The Effect of Instrumental Stray Light on Brewer and Dobson Total Ozone Measurements

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Abstract. Dobson and Brewer spectrophotometers are the primary, standard instruments for ground-based ozone measurements under the World Meteorological Organization's (WMO) Global Atmosphere Watch program. The accuracy of the data retrieval for both instruments depends on a knowledge of the ozone absorption coefficients and some assumptions underlying the data analysis. Instrumental stray light causes non-linearity in the response of both the Brewer and Dobson to ozone at large ozone slant paths. In addition, it affects the effective ozone absorption coefficients and extraterrestrial constants that are both instrument dependent. This effect has not been taken into account in the calculation of ozone absorption coefficients that are currently recommended by WMO for the Dobson network. The ozone absorption coefficients are calculated for each Brewer instrument individually, but in the current procedure the effect of stray light is not being considered. This study documents the error caused by the effect of stray light in the Brewer and Dobson total ozone measurements using a physical ~~mathematical~~ model for each instrument. For the first time, new ozone absorption coefficients are calculated for the Brewer and Dobson instruments taking into account the stray light effect. The analyses show that the differences detected between the total ozone amounts deduced from Dobson AD and CD pair wavelengths are related to the level of stray light within the instrument. The ~~error~~ discrepancy introduced by the assumption of a fixed height for the ozone layer for ozone measurements at high latitude sites is also evaluated. The ozone data collected by three Dobson instruments during the period of February ~~between~~ 2008 to ~~and~~ December ~~2012~~ 2014 are compared with ozone data from a collocated double monochromator Brewer spectrophotometer (Mark III). The results show the dependence of Dobson AD and CD pair measurements on stray light.

1 Introduction

Routine atmospheric total column ozone measurements started in the mid-1920s with a Féry spectrophotometer (Dobson, 1931). Following the International Geophysical Year (1958) a worldwide network was developed with a number of Dobson instruments that were installed around the world to monitor total ozone variations. In the early 1980s the automated Brewer became commercially available (Kerr et al., 1981). A similar network was also introduced for the Brewer as observing organizations started to use these instruments alongside the Dobson for long-term measurements. Although the principle behind the measurements of the Brewer and Dobson instruments is generally the same, seasonal and systematic differences in respective TOC (Total Ozone Column) products became evident after long-term co-incident measurements were accumulated (Staehelin et al., 1998; Vanicek, 2006). The adoption of the Bass and Paur (1985) ozone cross-sections (BP) for the Dobson instrument in 1992 put both instruments on the same reference scales (Brewer uses BP) and reduced the difference to 4 % (Kerr et al., 1988) but it did not resolve the seasonal and offset differences (Vanicek, 2006).

Temperature corrections to the ozone absorption cross-sections may reduce the systematic errors of Dobson ozone data by up to 4 % (Bernhard et al., 2005). The seasonal differences between the measurements by the two instrument types is related to the ozone effective temperature, which affects differently the ozone absorption measured by the Brewer and Dobson instruments (Bernhard et al., 2005; Kerr et al., 1988; Scarnato et al., 2009; Van Roozendael et al., 1998; Vanicek, 2006) because of the different wavelengths employed for the measurements. The impact of different laboratory-determined ozone cross-sections has also been investigated and showed up to a 3 % change for the Brewer and 1 % for Dobson data (Redondas et al., 2014).

To facilitate the replacement of Dobson instruments with Brewers, statistical methods have been developed to derive transfer functions for converting Dobson measurements to the Brewer scale (Staehelin et al., 2003). These methods have been partly successful, but they cannot entirely explain the differences between the measurements of the two instruments (Scarnato et al., 2010). Scarnato et al. (2010) found a 3 % drift over about 10-year period (1988-1997) between Arosa's Dobson and Brewer total ozone series unexplained.

Analysis of the data obtained by the Dobson at the South Pole showed that the assumption of the ozone layer being at a fixed height leads to an error in the air mass calculation. The errors caused by this assumption may exceed 4 % in ozone measurements when the ozone distribution is distorted by the "ozone hole" (Bernhard et al., 2005).

While The stray light has been demonstrated to affect measurements by both instrument types (Bais et al., 1996)., the effect of the stray light on measurements at large solar zenith angles (SZA), have not been analysed properly yet. Basher (1982) used a mathematical model to estimate stray light levels present in the measurements of a particular Dobson instrument. According to Basher (1982), errors of 1, 3 and 10% may be present at air mass values of 2.5, 3.2 and 3.8, respectively for direct sun AD measurements. Christodoulakis et al. (2015) employed Basher's model to estimate the stray light level of Dobson #118 at Athens Dobson station using the direct sun AD wavelength pair measurements collected over a large range of solar zenith angles. The result showed that the mean underestimation of ozone was 3.5 DU (or about 1% of the station's mean total ozone column value) for measurements with air mass values of up to 2.5. However, a single-pair parameter was not found for Basher's model that succeeded in calculating the stray light correction for all experimental days. Christodoulakis et al. (2015) concluded that Basher's model cannot quantify the effect of stray light on TOC measurements made by the Dobson instrument under all conditions and that further study was needed. This was also mentioned by Basher (1982) and Evans et al. (2009).

Karppinen et al. (2014) employed the method suggested by Kiedron et al. (2008) to correct the data collected by a single monochromator Brewer during an Intercomparison/Calibration campaign for Nordic Brewers and Dobsons held at Sodankylä 8–24 March 2011 and a follow up campaign at Izaña observatory, Tenerife, between 28 October and 18 November 2011. The method suggested relies heavily on the dispersion information for the instrument which is not available for all instruments, especially in the historical record.

The errors caused by stray light are particularly significant at high latitudes in the late winter and early spring when measurements are made at large SZA and large TOC. It is considerable importance if those data are to be used for trend analysis or satellite data validation. In particular, if such data are used in the case where Dobsons or single monochromator Brewers are replaced by instruments with a significantly lower level of stray light, such as double monochromator Brewers (Mark III), a significant false positive trend in ozone may result.

The main goal of this study is to investigate and document these sources of error in total ozone as measured by the Dobson and Brewer instruments at high latitudes.

2 Method

2.1 Retrieval Algorithm

According to the Beer-Lambert law, the spectral irradiance $I(\lambda)$ from a direct solar spectrum at the Earth's surface can be expressed as:

$$\boldsymbol{I(\lambda) = I_0(\lambda) exp(-\tau(\lambda))} \quad (1)$$

where $\tau(\lambda)$ is the optical thickness of the incident path and $I_0(\lambda)$ is the extraterrestrial irradiance at wavelength λ

$$\boldsymbol{\tau(\lambda) = \alpha(\lambda) X\mu + \beta(\lambda)\frac{P_s}{P_0} m_R + \delta(\lambda) m_a} \quad (2)$$

And

$\alpha(\lambda)$ - Monochromatic ozone absorption coefficient at wavelength λ

X - Total column ozone (TOC)

μ - Relative optical air mass corresponding to ozone absorption

$\beta(\lambda)$ - Rayleigh optical depth for a one-atmosphere path

P_s - Station pressure

P_0 - Mean sea level pressure (101.325 kPa)

m_R - Relative optical air mass corresponding to Rayleigh scattering (extinction)

$\delta(\lambda)$ - Aerosol optical depth

m_a - Relative optical air mass corresponding to aerosol scattering (extinction)

The Dobson spectrophotometer does not measure the intensity of sunlight at a single wavelength but instead determines the ratio between the irradiance at two wavelengths, one strongly absorbed and the other more weakly affected by ozone. Several wavelength pairs are used by the Dobson algorithm for calculating total column ozone. In order to minimize the effect of aerosol and other absorbers, two wavelengths pairs are used such as AD, AC or CD where the A pair is (305.5 / 325.4 nm), C is (311.5 / 332.4 nm) and D is (317.6 / 339.8 nm) (Evans and Komhyr, 2008; Komhyr et al., 1993). For example, the total ozone using AD wavelength pair observations is retrieved by following expression:

$$\boldsymbol{X = (N_A - N_D - K - \Delta\beta_{AD}\frac{P_s}{P_0}m_R - \Delta\delta_{AD}m_a)/(\mu\Delta\bar{\alpha}_{AD}\alpha_{AD})} \quad (3)$$

$$\boldsymbol{N_A = ln[I_0(305.5)/I_0(325.4)] - ln[I(305.5)/I(325.4)]} \quad (4)$$

$$\boldsymbol{N_D = ln[I_0(317.6)/I_0(339.8)] - ln[I(317.6)/I(339.8)]} \quad (5)$$

$$\boldsymbol{\Delta\beta_{AD} = [\beta(305.5) - \beta(325.4)] - [\beta(317.6) - \beta(339.8)]} \quad (6)$$

$$\boldsymbol{\Delta\delta_{AD} = [\delta(305.5) - \delta(325.4)] - [\delta(317.6) - \delta(339.8)]} \quad (7)$$

$$\boldsymbol{\Delta\bar{\alpha}_{AD}\alpha_{AD} = [\bar{\alpha}\alpha(305.5) - \bar{\alpha}\alpha(325.4)] - [\bar{\alpha}\alpha(317.6) - \bar{\alpha}\alpha(339.8)]} \quad (8)$$

where $\Delta\bar{\alpha}\alpha$ is the effective differential ozone absorption coefficient at -46.3° C and ***K*** is the instrument constant. Other double wavelength pairs such as CD can be used for the ozone calculation by modifying Eq. (3) accordingly (Komhyr et al., 1993).

The basic measurement principle for the Brewer instrument is the same as the Dobson. However, the Brewer measures the intensity of four operational wavelengths quasi-simultaneously. The total ozone is calculated using the following equation:

$$\boldsymbol{X = (MS9 + \Delta\beta\frac{P_s}{P_0}m_R - ETCB)/(\Delta\bar{\alpha}\alpha\mu)} \quad (9)$$

where $\Delta\bar{\alpha}$ ~~α~~ and ETC ~~B~~ are the effective differential ozone absorption coefficient at -45º C and Extra-Terrestrial Constant (ETC) respectively. Both are obtained from a linear weighted combination of the logarithms of their individual values at the four wavelengths used for the total ozone retrieval (Kerr, 2002). $MS9$ is calculated from a linear combination of the logarithms of the intensities ~~(F_i)~~ $(I(\lambda_i))$ measured at the four wavelengths $\lambda_i = (310.0, 313.5, 316.8, 320.0)$, multiplied by weighting coefficients w_i.

$$\boldsymbol{MS9 = \sum_{i=1}^{4} w_i . \ln I(\lambda_i)} \; \sout{F_i} \boldsymbol{= \ln[I(310.0)] - 0.5 \ln[I(313.5)]}$$

$$\boldsymbol{-2.2 \ln[I(316.8)] + 1.7 \ln[I(320.0)]} \quad (10)$$

$$\Delta\bar{\alpha} \; \sout{\alpha} = \sum_{i=1}^{4} w_i . \; \sout{\alpha_i} \; \bar{\alpha}(\lambda_i) \quad (11)$$

$$\Delta\beta = \sum_{i=1}^{4} w_i . \; \sout{\beta_i} \; \beta(\lambda_i) \quad (12)$$

The weighting coefficients, w_i = (1.0, -0.5, -2.2 and 1.7), have been selected to minimize the absorption of SO_2 and suppress any variations that change linearly with wavelength. Hence, the aerosol scattering effect, which is approximately linear with wavelength over a narrow wavelength range, is suppressed in the calculation. The w_i sum to zero, the requirement for the absorption function to be independent of absolute intensity. The ETC ~~(B)~~ of a primary standard instrument is determined using observations made at Mauna Loa observatory and are calculated using the zero air mass factor extrapolation (Langley plot method). It can be transferred to other instruments by comparisons with a traveling standard instrument (Fioletov et al., 2005).

2.2 Effective Ozone Absorption Coefficients

To calculate the effective ozone absorption coefficients, the laboratory-determined ozone cross-sections at an effective atmospheric ozone layer temperature must be convolved with the instrument slit function, weighted by the solar flux. The BP ozone cross-sections were recommended by the International Ozone Commission (IO_3C) in 1992 (http://www.esrl.noaa.gov/gmd/ozwv/dobson/papers/coeffs.html) for the Brewer and Dobson networks. The calculation of the absorption coefficients, which are currently recommended by WMO for Dobson instruments, is described by Komhyr et al. (1993) (K93 hereinafter) and the re-evaluation is described by Bernhard et al. (2005) (B05 hereinafter). Recently IO_3C has recommended the ozone cross-sections measured by Serdyuchenko et al. (2014), as they reduce the Dobson temperature sensitivity. In this study for consistency with previous works the BP cross-sections are used. A correction factor

$$\boldsymbol{f_c = 1.0112 - 0.6903/[87.3 - (T - T_0)]} \quad (13)$$

based on the results of Barnes and Mauersberger (1987), as suggested by K93, is used to adjust the BP cross-sections. T is the temperature in kelvin and T_0 is 273.15 K. For this study all BP cross-sections are multiplied by this factor and calculated at -46.3 for both instruments to be consistent. the relevant temperature. This correction has been implemented in the Dobson and Brewer networks. For wavelengths longer than 340 nm, where BP data are not available, the Brion et al. (1993), Daumont et al. (1992) and Malicet et al. (1995) (BDM) data are used. These data sets are available at individual temperatures and also with the associated quadratic coefficients of temperature dependence on the IGACO (Integrated Global Atmospheric Chemistry Observations) web page. For this study the quadratic coefficients on the file 'Bp.par' are used for BP cross-sections and (Liu et al., (2007) quadratic approximation which excludes -273° K data from the quadratic temperature dependence fitting are used For BDM cross-sections. The temperature dependence of the cross-sections is expressed as:

$$\boldsymbol{\sigma(\lambda, T) = C_0(\lambda) + C_1(\lambda)T + C_2(\lambda)T^2} \quad (14)$$

where $\sigma(\lambda, T)$ is the ozone absorption cross-section at wavelength λ and temperature T, and C_0, C_1 and C_2 are the quadratic coefficients at wavelength λ. The quadratic coefficients used throughout this study are consistent with the K93 and B05 calculations. The absorption coefficients are calculated from the ozone cross-sections $\sigma(\lambda, T)$ and the ozone number density $\rho(z)$:

$$\boldsymbol{\alpha(\lambda) = \frac{1}{X}\int_{z_0}^{\infty} \sigma\big(\lambda, T(z)\big)\rho(z)dz} \quad (15)$$

where z_0 is the altitude of the station and T is the temperature in Kelvin. The total ozone column, X, (in Dobson unit equal to 2.69×10^{16} ozone molecules per square centimetre) is defined as:

$$\boldsymbol{X = \frac{kT_0}{P_0}\int_{z_0}^{\infty} \rho(z)dz} \quad (16)$$

where T_0 is 273.15 K and $\boldsymbol{k}$ is the Boltzman constant (It should be noted that X is used in the equations whereas TOC is used in the text). In order to account for the finite bandwidth of the Brewer and Dobson slit functions, the effective ozone absorption coefficient $\bar{\alpha}_i$ $\bar{\alpha}(\lambda)$ is used instead of $\alpha(\lambda)$ in Eq. (2) and (3) the Brewer and Dobson retrieval algorithms (Basher, 1982; Vanier and Wardle, 1969):

$$\overline{\alpha}_i\ \overline{\alpha}(\lambda_i) = \frac{-1}{X\mu} ln\left(\frac{\int I_0(\lambda)S(\lambda,\lambda_i)exp(-\alpha(\lambda)X\mu - \beta(\lambda)\frac{P_s}{P_0}m_R)d\lambda}{\int I_0(\lambda)S(\lambda,\lambda_i)exp(-\beta(\lambda)\frac{P_s}{P_0}m_R)d\lambda}\right)$$

(17)

where $S(\lambda, \lambda_i)$ is the slit function for a nominal wavelength λ_i.

The Brewer operational method employs a simpler approximation, which is identical to the approximation method of B05 and the simplest approach of K93, and also used by Redondas et al. (2014), Van Roozendael et al. (1998), Scarnato et al. (2009) and Fragkos et al. (2013):

$$\overline{\alpha}_i^{apx}\overline{\alpha}^{apx}(\lambda_i) = \frac{\int \alpha(\lambda)S(\lambda,\lambda_i)\, d\lambda}{\int S(\lambda,\lambda_i)\, d\lambda}$$

(18)

2.3 Ozone Air Mass Calculations

Both Brewer and Dobson retrievals assume a fixed height for a thin layer of ozone to calculate the ozone air mass. The following expression is used by both instruments to calculate relative optical air mass at a solar zenith angle of ~~θ_0~~ θ:

$$\mu(\theta_0\theta) = (Re + h)/[(Re + h)^2 - (Re + r)^2 sin^2 \theta_0\theta]^{0.5} \qquad \textbf{(19)}$$

where *Re* is the radius of the Earth, *r* is the altitude of the station and *h* is the height of the ozone layer. Using the mean Earth radius for *Re* instead of the actual Earth radius at the station does not introduce a significant error in μ. However, it is important that the correct values for the station altitude and the height of the ozone layer are used in Eq. (19). The Dobson community has adopted a variable ozone layer height with latitude which, to some extent, is in agreement with ozone climatology, while a fixed height of 22 km is used in the Brewer network.

2.4 Slit Function and Stray Light Effect

Stray light is unwanted radiation from other wavelengths that arrives at the detector during measurements at a selected wavelength. Scattering by instrument optical elements and inefficient out-of-band (OOB) rejection of the light by dispersive elements, e.g. the grating, are the main sources of stray light in the spectrometers. Particulate scattering within the instrument~~s~~ and radiation scattered from the atmosphere within field of view of the instrument can also contribute a stray light effect (Josefsson, 1992).. ~~may also contribute to the stray light~~. Generally, holographic gratings with higher line densities generate lower stray light. The Mark II and IV versions of the Brewer demonstrate higher levels of stray light compared to the Mark III as the Mark III instruments utilize a double monochromator with higher line density gratings that leads to significantly better rejection of the OOB light. The stray light within the Dobson instrument is comparable to that of the Brewer Mark IV and II.

Since the gradient of ozone absorption is large in the ultraviolet spectral region, the stray light contribution from longer wavelengths can make up a significant fraction of the signal measured at shorter wavelengths where the intensity is reduced by ozone absorption. As the light path (air mass and ozone path) increases, stray light effects in the measurements also increase. Stray light results in an underestimated ozone column at larger ozone slant column amounts.

To characterize the stray light in an instrument it is necessary to measure the instrument slit function. The Brewer Mark III and IV can measure the wavelength range of 286.5 to 363 nm with 0.5 nm resolution. The Brewer slit function is characterized using a narrow band line source such as a laser as input source and scanning through all wavelengths. Measurements at 350 nm (not reported) have shown the slit function to be similar at all wavelengths in the Brewer measurement range. The slit function is reversed in wavelength space to account for the reciprocal nature of scanning the instrument versus scanning the wavelength of the line source. He-Cd laser commonly is used to measure the slit function of the Brewer (Karppinen et al., 2014; Kiedron et al., 2008; Pulli et al., 2018). For this study also Aa He-Cd laser (single line at 325.029 nm) has been used to measure the slit functions of the Brewer #009 and #119. Figure 1Figure 1 shows the measured slit functions of Brewer Mark IV #009 (single monochromator) and Mark III #119 (double monochromator) located at Mauna Loa Observatory (MLO). Several Brewer Mark IV, Mark II, and Mark III slit functions have been measured throughout various intercomparison campaigns (e.g. The Fourth North American Interagency Intercomparisons of Ultraviolet Monitoring near Boulder, Colorado, in 1997 and published by Lantz et al. (2002) and Intercomparison Campaigns of the Regional Brewer Calibration Centre-Europe (RBCC-E)). The slit function consists of a core (band-pass), the shoulders, and the extended wings (Fig. 1). The stray light measured from nearby wavelengths (the wings of the slit function) is typically below 10^{-6} times that of the primary wavelength in the Mark III double Brewers as compared to 10^{-4} in the Mark II and Mark IV single Brewers. To reduce the effect of stray light, the Brewer Mark II uses a cutoff filter which strongly attenuates wavelengths longer than 345 nm. A solar blind filter (SBF) made of nickel sulphate hexahydrate ($NiSO_4.6H_2O$) crystal sandwiched between two UV coloured glass filters (similar to Schott UG5 or UG11) is also used in the Mark IV. Figure 2 shows the transmission of a typical UG11-$NiSO_4$ filter measured by a Cary 5E spectrophotometer. The stray light level depends on the optical and mechanical configuration which is unique for each instrument, and thus two identically configured instruments can have somewhat different OOB light rejection.

In the Brewer operational wavelength calibration, the individual slit functions are characterized separately through dispersion analysis (Gröbner et al., 1998). For this study, a symmetrical trapezoid is fitted to the measured slit functions of Brewer #009 (Single – Mark IV) and Brewer #119 (Double – Mark III) (Figure 1Fig. 1). The model slit function fit to the data (red line) includes three parts: a trapezoid with 0.55 nm nominal FWHM (Table 1Table 1) at the core band-pass, the shoulders which are modelled by fitting a Lorentzian function (Table 1Table 1) to the measured data and two horizontal straight lines for the outer parts (wings). For simplicity, in this study, a modelled slit function – which is quite representative of most Brewers – with 0.55 nm FWHM is used for all slits. To investigate the effect of stray light, an ideal slit function which is a trapezoid shape with a flat top at 0.87 of the full height and two straight lines to zeros with 0.55 nm nominal FWHM also has been used (Figure 1Fig. 1, top left).

The slit functions of the world standard Dobson #83 were experimentally measured by Komhyr et al. (1993) Komhyr and recently verified by (Köhler et al., (2018) using a tuneable light source (Komhyr et al., 1993). However, the published slit functions are restricted to the core band-passes. It has been assumed that the Dobson instrument restricts OOB light from entering the slit. The extended wings have not been measured for the Dobson instrument. Basher (1982) attempted to estimate the level of stray light within the Dobson instrument by fitting a mathematical model to the AD pair direct sun measurements and analysing the total column ozone changes with Solar Zenith angle. His analysis suggested that for most Dobson instruments the level of stray light is 10^{-4} based on the non-linearity of the AD direct sun measurements beyond an air mass factor of 3.

Another approach has been used by Evans et al. (2009) to measure the stray light entering the Dobson instrument. They used a filter that is opaque to the C-pair nominal short wavelength band-pass, and transparent outside of this range (Fig. 6 in Evans et al. (2009)). The idea is the filter would remove the desired band-pass from the signal and any current remaining is from OOB light. This method was used to estimate the contribution of stray light in zenith sky measurements of Dobson #65 in Boulder, CO. They also used a model approach for the stray light contribution in zenith sky measurements and concluded that the level of stray light in Dobson #65 is likely 2×10^{-5}.

The Dobson slit functions for short and long wavelengths are approximately a triangle with FWHM of 1.06 nm and a trapezoid with FWHM of 3.71 nm respectively (Figure 3Fig. 3). For this study, symmetrical trapezoids centered at the nominal Dobson wavelengths were fitted to the experimentally determined slit functions of Dobson #83 and used as ideal slit functions. The characteristics of these trapezoids are given in Table 1Table 1. In order to account for stray light, for this study two straight lines were added to the outer parts of the ideal slit functions.

3 Discussion

3.1 Effect of stray light on ozone absorption coefficients

To calculate the ozone absorption coefficients, the standard values defined in Table 1Tables 1 and 2 are employed. In tables 3 and 4 the coefficients calculated for the Brewer single and double versions are shown. The values of $\bar{\alpha}_i^{apx}$ calculated with the ideal (trapezoid) slit functions are the same as the operational values which are currently being used for Brewer #009 and #119. To validate the calculations, the $\Delta\bar{\alpha}^{apx}$ is calculated for the double Brewer using an ideal trapezoid slit function and BP cross-sections at -45 °C without the Barnes and Mauersberger (1987) correction. Redondas et al. (2014) have calculated the ozone absorption coefficients for the nominal Brewer which is identical in terms of slit functions, nominal wavelengths and slit FWHMs with the double Brewer of this work using ideal trapezoid slit functions. The IGQ4 cross-sections used in Redondas et al. (2014) are the same as the BP cross-sections employed at this work. The value 0.3367 calculated using IGQ4 cross-sections at -45 ºC (Redondas et al. Table 6) has a difference of 0.06 % with the value 0.3365 calculated here with the same cross-sections at the same temperature (-45 ºC) (Table 3).

To be consistent with Dobson calculations, the BP cross-sections with Barnes (1987) correction and at -46.3 ºC are used for calculation of $\bar{\alpha}(\lambda_i)$ and $\bar{\alpha}^{apx}(\lambda_i)$ presented in Table 4 and Table 5 for the single and double Brewers.

The contribution of stray light in determining the ozone absorption coefficients can be seen from comparing the $\Delta\bar{\alpha}$ calculated using ideal slit functions (without stray light) with the values ($\Delta\bar{\alpha}$) calculated using modeled slit functions (including stray light). For the single Brewer the results show a 0.7 % difference (modeled slit functions including stray light are less than that of the ideal slit functions) while for the double Brewer the difference is less than 0.01 %.

Comparing $\Delta\bar{\alpha}$ with $\Delta\bar{\alpha}^{apx}$ for both Brewers (single and double using ideal and modeled slit functions) shows a minimum difference of 0.7 % ($\Delta\bar{\alpha}$ higher than $\Delta\bar{\alpha}^{apx}$) for the double Brewer and a maximum of 0.9 % for the single Brewer with ideal trapezoid slit functions, indicating the role of the solar spectrum in calculating the ozone absorption coefficients.

~~These values were calculated to test the retrieval that is used in this study. Comparing $\bar{\alpha}_i$ calculated using modeled slit functions with $\bar{\alpha}_i^{apx}$ calculated using ideal slit functions shows 0.7% difference for the single and less than 0.01 % for the double (highlighted in Bold at Table 3). Overestimating the coefficients according to Eq. (9) leads to underestimation of the total ozone amount.~~

The values of ~~$\bar{\alpha}_i$~~ $\bar{\alpha}(\lambda_i)$ and ~~$\bar{\alpha}_i^{apx}$~~ $\bar{\alpha}^{apx}(\lambda_i)$ calculated for the Dobson instrument using the modeled slit functions are provided in Table 6~~Table 6Table 4~~. ~~$\bar{\alpha}_i^{adj}$~~ $\bar{\alpha}^{adj}(\lambda_i)$ is the adjusted set of coefficients which are recommended by WMO to be used for the Dobson network. After applying the K93 data set to the observations made by World Standard Dobson Instrument #083 at Mauna Loa observatory, 0.8% for AD pair and 2.2 % for CD pair differences in the calculated total ozone values were detected. K93 realized that increasing $\Delta\bar{\alpha}_D$ by 2 % would decrease the discrepancies to below 0.5 %. Thus, the adjusted values were recommended by WMO to be used for the Dobson instruments.

The ~~$\bar{\alpha}_i^{apx}$~~ $\bar{\alpha}^{apx}(\lambda_i)$, and ~~$\bar{\alpha}_i$~~ $\bar{\alpha}(\lambda_i)$ calculated in this study using ideal (trapezoidal slit functions without stray light) slit functions and the slit functions with 10^{-5} level of stray light show less than 0.1% differences. However, the same comparison between the ideal slit values and the results using the slits with 10^{-4} level of stray light shows 4.0 % and 6.9 % difference between ~~$\bar{\alpha}_i$~~ $\bar{\alpha}(\lambda_i)$ values for AD and CD pair respectively. The values of ~~$\bar{\alpha}_i^{apx}$~~ $\bar{\alpha}^{apx}(\lambda_i)$ calculated using ideal slit functions and the slit functions with 10^{-5} level of stray light agree with the corresponding values of K93 to within ±2.0 %. In the case of ~~$\bar{\alpha}_i$~~ $\bar{\alpha}(\lambda_i)$, the comparison indicates agreement to within ±3.4 % except for ~~$\bar{\alpha}_{339.9}$~~ $\bar{\alpha}(339.9)$ where the difference is about 67 %. Approximately the same difference was reported by B05 for the same wavelength compared to K93. B05 have investigated this discrepancy by using Molina and Molina (1986) cross-sections to extend the BP datasets for Dobson calculations and concluded that the K93 value for ~~$\bar{\alpha}_{339.9}$~~ $\bar{\alpha}(339.9)$ is unreasonably high. As in B05, the calculated value, $\Delta\bar{\alpha}_D$, presented in this study agrees better with the empirically adjusted value, $\Delta\bar{\alpha}_D^{adj}$. The comparison shows agreement to within ±1.6 % between the values calculated for this work and the K93 adjusted values.

Generally, the differences between values presented here and those from K93 are slightly higher than the difference between B05 and K93. However, it should be noted that the slit functions and the parameters used in the calculations presented here are slightly different from those used by K93 and B05 (Table 1~~Tables 1~~ and Table 2~~2~~). The AD coefficient calculated for a Dobson instrument with 10^{-4} level of stray light shows a 3.6 % deviation compared to the adjusted values and for the CD pair the difference is about 7.2 %.

Clearly, the stray light level within each instrument has an effect on the ozone absorption coefficient calculations. This effect is negligible for instruments with a stray light level on the order of 10^{-5}. But the difference could be up to 4.0 % and 6.9 % for AD and CD pair coefficients respectively for instruments with levels of stray light on the order of 10^{-4} when compared with the values calculated using ideal slits. These differences translate to an underestimation of ozone values through Eq. (3). However, by applying the Dobson calibration procedure the difference between the AD measurements of the Standard instrument and a calibrated one is reduced to less than 0.7 % (Evans and Komhyr, 2008). In the Dobson AD pair calibration, scale factors are calculated for different ranges of airmass. The data from the instrument being calibrated are scaled to the data from the reference instrument. Then, using the quasi-simultaneous measurements of AD and CD pairs of the calibrated instrument a scaling factor can be calculated to reduce the CD measurements to the AD level.

~~It is advisable that the new measured slit functions are used to recalculate the absorption coefficients. The new values should be recommended by WMO to be applied in the Dobson retrieval algorithm.~~

It is advisable that the WMO assign a group to measure the Dobson stray light level at least for the reference instrument. Then, the absorption coefficients should be recalculated and recommended to be used instead of the values currently in use.

3.2 Stray light influence on low-sun measurements

To illustrate the effect of stray light on low-sun measurements, the percentage difference between ozone derived using Brewer and Dobson retrievals with assumed constant ozone in the atmosphere are depicted as a function of ozone slant path (OSP, total ozone times air mass) in Figure 4~~Fig. 4~~. Equation (1) along with parameters indicated in Table 2, are used to model the atmosphere and calculate the solar spectrum at the surface. To retrieve the ozone values, the absorption coefficients calculated in Sect. 3.1 are used. To calculate the ETC, the instrument absorption function using the solar spectrum (Chance and Kurucz 2010), Eqs. (1), (2) and retrieval algorithm of the Brewer (or Dobson) for an assumed constant amount ozone (325 DU in this study) is calculated and plotted as a function of ozone slant path. The best fit to the data with airmass less than 2 (less than 3 for the Dobson instruments) is found and extrapolated to zero airmass. Figure 5 shows the best fit to a single Brewer data. For the single Brewer the ETC is calculated as 1945.4 for a modelled trapezoid slit function with stray light which is comparable with 2020 as calculated by Kiedron et al. (2008) noting the slight differences in the slit functions and solar spectrum. Karppinen et al. (2015) have reported 3218 for ETC value for slit functions with stray light. However, they used LibRadtran 1.6-beta radiative transfer model to scale their data to be matched with real data. ~~The ETC values are calculated using the Langley method, considering data corresponding to air mass factors less than 2 and 3 for Brewer and Dobson respectively.~~ For Dobson models, the same ETC values as the one calculated using ideal slits are used for the other models (i.e. with 10^{-4} and 10^{-5} levels of stray light). Two versions of the Brewer are compared with the Dobson instrument measurements with two levels of stray light. AD measurements with 10^{-4} order of stray light show approximately 25 % discrepancy at 2000 DU OSP (air mass 6.2 in this case). The difference is about 5 % for a typical single Brewer at the same OSP. The underestimation of total ozone as measured by the AD pair of a Dobson instrument with 10^{-5} level of stray light could be up to 6 % at 2000 DU OSP. It has to be noted here that AD pair measurements are conducted for air mass factors less than 2.5 and thus, during the ozone hole period (total column ozone is less than 300 DU), Dobson data will be reported for OSP less than 750 DU (Evans and Komhyr, 2008).

Evidently, the CD pair is less influenced by scattered light than the AD pair because of the smaller ozone cross-sections at the CD wavelengths and the consequent smaller gradient with respect to wavelength in the spectrum measured. For a Dobson instrument with a minimum level of stray light (10^{-5}) the difference for the CD pair could be up to 1.8 % at 2000 DU OSP while it is less than 0.8 % for a typical double Brewer at the same OSP. It has to be noted that Dobson CD total ozone is reported for air mass values beween 2.4 and 3.5, and thus OSP is less than 1100 DU for total ozone (TOC) less than 300 DU (Evans and Komhyr, 2008).

3.3 Total ozone values retrieved from Dobson AD and CD pairs

For decades the Dobson community has faced a discrepancy between the ozone values deduced from quasi-simultaneous AD and CD pair measurements. As indicated by the Dobson operational handbook, AD observations are the standard for the Dobson instrument and all other observations must, therefore, be reduced to the AD level by determining a multiplying factor. For example, the ozone values deduced from measurements on CD wavelengths should be multiplied by the factor of X_{AD}/X_{CD} (where X_{AD} and X_{CD} are the average ozone measurements retrieved from AD and CD pairs derived from a large number of quasi-simultaneous observations covering a broad range of μ values greater than 2.0) to be reduced to those deduced from AD measurements.

Figure 6~~Figure 6Figure 5~~ illustrates the discrepancy in total ozone reduced from AD and CD pairs for two modeled Dobson instruments with different levels of stray light as a function of OSP. The ratio of the AD to the CD pair is also shown. The adjusted coefficients calculated by K93 and recommended by WMO are used to derive the total ozone amounts for this model. The ETC values that were calculated using the Langley method for an ideal instrument are used here as well. It can be seen that, as the level of stray light increases, the difference between the AD and CD values increases, indicating the role of stray light in the observed discrepancy between AD and CD values. Clearly, such a difference varies for different Dobson instruments as it depends on the level of stray light which is unique for each individual instrument. It should be noted that, as discussed in Sect. 3.1, these discrepancies are reduced during calibration using simultaneous measurements with a well-maintained, standard instrument.

3.4 Error Discrepancy caused by Air Mass Calculation

To retrieve the total ozone from direct sun measurements it is required that the ozone air mass value be calculated. For measurements at the South Pole, the following values are used by the Dobson community in Eq. (19): *Re* = 6356.912, *r* = 2.81 km, and *h* = 17 km. Figure 7Figure 6 shows the ratio of total ozone retrieved using air mass values calculated with four different sets of assumptions for *Re*, *r* and *h* to ozone values retrieved using air mass factor calculated for the South Pole employing the Dobson community's values for *Re*, *r* and *h* as a reference. Any discrepancy in the air mass is directly reflected in the Dobson and Brewer retrieved ozone via Eqs. (3) and (9) respectively. It is obvious that the fixed ozone layer height of 22 km, as used by Brewer retrieval, can cause up to a 2.2 % difference at an air mass of 5.4. In addition, the altitude of the site can introduce a significant difference at high solar zenith angles.

4 Comparison between Dobson and Brewer measurements at the South Pole

Total ozone measurements collected by three Dobson instruments (#82, #42, and #80) and one double Brewer Mark III, #085, collocated and operated simultaneously at the Amundsen-Scott site (24.80º W, 89.99º S, altitude 2810 m) are used for this comparison. Double Brewer #085 was installed at the South Pole station in 2008 and since then it was in routine operation. until it was replaced in 2016. The Brewer data for the South Pole site are available at the WOUDC website. Due to the logistic difficulties Brewer #085 was not replaced or calibrated until 2016.

The Dobson data used for this study are freely available at: ftp://aftp.cmdl.noaa.gov/user/evans/York_Omid/. For this study all direct sun Dobson measurements are used while only one measurement representative of the day is reported to the NDACC or WOUDC. A complete description of the South Pole dataset is provided by Evans et al., (2017). The reprocessed data using WinDobson software as described in Evans et al. (2017) are used for the analysis here. Generally, the Dobson instrument at the South Pole site is replaced with a calibrated instrument every four years. The instrument replaced is calibrated against the reference Dobson #83 and the calibration results are used to adjust and post-process the last four years of data collected at the South Pole. The calibration procedure can be found at Evans and Komhyr (2008) and the major calibration or instrument changes regarding the South Pole dataset can be seen in Fig. 5 of Evans et al. (2017).The Dobson instruments have been repeatedly calibrated against reference Dobson instrument #83.

Quasi-simultaneous direct sun measurements performed within 5 minutes during the period during the period of February 2008 and to December 2014 were used in the present analysis. The air masses calculated by the Brewer retrieval were corrected adjusted using Eq. (19) by applying the values used by Dobson instruments (Re = 6356.912 km, r = 2.81 km, and h = 17 km) to be consistent with the Dobson air masses. Figure 8 shows the total ozone column measured by double Brewer #085 and the total ozone retrieved using the adjusted airmasses. The ratio of total ozone columns retrieved using adjusted airmasses to the total ozone columns retrieved using unadjusted airmasses are also shown in the same figure.

The data presented here are the entire data collected by the instruments for research and maintenance purposes. The ozone absorption coefficients calculated by Komhyr et al. (1993) and recommended by WMO have been used to retrieve ozone values for the AD and CD pairs. It is necessary to mention that only the data collected with air mass factors less than 2.5 or OSP less than 800 DU would be reported for AD pair measurements to the World Ozone and Ultraviolet Data Centre (WOUDC) or other institutes for regular research purposes. The range of air mass factor for CD measurements is 2.4 to 3.5 and that means in the case of the South Pole station, the maximum OSP would be 1100 DU.

Figure 9Figure 9Figure 7 presents a comparison of the Brewer total ozone measurements with Dobson ozone observations reduced from the direct sun AD pair as a function of OSP. The ratios between the uncorrected unadjusted Brewer data and Dobson measurements are also shown in the same plot. The ratio between the Brewer adjusted corrected data and the Dobson values shows some dependence on OSP: the Dobson #82, #42, and #80 are on average 1 %, 0.46 % and 1.6 % higher respectively for OSPs below 800 DU. When the OSP is above 800 DU, Dobson measurements gradually become lower by up to 4 % for OSPs up to 1400 DU for Dobson #42 and #80 and up to 5 % for OSPs up to 1200 DU for Dobson number #82 (Figure 9Figure 9Fig. 8).

Figure 8 shows a box plot of the difference between double Brewer ozone measurements and Dobson values retrieved from AD and CD pairs. The data are binned for 100 DU from 400 to 2000 DU. On each box, the central red line is the median, the edges of the box are the 25th and 75th percentiles, the whiskers extend to the most extreme data points not considered outliers, and outliers are plotted individually. The ratio between Dobson CD pair measurements and the Brewer data also shows a dependence on OSP (Figure 9Figure 9Fig. 8). However, CD pair ozone values are on average 3.4 %, 4.5 %, and 2.5 % higher for almost the entire measurement set for Dobson #82, #42, and #80, respectively. It should be noted that the CD pair values are scaled to the AD pair for each individual Dobson instrument. The scaling factors calculated during calibration procedure and used for Dobson #82, #42, and #80 were 1.043, 1.025, and 1.03 respectively. The calibration procedures and the method for calculating the scaling factor are described and published by WMO in GAW report No. 183 (Evans and Komhyr, 2008). As illustrated by B05 (Fig. 4 of Bernhard et al. (2005)) the temperature dependence of the ozone absorption cross-sections may also cause deviations in Dobson total ozone column measurements. B05 assessed variability in the effective temperature using ozone profiles measured by Global Monitoring Division of NOAA (former Climate Monitoring and Diagnostics Laboratory, CMDL) at South Pole between 1991 and 2003. They found that the temperature adjusted AD and CD ozone absorption coefficients deviated from nominal values (K93) by up to ±4 % leading to underestimation or overestimation of the total ozone column through Eq. (3). B05 also found that the 1991-2003 collection of temperature adjusted CD ozone absorption coefficients exhibited a SZA dependence. The ozone absorption coefficient adjustment is likely magnified at low sun (large SZA) conditions (preferential for CD over AD measurements) when extreme changes in ozone and temperature profiles are observed during the ozone hole period.

It can be seen from this analysis that Dobson #42 TOC values show less dependence on OSP. Based on the physical model developed in this work, it could be concluded that this instrument has a significantly lower level of stray light than the other Dobson instruments #82 (#80 and #82). As it is shown in Figure 10, the physical model developed in this study suggests $10^{-3.7}$, $10^{-4.1}$, and $10^{-4.0}$ level of stray light for Dobson #82, 42, and 80, respectively.

Figure 11 shows a box plot of the difference between double Brewer ozone measurements and Dobson values retrieved from AD and CD pairs. The data are binned for 100 DU from 400 to 2000 DU. On each box, the central red line is the median, the edges of the box are the 25th and 75th percentiles, the whiskers extend to the most extreme data points not considered outliers, and outliers are plotted individually. In each bin the values with differences larger than three standard deviations from the mean of the bin have been removed from the calculation. The number of simultaneous measurements in each bin is summarized in Table 7.

5 Conclusions

Physical models of the Dobson instrument and two types of Brewer spectrophotometer were developed to help better understand the effects of stray light on ozone measurements. The influence of assuming a fixed ozone layer height on air mass calculations and the difference caused by this assumption its error contribution to the ozone retrieval were also examined. The target accuracy for ground-based ozone measurements is 1 %, while mathematical physical models show that the stray light effect can cause a discrepancy for a typical single Brewer and Dobson AD pair at large ozone slant paths of up to 5 % and 25 %, respectively. At 2000 DU OSP the difference for a double Brewer and a Dobson CD pair with minimum level of stray light (10^{-5}) is up to 0.8 % and 1.8 %, respectively. This effect restricts measurements at high latitudes, like such as polar stations, particularly in the late winter and early spring when the ozone slant column is particularly large. It is considerably important if those data are to be used for trend analysis. In particular, if such a data is used in the case where Dobsons or single Brewers are replaced by double Brewers, a significant false positive trend in ozone may result.

Stray light also can affect the calculation of ozone absorption coefficients. Currently, an approximation method is used to calculate the absorption coefficients for Brewer instruments. The analysis shows that using a measured slit function (instead of an idealized trapezoidal one) and taking into account the solar spectrum, leads to a 0.7 % difference in calculated coefficients for a typical single Brewer.

The analysis shows that using a modeled trapezoid slit function with stray light (instead of an idealized trapezoidal one) and taking into account the solar spectrum, leads to a difference of 0.7 % and 0.9 % in calculated coefficients for a typical double and single Brewer, respectively.

Absorption coefficients for the Dobson spectrophotometers, taking into account the effect of stray light, have been calculated and compared with the results of similar calculations by K93, which are the coefficients recommended by WMO. The slit functions of Dobson #83 have been measured using a tunable light source (K93). Recently, the measured slit functions and calculated coefficients are verified by measuring the slit functions of three Dobsons (#74, #64, and #83) at the Physikalisch-Technische Bundesanstalt (PTB) in Braunschweig in 2015 and at the Czech Metrology Institute (CMI) in Prague in 2016 within the EMRP ENV 059 project “Traceability for atmospheric total column ozone” (Köhler et al., 2018). Köhler et al. (2018) showed that the optical properties of these three Dobsons deviate from the specification described by G. M. B.

Dobson. However, the AD pair ozone absorption coefficents derived from new slit functions lead to less than 1 % deviation in total ozone column values. It is generally assumed that the slit functions of other Dobson spectrophotometers are similar to the standard one (#83). For the study presented here, the slit functions were modeled to examine the effect of stray light on the calculation of ozone absorption coefficients. The results show that 10^{-5} level of stray light has negligible effect on absorption coefficient calculations while the difference could be up 4.0 % and 6.9 % for AD and CD coefficients for an instrument with 10^{-4} level of stray light.

Coefficients for a Dobson with a minimum expected level of stray light (10^{-5}) agree to within $\pm$0.01 % and $\pm$1.7 % for $\Delta\bar{\alpha}_{AD}$ and $\Delta\bar{\alpha}_{CD}$ with K93 respectively, noting that the slit functions and parameters used by K93 and in this work (Table 1Tables 1 and Table 2 2) are slightly different. The calculation for $\bar{\alpha}_{339.9}$$\bar{\alpha}(339.9)$ shows a 67 % difference with K93's result leading to differences of 3.4 %, and -1.7 % in $\Delta\bar{\alpha}_{D}$, and $\Delta\bar{\alpha}_{CD}$. B05 also have found approximately the same difference for this value ($\bar{\alpha}(339.9)$ $\bar{\alpha}_{339.9}$) with K93's calculation. They concluded that K93's value for this wavelength is unreasonably large and likely caused by an error in K93's calculation. The adjusted value for $\Delta\bar{\alpha}_{D}$ recommended by WMO is K93's $\Delta\bar{\alpha}_{D}$ value, but increased by 2 %. The differences between the calculations in this work (using an ideal slit function and a slit function with 10^{-5} level of stray light) and the WMO values are 1.6 %, 0.5 %, and -2.6 % for $\Delta\bar{\alpha}_{D}$, $\Delta\bar{\alpha}_{AD}$, and $\Delta\bar{\alpha}_{CD}$, respectively.

Using modeled slit functions with 10^{-4} level of stray light, up to -3.5 %, and -7.2 % differences between calculated coefficients and WMO values for $\Delta\bar{\alpha}_{AD}$ and $\Delta\bar{\alpha}_{CD}$ are found. Overestimating the $\Delta\bar{\alpha}$ values translates to an underestimation of total ozone. However, it should be noted that the difference between Dobson AD values of the standard instrument and a calibrated one were reduced through the calibration procedure.

When quasi-simultaneous measurements are made using Dobson AD and CD wavelengths, the results may not agree. For decades the Dobson community has faced such differences. The AD pair is the standard for Dobson measurements and the observations using other pairs' data should be scaled to the AD pair before release. Our analysis indicates that the difference between quasi-simultaneous measurements using AD and CD pairs is related to the level of stray light inside each Dobson instrument. Higher levels of stray light lead to larger differences between the values deduced from AD and CD wavelengths.

Both Brewer and Dobson retrievals assume a fixed height for the ozone layer to calculate the ozone air mass. A fixed height of 22 km is used by the Brewer network for all sites while a variable ozone layer height changing with latitude is employed by the Dobson community. The assumption of a 22 km height for the ozone layer at the South Pole, compared to the 17 km height used in the Dobson analysis, leads to a 2.2 % difference in ozone column at an air mass of 5.4.

Comparisons with total ozone data from a double Mark III Brewer spectrophotometer located at the South Pole indicate some dependence on OSP for the Dobson measurements. For the OSPs below 800 DU the AD vales are generally 1 % higher. However, for OSPs larger than 800 DU the Dobson AD measurements are lower by up to 4 % at 1400 DU OPS.

The observations made at the CD wavelengths also show some dependence on OSP. Compared to Brewer data, the CD values are, on average, 4 % higher for almost the entire range of measurements. However, as is the case for the AD pair, the CD pair values also decrease at larger OSPs. It should be noted that the Dobson AD and CD pair measurements are not reported for air mass factors above 2.5 and 3.5 respectively due to the effect of stray light.

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References

Bais, A. F., Zerefos, C. S., and McElroy, C. T.: Solar UVB measurements with the double- and single-monochromator Brewer ozone spectrophotometers, Geophys. Res. Lett., 23(8), 833–836, doi:10.1029/96GL00842, 1996.

Barnes, J., and Mauersberger, K.: Temperature Dependence of the Ozone Absorption Cross Section at the 253.7-nm Mercury Line, J. Geophys. Res., 92(D12), 14861–14864, 1987.

Basher, R. E.: Review of the Dobson Spectrophotometer and its Accuracy, WMO Global Ozone Research and Monitoring Project, Report No. 13, World Meteorological Organization, Geneva, Switzerland, 1982.

Bass, A. M., and Paur, R. J.: The Ultraviolet Cross-Sections of Ozone: I. The Measurements, In Atmospheric Ozone, Springer, Netherlands, 606–610, doi:10.1007/978-94-009-5313-0_120, 1985.

Bates, D. R.: Rayleigh-scattering by air, Planet. Space Sci., 32(6), 785–790, doi:10.1016/0032-0633(84)90102-8, 1984.

Bernhard, G., Evans, R. D., Labow, G. J., and Oltmans, S. J.: Bias in Dobson total ozone measurements at high latitudes due to approximations in calculations of ozone absorption coefficients and air mass, J. Geophys. Res., 110, D10305, doi:10.1029/2004JD005559, 2005.

Bhartia, P. K., Silberstein, D., Monosmith, B., and Fleig, A. J.: Standard profiles of ozone from ground to 60 km obtained by combining satellite and ground based measurements, In Atmospheric Ozone, Springer, Netherlands, 243–247, 1985.

Brion, J., Chakir, A., Daumont, D., Malicet, J., and Parisse, C.: High-resolution laboratory absorption cross section of O3. Temperature effect, Chem. Phys. Lett., 213(5–6), 610–612, doi:10.1016/0009-2614(93)89169-I, 1993.

Chance, K., and Kurucz, R. L.: An improved high-resolution solar reference spectrum for earth's atmosphere measurements in the ultraviolet, visible, and near infrared, J. Quant. Spectrosc. Radiat. Transf., 111(9), 1289–1295, doi:10.1016/j.jqsrt.2010.01.036, 2010.

Christodoulakis, J., Varotsos, C., Cracknell, a. P., Tzanis, C., and Neofytos, A.: An assessment of the stray-light in 25 years Dobson total ozone data at Athens, Greece, Atmos. Meas. Tech., 8, 3037–3046, doi:10.5194/amt-8-3037-2015, 2015.

Daumont, D., Brion, J., Charbonnier, J., and Malicet, J.: Ozone UV spectroscopy I: Absorption cross-sections at room temperature, J. Atmos. Chem., 15(2), 145–155, doi:10.1007/BF00053756, 1992.

Dobson, G. M. B.: A Photoelectric spectrophotometer for measuring the amount of atmospheric ozone, In Proceedings of the Physical Society, Vol. 43, 324–339, doi:10.1088/0959-5309/43/3/308, 1931.

Evans, R., and Komhyr, W.: Operations Handbook - Ozone Observations with a Dobson Spectrophotometer, WMO/GAW Report No. 183, World Meteorological Organization, Geneva, Switzerland, 2008.

Evans, R., McConville, G., Oltmans, S., Petropavlovskikh, I., and Quincy, D.: Measurement of internal stray light within Dobson ozone spectrophotometers, Int. J. Remote Sens., 30(15), 4247–4258, doi:10.1080/01431160902825057, 2009.

Evans, R., Petropavlovskikh, I., Mcclure-begley, A., Mcconville, G., and Quincy, D.: Technical note : The US Dobson station network data record prior to 2015 , re-evaluation of NDACC and WOUDC archived records with WinDobson processing software, , 12051–12070, 2017.

Fioletov, V. E., Kerr, J. B., McElroy, C. T., Wardle, D. I., Savastiouk, V., and Grajnar, T. S.: The Brewer reference triad, Geophys. Res. Lett., 32, L20805, doi:10.1029/2005GL024244, 2005.

Fragkos, K., Bais, A. F., Balis, D., Meleti, C., and Koukouli, M. E.: The Effect of Three Different Absorption Cross-Sections and their Temperature Dependence on Total Ozone Measured by a Mid-Latitude Brewer Spectrophotometer, Atmosphere-Ocean, 1–10, doi:10.1080/07055900.2013.847816, 2013.

Furukawa, P. M., Haagenson, P. L., and Scharberg, M. J.: A Composite, High-Resolution Solar Spectrum from 2080 to 3600 A, NCAR TN-26, National Center for Atmospheric Research, Boulder, Colo., 1967.

Gröbner, J., Wardle, D. I., McElroy, C. T., and Kerr, J. B.: Investigation of the wavelength accuracy of brewer spectrophotometers., Appl. Opt., 37(36), 8352–60, doi:10.1364/AO.37.008352, 1998.

Josefsson, A. P.: Focused Sun Observations Using a Brewer Ozone Spectrophotometer, J. Geophys. Res., 97(D14), 15813–15817, 1992.

Karppinen, T., Redondas, A., García, R. D., Lakkala, K., McElroy, C. T., and Kyrö, E.: Compensating for the Effects of Stray Light in Single-Monochromator Brewer Spectrophotometer Ozone Retrieval, Atmosphere-Ocean, 1–8, doi:10.1080/07055900.2013.871499, 2014.

Kerr, J. B.: New methodology for deriving total ozone and other atmospheric variables from Brewer spectrophotometer direct sun spectra, J. Geophys. Res., 107(23), 1–17, doi:10.1029/2001JD001227, 2002.

Kerr, J. B., Asbridge, I. A., and Evans, W. F. J.: Intercomparison of total ozone measured by the Brewer and Dobson spectrophotometers at Toronto, J. Geophys. Res., 93(D9), 11129–11140, doi:198810.1029/JD093iD09p11129, 1988.

Kerr, J. B., McElroy, C. T., and Olafson, R. A.: Measurements of ozone with the Brewer ozone spectrophotometer, In Quadrennial Ozone Symposium, National Center for Atmospheric Research, Boulder, Colo., 74–79, 74–79, 1981.

Kiedron, P., Disterhoft, P., and Lantz, K.: NOAA-EPA Brewer network Stray Light Correction, , NOAA Earth System Research Laboratory, Retrieved from http://www.esrl.noaa.gov/gmd/grad/ neubrew/docs/StrayLightCorrection.pdf 2008.

Köhler, U., Nevas, S., McConville, G., Evans, R., Smid, M., Stanek, M., Redondas, A., and Schönenborn, F.: Optical characterisation of three reference Dobsons in the ATMOZ Project - Verification of G. M. B. Dobson's original specifications, Atmos. Meas. Tech., 11(4), 1989–1999, doi:10.5194/amt-11-1989-2018, 2018.

Komhyr, W. D., Mateer, C. L., and Hudson, R. D.: Effective Bass-Paur 1985 Ozone Absorption Coefficients for Use With Dobson Ozone Spectrophotometers, J. Geophys. Res., 98(D11), 20451–20456, doi:10.1029/93JD00602, 1993.

Lantz, K., Disterhoft, P., Early, E., Thompson, A., Deluisi, J., Berndt, J., Harrison, L., Kiedron, P., Ehramjian, J., Bernhard, G., Cabasug, L., Robertson, J., Mou, W., Taylor, T., Slusser, J., Bigelow, D., Durham, B., Janson, G., Hayes, D., Beaubien, M., and Beaubien, A.: The 1997 North American Interagency Intercomparison of Ultraviolet Spectroradiometers Including Narrowband Filter Radiometers, J. Res. Natl. Institue Stand. Technol., 107, 19–62, 2002.

Liu, X., Chance, K., Sioris, C. E., and Kurosu, T. P.: Impact of using different ozone cross sections on ozone profile retrievals from Global Ozone Monitoring Experiment (GOME) ultraviolet measurements, Atmos. Chem. Phys., 7(13), 3571—3578, doi:10.5194/acp-7-3571-2007, 2007.

Malicet, J., Daumont, D., Charbonnier, J., Parisse, C., Chakir, A., and Brion, J.: Ozone UV spectroscopy. II. Absorption cross-sections and temperature dependence, J. Atmos. Chem., 21(3), 263–273, doi:10.1007/BF00696758, 1995.

Molina, L. T., and Molina, M. J.: Absolute absorption cross sections of ozone in the 185-to 350-nm wavelength range, J. Geophys. Res. Atmos., 91(D13), 14501–14508, 1986.

Pulli, T., Karppinen, T., Nevas, S., Kärhä, P., Lakkala, K., Karhu, J. M., Sildoja, M., Vaskuri, A., Shpak, M., Manoocheri, F., Doppler, L., Gross, S., Mes, J., and Ikonen, E.: Out-of-Range Stray Light Characterization of Single-Monochromator Brewer Spectrophotometers, Atmosphere-Ocean, 56(1), 1–11, doi:10.1080/07055900.2017.1419335, 2018.

Redondas, A., Evans, R., Stuebi, R., Köhler, U., and Weber, M.: Evaluation of the use of five laboratory-determined ozone absorption cross sections in Brewer and Dobson retrieval algorithms, Atmos. Chem. Phys., 14(3), 1635–1648, doi:10.5194/acp-14-1635-2014, 2014.

Scarnato, B., Staehelin, J., Peter, T., Gröbner, J., and Stübi, R.: Temperature and slant path effects in Dobson and Brewer total ozone measurements, J. Geophys. Res., 114, D24303, doi:10.1029/2009JD012349, 2009.

Scarnato, B., Staehelin, J., Stübi, R., and Schill, H.: Long-term total ozone observations at Arosa (Switzerland) with Dobson and Brewer instruments (1988–2007), J. Geophys. Res., 115, D13306, doi:10.1029/2009JD011908, 2010.

Serdyuchenko, A., Gorshelev, V., Weber, M., Chehade, W., and Burrows, J. P.: High spectral resolution ozone absorption cross-sections – Part 2: Temperature dependence, Atmos. Meas. Tech, 7, 625–636, doi:10.5194/amt-7-625-2014, 2014.

Staehelin, J., Kegel, R., and Harris, N.: Trend analysis of the homogenized total ozone series of Arosa (Switzerland), 1926-1996, J. Geophys. Res., 103(D3), 8400–8389, doi:10.1029/97JD03650, 1998.

Staehelin, J., Kerr, J. B., Evans, R., and Vanicek, K.: Comparison of total ozone measurements of Dobson and Brewer spectrophotometers and recommended transfer functions, WMO/GAW Report No. 149, World Meteorological Organization, Geneva, Switzerland, 2003.

Van Roozendael, M., Peeters, P., Roscoe, H. K., De Backer, H., Jones, A. E., Bartlett, L., Vaughan, G., Goutail, F., Pommereau, J. P., Kyro, E., Wahlstrom, C., Braathen, G., and Simon, P. C.: Validation of ground-based visible measurements of total ozone by comparison with Dobson and Brewer spectrophotometers, J. Atmos. Chem., 29(1), 55–83, doi:10.1023/A:1005815902581, 1998.

Vanicek, K.: Differences between ground Dobson, Brewer and satellite TOMS-8, GOME-WFDOAS total ozone observations at Hradec Kralove, Czech, Atmos. Chem. Phys., 6, 5163–5171, doi:10.5194/acpd-6-5839-2006, 2006.

Vanier, J., and Wardle, D. I.: The effects of spectral resolution on total ozone measurements, Q. J. R. Meteorol. Soc., 95(404), 395–399, doi:10.1002/qj.49709540411, 1969.

Table 1: Brewer and Dobson optical parameters

	Brewer	Dobson
Nominal Wavelengths (nm)	310.05, 313.50, 316.80, 320.00	A: 305.5/325.0, C: 311.5/332.40, D: 317.5/339.9
Slit Function	Single~~:~~ trapezoid at centre 0.539,0.555,0.545,0.538 ~~0.55~~ nm FWHM, Lorentzian fitted to the measured slit of #009 for shoulders Double: trapezoid at centre 0.539,0.555,0.545,0.538 ~~0.55~~ nm FWHM, Lorentzian fitted to the measured slit of #119 for shoulders	Short Channels: trapezoid 1.66, 1.84, 2.02 nm at the base and 0.16, 0.16, 0.16 nm at the top Long Channels: trapezoid 4.60, 5.40, 5.75 nm at the base and 2.35, 2.50, 2.50 nm at the top
Stray light level	Single: ~ 1×10^{-4} Double: ~ 1×10^{-6}	1×10^{-5} and 1×10^{-4}
Filters	Single: UG-11 and NiSO4 filters – Zero below 280 and above ~330 nm Double: PMT sensitivity - Zero below 250nm and above 800 nm	Cobalt filter - zero above ~360 nm

Table 2: Parameters for calculation of ozone absorption coefficients.

Parameter	Komhyr et al. (1993)	This Work
Slit function	Measured slit functions (Fig. 1 of Komhyr et al. (1993))	Dobson: Parameterized from Fig. 1 of Komhyr et al. (1993) (Details in Table 1~~Table 1~~) Brewer: Parameterized from laser scan of #009 and #119 (Details in Table 1~~Table 1~~)
Effective temperature	-46.3º C	-46.3º C
Solar spectrum	Furukawa et al. (1967)	Chance and Kurucz (2010)*
Ozone cross-sections	Bass and Paur (1985)	Bass and Paur (1985)
Rayleigh Scattering	Bates (1984)	Bates (1984)
Ozone profile	Bhartia et al. (1985) for 45º N and 325 DU	Bhartia et al. (1985) for 45º N and 325 DU
Air mass	2	2

* For this study the wavelength range of 285-363 nm is used for calculations.

Table 3: Ozone absorption coefficients calculated here and the value calculated by Redondas et al. (2014)

		$\bar{\alpha}^{apx}(\lambda_i)$ (atm cm^{-1}) calculated for Double Brewer using ideal slits and BP cross-sections at -45 ^{o}C without Barnes (1987) correction	From Redondas (2014) Table 6; effective ozone absorption coefficient calculated using IQG4 B&P cross-sections
		Ideal (trapezoid)	Ideal (trapezoid)
Wavelength (nm)	FWHM (nm)	$\bar{\alpha}^{apx}(\lambda_i)$	$\bar{\alpha}^{apx}(\lambda_i)$
310.05	0.539	1.0044	
313.50	0.555	0.6793	
316.80	0.545	0.3760	
320.00	0.538	0.2935	
$\Delta\bar{\alpha}^{apx}$		0.3365	0.3367

Table 4: Single Brewer ozone absorption coefficients

		Ideal		Model (with Stray light)	
Wavelength (nm)	FWHM (nm)	$\bar{\alpha}^{apx}(\lambda_i)$	$\bar{\alpha}(\lambda_i)$	$\bar{\alpha}^{apx}(\lambda_i)$	$\bar{\alpha}(\lambda_i)$
310.05	0.539	1.0087	1.0127	1.0141	1.0102
313.50	0.555	0.6824	0.6842	0.6828	0.6833
316.80	0.545	0.3774	0.3789	0.3768	0.3789
320.00	0.538	0.2944	0.2962	0.2923	0.2959
$\Delta\bar{\alpha}^{apx} or \Delta\bar{\alpha}$		0.3377	0.3406	0.3407	0.3380

*BP cross-sections at -46.3 with Barnes (1987) correction.

Table 5: Double Brewer ozone absorption coefficients

		Ideal		Model (with Stray light)	
Wavelength (nm)	FWHM (nm)	$\bar{\alpha}^{apx}(\lambda_i)$	$\bar{\alpha}(\lambda_i)$	$\bar{\alpha}^{apx}(\lambda_i)$	$\bar{\alpha}(\lambda_i)$
310.05	0.539	1.0087	1.0127	1.0089	1.0126
313.5	0.555	0.6824	0.6842	0.6826	0.6841
316.8	0.545	0.3773	0.3789	0.3776	0.3789
320	0.538	0.2947	0.2962	0.2950	0.2962
$\Delta\bar{\alpha}^{apx} or \Delta\bar{\alpha}$		0.3384	0.3406	0.3384	0.3405

*BP cross-sections at -46.3 with Barnes (1987) correction.

Table 3: Brewer Ozone Absorption Coefficients

		Effective Ozone Absorption Coefficient (cm^{-1})			
		Operational	Slit Function: Ideal	Slit Function: Model	Ratio *
Single	$\bar{\alpha}_i^{approx}$	0.3390	0.3388	0.3409	0.994
	$\bar{\alpha}_i$		0.3398	0.3363	1.011
	$\bar{\alpha}_i^{approx}/\bar{\alpha}_i$		0.997	1.014	**1.007**
Double	$\bar{\alpha}_i^{approx}$	0.3395	0.3394	0.3394	1.000
	$\bar{\alpha}_i$		0.3398	0.3397	1.000
	$\bar{\alpha}_i^{approx}/\bar{\alpha}_i$		0.999	0.999	**0.999**

* Ideal/Model

Table 664: Dobson wavelengths and Ozone Absorption coefficients

	Effective Ozone Absorption Coefficient (atm cm)$^{-1}$								
	Komhyr et al. (1993)			This Work					
				Model (Ideal)		Model (10^{-5})*		Model (10^{-4})	
Wavelength, nm or pair	$\bar{\alpha}_i^{apx}$ $\bar{\alpha}^{apx}(\lambda_i)$	$\bar{\alpha}_i$ $\bar{\alpha}(\lambda_i)$	$\bar{\alpha}_i^{adj}$ $\bar{\alpha}^{adj}(\lambda_i)$	$\bar{\alpha}_i^{apx}$ $\bar{\alpha}^{apx}(\lambda_i)$	$\bar{\alpha}_i$ $\bar{\alpha}(\lambda_i)$	$\bar{\alpha}_i^{apx}$ $\bar{\alpha}^{apx}(\lambda_i)$	$\bar{\alpha}_i$ $\bar{\alpha}(\lambda_i)$	$\bar{\alpha}_i^{apx}$ $\bar{\alpha}^{apx}(\lambda_i)$	$\bar{\alpha}_i$ $\bar{\alpha}(\lambda_i)$
305.5	1.917	1.915		1.912	1.930	1.913	1.929	1.867	1.870
325	0.115	0.109		0.114	0.111	0.114	0.111	0.119	0.111
A	1.802	1.806	1.806	1.799	1.819	1.799	1.818	1.748	1.759
311.5	0.87	0.873		0.867	0.879	0.868	0.879	0.848	0.846
332.4	0.039	0.04		0.041	0.042	0.041	0.042	0.042	0.042
C	0.831	0.833	0.833	0.826	0.838	0.827	0.838	0.806	0.804
317.5	0.379	0.384		0.383	0.390	0.384	0.390	0.393	0.387
339.9	0.01	0.017		0.010	0.010	0.010	0.010	0.010	0.011
D	0.369	0.367	0.374	0.373	0.380	0.374	0.380	0.382	0.376
AD	1.433	1.439	1.432	1.426	1.439	1.425	1.438	1.366	1.383
CD	0.462	0.466	0.459	0.453	0.458	0.452	0.458	0.424	0.428

* The numbers inside the braces are showing the levels of stray light.

Table 7: The number of simultaneous measurements in each bin

	Dobson #82		Dobson #42		Dobson #80	
Bins (OSP)	AD	CD	AD	CD	AD	CD
[400 500)	39	33	0	0	45	41
[500 600)	171	143	7	0	63	63
[600 700)	172	113	101	70	57	72
[700 800)	439	313	258	179	11	8
[800 900)	174	235	153	178	5	6
[900 1000)	155	120	30	54	0	1
[1000 1100)	96	125	57	28	0	0
[1100 1200)	4	50	46	67	7	4
[1200 1300)	0	41	36	46	0	2
[1300 1400)	0	43	4	49	3	2
[1400 1500)	0	36	0	19	0	1
[1500 1600)	0	19	0	4	0	0
[1600 1700)	0	6	0	1	0	0
[1700 1800)	0	9	0	1	0	0
[1800 1900)	0	0	0	10	0	0
[1900 2000)	0	0	0	0	0	0
Total	1250	1286	692	706	191	200

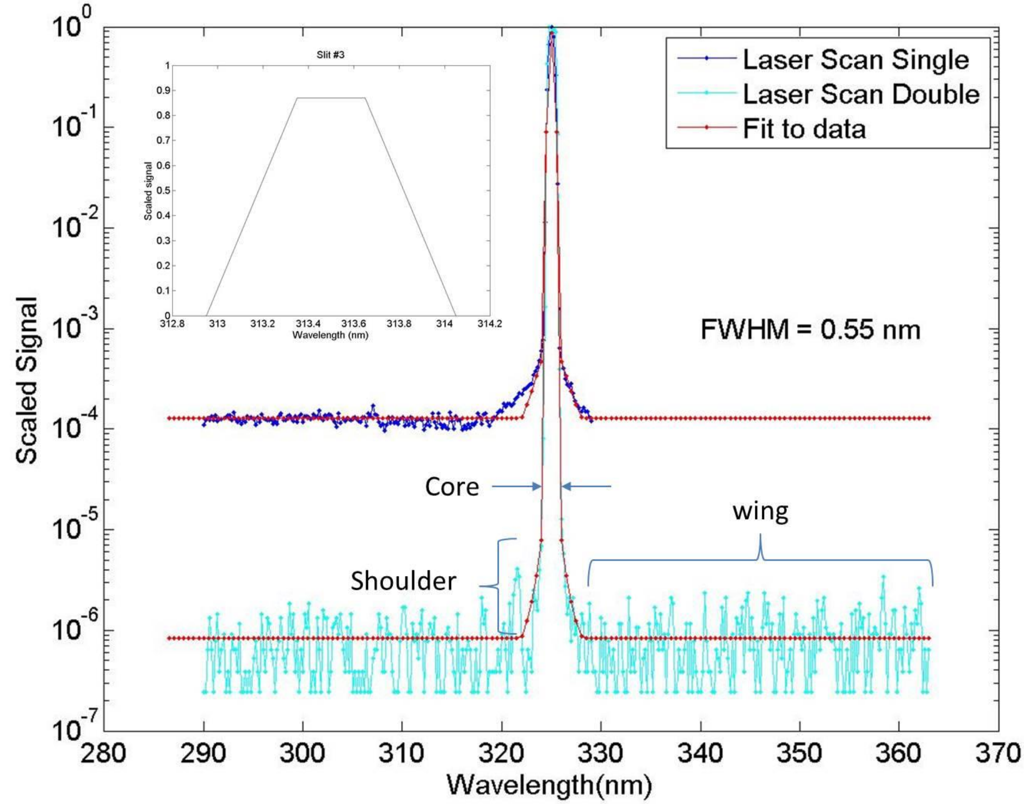
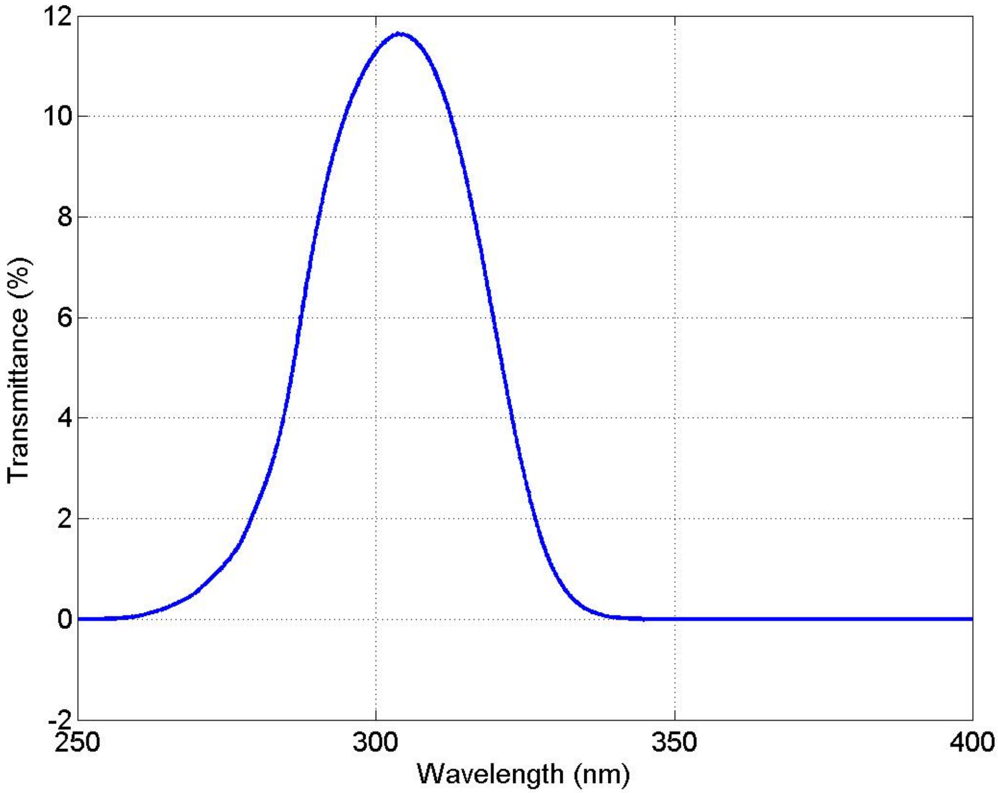


Figure 1: Slit functions measured with a He-Cd laser for single #009 and double #119 Brewers at Mauna Loa as well as fitted models; The ideal slit function is also shown inside the main graph.


12
10
8
6
4
2
0
-2
Transmittance (%)
250
300
350
400
Wavelength (nm)

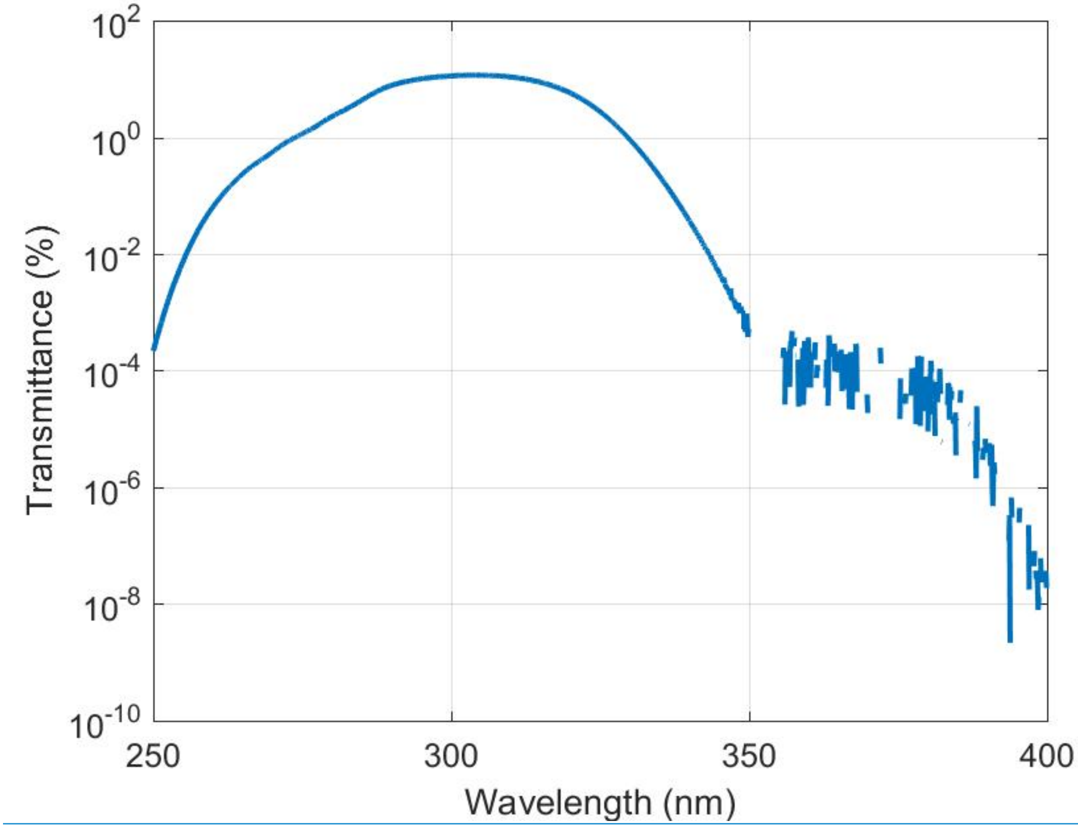


Figure 2: The transmission of a typical combined UG11-$NiSO_4$ filter utilized by Brewer Mark IV to reduce the stray light measured with a Cary 5E spectrophotometer for Brewer #154 filters.

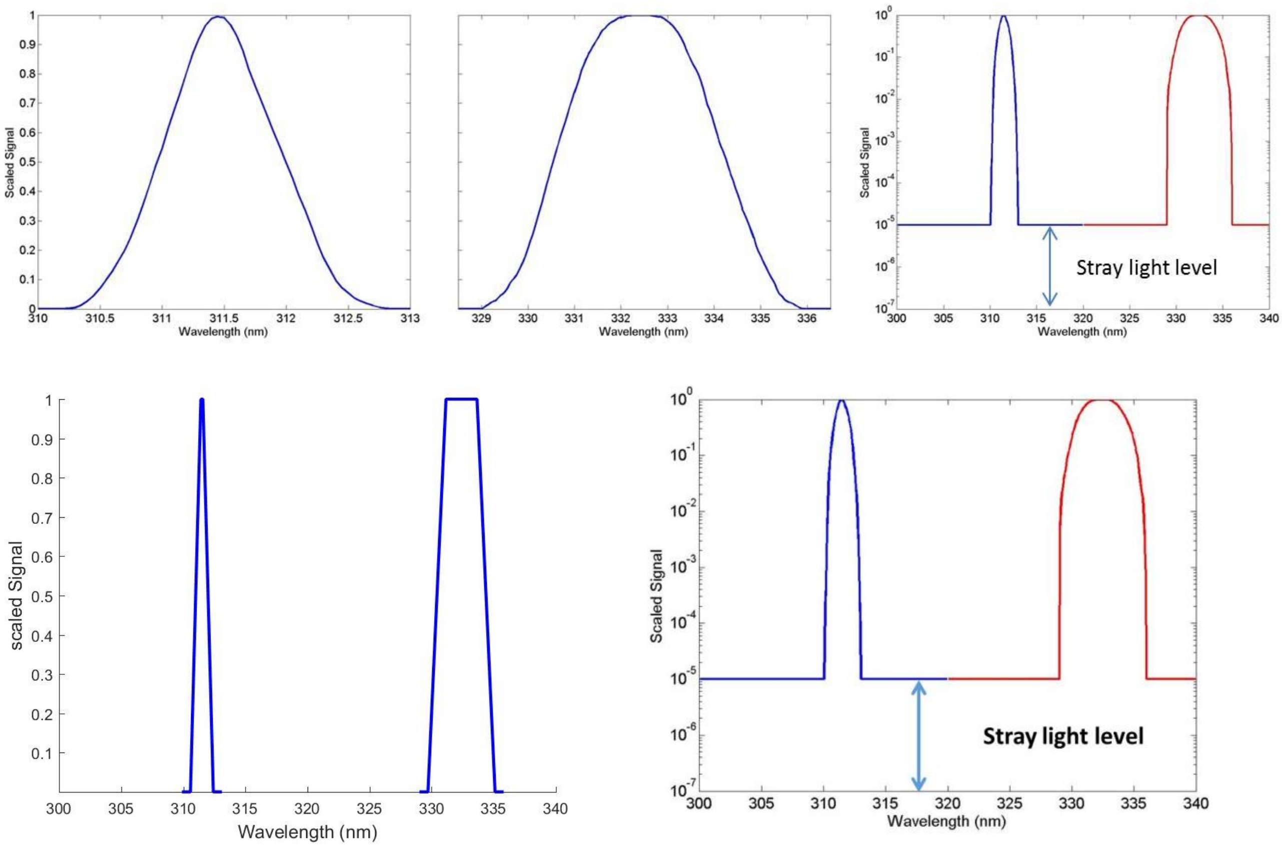


Figure 3: Dobson C-pair ideal slit functions (Left~~ and middle~~) parameterised from Figure 1 of Komhyr 1993. Dobson Modelled slit function (right). Two straight lines have been added to the core slit functions in order to account for stray light.

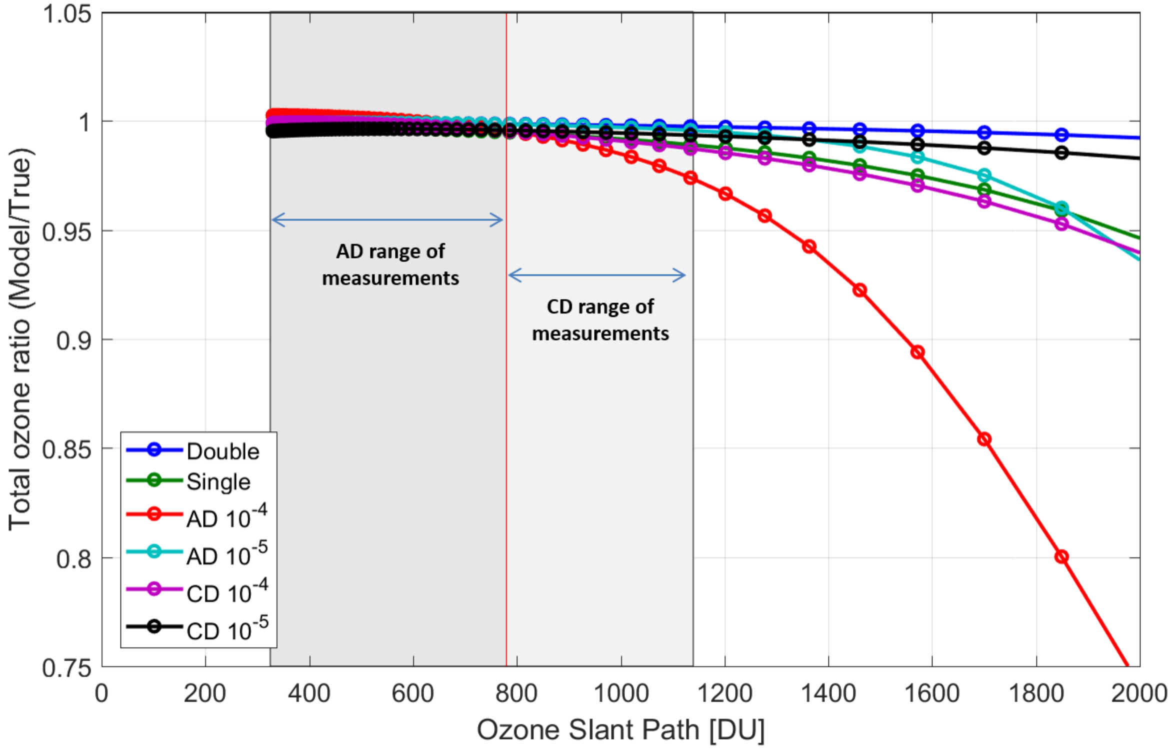


Figure 4: Ratio of the values retrieved from modeled single and double Brewers as well as a Dobson instrument with different levels of stray light (the numbers in front of the pairs are showing the levels of stray light) to assumed 325 DU ozone in the atmosphere (See text for details). The calculations reported in this study for the absorption coefficients have been used to retrieve total ozone. It should be noted that the air mass factor range recommended for AD measurements is 1.015 to 2.5 or less than 800 DU OSP and for CD measurements is 2.4 to 3.5 or less than 1200 DU OSP (Evans and Komhyr, 2008)**.**

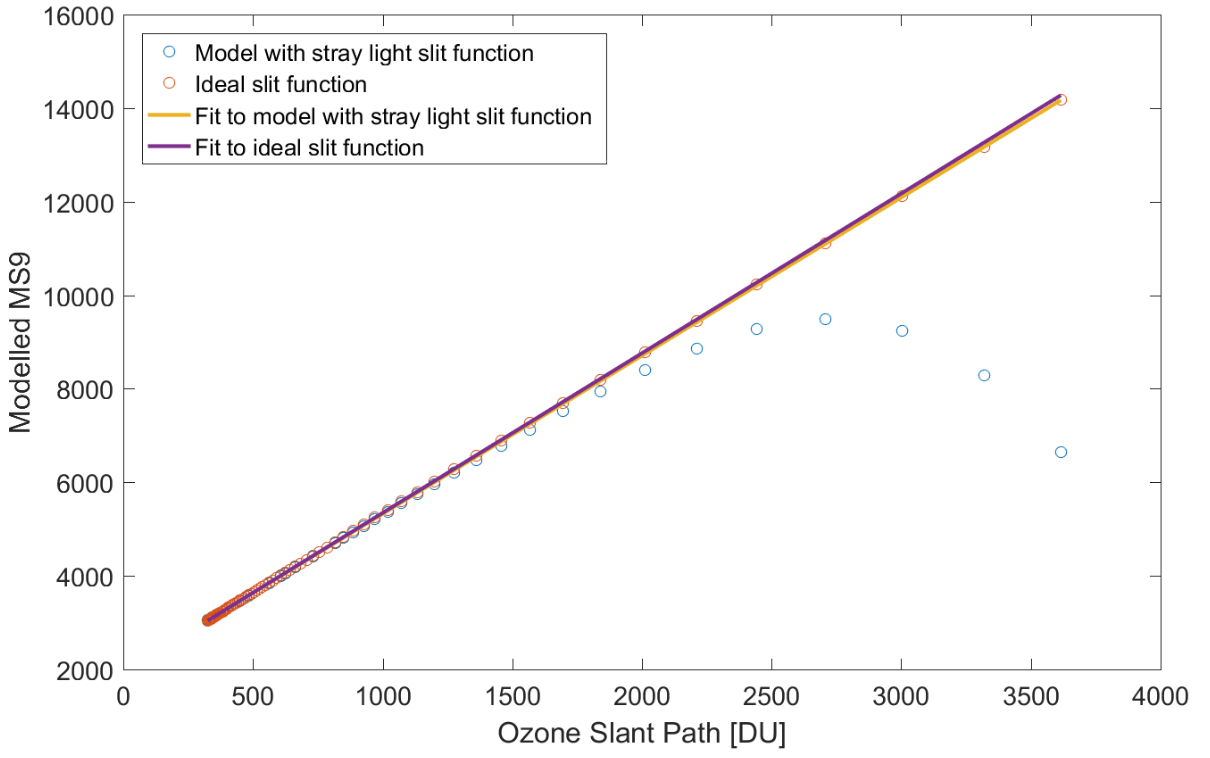


Figure 5: Example of Langley plot fitted to a modelled single Brewer data.

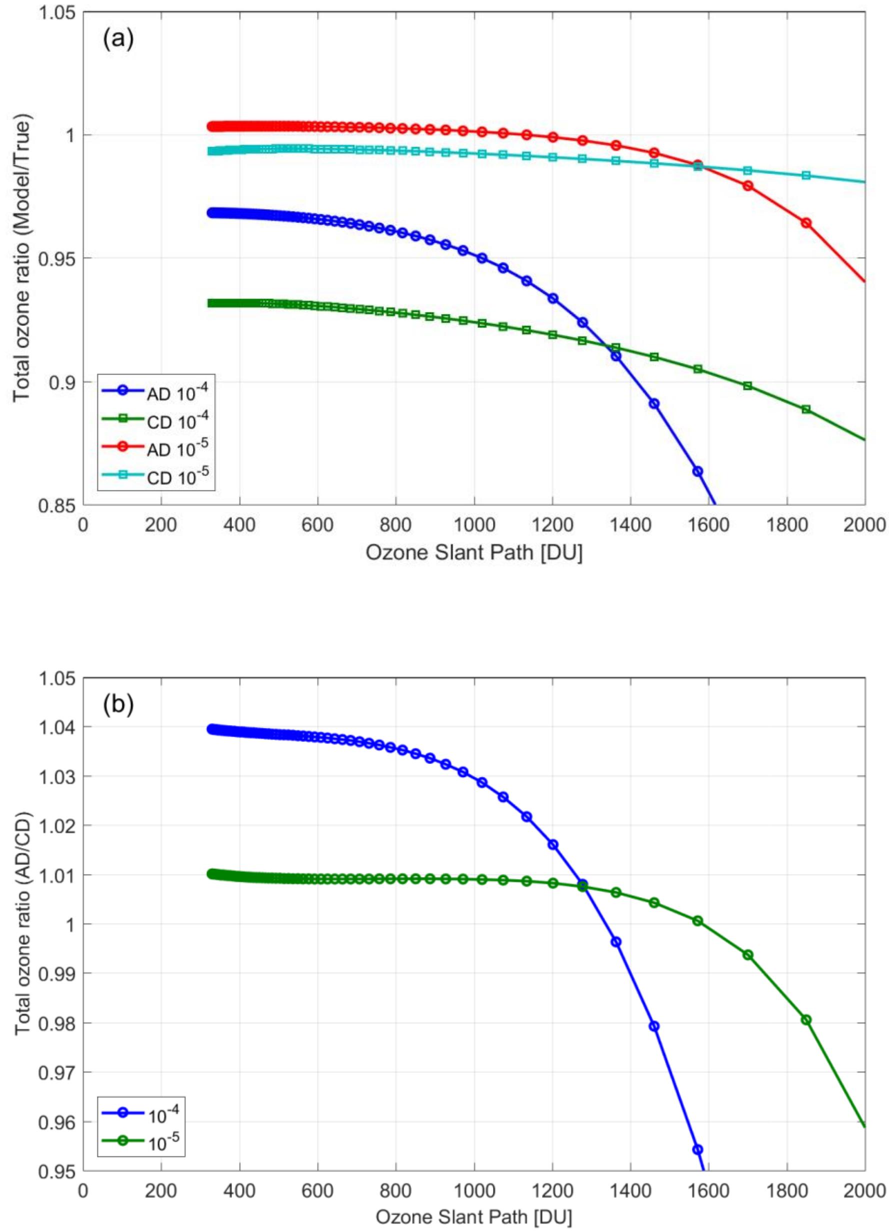


Figure 665: (a) The ratio of total ozone retrieved from modelled Dobson AD and CD pairs with different levels of stray light (10^{-4} and 10^{-5}) to true ozone as a function of OSP. (b) The ratio of total ozone retrieved from AD to CD wavelength pairs. The adjusted coefficients recommended by WMO are used to derive the total ozone amounts for these models. The ETC values calculated using the Langley method for an ideal instrument are used here as well.

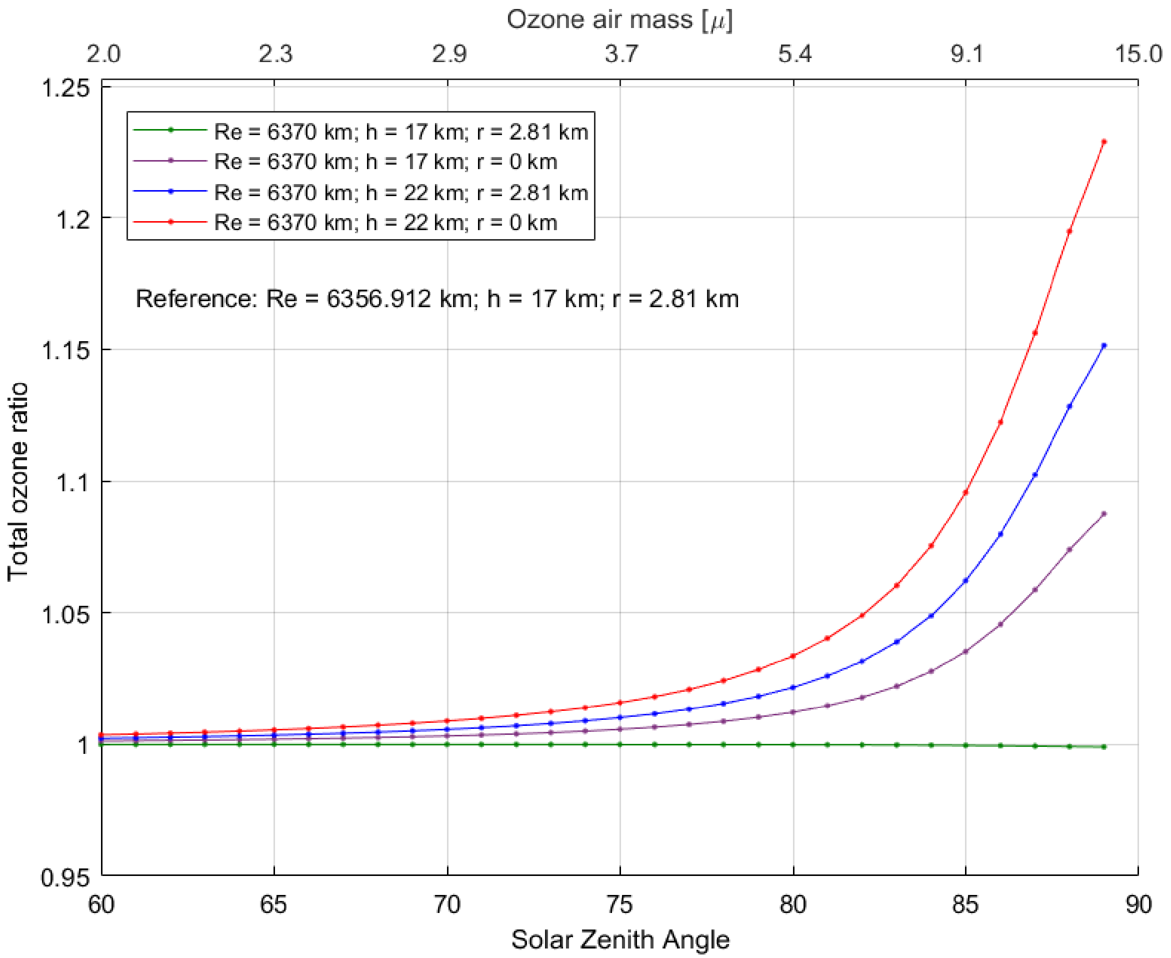


Figure 776: The ratio of total ozone retrieved from modelled Dobson using air mass factors calculated with a mean value for the radius of the Earth, *Re* = 6370 km as used in the Brewer retrieval, and different values for the altitude of site, '*r*', and the height of ozone layer, '*h*', to the ozone values retrieved using air mass factors calculated for the South Pole employing *Re* = 6356.912 km, *r* = 2.81 km, and *h* = 17 km as a reference. Any discrepancy in the air mass is directly reflected in the Dobson and Brewer retrieved total ozone via Eqs. (3) and (9) respectively.

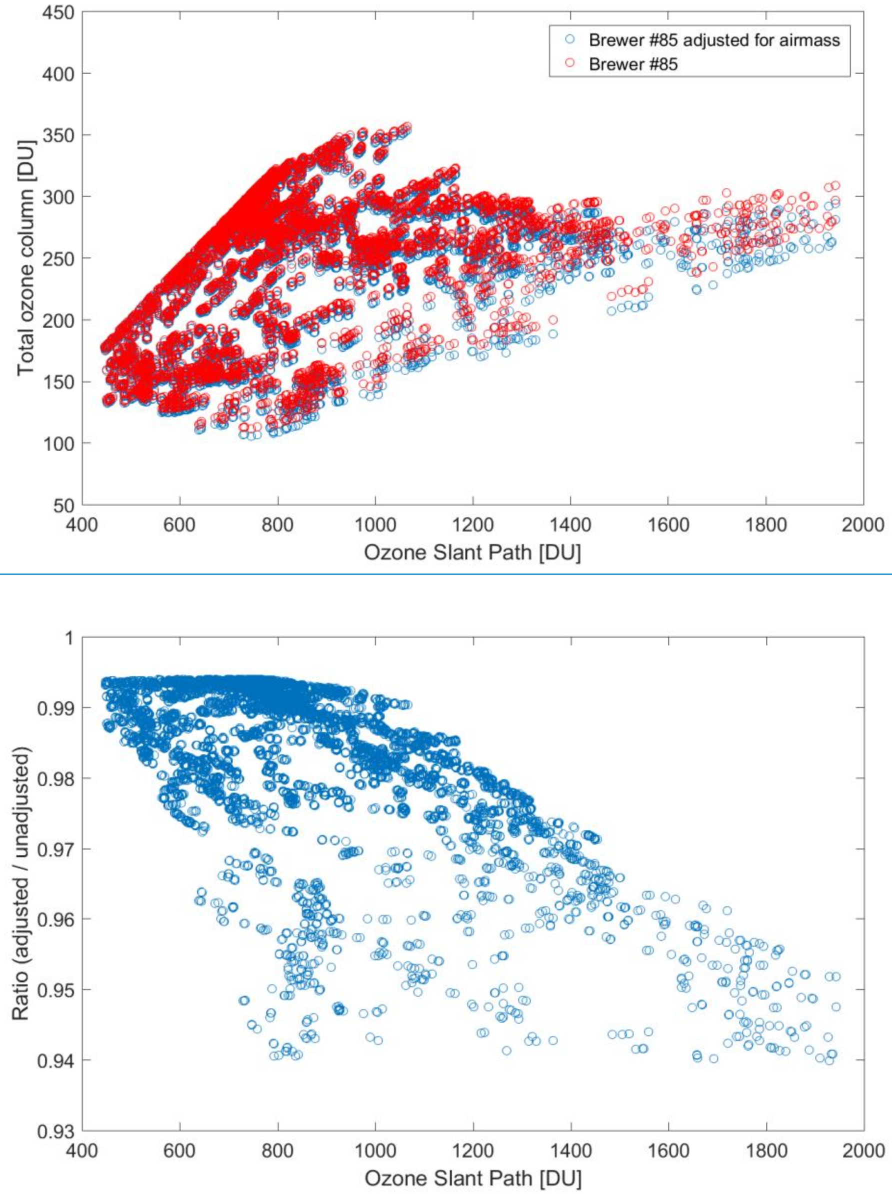
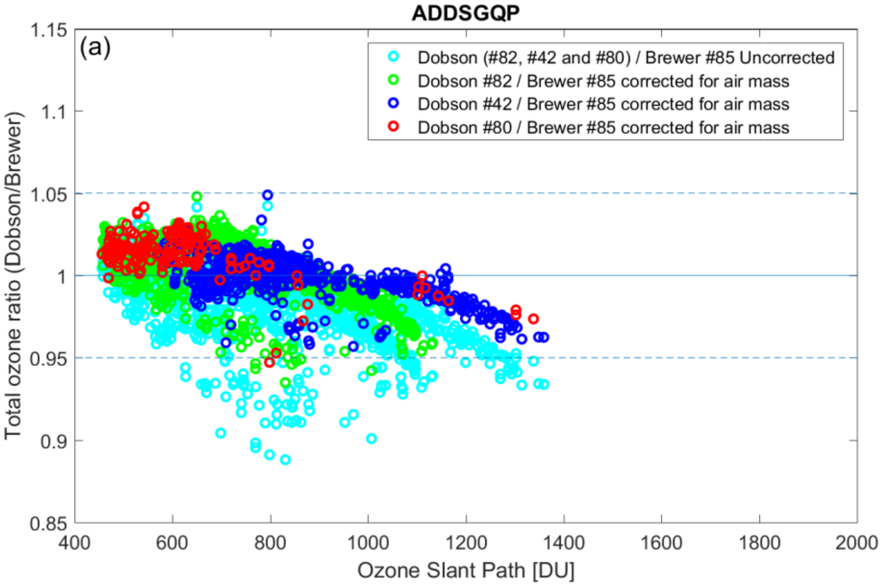
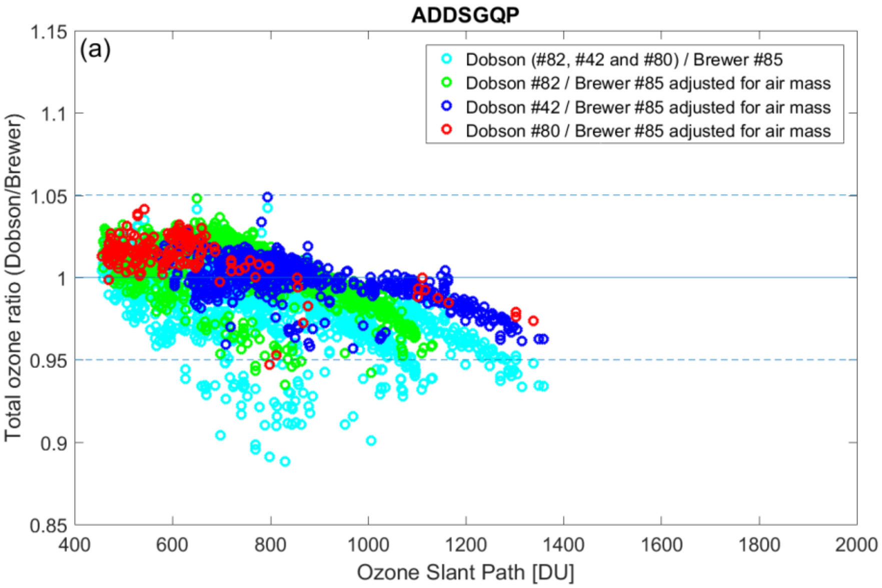
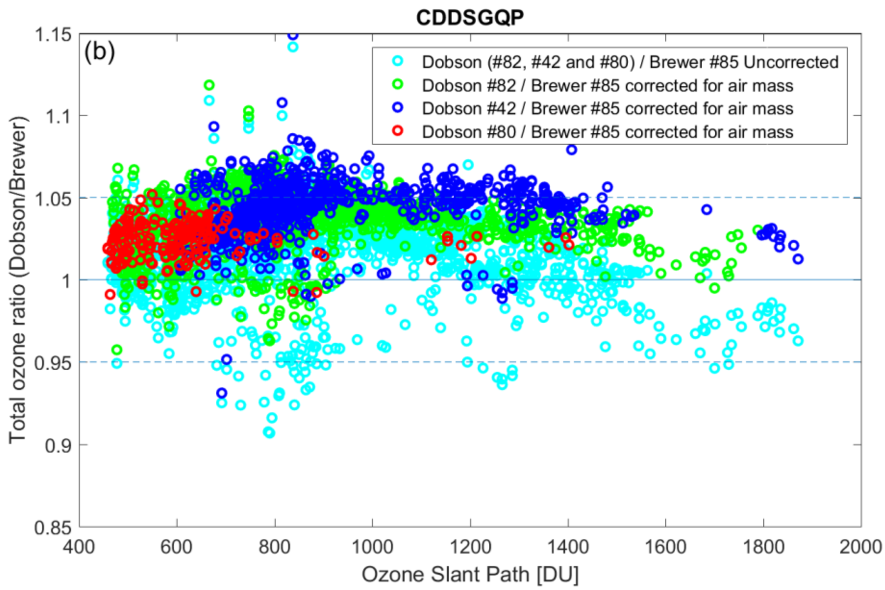


Figure 8: (Top) Total ozone column measured by double Brewer #085 versus total ozone slant path. Total ozone columns calculated using adjusted air masses are also shown (see the details in the text). (Bottom) Ratio of total ozone column retrieved using adjusted airmass to total ozone retrieved using unadjusted airmass.


ADDSGQP
(a)
Dobson (#82, #42 and #80) / Brewer #85 Uncorrected
Dobson #82 / Brewer #85 corrected for air mass
Dobson #42 / Brewer #85 corrected for air mass
Dobson #80 / Brewer #85 corrected for air mass
Total ozone ratio (Dobson/Brewer)
Ozone Slant Path [DU]
1.15
1.1
1.05
1
0.95
0.9
0.85
400
600
800
1000
1200
1400
1600
1800
2000


ADDSGQP
(a)
Dobson (#82, #42 and #80) / Brewer #85
Dobson #82 / Brewer #85 adjusted for air mass
Dobson #42 / Brewer #85 adjusted for air mass
Dobson #80 / Brewer #85 adjusted for air mass
Total ozone ratio (Dobson/Brewer)
Ozone Slant Path [DU]
1.15
1.1
1.05
1
0.95
0.9
0.85
400
600
800
1000
1200
1400
1600
1800
2000



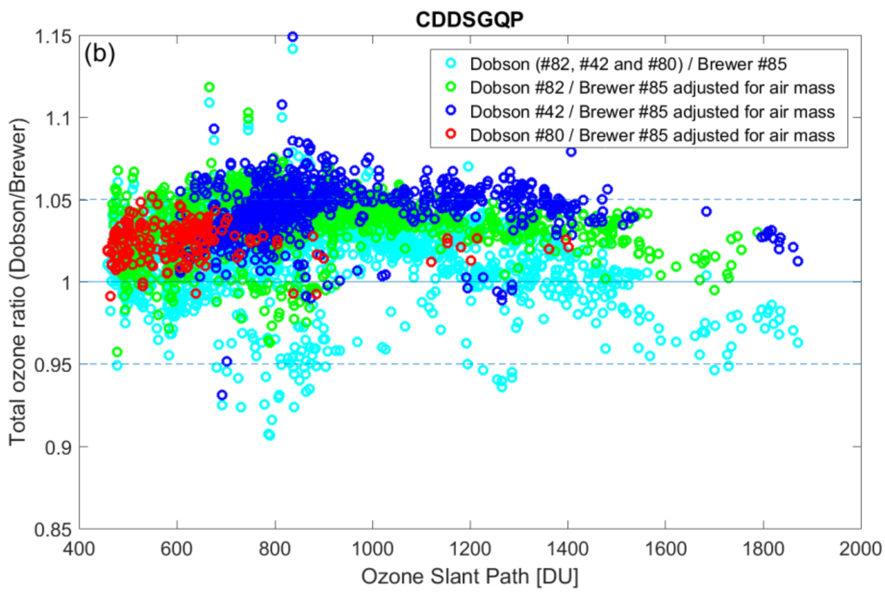


Figure 9~~97~~: (a) The ratio of quasi-simultaneous observations (within 5 min) using Dobson (#82, #42 and #80) AD wavelengths to double Brewer #085 data at the South Pole. (b) Same as (a) using Dobson CD pairs. Brewer air masses have been corrected using the values used for the Dobson measurements for the radius of the Earth, ozone layer height and the altitude of the site. The ratio of all data from three Dobson instruments and Brewer data before ~~corrections~~ adjustment for ozone layer height and station altitude are also depicted. ADDSGQP: AD direct sun measurement using a ground quartz plate, and CDDSGQP: CD direct sun measurement using ground quartz plate.

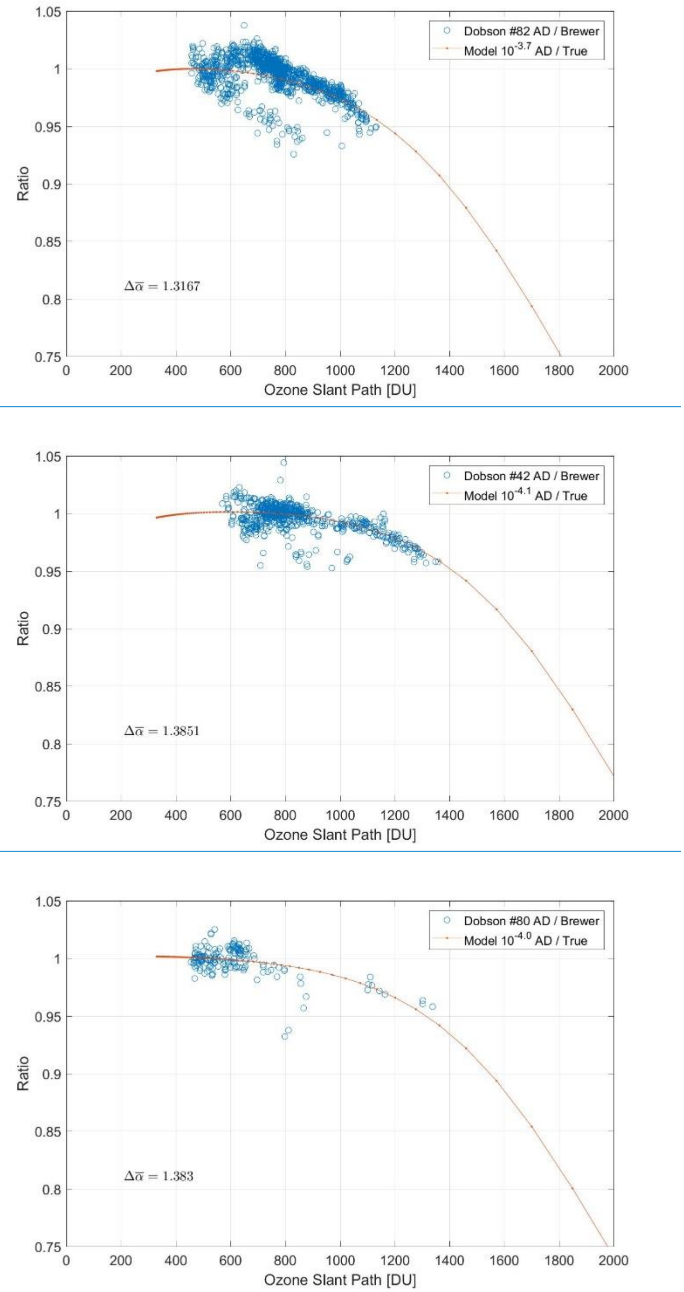
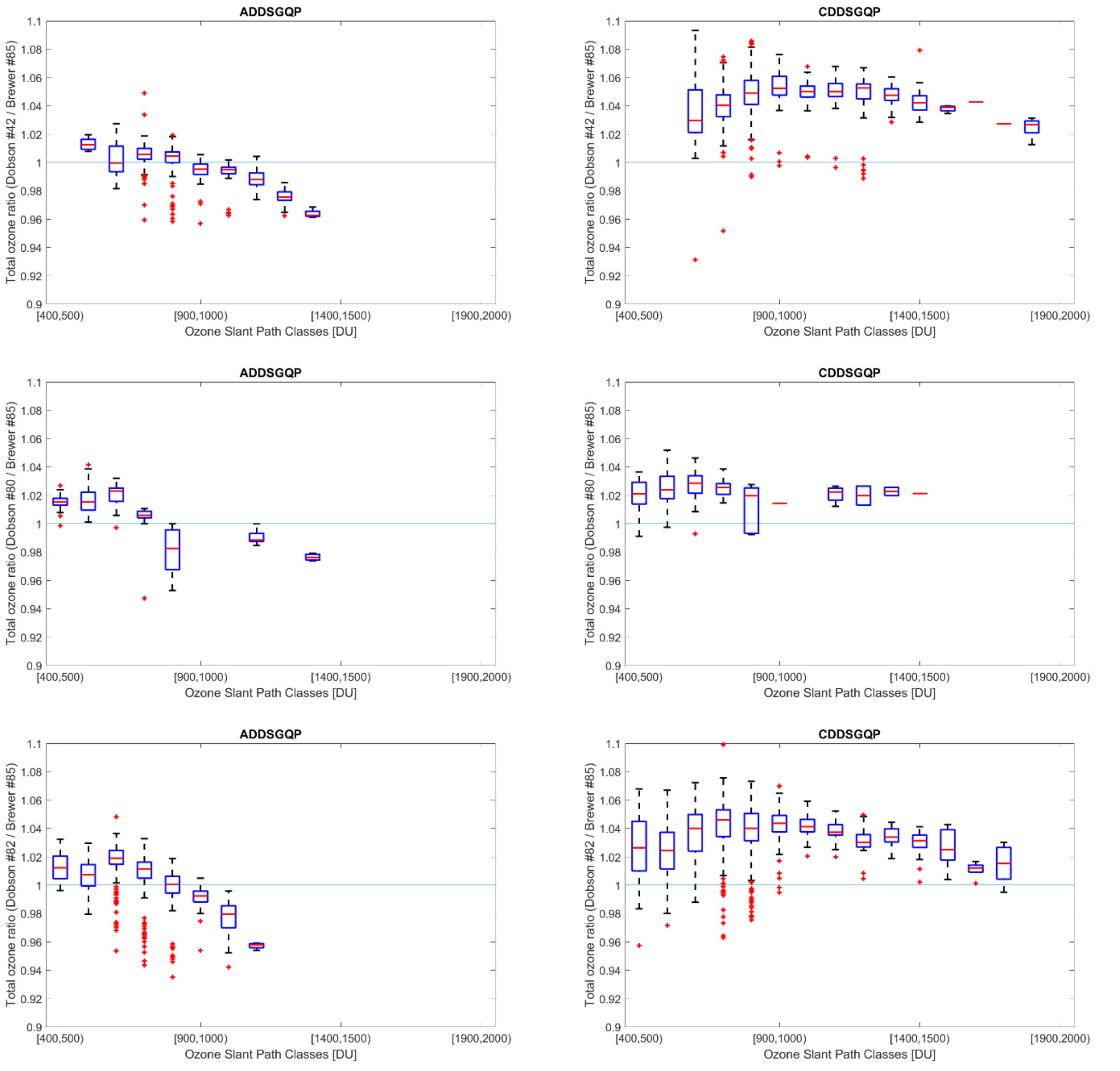


Figure 10: The ratio of quasi-simultaneous observations of Dobson #82, #42 and #80 AD wavelengths to double Brewer #085 data at the South Pole as well as the ratio of the values retrieved from the physical model developed in this study with certain amounts of stray light to the true value assumed in the atmosphere suggesting the level of stray light in each individual Dobson instrument. The ETC values and ozone absorption coefficients are calculated for each model separately using Langley method. Note that the average difference between the Brewer and Dobson data with OSPs less than 800 DU has been used to scale the Dobson data first. Then the model with stray light level that better matches with the Dobson data has been found. The scaling factors used for Dobson #82, #42 and #80 are 1, 0.46 and 1.6 respectively.


ADDSGQP
CDDSGQP
Total ozone ratio (Dobson #42 / Brewer #85)
Total ozone ratio (Dobson #80 / Brewer #85)
Total ozone ratio (Dobson #82 / Brewer #85)
Ozone Slant Path Classes [DU]
[400,500)
[900,1000)
[1400,1500)
[1900,2000)
1.1
1.08
1.06
1.04
1.02
1
0.98
0.96
0.94
0.92
0.9

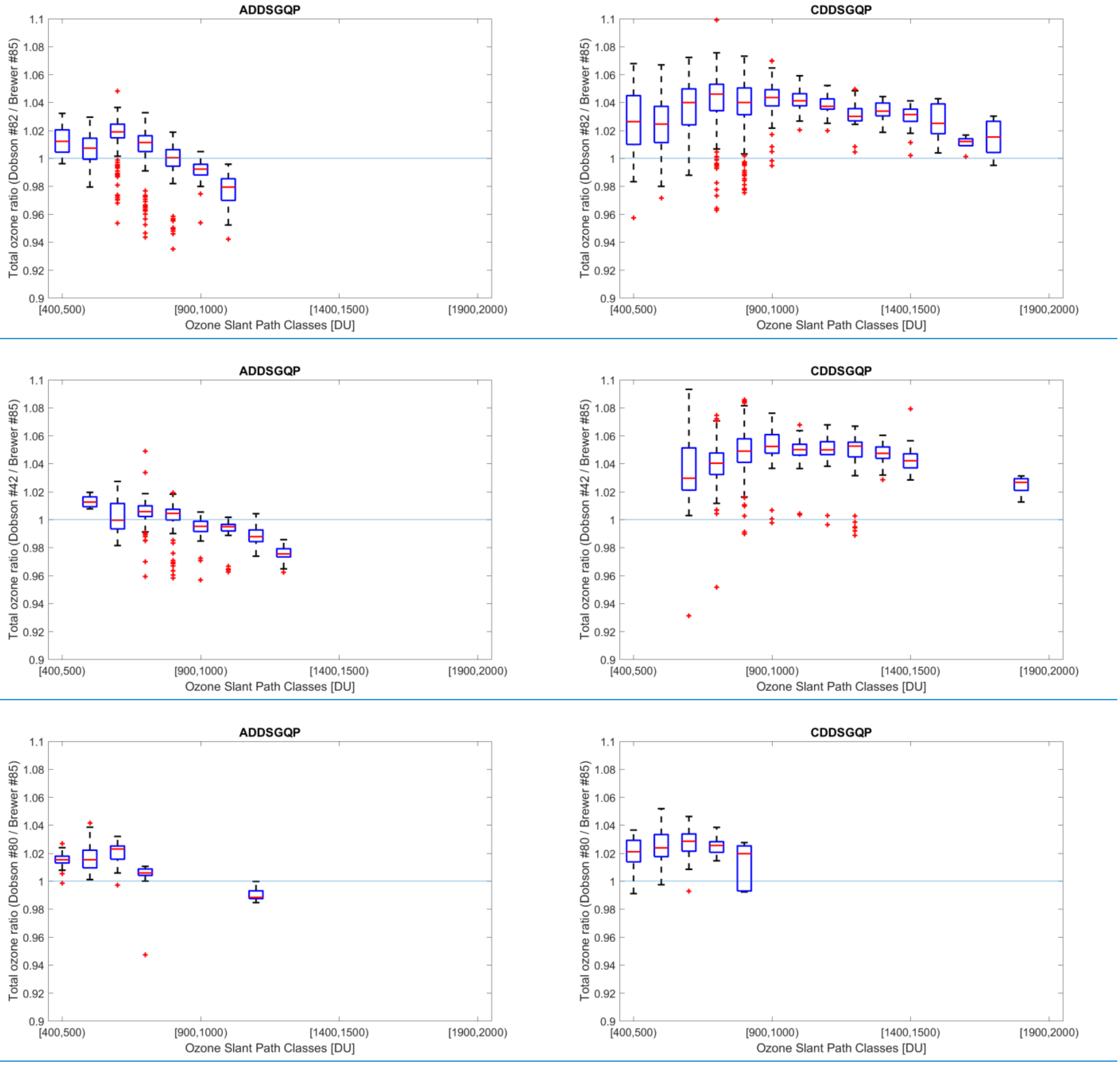


Figure 11~~118~~: The ratio of quasi-simultaneous direct sun observations (within 5 min) by Dobsons #82, #42, and #80, AD and CD wavelengths to data from double Brewer #085 at the South Pole. On each box, the central red line is the median, the edges of the box are the 25th and 75th percentiles, the whiskers extend to the most extreme data points not considered outliers, and outliers are plotted individually. In each bin the values with differences larger than three standard deviations from the mean of the bin have been removed from the calculation. Note that only bins with more than 6 simultaneous measurements are depicted. The title of plots is showing the type of measurements. ADDSGQP: AD direct sun measurement using a ground quartz plate, and CDDSGQP: CD direct sun measurement using ground quartz plate.

Interactive comment on "The Effect of Instrumental Stray Light on Brewer and Dobson Total Ozone Measurements" by Omid Moeini et al.

Omid Moeini et al. (omidmns@yorku.ca)

The authors would like to thank the reviewer for the thorough and useful review which we have gratefully considered in improving the paper.

Anonymous Referee #1

General Comments

This manuscript calculates the effect of stray light on the ozone absorption cross-sections, and hence the derived values of total ozone, from Dobson and Brewer spectrophotometers.
These two instruments have formed the basis of global ground-based measurements of total ozone for many decades and thus this is a very useful issue to address and well within the scope of AMT.
In its current form, however I feel the manuscript suffers from two major defects.
Firstly, I found the logic hard to follow, meaning I was often quite confused about how the different sections related to each other and what the purpose of each really was.
Results from different sections didn't seem to even be used in the following sections.
(More details are given in the specific comments).
The analysis of measurements at South Pole is only very partially linked back to the model calculations and not at all linked to the lab measurements. The connections and argument need to be made much more explicit.
The discussion (section 3) is revised to be explicit and clear and link different parts of the article. The model developed in this study is used to estimate the stray light level within each Dobson instrument located at South Pole (please see the response to the specific comments and also the response to A. Redondas (page 9,5)).

Secondly, the study seems to have been carried out largely in isolation from work that has been undertaken in the Brewer community over the last five years or so. Some recent references are missing, and others are cited but not sufficiently engaged with.

The recent studies have been discussed and the references have been added to the manuscript (please see the response to the specific comments).

In particular, I would insist the analysis be re-computed using Serdyuchenko cross-sections. This makes the work relevant to the current day concerns of the community and removes factors that are known to be caused by the use of Bass-Paur (Redondas et al. 2014).

The authors deliberately avoid the use of the Serdyuchenko (2014) cross-sections as it is not the intent of this study to presume to set the cross-section values to be used by the community to measure ozone, but only to provide some additional information about the impact of stray light on the measurements. Changing the cross-sections would not change the significance of this study. The cross-sections can be considered as a variable and the nature of the processes would remain the same. The paper is intended to show the connection between the physics of the instruments and the impact of stray light on the measurements. The first priority in using the results of this study is the provision of an algorithm for correcting the extant ozone historical record (described a paper currently in review) – particularly results measured at large slant column ozone amounts (e.g.: particularly at high latitudes in spring and fall). The inclusion of multiple results would obscure the basic intent of the paper and possibly create confusion in the community. Calculating the ozone absorption coefficients with new cross-sections is beyond the scope of this article and subject of another study which should be supported by WMO. To the best of our knowledge no new data have been submitted to the WOUDC using new cross-sections nor have the historical data been so corrected.

About the Dobson AD-CD difference: This work shows that higher levels of stray light lead to larger differences between AD and CD measurements. This fact is the same for all cross-sections. Redondas et al. (2014) have shown that for the ideal slit functions without stray light, the difference is somewhat lower for the Serdyuchenko (2014) cross-sections as compared with the results using other cross-sections.

Specific comments

Page 1

Line 20 – This needs to be done using Sedyuchenko cross-sections to be relevant and comparable to modern work.

Please see the response to the general comments.

Line 22 – I dispute that you have "evaluated" the error. The discrepancy between Dobson and Brewers as a result of their different assumptions is calculated but nothing here says what the deviation from the true value is.

Revised – "error" is replaced by "discrepancy". However, any difference between the actual height of the ozone layer and the assumption leads to an error in the measurements. The ozone climatology studies suggest that the ozone layer height is about 26 km and constant from -20 to 20 and then slopes toward the poles with the height around 17 km.

The authors believe that this assumption better matches with reality and is a good choice to be considered by both communities (Dobson and Brewer) as the height of the ozone layer. This leads to a reduction of discrepancies between Brewer and Dobson measurements and a more accurate ozone amount.

Line 24 Between 2008 and 2012 – this is quite misleading because you actually only use two distinct periods in 2008 and 2012 (Unless the description on page 11 is wrong?)

Description on page 11 is revised. All direct sun measurements available between 2008 and 2014 from three Dobsons and one double Brewer are used in this study.

Line 25 I can't see that you have shown this at all. You have shown the difference between the Dobson values and the double-Brewer values, but how have you actually attributed this difference to stray light? This is a serious defect that needs to be addressed.

The models developed in this study show that the documented instrumental stray light effect in Brewers causes a non-linearity in the modeled ozone measurements at large ozone slant paths consistent with the observations. In this study, the data from three Dobsons are compared to the measurements of a double-Brewer with a very low level of stray light. The discrepancies in the measurements clearly depend on ozone slant path which is an indicator of a stray light effect.

Line 30 I wouldn't say a "similar network" was introduced because of the more limited geographical coverage of Brewers even to today.

Revised – "similar" is removed.

Page 2

Line 15 Refer to Staehlin et al. GAW report

The reference is added to the manuscript.

Staehelin, J., J. B. Kerr, R. Evans, and K. Vanicek, (2003), COMPARISON OF TOTAL OZONE MEASUREMENTS OF DOBSON AND BREWER SPECTROPHOTOMETERS AND RECOMMENDED TRANSFER FUNCTIONS, *WMO/GAW Report No. 149*, World Meteorological Organization, Geneva, Switzerland.

Line 16 I think you need to be specific here – what fraction of the difference can be accounted for?

The following sentence has been added:

"They found a 3% drift over about a 10-year period (1988-1997) between the Arosa Dobson and Brewer total ozone series that remains unexplained."

Line 21 "properly" is not the right word, a lot of work has been done, eg at the RBCCE

Revised. Following statement is removed from the manuscript:

"the effect of the stray light on measurements at large solar zenith angles (SZA), have not been analyzed properly yet."

This paper reports the results of a physical model which demonstrates that the functional behavior of the non-linearity in ozone amounts at large slant ozone columns can be explained as being due to the measured stray light properties of the Brewer instruments and, by inference, a similar statement is made about the Dobson.

Page 3

Line 4 "large SZA and large TOC" – this is only true in the Northern Hemisphere. It is not true at all in Antarctica, which you use for your comparison. Was South Pole even a good choice for your study?

The South Pole is one of the most important sites to detect ozone recovery, trend analysis and satellite verifications. With ozone recovery in future more data measured at large ozone slant paths would be available which could cause an error in future studies. In addition, if the Dobson at that site is replaced with an instrument with a lower level of stray light, a false positive signal could be detected. There are six years of data collected by three Dobsons and one double Brewer which can be used for comparison. Using these data this study shows the dependence of the Dobson and Brewer difference to the ozone slant path which is an indicator of the impact of stray light.

Page 5

Line 24 It's fine to do the calculations using Bass-Paur so you can compare them to older work but you also have to do them using Serdyuchenko to be relevant to modern work, eg Redondas et al. 2014, Köhler et al. 2018)

The goal of this study is to show the effect of stray light at large ozone slant paths and also on effective ozone absorption coefficients for both Brewer and Dobson instruments. In our analysis the cross-section can be left as a variable and the whole process would be the same. Therefore, the authors believe that adding more numbers to the article would not be helpful and is beyond the scope of this study.

Line 29 the "relevant temperature" – you need to be explicit here – are you using the same temperature for both Dobsons and Brewers? Which is it? Otherwise won't this introduce a difference separate to what you're looking at?

The same temperature, -46.3, is used for both instruments. The manuscript is revised to clearly express this.

Page 6

Line 25-27 To be clear, you are not going to use this approximation? (equation 18). You should be explicit.

This approximation ($\bar{\alpha}^{apx}$) is used for the values in table 3 rows 1 and 4 and also in table 4 columns 4, 6, and 8.

Page 7

Line 4 Why do you use theta_0 not just theta?

Revised. Theta_0 is replaced with theta.

Line 9 You say "it is important" but don’t give any evidence as to why it’s important. Evidently the Brewer algorithm doesn’t think it’s important

The fixed ozone layer height of 22 km, as used by Brewer retrieval, causes up to a 2.2 % difference at an air mass of 5.4 with the value retrieved with ozone layer height of 17 km (Figure 6). This shows that this parameter is important for large-solar-zenith-angle measurements, especially at higher latitude sites where the ozone layer height is close to 17 km based on ozone climatology studies.

Line 9 You say the "correct" value of the height of the ozone layer but don’t show that the Dobson parameterisation is correct. I think you just mean that the Brewer and Dobson methods are different to each other and this will cause a slight difference in derived total ozone.

“correct” is replaced with “adjust” to prevent any confusion. No value is suggested by the authors as the correct value. But we believe that adopting a variable ozone layer height with latitude is in more agreement with ozone climatology. We suggest a constant value for -20 to 20 with slope toward the poles with 17 km at the poles.

Line 19 How do you know the stray light in a Dobson is similar to Mk IV and Mk II Brew-ers? Are you taking this from previous studies? This is one of my major confusions. I don’t think you measured it?

No, we have not measured it. That statement is removed from the manuscript. However, the stray light levels suggested by Basher (1982) for several Dobson instruments based on the non-linearity in their measurements reveal that the level of stray light in Dobson instruments are comparable with measured stray light of Brewers MKII and MKIV.

Line24 You should mention that He-Cd laser has been used before and give the references (see Pulli et al. 2018)

References are added.

Pulli, T., T. Karppinen, S. Nevas, P. Kärhä, K. Lakkala, J. M. Karhu, M. Sildoja, A. Vaskuri, M. Shpak, F. Manoocheri, L. Doppler, S. Gross, J. Mes, and E. Ikonen, (2018), Out-of-Range Stray Light Characterization of Single-Monochromator Brewer Spectrophotometers, *Atmosphere-Ocean*, *56*(1), 1–11, doi:10.1080/07055900.2017.1419335.

Karppinen, T., A. Redondas, R. D. García, K. Lakkala, C. T. McElroy, and E. Kyrö, (2014), Compensating for the Effects of Stray Light in Single-Monochromator Brewer Spectrophotometer Ozone Retrieval, *Atmosphere-Ocean*, 1–8, doi:10.1080/07055900.2013.871499.

Kiedron, P., P. Disterhoft, and K. Lantz, (2008), NOAA-EPA Brewer network Stray Light Correction, NOAA Earth System Research Laboratory.

Line 24-25 You should give at least a very brief description of the experimental set-up. For example, you should explain how you derive a slit-function from a single wavelength laser? What is the sensitivity of your detector? (This is important since you are measuring over such a wide dynamic range).

Revised. Following statement is added to the manuscript:

“The Brewer Mark III and IV can measure the wavelength range of 286.5 to 363 nm with 0.5 nm resolution. The Brewer slit function is characterized using a narrow band line source such as a laser as input source and scanning through all wavelengths. Measurements at 350 nm (not reported) have shown the slit function to be similar at all wavelengths in the Brewer measurement range. The slit function is reversed in wavelength space to account for the reciprocal nature of scanning the instrument v. scanning the wavelength of the line source.”

Page 8

Line 15 You need to refer to Köhler et al. 2018.

The reference is added.

Lines 29-32 I am very confused here about what is what. In Figure 3 the slit functions are curved, not trapezoids. Where did this shape come from?

Caption of the figure was not accurate. Those are Dobson C-pair slit functions parameterized from Figure 1 of Komhyr (1993) and brought here as an example but are not being used for the analysis. The accurate description of the slit functions used for this study can be found in Table 1.

The caption has been corrected.

Page 9

Line 3 It seems you are not using the approximation in equation 18. Did you use a radiative transfer model?

In section 3.1 the approximation in equation 18 is used and the results are compared with the results from equation 17.

For section 3.2 the values calculated from equation 17 are used.

No, a radiative transfer model is not used in this study. In section 3.2 the solar spectrum at the surface, assuming constant amount of ozone in the atmosphere, is calculated using equation 1. Then, the Brewer and Dobson algorithm plus ideal and model slit functions are employed to retrieve the total ozone.

Page 10

Lines 8-9 I find this statement completely baffling. What do you mean by "measured slit functions"? What value of stray light are you suggesting WMO use?

Revised. Following statement is used instead of the previous one:

“It is advisable that the WMO assign a group to measure the Dobson stray light level at least for the reference instrument. Then, the absorption coefficients should be recalculated and recommended to be used instead of the values currently in use.”

Line 15 I would like to see a plot showing what the Langely looked like without and without the stray light being added to the model

Following figure shows the Langley plot for Single Brewer with and without stray light. The plot is added to the manuscript:

“To calculate the ETC, the instrument absorption function using the solar spectrum (Chance and Kurucz 2010), Eqs. (1), (2) and retrieval algorithm of the Brewer (or Dobson) for an assumed constant amount ozone (325 DU in this study) is calculated and plotted as a function of ozone slant path. The best fit to the data with airmass less than 2 (less than 3 for the Dobson instruments) is found and extrapolated to zero airmass. Figure 5 shows the best fit to a single Brewer data:

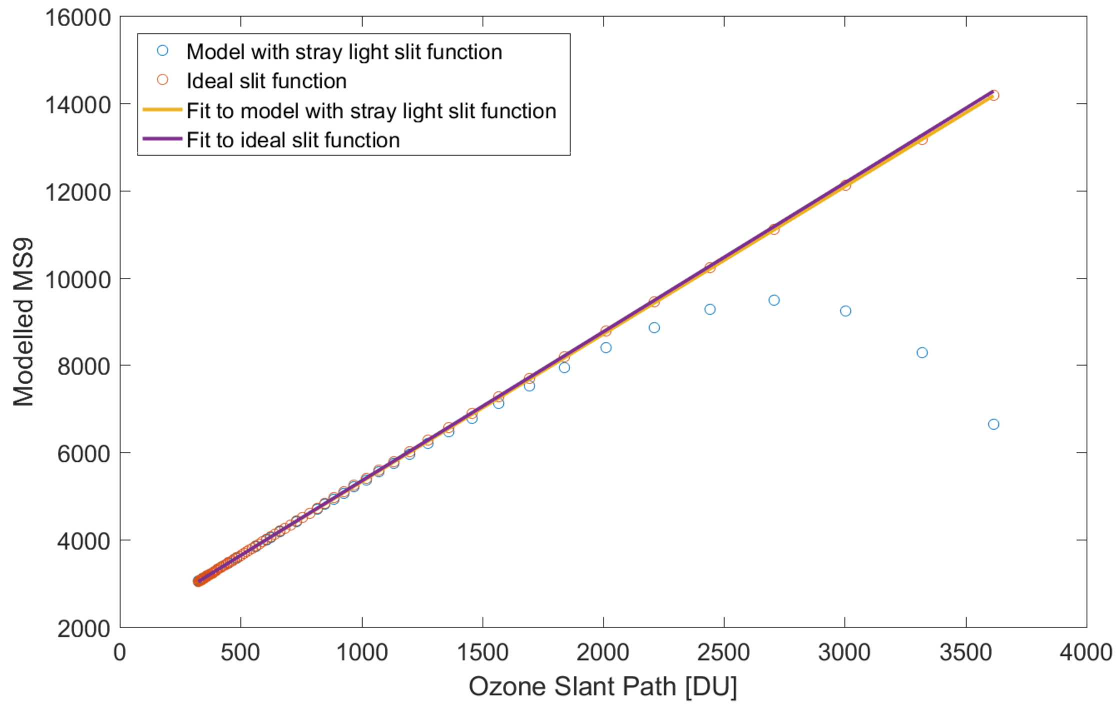


Figure 5: Example of Langley plot fitted to a modeled single Brewer data

Page 11

Line 3 It seems to me your results would imply the AD-CD correction should use an expression linear in mu rather than an average across the mu range?

Our model suggests that the AD-CD difference depends on the internal stray light level of the instrument and changes non-linearly above 800 DU OSP.

Line 15 You can't say "error" because you don't make any attempt to look at the what the true value is (for example by using South Pole ozonesonde data). You could call it a "discrepancy" between the Dobson and Brewer.

Revised. "discrepancy" is used instead of "error".

Line 30 Do you mean "February 2008 and December 2014" or is it actually meant to be "February 2008 to December 2014" ?

Revised. "February 2008 to December 2014" is correct.

Line 31 I don't think you can say "corrected" because you don't know that the Dobson value is any more correct than the Brewer value.

Revised. "adjusted" is used instead of "corrected".

Page 12

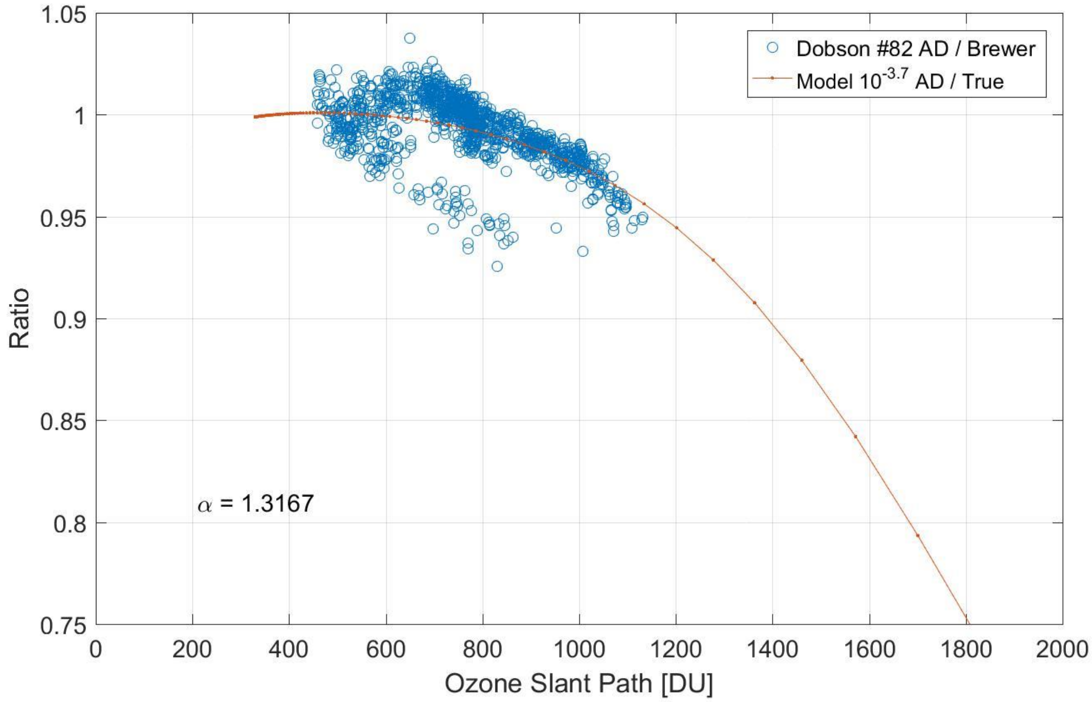
Line 9-14 It looks like a linear relation. Couldn't you then calculate the gradient and compare the value with your model? This is what I was expecting you to do to better finish off the study.

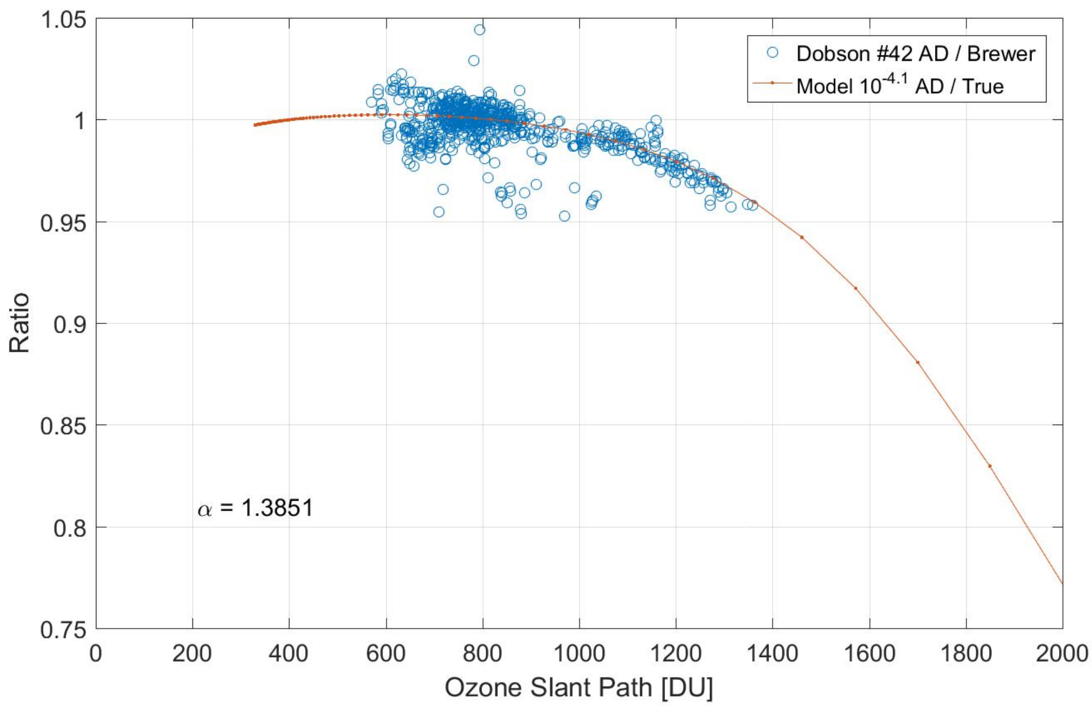
The comment is not clear. The stray light effect causes non-linearity in the measurements at large OSPs. There isn't a linear relation.

Line 24-26 It seems a bit curved. You need to calculate how close the measured values are to what you expect from your model.

The manuscript is revised and the following plots and statement are added:

"As it is shown in Fig. 9, the physical model developed in this study suggests $10^{-3.7}$, $10^{-4.1}$, and $10^{-4.0}$ level of stray light for Dobson #82, 42, and 80 respectively.


Dobson #82 AD / Brewer
Model 10^-3.7 AD / True
α = 1.3167
Ratio
Ozone Slant Path [DU]
1.05
1
0.95
0.9
0.85
0.8
0.75
0
200
400
600
800
1000
1200
1400
1600
1800
2000


Dobson #42 AD / Brewer
Model 10^-4.1 AD / True
α = 1.3851
Ratio
Ozone Slant Path [DU]
1.05
1
0.95
0.9
0.85
0.8
0.75
0
200
400
600
800
1000
1200
1400
1600
1800
2000

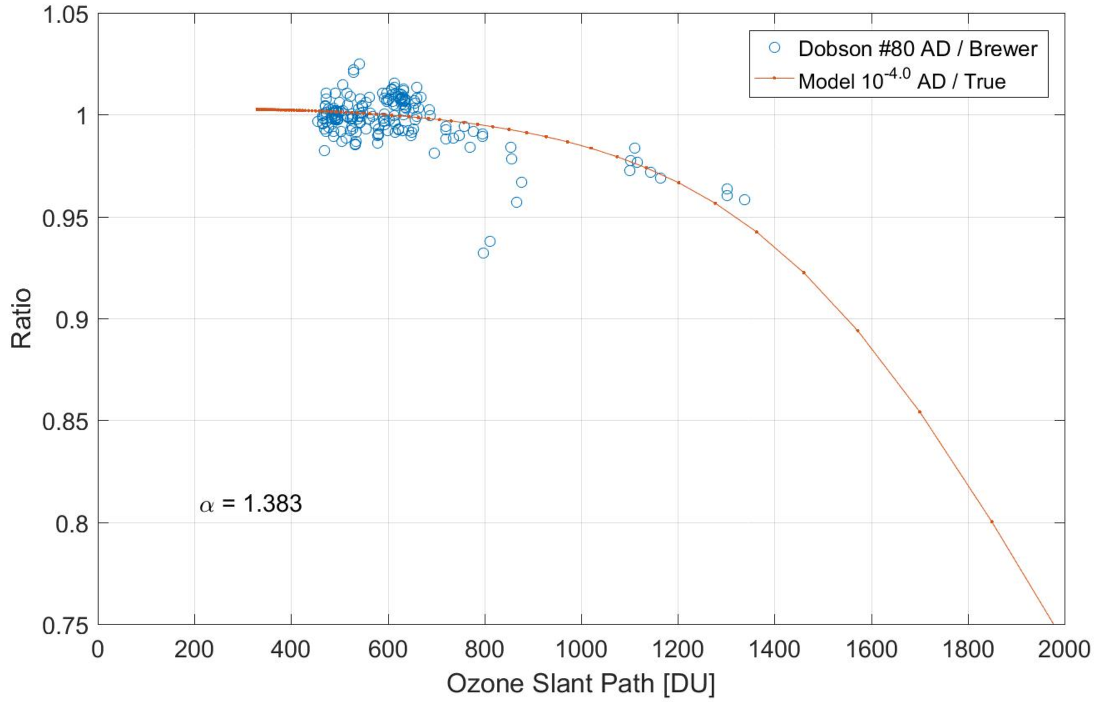


Figure 9: The ratio of quasi-simultaneous observations of Dobson #82, 42 and 80 AD wavelengths to double Brewer #085 data at the South Pole as well as the ratio of the values retrieved from the physical model developed in this study with certain amounts of stray light to the true value assumed in the atmosphere suggesting the level of stray light in each individual Dobson instrument. The ETC values and ozone absorption coefficients are calculated for each model separately using Langley method. Note that the average difference between the Brewer and Dobson data with OSPs less than 800 DU has been used to scale the Dobson data first. Then the model with stray light level that better matches with the Dobson data has been found. The scaling factors used for Dobson #82, #42 and #80 are 1, 0.46 and 1.6 respectively."

Line 28 "Physical model" but four lines later you say "mathematical model".

Revised. "Physical Model" is correct. (In reality it is both. The physics of the measurement is expressed in mathematical terms so that simulated observations can be produced.)

Line 30 Again, I don't think you have found anything about the "error" – only the difference between the Dobson and Brewer.

Revised. “difference” is used instead of “error”.

Line 32 But does this 25% relate to a realistic value of Dobson stray light?

This is the error at 2000 DU OSP. Experimental data discussed by Basher (1982), Varotsos (1998) and Christodoulakis et al. (2015) suggest an even larger error at the same OSP indicating a higher level of stay light in the Dobsons being used for the measurements.

Page 13

Line 2 "like polar stations" would be better worded as "such as polar stations"

Revised.

Line 2 This is misleading because the study has considered South Pole data where ozone is very low in spring

The location doesn’t really matter in the case of stray light. Wherever you have data with OSP (ozone slant path) larger than 800 DU you can see the effect of stray light. Even at South Pole there is enough data to show this effect.

Line 6 You say "stray light also can affect" but isn’t this just a different way of expressing the same thing? (ie stray light will affect total ozone, which alternatively you could express as the effect on the absorption coefficients).

There are two effects we discussed in this article. First, the models show that the stray light causes non-linearity in the measurements at large ozone slant paths. This feature happens even if the ozone absorption coefficients are accurately calculated.

It is also shown that the stray light affects the calculation of the effective ozone absorption coefficients which leads to an error in the measurements even at low airmass. This error is reduced during calibration of the instruments by comparing the coincidence measurements with the reference instrument.

Line 10-16 You need to discuss Köhler et al. 2018 here

Following sentences are added to the manuscript:

“Recently, the measured slit functions and calculated coefficients were verified by measuring the slit functions of three Dobsons (#74, #64, and #83) at the Physikalisch-Technische Bundesanstalt (PTB) in Braunschweig in 2015 and at the Czech Metrology Institute (CMI) in Prague in 2016 within the EMRP ENV 059 project “Traceability for atmospheric total column ozone” (Köhler et al., 2018). Köhler et al. showed that the optical properties of these three Dobsons deviate from the specification described by G.M.B. Dobson. However, the AD pair ozone absorption coefficents derived from the new slit functions lead to less than a 1% deviation in total ozone column values.”

Line 34 This calculation needs to be with Serdyuchenko cross-sections.
With ideal slit functions it was shown that the AD-CD difference minimizes with the Serdyuchenko cross-sections (Redondas, 2014) as compared to the results with other cross-sections. We show in this article that no matter which cross-sections are used, the AD-CD difference increases as the contribution of instrumental stray light level increases.

Page 14

Line 6 "high" should be "higher"
Revised.

Line 7 "low" should be "lower"
Revised.

Page 20 Table 3 Are the values for the single or double Brewer?
Both instruments are discussed in the table 3. “Single” for single Brewer and “Double” for double Brewer.

Page 23 Figure 2 Would this be better on a log scale as in Figure 1?
Revised.

Page 24 Figure 3 I am very confused about this figure. The shapes are cruved not straight lines. Did you measure these in the lab with the laser?

The caption of the figure is revised as discussed in previous comment (Page 8, line 29-32).

Page 29 Figure 8 How did you identify the outliers? (If they represent bad data, perhaps you shouldn't plot them?)

In each bin the values with differences larger than three standard deviations from the mean of the bin have been removed from the plot. This statement has been added to the caption of the figure.

REFERENCES

Köhler, U., Nevas, S., McConville, G., Evans, R., Smid, M., Stanek, M., Redondas, A., and Schönenborn, F.: Optical characterisation of three reference Dobsons in the ATMOZ Project – verification of G. M. B. Dobson's original specifications, Atmos. Meas. Tech., 11, 1989-1999, https://doi.org/10.5194/amt-11-1989-2018, 2018.

Koukouli, M. E., Zara, M., Lerot, C., Fragkos, K., Balis, D., van Roozendael, M., Allart, M. A. F., and van der A, R. J.: The impact of the ozone effective temperature on satellite validation using the Dobson spectrophotometer network, Atmos. Meas. Tech., 9, 2055-2065, https://doi.org/10.5194/amt-9-2055-2016, 2016.

T. Pulli, T. Karppinen, S. Nevas, P. Kärhä, K. Lakkala, J. M. Karhu, M. Sildoja, A. C6 Vaskuri, M. Shpak, F. Manoocheri, L. Doppler, S. Gross, J. Mes & E. Ikonen (2018) Out-of-Range Stray Light Characterization of Single-Monochromator Brewer Spectrophotometers, Atmosphere-Ocean, 56:1,1-11, DOI: 10.1080/07055900.2017.1419335

Staehelin, J., Kerr, J., Evans, K., and Vanicek, R.: Comparison Of Total Ozone Measurements of Dobson and Brewer spectrophotometers and Recommended Transfer Functions, WMO TD No. 1147, World Meteorological Organization, Global AtmosphereWatch, No. 149, available at: http://www.wmo.ch/web/arep/reports/gaw149.pdf., 2003.

Stübi, R., H. Schill, J. Klausen, L. Vuilleumier, and D. C. Ruffieux (2017), Reproducibility of total ozone column monitoring by the Arosa Brewer spectrophotometer triad, J Geophys. Res. Atmos., 122, 4735–4745, doi:10.1002/2016JD025735

Karppinen, T., A. Redondas, R. D. García, K. Lakkala, C. T. McElroy, and E. Kyrö, (2014), Compensating for the Effects of Stray Light in Single-Monochromator Brewer Spectrophotometer Ozone Retrieval, *Atmos. Ocean*, 1–8, doi:10.1080/07055900.2013.871499.

Christodoulakis, J., C. Varotsos, a. P. Cracknell, C. Tzanis, and A. Neofytos, (2015), An assessment of the stray-light in 25 years Dobson total ozone data at Athens, Greece, *Atmos. Meas. Tech., 8*, 3037–3046, doi:10.5194/amt-8-3037-2015.

Varotsos, C. A., (1998), Technical note On the influence of stray light on total ozone measurements made with Dobson spectrophotometer no. 118 in Athens, Greece, *Int. J. Remote Sens.*, *19*(17), 3307–3315, doi:10.1080/014311698213993.

Kiedron, P., P. Disterhoft, and K. Lantz, (2008), NOAA-EPA Brewer network Stray Light Correction, NOAA Earth System Research Laboratory.

Interactive comment on “The Effect of Instrumental Stray Light on Brewer and Dobson Total Ozone Measurements” by Omid Moeini et al.

Omid Moeini et al. (omidmns@yorku.ca)

The authors would like to thank the reviewer for the thorough and useful review which we have gratefully considered in improving the paper.

A. Redondas (Referee) aredondasm@aemet.es

General comments

The article is interesting as the effect of the stray light on the ozone cross section calculation were not studied on the past. I have a few comments which I would the authors to answer, pending those I support the publication of the manuscript. The principal comment i repeat from my first evaluation is why they don’t use the (Serdyuchenko 2014) cross section in his calculations, when is now the recommended ozone cross section for Brewer and Dobson. Moreover, some of the discussions of the paper like the AD/CD ozone difference in the Dobson measurements and the Brewer/Dobson differences are also affected with the change of cross section (Redondas 2014). The discussion (Section 3.1) is still difficult to follow especially the Dobson section (see specific comments).

The authors deliberately avoid the use of the Serdyuchenko (2014) cross-sections as it is not the intent of this study to presume to set the cross-section values to be used by the community to measure ozone, but only to provide some additional information about the impact of stray light on the measurements. Changing the cross-sections would not change the significance of this study. The cross-sections can be considered as a variable and the nature of the processes would remain the same. The paper is intended to show the connection between the physics of the instruments and the impact of stray light on the measurements. The first priority in using the results of this study is the provision of an algorithm for correcting the extant ozone historical record (described a paper currently in review) – particularly results measured at large slant column ozone amounts (e.g.: particularly at high latitudes in spring and fall). The inclusion of multiple results would obscure the basic intent of the paper and possibly create confusion in the community. Calculating the ozone absorption coefficients with new cross-sections is beyond the scope of this article and subject of another study which should be supported by WMO. To the best of our knowledge no new data have been submitted to the WOUDC using new cross-sections nor have the historical data been so corrected.

About the Dobson AD-CD difference: This work shows that higher levels of stray light lead to larger differences between AD and CD measurements. This fact is the same for all cross-sections. Redondas et al. (2014) have shown that for the ideal slit functions without stray light, the difference is somewhat lower for the Serdyuchenko (2014) cross-sections as compared with the results using other cross-sections.

The second point to mention is the ETC calculation in section 3.2, is not clear how is calculated, in particular how is related from Chance and Kurucz (table 2). As suggested by the referee Julian Groebner on the discussion on the paper also part of this special number (Redondas et al. 2018). The difference between the use of trapezoid slit and a triangular slit is about 0.7% in a double brewer. I think is usefull to include this case in your calculation.

The ETC calculation and its relation to solar spectrum are discussed and added to the manuscript (see response to specific comments).

The authors believe that repeating all this work with different minor variations (replacing trapezoid slit with triangular slit) and adding all those numbers to the manuscript actually obscures the point of the paper.

The error introduced by the assumption of the fixed air-mass is also showed but could be more illustrative to show the difference in ozone rather than in airmass. The effect on the Dobson record at South Pole was also studied by (Bernhard et al. 2005) a comparison with his results could be also illustrative.

The plot that shows the difference in airmass is replaced with a plot showing the difference in ozone.

Generally, Bernhard et al. (2005) has stated that the effective ozone absorption coefficients, $\Delta\bar{\alpha}_{AD}$ and $\Delta\bar{\alpha}_{CD}$, are smaller at large ozone slant path which is the same result as from the current analysis. They have compared the Dobson data with TOMS and SUV-100 data. To compare those results with this analysis, information about the TOMS and SUV-100 instruments would be required. This is beyond the scope of this article and could be a subject for another study.

Specific comments

Page 2, 30: A basic description of the method is worthwhile, the method is based on the characterization of the instrument and need both the spectral response and the Laser measurements of the slit rather than the dispersion information. A comparison between the Kiedrom/Karppinen model ant this work will be illustrative.

Kiedrom/Karppinen have tried to correct the stray light effect at large ozone slant paths for a single Brewer by changing the weighting coefficients. Here, two types of Brewers and a Dobson instrument are modeled to show the connection between the physics of the instruments and the impact of stray light on the measurements.

Page 3, 7: A reference of the false positive trend due different stray light is advisable.

This is difficult quantify in a really useful way until a reanalysis of an appropriate data set is done. It is considered beyond the scope of the paper and work that needs to be done.

Page 4: There is no explanation of the calibration of the Dobson as is done with the Brewer

The comment is not clear.

The Dobson calibration procedure is described in Evans and Komhyr (2008). Generally, the Dobsons are adjusted to make the slit functions as similar as possible and then only an extraterrestrial value is transferred from a reference instrument traceable to the World Standard Dobson.

Page 5: There is some confusion on the nomenclature of the formulas: please unify B or ETC, F or I.

Revised. “I” and “ETC” are used.

Page 5,29 : A reference of the application of the Barnes correction to the Brewer network will be advisable.

Revised. “the Brewer” is removed from the statement.

Page 6,1: There are several files available at IGACO, which ones are used in this study?.

The following statement has been added to the manuscript:

“For this study the quadratic coefficients on the file ‘Bp.par’ are used for BP cross-sections and the Liu et al. (2007) quadratic approximation, which excludes -273^{o} K data from the quadratic temperature dependence fitting, are used for BDM cross-sections.”

Page 6,20: Could clarify the relation between equations 11, 15,17 and 18. (see also 9,1).

The ozone absorption coefficients $\alpha(\lambda_i)$ are calculated from ozone absorption cross-sections and vertical profiles of ozone and temperature employing equation 15. Due to the finite bandpass of the Brewer and Dobson’s slit functions, the effective ozone absorption coefficients ($\bar{\alpha}(\lambda_i)$) must be calculated either using equation 17 or 18. Equation 17 considers the solar spectrum whereas equation 18 is the simplest approach that can be used to calculate the effective ozone absorption coefficients. The effective ozone absorption coefficients must be used in equation (11).

To prevent any confusion, $\alpha(\lambda_i)$ and $\bar{\alpha}(\lambda_i)$ are used instead of α_i and $\bar{\alpha}_i$ in all equations.

$\alpha(\lambda_i)$ is replaced with $\bar{\alpha}(\lambda_i)$ in equation (11) and $\Delta\alpha$ is replaced with $\Delta\bar{\alpha}$ in equations (3), (8), (9), and (11) to make clear that the effective differential ozone absorption coefficients must be calculated and used in Dobson and Brewer retrievals.

Page 7.15: A mention of a other sources of stray light could be mention, see for example Josefsson and discused.

Revised. The reference and following statement have been added to the manuscript:

“radiation scattered from the atmosphere within field of view of the instrument can also contribute a stray light effect (Josefsson, 1992).”

Josefsson, A. P., (1992), Focused Sun Observation Using a Brewer Ozone Spectrophotometer, *J. Geophys. Res.*, *97*(D14), 15813–15817.

Page 9,1: There is a confusing use of α_i vs α_i^{approx} where are talking about Δα. The same issue for table 3.

Revised.

Page 9,5: Is surprising that the calculation of the operational values agree with yours calculations. In this work you are using a different cross section temperature, brewer uses -45 C but you are using -46.3 C (Table 2). The same nominal wavelengths (Table 1) for both brewers whereas brewer operative wavelengths are slightly different for every instrument, and the same FWHM for all the slits. Can be also useful to have the brewer ozone absorption coefficient for for every wavelength (α_i vs α_i^{approx}) and not only the effective Δα.

Apparently it is a coincidence that those numbers are matched. To validate the procedure, the calculations are repeated for nominal wavelengths of 310.05, 313.50, 316.80 and 320.00 nm with FWHMs of 0.359, 0.555, 0.545 and 0.538 and BP cross-sections at -45 ^{o}C and compared with the value calculated by Redondas et al. (2014) using the same cross-sections for a nominal Brewer. There is a difference of 0.06 % between this value (0.3365) and the value calculated by Redondas et al. (2014) (0.3367) using IGQ4 cross-sections for a nominal Brewer (Table 6) which is identical with our double Brewer in terms of slit functions.

Also, the Brewer ozone absorption coefficients for every wavelength are calculated and reported as suggested by the referee.

The Brewer part of the discussion (section 3.1) is revised and following statements and tables are added to the manuscript:

"To validate the calculations, the $\Delta\bar{\alpha}^{apx}$ is calculated for the double Brewer using an ideal trapezoid slit function and BP cross-sections at -45 ^{o}C without the Barnes (1987) correction. Redondas et al. (2014) have calculated the ozone absorption coefficients for the nominal Brewer which is identical in terms of slit functions, nominal wavelengths and slit FWHMs with the double Brewer of this work using ideal trapezoid slit functions. The IGQ4 cross-sections used in Redondas et al. (2014) are the same as the BP cross-sections employed at this work. The value 0.3367 calculated using IGQ4 cross-sections at -45 ^{o}C (Redondas et al. Table 6) has a difference of 0.06 % with the value 0.3365 calculated here with the same cross-sections at the same temperature (-45 ^{o}C) (Table 3).

To be consistent with Dobson calculations, the BP cross-sections with Barnes (1987) correction and at -46.3 ^{o}C are used for calculation of $\bar{\alpha}_i$ and $\bar{\alpha}_i^{apx}$ presented in tables 4 and 5 for the single and double Brewers.

The contribution of stray light in determining the ozone absorption coefficients can be seen from comparing the $\Delta\bar{\alpha}$ calculated using ideal slit functions (without stray light) with the values ($\Delta\bar{\alpha}$) calculated using modeled slit functions (including stray light). For the single Brewer the results show a 0.7 % difference (modeled slit functions including stray light are less than that of the ideal slit functions) while for the double Brewer the difference is less than 0.01 %.

Comparing $\Delta\bar{\alpha}$ with $\Delta\bar{\alpha}^{apx}$ for both Brewers (single and double using ideal and modeled slit functions) shows a minimum difference of 0.7 % ($\Delta\bar{\alpha}$ higher than $\Delta\bar{\alpha}^{apx}$) for the double Brewer with ideal trapezoid slit functions and a maximum of 0.9 % for single Brewers with ideal triangle slit functions, indicating the role of the solar spectrum in calculating the ozone absorption coefficients.

Table 3: Ozone absorption coefficients calculated here and the value calculated by Redondas et al. (2014)

		$\bar{\alpha}_i^{apx}$ (atm cm^{-1}) calculated for Double Brewer using ideal slits and BP cross-sections at -45 ^{o}C without Barnes (1987) correction	From Redondas (2014) Table 6; effective ozone absorption coefficient calculated using IQG4 B&P cross-sections
Wavelength (nm)	FWHM (nm)	Ideal (trapezoid)	Ideal (trapezoid)
310.05	0.539	1.0044	
313.50	0.555	0.6793	
316.80	0.545	0.3760	
320.00	0.538	0.2935	
$\Delta\bar{\alpha}^{apx}$		0.3365	0.3367

Table 4: Single Brewer ozone absorption coefficients

		Ideal		Model (with Stray light)	
Wavelength (nm)	FWHM (nm)	$\bar{\alpha}_i^{apx}$	$\bar{\alpha}_i$	$\bar{\alpha}_i^{apx}$	$\bar{\alpha}_i$
310.05	0.539	1.0087	1.0127	1.0141	1.0102
313.50	0.555	0.6824	0.6842	0.6828	0.6833
316.80	0.545	0.3774	0.3789	0.3768	0.3789
320.00	0.538	0.2944	0.2962	0.2923	0.2959
$\Delta\bar{\alpha}^{apx}/\Delta\bar{\alpha}$		0.3377	0.3406	0.3407	0.3380

*BP cross-sections at -46.3 with Barnes (1987) correction.

Table 5: Double Brewer ozone absorption coefficients

		Ideal		Model (with Stray light)	
Wavelength (nm)	FWHM (nm)	$\bar{\alpha}_i^{apx}$	$\bar{\alpha}_i$	$\bar{\alpha}_i^{apx}$	$\bar{\alpha}_i$
310.05	0.539	1.0087	1.0127	1.0089	1.0126
313.5	0.555	0.6824	0.6842	0.6826	0.6841
316.8	0.545	0.3773	0.3789	0.3776	0.3789
320	0.538	0.2947	0.2962	0.2950	0.2962
$\Delta\bar{\alpha}^{apx}/\Delta\bar{\alpha}$		0.3384	0.3406	0.3384	0.3405

*BP cross-sections at -46.3 with Barnes (1987) correction.

Page 10,5: An explanation why the calibration method reduces the the discrepancy to 0.7% independent of the level of stray light of the instruments and can be illustrated for example in figure 5.

The following statement has been added:

“In the Dobson AD pair calibration, scale factors are calculated for different ranges of airmass. The data from the instrument being calibrated are scaled to the data from the reference instrument. Then the CD pair data of the calibrated instrument are scaled to its AD pair data.”

Page 10,15: Please describe the calculation of the ETC, how is compared with the calculation of Kiedrom and (Karppinen 2015).

The following statement and plot have been added to the manuscript:

“To calculate the ETC, the instrument absorption function using the solar spectrum (Chance and Kurucz, 2010), Eqs. (1) and (2) and the retrieval algorithm of the Brewer (or Dobson) for an assumed constant amount of ozone (325 DU in this study) is calculated and plotted as a function of ozone slant path. The best fit to the data with airmass less than 2 (less than 3 for the Dobson instruments) is found and extrapolated to zero airmass. Figure 5 shows the best fit to the single Brewer data:

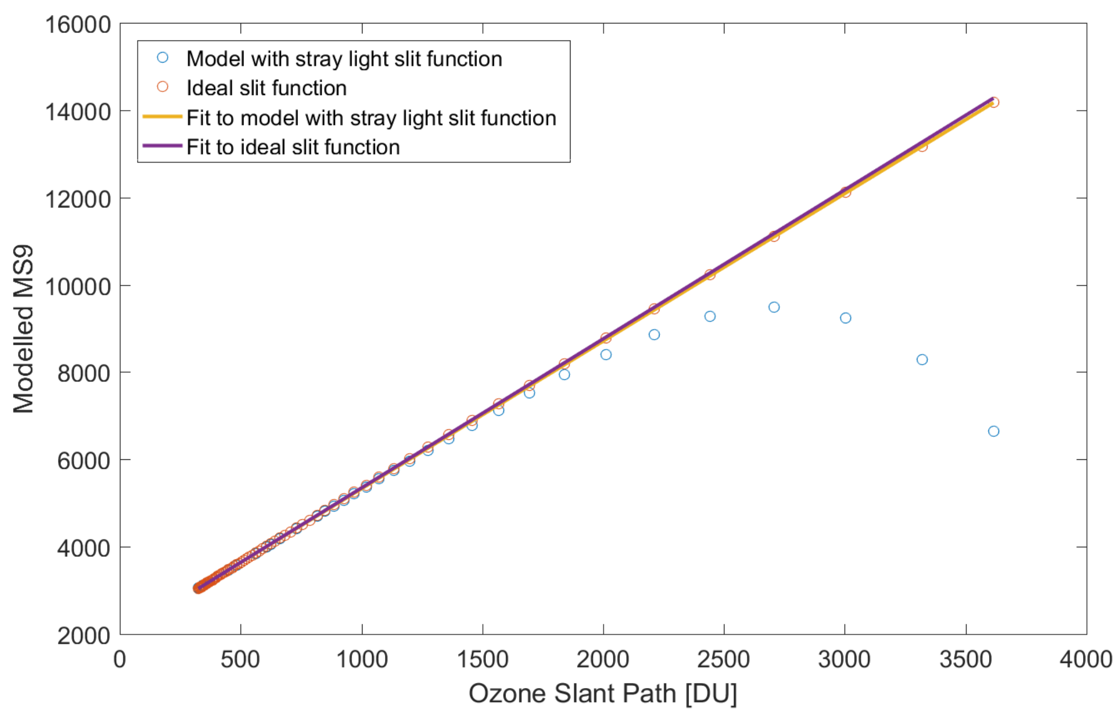


Figure 5: Example of Langley plot fitted to a modeled single Brewer data

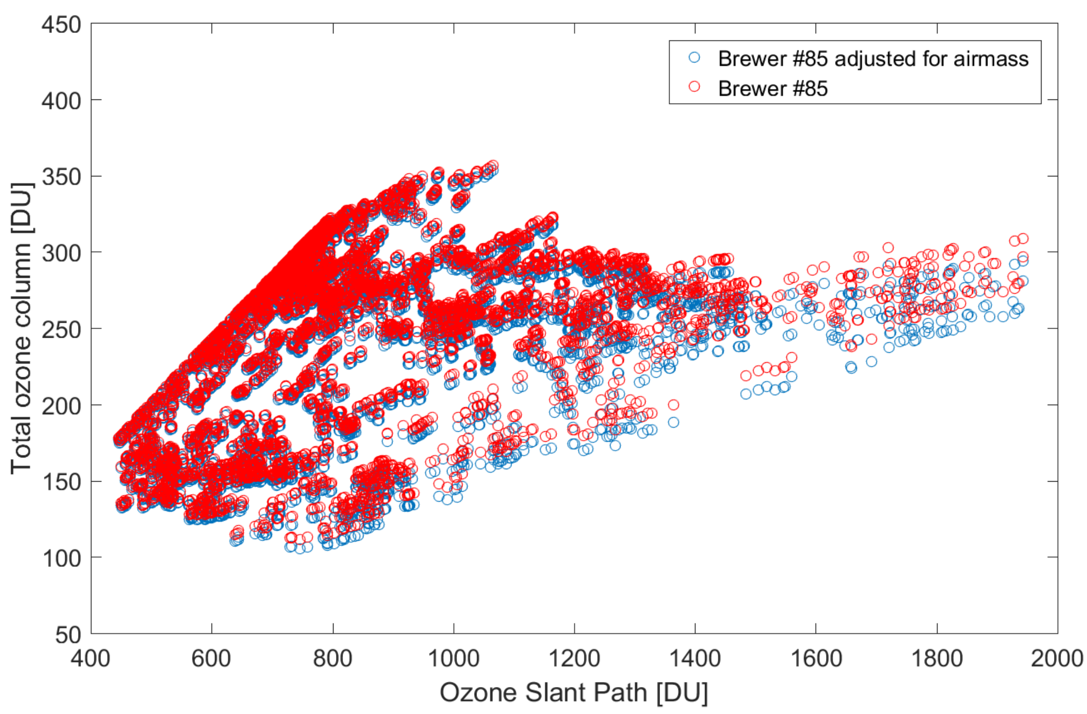
For the single Brewer the ETC is calculated as 1945.4 for a modeled trapezoid slit function with stray light which is comparable with 2020 as calculated by Kiedrom et al. (2008) noting the slight differences in the slit functions and solar spectrum. Karppinen et al. (2015) have reported 3218 for ETC value for slit functions with stray light. However, they used LibRadtran 1.6-beta radiative transfer model to scale their data to be matched with real data."

Page 10.25: Consider also to discuss the case of early spring at high latitudes, with low sun and high ozone content.

This is a good suggestion but beyond the scope of this study. We chose the South Pole as it is important for the detection of ozone recovery and is being used for trend analysis and satellite validations. With ozone recovery in future more data collected at large ozone slant paths would be available which may cause an error in the trend analysis or satellite validation due to the effect of stray light.

Page 11.15: Consider to plot corrected /uncorrected South Pole Brewer to illustrate the error due air mass calculation.

The following plot has been added to the manuscript.



Page 12: A better description of the data-set might be provided or referenced: number of simultaneous measurement, if the data are available at WOUDC/NDACC databases, the QA/QC results of calibrations and how stable are in time the comparison between Dodson instruments, and brewer-dobson will help to interpret the comparison.

The following statements have been added to the manuscript:

“The Brewer data for the South Pole site are available at the WOUDC website. Due to the logistic difficulties Brewer #085 was not replaced or calibrated until 2016.

The Dobson data used for this study are freely available at: ftp://aftp.cmdl.noaa.gov/user/evans/York_Omid/. For this study all direct sun Dobson measurements are used while only one measurement representative of the day is reported to the NDACC or WOUDC. A complete description of the South Pole dataset is provided by Evans et al. (2017). The reprocessed data using WinDobson software as described in Evans at al. (2017) are used for the analysis here. Generally, the Dobson instrument at the South Pole site is replaced with a calibrated instrument every four years. The instrument replaced is calibrated against the reference Dobson #083 and the calibration results are used to adjust and post-process the last four years of data collected at the South Pole. The calibration procedure can be found at Evans and Komhyr (2008) and the major calibration or instrument changes regarding the South Pole dataset can be seen in Fig. 5 of Evans et al. (2017).”

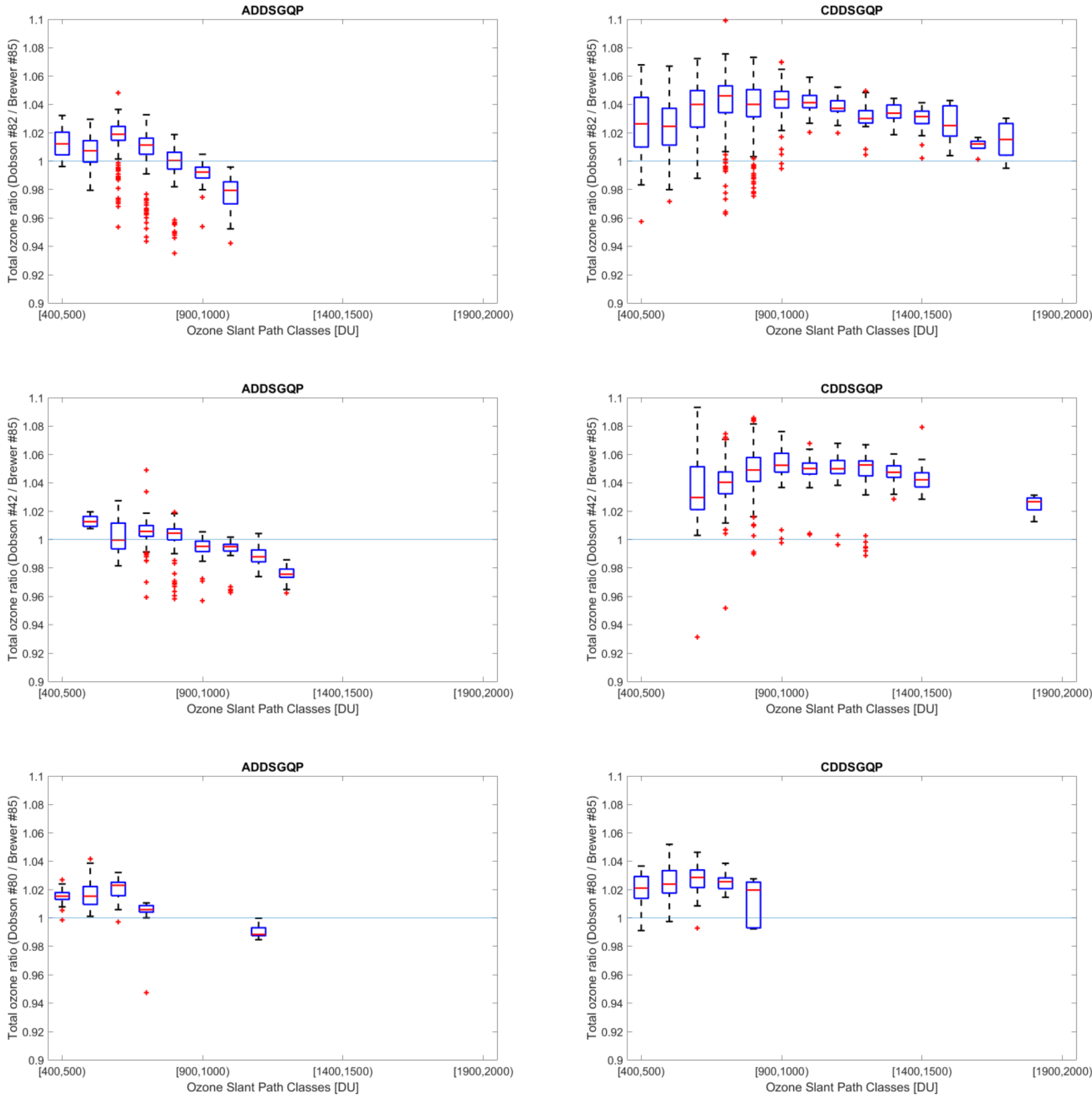
The simultaneous measurements available are summarized in a table and added to the manuscript:

“Table 7: The number of simultaneous measurements in each bin

	Dobson #82		Dobson #42		Dobson #80	
Bins (OSP)	AD	CD	AD	CD	AD	CD
[400 500)	39	33	0	0	45	41
[500 600)	171	143	7	0	63	63
[600 700)	172	113	101	70	57	72
[700 800)	439	313	258	179	11	8
[800 900)	174	235	153	178	5	6
[900 1000)	155	120	30	54	0	1
[1000 1100)	96	125	57	28	0	0
[1100 1200)	4	50	46	67	7	4
[1200 1300)	0	41	36	46	0	2
[1300 1400)	0	43	4	49	3	2
[1400 1500)	0	36	0	19	0	1
[1500 1600)	0	19	0	4	0	0
[1600 1700)	0	6	0	1	0	0
[1700 1800)	0	9	0	1	0	0
[1800 1900)	0	0	0	10	0	0
[1900 2000)	0	0	0	0	0	0
Total	1250	1286	692	706	191	200

Page 12.15: Concerning the analysis , the intervals with a reduced number of observations should be removed, this discard for example most of the Dobson #80 observation for high ozone slant column. Consider to use the same order of the Dobson instruments in plots and enumerations.

The boxes with less than 6 coincident measurements in each bin are removed from the plots.



Page 13,5 : In the conclusions refers that you are using the measured slit but in reality the central part of the slit is not measured, and are also model as trapezoid.

Revised.

References

Bernhard, G., Evans, R. D., Labow, G. J., and Oltmans, S. J.: Bias in Dobson total ozone measurements at high latitudes due to approximationsin calculations of ozone absorption coefficients and air mass, 110, https://doi.org/doi:10.1029/2004JD005559,.

Josefsson, W.: Focused sun observations using a Brewer ozone spectrophotometer, 97, 15 813–15 817, https://doi.org/10.1029/92JD01030,https://agupubs.onlinelibrary.wiley.com/doi/abs/10.1029/92JD01030.5

Karppinen, T., Redondas, A., García, R. D., Lakkala, K., McElroy, C., and Kyrö, E.: Compensating for the effects of stray light in single-monochromator Brewer spectrophotometer ozone retrieval, Atmosphere-Ocean, 53, 66–73, 2015.

Redondas, A., Evans, R., Stuebi, R., Köhler, U., and Weber, M.: Evaluation of the use of five laboratory-determined ozone absorption crosssections in Brewer and Dobson retrieval algorithms, Atmospheric Chemistry and Physics, 14, 1635–1648, 2014.

Redondas, A., Nevas, S., Berjón, A., Sildoja, M.-M., León-Luis, S. F., Carreño, V., and Santana, D.: Wavelength calibration of Brewer10spectrophotometer using a tuneable pulsed laser and implications to the Brewer ozone retrieval, Atmos. Meas. Tech. Discuss., 2018, 1–16,https://doi.org/10.5194/amt-2017-459, https://www.atmos-meastech-discuss.net/amt-2017-459/, 2018.

Serdyuchenko, A., Gorshelev, V., Weber, M., Chehade, W., and Burrows, J.: High spectral resolution ozone absorption cross-sections–Part2: Temperature dependence, Atmospheric Measurement Techniques, 7, 625–636, 2014.

Evans, R. D., Petropavlovskikh, I., Mcclure-begley, A., Mcconville, G., and Quincy, D.: Technical note : The US Dobson station network data record prior to 2015 , re-evaluation of NDACC and WOUDC archived records with WinDobson processing software, , 12051–12070, 2017.

Evans, R., and Komhyr, W.: Operations Handbook - Ozone Observations with a Dobson Spectrophotometer, WMO/GAW Report No. 183, World Meteorological Organization, Geneva, Switzerland, 2008.