

Evaluation of the use of five laboratory determined ozone absorption cross-sections in Brewer and Dobson retrieval algorithms

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Abstract

The primary ground-based instruments used to report total column ozone (TOC) are Brewer and Dobson Spectrophotometers, in separate networks. These instruments make measurements of the UV irradiances, and through a well-defined process a TOC value is produced. Inherent in the algorithm is the use of a laboratory determined cross-section data set. We used five ozone cross section data sets: three dataset that are based from measurements of Bass and Paur, one derived from Daumont, Malicet and Brion (DMB) and a new set determined by Institute of Environmental Physics (IUP), University of Bremen. The three Bass and Paur (1985) sets are: quadratic temperature coefficients from IGACO web page (IGQ4), the Brewer network operational calibration set (BOP), and the set used by Bernhard et al. (2005), in the reanalysis of the Dobson absorption coefficient values (B05). The ozone absorption coefficients for Brewer and Dobson are then calculated using the normal Brewer operative method which is essentially the same that used for Dobson instruments.

Considering the standard TOC algorithm for the Brewer instruments and comparing to the Brewer standard operational calibration data set, using the slit functions for the individual instruments: we find the IUP data set changes the calculated TOC by -0.5% , the DBM data set changes the calculated TOC by -3.2% , and the IGQ4 data set at $-45\text{ }^{\circ}\text{C}$ changes the calculated TOC by $+1.3\%$.

Considering the standard algorithm for the Dobson instruments, and comparing to results using the official 1992 ozone absorption coefficients values and the single set of slit functions defined for all Dobson instruments, the calculated TOC changes by $+1\%$; with little variation depending on which data set is used.

We applied the changes to the European Dobson and Brewer reference instruments during the Izaña 2012 Absolute Calibration Campaign. The application of a common Langley calibration and the IUP cross section the differences between Brewer and Dobson vanish whereas using Bass and Paur and DBM produce differences of 1.5% and 2% respectively. A study of temperature dependence of these cross-section (XS) data sets is presented using the Arosa, Switzerland total ozone record of 2003–2006, obtained from two Brewer instrument types and

a Dobson instrument, combined with the stratospheric ozone and temperature profiles from the Payerne soundings in the same period. The seasonal dependence of the differences between the results from the various instruments is greatly reduced with the application of temperature dependent absorption coefficients, with the greatest reduction obtained using the IUP data set.

1 Introduction

The routine measurement of TOC started in the mid-1920s with a prototype of the Dobson instrument (Dobson, 1968b) as part of studies of atmospheric circulation. A world-wide network grew up after the instrument re-design in 1947 and the International Geophysical Year in 1957. Until the late 1970s, this was the only optical dispersing instrument determining TOC. The Brewer Ozone Spectrometer was developed in Canada during the 1970s, and a commercial, automated version became available in the early 1980s (Kerr et al., 1981). As observing organizations purchased these instruments and placed them in service alongside the Dobson instrument for long term measurements, the seasonal and systematic bias in the results became evident. The initial difference (Kerr et al., 1985; Köhler, 1986) of 4 % was strongly reduced with the adoption of absorption coefficients based on the work of Bass and Paur (1985) for the Dobson instrument in 1992 (Kerr et al., 1988). As measurements continued, a seasonal and offset difference was still evident (Vanicek, 2006; Vaníček et al., 2012). With the consideration of the replacement of the manually operated Dobson with automated Brewer, some “transfer function” schemes were considered, using statistical regression methods (Scarnato et al., 2010). The methods can be quite successful, but do not fully explain the reasons for the differences.

The difference in the results of measurements made in the same place is not limited to the primary ground based networks. In 2009, the ozone community established the ACSO committee (“Absorption Cross Sections of Ozone”) to review the presently available cross-section data bases and to determine the impact of a change of the reference cross-section for the different instrument types (ground-based and satellite) used in the individual instrument retrieval algorithms. The cross-sections used in this study are accessible at the ACSO initiative web page (<http://igaco-o3.fmi.fi/ACSO/>). This ASCO committee is a joint commission of Scientific Advi-

sory Group for Ozone of the Global Atmosphere Watch of the World Meteorological Organization and the International Ozone Commission of the International Association of Meteorology and Atmospheric Sciences.

Our study will investigate the differences due to different determination of cross-sections, and the limitations of the retrieval algorithms. There are other instrumental issues that can cause differences between the instruments that this study does not address, but have some bearing on our results.

- Both instrument types have demonstrated levels of internal stray light, (Dobson, 1968a; Bais et al., 1996). The effect of the stray light is such that TOC is under-estimated at ozone high slant path values (μX , is defined as the product of the optical path length through the atmosphere with the calculated ozone). As high μX values correspond to low sun, and high TOC, the effect will be seasonal. Individual instruments have different levels of stray light. Brewer instruments are either single or double monochromators, the latter with version having demonstrably lower levels of internal straylight.
- The retrievals use a calculation for optical path length (μ) through the absorbing region in the atmosphere. The calculation is different in the Dobson algorithm than that used for Brewer retrievals. This small difference is dependent on the station, and the time of day, and produces a small difference in the calculated ozone that is correlated with μ .
- The SO_2 is a interfering absorber (Komhyr and Evans, 1980) in the spectral region used by both the Dobson and Brewer instruments. Our study is restricted to the results in unpolluted atmospheres; the real data examples are from high altitude, clean sites.
- The Dobson instrument uses three wavelength pairs designated as
 - A (A1:305.5/A2:325.0 nm)
 - C (C1:311.5/C2:332.4nm),
 - D (D1:317.5/D2:339.9nm).

To minimize the effect of atmospheric aerosols, measurements are made in double pair combinations (AD and CD). The resultant ozone from the AD and CD combinations do not agree under many conditions. This difference is well-known and instructions to account for this difference are described in the standard operating procedures (Komhyr and Evans, 2006). This study will concentrate on the results of AD combination.

2 Materials and methods

2.1 Theory of measurements

The basic measurement principle of both spectrometers is the same. The thickness of the ozone layer is determined by comparing the intensity of solar radiation that has passed through the atmosphere at wavelengths in the ultraviolet that are strongly and weakly absorbed by ozone. The Dobson utilizes a variable attenuator called an “optical wedge” to measure the intensity ratio of two wavelengths, whereas the Brewer directly measures the intensity of sunlight at multiple wavelengths and ratios are calculated.

The general ozone calculation in either the Dobson or Brewer retrieval algorithm can be summarized by this expression

$$X = \frac{N - B}{A\mu} \quad (1)$$

Where N is a linear combination of the logarithm of the measured spectral direct irradiances, extra-terrestrial (I_o), see 3.2.1, and at ground level (I) at selected n wavelengths, A is the ozone absorption coefficient or Differential Cross Section (DXS) and B is the Rayleigh coefficient, which are linear combinations of the ozone absorption (α) and Rayleigh molecular scattering (β), respectively, at corresponding wavelengths.

$$N = \sum_{i=1}^n w_i \log\left(\frac{I_i}{I_{oi}}\right), \quad (2)$$

$$A = \sum_{i=1}^n w_i \alpha_i \quad (3)$$

$$B = \nu \frac{p}{p_0} \sum_{i=1}^n w_i \beta_i \quad (4)$$

Where α_i and β_i are the convolution of the instrument slit function (S) with the ozone and Rayleigh cross-sections, w_i the weighting coefficients, p and p_0 are the atmospheric pressure at the station and sea level respectively and ν the Rayleigh airmass. As the Dobson only measure intensity ratios the weighting coefficients (w_i) are always 1 or -1 for the double pairs of wavelengths (λ_i). The coefficients for the Brewer were selected to eliminate the SO_2 absorption, and as the coefficients verify $\sum_{i=1}^n w_i \lambda_i = 0$ all linear effects with wavelengths, such as the aerosol absorption, are negligible.

The ozone cross section data base used for the Brewer and Dobson network is from Bass and Paur (1985) as were recommended by the International ozone commission (<http://www.esrl.noaa.gov/gmd/ozwv/dobson/papers/coeffs.html>). The Dobson absorption coefficients calculation is described in Komhyr et al. (1993) and the reevaluation is described by Bernhard et al. (2005). Our Dobson calculations are compared with these results referenced to as Komhyr et al. (1993) and Bernhard et al. (2005). The Brewer calculation follows the operative procedure (Gröbner et al., 1998; Kerr, 2002) used for Regional Brewer Calibration Center-Europe (RBCC-E) at the calibration campaigns. In summary the individual wavelengths in the Brewer measurement set are located at the focal plane of the spectrometer through the use of a stainless steel mask of seven slits, the particular wavelength is determined by analyzing the measurements of a series of discharge lamps. Then the wavelength setting is optimized to minimize the effect of wavelength shift during the operation of the instrument. This wavelength calibration process determines the central wavelength and Full Width Half Maximum (FWHM) of every slits. For this work for comparison we use the Brewer operative method, which is essentially

the same as the approximation method of Bernhard et al. (2005) (see Eq. 5).

$$\alpha_i = \frac{\int \sigma(\lambda) S_i(\lambda) d\lambda}{\int S_i(\lambda) d\lambda} \quad (5)$$

Where S is the instrument slit function for the corresponding wavelength and σ the ozone cross section at temperature, -46.3°C for Dobson Network and -45°C for Brewer instruments (Fig. 1).

In the Dobson network, all instruments are assumed to have the same wavelength registration and slit functions as the World Primary Dobson Spectrometer D083 and consequently each instrument uses the same absorption coefficients in the ozone retrieval. In contrast, the wavelengths and slit functions (and thus the absorption coefficient) for each individual Brewer instrument are determined during the calibration process and are slightly different from nominal values.

In this work the particular Dobson and Brewer instrument are labeled by D or B followed by the fabrication number. The reference Dobson is denoted by D064 and the RBCC-E brewers are B157, B183 and B185.

2.2 Ozone cross sections

There are three versions of Bass and Paur (1985) cross-sections used in this study which are denoted as Brewer operational (BOP), IGACO quadratic coefficient (IGQ4) and Bernhard (2005):

- Brewer operational (BOP) is the file provided by Environment Canada and used by the RBCC-E, and the rest of Brewer network to derive the individual instrument ozone absorption coefficients. This is equivalent to Bass and Paur (1985) published data without any other adjustment (Kerr, 2002). This data set has six temperatures per wavelength registration and agrees with the Fig. 2 of the Bass and Paur (1985) publication but the wavelength range is restricted to the Brewer instrument range (297–332 nm). This file is not available on the IGACO web page and can be downloaded at RBCC web page and at Mainz spectral database (<http://www.atmosphere.mpg.de/enid/2295>). The Mainz database

is in a different format, and some information at important temperatures and wavelengths is missing.

- IGQ4: there are two different sets available at the IGACO web page, one with the individual temperatures and the other with the coefficients of the quadratic fit of the temperature dependence on the file “Bp.par”. The six individual temperatures files do not agree with Bass and Paur (1985) original publication and do not include values at -45°C , which is used in Brewer calculations. This dataset appears to be calculated at selected temperatures using the quadratic polynomial obtained from the fit of the original data but excluding 218 K set (Weber et al., 2011). In this work we use the quadratic coefficients set, to be consistent with the Komhyr determination (Komhyr et al., 1993) of Bass and Paur (1985). Following the instructions on the IGACO web page, we extracted the values at -45°C from IGACO and compared to the BOP values also at -45°C . The values are similar to the BOP set but more variable.
- Bernhard (2005): in order to compare our results for the Dobson instrument with Bernhard dynamical results (Bernhard et al., 2005); this special dataset was obtained directly from the authors. The dataset is Bass and Paur (1985) corrected by temperature dependence based on the results of Barnes and Mauersberger (1987) and extended above 340 nm with the Molina and Molina (1986) cross section. Further refinement includes convolving the data set with the 1986 US Standard Atmosphere temperature profile, a mid-latitude ozone profile and top of the atmosphere solar spectrum.

In addition we use two high-resolution cross-sections available at IGACO web page:

- Daumont et al. (1992), Brion et al. (1993), and Malicet et al. (1995) (DBM), this high resolution set has been measured at 5 temperatures. We use the quadratic fit, labeled as DBMQ, for the temperature dependence studies. For comparison we also use the Liu et al. (2007) quadratic approximation (DBML) which excluded the 273°K data from the quadratic temperature fitting.

- The newly determined data set from Bremen University (IUP) (Serdyuchenko et al., 2013; Gorshelev et al., 2013), are also available at IGACO with ten temperatures files (IUP) and the quadratic polynomial approximation (IUPQ).

For consistency the wavelengths were referenced to air, using Bernhard tool in the “Libradtran” package (Mayer and Kylling, 2005), and using the -45°C temperature for Brewer and -46.3°C for Dobson calculations, when these temperatures were not available on the cross section set a linear interpolation was used. In the Fig. 2 the ratio to IGQ4 at -45°C of the various cross section data are shown and the values both interpolated values of IUP at -45°C and the values of the quadratic approximation IUPQ are displayed. The units of the cross sections in this work are $(\text{atm cm})^{-1}$ in logarithmic base 10 scale as is used in Dobson and Brewer network, using the value for the Loschmidt’s number $2.687 \times 10^{-19} \text{ cm}^{-3}$.

2.3 Slit functions

In the Dobson instrument, the spectrum is moved across two slits. The measurements are made with the wavelength selector in one of three defined positions. This means there are six slit functions used in the derivation of the absorption coefficients. Originally, there were two slit functions, estimated as a triangle for the short wavelength, and a trapezoid for the long wavelength. There are two measured slit function sets used for the Dobson instrument, the set measured on Dobson 083 (Komhyr et al., 1993) and the trapezoid parameterization of the Komhyr measured slits by Bernhard et al. (2005). For the Brewer we use also a parameterization for the slits, the slits are considered a truncated isosceles triangle where the central wavelength and FWHM are determined from the wavelength calibration. Note that in other works, different slit parameterizations for Brewer are used, Van Roozendaal et al. (1998) used a Gaussian fit, Serdyuchenko et al. (2013), used a rectangular parameterization while Redondas and Cede (2006) and Fragkos et al. (2013a) used laser measurements.

The RBCC-E has been conducting intercomparisons of Brewer instruments in the European region since 2003. In this work we use a set of 123 wavelength calibrations performed on 33 instruments during these campaigns. This allows us to define an average Brewer (Table 1)

very similar to the nominal wavelengths, 80 % of the analyzed instruments differ from these wavelengths less than 0.2\AA from the average Brewer (Fig. 3). The application of the DXS methodology to the average Brewer wavelengths characteristics gives a value which is the same as the average of the individual DXS.

The DXS for an individual Brewer instrument will differ slightly from this “average” Brewer. The difference is directly proportional to the difference in center wavelength from the nominal wavelength as shown in Fig. 3 (Savastiouk, 2010).

2.4 Temperature dependence

The ozone absorption coefficient is calculated from the ozone absorption cross section and the ozone $X(z)$ and the temperature $T(z)$ vertical profile:

$$\alpha(\lambda) = \frac{\int \sigma(\lambda, T(z)) X(z) dz}{\int X(z) dz} \quad (6)$$

Due to the finite bandwidth of Brewer and Dobson slit functions the ozone absorption coefficient has to be replaced by an effective ozone absorption (Vanier and Wardle, 1969; Basher, 1982)

$$\alpha(\lambda) = \frac{\log \left(\frac{\int E_o(\lambda) S(\lambda, \lambda_i) 10^{-\alpha(\lambda) X \mu - \beta(\lambda) \frac{P}{P_o} \nu} d\lambda}{\int E_o(\lambda) S(\lambda, \lambda_i) 10^{-\beta(\lambda) \frac{P}{P_o} \nu} d\lambda} \right)}{X \mu} \quad (7)$$

Where E_o is the extraterrestrial spectral irradiance.

For the complete calculation the ozone and temperature profiles are needed and applied in a radiative transfer model considering the complete transmission through the atmosphere (Komhyr et al., 1993). In this work we use the simplest approach of Komhyr et al. (1993), also used by Van Roozendaal et al. (1998), Scarnato et al. (2009), and Fragkos et al. (2013b) which is based on two simple assumptions

1. The temperature dependence of the cross section is approximated by a quadratic polynomial.

$$\sigma(T) = c_o + c_1 T + c_2 T^2 \quad (8)$$

2. The effect of the temperature and ozone profile integration can be simplified by the introduction of the effective temperature which is the ozone weighted temperature average (Thomas and Holland, 1977)

$$T_{\text{eff}} = \frac{\int_{z_o}^{\infty} T(z) X(z) dz}{\int_{z_o}^{\infty} X(z) dz} \quad (9)$$

The effective absorption coefficient is therefore

$$\alpha_i(T_{\text{eff}}) = C_{io} + C_{i1} * T_{\text{eff}} + C_{i2} * T_{\text{eff}}^2 \quad (10)$$

Where the coefficients C are

$$C_{ij} = \frac{\int c_j(\lambda) S_i(\lambda, \lambda') d\lambda}{\int S_i(\lambda, \lambda') d\lambda} \quad (11)$$

and finally the absorption coefficient

$$\begin{aligned} \alpha(T) &= \sum_{i=1}^n w_i \sum_{j=0}^2 C_{ij} * T^j \\ &= \sum_{i=1}^n w_i C_{io} + T \sum_{i=1}^n w_i C_{i1} + T^2 \sum_{i=1}^n w_i C_{i2} \end{aligned} \quad (12)$$

The quadratic approximation has the same accuracy (1 %) as the cross section (Orphal, 2003; Serdyuchenko et al., 2013) but the choice of the temperatures at which the fit is performed can give different results (Scarnato et al., 2009; Fragkos et al., 2013b). To avoid this issue, and considering that the operative temperature 228 K is available for most of the cross-sections of this study, for the operational retrieval a linear extrapolation is used. The temperature dependence of the cross section is generally expressed as the gradient of the cross section, with a quadratic dependence of temperature and for a particular measurement with n slits and weights w_i is equal

to

$$\frac{\Delta A}{\Delta T} = \sum_{i=1}^n w_i [C_{i1} + 2 * C_{i2} * T] \quad (13)$$

This is expressed as % change per degree Kelvin, where A_o is the operative (fixed temperature) cross section.

$$100 \frac{\Delta A}{A_o \Delta T} \quad (14)$$

The ratio of temperature corrected and uncorrected ozone due to cross section change is equal to the inverse of the absorption coefficients

$$X(T) = X_0 * \frac{A_o}{A(T)} \quad (15)$$

Where X_0 is the ozone at operative temperature.

3 Analysis of the results

3.1 Operational parameter

3.1.1 Dobson calculations

We used the various cross-section data sets with the measured and parameterized slit functions for D083. The values obtained are displayed in Table 2. There are small differences, except for the (Komhyr et al., 1993) value for the D2 (339.9 nm) setting. This was a known problem and addressed in 1993 by using the record of D083 measurements at Mauna Loa Observatory to empirically find a value that was more realistic. The reanalysis in 2005 verified that the empirical value was more correct, and there was an error in the 1993 analysis. Table 3 expresses

the per cent difference in calculated ozone that would occur with the use of the various cross-section data sets compared to that calculated using the operational values. As the wavelength range of the BOp does not extend to the C2 and D2 slit functions, BOp is omitted.

The comparison with the operational values shows that our derivations are consistent within 1 % for the AD. On CD pair the differences are bigger, 1.5 %, for IGQ4 and DBM with the values of IUP 0.5 % also higher. The results with parameterized slits are slightly lower than those measured slits (a lower value means that the calculated ozone value will be higher). As the Bernhard B & P cross-sections is available only for -46.3°C , it was only used in a derivation for the trapezoid approximation to assess the validity of our numerical method, the four remaining cross-sections were calculated for both slits. The validity of the calculation can be checked when we use the same ozone cross section and the same slit parameterization as Bernhard et al. (2005) on pair wavelengths and double pair we get a maximum difference of 0.15 %.

3.1.2 Brewer calculations

For the Brewer instruments, we take the results of 123 dispersion tests performed on 33 instruments during the RBCC-E campaigns (Fig. 4), and calculate the absorption coefficients using the operative Brewer procedure described in the previous section. The ratio of each new absorption coefficient to the one determined from the BOp dataset was also determined (Fig. 5). The statistics of the ratio results are displayed in Table 4. The statistics of this set confirm the results for other determinations such as those using the DBM XS during the Sodankylä Total Column Ozone Intercomparison (SAUNA) (Redondas and Cede, 2006); studies presented at ACSO meeting (Redondas, 2009; Savastiouk, 2010); and a recent study by Fragkos et al. (2013a). However, our results are not in agreement with those of (Scarnato et al., 2009), presented also at an ACSO meeting. The Scarnato et al. (2009) results are 4 % lower than our average DBM results, which have a range of ± 1.2 %. The IUP XS results are the closest to the operative value (producing 0.5 % higher TOC).

Instrumental differences in the Brewer operative XS determined DXS are mirrored in the DXS determined in the other XS data sets (Fig. 4), and is related to the difference of central

wavelengths to the nominal value (Fig. 3).

$$A_{i,op} = \widetilde{A}_{op} + a_{op} * (\lambda_i - \widetilde{\lambda}) \quad (16)$$

Where $A_{i,op}$ are the operative DXS of the instrument i and λ_i its central wavelength of the slit 6, the tilde values are DXS and wavelength referenced to the nominal instrument and a_{op} the proportional constant. The ratio of the different cross-sections A_{xs} to the operative ones A_{op} for a particular instrument are also related with the difference in wavelengths to the nominal value (Fig. 5).

$$A_{i,xs}/A_{i,op} = \frac{\widetilde{A}_{xs}}{\widetilde{A}_{op}} + a_{xs}(\lambda_i - \widetilde{\lambda}) \quad (17)$$

A summary of these linear relationships can be found in Table 6. This linear relationship allows us to correct past ozone measurements; if we know the operative differential cross-section of the instrument $A_{i,op}$, we can estimate the correction factor for the desired cross-section. If we were to apply the nominal Brewer absorption coefficients to all Brewer instruments, the maximum error in calculated TOC is 0.5 %. If this correction factor is applied, the error is reduced to 0.2 %. As the wavelength difference between the majority of the test Brewers and the nominal Brewer is less than 0.02 nm, the error is more like 0.1 %

3.1.3 Temperature dependence calculations

The temperature dependence calculations were performed with IGQ4, DBM and IUP cross-sections, as the temperature dependence is not available for the operative cross-sections. The results are summarized in Table 8, for the Dobson 083 and a nominal Brewer defined as having the mean central wavelengths and mean FWHM of the RBCC-E set. The absorption coefficient temperature dependence of this Brewer and the standard deviation of the 123 calibrations of the RBCC-E set are depicted in Fig. 6 with the Dobson temperature dependence.

These values of the temperature dependence are in general agreement with previous studies using the B & P and IUP cross-sections. In the use of DMB, the differences are larger, which

might result from the choice of four or five temperatures in the determination of the quadratic approximation for the DMB cross-section (Liu et al., 2007; Fragkos et al., 2013a) . We cannot explain the difference from the Scarnato study.

The main conclusions are:

- The calculated IUP temperature dependence for the Brewer is very low, less than 0.01 %. For the Dobson, the value is smaller than that published in (Komhyr et al., 1993).
- The calculated DBM temperature dependence is a small negative value for the Brewer, but is a small positive value for Dobson.
- The calculated B&P temperature dependence for Brewer is lower than that for Dobson.

The effect on the ozone observations of Dobson and Brewer using comparison data is examined in the next section.

3.2 Application to real measurements

3.2.1 Application to the 2012 Langley Campaign at Izaña Observatory

We can evaluate the effect on the Brewer Dobson comparison by applying the cross-sections determined in this study to the synchronized measurements made during the Izaña 2012 Langley Campaign. Both Dobson and Brewer instruments use the Langley plot method (Langley, 1884) applied to the measured ratios to verify the extraterrestrial constant used in the algorithms to convert measurements to total ozone (Komhyr et al., 1989). If the ozone and other interfering absorbers are constant over a half day, the plot of the measured ratios vs the airmass (μ) (see Eq. 1) is a straight line and extrapolation to airmass zero is possible to determine the extraterrestrial value.

This campaign was conducted from 20 September to 12 October 2012 at the Izaña Observatory (IZO) under very clear sky conditions. We use twelve “Langley” days, with clear and stable atmospheric conditions, as verified by ultraviolet aerosol optical depth less than 0.05,

measured at 340 nm by a CIMEL sunphotometer. The comparison of Brewer and Dobson during this campaign was in agreement with previous comparisons (Köhler et al., 2012), with an underestimation of 1.5 % of the Dobson with respect to the Brewer (Fig. 7). It's important to note that the reference for this calculation is the mean of Brewer and Dobson taken separately.

The comparison of the instruments do not show dependence on μX which suggests that the difference between instruments is due to cross-section. The effective temperature had a small variation as it was very close to the operative value so its effect is small on the measurements. The effect on the TOC calculated by Dobson and Brewer instruments based on change of ozone cross-section α to α' is simply the ratio between the old and new absorption coefficients (Eq. 15). The factors applied to the synchronized observations of Dobson and Brewer are shown in Table 7. The application of these factors is shown in Fig. 8 and summarized in Table 10. The use of the IGQ4 cross-sections does not change the Brewer Dobson comparison but slightly increases the Dobson CD/AD double pair difference. The DBM increases the difference between the instruments from 1.5 % for the operative algorithm to 2 and 3 % for the case of CD pair and AD pair respectively. Finally the IUP reduces significantly the differences between Brewer and Dobson and maintains the differences between CD/AD pairs of the operative set.

3.2.2 Application to the Arosa Brewer vs. Dobson series

To investigate the various temperature dependent absorption coefficients with real data, we use Dobson and Brewer observational data from Arosa Switzerland. This data set consists of three years of TOC observations with Dobson D101 and Brewer B040 (single monochromator) and Brewer B156 (double monochromator). For the stratospheric temperature at the time of the observations, the ozone weighted temperature, or effective temperature T_{eff} , was obtained from the Payerne Switzerland ozonesonde soundings for the same period (Fig. 9). Quasi-simultaneous set of the observations, taken within a 10 min time span was selected and the three times a week temperature information interpolated to the time of the Brewer/Dobson measurements. We tested several methods of interpolation, using linear, nearest day value, or considering only the days with soundings without finding any significant effect on the results. TOC values for the Dobson and Brewer are corrected according to this interpolated temperature measurements,

using Eq. (15), and we use the quadratic coefficients of T for a “generic Brewer” and the Dobson 083 (Table 8). We also investigated the data set using a DXS determined specifically for Brewer 040 and Brewer 156 and found little difference from the nominal Brewer results. The Brewer#156 is quite similar to the nominal Brewer, and Brewer 040 is $\sim 0.2\%$ different. The effect on the seasonal differences is shown in Fig. 10.

The results are similar to the Langley campaign results:

- The DBM derived absorption coefficients produce a difference of about 2–3 % between the instruments’ results.
- The Bass & Paur derived absorption coefficients produce a difference of about 2–3 %, but in the opposite direction to DBM.
- The IUP derived absorption coefficients produce a difference of about 0–1 % same direction as B & P.

The known seasonality of the difference (Vanicek, 2006; Scarnato et al., 2009) has in the past been investigated with the use of the temperature dependence of the Dobson absorption coefficients alone, as the Brewer wavelengths were chosen so that stratospheric temperature changes would have less effect on the measurement results (Kerr, 2002). The difference between the single and double monochromator Brewer is small and only apparent in the spring months. The better rejection of stray light by the internal optics of the double monochromator is more important for measurements at high TOC values encountered in the northern hemisphere spring. The difference in the calculation of μ was not addressed in this study, but the effect of changing the Brewer calculation would be small, and in the direction to decrease seasonality.

4 Conclusions

A new set of ozone absorption coefficients A_i for Dobson and Brewer spectrophotometers, using the five cross section laboratory data, was calculated and compared with the previous

calculations. The performance of these coefficients were evaluated using the data of simultaneous Brewer and Dobson observations during the CEOS Calibration campaign and the ozone observations at Arosa. The main conclusions of our study are

1. The Brewer and Dobson instrument results agree best when the absorption coefficients used are based on the IUP XS. The application of the temperature dependent absorption coefficients substantially reduces the seasonality found in the Arosa Brewer-Dobson record. The DBM set also reduces the seasonality but the change in absolute scale in the Brewer instrument results away from the Dobson results makes its use unsuitable for the network.
2. The temperature dependence values obtained confirm the hypothesis of Kerr (2002): the systematic annual differences between Brewer and Dobson are due to the different temperature dependence in the instrument's ozone retrieval algorithm. With the Brewer this is small; less than $0.01\% \text{ C}^{-1}$, Kerr et al. (1988) suggestion that this difference is due to the temperature dependence in the Dobson algorithm is also confirmed.
3. The Dobson record will change by less than 1% using any one of these XS dataset. A change to the temperature dependent absorption coefficients provides the most benefit by removing an artificial seasonality in the ozone record. The application of the temperature dependent absorption coefficients will be station dependent, as knowledge of the stratospheric temperature record over the station is required. The determination of the best method to determine this record is a subject for another study.
4. The calculation of the DXS for a particular Brewer instrument is very sensitive to both the XS and the handling of the XS (editing, smoothing, etc.); these differences can be as large as 1% in ozone.
5. As suggested by Kerr (2002) a direct measurement of the cross-section by the instrument can help to validate different calculations strategies of the DXS calculation for the network instruments. The method requires an independent source of stratospheric temperature

6. The existing Brewer record of TOC can be adjusted to the IUP scale through the record of the wavelength calibrations. Using the average Brewer value the maximum uncertainty based on 123 instruments was 0.4 %; using the known operational absorption coefficient that uncertainty can be reduced to 0.1 %.

Glossary

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|-----------|---|
| ACSO | Absorption Cross Sections of Ozone |
| B&P | Generally refers to the determination of an ozone cross-section data base determined by Bass, A. M. and Paur, R. J., published in 1985. |
| B05 | The B&P cross-section data base weighted by the top of the atmosphere solar spectrum, and mid-latitude ozone and temperature profiles. This set was using in the re-evaluation of the Dobson absorption coefficients in Bernhard et al. (2005). |
| BOp | The official cross-section data base used to determine the absorption coefficients for Brewer instruments |
| DBM | Generally refers to an ozone cross-section data determined by Daumont, D; Brion, J, and Malicet, J in the early 1990s. |
| DBML | The DMB ozone cross-section expressed as quadratic polynomial approximation in temperature at each wavelength registration, determined by Liu et al. (2007) |
| DBMQ | The DMB ozone cross-section expressed as quadratic polynomial approximation in temperature at each wavelength registration. |
| DXS | Differential Cross-Section |
| FWHM | Full Width at Half Maximum, a measure of the spectral band pass of a slit in a spectrometer. |
| IGACO | Integrated Global Atmospheric Chemistry Observations |
| IGQ4 | B&P cross-section data base published on the IGACO website |
| IUP | The ozone cross-section data base determined by Institute of Environmental Physics, University of Bremen at ten temperatures per wavelength registration. |
| IUPQ | The IUP ozone cross-section expressed as quadratic polynomial approximation in temperature at each wavelength registration. |
| RBCC/RDCC | Regional Brewer Calibration Center/Regional Dobson Calibration Center |
| TOC | Total Column Ozone |

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Table 1. Wavelengths and weighting coefficients used in the Dobson and Brewer operative algorithms. The Brewer values are the mean and standard deviation of central wavelength and Full Width Half Maximum (FWHM) of the slits of the “average” Brewer determined during RBCC-E campaigns . The Dobson values correspond to the nominal values published in the Dobson handbook. The values for the World Standard Dobson 83 are available from Komhyr et al. (1993). Note that only the last four wavelengths are used for the brewer ozone calculation.

| Brewer Slits | wavelength | std | FWHM | std | w_i | Dobson Slits | wavelength | FWHM | w_i AD | w_i CD |
|--------------|------------|-------|-------|-------|-------|--------------|------------|------|----------|----------|
| 0 | 303.001 | | | | 0 | A1 | 305.5 | 0.9 | 1 | 0 |
| 2 | 306.301 | 0.014 | 0.548 | 0.016 | 0 | C1 | 311.5 | 0.9 | 0 | 1 |
| 3 | 310.051 | 0.014 | 0.539 | 0.015 | 1 | D1 | 317.5 | 0.9 | 1 | 1 |
| 4 | 313.501 | 0.015 | 0.555 | 0.012 | -0.5 | A2 | 325.0 | 2.9 | -1 | 0 |
| 5 | 316.801 | 0.017 | 0.545 | 0.012 | -2.2 | C2 | 332.4 | 2.9 | 0 | 1 |
| 6 | 320.002 | 0.019 | 0.538 | 0.012 | 1.7 | D2 | 339.9 | 2.9 | -1 | 1 |

Table 2. Summary of Dobson ozone absorption coefficient in $(\text{atm cm})^{-1}$, determined from the five ozone cross-sections (see text for details), using measured slit functions and parameterized slit functions. Values from Komhyr and Bernard are also displayed for comparison. The calculations using B&P cross-sections by Bernhard 2005 (B05) are also calculated for the parameterized slit functions.

| | Measured slit | | | | Parameterized slit | | | | | Prior Determinations | | | | |
|-------|---------------|-------|-------|-------|--------------------|-------|-------|-------|------------|----------------------|----------------|---------------|----------------|-------|
| | BOp | IGQ4 | DBM | IUP | BOp | IGQ4 | DBM | IUP | B&P B05 | Komhyr approx. | Komhyr 1993 | Komhyr Op. | B05 approx. | B05 |
| A1 | 1.901 | 1.900 | 1.895 | 1.897 | 1.903 | 1.902 | 1.897 | 1.899 | 1.915 | 1.917 | 1.915 | | 1.915 | 1.914 |
| A2 | 0.109 | 0.109 | 0.107 | 0.107 | 0.116 | 0.116 | 0.114 | 0.114 | 0.117 | 0.115 | 0.109 | | 0.115 | 0.110 |
| Apair | 1.792 | 1.791 | 1.788 | 1.790 | 1.788 | 1.787 | 1.783 | 1.785 | 1.798 | 1.802 | 1.806 | 1.806 | 1.800 | 1.805 |
| C1 | 0.862 | 0.862 | 0.856 | 0.862 | 0.861 | 0.861 | 0.855 | 0.862 | 0.868 | 0.870 | 0.873 | | 0.868 | 0.871 |
| C2 | | 0.038 | 0.038 | 0.038 | | 0.039 | 0.039 | 0.039 | 0.040 | 0.039 | 0.040 | | 0.040 | 0.039 |
| Cpair | | 0.824 | 0.818 | 0.825 | | 0.822 | 0.816 | 0.823 | 0.828 | 0.831 | 0.833 | 0.833 | 0.828 | 0.832 |
| D1 | 0.382 | 0.382 | 0.376 | 0.379 | 0.380 | 0.380 | 0.374 | 0.377 | 0.384 | 0.379 | 0.384 | | 0.384 | 0.387 |
| D2 | | 0.010 | 0.010 | 0.010 | | 0.011 | 0.011 | 0.011 | 0.010 | 0.010 | 0.017 | | 0.010 | 0.010 |
| Dpair | | 0.373 | 0.366 | 0.369 | | 0.370 | 0.363 | 0.367 | 0.373 | 0.369 | 0.367 | 0.374 | 0.373 | 0.377 |
| AD | | 1.419 | 1.422 | 1.421 | | 1.417 | 1.420 | 1.419 | 1.425 | 1.433 | 1.439 | 1.432 | 1.427 | 1.428 |
| CD | | 0.451 | 0.452 | 0.455 | | 0.452 | 0.453 | 0.456 | 0.455 | 0.462 | 0.466 | 0.459 | 0.455 | 0.455 |

Table 3. Change in calculated ozone for the double wavelength pair combinations from the standard absorption coefficients to the ones derived from the various cross-section data sets.

| Wavelength setting | Measured slit | | | Parameterized slit | | | | Prior Determinations | | | |
|-----------------------|---------------|-------|-------|--------------------|-------|-------|------------|----------------------|--------|---------------------|----------|
| | IGQ4 B & P | DBM | IUP | IGQ4 | DBM | IUP | B05 B&P | Komhyr approx. | Komhyr | Bernhard approx. | Bernhard |
| AD | 0.9 % | 0.7 % | 0.8 % | 1.1 % | 0.8 % | 0.9 % | 0.5 % | -0.1 % | -0.5 % | 0.3 % | 0.3 % |
| CD | 1.7 % | 1.5 % | 0.8 % | 1.5 % | 1.3 % | 0.6 % | 1.0 % | -0.7 % | -1.5 % | 0.9 % | 0.9 % |

Table 4. Statistics of the ratio of the ozone absorption coefficient used for Brewer (Bass & Paur at -45°C) to the calculated with B&P from IGACO web page (IGQ4), Daumont, Malicet and Brion (DMB) and University of Bremen cross-sections (IUP).

| | IGAQ | DBM | IUP | IUPQ |
|-------|-------|-------|-------|-------|
| Mean | 0.987 | 1.032 | 1.005 | 1.009 |
| Std | 0.001 | 0.002 | 0.001 | 0.001 |
| Max | 0.988 | 1.037 | 1.009 | 1.013 |
| Min | 0.985 | 1.025 | 1.000 | 1.004 |
| Range | 0.003 | 0.012 | 0.009 | 0.009 |

Table 5. Ratio of the Differential Ozone Absorption Coefficient to the operative ones compared with results from other studies.

| Brewer | Redondas 2006 #185 | Redondas 2009 #157 | Savastiouk 2010 set average | Scarnato 2009 | | | Redondas 2013 set average |
|--------|-----------------------|-----------------------|--------------------------------|---------------|-------|-------|------------------------------|
| | | | | #040 | #072 | #156 | |
| DBM | 0.970 | 0.969 | 0.970 | 0.939 | 0.917 | 0.933 | 0.969 |

Table 6. Statistics of the linear relation of the differences based on Eqs. (16) and (17). The first column gives the differential cross-section A_{xs} of the different cross-section calculated for the nominal Brewer $(\text{atm cm})^{-1}$, the second column shows the ratio of the differential cross-section to the operative value for the nominal instrument and "a" is the slope of Eq. (17) $(\text{atm cm nm})^{-1}$. The last column is the R-square coefficient of the linear fit, (IGQ4 is flat).

| | A_{xs} | A_{xs}/A_{op} | a | R-square |
|------|----------|-----------------|-------|----------|
| BOp | 0.3412 | 1 | – | – |
| IGQ4 | 0.3367 | 0.9865 | 0.004 | – |
| DBM | 0.3521 | 1.0317 | 0.070 | 0.7879 |
| IUP | 0.3430 | 1.0048 | 0.047 | 0.6754 |
| IUPQ | 0.3445 | 1.0092 | 0.048 | 0.6816 |

Table 7. Coefficients used to convert the ozone operational observations of Dobson and Brewer to evaluated cross-sections.

| | IGQ4 | DMB | IUP |
|-----------|-------|-------|-------|
| Brewer | 1.013 | 0.969 | 0.995 |
| Dobson CD | 1.017 | 1.015 | 1.008 |
| Dobson AD | 1.009 | 1.007 | 1.011 |

Table 8. Quadratic coefficient of the ozone absorption coefficient ($C_2 \dots C_0$), the absorption coefficient for the operative temperature A_0 and the % gradient Δ for the three ozone cross-sections calculated for Dobson and Brewer. The operative value, is also indicated (A_{op}).

| | Brewer $A_{op}=0.3412$ | | | | Dobson $A_{op}=1.4320$ | | | |
|----------|--------------------------|--------------------------|--------------------------|--------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| | B&P | DBM | DBML | IUP | B&P | DBM | DBML | IUP |
| C_2 | -2.1989×10^{-6} | 1.9801×10^{-6} | 7.4771×10^{-6} | -4.9188×10^{-8} | 8.2385×10^{-6} | 2.4632×10^{-5} | 3.0829×10^{-5} | 1.0518×10^{-5} |
| C_1 | 1.1747×10^{-4} | 4.1821×10^{-5} | 3.7060×10^{-4} | 2.8781×10^{-5} | 2.6428×10^{-3} | 2.8713×10^{-3} | 3.2420×10^{-3} | 2.4502×10^{-3} |
| C_0 | 3.4667×10^{-1} | 3.5353×10^{-1} | 3.5632×10^{-1} | 3.4591×10^{-1} | 1.5216×10 | 1.5025×10 | 1.5057×10 | 1.5157×10 |
| α | 3.3693×10^{-1} | 3.5565×10^{-1} | 3.5478×10^{-1} | 3.4452×10^{-1} | 1.4172×10 | 1.4225×10 | 1.4217×10 | 1.4250×10 |
| Δ | 9.3601×10^{-2} | -3.8349×10^{-2} | -8.5217×10^{-2} | 9.6391×10^{-3} | 1.3285×10^{-1} | 4.2096×10^{-2} | 2.7975×10^{-2} | 1.0384×10^{-1} |

Table 9. Summary of temperature dependence of Dobson and Brewer from previous studies in $\% K^{-1}$.

| $\% K^{-1}$ | Kerr (1998) | | Kerr (2002) | | Rozendael | | Scarnato | | | Redondas | Fragkos | This work | |
|-------------|-------------|------|-------------|------|-----------|-------|----------|-------|--------|----------|---------|-----------|--------|
| | Dob | #008 | #014 | Dob | Brw | Dob | #040 | #072 | #156 | #185 | #005 | Dob | Brw |
| B&P | 0.13 | 0.07 | 0.094 | 0.13 | 0.11 | | 0.081 | 0.099 | 0.088 | 0.09 | 0.097 | 0.133 | 0.094 |
| DBM | | | | | | -0.11 | -0.131 | -0.12 | -0.128 | -0.04 | -0.07 | -0.042 | -0.038 |
| IUP | | | | | | | | | | | 0.019 | 0.104 | 0.009 |

Table 10. Izana Langley Dobson Brewer campaign, ten minutes simultaneous measurements relative differences of Dobson (CD and AD pair) and Brewer triad serial number (#157,#183,#185) using the Operative, IGACO B & P, DBM and IUP cross-section

| | D CD | D AD | B#157 | B#183 | B#185 |
|------|-------|-------|-------|-------|-------|
| Op. | -0.78 | -0.78 | 0.68 | 0.69 | 0.96 |
| IGQ4 | -0.37 | -1.18 | 0.68 | 0.69 | 0.96 |
| DBM | 1.76 | 0.94 | -1.45 | -1.44 | -1.17 |
| IUP | -0.20 | 0.10 | -0.05 | -0.04 | 0.24 |

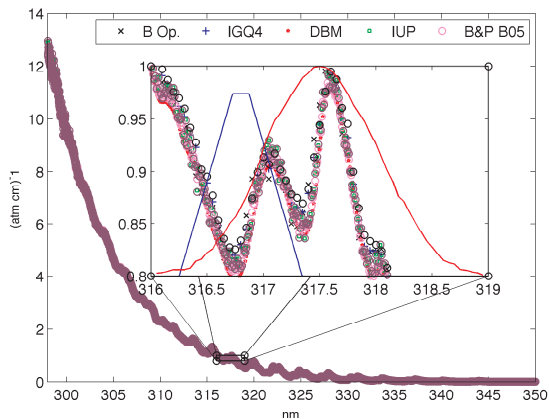


Fig. 1. The cross-sections used in this study Brewer Operative B&P (BOp), B&P IGACO quadratic fit (IGQ4), Daumont Brion and Malicet (DBM), Bremen Institute of Atmospheric Physics (IUP) and B&P of Bernhard (B05) at 228 K and slit functions of Brewer and Dobson in the region of 317 nm.

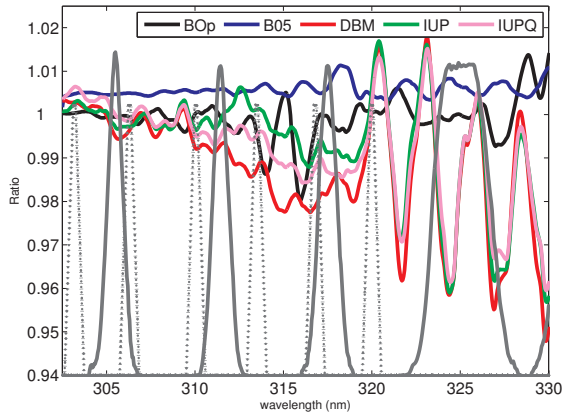


Fig. 2. Ratio of the cross-sections of this study to the IGACO Bass & Paur (IGQ4), the cross-sections are interpolated to a common resolution base on that of B&P (0.1 nm) and smoothed to the Brewer resolution (triangle slit with FWHM of 0.6 nm). In gray the Dobson (continuous) and Brewer (dotted) slit functions are shown. DBM and IUP show the same structures compared with B&P. There is a small but significant difference between the interpolated value of IUP and the values from the quadratic polynomial (IUPQ).

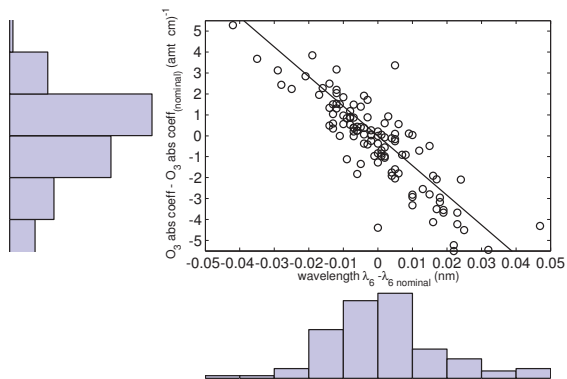


Fig. 3. Difference of the operative ozone absorption coefficient for each individual instrument to the nominal instrument vs the difference of the wavelength 6 (320 nm) to the nominal value. The DXS is proportional to the wavelength difference.

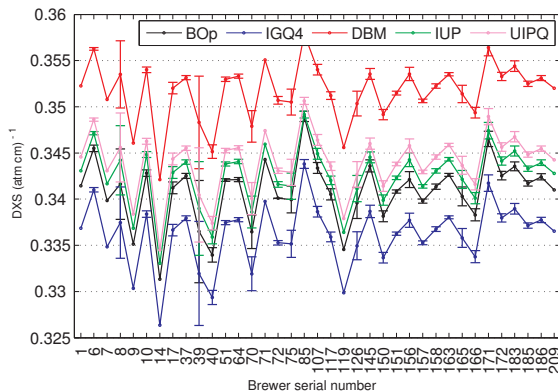


Fig. 4. Brewer ozone absorption coefficient or differential cross-section for the Brewers in the RBCC-E set, the values are the mean and the bars indicate the standard deviation for the analyzed cross-sections. Brewer labeled as #1 is the “nominal” Brewer; the x axis notation is the individual Brewer serial number

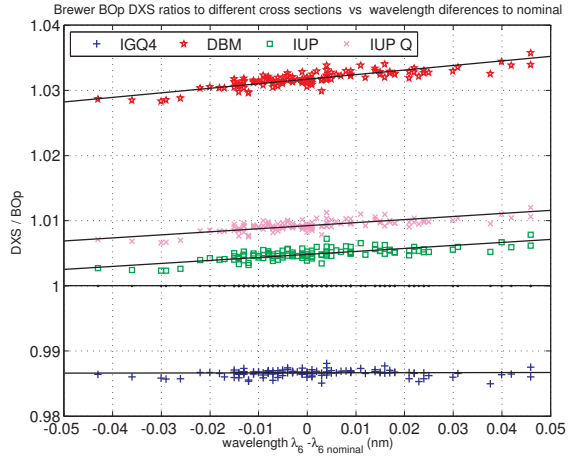


Fig. 5. Brewer operative differential cross-section ratio (BOp) to those calculated using various other cross-sections data sets vs. slit 6 wavelength difference to nominal in nm.

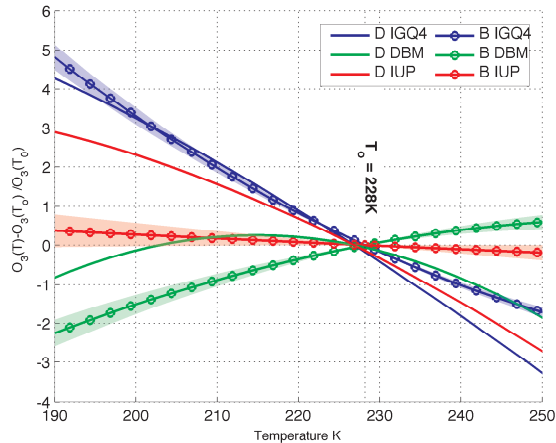


Fig. 6. Dobson AD pair and Brewer (average and shadowed the standard deviation of the RBCC-E set) total ozone error due temperature dependence of the various cross-section data set. In a cooler stratosphere the Dobson (labeled as D) and Brewer (labeled as B), underestimate the ozone using IGQ4 (B&P) and IUP cross section whereas they overestimate if we use DBM. The Brewer temperature dependence of IUP case is very small.

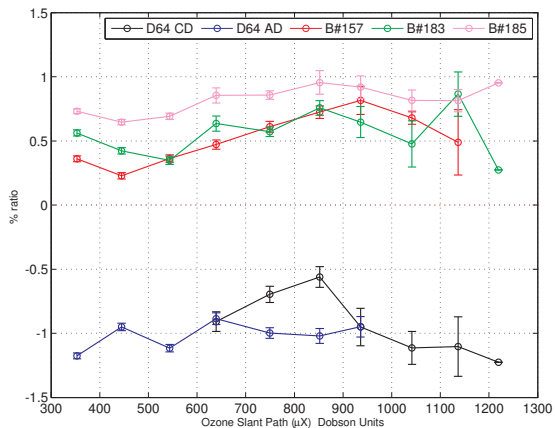


Fig. 7. Brewer–Dobson percent differences versus the mean of European references Brewers (labeled as B) and Dobson (Labeled as D) taken separately versus ozone slant path (μX), during 2012 Langley plot calibration 2012 campaign at IZO. There is no evident (μX) dependence with the exception of the Dobson CD pair at high (μX).

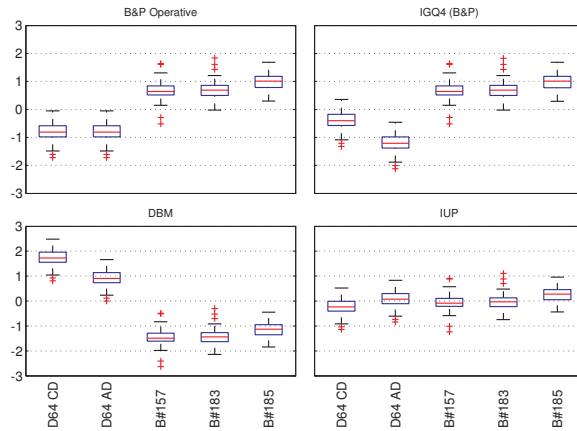


Fig. 8. Boxplot of the percentage differences versus the mean of Dobson and Brewer instruments, during 2012 Langley plot calibration campaign at IZO, with four cross-sections: 1) Bass & Paur Operative (BOP) 2) Bass & Paur from quadratic coefficients (IGQ4) 3) Daumont Malicet and Brion (DBM) and 4) University of Bremen (IUP), first two boxes in each panel correspond to Dobson CD and AD pair and the last three to the Brewer triad used at the RBCC-E.

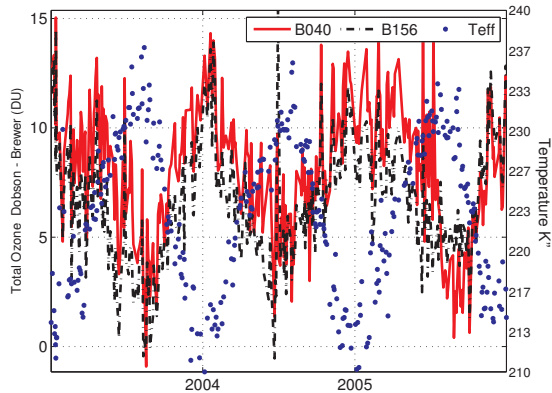


Fig. 9. Daily mean of the Dobson-Brewer total ozone difference for Arosa 2003–2006 and effective temperature, Brewer 040 (B040) is a single monochromator instrument; Brewer 156 (B156) is a double.

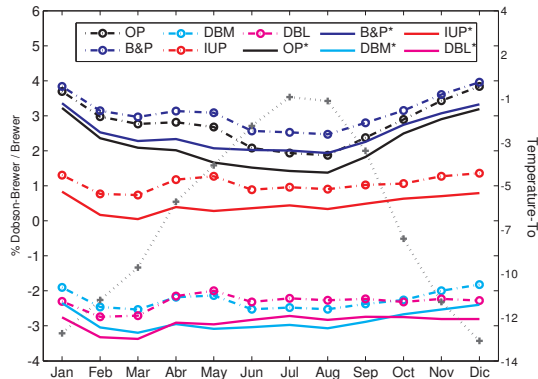


Fig. 10. Monthly means of the Brewer-Dobson differences for the Arosa observations. The different plot lines are derived from ozone calculated using the operational (fixed temperature) algorithms (black lines), and ozone calculated with temperature dependent algorithms (colored lines). The dotted lines are for single Brewer and the solid lines are for double Brewers. The stratospheric temperature difference from the nominal used in the algorithm, and the temperature determined from the Payerne ozonesonde record is also displayed (gray-dotted line with grey '+'s).