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Short- and long-term variability of spectral solar UV irradiance at Thessaloniki, Greece: effects of changes in aerosols, total ozone and clouds

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Abstract

In this study, we discuss the short- and the long-term variability of spectral UV irradiance at Thessaloniki, Greece using a long, quality-controlled data set from two Brewer spectrophotometers. Long-term changes in spectral UV irradiance at 307.5, 324 and 350 nm for the period 1994–2014 are presented for different solar zenith angles and discussed in association to changes in total ozone column (TOC), aerosol optical depth (AOD) and cloudiness observed in the same period. Positive changes in annual mean anomalies of UV irradiance, ranging from 2 to 6 % per decade, have been detected both for clear- and all-sky conditions. The changes are generally greater for larger solar zenith angles and for shorter wavelengths. For clear skies, these changes are, in most cases, statistically significant at the 95 % confidence limit. Decreases in the aerosol load and weakening of the attenuation by clouds lead to increases in UV irradiance in the summer, of 7–9 % per decade for 64° solar zenith angle. The increasing TOC in winter counteracts the effect of decreasing AOD for this particular season, leading to small, statistically insignificant, negative long-term changes in irradiance at 307.5 nm. Annual mean UV irradiance levels are increasing from 1994 to 2006 and remain relatively stable thereafter, possibly due to the combined changes in the amount and optical properties of aerosols. However, no statistically significant corresponding turning point has been detected in the long-term changes of AOD. Trends in irradiance during the two sub-periods are not discussed, because the length of the two datasets is too short for deriving statistically significant estimates. The absence of signatures of changes in AOD in the short-term variability of irradiance in the UV-A may have been caused by changes in the single scattering albedo of aerosols, which may counteract the effects of changes in AOD on irradiance. The anti-correlation between the year-to-year variability of the irradiance at 307.5 nm and TOC is clear and becomes clearer as the AOD decreases.

1 Introduction

Although ultraviolet (UV) radiation is only a small fraction ($< 10\,\%$) of the total solar radiation that reaches the earth's surface, it is vital for the life on earth (Asta et al., 2011; Hader et al., 2015; Lucas et al., 2015; Madronich et al., 2015; UNEP, 2010; Williamson et al., 2014). The amount of solar UV radiation reaching the atmosphere is changing periodically due to changes in the earth-sun distance and the solar activity. Solar radiation with wavelengths shorter than 290 nm is entirely blocked by the atmosphere, while for longer wavelengths the fraction that penetrates to the surface depends mainly on the solar zenith angle, the composition of the atmosphere and the characteristics of the surface (Kerr and Fioletov, 2008). The interaction between the UV radiation, the atmospheric constituents and the characteristics of the surface is complicated and not yet fully understood (Bernhard et al., 2007; Kerr and Fioletov, 2008; Meinander et al., 2009). The geophysical parameters that mainly affect the levels of the surface UV irradiance are: ozone, clouds, surface reflectivity and aerosols (Arola et al., 2003; Bais et al., 1993; Bernhard et al., 2007; WMO, 2007).

From the early 1980s until the mid-1990s, the sharp decline of the stratospheric ozone over the mid and high latitudes led to important increases in the surface UV irradiance (Kerr and McElroy, 1993; Madronich et al., 1998). The successful implementation of the Montreal protocol decelerated the weakening of the ozone layer (Egorova et al., 2013; Mäder et al., 2010; Newman and McKenzie, 2011) and many recent studies indicate the first signs of recovery over the northern hemisphere (Kuttippurath et al., 2013; McLinden and Fioletov, 2011; Newchurch et al., 2003; Smedley et al., 2012). Signs from the onset of ozone recovery since the late 1990s on surface UV-B irradiance have been mainly detected over the northern high latitudes; recent studies indicate that UV-B has been declining during the last two decades (Bernhard, 2011; Eleftheratos et al., 2014). However, during the same period, both the UV-B and the UV-A irradiance are increasing over many locations in the northern hemisphere mid-latitudes, mainly due to the negative trends in the amount of clouds and aerosols (De Bock et al., 2014;

Fitzka et al., 2012; Román et al., 2014; Smedley et al., 2012; Zerefos et al., 2012). In a recent study, Fragkos et al. (2015) showed that in Thessaloniki, even under extreme high (low) TOC conditions, the erythemal irradiance can be lower (higher) than its climatological values due to the dominant effect of aerosols. Zerefos et al. (2012) suggest that over Canada, Europe and Japan there is a statistically significant evidence of a slowdown or even a turning point in the upward UV-B trends after 2006, mainly due to a corresponding turning point in the negative trends of aerosols.

In the next decades, ozone, aerosols, clouds and surface reflectivity are projected to undergo important changes (IPCC, 2013). Changes in these factors may alter the levels of the surface UV irradiance (Bais et al., 2015, 2011; Hegglin and Shepherd, 2009; Tourpali et al., 2009; Watanabe et al., 2011) with important impacts on the human health and the balance of the ecosystems (UNEP, 2010; Williamson et al., 2014). However, the uncertainties in the spatial and temporal variability, the magnitude, and the direction of the projected changes of surface UV irradiance are still high (Bais et al., 2015). Thus, good quality measurements of the spectral UV irradiance and the main factors controlling its levels at the earth's surface are of great importance for achieving better understanding and more accurate modeling of the interactions among UV radiation, ozone, aerosols, clouds and surface reflectivity (García et al., 2015; Kreuter et al., 2014; Mayer and Kylling, 2005; Schwander et al., 1997).

Accurate knowledge of the levels of spectral surface UV irradiance is necessary in order to quantify effects on the health of humans (Kazantzidis et al., 2015; Webb et al., 2010) and ecosystems (Ballare et al., 2011; Hader et al., 2011), and prevent potential impacts from over- or under-exposure to UV radiation (Lucas et al., 2015). Additionally, reliable estimations of the trends of spectral surface UV irradiance provide useful information for assessing these impacts and for adopting proper measures (Morgenstern et al., 2008; Newman and McKenzie, 2011; van Dijk et al., 2013). Climatologies and trends of surface UV irradiance (spectral or broadband) can be derived either directly from ground based measurements (Fitzka et al., 2012; Glandorf et al., 2005; Zerefos, 2002), or indirectly from measurements of surface reflectivity, ozone, aerosols and cloudiness derived either form satellites (Damiani et al., 2014; Fioletov et al., 2004; Li et al., 2000), or from ground based instruments (Antón et al., 2011; Román et al., 2014; Walker, 2009). The uncertainties of these parameters and the applied methodologies increase the uncertainty of the indirectly derived UV irradiance, when compared to measurements (Cordero et al., 2013; Weihs and Webb, 1997). Thus, long records of good quality measurements of UV irradiance lead to more reliable estimations of its short-term and long-term changes (Arola et al., 2003; Weatherhead et al., 1998).

The present study aims at the quantification of the long-term changes in surface UV irradiance using spectral measurements which are recorded since 1990 at Thessaloniki (Bais et al., 2001; Garane et al., 2006; Gröbner et al., 2006), one of the longest time series globally (Glandorf et al., 2005). An important aspect is also the attribution of the trends and variability of UV irradiance to changes in the total ozone column (TOC), the aerosol optical depth (AOD) and cloudiness during the same period. Special emphasis is given to the reported slowdown of the aerosol decline over the northern hemisphere (Turnock et al., 2015; Zerefos et al., 2012).

2 Instrumentation and data

In the 1980s, the increased concern for the stratospheric ozone depletion (Farman et al., 1985; Solomon et al., 1986) and its effect on the levels of UV radiation at the Earth's surface (Kerr and McElroy, 1993; Madronich et al., 1995; Zerefos, 2002), led to increased deployment of ground-based instruments worldwide (Fioletov et al., 1999), to monitor the TOC and the surface UV irradiance. Among these instruments, several Brewer spectrophotometers (Brewer, 1973; Kerr et al., 1985) were deployed at different locations including Thessaloniki, Greece, where the first commercially available single-monochromator Brewer with serial number 005 (B005) was installed in 1982. Since then B005 performs continuous measurements of the TOC and the columnar SO_2 (Bais et al., 1993, 1985; Meleti et al., 2012; Zerefos, 1984). These measurements are also used to derive the aerosol optical depth at specific UV-B wavelengths (Kazadzis et al., 2007). Monitoring of spectral UV irradiance with B005 started in 1990 (Bais et al., 1996, 1993; Garane et al., 2006). Since 1993, a second, double-monochromator, Brewer spectrophotometer with serial number 086 (B086) is also operating at Thessaloniki for continuous monitoring of the spectral UV irradiance (Bais et al., 1996). Both instruments are located at the facilities of the Laboratory of Atmospheric Physics (latitude 40.634° N, longitude 22.956° N, altitude 60 m above sea level).

The spectral measurements of B005 cover the wavelength range 290–325 nm in steps of 0.5 nm and spectral resolution of about 0.55 nm (FWHM). The corresponding spectral range for B086 is 290–363 nm, with the same step and very similar spectral resolution. The UV dataset of both instruments was quality checked and re-evaluated up to the end of 2005 (Garane et al., 2006) and has been used in different studies (Kazadzis et al., 2009; Kazantzidis et al., 2006, 2009; Meleti et al., 2009). The estimated 1σ uncertainty of the measurements is about 5 % for B086 and ranges from 6.5 % near 305 nm to 5 % near 320 nm for B005 (Garane et al., 2006). Recently, the quality control and the re-evaluation of the post-2005 dataset have been completed and the time series is now extended to the end of 2014, comprising about 170 000 spectra for B005 and 140 000 spectra for B086.

Direct spectral irradiance measurements performed with B005 at 306.3, 310.0, 313.5, 316.8 and 320.1 nm are used to derive the TOC (Kerr et al. 1981) and the AOD (Gröbner and Meleti, 2004; Meleti and Cappellani, 2000). The uncertainty of the TOC measurements is estimated to about 1 % or less (Kerr et al., 1985), while for the AOD the uncertainty is of the order of 0.04 at 320 nm for air mass 1.4 (Kazadzis et al., 2007). Comparisons with AOD data for the period 2005–2014 provided from a collocated Cimel sun-photometer which is part of AERONET (http://aeronet.gsfc.nasa.gov/) revealed an overall agreement to within 0.1 for air mass values up to 3.2.

For the trend analysis, which will be discussed later, data for the 11-year solar cycle and the Quasi-Biennial Oscillation (QBO) of the winds in the equatorial stratosphere have been used. Monthly means for the solar flux at 10.7 cm were downloaded from the NOAA national geophysical data centre (http://www.ngdc.noaa.gov/stp/space-weather/solar-data/solar-features/solar-radio/noontime-flux/penticton/), while for the QBO wind data were downloaded from the Freie Universität Berlin (http://www.geo.fu-berlin.de/en/met/ag/strat/produkte/qbo/index.html).

The spectral irradiances used in this study are averages of five measurements (within ±1 nm about the nominal wavelength) and the analysis is performed for 307.5, 324 and 350 nm. The irradiance for the former two wavelengths is derived from both instruments while for 350 nm it is derived only from B086. The solar irradiance at 307.5 nm is strongly absorbed by ozone in contrast to the other two wavelengths where the ozone absorption is either weak (324 nm) or negligible (350 nm). In many studies, the irradiance at 305 nm has been used to estimate the effect of TOC on UVB irradiance. However, for large solar zenith angles and/or under cloudy conditions the effects from the dark signal and the stray light are very important for such low wavelength, especially for the single monochromator Brewers (Karppinen et al., 2014). Therefore, in the present study the irradiance at 307.5 nm has been chosen because it is stronger than at 305 nm, with significantly higher signal-to-noise ratio required for more accurate determination of trends, while the effect of ozone absorption remains very strong. Additionally, the changes in irradiance for 307.5 nm are more representative of the changes in the erythemal irradiance, which is an important, human health–related metric. Finally, the effect of SO_2 absorption in relation to the effect of ozone absorption at 307.5 nm is the weakest in the range 306–309 nm. The changes in irradiance at 324 and 350 nm for clear skies are mainly determined by the changes in the amount and optical properties of the aerosols. Thus the effect of TOC on the long-term trends can be estimated by comparing the trend in irradiance at 307.5 nm with the trend at these longer wavelengths. In order to detect the presence of clouds during measurements and separate the data under clear skies, data from a collocated pyranometer (type Kipp & Zonen CM-21) recorded at high temporal resolution (60 Hz) have been used (Bais et al., 2013).

The long-term variability of the spectral UV irradiance was investigated for specific solar zenith angles, in order to minimize interferences from the different paths of radiation in the atmosphere. Specifically, averages of measurements corresponding to SZAs within ±1° about the nominal SZA were used. In order to eliminate remaining biases induced by these slightly different SZAs, correction factors were derived with the radiative transfer model UVSPEC, which is included in version 1.7 of the libRadtran package (Mayer and Kylling, 2005). The simulations were made for a range of TOC and AOD values within the expected range of variability over Thessaloniki: 250–550 DU for TOC and 0–1.4 for the AOD at 320 nm, using the US standard atmospheric profile (Anderson et al., 1986), the aerosol profile suggested by Shettle (1989), and typical values of the surface reflectivity, the single scattering albedo and the asymmetry factor of 0.05, 0.85 and 0.7 respectively (Bais et al., 2005). The simulations revealed that while for small SZAs and long wavelengths the differences in clear-sky UV irradiance are small, at 305 nm the differences escalate to 60 % for a change in SZA from 69 to 71°. The following empirical relationship has been derived to correct the measured irradiance at SZAs different than the nominal:

$$\frac{I_0}{I_\theta} = 1 + a(\lambda, \theta_0) \cdot \left(\frac{1}{\cos\theta} - \frac{1}{\cos\theta_0}\right) \quad (1)$$

Where θ_0 is the nominal SZA, θ is the actual SZA, I_0 is the irradiance for θ_0, I_θ is the irradiance for θ and $\alpha(\lambda, \theta_0)$ is the correction factor which depends on wavelength λ and θ_0. After applying the correction, the differences between irradiances for SZAs which differ by up to 2° do not exceed 10 % (±5 % about the mean) for wavelengths ranging from 290 to 400 nm and SZAs from 15 to 80°. For the wavelengths above 310 nm and SZAs smaller than 70° the remaining discrepancies are generally below 2 %, while for the same SZAs and wavelengths between 305 and 310 nm the remaining discrepancies range between 1 and 5 %.

The monthly mean values of the irradiance at 307.5 and at 324 nm, the TOC, and the AOD derived from B005 since 1990 are presented in Fig. 1. The period from June 1991 until December 1993 has been shaded to highlight the low TOC values due to the Mt. Pinatubo volcanic eruption in June of 1991 (Hofmann et al., 1994; Randel et al., 1995).

The annual cycle of the irradiance at 307.5 nm is clearly anti-correlated with the annual cycle of TOC while for the irradiance at 324 nm the annual variability is mainly caused by changes in cloudiness. There is an indication of increasing tendency in irradiance, for both wavelengths since the beginning of the record, which will be further discussed in the following sections. The monthly mean TOC generally ranges between about 280 and 400 DU with no obvious long-term trend. The high aerosol load over Thessaloniki is depicted in the monthly mean values of AOD that range between about 0.3 and 0.9. However, during the last two decades, the mean levels of the AOD are decreasing and its inter-annual variability becomes weaker. As will be shown in the following, changes in aerosols play a key role in both the short- and the long-term variability of the UV irradiance over Thessaloniki.

3 Data analysis and results

3.1 Methodology

The present study has two main objectives: First, to quantify and discuss the long- and short-term changes in UV irradiance, and second, to investigate whether a turning point exists in the long-term variability of the UV time-series, during the period 1994–2014. Data before 1994 are not used in the analysis, to eliminate the effect on total ozone from the volcanic eruption of Mt. Pinatubo in June 1991. Large amounts of aerosols, mainly sulfuric, were injected into the stratosphere which led to decreases in TOC in the period 1991–1993, as can be seen from Fig. 1. In addition, measurements of spectral UV irradiance at Thessaloniki before June 1991 are sparse and available for less than two years.

Assuming that part of the long-term variability of the clear-sky UV irradiance is due to ozone, one would expect that there should be two modes in this trend: one for the period of decreasing total ozone and one for the period of stabilized or increasing total ozone. For some northern hemisphere locations, it was found (Zerefos et al., 2012) that surface UV-B irradiance increases faster in the period before 2006. If such a turning point exists also in the 20-year long UV data-series of Thessaloniki, the two sub-periods would be too short to derive reliable estimates of the trends in each sub-period (Arola et al., 2003; Weatherhead et al., 1998). Thus, in the following the long-term trends are comprehensively discussed only for the entire period 1994–2014.

With respect to the presence of autocorrelation in the time series of TOC and UV and its effects on trend analysis, Weatherhead et al. (1998) have reported that the deseasonalized monthly mean UV irradiance data are autocorrelated in the first order. For the station of Thessaloniki, the autocorrelation of the all-sky dataset is estimated to be small, less than 0.2 and should not affect significantly the magnitude of the trends. In contrast, for the clear-sky dataset the autocorrelation is larger, ranging between 0.3 and 0.5 for different SZAs; hence must be removed. As discussed in Yang et al. (2006) removing the autocorrelation from time series with large number of gaps, as in our case for the clear-sky UV data set, can induce artificial tendencies and biases in the derived trends. Therefore, the autocorrelation was treated differently in the calculation of the long-term changes in UV irradiance than in the detection of the turning point in its trends.

In order to accurately detect the turning point in the trends of the UV irradiance and to determine its statistical significance, the methodology of Yang et al. (2006) was applied on the monthly mean anomalies. This study aimed at detecting a turning point in a time series of TOC with a large number of gaps using a non-autoregressive model. The additional uncertainty due to the remaining autocorrelation was taken into account in the estimation of the statistical significance associated with the detection of the turning point.

For the analysis of long-term changes we calculated daily anomalies for TOC, AOD and spectral UV irradiance at different SZAs in order to remove the effect of SZA in the annual variability of irradiance. These daily anomalies were calculated by subtracting from each data point the climatological value which was derived from the entire dataset. Then using the daily anomalies we derived monthly mean anomalies for months with at least 10 days of available data. As a next step, the effects of QBO and the 11-year solar cycle were filtered from both the TOC and UV irradiance data sets, by applying a multi-linear regression analysis. The procedure described in, e.g., Zerefos et al. (2012) was followed with the only difference being that in the present study we did not use an autoregressive model, due to gaps in the clear-sky UV data set. It was found that the difference in the linear trends derived for the period 1994–2014 with and without filtering the effects of these two natural cycles is generally lower than 0.5 % per decade. The number of gaps in the time-series of the UV irradiance is higher in the first half compared to the second half of the period of study. In order to suppress the effect of the uneven distribution of the measurements, the long-term changes in UV irradiance were calculated from the yearly mean anomalies, instead of those derived from the multilinear model. After removing the effects of the solar cycle and the QBO from the monthly mean anomalies, the dataset was recomposed and the yearly mean anomalies were calculated. This way the problem of the autocorrelation was also solved since the yearly mean anomalies are not autocorrelated. However, it was found again that the difference in the linear trends derived from the yearly mean anomalies and directly from the multilinear model is small, with the former being higher by only 0.1–0.4 % per decade. The statistical significance of the trends is derived from the Mann-Kendall test (Burkey, 2006). In the following, a trend is considered significant when it is statistically significant at the 95 % confidence level.

3.2 Comparison between the trends from the two Brewers for different SZAs

Following the re-evaluation and quality control of the entire dataset, the trends of the UV irradiance were calculated separately for the two Brewers operating at Thessaloniki. Mean ratios between quasi-synchronous (within ±1 min) spectral UV irradiance measurements from B005 and B086 under all-sky conditions averaged over 5 nm spectral intervals were calculated for different SZA's. For the wavelength range 310–325 nm the ratios are very close to 1 with a standard deviation of about 5 %. For shorter wavelengths, the mean ratio gradually decreases and for the 300–305 nm range it is ∼ 0.96

with a standard deviation of about 10 %. The uncertainties and the deviations from unity arise from the different characteristics of the two instruments (e.g., angular response, stray-light rejection, spectral resolution and temperature) and from the imperfect synchronization of the measurements (Garane et al., 2006). No dependency of the ratio from the temperature or the solar zenith angle was found. The good agreement in the absolute levels of the measured irradiance by the two instruments is an indication for the quality of the re-evaluated data. It should be noted, however, that the synchronous measurements represent only about 50 % of the available data. The trends from both instruments for the entire period 1994–2014 were compared for different solar zenith angles from 30 to 70° in steps of 10°. The results for 307.5 and 324 nm are presented in Fig. 2 both for clear-sky and all-sky conditions.

For 307.5 nm, the clear-sky trends from both instruments are statistically significant while the all-sky trends are statistically significant only for B005 and for SZAs 30 and 70°. For 324 nm, the trends are generally smaller than those for 307.5 nm. For this wavelength and all SZAs the all-sky trends are not statistically significant for both instruments, as they are for clear skies and for SZAs between 50 and 70°. For smaller SZAs only the trends derived from B005 data are statistically significant.

The results are quite satisfactory and consistent since for the same wavelengths and SZAs the irradiance trends from B005 and B086 do not differ by more than 2 % per decade and in most cases they agree within 1σ. The derived trends both for clear- and all-sky data and for all SZAs are positive and range between 1 and 6 % per decade. Although the dependence of the trends on the SZA appears to be small and within the uncertainty limits, at large SZAs the trends are greater. This dependence can be partially attributed to the increasing optical path of radiation with SZA, which leads to stronger absorption from ozone or aerosols. However, for different SZAs, the datasets comprise data from different periods in the year (e.g. for SZA = 30° data exist only from April to August, while for SZA = 70° data are available during the entire year). Since the long-term changes of TOC, AOD and cloudiness are different for different seasons, the irradiance trends for different SZAs should be affected differently by these factors.

3.3 Seasonal trends

Since the results from both instruments are generally similar, only the data from B086 are used in the following, since this instrument has superior characteristics, at least with respect to the rejection of stray light and angular response. Seasonal trends of the spectral UV irradiance for 307.5, 324 and 350 nm (Fig. 3) were calculated and compared to the corresponding trends of the daily mean TOC and AOD (Fig. 4). For SZAs larger than 63° data are available during the whole year, thus, the irradiance for 64° SZA (data ranging from 63 to 65°) is used in the analysis of trends. The effect of the changes in cloudiness is assessed by comparing the trends of the clear-sky and the all-sky irradiance.

As expected, the seasonal trends for 324 and the 350 nm are similar for both, clear-sky and all-sky conditions. The changes of the solar irradiance at these wavelengths are practically unaffected by the changes of TOC, while they are mainly affected by the changes in aerosols and clouds. In general, the effects of changes in aerosol amount and/or properties on UV irradiance are stronger for shorter wavelengths. Thus, the important negative trends of the AOD at 320 nm that have been observed for Thessaloniki lead to slightly less positive trends for the irradiance at 350 nm than at 324 nm. It must be clarified at this point that the interaction of solar UV radiation with aerosols is very complex and the changes in the AOD cannot explain the changes in UV irradiance without taking into account the absorption efficiency of the aerosols (i.e., the single scattering albedo) for which no measurements are available for this period. For example, decreases in the single scattering albedo (greater absorption efficiency) counteract the effect of decreases in the AOD. As will be discussed later, the fact that the changes in clear-sky UV-A irradiance (324 and 350 nm) cannot be fully explained by the changes in the AOD is an indication that changes in other optical properties of aerosols, such as the single scattering albedo may have occurred.

The greatest changes in irradiance at 324 and 350 nm were found in summer both for clear-sky and all-sky conditions. The trend for clear skies at these wavelengths is about 3.5 % per decade, while for 307.5 nm it increases to about 5 % per decade. The main driver for the changes under clear skies appears to be the decreasing AOD, which for summer is more than 20 % per decade. For all skies, the positive trends are almost double than those for clear skies (about 7 % for 324 and 350 nm and about 9 % for 307.5 nm), suggesting that the attenuation of irradiance by clouds is decreasing during the last two decades. All these trends are statistically significant. For winter, the trends in irradiance for 324 and 350 nm are 3.5 and 3.0 % respectively both for clear skies and all-skies, suggesting that cloud effects during the last two decades are very small in winter and changes in aerosols are the dominant factor. This conclusion is confirmed by the negative trend of the AOD shown in Fig. 4. For 307.5 nm the increases in TOC counteract the effects of changing aerosols, leading to a negative trend of about −3 % per decade for irradiance under clear skies. However, none of the trends in winter is statistically significant.

For spring, the trends for clear skies are similar to those in summer for all three wavelengths, while for all skies trends are smaller; by 0.5–1 %. Thus, as for winter, the UV trends are due mainly to decreasing AOD. Although for that season the trend in TOC is about 1 % per decade, this not reflected in the trend of clear-sky irradiance at 307.5 nm which is slightly larger than in the UV-A wavelengths, instead of being smaller. For this season only the trend for 350 nm is statistically significant.

For autumn, the trends in clear-sky irradiance are approximately 7, 3 and 1.5 % for 307.5, 324 and 350 nm respectively, and statistically significant only for the first two wavelengths. For all skies, the trends are 3–4 % lower, suggesting an increasing attenuation by clouds during this season. However, the differences between the clear sky and the all sky trends are within the uncertainty limits of the later. The all-sky trends for autumn are not statistically significant. One of the possible reasons for the stronger increase of the irradiance at 307.5 nm compared to 324 and 350 nm is the small negative trend in TOC. Additionally, the relatively large difference between the trends for 324 and 350 nm is explained by the decreasing aerosols which have much stronger impact on shorter than on longer wavelengths.

Finally, the yearly averaged TOC is slightly increasing, by about 0.8 % per decade, but this change is not statistically significant. In contrast, the yearly mean AOD has been decreasing by about 17 % per decade, and therefore AOD is the dominant driver of the changes in the yearly mean UV irradiance. The trends in UV irradiance range from 3 to 4 % for clear skies, while for all skies they are about 0.5 % larger. At shorter wavelengths the trends are larger, possibly due to the negative trend in TOC and the stronger effect of aerosols on the irradiance at these wavelengths. A general conclusion is that the enhanced attenuation of UV radiation by clouds in summer is balanced by the decreased attenuation in autumn, leading to a negligible effect on the yearly mean UV irradiance.

3.4 The role of ozone and aerosols on short- and long-term variability of irradiance

In the following we discuss in more detail the short- and long-term variability of clear-sky UV irradiance at 307.5 and 350 nm in association with the evolution of factors causing this variability. Furthermore we explore a potential turning point in the time series of irradiance at Thessaloniki, in an attempt to confirm the findings of Zerefos et al. (2012). The analysis is performed on annual mean anomalies of UV irradiance at 64° SZA, TOC and AOD, as well as for mean anomalies for the periods December–May (winter–spring) and June–November (summer–autumn) since the first is affected strongly by ozone changes while the second is affected mainly by changes in aerosols.

The results for 324 nm are not discussed since they are similar to those for 350 nm. For the yearly mean anomalies, a turning point in the upward trend of irradiance at both 307.5 and 350 nm has been detected in 2006, statistically significant at the 95 % confidence level. Since the same pattern occurs at both wavelengths and since no statistically significant turning point has been detected for TOC, this piece-wise trend pattern in UV irradiance has likely been caused by changes in aerosols. However, the small negative trend in UV irradiance observed after 2006 (see Table 1 and Fig. 5) does not comply with the negative monotonic trend in AOD during the whole period of study which continues also after 2006. The behaviour of aerosols after 2006 has been verified by an independent dataset from a collocated Cimel sun-photometer, which revealed a decreasing trend of about 0.1 per decade in AOD at 440 nm from 2006 to 2014, similar to that of B005. Thus, the only factor that could explain the small negative trend in UV irradiance during this period would be a negative trend in the single scattering albedo (Bais et al., 2005; Nikitidou et al., 2013). This assumption cannot be easily verified since the SSA data from the Cimel and from satellite overpasses (e.g. http://disc.sci.gsfc.nasa.gov/giovanni) are sparse and inadequate to derive reliable trends. However, simulations with UVSPEC revealed that for SZAs greater than 60° and for typical aerosol properties and atmospheric conditions for Thessaloniki, the effect of a decrease in AOD at 320 nm by 0.1 can be reversed by a simultaneous decrease in SSA by less than 0.1.

As shown in Table 1, the trends for 350 nm for winter-spring, summer-autumn and the entire year are similar. For all the three cases the UV irradiance increases by about 10 % from 1994 to 2006 and then it slightly decreases from 2006 to 2014 resulting to a mean rate of decrease of about 3.5 % per decade for the entire period 1994–2014. For all the three cases the mean rate of decrease for the AOD is similar before and after 2006. Additionally, the year to year variability of the mean anomalies for the AOD is not clearly anti-correlated with the year to year variability of the mean anomalies for the UV irradiance at 350 nm, which can be only attributed to changes in SSA.

The changes of the UV irradiance at 307.5 nm are highly affected by changes in TOC and aerosols. For the winter-spring period no statistically significant turning point has been detected in the trend for this wavelength. Additionally, the mean trend in irradiance for the period 1994–2014 is weak (Table 1) compared to the corresponding trend for the period June–November, and is likely caused by the combined, but opposing, effects of a statistically significant positive trend in TOC and a negative trend in AOD. For the period June–November no trend was detected in TOC, thus, as for 350 nm, the UV irradiance at 307.5 nm increases steadily from 1994 to 2006 due to decreasing AOD and after 2006 remains unchanged. A similar with this period pattern appears also in the annual means, with changes in irradiance dominated again by changes in aerosols of opposite sign.

There are some interesting conclusions emerging from Fig. 5: By comparing Figs. 5a–c with 5g–i, one can notice an obvious anti-correlation between the year to year variability of TOC and the year to year variability of UV irradiance at 307.5 nm, which becomes stronger as the AOD decreases. Obviously, while the long-term changes in irradiance at 307.5 nm are mainly driven by the changes in aerosol, its year to year variability is mainly driven by the changes in TOC. For example, the yearly mean TOC in 2010 is the highest that has been recorded during the entire period 1994–2014 (Steinbrecht et al., 2011) and has led to extremely low yearly mean irradiance at 307.5 nm. However, the yearly mean irradiance at 307.5 nm in 2010 is still higher than mean levels in the period 1994–1998, mainly due to the very high levels of aerosols in the atmosphere in the mid-1990s. As the AOD decreases throughout the years, the anti-correlation between the short-term variability of the TOC and the UV irradiance becomes clearer. Finally, it is noteworthy that while the mean value of AOD for 2014 in the period summer–autumn is the lowest recorded since 1994, the corresponding value for the period winter–spring is the highest of the last seven years. These very high AOD values are probably due to the increased biomass-burning aerosols arising from a shift in the type of fuel owing to the economic crisis in Greece after 2009 (Saffari et al., 2013). As a consequence of the increased aerosols, the levels of irradiance at 350 nm for winter–spring 2014 are the lowest recorded during the last decade.

Since this paragraph aimed at attributing the short- and long-term variability of the UV irradiance to the corresponding variability of TOC and AOD, the analysis was restricted to clear-sky data. Although not shown here, a similar analysis has been performed for the irradiance under all-sky conditions and a statistically significant turning point in 2006 has also been detected in or the trends of yearly mean irradiance for 307.5 and 350 nm. As already discussed, changes in cloudiness do not have an important impact on the long-term changes of the UV irradiance at Thessaloniki but are the main driver of the short-term variations in the all-sky dataset.

4 Summary and conclusions

In the present study, spectral UV irradiance measurements from 1990 to 2014 at Thessaloniki, Greece have been used to investigate the short- and long-term variability of UV irradiance at specific wavelengths, affected differently by total ozone, aerosols and clouds. The analysis was restricted to the period 1994–2014, to avoid interferences in the trends from the volcanic aerosols injected into the stratosphere by the eruption of Mt. Pinatubo in 1991. Additionally, the parallel measurements from two co-located Brewer spectrophotometers after 1993 ensure data of superior quality. Trends of clear-sky and all-sky UV irradiance at 307.5 and 324 nm were derived for the period 1994–2014 from both B005 and B086 for SZAs from 30 to 70°. The difference between the trends from the two instruments was found to be smaller than their 1σ uncertainty boundaries.

According to the results, the annual mean UV irradiance has increased during the last two decades. The increasing trends are similar for both clear-sky and all-sky data and are larger at shorter wavelengths and higher SZAs. The calculated trends range between 2 and 6 % per decade, and for clear skies are statistically significant for most SZAs. For all skies, most of the irradiance trends are not statistically significant.

The impact of changes in TOC, aerosols and clouds on the changes in UV irradiance is different for different seasons. The negative trends in AOD, which are stronger in summer, lead to positive trends in UV irradiance at longer wavelengths (e.g., at 324 and 350 nm). For shorter wavelengths changes in TOC are also important. Thus, the effect of the small negative trend in AOD in winter is fully counteracted by the positive trend in TOC, resulting in a decreasing trend in clear-sky irradiance at 307.5 nm. Changes in clouds have a negligible effect on the trend of irradiance for winter and spring. The enhancement of the attenuation of irradiance by clouds in autumn is balanced by the reduced attenuation in summer, leading to similar changes in the annual means of clear-sky and all-sky irradiance. It is important to notice that the strongest changes in UV irradiance were found for summer when humans are more exposed to the Sun compared to the other seasons.

Moreover, it is shown that the period 1994–2014 can be divided in two sub-periods: during the first period (1994–2006) the annual mean UV irradiance is increasing fast while during the second period (2006–2014) the UV irradiance is relatively stable at 307.5 nm and is slightly decreasing at 350 nm. The long-term variability of UV irradiance for both short and long wavelengths is mainly driven by the changes in aerosols. The short-term variability of the clear-sky irradiance at 307.5 nm is mainly driven by the short-term variability of TOC. The effect of the TOC changes on the year to year variability of UV irradiance becomes clearer when AOD decreases. The short-term changes in irradiance at 350 nm cannot be fully explained by the short-term changes in AOD, as the absorption efficiency of aerosols may also change with time.

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Table 1. Trends of TOC, AOD at 320 nm and spectral UV irradiance at 307.5 and 350 nm, for different periods. Asterisks denote the statistically significant trends.

	period	winter–spring	summer–autumn	year
307.5 nm (change % per decade)	1994–2006	–	$11.0 \pm 3.3^*$	$7.1 \pm 2.1^*$
	2006–2014	–	-0.16 ± 7.7	-0.28 ± 5.0
	1994–2014	2.2 ± 1.9	$7.0 \pm 1.9^*$	$4.5 \pm 1.2^*$
350 nm (change % per decade)	1994–2006	$6.9 \pm 1.8^*$	$6.7 \pm 1.6^*$	$7.0 \pm 1.4^*$
	2006–2014	-2.8 ± 4.1	-2.5 ± 3.7	-3.3 ± 3.2
	1994–2014	$3.8 \pm 1.0^*$	$3.4 \pm 1.0^*$	$3.3 \pm 0.9^*$
TOC (change % per decade)	1994–2014	$1.7 \pm 0.8^*$	0.0 ± 0.6	0.8 ± 0.6
320nm AOD (absolute change per decade)	1994–2014	$-0.06 \pm 0.02^*$	$-0.11 \pm 0.02^*$	$-0.09 \pm 0.01^*$

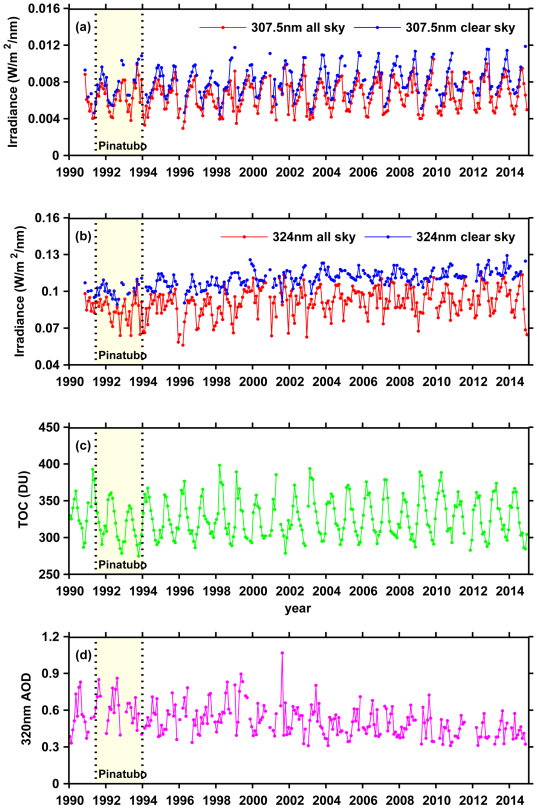

Figure 1. Time series of monthly means of **(a)** 307.5 nm irradiance, **(b)** 324 nm irradiance, **(c)** daily mean TOC, and **(d)** daily mean AOD. Monthly means were calculated only for months with at least 10 days of data. The UV irradiance is for 63° (±1°) SZA and for clear-sky and all-sky conditions.

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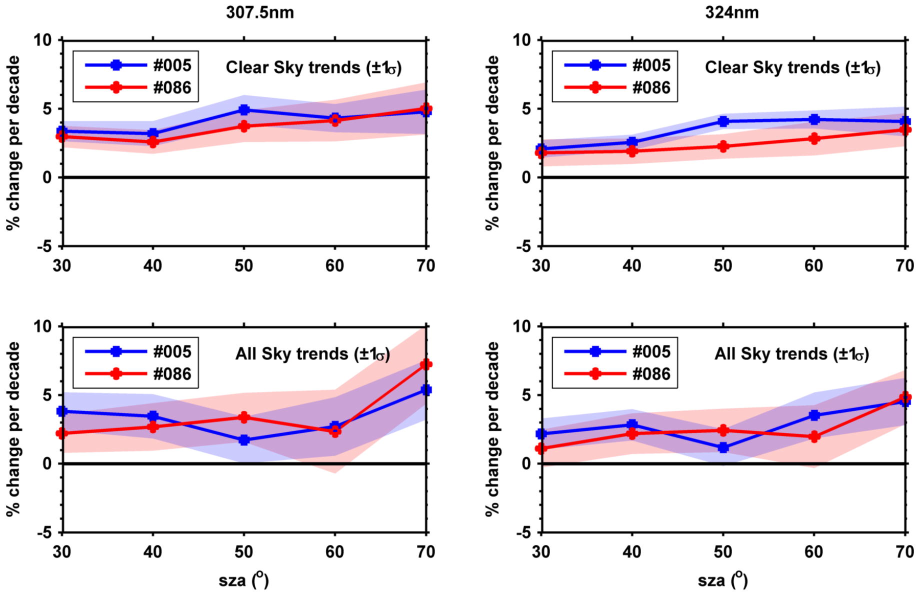

Figure 2. Linear trends (in % per decade) of spectral UV irradiance at 307.5 nm (left) and 324 nm (right) for clear-sky (upper) and all-sky (lower) conditions derived from Brewers #086 and #005, as a function of solar zenith angle. The shaded areas represent the ±1σ uncertainty of the derived trends.

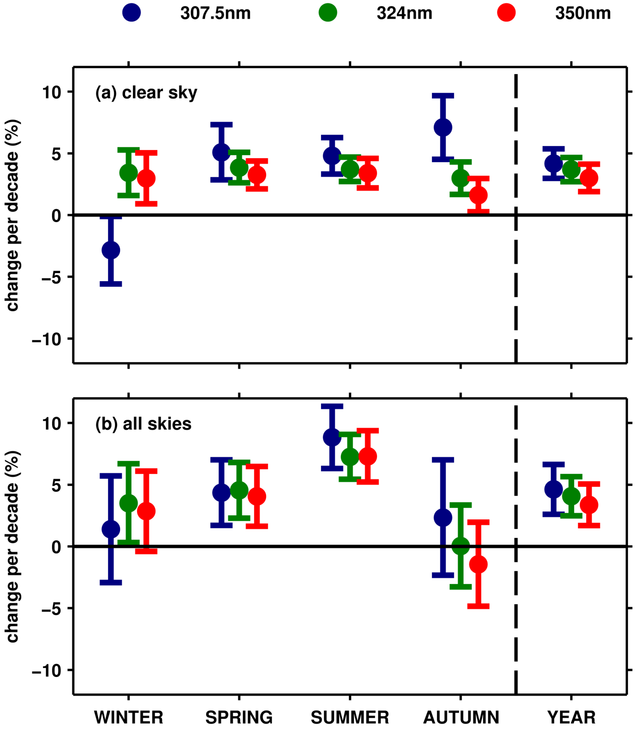

Figure 3. Long-term changes (in % per decade) and associated 1σ uncertainty of the seasonal and the yearly mean spectral irradiance for 307.5, 324 and 350 nm at 64° SZA, for clear skies **(a)** and all skies **(b)** at Thessaloniki.

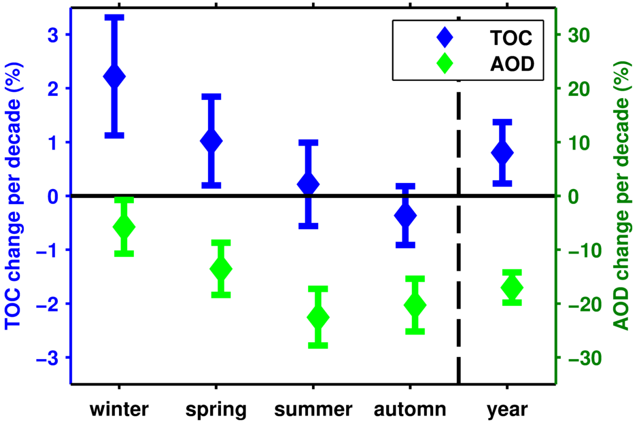

Figure 4. Long-term changes (in % per decade) and the associated 1σ uncertainty of the seasonal and the yearly mean of TOC (blue rhombs) and the AOD at 320 nm (green rhombs). The left (blue) axis corresponds to the changes in TOC while the right (green) axis to changes in AOD. The changes in AOD are statistically significant (95 %) while the changes in TOC are not.

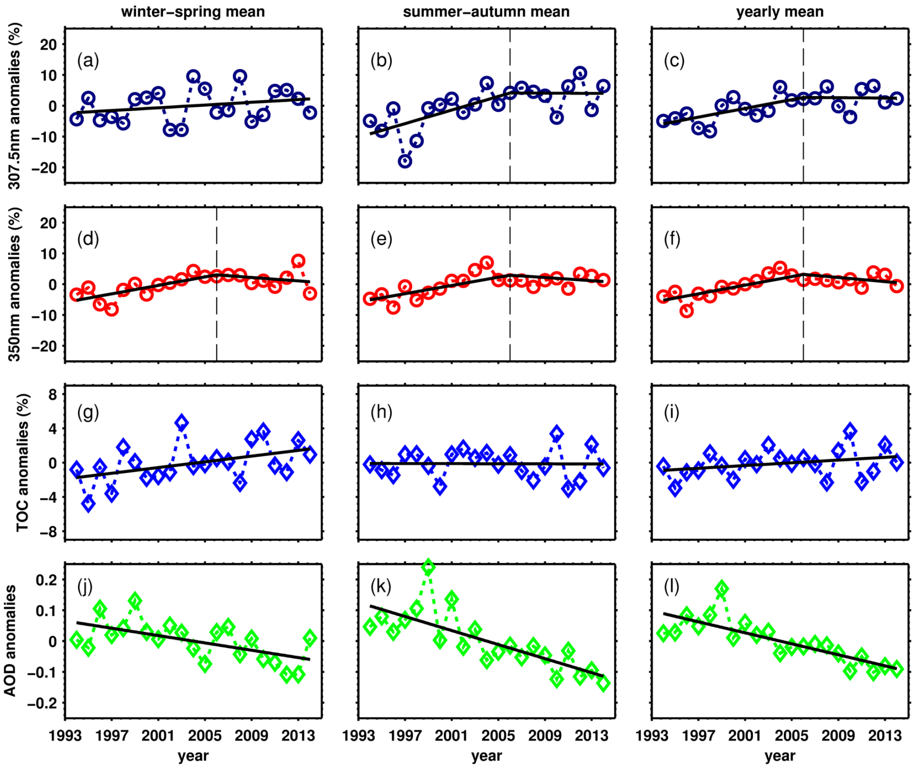

Figure 5. Yearly mean anomalies and corresponding trends for irradiance at 307.5 nm **(a, b, c)** and 350 nm **(d, e, f)**, TOC **(g, h, i)** and AOD at 320 nm **(j, k, l)** for December–May (left panels), June–November (middle panels) and for the entire year (right panels). A piece-wise trend consisting of two linear trends has been drawn when a statistically significant turning point has been detected; otherwise a linear trend for the entire period has been drawn.