Estimating Stratospheric and Tropospheric BrO columns using Ozone Monitoring Instrument

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Abstract: Distributions of tropospheric BrO columns are estimated by residual methods using OMI total BrO columns and stratospheric BrO columns obtained from several assumptions. The assumptions are (1) the lower 20th percentiles of latitudinally binned BrO columns; (2) SCIAMACHY stratospheric measurements extrapolated down to the NCEP tropopause; (3) SCIAMACHY stratospheric measurements assuming constant BrO between the NCEP tropopause and 15 km; and (4) a model simulation output by R. Salawitch and T. Canty. We conduct an integrated analysis of tropospheric BrO columns with observation data obtained during ARCTAS in order to understand the quality of satellite-derived tropospheric BrO and improve our knowledge on tropospheric halogen chemistry. The correlations of tropospheric columns to in situ observations of bromine species are used to evaluate the estimations of stratospheric BrO columns and the resulting tropospheric columns. Relationship between satellite-derived total and tropospheric BrO columns is also analyzed.

1. Introduction

Bromine radicals (BrOx = Br + BrO) are chemically important species in polar troposphere because of their ability to catalytically destroy ozone. Enhancements of BrO connected to ozone depletion events have been observed in the polar surface air during early springtime [Hausmann and Platt, 1994; Tuckermann et al., 1997; Kreher et al., 1996; 1997]. In addition, bromine radicals are responsible for mercury deposition events in the polar environments [Schroeder et al., 1998; Sander et al., 2003; Brooks et al., 2006]. An autocatalytic reaction pathway that oxidizes bromide to bromine radicals in acidic sea salt aerosols has been proposed [Fan and Jacob, 1992; Vogt et al., 1996; Foster et al., 2001].

Back trajectory studies indicate that activation of bromine is positively correlated with the duration of contact with the newly forming sea ice [Frieb et al., 2004; Simpson et al., 2007; Wagner et al., 2007]. However, the detailed mechanism to transport bromide salt to bromine radicals is still uncertain. Enhanced BrO in the polar boundary layer might be transported to the free troposphere by convection [McElory et al., 1992]. This may have global consequences for tropospheric ozone chemistry [von Glasow et al., 2004; Lavy et al., 2005], mercury oxidation [Holmes et al., 2006], and aerosol formation and cloud albedo by affecting DMS oxidation [von Glasow and Crutzen, 2004].

Satellite observations, with their global coverage, provide us with valuable information to study tropospheric BrO chemistry. The Global Ozone Monitoring Experiment (GOME), launched in 1995, provided the first global mapping of BrO total columns [Wagner et al., 1998; Richter et al., 1998; Wagner and Platt, 1998]. Since then, the Ozone Monitoring Instrument (OMI) [Levelt et al., 2006], the Scanning Image Absorption SpectroMeter for Atmospheric CHartographY (SCIAMACHY) [Sinnhuber et al., 2005], and the second Global Ozone Monitoring Experiment (GOME-2) [Loyala et al., 2008] have been used to monitor BrO total column amounts across the globe. Limb sounders including SCIAMACHY provide upper and middle stratospheric BrO profiles [Rozanov et al., 2005; Sioris et al., 2006]. Figure 1 shows mapping of total BrO column on Sep 2006. However, these satellite-derived BrO columns have rarely been independently validated, because only a limited amount ground-based data are available for this purpose.

Several studies suggested a connection between enhanced tropospheric BrO columns and ozone depletion events [Richter et al., 1998; 2002; Wagner et al., 2001; Hollwedel et al., 2004; Jacobi et al., 2006]. Zeng et al. [2003] derived tropospheric BrO columns from the BrO total column amounts using a 3-dimensional regional chemical transport model with GOME observations. They also simulated the effect of BrO on ozone depletion events [2003; 2006] and hydrocarbons [2006].

The NASA Arctic Research of the Composition of the Troposphere from Aircrafts and

Satellites (ARCTAS) and the NOAA Aerosol, Radiation, and Cloud Processes affecting Arctic Climate (ARCPAC) missions provide observations of BrO and relevant compounds on various platforms during the spring 2008 in the Arctic regions.

In this study, we derive tropospheric BrO vertical column densities (VCDs) from total BrO VCDs provided by OMI and GOME-2 using various approaches to prescribe stratospheric BrO VCDs. The total and tropospheric BrO VCDs are compared with aircraft- and ground-based measurements of bromine species during the spring 2008 in order to examine the capability of these instruments for tropospheric BrO. We also examine the stratospheric contribution to the variation of the total BrO VCD and assess the tropospheric BrO VCDs used in this study.

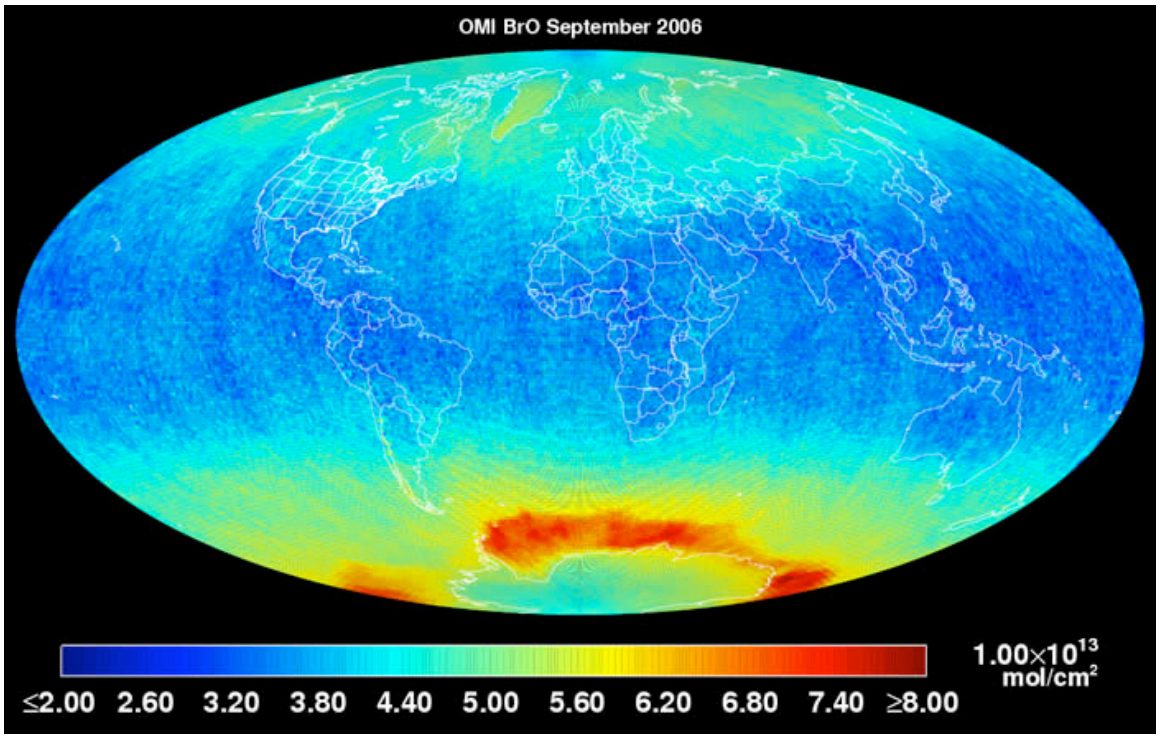

Figure 1. Total BrO column in September 2006 observed by OMI [T. Kurosu et al.]

2. Data Description

2.1 Aircraft and Ground-based Measurements

In situ measurements of bromine species were made from NASA DC-8 aircraft platform during the Arctic Research of the Composition of the Tropospheric from Aircraft and Satellite (ARCTAS) experiment in April 2008. Detailed descriptions of the instruments

are available in the ARCTAS and ARCPAC overview papers [Jacob et al., 2009 and Brock et al., 2010, respectively]. BrO and Br2 were observed using Chemical Ionization Mass Spectrometry (CIMS) during the both experiments [Liao et al., 2010; Neuman et al., 2010]. The CIMS technique has been described by Slucher et al. [2004] and Kim et al. [2007]. BrO was measured on two DC 8 flights (16 and 17 April 2008). On these flights, BrO was measured once every 30s.

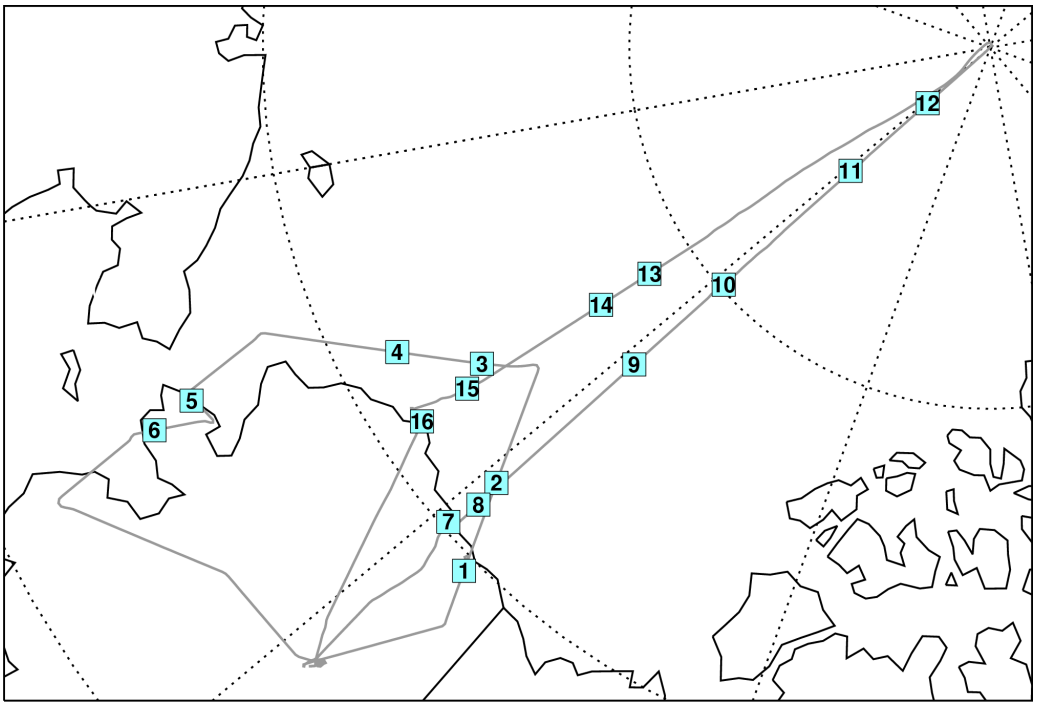

Figure 2. Flight tracks for NASA ARCTAS mission.

2.2 Total BrO Total Vertical Column Densities from OMI and GOME-2

We use total BrO VCD data provided by OMI and GOME-2 during March and April 2008 in this study. The Ozone Monitoring Instrument (OMI) and the Global Ozone Monitoring Experiment-2 (GOME-2) are space-based nadir viewing sensors in sun-synchronous polar orbit with equator crossing times of approximately 1:30 PM and 9:30 AM, respectively. They provide BrO total column mappings with nearly daily global coverage. OMI is aboard the NASA Aura satellite, and GOME-2 is aboard the operational EUMETSAT MetOp satellite. OMI has a nadir pixel size of ~13x24 km2 (13x13 km^2 in spatial zoom mode).

The BrO retrieval algorithm uses a spectral range of 344 to 360 nm within the UV-2 channel that has a spectra resolution of ~0.5 nm. The nadir pixel size of of GOME-2 is

40x80 $km^{2.}$. The GOME-2 BrO retrieval algorithm uses a spectral fitting window of 336-351.5 nm.. The OMI and GOME-2 BrO retrieval algorithms employ differential optical absorption spectroscopy (DOAS) approach. This approach involves first fitting backscattered UV radiance to BrO and other absorption spectra to obtain a BrO total slant column density (SCD). An initial total BrO vertical column density (VCD) is obtained by dividing the SCD by the air mass factor (AMF) calculated using a BrO profile that assumes BrO exists only in the stratosphere. This initial total vertical column is equal to total BrO column where there is no tropospheric BrO.

3. Deriving Tropospheric BrO Vertical Column Density

3.1 Estimates of Stratospheric BrO column density

In order to derive tropospheric BrO column, an estimate of stratospheric BrO column is needed. Here, we prescribe the spatial distribution of stratospheric BrO vertical column using several hypotheses. The details and naming conventions of each approach used in this study are described in detail below. Figure 3 shows the four stratospheric columns used in this study.

(1) 20th stratospheric column:

The simplest hypothesis is that stratospheric BrO is zonally constant. To provide a first-order estimate of the magnitude of the stratospheric BrO vertical column, we take the lower 20th percentile of zonally binned the initial BrO total columns. Here we assume that tropospheric column amounts for the lowest 20th percentile are negligible. A similar approach was used to derive tropical stratospheric columns of ozone with OMI and similar instruments [Ziemke et al., 2009]

However, addressing the structure of stratospheric BrO vertical column is necessary as observed total BrO VCD cannot explain the observed feature of halogen species and ozone depletion events during the ARCTAS. From SCIAMACHY limb soundings of stratospheric BrO, we produce two mappings of stratospheric BrO column amounts based on different assumptions on vertical structure of stratospheric BrO mixing ratio.

(2) SCIA-2nd stratospheric column:

Limb sounding of stratospheric BrO mixing ratio is used to obtain mapping of stratospheric BrO column. SCIAMACHY provides BrO number density and mixing ratio from 15km to 33km altitude. However, stratospheric BrO number density below 15km cannot be observed due to low sensitivity to the lower stratosphere. In order to obtain

stratospheric BrO profile between tropopause and 15km, we extrapolate the BrO mixing ratio profile from 15km to 33km as a secondary polynomial. The obtained stratospheric BrO profiles is integrated to yield stratospheric BrO column amounts. Pressure and temperature profile from NCAR/NCEP Reanalysis data is used for the integration.

(3) SCIA-Max stratospheric column:

Similarly to the SCIA-2nd stratospheric column, SCIAMACHY BrO mixing ratio profile from 15km to 33km is used as middle stratospheric BrO profile. But we use different assumption for the lower stratospheric BrO. In order to apply maximum loading of BrO at the lower stratosphere to the stratospheric column, we assume BrO mixing ratio between tropopause and 15km is the same as BrO mixing ratio at 15km observed by SCIAMACHY.

(4) UMD stratospheric column:

A model simulation for stratospheric bromine species [Salawitch et al., 2010] are taken to describe the spatial structure of stratospheric BrO VCD. They take CFC-12 from GEOS-5, and define Bry, the sum of inorganic bromine species, as a function of CFC-12 from an analysis of organic bromine measurements in the stratosphere. This provides profiles of Bry. Then they use WACCM values of BrO/Bry, for the time of OMI overpass, to find BrO mixing ratio. They obtain the baseline values of Bry vs CFC-12 which by definition equals zero at the tropopause. And they add 5 ppt to the baseline value of Bry at all values of CFC-12, then repeat the simulation to yield stratospheric BrO field.

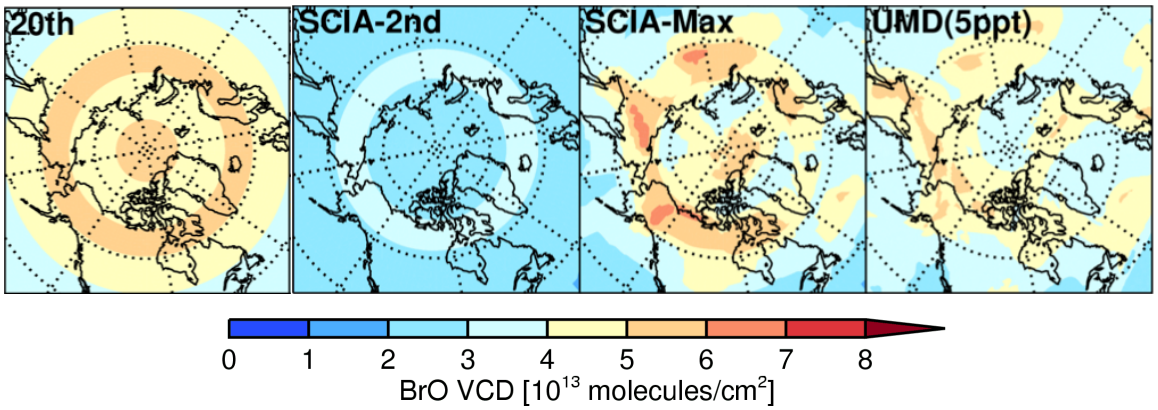

Figure 3. 20th stratospheric column, SCIA-2nd stratospheric column, SCIA-Max stratospheric column, and UMD stratospheric column on Apr 16th 2010.

3.2 Calculation of OMI tropospheric columns

Tropospheric BrO vertical column densities are obtained using OMI total BrO column and mappings of stratospheric BrO columns described in 3.1. In order to obtain the tropospheric portion of the total BrO column, the stratospheric portion need be subtracted from the total column. Correction for air mass factor is needed for accurate estimation of tropospheric column, as the air mass factor used to derive total BrO vertical column is calculated assuming tropospheric BrO mixing ratio is zero. So we derive tropospheric BrO slant column by multiplying the tropospheric portion of the total BrO vertical column by the air mass factor for the total BrO vertical column. Then tropospheric BrO vertical column is obtained by dividing tropospheric BrO slant column by tropospheric air mass factor which is calculated based on tropospheric BrO mixing ratio profile from *in-situ* BrO measurements during ARCTAS. Figure 4 shows the tropospheric BrO profile used in radiative transfer calculation for the tropospheric air mass factor.

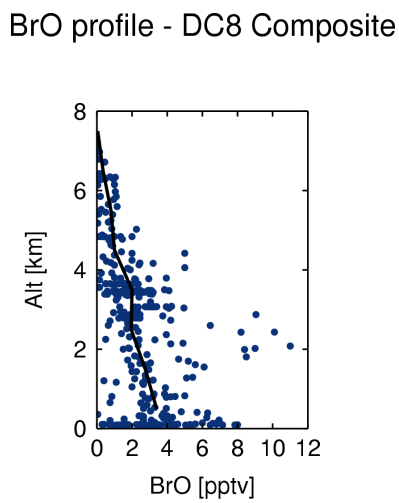

Figure 4. Tropospheric BrO profile obtained from *in-situ* measurements during ARCTAS

In this study, we are using four mappings of stratospheric BrO column. Therefore, combination of OMI total BrO column and the stratospheric BrO columns yields four mappings of tropospheric columns. Figure 5 shows the OMI total BrO column and these four tropospheric columns on Apr 16th 2010. Each tropospheric column reflects effects of assumption used to prescribe stratospheric BrO mapping. For example, tropospheric column derived using 20th stratospheric BrO column, which assumes constant zonal stratospheric BrO column, keeps spatial structure of OMI total BrO column, while tropospheric column derived from UMCP stratospheric BrO column shows different zonal structure from total BrO column. In addition, tropospheric BrO column using SCIA-Max, which assumes maximum BrO loading at lower stratosphere, shows

significantly less amount of tropospheric column compared to tropospheric BrO column using SCIA-2nd, which takes extrapolation of lower stratospheric BrO profile assuming stratospheric BrO profile as a secondary-order polynomial. In tropospheric BrO columns, difference in magnitudes of stratospheric column is amplified by air mass correction.

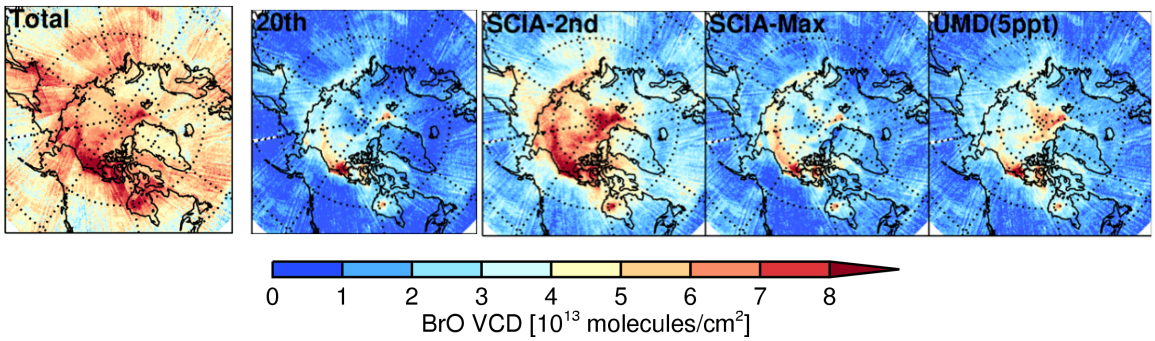

Figure 5. OMI Total BrO column on Apr 16th 2010, and OMI tropospheric BrO column from 20th stratospheric column, OMI tropospheric BrO column derived using SCIA-2nd stratospheric column, OMI tropospheric BrO column derived using SCIA-Max stratospheric column, and OMI tropospheric derived using UMCP stratospheric column on Apr 16th 2010.

4. Comparison of OMI tropospheric BrO columns to *in-situ* and ground-based observations during spring 2010

During ARCTAS, BrO mixing ratio is observed along the flight tracks. As the *in-situ* measurements provides BrO mixing ratio at multiple positions and altitudes, the BrO mixing ratios can be collected as tropospheric BrO profiles. We obtained 16 BrO profiles from ARCTAS BrO measurements, and the profiles are integrated to yield "*in-situ*" tropospheric BrO column. Median positions of the BrO profiles are shown in figure 1. Figure 6 shows shapes of the profiles and integrated columns. Profile #3, #9 #10, #12, and #14 show enhanced BrO at middle troposphere. Most of the profiles imply the existence of free tropospheric BrO.

We compared OMI Tropospheric BrO columns, which are calculated using OMI total column and the estimates of stratospheric columns, to in-situ tropospheric BrO column. Figure 7 shows mean ratios of OMI tropospheric BrO columns to in-situ tropospheric BrO columns at the 16 points on the flight tracks. Mean ratio of tropospheric BrO column using 20th percentile stratospheric column to in-situ tropospheric column is close to 1, which means the 20th percentile stratospheric BrO column is reasonable first-order

estimate of stratospheric BrO column. Also, ratios of tropospheric BrO columns using other estimates of stratospheric BrO columns to the in-situ column are in acceptable range, especially those three estimates are totally independent of OMI BrO total column. One important feature is that the magnitude of tropospheric column using SCIA-Max is far greater than the tropospheric column using SCIA-2nd, which means lower stratospheric BrO takes significant portion in magnitude of whole stratospheric BrO column. Therefore, taking structure of lower stratospheric BrO into account precisely is essential to obtain the accurate estimate of tropospheric BrO column.

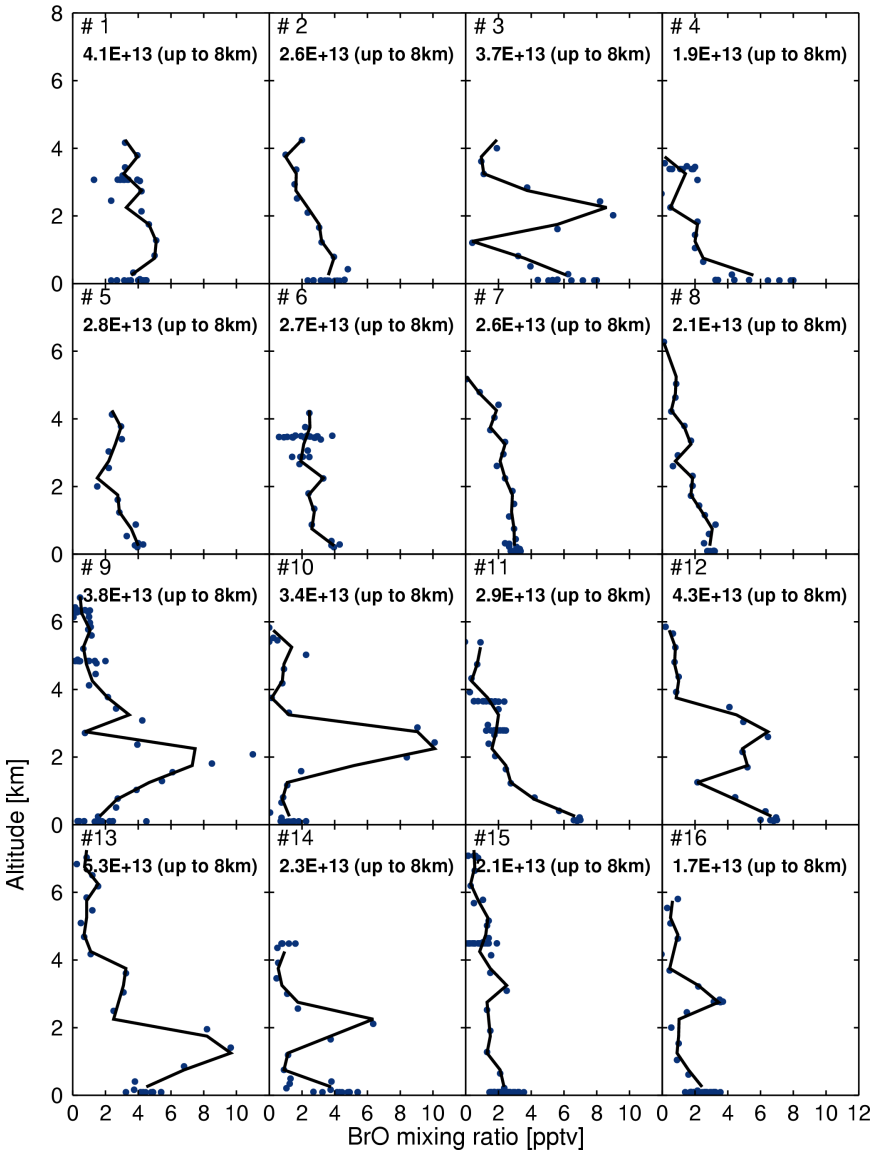

Figure 6. Tropospheric BrO mixing ratio profiles observed on Apr 16 and 17 2010 during ARCTAS.

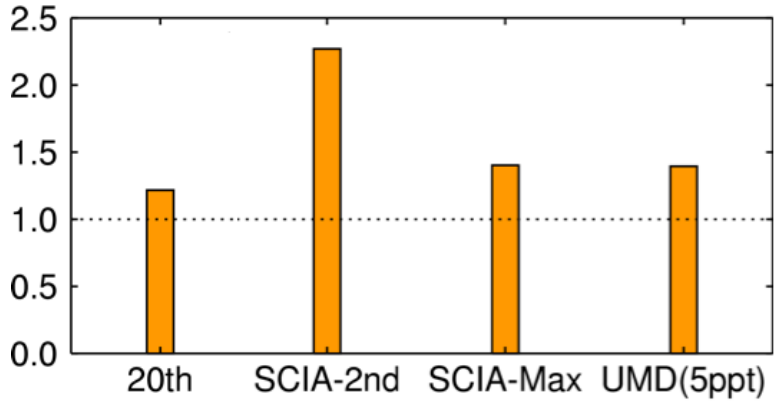

Figure 7. Ratios of OMI tropospheric BrO columns to in-situ tropospheric BrO columns.

Figure 8 shows scatter plots of OMI tropospheric BrO columns to in-situ BrO columns. However, due to limited number of in-situ columns, we cannot confirm that OMI tropospheric BrO columns capture the variation of tropospheric BrO column observed during ARCTAS.

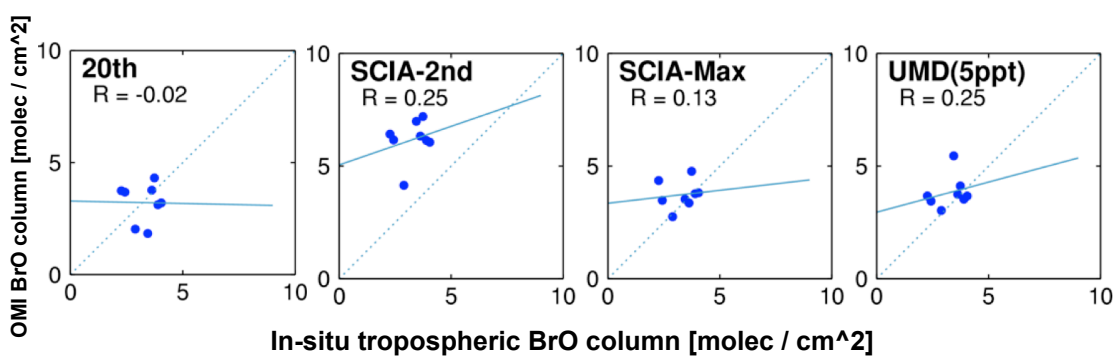

Figure 8. Scatter plots of OMI tropospheric BrO columns (Y-axis) and in-situ tropospheric BrO column (X-axis)

5. Conclusion

In this study, we calculate tropospheric BrO columns by residual methods using OMI total BrO columns and estimates of stratospheric BrO columns obtained from several assumptions. The tropospheric column using lower 20th percentiles stratospheric BrO columns shows good agreement to in-situ measurement in magnitude, but hard to reproduce zonal structure of tropospheric BrO column. Estimates of stratospheric BrO column from independent observation and simulation worked reasonably well.

Tropospheric columns applying SCIAMACHY stratospheric column implies importance of using accurate assumption for lower stratospheric BrO profile. Future goals of this study are to obtain more accurate estimates for stratospheric BrO column in terms of magnitude and variation, and to apply OMI tropospheric BrO columns to assess possible effects of BrO to the environments.

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