Total ozone measurements with Phaethon at Izaña including characterizations/calibrations and uncertainty estimations

Alkis Bais, Fani Gkertsi, Theano Drosoglou, Natalia Kouremeti*

Lab of Atmospheric Physics
Aristotle University of Thessaloniki
*PMOD/WRC Davos, Switzerland
• Brief introduction to DOAS-based retrieval of TOC by Phaethon

• Langley results from Izaña campaign in September 2016

• Comparisons with Brewer TOC data in Izaña and Thessaloniki

• Estimation of data uncertainties
The Phaethon mini-DOAS system

➢ Spectrometer
  • Cooled miniature CCD spectrograph
    AvaSpec-ULS2048LTEC
  • Operating temperature: 5 °C
  • Spectral range: 300 - 452 nm
  • Spectral resolution: ~0.25 nm

➢ Entrance Optics for total ozone measurements
  • Direct solar irradiance port with diffuser and ND filter
  • Far field stray light suppression: 475 nm short-pass filter
  • Spectral range modification: UV enhanced (300-370 nm)
  • Filed of View (~1°)
Range of TOC retrieval 315 - 337 nm

- TOC is retrieved from both regular and UV-enhanced spectra
- UV-enhanced range:
  - increases intensity by a factor of 5
  - reduces far-field stray-light effect from longer wavelengths
  - reduces DOAS retrieval error
Langley determination of $SCD_{REF}$

- $SCD_{REF}$: slant column ozone of the reference spectrum used in DOAS

- DOAS analysis provides the differential slant column density ($dSCD$) of ozone between the analyzed and the reference spectrum:

$$dSCD_i = SCD_i - SCD_{REF} = TOC_i \cdot AMF_i - SCD_{REF}$$

- $SCD_{REF}$ is derived from Langley extrapolation of $dSCD$ vs AMF

- Langley plots were derived from data of the Izaña ATMOZ campaign (14-27 September 2016)

- This dataset can be used to derive the $SCD_{REF}$ of any spectrum recorded by the same spectrometer
Phaethon Langley plot - Izaña

ALL DATA

$$\text{SCD ref} = 284.05 \times \text{AMF} - 320.59$$
Removal of outlier points

- Based on work of Kiedron and Michalsky 2016 (AMT)
- by “eye and mind”
- least-squares fitting (LSF) of $dSCD$ with respect to $AMF$ with sequential removal of outliers

Method 1 (LSF1):
Linear regression $y = ax + b$ with $y = dSCD$ and $x = AMF$

Method 2 (LSF2):
Linear regression $\frac{y}{x} = a \frac{b}{x}$ with $\frac{y}{x} = \frac{dSCD}{AMF}$ and $\frac{1}{x} = \frac{1}{AMF}$
Outlier removal based on RMS error

\[ RMS\% = \frac{RMS}{dSCD} \times 100 \]
$\text{SCD}_{\text{REF}}$ estimation

![Graph 1: LSF ($y=ax+b$) & RMS=1%](image1)

![Graph 2: LSF ($y/x=a+b/x$) & RMS=1%](image2)
Estimated $\text{SCD}_{\text{REF}}$ for different days/methods

- LSF1: 315.7 DU
- LSF2: 315.6 DU
- “eye and mind” 314.6 DU
✓ Small variation of TOC during the campaign (~30 DU) increases the uncertainty of the regression (r²=0.87)

✓ Phaethon overestimates TOC by ~0.7±0.8 % (~2 DU)

✓ Phaethon TOC is likely dependent on stratospheric temperature since in the DOAS retrieval all wavelengths in the range 315-337 nm are used
Temperature effect on $O_3$ x-sections
Effect of $O_3$ x-sections on Phaethon TOC

Phaethon vs Brewer 183 (BP based)

<table>
<thead>
<tr>
<th>$O_3$ absorption cross-section</th>
<th>Mean difference (%)</th>
<th>Std (% difference)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bass &amp; Paur (228K)</td>
<td>0.69</td>
<td>0.78</td>
</tr>
<tr>
<td>Bremen (223K)</td>
<td>-2.47</td>
<td>0.77</td>
</tr>
<tr>
<td>Bremen (233K)</td>
<td>1.65</td>
<td>0.79</td>
</tr>
</tbody>
</table>
SCD$_{\text{REF}}$ for Thessaloniki

\[ \text{SCD}_{\text{ref}} = 282.63 \times \text{AMF} - 424.44 \]

\[ \text{SCD}_{\text{ref}} = 276.96 \times \text{AMF} - 415.58 \]
Effective ozone temperature in Thessaloniki

228 K

218 K

Fragkos et al., 2013
Phaethon vs Brewer #005 - Thessaloniki

- Cold-period data (October 2015 – March 2017)

**Paur & Bass 228 K**

- Bias 3 DU (0.9±2.7 %)

**Paur & Bass 218 K**

- Bias 0.8 DU (0.2±2.4 %)
Regular spectra (without short pass filter)

- October 2015 – March 2107 (Paur & Bass 218 K)

**All data**

**Cold period**

Bias 0.2±2.1 %  
Bias 0.5±2.1 %
Uncertainty estimation of Phaethon TOC

- Factors contributing:
  - Spectral direct radiance measurements (very small)
  - Spectral characteristics of the measured spectra (mainly due to noise)
  - DOAS analysis
- Systematic uncertainties due to cross-section datasets of $O_3$ (& other absorbers)
  - Average bias in BP-based $dSCD$ relative to Bremen $\sim 1.5\%$ and BDM $\sim 1\%$
    (independent of SZA but increasing with decreasing $dSCD$)
- Random uncertainty of the DOAS analysis: on average $2.7\%$ in the $dSCD$
  - Effects on TOC are much smaller, due to division by the AMF
- Uncertainty in the $SCD_{REF} \sim 0.1\%$
  (estimated from the Langley regressions of the 14-day campaign in Izaña)
- Combined uncertainty of the respective vertical column densities:

\[
\sigma_{total}^2 = \frac{\sigma_{dSCD}^2}{AMF^2} + \frac{\sigma_{SCD_{REF}}^2}{AMF^2} = \frac{\sigma_{dSCD_{systematic}}^2}{AMF^2} + \frac{\sigma_{dSCD_{random}}^2}{AMF^2} + \frac{\sigma_{SCD_{REF}}^2}{AMF^2}
\]

- Average total uncertainty: $2.7\%$ (for large slant columns reduced to $0.9\%$)
DOAS retrieval with different temperature combinations

\[ y_1 = (0.9927) \times x_1 + (7.4739) \]
\[ r_1^2 = 0.93515 \]

\[ y_2 = (0.99776) \times x_2 + (3.7474) \]
\[ r_2^2 = 0.97424 \]

\[ y_3 = (1.0237) \times x_3 + (-0.31841) \]
\[ r_3^2 = 0.94922 \]

\[ y_4 = (1.0211) \times x_4 + (-1.2399) \]
\[ r_4^2 = 0.97057 \]
Conclusions

- Langley plots of the Izaña campaign dataset are used to derive the slant column of the reference spectrum used in the DOAS analysis for TOC retrieval

- The same dataset can be used for reference spectra recorded with the same spectrometer at other locations and times

- Total ozone data derived from Phaethon in Thessaloniki compare well with Brewer #005 (on average within 1%)

- Phaethon TOC shows higher noise compared to Brewer

- A small effect appears in TOC (~ 0.7 %) when BP cross-sections at different temperatures (218 vs 228 K) are used, implying a seasonal dependence in the derived TOC.
Thank you for your attention!