Quantification of Atmospheric BrO

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Motivation and Objectives:

- Enhanced total column BrO observed by satellites has been associated with Arctic surface ozone depletion; but, BrO "hotspots have also been observed NOT associated with surface events
- Locations of these hotspots in Arctic spring are consistent with observations of total column ozone and tropopause height (compression of stratospheric air to high pressure in regions of low altitude tropopause) → (?) a stratospheric origin for the elevation BrO
- Salawitch et al (2010) show closure of the budget for total column BrO can be achieved provided natural, short lived biogenic bromocarbons supply ~5 ppt of bromine to the Arctic lower atmosphere
- **Measurement objectives**
  - what is the vertical column density of BrO in Arctic spring – validation of OMI BrO
  - measurement location with no measurable tropospheric BrO
  - derive BrO vertical column density (VCD) by making use of all of direct sun (DS), MAXDOAS, and zenith sky measurements and use the synergies to nail down VCD BrO
  - measure the ozone profile directly by ozonesonde and Brewer
- **Analysis objectives**
  - evaluate effect of DOAS fitting parameters on VCD BrO retrievals from direct sun
  - use modeling results to select proper method for determining BrO in DOAS reference spectrum

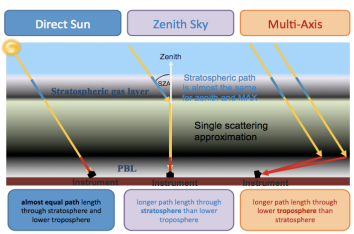
Instrumentation Fielded to U. Alaska

- WSU MFDOAS – direct sun (DS), zenith, MAXDOAS: BrO, O_3, NO_2, OClO, HCHO
- GSFC PANDORA – DS, zenith, MAXDOAS: BrO, O_3, NO_2, OClO, HCHO clear days
- GSFC – Brewer – O_3
- U Alaska mini MAXDOAS – MAXDOAS, zenith sky: BrO, O_3, NO_2, OClO, HCHO
- NOAA - ozonesondes

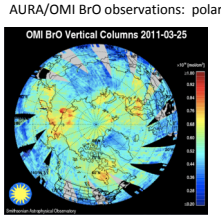
Observations

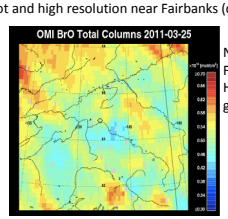
dates: 24 March – 9 April 2011
location: University of Alaska, Geophysical Institute roof
host: Dr. W. R. Simpson, Dept of Chemistry, U. Alaska

Observation Geometries



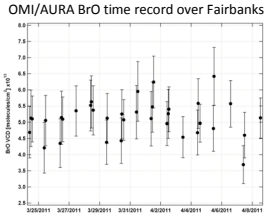
AURA/OMI BrO observations: polar plot and high resolution near Fairbanks (diamond)

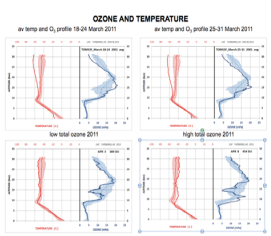




NRT BrO data over Fairbanks supplied by Harvard-Smithsonian group

OMI/AURA BrO time record over Fairbanks





Analysis of Ground-based Data to → Vertical Column Density (VCD) BrO

DOAS Non-linear least squares fitting:

$$\log[I(\lambda) - offset(\lambda)] - \log[Io(\lambda)] = -\sum_i [\sigma_i(\lambda)_{instrument} \cdot \Delta SCD_i] - P_{LO}$$

$I_o(\lambda)$ is a reference spectrum (typically measured at noon, with the "shortest" photon path)
ΔSCD is gas concentration integrated along the average photon (SCD_{true}) path relative to reference spectrum : $\Delta SCD = SCD_{true} - SCD_{ref}$

Parameters affecting derivation of ΔSCD in a specific wavelength fitting window:

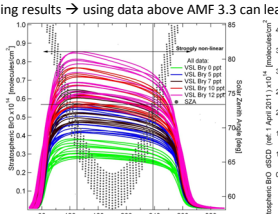
- Instrumental artifacts (e.g. errors in wavelength calibration, ISF)
- Errors in gas absorption cross sections (σ_i), e.g. wavelength scale, absolute value, temperature response
- Cross correlation between different gas absorption cross sections
- Approximation of the gas effective temperature in the non-isothermal atmosphere
- Polynomial order (P_{LO})
- Stray light and uncorrected dark current (offset)
- Random noise

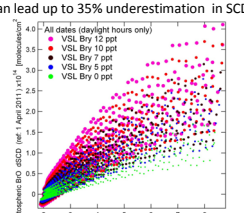
Determination of reference slant column:

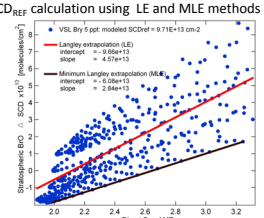
reference Fraunhofer spectrum (I_o in Beer's law) – trace gas abundance in reference spectrum is unknown
- typically taken under low absorption conditions
- short atmospheric path of photons (e.g. zenith for MAX and noon for direct sun and zenith)

- DIRECT SUN: information about the total vertical column (VCD) can be derived
  - SCD_{REF} must be estimated
  - air mass factor (AMF) has low dependence on gas profile (for SZA < 75°) and is accurately estimated
  - AMF does not depend on wavelength under most conditions
- MAX-DOAS: path length through stratosphere for zenith and MAX observations is almost the same (SZA < 75°):
  - information about lower troposphere can be derived without the knowledge about SCD_{REF}
  - AMF depends on gas and aerosol profile and wavelength
- VCD calculation is a two-step process:
  1. ΔSCD is calculated by DOAS non-linear least squares fitting
  2. AMF (MAX) and SCD_{REF} (direct sun) calculation

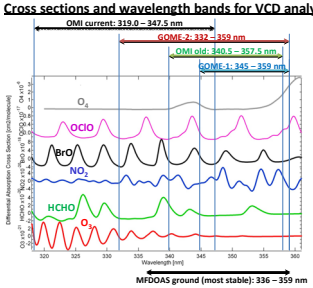
- Langley-like methods extrapolate measurements to extraterrestrial level (AMF = 0)
  $\Delta SCD = VCD * AMF - SCD_{REF}$; SCD_{REF} = - intercept; VCD = slope
- require constant column as a function of time at least for some days
- Below SZA ~ 73° (AMF ~ 3.3) almost linear decrease from morning to evening
- modeling results → using data above AMF 3.3 can lead up to 35% underestimation in SCD_{REF} calculation using LE and MLE methods



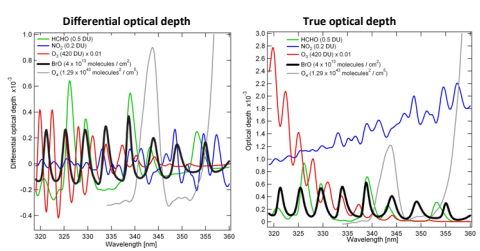




Cross sections and wavelength bands for VCD analysis



Typical vertical optical depths in the 319 – 359 nm range

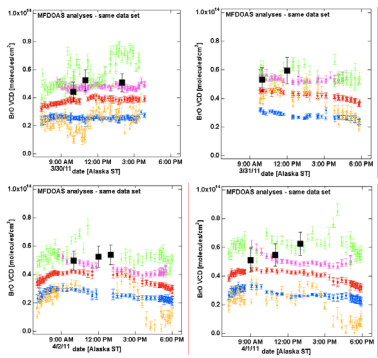


DOAS fitting settings varied in the BrO analysis:
- various spectral windows as shown above
- polynomial orders 3, 4, 5
- offset: linear/nonlinear/constant, 1st, 2nd order
- ozone xsec temp: 218, 228, 243K
- ozone I_o correction

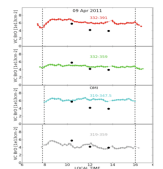
Species	Temperature [K]	Citation
O_3	218, 228, 243	Daumont, Brion, Malicet et al
NO_2	220, 270	Vandaele et al., 1998
O_2-O_2	296	Hermans et al., 2006
OClO	208	Wilmouth et al., 1998
BrO	228	Wilmouth et al., 1999
HCHO	298	Meller and Moortgat, 2000

Results

DS BrO VCD from MFDOAS and OMI: 30 March – 2 April 2011



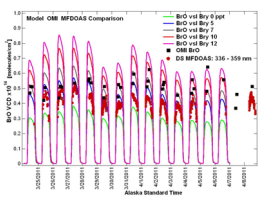
PANDORA 9 April 2011

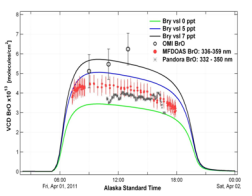


■ OMI BrO (319 – 347.5 nm)
MFDOAS direct sun BrO:
- ■ 319 -347.5 nm (current OMI)
- ▲ 332 -359 nm (GOME-2)
- ● 336 -359 nm (best for MFDOAS)
- ▼ 340 -357.5 nm (old OMI)
- ▶ 345.5 -359 nm (GOME-1)

- no HCHO
- O_3: 218, 243K
- OClO orth. BrO xsec
- NO_2 xsec 220K
- polynomial order 3
- nonlinear offset 0 and 1st order

BrO model, OMI and MFDOAS direct sun comparison

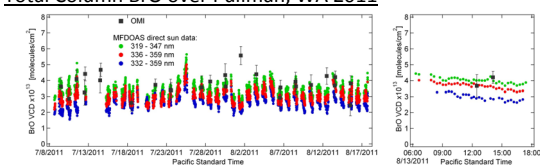




expected BrO diurnal variation is captured

- MAX-DOAS and zenith sky ΔSCD show similar fitting wavelength window/parameter dependence
- Effect of fitting parameters on VCD is wavelength dependent due to AMF

Total Column BrO over Pullman, WA 2011



- Similar dependence observed at a "clean" rural site: smaller contribution from all the absorbers
- Preliminary direct moon measurements used as a reference spectrum in direct sun analysis show good agreement (within a large error ± 1.5 x 10^{13} molec/cm² due to difference in illuminations and S/N) with the LE method

Conclusions:

- no BrO hotspots were observed by ground based or satellite instruments
- no BrO was detected in the lower troposphere (MAXDOAS)
- *strong (x 2 - 3)* spectral window dependence of direct sun VCD BrO → interplay of various DOAS parameters [e.g. spectral window, polynom. order, ref. spectrum column, cross section orthogolization etc] has strong effect on derived BrO. Spectral residual minimization is a requirement, but not a sufficient condition for correctness. All reductions in our analyses had residual levels < 0.05%
- use of different parameters within a given spectral window (e.g., HCHO, polyn orders) can change BrO ΔSCD by > 40%
- what are the DOAS parameter settings that produce a robust and accurate retrieval of BrO?
- **MFDOAS BrO VCD using the "best" MFDOAS DOAS parameters are about 0.75 OMI VCD → best agreement w/ source gas injection of ~2 ppt & product gas injection of ~3 ppt of Br_y from very short-lived Br_y sources**

This work supported by numerous NASA Aura Science Team grants.
This poster very similar to the poster presented at Fall 2011 AGU, prepared by George & Elena ☺