Intercomparison of MAXDOAS HCHO slant columns during the CINDI campaign

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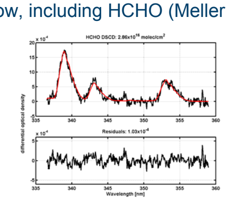
Introduction

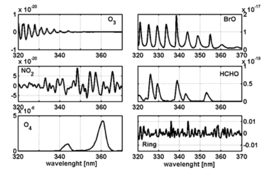
We present the results of a **formaldehyde** slant column intercomparison performed during the **Cabauw Intercomparison Campaign of Nitrogen Dioxide measuring Instruments** (CINDI) which took place in Cabauw (52 N, 5 E), The Netherlands, during summer 2009. Results from nine **MAX-DOAS** instruments (from BIRA-IASB, INTA, Bremen, Heidelberg, JAMSTEC, NASA, WSU, Toronto and Mainz research groups) are compared after application of common DOAS settings.

- **MAXDOAS**: quasi-simultaneous observations of scattered sunlight from the horizon to the zenith. Low viewing elevation measurements have a higher sensitivity to lower tropospheric layers, and thus the MAXDOAS have an increased sensitivity to atmospheric absorbers located near the surface, such as HCHO (Honninger et al. 2004).
- **HCHO**: the most abundant organic carbonyl compound in the atmosphere. A short-lived oxidation product of a large number of volatile organic compounds (VOCs), its abundance can be closely related to VOC emissions of natural origin or from human activities. These emissions, through their involvement in tropospheric ozone chemistry, are important in controlling air quality.
- **The CINDI campaign**: main focus on intercomparison of NO_2 measuring instruments (Piters et al., 2012), gathering of more then 20 MAXDOAS instruments. Opportunity to look on consistency of HCHO measurements. The concentrations are expected to be between one and several tens of ppbv (typical background levels in the continental boundary layer and urban regions).

1. Data Analysis

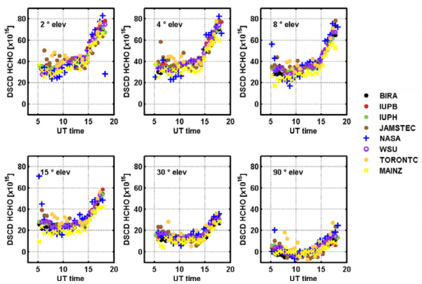
- **Instruments**: the characteristics of the various MAXDOAS instruments were quite diverse (Piters et al., 2012), ranging from commercial mini-DOAS systems to state-of-the-art scientific grade instruments equipped with thermoelectrically cooled CCD array detectors of large dimension.
- **Common observation geometry**: a set of prescribed elevation angles (2°, 4°, 8°, 15°, 30° and the zenith), and at a fixed azimuth angle of 287° relative to North. A full cycle of MAXDOAS measurements was generally obtained within half an hour.
- **Common analysis settings**: DOAS fit in the 336.5-359 nm window, including HCHO (Meller and Moortgat, 2000), NO_2 (Vandaele et al., 1996), O_3 (Bogumil et al., 2003 at 243 and 273K), O_4 (Hermans et al.), BrO (Fleischmann et al., 2004), and a pseudo absorption cross-sections for the Ring effect (Chance and Spurr, 1997). A linear intensity offset correction and a 3rd order polynomial are applied to account for the broadband contribution of the absorption and diffusion, and for possible instrumental straylight. Daily reference around noon.

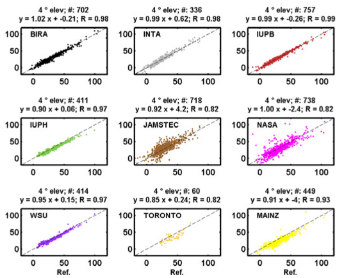


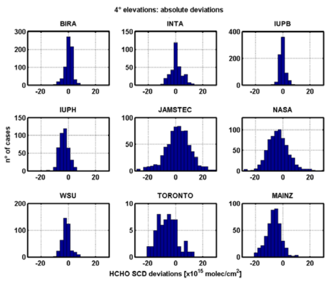


2. Slant column intercomparison

- a) slant columns average over intervals of 30-minutes to reduce instrumental and atmospheric noises, b) creation of a reference dataset grouping instruments with the best mutual agreement (BIRA, IUPB, INTA), c) comparison to the reference through scatter plots with statistic analysis and histograms (according to approach for NO_2 and O_4 blind intercomparison of Roscoe et al., 2010).

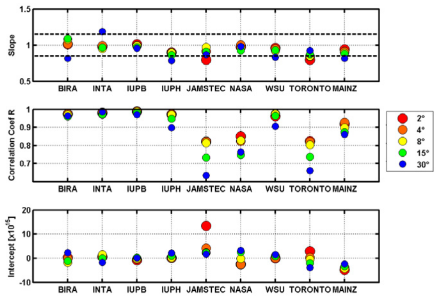






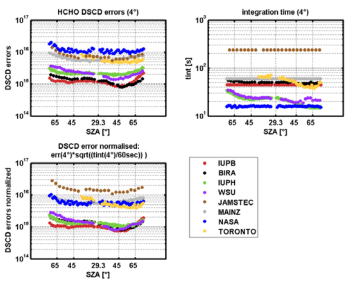
Direct impact on HCHO measurements of differences in stability and noise levels from one system to another: largest FWHM values are found for JAMSTEC, NASA and Mainz, consistent with their smaller and not cooled detectors.

- Overview of statistical results for all elevation angles:



The intercomparison shows a good agreement, with differences from the reference dataset generally within 15% for off-axis elevations.

2 groups of instruments show up, scientific grade MAXDOAS and mini-DOAS-like devices.

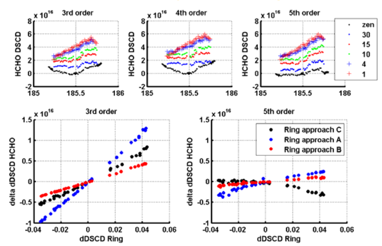


3. Sensitivity tests

- Test the impact of input parameters such as the polynomial terms, the molecular absorption cross-sections, corrections terms for the Ring effect and the width of the fitting interval.

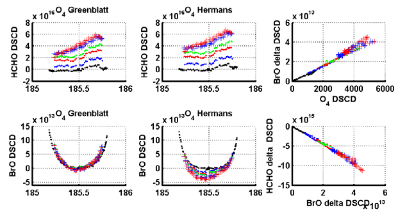
dDSCD = DSCD(off-axis) – DSCD(zenith of the scan)
delta dDSCD = difference with the baseline case

Impact of polynomial degree



The use of a polynomial of degree 5 reduces the strength of the interference between HCHO and Ring observed with a polynomial of degree 3. Optimized settings are weakly dependent on the details of the Ring correction applied.

Impact of O_4 cross-section

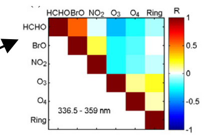


The use of the Hermans et al. O_4 cross-section activates a correlation between O_4, HCHO and BrO. This correlation is largely reduced using the Greenblatt et al. O_4 data set, as demonstrated by the smooth diurnal variation of BrO (expected for a stratospheric gas).

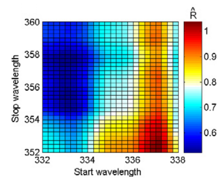
Sensitivity tests lead to the **recommendation** of new **HCHO analysis settings**:
- 336.5-359 nm window,
- polynomial of **degree 5**,
- O_4 (**Greenblatt et al. 1990**), HCHO (Meller and Moortgat, 2000), NO_2 (Vandaele et al., 1996), O_3 (Bogumil et al., 2003 at 243 and 273K), BrO (Fleischmann et al., 2004), Ring (Chance and Spurr, 1997)

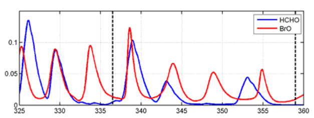
Ring in approach A: according to Wagner et al. (2009)
Ring in approach B: from SCIATRAN RTM using a Rayleigh atmosphere
Ring in approach C: Principal Component Analysis, according to Vountas et al. (1998)

Impact of fitting window and search for an optimal wavelength interval: theoretical search by minimizing the correlation matrix between all absorbers included in the fit. Major correlation in the 336.5-359nm window is between HCHO and BrO due to similarities in shape and position of their absorption cross-sections.

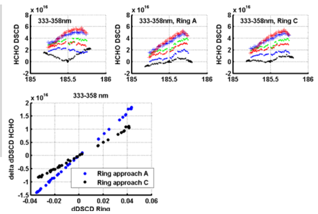


Investigation in the 332-360nm range points to a minimum in the total correlation around the 333-358nm window:





Sensitivity analyses in this wavelength interval however show larger instabilities, particularly as regards the correlation between Ring and BrO slant columns whatever the polynomial order.



Conclusions

- First and successful MAXDOAS HCHO intercomparison exercise. Result of 15% deviation from unity slope for off-axis elevations is very good, considering the lower optical thickness of HCHO and the challenge of retrieving HCHO DSCDs. Same order of magnitude than NO_2 and O_4 UV measurement comparisons (12% and 7%, Roscoe et al. (2010)).
- Sensitivity studies revealed possible optimizations of the HCHO DOAS retrieval, in order to minimize interferences and misfits with Ring, O_4 and BrO. Compared to the settings used during the intercomparison exercise, the use of a 5th degree polynomial and the O_4 Greenblatt cross-section are recommended.

Selected References

Roscoe et al.: AMT, 3, 1629-1646, 2010.
Piters et al.: AMT, 5, 457-485, 2012.
Honninger et al.: ACP, 4, 231-254, 2004.

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