Retrievals of formaldehyde from ground-based FTIR and MAX-DOAS observations at the Jungfraujoch station and comparisons with GEOS-Chem and IMAGES model simulations

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Formaldehyde (HCHO)

- Midday lifetime of a few hours

- Sources:
  - mainly by oxidation of:
    - CH₄
    - primary NMVOCs
  - (directly from various sources)

- Sinks:
  - photolysis
  - oxidation by OH radicals
    => yield CO and HO₂
  - (dry and wet deposition)

- Involved in the VOC – HOₓ – NOₓ chemistry
  generating or destroying tropospheric O₃

HCHO = indicator of NMVOCs emissions from continental sources

- biogenic (≈ 85 %)
- anthropogenic (≈ 12 %)
- pyrogenic (≈ 3 %)

- oxidative capacity of the atmosphere
- the global CO budget

Key role for air quality monitoring
Formaldehyde (HCHO)

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**Issues**

- Can we detect background levels of HCHO in the remote troposphere from ground-based FTIR and MAX-DOAS?

- Is there a good consistency between both instruments regarding HCHO at a high-altitude station?

- Validating an optimized FTIR retrieval strategy for HCHO above Jungfraujoch as a preparation for further studies e.g., multi-decadal timeseries at Jungfraujoch

Measurement site: *Jungfraujoch station* (Swiss Alps, 46.5° N, 8.0° E, 3580 m a.s.l.), part of the NDACC network

- Essentially located in the free troposphere during winter
- Frequent injections of air masses from the boundary layer, especially during summer
- More than 35 years of uninterrupted IR monitoring
Measurement site: Jungfraujoch station (Swiss Alps, 46.5° N, 8.0° E, 3580 m a.s.l.), part of the NDACC network

- Bruker IFS-120 HR operated by ULg
- Under clear-sky conditions
- Optical filter: 2400-3310 cm\(^{-1}\)
- Spectral resolution: 0.004 and 0.006 cm\(^{-1}\)
Measurement site: **Jungfraujoch station** (Swiss Alps, 46.5° N, 8.0° E, 3580 m a.s.l.), part of the NDACC network

- Operated by BIRA-IASB since 2010
- Pointing NE direction (city of Bern)
- Elevation angles used here: 0°, 1°, 3°, 4°, 5°, 8°, 10°, 12°, 15°, 30°
- Measurements from 85° SZA sunrise to 85° SZA sunset
- 20’ per scan

=> Focus on the mid-2010 – 2012 time period
FTIR retrieval strategy

- SFIT-2 v3.91 algorithm
- Spectroscopic line parameters from HITRAN 2008
  => updated line strength for HCHO from Perrin et al. (2009)
- A priori from 1980 – 2020 WACCM v.6 simulation
  => good consistency with 36.5 – 56.5° N zonal occultations from ACE-FTS
- Optimal Estimation Method for the retrieval process
  => covariance matrix derived from slightly « relaxed » WACCM values

<table>
<thead>
<tr>
<th>Microwindows (cm⁻¹)</th>
<th>Interfering species</th>
</tr>
</thead>
<tbody>
<tr>
<td>2763.425 – 2763.600</td>
<td>HDO, CH₄, O₃, N₂O, CO₂</td>
</tr>
<tr>
<td>2765.725 – 2765.975</td>
<td>HDO, CH₄, O₃, N₂O, CO₂</td>
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<tr>
<td>2778.200 – 2778.590</td>
<td>HDO, CH₄, O₃, N₂O, CO₂</td>
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<tr>
<td>2855.650 – 2856.400</td>
<td>HDO, CH₄, O₃, N₂O, H₂O</td>
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Based on Vigouroux et al. (2009), Atm. Chem. Phys.

- Individual FTIR fit example (22 August 2010, 6:40 UTC, SZA of 80°)
  => Very weak solar IR absorption + broad spectral lines

2. INSTRUMENTAL SETUP

NORS/NDACC/GAW workshop, 5 to 7 November 2014, Brussels
1. **DOAS spectral fitting** => DSCDs

- Fitting window: 328.5 – 358.0 nm
  => minimizing the HCHO/BrO correlation

- Zenith spectrum of each scan taken as reference
  => reducing the interference by O₃

- Fitted species:
  - HCHO at 293 K
  - NO₂ at 298 K
  - O₃ at 223 and 243 K
  - O₄
  - BrO at 223 K
  - Ring effect

- 5ᵗʰ-order polynomial fit and linear correction for off-set

2. **Profile retrieval** => OEM-based profiling tool bePRO

- Clémer et al. (2010), AMT
- Hendrick et al. (2014), ACP
- Wang et al. (2014), ACP

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<th>O₄ DSCDs</th>
<th>OEM</th>
<th>Aerosol extinction profiles</th>
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<td>HCHO DSCDs</td>
<td>OEM</td>
<td>DSCD weighting function</td>
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</table>
Characterization of FTIR retrievals

95.4% of the total column

DOFS = 1.04
\( \lambda_1 = 0.84; \lambda_2 = 0.15 \)

FTIR

3. DATA CHARACTERIZATION

NORS/NDACC/GAW workshop, 5 to 7 November 2014, Brussels
Characterization of MAX-DOAS retrievals

DOFS = 2.02
\( \lambda_1 = 0.97; \lambda_2 = 0.78; \lambda_3 = 0.25 \)

MAX-DOAS

3. DATA CHARACTERIZATION
NORS/NDACC/GAW workshop, 5 to 7 November 2014, Brussels
Characterization of the retrievals

- FTIR: mainly sensitive throughout the free troposphere
- MAX-DOAS: highly sensitive in the lowest layers

=> **Complementary** information content in the troposphere regarding HCHO

=> Direct comparisons between both instruments = little meaning

=> HCHO distributions from 3-D CTMs (GEOS-Chem and IMAGES) as **intermediates**

  Smoothened by the FTIR and MAX-DOAS AVK
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<th>GEOS-Chem (v9-01-03)</th>
<th>IMAGES v2</th>
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<td>Horizontal resolution</td>
<td>2.0° x 2.5°</td>
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<td>Meteorological forcings</td>
<td>GMAO GEOS-5</td>
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<td>EMEP (CO, NO$_x$, SO$_x$ and NH$_3$) RETRO and EMEP (NMVOCs)</td>
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3. DATA CHARACTERIZATION
Background provided by:
- CH$_4$
- Long-lived NMVOCs

Anthropogenic emissions (butane, toluene, ...)
- Northern Italy
- Southern France
- Southern Germany

- Higher photochemical oxidation rate
- Biogenic NMVOCs

e.g., methanol (Bader et al., 2014, AMT)
4. RESULTS

NORS/NDACC/GAW workshop, 5 to 7 November 2014, Brussels
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NORS/NDACC/GAW workshop, 5 to 7 November 2014, Brussels
4. RESULTS

- Sensitivity in the upper troposphere
- 25% of the total column above 8 km

1. Variability in higher tropospheric layers
   -> large-scale transport
   -> convective fluxes

2. Seasonality also driven by incursions of NMVOCs
   (rather than photolysis and CH$_4$ oxidation rate only)
Conclusion

- HCHO amounts from ground-based FTIR and MAX-DOAS
- HCHO distributions from 3-D CTMs as intermediates

  FTIR and MAX-DOAS => complementary and consistent

- FTIR retrieval strategy available now at Jungfraujoch

Perspectives

- Contribution of the different NMVOCs to the HCHO formation
- Optimized FTIR retrieval strategy
  => multi-decadal observational time series
    - inter-annual variability
    - long-term trend
    - statistics for intra-day investigations
Thank you for your attention
Characterization of the retrievals

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- MAX-DOAS: highly sensitive in the lowest layers

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<td>RETRO and EMEP (NMVOCs)</td>
<td>RETRO (NMVOCs)</td>
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Anthropogenic NMVOCs over Europe for 2011:
- RETRO = 25.7 Tg
- EMEP = 10.3 Tg
Anthropogenic emissions of NMVOCs common to both CTMs:
- GEOS-Chem = 4.7 Tg C yr\(^{-1}\)
- IMAGES = 15.7 Tg C yr\(^{-1}\)
# FTIR error budget

<table>
<thead>
<tr>
<th>Error source</th>
<th>Error (%)</th>
<th>Comments</th>
</tr>
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<tbody>
<tr>
<td>Assumed variability</td>
<td>49.7%</td>
<td>WACCM variability relaxed, commensurate with ACE-FTS variability down to 6 km</td>
</tr>
<tr>
<td><strong>Systematic errors</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Line intensity HCHO</td>
<td>9.7%</td>
<td>Assuming ±10% uncertainties</td>
</tr>
<tr>
<td>Air-broadening coefficient HCHO</td>
<td>8.0%</td>
<td>Assuming ±10% uncertainties</td>
</tr>
<tr>
<td>Line intensity interfering gases</td>
<td>5.2%</td>
<td>Assuming the maximal HITRAN 2008 uncertainties</td>
</tr>
<tr>
<td>ILS</td>
<td>2.5%</td>
<td>±10% misalignment and instruments bias</td>
</tr>
<tr>
<td>Forward model</td>
<td>1.0%</td>
<td>Retrieval algorithm-related</td>
</tr>
<tr>
<td>HCHO a priori profile</td>
<td>3.0%</td>
<td>Assuming HCHO a priori profiles derived from ACE-FTS, IMAGES and GEOS-Chem</td>
</tr>
<tr>
<td><strong>Total Systematic Error</strong></td>
<td><strong>14.2%</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Random errors</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature profile</td>
<td>5.0%</td>
<td>±4 K around NCEP noon profile</td>
</tr>
<tr>
<td>H$_2$O and HDO a priori profiles</td>
<td>10.1%</td>
<td>Changes by a factor 2 in a priori slope</td>
</tr>
<tr>
<td>SZA</td>
<td>0.7%</td>
<td>Assuming ±0.1° bias</td>
</tr>
<tr>
<td>Measurement noise</td>
<td>14.7%</td>
<td></td>
</tr>
<tr>
<td>Smoothing</td>
<td>10.2%</td>
<td></td>
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<tr>
<td>Model parameters</td>
<td>3.1%</td>
<td></td>
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<tr>
<td><strong>Total Random Error</strong></td>
<td><strong>21.3%</strong></td>
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## MAX-DOAS error budget

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<th>Error sources</th>
<th>Uncertainty on HCHO</th>
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<tr>
<td>Smoothing + noise errors</td>
<td>9.1%</td>
</tr>
<tr>
<td>Uncertainty related to aerosols</td>
<td>6.3%</td>
</tr>
<tr>
<td>Uncertainty related to the a priori</td>
<td>8.8%</td>
</tr>
<tr>
<td>Uncertainty related to the albedo</td>
<td>1.0%</td>
</tr>
<tr>
<td>Uncertainty on the HCHO cross sections</td>
<td>9.0%</td>
</tr>
<tr>
<td><strong>Total uncertainty</strong></td>
<td><strong>16.8%</strong></td>
</tr>
</tbody>
</table>
Better representation of the HCHO variability

≈25 % of the total column above 8 km