-2014) lower than 20%.

Based on the validation with ground-based measurements and the comparisons with correlative SCIAMACHY data, we concluded that the current GOME-2 GDP 4.8 BrO column product (for the all period 2007-2014) fulfill the user requirements in terms of accuracy, as stated in the Product Requirements Document: Threshold and Target accuracy (50% and 30%) virtually all the time; Optimal accuracy (15%) in a majority of cases (~80% of the time).

In the future, more work is needed to further reduce the impact of the degradation of the GOME-2 instrument on the quality of the total BrO column product and on the development of an improved BrO post-processing normalization procedure. We therefore recommend no to use the current data product for investigating BrO trends.

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