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ScienceDirect
Solar Energy 83 (2009) 280–286
SOLAR ENERGY
www.elsevier.com/locate/solener

UV-A (315–400 nm) irradiance from measurements at 380 nm for solar water treatment and disinfection: Comparison between model and measurements in Buenos Aires, Argentina and Almería, Spain

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Received 29 July 2007; received in revised form 12 September 2008; accepted 2 October 2008
Available online 4 November 2008

Communicated by: Associated Editor D. David Renne

Abstract

A linear correlation between UV-A and 380 nm was developed by means of the TUV 4.1 radiative transfer model. The prediction error of the correlation was evaluated with data from Buenos Aires, Argentina, 2001, and from 2006, Almería, Spain. Percent random mean square error (RMSE%) was calculated for intervals of 10° of solar zenith angles, ranging 4.75% at 20° to 37.70% at 90° in clear days and 22.16% at 20° to 26.17% at 90° for cloudy days in Buenos Aires Argentina, and 1.27% at 20° to 11.27% at 90° for clear days in Almeria, Spain. Clouded days were not assessed with the data from Spain. In Argentina, the UV-A radiometer is located in a rural area and the 380 nm radiometer is located in an urban area 6 km away. Hence the real error of the proposed model is closer to that found in Spain were both measurements were performed at the same site. The objective of the work is to achieve a simple and precise method to assess UV-A availability for environmental applications of solar energy, particularly for solar water treatment, at any desired latitude.

Keywords: UV-A; 380 nm; Irradiance; Measurements; Comparison

1. Introduction

In recent decades, much attention has been given the amount of ultraviolet (UV) radiation reaching the Earth's surface because of the thinning stratospheric ozone layer and the rapid advance of wastewater treatment mediated by the solar UV spectrum. Knowledge of the amount of UV radiation received by plants and animals near the Earth's surface is important in a wide range of fields such as cancer research, forestry, tropospheric chemistry, agriculture, oceanography and solar chemistry (Madronich and Flocke, 1995).

Such information is of crucial importance in the design of the solar photocatalytic systems used for water detoxification technologies (Blesa and Blanco, 2005). The detoxification of organic pollutants by solar UV radiation with

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0038-092X/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.solener.2008.10.010

catalysts is currently being studied by a number of laboratories, universities, and institutions throughout the world. Photocatalysis accelerates the oxidation of organic matter through the mediation of highly reactive species created on the surface of the photocatalyst, such as titanium dioxide, under UV illumination.

The principles of this process are well known, and have been described in the literature (Schiavello, 1985) and references therein. Strongly oxidizing radicals, such as ˙OH, are generated on the surface of the wideband-gap semiconductor (TiO_2) upon excitation with <400-nm UV light and formation of an electron–hole pair. These species are responsible for the non-selective oxidation of organic compounds. In the presence of dissolved oxygen, total mineralization is ideally achieved. Photocatalysis has been proven to destroy pesticides, organochlorinated compounds, waste water, dyes, and others causing heavy pollution (Pérez-Estrada et al., 2005; Malato et al., 2000; Tribusch, 1989).

Water disinfection may also be achieved by heterogeneous photocatalysis (Ibáñez et al., 2003; McLoughlin et al., 2004), through the attack of strongly oxidizing radicals on cell components. Again, there is a wealth of information in the literature about heterogeneous photocatalytic disinfection of water. An important limitation of heterogeneous photocatalysis is the need for UV light to excite the catalyst. Visible light is ineffective, and solar technologies must therefore provide means for efficient collection of the UV radiation present in the solar spectrum.

The efficiency of these systems depends on the availability of UV radiation at the selected location. Rapid development in this field of research and the construction of some pilot plants (Vidal et al., 1999) has lead to new requirements associated with proper system dimensioning as well as resource evaluation criteria. Dimensioning is dependent on the reaction rate among other factors. The reaction mechanism and the rate constants involved must be known for each particular wastewater. Once the kinetic constants are known, the monthly average UV radiation must be taken into account for proper siting and the total collector area needed.

In most of the systems described, the fluid to be treated circulates through transparent glass tubes with a UV-B light transmittance of about 45% and 90% for UV-A. Furthermore, the UV-A spectrum accounts for roughly 95% of the solar UV spectrum. Hence for solar photocatalysis systems, knowledge of UV-A is more important than knowledge of the whole UV spectrum.

Worldwide scarcity of information on the distribution of the UV-A resource makes it necessary to find this information indirectly through correlations of global and UV-A radiation, estimation from satellite databases, mathematical models, etc. (Cañada et al., 2003; Koronakis et al., 2002; Kudish et al., 2005; Ogunjobi and Kim, 2004). All the methods approximate real data within a certain error, but the need for statistically significant measurements and a reliable information resource is growing, not only for photocatalytic applications but also in fields such as photobiology and medicine.

This article reports and evaluates a method for finding UV-A irradiance at any latitude from measurements at 380 nm. The proposed methodology allows the UV-A irradiance to be calculated from measurements at 380 nm with a linear correlation. The model was validated using data from Buenos Aires, Argentina and Almería, Spain, in order to demonstrate model validity at different latitudes. The data evaluated in Argentina was from 2001 and in Spain from 2006. In the case of Argentina, a total of 249 days were analyzed of which 35 were clear days and the rest were cloudy days, either partially or overcast. The scarce clear days available is related to data acquisition problems and day choosing criteria. The instruments that perform the measurements at 380 nm and UV-A are located on different sites and only completely clear days without a single cloud in the sky were chosen. Out of the selected clear days, only those in which both measuring instruments registered information were used for the model validation. After both filtering conditions, only 35 clear days remained useful in the data base. The rest of the clear days was available only on one of the measuring instruments and could not be used for the purpose of this work. It is important to mention that the October and December UV-A data was not available in one of the radiometers and these are months were most clear days are available.

In the case of Spain, only 14 clear days were used due to the characteristics of the measuring instrument and also due to technical problems. The interval between measurement of this equipment is of 20 min. In a cloudy day, the attenuation due to clouds can be highly variable in this time interval, hence only clear days were used for model validation. The measuring instrument had some functioning problems in 2006 and only 14 of the total available days were available for validation. The detailed explanation of the obstacles encountered in data availability is further explained in the Section 2.

2. Materials and methods

2.1. TUV 4.1 radiative transfer model

The relationship between 380 nm and UV-A irradiance was analyzed with the TUV 4.1 radiative transfer model for different atmospheric conditions. According to Bais et al. (2003), this model has an accuracy of 95% at solar noon on clear days. One big advantage is that it can model the whole UV-A spectrum as well as discrete wavelengths such as 380 nm. This model uses a discrete ordinate method to solve the radiative transfer equation, and considers absorption and scattering as two independent phenomena (two-stream approximation). It divides the atmosphere in layers and then solves the equations for each layer. The model is widely used (Madronich and Flocke, 1995; Palancar and Toselli, 2004) for UV spectrum estimation. Some aerosol characteristics, the location (latitude, longitude, height above sea level) and time of the year (year, month, day, hour) must be entered. The aerosol parameters required are:

Aerosol optical depth (τ) is the product of particle density and the probability of interception of radiation, also being known as the cross section, and is usually between 0.1 and 1 (Madronich, 1993). Thick clouds can have values of 20–30.

Single-scattering albedo (ω) is a measure of the proportion of absorption and scattering caused by aerosols. It has values of 1 for pure scattering and 0 for pure absorption. Typical values for the wavelength range are 0.8–0.99 (Madronich and Flocke, 1995).

Alpha wavelength coefficient (α) measures the size of the aerosols and is between 0 for large particles and 4 for small particles, usually around 1.3 ± 0.5 (Iqbal, 1983).

The range of conditions for analysis was chosen to represent either general conditions, or those typical for Buenos Aires (Otero et al., 2003; Iqbal, 1983). Calculations were performed by varying one parameter at a time while the rest remain constant. Table 1 shows the values of the parameters analyzed. A total of 63 atmospheric situations at solar zenith angles ranging from 0° to 90° were modeled. This gives 5670 values of irradiance that were used to determine the correlation between 380 nm and UV-A irradiance.

2.2. Measurement of UV-A and 380 nm irradiance in Argentina

Measurements performed in Argentina in 2001 with multi-channel moderate-bandwidth GUV filter radiometers (Biospherical Instruments Inc., USA) in the Buenos Aires UV station (34°35'S; 58°28'W) were used to measure the horizontal total irradiance at 380 nm. The GUVs have four channels in the UV region, centered approximately at 305, 320, 340 and 380 nm, with bandwidths of approximately 10 nm. The instruments are kept at a stable 40 °C. A fifth channel measures photosynthetically active radiation (PAR) and is sensitive to visible radiation between 400 and 700 nm. The cosine error is less than 3% (±7.5%) for zenith angles of less than 65°. The radiometers are calibrated annually against a reference instrument. The reference instrument in turn is calibrated against an SUV100 spectroradiometer at Biospherical Instruments before and after the field calibration process (Bernhard et al., 2000; Diaz et al., 2002; Fuenzilda, 1998).

The horizontal total UV-A measurements in Buenos Aires were from a UV-A radiometer, model MS-210 from Eco Instruments Trading Co., Japan, with a spectral range of 315–400 nm, located at CEILAP-CITEFA (CC); 34°33'S; 58°30'W). This site is approximately 6 km away from the UV network B.A. station. The manufacturer did not provide the error of the equipment. The radiometer was calibrated in 1997 and according to the characteristics of the equipment an annual error of ±1% was estimated. Hence the maximum expected error was of ±3%.

Table 1
Atmospheric parameters used to model conditions with the TUV 4.1 program.

Parameter	Values
Aerosol optical thickness (τ)	0.1–0.5–1.0
Single-scattering albedo (ω)	0.85–0.99
Alpha wavelength exponent (α)	0.8–1.3
Total ozone column (DU)	200–250–300

Table 2
Distribution of the clear days in Argentina used to assess the correlation of Eq. (A1). N/A: data was not available either for climatic or equipment reasons.

Month	Clear days
January	5
February	N/A
March	4
April	4
May	N/A
June	4
July	7
August	3
September	3
October	N/A
November	5
December	N/A
Total	35

A total of 249 days were analyzed of which 35 were clear days and the rest were cloudy days, either partially or overcast. The number of clear days corresponds to those days on which the data from both instruments were available. The rest of the clear days was available only on one of the measuring instruments and could not be used for the purpose of this work. The annual distribution of clear days can be seen in Table 2. There was no data available from both equipments for the months of October and December.

2.3. Measurement of UV-A and at 380 nm in Spain

Measurements in Spain, during 2006 were performed by an Instrument Systems spectroradiometer, model SP320D USA, which measures the solar spectrum from 200 to 2500 nm with an accuracy of ±3%. The instrument is located at the Plataforma Solar de Almería (37°84'N and 2°34'W). This instrument allows total horizontal 380 nm and UV-A irradiance to be measured simultaneously. Hence there was no difference in geographic location.

The spectroradiometer spans the whole spectrum in about 7 min including processing time. As it performs the same operation for global, direct and diffuse radiation, global UV-A irradiance data are measured every 20 min. Attenuation due to cloudiness is higly variable in this time interval, therefore, only clear days were used to assess the model in this case. A total of 14 clear days were analyzed and their annual distribution can be observed in Table 3.

3. Results

3.1. Simulations with the TUV 4.1 model

Fig. 1 shows the results of the performed simulations with the TUV 4.1 model to analyze the sensibility of the

Table 3
Distribution of the clear days in Spain used to assess the correlation of Eq. (A1). N/A: data was not available either for climatic or equipment reasons.

Month	Clear days
January	2
February	2
March	2
April	1
May	1
June	1
July	2
August	1
September	2
October	N/A
November	N/A
December	N/A
Total	14

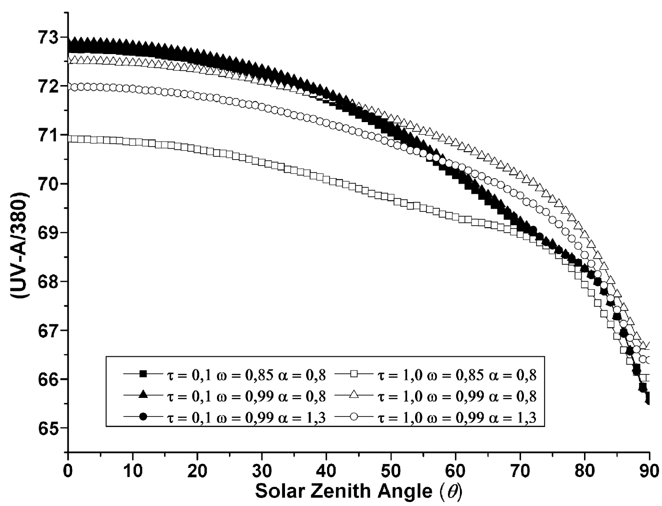

Fig. 1. Analysis of the 380/UV-A relation for the different modelled atmospheric conditions for each solar zenith angle. The value fluctuates ±1 unit around 72. All curves are shown for a total ozone column of 300 DU. The curves showed negligible variation for different total ozone columns.

relation 380/UV-A to changes in atmospheric conditions defined by the solar zenith angle (θ), aerosol optical thickness (τ), single-scattering albedo (ω) and the alpha wavelength coefficient (α). The results for $\tau = 0.5$ are not shown but lie in between the value of those observed in the graph.

All curves shown in Fig. 1 are for a total ozone column of 300 DU. The curves showed negligible variation for different total ozone columns.

Fig. 2 shows UV-A irradiance in units of W/m^2 against 380 nm irradiance in units of W/m^2 for each modelled situation.

The linear correlation according to the least squares method is given by Eq. (A1); where $I_{\text{UV-A}}$ is the UV-A irradiance in units of W/m^2, I_{380} is the 380 nm irradiance in the same units and N is the number of irradiances values used to develop the correlation.

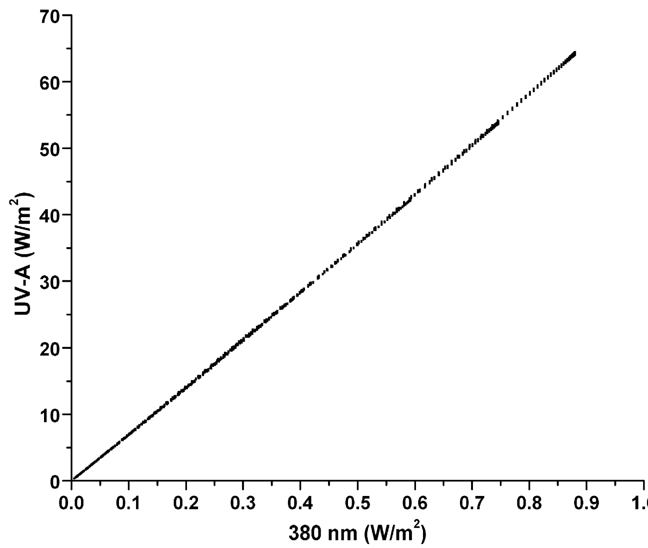

Fig. 2. Correlation between UV-A and 380 nm irradiance for all atmospheric situations simulated with the TUV 4.1.

3.2. Prediction error assessment with data measured in Argentina

Fig. 3 shows the results of the correlation evaluation in clear days and Fig. 4 shows the same results for cloudy days in Argentina.

The random mean square error expressed as percentage (RMSE%) of Eq. (A1) was calculated for clear and cloudy days for ranges of 10° of solar zenith angles. The number of irradiance values used to assess the error in each range is given by NSD for clear sunny days and by NCD for cloudy days. The results are shown in Table 4.

In the case of clear days, the error increases together with the zenith angle. This phenomenon has two reasons: first,

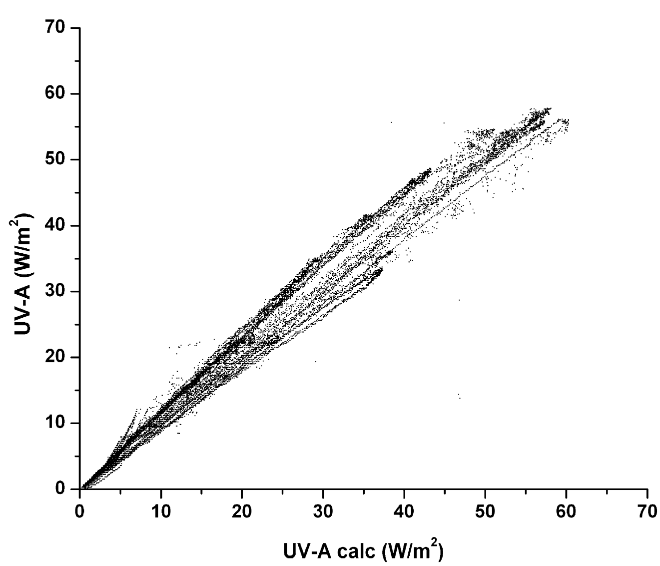

Fig. 3. Correlation between measured (UV-A) irradiance and calculated (UV-Acalc) irradiance using Eq. (A1) for clear days in Argentina.

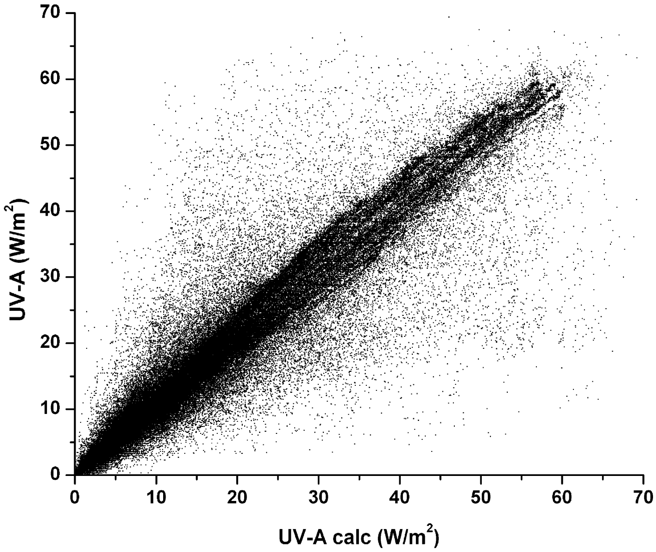

Fig. 4. Correlation between measured (UV-A) irradiance and calculated (UV-Acalc) irradiance using Eq. (A1) for cloudy days in Argentina.

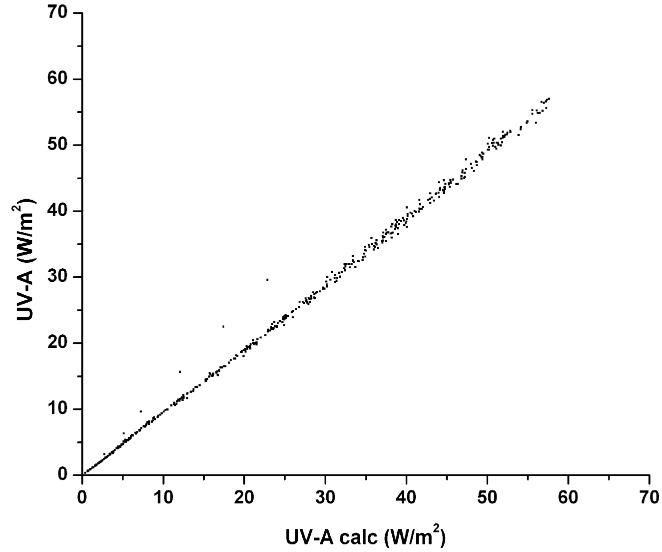

Fig. 5. Correlation between measured (UV-A) irradiance and calculated (UV-Acalc) irradiance using Eq. (A1) for clear days in Spain.

Table 4
Distribution of the RMSE (%) of Eq. (A1) for clear and cloudy days in Argentina for each range of solar zenith angle.

Solar zenith angle (°)	RMSE (%) in clear days	NSD	RMSE (%) in cloudy days	NCD
90–80	37.70	2423	26.17	23,745
80–70	21.65	2527	20.76	24,761
70–60	14.59	2925	19.70	28,332
60–50	12.77	2942	21.62	30,905
50–40	11.86	2140	22.85	21,715
40–30	9.90	1565	24.16	16,217
30–20	5.97	927	24.66	9569
20–00	4.75	908	22.16	5823
Total	11.13	16,357	27.98	161,067

the TUV 4.1 model is only precise up to zenith angles lower than 60°. At larger angles, the diffuse radiation becomes too complex to model. Second, the environmental context that surrounds both radiometers is completely different. The 380 nm radiometer is surrounded by buildings whereas the UV-A radiometer is in a rural area. The buildings do not project shadow on the radiometer but they block a great deal of the diffuse radiation which in the UV-A wavelengths can rise up to 40% on clear days.

In cloudy days, the error has homogeneous distribution in all zenith angles with an average value of 23%. The error increases at zenith angles higher than 70°. Again, this is due to the characteristics of the model. The similarity in the error at all zenith angles can be explained through cloud attenuation. In most of the cases, clouds have an attenuation independent of wavelength and on the other hand, they serve as a diffuser, illuminating everything isotropically. In clear days, the attenuation is dependant on the zenith angle due to the enlargement of the optical path in the atmosphere as is shown in the error distribution in Table 4, but in cloudy days, cloud attenuation is larger in comparison with that of the atmosphere so it dominates the process. The attenuation due to the variation of atmospheric pathlength is negligible with that generated by the occurrence of clouds.

The lower error values in cloudy days corresponds solar noon of completely covered skies in winter season. The larger error in cloudy days is when partial cloud cover occurs. Given the distance of separation of both radiometers, clouds can be covering one radiometer but not the other. Also some wavelength dependance may arise from multiple scattering phenomena in clouds (Mayer et al., 1998; Piacentini et al., 2003).

3.3. Prediction error assessment with data measured in Spain

Fig. 5 shows the result of the assessment of Eq. (A1) with measurements from Spain.

The prediction error of Eq. (A1) was calculated only for clear days for ranges of 10° of solar zenith angles. The number of data used to assess the error in each range is given by NSD for clear sunny days. The results are shown in Table 5.

Table 5
Distribution of the RMSE (%) of Eq. (A1) for clear days in Spain for each range of solar zenith angle.

Solar zenith angle (°)	RMSE (%) in clear days	NSD
90–80	11.18	63
80–70	7.89	80
70–60	8.75	85
60–50	4.81	82
50–40	3.39	74
40–30	2.95	41
30–20	2.25	41
20–00	1.27	22
Total	4.64	488

A similar error trend to that of Argentina is observed. Nevertheless, error values are less than 50% approximately. This is mainly because both measurements were performed at exactly the same site. In this way, they suffer atmospheric phenomena at the same time and measure under the same climatic influence. All effects due to the instrument separation are vanished.

4. Discussion

There is an important difference in the errors found at each location, so several factors must be considered before reaching some conclusions.

The measurements from Spain had a known error. This was not the case for the data in Argentina where the error had to be estimated. The estimated value may not be real, contributing to larger prediction errors.

In Argentina the 380 nm and UV-A radiometers were separated a distance of 6 km and surrounded by different environments. In addition, an error of a couple of minutes in data acquisition can happen since data is not recorded by the same computer. In clear days, the separation does not represent a problem but on cloudy days, different atmospheric situations can occur over both radiometers, e.g. cloudy on one and clear on the other. This effects contributes to the larger errors detected in Argentina.

The error of the radiative transfer model is large for values of solar zenith angles larger than 60°.

The error in Spain is approximately half of that in Argentina for clear days. This is mainly due to the separation between the UV and the 380 nm radiometers in Argentina.

In research experiments for solar water treatment, almost all experiences to assess the effect of sunlight are performed under clear skies and at zenith angles <60°. In this case the correlation presents a small error and is very useful given the simplicity and precision.

If the case is to know the solar UV-A resource availability for the design of a solar water treatment plant, the irradiance must be integrated over each day and then monthly means must be determined. In this case, and taking into account the real error described in the paragraph above, errors of 10–15% are well within the range of acceptance given that most water treatment plants work with security factors of around 5–15% (Tchoganoblus and Crites, 2000).

5. Conclusions

A correlation to assess the UV-A irradiance from measurements at 380 nm has been presented and evaluated. The correlation has been developed with data modelled with the TUV 4.1 program and the RMSE (%) has been assessed with data from Argentina and Spain. The error was calculated for intervals of 10° of the solar zenith angle (SZA). The error range for Argentina in clear days goes from 4.75% at 0–20° SZA to 37.70% for 80–90° SZA. In cloudy days, the range goes from 22.16% at 0–20° SZA to 26.17 at 80–90° SZA. In Spain the error was assessed in clear days only and the range goes from 1.27% at 0–20° SZA to 11.18% at 80–90° SZA.

On clear days the error increases with the SZA. In cloudy days, the error remains approximately constant around 23%.

The difference in the error obtained in Argentina and Spain evidences the influence of the separation of the radiometers. The error in Spain is about half of that in Argentina for clear days, mainly because 380 nm and UV-A irradiance are measured at the same site.

The correlation can be used in any location whose atmospheric parameters fall in the analyzed range.

A real conservative error value can be a mid point between that of Argentina and that of Spain, i.e. 7% for clear days and 14% for cloudy days.

Given the world scarcity of UV-A measurements, this correlation gives a simple way to determine UV-A irradiance from measurement at 380 nm with reasonable precision and can be applied in any desired location. The uses extend from solar water treatment to medical sciences.

Acknowledgements

Funded by European Union (Project INCO ICA4-2001-10022). Also supported by ANPCyT (Project PICT 12122).

Support through Doctoral Fellowship to C.N. from ANPCyT and BECAS MAE-AECI.

Appendix Equations

$$I_{\text{UV-A}} = 72.5679(\pm 0.0066) \cdot I_{380} - 0.0207(\pm 0.0116) \text{ with } R^2 = 0.9998 \text{ and } N = 5670 \quad \text{(A1)}$$

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