Table 1: Spectroscopic datasets used in the standard and new algorithms.

Species	standard algorithm	new algorithm
Rayleigh	same as for O_3 retrieval	Bodhaine et al. (1999)
NO_2	Johnston and Graham (1976), 298 K	Vandaele et al. (2002), 220 K
O_3	Vigroux (1952), 291 K	Bogumil et al. (2003), 223 K
O_2-O_2	not considered	Hermans et al. (2003)
H_2O	not considered	Rothman et al. (2009)

Table 2: Wavelengths and NO_2 weighting coefficients used within the old (Kerr, 1989) and new method at the corresponding grating positions (microsteps 1000 and 1012, respectively).

Slit	old wavelength (nm)	old γ_i	new wavelength (nm)	new γ_i
1	425.104	0	425.236	0.033
2	431.455	0.10	431.586	0.176
3	437.413	−0.59	437.542	−0.510
4	442.893	0.11	443.021	−0.044
5	448.150	1.2	448.276	0.741
6	453.272	−0.82	453.397	−0.396

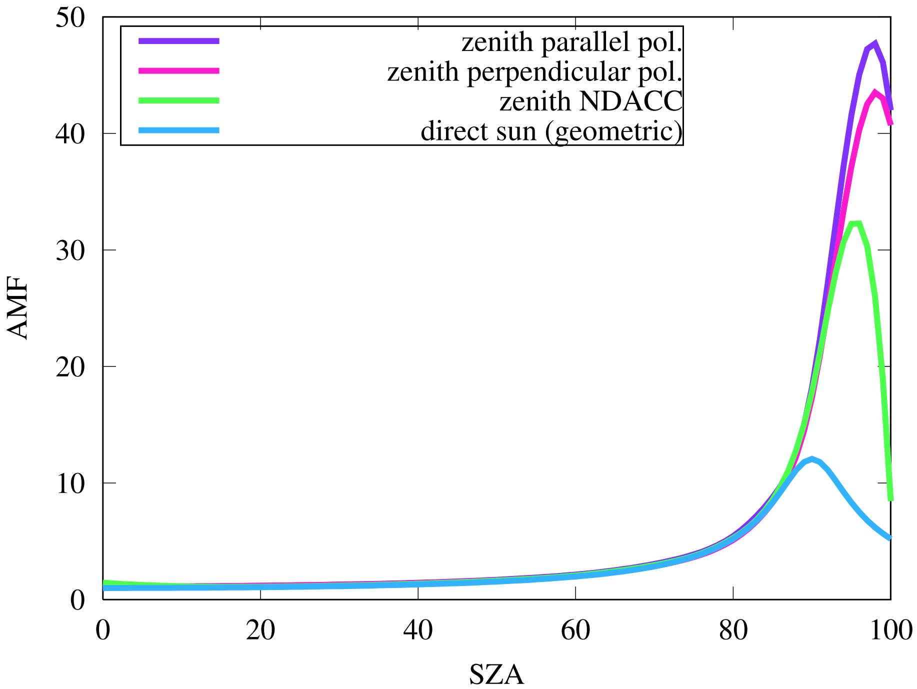

Figure 1: Air mass factors at 430 nm calculated in the zenith direction for both polarisations using the full-spherical SCIATRAN model (Rozanov et al., 2014) and the zenith AMFs suggested by NDACC for the Izaña station, as a function of the solar zenith angle. The geometric air mass as used by the standard Brewer algorithm is also depicted for comparison (the NO_2 effective height is assumed to be 22 km by the standard algorithm).

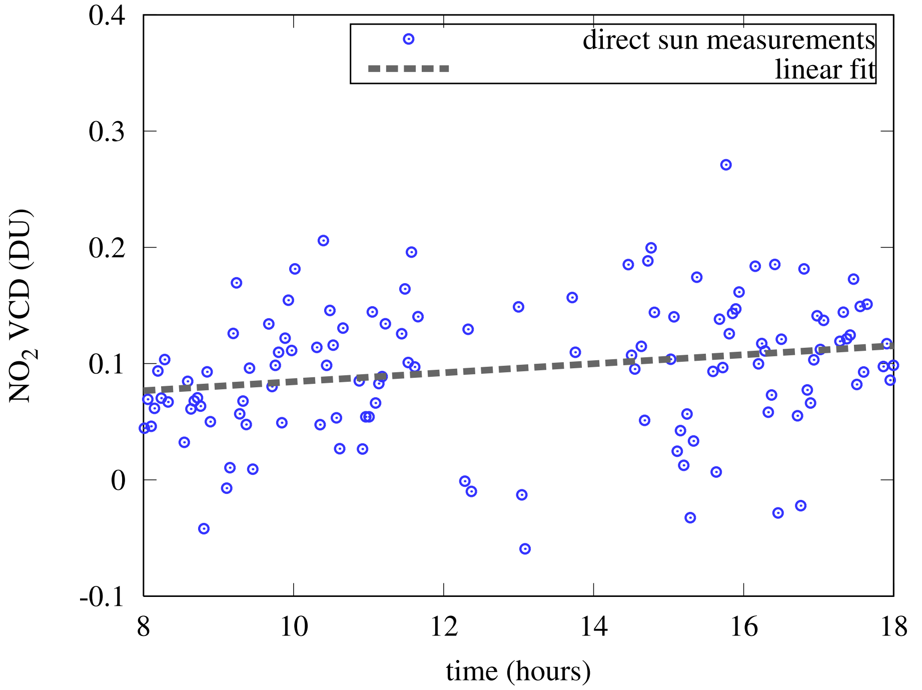

Figure 2: Direct sun VCD measurements at Izaña on day 269 together with a first-order regression line. Despite the high measurement noise, a slight daily evolution can be identified and is about 10^{14} molecules $\mathrm{cm}^{-2}\,\mathrm{h}^{-1}$ on the selected day.

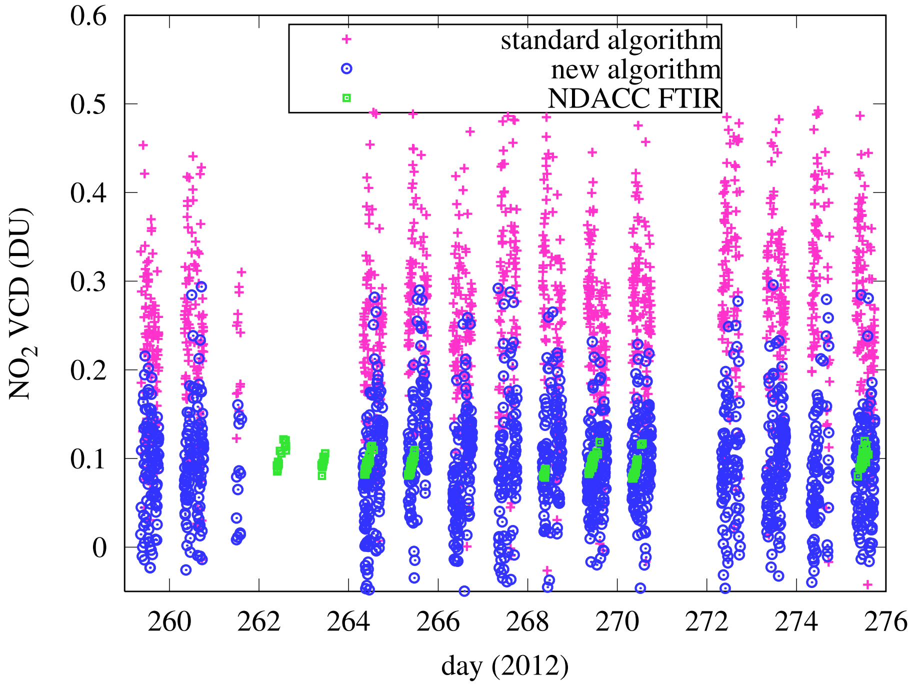

Figure 3: A subset of the NO_2 vertical column densities (VCDs) retrieved in the direct sun geometry during the Izaña calibration campaign. The Brewer data obtained with the grating at the standard position were analysed with the standard algorithm, while the data at the optimised grating position were processed with the new method. FTIR measurements are represented as green squares.

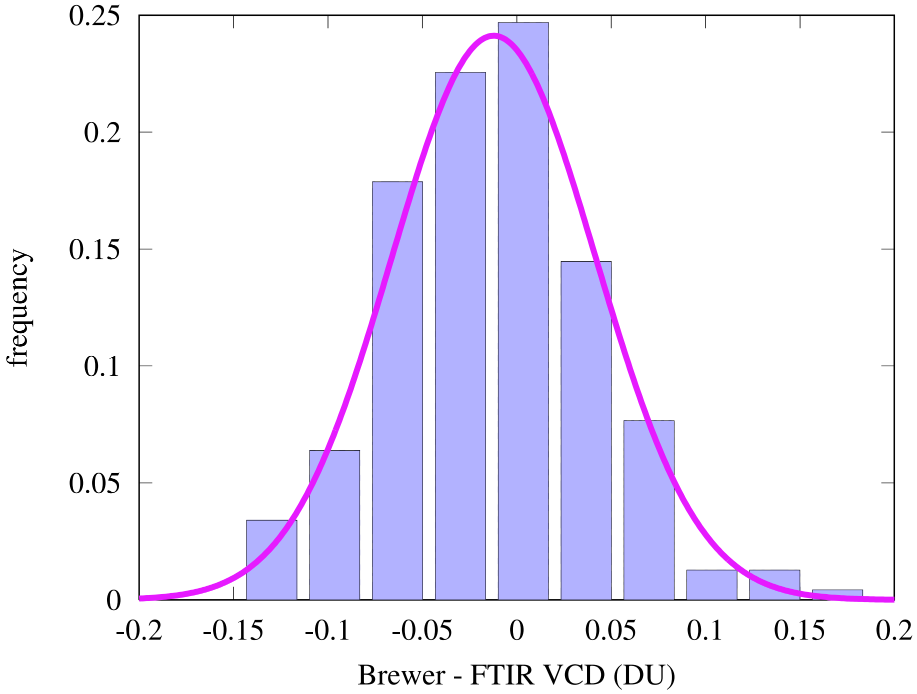

Figure 4: Histogram of the differences between the Brewer and the FTIR estimates in the direct sun geometry. The line represents a normal distribution with same mean (-0.01 DU) and standard deviation (0.05 DU) as the sample distribution.

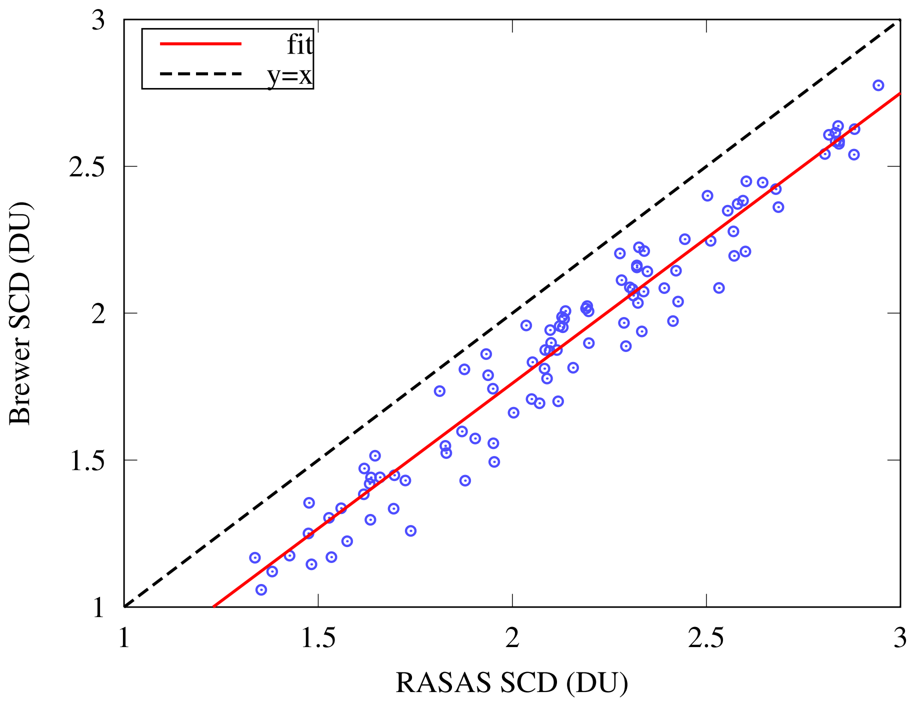

Figure 5: Scatterplot between twilight SCDs by the Brewer (zenith sky, perpendicular polarisation) and the reference RASAS-II spectrometer. Intercept: -0.2 DU; slope: 0.99; R^2: 0.95.

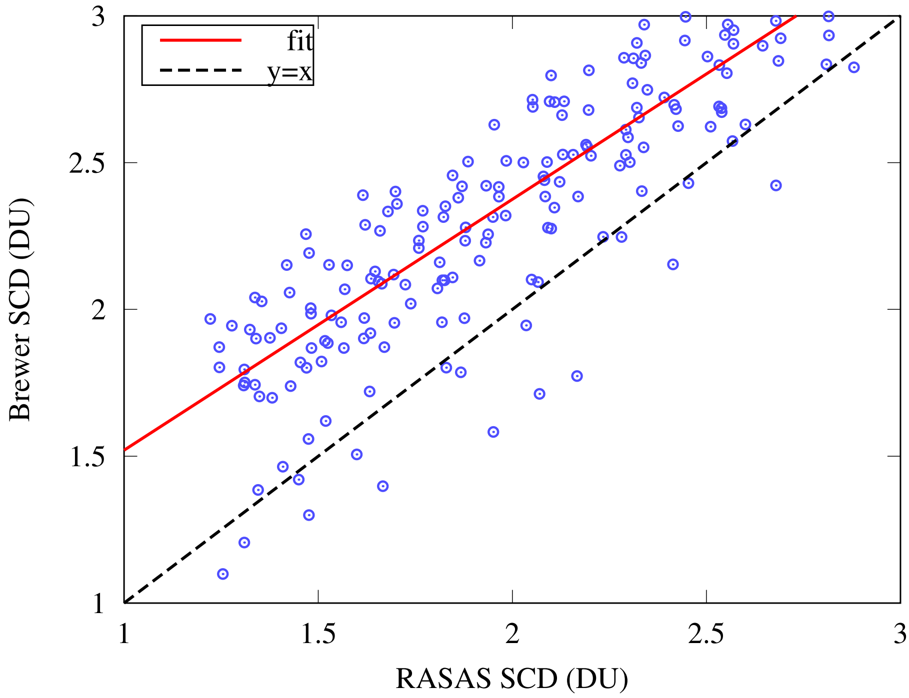

Figure 6: Same as in Fig. 5, with the Brewer operating in parallel polarisation. Intercept: 0.7 DU; slope: 0.85; R^2: 0.76.

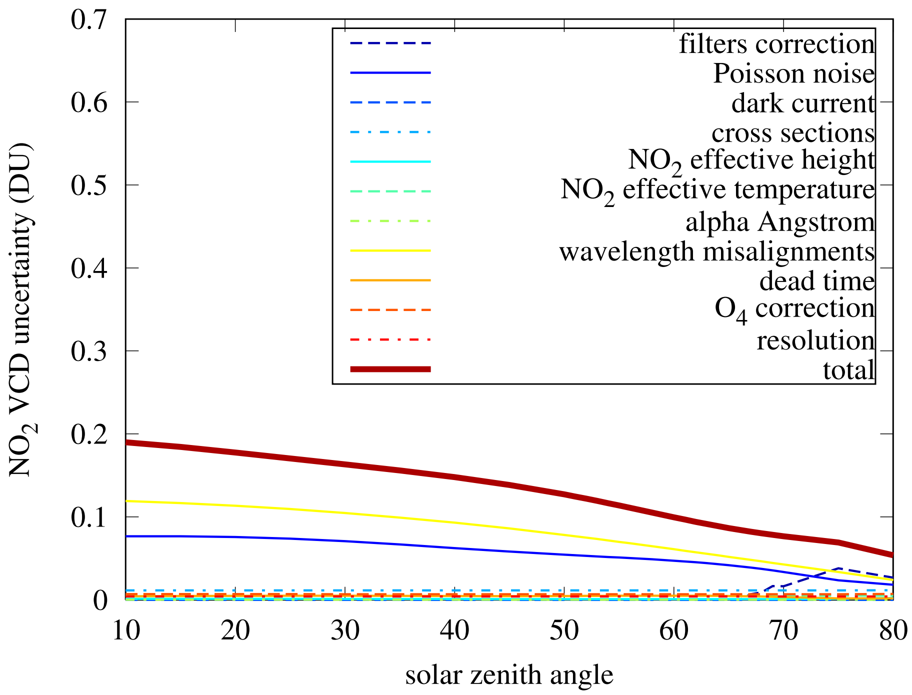

Figure 7: Monte Carlo standard uncertainty for Brewer NO_2 measurements in direct sun geometry in Izaña (NO_2 set to 0.1 DU).

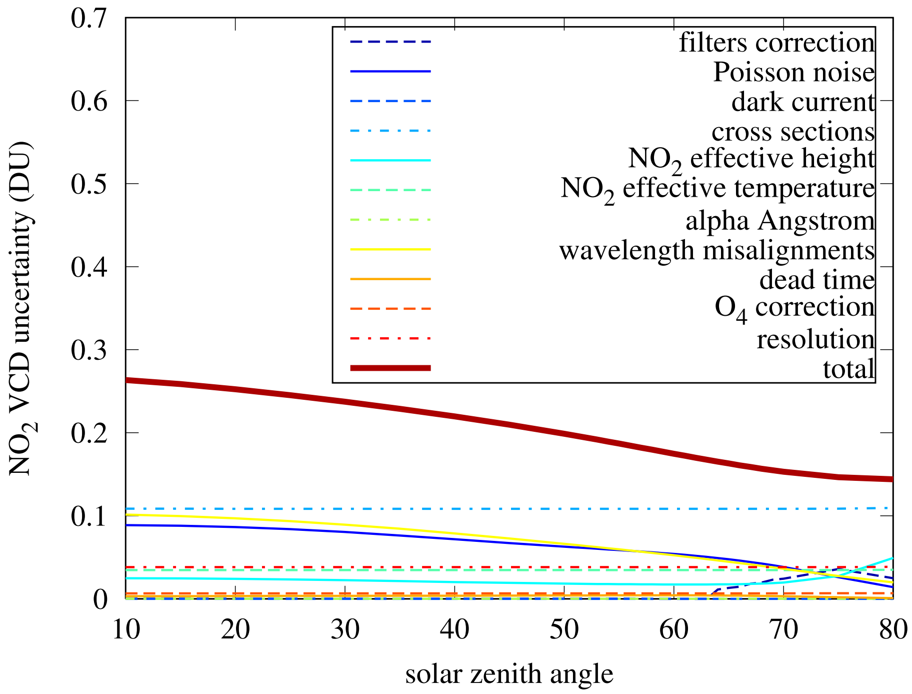

Figure 8: Monte Carlo standard uncertainty for Brewer NO_2 measurements in direct sun geometry in a polluted site (NO_2 VCD assumed to be 0.1 DU during the calibration phase and 1 DU during measurements).

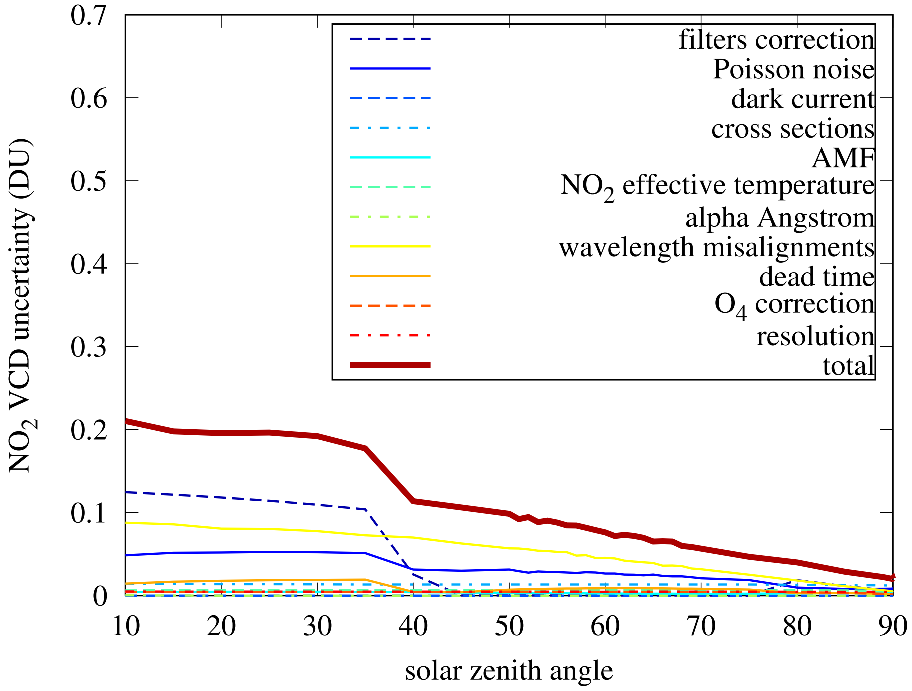

Figure 9: Monte Carlo standard uncertainty for Brewer NO_2 measurements in the zenith sky geometry and parallel polarisation in Izaña (NO_2 set to 0.1 DU).

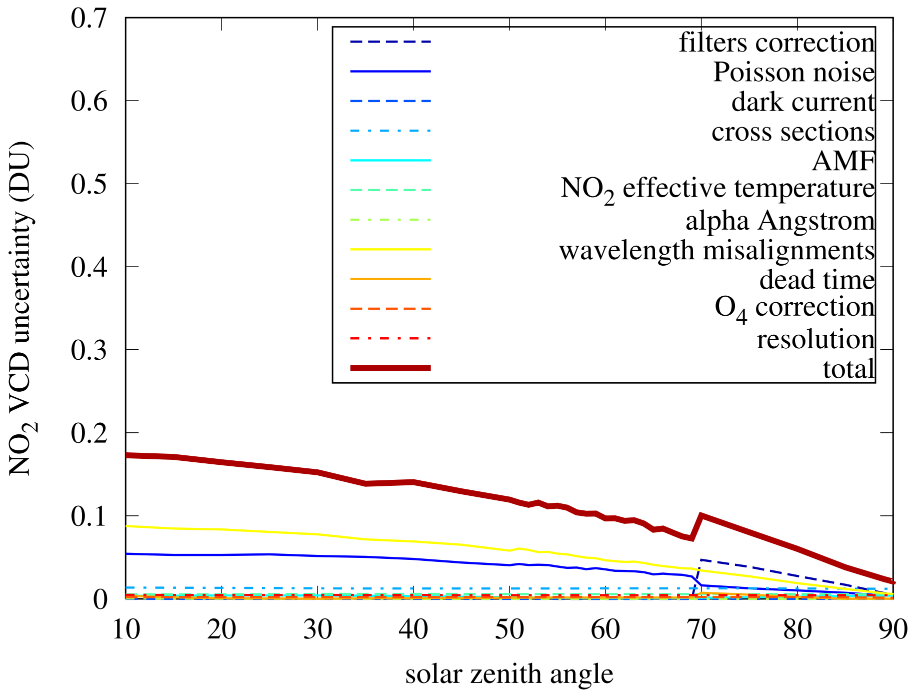

Figure 10: Monte Carlo standard uncertainty for Brewer NO_2 measurements in the zenith sky geometry and perpendicular polarisation in Izaña (NO_2 set to 0.1 DU).

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