Stability of the RBCC-E Triad during the period 2005 – 2016

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Answer to Tom McElroy

Thank you for your review. According to your suggestions and those of other referees, we submit a revised version of our manuscript entitled “Stability of the Regional Calibration Center for Europe Triad during the period 2005-2016” by Sergio Fabián León-Luis, Alberto Redondas, Virgilio Carreño, Javier López-Solano, Alberto Berjón, Bentorey Hernández-Cruz and Daniel Santana-Díaz. All issues brought up by the reviewers have been addressed.

Figures

In all the figures a colour legend has been introduced. For this reason, these are slightly different to the previous version of the article submitted.

Section 2 "Theoretical approach"

All referees have indicated that the section 2 is confused. Therefore, it has been rewritten taking into account all suggestions indicated by the referees. Also, a new figure has been introduced.

Grammatical errors

The authors appreciate the grammatical corrections indicated which have been introduced in the text. A co-worker, who is a native English speaker, has helped us with the use of language. In the new version, some paragraphs and sentences were modified to get a more fluid text.

We have were used both “behavior” and “behaviour”. In order to have a more consistent article we have replaced the word “behavior” by “behaviour” in the text.

-Similarly, "tractability" by "traceability". -Similarly, "centre" by "center".

Page 1 Line 1 “Total ozone column measurements can be made using ...” The text was modified
In 2003, ... The text was modified

... and since 2011 it has transferred ... The text was modified

... calibration, mainly to other European Brewers, using Brewer #185 ...” The text was modified

... annually, alternating ...” The text was modified

... focused on reporting on the stability... "The text was modified

... to the data from the Izana triad allows the comparison of the ...” The text was modified

... standard deviation of the mean equal ...” The text was modified

“In opposite, using...” Suggest “... Alternatively, using the procedure used to analyze the data from the Arosa Triad ...” The text was modified

... presents a relative standard deviation of about ...” The text was modified

... method used for the data from the World Triad Reference ...” The text was modified

... gives monthly values of 0.3% ...” The text was modified

... datasets were analyzed ...” “... second only included... “The text was modified

Furthermore, this paper also describes the Langley method used to determine the Extra-Terrestrial Constants (ETC) for the RBCC-E Triad, the necessary first step toward accurate ozone measurement.” The text was modified

... until a few decades ago, it was thought that the ozone concentration was constant in the stratosphere. However, after the discovery of the hole in the ozone layer in the mid-1980s, this idea was discarded (Farman et al., 1985)”. This is a problematic statement. Ozone is variable, it has annual cycles - and longer-term cycles - and a non-uniform global distribution. It is not clear how to accurately express the simple though the authors are searching for. Perhaps something like “Historical measurements - pre 1980 - indicated that the morphology of ozone was not changing significantly with time. However, the Antarctic measurements of Farman et al., published in 1985, changed that view....” The text was modified

... concerns related to the negative effects that UV radiation can have on terrestrial life ...” The text was modified

... agents that led to this decrease ...” The text was modified

... total ozone column abundance ...” The text was modified


... wavelength separation... “ Spelling: “... wavelength separation...” The text was modified

Although the prototype Brewer was developed in the early 1970s ...” “... has had on-going technical improvements to improve its accuracy...” The text was modified

Page 2 Line 20 Delete “concentration” The text was modified
Brewers present this ... Capitalize “Brewers present this ...”

... consisting of. ... “... consisting of. ...”

... (Fioletov et al., 2005) ...”

... parallel with the World Triad Reference ...”

... are calibrated by comparison with the travelling ...

... Observatory is located on the island of Tenerife ...

... campaigns through the travelling ...

These values were calculated using measurements in a range where Brewer #017 measurements are not strongly affected by stray light ...

... each Brewer at its local station ...

... which will allow the calculation of the TOC in near real time ...

Currently, approximately 40 Brewers ...

Also in this section the results of a study on the behavior of the RBCC-E Triad as a function of SZA range at which the measurements were performed.

... four spectral bands which ...

... with local maximum and minimum ozone absorption cross-sections.

... the contribution of Rayleigh ...

... more than one band is ...

The Beer-Lambert law ...

where J is the gas concentration ...

The equations in the PDF did not fare well.

Measurements on slits 2 to 6 are used for SO2 and ozone.

On behalf of the co-authors, thank you very much for your suggestions.

Alberto Redondas Marrero.

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Stability of the RBCC-E Triad during the period 2005 – 2016

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Answer to Referee #1

Thank you for your review. According to your suggestions and those of other referees, we submit a revised version of our manuscript entitled “Stability of the Regional Calibration Center for Europe Triad during the period 2005-2016” by Sergio Fabián León-Luis, Alberto Redondas, Virgilio Carreño, Javier López-Solano, Alberto Berjón, Bentorey Hernández-Cruz and Daniel Santana-Díaz. All issues brought up by the reviewers have been addressed.

Figures

In all the figures a colour legend has been introduced. For this reason, these are slightly different to the previous version of the article submitted.

Section 2 "Theoretical approach"

All referee have indicated that the section 2, where an approach to ozone retrieval (DS routine, slits) and Langley-technique are introduced, is confused. Therefore, it has been rewritten taking into account all the suggestions. Also, a new figure has been introduced.

Grammatical errors

The authors appreciate the grammatical corrections indicated which have been introduced in the text. A co-worker, who is a native English speaker, has helped us with the use of language. In the new version, some paragraphs and sentences were modified to get a more fluid text.

We have used both “behavior” and “behaviour”. In order to have a more consistent article we have replaced the word “behavior” by “behaviour” in the text.

-Similarly, "centre" by "center". - P1, l9: add ...from “two different” methods previously... done
- P1, l10: it should already be mentioned here that the World Reference is the Toronto triad. done
- P2, l5: “on” instead “in”. done
- P2, l6: “cause” instead “produce”. done
- P2, l9 and in references P20, l4: “Varotsos” instead “varotsos”. done
- P2, l9: “. . . . . which are considered to be reference instruments. . . .” Is not correct. The triads or Brewer #17 are references (or standards). May be “basic instruments in the global network” or similar is better. done
- P2, l10: “Brewer spectrophotometers are widely used” since when? This sentence was rewritten.
- P2, l12/13: “ozone concentration” is not correct, “TOC” is better. done
- P2, l16: Why is “although” used? Better “After the development of the first Brewer in the early 1980s it has had continu-
- P2, l21: 70 degrees as limit for single Brewer observations seems small, as it correspondsto µ-values of smaller than 3. Even single Brewers can measure reliable TOC up to 75 degrees (µ-values around 3.5) under normally clear air conditions. Perhaps it would be good, to describe the different stray light issues: internal straylight-problem, which is larger for single Brewers, and external stray light (diffuse sky light around the sun), which is similar for all Brewers, but larger for Dobsons.
- P2, l24: The calibration of the Brewer “in the first years” is traceable.
- P2, l31: by the “manufacturer” Kipp & Zonen.done
- P3, l5: Add “triad” behind RBCC-E.done
- P3, l9: Replace “in the island” with “on the island”.done
- P3, l16: “These values have been”.done
- P3, l20: “more than 150 Brewers have been calibrated”. done
- P4, l3 ff, p5: see under general comments (SO2!). The reference Dobson 1957 is out of place here and I think anywhere in the text. So omit it in the references. The presentation of the corresponding absorption spectra (O3 and SO2) might be helpful. This section was rewritten
- P5, l15: DS observations are done in 6, not in 7 slits: 4 ozone, 1 SO2 and 1 dark, the seventh slit is for HG-test. This section was rewritten
- P4/5/6: Use of m instead of µ is not correct. done
- P6, l7: “clear” instead of “clean”-sky.done
- P6, l11: Why does the use of 1/m (should also be µ) allow obtaining two ETCs? I thought it is the splitting in fore- and afternoon observations. This section was rewritten
- P6, l 32-35: no complete sentence. The sentence was corrected
- P8, l6: Giving a number for the low standard deviation would be helpful. **done**
- P8, l9: “Langley technique can be used” instead of “Langley-technique is used”. **done**
- P8, l18: correct “a an”. **done**

Chapter 4: - P10, 4: “mean of daily differences” or “daily mean of the difference”? **This sentence was rewritten**

5
- P10,l5: Replace “analyzed” with “analyze”. **done**
- P10, l10: replace “inconvenient” with “inconvenience”. **done**
- P10, l11 and P11, l11: isn’t Izana a subtropical station? **This sentences were rewritten**
- P10, l15: “another” instead of “other”. **done**
- P11, figure 4: The “A” from Eq. 10 is missed. Shouldn’t it be placed behind “ozone reference value”? The colors are not assigned to the Brewers. **done**
- P11, last section, P12, first section: Sorry, but I have problems to understand what is meant. The beginning of two consecutive sentence with “Therefore” does not sound good. It is described that the polynomial method show similar results regardless of the data set and the order of the fit. Why is then the daily mean method more appropriate? **This paragraph was rewritten**
- P15, Figure 6: The order of the panels does not coincide with the order of the mentioned methods in the figure caption. **done**
- P15, l10: correct “surprising”. **done**

**Answers at your specific questions:**

**Comment:** The description of the triad system is not profound and clear. Where is the second triad located? In Toronto too? How are this triad and in addition the travelling Brewer No. 17 calibrated? It is good to know how stable the RBCC-E triad is, but what about its accuracy? The agreement between this triad and the World Reference Triad is confirmed by the 0.5% - agreement with #017. But how good is the agreement of #017 with World Reference Triad? When was its last absolute Langley calibration performed?  

**Answer:** In the introduction we made reference to that both (World Reference and the Second Triads) work in parallel in Toronto. In order to clarify this questions, a new reference has been included in the text. An oral presentation where is shown some graphic about the agreement between both triads, and also some photos of the Brewers have been added too. In addiction, V. Savastiouk, who operated the Brewer #017, have indicated that “Brewer #017 is regularly compared with the World triad Reference in Toronto it is also absolutely and independently calibrated at the Mauna Loa Observatory in Hawaii, US. Some history of such calibrations can be found at http://www.io3.ca/Calibrations/Brewer/017”. (see interactive discussion of our article.)

**Comment:** P2, l21: 70 degrees as limit for single Brewer observations seems small, as it corresponds to µ-values of smaller than 3. Even single Brewers can measure reliable TOC up to 75 degrees (µ-values around 3.5) under normally clear air conditions. Perhaps it would be good, to describe the different stray light issues: internal straylight-
problem, which is larger for single Brewers, and external stray light (diffuse sky light around the sun), which is
similar for all Brewers, but larger for Dobsons. The effect is the same in both cases: drop of TOC, when the SZA
(\(\mu\)) increases and gets large depending on instrument and turbidity.

**Answer:** Yes, perhaps this value is a very extreme lower limit. This sentence was rewritten. We think that is better to say
that "...decrease in the TOC measurement at large ozone slant column".

**Comment:** - P8, l6: Giving a number for the low standard deviation would be helpful.

**Answer:** Following the suggestion of other referee this sentence was rewritten "despite this annual behaviour, the ozone
presents a lower daily variability as indicated our measurements".

**Comment:** - P8, l17: The criterion lower than 0.6 under item 4 is not clear: standard deviation of 0.6 DU? Seems to be
a very low standard deviation for a day with small ozone variation.

**Answer:** Yes, this condition was introduced in the article by mistake. It was written in a previous version (internal draft)
but it was not deleted from the uploaded article.

**Comment:**

- P8, l20: what does “(condition 3 above)” mean in the context with simultaneous? Does it mean, that in addition to
condition 3, these selected measurements should be simultaneous?

**Answer:** rephrased as additional condition.

**Comment:** - P10, l8/9: what does slight mechanical miscalculation mean?

**Answer:** Sorry, maybe this sentence is not the best translation into English. The text has been modified as follows:
Old version: “...it should be noted that the presence of slight mechanical miscalculations in the instrument...”
New Version: “... it should be noted that the presence of small drifts by its continued operation of the instrument...”

**Comment:** - P11, figure 4: The “A” from Eq. 10 is missed. Shouldn’t it be placed behind “ozone reference value”? The
colors are not assigned to the Brewers

**Answer:** A new figure with a colour legend has been upload. The “A” was included in the figure caption.

**Comment:** - P11, last section, P12, first section: Sorry, but I have problems to understand what is meant. The beginning
of two consecutive sentence with “Therefore” does not sound good. It is described that the polynomial method
show similar results regardless of the data set and the order of the fit. Why is then the daily mean method more
appropriate?

**Answer:** This paragraph was rewritten because, as you indicate, it is confusing. The "therefore" were replaced by other
connecters.
Comment: P13, Fig.5: Again the colors are not assigned to the Brewers

Answer: A new figure with a colour legend have been upload.

Comment: - P12 – P15: What about Brewer #183? Tables 3 and 4 (Data set 1) and Figures 5 and 6 show a larger ratio in 2007, which cannot be seen in the graph of Arosa method. Only the table 4 gives a negative shift median and larger percentile numbers for Brewer #183 data set 1. Is the reason known? The same is valid for the larger scattering of all RBCC-E Brewers around 2010.

Answer: Thank you! If the data in this graph was wrong. We have reviewed our calculations and now the results are more coherent with the previous graphs.

Comment: 2010: issues on 183, during that time only 157 and 185 were used for reference.

Answer: In 2010, the brewer #183 had some problem with their micrometer during some months. As in the previous questions, the fit can hide this problem. We have introduced this reference where some plot about this are shown. Roozen-dael, 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. http://repositorio.aemet.es/handle/20.500.11765/8886 (Accessed 5 April 2018), 2013.

Comment: - P14, l9 (and in abstract too): Where do the numbers for the RBCC-E triad come from? I cannot find them in the tables.

Answer: The values are the serial numbers of the brewer

Comment: - P14, l10: how is 40% lower dispersion determined?

Answer: This value was calculated as the ratio between both relative deviation (0.47-0.27)/0.47=0.42

Comment: - P14, l12: Is the 0.3% value for RBCC-E also calculated in the 2004 – 2012 period of the Stübi-paper

Answer: We’re sorry, but we cannot calculate that data. As we indicated in the introduction, brewers # 183 and # 185 were installed in 2005, hence there is not available data in the year 2004. In the article, the value reported corresponds with the period 2005-2016. In addition, it can be confusing to give values that do not correspond with the years defined in the datasets.

Comment: - P15, Figure 6: The order of the panels does not coincide with the order of the mentioned methods in the figure caption.

Answer: We have rewritten the Figure caption in the correct order.

Comment: - P15/16: The explanation for the larger scattering at high sun is good and comprehensible. But the obvious difference of low sun in the forenoon and in the afternoon is neither mentioned nor explained. Is there also an
explanation, why Brewer #183 shows larger scattering in the relative difference than the other two Brewers?

Answer: Honestly, we think that the Brewer #183 presents this large scattering because it was damaged in 2007, during the “Delta” storm and during 2008 it had an irregular behaviour and this data was used in this analysis. In addition, this difference is minimal or negligible and does not affect the calibration of the Triad. Moreover, this result is consistent with those presented in tables 3 and 4 where it is found that brewer 183 has the poorer values. It seems logical to think that if in average values (daily or monthly) this brewer is the worst, also depending on the SZA this difference is reflected.

Comment: - P16/17: The values in table 5 are not clear. Where do they come from? Fioletov daily of 0.47% is mentioned on P16, l8. In the same context the RBCC-E triad number is given as 0.41% in the Conclusion, but as 0.37 in the table, which is confusing.

Answer:
In order to clarify this question, a new table was generated.

On behalf of the co-authors, thank you very much for your suggestions.
Alberto Redondas Marrero.
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Stability of the RBCC-E Triad during the period 2005 – 2016

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Answer to V. Savastiouk

Thank you for your review. According to your suggestions and those of other referees, we submit a revised version of our manuscript entitled “Stability of the Regional Calibration Center for Europe Triad during the period 2005-2016” by Sergio Fabián León-Luis, Alberto Redondas, Virgilio Carreño, Javier López-Solano, Alberto Berjón, Bentorey Hernández-Cruz and Daniel Santana-Díaz. All issues brought up by the reviewers have been addressed.

Figures

In all the figures a colour legend has been introduced. For this reason, these are slightly different to the previous version of the article submitted.

General corrections

The authors appreciate the grammatical corrections indicated which have been introduced in the text. A co-worker, who is a native English speaker, has helped us with the use of language. In the new version, some paragraphs and sentences were modified to get a more fluid text.

- We have used both “behavior” and “behaviour” words. In order to have a more consistent article we have replaced “behavior” by “behaviour” in the text. Similarly, "centre" by "center".

- In addition, the expression "ozone concentration" was replaced by "Total ozone column (TOC)".

- The word "lines" was replaced by "bands" to indicate the wavelengths where the brewer measured.

References

New references have been included in the text where you and the other referees have indicated. However, we think that introducing a reference in the abstract as you suggest in your report is not habitual.
Abstract

P1- L9. This sentence was rewritten taking into account your suggestions. Also, the standard deviation symbol σ has been introduced together with the values reported.

Introduction

P2- L5. The sentence where we suggest that “. . . several countries agreed to reduce the agents that produces the decrease of . . .” was modified and, the number of countries agreed (197) was included.

P2- L12. The expression "Brewer is a spectrophotometer" was replaced by "Brewer ozone spectrophotometer". Also, this paragraph were rewritten.

P2- L21. 70 degrees as limit for single Brewer observations seems small, as it corresponds to -values of smaller than 3. We think that is better to say that "The single Brewer presents this problem for large ozone slant column (OSC)".

P2- L32. We think that is correct to duplicate the sentence “Since November 2003 and within the World Meteorological Organization (WMO) and the Global Atmosphere Watch . . . .” because in this paragraph it is used to talk about the history of the RBCC-E and, obviously, you must say: when was created it?, when the brewers were installed ?, which is our travelling Brewer?, etc.

P3- L11 We say that Izaña has “clean air and clear sky conditions around all the year and offers excellent conditions to perform the Langley-technique”. As you indicate we have not taken into account the dust intrusions. Therefore, the sentence was rewritten: “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 make difficult to measure the direct solar radiation”.

P3- L12. The sentence "Moreover, comparisons with the World Triad reference are carried out regularly..." was rewritten as "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."

P3- L19. The expression "annually alternating" was replaced by "annually, alternating"

P3- L23. The sentence "... on the measurements performed by each Brewer in its local station" was rewritten.

P4- L4. The sentence "... the precision between the measurements" was rewritten as "how similar are the measurements made by the Brewers"

Theoretical Approach

All referees have indicated that the section 2 is confused. Therefore, it has been rewritten taking into account all the suggestions about the approach to ozone retrieval (DS routine, slits) and Langley-technique. Also, a new figure has been introduced and the equations were modified, adding the symbol μ. In addiction, a clearer explanation about the procedure of the Langley technique was written. In it, we relate the Langley with the inverse of μ, and also explain how it affects the aerosols in this technique.
Now, we hope that the order of the section will be better.

**Ozone and dataset selected**

**P8- L6.** The sentence "Despite this annual behaviour, the ozone is stable during the day, with a low standard deviation for the recorded data." was rewritten as "Despite this annual behaviour, the ozone presents a lower daily variability as indicated by our measurements".

**P8- L17.** The criterion lower than 0.6 under item 4 is not clear: standard deviation of 0.6 DU? Seems to be a very low standard deviation for a day with small ozone variation.

Yes, this condition was introduced in the article by mistake. It was written in a previous version (internal draft) but it was not deleted from the uploaded article.

**Results and discussion**

**P10- L8/9.** What does slight mechanical miscalculation mean?

Sorry, maybe this sentence is not the best translation into English. The text has been modified as follows:

Old version: “...it should be noted that the presence of slight mechanical miscalculations in the instrument...”

New Version: “...it should be noted that the presence of small drifts by its continued operation of the instrument...”

**P12- L12.** The equation "mean value" was correct.

**P10- L15.** The expression "our experience suggest" was rewritten as "our experience suggests".

**Conclusions**

Some sentences were rewritten. The standard deviation symbol \( \sigma \) has been introduced to identify the values reported and a new table where all values are summarised is also included.
Stability of the Regional Brewer Calibration Center for Europe Triad during the period 2005 – 2016

Sergio Fabián León-Luis\textsuperscript{1,2}, Alberto Redondas\textsuperscript{1,2}, Virgilio Carreño\textsuperscript{1,2}, Javier López-Solano\textsuperscript{1,2,3}, Alberto Berjón\textsuperscript{2,3}, Bentorey Hernández-Cruz\textsuperscript{1,2,3}, and Daniel Santana-Díaz\textsuperscript{2,3}

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Abstract. Total ozone column \textsuperscript{2}measurements can be made using Brewer 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 \textsuperscript{3}since 2011 it \textsuperscript{4}transfers its own calibration, mainly to other European Brewers, using the Brewer \#185 as \textsuperscript{5}travelling reference. \textsuperscript{5}This work is focused on \textsuperscript{6}reporting on the stability of the measurements of the RBCC-E Triad (Brewers \#157, \#183 and \#185) \textsuperscript{7}made at the Izaña Atmospheric Observatory during the period 2005 – 2016. In order to study the long-term \textsuperscript{8}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 \textsuperscript{9}behaviour of the World Reference \textsuperscript{10}Triad (so-called Toronto Triad and Arosa Triad). Applying their procedures \textsuperscript{11}to the data from the RBCC-E Triad allows the comparison of the three instruments. In \textsuperscript{12}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 \textsuperscript{13}($\sigma_{\text{157}} = 0.362\%, \sigma_{\text{183}} = 0.453\%$ and $\sigma_{\text{185}} = 0.428\%$). Alternatively, using the procedure used to analyze

\footnotesize
\textsuperscript{*}removed: RBCC-E
\textsuperscript{2}removed: can be measured
\textsuperscript{3}removed: from
\textsuperscript{4}removed: has transferred
\textsuperscript{5}removed: reference instrument. The RBCC-E organizes regular inter-comparisons which are held annually alternating between Arosa (Switzerland) and El Arenosillo (Spain).
\textsuperscript{6}removed: showing
\textsuperscript{7}removed: in the
\textsuperscript{8}removed: stability
\textsuperscript{9}removed: stability
\textsuperscript{10}removed: and Arosa Triads
\textsuperscript{11}removed: in our triad allows us to compare the
\textsuperscript{12}removed: this way, the difference between the values calculated
\textsuperscript{13}removed: and the triad mean was analyzed. This also allows us to quantify the precision of each Brewer. The results obtained show that these differences are lower than 2 Dobson units in approx 90\% of the days evaluated. The daily and monthly difference between each Brewer and the Triad were calculated. We 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 [..14] include all the ozone measurements available while the second only includes the simultaneous measurements of all three instruments. Furthermore, [..15] this paper also describes the Langley method used [..16] to determine the Extra-Terrestrial Constant (ETC) [..17] for the RBCC-E Triad, the necessary first step [..18] toward accurate ozone measurement. Finally, the short-term, or intraday, stability is also studied to identify the effect of the solar zenith angle on the accuracy of the RBCC-E Triad.

1 Introduction[..19]

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. [..20] However, [..21] the Antarctic measurements of Farman et al. (1985) changed that view. Concerns related to the negative effects that UV can have on terrestrial life led to the signing of the Montreal Protocol in 1987, where [..22] 197 countries agreed to reduce the agents that [..23] led to this decrease (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 [..25] an accuracy of $\sim 1-3\%$ such as the Dobson and Brewer which are considered as [..26] ideal instruments for monitoring the ozone abundance (Basher, 1985; Varotsos and Cracknell, 1994; Fioletov et al., 2005; Scarnato et al., 2009).

Brewer [..27] 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 [..28] (Carvalho and Henriques, 2000; Gröbner et al., 2001; López-Solano et al., 2017). This instrument is mounted on an azimuth tracker that determines the TOC...
from a direct measurement of the solar radiation. The grating system separates the solar radiation and a slit mask mechanism is used to select the different UV bands to be measured which are associated with maximum and minimum ozone absorption.

After the development of the first Brewer in the early 1970s (Brewer, 1973; Kerr et al., 1985), it has had on-going technical improvements to improve its accuracy. For example, in the photomultiplier, diffraction gratings, operating software used as well as the incorporation of new measurement routines (Fioletov et al., 2005, 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 a decrease 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).

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 (Fioletov et al., 2005). 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 manufacturer by 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 hence can calibrate and transfer its own calibration. 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 to 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 this comparison, both instruments agree within 0.5%. These values have been calculated using measurements in a range where Brewer #017 measurements are not strongly affected by stray light (Redondas et al., 2015; Redondas and Rodríguez-Franco, 2015; Redondas and Rodriguez-Franco, 2016).

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 conducted (Cuevas et al., 2015). In these campaigns, the RBCC-E facilitates a new calibration for each instrument. Moreover, in order to obtain an ozone value with better accuracy, the RBCC-E advises on the need to reprocess the observations performed by 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 [61] recorded by the travelling reference #185 are used to calibrate the participating Brewers and also to conduct research works [62] (De La Casinière et al., 2005; Redondas et al., 2015; Redondas and Rodriguez-Franco, 2016).

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 [63] 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, [64] approximately 40 Brewers, mainly European, send their data automatically every 20 minutes to EUBREWNET’s dataserver. This dataserver also allows the reprocessing of data for homogenization and automatic quality control.

The present work [65] focused on investigating how similar are the measurements made by the Brewers #157, #183 and #185 [66] each day and how stable does this behaviour remain over time. This allows us to identify [67] 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 stability. 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 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.
Figure 1. Ozone and sulfur dioxide absorption cross sections. The solar radiation is measured for the intensity bands ($\lambda_{1-5} = 306.4, 310.1, 313.5, 316.8, 320.0 \text{nm}$). In contrast, the wavelength $\lambda_0 = 303 \text{nm}$ is used for a check routine.

2 Theoretical Approach

2.1 Ozone retrieval.

The standard (so-called DS) routine used to determine the TOC from direct sunlight radiation, measuring the signal intensity in five bands ($\lambda_{1-5} = 306.4, 310.1, 313.5, 316.8, 320.0 \text{nm}$) 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 $F$, in raw counts for each wavelength, 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.

\[ 73 \]

\[ \] Using standard Brewer operational variables, the TOC can be obtained as follows,

\[
O_3 = \frac{MS9 - ETC}{\alpha \cdot \mu} \tag{1}
\]

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

\[
MS9 = 10^4 \sum_i w_i \log F_i = 10^4 (\log F_2 - 0.5 \log F_3 - 2.2 \log F_4 + 1.7 \log F_5) \tag{2}
\]

The ozone absorption coefficient, \( \alpha \),

\[
\] is calculated from dispersion test (Redondas et al., 2014a) of the TOC and ETC and represent the solar radiation measured at the top of the atmosphere and the ground, respectively (Kipp & Zonen, 2008). Both parameters, and also the must be understood as values obtained from the weighted linear combination of the intensities \( F \), in logarithmic scale, of the four lines measured:

\[
\] The absorption intensity lines \( \alpha_i \) are
where $\alpha_i$ 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, $\lambda_i = (310.1, 313.5, 316.8, 320.0 \text{nm})$, used have been especially selected to suppress the aerosol and SO$_2$ effects in the measured signal (Dobson, 1957; Kerr et al., 1981). These $w_i$ and $\lambda_i$ 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 SO$_2$ on the ozone retrieval.

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

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

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. 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 solar radiation at the top of the atmosphere $ETC$, which must be estimated. The Langley calibration method is based on Lambert-Beer’s law (Eq. ??) written as a linear equation with the total optical air mass $m$ as the independent variable and $\log_e F_i^0$ as the intercept.
the extraterrestrial constant $ETC$. 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 $\mu$:

$$MS9 = ETC + O_3 \alpha \mu$$  \hspace{1cm} (6)

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

$$\frac{MS9 - (ETC + \Delta ETC)}{\mu} = O_3 \alpha$$  \hspace{1cm} (7)

where $\Delta ETC$ 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 $\mu$, 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 per day).

3. Individual measurements (not the average of 5) are considered with the cloud screen method of 2.5 ozone standard deviation.

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

---

104 removed: This procedure could be applied directly to calculate the solar extraterrestrial constant, in counts per second, for each one of the spectral lines measured, see Eq. 8. However

105 removed: ozone

106 removed: ETC is

107 removed: $m$.

111 removed: Although, in principle,

112 removed: This is because the atmospheric conditions are not stable throughout a day and this variability affects the ETC value calculated. Therefore, in practice, the

113 removed: stable atmosphere are selected. Redondas (2008) have shown that the

114 removed: Days with a stable ozone concentration (standard deviation lower than

115 removed: DU) and a large number of measurements (more than 50).

116 removed: Days with a low aerosol optical depth concentration and clean-sky conditions.
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 instrument recalibrates. 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 #.

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117 removed: In this respect, during a large part of the year, the Izaña Atmospheric Observatory presents the ideal atmospheric conditions required to use the Langley calibration method. However, and due to the low latitude of the Canary Islands, the number of measurements performed at low air mass (1 ≤ m ≤ 2) are more than those at large air mass (m ≥ 2). This produces a non-homogeneous data distribution. For this reason, Redondas (2008) suggest to make a Langley fit in the scale 1/m. This allows obtaining two ETC values per day.

118 removed: , when the ETC values obtained in
119 removed: its standard deviation is
120 removed: ETC introduced in the
121 removed: ETC mean.
122 removed: ozone concentration, the ETC
123 removed: So, in a period with a stable behavior, the ETC
124 removed: increasing
125 removed: losses its calibration
126 removed: On
127 removed: ETC
128 removed: RBCC-E Triad stability: Ozone and dataset selection criteria.
129 removed: Representative value of the Total ozone column.
130 removed: To our knowledge, there are only a few publications where the stability of the World Reference and Arosa Triads is analyzed. In these articles, and due to the large number of ozone measurements performed throughout day, the authors have calculated a representative value of all of them and, from it, the long-term stability of its triad has been analyzed (Fioletov et al., 2005; Stübi et al., 2017; Scarnato et al., 2010).
131 removed: Fioletov et al. (2005) studied the long-term stability 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:
134 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 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 Langley 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 in the calibration campaign reports (Redondas et al., 2015; Redondas and Rodriguez-Franco, 2016).

When a new ETC is given, the 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 identify the exact moment when a Brewer needs a new calibration. In addition, the traceability between the RBCC-E and the [..]

removed: where \( O_3 \) are the ozone concentrations 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 drifts of each instrument. The stability is studied from daily and monthly mean of these differences.

\[ \text{removed: Stübi et al. (2017) studied the long-term stability of the Arosa Triad in the period 1988 – 2015. In this study,} \]

\[ \text{removed: authors considered that the Triad is the most appropriate reference for each day. Therefore, the measurements of the three Brewers are modeled as a 3rd grade polynomial dependent on time :} \]

\[ \text{removed: where } t_0 \text{ corresponds to the 12 UTC time. In this case, each Brewer is characterized by a shift } \Delta, \text{ which is the mean of the difference between the values measured and obtained from the fit, and a standard deviation } \sigma. \text{ The standard deviation } \sigma \text{ evaluates the dispersion of these differences. Both parameters are used to analyzed the long-term stability of the Arosa Triad.} \]

\[ \text{removed: In order to compare the long-term stability of the RBCC-E Triad with respect to the World Reference and Arosa Triads, both expressions are used to fit our measurements in this work. In this work, the time reference } t_0 \text{ is the solar noon.} \]

\[ \text{removed: Although Eqs. 8 and 9 are valid to model the behavior of ozone, it should be noted that} \]

\[ \text{removed: presence of outliers can affect the final value of the adjustment. Given this problem, calculating the daily mean of the measurements} \]

\[ \text{removed: good strategy to avoid this inconvenient. In this work, and knowing that ozone presents a stable behaviour throughout the day at tropical latitudes,} \]

\[ \text{removed: mean of all measurement of each Brewer was used to calculate a representative value for each Brewer.} \]

\[ \text{removed: From these values, and following the procedure proposed by Fioletov et al. (2005), the long-term stability of our triad was also studied.} \]
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 diamond symbols and the error bars correspond to the ETC weekly mean and its standard deviation.

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

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.

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148 removed: Finally, the short-term, or intra-day, stability is also studied to identify the SZA ranges at which the differences between the measurements of
149 removed: 157, #183
150 removed: 185 are highest and lowest. This analysis was performed following the procedure proposed by Stübi et al. (2017), where the measurements are separated as a function of the SZA
151 removed: Dataset selection criteria.
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 produces an atmosphere free of anthropogenic pollutants and excellent weather conditions all the year, except for days with 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.

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.).

3. 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).

4. [..] 

The second dataset is obtained with the same conditions but also imposing the condition that the measurements must be simultaneous [..] in time. A measurement made by a Brewer is considered simultaneous if [..] in a temporal window of five minutes there is other measurement made by the other two [..] Brewers of the triad. 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 stability 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.

<table>
<thead>
<tr>
<th>Operational Days</th>
<th>Brewer #157</th>
<th>Brewer #183</th>
<th>Brewer #185</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operational Measurements</td>
<td>259534</td>
<td>204022</td>
<td>229201</td>
</tr>
</tbody>
</table>

[166] removed: The standard deviation of the measurements performed by each Brewer must be lower than 0.6. This is introduced to avoid days where the ozone presents an unusual behaviour.

[167] removed: (condition 3 above)

[168] removed: it is within 5 minutes of measurements performed

[169] removed: Brewers of the RBCC-E Triad

[170] removed: the

[171] removed: considered

[172] removed: higher

[173] removed: . Therefore, there is one for each day of the year. The routines
Table 2. Summary of the datasets used in this work.

<table>
<thead>
<tr>
<th>Dataset 1</th>
<th>Dataset 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Evaluated Days</td>
<td>2073</td>
</tr>
</tbody>
</table>

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

4 Results and discussion.

4.1 \cite{174}

\cite{174}

The stability of the measurements carried out by the RBCC-E Triad was evaluated from the datasets described in Sect. \cite{176}. 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.

4.1 Representative value of the Total ozone column.

To our knowledge, there are only a few publications where the stability 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 removed: Langley and ozone at RBCC triad.

removed: As mentioned

removed: 2.2, the ETC can be used as a probe of the internal state of a Brewer. In the period 2005–2016, the ETC used...
calculated a representative value of all of them and, from it, the long-term stability is analyzed (Fioletov et al., 2005; Scarnato et al., 2010; Stübi et al., 2017).

Fioletov et al. (2005) studied the long-term stability of the World Triad Reference in the period 1985 – 2003. In this work, the authors proposed to fit the measurements performed by each Brewer [177] (#008, #014 and #015) to a 2nd grade polynomial (see Fig.4):

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

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 stability is studied from the relative standard deviation of these differences. In this work, the [178] results using a 3rd grade polynomial have also been investigated, see Fig.4.

[179] Stübi et al. (2017) studied the long-term stability of the Arosa Triad in the period 1988 – 2015. In this study, the authors considered that the behaviour of the [180] 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 [181] Triad (see Fig.4):

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

where $t_0$ corresponds to the 12 UTC time. In this case, each Brewer can be characterized by a shift, $\Delta$, which is the daily mean of the difference between the values measured and obtained from the fit and a standard deviation, $\sigma$, which evaluates the dispersion of these differences. Both parameters are used to [182] analyze the long-term stability of the Arosa Triad.

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177 removed: has been modified several times. Different events can cause that a new calibration is necessary – e.g.

178 removed: replacement of components during maintenance tasks (micrometers, H. V. source, etc.) or by damages caused during bad weather situations (high winds, snowfall). Also, the ETC must be modified if a parameter of the Brewer configuration has been changed (dead time, temperature coefficients, filter attenuation, etc).

179 removed: 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

180 removed: instrument, while the horizontal line represents the operative ETC used to calculate the TOC concentration (Eq.1). As it can be observed, the ETC was changed two times,

181 removed: first time by maintenance tasks (performed by IOS service in July 2011), and the second one 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 Langley that satisfy the conditions indicated in Sect. 2.2

182 removed: calculate the weekly mean. Other examples of events that may affect the ETC can be found in the calibration campaign reports (Redondas et al., 2015; Redondas and Rodriguez-Franco, 2016)
In order to compare the long-term stability of the RBCC-E, 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.

$$A_M = \frac{\sum_i O_3}{N}$$

(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 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 $\Delta$) 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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removed: When a new ETC is given, the TOC concentration calculated from this new configuration can be compared with the values obtained by other instrument with similar resolution. This is the best strategy to check if the new ETC is the correct one and allows to identify the exact moment when a Brewer begins to have an irregular behaviour and needs a new calibration. At the RBCC-E this task is simple because the Brewers are constantly compared to each other. The tractability between the

removed: and the world Reference Triad during the calibration campaigns throughout the travelling references #185 and #017 which is a regular section of the calibration campaign reports.

removed: Operative ETC value for Brewer #183, after some events that could cause a change in the instrumental calibration during 2011. The dots in the figure denote ETC values calculated by the Langley method before and after solar noon each day. The diamond symbols and the error bars correspond to the ETC weekly mean and its standard deviation.

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

removed: Fig. 3 shows the daily (circles) and monthly (line) TOC means measured by Brewer #157. As it can be observed, 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 is stable during the day, with a low standard deviation for

removed: recorded values. This factor, together with a thermal inversion which produces an atmosphere free of anthropogenic pollutants and excellent weather conditions all the year, 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.

removed: In the next section it is shown that

removed: calibrations used for each Brewer and introduced after an event are correct, and then the long and short-term stability of the ozone values recorded by each Brewer is evaluated.
4.2 [..191]

[..192]

4.1.1 Long-term stability[..193]: daily averages

Following the procedure described by Fioletov et al. (2005) for the World [..199]Triad Reference, Datasets 1 and 2 (see Sect. 3) were fitted by a \(2^{nd}\) and \(3^{rd}\) grade polynomial[..201]. The distribution of the daily difference between the [..202]value, see Eq.8, obtained for each Brewer with respect to the Triad mean are plotted in Fig. 5. Also, in this plot, the [..203]difference calculated from 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 after applying a polynomial fit are similar regardless of the dataset[..204]. This can be explained by the small daily variation of the ozone [..205]what causes the \(2^{nd}\) and \(3^{rd}\) grade polynomial fit to give very similar [..206]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 stability [..207]plays an important role, because the Brewer-Triad mean differences are directly associated with [..208]fit. In this case, it may be more appropriate to use the daily mean to evaluate the RBCC-E Triad.

Regardless, independently 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 mean [..209]which indicates a good agreement among themselves.

Using the same procedure to evaluate the long-term stability can be the best strategy to compare different triads to each other. In this sense, Fioletov et al. (2005) only reported [..210]that the relative daily standard deviation of World triad reference is equal to 0.47%. This value [..211]was calculated as the mean of the relative standard [..212]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 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, [..213]4th column). This result indicates that the dispersion of the measurements of the

\[^{213}\text{removed: column } A_2(\%)\]
The present case the standard deviation does not show any seasonal component. Again, this result is explained by the low shift. A similar result was obtained for Dataset 2.

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

<table>
<thead>
<tr>
<th></th>
<th>2nd grade polynomial (DU)</th>
<th>3rd grade polynomial (DU)</th>
<th>Brewer Mean (DU)</th>
<th>2nd grade polynomial (%)</th>
<th>3rd grade polynomial (%)</th>
<th>Brewer Mean (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brewer #157</td>
<td>0.787 ± 1.04</td>
<td>0.796 ± 1.07</td>
<td>0.569 ± 0.744</td>
<td>0.276 ± 0.362</td>
<td>0.279 ± 0.372</td>
<td>0.1994 ± 0.26</td>
</tr>
<tr>
<td>Brewer #183</td>
<td>0.989 ± 1.29</td>
<td>1.01 ± 1.31</td>
<td>0.741 ± 0.956</td>
<td>[.222] 0.349 ± 0.453</td>
<td>[.223] 0.356 ± 0.463</td>
<td>[.224] 0.26 ± 0.35</td>
</tr>
<tr>
<td>Brewer #185</td>
<td>0.89 ± 1.21</td>
<td>0.90 ± 1.23</td>
<td>0.56 ± 0.78</td>
<td>[.225] 0.315 ± 0.428</td>
<td>[.226] 0.32 ± 0.438</td>
<td>[.227] 0.20 ± 0.27</td>
</tr>
</tbody>
</table>

Dataset 2

<table>
<thead>
<tr>
<th></th>
<th>2nd grade polynomial (DU)</th>
<th>3rd grade polynomial (DU)</th>
<th>Brewer Mean (DU)</th>
<th>2nd grade polynomial (%)</th>
<th>3rd grade polynomial (%)</th>
<th>Brewer Mean (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brewer #157</td>
<td>0.795 ± 1.00</td>
<td>[.234] 0.82 ± 1.05</td>
<td>0.534 ± 0.661</td>
<td>0.278 ± 0.349</td>
<td>0.286 ± 0.368</td>
<td>0.186 ± 0.23</td>
</tr>
<tr>
<td>Brewer #183</td>
<td>0.747 ± 0.942</td>
<td>0.784 ± 1.02</td>
<td>0.547 ± 0.719</td>
<td>[.235] 0.262 ± 0.331</td>
<td>[.236] 0.275 ± 0.36</td>
<td>[.237] 0.192 ± 0.29</td>
</tr>
<tr>
<td>Brewer #185</td>
<td>0.64 ± 0.87</td>
<td>0.67 ± 0.99</td>
<td>0.376 ± 0.526</td>
<td>[.238] 0.227 ± 0.311</td>
<td>[.239] 0.238 ± 0.333</td>
<td>[.240] 0.133 ± 0.1</td>
</tr>
</tbody>
</table>

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 measurements made by RBCC-E Brewers for Datasets 1 and 2. Then, for each Brewer its mean shift, $\Delta$, and standard deviation, $\sigma$, 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 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.

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. Contrary to the report in Stübi et al. (2017), in the present case the standard deviation does not show any seasonal component. Again, this result is explained by the low

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241 removed: the
242 removed: (Stübi et al., 2017).
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244 removed: (Stübi et al., 2017).
245 removed: )
246 removed: almost constant value
Figure 6. Time series of the mean shift $\Delta$ and the standard deviation $\sigma$, 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

daily variability of the ozone at [..247] sub-tropical latitudes. For the Brewers of the RBCC-E Triad, the standard deviation is more influenced by any anomalous internal [..248] behaviour of the instruments. For middle latitudes, e.g. in Arosa, there is a larger daily variation in ozone and the standard 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. [..249] 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[..250]. In comparison with the Arosa Triad, only Brewer #040 shows a better [..251] behaviour than the RBCC-E Brewers [..252] while their other Brewers (B#072, B#156) show similar values to [..253] ours.

4.1.2 Long-term stability: monthly averages

Although the histogram and the statistical parameters already presented suggest that the long-term stability of the RBCC-E[..334], Arosa and World Reference Triads are similar. It can be more interesting to [..335] present this study from the
monthly means. With this idea in mind, the [..336] daily difference plotted in Fig. 5 and [..337] the daily shift plotted in Fig.6 were monthly averaged. Fig.7 shows, in relative terms, the monthly values [..338] for the period 2005–2016 (Dataset 1). The results confirm that the RBCC-E Triad has a good long-term [..339] precision, regardless of the method selected. In order to compare with the World Triad Reference, Table 5 contains the relative standard deviation of the [..340] difference between the representative value A of each brewer, calculated from the 2nd grade polynomial fit, and the triad mean. As reported by Fioletov et al. (2005), 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 ([..341] 0.42% in mean). The RBCC-E Brewers have lower [..342] 1-monthly and 3-monthly relative standard deviation. The ratio between 3-monthly values is 40% lower for the RBCC-E.

Furthermore, Stübi et al. (2017) reported that in the period 2004–2012 the Arosa Triad presented monthly [..346] shift around ±0.4% [..347] while the RBCC-E are lower than [..348] ±0.3%.

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

<table>
<thead>
<tr>
<th>Brewer</th>
<th>P_{2.5}</th>
<th>P_{25}</th>
<th>Median</th>
<th>P_{75}</th>
<th>P_{97.5}</th>
<th>Brewer</th>
<th>P_{2.5}</th>
<th>P_{25}</th>
<th>Median</th>
</tr>
</thead>
<tbody>
<tr>
<td>#157</td>
<td>[..254]</td>
<td>-0.426</td>
<td>[..255]</td>
<td>-0.13</td>
<td>[..256]</td>
<td>0.017</td>
<td>[..257]</td>
<td>0.138</td>
<td>[..258]</td>
</tr>
<tr>
<td>#183</td>
<td>[..264]</td>
<td>-0.71</td>
<td>[..265]</td>
<td>-0.219</td>
<td>[..266]</td>
<td>0.016</td>
<td>[..267]</td>
<td>0.191</td>
<td>[..268]</td>
</tr>
<tr>
<td>#185</td>
<td>[..274]</td>
<td>-0.54</td>
<td>[..275]</td>
<td>-0.099</td>
<td>[..276]</td>
<td>0.0155</td>
<td>[..277]</td>
<td>0.147</td>
<td>[..278]</td>
</tr>
<tr>
<td>Triad</td>
<td>[..284]</td>
<td>-0.599</td>
<td>[..285]</td>
<td>-0.14</td>
<td>[..286]</td>
<td>0.008</td>
<td>[..287]</td>
<td>0.156</td>
<td>[..288]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Brewer</th>
<th>P_{2.5}</th>
<th>P_{25}</th>
<th>Median</th>
<th>P_{75}</th>
<th>P_{97.5}</th>
<th>Brewer</th>
<th>P_{2.5}</th>
<th>P_{25}</th>
<th>Median</th>
</tr>
</thead>
<tbody>
<tr>
<td>#157</td>
<td>[..294]</td>
<td>-0.573</td>
<td>[..295]</td>
<td>-0.265</td>
<td>[..296]</td>
<td>0.053</td>
<td>[..297]</td>
<td>0.084</td>
<td>[..298]</td>
</tr>
<tr>
<td>#183</td>
<td>[..304]</td>
<td>-0.475</td>
<td>[..305]</td>
<td>-0.093</td>
<td>[..306]</td>
<td>0.037</td>
<td>[..307]</td>
<td>0.214</td>
<td>[..308]</td>
</tr>
<tr>
<td>#185</td>
<td>[..314]</td>
<td>-0.341</td>
<td>[..315]</td>
<td>-0.103</td>
<td>[..316]</td>
<td>0.007</td>
<td>[..317]</td>
<td>0.114</td>
<td>[..318]</td>
</tr>
<tr>
<td>Triad</td>
<td>[..324]</td>
<td>-0.503</td>
<td>[..325]</td>
<td>-0.136</td>
<td>[..326]</td>
<td>0.001</td>
<td>[..327]</td>
<td>0.1386</td>
<td>[..328]</td>
</tr>
</tbody>
</table>

[336] removed: values plotted in Figs
[337] removed: 6 were
[338] removed: of A_2, A_3, A_4 and shift σ obtained for each Brewer in
[339] removed: stability, regardless
[340] removed: standard deviation obtained from the monthly values of the A_2 coefficients was calculated
[341] removed: 0.4
[342] removed: monthly values 0.33%, 0.34% and 0.23% for Brewers
[343] removed: values lower than
[344] removed: The corresponding monthly values for
[345] removed: ±0.1%
Table 5. RBCC-E and World Reference Triads: Relative monthly standard deviation.

<table>
<thead>
<tr>
<th>Brewer</th>
<th>1-Monthly</th>
<th>3-Monthly</th>
<th>3-Monthly</th>
</tr>
</thead>
<tbody>
<tr>
<td>#157</td>
<td>0.33%</td>
<td>0.29%</td>
<td>Brewer #008 0.40%</td>
</tr>
<tr>
<td>#183</td>
<td>0.34%</td>
<td>0.31%</td>
<td>Brewer #014 0.46%</td>
</tr>
<tr>
<td>#185</td>
<td>0.23%</td>
<td>0.20%</td>
<td>Brewer #015 0.39%</td>
</tr>
<tr>
<td>Mean</td>
<td>0.33%</td>
<td>0.27%</td>
<td>0.42%</td>
</tr>
</tbody>
</table>

Figure 7. Relative ratio of the monthly values with respect to the Triad mean for the method proposed for World Triad Reference, Fioletov et al. (2005), 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 their micrometers.

4.2 Short-term stability

Dataset 1 was used to study the short-term stability 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.
Figure 8. Experimental measurements and 3rd grade Triad fit (left) and relative difference by Brewer as function of the SZA (right).

polynomial as shown in Fig. 8. As previously commented, this polynomial represents the \[\text{behaviour}\] of the triad and allow \[\text{obtain the TOC as a function of}\] the time. Similarly to the previous study, each Brewer was characterized by a shift \(\Delta\). In this case, the \[\text{data were divided as a function of}\] 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. \(60^\circ<\text{SZA}<30^\circ\), the rest of ozone measurements.

In Fig. 8, the box-plot shows the statistical distribution of the mean shift calculated \[\text{for the ranges selected}\]. As can be observed, the greatest dispersion values are at low SZA \[\text{which indicates at solar noon}\] when more discrepancy can

\[\text{removed: behavior}\]
\[\text{removed: obtaining the ozone concentration in function on}\]
\[\text{removed: ozone measurements were divided in function on}\]
\[\text{removed: 60}\]
\[\text{removed: 30}\]
\[\text{removed: 60}\]
\[\text{removed: 30}\]
\[\text{removed: in function on the SZA. As it}\]
\[\text{removed: . This indicates that it is at the middle of the day}\]
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, $\mu$, is close to 1 and the ozone absorption $\alpha$ is a constant value. This implies that the 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 stability 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 (Roozendael et al., 2013).

5 Conclusions

The consistency of TOC measurements made by the RBCC-E Triad has been studied in order to check its long-term stability to compare it with the values reported for the World Reference and Arosa Triads. With this idea in mind, the 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 measurements made by each Brewer and the Triad mean present a relative daily standard deviation equal to $\sigma_{157} = 0.362\%$, $\sigma_{183} = 0.453\%$ and $\sigma_{185} = 0.428\%$ (mean $\sigma = 0.41\%$), lower than the reported value for the World Triad Reference ($\sigma = 0.47\%$). Using monthly averages of these differences, the relative standard deviation reports values slightly lower than those obtained from the

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365 removed: ozone concentration
366 removed: Brewers
367 removed: surprising
368 removed: instruments
369 removed: This
370 removed: Therefore, the denominator take a value almost constant. Thus
371 removed: ozone concentration recorded.
372 removed: In conclusion, the other range where the best stability can be observed. In this range, the solar radiation, the Rayleigh scattering and the optical mass are not in their extremes values and, consequently, a minimum variation of these does not produce important variations in the ozone concentration measured by the Brewer.
373 removed: the ozone measurements from Brewers #157, #183 and #185 of
374 removed: and compare with the behavior
375 removed: methods used to study the stability of
376 removed: Based on the procedure
377 removed: RBCC-E Triad presents
378 removed: mean equal to 0.41\% ( 379 removed: ), slightly
380 removed: 0.47 %
381 removed: , the standard deviation takes
Table 6. Summary of the three studies comparing the relative standard deviation of the World Triad Reference, Arosa and RBCC-E Triads

<table>
<thead>
<tr>
<th></th>
<th>daily</th>
<th>monthly</th>
<th>3-monthly</th>
</tr>
</thead>
<tbody>
<tr>
<td>World Triad Reference</td>
<td>0.42</td>
<td>-</td>
<td>0.47</td>
</tr>
<tr>
<td>Arosa Triad</td>
<td>0.5</td>
<td>0.36</td>
<td>-</td>
</tr>
<tr>
<td>RBCC-E</td>
<td>0.41</td>
<td>0.37</td>
<td>0.27</td>
</tr>
</tbody>
</table>

The standard deviation calculated from the procedure of Fioletov et al. (2005) 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 Fioletov et al. (2005) for the World Reference Triad.

daily data. In addition, applying the procedure used 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, except in the case of Brewer #040. However, the monthly means are better for the RBCC-E Triad. Despite these differences, the values reported for each Triad are fairly similar, see Table 6, which ensures the traceability of the ozone measurements all around the world.

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

Acknowledgements. The authors are grateful to the IZO team and especially all observers and PhD Students who have worked in the past at Izaña Atmospheric Observatory. This article is based upon work from the COST Action ES1207 “The European Brewer Network” (EU-BREWNET), supported by COST (European Cooperation in Science and Technology). This work has been supported by the European Metrology Research Programme (EMRP) within the joint research project ENV59 “Traceability for atmospheric total column ozone” (ATMOZ). The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

382 removed: Applying 383 removed: Brewers of the 384 removed: present 385 removed: interpercentiles for their mean shift which are 386 removed: Brewers 387 removed: The 388 removed: The values obtained for the different
References


