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Improved retrieval of nitrogen dioxide (NO_2) column densities by means of MKIV Brewer spectrophotometers

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Abstract

A new algorithm to retrieve nitrogen dioxide (NO_2) column densities using MKIV Brewer spectrophotometers is described. The method includes several improvements, such as a more recent spectroscopic dataset, the reduction of the measurement noise and interferences by other atmospheric species and instrumental settings, and a better determination of the air mass enhancement factors. The technique was tested during an ad-hoc calibration campaign at the high-altitude site of Izaña (Tenerife, Spain) and provided results compatible to those obtained from a spectrometer associated to the Network for the Detection of Atmospheric Composition Change (NDACC), with deviations of less than 0.02 DU. To determine the extraterrestrial constant, an easily implementable generalisation of the standard Langley technique was developed which takes into account the daytime linear drift of nitrogen dioxide due to the photochemistry. Estimates obtained from different observation geometries, by collecting the light from either the sun or the zenith sky, were found to be comparable within the measurement uncertainty. The latter was thoroughly determined by using a Monte Carlo technique. Finally, a method to retrieve additional products such as the degree of linear polarisation of the zenith sky and the oxygen dimer optical depth is presented. The new algorithm is backward-compatible, thus allowing for the reprocessing of historical datasets.

1 Introduction

Nitrogen dioxide (NO_2) is a key component of the Earth's atmosphere. Despite its low concentration, it drives several chemical reactions leading to both destruction and preservation of ozone (O_3) in the stratosphere (Hampson, 1964; Crutzen, 1970; Jones et al., 1989) and photochemical smog in the troposphere (Haagen-Smit, 1952). Furthermore, NO_2 absorbs solar radiation, thus impacting on the radiative balance of the planet (Solomon et al., 1999) and interfering with sun photometric measurements, such as the aerosol optical depth (Shaw, 1976).

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In 1985, an automated Brewer ozone spectrophotometer was modified to add capability to measure solar visible radiation and retrieve atmospheric nitrogen dioxide (Kerr, 1989), based on the differential optical absorption technique (Brewer and McElroy, 1973). Nowadays, the Brewer network consists of about 195 instruments installed in 44 different countries throughout the world (Kumharn et al., 2012). Among them, according to the World Ozone and Ultraviolet radiation Data Center (WOUDC, http://www.woudc.org/), more than 60 MKIV Brewer spectrophotometers have been put in operation and long-term nitrogen dioxide records have been collected at the respective stations. Unfortunately, the original algorithm has never been officially updated and exhibits several limitations that prevent the users from confidently employing the measured data for accurate analyses. Remarkable overestimations, up to 100 %, by the Brewer were detected in a wide range of intercomparison campaigns (McElroy et al., 1994; Barton, 2007) along with random deviations, as large as 30 % (Hofmann et al., 1995). Even comparisons between MKIV Brewers and satellite radiometers generally show similar issues (Francesconi et al., 2004).

Notable efforts have been done in the last years to improve the NO_2 retrieval by the Brewer, both in the UV-A band with direct sun measurements (Cede et al., 2006) and in the visible wavelength range by collecting the diffuse light from the zenith (Barton, 2007). Nevertheless, high-quality estimates of nitrogen dioxide by the Brewer are still difficult to acquire, mainly owing to the measurement noise drowning out the weak NO_2 signal, the effects of instrumental inaccuracies, such as slight wavelength misalignments, and the influence by the atmospheric species absorbing in the same wavelength range (e.g., the oxygen dimer, O_2–O_2, and water vapour, H_2O, in the visible). Finally, no on-site service exists to track the NO_2 calibration of the Brewer instruments operating worldwide.

A previous study (Diémoz et al., 2013) proved the feasibility of an updated method to retrieve nitrogen dioxide with MKIV Brewers. The present work describes the first application of this algorithm to real data and its validation during an ad-hoc field campaign at a high-altitude site. The results will help not only to henceforth collect high-accuracy data series, but also to reprocess with higher accuracy the long-term raw datasets recorded at the existing measuring stations.

2 Instrument

The MKIV Brewer spectrophotometer (Kipp & Zonen, 2007) collects the solar light reaching the ground from either the sun or the zenith sky. One of the two observation geometries is selected through the use of a reflective prism (to set the elevation angle of the field of view) and a solar tracker (adjusting the azimuth angle). Zenith sky measurements can be performed at two perpendicular, linear polarisations, depending on the tracker position, in a parallel or perpendicular direction to the scattering plane. The light is then dispersed into its spectrum by a holographic plane diffraction grating, rotated by a high-precision stepper motor and operated in the second order. A rotating slit mask at the exit of the monochromator allows the nearly simultaneous measurement of the intensity of the beam at up to six different wavelengths, whose spacing is defined by the distances between the six apertures and the wavelength dispersion at the focal plane. When measuring NO_2, the default grating position is normally chosen so that the wavelengths are between about 426 and 453 nm, a spectral range with strong differential structures and close to the maximum absorption by NO_2. However, the grating can be rotated to span a full spectral range of about 420–500 nm. The resolution usually ranges from 0.6 to 0.9 nm full width at half maximum (FWHM), depending on the slit and the Brewer type. A photomultiplier tube (PMT) is employed to analyse the intensity of the beam emerging from the monochromator and is maintained in its linearity regime with the help of a set of neutral density filters installed in the foreoptics.

One MKIV Brewer (serial number #066) was thoroughly characterised in the visible range. Several spectral lines from three discharge lamps (Hg, Cd and Ne) were scanned to assess the instrumental resolution and the wavelength dispersion. The latter was then parameterised with an accurate fitting function (Gröbner et al., 1998).

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Additionally, the spectral transmission of each neutral density filter was determined using the standard lamp installed inside the instrument.

3 Algorithm

This section summarises the updated NO_2 retrieval method described in more detail by Diémoz et al. (2013). As in the standard Brewer algorithm (Kerr, 1989), the Bouguer–Lambert–Beer formula (Bouguer, 1729) is applied to the solar irradiances I_i measured at several wavelengths λ_i and the logarithms of the irradiances are linearly combined to remove the interference of other species different from nitrogen dioxide, i.e.

$$\sum_i \gamma_i \log I_i = \sum_i \gamma_i \log I_{0_i} - \mu_{NO_2} X_{NO_2} \sum_i \gamma_i \sigma_{NO_2 i} - \sum_j \mu_j \sum_i \gamma_i \tau_{ji} \quad (1)$$

I_{0_i} denotes the flux that would be measured outside the Earth's atmosphere through the ith slit and represents a calibration constant typical of each instrument; μ indicates the air mass enhancement factor (AMF) of the different species; X_{NO_2} is the vertical column density (VCD) of nitrogen dioxide, the quantity to be determined by the retrieval procedure; the absorption cross sections of nitrogen dioxide at wavelength λ_i are expressed by $\sigma_{NO_2 i}$; the j subscript identifies the atmospheric species different from NO_2; finally, τ_{ji} is the optical depth of the jth species at wavelength λ_i. If the weighting coefficients γ_i are properly chosen, the last sum is cancelled out and X_{NO_2} can be determined provided that the extraterrestrial constant (ETC) of the instrument (first term at the right member) is known.

Compared to the standard algorithm, the new method brings several improvements:

1. while the former makes use of the irradiances recorded at only 5 wavelengths and minimises the influence by the Rayleigh scattering, ozone absorption, aerosol extinction and spectrally-flat factors, the new algorithm includes the measurements that are routinely performed (and recorded) through all the six slits. The additional

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degree of freedom, compared to the standard algorithm, is used to find a combination of the coefficients γ_i that maximise the sensitivity to NO_2 and minimise the measurement noise;

2. the spectroscopic dataset employed in the algorithm to calculate the weighting coefficients and the differential absorption cross section was updated to more recent laboratory results (Table 1) according to the recommendations by the Network for the Detection of Atmospheric Composition Change (NDACC) (Van Roozendael and Hendrick, 2012). Furthermore, since I_i is actually the convolution between the solar irradiance spectrum and the instrumental bandwidth at each slit, the cross sections have been downscaled to the Brewer resolution by adopting the formula by Aliwell et al. (2002):

$$\sigma_{\text{corrected}}(\lambda') = -\frac{1}{X}\log\left\{\frac{\int I_0(\lambda)\exp[-\sigma(\lambda)X]W(\lambda-\lambda')\mathrm{d}\lambda}{\int I_0(\lambda)W(\lambda-\lambda')\mathrm{d}\lambda}\right\} \quad (2)$$

where X is an a priori value for X, σ the laboratory cross section and W the slit function. This approach mitigates the so-called "I0-effect", since in actual measurements the spectra – and not their logarithm – are filtered by the slit function;

3. an optimal position of the grating, i.e. an optimal set of measuring wavelengths, was found that further reduces the measurement noise and minimises the interferences on the retrieval by the oxygen dimer, water vapour, the Ring effect (Grainger and Ring, 1962), the NO_2 effective temperature in the atmosphere and slight instrumental wavelength misalignments. This required to accurately simulate all the previous factors as a function of the grating position by perturbing the Brewer equation (Eq. 1). The resulting grating position depends on both the spectral dispersion and resolution of a specific instrument. The final set of wavelengths and weighting coefficients (γ_i) for Brewer #066 are presented in Table 2;

4. the residual interference by the oxygen dimer has been corrected through the use of a radiative transfer model (Rozanov et al., 2014) taking into account the

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atmospheric pressure at the measurement site, whereas the influence by O_2–O_2 is totally neglected in the standard algorithm;

5. the effect introduced by slight deviations from neutrality in the density filters is now taken into account in the retrieval as a correction factor which depends on the selected filter;

6. the air mass enhancement factors for zenith sky measurements were calculated in both polarisations with the help of a full-spherical vector radiative transfer model (Rozanov et al., 2014) using the finite difference method (Rozanov and Rozanov, 2010). Vertical profiles obtained from a 2-D chemo-dynamical model (Brühl and Crutzen, 1993) were employed for the purpose. It is worth citing, on the other hand, that the standard Brewer algorithm incorrectly uses direct sun AMFs for all geometries of observation.

4 Calibration campaign

A field measurement campaign took place at the Izaña Atmospheric Research Center, Tenerife, Canary Islands (28.31° N, 16.50° W, 2400 m a.s.l.) in September and October 2012. The site, which is described in more details by Gil et al. (2008), was chosen to achieve the maximum atmospheric stability necessary for an accurate calibration. Measurements in direct sun and zenith sky (at two polarisations) observation geometries were continuously taken during daylight hours for a total of 38 days, among which only 5 were discarded due to rain or fog. To collect as many points as possible, as required by the Langley technique, the number of samples to average for each measurement were reduced from 100 (default for direct sun) or 140 (zenith sky) to 16 for both geometries.

The standard Langley calibration technique can be rigorously applied only in the case when the absorber vertical column is constant during at least half a day. If this condition is met, Eq. (1) can be represented as a straight line when the linear combination (left

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side of the equation) is plotted as a function of the air mass factor μ. The calibration constant (first term at the right side) is then the intercept of the linear regression of the observations. However, in the present case, the NO_2 concentration increases during the day due to N_2O_5 photolysis (Evans et al., 1976) and the Langley technique cannot be applied in its standard formulation. To overcome the issue, many authors (e.g., Roscoe et al., 2001) modified the method by introducing photochemistry-corrected air mass factors. In order to avoid using complex photochemical models, we generalised the Langley technique to include a linear drift of the absorber with time. Indeed, previous studies at the same measurement station (Gil et al., 2008) have already confirmed that the NO_2 column linearly increases with time during the day for solar zenith angles below about 80°. Therefore, Eq. (1) was rewritten by explicitly taking into account the dependence on time, t:

$$\sum_i \gamma_i \log I_i = \sum_i \gamma_i \log I_{0_i} - \mu_{NO_2}(t) X_{NO_2}(t) \sum_i \gamma_i \sigma_{NO_2 i} \tag{3}$$

Assuming that

$$X_{NO_2}(t) = \eta(t - t_0) + \xi \tag{4}$$

where η is the NO_2 daytime increasing rate and ξ the NO_2 VCD at time t_0, the solution is easily provided by inverting an overconstrained system, e.g. by calculating a pseudoinverse matrix. The average increasing rate retrieved through the inversion is $(8.2 \pm 1.2) \times 10^{13}$ molecules cm^{-2} h^{-1} and agrees with previous literature (e.g., Sussmann et al., 2005; Gil et al., 2008; Peters et al., 2012), thus proving the effectiveness of the method.

The calibration constants for each geometry were calculated from the data gathered at AMFs between 1.5 and 3.5. Lower AMFs are not considered because the rate of change of the airmass and the NO_2 absorption are small, whilst atmospheric turbulence at midday is large. Higher AMFs are avoided due to possible shadows by the quartz window border in the field of view and steep variations of NO_2 owing to the photochemistry.

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5 Results

5.1 Comparison between standard and improved algorithm

A subset of the data series recorded in the direct sun geometry during the Izaña campaign is displayed, as an example, in Fig. 1. The same set of data was processed with both the standard algorithm and the new method taking into account the respective calibration constants. The results with the new algorithm agree well with both the expected stratospheric VCD for the clean site of Izaña and the climatological values reported by Gil et al. (2008), i.e. about 0.07–0.13 DU (morning and afternoon, respectively) in the campaign period. Conversely, the retrieval by the standard algorithm remarkably overestimates, with values about 200 % higher than the new algorithm. These results are in good agreement with previous model studies (Diémoz et al., 2013). Some negative VCDs may be found due to either the measurement noise, the atmospheric turbulence and thin clouds which were not filtered by the cloudscreening algorithm.

5.2 Comparison among different observation geometries

Results using different geometries are depicted in Fig. 2. Substantial agreement is visible between the retrieval in direct sun and perpendicular polarisation geometries in their respective AMF ranges (the average offset between direct sun and zenith sky measurements being 0.009 DU), while zenith sky estimates in parallel polarisation are generally higher (mean difference between zenith sky and direct sun measurements of 0.023 DU), although still within the measurement uncertainty (Sect. 6). In principle, the discrepancies between the retrievals could be due to inaccuracies in determining the ETC in either one or both polarisations. However, no better results throughout the full range of AMFs were found by perturbing the values of the calibration constants, which degrades the comparison at either low or high AMFs. Rather, the influence of the Ring effect on measurements in parallel polarisation may be the main reason of the

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observed behaviour, as found by Barton (2007), and further study is needed on this issue.

The retrieved VCDs generally show an increase from the morning to the evening, in agreement with the photochemistry of NO_2. Additionally, the plot clearly reveals that the measurement variability is higher at high AMFs (fewer photons recorded by the instrument and more noise) and at very low AMFs (higher turbulence at midday and lower absorption by NO_2 in the solar path).

5.3 Comparison to a reference NDACC instrument

Measurements taken at twilight by the Brewer can be compared to nearly-simultaneous ($\Delta t = 10$ min) estimates by a co-located UV-VIS spectrometer operated by the Instituto Nacional de Technica Aerospacial (INTA) and associated to the NDACC. The reference spectrometer, which is designed to retrieve the stratospheric column of NO_2, points to the zenith sky and is based on the Differential Optical Absorption Spectroscopy (DOAS) principle (Gil et al., 2008). Figure 3 shows the scatterplot between the data series recorded by both instruments (the Brewer operating in the perpendicular polarisation). Two groups of data can be identified and refer to dawn and dusk, respectively. Deviations of 0.01–0.02 DU may be noticed between the series (slope: 1.15; intercept: −0.03 DU). Although the discrepancies are very low and far below the uncertainties of both instruments, some possible reasons of the observed behaviour are worth being mentioned:

1. the spectroscopic datasets used to retrieve the NO_2 VCDs with both instruments are not responsible for the differences, since both algorithms use the same set of cross sections at the same temperatures;

2. different parameterisations of the AMFs by the two instruments could account for part of the deviations. Indeed, it is not possible to use the NDACC air mass factors with the Brewer, since the latter collects polarised radiances and requires vector calculations of the AMFs (different for parallel and perpendicular polarisations);

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3. due to the measurement schedule of the reference instrument, direct sun estimates by the Brewer could not be employed for the comparison. On the other hand, observations of diffuse light at the zenith by the Brewer are certainly affected by the Ring effect. The latter is, however, hard to quantify even using state-of-the-art radiative transfer models (which should include full-spherical, polarisation and rotational Raman scattering (RRS) capabilities at the same time);

4. finally, the spanned range of VCDs is rather short to allow an accurate comparison between both data series.

It must be noted that the root mean square (RMS) residual of the fit between the two datasets (0.10 DU) can be further decreased by averaging a larger number of the samples for each measurement.

5.4 Supplementary products

From the Brewer zenith measurements at both polarisations it is possible to determine without any further effort the degree of linear polarisation of the sky, defined as (Coulson, 1988)

$$L_p(\theta) \equiv \frac{I_\perp - I_\parallel}{I_\perp + I_\parallel} \quad (5)$$

where $I_\perp$ and $I_\parallel$ are the radiances measured in the perpendicular and parallel polarisations, respectively. L_p is a new product not included in the standard processing and can give useful information about aerosols properties (optical depth and effective radius of particles) in the atmosphere (McLinden et al., 2001) as well as about the cloud cover, since both factors affect the scattering characteristics in the atmosphere. Additionally, such measurements in the MKIV Brewer range are even more interesting than in the UV, since the interference by the Rayleigh scattering is less strong in the former case compared to the latter.

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Figure 4 shows the degree of linear polarisation along the zenith as a function of the solar zenith angle (SZA), as calculated with the radiative transfer model and measured by the Brewer. The figures represent a clear sky and a foggy day, respectively. The effects of the different atmospheric conditions on L_p are sharply distinguishable. Even in the clear sky case, some deviations between the model and the measurements persist. The latter are probably not due to the model (no reasonable change in the model input data provides the same shape), but rather to an efficiency of the Brewer polarising filters lower than 100 %. For example, an efficiency of about 95 %, which sounds quite realistic (A. Cede, personal communication, 2014), could reproduce the observed behaviour.

An additional and new product retrievable by MKIV Brewers is the optical depth of the oxygen dimer (O_2–O_2), which is an interesting parameter both in aerosol applications and for cloudscreening purposes (Daniel et al., 2003; Wagner et al., 2004). Indeed, a relatively strong absorption band falls within the instrumental wavelength range, with a maximum at about 477 nm. The O_2–O_2 retrieval may be performed by finding a set of weighting factors, as was done for NO_2, which maximise the sensitivity to the absorber, remove the contribution by ozone absorption, Rayleigh scattering, aerosol excintion and a spectrally flat term and minimise the other factors, including NO_2. The new set of weightings are shown in Table 3 together with the operational wavelengths used for the O_2–O_2 retrieval. The expected measurement noise is less than 7 % for 100 samples. An example of the retrieval during the last days of the Izaña campaign is shown in Fig. 5 as a ratio between the measured and expected O_2–O_2 optical depth for a standard tropical atmosphere (Anderson et al., 1986) at the Izaña altitude. The presence of clouds may be easily noticed in the plot as large scatter of the data, whereas measurements during clear sky days approach unity, as expected.

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6 Uncertainty budget

The uncertainty estimate in Brewer measurements is a complex task owing to the large number of the involved parameters and their reciprocal correlations. In this section, only the relatively simple case of direct sun measurements will be discussed as a proof of concept. Moreover, it is assumed that the Brewer operates at the same site where the Langley plot was performed and that the surrounding conditions do not relevantly changes compared to the calibration period. This case is likely to provide the minimum uncertainty attainable by the method proposed in the work.

Since an analytic assessment of the uncertainty is not feasible and the influence of the various factors on the retrieved NO_2 is expected to be non-linear, a Monte Carlo method (MCM) approach (BIPM et al., 2008) is adopted. Several sources of uncertainties, both in the calibration and the measurement phase, are considered taking into account the instrumental characteristics of Brewer #066:

1. to calculate the effect on the retrieval, random noise was artificially added to the measured count rates during both the Langley calibration and the measurements, using samples from a Poisson distribution centred at the measured number of photons, and scaled corresponding to the number of samples recorded at each measurement;

2. the standard deviation of the spectral attenuations of the neutral density filters measured during the diagnostic internal tests was used to assess the uncertainty in the filter correction. However, since potential uncertainties in the evaluation of the filter correction influence for the same amount the calibration and the measurement phases and cancel out if the same filter is used for a certain SZA, the measurements were randomly perturbed by simulating the effect of thin clouds successfully passing the cloudscreening algorithm. The filters were then simulated to switch as a function of the intensity of the solar light;

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3. an uncertainty in the operational wavelengths of 0.02 nm was assumed based on some tests and previous literature (e.g., Kerr and Davis, 2007). This value is higher than the accuracy provided by the internal mercury test;
4. the dead time was assumed to be determined within an uncertainty of 10 %;
5. diffuse light in the field of view of the instrument was assessed to be negligible in the visible range and for the Izaña conditions, according to radiative transfer calculations;
6. straylight in the monochromator was not considered in the study. It is however assumed to be negligible for visible wavelengths;
7. the uncertainties of the ozone and nitrogen dioxide laboratory cross sections were assumed to be 3 and 4 %, respectively, based on previous literature (see references in Table 1);
8. the effect of the aerosol Ångström exponent was assessed by varying its value between 0.2 and 1.6, based on the AERONET data gathered at Izaña in October 2012;
9. a conservative uncertainty of 10 % was assumed for the measured resolution at each slit;
10. 20 K and 5 km were taken as the uncertainties of the NO_2 effective temperature and height, respectively (Redondas and Cede, 2007);
11. an uncertainty of 30 % was assumed for the O_2–O_2 correction in the retrieval.

A large number (1000) of samples from the probability density functions (PDFs) of the above-mentioned factors were employed and the NO_2 retrieval was simulated at each iteration with a different set of variables. The standard deviation of all NO_2 retrievals was then taken as the standard (combined) uncertainty of the measurement as a function of the solar zenith angle. Figure 6 shows that the uncertainty ranges from 0.05

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to 0.19 DU with smaller values for large SZAs (due to the larger NO_2 absorption). It is worth noticing that the standard uncertainty can be approximately as high as twice the value of the measurements made in Izaña. The two largest contributions to the uncertainty are linked to the wavelength uncertainty and Poisson noise. The latter can be further reduced by increasing the number of samples (which were decreased for the Langley plot, as described in Sect. 4).

Finally, the relative uncertainty of the NO_2 retrievals is expected to drop for higher VCDs of nitrogen dioxide (i.e., more polluted conditions).

7 Conclusions

The new algorithm to retrieve the nitrogen dioxide by MKIV Brewers was tested using real data recorded during a calibration campaign at a high-altitude site. A generalisation of the Langley technique, taking into account the daytime increase of the NO_2 column, was developed to overcome issues related to the diurnal change in the absorber and was found provide results in agreement with the previous literature. The retrieval with the new algorithm no longer shows the overestimations which affect the standard method, which can be as large as 200 %, and is less influenced by the interferences from other species and instrumental factors. The method was validated by comparing the Brewer measurements to a reference NDACC spectrometer, with deviations of less than 0.02 DU. The results using different observation geometries (direct sun and zenith sky in parallel and perpendicular polarisations) were compared, providing estimates within their uncertainties (average deviations between direct sun and zenith sky estimates of 0.009 and 0.023 DU for perpendicular and parallel polarisations, respectively), those in the parallel polarisation being probably more affected by the Ring effect. Furthermore, a first attempt to fully address the assessment of the uncertainty of Brewer measurements was performed using the Monte Carlo technique. Although the combined uncertainty can be further reduced by increasing the number of samples for each measurement (thus decreasing the Poisson noise), a large contribution

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persists which is due to the uncertainty of the operating wavelengths and additional efforts are being done on this issue. Finally, the method was tested in a very clean environment, with a NO_2 contribution mostly from the stratosphere, however, the accuracy of the measurements is expected to improve in more polluted conditions. Partitioning between the stratospheric and the tropospheric NO_2 content, making use of nearly-simultaneous direct sun and zenith sky estimates by the Brewer, will be addressed in a future work.

Since every Brewer stores all raw data in its files, the method can be applied as well to reprocess past time series. A new set of weightings can be easily calculated for different Brewer instruments provided that the dispersion is well characterised. Additionally, statistical methods (e.g., Cede et al., 2006; Herman et al., 2009) are available to provide the necessary extraterrestrial calibration constant when a Langley campaign is not feasible.

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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)	Vandaele et al. (2002), 220 K
O_3	Vigroux (1952)	Bogumil et al. (2003), 223 K
O_2–O_2	not considered	Hermans et al. (2003)
H_2O	not considered	Rothman et al. (2009)

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Table 2. Wavelengths and NO_2 weighting coefficients used within the new method, together with the standard coefficients by Kerr (1989).

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

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Table 3. Wavelengths and weighting coefficients used to retrieve the O_2–O_2 optical depth.

Slit	wavelength (nm)	γ'_i (O_2–O_2)
1	454.961	−0.082
2	460.963	0.370
3	466.577	−0.380
4	471.728	−0.328
5	476.653	0.718
6	481.437	−0.298

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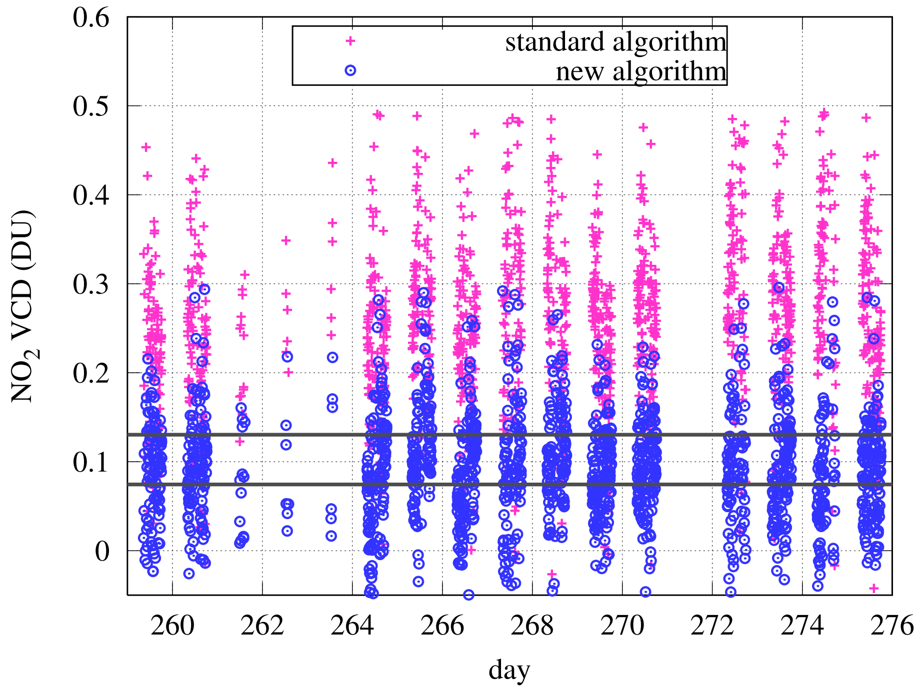

Figure 1. A subset of the NO_2 vertical column densities (VCDs) retrieved in the direct sun geometry during the Izaña calibration campaign. The same set of data was analysed with both the standard algorithm and the new method. The two horizontal lines represent the climatological VCDs for the morning (lower) and the afternoon (higher) in the period of the campaign according to Gil et al. (2008).

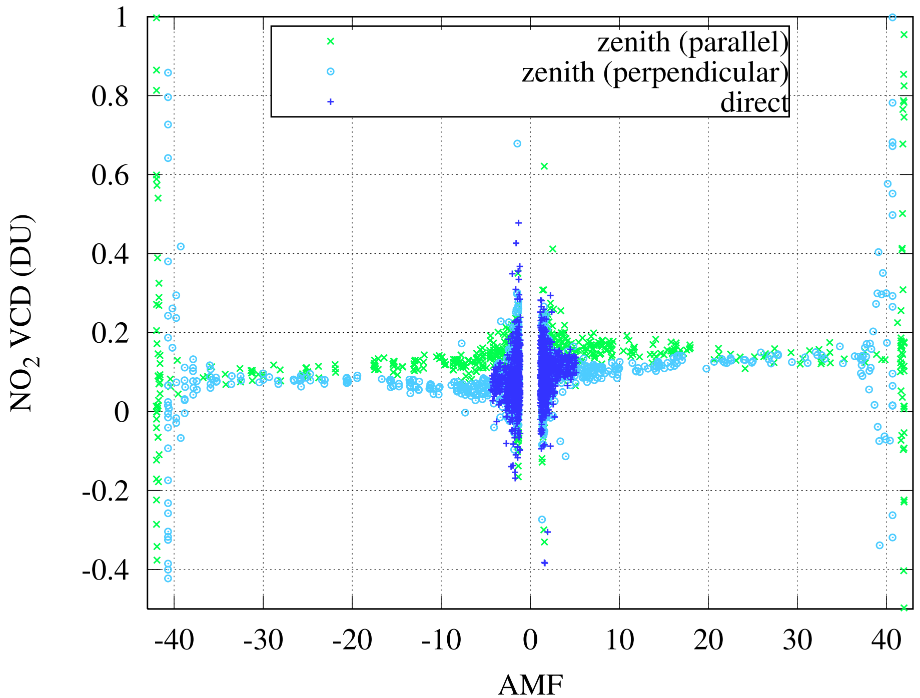

Figure 2. Retrieved NO_2 VCDs with three different observation geometries as a function of the air mass factor (AMF). Negative AMFs refer to the morning, positive to the afternoon.

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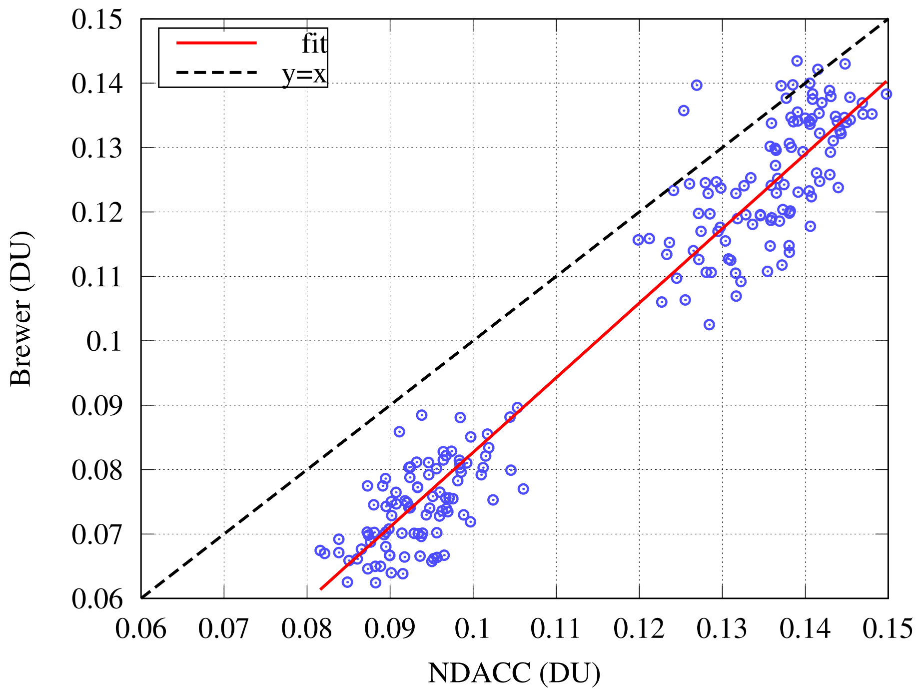

Figure 3. Scatterplot between measurements taken at twilight by the Brewer (zenith sky, perpendicular polarisation) and the reference NDACC spectrometer.

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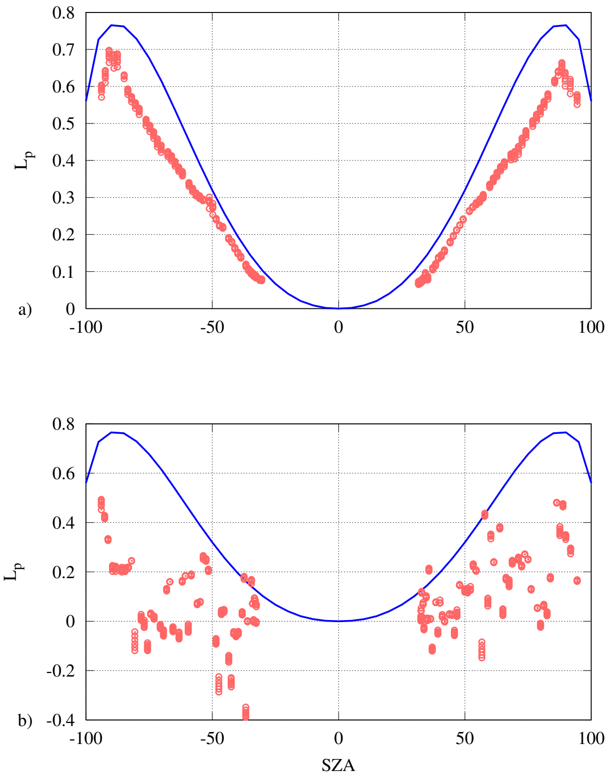

Figure 4. Degree of linear polarisation of the zenith sky as a function of the solar zenith angle (SZA) as measured by the Brewer in two different cases: **(a)** clear sky; **(b)** fog. The blue curve represents the polarisation degree as expected from the radiative transfer simulations.

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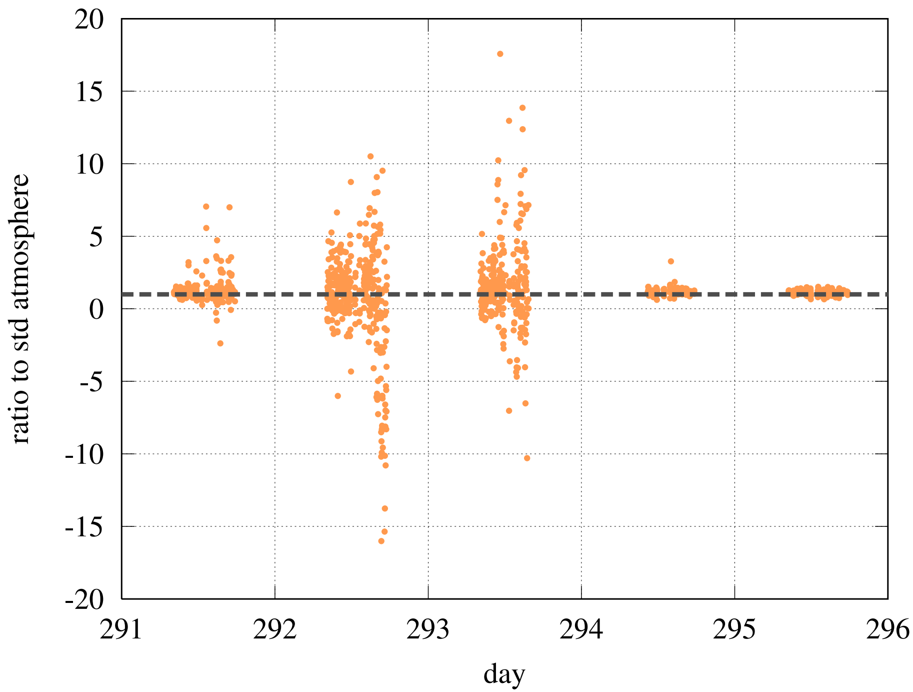

Figure 5. Ratio of the O_2–O_2 optical depth retrieved by the Brewer to the value expected for a standard tropical atmosphere at the same altitude as the Izaña observatory. The horizontal dashed line refers to a ratio of 1. The first three days are cloudy while the last two are sunny.

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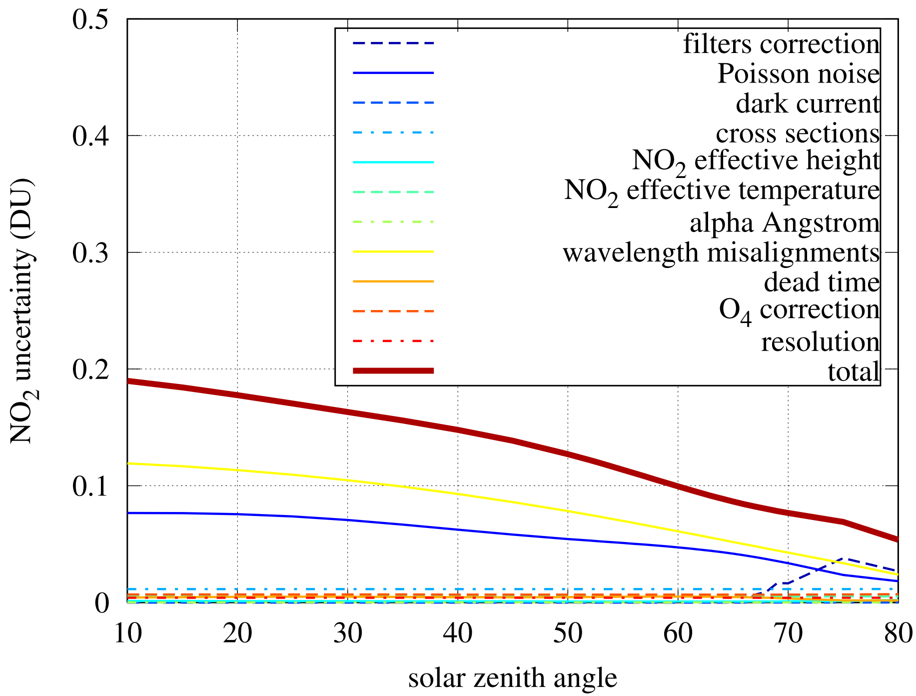

Figure 6. Monte Carlo standard uncertainty for Brewer NO_2 measurements in direct sun geometry in Izaña.

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