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Temperature and slant path effects in Dobson and Brewer total ozone measurements

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[1] There is a worldwide tendency to replace Dobson spectrophotometers in ground-based total ozone (TOZ) measurements by more advanced Brewer spectrophotometers. Ensuring the homogeneity of these data sets is of utmost importance if changes in TOZ of a few percent over long time periods are to be diagnosed accurately. Previous studies have identified a seasonal bias of a few percent between midlatitude Brewer and Dobson measurements. At Arosa (Switzerland), two Dobson and three Brewer instruments have been colocated since 1998, providing a unique data set of quasi-simultaneous observations, invaluable to study systematic differences between these measurements. The differences are partially attributed to the seasonal variability in atmospheric temperatures and ozone slant paths (OSP). The sensitivity to the temperature dependence of the ozone absorption cross section is calculated for each operational Brewer spectrophotometers at Arosa by using different high- and low-resolution reference spectra appropriately weighted with the instruments' slit functions, whereas the information on the primary standard instruments is used for all the Dobson instruments. The Brewer retrieval algorithm reveals a higher sensitivity to the reference spectra applied than the Dobson. When adopting the Bass and Paur (1985) or Malicet et al. (1995) ozone absorption spectra with their specific temperature dependence, and correcting for the OSP effect, the seasonal bias between Dobson and Brewer TOZ measurements is reduced to 0.6%. Conversely, these differences increase when using the spectral data of Burrows et al. (1999). This finding illustrates that the accuracy of ground-based spectrophotometric TOZ measurements is limited by the uncertainty in the ozone cross sections measured by different internationally leading laboratories.

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1. Introduction

[2] The depletion of the stratospheric ozone layer by anthropogenic activities has been a topic of scientific and public discussion since the 1970s [*Crutzen*, 1970; *Johnston*, 1971a, 1971b; *Molina and Rowland*, 1974]. The most dramatic effect is observed over Antarctica during austral spring [*Farman et al.*, 1985; *Solomon*, 1988, 1999], but significant ozone depletion is also found over midlatitudes [e.g., *Staehelin et al.*, 2001; *World Meteorological Organization* (*WMO*), 2007; *Harris et al.*, 2008], with halogens released from manmade chemicals such as chlorofluorocarbons (CFCs) and halons (containing bromine) seen as main responsible agents.

[3] Following the International Geophysical Year (1958), and especially when the discussion of the impact of human activities on the ozone layer started, many Dobson instruments were installed to form a worldwide network to monitor the ozone layer changes. In the 1980s an advanced instrument was introduced: the Brewer spectrophotometer [*Kerr et al.*, 1981], using a state-of-the-art technology that relies on the replacement of the prism used in the Dobson by a grating as the dispersing element. This allows the reduction of spectral range, thereby avoiding aerosol effects, and the use of absolute intensity measurements, thereby eliminating the difficult calibration of the logarithmic attenuator in the Dobson instrument.

[4] Though the Dobson instrument has served its purpose well since the 1930s, the Brewer ozone spectrophotometer is becoming more and more common for studying total ozone column (TOZ), sulphur dioxide column, and UV radiation. In the mid-1970s a data quality assurance program was introduced under the auspices of WMO, comparing Dobson and Brewer spectrophotometers with standard instruments on a regular basis. Although Dobson and

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Brewer instruments are based on the same general measurement principle, TOZ measurements exhibit characteristic differences in seasonal variation at midlatitudes [*Kerr et al.*, 1988; *Köhler*, 1999; *Staehelin et al.*, 1998; *Vanicek*, 2006]. The WMO recommends the simultaneous operation of both instruments in order to study these differences and to improve data quality [*WMO*, 2003]. At Arosa two Dobson and one Brewer instruments have been operated simultaneously since 1988, and since 1998 two Dobson and three Brewer spectrometers were installed providing a unique data base of quasi-simultaneous measurements.

[5] The primary goal of this paper is to study in detail the source of differences in TOZ measured by Dobson and Brewer instruments at Arosa. Section 2 includes a short overview about the measurement principle and the retrieval algorithms of Dobson and Brewer instruments. The data sets and the method used in this study are presented in section 3. The temperature sensitivity of the ozone absorption coefficients, used in Dobson and Brewer retrievals, has been calculated for absorption spectra determined by different laboratories and characterized by different spectral resolutions [*Bass and Paur*, 1985; *Malicet et al.*, 1995; *Burrows et al.*, 1999]. With this knowledge, TOZ time series have been corrected for the ozone absorption temperature dependence, and subsequently an empirical correction for the stray light interference is applied. The results are presented in section 4. Finally, conclusions are provided in section 5.

2. Dobson and Brewer Measurement Principle

2.1. Basic Instrumental Design

[6] The total ozone measurement by UV spectrophotometers is based on differential optical absorption spectroscopy (DOAS) utilizing spectral absorption differences of an absorbing gas, here of ozone: the intensities of the solar light reaching the Earth's surface are measured at different wavelengths and compared based on the known differences in laboratory-based ozone absorption cross sections [e.g., *Bass and Paur*, 1985; *Komhyr*, 1980b; *Komhyr and Evans*, 1980]. The solar light entering the spectrophotometers is dispersed by a quartz prism in Dobson and gratings in Brewer instruments, and its intensity is measured in a set of narrow spectral bands. Dobson spectrophotometers [*Dobson*, 1931; *Komhyr*, 1980a] are composed of two symmetric parts with two dispersive elements (prisms). The purpose of the first prism is the selection of the desired narrow wavelength bands, while the second prism is used for the rejection of the stray light in these bands, improving the wavelength selection. For the determination of TOZ, the wavelength selection in the Dobson is achieved with two slits. From the knowledge of ozone absorption spectrum between 305 and 340 nm [e.g., *Bass and Paur*, 1985], and the calibration of the instrument, the ozone column amount of the atmosphere is derived [*Komhyr et al.*, 1993]. The automated Brewer instrument measures intensities at selected wavelengths in the range of 306 to 318 nm to retrieve total columns of ozone and sulfur dioxide. At polluted sites the latter may interfere considerably with the TOZ measurement because of its absorption in this wavelength range [*Kerr*, 1985, 2002; *De Backer and Muer*, 1991]. The movement of holographic gratings (one in the single monochromator Brewer MKII instruments and two in the double Brewer MKIII instruments) ensures the wavelength selection more efficiently than a prism.

2.2. Retrieval Algorithms

[7] Beer's law expresses the attenuation of light by an absorbing or scattering medium. In application to the problem at hand it takes the form

$$I(\lambda) = I_0(\lambda)\exp\left(-\alpha(\lambda)X\mu - \beta(\lambda)\frac{p_s}{p_0}m_R - \delta(\lambda)m_a\right) \quad (1)$$

where

$$\alpha(\lambda) = \frac{1}{X}\int_{z_0}^{\infty}\sigma(\lambda, T(z))\rho(z)dz \quad (2)$$

$$X = \frac{kT_0}{p_0}\int_{z_0}^{\infty}\rho(z)dz \quad (3)$$

at the selected wavelength λ, $I(\lambda)$ is the direct normal irradiance at the Earth surface; $I_0(\lambda)$ is the intensity that would be measured outside the Earth's atmosphere; $\alpha(\lambda)$ is the monochromatic ozone absorption coefficient, where z_0 is the station elevation, T is the temperature in Kelvin, $\sigma(\lambda, T)$ is the ozone cross section, $\rho(z)$ is the altitude-dependent ozone number density and X is the total ozone column (in Dobson Units (DU) equal to 2.69×10^{16} ozone molecules per square centimeter). Note that we use X in the equations whereas TOZ is used in the text. In equation (3), T_0 is 273.15 Kelvin and k is the Boltzmann constant; μ is the relative slant path through ozone (air mass factor); $\beta(\lambda)$ is the Rayleigh scattering coefficient; p_s is the station pressure; p_0 is the mean sea level pressure at 1013.25 hPa; m_R is the relative optical air mass corresponding to Rayleigh scattering (extinction); $\delta(\lambda)$ is the aerosol optical depth; and m_a is the relative optical air mass corresponding to aerosol scattering (extinction). In equations (1) and (3), only the O_3 terms are introduced for clarity while similar terms exist to describe the extinction by SO_2.

[8] DOAS analysis requires a reference spectrum to which all measured spectra are compared. In this case, I_0 at the different wavelengths lambda is obtained from Langley extrapolations at high-altitude stations near the tropics where ozone is stable over the day. The combined $I_0(\lambda)$ values, resulting from the application of the TOZ retrieval algorithms of Dobson and Brewer spectrophotometers, are termed as extraterrestrial constants (ETCs). The ETC of the primary standard instruments is determined by the zero air mass factor extrapolation (Langley plot method) performed at the Mauna Loa observatory. The ETCs for the station instruments operated in the Global Atmospheric Watch (GAW) program are determined by comparison with standard instruments, and their values are updated in regular intervals by intercomparison with standard instruments.

[9] Beer's law applies to monochromatic radiation. However, both the Dobson and Brewer instruments measure fluxes in finite bandwidth. The error involved in using the single wavelength assumption underlying equation (1) is greatly reduced if the strongly λ-dependent cross section of

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Table 1. Comparison Between the Brewer Algorithm's Weighting Coefficients Adopted for the Whole Network w_i and the Weighting Coefficients Related to the Instrument Characteristics w_{i,r_i} Optimized by Equations (15), (16), and (17) for B040, B072, and B156

	Fabrication	F_3	F_4	F_5	F_6
w_i		1.00	−0.50	−2.20	1.70
w_{i,r_i}	B040	1.00	0.19	−3.55	2.36
w_{i,r_i}	B072	1.00	0.08	−3.32	2.24
w_{i,r_i}	B156	1.00	−0.06	−3.06	2.12

ozone is convolved with the appropriate slit function, also called the spectral sampling function [*Vanier and Wardle*, 1969; *Bernhard et al.*, 2005].

[10] Dobson spectrophotometers measure the ratio between the irradiance at two wavelengths bands, one strongly absorbed and the other weakly affected by ozone. In order to minimize interference with other absorbers (such as aerosols) in the retrieval algorithm, TOZ is retrieved using double wavelength pairs resulting from the combinations of AD, AC or CD wavelengths pairs, where A is the combination of wavelengths 305.5 nm and 325.4 nm, C is the combination of 311.5 nm and 332.4 nm and D is the combination of 317.6 nm and 339.8 nm [*WMO*, 2003; *Basher*, 1982]. For example TOZ derived by AD observations is calculated by the following equations:

$$X_{A,D} = \frac{N_A - N_D - (\Delta\beta_{AD})\frac{p_s}{p_0}m_R - (\Delta\delta_{AD})m_a}{\mu(\Delta\alpha_{AD})}, \quad (4)$$

$$N_A = \ln\left[\frac{I_0(305.5)}{I_0(325.4)}\right] - \ln\left[\frac{I(305.5)}{I(325.4)}\right], \quad (5)$$

$$N_D = \ln\left[\frac{I_0(317.6)}{I_0(339.8)}\right] - \ln\left[\frac{I(317.6)}{I(339.8)}\right], \quad (6)$$

$$\Delta\beta_{AD} = [\beta(305.5) - \beta(325.4)] - [\beta(317.6) - \beta(339.8)], \quad (7)$$

$$\Delta\delta_{AD} = [\delta(305.5) - \delta(325.4)] - [\delta(317.6) - \delta(339.8)], \quad (8)$$

$$\Delta\alpha_{AD} = [\alpha(305.5) - \alpha(325.4)] - [\alpha(317.6) - \alpha(339.8)], \quad (9)$$

where N is the instrumental readings and α_{AD} is the differential absorption coefficient at −46 degree Celsius [*Komhyr et al.*, 1993]. The Brewer TOZ retrieval algorithm is based on the following equation:

$$X = \frac{MS9 - B_1}{\Delta\alpha\mu}, \quad (10)$$

where α is the ozone absorption coefficient at the reference temperature of −44 degree Celsius [*Kerr*, 2002] and B_1 includes the ETCs and instrumental constants. $\Delta\alpha$ and B_1 are obtained from a linear combination of their single values at the four wavelengths used for TOZ measurements; B_1 is obtained by comparisons with standard instruments and updated by intercomparison with the traveling standard instruments. In equation (10), X is the TOZ amount (historically defined for Brewer retrieval algorithm as $MS11$) and $MS9$ is derived by a linear combination for $i = (3, \ldots, 6)$ of the logarithms of the intensities (F_i), at the nominal wavelengths in nm λ_i = (310.0, 313.5, 316.8, 320.0), multiplied by weighting coefficients w_i = (+1, −0.5, −2.2, +1.7).

$$\begin{aligned} MS9 &= MS5 - 0.5MS6 - 1.7MS7 \\ &= \ln[I(310.0)] - 0.5\ln[I(313.5)] - 2.2\ln[I(316.8)] \\ &\quad + 1.7\ln[I(320)] \\ &= F_3 - 0.5F_4 - 2.2F_5 + 1.7F_6, \end{aligned} \quad (11)$$

where

$$MS5 = F_5 - F_3, \quad (12)$$

$$MS6 = F_5 - F_4, \quad (13)$$

$$MS7 = F_6 - F_5. \quad (14)$$

[11] The coefficients w_i = (+1, −0.5, −2.2, +1.7), in equation (11), are adopted as operational coefficients in the Brewer network, and they have been selected to minimize the effect of the extinction due to aerosol (τ^{aod}), assumed to vary slowly and linearly with the wavelengths (Ångström formula), and the absorption of SO_2.

$$\sum_i w_i = 0, \quad (15)$$

$$\Delta\tau^{aod} = \sum_i w_i\tau_i^{aod} = \sum_i w_i(a\lambda_i) \approx 0, \quad (16)$$

$$\Delta\alpha^{SO_2} = \sum_i w_i\alpha_i^{SO_2} = 0. \quad (17)$$

[12] The nominal wavelengths can differ slightly from the operational one used in the retrieval algorithm (see SC test in section 3.3) and therefore the network weighting coefficients associated at the nominal wavelengths (w_i) can deviate considerably from the instruments related weighting coefficients ($w_{i,ri}$) as reported in the summary files of calibration tests (ls file; see Table 1 for w_i and w_{i,r_i} values of the Brewer instruments operated in Arosa).

[13] The accuracy of TOZ measurements depends on the knowledge of ozone absorption coefficients, see equations (4) and (10). The ozone absorption cross section in the Huggins band decreases strongly with the increasing wavelength and shows a pronounced temperature dependence (see Figure 1). The Huggins band is currently used for spectroscopic remote sensing of ozone by many experimental techniques (Dobson and Brewer spectrophotometers, satellite instruments, such as TOMS- or DOAS-based

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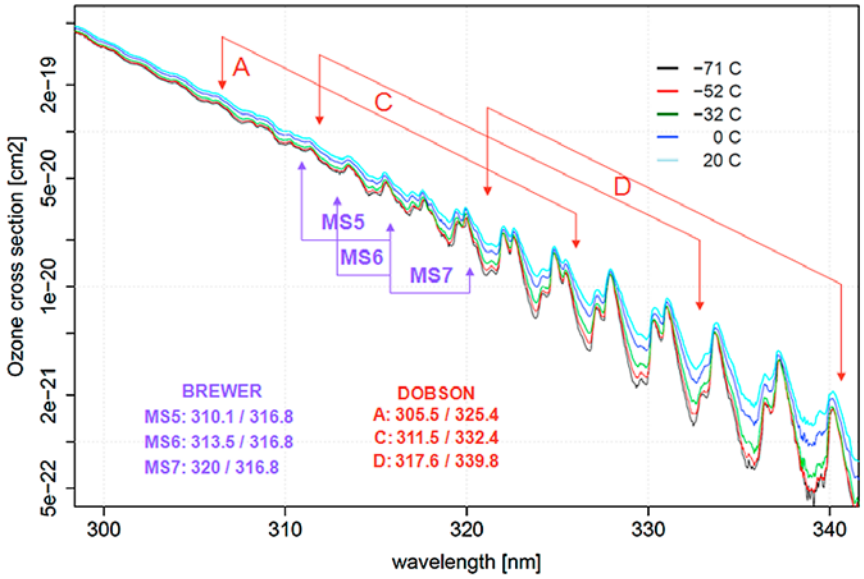

Figure 1. Ozone absorption cross section as a function of wavelength in the Huggins band according to *Bass and Paur* [1985]. Temperature dependence is shown by various colors. Arrows in red and violet indicate the nominal wavelengths used in Dobson and Brewer TOZ retrieval algorithms.

instruments, etc). The ozone spectral data used in this study are described in section 3.2.

3. Data and Method

3.1. Data

[14] At Arosa (46°46′58″N, 9°40′31″E, altitude 1850 m asl), two Dobson instruments (fabrication number D101 and D062, installed, respectively, in 1968 and 1992), two single Brewer MKII (fabrication number B040 and B072, operating, respectively, since 1988 and 1994) and one double Brewer MKIII (fabrication number 156 installed in 1998) instruments are colocated and operated simultaneously. These data sets allow a direct comparison for quality control and for studying the differences between the two types of spectrophotometers. In this study, we used the measurements from 1995 to 2004 because the intercomparisons with the Dobson and Brewer instruments provided evidence for instrumental stability (for more details see *Scarnato et al.* [2009]). In the present analysis we use quasi-simultaneous direct Sun measurements performed within 10 minutes, in order to minimize changes in atmospheric conditions in the comparison. As Arosa is above the inversion layer of the Swiss plateau, direct Sun observations are possible during approximately 70% of the days of the year. Arosa is located in an alpine environment far from pollution sources and therefore significant influences from SO_2 and AOD can been neglected.

[15] Ozone profile measurements are performed by small sondes carried aloft by meteorological balloons that bursts at an altitude of typically 30 to 33 km; the sondes are launched three times per week from Payerne (46°50′N, 6°58′E, 491 m asl), which is located in the center of the Swiss Plateau. The Brewer-Mast (BM) ozone sensors have been continuously used from November 1966 to August 2002, when they were replaced by Electrochemical Concentration Cell (ECC) ozonesondes [*Stübi et al.*, 2008]. Over the years, several modifications were made in order to improve the quality of the time series [*Jeannet et al.*, 2007]. The ozone profiles at Payerne are scaled by an altitude-independent correction factor to match the total ozone

Table 2. Spectral Absorption Cross Sections of Ozone Published by *Bass and Paur* [1985], *Malicet et al.* [1995], and *Burrows et al.* [1999]

	Bass and Paur [1985]	*Malicet et al.* [1995]	*Burrows et al.* [1999]
Instrument	1.8 m Ebert Scanning Monochromator	1.5 m Czerny-Turner Spectrometer	GOME-FM Monochromator with four diode-array detectors
Spectral Resolution (nm)	<0.025	not stated	0.2–0.4
λ range (nm)	245–343	245–343	231–794
Uncertainty (nm)	<0.025	not stated	0.03
Data step (nm)	0.05	0.01	0.12–0.21
Temperatures (°C)	−70, −55, −45, −30, 0, 25	−55, −45, −30, 0	−71, −52, −32, 0, 20
Uncertainty (°C)	0.25	0.05	2
Light source Absolute scaling	Hearn value at 253.65 nm and 1% increase between 25/−70°C *Orphal* [2003]	Measurements of total pressure	Chemical titration at 20°C assuming temperature independent
Stated uncertainty (%)	1.0	1.8	2.6–4.6

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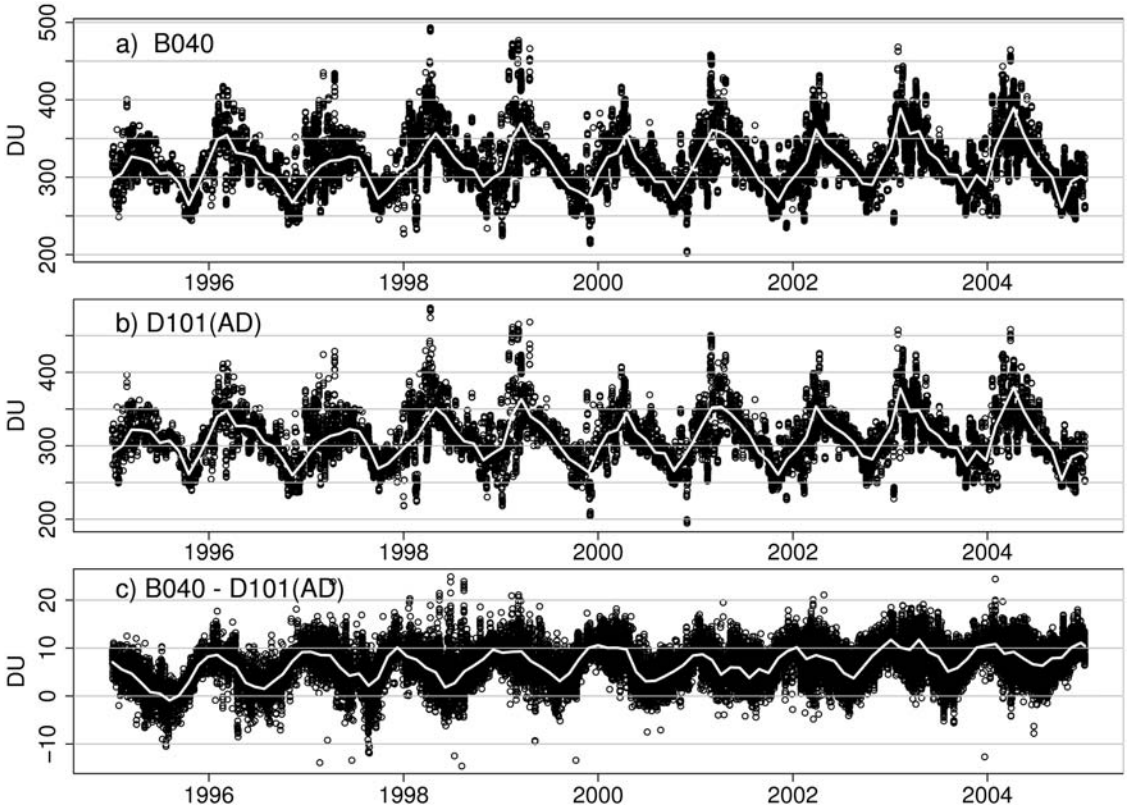

Figure 2. Total ozone time series of Arosa measured by (a) Brewer 040 (B040) and (b) Dobson 101 using AD wavelengths (D101 AD) and (c) their differences for quasi-simultaneous observations.

column, which is measured in Arosa with a Dobson spectrophotometer. Dobson data have been used for normalization because they cover the entire ozone sonde series. The ozone sonde measurements have been used to determine the temperature effect in the retrieved TOZ by Dobson and Brewer spectrophotometers.

3.2. Ozone Absorption Cross-Section Measurements

[16] We have used the absorption cross section of ozone including temperature dependencies derived by laboratory measurements published by *Bass and Paur* [1985], *Malicet et al.* [1995], and *Burrows et al.* [1999]. Laboratory measurements, using the same combination of absorption path and ozone pressure at high accuracy, are rendered difficult due to the strong variation of the absorption cross sections across the Huggins band of more than two orders of magnitude. Furthermore, the spectral resolution of the ozone absorption cross section depends on the experimental setup employed [*Orphal*, 2003]. Spectral absorption cross sections of ozone published by *Bass and Paur* [1985] have a high spectral resolution. This data set is the current remote sensing standard for ozone. The measurements of *Malicet et al.* [1995] have a resolution of an order of magnitude better than *Bass and Paur* [1985], whereas the measurements of *Burrows et al.* [1999] have a lower resolution, representative for most remote sensing measurements in the UV-visible, and they are used in the retrieval of the GOME instrument on the ERS-2 satellite. Table 2 specifies the measurements used here (and the instruments with which they were performed).

3.3. Temperature Influence on Total Ozone Measurements

[17] Dobson and Brewer retrieval algorithms have different sensitivities to temperature due to the different wavelength selection and different approximations in the TOZ calculation (see equations (4) and (10)) [*Komhyr et al.*, 1993; *Kerr et al.*, 1988]. Since 1992, the *Bass and Paur* [1985] spectra have been used as reference for the calculation of TOZ at all GAW stations [*Vanicek*, 2006]. Figure 1 describes the characteristics of the spectra measured by *Bass and Paur* [1985].

[18] The effective ozone cross section is here defined as

$$\sigma_{O_3,eff}(\lambda) = \frac{\int_{800hPa}^{10hPa} \sigma_{O_3}(\lambda, T(p)) \cdot O_3(p)dp}{\int_{800hPa}^{10hPa} O_3(p)dp}, \qquad (18)$$

where knowledge of the temperature and the ozone profile are required to convolve at each altitude the temperature dependent ozone absorption cross section and ozone. While equation (18) provides an accurate approach for calculating the effective ozone absorption cross sections, it is sufficient and more convenient to replace the evaluation of σ_{O_3}, *eff*(λ) by $\sigma_{O_3}(\lambda, T_{eff})$ with an effective temperature defined by

$$T_{eff} = \frac{\int_{800hPa}^{10hPa} T(p) \cdot O_3(p)dp}{\int_{800hPa}^{10hPa} O_3(p)dp}, \qquad (19)$$

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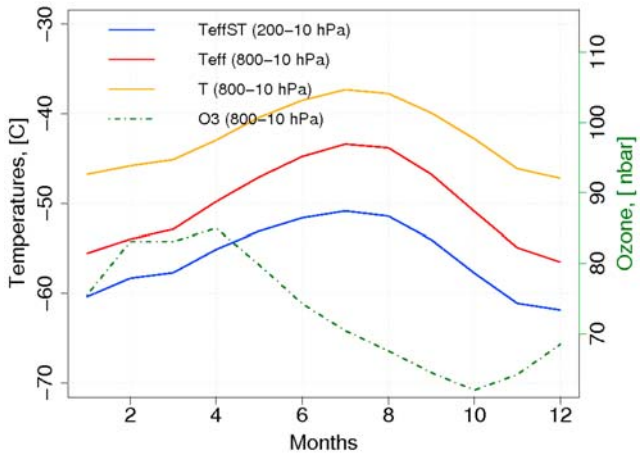

Figure 3. Seasonal variation (mean values for 1995–2004) of the key parameters used in this study: averaged ozone concentration from ozone sondes (O_3), averaged air temperature (T), and effective ozone temperature (T_{eff} and T_{eff}^{ST}).

where air temperature (T) and ozone profile (O_3) are both functions of pressure. We have looked at various approximation from T_{eff}: the resolution of the $T(p)$ and $O_3(p)$ profiles have been limited to few characteristic points and the integrals in equation (19) replaced by summation. If T and O_3 profiles are not available, corrections for temperatures at selected pressure levels may be used as a proxy for effective temperature. Different analytical expressions have been proposed in the literature to describe the temperature dependence of the ozone absorption cross section ($\sigma_{O_3}(\lambda, T)$) measured in the laboratory. Experimental data are better reproduced by a quadratic polynomial function, agreeing within 1% to the measurements in a range of 245 and 330 nm [*Orphal*, 2003]. Therefore, we can assume that the variation of ozone absorption cross section with respect to temperature ($\Delta\sigma_{O3}(\lambda, \Delta T)$) represents the error in TOZ retrieved if the ΔT is the difference between the values of T_{eff} and the retrieval temperatures (−44°C for Brewer and −46°C for Dobson). It can be calculated by the following equation:

$$\triangle\sigma_{O_3,eff}(\lambda, \triangle T) = c_0(\lambda) + c_1(\lambda) \triangle T + c_2(\lambda) \triangle T^2. \quad (20)$$

[19] Equation (20) must be convolved with the slit function of the instrument. Brewer instruments have 6 very narrow slits (approximately of optical width around 1.2 nm), one for each wavelength used to retrieve TOZ and SO_2 and one for dark counting. Brewer optics are designed to reduce aberrations and the slit function is nearly triangular.

[20] In Dobson instruments, two slits are used for TOZ observations, namely S2 and S3 [*Komhyr et al.*, 1993]. Shorter wavelengths pass through the narrow slit (S2) characterized by a slit function of triangular shape and optical width around 1.8 nm, and the large slit (S3) is characterized by a slit function with a trapezoidal shape and optical width around 5.8 nm. The only available information of slit function shapes from Dobson instruments originates from the World Primary Standard Dobson 083 (D083) [*Komhyr et al.*, 1993].

[21] The individual slit functions of the Brewer operational instruments have been characterized using the information stored in the dispersion test file for each Brewer. This test, performed usually every year during the ozone calibration process, establishes the relationship between the step number of the micrometer that moves the grating and the wavelengths seen through each exit slit. The retrieval wavelengths are selected in the Sun Scan test (SC test), which provides the optimal position of the micrometer for most of the measurements, in order to minimize the sensitivity of O_3 and SO_2 calculations to small changes in the angle of the grating. The slit function is measured by scanning through a laser line or discharge lamp with each of the slits. For single spectral lines, the shape of the scan represents the slit function of the instrument, which in general changes with wavelength. In equation (20), $c_i(\lambda)$ (i = 0, 1, 2) have been adapted for the slit function weights $S(\lambda', \lambda)$,

$$c_i(\lambda) = \frac{\int S(\lambda', \lambda) c_i(\lambda') d\lambda'}{\int S(\lambda', \lambda) d\lambda'} \quad (i = 0, 1, 2), \quad (21)$$

where λ are the operational wavelengths and λ' are those wavelengths within the slit width. In this way the slit function of each slit is convolved with the ozone absorption cross-section spectra to determine the effective coefficients $c_i(\lambda)$ (i = 0, 1, 2) and the values of $\sigma(\lambda, T)$ are used as the effective (slit-averaged) ozone absorption cross sections.

3.4. Stray Light Effect

[22] The so-called stray light effect includes any measured radiation which is not taken into account in the idealized ozone retrieval procedure described in section 2.2. It includes (1) radiation scattered within the instrument due to deficiencies in the optics, (2) a poor selection from the dispersive elements of the desired wavelengths, and (3) unwanted radiation scattered in the atmosphere by air molecules and aerosols entering in the field of view. Radiation at the short wavelengths end of the Huggins band is strongly attenuated by ozone, whereas at large air mass values is further attenuated by Rayleigh scattering in the air path. Stray light in the instrument affects mostly the short wavelengths since the intensity is orders of magnitude less than at longer wavelengths due to the strong wavelength dependent absorption by ozone and Rayleigh scattering. The method of Dobson instrument measurements was developed for monochromatic spectral bands and no account was made for the spectral variation of parameters, particularly of ozone absorption, across the instrument's finite bandwidths. The deficiency of this assumption of monochromaticity is its failure to account for the small

Table 3. Ozone Effective Temperature and Air Temperature Mean and Quantile Values Deduced From the Ozone Sondes of Payerne[a]

	Mean	First Quantile	Third Quantile
T_{eff}	−49	−53	−45
T_{eff}^{ST}	−56	−59	−53
T	−42	−45	−39

[a]Unit is degrees Celsius. Ozone effective temperature is T_{eff} and T_{eff}^{ST}, and air temperature is T.

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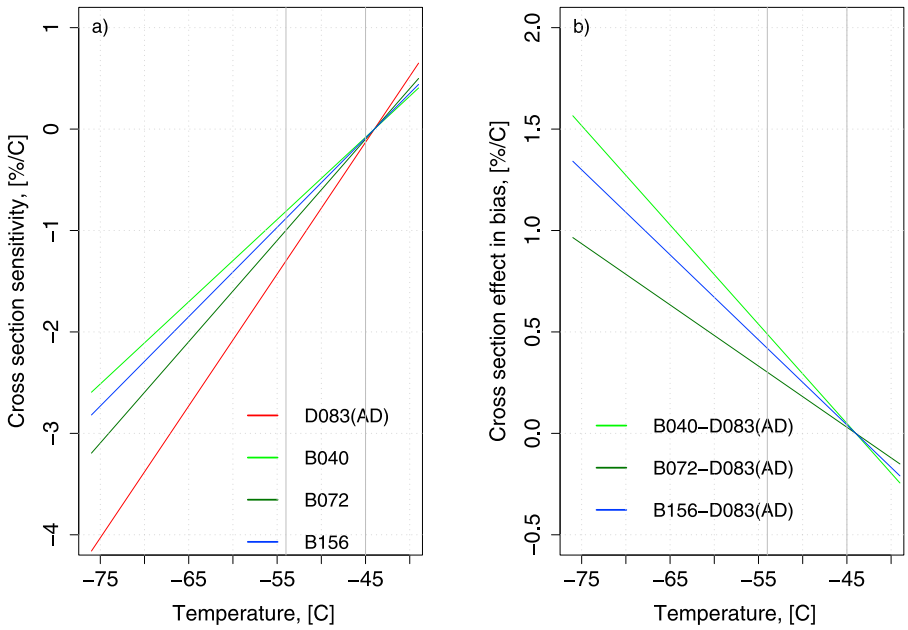

Figure 4. (a) Temperature sensitivity per degree Celsius of the ozone absorption cross section for B156, B072, B040, and D083 using *Bass and Paur* [1985] spectra as reference spectra. Here w_i are the weighting coefficients adopted in the Brewer retrieval algorithm. The ozone absorption cross-section temperature gradient results from application of equations (20) and (21). (b) Ozone absorption cross-section temperature effect in the bias between Brewer and Dobson TOZ measurements. (The two thin vertical lines mark the T_{eff} range typical in Arosa.)

apparent monotonic decrease in the effective absorption coefficient of a finite band with increasing air mass factor and absorber amount, the so-called bandwidth effect [*Vanier and Wardle*, 1969; *Komhyr et al.*, 1993]. For direct sunlight AD measurements, errors of +1%, +3%, and +10% may be present at air masses factors of 2.5, 3.2 and 3.8, respectively [*Basher*, 1982; *Varotsos et al.*, 1998]. As discussed by *Scarnato et al.* [2009], most of the Dobson observations at Arosa are in a range of air mass values between 1 and 2.5, therefore only a marginal number of observations at high air mass values are included in this study.

[23] Brewer and Dobson spectrophotometers have fields of view of 3 and 8 degrees, respectively. As consequence Dobson instruments are more influenced by light scattered into the field of view than Brewer. This can affect the retrieval of ozone values for Dobson measurements at high TOZ values and high solar zenith angles. The error due to the scattering is important when aerosol is present [*Thomas and Holland*, 1977]; this effect is neglected for measurements at Arosa, which is an Alpine unpolluted site. The Brewer MKIII spectrophotometers (B156 in Arosa) are more efficient in suppressing stray light due to their double dispersive elements than MKII instruments (B040 and B072). We use as a simple parameter to describe the stray light effects the air mass factor times total ozone, called ozone slant path (OSP).

4. Results and Discussion

4.1. Total Ozone Time Series

[24] The time series of Dobson and Brewer measurements at Arosa show very similar seasonal variability of TOZ (e.g., Figures 2a and 2b for B040 and D101 for AD observations). However, despite being quasi-simultaneous measurements within 10 min, TOZ values of the Brewer instrument are on average 2% higher. In addition, the differences of both instruments show a seasonal cycle of

Table 4. Temperature Dependence of the Ozone Absorption Coefficient Using *Bass and Paur* [1985] Spectra for B040 and B072 and B156 Compared With the Values Published by *Kerr et al.* [1988], *Van Roozendael et al.* [1998], and *Kerr* [2002][a]

	$\Delta\alpha/\Delta T$ (%/°C)				
	This Study All T, w_i, w_{i,r_i}, $w_{i,D}$	*Kerr et al.* [1988] All T	*Van Roozendael et al.* [1998] All T	*Kerr* [2002] Five Lowest T	This Study Four Lowest T, w_i, w_{i,r_i}
MKII	(B040) 0.081, 0.001, 0.213	(B014) 0.07	0.11	(B014) 0.094	0.226, 0.137
	(B072) 0.099, 0.032, 0.223	-	-	-	0.249, 0.182
MKIII	(B156) 0.088, 0.033, 0.212	-	-	-	0.114, 0.111

[a]The ozone absorption temperature dependence has been estimated using different sets of temperatures (T). The ratio $\Delta\alpha/\Delta T$ depends strongly on the weighting coefficient adopted in the retrieval and on the temperature range used for the determination of c_i. *Van Roozendael et al.* [1998] calculated $\Delta\alpha/\Delta T$ applying a Gaussian shape with a full width at half maximum (FWHM) of 0.6 nm [*WMO*, 1989] to convolve the *Bass and Paur* [1985] cross sections and not the real slit width functions.

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Table 5. Effect of the Ozone Absorption Coefficients in Function of the First and Third Quantile Values of T_{eff} on the Seasonal Bias Between Brewer and Dobson TOZ Measurements[a]

	w_i	w_{i,r_i}	$w_{i,D}$
First and third quantile (°C)	0–0.6	0.2–1.3	0–−1

[a]This contribution has been estimated using w_i, w_{i,r_i}, and $w_{i,D}$ in the retrieval algorithm.

±1% peak to peak with differences maximizing in winter (Figure 2c). Comparison with other instruments operated at Arosa show similar features and a comparable bias has also been documented earlier for several midlatitude stations [*Kerr et al.*, 1988; *Staehelin et al.*, 1998; *Köhler*, 1999; *WMO*, 2003; *Vanicek*, 2006].

[25] Possible sources for the observed differences are the instrumental design, the calibrations of individual instruments with different traveling standard instruments and the retrieval algorithms using different wavelengths with different ozone absorption cross-section temperature and OSP sensitivity. In the present study, we will investigate in detail on the source of differences in TOZ measured by Dobson and Brewer instruments at Arosa.

4.2. Effective Ozone Temperature Variation and Its Influence on Total Ozone Measurements

[26] The temperature cycle, shown in Figure 3 and Table 3, is ignored in both Dobson and Brewer retrieval algorithms [*Van Roozendael et al.*, 1998]. The absorption cross-sections values in TOZ retrievals are at fixed temperatures, such as −46.3°C in the Dobson [*Komhyr et al.*, 1993] and −44.0°C in the Brewer [*Kerr*, 2002] spectrophotometer.

[27] The error in TOZ retrieved can be estimated using equation (18). The temperature sensitivities of the effective absorption coefficients used in Dobson and Brewer retrieval (required in equations (4) and (10)) has been calculated by equations (20) and (21) based on temperature dependence of the *Bass and Paur* [1985] spectra (see Figure 4). The differences between the effective ozone cross section calculated convolving T and O_3 at each level as equation (18) or using ozone weighted temperature columns as in equation (19) and following equations (20) and (21) are negligible.

[28] The absorption in the Huggins band is strongly temperature dependent; therefore accurate measurements are needed in function of wavelengths and temperatures. The second-order polynomial fit in equation (20) leads to a significant difference in the temperature sensitivity of ozone absorption cross section, whether one uses c_i derived from a fit of six, five or four temperatures of *Bass and Paur* [1985] measurements. The ozone absorption gradient per degree Celsius ($\Delta\alpha/\Delta T$) calculated in this study, using different set of weighting coefficients, are compared in Table 4 with the values published by *Kerr et al.* [1988], *Van Roozendael et al.* [1998] and *Kerr* [2002]. The values of $\Delta\alpha/\Delta T$ are very sensitive to the weighting coefficients applied. The retrieval wavelengths can differ slightly from nominal wavelength and $w_{i,ri}$ are selected to better reduce the wavelength dependent interference of SO_2 and aerosols with TOZ measurements, see equations (16) and (17). The use of w_i, instead of $w_{i,ri}$, introduce on average less than 1% of difference in the seasonal temperature dependence of TOZ measurements by Brewer.

[29] The Brewer retrieval algorithm in general exhibits less temperature sensitivity than Dobson (see Figure 4a for c_i calculated using all the 6 temperatures measurements and w_i in the Brewer algorithms). The differences in the ozone absorption coefficients sensitivities within three Brewer instruments operated at Arosa are due to small differences in the optics, cutoff levels and in the operational retrieval wavelengths, which are used to minimize the sensitivity of TOZ and SO_2 calculations to small changes in the angle of the grating (SC test). The retrieval algorithm sensitivity to wavelengths and slit function widths variation (of 0.01 nm and 0.1 nm, respectively) can give uncertainty on the temperature dependence of the ozone cross sections (shown in Table 4) of ±0.022%/°C.

[30] In the period 1995–2003 SO_2 and AOD interference can be neglected in Arosa. If the same method of measurements as in Dobson spectrophotometers would be used to process Brewer data, the weighting coefficients would be $w_{i,D} = (1, -1, -1, 1)$. In this case the temperature sensitivity of ozone absorption coefficients $\Delta\alpha/\Delta T$ resulting from Brewer retrieval algorithm would be higher than for the Dobson (0.22%/°C versus 0.13%/°C cited by *Komhyr et al.* [1993]) and the uncertainty to small variation of retrieval wavelengths and slit widths would be ±0.012%/°C.

[31] The temperature effect of the ozone absorption coefficient on the difference of the Brewer and Dobson observations, considering the first and third quantile of T_{eff} (deduced form the measurements of Payerne) is shown in Figure 4b; Table 5 also illustrates the dependency of the temperature effect in the bias on the weighting coefficients applied in the retrieval algorithms.

[32] Dobson and Brewer spectrophotometer both have very narrow slit widths and resolution, on the other hand the ozone cross-section spectra have a high spectral variability. *Bass and Paur* [1985] experimental data have been extended to 344.9 nm to cover also the wavelength range of Dobson slit at 340 nm [see *Komhyr et al.*, 1993]. *Malicet et al.* [1995] measured the ozone spectra and their temperature

Table 6. Ozone Absorption Coefficients at the Retrieval Temperatures for B040, B072, and B156 Spectrophotometers Using *Bass and Paur* [1985], *Malicet et al.* [1995], and *Burrows et al.* [1999] Spectra as Reference[a]

	$\alpha_{B040}(MS9, -44)$ w_i, w_{i,r_i}, $w_{i,D}$ (cm^{-1})	$\alpha_{B072}(MS9, -44)$ w_i, w_{i,r_i}, $w_{i,D}$ (cm^{-1})	$\alpha_{B156}(MS9, -44)$ w_i, w_{i,r_i}, $w_{i,D}$ (cm^{-1})
Bass and Paur [1985]	0.336, 0.487, 0.342	0.342, 0.473, 0.409	0.347, 0.447, 0.406
Malicet et al. [1995]	0.358, 0.526, 0.252	0.373, 0.511, 0.402	0.372, 0.475, 0.409
Burrows et al. [1999]	0.309, 0.451, 0.304	0.361, 0.497, 0.409	0.344, 0.442, 0.407

[a]Differences due to the application in the retrieval algorithm of w_{i,r_i}, w_i, or $w_{i,D}$ are reported.

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Table 7. Ozone Absorption Coefficients at the Retrieval Temperatures for D083 Spectrophotometer Using *Bass and Paur* [1985], *Malicet et al.* [1995], and *Burrows et al.* [1999] Spectra as Reference

	$\alpha_{D083}(AD, -46)$ (cm^{-1})
Bass and Paur [1985]	1.421
Malicet et al. [1995]	1.451
Burrows et al. [1999]	1.456

dependence with an improved wavelength resolution and including the full range of Dobson slit widths. *Burrows et al.* [1999] spectra have a low resolution but a wide range as required in the satellite retrievals. Therefore the influence of the resolutions and uncertainties of different spectra in retrieving TOZ has been studied and summarized.

[33] The Brewer retrieval absorption coefficients are very sensitive to the instrument optics, to the weighting coefficients applied (w_i, w_{i,r_i}, $w_{i,D}$) and reference ozone absorption cross-sections spectra adopted (see Table 6). At typical retrieval temperatures, absorption cross sections can differ by up to 15% when applying different laboratory spectra to wavelengths used by Brewer spectrophotometers; conversely, the same value for Dobson spectrophotometers is only 2% (see Table 7). The ozone cross-section temperature gradient changes in magnitude and sign (Table 8) as a function of reference spectra applied (Figure 5 and 6). TOZ measurements by Brewer instruments show a more pronounced temperature sensitivity using *Malicet et al.* [1995] (except if $w_{i,D}$ is used) or *Burrows et al.* [1999] spectra instead of *Bass and Paur* [1985]. The higher variability of the ozone absorption coefficient for Brewer with respect to the spectra in use is due to its much higher slit width resolution, in combination with measurement noise in the experimentally determined ozone absorption cross sections. While for the Dobson instruments an average over many nanometers for each slit is relevant, in the case of the Brewer the resolution of the ozone cross-section data is more coarse, and therefore more sensitive to measurement uncertainties in these ozone cross-section data. We have also validated the retrieval algorithm sensitivity for *Malicet et al.* [1995] and *Burrows et al.* [1999] concerning wavelength or slit function variation. The retrieval algorithm sensitivity to wavelength or slit function width variation can lead to uncertainties in the temperature gradient of approximately ±0.033% for *Malicet et al.* [1995] and of ±0.005% *Burrows et al.* [1999].

4.3. Ozone Slant Path Effect and Its Influence on Observations

[34] In this section we extract information on stray light effects by simple parameterization with ozone slant path (OSP) defined as air mass factor times ozone (μ*TOZ). The readings of quasi-simultaneous measurements within the same types of instruments have been compared in function of the OSP in order to study the stray light effect due to optical components; 20469 direct Sun observations have been compared for Dobson D101 and D062 with AD wavelengths pair observations (for details, see *Scarnato et al.* [2009]). The differences of quasi-simultaneous TOZ measurements within the same type of spectrophotometers in function of the OSP do not show systematic differences, showing that measurements taken by the same type of instruments are not subjected to different effects of internal stray light problems. Brewer and Dobson TOZ observations have been corrected for the ozone cross-section temperature dependence in function of the reference spectra. In Figure 7 the differences between Dobson and Brewer MKII (B040) observations (corrected for *Bass and Paur* [1985] ozone cross-section temperature dependence as shown in Figure 4) increase up to almost 4% with the increase of the OSP. Even slightly higher values have been found in the differences between the observations of D101(AD) and B156 MKIII. Instrumental discrepancies at low OSP values (not explainable in terms of stray light effect) are around 2%. At higher OSP values than 800 DU the differences of the measurements show a OSP dependence between 1 and 2%.

4.4. Effect of Temperature Variability and Stray Light on Seasonal Cycle

[35] At Arosa, the difference of TOZ observations by the Brewer triad and Dobson instruments have monthly means values of 2.25% with a seasonal bias of ±1.15% peak to peak. Aiming to explain this seasonal bias, we removed from the measurements stepwise the expected effect of the temperature variability using the *Bass and Paur* [1985] spectra (see section 4.2) and the effect of OSP (see section 4.3). A polynomial second-order function fits the difference of the observations (already corrected for temperature effect; see Figure 4) versus OSP. Only the residual between the instrumental offset (of about 2%; see Figure 4) and OSP dependency (evident for OSP classes above 800 DU) has been eliminated.

[36] The contribution in the seasonal differences of the temperature effect results to be comparable with the stray light effect (see Figures 4 and 7). Note, that this analysis is restricted to conditions typical to midlatitudes and therefore it cannot be directly transferred to high-latitude sites, where the air masses are much larger in the cold season. Each single measurement by B040 and D101 has been reprocessed in function of the temperature and OSP effect; the difference of TOZ time series measured by B040 and D101 is shown in Figure 8 without and with the application of the discussed corrections. An absolute shift and drift of about

Table 8. Temperature Sensitivity of the Ozone Absorption Coefficients for B040 and B072, B156, and D083 Using *Malicet et al.* [1995] and *Burrows et al.* [1999] Spectra as Reference[a]

	$\Delta\alpha/\Delta T$ (°C)	
	Malicet et al. [1995] w_i, w_{i,r_i}, $w_{i,D}$	*Burrows et al.* [1999] w_i, w_{i,r_i}, $w_{i,D}$
MKII (B040)	−0.131, −0.162, −0.045	0.093, 0.020, 0.156
MKII (B072)	−0.120, −0.146, −0.025	0.085, 0.023, 0.148
MKIII (B156)	−0.128, −0.152, −0.029	0.057, 0.010, 0.174
	$\Delta\alpha/\Delta T$ (°C)	
	Malicet et al. [1995]	*Burrows et al.* [1999]
D083	−0.110	−0.018

[a]The ozone absorption cross-section temperature gradient results from application of equations (20) and (21). For *Burrows et al.* [1999], only four temperatures are used to calculate c_i.

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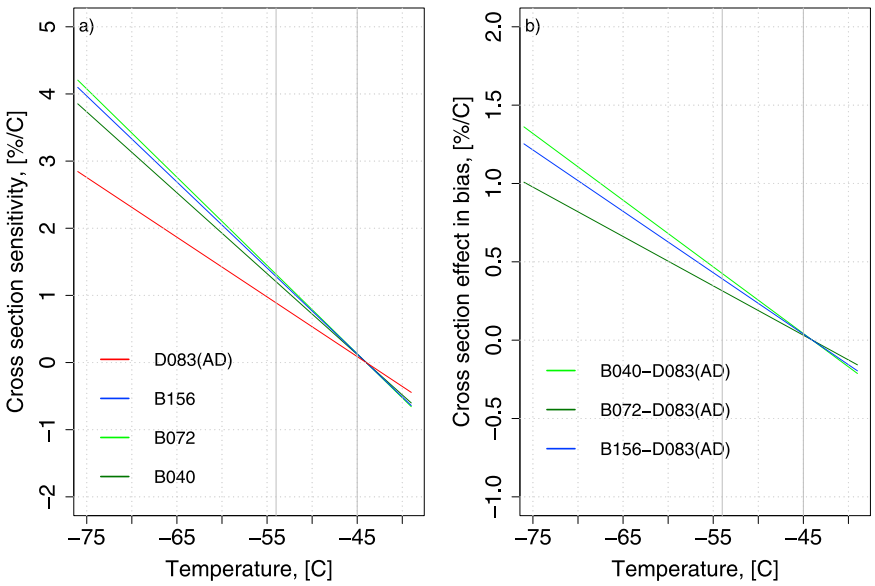

Figure 5. (a) Temperature sensitivity per degree Celsius of the ozone absorption cross section for B156, B072, B040, and D083 using *Malicet et al.* [1995] spectra as reference spectra. (b) Ozone absorption cross-section temperature effect in the bias between Brewer and Dobson TOZ measurements. (The two thin vertical lines mark the T_{eff} range typical in Arosa.)

2.25% is also documented in Figure 8, and the possible sources of this shift are discussed and analyzed by *Scarnato et al.* [2009]. Monthly means can be reduced to 2.05% with a seasonal bias of ±0.6% peak to peak using the ozone cross sections of *Bass and Paur* [1985] and the estimated OSP effect. Instrumental seasonal discrepancies remain unexplained on the order of 1%, (see Figure 9).

[37] The use of $w_{i,ri}$ as well as $w_{i,D}$, in the retrieval algorithm, would better minimize the seasonal bias in the monthly mean difference (see Table 5). If $w_{i,ri}$ or $w_{i,D}$ are applied in the retrieval algorithm, ETCs need to be calculated for the new weighting of the extraterrestrial constants. Note, that w_{i,r_i} differ from the w_i considerably, and using $w_{i,ri}$ the information on TOZ amount from wavelength 313 nm would be neglected. The use of T_{eff}^{ST} instead of T_{eff}

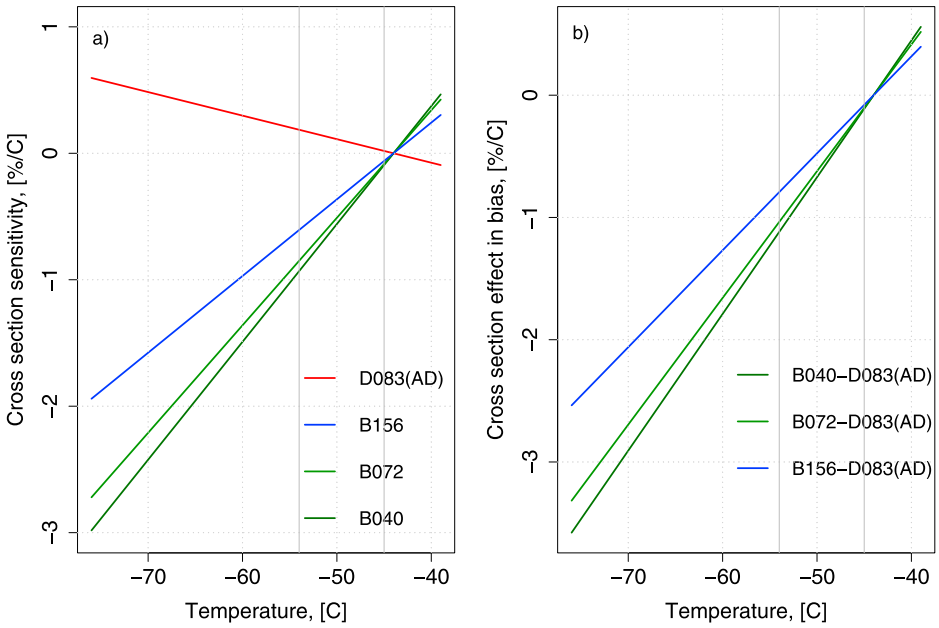

Figure 6. (a) Temperature sensitivity per degree Celsius of the ozone absorption cross section for B156, B072, B040, and D083 using *Burrows et al.* [1999] spectra as reference spectra. (b) Ozone absorption cross-section temperature effect in the bias between Brewer and Dobson TOZ measurements. (The two thin vertical lines mark the T_{eff} range typical in Arosa.)

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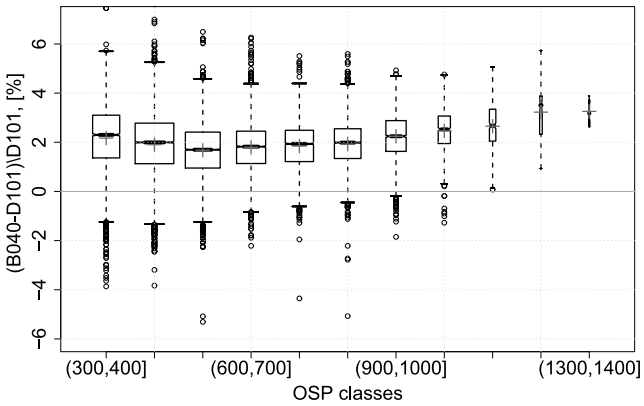

Figure 7. Difference of direct Sun TOZ observations (1995–2005) by B040 and D101(AD) versus ozone slant path. Coincident data within 10 min are used. The observations have been corrected for the *Bass and Paur* [1985] ozone absorption cross-section temperature effect (see Figure 4). The box plots are drawn with widths proportional to the square roots of the number of observations in the groups. The cross indicates the mean value; minimum and maximum value, lower and upper hinge, and median are also indicated with the shape of boxes. Number of observations per classes: 4606, 9361, 7610, 5289, 4975, 4441, 2579, 931, 258, 43, 4 for OSP classes (300, 400) to (1300, 1400).

would lead to an overcorrection for temperature effect in TOZ (see *Scarnato et al.* [2009] for discussion of different temperature scales). The TOZ data sets have also been reprocessed by using other spectra references (see Figures 10 and 11). Retrieving using *Malicet et al.* [1995] spectra, monthly means differences of the TOZ observations by the Brewer and Dobson instruments are −1.8% with a seasonal bias of ±1.05% peak to peak. Correction for temperature and OSP effect lead to mean values around −1.9±0.6%. Retrieving using *Burrows et al.* [1999] spectra, monthly means difference are −3.63±1.09% peak to peak. The temperature gradient applied is too strong to reduce the bias. The error in TOZ retrieved due to temperature variation in equation (20) has been calculated using only three of the lowest temperatures of the ozone absorption cross-sections measurements, because of wavelengths shifts in the spectra at 0 and 20 degrees Celsius.

[38] Modifications based on *Bass and Paur* [1985] and *Malicet et al.* [1995] ozone absorption cross sections and their temperature dependencies allow us to explain a substantial part of the seasonal differences between TOZ measurements.

5. Conclusions

[39] A systematic seasonal cycle in the difference of TOZ measurements of Brewer and Dobson instruments has been documented at many sites at midlatitudes [e.g., *Vanicek*, 2006]. The differences can be attributed to differences in the optics, in the retrieval wavelengths and consequent different sensitivities of the retrieval algorithms to temperature dependence. The ozone mean temperature has a substantial variability over the year but the presently used Dobson and Brewer retrieval algorithms ignore this influence. We have calculated the temperature sensitivity for each operational instrument, taking into account the operational retrieval wavelengths and the slit width functions. The ozone absorption coefficients for Brewer and their temperature dependencies can strongly vary from one instrument to another. The retrieval algorithm sensitivity to wavelengths and slit function widths variation (of 0.01 nm and 0.1 nm, respectively) can lead to uncertainties in the temperature gradient of the ozone absorption coefficients of approximately ±0.022%/°C. Furthermore, the Brewer retrieval algorithm is very sensitive to the weighting coefficients applied. Based on this work we recommend an optimization

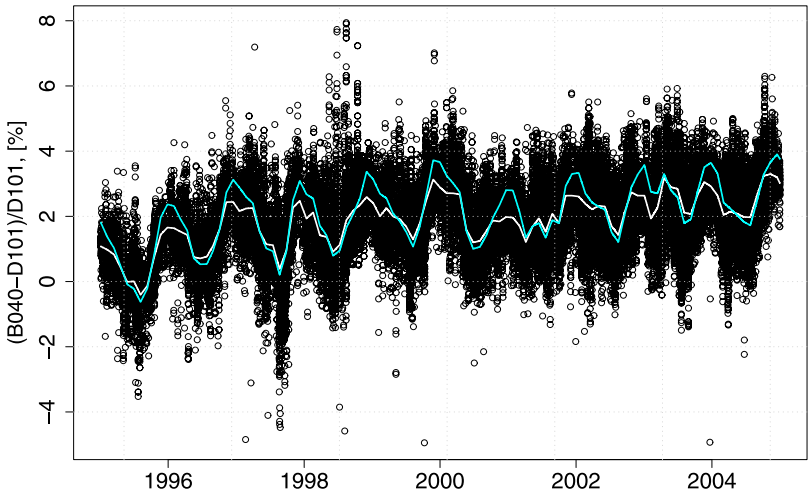

Figure 8. Difference of TOZ time series measured by B040 and D101(AD) using as reference spectra those of *Bass and Paur* [1985]. Light blue line is running mean of the difference of the observations with no correction applied. White line is running mean of the difference of the observations corrected for *Bass and Paur* [1985] ozone cross-section temperature dependence and OSP. Data are 1995–2003, coincident data within 10 min.

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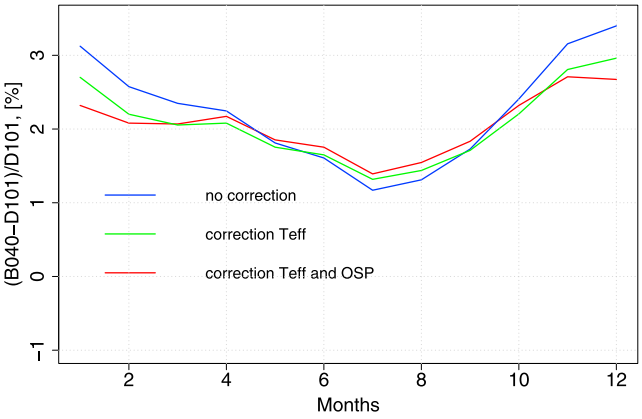

Figure 9. Monthly mean values of the difference of the B040 and D101(AD) observations (in blue) retrieved with *Bass and Paur* [1985] reference spectra, eliminating first the temperature contribution (in green) and second also the ozone slant path effects (in red). Data are 1995–2003, coincident data within 10 min.

of the weighting coefficients for background pollution conditions and for the instrumental operational wavelengths to better minimize the seasonal bias in TOZ observations (see Table 5). In this case, Brewer TOZ observations need to be reprocessed using proper ETCs. The optimization of the weighing in individual Brewer instruments is possibly a way to overcome some of the described problems. However, such an adaption requires the re-recalibration (ETC values) of the Brewer instruments for the respective wavelengths. If Brewer instruments are operated in this way, the required information must be communicated to WOUDC in order ensure the comparability of the Brewer network. The use of these coefficients decrease uncertainties for small slit widths and wavelength variation of interest for the Arosa-type instruments. The ozone absorption coefficients uncertainties for individual Dobson spectrophotometers are difficult to estimate because of the lack of slit function characterization for the operational instruments, and the relation between the Dobson 083 slit functions [*Komhyr et al.*, 1993] and the Dobson 101 and 062 instruments at Arosa is unknown. However, a sensitivity test to small slit widths and retrieval wavelengths variation confirms a lower sensitivity of Dobson than Brewer spectrophotometers.

[40] If the *Bass and Paur* [1985] ozone absorption cross section in Brewer instruments is replaced with any other reference spectra, it would be optimal a new selection of the weighting coefficients (see equations (15), (16) and (17)). This selection should be done in order to maximize the scalar product between the weighting coefficients and the new reference of ozone absorption cross-section values at the operational wavelengths.

[41] We show that the retrieval sensitivity of temperature strongly depends on the ozone absorption cross-section spectra and on the weighting coefficients applied. At typical retrieval temperatures, absorption cross sections can differ by up to 15% when applying different laboratory spectra to wavelengths used by Brewer spectrophotometers, while the respective sensitivity for Dobson spectrophotometers is only 2%. Moreover, the TOZ observations at large OSP values can be influenced by stray light problems, caused by different field of views, optics and suboptimal wavelength selection. We have tried to attribute the observed seasonal differences of the TOZ measurements at Arosa to temperature dependence of the ozone cross sections of the used wavelengths and to OSP. This requires a parameterization of the stray light effect. To this end we have used a OSP polynomial second-order fit. When we account for the effects of the ozone effective temperature based on the spectra by *Bass and Paur* [1985] as well as by *Malicet et al.* [1995] and of the OSP, the seasonal amplitude in the difference of the measurements reduces from about 1% to 0.6%. The temperature sensitivity of the ozone absorption cross section leads to a seasonal bias of about 0.5% in the difference of Dobson and Brewer measurements; a similar amount is also found for the OSP effect. The latter results in less weight in the seasonal bias due to the minor number of observations at high OSP values. Conversely, the use of the spectral data of *Burrows et al.* [1999] increases the differ-

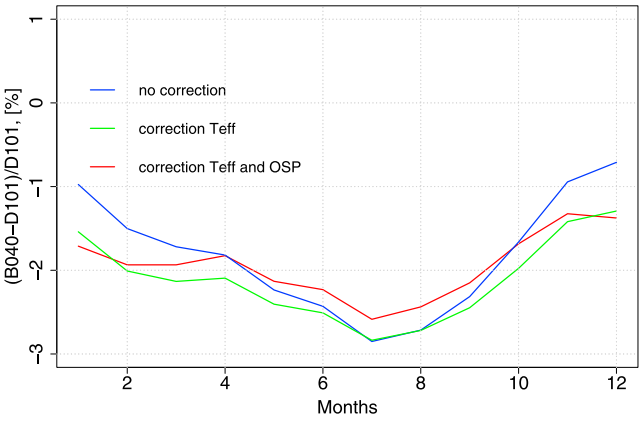

Figure 10. Monthly mean of the difference of the B040 and D101(AD) observations (in blue) retrieved with *Malicet et al.* [1995] reference spectra, eliminating first the temperature contribution (in green) and second also the ozone slant path effects (in red). Data are 1995–2003, coincident data within 10 min.

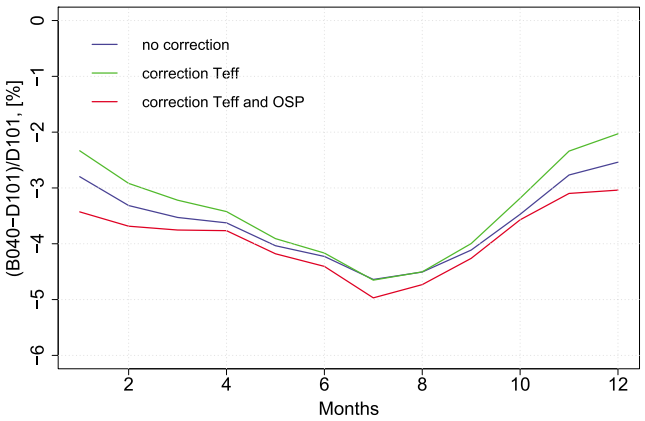

Figure 11. Monthly mean of the difference of the B040 and D101(AD) observations (in blue) retrieved with *Burrows et al.* [1999] reference spectra, eliminating stepwise the temperature contribution (in green) and also the ozone slant path effects (in red). Data are 1995–2003, coincident data within 10 min.

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ences between Dobson and Brewer TOZ observations at Arosa. These findings illustrate that the accuracy of ground-based spectrophotometric TOZ measurements is presently strongly limited by knowledge of the ozone absorption cross section derived from laboratory experiments. Absolute discrepancies between the different laboratory spectra are higher than 3%, leading to a significant offset in TOZ when used for derivation from Brewer measurements (irrespective of the temperature and therefore seasonal dependence). These data are also critical for comparison of ground-based and satellite TOZ measurements. The Brewer retrieval algorithm shows stronger sensitivity with respect to uncertainties within the published ozone absorption cross sections in the Huggins bands. This is the backside of the much of narrower slit width and the weighting optimization of the wavelengths in the Brewer retrieval algorithm, which was selected such as to minimize the effect of sulfur dioxide and AOD interferences.

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