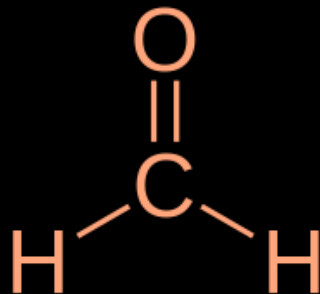**Borovski A.[1,2],**

Postylyakov O.[1], Ivanov V.[3], Kanaya Y.[4], Elokhov A.[1], Borodko S.K.[2]

[1]A.M. Obukhov Institute of Atmospheric Physics RAS, Moscow,
[2] National Ozone Monitoring Research and Educational Center of Belarussian State University, Minsk
[3]A. N. Sevchenko Institute of Applied Physical Problems of Belarusian State University, Minsk,
[4]Department of Environmental Geochemical Cycle Research, Japan Agency for Marine-Earth Science and Technology, Yokohama

Measurements of formaldehyde integral content in troposphere at Moscow Region
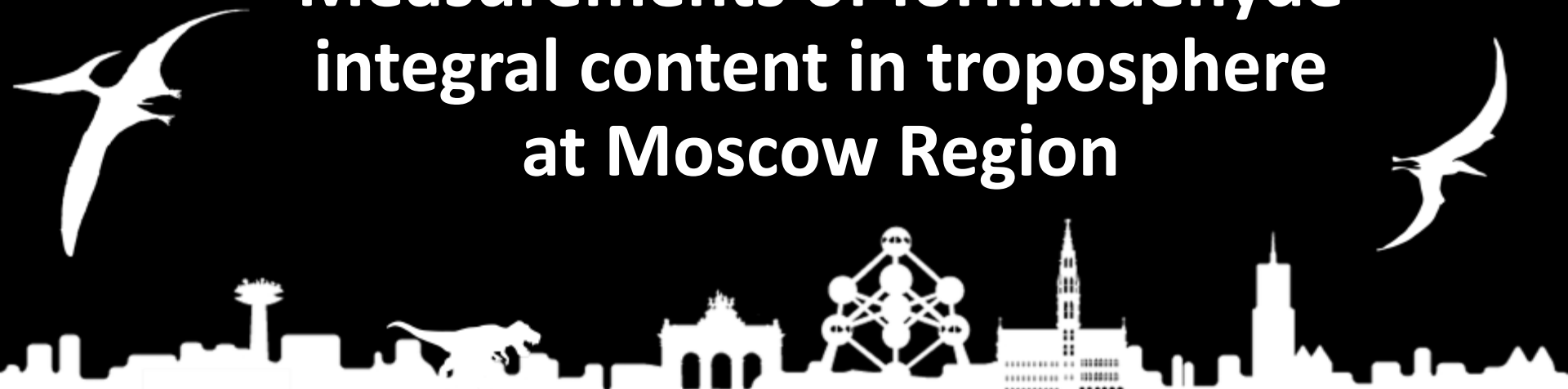
alexander.n.borovski@gmail.com

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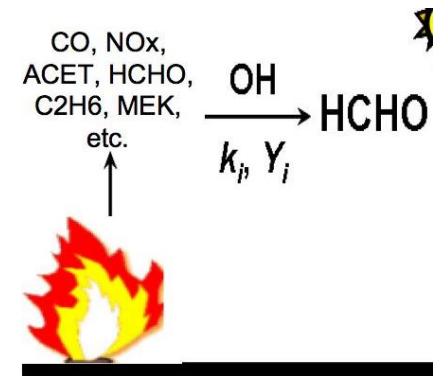b) photochemical activity in the atmosphere.

Sources

a) direct emissions:
- biomass burning;
- fossil fuel burning;

b) indirect emissions by oxidation of:
- methane (source of the background HCHO);
- VOC (tropospheric emissions).

CO, NOx, ACET, HCHO, C2H6, MEK, etc. $\xrightarrow[k_i,\ Y_i]{OH}$ HCHO

Sinks
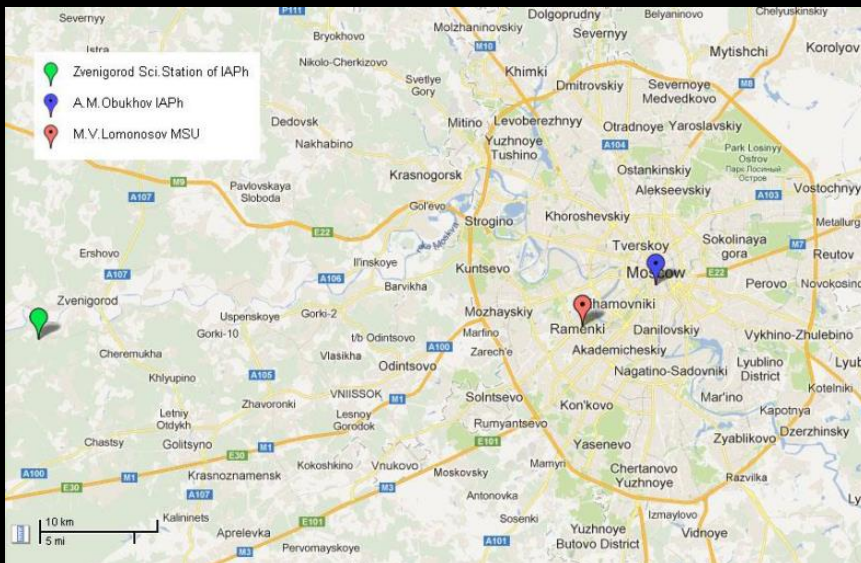
Oxidation by free radical (OH, HO$_2$);
photolysis (<400 nm).

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

Typical total content 10^{16} mol/cm^2
Remote background regions 0.2×10^{16} mol$\times$cm^{-2}
Concentration **(3-4 ppbv)**

Formaldehyde (HCHO)

NO2 observations

Zvenigorod Scientific Station is located
in 38 km western from Moscow

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

*Kanaya, Y. et al. Long-term MAX-DOAS network observations of
NO2 in Russia and Asia (MADRAS) during the period 2007–2012:
instrumentation, elucidation of climatology, and comparisons with
OMI satellite observations and global model simulations, Atm. Chem.
Physics, 14, 7909-7927, doi:10.5194/acp-14-7909-2014 (2014).
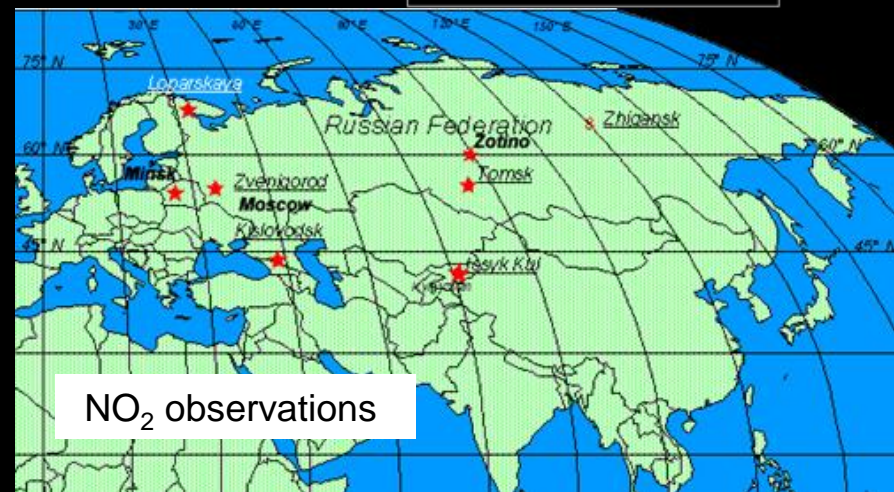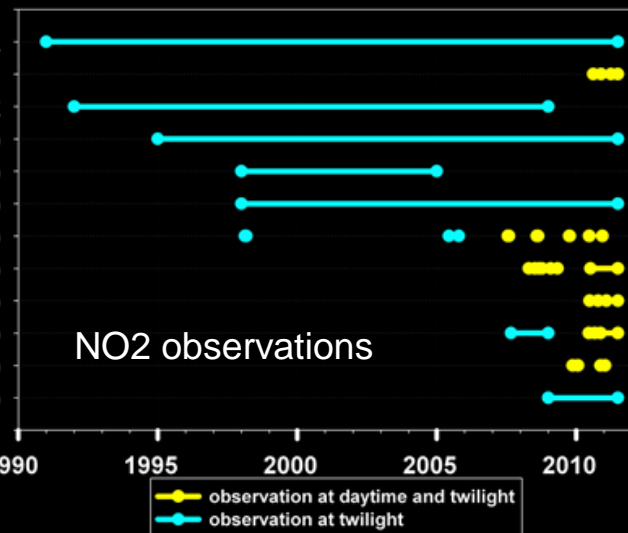
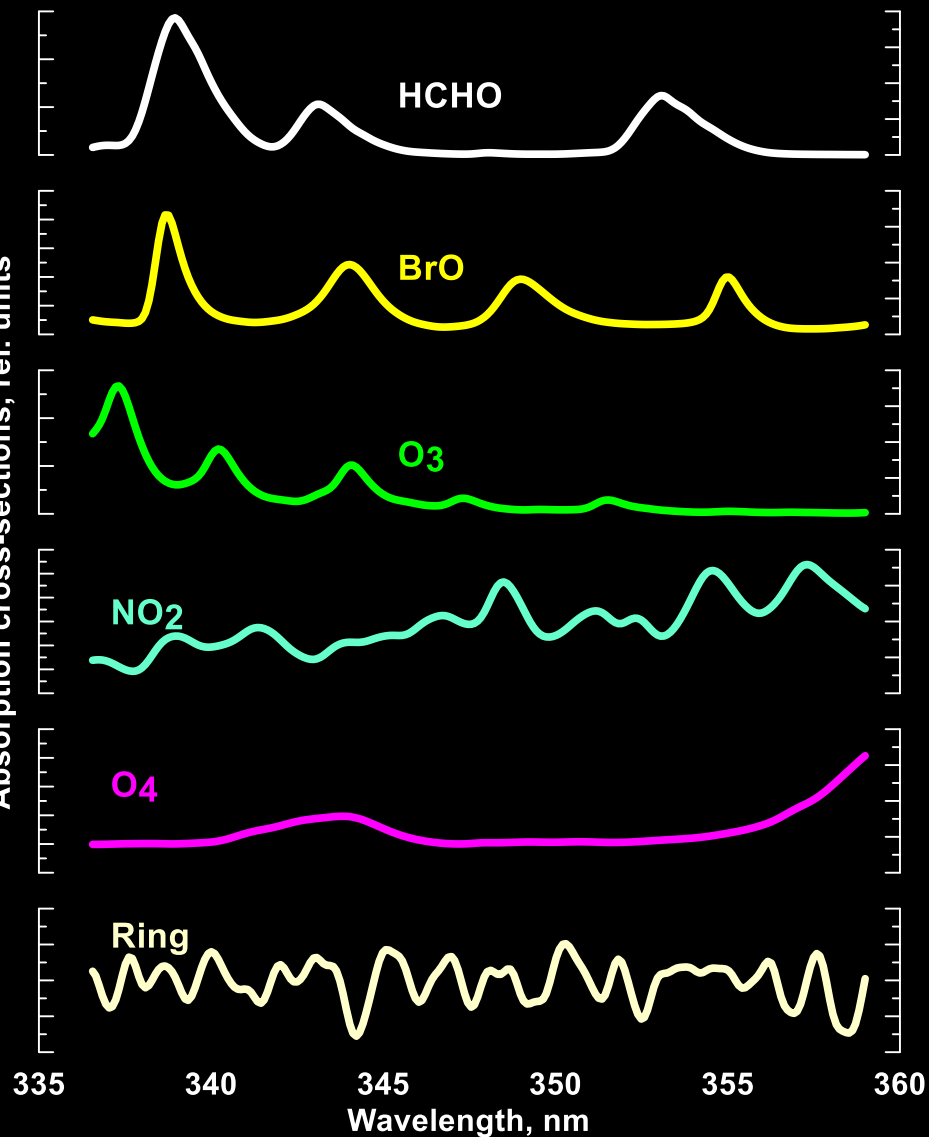NO$_2$ observations

IAP – Insitute of Atmospheric Physics
MSU – M.V. Lomonosov State University
DOAS – Differential Optical Absorption Spectroscopy
TROICA – TRanscontinental Observations Into the Chemistry of the Atmosphere

A.M. Obukhov IAP DOAS network

Absorption cross-sections, rel. units

HCHO

BrO

O$_3$

NO$_2$

O$_4$

Ring
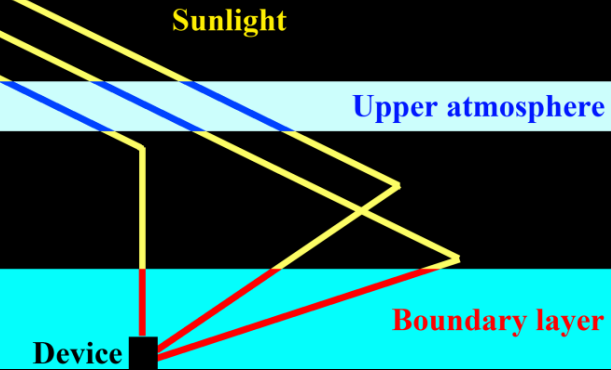
335 340 345 350 355 360

Wavelength, nm

- 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

JAMSTEC MAX-DOAS

Sunlight

Upper atmosphere

Boundary layer

Device

$$DS^{(i)} : \sum_k \left[\ln\left(\frac{I_{REF}(\lambda_k)}{I_\alpha(\lambda_k)} \right) - \sum_i \sigma_i(\lambda_k) DS_\alpha^{(i)} \right]^2 \to \min$$

$$S_\alpha = DS_\alpha + S_{REF} \qquad (1)$$

$$S_\alpha = \int_{h_0}^{h_1} a_\alpha(h) N(h)\, dh = \boldsymbol{V} \cdot \int_{h_0}^{h_1} a_\alpha(h) n(h)\, dh \equiv \boldsymbol{V} \cdot A_\alpha \quad (2)$$

We use non-zenith measurements for S_{REF} estimation only

(1) and (2) together for any pair of α for whole dataset:

$$\begin{cases} DS_{\alpha 1} + S_{REF} = V \cdot A_{\alpha 1} \\ DS_{\alpha 2} + S_{REF} = V \cdot A_{\alpha 2} \end{cases} \to S_{REF} = \frac{DS_{\alpha 1} A_{\alpha 2} - DS_{\alpha 2} A_{\alpha 1}}{A_{\alpha 1} - A_{\alpha 2}}$$

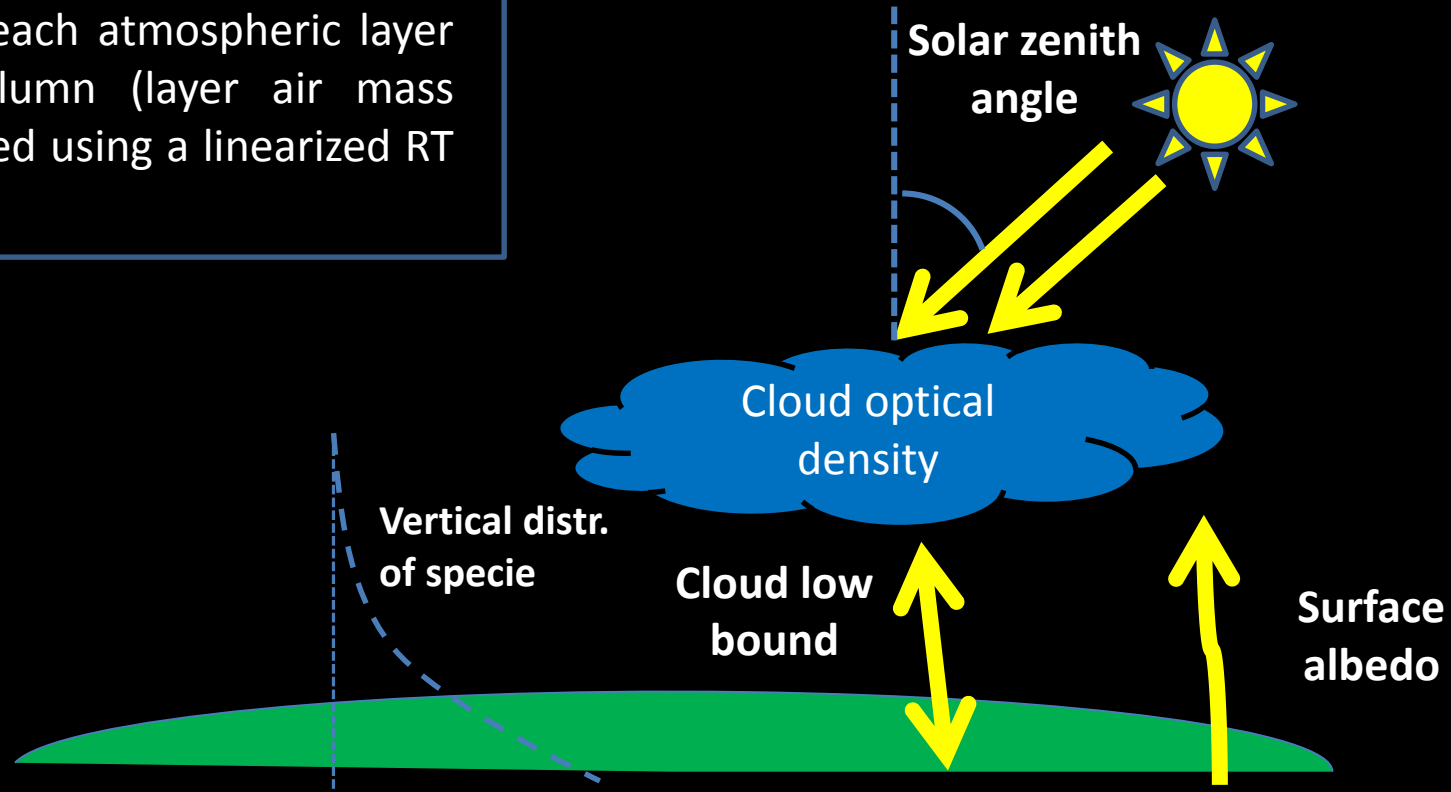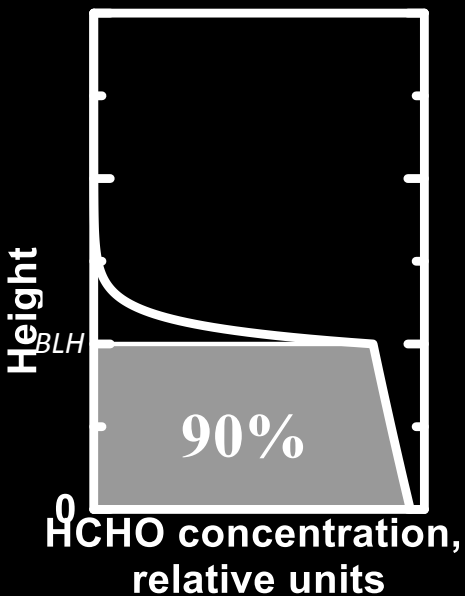S – slant column density of specie; DS - differential S; S_{REF}– S during reference spectrum registration; α – elevation angle; A – air mass factor; $a(h)$ – layer air mass factor, $n(h)$ and $N(h)$ – normalized and real vertical distribution of specie in the atmosphere; I and I_{REF} – signal and reference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

HCHO retrieval

$$V = \frac{S}{A} \qquad A = \int_{h_0}^{h_1} a(h) n(h) \, dh$$

$a(h)$ - 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++.

Solar zenith angle

Cloud optical density

Vertical distr. of specie

Cloud low bound

Surface albedo

Height

BLH

90%

0

HCHO concentration, relative units

Air-mass factor calculating

$$V = \frac{S}{A}$$

Introduce K-value: $K \equiv \frac{1}{A}$ ⟹ $V = S \cdot K$ ⟹ $\varepsilon_{VCD}^{(AMF)} = S \cdot \varepsilon_K$

K-value used for retrieval is estimated as

$$\overline{K} = \frac{K_{\max} + K_{\min}}{2}$$

$$K_{\max} = \max(K_n), \ K_{\max} = \max(K_n), \ n = \overline{0...N}$$

K_n – inverted RTM calculation results for different scenarios

Error related to uncertainty of RTM parameter estimated as:

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

ε_K up to **1%** during winter or summer (known albedo)
ε_K up to **10%** during demi season (unknown albedo)

Analysis of error caused by AMF parameter uncertainties

Thermostat mode in 2010 year

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

Parameter	Specification
Fitting interval	336.5-359 nm
Cross-sections	
HCHO	Meller and Moortgat (2000), 293°K
O3	Bogumil et al. (2003), 223, I_0-corrected
NO2	Vandaele et al. (1996), 298°K, I_0-corrected
BrO	Fleischmann et al. (2004), 223°K
O4	Hermans et al. (2003)
Ring effect	QDoas Software
Closure term	Polynomial of order 3 (corresponding to 4 coefficients)

HCHO retrieval was carried out using own-developed software

DOAS settings for the HCHO DSCDs retrieval are almost the same as used at CINDI campaign (G. Pinardi et al., 2013).

➢ We do not use the additional O_3 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.

DOAS settings

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

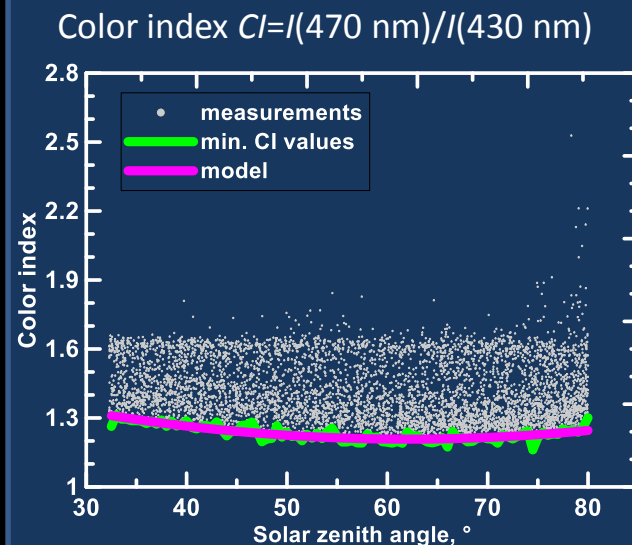**Dispersion of DOAS residual $\sigma^2 \leq 1.5 \times 10^{-5}$**

SZA $\leq 83.5°$
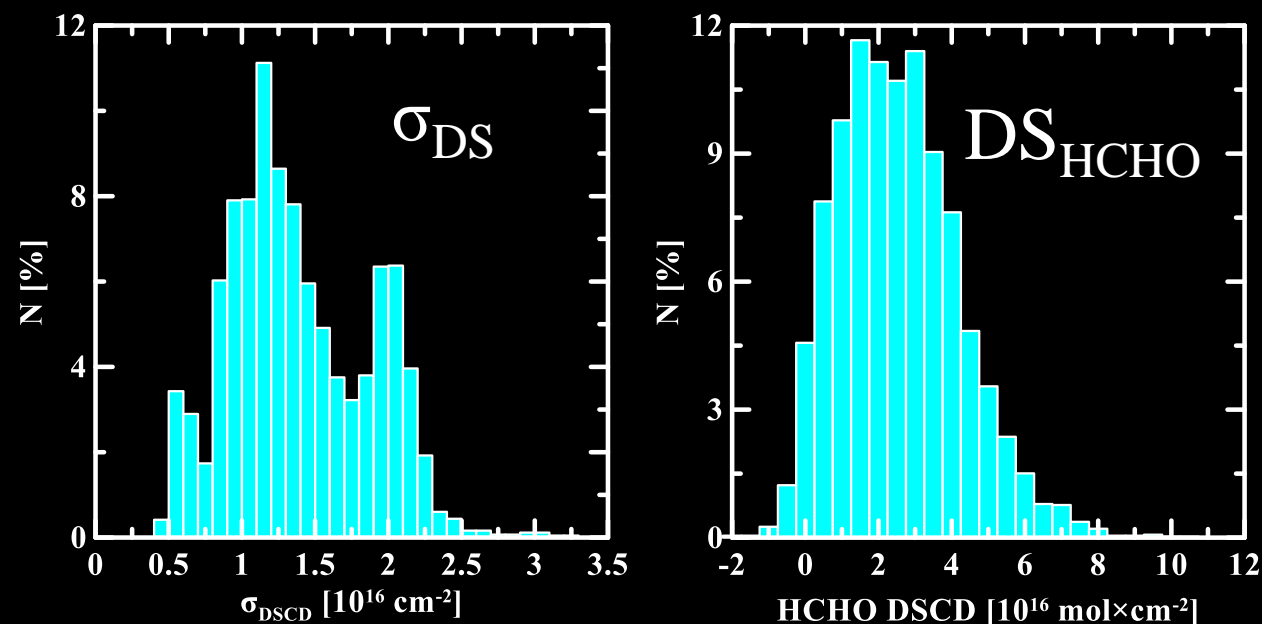
Cloud influence

1. Cloud coverage $\leq 20\%$ (METAR database of Vnukovo airport, 30 km from measurement site)
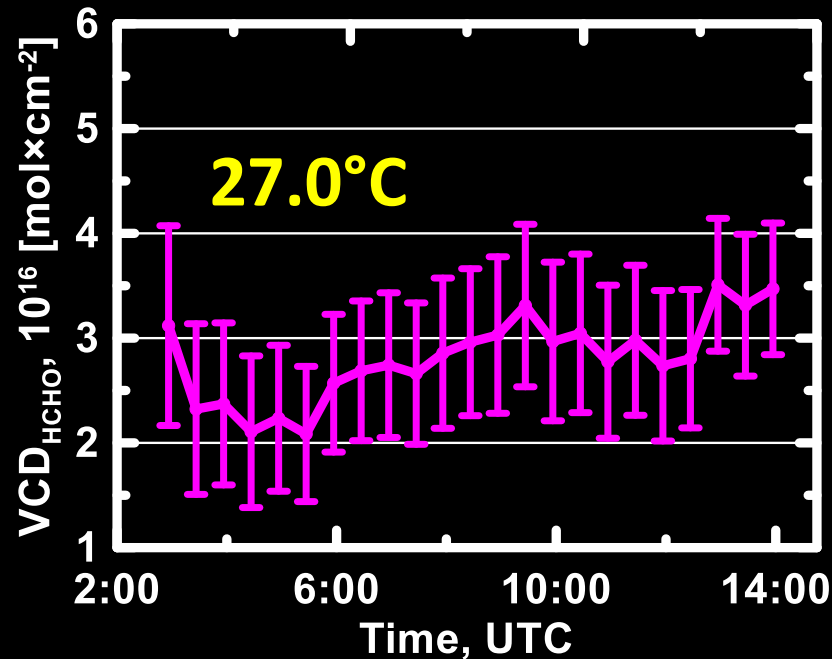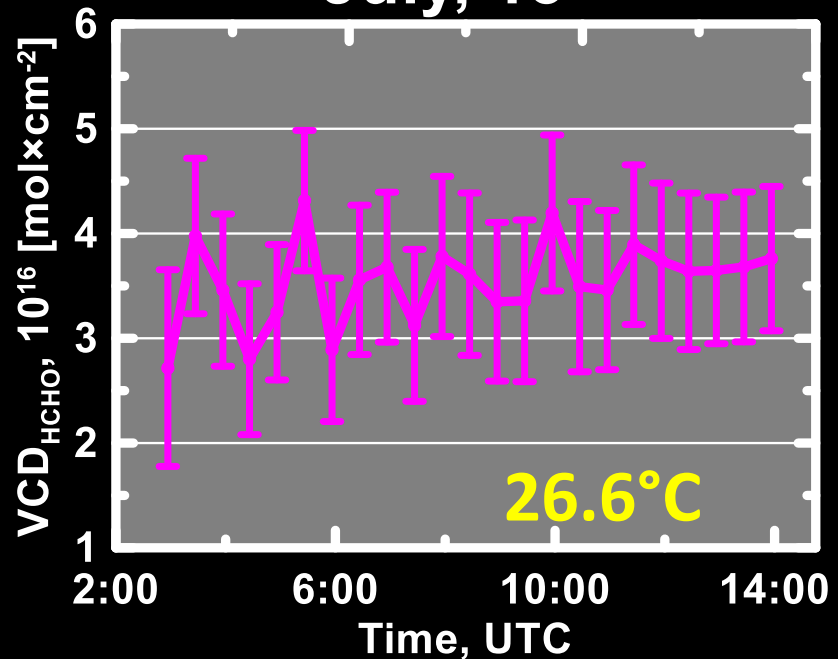
2. Color index $\leq$ Model color index + 0.2

Color index $CI = I(470 \text{ nm})/I(430 \text{ nm})$

4318 data points left

Data used in analysis

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

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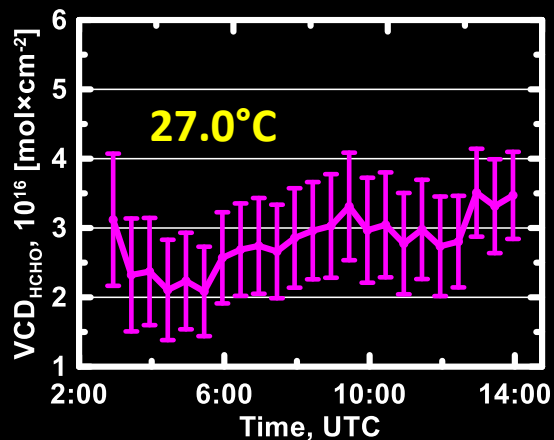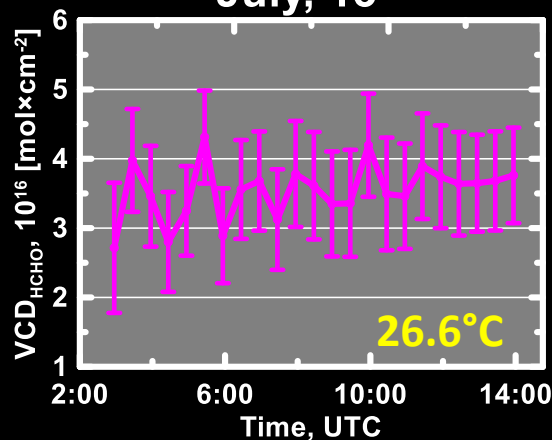12 July: non-east wind directions prevailed

July, 12th

27.0°C

July, 13th

26.6°C

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

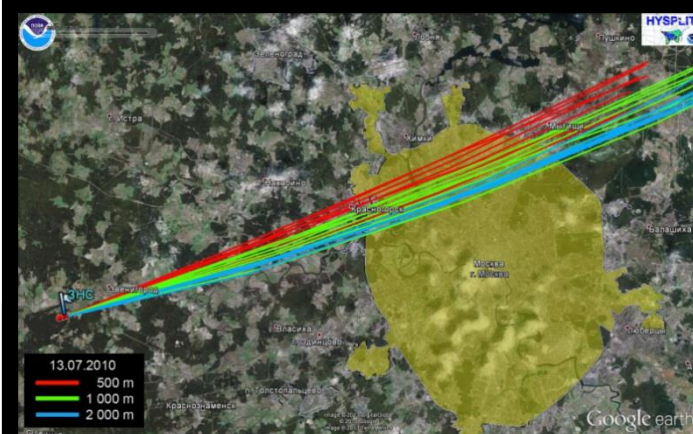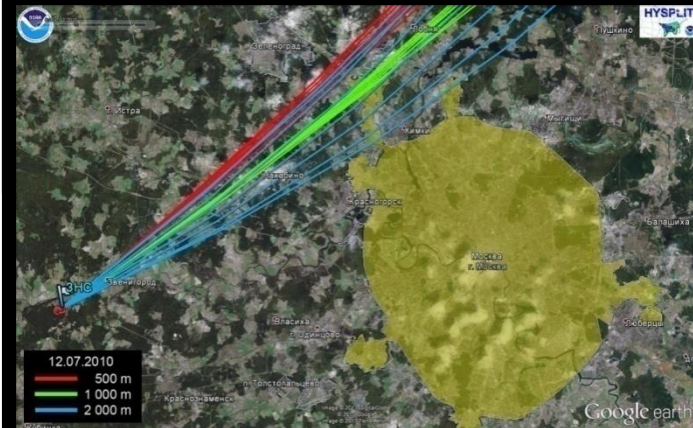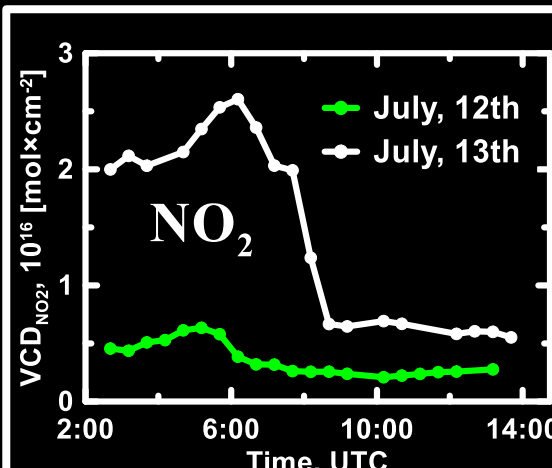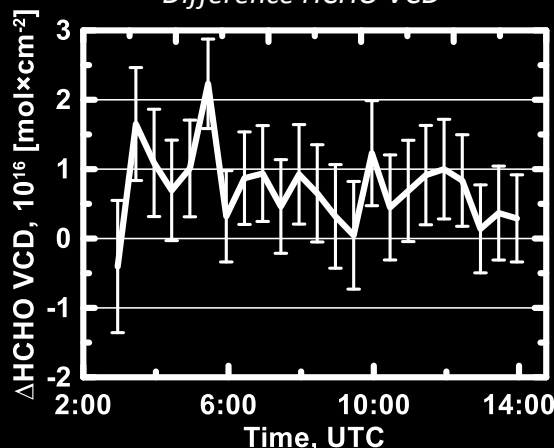July, 12th

27.0°C

July, 13th

26.6°C

14:00

Difference HCHO VCD
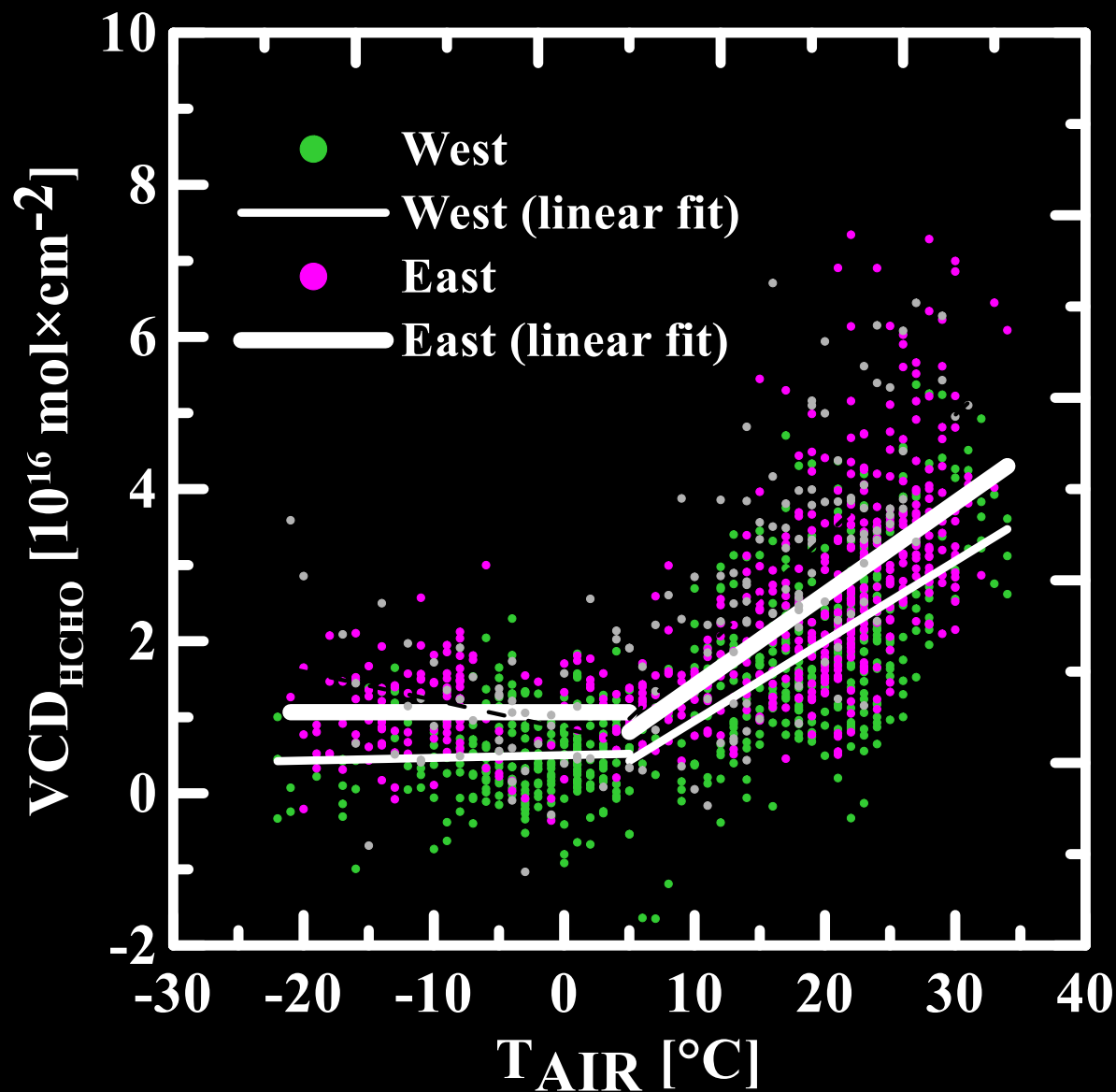
ΔHCHO VCD, 10^{16} [mol×cm^{-2}]

Time, UTC
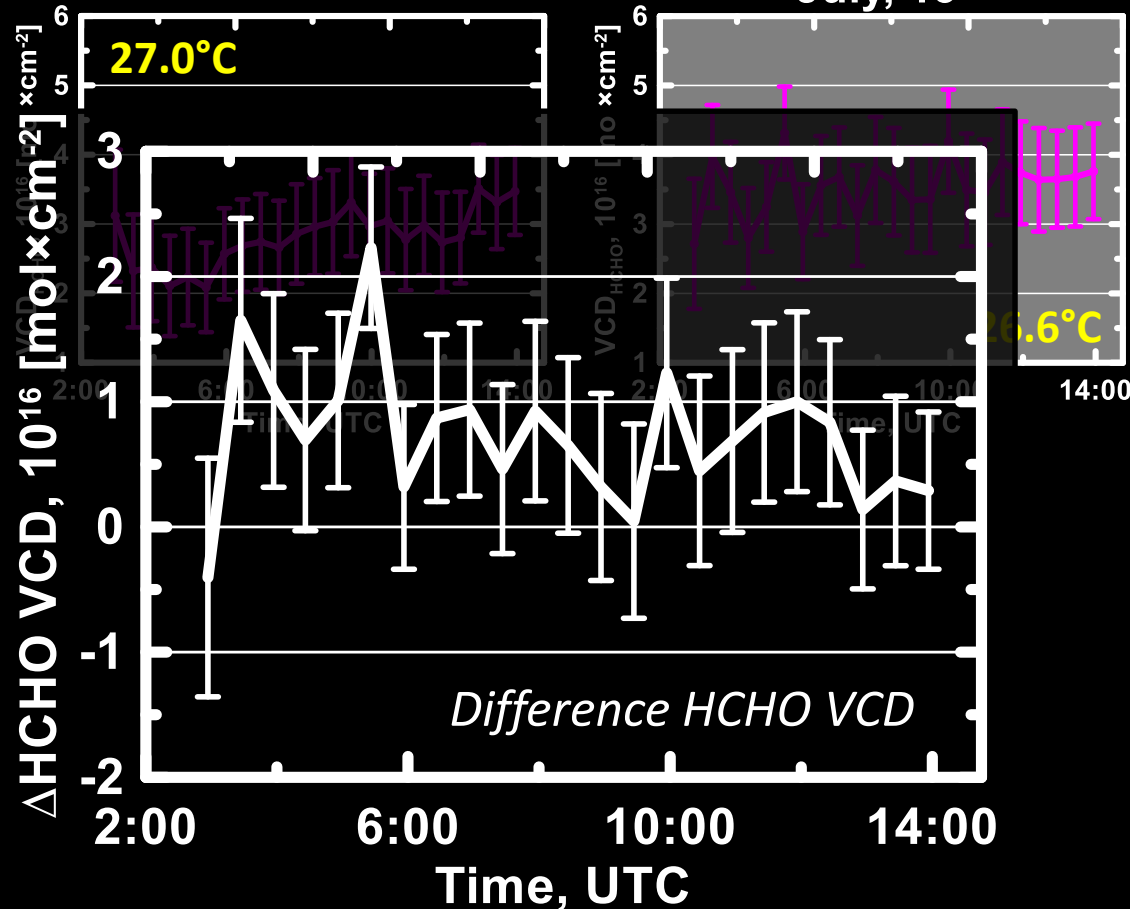
Moscow megacity influence: individual measurements
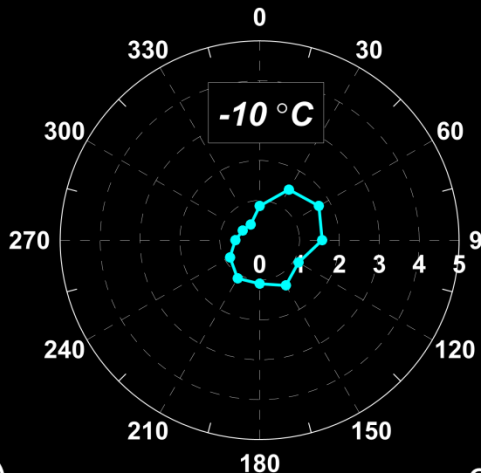
Cloud-free conditions

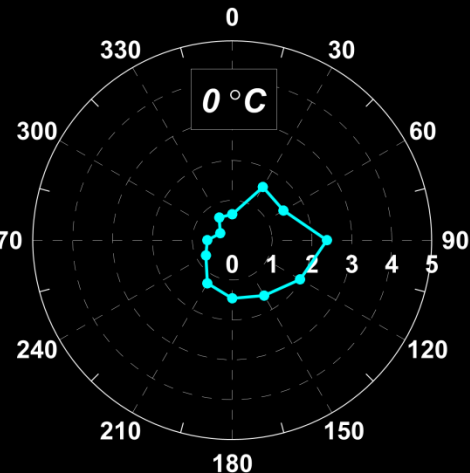# HCHO total column measurements at Zvenigorod

Temperature trend in HCHO data

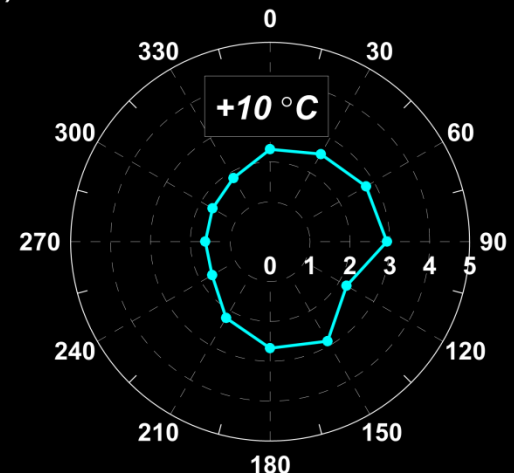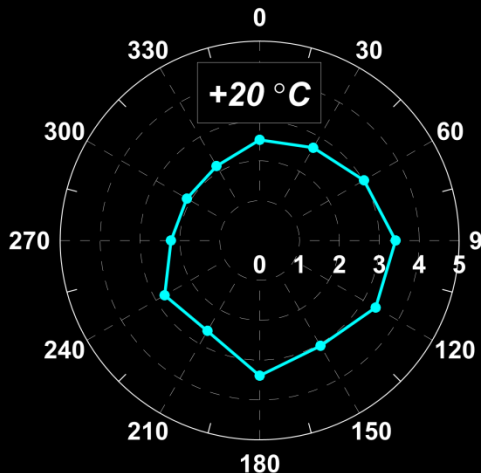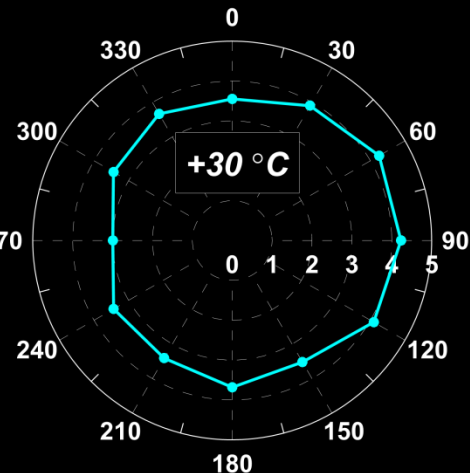# HCHO and air temperature variations

a)
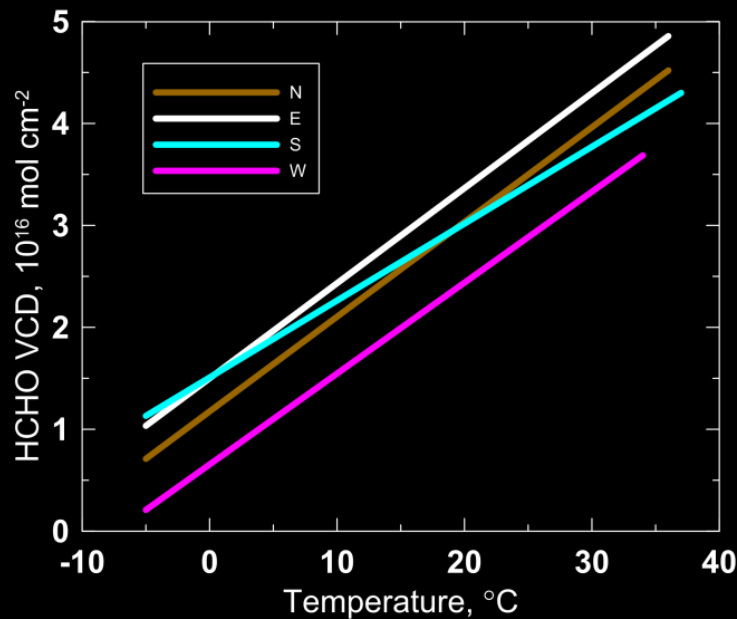

b)

c)

d)

e)

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).

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

*) 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 **0.85×10^{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 7.5×10^{14} and 9.3×10^{14} mol×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

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THANK YOU FOR YOUR ATTENTION!