

Internal consistency of the Regional Brewer Calibration Center for Europe Triad during the period 2005 – 2016

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General Comments:

Comment: My first impression reading the first pages of the manuscript was, that its rewriting significantly improves not only the English but also the content and structure. All addressed issues in the first review(s) have been incorporated. Abstract and introduction are now in an acceptable form. However, coming to chapter 2, 3 and 4 more and more still unsatisfying issues showed up. Thus I am not able to recommend now its publication without further major revision.

Description of the data retrieval and Langley calibration method (chapter 2) and of the selected data sets (chapter 3) is still not perfect, but better than in the first version and more or less acceptable with some minor corrections. Chapter 4 is still difficult to read and it is hard to understand the presented findings and conclusions. Some sentences are confusing, some statements do not reflect the results (e.g. p13, 15 and figure: no seasonal component in the relative standard deviation is in my opinion a very optimistic statement).

Answer: The authors are grateful for the comments of the referee and his description about the problems that he has found in each chapter. To solve them, we have improved the wording of some paragraphs in the text.

Comment: In addition results of the regular standard lamp tests of the Brewers are missing, which are normally a good indicator of the consistency of the instrumental calibration (sorry that I did not mention this issue in my first review). A comparison of these measured SL-test records with the presented statistical parameters should be included and hopefully show the same good consistency.

Answer: The results of the SL-test will not be included in the article but as supplementary information. We think (as the editor) that including them in the text can lead to a more complex article where the reader can get lost more easily. Moreover, at the RBCC-E, the SL-test is not the best indicator of the status of a Brewer (they are a secondary indicator for us). This is due to there are changes on the characteristics of the instrument that can be not detected with a SL-test such as variations on the attenuation filters, iris and pointing. The importance of having established the Regional

Brewer Calibration Center in the Izaña Atmospheric Observatory is because this place presents the ideal conditions for the Langley technique which allows us to absolutely and independently derive the Extraterrestrial constant (ETC) of each Brewer. These ETC values calculated from Langley are used to identify the possible changes on the spectral sensitivity of our instruments.

- 5 **Comment:** Chapter 5 Conclusion is a little on the short side and especially the statement in the last sentence is based mainly on one mention of the 0.5%-agreement of BR17 and BR185 (P3, l 12) during some campaigns. The results in the tables (especially table 6) only show the internal consistency within the Brewers of the various triads and that their long term consistency is good. But it does not say anything about their accuracy and the comparability of the triads' calibration levels, which is a condition for the traceability of the ozone measurements all around the world, when different triads are used for calibration of the field instruments in the global network.

10 **Answer:** The compatibility of the Triads is a pending topic due to the lack of intercomparisons between triads, we can only address by indirect intercomparisons with BR17, the conclusion has been rewritten accordingly.

Specific Comments (recommended text in “text”)

- P2, 110: This instrument is mounted on an azimuth tracker “and instead that” determines the TOC. **The wording of this sentence has been changed**
- 15 - P2, 113 - 14: better “(1985), it has been subjected on-going technical improvements to enhance its accuracy”. **The wording of this sentence has been changed**
- P2, 114 – 15: no complete sentence. **The wording of this sentence has been changed**
- P2, 128: replace manufacturer by with “by manufacturer”. **done**
- 20 - P3, 13: “is used for developing and tests”. **done**
- P3, 112: “in these comparisons”. **done**
- P3, 113: what kind of range? SZA!**Not, in this point we reference to the ozone slant column (OSC). The wording of this sentence has been changed**
- P3, 117/18: “Moreover, in order to obtain ozone values with higher accuracy, the RBCC-E advises on the need to reprocess the preceding observation records of each Brewer at its local station”. **done**
- 25 - P3, 120/21: no complete sentence. Perhaps it would be nice to mention ATMOZ already here in the context of Absolute Calibration Campaigns of the Brewer and Dobson reference instruments. **Now, in the introduction, we reference to this project and about the Absolute Calibration Campaigns of the Brewer and Dobson reference instruments**
- P3, 133 – 34: not a good English sentence. **The wording of this sentence has been changed**
- 30 - P4, 14: “includes” **done**
- P4, 111: “< 5 D.U.”. **done**
- P5, 11: “the measured intensities F_i in raw counts for each wavelength i ”. **done**

- P5, l24: The Langley technique is most popular only for reference instruments' calibration, but not for field instruments.
The wording was changed to indicate that only the reference instrument used this calibration technique
- P5 – P6 general statement: description is still not perfect, but better than the first version, therefore generally acceptable.
We have written both pages, a now a better description is given.
- 5 - P6, l14: (2 Langley “plots” per day). **done**
- P6, l15 ff: Meaning of bullet point 3 is not clear. Normally a regular Brewer TOC observations is calculated as average out of 5 single measurements and can be used if the standard deviation is less than 2.5 D.U. What is meant with individual measurements? These do not have a standard deviation. P6, l17 ff: Bullet point 4: Misleading formulation, as this daily standard deviation limit of 2.5 D.U. does not come from the description under bullet point 3, which refers to individual observations.
- 10 **We have rewritten the point 3 where the cloud screening filter and the single measurements are introduced. The point 4 has been deleted**
- P6, l24/25: Wording Only when the instruments recalibrates is uncommon. I would say “changing only when the calibration of the instrument drifts”. **done**
- General comment on the above discussed section: Here it would be proper to mention the SL-test as a simple alternative to
15 monitor the instrument's calibration level. **We have prepared an additional document with the SL and Langley values of each instruments during the period 2005-2016.**
- P7, Figure 2: Error bars hardly discernible, quality of the graph is not optimal. **A new Figure, with better resolution, has been added.**
- P8, l4: add “Saharan” dust **done**
- 20 - P8, l15 ff: Construction of this sentence is not good. **The wording of this sentence has been changed**
- P11, l5: “daily” mean? **done**
- P11, l15 – 23: Sorry but I have problems to understand the conclusion. Somewhat confusing! **We have rewritten the conclusion of this paragraph**
- P12, Figure 5: more detailed caption needed. Perhaps it helps to assign the different procedures to the shown panels. For a
25 better comparability it will be helpful to use the same y-axis maximum in all sub-graphs. **A new Figure, with the same Y-axis, has been uploaded**
- P13, l5/figure 6 on P14: It is stated there is no seasonal component in the standard deviation. This IMHO not the reality, as I can see a seasonal variation. **Yes a small seasonal component in the Std can be identified. The sentence has been rewritten as "Similarly to report by Stübi et al. (2017) the standard deviation shows an small seasonal component."**
- 30 - P13-14, l10, table 4: The mentioned 1.1% in table 4 is not clear. How is it determined? I see only numbers less than $\pm 1\%$. It is not possible for me follow the conclusion of consistency **This number corresponds to the sum of the percentile values, $P_{2.5} + P_{97.5}$, in absolute value (see Table 4). this factor was used by Stübi et al. (2017) to describe the behaviour of the Arosa triad.**
- P13 & 14 – 15: An explanation for the higher Arosa standard deviation is given, but isn't it the same reason for the Toronto
35 standard deviation? Honestly, this explanation we believe that only valid to explain why the RBCC-E presents a smaller

- deviation than the Arosa Triad, using its procedure to study the consistency of its measurements. The Toronto Triad used another procedure to study the consistency of their measurements and, hence, the standard deviation is calculated differently. Moreover, this triad is formed by single Brewers and each instrument underestimates the TOC for large SZA differently. In this case, we don't know how affect this on the standard deviation, Fioletov et al. (2005) only indicated the daily value of this
- 5 parameter but we can not find more informationfigures, tables, etc. In constant, the the RBCC-E uses double brewer which do not need stray light correction and, hence, the standard deviation only depends on the daily variability of the ozone at sub-tropical latitudes.
- P15, Figure 7: in figure caption please use the plural “methods” and “its micrometers” instead of their micrometers. **done**
 - P15, l3: Be more precise, as it is 36% lower than 40%. **The sentence was rewritten as "The ratio between 3-monthly**
- 10 **standard deviation is 36% lower for the RBCC-E"**
- P16, l4: “allows to” **done**
 - P16 – 17: What about the afternoon drop in figure 8, left panel? It is not explained. **In this section "Short-term consistency", we study the consistency of our data as a function of the SZA used the Dataset 2 (only simultaneous measurements between 2010-2016). The drop observed in the Figure 8 is due to that one instrument was not operative during**
- 15 **few minutes and, hence, we do not have simultaneous measurements between the Brewers. This information have been written in the Figure Caption.**
- P17: As already mentioned under general comments the conclusion is a little bit short. **The conclusion has been rewritten**
 - P21, references: please write “Köhler” and “Kyrö”. **done**

References

Fioletov, V. E., Kerr, J., McElroy, C., Wardle, D., Savastiouk, V., and Grajnar, T.: The Brewer reference triad, *Geophysical Research Letters*, 32, <https://doi.org/10.1029/2005GL024244>, <http://doi.wiley.com/10.1029/2005GL024244>, 2005.

Stübi, R., Schill, H., Klausen, J., Vuilleumier, L., and Ruffieux, D.: Reproducibility of total ozone column monitoring by the Arosa

- 5 Brewer spectrophotometer triad: AROSA BREWER TRIAD, *Journal of Geophysical Research: Atmospheres*, 122, 4735–4745, <https://doi.org/10.1002/2016JD025735>, <http://doi.wiley.com/10.1002/2016JD025735>, 2017.

Internal consistency of the Regional Brewer Calibration Center for Europe Triad during the period 2005 – 2016

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General comments

Comment: The revised text shows significant improvements compared to the originally submitted. The revised manuscript still reads a little too much as popular science with unconventional terminology and loosely used words (“measuring the signal intensity” or “The grating system separates the solar radiation”). If the reader overlooks this then it is possible to understand the significance of the good long-term agreement of the RBCC-E triad of Brewers.

Answer: We have rewritten these phrases to get a text with a better scientific language.

Comment: Title: The word stability in the title implies that the Brewer triad at RBCC-E was stable, but this is not what the content of the paper shows. It shows good agreement between the three Brewers that were regularly absolutely and independently calibrated, or re-calibrated. The paper doesn’t claim or show that the triad was not changing, however it does show that the changes did not affect the agreement between the Brewers once they have been properly calibrated. I suggest using something like “consistency” instead of “stability”.

Answer: The editor and you agree that the word "stability " is not the best to describe the objective of this article. Therefore, we have changed the title of "Stability of the Regional..." by "Internal consistency of the regional...". In text, we think that is better used only "consistency" to speak about the agreement of our measurements..

Comment: P1L4 “its own calibration” may be interpreted as “different” from others. I suggest saying that RBCC-E is using traveling standard(s) that are absolutely and independently calibrated at Izaña.

Answer: We rewritten this sentence as "the RBCC-E transfers its calibration based on Langley using travelling standard(s) that are absolutely and independently calibrated at Izaña".

Comment: P1L19 replace “measurement” with “calculation”

Answer: The text has been modified following your suggestion

Comment: P1L20 “accuracy” implies that you are comparing to the true value of some sort. What you are investigating is sensitivity or precision (or uncertainty)

Answer: The text has been modified following your suggestion

Comment: P2L1-3 these sentences are not connected to each other. It looks like you’ve removed some text and didn’t rephrase what’s left. E.g. what “decrease”?

Answer: We have modified the paragraph and, now, the wording is better.

Comment: P2L10 “This instrument is mounted on an azimuth tracker that determines the TOC...” the tracker definitely does not determine the TOC!

Answer: We have modified this paragraph and, now, the wording is better.

Comment: P2L11 “The grating system separates the solar radiation” separates into/from what? Please use the established scientific terminology. “The grating system” as you called it is in fact a diffraction grating that can be turned with a stepper motor that together with a slit mask allows the selection of solar radiation bands at the exit slit(s) of the monochromator.

Answer: The wording of this paragraph was changed **Comment:** P2L17 Stray light certainly doesn’t cause any decrease in TOC. It causes underestimation of TOC in the calculations when no stray light correction is applied.

Answer: The text has been modified following your suggestion

Comment: P2L32 “its own” see comment above

Answer: The text has been modified following your suggestion

Comment: P3L16 “conducted”

Answer: The text has been modified following your suggestion

Comment: P5EQ1 what are the units of O3 in this equation? Be careful, this is a trick question (but important!).

Answer: We have rewritten the equations. Now, the TOC is given in Dobson units.

[..*]Internal consistency of the Regional Brewer Calibration Center for Europe Triad during the period 2005 – 2016

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Abstract. Total ozone column measurements can be made using Brewer [..²]spectrophotometers which are calibrated periodically in intercomparison campaigns with respect to a reference instrument. In 2003, the Regional Brewer Calibration Centre for Europe (RBCC-E) was established at the Izaña Atmospheric Research Centre (Canary Islands, Spain) and since 2011 [..³]the RBCC-E transfers its calibration based on Langley using travelling standar(s) that are absolutely and independently calibrated at Izaña. This work is focused on reporting on the [..⁴]consistency of the measurements of the RBCC-E Triad (Brewers #157, #183 and #185) made at the Izaña Atmospheric Observatory during the period 2005 – 2016. In order to study the long-term precision of the RBCC-E Triad, it must be taken into account that each Brewer performs a large number of measurements every day and, hence, it becomes necessary to calculate a representative value of all of them. This value was calculated from two different methods previously used to study the long-term behaviour of the World Reference Triad (so-called Toronto Triad) and Arosa Triad. Applying their procedures to the data from the RBCC-E Triad allows the comparison of the three instruments. In daily averages, applying the procedure used for the World Triad Reference, the RBCC-E Triad presents a relative standard deviation equal to $\sigma=0.41\%$ which is calculated as the mean of the individual values for each Brewer ($\sigma_{157} = 0.362\%$, $\sigma_{183} = 0.453\%$ and $\sigma_{185} = 0.428\%$). Alternatively, using the procedure used to analyze the Arosa Triad, the RBCC-E presents a relative standard deviation of about $\sigma = 0.5\%$. In monthly averages, the method used for the data from the World Triad Reference give a relative standard deviation mean equal to $\sigma=0.3\%$ ($\sigma_{157} = 0.33\%$, $\sigma_{183} = 0.34\%$ and $\sigma_{185} = 0.23\%$). Whereas, the procedure of the Arosa Triad gives monthly values $\sigma=0.5\%$. In this work, two ozone datasets are analyzed: the first include all the ozone measurements available while the second only includes the simultaneous measurements of all three instruments. Furthermore, this paper also describes the Langley method used to determine the Extra-Terrestrial Constant (ETC) for the RBCC-E Triad, the necessary first step toward accurate ozone [..⁵]calculation. Finally, the short-term, or

*removed: Stability

²removed: sprectrophotometers

³removed: it transfers its own calibration , mainly to other European Brewers, using the Brewer #185 as travelling reference

⁴removed: stability

⁵removed: measurement

intraday, [..⁶]consistency is also studied to identify the effect of the solar zenith angle on the [..⁷]precision of the RBCC-E Triad.

1 Introduction

The ozone layer is a region of the Earth's stratosphere that absorbs most of the Sun's Ultraviolet (UV) radiation (Anwar et al., 2016). Historical measurements -pre 1980- indicated that the morphology of ozone was not changing significantly with time. However, the Antarctic measurements of Farman et al. (1985) changed that view. [..⁸]The negative effects that UV can have on terrestrial life led to the signing of the Montreal Protocol in 1987, where 197 countries agreed to reduce the agents that led to this decrease of the ozone layer (Sarma and Andersen, 2011). From this date, the monitoring and control of the total ozone column abundance has been a priority of the World Meteorological Organization (WMO). This task requires instruments that can measure the total ozone column concentration with an accuracy of $\sim 1\text{-}3\%$ such as the Dobson and Brewer which are considered as ideal instruments for monitoring the ozone abundance [..⁹](Basher, 1985; Varotsos and Cracknell, 1994; ?; Scarnato et al., 2009).

Brewer ozone spectrophotometers are used to measure the total ozone column (TOC), ultraviolet irradiance (Fioletov, 2002) and, more recently, the aerosol optical depth in the ultraviolet range (Carvalho and Henriques, 2000; Gröbner et al., 2001; López-Solano et al., 2018). This instrument [..¹⁰]determines the TOC from a direct measurement of the solar radiation. [..¹¹]A diffraction grating together with a slit mark allows the selection of UV radiation bands to be measured[..¹²].

After the development of the first Brewer in the early 1970s (Brewer, 1973; Kerr et al., 1985), it has [..¹³]been subjected to on-going technical improvements to [..¹⁴]enhance its accuracy. For example, there have been improvements in the photo-multiplier, diffraction gratings [..¹⁵]and operating software used as well as the incorporation of new measurement routines [..¹⁶](?Fioletov et al., 2011; Karppinen et al., 2015; Fountoulakis et al., 2017). However, possibly the greatest improvement has been the transition from a single to a double monochromator. This eliminates the presence of stray light in the measurements which causes [..¹⁷]an underestimation in the TOC at large solar zenith angles (Karppinen et al., 2015). In practice, the single Brewer presents this problem for large ozone slant column (OSC). Although, depending on the instrument, this effect may be greater or lesser (Redondas et al., 2015; Redondas and Rodríguez-Franco, 2015; Redondas and Rodríguez-Franco, 2016).

⁶removed: stability

⁷removed: accuracy

⁸removed: Concerns related to the

⁹removed: (Basher, 1985; Varotsos and Cracknell, 1994; Fioletov et al., 2005; Scarnato et al., 2009)

¹⁰removed: is mounted on an azimuth tracker that

¹¹removed: The grating system separates the solar radiation and a slit mask mechanism is used to select the different UV

¹²removed: which are associated with maximum and minimum ozone absorption cross-sections

¹³removed: had

¹⁴removed: improve

¹⁵removed: ,

¹⁶removed: (Fioletov et al., 2005, 2011; Karppinen et al., 2015; Fountoulakis et al., 2017)

¹⁷removed: a decrease

The calibration of the Brewer is traceable from the World Triad Reference, managed by Environment and Climate Change Canada, consisting of Brewers #008, #014 and #015, and located at Toronto. These single Brewers are calibrated every few years at the Mauna Loa Observatory (Hawaii) using the Langley-technique [..¹⁸](?). A second triad formed by double Brewers #145, #187 and #191 is also operated in parallel with the World Triad Reference (Netcheva, 2014; Fioletov and Netcheva, 2014; Zhao et al., 2016). Also, the Swiss Federal Office of Meteorology and Climatology (Meteo Swiss) has the Arosa Triad formed by the singles (#040 and #072) and double (#156) Brewers (Stübi et al., 2017). However, the Brewers distributed around the World are calibrated by comparison with the travelling standard reference, Brewer #017, managed by International Ozone Services (IOS) and Brewer #158 [..¹⁹]by manufacturer Kipp & Zonen.

In addition, since November 2003 and within the World Meteorological Organization (WMO) and the Global Atmosphere Watch (GAW) Programme, the Regional Brewer Calibration Centre (RBCC-E) for RA-VI Region was established at the Izaña Atmospheric Observatory (IZO) which is located on the island of Tenerife, managed by the State Meteorological Agency of Spain (AEMET). The RBCC-E is the European Brewer Reference and [..²⁰]is using travelling standard(s) that are absolutely and independly calibrated at Izaña. Its trajectory started in the year 1997 when the first double Brewer #157 was installed at IZO, running in parallel with a single Brewer #033 for six months. In January 2005, a second double Brewer, the #183, was installed and designated as the travelling reference. The single Brewer #033 was moved to Santa Cruz Meteorological Station (CMT) in December 1997, leaving the RBCC-E with only two instruments. In July 2005, a third double Brewer #185 was installed. Since that moment, the RBCC-E has been formed by the Brewers #157, #183 and #185. The TOC measured by Regional Primary Reference #157 are sent regularly to different world data servers. The Regional Secondary Reference #183 is used [..²¹]for developing and test. Whereas, the Regional Travelling Reference corresponds to Brewer #185.

The Izaña Atmospheric Observatory is located on the island of Tenerife, on the top of a mountain plateau at 2373 m a.s.l. The observatory is thus located on the region below the descending branch of the Hadley cell, typically above a stable inversion layer, and on an island far away from any significant industrial activities. This ensures clean air and clear sky conditions around all the year and offers excellent conditions to perform the Langley-technique, except for some days where the Saharan dust intrusions inhibit the measurements of the direct solar radiation. Each Brewer can be calibrated “in situ” and independently using the Langley-technique, without the need to move them to other locations. Moreover, the traceability between the RBCC-E Triad and the World Triad Reference is checked during the calibration campaigns through the travelling references #185 and #017. In [..²²]these comparisons, both instruments agree within 0.5%. These values have been calculated using measurements in [..²³]the ozone slant column (OSC) range (100-900) where Brewer #017 measurements are not strongly affected by stray light (Redondas et al., 2015; Redondas and Rodríguez-Franco, 2015; Redondas and Rodríguez-Franco, 2016)

¹⁸removed: (Fioletov et al., 2005)

¹⁹removed: manufacturer by

²⁰removed: hence can calibrate and transfer its own calibration

²¹removed: to

²²removed: this comparison

²³removed: a range

The RBCC-E also organizes inter-comparisons which are held annually, alternating between Arosa (Switzerland) and El Arenosillo (Spain). Since 2011, more than 150 calibrations have been ^[..²⁴]conducted (Cuevas et al., 2015). In these campaigns, the RBCC-E facilitates a new calibration for each instrument. Moreover, in order to obtain ^[..²⁵]ozone values with higher accuracy, the RBCC-E advises on the need to reprocess the ^[..²⁶]preceding observation records of each brewer at its local station (Redondas et al., 2018). Aside from regular inter-comparisons, the RBCC-E has carried out other research campaigns supported by the ESA CalVal project. The NORDIC campaigns, with the objective to study the ozone measurements at high latitudes, and the Absolute Calibration Campaigns performed at IZO with the participation of Brewer and Dobson reference instruments. The participating Brewers and the travelling reference #185 operate with the same schedule throughout these campaigns. The TOC recorded by the travelling reference #185 are used to calibrate the participating Brewers and also to conduct research works (De La Casinière et al., 2005; Redondas et al., 2015; Redondas and Rodriguez-Franco, 2016). Recently, the RBCC-E has participated in the ATMOZ project (Traceability for the total atmospheric ozone column) where it organized an absolute calibration campaign with the Brewers and Dobsons reference instruments (research Programme, 2014).

Finally, it should be also mentioned that within the framework of COST Action ES1207, “A European Brewer Network” (EUBREWNET), the RBCC-E and AEMET are developing a dataserver for EUBREWNET (<http://rbcce.aemet.es/eubrewnet>) which will allow the calculation of the TOC in near real time (Rimmer et al., 2017). This completes the objectives of this COST action, whose aim is establishing a coherent network of Brewer monitoring stations in order to harmonise operations and develop approaches, practices and protocols to achieve consistency in quality control, quality assurance and coordinated operations. Currently, approximately 40 Brewers, mainly European, send their data automatically every 20 minutes to EUBREWNET’s dataserver. ^[..²⁷]

The present work focused on investigating how similar are the measurements made by the Brewers #157, #183 and #185 each day and how stable does this behaviour remain over time. This allows us to identify periods with lower or higher agreement between the Brewers. The RBCC-E measurements are evaluated from the methods described for the World Reference and Arosa Triads to study its ^[..²⁸]consistency. With this idea in mind, this work has been structured as follows: an approach to ozone retrieval and Langley method is presented in Section 2. The ozone values recorded in the period 2005-2016 and datasets used are shown in Section 3. The methods used to calculate the daily ozone value and the results obtained from these values and its discussion are presented in Section 4. Also, this section ^[..²⁹]includes results of a study on the behaviour of the RBCC-E Triad as a function of SZA range at which the measurements were performed. Finally, the conclusions are presented in Section 5.

²⁴removed: conduted

²⁵removed: an ozone value with better

²⁶removed: observations performed by

²⁷removed: This dataserver also allows the reprocessing of data for homogenization and automatic quality control.

²⁸removed: stability

²⁹removed: includes

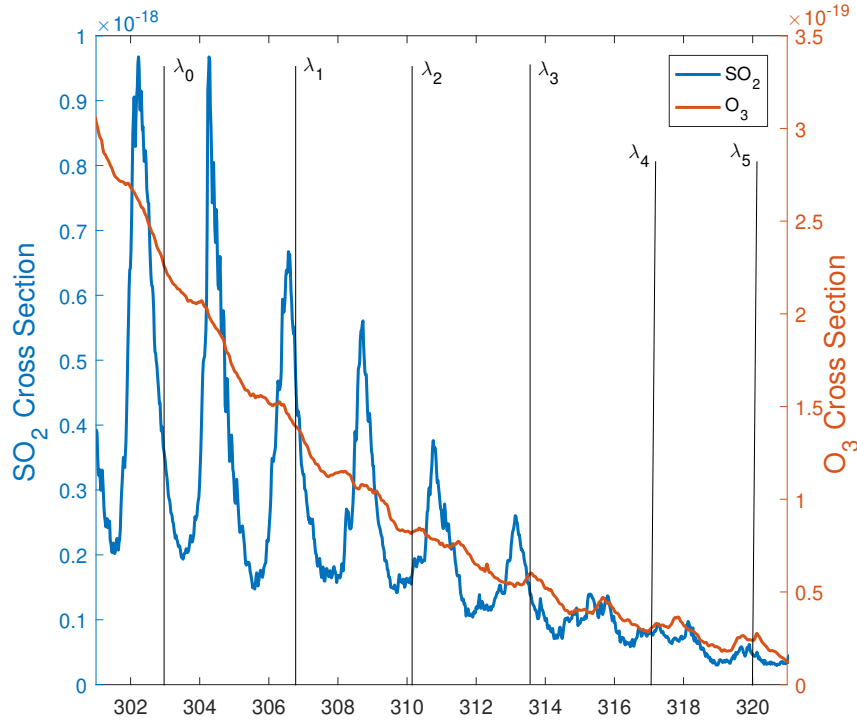


Figure 1. Ozone and sulfur dioxide absorption cross sections. The solar radiation is measured for the intensity bands ($\lambda_{1-5} = 306.4, 310.1, 313.5, 316.8, 320.0nm$). In contrast, the wavelength $\lambda_0 = 303nm$ is used for a check routine.

2 Theoretical Approach

2.1 Ozone retrieval.

The standard (so-called DS) routine [\[. ³⁰ \]](#) used to determine the TOC from direct sunlight radiation, [\[. ³¹ \]](#) measuring the signal intensity in five bands ($\lambda_{1-5} = 306.4, 310.1, 313.5, 316.8, 320.0nm$) which are associated with maximum and minimum O_3 and SO_2 absorption cross sections, see Fig. 1. Despite that SO_2 presents a more efficient absorption, its lower presence in the atmosphere (<5 D.U.) compared to the ozone (200-500 D.U.) causes that the greater absorption of UV radiation is due to the latter (Kerr, 2010). The intensity measured [\[. ³² \]](#) F_i in raw counts for each wavelength i , can be expressed in terms of counts per second, after applying some instrumental corrections (dark counts, dead time and temperature coefficients) and, also, taking into account the contribution of Rayleigh scattering.

³⁰removed: ,

³¹removed: measures five intensity

³²removed: F ,

Using standard Brewer operational variables, the TOC (in Dobson units) can be obtained as follows,

$$O_3 = \frac{MS9 - ETC}{\alpha \cdot \mu} \quad (1)$$

where MS9 (so-called double ratio) is calculated as follows, (Brewer, 1973; Kerr et al., 1981, 1985; Kipp & Zonen, 2008).

$$MS9 = [..^{33}] \sum_i w_i \log F_i [..^{34}] - \frac{P}{P_o} \beta_i \mu \quad (2)$$

5 The ozone absorption coefficient, α , is calculated from dispersion test (Redondas et al., 2014a)

$$\alpha = [..^{35}] \sum_i w_i [..^{36}] \alpha_i [..^{37}] \quad (3)$$

where α_i represents the band intensity calculated for each wavelength indicated in Fig. 1.

The weights, $w_i = (-1, 0.5, 2.2, -1.7)$ and the wavelengths, $\lambda_i = (310.1, 313.5, 316.8, 320.0nm)$, used have been especially selected to suppress the aerosol and SO₂ effects in the measured signal (Dobson, 1957; Kerr et al., 1981). These w_i and [..³⁸

10] λ_i fulfill the equations 4 and 5 ensuring that any linear effects with wavelength are suppressed and also allow to minimize any small shift in wavelength and the influence of SO₂ on the ozone retrieval.

$$\sum_{i=1} w_i = 0 \quad (4)$$

$$\sum_{i=1} w_i \lambda_i \approx 0 \quad (5)$$

15 [..³⁹] A more extensive description about dispersion test and the mathematical procedure to calculate the ozone concentration can be found in (Gröbner et al., 1998; Kipp & Zonen, 2008). Finally, the *ETC* (so-called Extra-Terrestrial Constant) must be calculated directly using the Langley-technique or transfers by comparison with a reference instrument.

2.2 Langley calibration method for the RBCC-E Triad

The Langley-technique is the most popular procedure to estimate the extraterrestrial constant *ETC* used by the reference

20 instruments. In practice, with respect to TOC measurements, the *ETC* can be calculated directly fitting a linear equation to the *MS9* values respect to air mass μ :

$$MS9 = ETC + O_3 \alpha \mu \quad (6)$$

or using the Dobson method (Dobson and Normand, 1958; Komhyr et al., 1989):

$$\frac{MS9 - (ETC + \Delta ETC)}{\mu} = O_3 \alpha \quad (7)$$

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³⁹removed: It is important to note that the factor 10^4 introduced in Eq. 2 is because the Brewer algorithm works in an internal base 10 logarithmic space multiplied by this factor.

where ΔETC represents the variation of this parameter respect to a reference value.

Both equations can be used to calculate the ETC value to be used in Eq.1 but Eq.7, where the slope is inverse to μ , has the advantage of presenting a better data distribution (Kiedron and Michalsky, 2016). This is because the number of measurements performed at low air mass ($1 \leq \mu \leq 2$) are more than those at large air mass ($\mu \geq 2$). Although all measurements could be used for this calculation, experience suggests that is better to select a subset of measurements. The days with a high aerosol optical depth concentration, i. e. during Saharan dust intrusions, are removed from this study with the help of data reported by other instruments.

The methodology used is essentially the same as described in (Redondas, 2008; Redondas et al., 2014b). The following criteria, listed in order of application, can be used to get a good agreement between the ETC values calculated:

1. The regression is performed on the [1.25 , 3.5] airmass range, using the brewer astronomical formulas for the airmass determination.
2. The data recorded during the morning and afternoon are taken separately (2 Langley plots per day)
3. ^[.40] The TOC observation is calculated in the DS routine as the average of 5 ^[.41] single measurements, applying a cloud-screening filter (std< 2.5 ^[.42] D.U.). However, in the Langley regression is used the individual measurements (and not the average) only if these pass the cloud filter.
4. ^[.43]
5. MS9 double ratios are corrected for filter non linearity.

It is important to indicate that despite selecting the better days when the ETC values obtained for different days are compared, these present a standard deviation around ± 5 . This difference is considered normal and the ETC introduced in Eq. 1 corresponds to the ETC mean. Although the median can be another option to get the ETC , the previous criteria guarantee that the difference between both methods are not significantly.

Aside from the interest to determine the TOC, the ETC is considered as a probe to check the correct state of the instrument. The ETC calculated from the Langley method presents a near constant value (std. ± 5), changing only when the ^[.44] calibration of the instrument drifts. This may happen, for example, after replacing a damaged component or due to normal drifts by its continued operation. In both cases, and after a stabilization period, a new ETC value can be calculated.

As an example, Fig. 2 shows the operative value of the ETC for the Brewer #183 during the year 2011. The vertical lines represent situations which can produce a change in the behaviour of the instrument, while the horizontal line represents the operative ETC used to calculate the TOC (Eq.1). As it can be observed, the ETC changed twice, the first time by maintenance

⁴⁰removed: Individual measurements (not the

⁴¹removed:) are considered with the cloud screen method of

⁴²removed: ozone standard deviation.

⁴³removed: This daily standard deviation limit (2.5 DU)are used to select the Langley events.

⁴⁴removed: instrument recalibrates

tasks (performed by IOS service in July 2011), and the second time due to changes in the Brewer configuration (to be more precise, changes in the so-called “Cal-Step” in August 2011). On the contrary, during the maintenance tasks (June 2011) or after UV calibration in our facilities (November 2011), the ETC remained constant. Only the Langleys that satisfy the conditions indicated in Sect. 2.2 are used to calculate the weekly mean. Other examples of events that may affect the ETC can be found

5 in the calibration campaign reports (Redondas et al., 2015; Redondas and Rodriguez-Franco, 2016).

[..⁴⁵] Routinely since 2009, monthly calibrations are performed for the three instruments. This task is based on evaluating the following points:

1. The internal lamps test historical record are analyzed.
2. The Langleys values obtained in this period and its comparison with the [..⁴⁶] ETC operative.
- 10 3. The values reported by the check routines of each instrument.
4. The intercomparison between our Brewers.

This procedure allow us to identify the exact moment when a Brewer [..⁴⁷] requires a new calibration. The calibration reports are available on the RBCC-E website, see for example (León-Luis et al., 2016). In addition, [..⁴⁸] before and after the calibration campaign our travelling reference (Brewer#185) is compared with the Brewer#157 and #183 which

15 remain at the observatory. The traceability between the RBCC-E and the World Reference Triads is checked in the calibration campaigns, organized by the RBCC-E, comparing the data of the travelling references: Brewers #185 and #017. The results of these comparisons are shown in the calibration campaign reports (Redondas et al., 2015; Redondas and Rodríguez-Franco, 2015; Redondas and Rodriguez-Franco, 2016).

3 Ozone and Dataset selected

20 In order to summarize the history of the RBCC-E Brewers, Table 1 provides the total number of days and measurements performed by these instruments since they became operational at IZO and as long as the weather conditions allowed them to operate. Fig. 3 shows the daily and monthly TOC means measured by Brewer #157. The ozone presents an annual cycle with a sawtooth profile with maximum and minimum values in spring and autumn, respectively. Despite this annual behaviour, the ozone presents a lower daily variability as indicated by our measurements. This factor, together with a thermal inversion which

25 produces an atmosphere free of anthropogenic pollutants and excellent weather conditions all the year, except for days with Saharan dust intrusions, explain why Izaña Atmospheric Observatory is an excellent location for a Brewer reference centre and, also, why the Langley-technique is used as calibration method.

⁴⁵removed: When a new *ETC* is given,

⁴⁶removed: TOC calculated from it can be compared with the data obtained by other instrument with similar precision. This can be a strategy to check if the new ETC is correct. At the RBCC-E Triad, this task is simple because the Brewers are constantly compared to each other, allowing to

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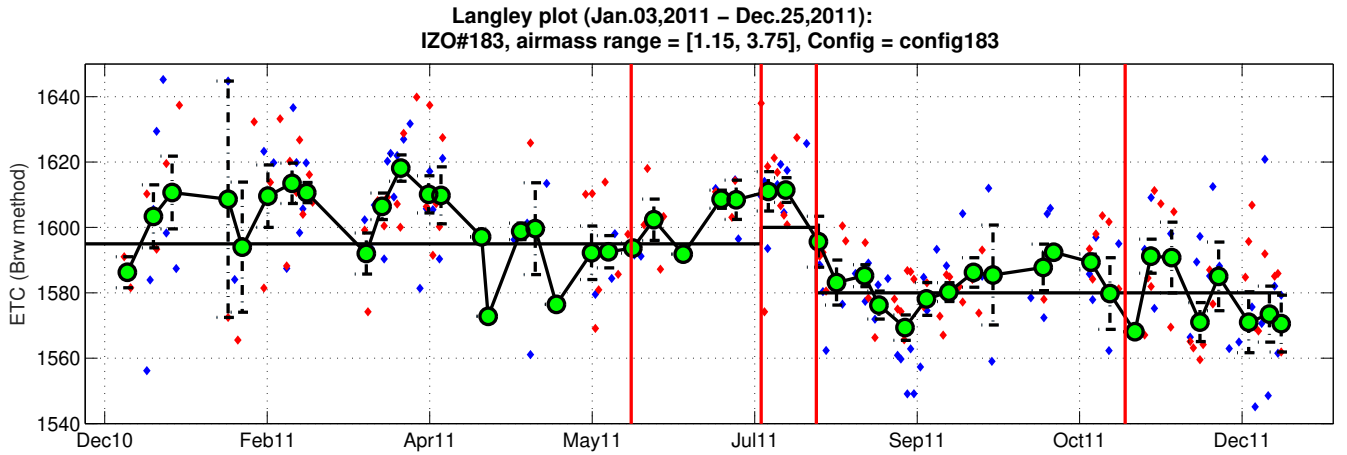


Figure 2. Operative ETC value for Brewer #183, after some events that could cause a change in the instrumental calibration during 2011. The red and blue dots denote daily ETC values calculated by the Langley method before and after solar noon, respectively. The [..⁴⁹] circles and the error bars correspond to the ETC weekly mean and its standard deviation.

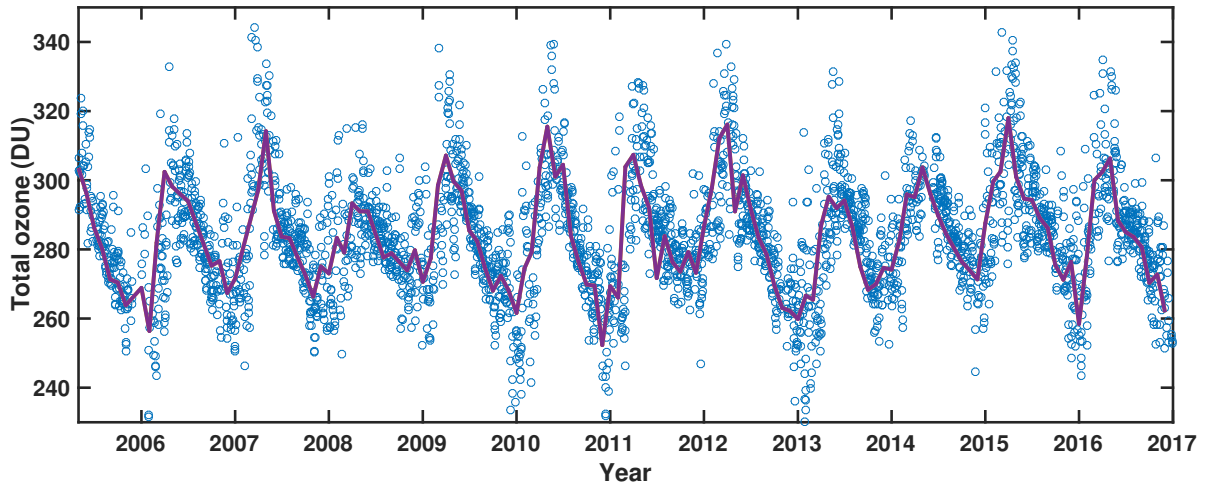


Figure 3. Time series of the ozone concentrations measured by Brewer #157 at Izaña Atmospheric Observatory, showing daily (dots) and monthly (line) means.

In this work, the ozone datasets have been analyzed. The first dataset is obtained directly, after applying several conditions, listed next in order of application:

1. Only include measurements performed at Izaña Atmospheric Observatory.
2. Remove days with problems clearly identified (wrong alignment, etc.).

- Only the days where the three Brewers have performed measurements are considered in this work. Moreover, each Brewer must have more than 12 measurements, with a minimum of 4 before and after the solar noon (homogeneous distribution).

The second dataset is obtained with the same conditions but also imposing the condition that the measurements must be simultaneous in time. A measurement [..⁵⁰] is considered simultaneous if we have one observations of each instrument in a temporal window of [..⁵¹] 5 minutes. Therefore, this second dataset can be considered a subset of the first. Table 2 gives a summary of both datasets. The entry “Evaluated Days” denotes the number of days used in each dataset to study the [..⁵²] consistency of the RBCC-E Triad. It is important to note that Dataset 1 includes the measurements made in the period 2005-2016 while Dataset 2 only considers simultaneous measurements from 2010 onwards. Before 2010, a large part of the measurement time was focused on the UV spectrum, and, hence, there are fewer ozone direct sun measurements in the instrument schedule. This means that the likelihood of finding 12 simultaneous measurements between the three instruments is low, particularly in winter where the presence of clouds is greater. After 2010, The RBCC-E started using the same synchronization schedule in their Brewers. These schedules take into account the sunrise and sunset times of each day and the routines, introduced in it, are distributed in function of the solar zenith angle (SZA).

Table 1. Number of operational days and measurements since their setup for the Brewers of the RBCC-E Triad.

	Brewer #157	Brewer #183	Brewer #185
Operational Days	3173	2740	2780
Operational Measurements	259534	204022	229201

Table 2. Summary of the datasets used in this work.

	Dataset 1	Dataset 2
Evaluated Days	2073	1325
Period studied	2005–2016	2010–2016

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⁵¹removed: five minutes there is other measurement made by the other two brewers of the triad

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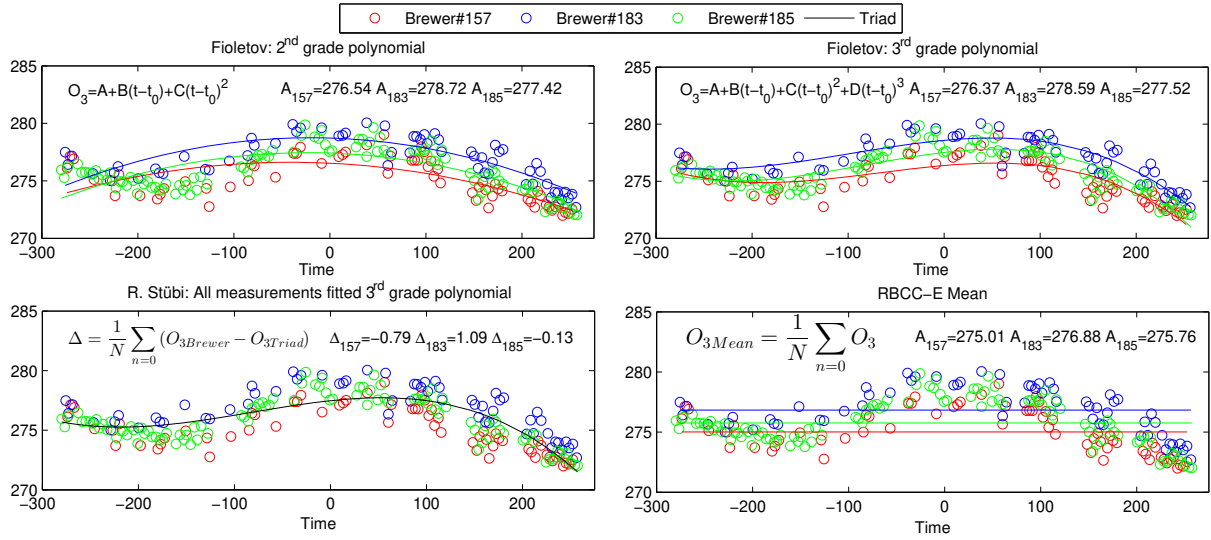


Figure 4. Method used to calculate the daily representative value. The ozone values plotted were measured the 16th November 2016.

4 Results and discussion.

The [⁵³]consistency of the measurements carried out by the RBCC-E Triad was evaluated from the datasets described in Sect. 3. In the case of the long-term behaviour, it was studied using both datasets, while the short-term behaviour was analyzed using only Dataset 1. The results obtained are shown in statistical terms.

5 4.1 Representative value of the Total ozone column.

To our knowledge, there are only a few publications where the [⁵⁴]consistency of the World Reference and Arosa Triads are analyzed. In these articles, and due to the large number of ozone measurements performed each day, the authors have calculated a representative value of all of them and, from it, the long-term [⁵⁵]consistency is analyzed (?Scarnato et al., 2010; Stübi et al., 2017).

- 10 [⁵⁶] ? studied the long-term [⁵⁷]consistency of the World Triad Reference in the period 1985 – 2003. In this work, the authors proposed to fit the measurements performed by each Brewer (#008, #014 and #015) to a 2nd grade polynomial (see Fig.4):

$$O_3 = A + B \cdot (t - t_0) + C \cdot (t - t_0)^2 \quad (8)$$

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⁵⁵removed: stability is analyzed (Fioletov et al., 2005; Scarnato et al., 2010; Stübi et al., 2017)

⁵⁶removed: Fioletov et al. (2005)

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where O_3 is the TOC measured and $t - t_0$ corresponds to the difference between the time of the measurement and the solar noon. The independent coefficient A obtained through the adjustment is used as a representative ozone value of each instrument. The difference between this coefficient for each Brewer and the Triad mean represents the daily drifts of each instrument. The ⁵⁸consistency is studied from the relative standard deviation of these differences. In this work, the results using a 3rd grade polynomial have also been investigated, see Fig.4.

Stübi et al. (2017) studied the long-term ⁵⁹consistency of the Arosa Triad in the period 1988 – 2015. In this study, the authors considered that the behaviour of the Triad is the most appropriate reference for each day. Therefore, all the measurements made by the three Brewers are modeled as a 3rd grade polynomial dependent on time which represents to the Triad (see Fig.4):

$$O_3 = A + B \cdot (t - t_0) + C \cdot (t - t_0)^2 + D \cdot (t - t_0)^3 \quad (9)$$

where t_0 corresponds to the 12 UTC time. In this case, each Brewer can be characterized by a shift, Δ , which is the daily mean of the difference between the values measured and obtained from the fit and a standard deviation, σ , which evaluates the dispersion of these differences. Both parameters are used to analyze the long-term ⁶⁰consistency of the Arosa Triad.

In order to compare the long-term ⁶¹consistency of the RBCC-E Triad with respect to the World Reference and Arosa Triads, both methods are used to fit our measurements. However, in this work, the time reference t_0 is the solar noon.

Although Eqs. 8 and 9 are valid to model the behaviour of ozone, it should be noted that the normal drifts by its continued operation of the instrument can affect the final value of the adjustment. Given this problem, calculating the daily mean of the measurements can be a good strategy to avoid this inconvenience. In this work, and noting by our measurements that ozone presents a reduced daily variability, see Fig.4, the mean of the all measurements, N , made by each Brewer was used as a representative value.

$$A_M = \frac{\sum_i O_3}{N} \quad (10)$$

The difference between the value obtained for each Brewer and the Triad mean represents the drifts of each instrument. Although the median can be another possibility to study the behaviour of the RBCC-E Triad, our experience suggests that the daily mean is robust. Moreover, since 2003, the mean has been used to detect when one of our Brewer loses its calibration, therefore, it has been interesting to include it in this work. At this point, it is important to note that for the World Triad Reference as for the RBCC-E, the representative value of each instrument is calculated, directly, from their measurements. In contrast, in the Arosa Triad, the representative value of each instrument (denoted as shift Δ) is calculated with respect to the behaviour of the three instruments, obtained by adjusting to a polynomial of the third degree (see Fig.4).

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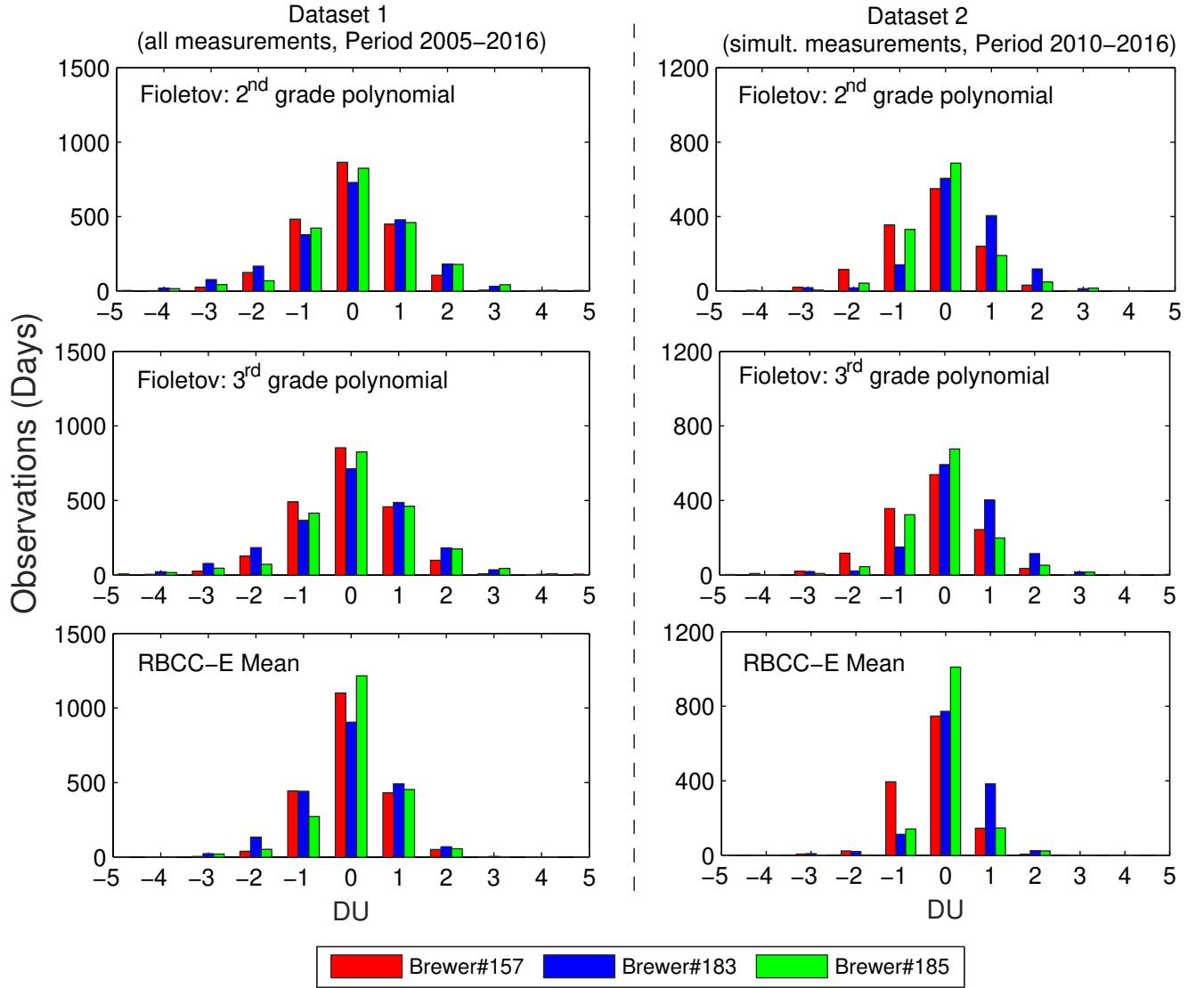


Figure 5. Daily difference of the ozone reference value A of each Brewer with respect to Triad. The values were obtained from the procedure proposed by Fioletov (World Triad Reference) and by daily mean (RBCC-E).

4.1.1 Long-term ⁶²consistency: daily averages

Following the procedure described by ⁶³? for the World Triad Reference, Datasets 1 and 2 (see Sect. 3) were fitted by a 2nd and 3rd grade polynomial ⁶⁴as is shown in Fig.4. The distribution of the daily difference between the A value, see Eq.8, obtained for each Brewer with respect to the Triad mean are plotted in Fig. 5. Also, in this plot, the difference calculated from
5 the daily mean of each instrument was included, see Eq.10.

It is important to take into account that the individual coefficients obtained for each Brewer, and also the Triad mean calculated from them, depend on the method used.

As Fig.5 shows, the histograms that represent the results obtained ⁶⁵when a polynomial fit ⁶⁶is used in each dataset are independent of its grade. This can be explained by the small daily variation of the ozone ⁶⁷which causes the 2nd and 3rd
10 grade polynomial fit to give very similar A coefficients, see Fig.4. In contrast, the histograms associated with the daily mean suggest that the differences between the brewers are less. This allows us to conclude that the method selected to evaluate the ⁶⁸consistency plays an important role, because the Brewer-Triad mean differences are directly associated with it. In this case, it may be more appropriate to use the daily mean to evaluate the RBCC-E Triad. ⁶⁹Independently of the method used, Fig. 5 shows that, for the great majority of days, the Brewers present less than 2 DU of difference with respect to the Triad
15 mean which indicates a good agreement among themselves.

Using the same procedure to evaluate the long-term ⁷⁰consistency can be the best strategy to compare different triads to each other. In this sense, ⁷¹? only reported that the relative daily standard deviation of World triad reference is equal to 0.47%. This value was calculated as the mean of the relative standard deviation of each brewer. Table 3 contains the difference mean, calculated from the mean Brewer-Triad difference plotted in Fig. 5, and its standard deviation. The RBCC-E Triad
20 presents a relative standard deviation mean equal to 0.41% ($\sigma_{157} = 0.362\%$, $\sigma_{183} = 0.453\%$ and $\sigma_{185} = 0.428\%$; see Table 3, Dataset 1, 4th column). This result indicates that the dispersion of the measurements of the RBCC-E Brewers presents a similar behaviour to those of the World Triad Reference. Furthermore, the standard deviation values obtained confirm that the daily mean is the best method to evaluate the RBCC-E Triad.

In order to compare the daily behaviour of the Arosa and RBCC-E Triads, a 3rd grade polynomial was fitted to all the daily
25 measurements made by RBCC-E Brewers for Datasets 1 and 2. Then, for each Brewer its mean shift, Δ , and standard deviation, σ , were calculated (see Sect. 3). The values obtained for the Dataset 1 are shown in Fig. 6. Because Brewer #183 was damaged by a storm and was inoperative between December 2005 and September 2006, the data plotted in that period were calculated

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Table 3. Absolute and relative values of the mean shift and the standard deviation.

Dataset 1						
	2 nd grade polynomial (DU)	3 rd grade polynomial (DU)	Brewer Mean (DU)	2 nd grade polynomial (%)	3 rd grade polynomial (%)	Brewer Mean (%)
Brewer #157	0.787 ± 1.04	0.796 ± 1.07	0.569 ± 0.744	0.276 ± 0.362	0.279 ± 0.372	0.1994 ± 0.26
Brewer #183	0.989 ± 1.29	1.01 ± 1.31	0.741 ± 0.956	0.349 ± 0.453	0.356 ± 0.463	0.26 ± 0.337
Brewer #185	0.89 ± 1.21	0.90 ± 1.23	0.56 ± 0.78	0.315 ± 0.428	0.32 ± 0.438	0.20 ± 0.279

Dataset 2						
	2 nd grade polynomial (DU)	3 rd grade polynomial (DU)	Brewer Mean (DU)	2 nd grade polynomial (%)	3 rd grade polynomial (%)	Brewer Mean (%)
Brewer #157	0.795 ± 1.00	0.82 ± 1.05	0.534 ± 0.661	0.278 ± 0.349	0.286 ± 0.368	0.186 ± 0.23
Brewer #183	0.747 ± 0.942	0.784 ± 1.02	0.547 ± 0.719	0.262 ± 0.331	0.275 ± 0.36	0.192 ± 0.254
Brewer #185	0.64 ± 0.87	0.67 ± 0.99	0.376 ± 0.526	0.227 ± 0.311	0.238 ± 0.333	0.133 ± 0.189

from measurements of Brewers #157 and #185 only. Similarly, when Brewer #185 is away from IZO in calibration campaigns, the values plotted correspond to Brewers #157 and #183. Note that although these data were introduced in Fig. 6 to avoid gaps in the plot, they are not considered in the statistical study. Therefore, the dates evaluated correspond with the days when the full RBCC-E Triad is operative, and the criteria established in Sect. 3 are still used.

- 5 As can be observed in Fig. 6, the results obtained for all instruments in Dataset 1 show a (± 0.5) value for the mean shift. A similar result was obtained for Dataset 2, figure not shown. [..⁷²] Similarly to report by Stübi et al. (2017), the standard deviation shows an small seasonal component. [..⁷³] This result is explained by the low daily variability of the ozone at sub-tropical latitudes. For the Brewers of the RBCC-E Triad, the standard deviation is more influenced by any anomalous internal behaviour of the instruments. For middle latitudes, e.g. in Arosa, there is a larger daily variation in ozone and the standard
- 10 deviation shows it.

- Following Stübi et al. (2017), Table 4 shows the distribution of percentiles of the mean shift and the standard deviation values plotted in Fig. 6. The Brewers present a similar interpercentile range $P_{2.5} - P_{97.5}$, with a mean value close to 1.1%. This result is consistent with the standard deviation shown in Table 3 for the polynomial fits. In comparison with the Arosa Triad, only Brewer #040 shows a better behaviour than the RBCC-E Brewers while their other Brewers (B#072, B#156) show similar
- 15 values to ours.

⁷²removed: Contrary to the report in Stübi et al. (2017), in the present case the standard deviation does not show any

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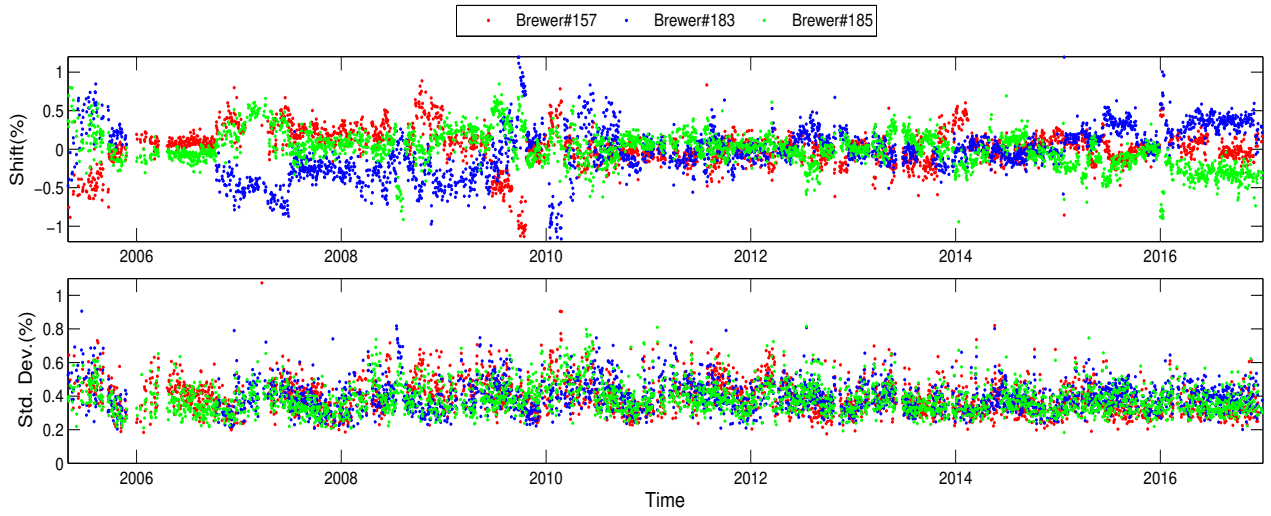


Figure 6. Time series of the mean shift Δ and the standard deviation σ , in terms relative to the TOC calculated from measurements performed by the three Brewers of the RBCC-E Triad (#157, #183 and #185) fitted with a 3rd grade polynomial

Table 4. Percentiles of the difference distribution (%) for the RBCC-E Triad.

Dataset 1		Shift Δ					Standard Deviation σ				
Brewer	$P_{2.5}$	P_{25}	Median	P_{75}	$P_{97.5}$	Brewer	$P_{2.5}$	P_{25}	Median	P_{75}	$P_{97.5}$
#157	-0.426	-0.13	0.017	0.138	0.464	#157	0.25	0.32	0.37	0.426	0.595
#183	-0.71	-0.219	-0.016	0.191	0.58	#183	0.25	0.327	0.377	0.439	0.599
#185	-0.54	-0.099	0.0155	0.147	0.51	#185	0.24	0.316	0.375	0.451	0.631
Triad	-0.599	-0.14	0.008	0.156	0.524	Triad	0.248	0.321	0.373	0.439	0.609

Dataset 2		Shift Δ					Standard Deviation σ				
Brewer	$P_{2.5}$	P_{25}	Median	P_{75}	$P_{97.5}$	Brewer	$P_{2.5}$	P_{25}	Median	P_{75}	$P_{97.5}$
#157	-0.573	-0.265	-0.053	0.084	0.365	#157	0.25	0.33	0.389	0.459	0.651
#183	-0.475	-0.093	-0.037	0.264	0.559	#183	0.265	0.349	0.405	0.473	0.627
#185	-0.341	-0.103	0.007	0.114	0.513	#185	0.247	0.33	0.389	0.479	0.6509
Triad	-0.503	-0.136	-0.001	0.1386	0.517	Triad	0.242	0.33	0.38	0.464	0.639

4.1.2 Long-term [..⁷⁴]consistency: monthly averages

Although the histogram and the statistical parameters already presented suggest that the long-term [..⁷⁵]consistency of the RBCC-E, Arosa and World Reference Triads are similar. It can be more interesting to present this study from the monthly means. With this idea in mind, the daily difference plotted in Fig. 5 and the daily shift plotted in Fig.6 were monthly averaged.

5 Fig.7 shows, in relative terms, the monthly values for the period 2005–2016 (Dataset 1). The results confirm that the RBCC-E Triad has a good long-term precision, regardless of the method selected. In order to compare with the World Triad Reference, Table 5 contains the relative standard deviation of the difference between the representative value *A* of each brewer, calculated from the 2nd grade polynomial fit, and the triad mean. As reported by [..⁷⁶]?, the relative standard deviation of the 3-monthly mean for the World Triad Reference is 0.40%, 0.46% and 0.39% for Brewers #008, #014, and #015, respectively (0.42% in
10 mean). The RBCC-E Brewers have lower 1-monthly and 3-monthly relative standard deviation. The ratio between 3-monthly [..⁷⁷]standard deviation is 36% lower for the RBCC-E.

Table 5. RBCC-E and World Reference Triads: Relative monthly standard deviation.

	RBCC-E		WORLD REFERENCE	
	1-Monthly	3-Monthly	3-Monthly	
Brewer #157	0.33%	0.29%	Brewer #008	0.40%
Brewer #183	0.34%	0.31%	Brewer #014	0.46%
Brewer #185	0.23%	0.20%	Brewer #015	0.39%
Mean	0.33%	0.27%	0.42%	

Furthermore, Stübi et al. (2017) reported that in the period 2004–2012 the Arosa Triad presented monthly shift around at $\pm 0.4\%$ while the RBCC-E are lower than $\pm 0.3\%$.

4.2 Short-term [..⁸¹]consistency

15 Dataset [..⁸²]2 was used to study the short-term [..⁸³]consistency of the RBCC-E Triad, with a view to determine in which SZA range the consistence of the measurements is higher. The measurements made by the three Brewers every day were fitted by 3rd grade polynomial as shown in Fig. 8. As previously commented, this polynomial represents the behaviour of the triad

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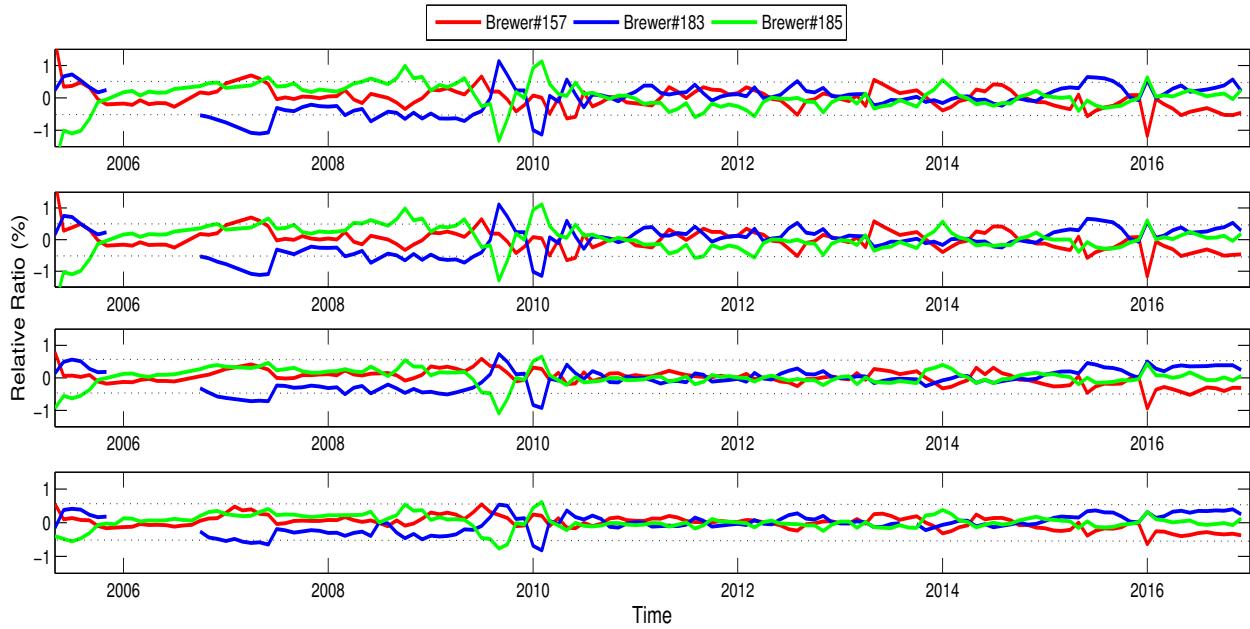


Figure 7. Relative ratio of the monthly values with respect to the Triad mean for the [..⁷⁸] methods proposed for World Triad Reference, [..⁷⁹], Daily Mean (RBCC-E) and Arosa Triad, Stübi et al. (2017). The gap for the Brewer #183 data was caused by the tropical storm “Delta” which damaged the instrument. In 2010, the Brewer #183 had a problem with [..⁸⁰] its micrometers

and [..⁸⁴] allows to obtain the TOC as a function of the time. Similarly to the previous study, each Brewer was characterized by a shift Δ . In this case, the data were divided as a function of the SZA. Different SZA ranges were checked, finding that the analysis can be reduced to just three broad ranges:

1. $SZA > 60^\circ$ corresponds to the first and last ozone measurements of every day, when solar radiation presents a low intensity and high Rayleigh scattering.
2. $SZA < 30^\circ$ corresponds to the measurement in the middle of the day, when the air mass is close to 1 and, hence, there is less Rayleigh scattering.
3. $60^\circ < SZA < 30^\circ$, the rest of ozone measurements.

In Fig. 8, the box-plot shows the statistical distribution of the mean shift calculated for the ranges selected. As can be observed, the greatest dispersion values are at low SZA which indicates at solar noon when more discrepancy can be observed between the data recorded by the instruments. This result may seem surprising because in these conditions the solar radiation on the Earth’s surface is maximum and the Rayleigh scattering is minimum but it can be easily explained from Eq. 1. In this expression, at low SZA the optical mass, μ , is close to 1 and the ozone absorption α is a constant value. This implies that the

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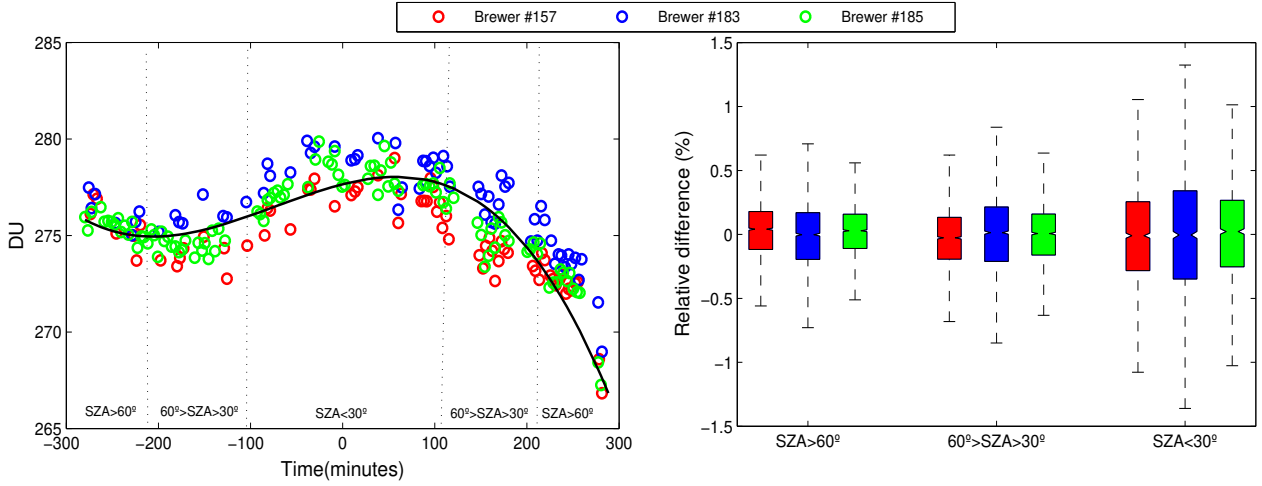


Figure 8. (left) Experimental measurements and 3rd grade Triad fit and ([..⁸⁵]right) [..⁸⁶]relative difference by Brewer as function of the SZA[..⁸⁷]. The drop is due to that one Brewer was not operative during few minutes and, hence, there are not simultaneous measurements between the three instruments.

denominator takes an almost constant value. Therefore, a small fluctuation (noise) associated with the MS9 values may affect significantly the TOC recorded. In contrast, for the other ranges the denominator takes a significant value and the effect of the noise on MS9 is less, increasing the [..⁸⁸]consistency of the measurements. In addition, the Fig. 8 shows that the Brewer #183 presents the poorer results which can be explained if it is taken into account that this instrument was damaged in 2007, and during 2008 it had an irregular operation. Moreover, in 2010, it had a problem with their micrometers (Roozendaal et al., 2013).

5 Conclusions

[..⁸⁹]

The long-term consistency of the TOC measurements made by the RBCC-E [..⁹⁰]triad has been studied [..⁹¹]and compared with the values reported for the World [..⁹²]reference and Arosa triads. With this idea in mind, the [..⁹³]procedure

⁸⁸removed: stability

⁸⁹removed: The consistency of

⁹⁰removed: Triad

⁹¹removed: in order to check its long-term stability to compare it

⁹²removed: Reference and Arosa Triads

⁹³removed: procedures used by these triads were reproduced in this work to analyze the RBCC-E data. From the method used to evaluate the World Triad Reference, the difference between the

Table 6. Summary of the three studies comparing of the relative standard deviation of the World Triad Reference, Arosa and RBCC-E Triads

	daily	monthly	3-monthly
World Triad Reference	0.42	-	0.47
Arosa Triad	0.5	0.36	-
RBCC-E	0.41	0.37	0.27

The standard deviation calculated from procedure of ? and Stübi et al. (2017) are not equal but they are similar enough to compare the three triads. In this table, the values introduced for the RBCC-E were obtained from the procedure used by ? for the World Reference Triad.

described by ? to evaluate the TOC measurements made by [..⁹⁴] the World Triad Reference was used in this work. The relative daily standard deviation [..⁹⁵] for each Brewer, $\sigma_{157} = 0.362\%$, $\sigma_{183} = 0.453\%$ [..⁹⁶], and the triad mean $\sigma = 0.41\%$ [..⁹⁷] were calculated. The values obtained for RBCC-E are lower than the reported value for the World Triad Reference [..⁹⁸]. Also, in this work has been investigated the possibility of extending the fitting proposed by (?) to a 3rd grade polynomial.

5 In this case, for our TOC measurements, there is no significant improvement of the results, compared to the initially proposed fitting. As the World Reference, the RBCC-E calculated the relative 1-monthly and 3-monthly standard deviation as the average of the daily values.

In addition, applying the procedure [..⁹⁹] described by Stübi et al. (2017) to study the Arosa Triad, the RBCC-E Triad presents a similar interpercentile range $P_{2.5} - P_{97.5}$, with a value close to 1.1%, similar to those reported for the Arosa Triad,

10 except in the case of Brewer #040. [..¹⁰⁰] Although the methodology used to study the World Reference and Arosa triads are different, the standard deviation reported for these and RBCC-E [..¹⁰¹] triads are fairly similar, [..¹⁰²] which indicate a large level of internal consistency between their instruments. However, in order to guarantee a correct traceability of the ozone measurements all around the world, a greater frequency of Absolute Calibration Campaign between the calibration center and the travelling standard reference are necessary.

15 Finally, the short-term consistency between the TOC measurements made by our Brewers is investigated. For this, the TOC observations were divided as a function of the SZA. The results obtained indicate that a greater difference between observations is observed at midday.

⁹⁴ removed: each Brewer and the Triad mean present a
⁹⁵ removed: equal to
⁹⁶ removed: and $\sigma_{185} = 0.428\%$ (
⁹⁷ removed:),
⁹⁸ removed: ($\sigma = 0.47\%$). Using monthly averages of these differences, the relative standard deviation reports values slightly lower than those obtained from the daily data.
⁹⁹ removed: used
¹⁰⁰ removed: However, the monthly means are better for the
¹⁰¹ removed: Triad. Despite these differences, the values reported for each Triads
¹⁰² removed: see Table 6, which ensures the

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References

- Anwar, F., Nazir Chaudhry, F., Nazeer, S., Zaman, N., and Azam, S.: Causes of Ozone Layer Depletion and Its Effects on Human: Review, *Atmospheric and Climate Sciences*, 06, 129–134, 2016.
- Basher, R. E.: Review of the Dobson Spectrophotometer and its Accuracy, in: *Atmospheric Ozone*, pp. 387–391, Springer, Dordrecht, 1985.
- 5 https://link.springer.com/chapter/10.1007/978-94-009-5313-0_78, doi: 10.1007/978-94-009-5313-0_78, 1985.
- Brewer, A. W.: A replacement for the Dobson spectrophotometer?, *Pure and Applied Geophysics*, 106–108, 919–927, <https://doi.org/10.1007/BF00881042>, <http://link.springer.com/10.1007/BF00881042>, 1973.
- Carvalho, F. and Henriques, D.: Use of Brewer ozone spectrophotometer for aerosol optical depth measurements on ultraviolet region, *Advances in Space Research*, 25, 997–1006, [https://doi.org/10.1016/S0273-1177\(99\)00463-9](https://doi.org/10.1016/S0273-1177(99)00463-9), <http://www.sciencedirect.com/science/article/pii/S0273117799004639>, 2000.
- 10 Cuevas, E., Milford, C., Bustos, J. J., del Campo-Hernández, R., García, O. E., García, R. D., Gómez-Peláez, A. J., Ramos, R., Redondas, A., Reyes, E., Rodriguez, S., Romero-Campos, P. M., Schneider, M., Belmonte, J., Gil-Ojeda, M., Almansa, F., Alonso-Pérez, S., Barreto, A., González-Morales, Y., Guirado-Fuentes, C., López-Solano, C., Afonso, S., Bayo, C., Berjón, A., Bethencourt, J., Camino, C., Carreño, V., Castro, N. J., Cruz, A. M., Damas, M., De Ory-Ajamil, F., García, M. I., Fernández-de Mesa, C. M., González, Y., Hernández, C., Hernández, Y., Hernández, M. A., Hernández-Cruz, B., Jover, M., Köhl, S. O., López-Fernández, R., López-Solano, J., Peris, A., Rodriguez-Franco, J. J., Sálamo, C., Sepúlveda, E., and Sierra, M.: Izaña Atmospheric Research Center Activity Report 2012–2014, no. 219 in GAW Report, State Meteorological Agency (AEMET), Madrid, Spain, and World Meteorological Organization, Geneva, Switzerland, http://www.wmo.int/pages/prog/arep/gaw/documents/Final_GAW_Report_No_219.pdf, 2015.
- 15 De La Casinière, A., Cachorro, V., Smolskaia, I., Lenoble, J., Sorribas, M., Houët, M., Massot, O., Antón, M., and Vilaplana, J.: Comparative measurements of total ozone amount and aerosol optical depth during a campaign at El Arenosillo, Huelva, Spain, *Ann. Geophys.*, 1–23, 2005.
- 20 Dobson, G. and Normand, C.: Determination of Constants Used in the Calculation of the Amount of Ozone from Spectrophotometer Measurements and the Accuracy of the Results, International Ozone Commission (I. A.M.A.P.), 1, <http://www.o3soft.eu/dobsonweb/messages/1957langleydobsonl.pdf>, 1958.
- 25 Dobson, G. M. B.: Observers' handbook for the ozone spectrophotometer, in: *Annals of the International Geophysical Year*, V, pp. 46–89, Pergamon Press, 1957.
- Farman, J. C., Gardiner, B. G., and Shanklin, J. D.: Large losses of total ozone in Antarctica reveal seasonal ClO x /NO x interaction, *Nature*, 315, 207–210, <https://doi.org/10.1038/315207a0>, <http://www.nature.com/articles/315207a0>, 1985.
- Fioletov, V. and Natcheva, S.: The Brewer Triad and Calibrations; The Canadian Brewer Spectrophotometer Network, http://kipponen-brewer.com/wp-content/uploads/2014/10/Status-of-the-Canadian-Network-Brewer-Triad_StoykaNatcheva.pdf, 2014.
- 30 Fioletov, V. E.: Comparison of Brewer ultraviolet irradiance measurements with total ozone mapping spectrometer satellite retrievals, *Optical Engineering*, 41, 3051, <https://doi.org/10.1117/1.1516818>, <http://opticalengineering.spiedigitallibrary.org/article.aspx?doi=10.1117/1.1516818>, 2002.
- Fioletov, V. E., Kerr, J., McElroy, C., Wardle, D., Savastiouk, V., and Grajnar, T.: The Brewer reference triad, *Geophysical Research Letters*, 32, <https://doi.org/10.1029/2005GL024244>, <http://doi.wiley.com/10.1029/2005GL024244>, 2005.
- 35

- Fioletov, V. E., McLinden, C. A., McElroy, C. T., and Savastiouk, V.: New method for deriving total ozone from Brewer zenith sky observations, *Journal of Geophysical Research*, 116, <https://doi.org/10.1029/2010JD015399>, <http://doi.wiley.com/10.1029/2010JD015399>, 2011.
- Fountoulakis, I., Redondas, A., Lakkala, K., Berjon, A., Bais, A. F., Doppler, L., Feister, U., Heikkila, A., Karppinen, T., Karhu, J. M., Koskela, T., Garane, K., Fragkos, K., and Savastiouk, V.: Temperature dependence of the Brewer global UV measurements, *Atmospheric Measurement Techniques*, 10, 4491–4505, <https://doi.org/10.5194/amt-10-4491-2017>, <https://www.atmos-meas-tech.net/10/4491/2017/>, 2017.
- Gröbner, J., Wardle, D. I., McElroy, C. T., and Kerr, J. B.: Investigation of the wavelength accuracy of Brewer spectrophotometers, *Appl. Opt.*, 37, 8352–8360, <https://doi.org/10.1364/AO.37.008352>, 1998.
- 10 Gröbner, J., Vergaz, R., Cachorro, V. E., Henriques, D. V., Lamb, K., Redondas, A., Vilaplana, J. M., and Rembges, D.: Intercomparison of aerosol optical depth measurements in the UVB using Brewer Spectrophotometers and a Li-Cor Spectrophotometer, *Geophysical Research Letters*, 28, 1691–1694, <https://doi.org/10.1029/2000GL012759>, <http://onlinelibrary.wiley.com/doi/10.1029/2000GL012759/abstract>, 2001.
- Karppinen, T., Redondas, A., García, R. D., Lakkala, K., McElroy, C. T., and Kyrö, E.: Compensating for the Effects of Stray Light in Single-Monochromator Brewer Spectrophotometer Ozone Retrieval, *Atmosphere-Ocean*, 53, 66–73, <https://doi.org/10.1080/07055900.2013.871499>, <http://www.tandfonline.com/doi/abs/10.1080/07055900.2013.871499>, 2015.
- 15 Kerr, J. B.: The Brewer Spectrophotometer, in: *UV Radiation in Global Climate Change*, pp. 160–191, Springer, Berlin, Heidelberg, https://link.springer.com/chapter/10.1007/978-3-642-03313-1_6, dOI: 10.1007/978-3-642-03313-1_6, 2010.
- Kerr, J. B., McElroy, C. T., and Olafson, R. A.: Measurements of ozone with the Brewer ozone spectrophotometer, in: *Proceedings of the Quadrennial Ozone Symposium held in Boulder, Colorado, August 1980*, pp. 74–79, J. London, ed., 1981.
- 20 Kerr, J. B., McElroy, C. T., Wardle, D. I., Olafson, R. A., and Evans, W. F. J.: The Automated Brewer Spectrophotometer, in: *Atmospheric Ozone*, pp. 396–401, Springer, Dordrecht, https://link.springer.com/chapter/10.1007/978-94-009-5313-0_80, dOI: 10.1007/978-94-009-5313-0_80, 1985.
- Kiedron, P. W. and Michalsky, J. J.: Non-parametric and least squares Langley plot methods, *Atmospheric Measurement Techniques*, 9, 215–225, <https://doi.org/10.5194/amt-9-215-2016>, <https://www.atmos-meas-tech.net/9/215/2016/>, 2016.
- 25 Kipp & Zonen: Brewer MKIII Spectrophotometer Operators Manual., Tech. rep., Kipp & Zonen Inc., <http://www.kippzonen.com/Download/207/Brewer-MkIII-Operator-s-Manual>, 2008.
- Komhyr, W., Grass, R., and Leonard, R.: Dobson spectrophotometer 83: A standard for total ozone measurements, 1962–1987, *Journal of Geophysical Research: Atmospheres*, 94, 9847–9861, <https://doi.org/10.1029/JD094iD07p09847>, <https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/JD094iD07p09847>, 1989.
- 30 León-Luis, S. F., Carreño Corbella, V., Hernández Cruz, B., Berjón, A., López-Solano, J., Rodríguez Valido, M., and Redondas, A.: RBCC-E Triad, in: *Brewer Ozone Spectrophotometer/Metrology Open Workshop*, <http://repositorio.aemet.es/handle/20.500.11765/7602>, 2016.
- López-Solano, J., Redondas, A., Carlund, T., Rodriguez-Franco, J. J., Diémoz, H., León-Luis, S. F., Hernández-Cruz, B., Guirado-Fuentes, C., Kouremeti, N., Gröbner, J., Kazadzis, S., Carreño, V., Berjón, A., Santana-Díaz, D., Rodríguez-Valido, M., De Bock, V., Moreta, J. R., Rimmer, J., Smedley, A. R. D., Boulkelia, L., Jepsen, N., Eriksen, P., Bais, A. F., Shiroto, V., Vilaplana, J. M., Wilson, K. M., and Karppinen, T.: Aerosol optical depth in the European Brewer Network, *Atmos. Chem. Phys.*, 18, 3885–3902, <https://doi.org/10.5194/acp-18-3885-2018>, <https://www.atmos-chem-phys.net/18/3885/2018/>, 2018.

- Netcheva, S.: Canada's Ozone Science Program. 9th Ozone Research Manager's Meeting. Oral Presentation., http://conf.montreal-protocol.org/meeting/orm/9orm/presentations/English/1400b_Canada_NationalRpt_9ORM_v3.pdf, 2014.
- Redondas, A.: Ozone Absolute Langley Calibration, in: The Tenth Biennial WMO Consultation on Brewer Ozone and UV Spectrophotometer Operation, Calibration and Data Reporting, no. 176 in GAW Report, World Meteorological Organization, ftp://ftp.wmo.int/Documents/PublicWeb/arep/gaw/gaw176_10thbrewer.pdf, 2008.
- Redondas, A. and Rodríguez-Franco, J.: Ninth Intercomparison Campaign of the Regional Brewer Calibration Center Europe (RBCC-E), no. 224 in GAW Report, World Meteorological Organization, http://library.wmo.int/pmb_ged/gaw_224_en.pdf, 2015.
- Redondas, A. and Rodríguez-Franco, J.: Eighth Intercomparison Campaign of the Regional Brewer Calibration Center for Europe (RBCC-E) (El Arenosillo Atmospheric Sounding Station, Heulva, Spain, 10-20 June 2013), doi: 10.13140/RG.2.1.2304.7443, 2016.
- 10 Redondas, A., Evans, R., Stüebi, R., Köhler, U., and Weber, M.: Evaluation of the use of five laboratory-determined ozone absorption cross sections in Brewer and Dobson retrieval algorithms, *Atmospheric Chemistry and Physics*, 14, 1635–1648, <https://doi.org/10.5194/acp-14-1635-2014>, <http://www.atmos-chem-phys.net/14/1635/2014/>, 2014a.
- Redondas, A., Rodríguez, J., Carreno, V., and Sierra, M.: RBCC-E 2014 langley campaign the triad before Arosa/Davos campaign, <https://repositorio.aemet.es/bitstream/20.500.11765/2599/1/Alberto%20TriadArosaDavos.pdf>, 2014b.
- 15 Redondas, A., J. Gröbner, U. Köhler, and Stübi, R.: Seventh Intercomparison Campaign of the Regional Brewer Calibration Center Europe (RBCC-E), doi: 10.13140/RG.2.1.4795.1128, 2015.
- Redondas, A., Carreño, V., Lui-León, S. F., Hernandez-Cruz, B., López-Solano, J., Rodríguez-Franco, J. J., Vilaplana, J. M., Gröbner, J., Rimmer, J., Bais, A. F., Savastiouk, V., Moreta, J. R., Boukelia, L., Jepsen, N., Wilson, K. M., Shirotov, V., and Karppinen, T.: EUBREWNET RBCC-E Huelva 2015 Ozone Brewer Intercomparison, *Atmos. Chem. Phys. Discuss.*, 2018, 1–18, <https://doi.org/10.5194/acp-2017-1210>, <https://www.atmos-chem-phys-discuss.net/acp-2017-1210/>, 2018.
- 20 research Programme, E. E. M.: Traceability for atmospheric total column ozone (ATMOZ), <http://projects.pmodwrc.ch/atmoz/index.php>, 2014.
- Rimmer, J., Redondas, A., Gröbner, J., Karppinen, T., De Bock, V., and Bais, A.: The European COST Action EUBrewNet, http://conf.montreal-protocol.org/meeting/orm/10orm/presentations/Observer%20Publications/Tu1745_Rimmer_EUBrewNET.pdf, 2017.
- 25 Roozendael, M. V., Köhler, U., Pappalardo, G., Kyrö, E., Redondas, A., Wittrock, F., Amodeo, A., and Pinardi, G.: CEOS Intercalibration of Ground-Based Spectrometers and Lidars: Final report, Tech. rep., ESA-CEOS, <http://repositorio.aemet.es/handle/20.500.11765/8886>, 2013.
- Sarma, K. M. and Andersen, S. O.: Science and Diplomacy: Montreal Protocol on Substances that Deplete the Ozone Layer, in: *Science diplomacy : science, Antarctica, and the governance of international spaces*, pp. 123–131, Smithsonian Institution Scholarly Press, <https://repository.si.edu/handle/10088/16168>, doi: 10.5479/si.9781935623069.123, 2011.
- 30 Scarnato, B., Staehelin, J., Peter, T., Gröbner, J., and Stübi, R.: Temperature and slant path effects in Dobson and Brewer total ozone measurements, *Journal of Geophysical Research*, <https://doi.org/10.1029/2009JD012349>, 2009.
- Scarnato, B., Staehelin, J., Stübi, R., and Schill, H.: Long-term total ozone observations at Arosa (Switzerland) with Dobson and Brewer instruments (1988–2007), *Journal of Geophysical Research*, 115, <https://doi.org/10.1029/2009JD011908>, <http://doi.wiley.com/10.1029/2009JD011908>, 2010.
- 35 Stübi, R., Schill, H., Klausen, J., Vuilleumier, L., and Ruffieux, D.: Reproducibility of total ozone column monitoring by the Arosa Brewer spectrophotometer triad: AROSA BREWER TRIAD, *Journal of Geophysical Research: Atmospheres*, 122, 4735–4745, <https://doi.org/10.1002/2016JD025735>, <http://doi.wiley.com/10.1002/2016JD025735>, 2017.

Varotsos, C. and Cracknell, A. P.: On the accuracy of total ozone measurements made with a Dobson spectrophotometer in Athens, *International Journal of Remote Sensing*, 15, 3279–3283, <https://doi.org/10.1080/01431169408954327>, <https://doi.org/10.1080/01431169408954327>, 1994.

- 5 Zhao, X., Fioletov, V., Cede, A., Davies, J., and Strong, K.: Accuracy, precision, and temperature dependence of Pandora total ozone measurements estimated from a comparison with the Brewer triad in Toronto, *Atmospheric Measurement Techniques*, 9, 5747–5761, <https://doi.org/10.5194/amt-9-5747-2016>, <http://www.atmos-meas-tech.net/9/5747/2016/>, 2016.