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Measurements of formaldehyde integral content in troposphere at Moscow Region

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Important detector of:
a) volatile organic compounds (VOCs) emissions;
b) photochemical activity in the atmosphere.

**Sources**
a) direct emissions:
   - biomass burning;
   - fossil fuel burning;
b) indirect emissions by oxidation of:
   - methane (source of the background HCHO);
   - VOC (tropospheric emissions).

**Sinks**
Oxidation by free radical (OH, HO₂); photolysis (<400 nm).

HCHO life-time in the atmosphere is about from 1 to 4 hours.

Typical total content $10^{16}$ mol/cm²
Remote background regions $0.2 \times 10^{16}$ mol×cm⁻²
Concentration (3-4 ppbv)
Zvenigorod Scientific Station is located in 38 km western from Moscow

JAMSTEC MAXDOAS mounted at Zvenigorod in 2008. Included also in MADRAS network*

• Measurement technique: MAX-DOAS.
• 6 off-axis: 3, 5, 10, 20, 30 and 90 degrees.
• 6-spectra series is registering during 30 min.
• Thermostat: summer +40…45°, winter +20…+25°

• UV-Vis spectra region (223-528 nm)
• Linear CCD, 3648 elements
• FWHM ~0.5 нм

Zvenigorod, from 2008
We use non-zenith measurements for $S_{REF}$ estimation only (1) and (2) together for any pair of $\alpha$ for whole dataset:

\[
\begin{align*}
\left\{ \begin{array}{l}
DS_{\alpha_1} + S_{REF} = V \cdot A_{\alpha_1} \\
DS_{\alpha_2} + S_{REF} = V \cdot A_{\alpha_2}
\end{array} \right. \quad \rightarrow \quad S_{REF} = \frac{DS_{\alpha_1}A_{\alpha_2} - DS_{\alpha_2}A_{\alpha_1}}{A_{\alpha_1} - A_{\alpha_2}}
\end{align*}
\]

$S$ – slant column density of specie; $DS$ - differential $S$; $S_{REF}$ – $S$ during reference spectrum registration; $\alpha$ – elevation angle; $A$ – air mass factor; $a(h)$ – layer air mass factor, $n(h)$ and $N(h)$ – normalized and real vertical distribution of specie in the atmosphere; $I$ and $I_{REF}$ – signal and reference spectra; $\sigma$ – absorption cross-section; $V$ – vertical column density

HCHO retrieval
Air-mass factor calculating

\[ V = \frac{S}{A} \]

\[ A = \int_{h_0}^{h_f} a(h)n(h) \, dh \]

\( a(h) \) - the weight coefficient of contribution for each atmospheric layer to the slant column (layer air mass factor) is calculated using a linearized RT model MC C++.
Analysis of error caused by AMF parameter uncertainties

\[
V = \frac{S}{A}
\]

Introduce K-value: \( K \equiv \frac{1}{A} \)

\[
V = S \cdot K
\]

\[
\varepsilon_{VCD}^{(AMF)} = S \cdot \varepsilon_K
\]

\[
\overline{K} = \frac{K_{\text{max}} + K_{\text{min}}}{2}
\]

\[
K_{\text{max}} = \max(K_n), \quad K_{\text{max}} = \max(K_n), \quad n = 0 \ldots N
\]

\( K_n \) – inverted RTM calculation results for different scenarios

Error related to uncertainty of RTM parameter estimated as:

\[
\varepsilon_K = \left( \frac{K_{\text{max}} - K_{\text{min}}}{K_{\text{max}} + K_{\text{min}}} \right) \cdot 100, \ [%]
\]

\( \varepsilon_K \) up to 1% during winter or summer (known albedo)

\( \varepsilon_K \) up to 10% during demi season (unknown albedo)
DOAS settings for the HCHO DSCDs retrieval are almost the same as used at CINDI campaign (G. Pinardi et al., 2013).

We used single reference spectra for each thermostat mode for the HCHO retrieval.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fitting interval</td>
<td>336.5-359 nm</td>
</tr>
<tr>
<td>Cross-sections</td>
<td></td>
</tr>
<tr>
<td>HCHO</td>
<td>Meller and Moortgat (2000), 293°K</td>
</tr>
<tr>
<td>O3</td>
<td>Bogumil et al. (2003), 223, I₀-corrected</td>
</tr>
<tr>
<td>NO2</td>
<td>Vandaele et al. (1996), 298°K, I₀-corrected</td>
</tr>
<tr>
<td>BrO</td>
<td>Fleischmann et al. (2004), 223°K</td>
</tr>
<tr>
<td>O4</td>
<td>Hermans et al. (2003)</td>
</tr>
<tr>
<td>Ring effect</td>
<td>QDoas Software</td>
</tr>
<tr>
<td>Closure term</td>
<td>Polynomial of order 3 (corresponding to 4 coefficients)</td>
</tr>
</tbody>
</table>

HCHO retrieval was carried out using own-developed software.

- We do not use the additional O₃ cross-section at the 243 K.
- Ring cross-section is generated by QDoas software (Fayt C. et al., 2012).
- Other settings correspond to the same of CINDI.
**Data used in analysis**

**DateTime:** from Dec 2009 to Apr 2013

**Dispersion of DOAS residual \( \sigma^2 \leq 1.5 \times 10^{-5} \)**

**SZA \( \leq 83.5^\circ \)**

4318 data points left

1. Cloud coverage \( \leq 20\% \)
   (METAR database of Vnukovo airport, 30 km from measurement site)

2. Color index \( \leq \) Model color index + 0.2

Color index \( CI = \frac{I_{470 \text{ nm}}}{I_{430 \text{ nm}}} \)

**Cloud influence**

- **\( \sigma_{DS} \)**
- **\( DS_{HCHO} \)**
HCHO VCD: Individual results

HCHO DSs on 13 July is larger than ones on 12 July

13 July: east wind directions prevailed
12 July: non-east wind directions prevailed

July, 12th

27.0°C

July, 13th

26.6°C
Moscow megacity influence: individual measurements

HCHO DSs on 13 July is larger than ones on 12 July

13 July: east wind directions prevailed
12 July: non-east wind directions prevailed

June, 12th

27.0°C

Difference HCHO VCD

Time, UTC

2:00  6:00  10:00  14:00

ΔHCHO VCD, $10^{16}$ [mol·cm$^{-2}$]

2.5  2.0  1.5  1.0  0.5  0.0  -0.5  -1.0

July, 13th

6.6°C
Moscow megacity influence: individual measurements

- 13 July – air masses formed in Moscow comes to Zvenigorod during 3-4 hours. This time is comparable with HCHO life-time (1-4 hours).
- 12 July – air masses formed in supposable free of pollutant regions.

HCHO DSs on 13 July is larger than ones on 12 July
HCHO and air temperature variability

Cloud-free conditions

HCHO total column measurements at Zvenigorod
Temperature trend in HCHO data
HCHO and air temperature variations

Wind speed > 2 m/sec, the air mass comes in less than 5.3 hours from Moscow.

Temperature effect is noticeable in our HCHO data.

Depending HCHO on wind direction is less noticeable.

Formaldehyde measurements at Zvenigorod Scientific Station
Linear approximation of HCHO VCD temperature dependence at different wind directions (HCHO=A+B×T).

<table>
<thead>
<tr>
<th>Wind direction</th>
<th>Count</th>
<th>Intercept A, $10^{16}$ mol cm$^{-2}$</th>
<th>Error of intercept A*), $10^{15}$ mol cm$^{-2}$</th>
<th>Gradient B, $10^{14}$ mol cm$^{-2}$ °C$^{-1}$</th>
<th>Error of gradient B*), $10^{14}$ mol cm$^{-2}$ °C$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>North</td>
<td>2377</td>
<td>1.175</td>
<td>0.132</td>
<td>9.292</td>
<td>0.757</td>
</tr>
<tr>
<td>East</td>
<td>1329</td>
<td>1.501</td>
<td>0.180</td>
<td>9.323</td>
<td>0.894</td>
</tr>
<tr>
<td>South</td>
<td>1598</td>
<td>1.509</td>
<td>0.120</td>
<td>7.543</td>
<td>0.682</td>
</tr>
<tr>
<td>West</td>
<td>1363</td>
<td>0.655</td>
<td>0.098</td>
<td>8.918</td>
<td>0.651</td>
</tr>
</tbody>
</table>

*) 95% confidential interval.

Formaldehyde measurements at Zvenigorod Scientific Station
• Beginning from 2008 the MAX-DOAS measurements in the visible and UV spectral regions are performed at Zvenigorod Scientific Station, Moscow Region, Russia. We developed a new algorithm for retrieval of HCHO using MAX-DOAS or ZDOAS measurements. The current version of the algorithm uses information on the surface albedo and the height of the atmospheric boundary layer provided by other measurements.

• We presented the first measurements of the formaldehyde total content in the atmosphere in Russia. Analyzed observations cover 2010-2012, including extremely hot summer.

• The average HCHO vertical column density observed at the east winds is larger than one at the west winds. **Moscow megapolis** influence on air quality at Zvenigorod causes the observed difference of about $0.85 \times 10^{16}$ mol cm$^{-2}$ between these values. This difference slightly depends on the air temperature and the season.

• **A temperature effect** is noticeable in the HCHO VCD. Our data show statistically significant positive temperature effect in HCHO for the background and polluted conditions for temperatures from -5°C to +35°C. The temperature trend in HCHO data at Zvenigorod Scientific Station varies between $7.5 \times 10^{14}$ and $9.3 \times 10^{14}$ mol$\times$cm$^{-2}$ °C$^{-1}$ for all wind directions. The increase of the HCHO VCD with the increase of the air temperature can be caused by the HCHO formation from non-methane biogenic VOCs (mainly - isoprene) for which more emission is expected at higher temperatures, and by growth of areas of forest and turf fires.

**Conclusion**
THANK YOU FOR YOUR ATTENTION!