Case studies of spectral atmospheric transmittance in the ultraviolet and visible regions in Athens, Greece
II. Aerosol transmittance

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Abstract

This work accounts for an investigation about the diurnal variation of aerosol spectral transmittance of solar irradiance under dominant wind conditions as case studies. Such a work is carried out in Athens for the first time. The spectral transmittance values estimated were derived using ground-based spectral measurements of beam irradiance in the range 310–575 nm (UV and VIS). The data were recorded by a system consisting of an automatic solar tracker and a spectrometer. All data were recorded under clear-sky conditions in the city center of Athens and the aerosol spectral transmittance was estimated towards zenith to avoid optical mass effects. The comparison reveals that the aerosol transmittance is higher under the influence of strong Etesian compared to sea-breeze conditions. The influence of low-pressure systems also plays a depollution role in the basin. Various features of diurnal variation are discussed with respect to emission sources, topographic peculiarities and wind pattern. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Aerosols exhibit spatial and temporal variations in urban environments like Athens area. Scientific interest has focused on the evaluation of atmospheric turbidity, a measure of the aerosol load in the atmosphere. Various turbidity definitions have been proposed such as the Linke turbidity factor, $T_L$, (Linke, 1922; 1929), the Unsworth–Monteith turbidity factor, $T_U$ (Unsworth and Monteith, 1972), the Ångström turbidity parameters, $\alpha$ and $\beta$ (Ångström, 1929), the Schüepp coefficient $B$, (Schüepp, 1949), and the horizontal visibility $V$ (McClatchey and Selby, 1972). Many studies dealing with aerosol optical properties appear in the literature (e.g. Louche et al., 1987; Kocifaj, 1994; Bokoye et al., 1997; Schmid et al., 1997; Tomasi et al., 1997; Devara, 1998; Kambezidis et al., 1998b; Jacobson, 1999). Some of those appear as spectral narrowband studies (e.g. McCartney and Unsworth, 1978; Cachorro et al., 1987; Lorente et al., 1994; Adeyefa et al., 1997; Kambezidis et al, 1997b; Marenco et al., 1997). Furthermore, a variety of atmospheric aerosols absorbing solar radiation are known (Jacobson, 1999).

The necessity in estimating the total atmospheric transmittance is discussed in the companion paper (Kambezidis et al., 2000). In addition, the effect of wind regime on the above quantity is studied. Here, an attempt is made to model the extinction of solar irradiance, taking into account various attenuation processes and constituents.

Starting with Leckner (1978), the total atmospheric transmittance was analyzed as a product of partial transmittance functions due to various atmospheric constituents considering Rayleigh scattering, absorption by ozone, water vapor and mixed gases as well as aerosol scattering. However, there was a special need to include nitrogen dioxide, the contribution of which to the extinction procedure is very significant in polluted areas. Therefore, Gueymard (1995) added one more term in his spectral radiative code SMARTS2, the transmittance function due to atmospheric NO$_2$.

2. Methodology

In this study, we use the spectral measurements of solar beam irradiance taken by PPS on the same selected days as described in the companion paper (Kambezidis et al., 2000). Based on SMARTS2 algorithm proposed by Gueymard (1995), a new radiative transfer model was first developed by Kambezidis et al (1997a). This calculates spectral radiative properties such as atmospheric optical thickness and transmission and also estimates atmospheric constituents such as O$_3$ and NO$_2$ (Kambezidis et al., 1996, 1997a). Ground-based multispectral measurements of direct solar irradiance are required as input values to the model. Such measurements were performed every 30 min in the spectral range 310–575 nm with a resolution of about 0.5 nm.

The total spectral atmospheric transmittance, $T(\lambda, \theta_z)$ (in the sun-sensor direction), considering single scattering, can be written as follows:

$$ T(\lambda, \theta_z) = \frac{H(\lambda, \theta_z)}{H_0(\lambda)} S $$  \hspace{1cm} (1)

where $H(\lambda, \theta_z)$ is the measured beam irradiance calibrated in W m$^{-2}$ (a function of wavelength, $\lambda$, and zenith angle, $\theta_z$), $H_0(\lambda)$ the spectral extraterrestrial radiation after
Gueymard (1995), and \( S \) is the correction factor for the sun–earth distance (Kambezidis et al., 1997a).

The spectral optical thickness (towards zenith), \( \delta'(\lambda) \), is determined from the equation:

\[
\delta'(\lambda, \theta_z) = 1/m \ln \left[ 1/\tau(\lambda, \theta_z) \right]
\]

where \( m \) stands for the atmospheric optical mass.

The total spectral transmittance function (towards zenith with \( m = 1 \)), \( \tau' \), is, therefore, given by the following equation:

\[
\tau'(\lambda, \theta_z) = \exp \left[ -\delta'(\lambda, \theta_z) \right].
\]

To model the atmospheric transmittance in any spectral range, six individual atmospheric processes are considered here: Rayleigh scattering, absorption by ozone, nitrogen dioxide, uniformly mixed gases (such as CO, \( O_2 \)), water vapor as well as aerosol extinction. Their respective spectral transmittance functions are denoted \( \tau_r, \tau_o, \tau_n, \tau_w, \) and \( \tau_a \). Within narrow spectral regions, these atmospheric processes can be considered independent of each other, so that the total transmittance function can be derived as the product of these individual spectral transmittance functions (Kambezidis et al., 1997a, 1998a; Gueymard, 1995). Thus:

\[
\tau(\lambda, \theta_z) = \tau_r(\lambda, \theta_z) \tau_o(\lambda, \theta_z) \tau_n(\lambda, \theta_z) \tau_w(\lambda, \theta_z) \tau_a(\lambda, \theta_z).
\]

For each \( i \)th atmospheric extinction process (\( i = r, o, n, g, w, a \)) mentioned above, the transmittance function \( \tau_i \) can be written in terms of optical thickness \( \delta_i \), and the optical mass \( m_i \), as follows:

\[
\tau_i = \exp(-m_i \delta_i).
\]

According to Eq. (5) the atmospheric transmittance due to Rayleigh scattering is retrieved as follows:

\[
\tau_r(\lambda, \theta_z) = \exp\left[ -m(\theta_z) \delta_r(\lambda) \right]
\]

where the molecular optical thickness is calculated from Leckner (1978):

\[
\delta_r(\lambda) = 0.008735 \lambda^{-1.08}.
\]

The units of \( \lambda \) in all the expressions are microns. The relative optical air mass, \( m' \), for standard pressure \( P_0 = 1013.25 \) hPa at sea level, is calculated from Gueymard (1995):

\[
m'(\theta_z) = \left[ \cos \theta_z + 0.45665 \theta_z^{0.07} (96.4836 - \theta_z)^{-1.697} \right]^{-1}
\]

where \( \theta_z \) is in degrees. The pressure corrected air mass, \( m \), is calculated from:

\[
m = m' P/P_0,
\]

where \( P \) is the measured surface pressure in hPa.

The water vapor transmittance and air mass are after Gueymard (1995):

\[
\tau_w(\lambda, \theta_z) = \exp\left[ -k_w \left( m_w J \right)^{1.05} f^n B \right]
\]
where the atmospheric mass due to water vapor is calculated from:

\[ m_w(\theta) = \left[ \cos \theta + 0.031141 \theta_w^{0.5} (92.471 - \theta) - 1.38140.1 \right]^{-1} \] (10)

where:

\[ J = 0.493 (\text{RH} \times \frac{P}{P_\text{m}})^{0.75} \times \sqrt{273.15/T} \text{ in cm.} \] (11)

RH is the relative humidity (in %), \( e_s \) is the saturation water vapor (in hPa) calculated from Gueymard (1994):

\[ e_s = \exp(22.329699 - 49.140396 T_v^{-1} - 10.921853 T_v^{-2} - 0.39015156 T_v^{12}) \] (12)

with \( T_v = T/100 \), \( T \) being the absolute air temperature (in K)

\[ f = A \left[ 0.394 - 0.26946 \lambda + (0.46478 + 0.23757 A) \left( \frac{P}{P_\text{m}} \right) \right] \] (13)

is a pressure scaling factor that compensates for inhomogeneities in the water vapor path length according to the Curtis–Godson approximation, and:

\[ A = 1 \text{ for } \lambda < 670 \text{ nm.} \]

In addition:

\[ n = 0.88631 + 0.025274 \lambda - 3.5949 \exp(-4.5445 \lambda) \] (14)

\[ c = 0.53851 + 0.003262 \lambda + 1.5244 \exp(-4.2892 \lambda). \] (15)

The correction factor \( B \) takes into account the variation of the absorption with distance from the band center:

\[ B = f'(m_u J) \exp(0.1916 - 0.0785 m_u + 4.706 \times 10^{-4} m_u^2) \] (16)

with:

\[ f'(m_u J) = 0.624 m_u J^{0.457} \text{ for } k_u < 0.01 \] (17a)

\[ f'(m_u J) = (0.525 + 0.246 m_u J)^{0.45} \text{ for } k_u \geq 0.01 \] (17b)

\( k_u \) being the water vapor absorption coefficient, in \( \text{cm}^{-1} \).

Since mixed gases possess no absorption lines in the spectral range under consideration, the respective formulas are not taken into account here.

The transmittance function due to absorption by \( \text{NO}_2 \) is:

\[ \tau_0 = \exp(-k_u l_u m_u). \] (18)

where \( l_u \) is the total column of \( \text{NO}_2 \) in the atmosphere. The corresponding atmospheric mass is calculated from Gueymard (1995):

\[ m_u(\theta) = \left[ \cos \theta + 602.3 \theta_w^{0.5} (117.96 - \theta) - 3.4536 \right]^{-1}. \] (19)

The corrected absorption coefficient is calculated from the data of \( k_u(\lambda, T_v) \) via the relationship (Gueymard, 1995):

\[ k_u(\lambda, T_v) = \max \left\{ 0, k_u(\lambda, T_v) \left[ 1 + \left( T_v - T_v \right) \sum_{i=0}^{5} f_i \lambda^{i} \right] \right\}, \text{ in } \text{cm}^{-1}. \] (20)
where \( k_s(\lambda, T) \) is the absorption coefficient for the reference temperature of \( T_s = 243.2 \) K, \( T_a = a_0 + a_1 T \) (\( a_0 = 332.41 \) K, \( a_1 = -0.34467 \) for summer and \( a_0 = 142.68 \) K, \( a_1 = 0.28498 \) for winter). The coefficients \( f_i \) are: \( f_0 = 0.69773, f_1 = -8.1829, f_2 = 37.821, f_3 = -86.136, f_4 = 96.615, f_5 = -42.635 \) for \( \lambda < 625 \) nm.

The atmospheric transmittance due to \( O_3 \) absorption is calculated from:

\[
\tau_o(\lambda, \theta_z) = \exp\left[-k_o(T, \lambda)l_o m_o\right].
\]

(21)

\( l_o \) is the total ozone column in atm-cm calculated as in Kambezidis et al. (1997a).

The ozone air mass is calculated from Gueymard (1995):

\[
m_o(\theta_z) = \left[\cos \theta_z + 268.45 \theta_z^{0.5} (115.42 - \theta_z)^{-3.2923}\right]^{-1}.
\]

(22)

The temperature-dependent absorption coefficients, \( k_o \), are calculated from:

\[
k_o(\lambda, T) = \max\left[0, \left[k_o(\lambda, T_s) + C_1(T_s - T) + C_2(T_s - T)^2\right]\right] \text{cm}^{-1}
\]

(23)

where \( T_s = a_0 + a_1 T \) (\( a_0 = 332.41 \) K, \( a_1 = -0.34467 \) for summer and \( a_0 = 142.68 \) K, \( a_1 = 0.28498 \) for winter), \( T \) (K) is the temperature at which the ozone absorption coefficient is to be estimated. The constants \( C_1 \) and \( C_2 \) are:

\[
C_1 = (0.39626 - 2.3272 \lambda + 3.4176 \lambda^2) \quad \text{for} \ 310 \ < \lambda < 344 \text{ nm}
\]

(24a)

\[
C_2 = (1.8268 \times 10^{-2} - 0.10928 \lambda + 0.16338 \lambda^2) \quad \text{for} \ 310 \ < \lambda < 344 \text{ nm}.
\]

(24b)

In the spectral range \( 344 < \lambda < 560 \text{ nm} \), \( k_o \) is given by:

\[
k_o(T, \lambda) = \max\left[0, \left[k_o(T_s, \lambda)\left[1 + 0.0037083(T_e - T)\right] \times \exp(28.04(0.4474 - \lambda))\right]\right].
\]

(25)

If the calculations are made for optical masses, \( m_s = 1 \), the individual spectral transmission functions \( (\tau'_i) \) are derived in the direction towards zenith, and therefore, are independent of the solar elevation angles at the times of the measurements. Thus, Eq. (4) can also be written as:

\[
\tau'(\lambda) = \tau'_s(\lambda) \tau'_o(\lambda) \tau'_e(\lambda) \tau'_w(\lambda) \tau'_l(\lambda).
\]

(26)

Making the aerosol transmittance subject of the formula, we can estimate this parameter:

\[
\tau'_s(\lambda) = \tau'(\lambda)/\left[\tau'_o(\lambda) \tau'_e(\lambda) \tau'_w(\lambda) \tau'_l(\lambda)\right].
\]

(27)

3. Results and discussion

The above-described algorithm requires simultaneous observations of dry-bulb temperature, relative humidity, barometric pressure and visibility as input values in addition to the spectral data of solar beam irradiance. Substituting all the appropriate values taken simultaneously at the time of measurements in the model presented in Section 2, aerosol spectral transmittances were derived.
To highlight the influence of wind regime on aerosol transmittance values (Adamopoulos et al., 1998), we present case studies during a pure-sea-breeze day (20th May 1997), a pure Etesian day (5th September 1997), a day with competing wind flows (1st July 1997) and a day under the influence of a low-pressure system (11th July 1997). Details are discussed in the companion paper (Kambezidis et al., 2000).

During the 20th of May 1997, the synoptic wind flow was very weak thus favoring the development of a sea-breeze cell. The calculated transmittances due to aerosols are shown in Fig. 1. These are very low because of the appearance of an air-pollution episode. The results are supported by high levels of ground-based air-pollutant measurements performed on a 24-h basis by the Greek Ministry of Environment (EARTH, 1998) and are consistent with the reduction in visibility observed in the city center. As for the diurnal variation of the aerosol transmittance (Fig. 1), the morning peak of aerosol load centered at 9:00 coincides with the rush hour of the city (Kambezidis et al., 1995; EARTH, 1998). This is due to automobile-originated aerosols since this peak appears mainly in the VIS. The weak synoptic wind flow favored the appearance of a temperature inversion with a low mixing-layer height. As a result, a substantial aerosol burden was trapped at low heights. The second peak in aerosol concentration is observed at 13:00. This time coincides with the time of observation of maximum concentrations of secondarily produced photochemical products (EARTH, 1998) which are considered here as aerosols. The photochemically produced aerosols should be the cause for this

Fig. 1. Aerosol spectral transmittance contours in Athens during the 20th of May 1997.
peak, since this is observed throughout the considered spectral range. However, soil- and marine-originated aerosols must be present in the ambient air as well (Scheff and Valiozis, 1990; Eleftheriadis et al., 1998). After 15:00, aerosol transmittance rapidly improves. This is explained by the fact that aerosols are swept by sea-breeze northwards. This is also supported by the results of other studies that showed high levels of secondary-photochemical-pollutant concentrations at the foothills of Mts Parnitha and Penteli in the early afternoon hours (Suppan et al., 1998). There, a convergence zone develops and large air masses are lifted at an altitude from where they can take part in a long-range transport by the synoptic wind flow (Klemm et al., 1998). Furthermore, the relatively high transmittances observed over 500 nm compared to those at shorter wavelengths in the late afternoon hours indicate that the basin may contain a large quantity of marine aerosols (Vaxelaire et al., 1991; Eleftheriadis et al., 1998).

In sharp contrast, the aerosol transmittances calculated during the 5th of September 1997 obtain much higher values (Fig. 2). This day was characterized by a relatively strong Etesian wind flow with speeds varying in the range 4.5–6.8 m s\(^{-1}\). This was expected since Etesian winds are responsible for cleansing the atmosphere of the Athens basin (Gagaoudaki, 1979; Lalas et al., 1983; Katsoulis, 1988; Ziomas, 1998; Suppan et al., 1998; Svensson and Klemm, 1998). The results are in accordance with the high visibility observed and the low levels of air-pollutant concentrations recorded by EARTH (1998). They are also supported by the findings of another work that derived turbidity parameters much higher during sea-breeze days than those under the existence

![Fig. 2. As in Fig. 1 but for the 5th of September 1997.](image-url)
of strong Etesians (Kambezidis et al., 1998b). Furthermore, a fair peak in aerosol load is observed in the morning due to traffic circulation. As the day progresses, the aerosol transmittance becomes higher and higher eventually reaching the value of 0.9 in the late afternoon. Moreover, aerosol transmittance turns out to be almost independent of the wavelength. This means that aerosols deplete solar irradiance almost equally throughout UV and VIS indicating a homogeneous atmosphere over Athens with respect to aerosols, due to the strong synoptic forcing.

During the 1st of July 1997, a high-pressure system centered over Italy. The resultant wind flow was a combination of both Etesian wind forcing and sea-breeze circulation. Fig. 3 presents the aerosol transmittance having characteristics of both previous two wind regimes (Figs. 1 and 2) as also found for total transmittance in the companion paper. The values derived are moderate and are comparable to those of pure-Etesian day in some cases. A peak in aerosol load is still observed in the morning due to increased anthropogenic emissions. The midday peak is not well pronounced as in the companion paper, too. In addition, unlike the findings during the pure-Etesian day, the aerosol transmittance depends here on the wavelength suggesting that aerosols of different origin are present in the ambient air. After 15:00, the atmosphere becomes cleaner.

The next case study shows the influence of a low-pressure system situated north of Greece during the 11th of July 1997. The predominant wind direction was from the S sector. The derived aerosol transmittances (Fig. 4) are much higher compared to those

![Figure 3](image-url)

Fig. 3. As in Fig. 1 but for the 1st of July 1997.
obtained during the sea-breeze day (Fig. 1) and in some cases, comparable to those calculated during the Etesian day (Fig. 2). A peak in atmospheric aerosol burden is observed at around 8:30 in the morning as found in all cases examined, suggesting that traffic is its origin. In the late afternoon hours, the cleansing effect of this low barometric system is more obvious. The peak in air pollution observed in the afternoon in the companion paper, is only found here in the VIS. We can invoke sea-spray transport as the cause.

4. Concluding remarks

The contribution of aerosols to the air-pollution of the Athens basin can be estimated from ground-based spectral measurements of solar beam irradiance using a radiative transfer model.

The aerosol transmittance achieves values roughly varying in the range 0.2–0.9. This turns out to depend on the time of measurement, the wavelength and the wind regime prevailing at the time of measurement. In the warm period, the highest values of aerosol transmittance are observed under the influence of strong Etesian winds throughout the considered spectral range, while during sea-breeze circulation the values are the lowest and are mainly attributable to photochemical, soil- and marine-origin aerosols. A cleansing effect on aerosols is found under the presence of low-pressure systems.
An atmospheric aerosol burden is observed in the morning under all examined wind regimes and coincides with the rush hour of the city. Nevertheless, various wind regimes cause different diurnal variations of spectral aerosol transmittance due to the various pollution sources involved, climatic and topographic peculiarities of the Athens basin.

References


