Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2017-441
Manuscript under review for journal Atmos. Meas. Tech.
Discussion started: 12 January 2018

Atmospheric Measurement Techniques
Discussions

Examination on total ozone column retrievals by Brewer spectrophotometry using different processing software.

Anna Maria Siani[1*], Francesco Scarlatti[2], Ariana Religi[3], Henri Diémoz[4],' Giuseppe.R. Casale[1], Massimiliano Pedone[5], Volodya Savastiouk[6]

[1]Department of Physics, Sapienza Università di Roma, Rome, Italy
[2]Independent scientist
[3]Institute of Services Science, University of Geneva, Geneva, Switzerland
[4]Aosta Valley Regional Environmental Protection Agency (ARPA), Saint-Christophe, Italy
[5]Infosapienza Settore per i Sistemi Centrali e per l'Office Automation, Sapienza Università di Roma, Rome, Italy
[6]International Ozone Services Inc., Toronto, Ontario, Canada

*Correspondence to: Anna Maria Siani (annamaria.siani@uniroma1.it)

Abstract. The availability of long-term records of the total ozone content (TOC) represents a valuable source of information in studies on the assessment of short and long-term changes and their impact on the terrestrial ecosystem. In addition, ground-based observations represent a valuable tool to validate satellite-derived products. To our knowledge, details about processing software packages to retrieve the TOC from Brewer spectrophotometer measurements are seldom specified in studies concerning such datasets, although some discrepancies can arise from the use of different algorithms and implementations. The deviations among retrieved TOCs from the Brewer instruments located at Rome and Aosta (Italy), using different processing software (Brewer Processing Software, O3Brewer software and EUBREWNET products (Level 1.5) are investigated. Ground-based TOCs are also compared with the Ozone Monitoring Instrument (OMI) TOC retrievals used as an independent dataset since no other instruments near the Brewer sites, are available.

Although the overall agreement of the BPS and O3Brewer TOC data with EUBREWNET data is clearly very good (as expected) and in most cases within the Brewer declared uncertainty less than 2%, it is worth noticing that slight differences have been seen depending on the software in use. Such differences become larger when the instrumental sensitivity exhibits a long-term drift and even in short-term episodes due to the different algorithm for the standard lamp correction. This work aims to provide useful information both for scientists engaged in ozone measurements with Brewer spectrophotometry and for stakeholders of the Brewer data products available at web-based platforms.

Key words: ozone, Brewer spectrophotometry, standard lamp correction, processing software, calibration

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1.INTRODUCTION

Although ozone (O_3) is present in small amounts in the terrestrial atmosphere, it plays a crucial role in the attenuation of solar ultraviolet (UV) radiation (200 - 400 nm) reaching the surface and in radiative processes controlling the energy balance on the Earth (Ramanathan and Dickinson, 1979; Dessler, 2000; Bordi et al., 2012; WMO, 2015).

The cumulative amount of stratospheric and tropospheric ozone represents the total ozone column (TOC). The most common ground-based instruments to measure TOC are spectrophotometers which are designed to measure ground level intensities of attenuated incident solar ultraviolet radiation in the ozone absorption spectra, from which it is possible to retrieve the TOCs. The first TOC observations were recorded using the Dobson spectrophotometer (Dobson and Harrison, 1926) in the late 1920s but only in a few places. Since then, a growing number of sites were equipped with the Dobson spectrophotometer and later in the 1980s with the automated Brewer spectrophotometer (Brewer, 1973). Nowadays, both the Dobson and the Brewer spectrophotometers are used all over the world and if properly maintained and calibrated they provide TOC data within 1-2% accuracy (Fioletov et al., 2005, Vanicek, 2006).

Satellite-based ozone measurements are made by use of the sun UV light backscattered from the Earth's atmosphere. These measurements have the advantage of quasi-global coverage by one and the same instrument. On the other hand, ground-based instruments regularly undergo calibrations with an absolute reference instrument and have longer lifetimes.

It has to be stressed that high-quality TOC retrievals from ground-based stations are necessary not only in support of the validation of satellite derived products but also for the assessment of the long-term ozone trend and to verify to what extent policy measures of the Montreal Protocol on substances that deplete the ozone layer, are effective. Moreover, ground–based TOC data are also necessary to calibrate the parameters in the global climate models used to predict the expected behaviour of the ozone layer in the future (Stübi et al., 2017). The above issues show the importance to measure the ozone amount from ground-based stations with a very good performance.

Even though the same TOC retrieval algorithm, based on the same and acknowledged physical principle (i.e. Bouguer-Lambert-Beer law), is adopted by all available processing software packages, slightly different implementations can trigger some differences in the processed TOC data.

The largest part of the TOC datasets used in the current/available scientific literature is obtained from the WOUDC (World Ozone and Ultraviolet Radiation Data Centre) (2017), in which detailed information on the used processing software is not always available. In addition, to our knowledge, processing software of Brewer TOC data varies from site to site and the processing algorithm is seldom specified. This can be due to the fact that currently a standard processing software of Brewer raw data has not been adopted yet. Recently, the COST Action ES1207 “A European Brewer Network” (EUBREWNET) was established aiming at defining, among the others, a standard procedure for processing the raw Brewer data, thus ensuring the quality of the data and harmonizing the products from the European Brewer (EUBREWNET, 2017).

The purpose of the present study is to: 1) investigate the differences among the TOCs retrieved by three different processing software packages (the Brewer Processing Software, hereafter called BPS) developed by Dr Fioletov V. and Ogyu A. (Environment Canada), O3Brewer software developed by Dr Stanek M. (Solar and Ozone Observatory of CHMI/International Ozone Service) and the EUBREWNET products (ozone Level 1.5). To the purpose of the intercomparison, we tested the mentioned software on the datasets collected by the Brewer instruments located at Rome and Aosta, Italy; 2) compare Brewer ozone recalculations with the Ozone Monitoring Instrument (OMI) TOC retrievals to investigate at which extent the ground-based and satellite-based retrievals are similar. The OMI data were used owing to the fact that no other independent instruments to measure TOCs collocated near the Brewer instruments, are available.

This paper is structured as follows: the theory on the ozone estimates from Brewer direct sun (DS) measurements is first briefly described (Section 2.1); furthermore, the methods to correct the ozone data using the three different ground-based processing software packages are presented in Section 2.2 and the measuring instruments sites in Section 2.3 and 2.4; then, TOC retrievals by the processing software are compared with the purpose to understand the reasons of the differences in ozone retrievals; finally a comparison between ground-based data and OMI products is carried out to investigate at which extent the ground-based and satellite-based retrievals are similar (Section 3); the last section summarizes the main conclusions.

2. DATA AND METHOD

2.1 Theory of direct sun (DS) measurements with Brewer spectrophotometry

The Brewer instrument is a spectrophotometer designed to retrieve the total ozone column by means of measurements of direct sunlight, zenith sky light, focused moonlight or using the global irradiance method (Kerr and Davis, 2007) in the UV region.

The most accurate method to determine the total column amount of an atmospheric gas is based on the direct sun (DS) measurements. It was shown that the accuracy of TOC with DS measurements taken with a well-maintained Brewer spectrophotometer is better than 2% (Fioletov et al., 2005, Vanicek, 2006).

The algorithm to retrieve the total ozone column from the Brewer in DS mode is based on a differential measurement method involving 4 selected wavelengths in the ozone absorption spectra (nominally: 310.1, 313.5, 316.8 and 320.0 nm). A photomultiplier registers photon counts of radiation that pass through the exit slits from 3 to 6 corresponding to the operational wavelengths. The raw photon counts are then converted into count rates and corrected for the dark count, the dead time, the internal Brewer temperature (Kerr, 2010). In addition, a correction for the spectral transmittance of the attenuation filters can be added depending on the filter used, if the respective characterization is available.

A linear combination (F) of the logarithms of the measured spectral direct irradiances at the four longer wavelengths (F_i) intensities is computed by weighting the F_i with coefficients -

(w_i=-1, +0.5, +2.2, -1.7) chosen in order to minimize the effect of the aerosol scattering and to eliminate the effect of the sulphur dioxide absorption (Kerr et al., 1981; Kerr, 2010):

$$F = \sum_{i=1}^{4} w_i \log F_i \qquad (1)$$

F_i is also compensated for the effect of the Rayleigh scattering by subtracting:

$$\frac{p}{p_o} \mu_R \sum_{i=1}^{4} w_i \beta_i \qquad (2)$$

where p is the climatological pressure at the measurement site and p_o is the pressure at the sea level; μ_R is the Rayleigh air mass factor (i.e. the slant path of direct radiation through air), calculated for a thin layer at 5 km altitude, β_i is the Rayleigh scattering coefficient at the wavelength, λ_i.

According to the Bouguer-Lambert-Beer law, it is possible to retrieve the total ozone column (TOC) as:

$$TOC = \frac{F - Fo}{\Delta\alpha\mu} \qquad (3)$$

where Δα is the weighted ozone absorption coefficient, i.e. the linear combination of the ozone cross sections using the same weighting coefficients employed for F. Δα is determined by performing a specific test using spectral lamps providing the precise operational wavelengths for each individual spectrophotometer. Then Δα is obtained for these wavelengths using Bass-Paur ozone absorption spectrum (Bass and Paur, 1985) at the fixed temperature of -45°C (Kerr, 2010).

The standard Brewer algorithm assumes that the ozone is concentrated in a thin layer at the altitude of 22 km, thus the air mass factor (μ) is expressed by:

$$\mu = \sec\left[\arcsin\left(\frac{R_E}{R_E + 22}\sin Z\right)\right] \quad (4)$$

where R_E is the Earth's radius and Z is the solar zenith angle.

F_o is also expressed as the linear combination of the extraterrestrial irradiance at the operational Brewer wavelengths with the same weighting coefficients used for F. F_o corresponds to F at the top of the atmosphere and it is usually named "extraterrestrial constant" (ETC).

There are two methods to determine the ETC. The first is based on the use of the Langley plot technique i.e. plotting F versus μ, then the ETC value is extrapolated at zero air mass. This method is used for the calibration of primary standards and requires to be carried out under stable atmospheric conditions, small day-to day stratospheric ozone variability and low pollution concentrations. The second method is based on transferring the calibration from a reference Brewer instrument with a known ETC to a candidate instrument during field campaigns. This latter technique is the most common way for regularly calibrating the instruments which belong to the Brewer network. In between the calibration audits with a travelling standard, the TOC data are processed adjusting the ETC according to the changes of the radiometric sensitivity of the instrument, if needed. The correction uses the time series of the intensities of the internal standard lamp test (see the following section).

Direct-sun measurements are carried out at specific solar zenith angles through the day depending on the user schedule (a sequence of commands written by the operator), allowing the Brewer to make observations continuously and automatically. During a DS sequence, five consecutive measurements are taken in less than five minutes. Then the mean and the standard deviation of the five ozone values are computed and associated to that DS measurement. An individual TOC value is considered acceptable if the standard deviation of the five measurements is lower than 2.5 DU. In this case, the value is included in the number of accepted DS measurements to provide the daily TOC mean.

2.2 Standard lamp correction

Several tests are performed on a daily and weekly basis to verify if the Brewer operates correctly and to take under control the changes in instrumental properties. The main standard tests included in the diurnal operational schedule are: shutter motor run/stop (RS), photomultiplier dead time (DT), mercury lamp (Hg) and standard lamp (SL).

The RS test verifies that the slit-mask motor is operating properly. It calculates the ratio of irradiances at the operational wavelength (using as the light source a quartz-halogen lamp of 20 W) in a dynamic mode and in a static mode. This ratio should be as close as possible to unity. The DT test measures the dead-time of the photomultiplier and the photon-counting circuitry (the result of the test value should be within 5 ns with respect to the instrument constant). Also during the DT test, the halogen lamp is turned on. The Hg test (in which a mercury lamp is used) ensures the correct wavelength alignment of the Brewer, i.e. that the instrument is usually making direct sun measurements at the proper wavelengths. This test is usually carried out several times every day.

The standard lamp test (SL) is used to monitor the stability of the instrument response after the calibration with the reference spectrophotometer. The test is performed by the use of a quartz-halogen internal lamp (20 W) as the light source. The photon counts are recorded at the same operational wavelengths employed in the DS measurement and the result of the SL test, the so-called R6 ratio, is determined using Eq.(1). In this way changes in the instrument response are constantly tracked (i.e. changes with respect to $R6_{ref}$ and hence to the corresponding ETC, both established during each calibration campaign).

If a change in R6 is experienced, this results in a corresponding change in the ETC (assuming that the relative lamp intensities at the four wavelengths do not change) and a correction in the reference ETC should be applied to determine the ozone values in between each calibration, as follows:

$$TOC = \frac{F - ETC + \Delta SL}{\Delta \alpha \mu} \qquad (5)$$

where ΔSL is the correction factor measuring the difference between $R6_{ref}$ (from the last intercomparison) and R6 for a specific day.

Depending on the processing software used by the station operator, ΔSL is computed in different ways:

- the BPS adjusts the ETC taking into account the difference between the $R6_{ref}$ (calculated with a triangular smoothing filter of SL-test values from 15 consecutive days since that calibration) and the present daily mean values of R6, if the difference between the $R6_{ref}$ and the current value is ≥ 250; if the difference is ≤ 250 units then a median of R6 data before 15 days and after 15 days is used for the correction. That correction is reported in the file named "o3data" produced by the BPS. The threshold and the time window are however not adjustable by the users.
- O3Brewer adjusts the ETC using a Gaussian smoothing filter on R6 values (Stanek M., 2016). The program reads the R6 daily means of the SL test 10 days before and 10 days after the selected date period, and creates the smoothed R6 time series (hereafter named $R6_{smooth}$) which is used for ETC adjustment. O3Brewer applies the Gaussian low-pass filter when the difference between R6 and the reference $R6_{ref}$ does not exceed a certain threshold (500 units, Stanek personal communication, 2016). The threshold and the time window are however not adjustable by the users. If this difference exceeds the threshold, then the software applies a correction equal to the $R6_{ref}$ plus 500 (see the figure in the following Section). This option can be turned off and then the daily mean values for SL are used for the correction of the ETC.

- The EUBREWNET architecture is based on three different data-quality/processing levels of TOC estimates from DS measures. Level 0: the TOC is taken directly from the Brewer files (named Bfiles) as calculated by the standard algorithm (Eq. (3)); Level 1: the TOC is recalculated with the standard algorithm applying the set of constants verified by the operator and the spectral attenuation of each filter is added in Eq. (5); Level 1.5: the TOC is filtered for the standard deviation of five consecutive observations (default value is 2.5 DU) and the maximum ozone air mass (the default maximum value is 3.5). Additionally, the wavelength alignment of the spectrometer must be within ±2 microsteps (valid Hg tests) before and after the ozone measurement to ensure the quality of TOC measurements. In addition, TOC values less than 100 DU and greater than 500 DU are discarded. The TOC is calculated taking into account Eq. (5) and adding the spectral attenuation of the filters and, if available, the stray-light correction is applied (Karppinen et al., 2015; Redondas et al., 2016). The ΔSL correction is determined applying a triangular moving average over the daily median values of R6 in a window of seven days (default time window). The correction is applied if the difference between $R6_{ref}$ and the calculated value exceeds 5 units. Level 2.0: ozone products are consistent with Level 1.5 products validated with a posterior calibration. If the reference constants of a posteriori calibration do not differ significantly from the values in use then level 1.5 product is not reprocessed and it represents the most reliable product.

  At the present time, tools for Level 2.0 are developed but not yet implemented. A complete description of the processing can be found at the website of EUBREWNET (2017).

2.3 Measuring instruments and sites

Brewers MKIV serial numbers 067 and 066 have been operating at the Solar Radiometry Observatory of Sapienza University of Rome (hereafter Rome) and at the headquarter of Aosta Valley Regional Environmental Protection Agency (ARPA) at Saint Christophe-Aosta (hereafter Aosta), respectively. The former has been recording TOCs since 1992 whereas the latter since 2007 (Siani et al., 2013).

In this study the above sites were selected because both Brewers belong to Sapienza University of Rome, both Brewers have been calibrated with the same reference spectrophotometer since their installation, both regularly submit data to the WOUDC and took part to the COST Action ES1207 “EUBREWNET”. The station characteristics are reported in Table 1.

Table 1. Characteristics of the two Italian Brewer sites

Station name (GAW ID)	**Brewer Serial number**	**Coordinates** (latitude, longitude, elevation (m above sea level)	**Observation period**	**Environmental context**
Aosta (AST)	066	45°N, 7.4°E, 569 m a.s.l.	29/01/2007 - 31/12/2015	semi-rural
Rome University (ROM)	067	41.9°N, 12.5°E, 75 m a.s.l.	01/01/1992 - 31/12/2015	urban

Since their installation, both Italian Brewers have been calibrated every one or two years by an intercomparison with the traveling reference Brewer 017 from International Ozone Services Inc. (IOS), (2017). This Brewer is in turn calibrated against the World Brewer Reference Triad in Toronto (Fioletov et al., 2005). In this way the ozone calibration of Italian spectrophotometers is also traceable to the Brewer Reference Triad. The calibration history of the Italian sites is reported in Table 2.

Although zenith sky and global irradiance measurements were available, only DS measurements were selected in this study because they have a lower uncertainty compared to the other types of measurements (Fioletov, 2005). Individual DS observations for each Brewer were recalculated with BPS (Fioletov and Ogyu , 2007), O3Brewer software packages (Stanek, 2016), satisfying the standard deviation criteria ≤ 2.5 DU and air mass factor ≤ 4. TOC real time values Level 1.5 were also downloaded from EUBREWNET platform over the period 2005-2015 at Rome and 2007-2015 at Aosta. The stray –light correction was not applied because it requires the calibration against a double monochromator Brewer and the instrumental characterization (Redondas et al., 2016) which is not available.

Daily means were then calculated from all available data sets (hereafter named TOC BPS, TOC O3Brewer and TOC EUBREWNET). We used daily TOC averages because the applied ETC correction is the same for all individual measurements within the same day.

Table 2. Calibration history of Brewer 066 and 067. In brackets it is reported the month of the calibration for Brewer 067 (*The recalculation of the constants was performed by IOS after the calibration on July 2009). In one case the calibration of Italian Brewers was performed in Arosa (Switzerland) at the Lichtklimatisches Observatorium during the Seventh Intercomparison campaign of the Regional Brewer Calibration Center Europe (WMO-GAW, 2015). In 2013 the calibration of both Brewers was carried out at Aosta.

Year	Period	Location (Brewer 066)	Location (Brewer 067)
1992	January		Rome
1993	September		Rome
1995	May		Rome
1996	April		Rome
1997	May		Rome
1998	July		Rome
1999	September		Rome
2000	September		Rome
2002	March		Rome
2003	September		Rome
2006	September		Rome
2007	April	Aosta	Rome
2009	July	Aosta	Rome
2010*	January	Aosta	Rome
2011	August (July)	Aosta	Rome
2012	August (July)	Arosa	Arosa
2013	May (June)	Aosta	Aosta
2014	July		Rome
2015	July	Aosta	Rome

2.4 Satellite TOC data

The Ozone Monitoring Instrument (OMI) products were used as an ancillary dataset with the purpose of helping understand the difference among the investigated Brewer retrievals and the comparison should not be regarded as exhaustive validation exercises of satellite total ozone data. Daily averages of the Brewer TOC were compared with satellite ozone values obtained during the overpass. The use of daily means instead of Brewer TOC observations taken close to the OMI overpass is reasonable owing to the well- known long-term chemical stability of the stratospheric ozone (Antón et al., 2009). This allows to compare a large number of pair measurements (Antón et al., 2009; Vaz Peres et al., 2017) because there are only one or two daily satellite values.

Satellite overpass data at Rome and Aosta were derived from OMI, on board NASA EOS-Aura spacecraft launched in July 2004. The OMI instrument is a nadir-viewing spectrometer measuring solar reflected and backscattered light from the Earth atmosphere and surface in the wavelength range from 270 nm to 500 nm, providing global daily coverage with a spatial resolution of 13×24 km^2 in nadir. The Aura satellite describes a sun-synchronous polar orbit, crossing the equator at 13:45 local time. Two algorithms, OMI-TOMS (Total Ozone Mapping Spectrometer) and OMI-DOAS (Differential Optical Absorption Spectroscopy), are used to produce OMI daily total ozone datasets.

In our study OMI-TOMS ozone overpasses based on TOMS V8.5 algorithm (Bhartia and Wellemeyer, 2002) at the stations under study over the period 01/10/2004-31/12/2015 were downloaded from the NASA –AURA validation data center platform. Here we used OMI-TOMS for the reason that the comparison between ground-based Brewer and Dobson data and OMI satellite ozone data showed an agreement of better than 1% for OMI-TOMS and better than 2% for OMI-DOAS data (Balis et al., 2007).

2.5 Statistical parameters

To estimate the difference between the TOC datasets, the following statistical parameters are used for all the possible data pairs: nonparametric Spearman coefficient (RHO), Mean Bias (MB), Mean Percentage Error (MPE), Root Mean Square Error (RMSE). RHO was used to measure the correlation between two variables without making any assumption about their distribution. MB represents the systematic differences (or bias) between two selected datasets; MPE provides the average of percentage errors with respect to TOC values taken as the reference. RMSE is an estimate of the standard deviation of the difference (residuals) between two dataset.

$$MB = \frac{1}{N}\sum_{1}^{N}(y_i - y'_i) \qquad (6)$$

$$MPE = 100 * \frac{1}{N}\sum_{1}^{N}\frac{(y_i - y'_i)}{y'_i} \qquad (7)$$

$$RMSE = \sqrt{\sum_{1}^{N}\frac{(y_i - y'_i)^2}{N}} \qquad (8)$$

The previous equations show the formulas of the mentioned statistical parameters, where y_i is the i-th TOC value (O3Brewer, or OMI) value, $y'_i$is the i-th TOC value of the BPS (or EUBREWNET) series, N the number of all the possible data pairs analysed.

3. RESULTS AND DISCUSSION

The time series of TOC daily means from BPS, O3Brewer and EUBREWNET are presented in Fig. 1 (upper panel Rome, bottom panel Aosta).

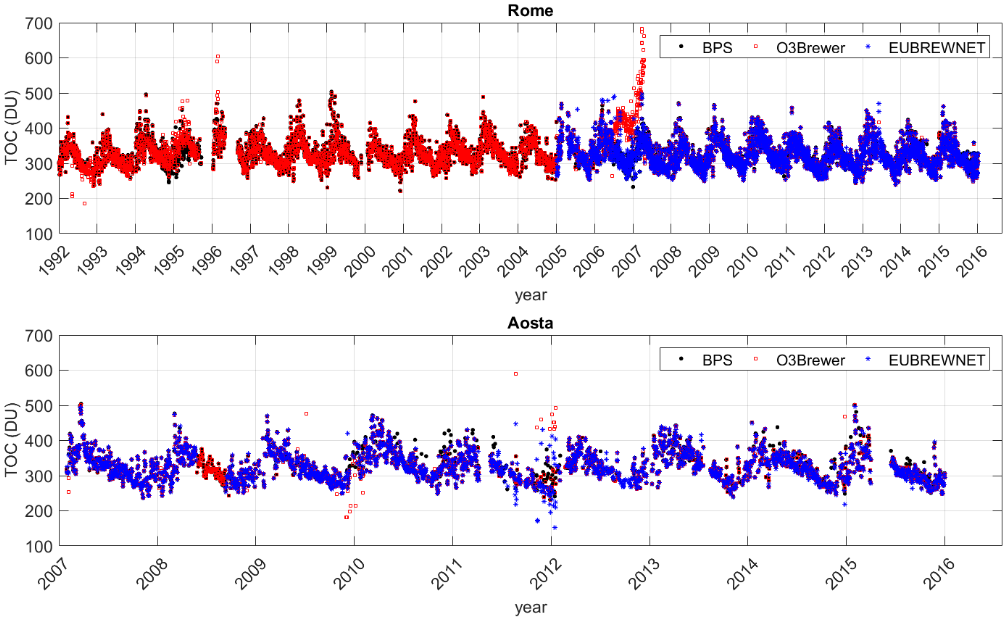
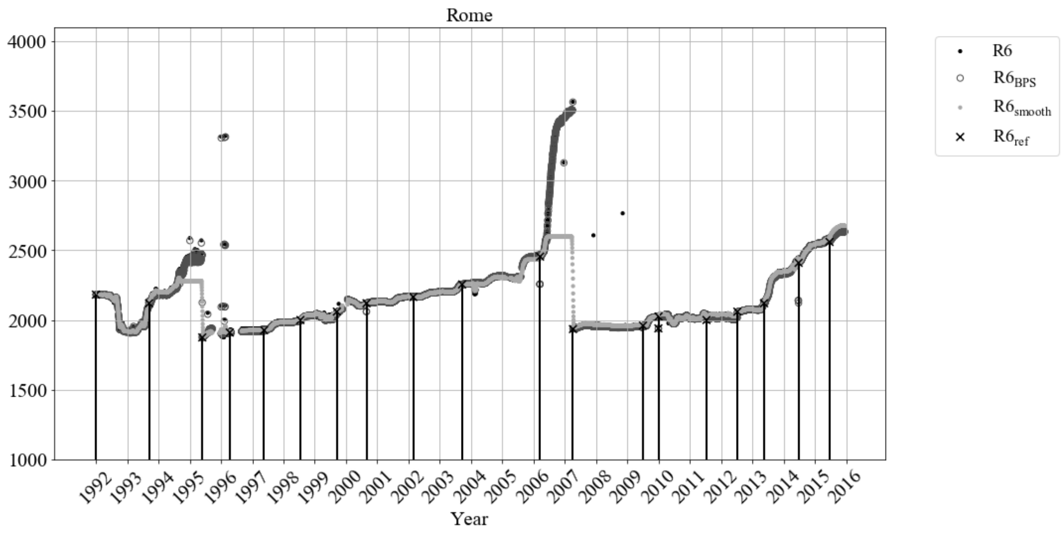


Figure 1. Time series of TOC daily means from BPS and O3Brewer and EUBREWNET at Rome (upper panel) and at Aosta (lower panel). The daily means are obtained taking into account individual direct Sun measurements satisfying std≤ 2.5 DU and μ≤4.

It is worth noticing that ozone seasonal cycles show an overall similarity between the two sites with maximum value in late Spring and minimum in late Autumn. However it is clearly visible that there are some periods in which TOC daily means, obtained by the three processing software are different (e.g. between 1994 and 1995, and between 2006 and 2007 at Rome).

With the aim at controlling the stability of the Brewer instruments, the R6 ratios are plotted in Fig. 2. In the same figure $R6_{BPS}$ (obtained as the sum of BPS correction and $R6_{ref}$), $R6_{smooth}$ series and the $R6_{ref}$ established during the calibration campaigns, are also shown.



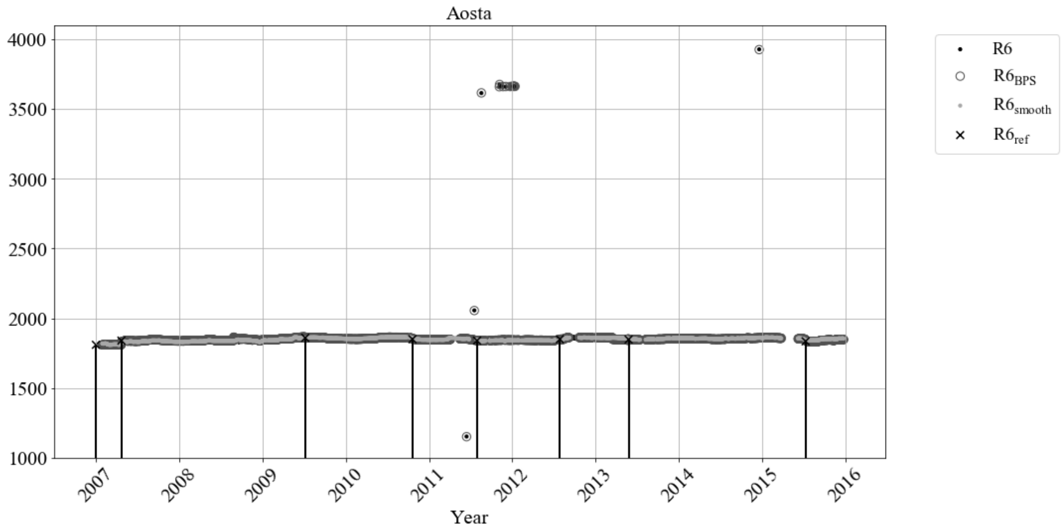


Figure 2. Daily series of the ratios R6, R6$_{BPS}$ and R6$_{smooth}$ at Rome (upper panel) and at Aosta (bottom panel). Vertical lines represent R6$_{ref}$ established during each calibration campaign.

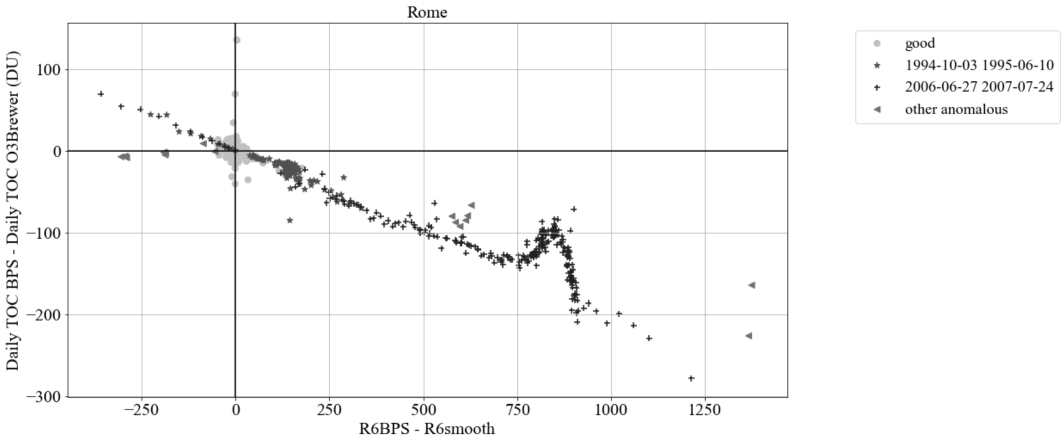
In order to investigate the effect of the standard lamp correction on TOCs retrievals, first we analyzed BPS and O3Brewer TOC series, then we compared both TOC retrievals with EUBREWNET data. Finally, the processed Brewer data were compared with OMI products. In this study we analyzed the recalculated TOC with the standard lamp correction and compared them to the reference constants derived during the calibration visits with the purpose to clarify how the effect of the processing software in use is reflected in the recalculated TOC values.

3.1 Comparison between BPS and O3Brewer TOC retrievals

Looking at the standard lamp test results (Fig. 2), it can be noticed that the sensitivity of the instrument at Rome has changed mainly in two periods (between 1994 and 1995, and between 2006 and 2007). The problem turned out to be the deterioration of the filter (NiSO4/UG11) which was replaced during the calibration visits both in 1995 and 2007. Brewer 066 (Aosta) exhibited a better stability except in some occasional cases, where unusual R6 ratios were experienced. R6$_{BPS}$ shows a very similar behaviour to R6 at both stations due to the calculation method of the standard lamp correction by the BPS, whereas R6$_{smooth}$ time series displays a different trend with respect to R6. In particular, at Rome (Fig.

2, upper panel) R6smooth becomes a constant offset when the sensitivity of the instrument starts to change. This is due to the fact that the Gaussian low-pass filter in O3Brewer software is not applied when the difference between the reference $R6_{ref}$ and R6 exceeds a certain threshold (500 units, Stanek personal communication, 2016). In this case the correction is equal to the $R6_{ref}$ plus 500. Consequently, the temporal behaviour of R6smooth during these time intervals appears as a plateau. Once a new calibration is performed (i.e. new references of R6 and the ETC are defined) R6 and R6smooth show a similar behaviour again. At Aosta the R6smooth temporal evolution (Fig. 2, bottom panel) shows a stable behaviour.

A better visualization of the effect of the correction factor on TOCs is provided plotting the difference between the TOC retrievals (TOC BPS – TOC O3Brewer) as a function of the difference between $R6_{BPS}$ and $R6_{smooth}$ (Fig. 3). Large deviations between the two reprocessed TOC daily means appear when there is a large difference between $R6_{BPS}$ and $R6_{smooth}$, as expected.



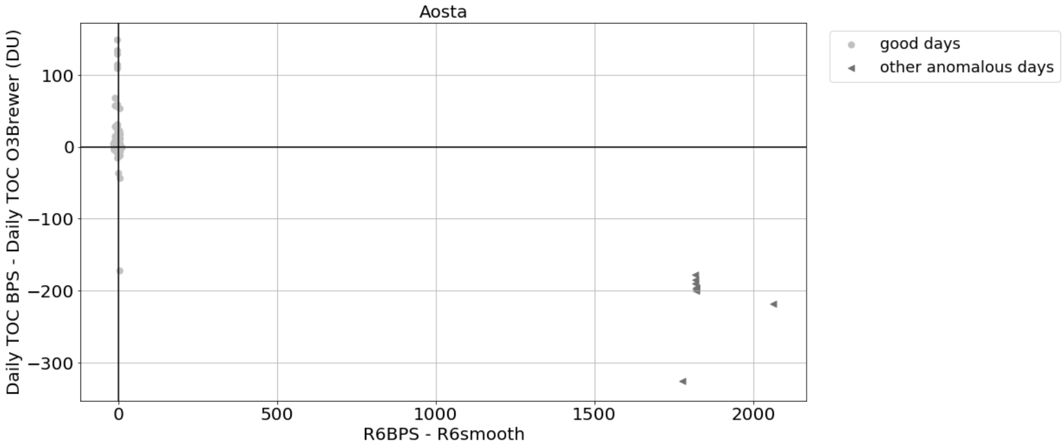


Figure 3. Differences between TOC BPS and TOC O3Brewer vs $R6_{BPS}$-$R6_{smooth}$ at Rome (upper panel) and at Aosta (bottom panel).

A further step consisted in distinguishing those days in which the standard lamp worked well (hereafter named “good” cases) i.e. when $R6_{BPS}$ and $R6_{smooth}$ show a similar behaviour as R6, from those in which $R6_{smooth}$ differed significantly from R6 and $R6_{BPS}$ (hereafter called “anomalous”). Two different conditions can be detected for the latter group: 1) $R6_{smooth}$ is a constant value and hence the O3Brewer recalculation provides unusual TOC values; 2) occasional failure of the SL test.

Two distinct periods were found at Rome belonging to the first condition (3rd October 1994 - 10th June 1995; 27th June 2006 - 24th July 2007), due to the deterioration of photomultiplier filter which was replaced during the calibration visit both in 1995 and in 2007. In those cases the standard lamp correction should not be applied. Some days that belong to anomalous cases were found at Aosta. Occasional anomalous R6 ratios can occur for several reasons, such as wrong wavelength selection by the micrometer, communication problems or incorrect zenith drive position in relation to the lamp.

A better visualization of “good” TOC data is provided by a scatterplot of TOC O3Brewer versus TOC BPS in Fig. 4. Although a lower dispersion can be seen if anomalous days are not considered, however there are cases in which a large difference still persists between the TOCs processed by the two software.

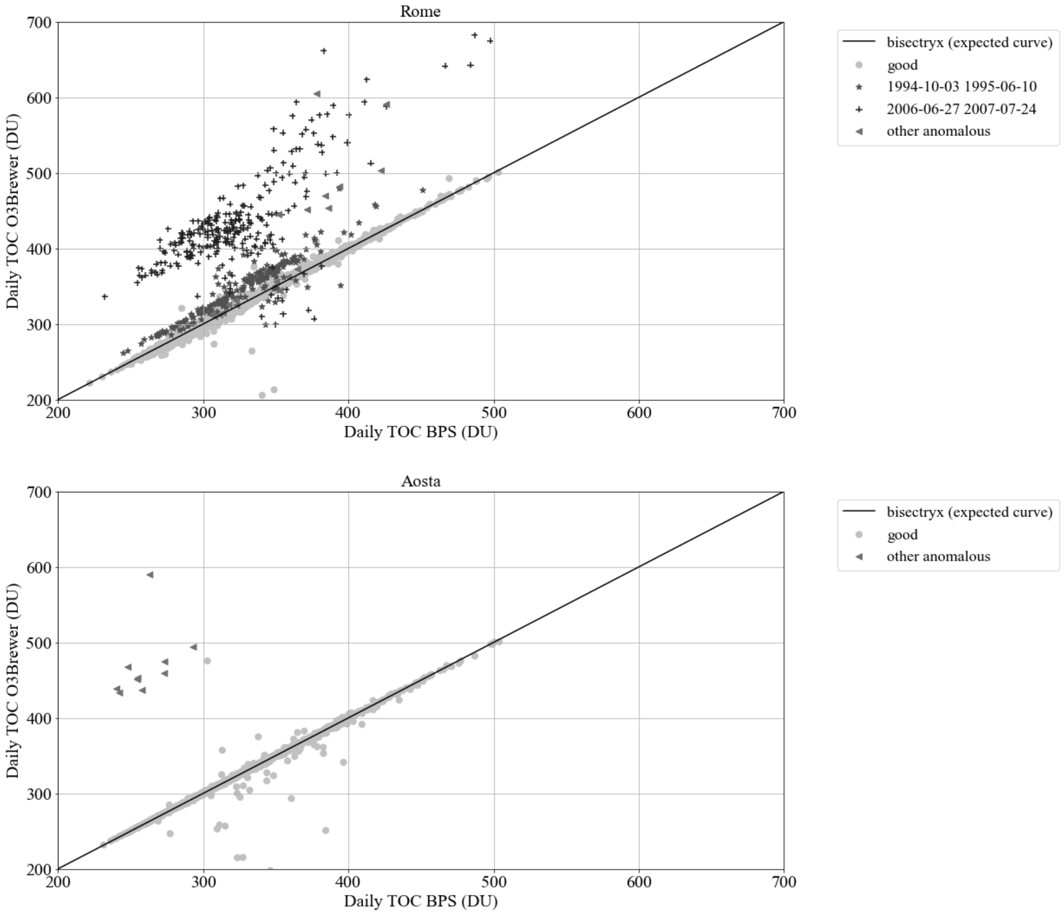


Figure 4. TOC O3Brewer *vs* TOC BPS at Rome (upper panel) and at Aosta (lower panel)

The next step was to flag the O3Brewer TOC daily means ≤180 DU and ≥ 550 DU as outliers, since the condition on maximum and minimum ozone has already been set in the BPS configuration. The data discarded by the above condition underwent an inspection of raw data in order to be sure that they were only due to a misbehaviour of the instrument and they were not "Black Swan" events (Taleb, 2007), i.e. events with a very low probability that come as a surprise in the field in which it occurs as it happened in the case of the Antarctic ozone hole (Barthia, 2017).

Then, TOC daily means with daily std ≥50 DU were also discarded since large daily variability often occurs in case of ozone spikes in that particular day. This high threshold was chosen because the diurnal TOC variability can reach 40–50 DU at mid- to high-latitude locations during late spring and summer (Siani et al., 2002; Tzortziou et al., 2012). TOC daily means without R6 values (no SL test was performed in that day) were also discarded.

Table 3 shows the comparison between O3Brewer and BPS when all data are considered (row “all” data), in the case of “good” data and also in the case of filtering outliers (row “good with filter flag”).

Table 3. Summary of the statistics O3Brewer vs BPS (N= number of pairwise TOCs). “all” data indicates all the possible data pairs, “good” days in which $R6_{BPS}$ and $R6_{smooth}$ show a similar behaviour with respect to R6; “good with filter flag” are related TOC daily means which are not above 550 DU and below 180 DU, daily means with daily std ≥50 DU and without R6 values are also discarded.

O3Brewer_vs_BPS	N	RHO	MB (DU)	MPE (%)	RMSE (DU)
Rome					
all	6483	0.919	4.32	1.33	24.32
good	6312	0.995	-0.66	-0.21	3.69
good with filter flag	6034	0.997	-0.62	-0.20	2.59
Aosta					
all	2432	0.967	0.36	0.19	15.85
good	2418	0.989	-0.51	-0.14	8.05
good with filter flag	2306	0.999	-0.13	-0.03	1.99

A good overall agreement is found when anomalous and flagged data were removed, the correlation improves from 0.92 (Roma) and 0.97 (Aosta) to close the unity at both stations; MB values move from about 4 DU to -0.6 DU at Rome and from 0.3 DU to -0.1 at Aosta. RMSE also decreases from an average value of about 25 DU to 2 DU at Rome and from 16 DU to about 2 DU at Aosta. In the former case the above difference can affect the validation of satellite derived products, the comparison with other ozone data sources and the assessment of the long-term ozone trend

3.2 Comparison of BPS and O3Brewer TOC retrievals with EUBREWNET data

The TOC daily means retrieved by O3Brewer and BPS (both “all” and “good with filter flag”) data were compared with those derived from EUBREWNET retrievals (including also the questionable data). The EUBREWNET data set used in this comparison was downloaded by the EUBREWNET platform without adding any additional filter. Table 4 shows the results of the two processed TOC data sets against the EUBREWNET data set.

There is no significant difference among the TOC retrievals (less than 1%) except in the comparison O3Brewer *vs* EUBREWNET in the case of “all” at Rome in which MPE is 2.5%. This is mainly due to the TOCs over the period 27th June 2006 - 24th July 2007, when the O3Brewer processing software applied a constant correction value. Although the overall agreement of the BPS and O3Brewer TOC data with EUBREWNET data is clearly very high (as expected), it is worth noticing from RMSE results that slight differences are still experienced depending on the software in use and, specifically, on the standard lamp correction algorithm.

Table 4. Summary of the statistics of the comparison between BPS and O3Brewer daily means with vs EUBREWNET, N= number of pairwise TOCs; all indicates the whole data set; “good with filter flag” includes TOC reprocessed by O3Brewer selecting $R6_{smooth}$ with a similar behaviour with R6. Filter flag is related to daily means with std ≥50 DU which are excluded. Notice that at Aosta all daily means have std <50 DU.

O3Brewer *vs* EUBREWNET	N	RHO	MB (DU)	MPE (%)	RMSE (DU)
Rome					
all	3260	0.877	7.98	2.50	32.99
good with filter flag	2870	0.995	-0.27	-0.05	6.21
Aosta					
all	2225	0.985	0.51	0.26	11.67
good with filter flag	2124	0.995	0.16	0.14	6.48
BPS vs EUBREWNET					
Rome					
all	3239	0.989	0.39	0.18	8.39
good with filter flag	3100	0.989	0.38	0.18	8.43
Aosta					
all	2240	0.975	-0.03	0.11	10.90
good with filter flag	2240	0.975	-0.03	0.11	10.90

3.3 Comparison of BPS, O3Brewer and EUBREWNET TOC retrievals with OMI data

OMI overpasses were compared with the investigated Brewer TOC retrievals. The comparison was performed taking into account the same design criteria described in the previous session. The scatterplots of OMI *vs* Brewer data are shown in Fig. 5 (all data are plotted on the left panel whereas only data marked as “ good” are plotted in the right panel). In the latter case a high degree of proportionality between OMI and the ground-based total ozone column data can be noticed. However depending on the Brewer processing software a different behaviour is visible, even when only “good” data are considered.

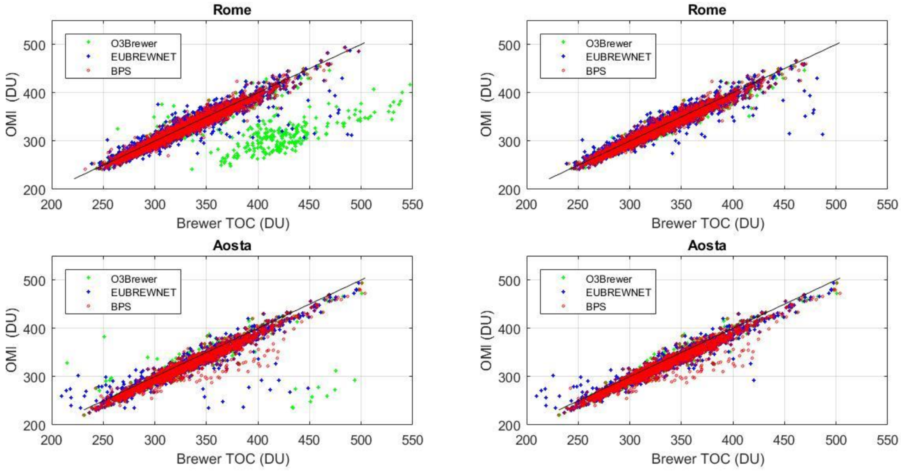


Figure 5. Scatterplots OMI versus Brewer total ozone column. The solid line represents the bisectrix

The results of the statistical analysis are summarized in Table 5. In general in both sites, the TOCs retrieved by the three processing software show an excellent agreement with OMI products (the Spearman coefficient is very high). However, OMI products show a systematic underestimation with respect to ground-based data. Taking into account only data over the periods showing small R6 deviations from the reference values, OMI data were on average smaller than good Brewer values: about less than 1 % and about 2.5% for both O3Brewer and EUBREWNET at Rome and Aosta respectively; about 1% (Rome) and 2.8% (Aosta) in the case of BPS data. These results are in agreement with previous studies on validation of the OMI total ozone column by Brewer spectrophotometry conducted at the same latitudes (Ialongo et al., 2008; Anton et al., 2009).

Table 5. Summary of the statistics of the comparison between BPS, O3Brewer and EUBREWNET and OMI; N= number of pairwise; "all" indicates that all data were used; "good with filter flag" includes TOC reprocessed by O3Brewer selecting R6smooth with a similar behaviour with R6. Filter flag is related to daily means with std ≥50 DU which are excluded. Notice that all daily means obtained by EUBREWNET have std <50 DU.

Rome	n	RHO	MB (DU)	MPE (%)	RMSE (DU)	**Aosta**	n	RHO	MB (DU)	MPE (%)	RMSE (DU)
	OMI vs BPS										
all	2894	0.977	-3.72	-1.13	8.59		2159	0.969	-9.44	-2.84	13.89
good with filter flag	2514	0.979	-3.61	-1.10	8.39		2141	0.969	-9.54	-2.87	13.92
	OMI vs O3Brewer										
all	2907	0.821	-12.49	-2.97	37.63		2068	0.950	-8.83	-2.54	19.71
good with filter flag	2524	0.972	-2.78	-0.82	8.80		1954	0.982	-8.35	-2.56	11.12
	OMI vs EUBREWNET										
all	2846	0.962	-3.37	-0.95	12.89		1922	0.957	-8.52	-2.47	16.01
good days	2594	0.967	-2.80	-0.78	11.45		1878	0.977	-8.14	-2.40	12.79

When comparing RMSE values it can be noticed that RMSE changes at Rome from 8.39 DU to 37.63 DU, at Aosta from 11.12 19.71 DU (higher in the case of all data reprocessed by O3Brewer) which supports the observed scatter plot shown in Fig. 5.

The slight differences among the statistical parameters used in the comparison of "good" cases are observable. A possible explanation is that the comparison was performed using Brewer data averaged on daily basis which includes local and temporal fluctuations that cannot be detected by overpasses and from approaches of the standard lamp correction in the software in use. Besides, systematic differences between ozone estimated from OMI and from Brewer at Aosta could be related to the ground pixel size which can affect ozone amounts probed by the satellite, due to the complex orography of the valley.

4.Conclusions

This study analyzed the total ozone column recalculations at Rome and Aosta using three different software packages. We found that large difference in total ozone column retrievals can be experienced when the instrumental sensitivity exhibits a long-term drift. The variability in TOCs retrievals depends on the algorithm of the standard lamp correction. When anomalous R6 values occur, the correction applied by O3Brewer software is a constant value producing anomalous TOCs. Similarly, the current Level 1.5 in the EUBREWNET can produce erroneous ozone recalculations when anomalous R6 values are experienced. This can be avoided if days with R6 outliers are removed manually The issue is expected to be solved in Level 2.0 products, when they will be released. The BPS ozone recalculations are less affected by abrupt changes in the sensitivity, even in case of R6 drifts. After discarding the periods with drifts or occasional abrupt changes in R6, a good overall agreement is found between BPS, O3Brewer and EUBREWNET (MPE about <0.3%). However a spread among the processing software was still found.

The analysis of the differences between recalculated TOCs and OMI overpasses showed that the latter dataset underestimate less than 2% ground –based total ozone columns at Rome and less than 3% at Aosta (using “good” cases).

The operators should constantly monitor the sensitivity of the instrument and know carefully the processing software used to recalculate the total ozone. This means that the quality-controlled data cannot be assured only by automatic data rejection rules of the adopted software, but a rigorous manual data inspection is always necessary to prevent inconsistent data produced by the processing software package in use. Alternately, users could use more than one package as a cross validation of own data, even if time consuming. Another solution consists in dividing the periods of R6 drifts into shorter time intervals and for that period a new set of constants ($R6_{ref}$ and ETC) could be established by the user as the averages of R6 ratios in that time interval. This process (“synthetic calibration”) allows the user to introduce standard lamp corrections larger than the software hardcoded thresholds. In any case the synthetic constants in use must be confirmed at the next calibration with the reference instrument.

Data availability. The data used for the present study can be asked to the authors of the present paper.

Competing interests. The authors declare that they have no conflict of interest.

Acknowledgments: We thank the European Brewer Network (http://rbcce.aemet.es/eubrewnet/) for providing access to the data used in this investigation, and the COST Action ES1207 “A European Brewer Network (EUBREWNET)”, supported by COST (European Cooperation in Science and Technology). We also thank NASA Goddard Space Flight Center for OMI data available (https://avdc.gsfc.nasa.gov/).
This paper is dedicated in memory of Ken Lamb, founder of International Ozone Services Inc. (IOS), who zealously delivered accurate ozone and UV calibrations to the worldwide Brewer community.

Author Contributions: All authors have helped to develop the paper. A.M. S played the major role supervising and coordinating the whole work; G.R. C. and H. D. have equally provided helpful comments on the draft. F. S. and A. R. have contributed in the elaboration of the Brewer and satellite data. A.M. S and G.R. C. are responsible of establishing and maintaining Brewer 067; H. D. has contributed with data of Brewer 066 and in establishing and maintaining the site; M. P. has given Matlab support; V. S. has given support with the Brewer processing software.

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