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Discussions

Advanced NO_2 retrieval technique for the Brewer spectrophotometer applied to the 20-year record in Rome, Italy

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Abstract. A re-evaluated data set of nitrogen dioxide (NO_2) column densities over Rome for the years 1996 to 2017 is here presented. This long-term record is obtained from ground-based direct sun measurements with a MkIV Brewer spectrophotometer (#067), further reprocessed using a novel algorithm. Compared to the original Brewer algorithm, the new method includes updated NO_2 absorption cross sections and Rayleigh scattering coefficients, and accounts for additional atmospheric com-

5   pounds and instrumental artefacts, such as the spectral transmittance of the filters, the alignment of the wavelength scale and internal temperature. Moreover, long-term changes in the Brewer radiometric sensitivity are tracked using statistical methods for in-field calibration. The resulting series presents only few (about 30) periods with missing data longer than one week and features NO_2 retrievals in more than 6100 days, covering nearly 80 % of the considered 20-year period. The high quality of the data is demonstrated by two independent comparisons. In a first intensive campaign, Brewer #067 is compared against another

10   Brewer (#066), recently calibrated at the Izaña Atmospheric Observatory through the Langley method and there compared to reference instrumentation from the Network for the Detection of Atmospheric Composition Change (NDACC). Data from this campaign show a highly significant Pearson's correlation coefficient of 0.90 between the two series of slant column densities, slope 0.98 and offset 0.05 DU (1.3×10^{15} molec cm^{-2}). The average bias between the vertical column densities is 0.03 DU (8.1×10^{14} molec cm^{-2}), well within the combined uncertainty of both instruments. Brewer #067 is also independently com-

15   pared with new-generation instrumentation, a co-located Pandora spectrometer (#117), over a 1-year long period (2016-2017) at Sapienza University of Rome, showing linear correlation indices above 0.96 between slant column densities, slope of 0.97 and offset of 0.02 DU (5.4×10^{14} molec cm^{-2}). The average bias between vertical column densities is negligible (-0.002 DU or -5.4×10^{13} molec cm^{-2}). This, incidentally, represents the first intercomparison of NO_2 retrievals between a MkIV Brewer and a Pandora instrument. Owing to its accuracy and length, the Brewer data set collected in Rome can be useful for satellite

20   cal/val exercises, comparison with photochemical models, and for better aerosol optical depth estimates (NO_2 optical depth climatology). In addition, it can be employed to identify long-term trends in NO_2 column densities over a metropolitan en-

vironment, during two decades witnessing important changes in environmental policies, emission loads and composition, and the effect of a worldwide economic recession, to offer just a few examples. The method can be replicated on the more than 80 MkIV spectrophotometers operating worldwide in the frame of the international Brewer network. The NO_2 data set described
25 in this manuscript can be freely accessed at https://doi.org/10.5281/zenodo.4715219 (Diémoz and Siani, 2021).

1   Introduction

Few trace gases are as ubiquitous in the atmospheric chemistry as nitrogen oxides. These are released by both natural sources, such as microbiological activity, biomass burning, lightnings and volcanoes (Bates and Hays, 1967; Lee et al., 1997; Schumann and Huntrieser, 2007), and anthropogenic sources, like high-temperature combustion in vehicle engines, power plants, industry,
30 and use of fertilisers. The different nitrogen oxides species are transported and mixed, not without reacting, into the different layers of the atmosphere. Among them, nitrogen dioxide (NO_2), one of their most abundant form, is involved in the catalytic cycles accounting for almost half of the ozone removal by gas-phase reactions in the high stratosphere, between 25 and 40 km altitude (Crutzen, 1970; Garcia and Solomon, 1994), while below 25 km it moderates the ozone loss by converting active ozone-depleting species into inactive reservoir forms (Chartrand et al., 1999; Portmann et al., 1999). In the lower troposphere,
35 nitrogen oxides control the abundance of ozone through the reactions leading to photochemical smog (Haagen-Smit, 1952), participate to aerosol (nitrates) formation (Seinfeld and Pandis, 2006), and can be adsorbed on dust particles (Zhou et al., 2015). Since they are also directly harmful to human health (Krzyzanowski and Cohen, 2008) and to the environment (Bell and Treshow, 2002), nitrogen oxides are notoriously known air pollutants and routinely monitored in the ambient air, to evaluate compliance with air quality standards, by environmental protection agencies. Last, but not least, owing to its ability of absorbing
40 solar radiation in the ultraviolet (UV) and visible bands, NO_2 is also known for its radiative effect (Solomon et al., 1999) and for its capacity of interfering with the estimate of other atmospheric compounds in solar photometry (Shaw, 1976).

Based on its peculiar spectral absorption of the solar radiation, the NO_2 vertical column density (VCD) can be estimated by ground-based spectroscopy (Brewer and McElroy, 1973; Noxon, 1975; Kerr et al., 1977) and from spaceborne instruments (Richter et al., 2005; Celarier et al., 2008; Griffin et al., 2019). Remote sensing techniques are able to probe the whole at-
45 mospheric column (or specific portions of it), whereas surface in-situ instrumentation (e.g., air quality monitors) provides information on the NO_2 burden at the surface and is sensitive to the mixing layer height (Petritoli et al., 2004). Estimates from satellite radiometers are usually associated with large uncertainties over complex terrains or very polluted areas (Boersma, 2004; Leitão et al., 2010) due to assumptions on the air mass factors (AMFs) based on climatologies, and might underestimate the local amounts owing to their generally low spatial and temporal resolution (Herman et al., 2019; Judd et al., 2019). For
50 example, Verhoelst et al. (2021) found strong negative biases of -50 % in the NO_2 total columns measured by Copernicus Sentinel-5P TROPOMI over Rome compared to ground-based Pandora spectrometers. Hence, improvement of observations from space requires a continuos validation of satellite retrievals against column densities from ground-based, remote-sensing instrumentation.

However, whilst surface air quality monitors and satellites often benefit from long-term records, accurate multi-decennial
55 data sets from ground-based spectrometers are not yet widely available (Wang et al., 2020; Gruzdev and Elokhov, 2021). Such
series are also beneficial for assessing trends in the NO_2 stratospheric concentration (Gruzdev, 2009; Werner et al., 2013), e.g.
for climate studies, and for evaluating the abatement effects on the tropospheric loads resulting from environmental policies
and emission controls, vehicle fleet renovation, and even worldwide crises such as the recent (2008) economic recession or
the confinement due to SARS-CoV-2 pandemic (Castellanos and Boersma, 2012; Russell et al., 2012; Hilboll et al., 2013;
60 Vrekoussis et al., 2013; Macdonald et al., 2021; Bassani et al., 2021).

Among other instruments to measure NO_2 columns, such as the Système d'Analyse par Observation Zénithale (SAOZ)
employed in the Network for the Detection of Atmospheric Composition Change (NDACC) and the Pandora spectrometers
constituting the Pandonia Global Network (PNG), the Brewer global network represents a possible, and undervalued, source of
information on total nitrogen dioxide column amounts. Indeed, NO_2 estimates from both direct sun and zenith sky observation
65 geometries have been proven possible with Brewers spectrophotometers, beside ozone retrievals for which they are well-
known reference instruments. Cede et al. (2006), for example, used MkIII Brewers to retrieve nitrogen dioxide VCDs from
direct sun measurements in the UV-A range (nominally, 315-400 nm), although the spectral structure of the NO_2 absorption
cross sections at these wavelengths is rather weak and does not provide high signal-to-noise ratios. MkIV Brewers, on the
contrary, were conceived in 1985 for the exact purpose of deriving both ozone in the UV-B (nominally, 280-315 nm) and
70 nitrogen dioxide in the visible range (wavelengths larger than 400 nm), which enhances the Brewer sensitivity to this trace
gas owing to the pronounced spectral structures of the NO_2 cross section in that band (Kerr, 1989). We estimate that more
than 50 MkIV Brewer spectrophotometers from 22 countries have been collecting raw (unprocessed) data in the visible range
and sending them to the World Ozone and Ultraviolet radiation Data Center (WOUDC) since the establishment of the Brewer
network in the 1990's. These data sets can be potentially used to extract information on past NO_2 total columns. Moreover,
75 another 30 MkIV Brewers have been programmed to retrieve ozone VCDs only, and can start collecting NO_2 data from now
on, which would enlarge the potential network to more than 80 spectrophotometers. Accurate NO_2 data processing from the
Brewer, however, is hampered by the lack of algorithm updates in the operating software since the 1980's and by the absence
of a travelling NO_2 reference such as for ozone. Nevertheless, considerable progress have been made in the last decades by
Barton (2007) and Diémoz et al. (2014), who improved the Brewer NO_2 algorithm and applied it to short-term series for
80 demonstration purposes.

In this study, we prove that it is possible to extract accurate information on NO_2 VCDs even from long-term data sets
collected with MkIV Brewers. To this end, we employ the Brewer spectrophotometer (serial number #067) operating at the
Atmospheric Physics Laboratory (APL), located at the Physics Department of Sapienza University of Rome. The instrument
has been providing UV global irradiance (Vitt et al., 2020) and ozone retrievals (Siani et al., 2018) since 1992 and has been
85 measuring direct solar radiation in the visible range for NO_2 estimates since 1996 (Francesconi et al., 2004). This series is
of particular interest owing to the characteristics of the station, located in the Italian capital city, a populated and trafficked
metropolis, and to the continuity and length of the data set. We reprocess this series based on the algorithm developed by
Diémoz et al. (2014, hereafter referred to as "reference paper", or RP2014), further improved to reduce the Brewer sensitivity to

some instrumental parameters such as the alignment of the wavelength scale and the Brewer internal temperature. Radiometric

90   sensitivity changes with time are also tracked using state-of-the-art methods for calibration in the field (since no other proxy or reference instrument is available during the whole period). The series analysed here covers the period 1996-2017, however measurements are still being performed and will be processed in a future study. An intensive intercomparison campaign with another MkIV Brewer recently calibrated at a pristine site through the Langley method and a 1-year long comparison with a more modern instrument, a collocated Pandora spectrometer, demonstrate the high quality of the Brewer data set in Rome.

95   The paper is structured as follows: Sect. 2 introduces the data and methods, i.e. the measuring site (Sect. 2.1), the involved instruments (Sect. 2.2) and the updates to the processing technique (Sect. 2.3). The new data set is then presented in Sect. 3.1, together with the description of the uncertainty estimation (Sect. 3.2). We compare the Brewer retrievals with other instruments in Sects. 3.3 and 3.4. Finally, the significance of the new data set and perspectives of further applications are discussed in Sect. 4.

The main results are expressed in both Dobson Units (DU), for direct comparison with previous literature on Brewers, and

100   in $\mathrm{molec\,cm^{-2}}$, as common in the DOAS and satellite scientific communities. Furthermore, the final data set is also provided in $\mathrm{mol\,m^{-2}}$.

2 Data and methods

2.1 Site description

Brewer #067 has been operating since 1992 at Sapienza APL (41.901N, 12.516E, 75 m asl). The observatory is located on a

105   wide terrace of the "Fermi" building on the university campus, in an urban context (Meloni et al., 2000). Rome, the Italian capital city, represents the most populated municipality in Italy, with almost 3 million inhabitants in the urban area, and more than 4 million inhabitants including the suburban areas. Nitrogen dioxide emissions are mainly imputable to human activities, such as road traffic, which in Rome is responsible for 80 % of the NO_2 emissions (Municipality of Rome, 2017) due to widespread use of private cars, and domestic heating. As a result, despite the NO_2 surface concentrations have nearly halved in the last 20

110   years (ARPA Lazio, 2020), exceedances of the annual limit value of 40 $\mu\mathrm{g\,m^{-3}}$ are still detected by some air quality stations in the city centre (ARPA Lazio, 2021). Other anthropogenic emission sources of nitrogen dioxide include air and sea traffic in proximity of the city, as well as combustion in energy and industry plant (Bassani et al., 2021). As for the natural sources, wildfire plumes might also occasionally contribute to the observed tropospheric NO_2 levels (Campanelli et al., 2021). The site is characterised by hot-summer Mediterranean climate (Csa, according to the Köppen-Geiger classification), also known as

115   a "typical Mediterranean climate", with strong solar radiation expected to relevantly impact the NO_2 surface concentrations through photochemical processes, as also common in other southern European locations. Pollutant dispersion, and notably the near-surface and tropospheric amounts of nitrogen dioxide, are additionally influenced by temperature inversions, the heat island effect (Di Bernardino et al., 2021) and by penetration of the breeze front in the urban area (Petenko et al., 2011).

In the last few years, APL serves as the main measuring headquarter of the Boundary layer Air Quality Using Network

120   of INstruments (BAQUNIN) project (https://www.baqunin.eu/, last access: 26 April 2021), beside two additional stations in semi-rural (CNR-ISAC, Tor Vergata) and rural (CNR-IIA, Montelibretti) context. Indeed, various ground-based instruments

dedicated to monitoring of the main trace gases and aerosols along the atmospheric column and at the surface are in operation at APL, for purely scientific purposes or in the frame of calibration and validation of satellite products. Among them, a Pandora spectrometer (#117, Sect. 2.2.2) has been operating since 2016.

125   In June 2013, Brewer #067 was moved for one month to the atmospheric observatory of Aosta–Saint-Christophe, Italy (Fountoulakis et al., 2020a, b), in the northwestern Alps, for comparison with Brewer #066, routinely operated there. The observatory is located on the roof of the local Environment Protection Agency (45.742N, 7.357E, 570 m asl, WIGOS ID 0-380-5-1) at the bottom of an Alpine valley with a wide horizon, in a semi-rural context. The local pollution sources only include road traffic and wintertime domestic heating from the nearby city of Aosta (34,000 inhabitants). Although transport of

130   NO_2 from the Po Valley, one European pollution hotspot, is observed to take place on fair-weather days owing to development of thermal winds (Diémoz et al., 2019), the tropospheric concentrations of this trace gas hardly ever reach large amounts (the yearly averages of NO_2 surface concentrations being about half of the annual limit value of $40\,\mu g\,m^{-3}$).

2.2   Instruments

The data set presented in this study is obtained from Brewer #067 in Rome, which is accurately described here below. In

135   addition, we provide information about Brewer #066 and Pandora #117, whose NO_2 retrievals are compared to the ones from Brewer #067.

2.2.1   MkIV Brewer spectrophotometers

Brewer spectrophotometers, and notably MkIV Brewers, are described in detail elsewhere, e.g. in RP2014. In short, the instruments collect solar radiation directly from the sun ("direct sun mode") or from the zenith ("zenith sky mode"), depending on

140   rotation of a reflective prism, which selects the elevation angle of the field of view. In the direct sun configuration, which is the only discussed in the present study, the sun light is directed on a diffusing filter and, possibly, on one of the available neutral-density filters, chosen so as to regulate the beam intensity to suitable levels for detection by a photomultiplier tube (PMT) in its linearity range. The filters available on a Brewer provide attenuations from 0 up to 2.5 decades, and are considered spectrally neutral in the default ozone and NO_2 retrieval algorithms. Actually, as discussed in RP2014, the filter transmittance is

145   not spectrally flat, therefore corrections are needed to achieve high-accuracy retrievals, especially of weakly absorbing species such as NO_2. MkIV Brewers are "single" Brewers, i.e. equipped with only one monochromator, which disperses, through a holographic diffraction grating, the incoming radiation into its wavelength spectrum. A rotating slit mask allows the PMT to sequentially measure the solar spectral irradiance at up to six different wavelengths at high speed (0.1147 s integration time for each slit). Twenty slit cycles are scheduled for each individual measurement, and five individual measurements are then

150   collected to obtain a direct sun retrieval (as the average of the samples) and its standard deviation, for a total of 100 cycles for each complete measurement loop. To retrieve the ozone total column, MkIV Brewers use the grating in the third order of diffraction, which provides output wavelengths in the ultraviolet range, and only solar irradiance recorded at the four longest wavelengths (about 310–320 nm) is employed in ozone retrievals. Conversely, to retrieve nitrogen dioxide, the diffraction

Table 1. Operating wavelengths and weightings employed with Brewer #067 for the retrieval of nitrogen dioxide. BNALG0 refers to the algorithm by Kerr (1989), BNALG1 to the algorithm by Diémoz et al. (2014), and BNALG2 to the updates proposed in this paper.

Wavelength (nm)	425.02	431.40	437.35	442.83	448.08	453.20
Weightings (BNALG0)	0	1×10^{-1}	-5.9×10^{-1}	1.1×10^{-1}	1.2	-8.2×10^{-1}
Weightings (BNALG1)	4.353×10^{-2}	1.489×10^{-1}	-4.925×10^{-1}	-4.929×10^{-2}	7.534×10^{-1}	-4.041×10^{-1}
Weightings (BNALG2)	6.657×10^{-2}	2.632×10^{-2}	-2.528×10^{-1}	-2.603×10^{-1}	8.326×10^{-1}	-4.124×10^{-1}

grating is used in the second order, and the emerging visible light has wavelength ranging between 425 and 435 nm (Table 1),
155   where the differential structure of the NO_2 absorption cross sections is pronounced.

Some tests are regularly alternated to measurements to check that the Brewer is stable over time. For example, due to temperature changes within the instrument, the wavelength alignment may vary during the day, hence tests using a line emission source (provided by an internal mercury lamp), representing a stable wavelength reference, are important to keep the wavelength registration within ± 0.01 nm. It is worth noting that, while the sensitivity of the Brewers to slight wavelength changes is
160   minimised for ozone retrievals by choosing a suitable grating position ("sun scan test"), this is not possible for NO_2 retrievals because the solar and NO_2 absorption spectra do not give rise to a similar effect in the visible range. Along with the wavelength registration, the spectral sensitivity of a Brewer can also change with the age of an instrument. To track these changes and correct them, some "standard lamp tests" (SL test) are included in the daily measurement schedule. During the test, which can be carried out in both "ozone" and "nitrogen dioxide" modes, the irradiance from an internal halogen lamp is collected instead
165   that of the sun, and is processed similarly to the solar measurements. The results (called "F-ratios" for the NO_2 measuring mode, cf. Fig. 1 as an example) are then used to monitor the Brewer stability and correct the retrievals, if needed (Siani et al., 2018).

Two major events impacted on the sensitivity of Brewer #067. In July 2012, the instrument was temporarily moved to Arosa (CH) and took part in an international intercomparison. There, during the maintenance operations, focusing of the
170   monochromator in the UV was improved by moving the mirror closer to the grating. This operation also likely affected focusing in the visible range and the energy distribution among the slits, thus introducing a strong discontinuity in the Brewer spectral sensitivity, though well compensated by the proposed algorithm (Sect. 2.3.2). The second event occurred some years later, in July 2017, when extraordinary servicing was performed on the PMT, with the aim of improving the stability of ozone retrievals. Unfortunately, the procedure degraded the quality of NO_2 retrievals by introducing short-term instabilities, strongly dependent
175   on the internal temperature in a non-linear way. Hence, we reprocess the data set only until that date to include retrievals with the highest possible accuracy in this data set. In the forthcoming future, the addition of a thick diffusing filter, which will lead to decreased photon counts, is expected to fix the issue.

Before carrying out NO_2 retrievals, both Brewers involved in this study, #066 (routinely operated in Aosta–Saint-Christophe) and #067, were accurately characterised. The wavelength dispersion function in the visible range is obtained from measure-

180   ments of emission lines in that band, as illustrated in RP2014. The stability of the dispersion function over the whole period

is monitored using the UV dispersion, regularly measured during the audits, as a proxy. This test shows that the wavelength

scale of Brewer #067 is stable within ± 0.03 nm for the whole considered period (1996–2017). Although the new algorithm

presented in this study (BNALG2, Sect. 2.3.1) is insensitive to such a small amount, the contribution to the overall uncertainty

on NO_2 retrievals owing to slight wavelength changes is anyway taken into account in Sect. 3.2. The dispersion test is also

185   employed to assess the spectral resolution provided by each slit and to degrade the absorption cross-sections to the instrumental

resolution. The spectral transmittance of the density filters was assessed using the internal standard lamp in 2013. In principle,

this measurement provides accurate estimates only for the thinnest filters, since the irradiance measured with the thickest filters

is very low. However, the procedure was iterated every day for nearly two months, thus collecting a large number of samples.

Moreover, to further check the accuracy of the filter characterisation, nearly-simultaneous retrievals using different filters are

190   compared in the final data set, showing no systematic deviations. Nevertheless, we discuss the uncertainty on the filter trans-

mittance in Sect. 3.2. In addition to the previous characterisation, Brewer #066 was furthermore calibrated for NO_2 retrievals

at the Izaña observatory (Tenerife, Canary islands). This was achieved using a modified version of the Langley plot accounting

for approximately daily linear trends in the stratospheric NO_2 VCD (due to photochemistry), as explained in RP2014.

The measurement schedule operating on Brewer #067 includes ozone measurements in direct sun and zenith sky geometries,

195   Umkehr observations, UV scans, nitrogen dioxide measurements in both geometries, and tests. As a result, about 10–30 NO_2

measurements are performed each day, depending on the available solar zenith angles (SZAs) and sunshine hours.

2.2.2   Pandora spectrometer

The Pandora-2S instrument (serial number 117) employed in this study consists of two optical paths and spectrometers. The

UV (VIS) spectrometer has a nominal wavelength range from 280 (380) to 530 (900) nm with an average spectral resolution of

200   0.6 (1.1) nm. For this study, only data from the UV channel are used. The field of view of the telescopes is 2.5° FWHM and the

direct sun beam is further adjusted using a diffuser and, if needed, neutral density filters. The instrument has been characterized

following the Pandonia Global Network (PGN) calibration procedures (Müller et al., 2020). The considered data correction

steps (raw L0 data to corrected L1 data) are explained in the Blick Software Suite manual (Cede, 2019). Pandora direct sun

NO_2 retrievals have been compared to spaceborne radiometer estimates and to other ground-based instruments during field

205   campaigns (Herman et al., 2009; Wang et al., 2010; Flynn et al., 2014; Reed et al., 2015; Martins et al., 2016; Lamsal et al.,

2017; Bösch et al., 2018; Tirpitz et al., 2021).

The Pandora data available for the present study, downloaded from http://data.pandonia-global-network.org (last access: 26

April 2021), are obtained using the direct sun retrieval code "nvs1" with Blick processor version 1.7 (Cede et al., 2021).

2.3   Nitrogen dioxide retrievals with Brewer #067

210   Accurate retrievals are generally the result of a reliable algorithm and careful calibration of the measuring instrument. Unfor-

tunately, in the case of nitrogen dioxide, none of them is available for the vast majority of the MkIV spectrophotometers in the

Brewer network. Indeed, the only algorithm implemented in the Brewer operating software is the one by Kerr (1989) (here-

after referred as to Brewer nitrogen dioxide algorithm version 0, or BNALG0 in short), based on now obsolete spectroscopic data sets, and relying on the characterisation of the specific spectrophotometer used by the authors (not necessarily similar to

215 other instruments in the network). Previous studies found that retrievals using BNALG0 show both overestimations (McElroy et al., 1994; Barton, 2007) and random deviations (Hofmann et al., 1995), these latter due to interfering atmospheric species or instrumental artifacts, compared to different types of instruments. Moreover, no travelling standard calibrated for NO_2 retrievals is available to homogenise the retrievals within the network. In our reference publication, we focused on both issues, proposing an improved algorithm (hereafter referred as to BNALG1), specially developed for pristine sites, and a technique to

220 calibrate MkIV Brewers at high-altitude, unpolluted stations. Here we aim at further overcoming the limitations of BNALG1, such as high sensitivity to wavelength misalignments, by introducing some improvements (BNALG2), and at testing statistical methods that sort out the issue of moving the Brewer to isolated locations in order to calibrate it, thus allowing the reprocessing of historical data sets.

2.3.1 Algorithm

225 Following the same notation as in RP2014, we can write the fundamental Brewer equation as

$$
\begin{aligned}
\sum_i \gamma_i \log I_i \;=\; & \sum_i \gamma_i \log I_{0_i} \\
& -\mu_{NO_2} X_{NO_2} \sum_i \gamma_i \sigma_{NO_2 i} \\
& -\sum_j \mu_j \sum_i \gamma_i \tau_{ji}
\end{aligned}
\tag{1}
$$

This represents a linear combination of the Bouguer-Lambert-Beer law (Bouguer, 1729) at the various wavelengths λ_i

230 measured by the Brewer (the number of wavelength i extending from 1 to 5 or 6, depending on the algorithm, cf. Tables 1 and 2). I_i represents the count rates, proportional to the direct sun irradiance, measured at wavelength λ_i, I_{0_i} the count rates that would be measured if no extinction took place within the Earth atmosphere (extraterrestrial coefficient, Sect. 2.3.2), μ_{NO_2} the airmass factor relative to NO_2 (enhancement of the light optical path, compared to the zenith, in the NO_2 layer at an effective height h_{eff}), X_{NO_2} the unknown amount of nitrogen dioxide, $\sigma_{NO_2 i}$ the NO_2 absorption cross section, and $\sum_j \mu_j \sum_i \gamma_i \tau_{ji}$

235 the contribution of other species, such as Rayleigh scattering, ozone absorption, aerosols, and factors affecting all wavelengths in a similar way (such as the Earth-sun distance and, to a first approximation, clouds). With a proper choice of the set of weightings γ_i employed in the linear combination, we can remove the last term and make Eq. (1) only sensitive to NO_2.

From the equation above, incidentally, we can derive in few steps the Brewer sensitivity to an unaccounted species x:

$$
\epsilon_x \;=\; \frac{\mu_x \sum_i \gamma_i \tau_{xi}}{\mu_{NO_2} \sum_i \gamma_i \sigma_{NO_2 i}}
\tag{2}
$$

240 τ_{xi} being the optical depth of species x at wavelength λ_i. In other words, the larger is the optical depth of the unaccounted species x in the atmosphere and the stronger is its contribution to the derived NO_2. The Brewer sensitivity to slight wavelength

Table 2. Working principles of various algorithm for NO_2 direct sun retrievals with MkIV Brewers.

	BNALG0 (Kerr, 1989)	BNALG1 (Diémoz et al., 2014)	BNALG2 (present study)
Number of used wavelengths	5	6	6
NO_2 absorption cross sect.	Johnston and Graham (1976)	Vandaele et al. (2002), 220 K	Vandaele et al. (1998), 254.5 K
O_3 absorption cross sect.	Vigroux (1952)	Bogumil et al. (2003), 223 K	–
Rayleigh scattering coeff.	Brewer standard coeff.	Bodhaine et al. (1999)	Bodhaine et al. (1999)
Aerosols	Linear	λ^{-1}	λ^{-1}
Spectrally flat factors	Accounted for	Accounted for	Accounted for
O_2-O_2 absorption cross sect.	–	Hermans et al. (2003)	Hermans et al. (2003)
I0 effect (Aliwell et al., 2002)	–	Accounted for	Accounted for
SNR maximisation	–	Yes	Yes
Wavelength misalignments	–	–	Minimised
Filter non-neutrality	–	Accounted for	Accounted for
NO_2 effective layer height	22 km	27 km	7.2 km

misalignments can be treated likewise, as a fictitious absorber. In effect, by linearising Eq. (1) around wavelength λ_i, we can estimate the error ϵ_λ induced on X_{NO_2} when measuring solar irradiance at wavelengths $\lambda_i + \Delta\lambda$ instead of λ_i as

$$\epsilon_\lambda = -\Delta\lambda \frac{\sum_i \gamma_i \frac{\partial \log I_i}{\partial \lambda}}{\mu_{NO_2} \sum_i \gamma_i \sigma_{NO_2 i}} \qquad (3)$$

245 Thus, to reduce the Brewer wavelength sensitivity, we must choose a set of weightings γ_i minimising the numerator of Eq. (3). The equations above will be useful in the next paragraphs.

In BNALG0, the number of measured wavelengths employed in the algorithm is 5, which enables removal of interference by Rayleigh scattering, ozone, aerosol, and spectrally-flat factors. In BNALG1, we increased the used wavelength to 6, i.e. all wavelengths routinely measured by the Brewer in the visible range. The spectroscopic data sets were also updated (Table 2),

250 and the respective cross sections are convoluted to the Brewer resolution taking the I0-effect into account (Aliwell et al., 2002), and more absorbing species are considered (as corrections in the post-processing), along with the non-neutrality of the density filters. The remaining degree of freedom 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 (denominator in Eqs. 2 and 3). One of the main unsolved issues of BNALG1 is the sensitivity to small wavelength misalignments (Eq. 3), as discussed in the uncertainty estimation in

255 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 further improvements:

1. To minimise the instabilities due to sensitivity to wavelength misalignments, we determine new weightings (γ_i) by including the spectral derivative of the solar spectrum in the fit (Eq. 3), as also done by Kerr (2002) and Cede et al. (2006). 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). When the derivative of the solar spectrum is included in the Brewer fit, the absolute value of the weighting relative to the second wavelength (γ_2) correctly decreases (more than 5 times compared to BNALG1, i.e. from 1.489×10^{-1} to 2.632×10^{-2}, Table 1), thus reducing, in the linear combination, the relative importance of solar irradiance collected at 431 nm wavelength. An example of the improved stability provided by BNALG2 compared to BNALG1 is given in Sect. 3.4 (Fig. 9) based on comparison with the Pandora spectrometer;

2. In order to keep one degree of freedom available for SNR optimisation and not to overconstrain the system, we drop the ozone absorption from the fit. We estimate that this triggers an error of about 0.01 DU (2.7×10^{14} molec cm^{-2}) on NO$_2$ for a 200 DU range of total ozone column amounts. Such a low sensitivity is due to the fact that the ozone cross sections are quite flat in the considered spectral range. If needed, that amount can be taken into account and corrected by considering the closest ozone retrieval in time, or even the daily average O$_3$, from the Brewer (in the UV range);

3. To make the retrievals by Brewer #067 consistent with the co-located Pandora spectrometer (Cede et al., 2021), the same spectroscopic data set as in the Pandora is employed (Table 2, rightmost column). The new cross sections at higher temperatures and the lower NO$_2$ effective height used for airmass calculations are more suitable, compared to BNALG1, to operation at polluted sites, where the contribution of tropospheric nitrogen dioxide can be relevant;

4. We found that Brewer NO$_2$ retrievals are slightly sensitive to the instrument internal temperature, similarly to ozone retrievals. Temperature sensitivity is not accounted for in either BNALG0 or BNALG1, and absolute temperature dependence at only single wavelengths have been reported until now (e.g., Diémoz et al., 2016). Slight differences of the absolute sensitivity among wavelengths give rise to spectral dependence able to affect NO$_2$ retrievals. By analysing the multi-year data set of SL tests (Sect. 2.2.1) we are able to quantify this effect for Brewer #067 to -0.012 DU K^{-1} (-3.2×10^{14} molec cm^{-2} K^{-1}, Fig. 1). We then use this coefficient to correct the linear combination of the count rates in solar measurements. Since the results of the SL tests after the temperature correction show very stable behaviour, and since the extraterrestrial coefficients are retrieved on a regular basis (Sect. 2.3.2), we do not correct the calibration coefficient based on the results of the SL tests (as normally done for ozone measurements between one calibration and the next);

5. As in BNALG1, the interference by the oxygen dimer (O2−O2, with only a weak absorption band within the Brewer spectral range, at about 446 nm) is considered as a correction term to the retrieved NO$_2$ VCD, following Eq. (2). This is calculated from the Hermans et al. (2003) cross sections and the mean average pressure of the Rome site, and accounts for about 0.04 DU (1×10^{15} molec cm^{-2}).
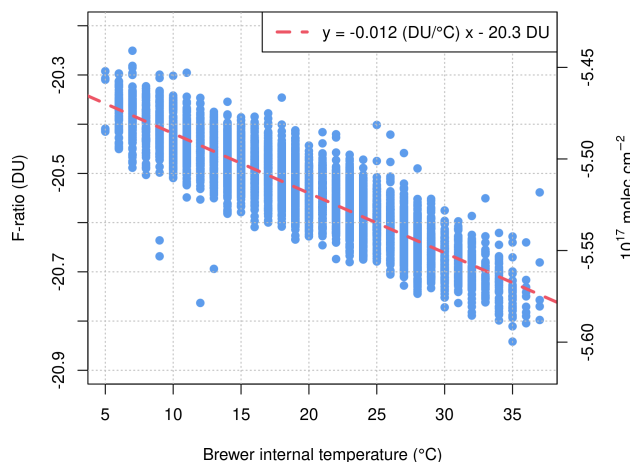
Figure 1. Results from the standard lamp (SL) test (blue dots, "F-ratio"), in both Dobson Units (DU, left axis) and $molec\,cm^{-2}$ (right axis), as a function of the Brewer internal temperature. The slope of the regression line is used in BNALG2 to correct the Brewer sensitivity to the internal temperature in solar measurements. Only variations (differences) of the SL results on the y-axis, and not their absolute values, have a physical meaning.

2.3.2 Calibration

As explained in Sect. 2.3.1, a time series of extraterrestrial calibration coefficients (ETCs) is needed in order to accurately retrieve the NO_2 column from spectrophotometric measurements. The usual method employed to this purpose in well-established measurement networks is to transfer the calibration from a reference instrument (e.g., a travelling standard) to a field instrument. The former, in turn, is generally calibrated using the Langley plot technique (Langley, 1903) at a pristine, high-altitude site. Neither of the two methods can be used in the present case. First, a travelling Brewer acting as a reference for NO_2 calibrations does not exist. Second, Brewer #067 was never moved to a suitable site for a Langley campaign, and, even if this were the case, regular calibrations should have been organised throughout the 20-year long period to accurately track possible sensitivity changes with the instrument. As a consequence, to reprocess this long-term record, we are forced to use "field" calibration techniques based on statistical analysis of the data collected at Sapienza APL. 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 ($X_{NO_2}^p$). Equation 1 can thus be written as

$$F \quad = \quad ETC - \mu_{NO_2}\left(X_{NO_2}^b + X_{NO_2}^p\right) \tag{4}$$

where F is the linear combination of the irradiances corrected for absorption by other species and divided by the differential NO_2 absorption coefficient,

$$F \quad = \quad \frac{1}{\sum_i \gamma_i \sigma_{NO_2 i}} \left[\sum_i \gamma_i \log I_i + \sum_j \mu_j \sum_i \gamma_i \tau_{ji} \right] \tag{5}$$

and

$$ETC \quad = \quad \frac{\sum_i \gamma_i \log I_{0_i}}{\sum_i \gamma_i \sigma_{NO_2 i}} \tag{6}$$

We choose to divide the quantities in both F and ETC by the differential NO_2 absorption coefficient to have their respective

310 values in DU (or molec cm^{-2}), i.e. in the same units as X_{NO_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 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} is well defined and corresponds to a straight line whose intercept is ETC,

315 whereas the points below that envelope are due to the additional contribution of pollution ($\mu_{NO2} X^p_{NO_2}$). In our implementation, we group the available data into air mass bins (with at least 500 points per bin) and, to exclude outliers in the identification of the upper envelope, we determine the 97 % percentile of F for each bin for the regression (corresponding to the third percentile in Herman's formulation). The regression over these points is performed employing a robust method, i.e. the iterated re-weighted least squares technique, implemented in the `rlm` function from the MASS library of the R package (Venables and Ripley,

320 2013). In order to track possible changes of the Brewer radiometric sensitivity with time, we apply the MLE every six months (between the two solstices, to have sub-periods of similar air mass range), with a forced discontinuity in July 2012, when we clearly notice a sudden change (Sect. 2.2.1). Results from the MLE methods are shown in Fig. 2 with triangular markers. The average of the background VCD ($X^b_{NO_2}$), provided by the slope of the MLE regression (not shown), is 0.2±0.1 DU (5.4±2.7 ×10^{15} molec cm^{-2}), which is similar to the value obtained by Herman et al. (2009) at Goddart Space Flight Center and

325 approximately corresponds to the expected average stratospheric NO_2 VCD. A major drawback of this technique, however, is the large scatter of the ETCs with no apparent link to instrumental changes, which cannot be reduced even increasing the length of the sub-periods considered for the regression (e.g., up to several years).

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:

330 $$F + \mu_{NO_2} X^b_{NO_2} \quad = \quad ETC - \mu_{NO2} X^p_{NO_2} \tag{7}$$

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. We assume a background VCD $X^b_{NO_2}$ of 0.2 DU (5.4×10^{15} molec cm^{-2}), i.e. the average of the values previously determined by the MLE method. As apparent from Fig. 2, the BE method is more stable. Therefore, to
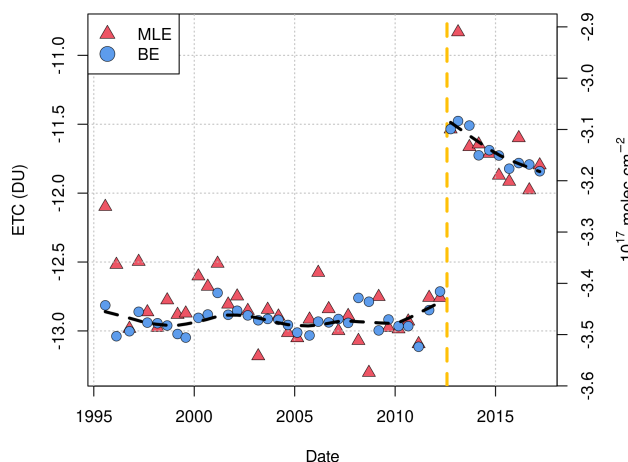
Figure 2. Extraterrestrial coefficients of Brewer #067 determined with the Minimum-Amoung Langley-Extrapolation (MLE, triangles) and Bootstrap-Estimation (BE, circles). The yellow vertical line indicates the discontinuity occurring in correspondence of the Arosa campaign in July 2012 (Sect. 2.2.1). The black dashed line represents a LOESS interpolation through the ETCs estimated by the BE method.

obtain the final series of ETCs, we take the results of this last method, further interpolated with a locally estimated scatterplot

335   smoothing (LOESS) curve to only keep the slowly-varying component of the calibration data set and not to introduce the short-term statistical noise (indeed, we have verified that these fast variations are not related to maintenance operations or changes in the instrument configuration).

It is worth noticing that the sudden variation in July 2012 (vertical dashed line in Fig. 2) is detected by both methods. If only an average ETC had been considered for the overall period, a step change larger than 1 DU or 27×10^{15} molec cm^{-2} (at

340   AMF$= 1$) in the NO$_2$ VCDs would have been introduced in the series. Instead, since we take that variation into account, no discontinuities can be noticed in the final NO$_2$ data set (Fig. 3).

2.3.3 Quality filter and cloudscreening

To ensure the highest retrieval accuracy and remove obviously erroneous measurements, always possible with automated instrumentation, we apply several checks:

345   1. A first set of controls is inspired by the Brewer Processing Software, developed by Environment and Climate Change Canada and described, e.g., by Siani et al. (2018). Raw counts lower than 2500 at the brightest slit, as well as differences between bright and dark counts lower than 250 (or 10 times the dark counts), are suggestive of incorrect pointing or very thick clouds. Measurements corresponding to these conditions are removed from the data set;

2. Spikes are corrected on the same principle as the Brewer operating software, i.e. by limiting the range of the measured

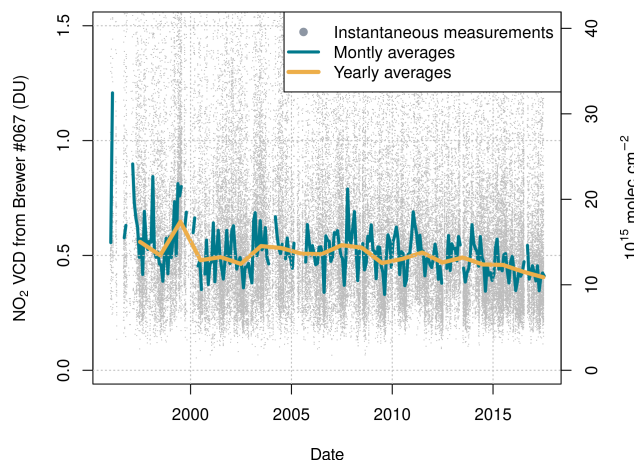350   count rates between 2 and 10^7 photons s^{-1};

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Figure 3. VCDs retrieved using BNALG2 from Brewer #067: instantaneous measurements (grey dots), monthly and yearly averages (lines).

3. To remove fast moving clouds between the sun and the observer, or erroneous measurements, the ratio between the standard deviation of the NO_2 retrieved from 5 consecutive samples and their average should be lower than 0.3. This empirical threshold is taken from previous studies (RP2014);

4. In the Brewers used here, the lower border of the quartz window casts a shadow on the zenith prism at solar zenith angles
355 larger than 78 °. Thus, only direct sun measurements at SZA lower than this limit are analysed here.

The procedure described above does not filter out all clouds, and slowly moving, moderately thick clouds can still contaminate the data set. Therefore, we tighten the threshold for the first criterion and we consider only measurements characterised by count rates at the brightest slit, compensated for the filter transmittance, higher than 10^6 photons s^{-1}. This threshold is determined by examination of the frequency histogram of the count rates, which shows two distinct distributions, likely corre-
360 sponding to clear-sky and residual clouds, well separated around the chosen threshold. Detailed visual inspection of the data set, together with comparison with Pandora (Sect. 3.4), confirm the accuracy of the quality screening algorithm.

3 Presentation of the re-evaluated data set

3.1 NO$_2$ vertical column densities

The NO_2 retrievals from Brewer #067 derived from algorithm BNALG2 are shown in Fig. 3. The record presents only few
365 periods (about 30) with missing data longer than one week, and mostly concentrated in the initial period of NO_2 measurements. It includes more than 6100 days, covering nearly 80 % of the considered 20-year period. 95 % of the instantaneous VCDs (single points in the figure) range from 0.2 to 1.6 DU (5.4 to 43 $\times 10^{15}$ molec cm^{-2}). The baseline VCDs are rather constant throughout the observation period, as expected from the application of the BE technique, and their value reflect the amount

given as input to the calibration method. Measurements accumulate in summer, thanks to the wider daily range of air masses and
- likely - to the sunnier weather, and become sparser in winter. Monthly (yearly) averages, calculated when at least 50 % of the
daily (monthly) averages are available, are also shown on the same figure as lines. A decreasing trend, still to be quantitatively
assessed and discussed in more depth in future studies, is clearly perceptible, as expected from the tropospheric NO_x emission
reductions.

The daily and weekly average cycles of Brewer retrievals are represented in Fig. 4a, to demonstrate the reasonableness
of the retrieval results. The most apparent feature is the inverse-U daily shape in the VCD amounts. This behaviour is not
an indication of a wrong ETC, since the cycle is not centred at the solar noon (minimum AMF). Rather, as also detected
by surface air quality monitors (not shown), the maximum is defined by the coupled effect of increased NO_x emissions at
the surface during the morning rush hours and photochemical reactions involving generation of NO_2. Moreover, the peak is
shifted towards midday on Sundays, as expected from a later start of the activities on such a day of the week. The beginning
of another ascending phase is visible in the late afternoon of each day, however the effect of the measurement schedule and of
the sunset does not enable the Brewer to sample the whole secondary peak. The same figure also illustrates the weekly cycle,
with higher loads during work days and minima during the week end. Figure 4 additionally shows the monthly evolution of
the NO_2 VCDs (b), as an average of the whole 1996-2017 period, and of the surface concentrations (c) determined by the
local Environment Protection Agency in the period 1999-2017 at the Magna Grecia station, 2.6 km away from APL. The two
plots share common features, the most evident being a minimum in August, the typical summer holiday month. However,
the evolution of column densities and surface concentrations remarkably differs in winter. This is an expected feature and
depends on the fact that spectrophotometric estimates are representative of the whole atmosphere while surface concentrations
are sensitive to the mixing layer height, and thus to more stable meteorological conditions and reduced tropospheric mixing
in winter. Moreover, the sampling time differs between the two techniques, since Brewer retrievals are only available during
daylight hours, whilst surface data are collected all day round, this difference becoming maximum in winter.

A more in depth analysis of the re-evaluated data is out of the scope of this paper and will be the subject of future investigations.

3.2 Uncertainty estimation

The uncertainty estimation of NO_2 retrievals from the Brewer is complex owing to the numerous factors contributing to the
uncertainty in both the calibration and measurement phases, and to their respective correlations. For this reason, in RP2014
we took advantage of a Montecarlo technique to characterise the uncertainty of a Brewer calibrated with the Langley method
at a pristine site, and then used at the same site or in a more polluted environment. In the present study, however, both the
calibration procedure and the purpose of the uncertainty estimation are different. In particular, here we are not interested in a
typical and general uncertainty assessment, but we want every measurement to be accompanied by its respective uncertainty,
which is needed, for example, if the data set is employed for data reanalysis or trend assessment purposes. Hence, we use
analytical formulas (rather than a Montecarlo technique) and we consider the calibration and the measurement uncertainties
separately, since in this case the former is primarily driven by statistical fluctuations and a-priori assumptions.
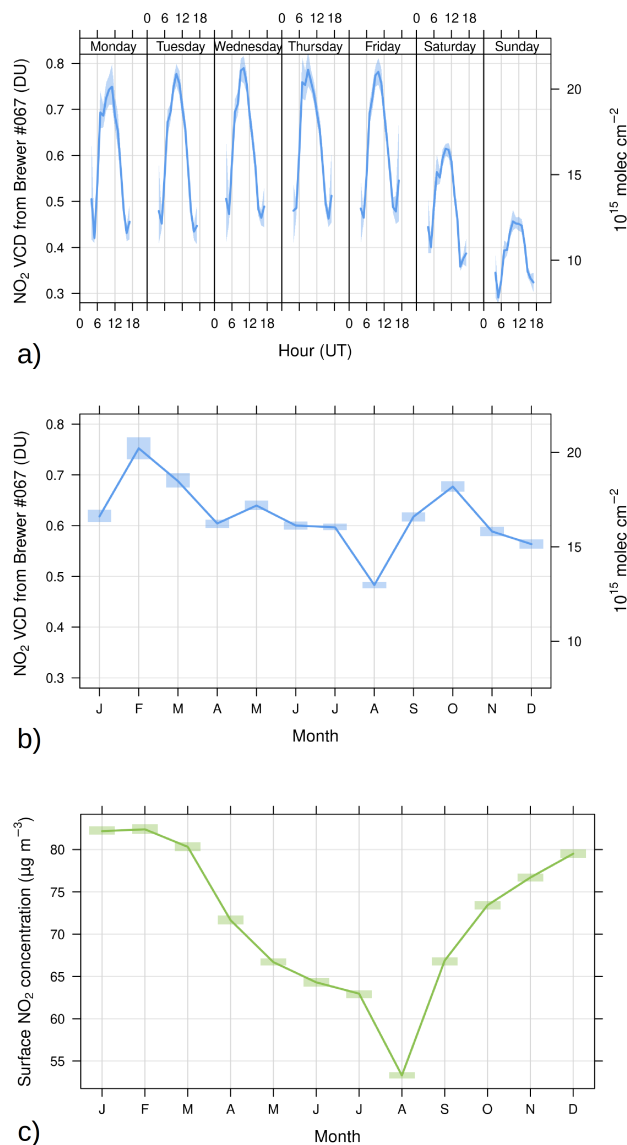
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Figure 4. Daily, weekly (a) and monthly (b) cycles of NO_2 VCDs from Brewer #067 (averages from period 1996-2017), and monthly cycle of NO_2 surface concentrations (averages from period 1999-2017) measured by the local Environment Protection Agency at the Magna Grecia station (c), 2.6 km away from APL.

1. Calibration. The ETC values from the BE calculation depend on some assumptions, such as the chosen percentile (e.g., selecting the 99th or the 95th percentile instead of the 97th already introduces differences of about ±0.05 DU or 1.3×10^{15} molec cm^{-2}) and the background VCD $X^b_{NO_2}$. Changes of ±0.05 DU in this latter translate into differences of ±0.1 DU (2.7×10^{15} molec cm^{-2}) on the ETC values. The choice of the air mass range also influences the

405

results for another 0.05 DU due to differences in the sampled set and, possibly, to systematic diurnal changes of the NO_2 tropospheric (and stratospheric) column, already mentioned above. Given the fact that these boundaries represent extreme conditions (and can be thus assimilated to the extremes of a uniform distribution), and that the above factors are

410 probably correlated, we think that a (1 standard deviation) value of 0.08 DU (2.2×10^{15} molec cm^{-2}) is a conservative estimate of the overall ETC uncertainty. This value also reflects the experimental ETC variability in periods when the instrument is believed to be stable. This estimate, however, is higher than the (2-sigma) value of 0.05 DU assumed by Herman et al. (2009) for similar field calibration methods. This translates into an uncertainty of 0.08 DU AMF^{-1} on VCDs;

415 2. Radiometric stability. Since the ETCs are determined on a regular basis, and since results from the SL tests, after correcting for temperature, are very stable within the considered sub-periods, we do not consider any further uncertainty resulting from Brewer instabilities over time;

3. Poisson noise. The effect of instrumental noise on NO_2 VCDs is estimated using Poisson statistics on the recorded count rates (accumulated from 20 cycles for each sample) and propagating the resulting uncertainty to the linear combination of

420 the logarithm of the count rates. Both bright measurements and dark count measurements are considered, and the results are further divided by $\sqrt{5}$, since each measurement loop is repeated 5 times. The contribution of Poisson noise on NO_2 VCDs (about 0.03 DU or 8.1×10^{14} molec cm^{-2} at AMF close to 1 and less than 0.01 DU or 2.7×10^{14} molec cm^{-2} at the largest SZAs, this behaviour originating from the contrasting effect of stronger light at low SZAs and increased NO_2 absorption at larger air masses) is lower than the one stated in RP2014. Indeed, in that preliminary study the

425 number of data averaged in each measurement loop was reduced from 100 to 16 for practical purposes, i.e. to obtain more Langley measurements at twilight, when the air mass factor changes faster. If the values obtained in the present work are multiplied by a factor $\sqrt{100}/\sqrt{16} = 2.5$, then the same results as in RP2014 are found. Comparison of the expected Poisson uncertainty with the experimental standard deviation of the mean of the 5 samples provides similar results, with discrepancies smaller than 0.004 DU (1.1×10^{14} molec cm^{-2}) presumably due to additional atmospheric

430 variability during the measurements (not taken into account by Poisson statistics on count rates), thus confirming that the estimate of the instrumental noise is realistic;

4. Differential absorption coefficient. As for the uncertainty related to NO_2 cross sections, Vandaele et al. (2002) report values of 4-5 %. However, most of the factors influencing that estimation are likely to affect all wavelengths in a correlated way, therefore the propagation of that uncertainty on the differential absorption coefficient, as used in the Brewer

435 algorithm, is lower. In our case, the main sources driving the uncertainty of the differential absorption coefficient are the unknown effective temperature of the NO_2 layer and the characterisation of the instrumental resolution used to scale the NO_2 cross sections. Concerning the first factor, an extreme variability range of ± 25 K around the 254.5 K temperature used for the evaluation of the cross sections would lead to a 1-sigma uncertainty of 4 % on the absorption coefficient. This estimate is obtained in the case of a uniform temperature probability distribution and assuming a temperature de-

440 pendence of the absorption coefficient of 0.285 % K^{-1}, as can be derived from the Vandaele et al. (2002) spectroscopic

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data set using the weighting coefficients from Table 1. As for the second factor, a similar amount should be added if an uncertainty of 10 % is assumed on the characterisation of the Brewer resolution, as in RP2014. Accounting for both factors translates into an uncertainty of $0.06 \cdot X_{NO_2}$ on the retrieved column;

5. Neutral density filters. To check whether the spectral transmission of every neutral density filter is correctly characterised, all NO_2 retrievals from consecutive measurements (within an interval of 30 minutes maximum) using different filters are compared and their average differences are studied to identify any systematic offset. The average discrepancy between nearly-simultaneous data collected with different filters is smaller than 0.02 DU (5.4×10^{14} molec cm^{-2}). This will be taken as the uncertainty on the neutral density filters, thus accounting for 0.02 DU AMF^{-1} on VCDs;

6. Wavelength misalignments. This is one of the largest sources of uncertainty in the BNALG1 algorithm, accounting for about 0.1 DU (2.7×10^{15} molec cm^{-2}) at low SZAs for an uncertainty of ± 2 steps in the micrometer operating position (RP2014). Conversely, BNALG2 was already conceived to minimise this factor (Eq. 3). To verify if the algorithm updates are successful, we perform radiative transfer simulations using the new weightings (Table 1), and we find that the effect of wavelength misalignments is reduced by about 20 times compared to BNALG1. For example, when the wavelength scale is shifted by ± 2 microsteps, a maximum discrepancy of only 0.006 DU (1.6×10^{14} molec cm^{-2}) is found (at low solar zenith angles), while for an extreme change of ± 4 microsteps the effect amounts to 0.018 DU (4.8×10^{14} molec cm^{-2}). The contribution of this factor to the overall uncertainty is then set to 0.01 DU AMF^{-1} (2.7×10^{14} molec cm^{-2} AMF^{-1}), and represents one major improvement compared to BNALG1;

7. Oxygen dimer. NO_2 retrievals with BNALG2 are corrected for interference by O2$-$O2. Assuming a 30 % uncertainty on the oxygen dimer cross sections, as done in RP2014, the respective contribution to the NO_2 uncertainty is of the order of 0.01 DU (2.7×10^{14} molec cm^{-2}). This value is added to the overall uncertainty;

8. Unaccounted absorbers. Ozone and water vapour are not explicitly included in the fit, although they can interfere with the retrieval. According to Eq. (2), a change of ± 200 DU in ozone triggers an error of about 0.01 DU (2.7×10^{14} molec cm^{-2}) in NO2. The maximum estimate of the interference effect for water vapour is obtained by calculating the WV optical depth under saturation conditions at all altitude levels. This is performed using the HITRAN 2008 database (Rothman et al., 2009). Under these circumstances, the current algorithm might underestimate the NO_2 VCD by 0.08 DU (2.2×10^{15} molec cm^{-2}). However, it must be noted that the final data set is cloudscreened and that WV saturation conditions rarely occur in Rome in sunny conditions. Thus, a value of 0.02 DU (5.4×10^{14} molec cm^{-2}) accounting for both ozone and water vapour is added to the combined uncertainty only as a precautionary measure;

9. AMF. The NO_2 air mass factor is a fundamental parameter in the retrieval (Eq. 1). The data analysed here only extend to solar zenith angles lower than 78 °, as explained in Sect. 2.3.3. At these large angles, the AMF might be sensitive to the NO_2 effective height. If an uncertainty of ± 5 km (as in RP2014) is taken as representative for the effective layer height, this leads to a maximum uncertainty of about $0.015 \cdot X_{NO_2}$ on VCDs at very large SZAs. Moreover, Since the Brewer
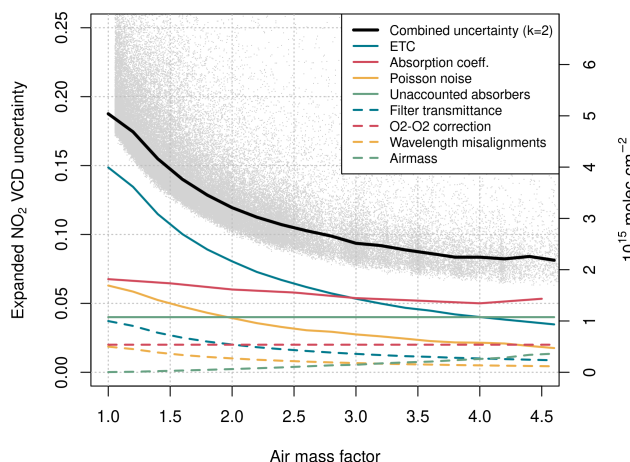
Figure 5. Total expanded uncertainty (black line) and its components, discussed in the text. The lines represent the median values for each air mass bin. Uncertainties are actually estimated for each individual measurement, here represented as grey dots.

PC is synchronised to the universal time by Network Time Protocol, we assume no uncertainty on the registration time and negligible uncertainty on the calculation of the SZA;

475   10. Instrumental temperature. Analysis of SL tests in different periods leads to differences in the determination of the temperature coefficient lower than $\pm 5 \times 10^{-4}$ DU K^{-1} (1.3×10^{13} molec cm^{-2} K^{-1}). Even for temperature extremes of ± 20 K from the average, the resulting uncertainty is lower than 0.01 DU (2.7×10^{14} molec cm^{-2}), and thus negligible. Moreover, visual inspection of temperature measurements in the instrument does not show any trend in more than 20 years, therefore we assume that the response by the internal temperature sensor is stable;

480   11. Based on RP2014, the uncertainties related to the photomultiplier dead time, to the assumed aerosol Ångström exponent, to spectral and geometrical straylight, and to the Rayleigh correction in the visible range are deemed negligible.

Figure 5 depicts the expanded ($k = 2$) measurement uncertainty and its components previously described as a function of the AMF, which is the dominant factor of variability for VCD uncertainties. For sake of clarity, the uncertainties associated to each NO_2 retrieval (grey dots) are grouped in air mass bins and their median is plotted as a line. The expanded uncertainties

485 of individual measurements mostly rely between 0.06 DU (1.6×10^{15} molec cm^{-2}) at large SZAs and 0.23 DU (6.2×10^{15} molec cm^{-2}) at small SZAs, and are much lower (less than 50 %) than the ones obtained with BNALG1 in RP2014.

3.3 Comparison with Brewer #066

To illustrate the accuracy of the new series, we compare two subsets of the BNALG2 record with simultaneous NO_2 estimates obtained with reference instrumentation. A first campaign is organised from 3 to 27 June 2013, when Brewer #067 was moved

490 to the Aosta–Saint-Christophe observatory and compared to Brewer #066. This latter, in turn, was calibrated in September and
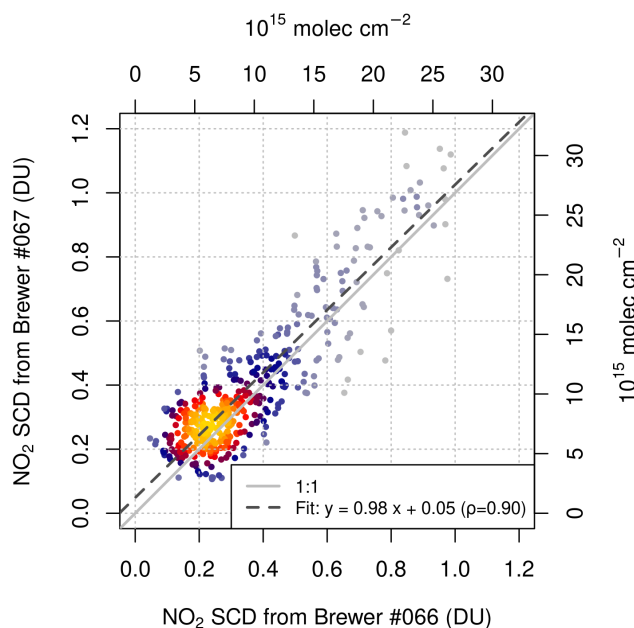
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Figure 6. Comparison of the NO_2 slant column densities retrieved from Brewer #067 and Brewer #066 (considered as the reference) at the Aosta–Saint-Christophe observatory. Colours represent the density of the points based on a two-dimensional Kernel Density Estimation (Venables and Ripley, 2013). The Pearson's correlation coefficient between the two SCD series is $\rho = 0.90$.

October 2012 at the Izaña observatory (Canary island), where its retrievals were also validated against two instruments from the NDACC network: a Fourier Transform Infrared Spectrometer and a RASAS-II Multi Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) spectrometer (cf. RP2014 for further details). In the months following the Langley calibration, the stability of Brewer #066 was carefully checked through the internal (SL) tests.

Brewers #066 and #067 were programmed to take simultaneous measurements in both direct sun and zenith sky geometries. Here we only consider direct sun data collected on fair weather days, which consist in 445 simultaneous retrievals. Since measurements from Brewer #066 were validated in Izaña using BNALG1, we do not reprocess them with BNALG2, but we only rescale them to the new differential absorption coefficient and use the new NO_2 effective layer height in the air mass factor formulation (Table 2). The retrievals from Brewer #067 are instead performed with BNALG2, as in Rome.

The maximum NO_2 Slant Column Density (SCD), i.e. the product between VCD and air mass (which is the real quantity the two instruments are sensitive to), estimated by both Brewers in Aosta–Saint-Christophe is 1.3 DU (35×10^{15} molec cm^{-2}). This first comparison features a Pearson's correlation coefficient of 0.90 between the two sets (Fig. 6, p-value $< 2.2 \times 10^{-16}$, slope 0.98 and offset 0.05 DU, or 1.3×10^{15} molec cm^{-2}). VCDs derived with Brewer #067 are slightly larger than the ones from Brewer #066 (by 0.03 DU or 8.1×10^{14} molec cm^{-2}), however it must be considered that Poisson's noise already accounts for 0.03 DU (at AMF$= 1$) and that the uncertainty related to wavelength misalignments with BNALG1 (Brewer #066) accounts
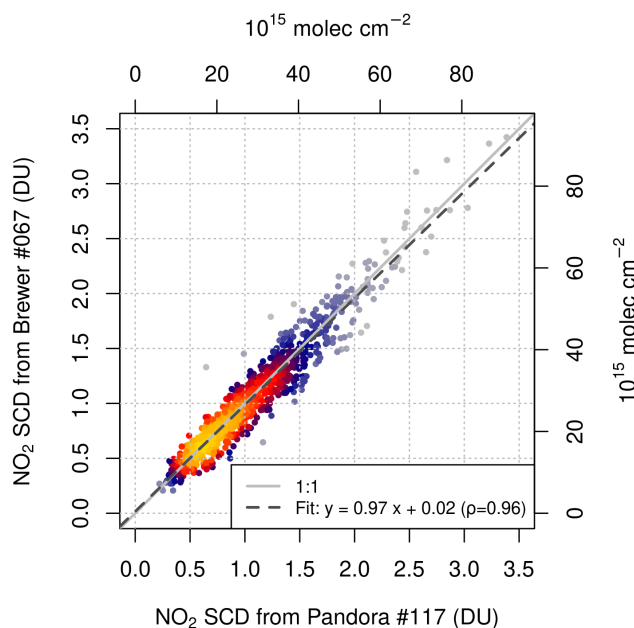
Figure 7. Comparison of the NO_2 slant column densities retrieved from Brewer #067 and Pandora #117 (considered as the reference) at APL (Rome). The Pearson's correlation coefficient between the two SCD series is $\rho = 0.96$. Notice that the range of the axes is wider than in Fig. 6.

for 0.08 DU (2.2×10^{15} molec cm^{-2}). Thus, the mean bias is well within the combined uncertainty, and the comparison results can be defined very satisfactory.

3.4 Comparison with Pandora

The second comparison proposed here is between Brewer #067 and Pandora #117 in Rome. The overlapping period of operation of both instruments extends from May 2016 to July 2017, and accounts for 185 fair weather days and more than 1000 simultaneous measurements (i.e., within a 2-minute time difference). Slant column densities (SCDs) are depicted in Fig. 7. Quite consistently with the results in Aosta–Saint-Christophe, the comparison shows a Pearson's correlation coefficient of 0.96 between the two sets (p-value $< 2.2 \times 10^{-16}$), a slope of 0.97 and an offset of 0.02 DU (5.4×10^{14} molec cm^{-2}). The differences between VCDs from Brewer and Pandora are represented in Fig. 8 as a function of the air mass, to show that their dependence on the AMF is negligible. The median VCD bias by Brewer #067 is -0.002 DU (-5.4×10^{13} molec cm^{-2}), clearly much lower than the combined uncertainty of both instruments, and 90 % of retrievals from Brewer #067 also fall within the nominal confidence levels of Pandora (0.1 DU or 2.7×10^{15} molec cm^{-2}, 2-sigma estimate).

The comparison between the two instruments also allow to appreciate the better stability of BNALG2 compared to the previous version of the algorithm, BNALG1. Figure 9 shows the difference between the Brewer and Pandora on a portion of the data set, using both algorithms. In June 2017, the internal mercury lamp of Brewer #067, representing its wavelength reference,
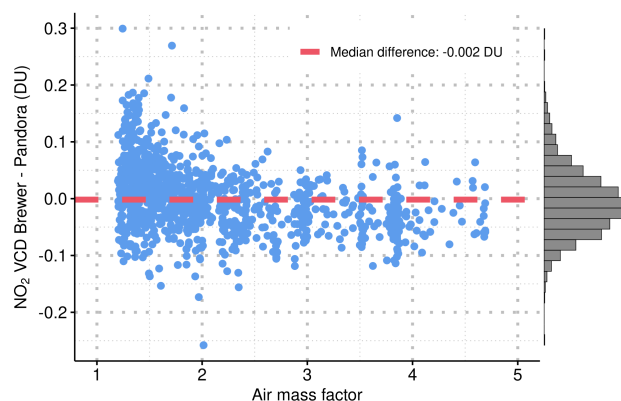
Earth System
Science
Data

Figure 8. Difference between NO_2 VCD retrievals from Brewer #067 and Pandora #117 as a function of the air mass factor (AMF). The median of the differences (-0.002 DU or -5.4×10^{13} molec cm^{-2}) is plotted as a dashed line.
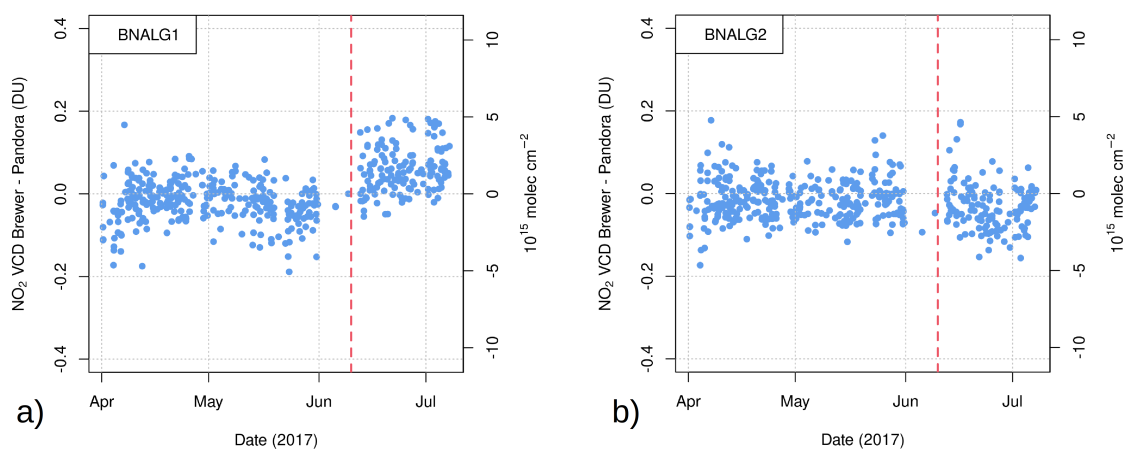

Figure 9. Difference between NO_2 retrievals from Brewer #067 - using BNALG1 (a) and BNALG2 (b) - and Pandora #117, on a portion of the data set. The vertical line shows the moment when the internal mercury lamp of Brewer #067, representing its wavelength reference, was replaced. This is sufficient to trigger a change with BNALG1, which is very sensitive to slight wavelength misalignments.

burned out and was replaced with a new one. This operation is sufficient to trigger an offset of 0.1 DU (2.7×10^{15} molec cm^{-2}) between the two instruments with BNALG1, which is very sensitive to small wavelength misalignments. The retrievals from BNALG2, instead, do not reflect such a large variation.

4 Discussion and conclusions

525 Although new generations of instruments have emerged in the last decades, and more specific, accurate and faster spectrometers have been made available to measure nitrogen dioxide in the atmosphere, the greatest asset from NO_2 data sets from Brewer

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spectrophotometers is the already existing network and the potential length of the recorded series. The data set from Rome represents an exemplary case, since the series covers - with an impressive continuity and only few interruptions - the period from 1996 to the present, when important changes in tropospheric NO_2 emissions are expected to have occurred, especially in this

530   European capital, in connection with technological upgrades (e.g., vehicle fleet and domestic heating sources), environmental control measures and other contingencies.

This justifies the effort made in this study to further improve the Brewer algorithm from BNALG1 to BNALG2. Experimental and modelling findings suggest that the data set obtained with the new method is less sensitive to instrumental interferences, such as wavelength misalignments and changes in the internal temperature, which also contributed to reduce the overall mea-

535   surement uncertainty compared to RP2014. Additional innovations brought by BNALG2 are optimisation for polluted sites and use of the bootstrap estimation method to reconstruct the series of the extraterrestrial calibration coefficients and to track their temporal evolution. In this regard, a fortuitous example is offered by the change of the spectral radiometric sensitivity resulting from maintenance on the Brewer spherical mirror in July 2012, which is correctly tracked by the bootstrap technique.

Although not abundant, and mostly concentrated in the last years of the data set, all available data collected by "reference"

540   instrumentation operating alongside with Brewer #067, during intensive campaigns or much longer periods, were exploited to check the quality of our record. Comparisons with a Brewer (#066) calibrated using the Langley method at a pristine site and validated against NDACC instruments, and with a Pandora (#117) spectrometer show high and largely significant Pearson's correlation coefficients (>0.90), slopes close to 1 and offsets well within the stated uncertainty. The latter was thoroughly calculated taking several instrumental, calibration and algorithmic factors into account, and assigned to each of the >71000

545   measurements. Since calibration provides the largest contribution to the overall uncertainty, one way of further reducing it is to establish new travelling reference instruments calibrated for NO_2 allowing harmonised retrievals within the network. A calibration protocol for NO_2 using a travelling standard MkIV Brewer is being developed by the authors using the current algorithm results. This will bring more consistency to the existing global Brewer NO_2 data and will make it easier to expand the usage of this algorithm in the future. Additionally, an ad hoc characterisation of MkIV Brewer spectrophotometers can be

550   envisaged during international intercomparison campaigns (e.g., Redondas et al., 2018) to facilitate the implementation of our new algorithm and operational NO_2 retrievals on a network basis, such as in EUBREWNET (Rimmer et al., 2018).

This new data set can be used for calibration / validation exercises with satellite radiometers, comparison with models, and to calculate a climatology of the optical depth imputable to NO_2, which is useful, e.g., to improve the accuracy of aerosol optical depths from sun photometers. Further studies are needed to quantitatively determine the magnitude and the significance

555   of the long-term trends that can be identified in the record, and their influencing factors. Since zenith sky measurements have also been recorded throughout the period of operation, they should be explored in future works, with the aim of developing and testing algorithms to partition the NO_2 column densities in the troposphere and in the stratosphere.

Thanks to the general formulation of the method and similar principles of operation of other MkIV spectrophotometers, the algorithm described here and applied to the record in Rome can be implemented at other stations of the international Brewer

560   network, notably the ones with the longest historical data sets.

5   Data availability

The data described in this manuscript can be freely accessed at https://doi.org/10.5281/zenodo.4715219 (Diémoz and Siani, 2021). The series is available as a Comma-Separated Value (CSV) file including vertical and slant column NO_2 densities, in different measurements units ($\mathrm{molec\,cm^{-2}}$, $\mathrm{mol\,m^{-2}}$ and DU), their respective expanded (k= 2) uncertainties, and other ancillary information.

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