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## Response to Referee #1

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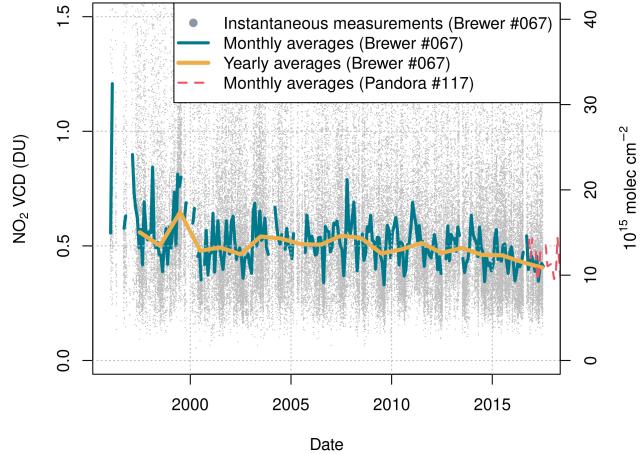
We thank the reviewer for taking the time to revise our manuscript and for his constructive comments. Our point-to-point reply is given hereafter (the text in italics represents a citation of the revised manuscript and the figure references follow the updated numbering).

**Referee's comment 1. The paper is mostly well written with minor language corrections needed (see attached document with corrections marked in green).**

Author's response 1. All language corrections (marked in green by the reviewer) were applied to the text.

**RC2. Figure 3. What are the corresponding Pandora measurements?**

AR2. Figure 3 was updated, it now includes the corresponding Pandora measurements. The new figure is reported here below.



**Figure 3:** VCDs retrieved using BNALG2 from Brewer #067: instantaneous measurements (grey dots), monthly and yearly averages (continuous lines). The monthly averages of the retrievals from Pandora #117 (Sect. 3.4), operating at APL since 2016, are also shown for comparison (dashed line).

### RC3. How is time matching accomplished in Figs. 8 and 9?

AR3. We clarified that “*Time matching between the two data sets is accomplished by considering retrievals within a 2-minute time difference*” in the figure captions. This was already explained in the main text, which was not changed.

RC4. The description of the equations used in the new algorithm is deficient. This needs to be fixed before publication. [...] As it is now, it is not possible to follow the derivation of equations 1 to 3 and more detail for the remaining equations 4 - 7.

AR4. 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  $\epsilon_U$  was dropped since we assume that it has been minimised):

$$X_{NO_2} = \frac{\sum_i \gamma_i \log I_{0i} - \sum_i \gamma_i \log I_i^*}{\mu_{NO_2} \sum_i \gamma_i \sigma_{NO_2i}} \quad (1)$$

This is obtained from a linear combination of the Bouguer-Lambert-Beer law (Bouguer, 1729) at the various wavelengths  $\lambda_i$  measured by the Brewer. The coefficients of the linear combination,  $\gamma_i$ , 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).  $I_{0i}$  represents the count rates that would be measured if no extinction took place within the Earth atmosphere (Sect. 2.3.2).  $\mu_{NO_2}$  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  $\sigma_{NO_2i}$  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  $I_0$ -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 ( $X_{NO_2}^b$ , e.g. the stratospheric VCD), always present, and a variable fraction due to tropospheric pollution ( $X_{NO_2}^p$ ). As the sum of  $X_{NO_2}^b$  and  $X_{NO_2}^p$  provides the total column, i.e.  $X_{NO_2}$ , Eq. (1) can be rewritten as

$$X_{NO_2}^b + X_{NO_2}^p = \frac{\sum_i \gamma_i \log I_{0i} - \sum_i \gamma_i \log I_i^*}{\mu_{NO_2} \sum_i \gamma_i \sigma_{NO_2i}} \quad (2)$$

By defining the measurement term,  $F$ , as

$$F = \frac{\sum_i \gamma_i \log I_i^*}{\sum_i \gamma_i \sigma_{NO_2i}} \quad (3)$$

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

$$ETC = \frac{\sum_i \gamma_i \log I_{0i}}{\sum_i \gamma_i \sigma_{NO_2i}}, \quad (4)$$

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

$$F = ETC - \mu_{NO_2} (X_{NO_2}^b + X_{NO_2}^p) \quad (5)$$

Since we have divided the two terms in Eqs. (3)–(4) by the  $NO_2$  differential absorption coefficient ( $\sum_i \gamma_i \sigma_{NO_2i}$ ), both  $F$  and  $ETC$  are now expressed in the same units as  $X_{NO_2}$ , e.g. DU or molec cm<sup>-2</sup>.

The first method by Herman *et al.* (2009), called “Minimum-Amount Langley-Extrapolation” (MLE), assumes that the (a-priori unknown) background  $NO_2$  VCD ( $X_{NO_2}^b$ ) 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  $\mu_{NO_2}$ , i.e. (refer to Eq. 5)

$$F^b = ETC - \mu_{NO_2} X_{NO_2}^b \quad (6)$$

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

$$F = F^b - \mu_{NO_2} X_{NO_2}^p \quad (7)$$

are due to the additional, and variable, contribution of pollution ( $\mu_{NO_2} X_{NO_2}^p$ ) 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

$$F + \mu_{NO_2} X_{NO_2}^b = ETC - \mu_{NO_2} X_{NO_2}^p \quad (8)$$

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  $X_{NO_2}^p = 0$ . 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:

$$\begin{aligned} \log I_i &= \log I_{0i} - \mu_{NO_2} X_{NO_2} \sigma_{NO_2i} \\ &\quad - \mu_R \tau_{Ri} \\ &\quad - \mu_a \tau_{ai} \\ &\quad - \sum_j \mu_j \tau_{ji} \\ &\quad - D_{fi} \\ &\quad - \Lambda \end{aligned} \quad (A1)$$

The spectral dependence of the equation is expressed by the index  $i$ , which refers to the considered wavelength ( $\lambda_i$ ) 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).  $I_{0i}$  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  $\text{NO}_2$ ,  $\text{R}$ , 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  $h_{\text{eff}}$  is represented by  $\mu$ . The letter  $X$  represents the VCD of a species,  $\sigma_i$  its spectral cross section, and  $\tau_i$  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 “ $I_0$ -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  $\lambda_i$  is denoted by  $D_{fi}$  and the spectrally-invariant factors (such as the Earth-sun distance and, to a first approximation, clouds) by  $\Lambda$ .

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  $X_{\text{NO}_2}$  using the addition method (linear combinations), i.e. by multiplying each equation by a coefficient  $\gamma_i$  (“weighting”). The set of coefficients should be chosen in order to minimise the contribution of species other than  $\text{NO}_2$ . 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:

$$\begin{cases} \sum_i \gamma_i \equiv 0 \\ \sum_i \gamma_i \tau_{Ri} \equiv 0 \\ \sum_i \gamma_i \lambda_i^{-1} \equiv 0 \\ \sum_i \gamma_i \frac{\partial \log I}{\partial \lambda} \Big|_{\lambda_i} \equiv 0 \end{cases} \quad (\text{A2})$$

The first equation ensures that all spectrally flat factors ( $\Lambda$ ) 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  $\lambda_i$  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  $\lambda_i$ :

$$\log I(\lambda_i + \Delta\lambda) \simeq \log I(\lambda_i) + \frac{\partial \log I}{\partial \lambda} \Big|_{\lambda_i} \Delta\lambda, \quad (\text{A3})$$

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  $\pm 2$  micrometer steps (corresponding to about 0.02 nm).

The constraints over the  $\gamma_i$ ’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:

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

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:

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

and the  $NO_2$  VCD can be calculated as

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

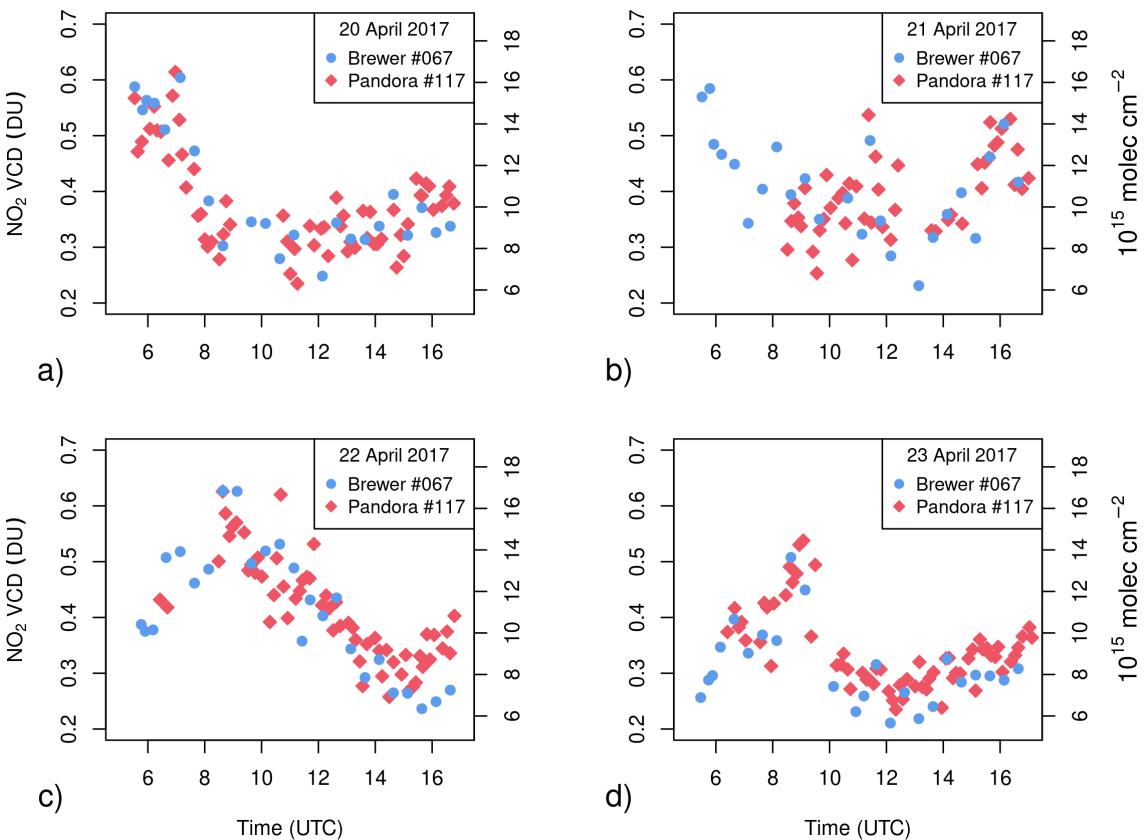
where we have indicated with  $\epsilon_U$  the effect of the unaccounted species. In other words, when neglecting this  $\epsilon_U$  contribution, the error on the  $NO_2$  VCD estimation will be

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

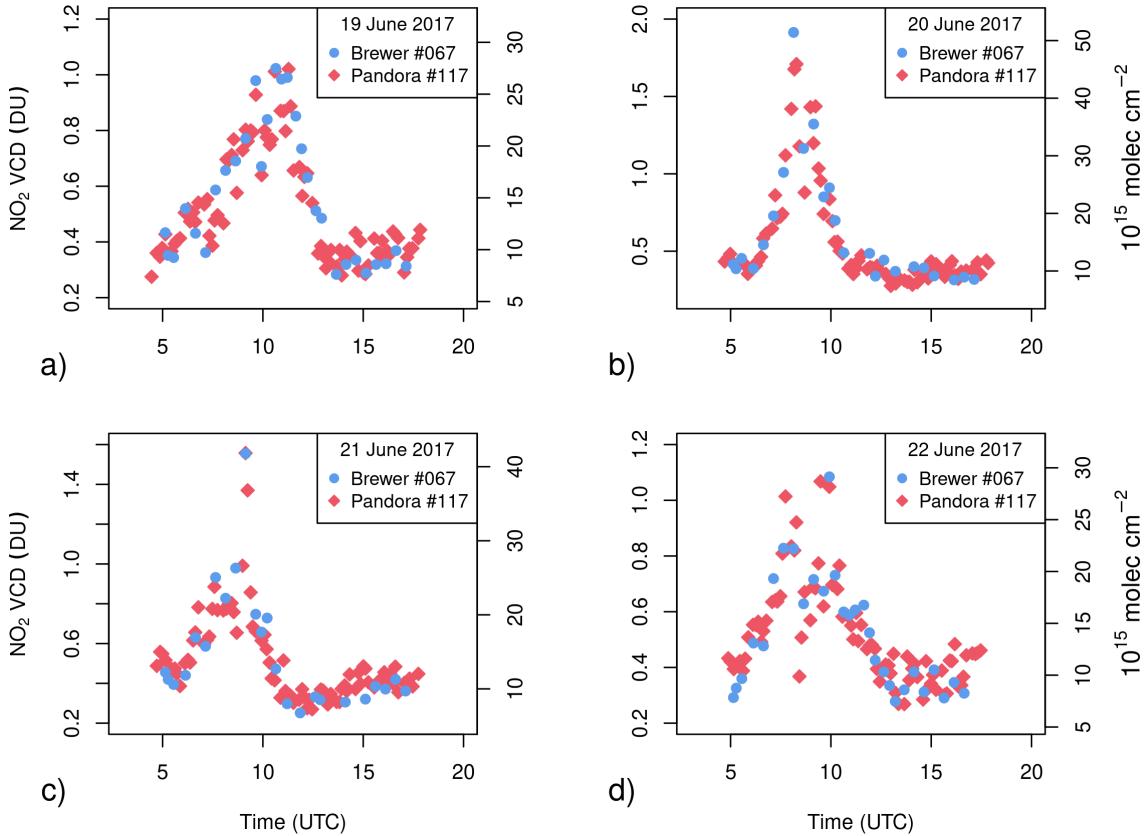
Therefore, in order to minimise the influence of the unaccounted interfering species, we must maximise the  $NO_2$  differential cross section, i.e. the term  $\sum_i \gamma_i \sigma_{NO_2 i}$ . This represents the fifth constraint in addition to the ones listed in Eq. (A2). The same condition also maximises 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.

RC5. The comparison with Pandora 117 is quite good, However, even more interesting is a comparison of Brewer 067 with the daily files from Pandora 117.

AR5. We thank the reviewer for spotting this. We have replicated his figures, as shown here below, and included them in the paper. Notice that Pandora measurements are missing on 21 April 2017 before 8 UTC due to power supply issues occurred during the night (as noted in the instrument logbook), not due to clouds.



**Figure 9:** Independent retrievals from instantaneous measurements by Brewer #067 and Pandora #117 on four selected days (20–23 April 2017). Notice that some Pandora data are missing on 21 April before 8 UTC due to a power supply issue.



**Figure 10:** Independent retrievals from instantaneous measurements by Brewer #067 and Pandora #117 on four selected days (19–22 June 2017). Notice that the range of the vertical axis on 20 and 21 June is different from the other two days and that in subfigure c) the Brewer and Pandora measurements corresponding to the daily maximum (just before 10 UTC) perfectly overlap at about 1.5 DU and are not easily distinguishable.

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