On the sources of bias in aerosol optical depth retrieval in the UV range

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[1] In this paper we discuss and evaluate the systematic sources of bias in aerosol optical depth (AOD) values in the UV range due to (1) the entrance of diffuse light into the finite field of view, (2) diurnal atmospheric changes of ozone under urban conditions, (3) the influence of omitting the effect of NO_2 absorption, and (4) stray light of a single monochromator. These error sources have been neglected before in Brewer AOD retrieval. However, if these bias estimates are added together, it appears likely that the main reason for the recent results, that is, an AOD wavelength dependency that is in contradiction to the Ångstrom law, lies in the omitted sources of systematic error in the AOD retrieval. For instance, the estimated negative bias in AOD difference between 306.3 and 320.1 nm is ~0.0772, while between 310.1 and 320.1 nm it is ~0.0346. If the true Ångstrom α was 1 and the AOD at 320.1 was 0.5, then the actual difference between 306.3 and 320.1 nm would be positive and equal to 0.022, while between 310.1 and 320.1 nm it would be 0.016. Therefore the neglected source of bias can mask this difference and result in a negative Ångstrom exponent (AE) value. In addition to these sources of bias, we also discuss other potential sources of uncertainty that have been previously neglected. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0360 Atmospheric Composition and Structure: Transmission and scattering of radiation; 3359 Meteorology and Atmospheric Dynamics: Radiative processes; *KEYWORDS:* aerosol optical depth, ultraviolet irradiance, surface ultraviolet measurements

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1. Introduction

[2] Recently, the optical properties of aerosols in the UV range have begun to receive more attention. Aerosol effects on radiative transfer and climate in general have been recognized as a research area with still-remaining uncertainties and scientific questions that need further study. To this end, measurement networks have been established (e.g., Aerosol Robotic Network (AERONET) and Global Atmosphere Watch) whose aim is to improve our knowledge of aerosol properties on a global scale. In the current AERONET network the shortest wavelength that is measured in almucantar mode is typically 440 nm (optical depth, single-scattering albedo, and particle size distribution); in some cases, measurements are also performed at 340 nm to determine only optical depth from direct Sun measurements. While, in general, the properties, climate effects, and radiative transfer of aerosols in the atmosphere pose challenges for further research, the need is particularly acute at the shortest wavelengths. This is due to the fact that the significance of essentially all the sources of uncertainty in the aerosol measurements is strongly magnified in the UV range.

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[3] Although, so far, the AERONET network mostly has not offered measurements on aerosol optical properties in the UV, some other measurement approaches are available. The global network of Brewer spectrophotometers consists of nearly 200 instruments originally intended for the monitoring of the total column ozone and spectral UV irradiance. Their additional capability for retrieving the aerosol optical depth (AOD) has long been neglected. In recent years the technique of using the Brewer direct Sun (DS) observation for this purpose has evolved and has been reported in several papers [e.g., *Marenco et al.*, 1997, 2002; *Carvalho and Henriques*, 2000; *Jaroslawski et al.*, 2003; *Cheymol and De Backer*, 2003; *Kirchhoff et al.*, 2001, 2002; *Kerr*, 1997; *Bais*, 1997; *Gröbner et al.*, 2001]. One of the results that has been obtained by many of them is an AOD wavelength dependency that is in contradiction to the Ångstrom law. According to the Ångstrom law, the aerosol optical depth increases with the decreasing wavelength, following a theoretical $\lambda^{-\alpha}$ law where α is the so-called Ångstrom exponent (AE). However, by using Brewer DS measurements, negative α values have been obtained by *Marenco et al.* [1997], *Jaroslawski et al.* [2003], and *Kirchhoff et al.* [2001, 2002]; in most cases, no explanation has even been attempted. Negative AE values could be examined with the Mie theory by using size distribution and refractive index measurements. Negative AE values would require a very

large mean radius of aerosol particles (in the accumulation mode) together with a large real part of the refractive index. We examined a set of AERONET size distribution and refractive index measurements of urban stations, including Belsk and Sao Paolo, and did not find support for this.

[4] In all of the above mentioned papers a thorough error analysis has been lacking. In some papers the effect of random errors is discussed to some extent. However, there are several error sources in this methodology that are systematic rather than random, and we argue that the observed wavelength dependency could be due to these effects that have not so far been taken into account. In this paper we discuss the systematic errors that arise in the AOD retrieval from Brewer DS measurements that need to be considered and taken into account in order to achieve more accurate measurements of aerosol properties in the UV.

2. Methodology and Sources for Systematic Errors

[5] The details of the methodology to retrieve AOD from Brewer measurements are most comprehensively described in *Marenco et al.* [2002]. We give here only a brief description of the main points.

[6] When the Brewer retrieves the total column ozone, it uses a so-called DS measurement: In this, the instrument is directed toward the Sun, and twenty samples of the direct solar beam irradiance are collected at wavelengths centered typically at 306.3, 310.1, 313.5, 316.7, and 320.1 nm. (There are some slight differences in the wavelengths between the instruments.) The total optical depth is inferred from measurements for each wavelength with the use of the Beer-Bouguer law:

$$\tau_{\mathrm{tot}}(\lambda) = \frac{1}{m}\ln\left(\frac{I_0(\lambda)}{I(\lambda)}\right), \tag{1}$$

where $\tau_{\mathrm{tot}}(\lambda)$ is the total optical depth (TOD), m is the air mass factor taking into account the slant path of the direct irradiance, and $I_0(\lambda)$ is the intensity at the top of the atmosphere (the extraterrestrial constant), while $I(\lambda)$ is the measured direct irradiance at the wavelength λ. For small solar zenith angle (SZA) the air mass factor can be approximated by sec(SZA), while for larger SZA (>60°) the Earth's curvature (and refraction in higher SZA values) causes an error in this approximation. Most authors calibrate their AOD measurements by using the Langley method to get the extraterrestrial constant. The Langley method is an application of the Beer-Bouguer law and linear regression. Measured direct irradiances are plotted against the air mass factor; extrapolation to zero air mass yields an estimate of $I_0(\lambda)$, and the slope of the line gives an estimate of the total optical depth of the atmosphere.

[7] The AOD can then be calculated as a residual if all of the other contributions are subtracted from the total optical depth:

$$\tau_{\mathrm{aer}} = \tau_{\mathrm{tot}} - \tau_R - \tau_{\mathrm{O_3}} - \tau_{\mathrm{SO_2}} - \tau_{\mathrm{NO_2}}, \tag{2}$$

where τ_{aer} is the aerosol optical depth, τ_R is the Rayleigh scattering optical depth from sea level to infinity at standard conditions, $\tau_{\mathrm{O_3}}$ is the ozone absorption optical depth, $\tau_{\mathrm{SO_2}}$ is the sulphur dioxide optical depth, and $\tau_{\mathrm{NO_2}}$ is the nitrogen dioxide optical depth. In all the earlier studies, SO_2 has been stated as being small enough to be ignored. In none of them has NO_2 even been mentioned as a potential absorbing gas to be considered. We included it here for a purpose that will be explained in section 2.3.

[8] Equations (1) and (2) can be used to retrieve TOD if clear-sky conditions for a large enough range of air mass factors exist. One can then estimate the extraterrestrial constant and the atmospheric total optical depth; in turn, the aerosol optical depth can then be calculated as a residual. *Kirchhoff et al.* [2001, 2002] retrieved AOD from the Langley plots; that is, their values were representative for the period of morning or afternoon. Moreover, instantaneous values of AOD can be estimated if the extraterrestrial constant is determined in advance on the basis of the Langley method. This latter approach is somewhat more robust since the Langley plots are made only on selected days with the purpose of estimating the extraterrestrial constant only.

[9] Equations (1) and (2) can then be combined as follows:

$$\tau_{\mathrm{aer}} = \frac{1}{m_{\mathrm{aer}}}\left[\ln\left(\frac{I_0(\lambda)}{I(\lambda)}\right) - m_R\frac{p}{p_0}\tau_R(\lambda) - m_{\mathrm{O_3}}D_{\mathrm{O_3}}k_{\mathrm{O_3}}(\lambda) - m_{\mathrm{NO_2}}D_{\mathrm{NO_2}}k_{\mathrm{NO_2}}(\lambda)\right], \tag{3}$$

where

- m_{aer} and air mass factor for the aerosol optical depth;
- m_R air mass factor for the Rayleigh scattering optical depth;
- $m_{\mathrm{O_3}}$ air mass factor for the ozone absorption optical depth;
- $m_{\mathrm{NO_2}}$ air mass factor for the nitrogen dioxide optical depth;
- p atmospheric pressure at the station;
- p_0 standard atmospheric pressure (1013 hPa);
- $\tau_R(\lambda)$ Rayleigh scattering optical depth from sea level to infinity at standard conditions;
- $D_{\mathrm{O_3}}$ ozone column measured with the Brewer instrument;
- $k_{\mathrm{O_3}}$ ozone absorption coefficient;
- $D_{\mathrm{NO_2}}$ total nitrogen dioxide column;
- $k_{\mathrm{NO_2}}$ nitrogen dioxide absorption coefficient.

Here the different air mass factors have been written explicitly for each component to show the more precise form of equation (3).

[10] In the Langley method, sources of random errors exist that arise from atmospheric and instrumental instability. More importantly, there are also sources of systematic wavelength-dependent errors that have been neglected in previous work. The basic requirements for the Langley method are as follows: (1) direct irradiance, (2) monochromatic irradiance, (3) the necessity for extraterrestrial conditions to remain stable during the measurements of air mass factors included in the plot, and (4) the necessity for atmospheric conditions to remain constant during the time interval selected for the Langley plot.

[11] Requirement 3 is naturally always met. Usually, the Langley method is applied at high-altitude stations with a clear atmosphere; otherwise, the rest of the requirements

above are not well satisfied, particularly when UV wavelengths are measured. The various systematic errors introduced by these effects, particularly when the method is applied at a low-altitude station in urban conditions, are now discussed further. First, requirement 1 is not precisely met since diffuse irradiance can enter the instrument's finite field of view (FOV). Second, earlier work has mostly been carried out in urban environments, where the conditions for requirement 4 are hardly ever met. The violation of these two requirements is most apparent; in both cases a wavelength-dependent error is caused that can partly explain the observed wavelength dependency, i.e., the negative AE. Requirement 2 is not strictly true either since the Brewer measures through a slit function with a full width at half maximum of ~0.6 nm.

[12] In addition to the requirements of the Langley method itself, there are error sources related to inappropriate use of equation (2). In other words, since AOD is calculated as a residual, it is very important to accurately consider all the necessary components that compose the total optical depth. The ozone optical depth and the Rayleigh extinction optical depth are both typically larger than AOD values in the UV. Moderate errors in the ozone term in equation (3) may therefore result in considerable errors in the estimated AOD.

[13] The sources of systematic error in AOD estimated in this paper result mostly in biases having the same direction so that they do not compensate each other. Although any single source of systematic error may not necessarily be very large, the combined effect of more than one source can explain the observed negative AE values reported in the earlier studies.

[14] In this study we used the UVspec radiative transfer model from the LibRadtran 0.99 version (available from http://www.libradtran.org). The model was used to generate synthetic Langley plots under different atmospheric conditions, allowing one to estimate the magnitude of each error separately, as discussed in the following sections.

2.1. Diffuse Irradiance Entering the Instrument's Field of View

[15] Brewer DS measurements are performed with a finite field of view. Therefore there is inherently some fraction of the diffuse irradiance (aureole and Rayleigh components) entering the instrument measuring the direct irradiance. The magnitude of this effect depends on the field of view and the wavelength but also on the SZA. The need to correct this effect has been discussed with regard to AERONET measurements that are mostly in the visible band and have a full field of view of 1.2° [*Eck et al.*, 1999]. These effects are clearly more severe at UV wavelengths since a considerably larger fraction of global irradiance is received as a diffuse component. Moreover, the full field of view of a Brewer is 2.6° [*Cede et al.*, 2003]. Therefore it is rather surprising that the effect of diffuse irradiance on the Brewer AOD values has not been discussed before.

[16] If the field of view is 2.6°, then the corresponding solid angle is ~0.0257% of the full hemispheric solid angle of 2π. This is not a large fraction; however, when SZA (and thus the air mass factor on the x axis of the Langley plot) increases, the ratio of direct/diffuse decreases strongly. Even a relatively small part of the diffuse irradiance entering the instrument's field of view could alter the Langley plot. We estimated this effect on the Langley plot method by generating direct irradiance values at different SZA values and adding diffuse radiance around the Sun integrated over the FOV of 2.6°. This plot was then compared to the plot with the direct component only. Figure 1 shows this kind of comparison when the input variables for the radiative transfer (RT) model were as follows: clear sky, 300 Dobson units (DU) of ozone, an AOD of 0.65 at 306.3 nm, a single-scattering albedo of 0.96, and an asymmetry factor of 0.75. The U.S. standard atmosphere [*Anderson et al.*, 1986] was assumed for the temperature and ozone profiles and was scaled to match the total column ozone.

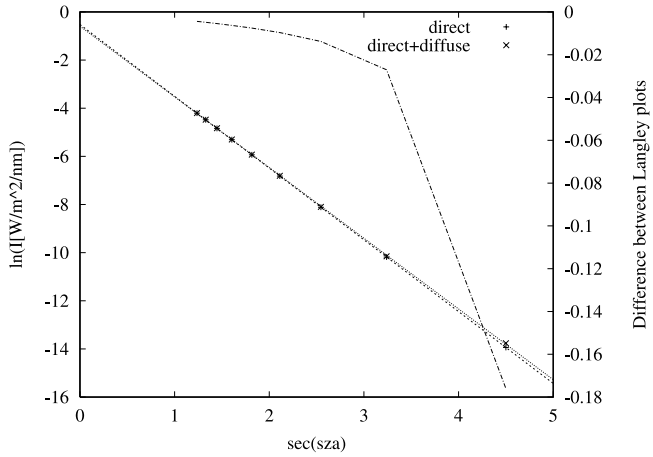

Figure 1. Langley plots generated by the radiative transfer (RT) model. Two cases are included: (1) direct irradiance at 306.3 nm only and (2) direct irradiance at 306.3 nm added to the diffuse component entering the instrument's field of view. The difference between cases 1 and 2 is shown in the right y axis (dash-dotted curve).

[17] The error in AOD caused by the diffuse light is twofold. First, an error results from a systematic underestimation of the extraterrestrial constant (which leads to an underestimation in AOD). Second, it appears as an overestimation of measured direct irradiance ($I(\lambda)$ in equation (1), also an underestimation of AOD). In both cases the effect's magnitude depends on the SZA of the direct Sun measurements. In Figure 1 the largest allowed air mass factor was 4.5. (*Marenco et al.* [1997] used a limit of 4.5 for the maximum air mass factor, while *Jaroslawski et al.* [2003] used 5.) In this example case, τ_{tot} is underestimated by 0.0466 at 306.3 nm and by 0.0130 at 320.1 nm. The sea level AOD difference between 306.3 and 320.1 nm is therefore underestimated by 0.034, and this contributes directly to the bias in Ångstrom α. If the observing altitude were increased to 2.5 km, the resulting AOD difference would be ~0.010, so clearly, the effect of diffuse light is enhanced at lower altitudes. We would also like to stress that this effect introduces monotonic changes in the Langley plot that are difficult to detect from the Langley plot itself. This effect increases strongly if larger air mass factors are allowed. For instance, if the maximum included air mass factor were 5, the bias in the AOD difference between 306.3 and 320.1 nm would be more than doubled. It should also be noted that for the aerosols with more forward scattering phase functions (i.e., maritime) these values are higher.

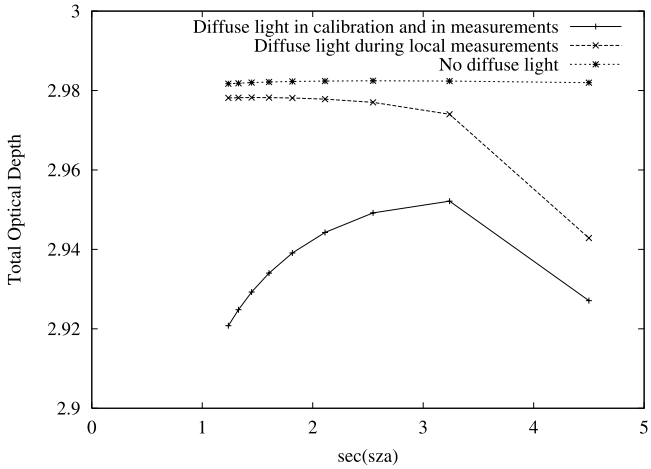

Figure 2. Total optical depth (TOD) against the air mass factor, calculated by equation (1) for the following different cases: (1) Both $I_0(\lambda)$ and $I(\lambda)$ are correct; (2) $I_0(\lambda)$ is correct, and $I(\lambda)$ is biased by the diffuse radiation; and (3) Both $I_0(\lambda)$ and $I(\lambda)$ are biased.

[18] Using equation (1), we calculated the total optical depth separately for each air mass factor of the case in Figure 1. In Figure 2, three different cases are shown. The first, a true TOD, refers to the case in which both the extraterrestrial constant and the actual irradiance measurement ($I_0(\lambda)$ and $I(\lambda)$ in equation (1), respectively) are correct. In the second plot the extraterrestrial constant is assumed to be correct, while the irradiance measurements are affected by the diffuse irradiance fraction in the field of view. This illustrates the case in which $I_0(\lambda)$ has been calibrated in the appropriate conditions (at high altitude with a clear and stable atmosphere). The third case, in which both $I_0(\lambda)$ and $I(\lambda)$ are influenced by the diffuse irradiance, corresponds to the situation discussed in this paper, i.e., the use of Brewer DS measurements together with the Langley method near the sea level to retrieve AOD. Figure 2 illustrates the TOD errors against the air mass factor. However, the mean of the TOD values, calculated separately for each air mass factor, is very close to the TOD calculated as the slope of the Langley plot in Figure 1. The errors made in the TOD estimate convert directly to the bias in AOD after nonaerosol effects are subtracted. The air mass factor dependency of TOD in Figure 2 is a characteristic of the effect of diffuse irradiance in the FOV. The effect of $I_0(\lambda)$ alone is such that the underestimation of TOD increases with decreasing air mass factor, while the effect of $I(\lambda)$ increases nearly exponentially as the air mass factor increases. This is the reason why the combined effect exhibits this peculiar behavior. In the other sources of bias, discussed below, the combined effect results essentially in a constant underestimation with changes in the air mass factor.

2.2. Diurnal Variability in an Urban Atmosphere

[19] One of the requirements for the Langley method is that the atmospheric conditions stay constant during the time interval chosen for making the measurements over the air mass range of the Langley plot. All of the earlier studies that have resulted in negative values of AE from Brewer measurements have been done in urban environments. There are numerous papers that report on the diurnal variability of tropospheric ozone and its precursors in urban environments [e.g., *Massambani and Andrade*, 1994; *Jaroslawski*, 1995; *Lorenzini et al.*, 1994]. They show clear diurnal trends, for instance, *Massambani and Andrade* [1994] in Sao Paolo, which, interestingly, is one of the stations included in the study of *Kirchhoff et al.* [2001, 2002]. On average the diurnal surface ozone peaks at $\sim$14 local standard time and the increase from the morning values is about 0.025–0.05 ppm, the peak value depending on the season. In any season the average pattern is clear.

[20] If we assume a mixing height of 1 km at noon and a surface ozone increase of 0.04 ppm from the morning to noon, this converts to an ozone change of 4 DU in the total column ozone (or $\sim$1.2% change relative to a typical midlatitude value of 330 DU). This is a systematic diurnal change that cannot be overlooked if the Langley method is applied at populated urban stations.

[21] The above approach may slightly overestimate the ozone change, since not all the surface ozone changes are due to photochemical production and its diurnal variability. On the other hand, the actual ozone change takes place in the planetary boundary layer and thus at higher temperatures than the column average temperature. We estimated the effect of diurnal ozone change by changing the total column ozone only; thus we argue that 4 DU is a reasonable value to demonstrate this effect in densely populated regions. We also want to stress that this effect can occasionally be larger [e.g., *Plaza et al.*, 1997].

[22] We generated the Langley plots with the input data of the previous case, but changing the ozone column by 4 DU from morning to noon. This results in an underestimation of the extraterrestrial constant and total optical depth at all wavelengths, with the underestimation increasing with decreasing wavelength. From this cause the AOD difference between 306.3 and 320.1 nm is underestimated by 0.0279. Again, this bias is in a direction that can partly explain the observed negative Ångstrom α values. This type of change is also monotonic and therefore difficult to detect from the Langley plots themselves. Possible random variabilities in the extraterrestrial constant can be reduced by averaging it over several days [e.g., *Marenco et al.*, 2002]. However, this does not reduce the systematic error, which is due to the systematic diurnal ozone variability. On the other hand, since the total column ozone is known at any instant of time from the Brewer data, the diurnal ozone change could be accounted for in the Langley plot if applied as in *Cheymol and De Backer* [2003].

2.3. NO_2 Influences

[23] When the nonaerosol components are subtracted from the total observed optical depth (equation (2)), typically, only ozone and Rayleigh scattering are considered. Except in highly polluted areas, the effect of SO_2 is assumed to be small enough to be ignored. NO_2 has not been taken into account or even mentioned in any of the previous work. We argue that, in urban conditions, it cannot be simply omitted without considering its local magnitude.

[24] The UV absorption coefficients of SO_2 and NO_2 have different wavelength dependencies, but both have similar

magnitudes in the UV-B. NO_2 absorption increases with increasing wavelength (having a maximum at about 390–400 nm). In other words, if significant amounts of SO_2 were present, its influence on AE would be the opposite. It is evident from the measurements in urban environments available on the Internet (e.g., for Brussels, Belgium from http://www.irceline.be/~celinair/airact_table.html) or from annual air quality reports in various states of the United States (e.g., for Wilmington, Delaware from http://www.dnrec.state.de.us/air/aqm_page/docs/pdf/anrpt00.pdf), as well as from published studies [e.g., *Massambani and Andrade*, 1994], that urban NO_2 concentrations in ppb are typically much higher than those of sulphur dioxide.

[25] We estimated the effect of neglected NO_2 absorption with the data reported by *Massambani and Andrade* [1994]. The measured surface NO_2 amounts are on average from 0.05 to 0.07 ppm. If 0.05 ppm of NO_2 is converted into a total column amount (with a mixing height of 1 km), it corresponds to 5 DU. This seems to be a good estimate for urban conditions, further justified by *Alexandrov et al.* [2002], for instance, who presented total column NO_2 measurements both in New York City and in Big Bend National Park in Texas.

[26] At 298 K the NO_2 absorption coefficient at 306.3 nm is 1.544×10^{-19} cm^2, and at 320.1 nm the coefficient is 2.544×10^{-19} cm^2 [*Schneider et al.*, 1987]. The optical depths caused by 5 DU of NO_2 at 306.3 and 320.1 nm are therefore 0.02086 and 0.03414, respectively. Due to its wavelength dependency the resulting negative bias on the AOD difference between 306.3 and 320.1 nm can be ~0.0133. Three-band Brewer spectrophotometers are able to measure NO_2 absorption, allowing this effect to be included. However, this effect is omitted in all of the earlier works on Brewer AOD.

2.4. Effect of Stray Light

[27] All spectroradiometers suffer from a degradation of the signal due to a small amount of light arriving from outside the intended wavelength. The problem is called stray light, out-of-band leakage, or spectral scattering [e.g., *Kostkowski*, 1997]. It is caused by photons not following the desired path inside the monochromator due to scattering from the grating, the mirror, or the housing. Double monochromators normally overcome the problem satisfactorily, but for single monochromators, like most of the Brewers, it is always present.

[28] There is no direct way of estimating the proportion of stray light in a Brewer DS measurement. We estimated it indirectly from the measurements of global UV spectra. We analyzed 200 clear-sky UV spectra from Brewer Mk-II 037 at Sodankylä, Finland. We assumed that at the lowest wavelengths, i.e., below 292 nm, due to the absorption in the atmosphere, there is no true irradiance on the surface of the Earth and any signal measured must therefore be stray light. We also used the common assumption that the magnitude of the stray light is the same and constant at all wavelengths. The fraction of the stray light in the irradiance at the five DS wavelengths could then be calculated. It is plausible to assume that this fraction is applicable to the DS measurements, too, because the light path is the same for both UV and DS measurements in the monochromator where the undesirable spectral scattering occurs. The path of light in the foreoptics or the geometry of the light source (i.e., full sky or solar beam) should therefore have no effect.

[29] The fraction of stray light seemed to be negligible (<0.2%) at or above a wavelength of 313.5 nm. At shorter wavelengths a quasi-linear dependence on the SZA could be seen. The effect is at its worst at 306.5 nm and at an air mass of 3–5, where 1–2% of the signal is due to stray light. This result may be true for this particular instrument only, but it gives an idea of the magnitude of the problem.

[30] This SZA-dependent estimate of the stray light was added to the model-generated beam irradiances described before. The Langley plot was biased, again causing an underestimation of the extraterrestrial constant, but only by <1%. TOD was low by 0.0046 at 306.5 nm and by 0.0008 at 310 nm, which, again, are relatively small errors for the total optical depth but transfer directly into the aerosol optical depth and its wavelength dependence. The bias is negligible at higher wavelengths where the stray light has a relatively small contribution.

[31] This error source is present in the single monochromator Brewer independent of where the Langley calibration is performed. Therefore both the calibration and the calculation of AODs from individual observations are normally influenced. If the extraterrestrial constants are unbiased, i.e., obtained from a comparison with a double monochromator Brewer, the stray light has a smaller but more wavelength-dependent influence on the AOD.

2.5. Effect of Air Mass Factor

[32] As stated in connection with equation (3), strictly speaking, different air mass factors should be considered for different attenuating substances, since they have different vertical distributions. The bias caused by using sec(SZA), instead of the actual air mass factor, increases at solar zenith angles larger than 60°. The largest amounts of ozone are found at an altitude of ~22 km, for which reason the ozone air mass factor deviates most strongly from sec(SZA) at large SZA. A good approximation for the true air mass factor can be estimated by

$$m = \sec\left\{\sin^{-1}\left[\frac{R}{R+h}\sin(\mathrm{SZA})\right]\right\}, \tag{4}$$

where R is the mean radius of the Earth (6370 km) and h is the height above the surface of the substance under consideration (e.g., ozone) [*Cheymol and De Backer*, 2003]. Approximations that are even better for very large SZA are available [e.g., *Smith and Smith*, 1972].

[33] *Thomason et al.* [1983] discussed the effect of the ozone air mass factor on the Langley plot estimation of the extraterrestrial constant. They showed that at 320 nm an underestimation of 2% results if sec(SZA) is assumed for the ozone air mass factor instead of the true value. It should be remembered that this is again a systematic error, not a random one. We studied that the effect on the extraterrestrial constant is essentially the same at 306 nm. *Thomason et al.* [1983] included a maximum air mass factor of 6, while the effect is clearly reduced with the maximum value of 4.5. Therefore it is clear that this is a minor effect, if compared to those that have been discussed in this paper, and does not introduce any clear wavelength dependency. On the other

hand, we can see from equation (3) that if AOD is estimated separately for direct measurements at a large enough SZA (>60°), there is an additional underestimation in AOD if in the ozone subtraction the actual air mass factor is not used.

2.6. Additional Error Sources

[34] There are also other sources of error. However, these have a minor influence if compared to the four previous error sources. For the sake of completeness they are discussed here as well.

[35] In the ozone algorithm of Brewer the ozone absorption coefficients of *Bass and Paur* [1985] are used. The same ozone absorption coefficients should therefore also be used in equation (3), when the ozone optical depths are subtracted from the total optical depth. However, *Marenco et al.* [1997, 2002] and *Kirchhoff et al.* [2001, 2002] have used the absorption coefficients by *Molina and Molina* [1986], while *Jaroslawski et al.* [2003] and *Cheymol and De Backer* [2003] incorporated those of Bass and Paur consistently with the Brewer.

[36] The selection of the ozone absorption coefficients influences the reading obtained for the total ozone abundance, that is, the measurement scale. Currently the Dobson and the Brewer networks are instructed to use the Bass and Paur scale. Should they use some other scale, the calibration would result in readings that differ from the present ones. Therefore the same scale, or absorption coefficients, should be used in removing the effect of ozone in the measurement.

[37] We estimated the ozone optical depths with the absorption coefficients of Molina and Molina and Bass and Paur at different wavelengths. If, for instance, the work of Molina and Molina is used (and 300 DU of ozone is assumed), ozone optical depths at 306.3 and 320.1 nm are 1.267 and 0.216, respectively. On the other hand, with the use of Bass and Paur the corresponding values are 1.250 and 0.208. Therefore the resulting negative bias in AOD difference between 306.3 and 320.1 nm is ~0.009.

[38] Ozone absorption coefficients should be calculated as a slit function averaged for each of the wavelengths. However, we found that this effect strongly depends on the given wavelength and thus does not result in clear wavelength dependence. For instance, assuming an ozone column of 300 DU and the ozone absorption coefficients of *Bass and Paur*, [1985], the ozone optical depth is overestimated by 0.0189 at 306.3 nm if ozone absorption coefficient at the nominal wavelength is used instead of the slit function-averaged one. On the other hand, at 306.1 nm (the shortest wavelength of Brewer DS measurements at Belsk [*Jaroslawski et al.*, 2003]) the overestimation is significantly smaller, 0.0036.

[39] As a further point, the wavelengths for the Brewer DS measurements are given precisely and can be found from the Brewer setup, which also may have changed over the years. For example, step 284 for the Brewer 107 operating at Jokioinen, Finland sets the following wavelengths for the direct Sun measurements: 306.309, 310.063, 313.53, 316.815, and 320.018 nm. The ozone absorption coefficient for equation (3) should be calculated for exactly these same wavelengths.

[40] Equation (3) describes the Rayleigh scattering optical depth and its dependency on the station pressure. In the Brewer algorithm, constant pressure is assumed. For example, at Jokioinen, p equals 1000 (the altitude of the station is 103 m). However, the actual pressure exhibits some variability. At a given site this effect has a tendency to be biased in one direction, since lower pressure results in a higher probability of clouds and thus fewer direct Sun measurements. We investigated the pressure distribution for cloud-free days at Jokioinen. Typically the pressure varies from 1000 hPa up to 1020 hPa. This results in an overestimation in AOD, which can reach a maximum of ~0.03 at the UV wavelengths. However, it can contribute only ~0.001 to the AOD difference between 306.3 and 320.1 nm. This is the only systematic effect that results in an overestimation in the AOD difference between 306.3 and 320.1 nm and thus an overestimation in Ångstrom α. In contrast, all the other above mentioned sources of systematic error are in the opposite direction and can explain the observed wavelength dependency found in recent Brewer DS measurements.

Table 1. Bias in the AOD Differences Between 306.3 and 320.1 nm and Between 310.1 and 320.1 nm due to the Different Error Sources[a]

Source of Bias in AOD	306.3–320.1, nm	310.1–320.1, nm
Diffuse irradiance in FOV[b]	−0.0336	−0.0111
Diurnal ozone change	−0.0279	−0.0133
NO_2 influence	−0.0133	−0.0095
Stray light influence	−0.0046	−0.0008
Total bias	−0.0794	−0.0347
Theoretical (positive) difference	0.0224	0.0160

[a]The theoretical (based on the Ångstrom law) difference in AOD is also shown, assuming AOD of 0.5 at 320 nm and AE of 1.
[b]FOV is field of view.

3. Discussion and Conclusions

[41] If the systematic error estimates (in near-sea level urban environments) are added together, they can explain the observed AE dependency. In Table 1 the components of the four main sources for bias are added for two wavelength pairs. For instance, the estimated negative bias in AOD difference between 306.3 and 320.1 nm is ~0.0794, while between 310.1 and 320.1 nm it is ~0.0347. If the true Ångstrom α was 1 and the AOD at 320.1 was 0.5, then by the Ångstrom relation the AOD at 306.3 nm would be 0.522. Thus the actual difference between 306.3 and 320.1 nm would be positive and equal to 0.022, while between 310.1 and 320.1 nm it would be 0.016. It is thus clear that the systematic errors introduced by the diffuse irradiance, the diurnal variability in urban environments, the effect of stray light, and the effect of NO_2 can mask this difference and result in a negative AE value.

[42] On the other hand, the wavelength range from 306.3 to 320.1 nm is likely too narrow to draw accurate AE estimates, even after the systematic errors are corrected. The random errors estimated in *Kirchhoff et al.* [2002] are about the same magnitude or more than the estimated theoretical positive difference between 306.3 and 320.1 nm in Table 1.

[43] We want to emphasize that it is likely that the reason for the recent results on the wavelength dependency of AOD in the UV range may lie in the omitted sources of uncertainty. Therefore it is suggested that in AOD retrievals from Brewer DS measurements these effects are considered in order to obtain more accurate estimates. Moreover, all but

the stray light-induced bias apply to Sun photometers in general when Langley calibrations are attempted.

[44] In summary, there are some major issues to be considered in the AOD retrieval in the UV range: (1) The extraterrestrial constant should not be estimated at a low-altitude station in urban conditions if accurate corrections for ozone and diffuse light are not available; (2) The maximum air mass factor included should not exceed 3, in accordance with *Slusser et al.* [2000], who concluded that air mass range of 1.2 to 2.2 was suitable for the UV instead of the range of 2 to 6 commonly used in the visible wavelengths of *Harrison and Michalsky* [1994]; (3) The possible diurnal ozone changes should be accounted for, as in *Cheymol and De Backer* [2003]; and (4) A reasonable estimate (preferably based on measurements) should be considered for NO_2 absorption.

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