Response to Referee #2

We thank the reviewer for taking the time to revise our manuscript and for her constructive comments. Our point-to-point reply is given hereafter (the text in italics represents a citation of the revised manuscript).

Referee's comment 1. I agree with the first reviewer – the equations need to be written out further to explain intermediate steps. If needed, this can be addressed in the Appendix.

Author's response 1. Section 2.3.1 (Algorithm) was rewritten and a new Appendix (Detailed derivation of the Brewer equation) was added at the end of the manuscript. Section 2.3.2 was expanded to provide more details on the calibration techniques. They are reported here below.

2.3.1 Algorithm

The NO_2 VCD (X_{NO_2}) is calculated from the fundamental Brewer equation, derived in Appendix A (Eq. A6) and reported here below (the term ϵ_U was dropped since we assume that it has been minimised):

$$X_{NO_2} = \frac{\sum_i \gamma_i \log I_{0_i} - \sum_i \gamma_i \log I_i^*}{\mu_{NO_2} \sum_i \gamma_i \sigma_{NO_2 i}} \tag{1}$$

This is obtained from a linear combination of the Bouguer-Lambert-Beer law (Bouguer, 1729) at the various wavelengths λ_i measured by the Brewer. The coefficients of the linear combination, γ_i, are chosen so that interference by known atmospheric absorbers is minimised (Eq. A2). I_i^* represents the count rates, proportional to the direct sun irradiance, measured by the Brewer at the Earth surface. The asterisk indicates that this term can include slight adjustments for instrumental artefacts and interference by the atmospheric species (Eq. A4). I_{0_i} represents the count rates that would be measured if no extinction took place within the Earth atmosphere (Sect. 2.3.2). μ_{NO_2} is the NO_2 airmass factor (lengthening of the light optical path due to the inclination of the solar beam relative to the zenith, in the NO_2 layer) and $\sigma_{NO_2 i}$ is the NO_2 absorption cross section.

In BNALG0, the number of measured wavelengths employed in the algorithm is 5, which enables removal of interference by Rayleigh scattering, ozone, aerosols, and spectrally-flat factors. In BNALG1, we increased the used wavelengths to 6, i.e. all wavelengths routinely measured by the Brewer in the visible range. The spectroscopic data sets were also updated (Table 2), and the respective cross sections are convoluted to the Brewer resolution taking the I0-effect into account (Aliwell et al., 2002). More absorbing species are considered (as adjustments in I_i^*), along with the non-neutrality of the density filters. The additional degree of *freedom compared to BNALG0 is employed to maximise the Signal-to-Noise Ratio (SNR) by maximisation of the scalar product between the* NO_2 *cross section and the weightings (Eq. A7). One of the main unsolved issues of BNALG1 is the sensitivity to small wavelength misalignments, as discussed in the uncertainty estimation in RP2014. This is due to a deep Fraunhofer line in the solar spectrum in the proximity of one of the measured wavelengths (431 nm) (Diémoz et al., 2016).*

The algorithm proposed in the present article (BNALG2) includes the following improvements [...]

2.3.2 Calibration

As shown by Eq. (1) and explained in Sect. 2.3.1, an extraterrestrial calibration (ETC) coefficient is needed to accurately retrieve the NO_2 *column from spectrophotometric measurements. Furthermore, since the spectral sensitivity of a specific instrument can change with time, this term cannot be determined once and for all, but a series of ETCs covering the whole length of the* NO_2 *data set is needed. [...]*

Herman et al. (2009) developed two methods for DOAS measurements that can be adapted to our case. Both methods rely on the fact that the total NO_2 *column can be partitioned into a background contribution (*$X^b_{NO_2}$*, e.g. the stratospheric VCD), always present, and a variable fraction due to tropospheric pollution (*$X^p_{NO_2}$*). As the sum of* $X^b_{NO_2}$ *and* $X^p_{NO_2}$ *provides the total column, i.e.* X_{NO_2}*, Eq. (1) can be rewritten as*

$$X^b_{NO_2} + X^p_{NO_2} = \frac{\sum_i \gamma_i \log I_{0_i} - \sum_i \gamma_i \log I^*_i}{\mu_{NO_2} \sum_i \gamma_i \sigma_{NO_2 i}} \tag{2}$$

By defining the measurement term, F, as

$$F = \frac{\sum_i \gamma_i \log I^*_i}{\sum_i \gamma_i \sigma_{NO_2 i}} \tag{3}$$

and the (hitherto unknown) extraterrestrial calibration (ETC) term as

$$ETC = \frac{\sum_i \gamma_i \log I_{0_i}}{\sum_i \gamma_i \sigma_{NO_2 i}}, \tag{4}$$

we can rearrange Eq. (2) in the following way:

$$F = ETC - \mu_{NO_2} \left(X^b_{NO_2} + X^p_{NO_2} \right) \tag{5}$$

Since we have divided the two terms in Eqs. (3)–(4) by the NO_2 *differential absorption coefficient (*$\sum_i \gamma_i \sigma_{NO_2 i}$*), both F and* ETC *are now expressed in the same units as* X_{NO_2}*, e.g. DU or molec* cm^{-2}*.*

The first method by Herman et al. (2009), called "Minimum-Amount Langley-Extrapolation" (MLE), assumes that the (a-priori unknown) background NO_2 *VCD (*$X^b_{NO_2}$*) measurable along the atmospheric column is constant over a considered portion of the data set and that this minimum amount does not depend on the considered air mass. Hence, the upper envelope (lower envelope, in Herman's DOAS formulation) of F against* μ_{NO_2}*, i.e. (refer to Eq. 5)*

$$F^b = ETC - \mu_{NO_2} X^b_{NO_2} \tag{6}$$

is well defined and corresponds to a straight line whose intercept is ETC. Conversely, the points below that envelope, i.e.

$$F = F^b - \mu_{NO_2} X^p_{NO_2} \tag{7}$$

are due to the additional, and variable, contribution of pollution ($\mu_{NO2} X^p_{NO_2}$) to the NO_2 slant column density. [...]

We therefore test the second statistical field method, the "Bootstrap Estimation" (BE) technique. In this case, the background NO_2 column is fixed on an a priori basis, and the corresponding slant column is added to F. By simply rearranging Eq. (5), we obtain

$$F + \mu_{NO_2} X^b_{NO_2} = ETC - \mu_{NO2} X^p_{NO_2} \tag{8}$$

We observe that the term at the right-hand side increases in pristine conditions reaching the maximum value of ETC in the limiting case when $X^p_{NO_2} = 0$. Hence, ETC can be simply calculated by a robust estimation of the maximum (e.g., 97 % percentile) of the quantity at the left-hand side of the equation above. [...]

A Detailed derivation of the Brewer equation

The extinction of the direct sun irradiance within the Earth atmosphere is described by the Bouguer-Lambert-Beer law (Bouguer, 1729), written here below in a general form. This will be solved in the following based on BNALG2 and by accounting for the most relevant species interacting with solar radiation in the MkIV Brewer measurement range:

$$\begin{aligned}\log I_i = \; & \log I_{0_i} - \mu_{NO_2} X_{NO_2} \sigma_{NO_2 i} \\ & -\mu_R \tau_{Ri} \\ & -\mu_a \tau_{ai} \\ & -\sum_j \mu_j \tau_{ji} \\ & -D_{fi} \\ & -\Lambda \end{aligned} \tag{A1}$$

The spectral dependence of the equation is expressed by the index i, which refers to the considered wavelength (λ_i) among the ones measured by the Brewer (the total number of wavelengths extending up to 5 or 6, depending on the algorithm, cf. Tables 1 and 2). I_i represents the count rates measured by the instrument at the Earth surface, proportional to the direct sun irradiance. These are assumed to have already undergone the preliminary data reduction (e.g., Kipp&Zonen, 2007; Siani et al., 2018), i.e. to have been corrected for the photomultiplier dark current, scaled for the integration time, and compensated for the deadtime from the photomultiplier and the counting system (electronics). I_{0_i} is the count rate that would be measured if no extinction took place within the Earth atmosphere (Sect. 2.3.2). We denote with the subscripts NO_2, R, and a the contributions by nitrogen dioxide, Rayleigh scattering, and aerosols, respectively. The other species interacting with solar radiation in the considered wavelength range (e.g., ozone, the oxygen dimer, water vapour, glyoxal, etc.) are marked with the subscript j. The airmass factors of a species, i.e. the enhancement of the light optical path, compared to the zenith, in the corresponding atmospheric layer at an effective height h_{eff} is represented by μ. The letter X represents the VCD of a species, σ_i

its spectral cross section, and τ_i its optical depth (i.e., the product of VCD and cross section). In BNALG2, the cross sections are calculated as the convolution of high-resolution spectroscopic data sets with the instrumental slit function, by also accounting for the "I0-effect" (Aliwell et al., 2002), i.e. the fact that in actual measurements the spectra – and not their logarithm – are filtered by the slit function. Finally, the spectral attenuation of a density filter f at wavelength λ_i is denoted by D_{fi} and the spectrally-invariant factors (such as the Earth-sun distance and, to a first approximation, clouds) by Λ.

We can rewrite Eq. (A1) once for each of the wavelengths collected in the course of a measurement. In this way, we obtain a system of equations, which can be solved for X_{NO_2} using the addition method (linear combinations), i.e. by multiplying each equation by a coefficient γ_i ("weighting"). The set of coefficients should be chosen in order to minimise the contribution of species other than NO_2. It should be noted that, since these weightings ultimately depend on the Brewer resolution and exact wavelengths, they can slightly change among instruments.

Unfortunately, in the above system there are fewer equations (measurement wavelengths) than the unknowns, therefore some of the interfering species will be cancelled out by the linear combination, others will be accounted for with a correction term, and still others will be simply ignored based on their limited contribution. For example, in BNALG2 we use the following constraints to determine the weightings:

$$\begin{cases} \sum_i \gamma_i \equiv 0 \\ \sum_i \gamma_i \tau_{Ri} \equiv 0 \\ \sum_i \gamma_i \lambda_i^{-1} \equiv 0 \\ \sum_i \gamma_i \frac{\partial \log I}{\partial \lambda}\big|_{\lambda_i} \equiv 0 \end{cases} \tag{A2}$$

The first equation ensures that all spectrally flat factors (Λ) are correctly cancelled out in the linear combination. The second condition removes the effect by Rayleigh scattering. The third equation minimises the effect of Mie scattering by particles, assuming an aerosol Ångström exponent of 1 (i.e., $\tau_{ai} \equiv \beta \lambda_i^{-1}$). Notice that in the standard Brewer algorithm a linear dependence with λ_i is used instead (i.e., $\sum_i \gamma_i \lambda_i \equiv 0$). The fourth condition minimises the algorithm sensitivity to small shifts in the Brewer wavelength scale (see main text for an in-depth discussion). This can be easily shown by linearising the logarithm of the measured irradiance around a wavelength λ_i:

$$\log I(\lambda_i + \Delta\lambda) \simeq \log I(\lambda_i) + \frac{\partial \log I}{\partial \lambda}\big|_{\lambda_i} \Delta\lambda\,, \tag{A3}$$

and by noting that, in this way, an extra term $\Delta\lambda \sum_i \gamma_i \frac{\partial \log I}{\partial \lambda}\big|_{\lambda_i}$ is introduced in the linear combination and must be minimised with a correct choice of the weightings. Here, the spectral derivative is calculated with the finite difference method by simulating the solar spectrum at ground with the libRadtran radiative transfer code (Emde et al., 2016) and shifting it by ±2 micrometer steps (corresponding to about 0.02 nm).

The constraints over the γ_i's in Eq. (A2) form themselves a homogeneous system of equations. In order to avoid the trivial (null) solution, we must leave one degree of freedom available. Hence, we can only fix one additional constraint, which in BNALG2 we use to maximise the signal-to-noise ratio, as explained later on.

Setting aside, for a moment, the determination of the linear combination coefficients, we rewrite Eq. (A1) as follows:

$$\begin{aligned} \sum_i \gamma_i \log I_i \quad &+ \quad \sum_i \gamma_i \mu_{O_4} X_{O_4} \sigma_{O_4 i} \\ &+ \quad \sum_i \gamma_i D_{fi} \\ &= \quad \sum_i \gamma_i \log I_{0_i} - \sum_i \gamma_i \mu_{NO_2} X_{NO_2} \sigma_{NO_2 i} \\ &- \quad \sum_i \gamma_i \sum_u \mu_u \tau_{ui} \end{aligned} \tag{A4}$$

where the terms cancelled out or minimised by the linear combination are neglected, and the terms that can be interpreted as small corrections to the measured irradiance (i.e. oxygen dimer and filter transmittance) are moved to the left-hand side. Indeed, once the Brewer has been characterised (Sect. 2.2.1) and the weightings are determined as described above, those terms can be easily calculated. Notably, in BNALG2 we estimate the contribution by the oxygen dimer based on surface pressure and the contribution by the density filter based on its spectral transmittance. The dependence of the Brewer spectral sensitivity on the instrument internal temperature (Sect. 2.3.1 and Fig. 1) can also be corrected at this stage. Finally, the species unaccounted for in BNALG2, e.g. ozone and water vapour (u subscript), are included in the last term of Eq. (A4). Their effect is investigated in the main text.

After adjusting the linear combination of the measured irradiances for the correction terms (thus obtaining the corrected $\sum_i \gamma_i \log I_i^*$*), the equation becomes:*

$$\begin{aligned}\sum_i \gamma_i \log I_i^* &= \sum_i \gamma_i \log I_{0_i} - \mu_{NO_2} X_{NO_2} \sum_i \gamma_i \sigma_{NO_2 i} \\ &- \sum_i \gamma_i \sum_u \mu_u \tau_{ui}\end{aligned} \tag{A5}$$

and the NO_2 *VCD can be calculated as*

$$\begin{aligned}X_{NO_2} &= \frac{\sum_i \gamma_i \log I_{0_i} - \sum_i \gamma_i \log I_i^*}{\mu_{NO_2} \sum_i \gamma_i \sigma_{NO_2 i}} \\ &- \epsilon_U\end{aligned} \tag{A6}$$

where we have indicated with ϵ_U *the effect of the unaccounted species. In other words, when neglecting this* ϵ_U *contribution, the error on the* NO_2 *VCD estimation will be*

$$\epsilon_U = \frac{\sum_i \gamma_i \sum_u \mu_u \tau_{ui}}{\mu_{NO_2} \sum_i \gamma_i \sigma_{NO_2 i}} \tag{A7}$$

Therefore, in order to minimise the influence of the unaccounted interfering species, we must maximise the NO_2 *differential cross section, i.e. the term* $\sum_i \gamma_i \sigma_{NO_2 i}$*. This represents the fifth constraint in addition to the ones listed in Eq. (A2). The same condition also maximises the signal-to-noise ratio of the* NO_2 *retrieval. This is not demonstrated here for sake of brevity, but can be easily shown by propagating Poisson noise from the* I_i *to* X_{NO_2} *in Eq. (A6), as also described in Sect. 3.2.*

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