Intercomparison of MAX-DOAS retrieval algorithms using MAD-CAT NO_2 campaign data

E. Peters (1), G. Pinardi (2), T. Bösch (1), F. Wittrock (1), A. Richter (1), J. P. Burrows (1), M. Van Roozendael (2), A. Piters (3), T. Wagner (4), T. Drosoglou (5), A. Bais (5), S. Wang (6), A. Saiz-Lopez (6), and the Extended QA4ECV MAXDOAS Team

(1) University of Bremen, Institute of Environmental Physics, Germany, (2) Belgian Institute for Space Aeronomy, IASB-BIRA, Brussels, Belgium, (3) Royal Netherlands Meteorological Institute, KNMI, De Bilt, The Netherlands, (4) Max Planck Institute for Chemistry, Mainz, Germany, (5) Aristotle University of Thessaloniki, Greece, (6) CSIC, Instituto de Química Física Rocasolano, Madrid, Spain

Introduction

Measurement principle: **Differential Optical Absorption Spectroscopy (DOAS)**

- Based on Lambert-Beer's law
- High-frequency part of (known) absorption structures σ are fitted to optical depth τ
- DOAS equation (I and I_0 are measured):

$$\tau_{meas} = \ln\left(\frac{I_0}{I}\right) = \sum_i \sigma_i \cdot SC_i + polynomial + residual$$

- Result: Slant columns $SC_i = \int \rho_i \cdot ds$ (absorber concentration ρ_i integrated over light path s)
- I_0 measured usually in zenith direction

Intercomparison and harmonization efforts in the past:

- DOAS is a widely used remote sensing technique
- Groups use their own instruments and (mostly) their own retrieval codes
- Intercomparison campaigns (e.g., CINDI, MAD-CAT etc.) attempted to evaluate the agreement between groups (i.e. using different instruments and different retrieval codes, e.g. [1,2])

Objective and approach here:

- Spectra measured by IUPB MAX-DOAS during the MAD-CAT campaign were provided
- Every group performs DOAS analysis using their own retrieval software
- Results (slant columns) are then intercompared

→ Estimation of agreement of different DOAS retrieval codes (not biased by instrumental effects)
→ Identification of systematic differences

MAD-CAT campaign & intercomparison exercise

MAD-CAT campaign:

- Multi-Axis DOAS Comparison campaign for Aerosols and Trace gases (MAD-CAT, e.g. [3])
- Carried out at Max-Planck institute for Chemistry (MPIC) in Mainz, Germany
- 11 international groups participated with their own instruments
- IUPB instrument was deployed from 7 June to 6 July 2013

Intercomparison exercise:

- Not restricted to campaign participants
- Data provided: Off-axis and zenith spectra measured by IUPB instrument at 18 June (best viewing conditions during campaign), slit function, cross sections
- 4 different fits were intercompared (Tab.1)
- Participants: 16 institutes (IUPB, MPIC, IUPHD, U Toronto, CU Boulder, Jamstec, KNMI, INTA, AUTH, BIRA, CSIC, NIWA, IAP, BSU, USTC, UNAM)
- A questionnaire was sent around in order to understand differences

Tab 1: Fit settings used in the intercomparison

Fit	Reference	Fit window	Polynomial	Cross sections	Calibration
v1	noon	425-490 nm	5 (6 coefs)	O_3, NO_2 (298K and 220K ortho), O_4, H_2O, Ring, 0th order intensity offset correction	Based on solar atlas provided
v1a	sequential				
v2	noon	411-445 nm	4 (5 coefs)		
v2a	sequential				

Fig 1: Instruments deployed at MPIC roof during the MAD-CAT campaign. The IUPB instruments providing measurements for this study is the one on the left side.

Acknowledgements

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- Many thanks to all contributing Co-authors providing data for this intercomparison exercise.
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Intercomparison results

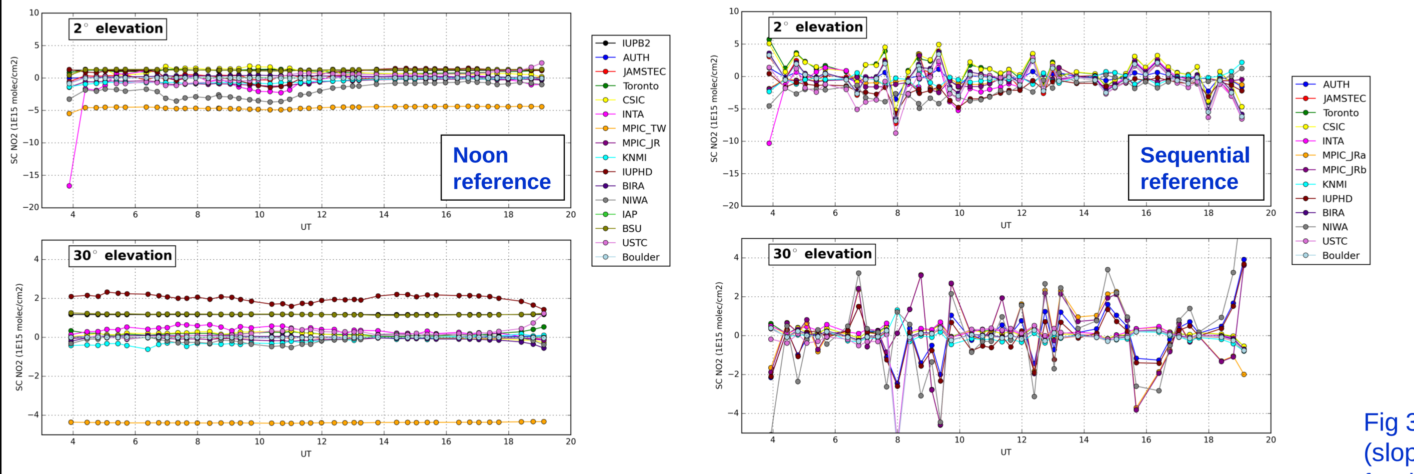


Fig 2: Time series of NO_2 SCs (w.r.t. IUPB NO_2 SCs) in 2° and 30° elevation from 18 June 2013, 425-490 nm fit, noon reference and sequential reference (i.e., v1 and v1a fit, see Tab. 1)

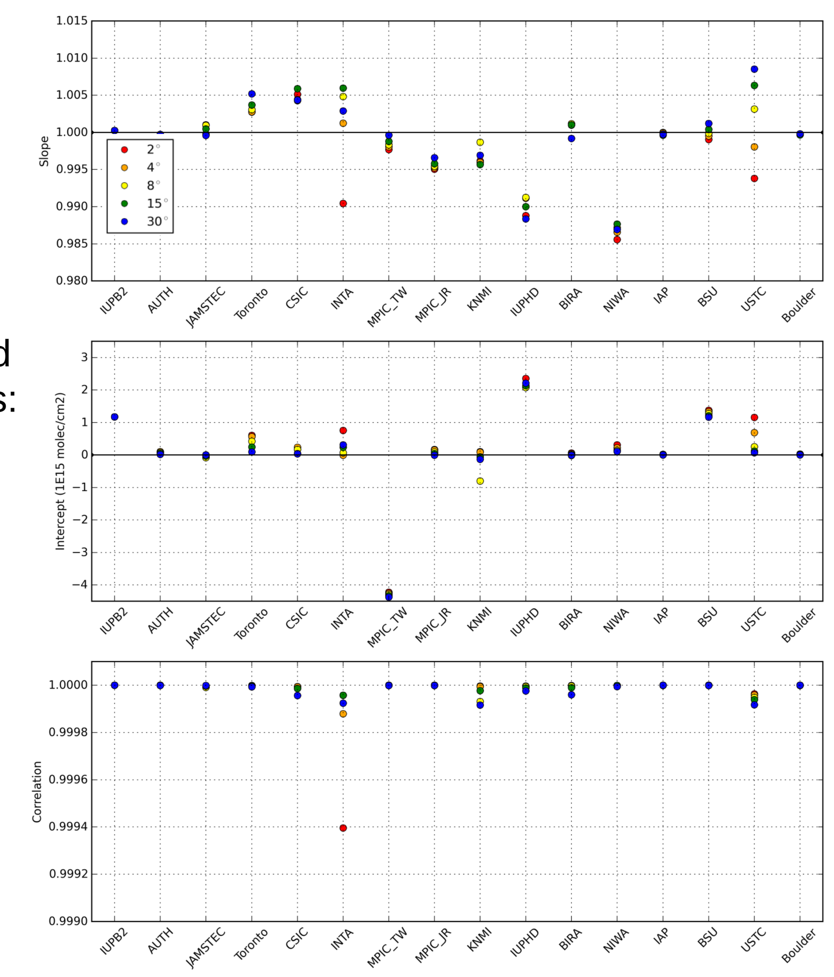


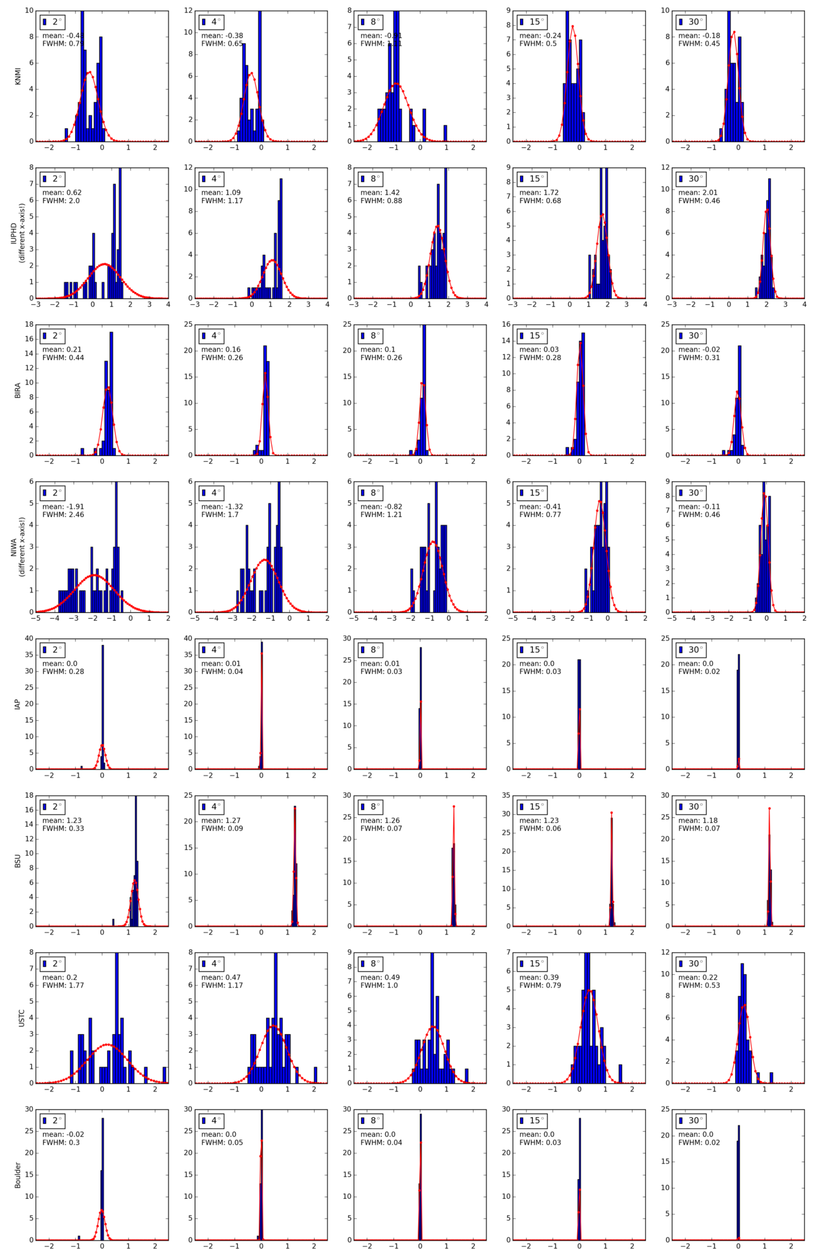
Fig 3: Linear regression results (slope, intercept, correlation) for different elevation angles (w.r.t. IUPB) using fit setting v1 (see Tab. 1).

- As a reference for the intercomparison, IUPB results have been used. (IUPB2 estimates the effect of using a different reference in Fig. 2, 3, 5).
- Agreement and correlation for sequential reference worse than noon (Fig. 2 and Tab. 2)
- Large fit range shows slightly better correlation (more information → less statistical scatter)
- NO_2 differences are < 5E15 molec/cm² (Fig. 2,3, Tab. 2) and depend on elevation angle (Fig. 2,5)
- Histograms (Figs. 4,5) and questionnaires allowed to identify most important systematical differences:

1. Treatment of reference (a few 10^{15} molec/cm²)
2. Differences in wavelength calibration
3. Different treatment of the slit function

	Corr (%)	Slope range	Intercept (absolute)
v1	> 99.98 (outlier)	0.985 - 1.01	2-3E15
v1a	> 99.2	0.96 - 1.01	2E15
v2	> 99.94	0.985 - 1.005	2-3E15
v2a	> 99.2	0.96 - 1.005	2E15

Tab. 2: Summary of statistics (Fig. 3) for each fit setting



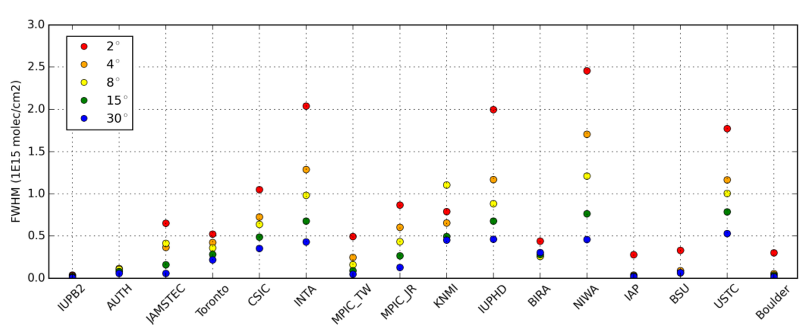


Fig. 4 (left): Subset of histograms for different groups w.r.t. IUPB using fit setting v1 (Tab. 1) for different elevation angles. Red: Calculated Gauss distributions of histograms.
Fig 5 (top): FWHM of Gauss curves in histograms (Fig. 4) for each group and fit setting v1.

Selected references

[1] Roscoe, H. K., et al.: Intercomparison of slant column measurements of NO2 and O4 by MAX-DOAS and zenith-sky UV and visible spectrometers, Atmos. Meas. Tech., 3, 1629-1646, doi:10.5194/amt-3-1629-2010, 2010.
[2] Piters, A. J. M., et al.: The Cabauw Intercomparison campaign for Nitrogen Dioxide measuring Instruments (CINDI): design, execution, and early results, Atmos. Meas. Tech., 5, 457-485, doi:10.5194/amt-5-457-2012, 2012.
[3] Ortega, I., Koenig, T., Sinreich, R., Thomson, D., and Volkamer, R.: The CU 2-D-MAX-DOAS instrument – Part 1: Retrieval of 3-D distributions of NO2 and azimuth-dependent OVOC ratios, Atmos. Meas. Tech., 8, 2371-2395, doi:10.5194/amt-8-2371-2015, 2015.

Evaluating the effect of slit function treatment

- Different groups are treating the provided slit function in different ways (e.g. Fig. 6)
- Tests were performed using a fixed retrieval code (Bremen code) in order to evaluate the effect of the slit function treatment (Tab. 3)
- Test measurement: 5° spectrum from 18 June 2013 9:20 UT, noon zenith reference, 425-490 nm fit window

	T1	T2	T3	T4	T5	T6	T7
use as is	■						
sub offset		■		■	■		
geometric centering			■	■	■		
cut-off value = 0					■		
fit gauss						■	
fit gauss (mu = 0)							■

Tab 3: Different tests performed in order to evaluate the effect of different slit function treatments on NO_2.

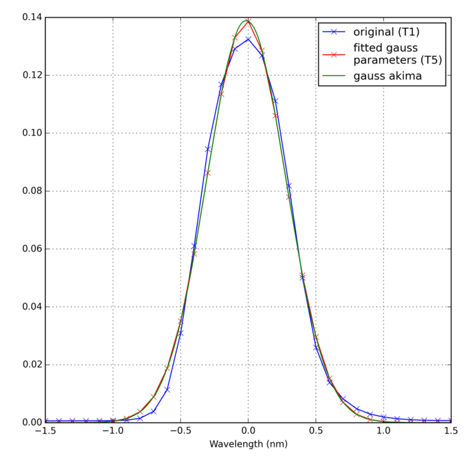


Fig 6: Example of slit functions used in tests T1 and T6 (Tab. 3).

→ Effect is small (Tab. 4), but in the same range or even larger than the fit error (SC_{error} ≈ 0.35% here)

→ Produces disagreements between groups in the same order of magnitude

→ Open for discussion which is the most correct result (i.e. recommendable treatment)

	SC NO_2 (10^{17} molec/cm²)	Relative diff to T1
T1	1.506376	-
T2	1.498138	-0.55%
T3	1.506375	<0.01%
T4	1.498138	-0.55%
T5	1.501436	-0.33%
T6	1.506642	0.02%
T7	1.508762	0.16%

Tab 4: NO_2 slant column changes In different tests (w.r.t. test T1)

QA4ECV MAX-DOAS fit recommendations

	NO_2*lambda (ortho)	Ring*lambda	Linear offset term (slope)
Base fit*			
rec2	■		
rec3	■	■	
rec4	■		■

Tab 5: Fit settings shown in Fig. 7 for final QA4ECV MAX-DOAS NO_2 fit recommendation.

*Base fit: 425-490 nm, p6, O_3, NO_2, O_4, H_2O, Ring,
Intensity offset: Constant

- Intercomparison fits are reasonable, but improvements possible
- RMS reduction by NO_2 AMF wavelength-dependence: NO_2*lambda (orthogonalized, rec2 fit in Tab. 5) largely reduces the RMS in small elevations (Fig. 7)
- Ring*lambda (rec3) yields small further RMS reduction
- Linear offset term instead of Ring*lambda has same effect

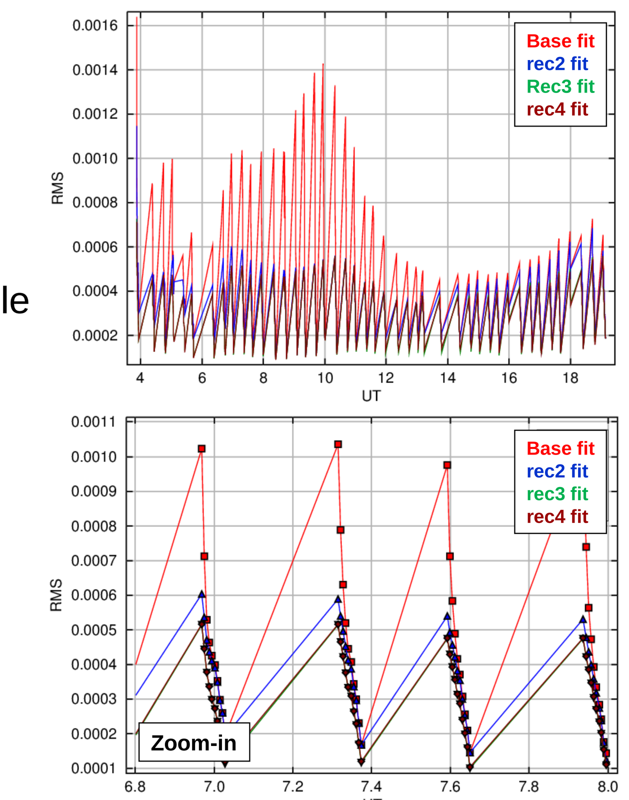
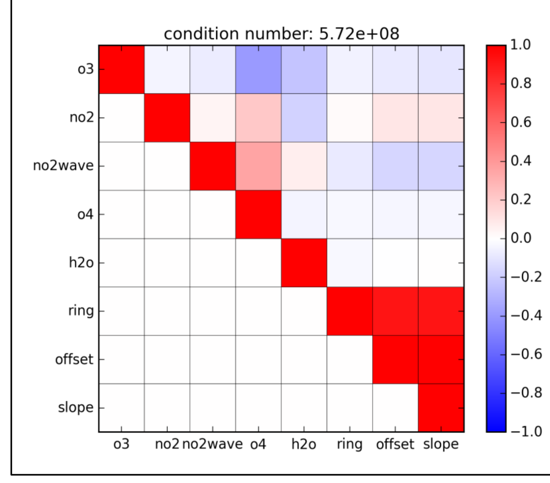


Fig 7: RMS of different NO_2 fits (data from 18 June 2013). Red line: Base fit. Blue line: rec2 fit. Green line: rec3 fit. Brown line: rec4 fit (see Tab. 5).



- rec4 fit shows very small interferences between cross sections included (Fig. 8)

→ rec4 is QA4ECV final fit recommendation for tropospheric NO_2

Fig 8: Correlation matrix of differential cross sections used in the final recommended QA4ECV MAX-DOAS tropospheric NO_2 fit (rec4 fit, Tab. 5)

Summary and conclusions

- 16 international groups participated in an intercomparison exercise of DOAS retrieval codes.
- In contrast to former intercomparison campaigns, findings characterize differences in retrieval codes only (not biased by instrumental differences).
- Systematical differences are mainly caused by 1) use of the reference spectrum, 2) differences in wavelength calibration, 3) different treatment of the slit function.
- The effect of slit function treatment was found to produce systematic differences up to the range of typical NO_2 fit errors (≈ 1%).
- Based on the intercomparison fit, recommendations for tropospheric NO_2 DOAS fits were elaborated.

This poster as pdf:

Universität Bremen
www.iup.uni-bremen.de/doas

Email: Enno.Peters@iup.physik.uni-bremen.de

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