Improvements to the nitrogen dioxide observations by means of the MKIV Brewer spectrophotometer

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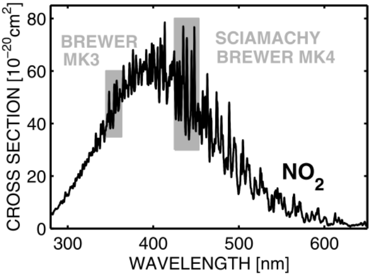
Tenerife, March 2014

MKIV

- 426 – 453 nm (visible)
- original algorithm: Kerr (1989)
- updates (not implemented): Barton (2007)

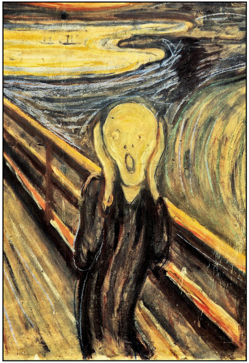
MKIII

- 349 – 363 (UV-A)
- Cede et al. (2006)



What's wrong with NO_2 measurements using the Brewer?

- overestimations (>200%) with the current algorithm
  - other ground-based instruments
  - satellite radiometers
- random deviations
  - due to interferences (O_4, H_2O, Ring)
  - sensitivity to instrumental settings (e.g. wavelength misalignments)
- noise
  - depends on both the algorithm and used wavelengths
- no calibration service for NO_2



Open questions

- can we obtain better performances by changing the operational wavelengths?
- how large is the measurement uncertainty?
- do direct sun and zenith sky estimates agree within their uncertainties?
- how to perform a Langley plot with a variable absorber?
- is it possible to reprocess long-term series?

What was done

1. mathematical framework and numerical simulations
   - accurate characterisation of Brewer #066
   - parameterisation of all influencing factors
2. updated spectroscopic dataset
3. new (polarised) AMFs for ZS geometry
4. variable-Langley calibration (Izaña)
5. Montecarlo uncertainty budget
6. reprocessing of 4 long-term series

Instrumental characterisation

Fundamental to reveal the weak signal of NO_2

- dispersion
- "neutral density" filters
- temperature dependence
- etc.

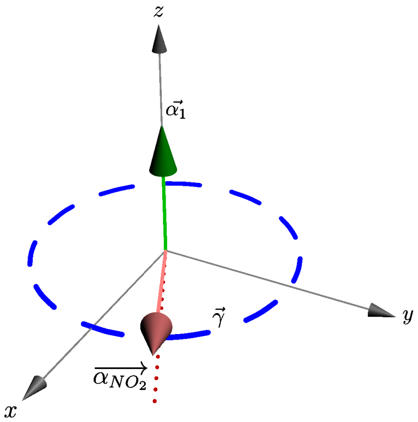
[Diémoz et al., 2011, Brewer Meeting, Beijing]

Updates to the algorithm

Noise reduction

$$\begin{cases} \vec{\gamma} \cdot \overrightarrow{\beta_R} \equiv 0 \\ \vec{\gamma} \cdot \overrightarrow{\alpha_{O_3}} \equiv 0 \\ \vec{\gamma} \cdot \overrightarrow{\delta_A} \equiv 0 \\ \vec{\gamma} \cdot \vec{1} \equiv 0 \\ \vec{\gamma} \parallel \alpha_{NO_2} \end{cases}$$

6 slits =
more degrees of freedom =
noise reduction

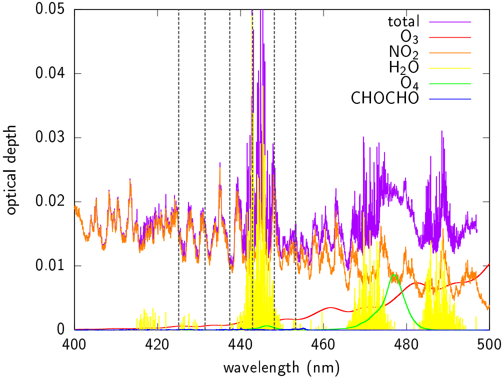


Updates to the algorithm

Interfering factors

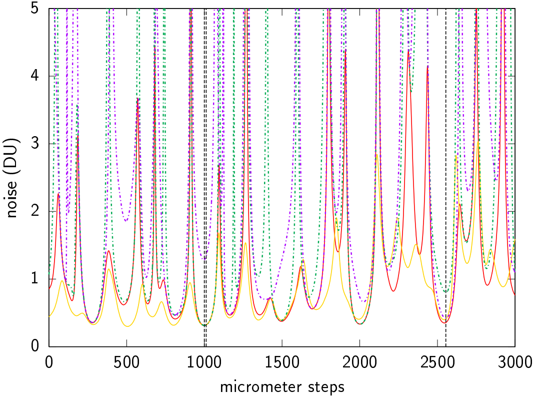
Considered factors

- noise
- oxygen dimer (O_4)
- water vapor (H_2O)
- Ring effect
- sensitivity to NO_2 effective temperature
- wavelength misalignments



Updates to the algorithm

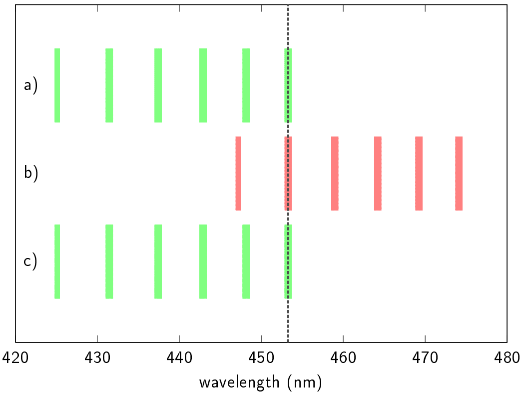
Increasing the DOF



For every influencing factor a diagram was assessed and the optimal grating positions (i.e. wavelengths) were found

Updates to the algorithm

Jump scans



11 slits

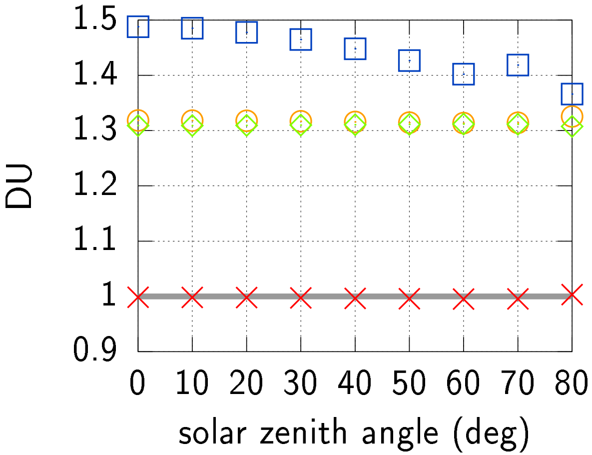
O_4 and H_2O included in the retrieval

Updates to the algorithm

Further updates

- all cross sections were updated to recent laboratory measurements (NDACC 2012 guidelines)
  - NO_2 - Vandaele 2002 @ 220 K (instead of Graham 1976)
  - O_3 - Bogumil 2003 @ 223 K (instead of Vigroux 1952)
  - Rayleigh - Bodhaine et al. 1999 (instead of UV Brewer coefficients)
  - O_4 - Hermans 2003 (previously neglected)
  - H_2O - Hitran + Py4CATS (previously neglected)
- I0-effect taken into account
- new weighting factors
- polarised AMFs for ZS geometry (SCIATRAN, full-spherical)

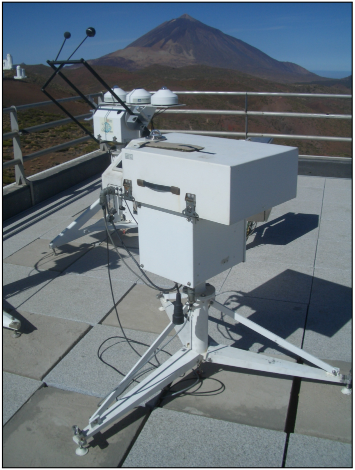
Updates to the algorithm
Radiative transfer calculations



[Diémoz et al., 2013, SPIE, Dresden]

Field measurement campaigns

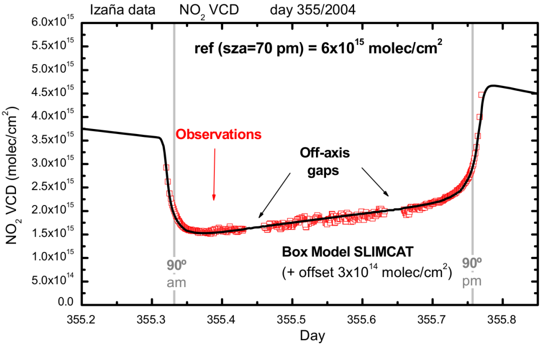
The Izaña campaign



- 38 days of measurements
- 5 days removed because of fog/rain
- no relevant contamination by Saharan dust on ratios
- 2 days for initial checks
- 16 days for direct-sun measurements (3 steps)
- 15 days for zenith-sky measurements (3 steps and 2 polarizations)
- 5 days for O_3 and O_4 direct-sun measurements

Field measurement campaigns

Langley in varying conditions

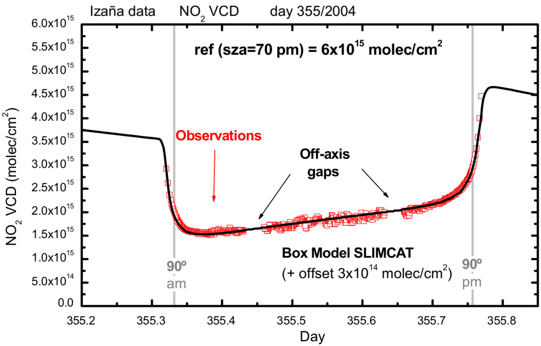


Improving the Langley: linear changes with time

$$\begin{aligned}\frac{y(t)}{\mu(t)} &= a\frac{1}{\mu(t)} + b(t) \\ &= a\frac{1}{\mu(t)} - \delta - \xi t\end{aligned} \tag{1}$$

Field measurement campaigns

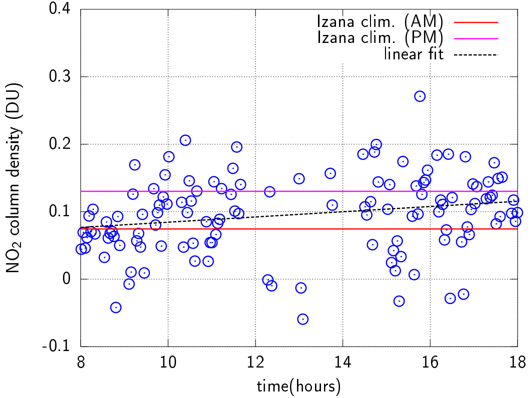
Langley in varying conditions



$$\begin{pmatrix} a & \delta & \xi \end{pmatrix}^T = A^\dagger \begin{pmatrix} \frac{y_1}{\mu_1} & \dots & \frac{y_n}{\mu_n} \end{pmatrix}^T \tag{2}$$

Field measurement campaigns

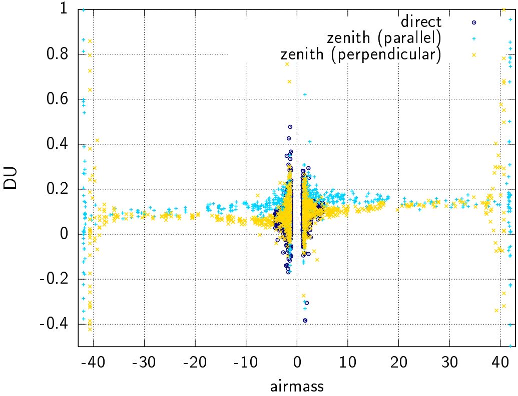
Langley in varying conditions



site	reference	daytime increasing rate ($10^{13} \frac{molec}{cm^2\ h}$)
Zugspitze/Garmisch	Sussmann et al. (2005)	5–15
Izaña	Gil et al. (2008)	6
Pacific Ocean	Peters et al. (2012)	8.7±0.5
Izaña	present study	7.0–12.5

Field measurement campaigns

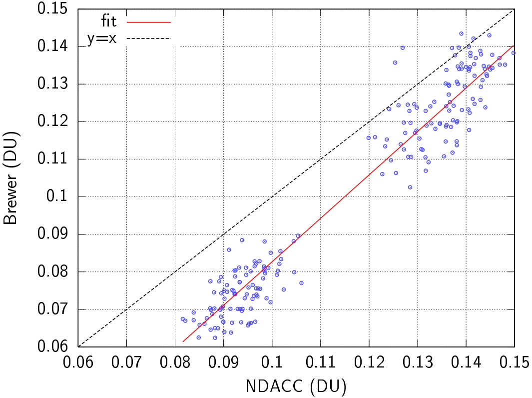
The Izaña campaign



Measurements using the three different geometries are equivalent within their respective uncertainties (airmass < 0 morning; > 0 afternoon)

Field measurement campaigns

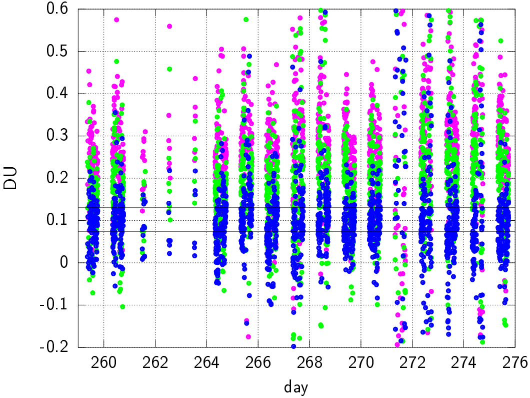
The Izaña campaign



The Brewer does not overestimate anymore

Field measurement campaigns

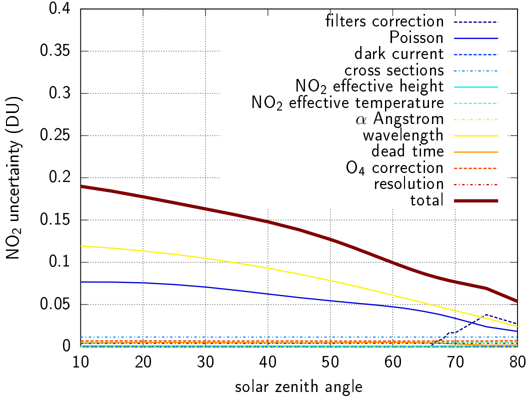
Comparison among different algorithms



Izaña (2012) – **Pink**: Kerr's algorithm; **green**: filters and Rayleigh updates; **blue**: new algorithm.

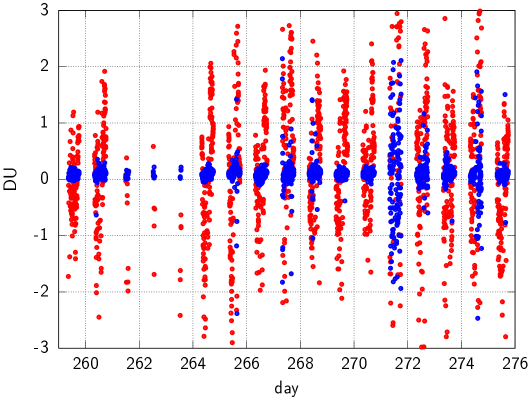
Field measurement campaigns

Uncertainty budget



Monte Carlo uncertainty budget

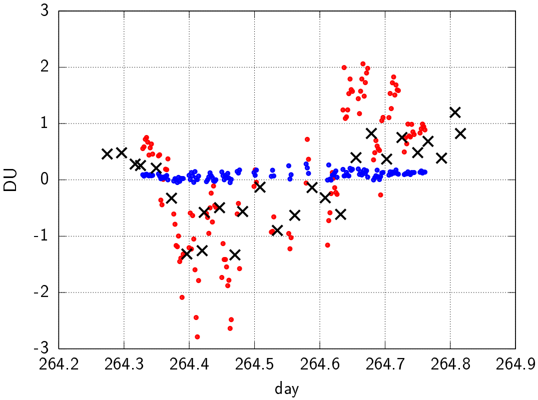
$>$ 10 factors taken into account



Much less noise than Barton's algorithm (2007)...

Field measurement campaigns

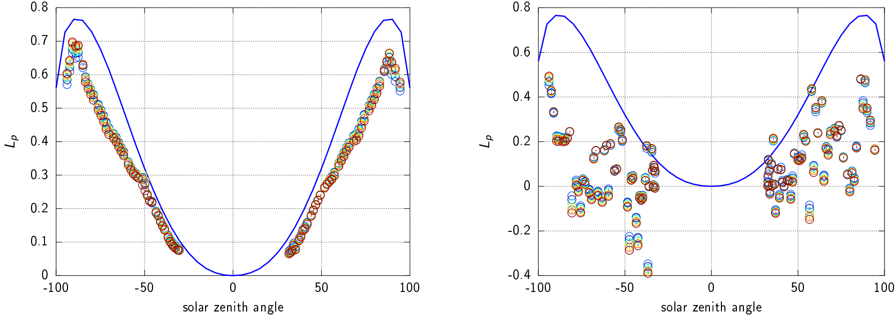
Comparison among different algorithms



... and much smaller dependence on wavelengths misalignments (**crosses**: `hg` test misalignments on same scale)

Field measurement campaigns

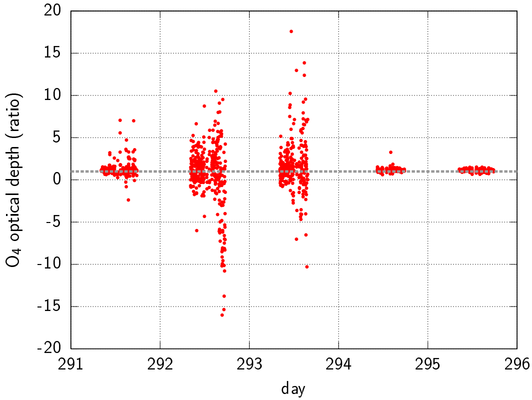
Other retrievable quantities



New product: degree of linear polarisation of the sky
(**left**: clear sky; **right**: fog)

Field measurement campaigns

Other retrievable quantities



New product: oxygen dimer (O_2–O_2) optical depth
(too weak absorption by H_2O in the blue band)

The Brewer #066 calibration can be successfully transferred

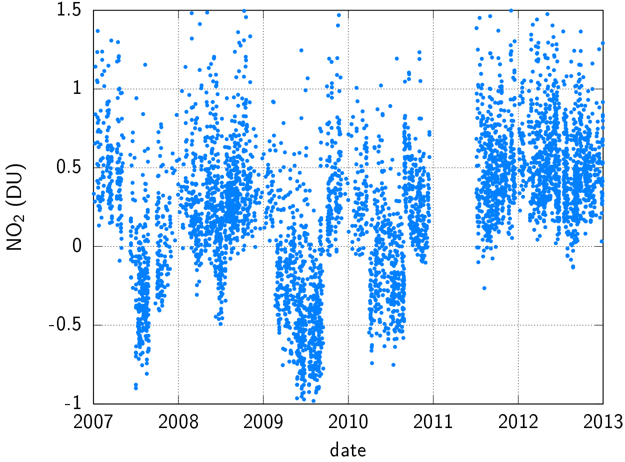
Reprocessing of long-term data sets

The stations

"Minimum-Amount Langley Extrapolation"
and "Bootstrap Estimation" techniques
Herman (2009)

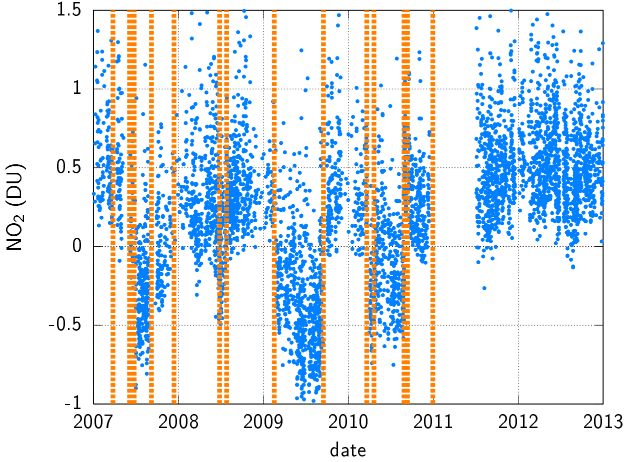
Reprocessing of long-term data sets

Wavelength misalignments



Athens, Brewer #001

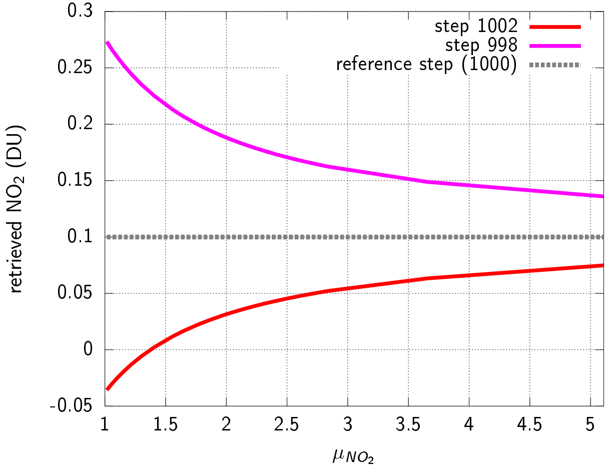
Reprocessing of long-term data sets
Wavelength misalignments



Athens, Brewer #001

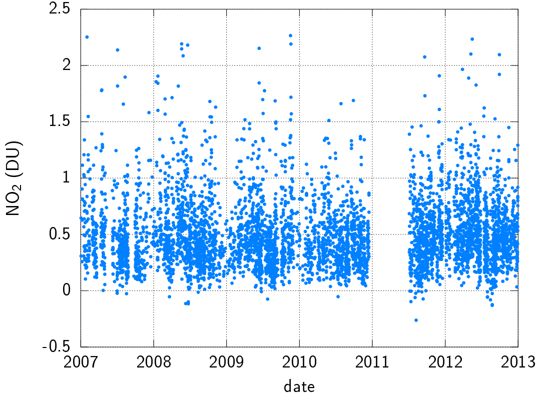
Reprocessing of long-term data sets

Wavelength misalignments



Reprocessing of long-term data sets

Wavelength misalignments



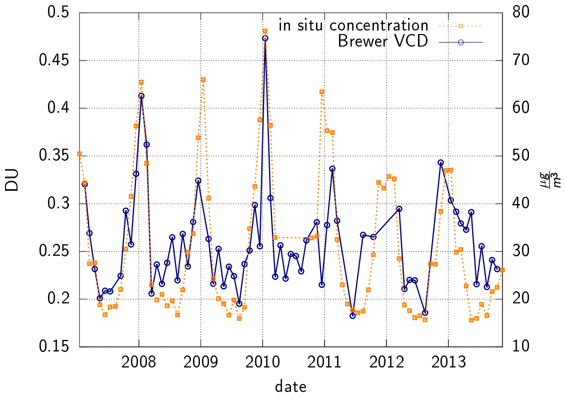
“Piecewise” calibration
Athens, Brewer #001

station	IQR (DU) new algorithm	IQR (DU) old algorithm	overestimation by old algorithm
Saint-Christophe	0.19–0.3	1.0–1.3	340%
Hradec Králové	0.3–0.5	1.3–1.9	275%
Rome	0.28–0.6	1.2–1.8	275%
Athens	0.3–0.7	0.8–1.5	120%

Years: 2007–2013

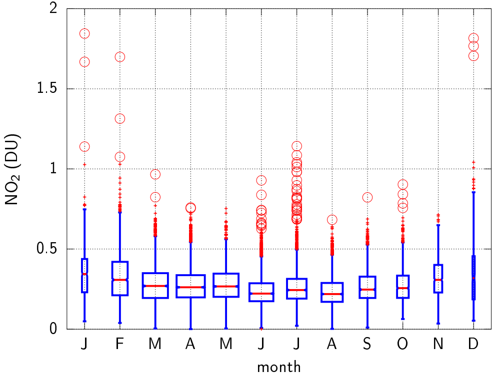
Reprocessing of long-term data sets

Correlation with in situ concentrations



Aosta, Brewer #066 (monthly averages)

Spearman's $r_s = 0.7$ when compared to *in situ* concentrations

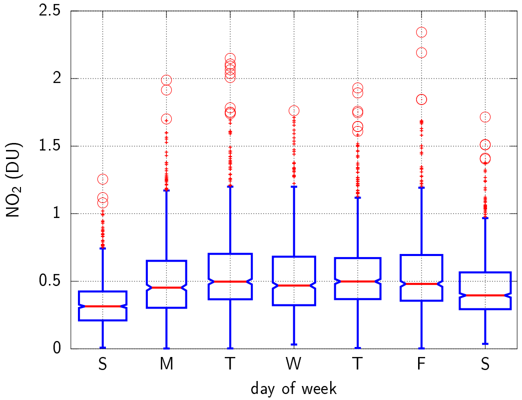


Aosta, Brewer #066

- temperature inversions and stagnation
- increased photolysis during summer
- increased NO_2 lifetime during winter (lower temperatures)
- increased emissions in winter

Reprocessing of long-term data sets

Weekly cycle

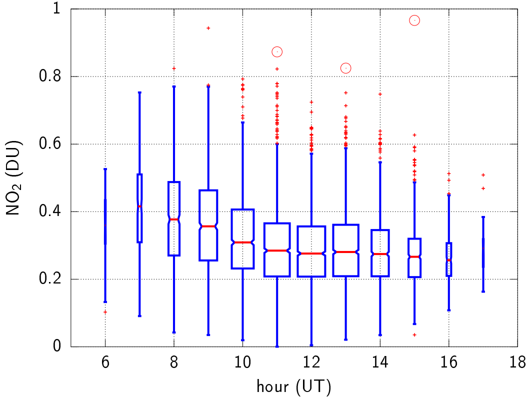


Rome, Brewer #067

Significant differences between weekdays and weekends in all analysed stations

Reprocessing of long-term data sets

Daily cycle



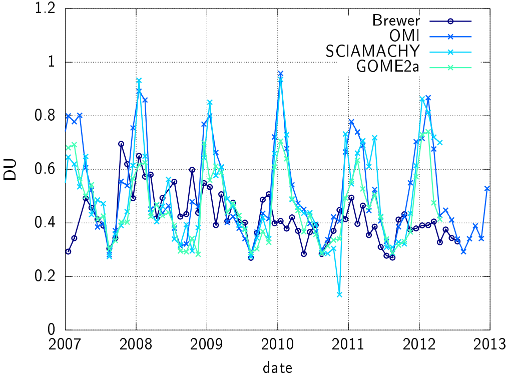
Aosta, Brewer #066

Morning rush hours – No (inverse-)U shape

Reprocessing of long-term data sets

Spaceborne estimates

- much more comparable, now overall bias -2.4%
- low correlation
- lack of seasonality compared to satellites



Rome, Brewer #067
Monthly averages

Future research

- AOD retrieval at 440 nm (STSM)
- more accurate Brewer-satellites comparison (STSM)
- Ring effect
  - more accurate zenith sky measurements
- stratosphere-troposphere partitioning (ds + zs)
- Moon measurements (already started)