Long-term monitoring of stratospheric composition by UV-visible spectrometry and contribution to satellite validation

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OVERVIEW

- Introduction
  - Context of the long-term ground-based UV-visible observations
  - BIRA-IASB UV-vis Network and contribution to the NDACC
- Satellite validation
- 3D-CTM validation
- Trend studies
- Conclusions and perspectives
Since the 1970’s, ground-based UV-visible absorption spectrometry has been a key component in the long-term monitoring effort of the atmospheric composition.

When operating in zenith-sky geometry, UV-visible spectrometers are mainly sensitive to the stratosphere.

This technique is widely used to monitor key stratospheric variables relevant to the stratospheric ozone depletion issue: 

\[ \text{O}_3, \text{NO}_2, \text{BrO}, \text{and OCIO} \]
UV-Visible absorption spectroscopy

- Analysis of the absorption spectra using the DOAS (Differential Optical Absorption Spectroscopy) method
- DOAS method based on the Beer-Lambert law:

\[ I(\lambda) = I_0(\lambda) e^{-\sigma(\lambda) \cdot SCD - \tau_{\text{Rayleigh}} - \tau_{\text{Mie}}} \]

\[ \ln \frac{I(\lambda)}{I_0(\lambda)} = -\sigma(\lambda) \cdot SCD - \tau_{\text{Rayleigh}} - \tau_{\text{Mie}} \]

- SCD can be converted to VCD using calculated AMF (VCD=SCD/AMF)
- Vertical profiles can be also retrieved by applying the Optimal Estimation Method to twilight SCDs (70-93°SZA)
About 70 stations from pole to pole, more than 35 equipped with UV-vis spectrometers

NDACC UV-vis database (O₃, NO₂) extensively used for satellite validation and trend analyses
BIRA-IASB contribution to the NDACC UV-VIS Network

NDACC Sites

Harestua (60°N, 11°E) - NDACC

Jungfraujoch (46.5°N, 8°E) - NDACC

Haute Provence (43.5°N, 5.5°E)

Reunion Island (21°S, 55.5°E)

Workshop « Spawning the Atmosphere Measurements at Jungfraujoch », 25-26 November 2008, Bern
## Data sets overview (zenith-sky)

<table>
<thead>
<tr>
<th>Station</th>
<th>Observed species in zenith-sky geometry</th>
<th>Operation period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Harestua (60°N, 11°E):</td>
<td>-O$_3$ (C) + NO$_2$ (C) provided to the NDACC database</td>
<td>1990 1995 2000 2005</td>
</tr>
<tr>
<td><em>BIRA zenith-sky UV + visible spectrometers (cooled detectors)</em></td>
<td>-NO$_2$ (P), BrO (P+C), OCIO (C)</td>
<td></td>
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<tr>
<td>Jungfraujoch (46.5°N, 8°E):</td>
<td>-O$_3$ (C) + NO$_2$ (C) provided to the NDACC database</td>
<td></td>
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<tr>
<td><em>SAOZ spectrometer (zenith-sky; room t° detector)</em></td>
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<tr>
<td>OHP (44°N, 5.5°E):</td>
<td>-O$_3$ (C), NO$_2$ (C), BrO (P+C)</td>
<td></td>
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<tr>
<td><em>BIRA MAX-DOAS spectrometer</em> (cooled detector)</td>
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<td></td>
</tr>
<tr>
<td>Reunion Island (21°S, 55°E):</td>
<td>- O$_3$ (C), NO$_2$ (P+C), BrO (P+C)</td>
<td></td>
</tr>
<tr>
<td><em>BIRA MAX-DOAS spectrometer</em> (cooled detector)</td>
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</table>

C: vertical column; P: vertical profile
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Satellite instruments validation

Satellite instruments must be validated during their entire lifetime in order to:

- Assess the on-going quality of the measured data
- Avoid long-term drifts due to instrumental aging
- Determine how well the measurements represent geophysical signals (meridional, zonal, and vertical structures, temporal cycles, special events)

Validation is most of the time not straightforward due to:

- Difference in sampling of the atmosphere (time and space)
- Difference in sensitivity to ancillary atmospheric and instrumental parameters

Sophisticated methods might be needed (vertical and horizontal smoothing, photochemical modelling,...)
Stratospheric O$_3$: TOMS

N7-TOMS, M3-TOMS, EP-TOMS v8 vs. IASB UVVIS at Jungfraujoch (46.55°N, 7.98°E)

Mean and Median Relative Differences

Mean and Median Standard Deviations

Data source: NDACC
NO$_2$: GOME, SCIAMACHY, and GOME-2

SCIAMACHY SGP3.01, GOME GDP4.1, GOME2 GDP4.2 vs. IASB UVVIS at Jungfraujoch (46.55°N, 7.98°E)

Data source: NDACC
- Sunrise
- Sunset

Mean and Median Relative Differences

Mean and Median Standard Deviations
Stratospheric NO$_2$: ACE-FTS

ACE-FTS 2.2 vs. Ground-based UV-vis at Harestua (60°N, 11°E)  
2004-2005 period

Kerzenmacher et al., ACP, 2008
Stratospheric BrO: SCIAMACHY limb

- ENVISAT/SCIAMACHY limb stratospheric BrO profiles retrieved at the IUP/University of Bremen (scientific product version 3.2)

- 15-27 km BrO partial columns (altitude range with high sensitivity to BrO profile for both instruments)

- Good overall agreement:
  - Mean relative difference: < 11%
  - BrO seasonality and latitudinal variation consistently captured

Hendrick et al., submitted to Atmos. Meas. Tech., 2008
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Validation of the BASCOE 3D-CTM: \( \text{O}_3 \)

Ground-based data from the NDACC UV-vis database

Theys et al., ACPD, 2008

Workshop « Spawning the Atmosphere Measurements at Jungfraujoch », 25-26 November 2008, Bern
Validation of the BASCOE 3D-CTM: NO$_2$

[BrO] in the lower stratosphere controlled by: BrO + NO$_2$ + M $\rightarrow$ BrONO$_2$

Ground-based data from the NDACC UV-vis database

Theys et al., ACPD, 2008
Validation of the BASCOE 3D-CTM: BrO

HARESTUA / 80° SZA Sunset

BrO partial columns [10^{13} molec/cm^2]

12–20 km

2003  2004  2005

20–28 km

2003  2004  2005

Theys et al., ACPD, 2008

Workshop « Spawning the Atmosphere Measurements at Jungfraujoch », 25-26 November 2008, Bern
Validation of the BASCOE 3D-CTM: BrO

Observatoire de Haute-Provence / 80° SZA Sunset

BrO partial columns [10^{13} molec/cm^2]

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Theys et al., ACPD, 2008
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**NO₂ trends**

- WMO 2006: Trend analysis of long-term observation of NO₂ made at Lauder (45°S), New Zealand (UV-vis data) and Jungfraujoch (46.5°N), Switzerland (FTIR data) suggested that the NO₂ trends in the SH are significantly larger than in the NH:
  - Lauder: +6.2 ± 1.8% (am) and +5.7 ± 1.1% (pm) per decade
  - Jungfraujoch: +1.5 ± 1.1% per decade

- The origin of this hemispheric difference in trend remained unexplained

- Recently, Kreher et al. (NIWA, NZ) studied again the NO₂ trends using ground-based UV-vis data at seven stations

Statistical model of the form:

\[ m(t) = A + B(t - t_0) + \sum_{n=1}^{3} C_n \cos(n2\pi(t - t_0)) + \sum_{n=1}^{3} D_n \sin(n2\pi(t - t_0)) \]
Hemispheric difference in NO₂ trends

Northen hemisphere

Jungfraujoch (46.5°N, 8.5°E)

-11.2 ± 2.4 % per decade (pm)

-13.7 ± 2.5 % per decade (am)

Moshiri (44.4°N, 142°E)

-7.2 ± 1.8 % per decade (pm)

-7.6 ± 2.4 % per decade (am)

Southern hemisphere

Macquarie Island (54.5°S, 159°E)

14.0 ± 2.4 % per decade (pm)

14.8 ± 4.1 % per decade (am)

Lauder (45.0°S, 170.0°E)

4.6 ± 0.8 % per decade (pm)

5.4 ± 1.1 % per decade (am)
### Hemispheric difference in NO$_2$ trends

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<tbody>
<tr>
<td></td>
<td>Sunrise</td>
<td>Sunset</td>
<td>Sunrise</td>
</tr>
<tr>
<td>Kiruna (67.8°N)</td>
<td>-3.7</td>
<td>4.3</td>
<td>-2.6</td>
</tr>
<tr>
<td>Jungfraujoch (46.5°N)</td>
<td>-9.8</td>
<td>2.9</td>
<td>-7.8</td>
</tr>
<tr>
<td>Moshiri (44.4°N)</td>
<td>-7.1</td>
<td>3.4</td>
<td>-6.4</td>
</tr>
<tr>
<td>Mauna Loa (19.5°N)</td>
<td></td>
<td></td>
<td>-1.6</td>
</tr>
<tr>
<td>Lauder (45°S)</td>
<td>8.3</td>
<td>1.6</td>
<td>7.1</td>
</tr>
<tr>
<td>Macquarie Island (54.5°S)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Arrival Heights (77.8°S)</td>
<td></td>
<td></td>
<td>15.8</td>
</tr>
<tr>
<td>Jungfraujoch FTIR</td>
<td>3.1</td>
<td>1.5</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Bromine contributes significantly to the global ozone loss (by about 25%) – BrO is the most abundant bromine species during daytime.

Stratospheric BrO columns retrieved by applying a profiling technique to the ground-based zenith-sky DOAS observations.

Trend values at both stations agree within their combined error bars.

First observational evidence that the Montreal Protocol restrictions on brominated substances have now reached the stratosphere.
Conclusions and perspectives

- Since early 90’s, BIRA-IASB has been operating UV-vis spectrometers at four sites: Harestua (60°N), Jungfraujoch (46°N), OHP (45°N), and Reunion Island (21°S).
- The Jungfraujoch and Harestua instruments are part of the NDACC UV-vis Network.
- Long-term observations of O₃, NO₂, and BrO columns (+profiles when possible) at the four stations are widely used in satellite instruments and 3-D CTM’s validation and in trend studies.
- Plans for installation of MAX-DOAS spectrometers at Harestua and Jungfraujoch (cf. M. Van Roozendael’s talk).
Acknowledgements

- Belgian PRODEX contracts NOy-Bry and SECPEA
- EC project GEOMON (6th Framework Program)
- New Zealand Foundation for Research Science and Technology
- M. P. Chipperfield (SLIMCAT data)

Thank you for your attention!
Extra material
Global monitoring of predicted ozone recovery

Global ozone column monitoring by satellites:
- SCIAMACHY / Envisat (2002-2013?)
- OMI / EOS-Aura (2004-?)
- OMPS / NPOESS (2009-?)

Global ozone change from pre-1980 values
- Decreasing ozone
- Increasing ozone

Expected return of ozone-depleting gases to 1980 levels

Range of model projections

Adapted from WMO 2006

Stage 1: Initial slowing of ozone decline
Stage 2: Onset of ozone increases
Stage 3: Full recovery of ozone from ozone-depleting gases

End of 21st century
Test of our understanding of the polar ozone photochemistry

SLIMCAT 3D-CTM versus DOAS data at Harestua (60°N)

THird European Stratospheric Experiment on Ozone (THESEO) EC campaign
Total BrO column: GOME and SCIAMACHY nadir

- GOME and SCIAMACHY nadir BrO total columns: BIRA-IASB scientific products (http://www.temis.nl)
- Reasonably good overall agreement: relative difference < 20%

(Hendrick et al., ACP, 2007)
(Theys et al., ACP, 2007)