Photovoltaic Spectral Responsivity and Efficiency under Different Aerosol Conditions

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Abstract: While solar power applications are growing rapidly worldwide, information about solar energy availability, its characteristics and the factors that affect it are essential. Among other parameters, a reference spectrum (ASTMG-173-03) is adopted, relying on Standard Test Conditions (STC), under which Photovoltaic (PV) devices are evaluated. However, these rigorously defined conditions can vary considerably from realistic environmental conditions. The objective of the present work is to assess the impact of the variability of atmospheric composition on the spectral distribution of the incident solar spectral irradiance (SSI) and, therefore, its implication on various PV materials performance. Ground-based measurements of global horizontal SSI have been conducted using a Precision Spectroradiometer (PSR) in the framework of the ASPIRE (Atmospheric parameters affecting SPectral solar IRRadiance and solar Energy) project in Athens, Greece. The gathered data in combination with spectrally resolved radiative transfer under clear-sky conditions contributed to the investigation of the atmospheric variables that attenuate irradiance (e.g., aerosols). In addition, since PV modules’ spectral absorptivity differs according to the semiconductor material used, the impact of the above-mentioned spectral features on PV performance has been investigated in order to estimate the spectral impact between the theoretical and outdoor conditions on the yield of different PV technologies. Overall, the results denote that smoke has a more significant effect than dust, while the effect on various technologies varies. The highest deviation compared to the STC was observed in the case of a-Si, reaching an absolute difference of 45% in the case of smoke particles in the atmosphere, while the maximum deviation between the different technologies reached approximately 7%.

Keywords: spectral solar irradiance; solar energy; aerosols; PV spectral response; PV performance

1. Introduction

The ever-increasing contribution of solar power applications in the field of energy production induces new challenges to industry and science branches in terms of the development of new PV technologies and materials and the optimization of those that already exist, in order to maximize their performance.

According to the International Energy Agency (IEA) [1], solar power applications are estimated to reach the highest installed capacity worldwide in the next five years, surpassing that of coal and natural gas. In line with these predictions, according to re-
cent publications of IEA [2], the global investment in solar power will exceed that of oil production, denoting the increased scale and speed of energy transformation. Based on the expected capacity expansion, in 2050, its cumulative capacity will be capable of contributing to the coverage of the total electricity demand by more than 25% [3].

Photovoltaic (PV) power yield strongly depends on both the atmospheric conditions and the characteristics of the employed technology [4,5]. Hence, especially in regions prone to high solar power potential, the accurate estimation of incident solar radiation and further research and effort to enhance the efficiency of such systems are vital.

While the solar radiation reaching the top of the Earth's atmosphere is relatively constant [6], the intensity and the spectral characteristics of the irradiance reaching the ground are spatially and temporally dependent on numerous factors. The most important aspects are solar elevation, which can be specified using the air mass factor (AM), and time-varying atmospheric constituents, such as clouds, aerosols, precipitable water, ozone and absorption of trace gases [7,8].

In a cloud-free atmosphere, aerosols can be considered as the main cause of atmospheric attenuation for solar radiation. In fact, aerosol effects (direct and indirect) have been studied a lot in the past and were found to have the most dominant effect on SSI fluctuation [7–10]. The effect of aerosols on solar irradiance strongly depends on their physical and chemical composition as well as on their concentration and optical properties. High aerosol loads emerging from increasing anthropogenic emissions, wildfires and winds that transfer desert dust cause a substantial impact on downwelling surface radiation [11,12]. Especially, the Mediterranean region, and therefore Greece and Athens city, is considered highly affected by aerosols generated by different sources [13,14]. Furthermore, due to their spectrally dependent absorption, lying mostly in the lower wavelength regions, aerosols are capable of conditioning the incident solar spectrum distribution.

Aerosol optical depth, hereinafter noted as AOD, is the parameter that describes the amount of radiation attenuated by the aerosol particles in the atmospheric column, while the Ångström exponent (AE) is used to represent the extinction's spectral behavior [15]. Lower values of AE (AE < 1) indicate the presence of big particles in the atmosphere [16,17], such as mineral dust, whereas large values are typical of small particles, such as emissions from urban areas or biomass burning. Another important parameter is the Single Scattering Albedo (SSA). SSA is spectrally dependent, while high values of SSA indicate more scattering aerosols in contrast to lower values that indicate more absorbing types. The high spatiotemporal variability of aerosols and the complex atmospheric interactions have been of great concern to the scientific community in the past, and diverse studies have attempted to enhance the knowledge on this topic (e.g., [18–21]).

Measurements of AOD, AE and SSA are available in a variety of databases, such as the Aerosol Robotic Network (AERONET) [22], the SKYNET network [23] and the GAW-PFR network [24]. AERONET provides information about AOD and other optical properties at thousands of sites worldwide and at high temporal resolutions.

To account for the effects of all the aforementioned parameters on the total solar radiation at the ground level is a complex procedure. Until today, ground-based measurements of solar radiation are still considered as the most reliable for his purpose [25]; however, precise measurements combining all the above aerosol and solar irradiance parameters and knowledge related to the spectral distribution under real conditions over different sites are still limited.

PV panels and modules are semiconductor devices that convert solar energy to electricity, while a wide range of parameters condition their characteristics and, finally, their efficiency. Amongst other features that have been studied in the past (e.g., [26]), such as solar irradiance (light intensity), temperature and soiling, the performance of PV cells and systems is known to be highly dependent on the spectral distribution of the incident solar irradiance in a complex way. This work is focused on this last parameter in relation
to the semiconductor material used and, more precisely, the spectral absorptivity of the different PV technologies.

In order to test, validate and, moreover, to compare the relative optical performance of different PV devices from different manufacturers, the PV community has agreed on the use of reference standard solar spectra. These spectra represent the solar spectral irradiance at the Earth’s surface and have been established using different spectral models and a set of specified atmospheric conditions, known as Standard Test Conditions (STC). By definition, STC corresponds to 1000 W/m², 25 °C cell temperature and Air Mass 1.5 (AM1.5), as defined in IEC 60904-3 [27]. However, although such indicators are essential, they do not always reflect the actual performance of the PV systems since these defined conditions rarely occur under real operating conditions.

These standard spectra have been modified throughout the years in order to improve accuracy and to represent a broader range of conditions, aiming to meet the continuously incrementing technical demands of the industry and users. A more detailed review of the previous versions and the parameters involved is provided by Myers et al. [28].

Nowadays, the most widely adopted reference spectrum to certify photovoltaic panels under STC is the ASTM-G-173-03 [29] reference spectrum, which has been generated using the Simple Model of the Atmospheric Radiative Transfer of Sunshine (SMARTS, Version 2.9.2) [30,30,31] and provided by the American Society for Testing and Materials (ASTM) [32]. The 1976 U.S. Standard Atmosphere Model [33] with the rural Shettle and Fenn Aerosol [34] was used for the configuration of the standard spectra. Additional information related to these standard spectra and the STC that were used in the present study can be found in the following section (Section 2.1).

The spectral responsivity of the PV materials, their ability to absorb different parts of the spectral irradiance and convert them into electrical energy, is obtained with respect to the STC and depends on the bandgap of each PV device [35]. The spectral sensitivity of each PV module is different; nevertheless, the optimum absorption for the majority of PV materials is detected in the visible range of the electromagnetic spectrum, where the highest amount of solar energy is concentrated. Consequently, the spectral response (SR) of PV materials is a vital factor in determining their performance and output and is defined by their electronic band structure, which determines their ability to absorb photons and generate electron–hole pairs.

A number of studies have previously focused on the effect of aerosol-induced solar spectrum variability on photovoltaic performance, most of them using radiation transfer models (RTM) (e.g., [36–39]), but only a few used ground-based spectral irradiance measurements (e.g., [40–42]).

Understanding the differences in PV efficiency due to air pollution and associated aerosol loads is of great importance for the performance and planning of PV installations. Precise spectrum measurements are scarce, although they are a key factor considering the sensitivity of the various PV module technologies to spectral irradiance. To address this issue, in our study, we use in situ-measured spectral and broadband solar irradiance for clear-sky (cloudless) conditions from the one-year experimental campaign that was held in the framework of the ASPIRE project in Athens, Greece, from December 2020 to November 2021 (https://aspire.geol.uoa.gr, accessed on 11 September 2023). Furthermore, in order to achieve a better understanding of the influence of the spectral variations of the incident solar irradiance on the performance of PV modules, an individualized analysis for each of the atmospheric parameters (AOD, AE and SSA) was performed. The research is focused only on the spectral sensitivity of the different PV materials, not on any other parameters that affected their efficiency.

The paper is organized as follows. Section 2 introduces the employed datasets and describes the methodology followed for the purposes of this work. In Section 3, the related results are presented, based on the ground-based measurements from the PSR and RTM simulations—both compared to the STC—and focused on the effect on the various
PV technologies along with a discussion on the observed deviations from the standard spectrum. Concluding remarks are finally drawn in Section 4.

2. Data and Methodology
2.1. Standard Test Conditions (STC)

As mentioned in the preceding section, the validation of the PV devices is achieved according to the adopted STC. Nominally, these conditions are characterized by a 25 °C junction temperature, air mass (AM) equal to 1.5, global irradiance equal to 1000 W/m² and representation of cloudless atmospheric conditions. Additionally, some pivotal reference parameters include AOD at 500 nm equal to 0.084, being of rural aerosol type, and having precipitable water equal to 1.42 cm and spectral albedo equal to 0.2 at 500 nm.

In the framework of this study, only the hemispherical solar irradiance, consisting of direct and diffuse components, in the wavelength range between 300 and 1200 nm of the ASTM G173-03 standard spectrum was employed [29]. The provided incident radiation refers to a sun-facing, 37°-tilted surface. The wavelength interval of the obtained reference spectrum was 0.5 nm for the spectral range between 300 and 400 nm and 1 nm between 400 nm and 1200 nm.

Spectral Responses

The spectral responses of five widely adopted high-efficiency technologies were considered for the objectives of the following analysis: GaAs (Gallium arsenide), CdTe (Cadmium telluride), a-Si (amorphous Silicon), mono c-Si (monocrystalline silicon) and poly c-Si (polycrystalline silicon). Other promising materials could be investigated in addition such as perovskite, which has experienced remarkable progress in recent years; however, it is not included in the current work since perovskite PVs are in an experimental phase, and a number of challenges remain before they can become a competitive commercial technology [43,44]. The respective SRs of the selected materials were acquired from the PV Performance Modeling Collaborative, Sandia National Laboratories (pvpmc, https://pvpmc.sandia.gov/, accessed on 24 March 2022) and are depicted in Figure 1 for the wavelength range under study (300–1200 nm), along with an instantaneous measurement of SSI during a cloudless day.

![Spectral Responses of PV materials and SSI](image)

**Figure 1.** Relative spectral responses of the five PV materials taken into account for this work (left y-axis) and measured SSI under clear-sky conditions (right y-axis) with respect to the wavelength.

Based on the different materials’ absolute spectral responses, the spectral contribution to Global Tilted Irradiance according to the ASTM G173-03 spectrum was calculated using the following formula (Formula (1)):

\[ \frac{S_{\text{STC}}(\lambda) \cdot \text{SR}_{\lambda}(\lambda)}{\int_{\lambda} S_{\text{STC}}(\lambda) \cdot \text{SR}_{\lambda}(\lambda) \, d\lambda} \times 100 \% \]  

(1)
where the parameter $I_{SC}^{b}\text{Stc}(\lambda) = SR_T(\lambda)d\lambda$ stands for the short circuit current at STC ($I_{SC}$), which is the maximum current from a solar cell and occurs when the voltage across the solar cell is zero. In general, the short circuit current ($I_{SC}$) depends on a number of factors, such as the incident light intensity, its spectral characteristics, the optical properties of the PV cell and the area of the solar cell, which was considered equal to 1 m$^2$ [45]. SR$_T$ stands for the absolute spectral response (in A/W) for each technology (T), $\lambda$ is the wavelength (in nm) and SI$_{Stc}$ stands for the reference spectrum under STC in W/m$^2$/nm for the selected wavelength range under study ($a = 300$ nm and $b = 1200$ nm). The results of the contribution of each material can be observed with respect to the wavelength in Figure 2. Additionally, the entire spectral range was divided into smaller wavelength regions (300–400 nm, 400–700 nm, 700–900 nm and 900–1200 nm) reflecting the UV, visible, near-infrared (NIR) and short-wave infrared (SWIR), respectively, for a better understanding of the contribution in each spectral region (Table 1).

![Figure 2: Spectral contribution of PV materials according to ASTM G173-03 for tilted surfaces.](image)

**Table 1.** The contribution of PV materials to total ASTM G173-03 irradiance according to the wavelength range.

<table>
<thead>
<tr>
<th>PV Techn.</th>
<th>300–400 nm</th>
<th>400–700 nm</th>
<th>700–900 nm</th>
<th>900–1200 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Si</td>
<td>4.6</td>
<td>88.7</td>
<td>6.7</td>
<td>0</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.6</td>
<td>61.5</td>
<td>36.8</td>
<td>0.1</td>
</tr>
<tr>
<td>CdTe</td>
<td>0.7</td>
<td>62.1</td>
<td>37.2</td>
<td>0</td>
</tr>
<tr>
<td>mono c-Si</td>
<td>1.8</td>
<td>45.8</td>
<td>32.9</td>
<td>19.6</td>
</tr>
<tr>
<td>poly c-Si</td>
<td>1.6</td>
<td>47.3</td>
<td>33.6</td>
<td>17.5</td>
</tr>
</tbody>
</table>

2.2. Ground-Based Measurements

2.2.1. Location

The experimental setup was located at the Actinometric Station of the National Observatory of Athens (ASNOA) (38°00’ N, 23°43’ E, 110 m a.s.l.), at Thissio, the historical center of Athens. Although the station is surrounded by areas of greenery, where the emissions in a range shorter than approximately 300 m are negligible, it is considered an urban area accurately representing the central Athens area.

According to AERONET climatology tables of level 2 retrievals, the average AOD at 500 nm and Ångström exponent in the wavelength range of 440–870 nm, for the specific station (‘ATHENS-NOA’), are equal to 0.19 and 1.4, respectively [14]. The aerosol species that are most frequent over the station region originate from urban emissions, which are often trapped in the basin due to the city’s topography, as well as desert dust particles, transported via air masses from Africa [14,46].
2.2.2. Instruments

In order to assess the impact of the variability of atmospheric composition on solar energy based on in situ, ground-based measurements under real outdoor conditions, two state-of-the-art instruments have been used, a Precision solar Spectroradiometer (PSR 007), providing measurements of spectral Global Horizontal Irradiance (GHI), and a CIMEL sun photometer, providing columnar aerosol optical properties (Table 2). In general, both the aforementioned instruments are suitable for continuous outdoor exposure and capable of measuring in all conditions.

Table 2. Instruments that contributed to the current study.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Measurements</th>
<th>Parameters Retrieved</th>
<th>Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSR</td>
<td>GHI and DNI</td>
<td>Spectral GHI, DNI</td>
<td>1 min</td>
</tr>
<tr>
<td></td>
<td>spectral 300–1020 nm (step 0.7 nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CIMEL440 *</td>
<td>Direct sun 8 bands 340–1024 nm</td>
<td>Columnar aerosol optical properties</td>
<td>15 min</td>
</tr>
</tbody>
</table>

* A CE-318 CIMEL sun photometer with serial number 440.

Precision Solar Spectroradiometer (PSR)

The PSR is a prototype precision spectroradiometer, developed and calibrated in the World Radiation Center (WRC, Davos, Switzerland), and it is able to measure direct (DNI) and global horizontal (GHI) spectral irradiance (in W/m²/nm) in the spectral region between 300 and 1020 nm (with a step of 0.7 nm) at 1024 channels [47]. Each cycle of measurements consists of 10 GHI spectra, 10 DNI spectra and 5 dark signal measurements, in order to perform dark-signal corrections. The average spectra in each case (GHI and DNI) were stored before applying the calibration.

PSR was last calibrated in June 2019 at the WRC using a calibrated standard 1000 W tungsten–halogen FEL lamp. The uncertainty of the instrument was found to be less than 1% in VIS, less than 1.7% in UV-A and higher than 2% in UV-B. Detailed analysis regarding the uncertainty budget of the instrument was published by Gröbner and Kouremeti [47]. In addition, three field instrument calibrations were performed during the ASPIRE campaign, while one of them was performed during the under-study period (7 July 2021), using a 200 W Quartz Halogen lamp, traceable to Physikalisch-Technische Bundesanstalt (PTB) [48].

CE-318 CIMEL Sun Photometer

The CE-318 sun photometer by CIMEL Electronique is a filter radiometer and the standard instrument of AERONET [22] that records direct sun and sky radiance at almucantar planes and retrieves columnar aerosol optical properties. A CE-318 photometer with serial number 440, which contributed to this work as part of the ATHENS-NOA AERONET station, provides AOD retrievals at eight narrow spectral bands. Each band has a full width of approximately 10 nm at half maximum (FWHM) with central wavelengths of 340, 380, 440, 500, 675, 870, 1020 and 1640 nm. For the comparisons between the measured and simulated spectra, the AOD at 500 nm, as given from the STC, was used. Moreover, Ångström exponent (AE) in the range of 440–870 nm data (Level 2.0) from AERONET Version 3.0 [49] of the retrieval algorithm were used. According to the inversion products, A Level 2.0 SSA requires a value of AOD higher than 0.4 and SZA bigger than 50° [50]. Since the limitation of Level 2.0 can out an important part of the retrievals, and in the current work we investigate the cases where SZA = 48.19° (<50°), the mean value of the retrieved Level 1.5 SSA was calculated in four wavelengths (440, 675, 870 and 1020 nm).
2.2.3. Methodology

The current analysis focuses only on the GHI-measured parameter. An overview of some selected days under cloud-free and different turbidity conditions during the year 2021 is presented in Section 3.1. Moreover, greater emphasis is placed on radiation measurements at AM1.5, which indicates a solar zenith angle (SZA) equal to 48.19°, in order to meet the specified criteria of the standard spectra as introduced in the previous section (Section 2.1).

The three chosen cases are characterized in terms of aerosol load in the atmosphere as follows: clean conditions (low AOD), hazy conditions (high dust concentration) and the presence of wildfire-generated particles (smoke). One example of the measured SSI depicting the attenuation in the case of the three aforementioned conditions can be illustrated in Figure 3. Especially during the summer of 2021, Greece experienced severe wildfire events that significantly affected the air quality of the city of Athens. Some cases are investigated in the present study; however, considerable and detailed research has already been conducted on the impact of those specific events on solar irradiance by Masoom et al. [12].

![Figure 3. Variation of solar spectral irradiance as measured with the PSR instrument at ASNOA, Athens, for three selected cases (low AOD, presence of dust particles and presence of smoke particles) for AM 1.5.](image)

Ground-based measurements of SSI (AM1.5) were used to calculate the deviation of the performance of the different PV technologies in comparison to the expected performance according to the reference spectrum.

However, to overcome the PSR limitations (300–1020 nm) and in order to obtain data in the whole range of interest (300–1200 nm, where the SR of the selected PV technologies is observed), the measured spectra were extrapolated and converted according to the ratio between the measured and the reference spectrum. We can estimate that the uncertainty of the conversion to a 37-degree angle is less than 5%.

The relative difference for each material was calculated using Equation (2):

\[
R = \left( \frac{\int_a^b G(\lambda) \cdot SR(\lambda) \, d\lambda - \int_a^b S_{STC}(\lambda) \cdot SR(\lambda) \, d\lambda}{\int_a^b S_{STC}(\lambda) \cdot SR(\lambda) \, d\lambda} \right) \times 100 \%
\]

where \( G(\lambda) \) and \( S_{STC}(\lambda) \) represent the spectral solar irradiance measured with PSR and obtained from the reference spectrum, respectively. The wavelength limits a and b are determined by the extended spectroradiometer wavelength range (a = 300 nm and b = 1200 nm) here, with respect to the full range of spectral sensitivity of the selected PV technologies.

Thereafter, in order to calculate the spectral impact on each PV technology compared to total broadband irradiance measured using PSR compared to the reference spectral irradiance, the spectral mismatch factor (MM) according to IEC 60904-7 standard [51] is given in Equation (3):
\[
\text{MM} = \frac{\int_{\lambda}^{b} \text{SR}_\text{ref}(\lambda)g(\lambda) \, d\lambda}{\int_{\lambda}^{b} \text{SR}_\text{ref}(\lambda)s_{\text{STC}}(\lambda) \, d\lambda} \times \frac{\int_{\lambda}^{b} \text{SR}_\text{ref}(\lambda)s_{\text{STC}}(\lambda) \, d\lambda}{\int_{\lambda}^{b} \text{SR}_\text{ref}(\lambda)g(\lambda) \, d\lambda}
\]

was employed, where \(\text{SR}_\text{ref}\) is the relative spectral response of the reference device, the spectroradiometer, which technically does not have a short circuit current. However, the spectroradiometer signal can be thought of as the short circuit current of a theoretical PV device with SR being the unity for all wavelengths [14,36]. \(G(\lambda)\) is the measured spectral irradiance under actual conditions, and \(s_{\text{STC}}\) is the reference spectral irradiance according to ASTM (both in W/m²/nm) [52–54].

MM essentially expresses the energetic gain or loss in effective irradiance available at current conditions compared to the reference device’s indication (referring solely to spectral differences), determined with the following values:

- MM > 1: spectral gain compared to STC, which indicates the better performance of the considered material under the actual spectrum than under the standard AM1.5 spectrum;
- MM < 1: spectral loss compared to STC, indicating power loss.

This approach was already used by various authors and is considered as a useful approximation to quantify the spectral impacts on the energy output. Equation (3) can also be written as follows:

\[
\text{MM} = \frac{I_{sc}'}{I_{sc}} \cdot \frac{G_{int}'}{G_{int}}
\]

where \(I_{sc}\) stands for the short circuit current at the outdoor conditions, \(I_{sc}'\) for the short circuit current at STC, \(G_{int}\) for the broadband irradiance as measured with PSR and \(G_{int}'\) for the reference broadband irradiance derived from STC. Finally, the short circuit current when considering only the irradiance and spectral effects is approximately equal to the maximum power (\(P_{\text{max}}\)) [36].

Nann and Emery [55] used the ratio \(\eta/\eta_{\text{STC}}\) to estimate the spectral efficiency, which is the relative change in efficiency when a transition is made from STC (\(\eta_{\text{STC}}\)) to real outdoor conditions (\(\eta\)), considering only the spectral effect. As efficiency is the ratio of the electrical power (\(P_{\text{max}}\) or \(P_{\text{max}}'\) for outdoor and STC, respectively) to the incident irradiance power (where \(A\) stands for the solar cell area), the spectral efficiency is given using Equation (5):

\[
\frac{\eta}{\eta_{\text{STC}}} = \frac{P_{\text{max}}/G_{\text{int}} * A}{P_{\text{max}}'/G_{\text{int}}' * A}
\]

which is equal to the MM (Equation (4)).

### 2.3. Model Simulations — Library for Radiative Transfer (libRadtran)

In order to analyze the individual influence of each atmospheric parameter, several solar spectra were simulated using the Radiative Transfer Model (RTM) and more specifically, the libRadtran package [56,57] version 2.0.4. To solve the radiative transfer equation, the numerical solver DISORT (DIScrete Ordinates Radiative Transfer) [58,59] pseudospherical approximation of the uvspec radiative transfer model was used, with 32 streams. For the molecular absorption, REPTRAN band parametrization [60] was applied in the wavelength range between 300–1200 nm with a fine spectral resolution. The selected spectral resolution corresponds to a band width of 1 nm, with respect to the spectral range that is relevant to the spectral response of the PV materials under study. Finally, the extraterrestrial spectrum from Kurudz [61] and the standard US atmospheric profile [62] were applied.

The libRadtran simulations were performed for seven different groups of inputs (Table 3). Downward spectral solar irradiance (DSSI) was estimated with some explicitly defined parameters that varied individually while keeping the rest fixed according to the
reference values corresponding to the standard AM1.5G ASTM G-173-03 reference spectrum (AM1.5, precipitable water vapor column (PWC) of 1.42 cm, total ozone column (TOC) of 340 DU and surface albedo of 0.2 at 500 nm). Other variables taken into account in setting up the model simulations were profiles of temperature, air density and other atmospheric gases that were left to their default values.

The different scenarios that were performed are presented in Table 3.

<table>
<thead>
<tr>
<th>Table 3. The different RTM scenarios used in this study.</th>
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<tbody>
<tr>
<td><strong>Variable Input Parameters in RTM</strong></td>
</tr>
<tr>
<td><strong>Scenarios</strong></td>
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<td>1</td>
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<td>7</td>
</tr>
</tbody>
</table>

In all cases, simulations were performed for clear-sky conditions neglecting the effect of clouds for a better assessment of the impact of the aerosol properties on the spectral distribution.

Moreover, in order to convert, as a next step, the spectrally resolved GHI to Global Tilted Irradiance (GTI) at 37° (with respect to the ASTM G-173-03 reference spectrum), both the cosine of the viewing zenith angle (umu) between ~90 and 90 degrees (with a resolution of 1 degree) as well as the sensor azimuth (phi) intervals between 0 and 360 degrees (with a resolution of 10 degrees) were included in uvspec. Then, to generate the required angular, resolved radiances, the uvspec outputs were used as inputs to the angres tool [54], which integrates the simulated irradiances using Monte Carlo methods for the specified geometry. Finally, the angres tool reads the input files, tilts and rotates the surface according to the required conditions and integrates the radiance field over the zenith and azimuth angle. More specifically, for the purposes of the current work, angres was called for each wavelength of the selected spectral range given the tilt angle (t = 37°) and rotation angle (r = 90°). In addition, in order to include the direct irradiance contribution to the results apart from the diffused, the solar zenith angle (SZA = 48.19°, as AM1.5 indicates) and solar azimuth angle (AZ = 180°) were also provided as inputs to the angres tool.

3. Results and Discussion

3.1. Ground Based Measured SSI—Reference Spectrum

An overview of the spectral mismatch factor as calculated for all the measurements during some selected days under cloud-free and a variety of turbidity conditions during the year 2021 are presented in Figure 4a–e.
Figure 4. The Spectral mismatch factor based on measured SSI during some cloudless days related to broadband irradiance (as measured with PSR); SZA and AOD (at 500 nm) for (a) a-Si, (b) GaAs, (c) CdTe, (d) mono c-Si and (e) poly c-Si technologies. The filled circles and triangles indicate AOD values lower and higher than 1, respectively.

According to the observed values, it is evident that in most cases, lower irradiance intensity is related to high zenith angles. However, some occasions of higher AOD values (AOD > 1) can be the cause of the lower irradiances. Considering the three technologies, a-Si is of the utmost interest, since it experiences the highest spectral losses, especially in the lower broadband irradiance range (e.g., below 300 W/m²) and high AOD values. However, when measured intensity is higher than 500 W/m², it is illustrated that a-Si performs efficiently under real outdoor conditions, whereas the effect of high AOD is still significant. On the other hand, CdTe and mono c-Si indicate a more constant performance under the different conditions and in comparison, to the STC.

Furthermore, as described in Section 2.2.3, in order to investigate the effect of various events that occur in the broader area of Athens in spectral solar irradiance and, therefore, in the performance of different PV materials, some specific cases were selected for further investigation. The results of the relative differences, as calculated using Equation (3), are presented in Figure 5.
The absolute AOD values at 500 nm, approximately at the time of the SSI measurements (mean AOD for SZA ± 5°), were 0.52, 0.79, 0.80 and 0.89 in the case of dust, and 0.32, 0.44, 0.64 and 2.02 in the case of smoke particles. Accordingly, AE for the dust cases was 0.20, 0.24, 0.14 and 0.17 and 1.62, 1.78, 1.95 and 2.14 for smoke.

The performance of all technologies degrades with the presence of (aerosol) dust and smoke in the atmosphere. More precisely, the differences can reach 45% considering the detected conditions, while in the case of smoke the effect is more significant, not only overall but with respect to the different technologies as well. For instance, the deviation from the theoretical values on 1 July 2021 afternoon (differences reaching 20% at most) is lower than the one on the 19 August 2021 morning (differences 20–25%), although in the first case, AOD is higher by 0.2. Furthermore, differences based on PV materials are approximately 7% in the second case and lower than 5% in the first. This can be explained by the higher sensitivity of some materials at shorter wavelengths and more specifically between 300–500 nm (Figure 1), for instance a-Si, since the effect of smoke is stronger in the ultraviolet (UV) and the visible range to total irradiance (e.g., Masoom et al. [12]), whereas the contribution of infrared is higher when compared to the presence of dust particles. More information about the differences of the aforementioned comparison on the different technologies is listed in detail in Table 4.

Table 4. Mean and maximum aerosol-based differences for each technology, with respect to the three examined atmospheric conditions (low aerosol load, dust particles and smoke particles).

<table>
<thead>
<tr>
<th>AOD&lt;sub&gt;500 nm&lt;/sub&gt;</th>
<th>Clean</th>
<th>Dust</th>
<th>Smoke</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Si</td>
<td>-5</td>
<td>-20</td>
<td>-22</td>
</tr>
<tr>
<td>GaAs</td>
<td>-5</td>
<td>-23</td>
<td>-44</td>
</tr>
<tr>
<td>CdTe</td>
<td>-6</td>
<td>-21</td>
<td>-20</td>
</tr>
<tr>
<td>mono c-Si</td>
<td>-6</td>
<td>-18</td>
<td>-39</td>
</tr>
<tr>
<td>poly c-Si</td>
<td>-5</td>
<td>-18</td>
<td>-38</td>
</tr>
</tbody>
</table>

The higher differences illustrated in Figure 5 based on the different materials can be explained by their different spectral responses (Figure 1). To understand the issue, Figure 6 shows some examples of the spectral dependence of the under-study PV materials,
exhibiting the maximum of their spectral response in different spectral areas. Although mono c-Si is known to absorb the solar irradiance more efficiently, since it is characterized by higher absolute SR than a-Si, a drawback on its performance is the fact that its sensitivity peaks at approximately 950 nm (right y-axis, Figure 7b), whereas a-Si maximum absorption is detected at shorter wavelengths and more specifically at approximately 600 nm (right y-axis, Figure 7a), where the radiation intensity is higher (Figure 6).

For the clean conditions, retrieved AOD reached 0.05, while AE and SSA values were 1.33 and 0.89, respectively. Similarly, in the case of dust, AOD is 0.89, AE 0.17 and SSA 0.90, where the low value of AE signifies the dominance of big particles in the aerosol mixture. Finally, in the case of smoke, AOD was 2.02, AE 2.14 and SSA 0.88. The SSI for each of the presented cases is shown in Section 2.2.3, Figure 3.

![Graphs of different PV materials under varying atmospheric conditions.](image)

**Figure 6.** Effect of the different atmospheric conditions on the under-study PV materials with different optimum absorption wavelength areas based on their absolute SR (AW⁻¹), given from the measured spectral irradiance multiplied with the absolute spectral response of the respective material for: (a) a-Si, (b) GaAs, (c) CdTe, (d) mono c-Si and (e) poly c-Si.
3.2. Radiative Transfer (libRadtran) Simulations—Reference Spectrum

We assessed the impact of the different atmospheric conditions that occurred in Athens in the performance of the under-study PV technologies, and AOD is proved to have the utmost impact on SSI, which can cause a decrease in the PV performance, up to 45% considering the detected conditions (see Figure 5). However, the results indicate that other optical properties of aerosols can also play a notable role.

In order to analyze the influence of the main atmospheric parameters in the performance of solar energy applications (e.g., PV applications) in previous studies, e.g., [37,43,63–66], several spectra have been simulated by varying one of the atmospheric parameters while the rest were kept constant at the reference values defined by the AM1.5G ASTMG-173-03 reference spectrum. Therefore, for a better understanding of the impact of these properties, we also examined the effect of AE and SSA on the DSSI, using RTM simulations based on values observed in measurements that were performed during dust and smoke aerosol events.

In the case of a change on AE by 1.5 (from 0.5 to 2), we observed a 3.8–11.7% decrease based on different technologies per unit of AOD in the case of SSA = 0.85 and about 3–8.6% when SSA equals 0.99. Furthermore, differences among the two cases in aerosol absorption (SSA = 0.85 and SSA = 0.99) could enhance the attenuation and increase the differences in technologies by approximately 2% when AE = 0.5 (dust scenario) and 4% when AE = 2 (smoke scenario) (Table 5).

**Table 5.** AE and SSA effect on the deviation of the performance of the under-study technologies compared to the reference conditions (STC). Where AE0.5 and AE2 stand for AE equal to 0.5 and 2, respectively, and similarly, SSA0.85 and SSA0.99 stand for SSA equal to 0.85 and 0.99, respectively.

<table>
<thead>
<tr>
<th>SSA</th>
<th>AE Effect</th>
<th>SSA Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Difference</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AE0.5–AE2</td>
<td>SSA0.85–SSA0.99</td>
</tr>
<tr>
<td></td>
<td>(%)</td>
<td>(%)</td>
</tr>
<tr>
<td>SSA0.85</td>
<td>min</td>
<td>max</td>
</tr>
<tr>
<td></td>
<td>−3.8</td>
<td>−11.7</td>
</tr>
<tr>
<td>SSA0.99</td>
<td>−2.9</td>
<td>−8.6</td>
</tr>
</tbody>
</table>

More outdoor (measured) clear-sky conditions at AM 1.5 were investigated for the selected days that are presented in Figure 4, in order to examine the impact of the different atmospheric conditions on the PV performance and the relative difference from the
expected. As a general trend, STC overestimate the real outdoor conditions in most of the cases (Figure 7). For a low AOD load (up to 0.2), only some exceptions were detected where the comparison signifies that STC underestimate the actual conditions (by 4% at most). Moreover, the differences between the different materials tend to enhance with respect to AOD, climbing up to 10%. Both Figures 5 and 7 denote that higher bandgap PV materials such as a-Si, GaAs and CdTe experience the most significant variations, which is in good agreement with previous studies, e.g., [33].

Furthermore, the difference when comparing the effect of simulated DSSI (for AOD equal to 1, AE equal to 1.30 and two SSA values, 0.85 and 0.90, respectively) with the standard conditions is shown in Figure 7 for mono c-Si, as a reference material. A 5% decrease in the difference is illustrated, respectively, to a raise in SSA by 0.05.

Finally, the spectral efficiency as calculated from simulated irradiances for different AOD scenarios (AE equal to 1.30, and SSA equal to 0.90) and the different technologies are presented in Figure 8. The estimated behavior of each material to the specific conditions is in line with the respective results based on measured SSI (Figure 4). Higher AOD values increase the spectral losses of a-Si up to 5%, whereas the rest of the technologies are not significantly affected, and MM remains close to 1.

![Figure 8](image.png)

**Figure 8.** The spectral mismatch factor based on simulated DSSI for cloudless conditions related to AOD at 500 nm for different PV technologies.

### 4. Conclusions

This study is focused on the investigation of different aerosol conditions (clean sky, dust and smoke) in the city of Athens, in Southeast Europe, over a one-year period. More specifically, we focused on the impact of the variability of atmospheric composition on the spectral distribution of the incident solar irradiance and, therefore, its implication on various PV materials.

Overall, higher bandgap PV materials such as a-Si, GaAs and CdTe experience the most significant variations when aerosol load in the actual operating conditions of the PV devices is higher than the standard conditions. This result is more evident for extreme, smoke and dust conditions. In contrast, the investigation of crystalline silicon technologies (monocrystalline and polycrystalline) revealed the smaller sensitivity of these materials. In addition, the spectral impact on each PV technology compared to the reference spectral irradiance was determined in the frame of the spectral mismatch factor, verifying the more considerable effect in a-Si technologies, which is in line with previous studies. More precisely, in the case of a-Si, values of MM lower than 0.9 were observed for high AOD conditions, whereas, in the case of crystalline silicon, the respective values were closer to 1 in all conditions, with deviations lower than 0.5.

Moreover, we assessed the effect of different atmospheric composition cases, such as dust and smoke. Results indicate that STC overestimate the outdoor existing condi-
tions in most of cases, especially in cases of high dust concentration and the presence of smoke particles in the atmosphere, and the difference from the expected performance can climb even up to 45%. A more extended analysis on the effect of the aerosol properties (AE and SSA) proves that SSA has a significant effect on this deviation, reaching 15% in the case of a-Si under dust conditions, only 1% more than in the case of smoke particles, while AE differences are responsible for a maximum difference of approximately 12% for some of the considered materials (e.g., mono c-Si and poly c-Si).

Still, today, ground-based measurements of solar radiation are considered the most reliable for this purpose. Differences based on the various atmospheric conditions that occurred in Athens during the one-year period from 2020 to 2021 as well as the general increase in the frequency of these events worldwide highlight the importance of accurate and reliable SSI measurements for the optimum operation of the PV devices, accurate power production prediction and, therefore, profitable performance of the various solar-energy-related applications.


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**Data Availability Statement:** All data collected during the ASPIRE campaign are available through the ASPIRE website (https://aspire.geol.uoa.gr/, accessed on 11 September 2023) or upon request from the authors. Data concerning aerosol properties are available on the AERONET website (ATHENS-NOA site, https://aeronet.gsfc.nasa.gov/, accessed on 10 October 2022).

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**Conflicts of Interest:** The authors declare no conflicts of interest.

**Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AE</td>
<td>Ångström exponent</td>
</tr>
<tr>
<td>AERONET</td>
<td>Aerosol Robotic Network</td>
</tr>
<tr>
<td>AM</td>
<td>air mass</td>
</tr>
<tr>
<td>AOD</td>
<td>aerosol optical depth</td>
</tr>
<tr>
<td>a-Si</td>
<td>amorphous silicon</td>
</tr>
<tr>
<td>ASNOA</td>
<td>Actinometric Station of the National Observatory of Athens</td>
</tr>
<tr>
<td>ASPIRE</td>
<td>Atmospheric parameters affecting Spectral solar Irradiance and solar Energy</td>
</tr>
<tr>
<td>ASTM (-G)</td>
<td>American Society of Testing and Materials (Global)</td>
</tr>
<tr>
<td>AZ</td>
<td>solar azimuth angle</td>
</tr>
<tr>
<td>CdTe</td>
<td>cadmium telluride</td>
</tr>
<tr>
<td>CIS</td>
<td>copper indium selenide</td>
</tr>
<tr>
<td>DNI</td>
<td>direct normal irradiance</td>
</tr>
<tr>
<td>DSSI</td>
<td>downward spectral solar irradiance</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>GaAs</td>
<td>Gallium arsenide</td>
</tr>
<tr>
<td>GAW</td>
<td>Global Atmospheric Watch</td>
</tr>
<tr>
<td>GHI</td>
<td>global horizontal irradiance</td>
</tr>
</tbody>
</table>
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GTI Global Tilted Irradiance
IEA International Energy Agency
IEC International Electrotechnical Commission
MM spectral mismatch factor
mono c-Si monocrystalline silicon
PFR Precision Filter Radiometer
poly c-Si polycrystalline silicon
FSR Precision solar Spectroradiometer
PTB Physikalisch-Technische Bundesanstalt
PV photovoltaic(s)
pvpmc PV Performance Modeling Collaborative
PWC precipitable water vapor column
RTM radiative transfer model
SI spectral irradiance
SMARTS Simple Model of the Atmospheric Radiative Transfer of Sunshine
SR spectral response
SSA single scattering albedo
SSI solar spectral irradiance
STC Standard Test Conditions
SZA solar zenith angle
TOC total ozone column
UV ultraviolet
WRC World Radiation Center

References


62. Anderson, G.; Clough, S.; Kneizys, F.; Chetwynd, J.; Shettle, E. *AFGL Atmospheric Constituent Profiles (0.120 km)*; Air Force Geophysics Lab.: Bedford, MA, USA, 1986; p. 46.


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