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

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10 **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

15 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 mathematical model for each instrument. For the first time, new ozone absorption coefficients are

20 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 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 between 2008 and 2012 are compared with ozone data from a collocated double monochromator Brewer spectrophotometer (Mark

25 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

30 became commercially available (Kerr et al., 1981). A similar network was 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

5   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

10 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

15 functions for converting Dobson measurements to the Brewer scale. These methods have been partly successful, but they cannot entirely explain the differences between the measurements of the two instruments (Scarnato et al., 2010).

 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).

20 While 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

25 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

30 instrument under all conditions and that further study was needed. This was 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:

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

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

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

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 /

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:

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

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

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

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

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

$$\Delta\alpha_{AD} = [\alpha(305.5) - \alpha(325.4)] - [\alpha(317.6) - \alpha(339.8)] \tag{8}$$

20   where $\Delta\alpha$ is the differential ozone absorption coefficient at -46.3º 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:

25   $$X = (MS9 + \Delta\beta\frac{P_s}{P_0}m_R - B)/(\Delta\alpha\mu) \tag{9}$$

where $\Delta\alpha$ and B are the 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

30   intensities (F_i) measured at the four wavelengths $\lambda_i = (310.0, 313.5, 316.8, 320.0)$, multiplied by weighting coefficients w_i.

$$MS9 = \sum_{i=1}^{4} w_i . lnF_i = ln[I(310.0)] - 0.5\, ln[I(313.5)]$$

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

$$\Delta\alpha = \sum_{i=1}^{4} w_i . \alpha_i \tag{11}$$

$$\Delta\beta = \sum_{i=1}^{4} w_i . \beta_i \tag{12}$$

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

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

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 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. The temperature dependence of the cross-sections is expressed as:

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

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 $\rho(z)$:

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

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:

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

where T_0 is 273.15 K and 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

20 absorption coefficient $\bar{\alpha}_i$ is used instead of $\alpha(\lambda)$ in Eq. (2) and (3) (Basher, 1982; Vanier and Wardle, 1969):

$$\bar{\alpha}_i = \frac{-1}{X\mu} ln \left(\frac{\int I_0(\lambda)S(\lambda,\lambda_i)exp(-\alpha(\lambda)X\mu - \beta(\lambda)\frac{P_S}{P_0}m_R)d\lambda}{\int I_0(\lambda)S(\lambda,\lambda_i)exp(-\beta(\lambda)\frac{P_S}{P_0}m_R)d\lambda} \right) \tag{17}$$

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

25 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):

$$\bar{\alpha}_i^{apx} = \frac{\int \alpha(\lambda)S(\lambda,\lambda_i)\,d\lambda}{\int S(\lambda,\lambda_i)\,d\lambda} \tag{18}$$

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:

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

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

10   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

15   elements, e.g. the grating, are the main sources of stray light in the spectrometers. Particulate scattering within the instruments 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.

20   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. A He-Cd laser (single

25   line at 325.029 nm) has been used to measure the slit functions of the Brewer. Figure 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

30   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

5   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) (Fig. 1). The model slit function fit to the data (red

10   line) includes three parts: a trapezoid with 0.55 nm FWHM at the core band-pass, the shoulders which are modelled by fitting a Lorentzian function (Table 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 FWHM also has been used (Fig. 1, top left).

15   The slit functions of the world standard Dobson #83 were experimentally measured by Komhyr using a tunable 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

20   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

25   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 (Fig. 3). For this study, symmetrical trapezoids centered at the nominal

30   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 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 1 and 2 are employed. In Table 3 the coefficients calculated for the Brewer single and double versions are shown. The values of $\bar{\alpha}_i^{apx}$ calculated with the ideal

5 (trapezoid) slit functions are the same as the operational values which are currently being used for Brewer #009 and #119. 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.

10 The values of $\bar{\alpha}_i$ and $\bar{\alpha}_i^{apx}$ calculated for the Dobson instrument using the modeled slit functions are provided in Table 4. $\bar{\alpha}_i^{adj}$ 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 $\bar{\alpha}_D$ by 2 % would decrease the discrepancies to below 0.5 %. Thus, the adjusted values were recommended by WMO to be

15 used for the Dobson instruments.

The $\bar{\alpha}_i^{apx}$, and $\bar{\alpha}_i$ 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 $\bar{\alpha}_i$ values for AD and CD pair respectively. The values of $\bar{\alpha}_i^{apx}$ calculated using ideal slit functions and the slit functions with 10^{-5} level of

20 stray light agree with the corresponding values of K93 to within ±2.0 %. In the case of $\bar{\alpha}_i$, the comparison indicates agreement to within ±3.4 % except for $\bar{\alpha}_{339.9}$ 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 $\bar{\alpha}_{339.9}$ is unreasonably high. As in B05, the calculated value, $\bar{\alpha}_D$, presented in this study agrees better with the empirically adjusted

25 value, $\bar{\alpha}_D^{adj}$. 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 (Tables 1 and 2). The AD coefficient calculated for a Dobson

30 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).

5   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). Then, using the quasi-simultaneous measurements of AD and CD pairs 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.

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 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

15   calculated in Sect. 3.1 are used. 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

20   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

25   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

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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

5   deduced from AD measurements.

Figure 5 illustrates the percentage 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

10   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.

15   **3.4 Error 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 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

20   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

25   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 Dobson instruments have been repeatedly calibrated against reference Dobson instrument #83.

30   Quasi-simultaneous direct sun measurements performed within 5 minutes during the period February 2008 and December 2014 were used in the present analysis. The air masses calculated by the Brewer retrieval were corrected 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.

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

5   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 7 presents a comparison of the Brewer total ozone measurements with Dobson ozone observations reduced from the

10 direct sun AD pair as a function of OSP. The ratios between the uncorrected Brewer data and Dobson measurements are also shown in the same plot. The ratio between the Brewer 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 (Fig. 8).

15 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 (Fig. 7). However, CD pair ozone values are on average 3.4 %, 4.5 %, and 2.5 % higher for

20 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).

It can be seen from this analysis that Dobson #42 TOC values show less dependence on OSP. Based on the physical model

25 developed in this work, it could be concluded that this instrument has a significantly lower level of stray light than the other Dobson instruments (#80 and #82).

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

30 air mass calculations and its error contribution to the ozone retrieval were also examined. The target accuracy for ground-based ozone measurements is 1 %, while mathematical 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 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 are used in the case where Dobsons or single Brewers are replaced by double Brewers, a

5   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.

10   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). It is assumed that the slit functions of other Dobson spectrophotometers are similar to the standard one. 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

15   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 ± 0.01 % and ± 1.7 % for $\bar{\alpha}_{AD}$ and $\bar{\alpha}_{CD}$ with K93 respectively, noting that the slit functions and parameters used by K93 and in this work (Tables 1 and 2) are slightly different. The calculation for $\bar{\alpha}_{339.9}$ shows a 67 % difference with K93's result leading to differences of 3.4 %,

20   and -1.7 % in $\bar{\alpha}_{D}$, and $\bar{\alpha}_{CD}$. B05 also have found approximately the same difference for this value ($\bar{\alpha}_{339.9}$) 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 $\bar{\alpha}_{D}$ recommended by WMO is K93's $\bar{\alpha}_{D}$ 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 $\bar{\alpha}_{D}$, $\bar{\alpha}_{AD}$, and $\bar{\alpha}_{CD}$, respectively.

25   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 $\bar{\alpha}_{AD}$ and $\bar{\alpha}_{CD}$ are found. Overestimating the $\bar{\alpha}$ values translates to an underestimation of total ozone. However, 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

30   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.

5 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 % high. However, for OSPs larger than 800 DU the Dobson AD measurements are low 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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Table 1: Brewer and Dobson optical parameters

	Brewer	Dobson
Nominal Wavelengths (nm)	310.0, 313.5, 316.8, 320.0	A: 305.5/325.0, C: 311.5/332.40, D: 317.5/339.9
Slit Function	Single: trapezoid at centre 0.55 nm FWHM, Lorentzian fitted to the measured slit of #009 for shoulders Double: trapezoid at centre 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) Brewer: Parameterized from laser scan of #009 and #119 (Details in Table 1)
Effective temperature	-46.3° C	-46.3° 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 45° N and 325 DU	Bhartia et al. (1985) for 45° N and 325 DU
Air mass	2	2

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

Table 3: Brewer Ozone Absorption Coefficients

		Operational	Slit Function		Ratio [*]
			Ideal	Model	
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 4: Dobson wavelengths and Ozone Absorption coefficients

Wavelength, nm or pair	Effective Ozone Absorption Coefficient (atm cm)⁻¹								
	Komhyr et al. (1993)			This Work					
				Model (Ideal)		Model (10⁻⁵)*		Model (10⁻⁴)	
	$\bar{\alpha}_i^{apx}$	$\bar{\alpha}_i$	$\bar{\alpha}_i^{adj}$	$\bar{\alpha}_i^{apx}$	$\bar{\alpha}_i$	$\bar{\alpha}_i^{apx}$	$\bar{\alpha}_i$	$\bar{\alpha}_i^{apx}$	$\bar{\alpha}_i$
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.
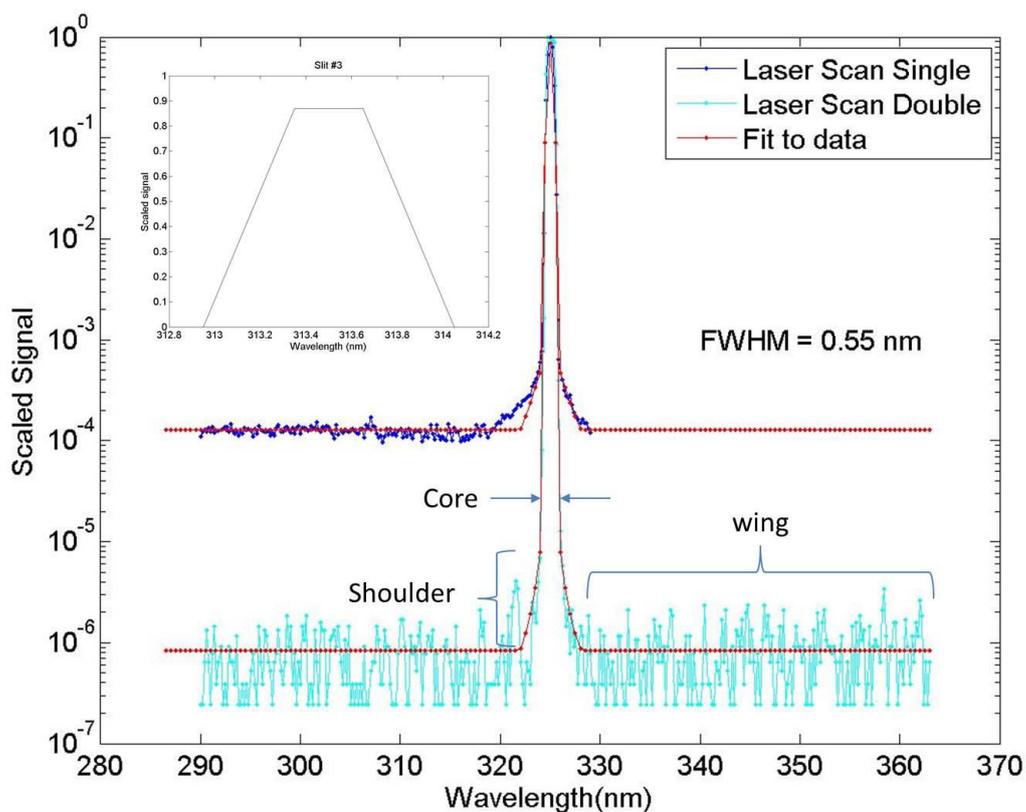
Figure 1: Slit functions measured with a He-Cd laser for single #009 and double #119 Brewers at Mauna Loa as well as fitted models; The ideal slit function is also shown inside the main graph.
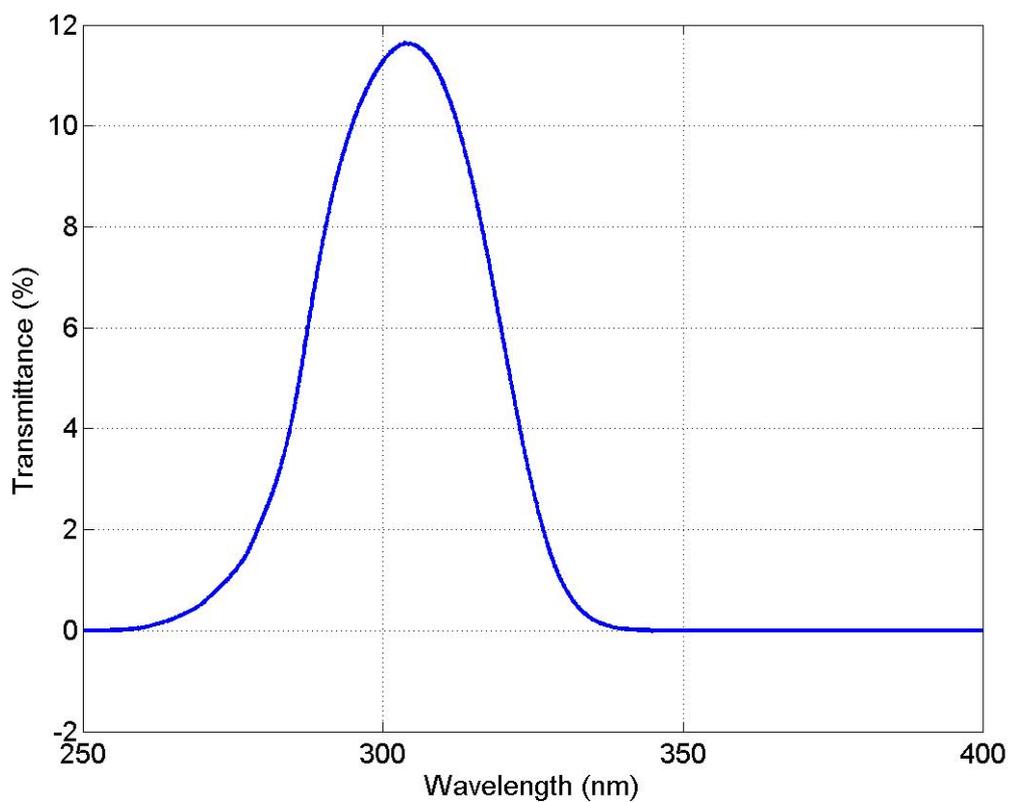
Figure 2: The transmission of a typical combined UG11-NiSO₄ filter utilized by Brewer Mark IV to reduce the stray light measured with a Cary 5E spectrophotometer for Brewer #154 filters.
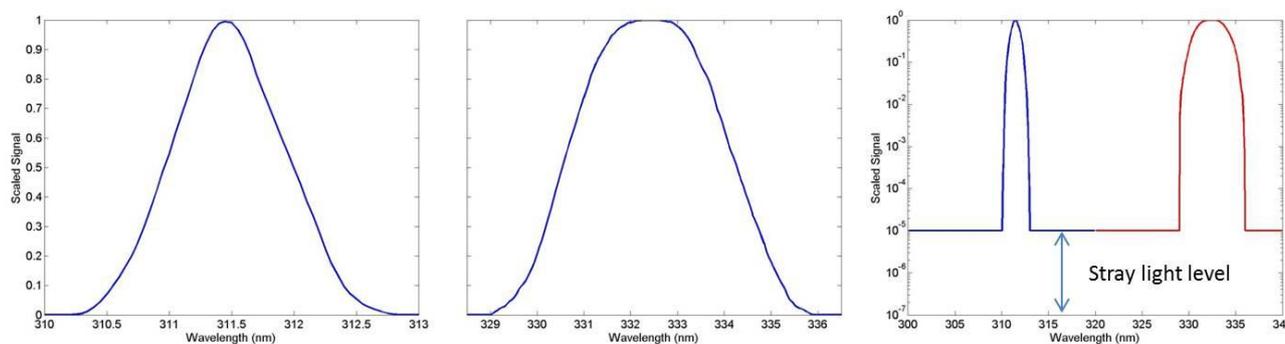
Figure 3: Dobson C-pair ideal slit functions (Left and middle). Dobson Modelled slit function (right). Two straight lines have been added to the core slit functions in order to account for stray light.
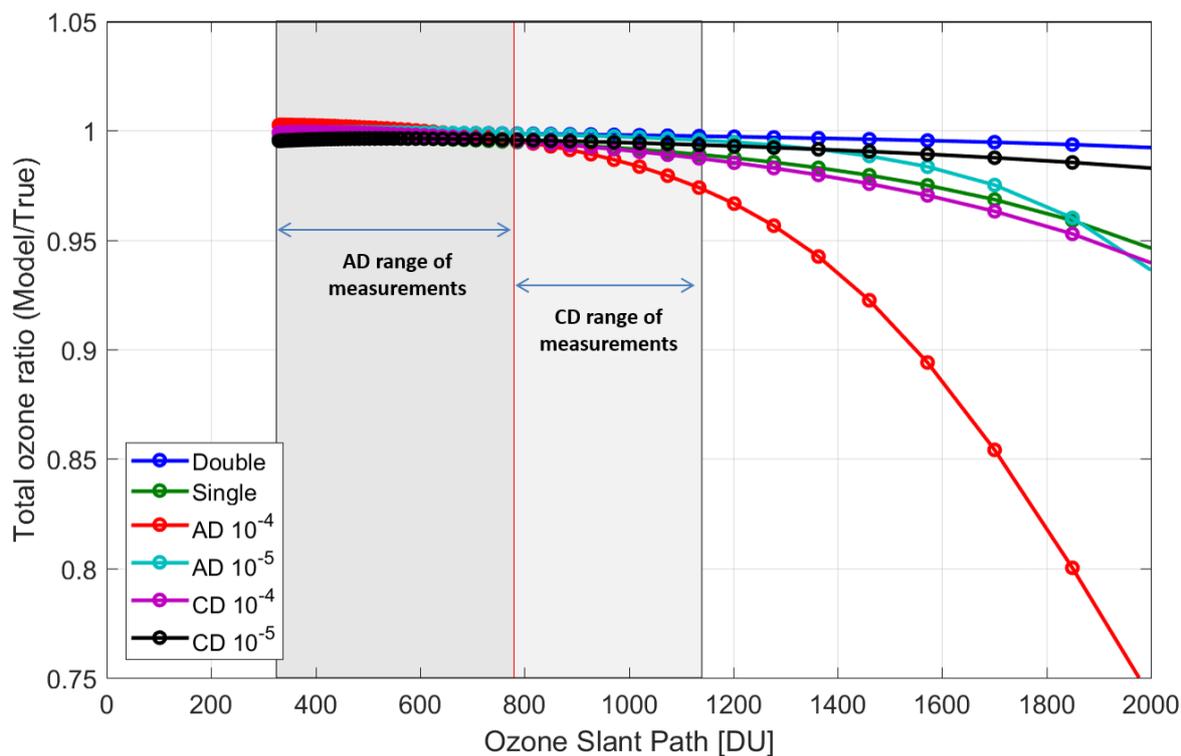
Figure 4: Ratio of the values retrieved from modeled single and double Brewers as well as a Dobson instrument with different levels of stray light (the numbers in front of the pairs are showing the levels of stray light) to assumed 325 DU ozone in the atmosphere (See text for details). The calculations 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).
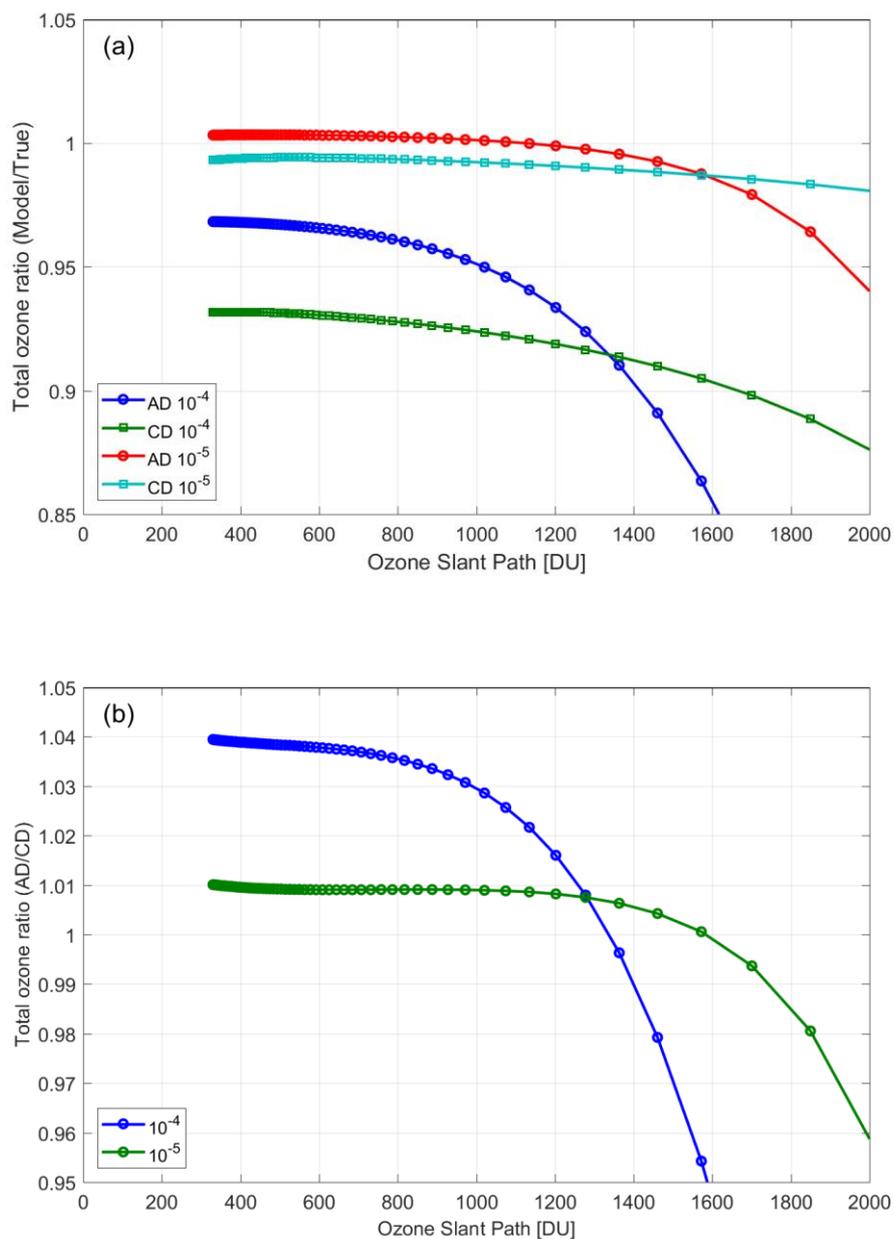
Figure 5: (a) The ratio of total ozone retrieved from modelled Dobson AD and CD pairs with different levels of stray light (10^{-4} and 10^{-5}) to true ozone as a function of OSP. (b) The ratio of total ozone retrieved from AD to CD wavelength pairs. The adjusted coefficients recommended by WMO are 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.
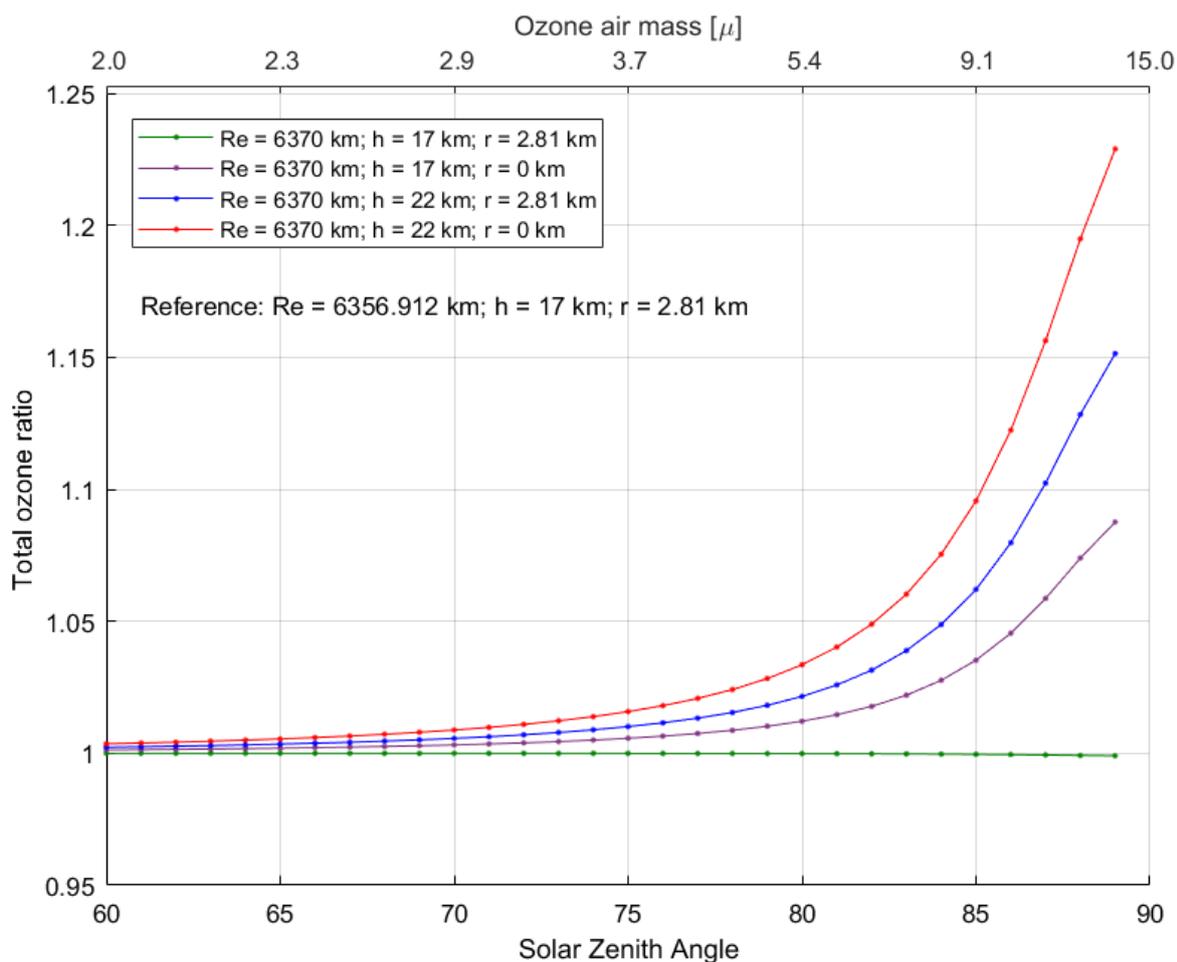
Figure 6: The ratio of total ozone retrieved from modelled Dobson using air mass factors calculated with a mean value for the radius of the Earth, *Re* = 6370 km as used in the Brewer retrieval, and different values for the altitude of site, '*r*', and the height of ozone layer, '*h*', to the ozone values 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

10 **total ozone via Eqs. (3) and (9) respectively.**
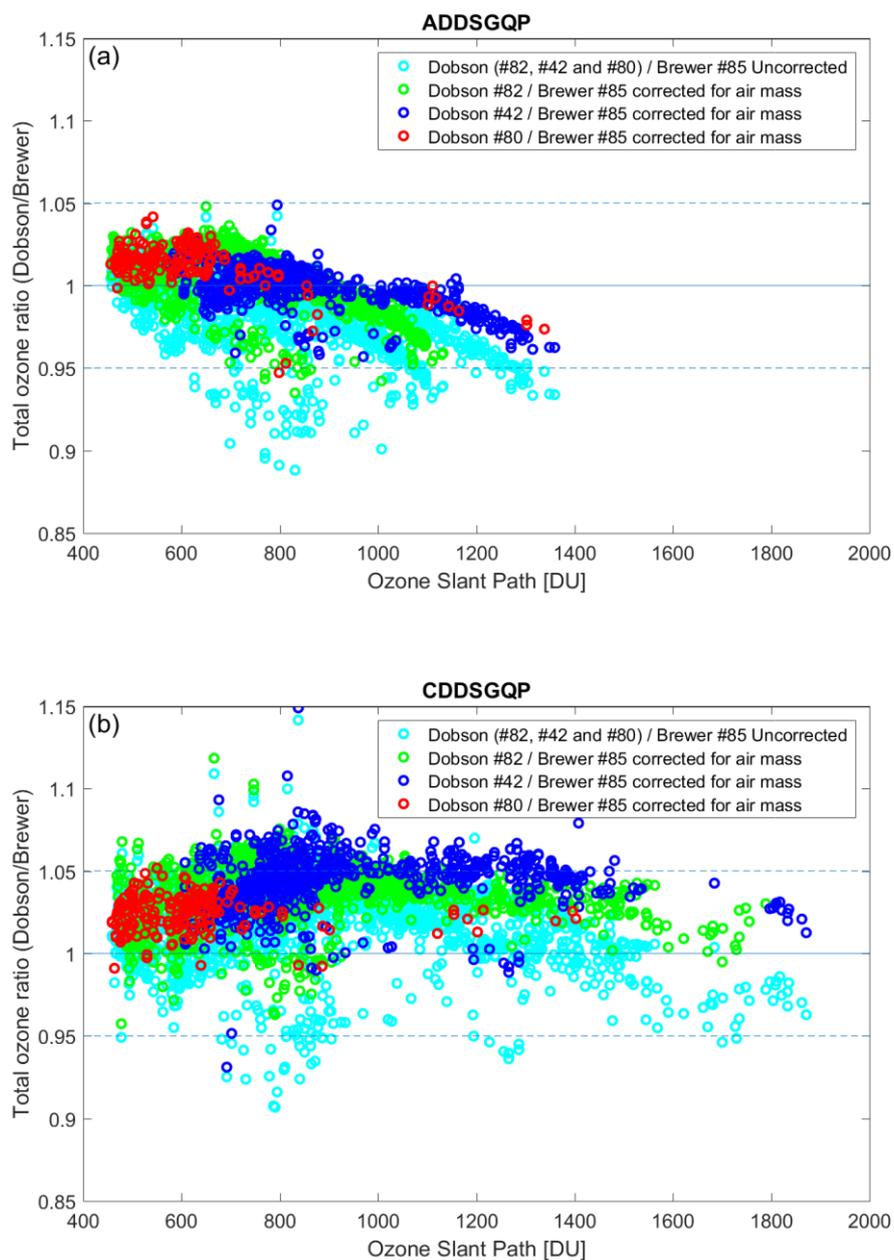
Figure 7: (a) The ratio of quasi-simultaneous observations (within 5 min) using Dobson (#82, #42 and #80) AD wavelengths to double Brewer #085 data at the South Pole. (b) Same as (a) using Dobson CD pairs. Brewer air masses have been corrected using the values used for the Dobson measurements for the 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 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.
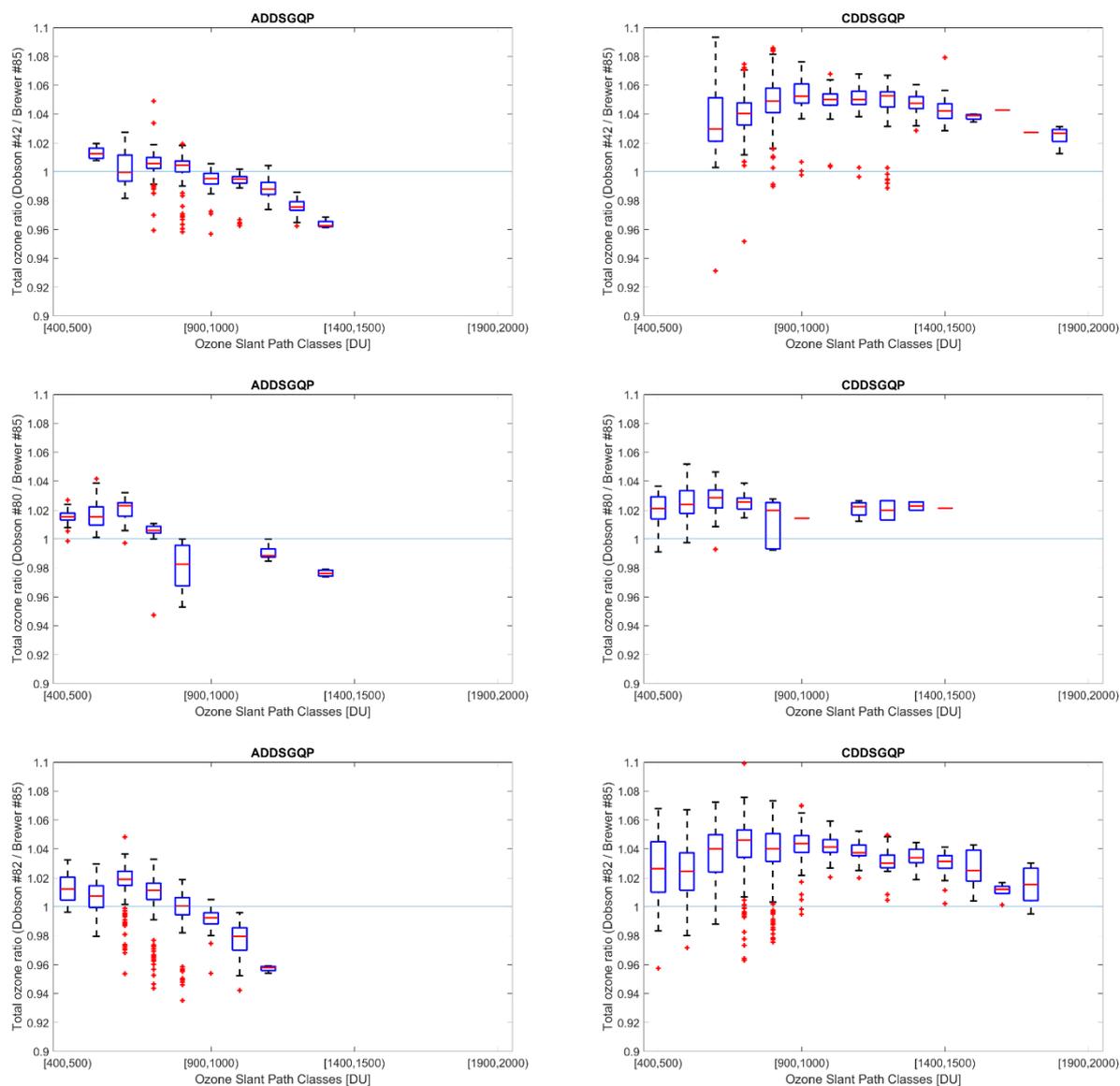
Figure 8: The ratio of quasi-simultaneous direct sun observations (within 5 min) by Dobsons #82, #42, and #80, AD and CD wavelengths to data from double Brewer #085 at the South Pole. On each box, the central red line is the median, the edges of the box are the 25th and 75th percentiles, the whiskers extend to the most extreme data points not considered outliers, and outliers are plotted individually. 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