FORMAT Campaign

Alzate (Po Basin, Northern Italy)
July – August, 2002

first analysis results

2002, Dec. 4
Tibi Tarsu
Outline

• motivation for studying formaldehyde (HCHO)
• sources & chemistry of formaldehyde in the atmosphere
• scientific objectives of the project and aims of the campaigns
• campaign (summer – 2002)
• data analysis
• next campaign (2003?)

FORMAT = Formaldehyde as a tracer of (photo)oxidation in the troposphere
Motivation of project

HCHO – most abundant of the carbonyl compounds in the atmosphere

HCHO - indicator of photochemical smog

HCHO, O₃, NO₂ and SO₂ dominate the tropospheric photochemistry

HCHO → influence on the oxidizing capacity of the atmosphere

HCHO – dangerous for health at concentrations above 0.1 ppm
Atmospheric Formaldehyde Production (Sources)

Background troposphere: major product of the photooxidation of methane (CH$_4$ is the dominant precursor of HCHO)

Close to the surface:
- generated by the photooxidation of both methane & NMHC (biogenic & anthropogenic sources)
- byproduct of incomplete combustion processes (anthropogenic sources)
- naturally occurring: biogenic emissions (released in air by plants)
- generated by atmospheric chemical reactions of other pollutants
  \[(\text{HOCH}_2\text{CH}_2\text{O} \rightarrow \text{HCHO} + \text{CH}_2\text{OH}, \quad \text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2)\]
Atmospheric Formaldehyde Chemistry (Sinks)

1. Photolysis (in the near UV):

\[
\text{HCHO} + h\nu (\lambda < 360 \text{ nm}) \rightarrow \text{H}_2 + \text{CO} \quad \text{ (ca. 55\%)}
\]

\[
\text{HCHO} + h\nu (\lambda < 338 \text{ nm}) \rightarrow \text{H} + \text{HCO} \quad \text{ (ca. 45\%)}
\]

\[
(\tau_{\text{atm}} = 3.8 \div 8.6 \text{ h})
\]

\[
\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}
\]

\[
\text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}, \quad \text{ (CO + OH} \rightarrow \text{H} + \text{CO}_2)
\]

\[
(\tau_{\text{atm}} \sim \text{ months})
\]

2. HCHO + OH → H$_2$O + HCO

\[
(\tau_{\text{trop}} \approx 1.5\text{ days})
\]

3. HCHO + HO$_2$ ↔ OOCH$_2$OH

\[
(\tau \approx 7\text{ hrs at } [\text{HO}_2]=5\times10^8\text{cm}^{-3})
\]

4. Hydrolysis: HCHO (aq.) + H$_2$O ↔ H$_2$C(OH)$_2$
Scientific objectives of the project

- improvement of experimental techniques used as measurement methods for formaldehyde atmospheric determinations
- better knowledge about (regional- and global-scale) formaldehyde distribution and concentrations in the troposphere

Goals of the campaign

- validation of satellite data (GOME, SCHIAMACHY) regarding formaldehyde distributions in the area
- improvement of atmospheric chemistry models capabilities for calculating formaldehyde distributions and for using it as tracer of fossil fuel and biomass burning
FORMAT Campain (July – August 2002)

Alzate: 45°46’N, 09°09’E, 384m altitude
Bresso: 45°32’N, 09°12’E
Pavia: 45°18’N, 09°17’E
Bremen Univ: MAX-DOAS (Alzate, July 20 – August 19) & AMAX-DOAS

Viewing directions: elevation angles: 3°, 6°, 10°, 18° & 90° (zenith)
azimuth: west (20.07. – 26.07. morning)
south (SSW: 35° azimuth S) (26.07. morning – 19.08)

MAX-DOAS measurement parameters
- wavelength interval: 311.5 – 396.5nm
- temporal resolution: min: 60 s, max: 550 s, typical: 300 s

Intercomparison period: July 20 – August 3
Ozone measurements

Microtops measurements → depending on clouds 
in situ determinations – every 10 min.
Data analysis

- wavelength fit range:
  - HCHO: 335.0 – 357.0nm
  - O₄ & NO₂: 355.0 – 390.5nm

Analyzed trace gases absorption spectrum in the fitting intervals
### Reference Spectra for HCHO analysis

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Temperature [K]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCHO</td>
<td>293</td>
<td>Meller and Moortgaat</td>
</tr>
<tr>
<td>NO2</td>
<td>220</td>
<td>Van Daele et al. (1997)</td>
</tr>
<tr>
<td>O3</td>
<td>241</td>
<td>GOME</td>
</tr>
<tr>
<td>O3</td>
<td>221</td>
<td>GOME</td>
</tr>
<tr>
<td>04</td>
<td>296</td>
<td>Greenblatt et al. (1996), corrected</td>
</tr>
<tr>
<td>BrO</td>
<td>228</td>
<td>Wahner (1990)</td>
</tr>
<tr>
<td>Ring</td>
<td>-</td>
<td>Vountas (1997)</td>
</tr>
</tbody>
</table>

**Polynomial:** degree 5 (6 coefficients)
Comparing between luminosity conditions

Light intensity, August 11, 2002

HCHO Analysis, August 11, 2002

Light intensity, August 13, 2002

HCHO Analysis, August 13, 2002
Intercomparison period (July 22 – August 3)

MAXDOAS Comparison Alzate, HCHO, zenith, July 23, 2002

MAXDOAS Comparison Alzate, HCHO, 10 deg., July 23, 2002

MAXDOAS Comparison Alzate, NO2, zenith, July 23, 2002

MAXDOAS Comparison Alzate, NO2, 10 deg., July 23, 2002

MAXDOAS Comparison Alzate, O4, zenith, July 23, 2002

MAXDOAS Comparison Alzate, O4, 10 deg., July 23, 2002
Typical DOAS analysis for HCHO evaluation

(3° elevation, 13.08.2002, 15:21 UT)
Improving $O_4$ evaluation

File 020812ALRG6, 11:46:35, SZA = 31.07°

File 020812ALRGX, 11:46:35, SZA = 31.07°

File 020812ALRG6, 11:46:35, SZA = 31.07°

File 020812ALRGX, 11:46:35, SZA = 31.07°

File 020812ALRG6, 11:46:35, SZA = 31.07°

File 020812ALRGX, 11:46:35, SZA = 31.07°
Influence of improved Ring upon HCHO evaluation

Schräge Säule HCHO, 13.08.02

Schräge Säule RING, 13.08.02

Chi-Square, 13.08.02

R/IEX(Residuals)/R/IEX(abs.Abs.), 13.08.02

File 020813AL.A16, 05:24:02, SZA = 80.24°

File 020813AL.RFI, 05:24:02, SZA = 80.24°