Trend analysis of stratospheric BrO: Comparison between SCIAMACHY limb and ground-based UV-visible observations

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Stratospheric bromine

• Bromine (together with chlorine), are known to be largely responsible for stratospheric ozone depletion through catalytic cycles, e.g.:

\[ \text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{Cl} + \text{O}_2 \]
\[ \text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \]
\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]

\[ \text{BrO} + \text{HO}_2 \rightarrow \text{HOBr} + \text{O}_2 \]
\[ \text{HOBr} + h\nu \rightarrow \text{Br} + \text{OH} \]
\[ \text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \]
\[ \text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2 \]

\[ \text{BrO} \text{ Net: } 2 \text{ O}_3 \rightarrow 3 \text{ O}_2 \]

• Bromine monoxide (BrO) is the most abundant inorganic bromine species during daytime (BrO/Br\text{y} \sim 0.6 with Br\text{y} = \text{Br} + \text{BrO} + \text{BrONO}_2 + \text{HBr} + \text{HOBr} + \text{BrCl})

\[ \text{BrO is representative of the total inorganic bromine loading Br}_{\text{y}} \]
Trend in stratospheric bromine

Total bromine inferred from ground-based UV-vis observations of BrO at Harestua (60°N) and Lauder (45°S)

Total bromine inferred from balloon-borne BrO observations

Is this decline also detected by satellite instruments??

Hendrick et al., GRL, 2008

Dorf et al., GRL, 2006 with recent update
SCIAMACHY/ENVISAT limb instrument and data

- In his limb mode, SCIAMACHY provides vertical profiles of stratospheric BrO

  No contamination by the troposphere in contrast to the nadir mode

- Version 3.2 of the IUP/IFE Bremen SCIAMACHY limb BrO product:
  - Level 1 data: ESA version 6.03
  - Differential two-step inversion approach
  - Spectral range: 338.0-356.2 nm
  - Reference tangent height: ~ 35km
  - Additional information on pressure and temperature from ECMWF
  - More details at http://www.iup.physik.uni-bremen.de/~sciaproc/CDI/DOCU/PSD_BrO_v3_2.pdf or in Hendrick et al., AMT, 2009
  - Period covered by the data is 2002-2008 (7 years)
Ground-based UV-visible observations (1)

Network for the Detection of Atmospheric Composition Change

NDACC Sites

OHP (44°N, 5.5°E)
BIRA-IASB

Harestua (60°N, 11°E)
BIRA-IASB

Izaña (28°N, 16°W)
INTA

Lauder (45°S, 170°E)
NIWA
Ground-based UV-visible observations (2)

- **DOAS settings for BrO (zenith-sky observations):**
  - Fitted species: (BrO), NO\textsubscript{2}, O\textsubscript{3}, O\textsubscript{4}, OCIO (Harestua)
  - BrO cross sections: Wilmouth et al. (1999)
  - Wavelength range: 336-359 nm (Harestua), 345-359 nm (OHP), 342-357 nm (Lauder), 342-357 nm (Izaña)
  - Daily reference spectra

- **Use of 80° SZA PM stratospheric columns derived by integrating low resolution BrO vertical profiles retrieved by applying an optimal estimation profiling technique to sunset (70-94° SZA) BrO zenith-sky observations (Hendrick et al., AMT, 2009)**

  ➔ SCIAMACHY profiles integrated in the 13-30 km (Harestua, OHP, and Lauder) and 15-30 km (Izaña) altitude range in order to perform a trend comparison study with similar physical quantities
Statistical model for trend analysis

- Stratospheric BrO shows a marked seasonality (maximum in winter and minimum in summer) related to the NO₂ seasonal cycle
  ⇒ a model with a linear trend and seasonal components needed:

\[
m(t) = A + B(t - t_0) + \sum_{n=1}^{3} C_n \cos(n2\pi(t - t_0)) + \sum_{n=1}^{3} D_n \sin(n2\pi(t - t_0))
\]

Bergamaschi et al., JGR, 2000

- Number of cosine and sine functions (3) optimized through minimization of the fit residuals

- Standard deviation \(\sigma_B\) on the trend \(B\) estimated using the remainders of the fit \(\sigma_N\) (differences between the modeled and measured columns) and their autocorrelation coefficient \(\phi\) (more details in Hendrick et al., GRL, 2008):

\[
\sigma_B = \frac{\sigma_N}{N^{3/2}} \sqrt{\frac{1 + \phi}{1 - \phi}}
\]
Trend of stratospheric BrO: Harestua (60°N,11°E)

GB UV-vis

Stratospheric BrO
VCDs at 80°SZA PM

Trend 1998-2001: +2.1 ± 0.5%/year
Trend 2001-2008: -0.9 ± 0.4%/year
Trend 2002-2008: -0.7 ± 0.3%/year

SCIAMACHY limb
(IUP-Bremen v3.2)

13-30km partial
columns at ~10h LT

Trend 2002-2008: -0.6 ± 0.3%/year

Very good consistency over the 2002-2008 period
Trend of stratospheric BrO: Lauder (45°S, 170°E)

GB UV-vis

Stratospheric BrO VCDs at 80°SZA PM

Trend 1995-2001: +2.2 ± 0.2%/year
Trend 2001-2005: -1.3 ± 0.3%/year
Trend 2002-2005: -0.9 ± 0.5%/year

SCIAMACHY limb (IUP-Bremen v3.2)

13-30km partial columns at ~10h LT

Trend 2002-2005: -0.5 ± 0.5%/year

Good consistency over the 2002-2005 period
Trend of stratospheric BrO: Lauder (45°S, 170°E)

GB UV-vis

Stratospheric BrO VCDs at 80°SZA PM

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GB UV-vis

Stratospheric BrO VCDs at 80°SZA PM

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13-30km partial columns at ~10h LT

Trend 2005-2008: -2.3 ± 0.7%/year

Trend 2005-2008: -3.6 ± 1.4%/year

SCIA larger than G-B but not significant
Trend of stratospheric BrO: OHP (44°N, 5.5°E)

GB UV-vis

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ESA Atmospheric Science Conference, 7-11 September 2009, Barcelona, Spain
Trend of stratospheric BrO: Izaña (28°N, 16°W)

! Preliminary results!

GB UV-vis

Stratospheric BrO VCDs at 80°SZA PM

SCIAMACHY limb (IUP-Bremen v3.2)

13-30km partial columns at ~10h LT

Trend 2004-2007: \(-1.9 \pm 0.9\%\)/year

DOAS analysis still preliminary

Trend 2004-2007: \(-3.2 \pm 0.5\%\)/year

Preliminary results!
Trend of stratospheric BrO: Izaña (28°N, 16°W)

! Preliminary results!

GB UV-vis

Stratospheric BrO VCDs at 80°SZA PM

SCIAMACHY limb (IUP-Bremen v3.2)

13-30km partial columns at ~10h LT

Trend 2004-2007: -1.9 ± 0.9%/year

Trend 2004-2007: -3.2 ± 0.5%/year

Trend 2002-2008: -2.1 ± 0.4%/year

DOAS analysis still preliminary

Trend 2004-2007: -3.2 ± 0.5%/year

Trend 2002-2008: -2.1 ± 0.4%/year

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### Summary (1)

- **Stratospheric BrO trend over common periods:**

<table>
<thead>
<tr>
<th>Station</th>
<th>Period</th>
<th>SCIAMACHY (%/year)</th>
<th>GB UV-vis (%/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Harestua (60°N, 11°E)</td>
<td>2002-2008</td>
<td>-0.6 ± 0.3</td>
<td>-0.7 ± 0.3</td>
</tr>
<tr>
<td>OHP (44°N, 5.5°E)</td>
<td>2005-2008</td>
<td>-3.6 ± 1.4</td>
<td>-2.3 ± 0.7</td>
</tr>
<tr>
<td>Lauder (45°S, 170°W)</td>
<td>2002-2005</td>
<td>-0.5 ± 0.5</td>
<td>-0.9 ± 0.5</td>
</tr>
<tr>
<td>Izaña (28°N, 16°W)</td>
<td>2004-2007</td>
<td>-3.2 ± 0.5</td>
<td>-1.9 ± 0.9</td>
</tr>
</tbody>
</table>

- A decline of stratospheric BrO is observed at the four stations for all the different periods.

- Good consistency between SCIAMACHY and ground-based UV-vis observations except at Izaña (28°N).

The good agreement between the results of both measurement techniques at high- and mid-latitudes shows that the IUP-Bremen SCIAMACHY limb BrO profile data set is reliable for trend analysis.
Summary (2)

• **Stratospheric BrO trend over the 2002-2008 period:**

**SCIAMACHY limb:**

<table>
<thead>
<tr>
<th>Location</th>
<th>Change Rate (%/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Harestua (60°N)</td>
<td>-0.6 ± 0.3</td>
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</tbody>
</table>

**Ground-based UV-vis:** -0.7 ± 0.3%/year (Harestua, 60°N)

- This decline of ~1%/year at high- and mid-latitudes is consistent with the estimated decrease of bromine source gases (CH$_3$Br and halons) at the Earth’s surface (WMO 2006)

• Further work:
  - Consolidation of the Izaña comparison; Comparison with 3D CTMs
  - A more refined trend analysis of stratospheric bromine can be done with SCIAMACHY limb, e.g., investigating on possible latitude and altitude dependences of the stratospheric bromine trend.
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- EC projects SHIVA (7th Framework Program) and GEOmon (6th Framework Program)
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- ECMWF
- New Zealand Foundation for Research Science and Technology
- M. P. Chipperfield (SLIMCAT data for ground-based retrieval)

More on SCIAMACHY limb BrO: see A. Rozanov et al.’s poster
Backup material
SCIAMACHY limb versus ground-based UV-vis observations

15-27 km partial columns

Harestua (60°N, 11°E)

Update of Hendrick et al., AMT, 2009

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