ABSTRACT

PETTERS, JONATHAN LEONARD. Investigation of Aerosol Single Scattering Albedo in the Ultraviolet Spectrum. (Under the direction of Vinod K. Saxena)

Single scattering albedo (ω), the ratio of scattering coefficient to total extinction coefficient, at UV wavelengths is an important aerosol radiative parameter in determining surface UV irradiance. Surface measurements of total and diffuse UV irradiance in the summer and fall of 1999 at the seven narrowband wavelength channels of an UV multifilter rotating shadowband radiometer (UVMFR-SR) at Black Mountain, NC were coupled with a tropospheric ultraviolet radiative transfer model to produce values of ω. Its value ranged from 0.53 – 0.94 at 300 nm to 0.55 – 1.00 at 368 nm. Error in this procedure decreases with increasing aerosol optical depth (AOD), from +/-0.19 at AOD = 0.05 to +/-0.02 at AOD=1.0. Values of ω were not found to be correlated with air mass origin. The current values of ω have a wider variation than values reported from a previous study at the same site, possibly attributable to changes in aerosol chemical composition over time. The value of ω was found to be quadratically correlated with wavelength. Little research has been conducted in the scattering and absorption properties of aerosols in the UV wavelengths, but what has been done suggests such a correlation is possible. More values of ω in the UV spectrum will allow for better estimation of this parameter for UV radiative transfer modeling and will lessen error in estimation of surface UV irradiances.

INVESTIGATION OF AEROSOL SINGLE SCATTERING ALBEDO IN THE ULTRAVIOLET SPECTRUM

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Chair of Advisory Committee

(Dr. Vinod K. Saxena)

Biography

Jonathan Leonard Petters was born on September 8, 1978 in Raleigh, North Carolina. He spent his childhood engaged in television watching, video game and role-playing game playing, and roughhousing. He also spent a good deal of time reading books on paleontology, astronomy and meteorology. When confronted with the decision of what major to choose as he entered North Carolina State University in 1996, he choose meteorology, although he hadn't read much concerning the weather in several years. It was a good a choice as any, he surmised. After spending three more years toiling in classes and at The Fresh Market, he decided to study abroad in his senior year in the United Kingdom at the University of Hull, East Yorkshire. It was an excellent decision, and was enjoyable in so many ways. After returning to America, he decided to spend more time in his hometown of Raleigh, and enrolled in graduate school at North Carolina State University in August 2000.

Acknowledgements

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I would like to thank the head of my graduate committee Dr. V.K. Saxena for his help and input into my work over the last two years. He got a lot more than he bargained for when he offered me an assistantship. I would also like to thank my committee members, Dr. John J. DeLuisi and Dr. Sethu Raman, for their input.

Brian Wenny, whose work this thesis follows, deserves much of the credit for getting my research started and keeping it moving in the right direction. Without his help I would probably still be trying to figure out a good thesis topic. His work under V.K. Saxena at this university has been the model I have followed to see the completion of this thesis and my Master's degree.

Sasha Madronich and Luca Cinquini of the ACD at NCAR graciously helped me modify the TUV radiative transfer model, and gave much needed insight into my research. James Slusser of the USDA UV-B Radiation Monitoring Network gave me many ideas that I put into practice concerning my error and sensitivity analysis. The unpublished report I obtained from him crystallized many of the uncertainties I had while researching. Peter Bloomfield and David Dickey of our own Statistics department helped me with the error analysis and the statistical regressions. Bill Barnard also deserves thanks for sharing his wide knowledge of UV radiation and for giving advice when I needed it. His knowledge of instrumentation is indispensable. Jung-Sun Im deserves thanks for her advice and input.

Mark Modrak shared most of my ups and downs over the last two years, gave me reasons to keep working when I wanted to quit, and was constantly fun to be around. Our debates on atmospheric radiation and college basketball kept my mind at ease. I can't imagine finishing this thing if he wasn't around to keep me somewhat sane. The other graduate students I met and befriended in this department helped to make my extended time in Raleigh more tolerable, which was oh so very important.

I give thanks to my family members, especially my mother, for listening to my incessant whining and complaining and giving me positive encouragement when I most needed it.

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Introduction

The study of atmospheric ultraviolet (UV) radiation has been the focus of scientific interest in recent years. After the phenomenon of stratospheric ozone depletion was discovered, concern for the effects of increased UV radiation at the surface spread [*Warneck*, 2000]. UV irradiance comprises roughly 10% of the total solar irradiance reaching the surface [*Lenoble*, 1993], and is therefore not the most significant part of solar insolation as it relates to climate forcing. However, it is important to biological activity at the surface and to photochemical activity in the atmosphere. Increased surface UV irradiance can lead to increases of incidences of skin cancer and cataracts in animal life, including humans. It can also damage terrestrial and oceanic vegetation, alter formation of photochemical smog and change bio-geochemical cycles of organic and non-organic matter [*Madronich*, 1998].

The amount of surface UV irradiance at a location is highly variable and dependent on several factors. The value of the solar constant and the solar elevation angle play primary roles. Absorption by ozone is also a significant factor. Values of total ozone column (TOC) have been well characterized through long-term surface measurements and satellite sensing systems such as the Total Ozone Mapping Spectrometer (TOMS, http://toms.gsfc.nasa.gov). Ground reflectance, or albedo (ga), plays a smaller role, and is dependent on the type of surface (grassland, snow-covered, etc.) [*Blumthaler and Ambach*, 1988; *Diffey et al.,* 1995]. Clouds and aerosols have been shown to significantly attenuate UV radiation, and are believed to mask the increase of UV irradiance expected due to stratospheric ozone depletion [*Frederick et al.*, 1993;

Schafer et al., 1996; *Meleti and Cappellani*, 2000]. The effect of clouds and aerosols is at present poorly characterized due to their high spatial and temporal variability [*Schwartz et al.*, 1995; *Madronich et al*, 1998].

Tropospheric aerosols' effect on UV radiation varies widely in time and space due to their short residence time (2-7 days), variability in size, shape, and chemical composition, and dependence on relative humidity [*Reuder and Schwander*, 1999]. For this reason, an extensive ground-based network of UV radiation measuring instruments is required to obtain a spatial and temporal variation of UV irradiance at the surface. Such networks do exist; however, radiative transfer modeling offers a much cheaper alternative to quantifying UV surface irradiance. Also, it is difficult to obtain ground-based measurements over the oceans. However, radiative transfer models are only as accurate as their inputs. More information on aerosol radiative properties is required if they are to be effectively parameterized for use in radiative transfer models.

In radiative transfer modeling, aerosol effects are usually parameterized by the aerosol optical depth, asymmetry parameter, and single scattering albedo. These three parameters are usually allowed to vary with altitude. Aerosol optical depth, τ, is defined as

$$\tau(\lambda) = \int_0^\infty \beta(\lambda,z)\, dz$$

where β is the total volume extinction (scattering + absorption) coefficient at wavelength λ and length z [*Liu*, 1980]. Aerosol optical depth (AOD) is most closely related to the amount of aerosol that attenuates radiation at a specific wavelength. AOD is one of the most important aerosol radiative parameters in determining surface irradiance [*Kiehl and Rodhe*, 1995; *Schwartz et al.*, 1995]. Through sensitivity analysis of the radiative transfer model STAR, it has been

demonstrated that AOD is the most decisive parameter in describing the aerosol effect on UV radiation, contributing to more than 50% of the aerosol effect [*Reuder and Schwander*, 1999]. AOD typically varies between 0 and 1 in the UV wavelengths in a relatively clean atmosphere in a rural location, but can be higher in polluted urban air.

Asymmetry parameter, g, is an approximation of the directionality of scattering of radiation off of a particle. A full description of scattering direction is given by the phase function $P(\theta,\phi,\theta',\phi')$, which is the probability that an incident photon from angular coordinates (θ,ϕ) will scatter in the direction (θ',ϕ'). If Θ is defined as $\theta-\phi$, g is defined as

$$g = 0.5\int_{-1}^{+1} P(\Theta)\cos\Theta \, d(\cos\Theta)$$

where g = 1 indicates complete forward scattering, g = -1 indicates complete backward scattering, and g = 0 indicates isentropic scattering by a particle [*Madronich and Flocke*, 1997]. For UV wavelengths, g typically falls between 0.6 and 0.8 [*Madronich*, 1993].

Single scattering albedo (ω), the ratio of scattering coefficient to total extinction (scattering + absorption) coefficient, varies between 0, indicating a totally absorbing aerosol, and 1, indicating a totally scattering aerosol. Realistically, the value of ω is between 0.5 and 1.0 in the visible and UV wavelengths. The use of single scattering albedo assumes that incoming solar radiation is scattered only one time by matter before they reach the earth's surface. In turbid atmospheres ($\tau>1.0$), multiple scattering of radiation by aerosols becomes appreciable, thereby complicating the scattering process [*Yu et al.*, 2000].

Single scattering albedo is an important aerosol parameter as it distinguishes between the amount of absorbing aerosol and scattering aerosol in the atmosphere. In relation to climate

forcing, *Hansen et al.* [1997] found a critical value of ω of 0.86 for the entire solar spectrum, where effects of aerosols on surface temperature shifts from warming (ω<0.86) to cooling (ω>0.86). Because of its importance in climate forcing, several studies have obtained values of ω in the visible wavelengths for specific locations and times [*Anderson et al.*, 1999; *Devaux et al.*, 1998; *Dubovik et al.*, 1998; *Eck et al.*, 1998; *Gras et al.*, 1999; *Im et al.*, 2001; *Ogren and Sheridan*, 1996; *Yu et al.*, 2000]. However, less research has been conducted to determine values of ω in the UV wavelengths [*Kylling et al.*, 1998; *Wenny et al.*, 1998; Slusser et al., unpublished report, 2002]. *Reuder and Schwander* [1999] found single scattering albedo to be the second-most decisive parameter in determining the aerosol effect on UV radiation. Additionally, for an AOD of 0.1, *Gröbner et al.* [2000] found that changing ω from 1.0 to 0.85 decreases irradiance at 320nm by 4.49%, a non-negligible effect. Therefore, a need for representative values of ω exists. Such information is required to assess the impact of aerosols in these wavelengths [*Kylling et al.*, 1998; *Schwander et al.*, 1997; *Schwartz et al.*, 1995]. Better estimates of this parameter can serve as input into radiative transfer modeling studies of surface UV trends. Furthermore, knowledge of the characteristics of ω will lead to the reduction of errors in satellite estimation of surface UV irradiance [*Krotkov et al.*, 1998].

The objective of this thesis is to investigate aerosol single scattering albedo in the ultraviolet spectrum. A novel procedure was devised to retrieve single scattering albedo in UV-B (280 - 300nm) and UV-A (320-400nm) wavelengths. The values of ω found for this thesis were compared with values of ω found in the literature. Error and sensitivity analysis was conducted on this procedure to determine under what conditions it could be useful. Back trajectory analysis was used to see if values of ω could be correlated with air mass origin.

Validation of the air mass classifications used is described in detail. Statistical analysis was used to ascertain if single scattering albedo in the UV has any dependence on wavelength.

Research Sites and Instrumentation

Mount Gibbes Research Site

The Mount Gibbes research site is located on the peak of Mount Gibbes (35.78° N, 82.29° W, 2006m amsl), in the Blue Ridge Mountains of Western North Carolina. The site is approximately 4 km southwest of Mount Mitchell, NC (elevation 2038m), the highest peak in the eastern United States. This site was chosen because high elevation sites like Mount Gibbes remain in the free troposphere throughout much of the year. Therefore, local pollution sources generally need not be considered, and long-range transport characteristics can be studied [*Marti,* 1990; *Schwikowski et al.,* 1995; *Dutkiewicz et al.,* 2000; *Plessow et al.,* 2001]. Hence, back trajectory analysis at sites such as these can reveal what air masses influence the region surrounding the site.

The site was manned during the summers of 1993-96. A 17.1 m walkup tower at the site was equipped with temperature, pressure, wind speed, wind direction, and humidity instruments, which provided continuous measurements at the top of the tower. A vertically movable carriage was positioned on the north side of the tower that carried an Atmospheric Science Research Center (ASRC) cloud water collector. The carriage was capable of maneuvering from the ground to as high as one meter above the tower. Figure 1 shows a picture of the tower. On top of this tower can be seen the ASRC cloud water collector.

A Magee Scientific Aethalometer was operated at the site from a cabin near the tower. The aerosol sampling inlet was located approximately 2 m above the ground, with an inverted funnel at the opening.

Black Mountain Research Site

A second field site is adjacent to the Burnett Reservoir near the town of Black Mountain, North Carolina at 35.63° N, 82.33° W, 951 m amsl. The site is approximately 10 km south-southwest of the Mount Gibbes site.

Here a Yankee ultraviolet multifilter rotating shadowband radiometer (UVMFR-SR) was located on top of a 30-foot tower. Computer hardware used to collect data is located in a shed next to the tower. Figure 2 illustrates the site set-up. Before previous atmospheric radiation research was conducted at the site [*Schafer et al.*, 1996; *Wenny et al.*, 1998], a theodolite was used to measure the angular heights of obstructions, such as hills and trees, in the surrounding area. These measurements revealed a 1.7% obstruction in the total hemispheric solid angle around the site [*Wenny*, 1996].

The Atmospheric Science Research Center passive cloud water collector

The Atmospheric Science Research Center (ASRC) passive cloud water collector was used during the months of May to June from 1993 to 1995. The ASRC is a passive collector (no inlet fan), has no wind direction dependence and can collect cloud, drizzle, and rain droplets. The collector works by allowing water droplets to impact on Teflon™-coated strings and fall into a replaceable nalgene bottle. During cloud events on the mountain peak collection bottles were replaced every hour and then sealed and refrigerated for analysis. Analysis of cloud water included a check of pH as well as ion chromatography [*Ulman and Saxena*, 1997; *Deininger and Saxena*, 1997].

Magee Scientific Aethalometer

A Magee Scientific Aethalometer was deployed at the Mt. Gibbes site during portions of 1996, 1997, 1998, and 1999 to provide real time measurements of black carbon (BC) aerosol concentration. [*Bahrmann and Saxena,* 1998; *Im et al.,* 2001].

The aethalometer measures the fraction of the carbonaceous aerosol that absorbs light over a broad region of the visible spectrum by determining the attenuation of light transmitted through the sample when collected on a fibrous filter [*Hansen*, 1996]. Other authors [*Gundel et al*., 1984; *Japar et al*., 1986] have found that optical absorption is proportional to BC concentration by the following:

$$[BC] = ATN/\sigma$$

where ATN is the absorption coefficient (or measured absorption, in m^{-1}), and σ is the specific absorption, or ATN per unit mass of BC. It has been found that the value of σ is dependent on a number of factors such as origin and age of the aerosol, and whether the absorbing aerosol is internally or externally mixed with a scattering aerosol species [*Liousse et al.,* 1993]. *Lavanchy et al.* [1999] found a value of 9.3 m^2g^{-1} for σ using a thermal measuring method. The aethalometer uses a value of 19 m^2g^{-1}, which should be considered a first-step approximation in determining BC mass concentration.

Yankee Ultraviolet Multifilter Rotating Shadowband Radiometer

The Yankee ultraviolet multifilter rotating shadowband radiometer (UVMFR-SR) works under the same principles as the original visible wavelength version described in *Harrison et al.* [1994]. It is described in detail on the Yankee Environmental Systems web site [http://www.yesinc.com/products/raduv.html]. The instrument consists of a rotating

shadowband of a 3.3° umbral angle that systematically shades a Teflon™ diffuser disk. This diffuser disk is directly coupled to an optical integrating cavity that is viewed by seven different filter detectors. These filter detectors convert the incident radiation to voltage signals. The voltage signals can then be converted back to irradiance values through software.

A stepped motor moves the shadowband systematically over the diffuse disk. Four separate measurements are taken with each pass of the shadowband. The first measurement is taken as the shadowband is at its rest (nadir) position, giving total irradiance. The other three measurements are taken with direct sunlight completely blocked from reaching the diffuser disk and one taken 9° to either side of the sun. These measurements allow for correction of sky blocked by the shadowband when the sun-blocking measurement is made. These three measurements give diffuse irradiance. Direct irradiance is computed by subtracting diffuse irradiance values from total irradiance values.

For each measurement interval, the solar position is calculated by a self-contained microprocessor. Each measurement of irradiance is corrected for the solar position and the cosine response of the instrument. The UVMFR-SR's cosine response has been laboratory characterized and is accurate to within 5% for solar zenith angles between 0 and 80°.

The UVMFR-SR measures both total and diffuse irradiance for seven specified wavelengths (300, 305.5, 311.4, 317.6, 325.4, 332.4, and 368 nm) with a 2 nm nominal full width at half maximum (FWHM) bandwidth. These measurements provide a good survey of irradiance in the longer half of the UV-B wavelengths as well as the shorter half of the UV-A wavelengths. Measurements of total and diffuse irradiance were recorded every 20 s, and

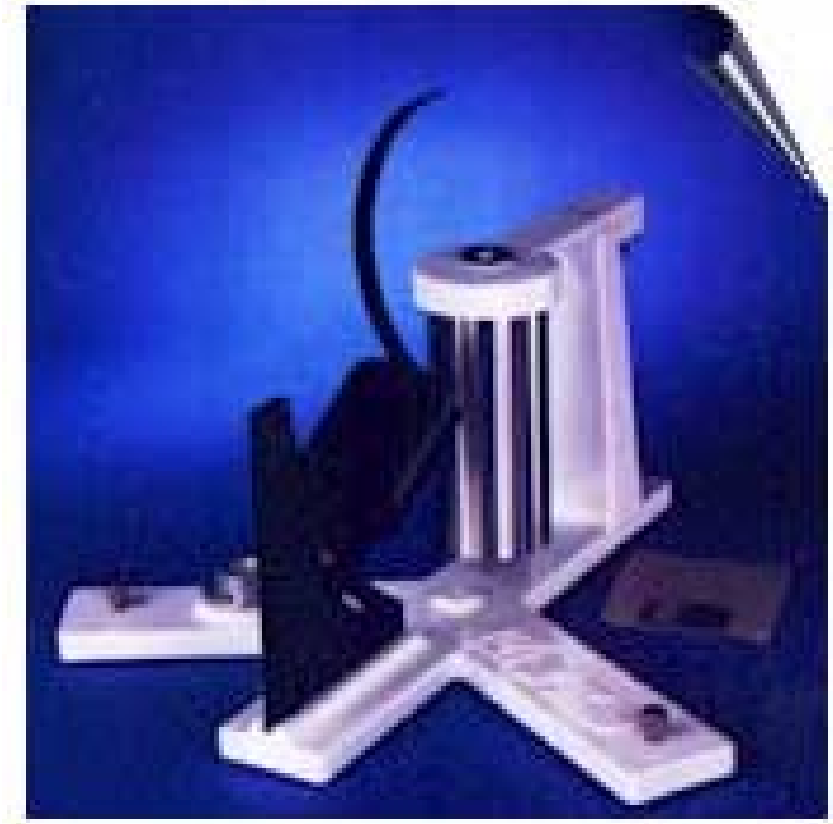
stored as 2 m averages along with a computed direct irradiance. Data were remotely downloaded by modem. The cosine response and irradiance calibration of the UVMFR-SR was conducted before deployment at the field site. Figure 3 displays a picture of the UVMFR-SR and a simple diagram of the detector assembly's geometry. The database used for this study was collected between July and December 1999.

Figure 1. Picture of 17.1m walk-up tower at Mount Gibbes.

2a.  2b. 

Figure 2. a) picture of tower and cabin at Black Mountain research site, North Carolina. b)close-up of 30-foot tower.

3a.



3b.

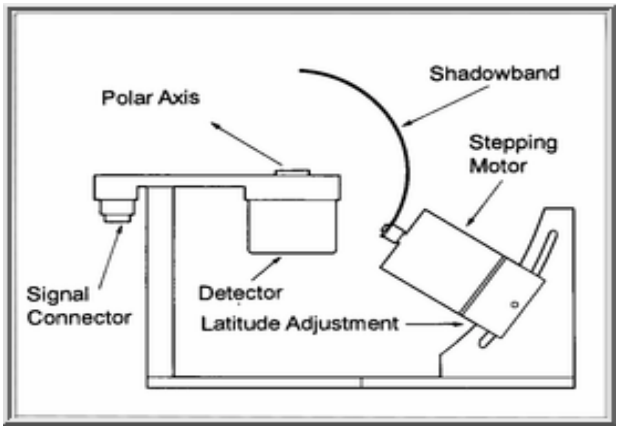


Figure 3. a)Yankee Environmental Systems (YES) Ultraviolet Multifilter Rotating Shadowband Radiometer (UVMFR-SR). b) UVMFR-SR Detector Assembly Geometry. [http://www.yesinc.com/products/raduv.html]

Methodology

Retrieval of Single Scattering Albedo

The ω retrieval procedure employed the data collected by the UVMFR-SR and the tropospheric ultraviolet radiative transfer model TUV4.1 [*Madronich*, 1993]. The TUV4.1 uses a discrete ordinate method of determining radiative transfer through the atmosphere, and was run in the 8-stream mode. This model has been used in other UV radiation studies conducted at the site [*Wenny et al*., 1998; *Wenny et al*., 2001]. The original code was modified to output diffuse-to-direct ratio (DDR) at the wavelengths of the UVMFR-SR. The model inputs relevant to the study are the time of solar noon, AOD, TOC, g, ga and ω. The initial output of DDR at solar noon from TUV4.1 was compared with measurements taken by the UVMFR-SR. The DDR was derived from the UVMFR-SR measurements as the ratio between the recorded diffuse and direct irradiances. The TUV4.1 was iterated by varying ω until the output matched that of the UVMFR-SR, ultimately yielding ω for each wavelength for each day. Figure 4 outlines the inversion process of ω retrieval in a flow chart. It is assumed that the value of ω retrieved does not vary with altitude. TUV4.1 does allow for varying ω or g values with altitude, but there is little data on how these radiative parameters vary with height in the UV wavelengths. *Ogren and Sheridan* [1996] found that ω and g varied little with altitude in the visible wavelengths. In addition, we can assume that at solar noon the boundary layer has undergone some mixing and that the air above the surface is fairly homogeneous.

Because of the inherent difficulties clouds bring to radiation studies, their influence are neglected here. Overcast sky conditions have been shown to attenuate 70% of UV-B

(280-320 nm) irradiance at a solar zenith angle of 50º [*Schafer et al.*, 1996]. However, the three dimensional distribution of clouds over a region is difficult to obtain and, under the right circumstances, can increase UV irradiance reaching the surface [*Schafer et al.*, 1996; *Weihs et al.*, 2000]. To ensure cloudless conditions at solar noon, each day's diffuse irradiance was plotted against time of day. If the top of the characteristic 'bell curve' of the irradiance plot was seen as uninterrupted for some time before and after solar noon, that day was deemed usable for ω retrieval. Figure 5 displays an example of an irradiance curve that met these requirements. A 'bell curve' does not entirely eliminate the possibility that clouds are in the sky but not covering the disk of the sun. This contributes to possible error in DDR measurements.

The inputs used in TUV4.1 were obtained or assumed as follows. AOD was calculated from the irradiance measurements at the seven wavelengths of the UVMFR-SR's by *Wenny et al.* [2001] for 74 clear sky days in the observation period of 1999. Langley plot analysis was used to obtain a value of V_o (the voltage signal the UVMFR-SR would record at the top of the atmosphere) as prescribed by *Harrison and Michalsky* [1994]. Given these values for each wavelength channel, the following formula can be used to obtain total optical depth (TOD):

$$\tau = -(\cos Z) * \ln(V_\lambda / V_{\lambda o})$$

where V_λ is the UVMFR-SR voltage signal at wavelength λ, $V_{\lambda o}$ is the extraterrestrial voltage signal at wavelength λ, and Z is the solar zenith angle. From TOD, Rayleigh and ozone optical depths are subtracted, leaving AOD. Absorption by other atmospheric gases is considered negligible for the wavelength channels of the UVMFR-SR. Rayleigh optical

depth is assumed constant for the site's elevation, and ozone optical depth is calculated from total ozone column and ozone absorption coefficients. This process was conducted for each 2 min measurement. The model input of AOD is at 340 nm, and Angstrom's formula was used to extrapolate AOD to this wavelength. Only AOD at the four longer wavelength channels were used for extrapolation because of larger uncertainty in AOD at the shorter wavelengths. This is described in the following error analysis. The AOD inputs were morning averages using clear-sky measurements for $Z \leq 60^{o}$. TUV4.1 assumes that AOD varies inversely with the first power of wavelength [*Madronich*, 1993], and that it varies with altitude according to the *Elterman* [1968] profile.

TOC was derived from measurements of the UVMFR-SR, and its retrieval is detailed in *Wenny et al.* [2001]. The technique used to retrieve TOC will not be described here, as TOC will be shown in the result of the error and sensitivity analysis to be an insignificant input, and could have been assigned a constant value of 300 Dobson Units, with no change in retrieved ω values.

Asymmetry parameter, g, was assumed a value of 0.70, for all wavelengths and altitudes. This was the average of nine values from a previous UV-B radiation study conducted at the same site [*Wenny et al.*, 1998]. These values were calculated at 312 nm in the same months of the year as the current study. Also, *Madronich* [1993] states that g typically falls between 0.6 and 0.8 for the UV wavelengths, of which the median is also 0.70.

Ground albedo, ga, was assumed a value of 0.04, for all wavelengths and altitudes. This value was originally taken from *Schwander et al.* [1997]. The tower and cabin at the research site are surrounded by grassy meadows. Above grassland, the ground albedo in UV

wavelengths has typically been found to be between 0.01 and 0.03 [*Blumthaler and Ambach*, 1988; *Diffey et al.*, 1995; *Feister and Grewe*, 1995; *McKenzie et al.*, 1996]. A more recent study by *Kylling et al.* [2000] gives a value of 0.08 for the same ground cover.

Error/Sensitivity Analysis

It is necessary to perform sensitivity studies so that error in this technique to retrieve ω can be determined. Tests were conducted to see which input played the greatest role in determining DDR. One parameter was varied holding the others constant. The other stock inputs, when not being tested, were g = 0.70, ga = 0.04, ω = 0.85, and TOC = 300 DU. TUV4.1's output of DDR was expected to be more sensitive to a more turbid atmosphere [Slusser et al., unpublished report, 2002], so two AOD scenarios (0.3 and 0.8) were used. An example of the results of these tests can be seen in figure 6, which shows the sensitivity of DDR to ω for the two aerosol optical depths. From these tests the order of importance for parameters for determining DDR, based on the rate of increase of DDR with respect to the variable in question, is: AOD, ω, g, ga, and TOC. It was found that DDR has little dependence to realistic values of TOC. Ozone plays a major role in absorbing UV radiation in the stratosphere, taking out a lot of incident photons. Variations of tropospheric ozone do little to influence UV radiation when compared to stratospheric ozone [*Barnard*, 2001]. Nitrogen, oxygen, and aerosol particles are the dominant scatterers of incoming solar radiation in the troposphere. Figure 6 shows that the sensitivity of DDR to ω increased from AOD = 0.3 to AOD = 0.8, and this was also found to occur for g and ga. A further test was conducted to see how much a change in DDR of 0.02 would affect the retrieval of ω as AOD

is varied. Figure 7 shows these results. It can be seen that, as AOD decreases, the change in ω increases. Hence, error analysis in ω retrieval was conducted at several aerosol optical depths, from 0.05 to 1 in 0.05 increments to see how AOD affects the error. A threshold of AOD values was decided upon to give reasonable single scattering albedo values.

At each AOD, the uncertainty in DDR values due to uncertainty in g, ga, and AOD was determined. This was done by summing together the greatest possible error in DDR due to these three parameters. This error in DDR was combined with the uncertainty in the instrument's DDR measurements through the root mean square error (RMSE) formula. After the total error in DDR was found, how much this error in TUV4.1 output of DDR affected the ω values retrieved could be determined (Bloomfield, personal communication). The value of ω was allowed to vary from a value of 0.86. Table 1 displays the assumed values of the model parameters and the uncertainty assigned to these parameters and the instrument measurements.

Uncertainty in AOD was taken from *Kato et al.* [2000]. Uncertainty due to V_o relates to the Langley analysis used in AOD retrieval; error in a V_o value will transfer to a slight error in AOD of +/-0.01. Another source of error for AOD retrieval in the UV wavelengths is that AOD is not the dominating attenuator in the UV wavelengths, and is subject to changes in the other attenuators. Ozone absorption is most important in the two shortest wavelengths of the UVMFR-SR, and Rayleigh scattering is most important in the five longest wavelengths. AOD accounts for only 7% of the total optical depth at 300 nm, increasing to 34% at 368 nm [*Wenny et al.*, 2001]. The error related to this phenomenon has

not yet been quantified, but is expected to give greater uncertainty in AOD measurements in the UV spectrum as wavelength decreases.

The uncertainty assigned to asymmetry parameter, +/-0.05, is one standard deviation of the values of g from *Wenny et al.* [1998] at 312 nm. The uncertainty for ground albedo, +/-0.02, was chosen so as to encompass most of the values found in the literature for open grassland in the UV spectrum. Uncertainty in DDR, +/-0.02, was taken directly from Slusser et al. [unpublished report, 2002]. This helps to account for blockage of diffuse light by the shadowband of the UVMFR-SR, as well as possible intensification of diffuse irradiance by broken clouds.

Correlation with Air Mass Type

Figure 8 shows the demarcation of geographical sectors of different air mass types influencing the two research sites. If due north is defined as 0°, the three sectors are identified as continental from 240º to 290º azimuth relative to the site, highly polluted from 290º to 65º azimuth, and marine from 65º to 240º azimuth. Over the years several studies conducted at Mount Gibbes have demonstrated air masses originating from these marine, continental and highly polluted sectors exhibit different phyisco-chemical properties. Also, it is assumed that the air between Mount Gibbes and Black Mountain is relatively homogeneous, and air mass classifications used for Mount Gibbes are representative of air masses influencing the Black Mountain site.

Ulman and Saxena [1997] established the air mass sectors based on the United States Environmental Protection Agency's source inventory data on SO_x and NO_x emissions [*EPA*, 1993]. It was assumed that air parcels at the same altitude as Mount Gibbes travel 25 km/h,

and therefore a 1200 km radius around the site (how far air could travel at that speed in 48 hours) was sufficient to total emissions from each sector. It was evident that the polluted sector contained the highest emissions of SO_x and NO_x, followed by the marine and the continental sector. Cloud water collected and analyzed during the field season of 1993 lends credence to the air mass classifications. It was found that the pH of cloud water that spent time in the polluted sector had the lowest average pH, followed by the marine and continental sectors. The same correlation to air mass sector was found with respect to both sulfate and nitrate concentrations in the cloud water [*Ulman and Saxena*, 1997].

Deininger and Saxena [1997] conducted a broad-based study to validate the demarcation of the marine, continental, and highly polluted sectors through principal component analysis of ion concentrations in cloud water collected during the field seasons of 1993 and 1994. The marine sector was found to be dominated by salt aerosols, the continental sector by a combination of silicate and soot aerosols, and the polluted sector is dominated by soot and sulfate aerosols. The polluted sector was also found to have a much higher total ion concentration of cloud water as compared to the other two sectors.

Measurements of black carbon (BC) concentrations were also found to be correlated with air mass, and thereby further validate the sector classification. Aethalometer data from the summers of 1996 and 1997 revealed the following BC concentrations: 216.6 ± 47.8 ngm^{-3} for polluted air masses, 169.9 ± 50.6 ngm^{-3} for continental air masses, and 65.6 ± 23.5 ngm^{-3} for marine air masses [*Bahrmann and Saxena*, 1997]. *Im et al.* [2001] gathered aethalometer data during the summer of 1998 and corroborated the previous findings concerning BC concentration with air mass.

For the current study, 48 hour back trajectories were computed from the site using the HYbrid Single-Particle Lagrangian Integrated Trajectory (HY-SPLIT) Model for each value of ω to see which sector the air over the site came from [*Draxler and Hess*, 1998]. Back trajectories were computed as if the parcel reached the altitude of 1000 m over the research site. If the computed trajectory went over more than one sector, that trajectory was classified by which sector it remained longest over.

Statistical Analysis

The values of ω retrieved were averaged over each wavelength. These means were intoduced into the Statistical Analysis System (SAS) and different polynomial regressions were applied to them, starting from the simplest (linear) and adding higher order terms as needed. In this way, it could be seen if ω exhibits any dependency upon wavelength. If the regression coefficients were found to be significant at the 0.05 level, that regression was deemed to be reasonable. None of the previous studies of ω in the UV wavelengths attempted to look at its spectral dependency, and knowledge of spectral dependency could ease parameterization of ω.

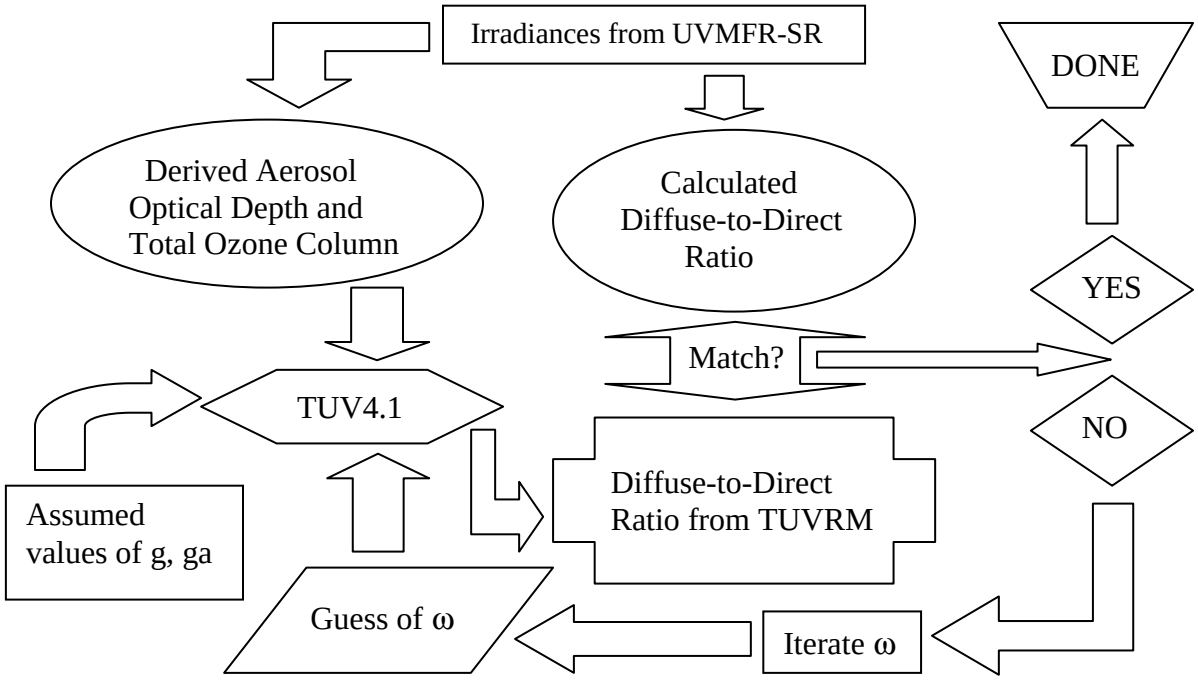


Figure 4. Diagram outlining the inversion process of single scattering albedo (ω) retrieval.

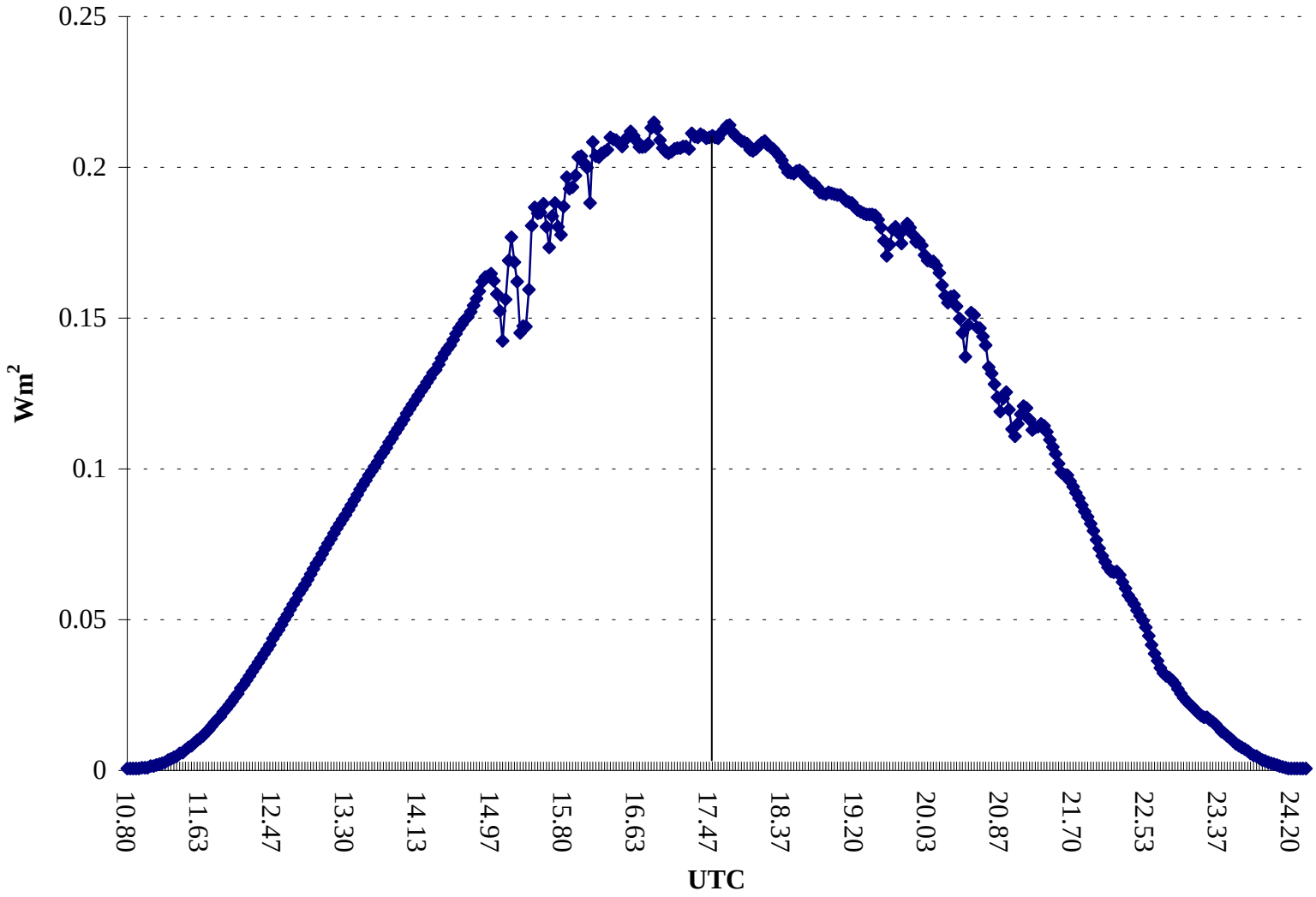


Figure 5. Plot of diffuse irradiance at 317.6 nm vs. time of day, August 10, 1999. Solar noon is indicated by the vertical line at the center of the plot.

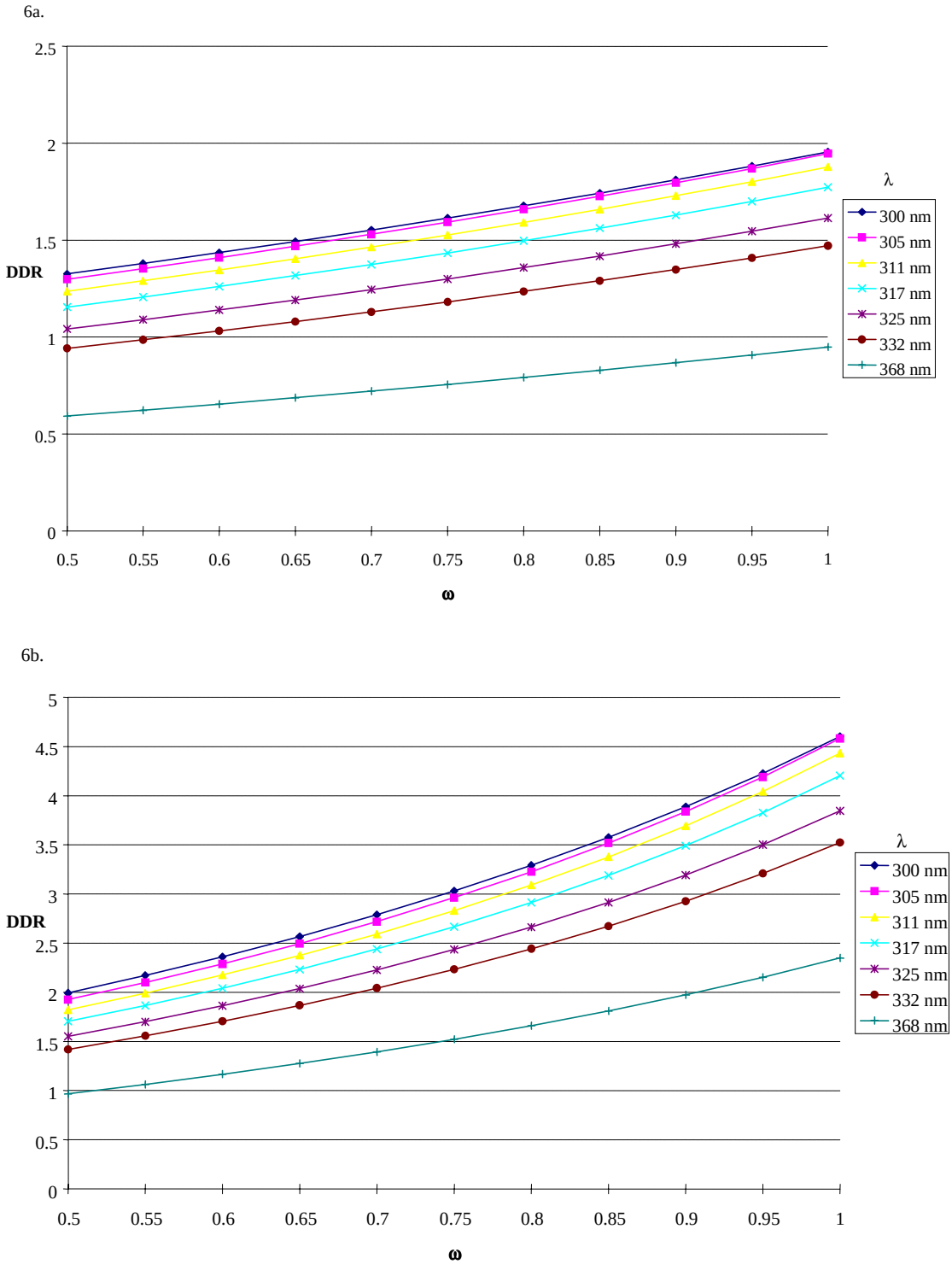


Figure 6. a) Sensitivity of diffuse-to-direct (DDR) ratio to single scattering albedo(ω) in TUV4.1 at aerosol optical depth (AOD) = 0.3. b) same as a) at AOD = 0.8.

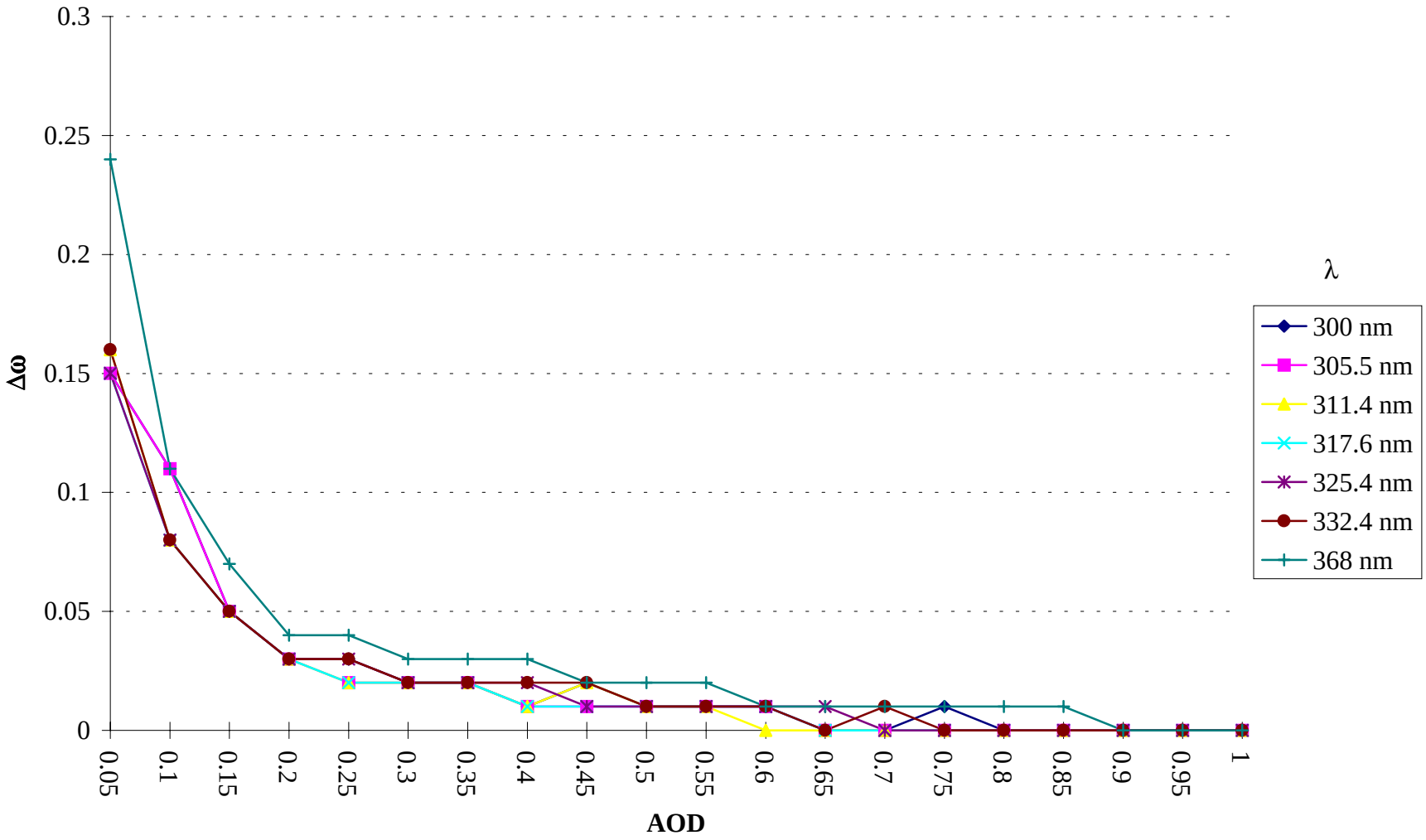


Figure 7. Change in single scattering albedo value (Δω) with an increase of 0.02 in diffuse-to-direct ratio (DDR) at various aerosol optical depths (AOD).

Table 1. Assumed values and related assumed uncertainties of model parameters for use in error analysis.

Radiative Parameter	Assumed Value	Error (+/-)
uncertainty in aerosol optical depth (AOD) due to V_o		0.01
asymmetry parameter (g)	0.7	0.05
ground albedo (ga)	0.04	0.02
diffuse-to-direct ratio (DDR)		0.02
single scattering albedo (ω)	0.86	

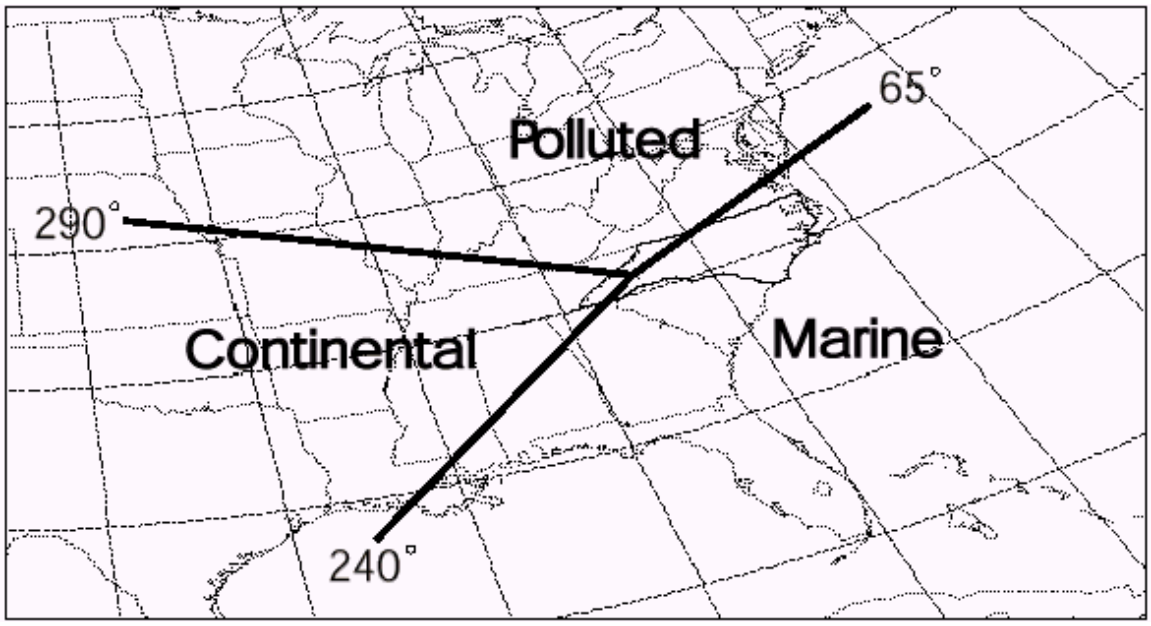


Figure 8. Map of the United States illustrating the geographical location and classification of the different air mass types influencing the research sites in western North Carolina.

Results/Discussion

Error/Sensitivity Analysis

Figure 9 shows the results of the error analysis. Displayed is the estimated uncertainty in ω as it varies with AOD and wavelength. For the analysis conducted here, there is no correlation between wavelength and uncertainty in ω. However, the increasing uncertainty in AOD retrieval with decreasing wavelength in the UV spectrum is expected to also increase uncertainty in ω retrieval as wavelength decreases. Uncertainty in this technique seems to decay exponentially with increasing AOD, from an average error of +/- 0.19 for AOD = 0.05 to an average error of +/-0.2 for AOD = 1.0. Error in ω retrieval is expected to monotonically decrease with increasing AOD, but does not necessarily do so here due to truncations throughout the error analysis. For AOD<0.3, the estimated error is +/-0.04. This was deemed to be the threshold for a reasonable ω retrieval, so results from days with AOD<0.3 were excluded. The AOD values retrieved from the UVMFR-SR used for extrapolation to AOD at 340 nm and subsequently used as input into TUV4.1 are displayed in Table 2.

Values/Air Mass Correlation

Single scatter albedo (ω) values were obtained for the seven wavelengths of the UV-MFRSR for nine days from July 26 to October 5 of 1999. The value of ω ranged from 0.53 - 0.94 at 300 nm, 0.58 - 0.99 at 305.5 nm, 0.59 - 1.00 at 311.4 nm, 0.59 - 1.00 at 317.6 nm, 0.59 - 1.01 at 325.4 nm, 0.59 - 1.01 at 332.4 nm, and 0.55 - 1.03 at 368 nm. These results are displayed in Table 3. For a few of the days, the upper range of ω for the longer wavelengths (325.4, 368 nm) is not physically possible. However, if the uncertainty in the procedure used

to obtain these values is factored in, they can be said to be unity or very close to unity. The error in each day's single scattering albedo is dependent on the aerosol optical depth of that particular day, and can be determined from Figure 7.

Table 4 displays the values of diffuse-to-direct ratio (DDR) measured by the UVMFR-SR at solar noon that were matched as output from TUV4.1. As can be seen by the averages of DDR at each wavelength, DDR tends to increase from 300.0 to 305.5 nm, and then decrease as wavelength increases from 305.5 to 368.0 nm. It is not necessarily correlated with the AOD retrieved from the UVMFR-SR. DDR can be expected to vary widely with aerosol optical depth, size distribution, shape, and chemical composition, as other aerosol radiative properties do.

As can be seen in Table 3, there is no evidence of correlation between air mass type and ω at these wavelengths. This can be attributed to the widely varying aerosol content of air masses coming from each sector. This is especially true for air masses originating in the polluted sector, where efficient scatterers (sulfate) and absorbers (soot) abound [*Deininger and Saxena*, 1997]. An extensive knowledge of the source inventories within the three sectors is required if a range of expected ω values is to be known.

Relative humidities taken at Asheville Airport (~10 miles southwest of the site) at concurrent times with other observations can be said to be representative of relative humidity at the site. These values are also displayed in Table 3. Large relative humidities, greater than 70%, have been shown to increase aerosol scattering coefficient in the visible wavelengths [*Waggoner et al.*, 1981], and therefore increasing values of ω. For this study,

the relative humidity varies between 46.0 and 59.5%, below the 70% benchmark, and therefore such humidity effects can be neglected.

The values of ω in the UV found in this study vary more widely than previous studies established. *Wenny et al.* [1998] determined ω for nine days in 1995 at 312 nm at the same site as this study. An iterative modeling procedure was used, involving a UV-B Radiative Transfer Model, very similar to the one used in this study, along with a Mie code. Single scattering albedo, asymmetry parameter, and the refractive index were the result of this procedure. Values of ω ranged from 0.75 - 0.93 with no discernible dependence on air mass type. This range of values is more limited than the values presented in this study (0.59 - 1.00 at 311.4 nm). They found a dependence on the relative humidity, as days with relative humidities above 80% yield the higher single scattering albedo values.

Kylling et al. [1998] matched spectral UV irradiance from two spectroradiometers with a radiative transfer model that uses a discrete ordinate algorithm (similar to TUV4.1). This was conducted on two different Greek islands for data from June 1996. To get the best correlation between model and measurement, an ω value for a specific day was taken to be the value that gave the best agreement between the two at noon. The value of ω was assumed to be independent of wavelength. Both instruments measure spectral irradiance at wavelengths covering the wavelengths measured by the UVMFR-SR (Bentham DM 150, 290-500 nm; Brewer MK III, 287.5-366 nm). The value of ω ranged from 0.83 to 0.99 in this study, and falls within the range of the values retrieved in the current study.

Slusser et al. [unpublished report, 2002], in a study very similar to the current study, measured aerosol optical depths and direct-to-diffuse irradiances from a UVMFR-SR and

paired those with a radiative transfer lookup table to determine single scattering albedo at 368 nm. The value of ω was retrieved for two days in May 1998 in Baton Rouge, LA, in a period of very high aerosol loading, and found to be 0.72 and 0.86. The same process was used in Beltsville, MD for July 17, 1999, and ω was found to be 1.00. These values lie in the range of the current study.

One possible cause of the wide range of values of single scattering albedo in this study, as compared to previous work, is the high temporal and spatial variability of tropospheric aerosols. The vast differences in sources, transformation and removal processes, and lifetimes all contribute to this variability [*Kiehl and Rodhe,* 1995]. Through comparison of the values of ω found here to the values found by *Wenny et al.* [1998], it is possible that there has been a recent change in the aerosol composition in the air masses influencing the site. An increase in the scattering ability or decrease in the absorbing ability of the aerosols at the site would explain higher values of ω, and vice versa for lower values. An additional but unquantified error in ω retrieval due to error in retrieved aerosol optical depth also contributes to the wide variation in single scattering albedo values.

Statistical Analysis

Figure 10 shows that, on average, ω increases with increasing wavelength in the first six channels of the UVMFR-SR from 0.75 at 300 nm to 0.83 at 332 nm, but then remains 0.83 at 368 nm. A quadratic regression proved significant at the 0.05 level, with the following equation:

$$\omega = -3.47E\text{-}5\lambda^2 + 0.0242\lambda - 3.360$$

The value of λ is in nm. The value of R^2 was 0.896, and the p-values of the regression coefficients (from highest to lowest order) were 0.0329, 0.0185, and 0.0209 respectively. None of the previous studies of ω in the UV wavelengths looked at its spectral dependency. There is some evidence that absorption by soot, the most abundant absorbing aerosol in the region, decreases with wavelength in the wavelengths of the UVMFR-SR [*Martins et al.*, 1998]. In studies centered on visible wavelengths, *Lacis and Mishchenko* [1995] conducted modeling work that found single scattering albedo is positively correlated with UV wavelengths for different types of aerosols, except for soot; conversely, *DeLuisi* [1997], from aerosol size distribution data taken on Whiteface Mountain in New York, did Mie theory calculations that gave either constant or negatively correlated values of ω in the UV wavelengths. Some studies of single scattering albedo in the visible wavelengths have investigated spectral dependency. *Eck et al.* [1998] found that ω decreased with increasing wavelength from 400 nm to 700 nm on two separate days during the SCAR-B (Smoke, Clouds, and Radiation – Brazil) campaign in 1995. *Dubovik et al.* [1998], also during SCAR-B, found that ω could either increase or decrease with wavelength from 440 to 1020 nm in yearly averages of retrieved values from 1993-1995. There the authors suggest that an assumption that black carbon absorption is independent of wavelength can force ω to decrease with wavelength. This may explain the dependency on wavelength of the current study, as TUV4.1 has no unique input for black carbon aerosol properties. Absorption and scattering properties of soot aerosols are allowed to vary within the input of single scattering albedo in TUV4.1.

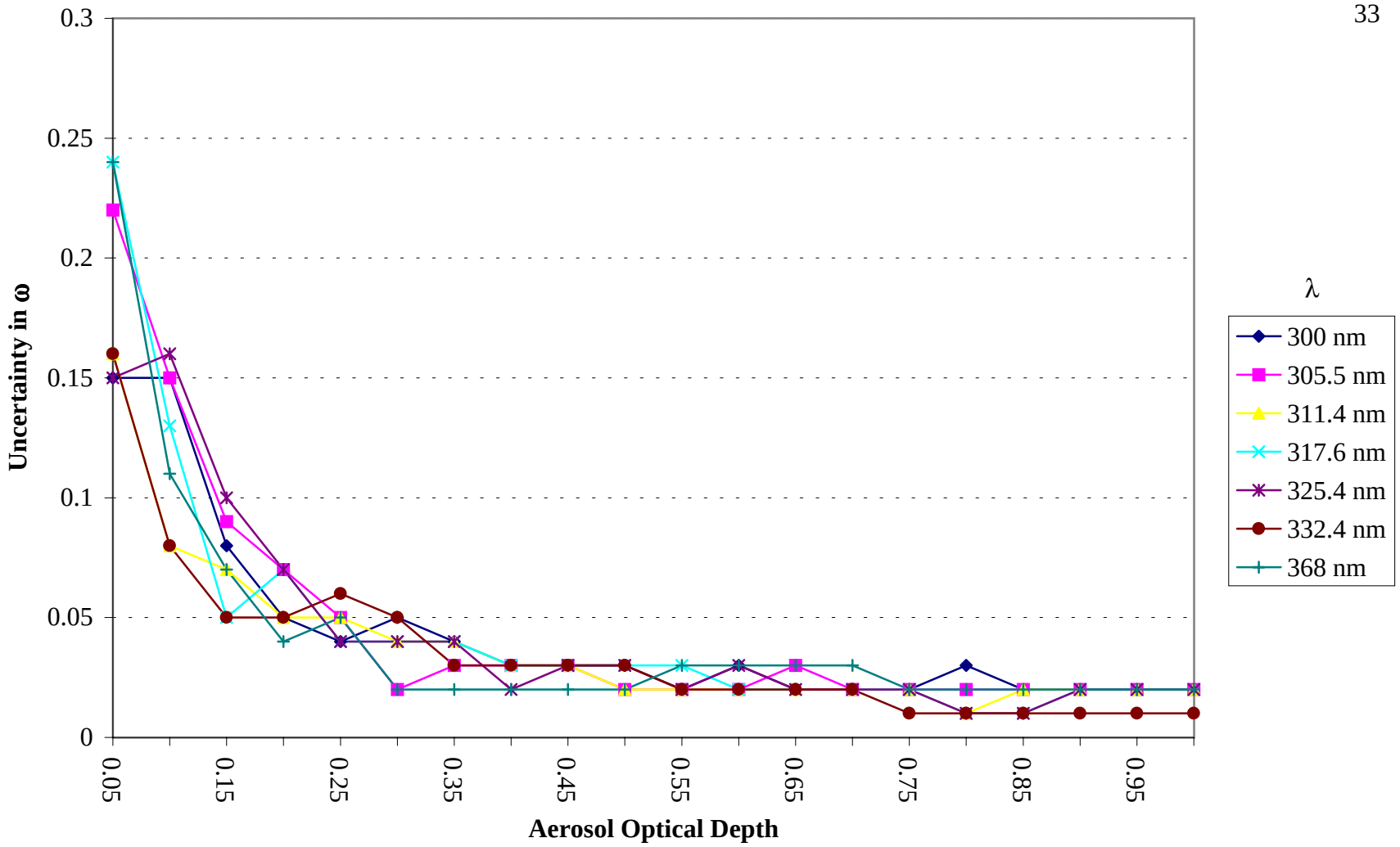


Figure 9. Estimated uncertainty in single scattering albedo (ω) as functions of wavelength (λ) and aerosol optical depth (AOD).

Table 2. Aerosol optical depth values retrieved from the four longer wavelength channels of the UVMFR-SR. These values were used for extrapolation to aerosol optical depth at 340 nm using Angstrom's formula (data reproduced from preliminary data for *Wenny et al.*, 2001).

Wavelength	7/26/1999	8/10/1999	8/14/1999	8/15/1999	8/16/1999	8/26/1999	8/30/1999	9/13/1999	10/5/1999
317.6 nm	0.775	0.525	0.349	0.597	0.830	0.554	0.550	0.462	0.459
325.4 nm	0.732	0.498	0.313	0.568	0.793	0.525	0.510	0.418	0.430
332.4 nm	0.731	0.504	0.313	0.573	0.792	0.527	0.505	0.405	0.426
368.0 nm	0.648	0.468	0.258	0.540	0.723	0.472	0.441	0.322	0.396

Table 2. Single scattering albedo values retrieved at the seven wavelengths of the UV-MFRSR. Asymmetry parameter = 0.70, ground albedo = 0.04. To the left are the values of aerosol optical depth (AOD). To the right are the relative humidities during the measurement times (RH) and the air mass classifications as determined by the HY-SPLIT 48 hour back trajectories (HP=highly polluted, C=continental, M=marine).

DATE	AOD	300.0 nm	305.5 nm	311.4 nm	317.6 nm	325.4 nm	332.4 nm	368.0 nm	RH	Air Mass
7/26/1999	0.707	0.64	0.69	0.7	0.71	0.71	0.71	0.7	48.0%	HP
8/10/1999	0.491	0.87	0.91	0.93	0.93	0.95	0.97	1.03	54.5%	HP
8/14/1999	0.298	0.94	0.99	1	1	1.01	1.01	1.01	46.0%	C
8/15/1999	0.562	0.68	0.73	0.75	0.76	0.78	0.79	0.82	59.5%	HP
8/16/1999	0.772	0.88	0.91	0.92	0.93	0.94	0.96	0.99	58.5%	M
8/26/1999	0.509	0.71	0.74	0.77	0.78	0.79	0.8	0.8	56.5%	C
8/30/1999	0.489	0.55	0.58	0.59	0.59	0.59	0.59	0.55	46.5%	HP
9/13/1999	0.384	0.94	0.96	0.96	0.95	0.94	0.93	0.88	46.0%	M
10/5/1999	0.421	0.53	0.62	0.63	0.63	0.64	0.67	0.69	54.0%	C
AVERAGE		0.75	0.79	0.81	0.81	0.82	0.83	0.83		

Table 4. Values of diffuse-to-direct ratio (DDR) retrieved from the seven wavelength channels of the UVMFR-SR. These values are matched with the output of TUV4.1 as part of the inversion process to determine single scattering albedo.

DATE	AOD@340 nm	300.0 nm	305.5 nm	311.4 nm	317.6 nm	325.4 nm	332.4 nm	368.0 nm
7/26/1999	0.707	1.43	1.53	1.53	1.47	1.37	1.28	0.90
8/10/1999	0.491	1.57	1.67	1.67	1.61	1.52	1.44	1.06
8/14/1999	0.298	1.27	1.34	1.33	1.27	1.18	1.09	0.73
8/15/1999	0.562	1.39	1.49	1.49	1.44	1.36	1.28	0.94
8/16/1999	0.772	2.38	2.50	2.50	2.43	2.30	2.17	1.61
8/26/1999	0.509	1.43	1.50	1.50	1.45	1.36	1.27	0.88
8/30/1999	0.489	1.19	1.24	1.21	1.15	1.05	0.97	0.62
9/13/1999	0.384	1.75	1.80	1.74	1.64	1.49	1.36	0.86
10/5/1999	0.421	1.53	1.63	1.57	1.48	1.36	1.27	0.85
AVERAGE		1.55	1.63	1.62	1.55	1.44	1.35	0.94

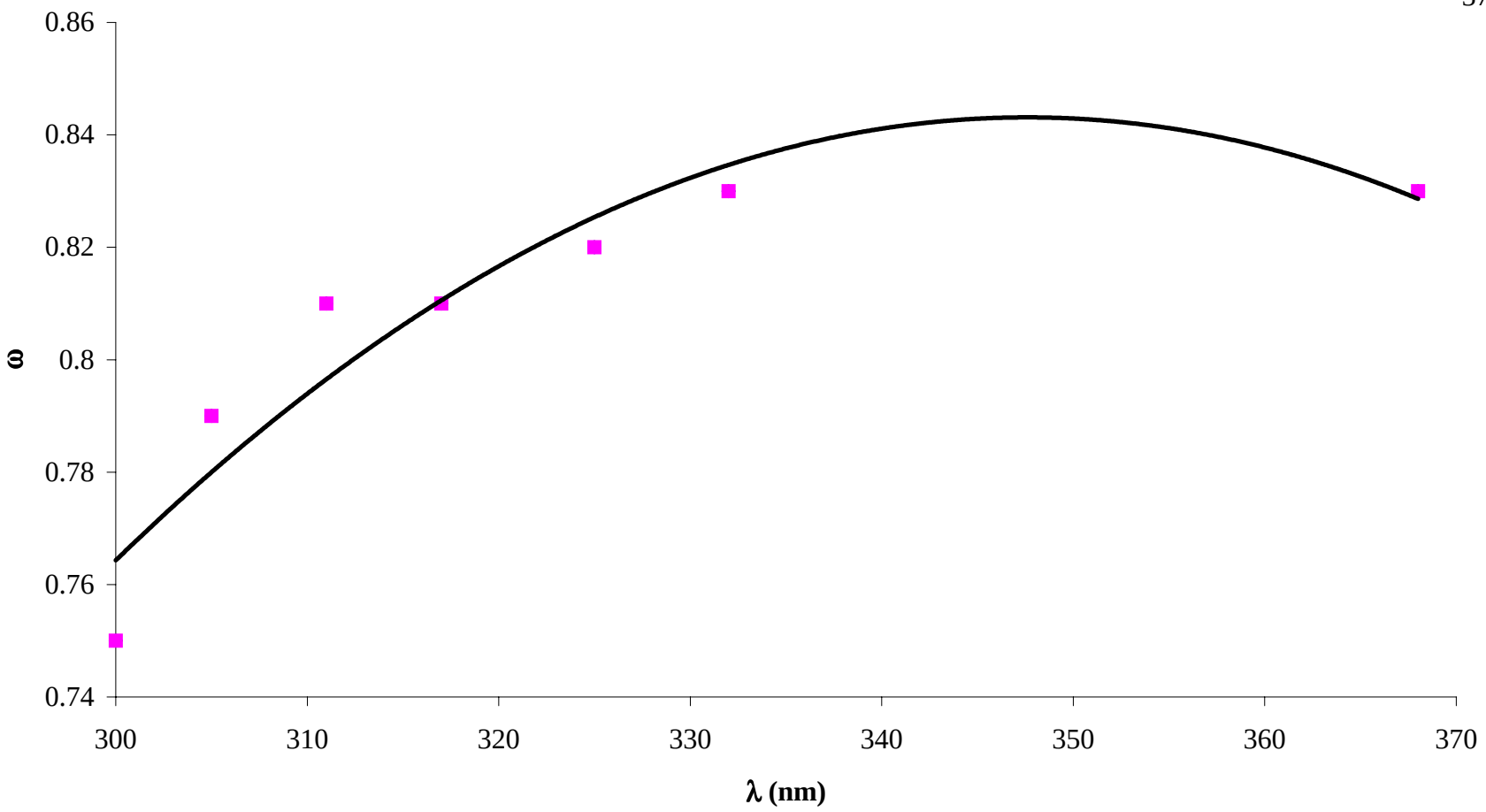


Figure 10. Mean single scattering albedo (omega) values as a function of wavelength. Dark line is quadratic regression of data.

$\lambda = -3.47E\text{-}5\lambda^2 + 0.0242\lambda - 3.360$; $R^2 = 0.896$.

Future Work

As previously stated, the technique used to retrieve AOD values at the wavelengths of the UVMFR-SR has a yet unquantified amount of error that is expected to be greater for the shorter wavelengths. Brewer ozone spectrophotomer measurements of spectral irradiance have also been used to derive AOD in the UV spectrum [*Carvalho and Henriques*, 2000], but the error in this retrieval has not been determined either. It is important to gain knowledge of this uncertainty, as it can modify the error analysis conducted for the procedure of single scattering albedo retrieval described in this thesis. The retrieval of ω will have more power when this error is quantified.

The values of ω found here are in the summer and early autumn months. Long-term UVMFR-SR measurements will allow for investigation of both seasonal and annual variation of single scattering albedo. This retrieval procedure could be conducted in the visible wavelengths with a visible multifilter rotating shadowband radiometer (VISMFR-SR). As single scattering albedo in the visible wavelengths plays an important role in climate forcing [*Hansen et al.*, 1997], information concerning its value would prove most useful. This procedure could also be utilized in conjunction with in-situ airborne measurements of single scattering albedo through scattering and absorption coefficients. The two processes could be compared and would hopefully validate each other as being more accurate.

A method has been devised to identify clear-sky periods using downwelling total and diffuse irradiance measurements such as those from the UVMFR-SR [*Long and Ackerman*, 2000]. This procedure is more rigorous than the ‘eye-balling’ procedure used in the current study, and could well be utilized with the current methodology to allow for determination of

single scattering albedo on days when clouds are more prevalent. Aerosol optical depth could be extrapolated from irradiance measurements made during only the clear-sky periods and subsequently used as input into TUV4.1. This could allow for a wider database of single scattering albedo values from the database analyzed for this study.

Summary

In this thesis aerosol single scattering albedo was investigated in the UV wavelengths. A procedure was devised to retrieve single scattering albedo from UVMFR-SR measurements coupled with the radiative transfer model TUV4.1. Values of ω were determined for the seven wavelengths of the UVMFR-SR for nine days in 1999. The values retrieved vary from 0.53 to 1.03 and vary quadratically with increasing wavelength. There was no discernible dependence of ω on the air mass classifications used. The range of values is larger than previous studies have found, and this can possibly be attributed to changes in aerosol size, composition, and distribution in the air masses influencing the site, as well as error in both the instrument and model. Uncertainties in estimations of asymmetry parameter and ground albedo also contribute, as do errors in AOD inputs. Some of the error in AOD measurements has been quantified, but uncertainty in AOD is expected to be higher than what was used here, due to changes in the more dominant ozone and Rayleigh optical depths. Quantification of this error is needed. Error and sensitivity analysis was conducted to determine the uncertainty in the retrieval of single scattering albedo. Error in this procedure was found to decrease with increasing aerosol optical depth, suggesting that this process works best for more turbid atmospheres (AOD>0.3). The error was determined to be +/-0.19 for AOD=0.5 and +/-0.2 for AOD=1.0. Long term UVMFR-SR measurements would allow for observation of trends in UV aerosol radiative properties. The values of ω found here can be used for better estimation of the parameter in these wavelengths for the southeastern US. This will lead to further development of UV radiative transfer models and lessen error in estimation of surface UV irradiances for the region.

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