Long-term UV dosimeter based on polyvinyl chloride for plant damage effective UV exposure measurements

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Highlights

- UV dosimeters based on PVC are compared with PPO dosimeters for measuring the UV exposure of the leaves on a plant
- The performance of the PVC dosimeters in assessing UV exposure is comparable to those of the PPO dosimeters
- PVC dosimeters have a useable range four times higher (up to 1 month) than PPO dosimeters

Abstract

Research on the influence of ultraviolet radiation (UV) on terrestrial plants and on its link with other influencing environmental factors requires information on UV exposures, both for a horizontal plane and specific portions of a plant, above and under the canopy. In this research, one set of UV dosimeters based on unstabilized polyvinyl chloride (PVC) were employed to measure the unweighted UVB (UVB) and the biologically effective UV radiation for plant damage ($UVBE_{plant}$) incident on the leaves of a plant for a month, without having to change the dosimeters. The exposures were compared to the cumulative exposure concurrently measured with six sets of unstabilized polyphenylene oxide (PPO) dosimeters that required changing every four to six days. The difference in exposures between the two types of dosimeters was on average within 11%. The PVC dosimeter is the first reported polymer film dosimeter with a useable range of a month for measuring the plant damaging UV and the UVB exposures to specific parts of a plant. The exposure period of a month for the PVC dosimeter is an extension by a factor of four over the useable range of dosimeters previously reported in the literature for evaluation of the exposure of plants to UV radiation.

1. Introduction

Ultraviolet radiation has some negative impacts on plant growth but also provides some positive influences, for example increasing the hardiness of plants resulting in less susceptibility to pest and disease attack (Bornman et al., 2015). The influence of solar UVB (280-320 nm) on terrestrial ecosystems and on cultivated plants is interlinked with the total column ozone and with climate change (Bornman et al., 2015). Any research on the influence of UV on terrestrial plants and ecosystems and on its link with other influencing environmental factors requires long term information on UV exposures; in particular are required UV exposures integrated over periods of time (Kakani et al., 2003). Other than UV exposures over a horizontal plane are required exposures over specific portions of a plant above and under the canopy. Specific portions of a plant can receive significantly different amounts of UV radiation due to factors such as orientation, shading and canopy structure (Bornman et al., 2015). Previous research has reported on the measurements of solar UV exposures to plants with spectroradiometers (Grifoni et al., 2008), radiometers (Webb, 2003) and dosimeters (Parisi et al., 2010; 2003; 1998; Turner et al., 2013). Spectroradiometers are expensive sophisticated pieces of equipment that measure the spectral irradiances in narrow wavebands. Radiometers measure the broadband UV in a given waveband. Dosimeters are small devices that are based on passive polymer films (Parisi and Wong, 1994) or electronic dosimeters (Thieden et al., 2005) for measuring in a given waveband. Other research has measured the radiation at the canopy level and applied a radiative transfer approach to determine the exposures to specific parts of a plant (Gao et al., 2001). However, the approach in this current research is to apply physical simultaneous multi-site measurements to different parts of a plant. The use of electronic dosimeters (Thieden et al., 2005) for the monitoring of UV radiation can have a significant cost for the use of these for simultaneous multi-site measurements. Consequently, the approach in this research is the use of dosimeters based on polymer film.

The influence of ultraviolet radiation is wavelength specific and this can be represented by a specific action spectrum for each biological process (Coohill, 1991). The action spectrum is multiplied by the incident solar radiation at each wavelength and then integrated over the wavelength interval to calculate the biologically effective UV (UVBE). There are a number of plant damage action spectra that have been previously developed for different purposes. These can be categorized into those that have responses predominantly in the UVB and no response in the UVA (320-400 nm), those with responses lower in the UVA than in the UVB (up to by several orders of magnitude) such as the generalized plant damage action spectrum (Caldwell, 1971), the DNA damage action spectrum (Setlow, 1974) and the action spectrum for DNA damage in alfalfa seedlings (Quaite et al., 1992) and finally those with a significant response in the UVA such as the action spectrum for damage to plant growth (Flint and Caldwell, 2003) and that for damage to photosynthesis (Rundel, 1983)..

The current range of chemical dosimeters based on polymer film have a useable range of one day to a week and then require changing and readout as a result of saturation of the UV induced response. Examples of these dosimeters are those based on polysulphone (Davis et al., 1976) and polyphenylene oxide (PPO) (Lester et al., 2003; Wainwright et al., 2013; Schouten et al., 2007). This is suitable for research requiring short term exposure measurements. However, for research requiring evaluation of long term exposures over extended periods, it has the cost and time required for the producing, changing and measurement either on a daily or weekly basis, with a possible increase in uncertainty due to the necessity of changing over dosimeters. The chemical dosimeters that have been employed over longer growth periods require the change and read out of the dosimeters on a regular basis in order to measure the exposure over an extended period. A new dosimeter based on unstabilized polyvinyl chloride (PVC) for the measurement of solar UV with a useable range of the order of a month has been reported for the evaluation of the UVB exposures to humans (Amar and Parisi, 2013a). These dosimeters have been shown to have the properties required for a UV dosimeter (Amar and Parisi, 2012) and have a spectral response predominantly in the UVB and a cosine response error less than 6.5% for angles up to 40º, increasing to 16% at 50º (Amar and Parisi, 2013b). The aim of this research is to evaluate a dosimeter based on PVC for the measurement of the biologically effective UV for plant damage ($UVBE_{plant}$) (Caldwell, 1971) and the UVB over an extended period of time. This will be undertaken by the comparison and evaluation of the plant damage UV exposures and the unweighted UVB (UVB) exposures measured at a number of leaves on a plant with the proposed dosimeter over a period of a month during summer compared to the corresponding cumulative exposures measured with a series of the existing PPO dosimeters that have been previously characterized for use in measuring plant damaging UV exposures with a useable range of four to six days (Wainwright et al., 2013).

2. Materials and Methods

2.1 Calibration

In order to evaluate the long-term UV dosimeter based on unstabilized PVC for measuring $UVBE_{plant}$ exposures and UVB exposures, PVC dosimeters were fabricated from 16 µm thick PVC film in 3 cm x 3 cm holders as described by Amar and Parisi (2013a). Previously reported PPO dosimeters (Lester et al. 2003; Wainwright et al., 2013) were employed to evaluate the exposures recorded by these PVC long-term dosimeters as it is not possible to measure with radiometers the concurrent plant damage and UVB exposures to a number of leaves simultaneously over a period of a month due to both the size of the radiometers and the need to have multiple instruments for simultaneous measurements on a number of leaves. As PPO dosimeters saturate after four to six days, they were used as sets of a series of dosimeters that were replaced every four to six days and the cumulative UVB and $UVBE_{plant}$ exposures evaluated over the long term exposure period. Forty four PPO dosimeters with a film thickness of 40 µm in a 3 cm x 3 cm holder were fabricated for this purpose.

The field trial was carried out for an entire month during summer 2015 in Toowoomba near the University of Southern Queensland (27.56 °S, 151.95 °E, 690 m), just after perihelion. The site of the exposures was an unshaded lawn surrounded by a house and fence, with partial shading before 08:00 and after 18:00 Australian Eastern Standard Time (AEST). The UV induced response of the PPO dosimeters was quantified by the change in their optical absorbance at 320 nm (Lester et al. 2003) measured using a UV spectrophotometer (model UV-2700, Shimadzu Co., Kyoto, Japan), while the PVC dosimeters response was taken as the percentage change in the 1064 cm^{-1} peak intensity (Amar and Parisi, 2012), measured using a Fourier Transform Infrared (FTIR) spectrophotometer (IRPrestige-21/FTIR-8400S, Shimadzu Co., Kyoto). These wavelengths were employed as previous research has established that the maximum UV induced change occurs at these wavelengths.

The calibration curves relating the change in absorbance to the $UVBE_{plant}$ and to the UVB exposures for both the PVC and PPO dosimeters were determined at the time of exposure measurements by exposing a series of PVC and PPO dosimeters on a horizontal unshaded plane near a calibrated UV meter and regularly recording the UV induced response of the two types of dosimeters as a function of the UV exposure. The PPO and PVC dosimeters were calibrated in the same month that the measurements on the plant were performed. Two batches of dosimeters were employed for the PPO with one batch exposed for a period of four days and a second batch exposed over a second period of six days and the results combined for one calibration. The change in absorbance of the PVC dosimeters and the accumulated exposure were recorded at the end of each day. For the PPO dosimeters, the change in absorbance and the accumulated exposure were measured twice a day for the first two days and then once a day after that. For both dosimeters, a polynomial curve was fitted to the calibration data. The UV meter is a meter (model IL1400 ‘A’ Series, International Light, Newburyport, MA, USA) fitted with a broadband waterproof detector (SUD240, International Light) with a UVB filter (UVB1 filter, International Light). This setup of the IL1400 meter with the SUD detector and UVB filter has a response in the UVB with a negligible response in the UVA waveband and is referred to as the UV meter in the following. This provides the integrated exposures in the UVB waveband. In order to obtain an integrated $UVBE_{plant}$ exposure from the IL1400 UVB meter output, the meter was calibrated on a cloud free day, following the approach of Wainwright et al., (2013) directly to a scanning double grating spectroradiometer (model DTMc300, Bentham Instruments, Ltd, Reading, UK) measuring the terrestrial solar spectrum from 280 to 400 nm. The solar zenith angles over the calibration period were representative of those over the month. The spectroradiometer is permanently located near the exposure site, in an environmentally sealed box on the roof of a building at the University of Southern Queensland. The spectroradiometer was calibrated at least twice a year to a standard lamp with calibration traceable to the National Physical laboratory standard, UK and the stability of the spectroradiometer is of the order of ±6% (Parisi and Downs, 2004).

The UV spectrum was recorded between mid-morning to noon at every ten minutes on the calibration day and the cumulative exposures on the IL1400 meter were also recorded at each ten minute point. The UV spectra were weighted with the plant damage action spectrum (Caldwell, 1971) (Figure 1) to evaluate the $UVBE_{plant}$ exposures and used unweighted to calculate the UVB exposures for each ten minute point. There was a strong linear correlation ($R^2 = 0.99$) between the output of the IL1400 and the $UVBE_{plant}$ exposures and the UVB exposures evaluated from the spectroradiometer data.

The spectral response of the PVC dosimeter does not exactly match the plant damage action spectrum (Figure 1) and also has a response extending into the UVA. The spectral responses of the dosimeters are linearly interpolated between the data points to 0.5 nm increments in the following processing. A factor (*g*) has previously been described to account for the difference between the spectral response of a dosimeter and the relevant action spectrum (Krins et al., 2001; CIE, 1992; Siani et al., 2014). In this case, this factor is the ratio between the biologically effective UV ($UVBE_{plant}$) weighted with the plant damage action spectrum ($A_{plant}(\lambda)$) and the dosimeter effective UV ($UVBE_{PVC}$) (Krins et al., 2001):

$$g = \frac{UVBE_{plant}}{UVBE_{PVC}} = \frac{\int S(\lambda)A_{plant}(\lambda)d\lambda}{\int S(\lambda)R_{PVC}(\lambda)d\lambda}$$

where $R_{PVC}(\lambda)$ is the spectral response of the dosimeter, $S(\lambda)$ is the global or diffuse solar spectral horizontal plane irradiance in full sun and λ is wavelength. The influence of the variability of the solar spectral irradiance on g was investigated by evaluating this factor for the range of global UV and diffuse UV spectra measured with the spectroradiometer for the solar zenith angle (SZA) range of 5.1 to 71 degrees (Geoscience Australia, 2015) and the range of cloud cover over the month of the exposure of the dosimeters in this research. The spectral irradiances to a horizontal plane were measured from 280 to 400 nm in 0.5 nm increments at every ten minutes of the day for the global UV spectrum and at every ten minutes for the diffuse UV spectrum. The SZA range of 5.1 to 71 degrees takes into account the changes in the UV incident angle due to the orientation of each leaf with respect to the incident radiation.

The dosimeters have been calibrated at the location and in the season of the exposure measurements. This is based on the approach previously employed to measure erythemal UV exposures with polysulphone dosimeters where the mismatch between the erythemal action spectrum and the spectral response of polysulphone is taken into account by calibrating the dosimeters under the same atmospheric conditions and same site as measurement dosimeters exposed in the field (Casale et al., 2006). The approach has been previously employed for the calibration and use of the PVC and PPO dosimeters at the same site and same season as the measurement dosimeters (Amar and Parisi, 2013a; Schouten et al., 2010).

2.2 Plant Measurements

The plant used in this research was a frangipani plant, about one meter high which has a summer time growth phase and is characterized by broad glossy leaves. The large leaves of this plant were wide enough so that a pair of side by side PVC/PPO dosimeters could be attached using tape on each selected leaf (Figure 2). The plant was in a pot and taken indoors to replace and/or measure the dosimeters and also to protect the plant in case of extreme weather conditions.

Five side by side pairs of PVC/PPO dosimeters were attached by tape to the top side of leaves on the plant with a variety of angles and degrees of shading (Figure 2). A sixth pair was positioned on a horizontal unshaded plane near the plant to measure the ambient exposure. The dosimeters were mounted about half a centimeter above each leaf to avoid any possible heat accumulation due to the buildup of heat between the leaf and the dosimeter polymer film. The exposure was carried out from 07 January to 07 February 2015. The range of the noon solar zenith angle over this period was 5.1^{o} to 12.2^{o} (Geoscience Australia, 2015). The PVC dosimeters were not replaced over this period and remained on the leaves the whole month, while six sets of PPO dosimeters where required for the same period. Every 4-6 days (depending on the weather conditions) the plant was taken indoors to remove the PPO dosimeters and attach another set of PPO dosimeters. The PPO dosimeters used to establish the PPO calibration curve were also exposed for up to six days only. This maximum exposure period was necessary as PPO dosimeters are normally saturated after about five days of exposure to solar UV radiation under clear sky conditions (Lester et al. 2003). All of the absorbances of the dosimeters were measured at the relevant wavelengths immediately after exposure.

At the end of the exposures, the measured absorbance change within the PVC and PPO dosimeters were converted into a UVB exposure and a $UVBE_{plant}$ exposure in Jm^{-2} using the respective calibration. For each leaf, the exposure evaluated from the PVC dosimeter was then compared with the summation of exposures measured by six sequentially exposed PPO dosimeters.

3. Results and Discussion

The variation of the g ratio for a horizontal plane during 30 consecutive days of the measurement with the dosimeters on the plants between the times 0700 to 1700 AEST each day are provided in Figure 3, covering the SZA range of 5 to 71 degrees. The dark data points are for the peak UV times of 1000 to 1400 AEST each day and the data points for the remainder of the day are shown by the grey data points. The data is for both the global UV at 10 minute intervals and the diffuse UV at ten minute intervals for all of the cloud and clear sky conditions encountered. The average g ratio is 0.0633 ± 0.019, where the error is represented as the standard deviation. Extraction of the g ratios for the diffuse UV spectra only, provides an average g ratio of 0.0647 ± 0.019. There is practically no difference in the g ratio for the dataset from the diffuse UV spectra compared to the dataset that contains both the global and diffuse UV spectra.

The results show that the g ratio is influenced by the incident angle of the radiation and not whether it is the global spectrum or the diffuse spectrum. The range of solar incidence angles for each surface has the full range of angles as the solar zenith angle changes throughout each day from dawn to solar noon to dusk.

The dark data points in Figure 3 are for the peak UV times of 1000 to 1400 AEST each day. For this data, the average g ratio is 0.0760 ± 0.009. As the dosimeters measure the integrated UV over the exposure period, it is the irradiances over the peak UV times that contribute the most to the total exposure. The variation within one standard deviation of the mean for this UV during the peak UV times is ±12%. This variation has been addressed in this research by calibrating the dosimeters at the site and for the atmospheric conditions of the measurement dosimeters (Casale et al., 2006).

A comparison between the plant damage effective UV exposures received by the five selected leaves during 30 consecutive days in summer as measured using the PVC dosimeters and the cumulative exposure evaluated with the sets of PPO dosimeters are presented in Figure 4. In this case the post-exposure absorbances were measured directly after exposure. However, the critical aspect is that the time period between the removal and measurement of the dosimeter absorbances is consistent for all the dosimeters. The actual measured exposures for each leaf surface were those measured with the series of PPO dosimeters that were changed every four to six days. These cumulative exposures take into account the range of exposures due to changes in solar incidence angle to each leaf. The exposures measured with the long-term PVC dosimeters have been compared to the cumulative exposures measured with the series of PPO dosimeters.

The error bars are the errors due to the combined errors of calibration, angular response error, reciprocity and dark reaction of the dosimeters. These have been estimated to be of the order of ±15% (Lester et al., 2003) for the PPO dosimeters. For the PVC dosimeters, these have been evaluated as ±16% using the technique described in Amar (2014).

The atmospheric ozone for this site over this period as measured by the OMI satellite averaged 268 Dobson Units (DU) with a standard deviation of 8 DU (http://giovanni.gsfc.nasa.gov/giovanni/). The plant damage UV exposure as measured by the PVC dosimeters on a horizontal plane was 26,778 Jm^{-2}, with the exposures to each of the leaves on the plant being less than this. Apart from the set of dosimeters at site 3, the maximum difference is 14% with the average difference being 11%. The exception to this is the set of dosimeters on site 3 which, as seen in Figure 2 is the most shaded leaf of the leaves selected for the measurements. This is due to differences in the amount of time the PVC dosimeter is shaded compared to the period of time of shading of the PPO dosimeters. The average difference of 11% and the maximum difference of 14% are within the estimated errors for PPO dosimeters which have been estimated to be of the order of 15% (Lester et al., 2003).

The exposures to each leaf in Figure 4 relative to the exposures on a horizontal plane measured by the respective dosimeters are provided in Figure 5. Apart from site 3 which has the factor of the differences in shading to the PPO and PVC dosimeters, the agreement is within 5%. Figure 6 provides the UVB exposures to each of the five sites on the plant and to the horizontal plane. This figure provides a comparison of the UVB exposures measured with the single set of PVC dosimeters exposed for a month and the cumulative exposures from six sets of PPO dosimeters. Apart from site 3 which has the previously mentioned shading of the leaf, the maximum difference between the two sets of exposures is 14%. The UVB exposures to each leaf relative to those on a horizontal plane are similar to those in Figure 5 for the $UVBE_{plant}$ values.

The comparison that has been undertaken in this paper is against the month's cumulative exposures measured with the PPO dosimeters that were replaced every four to six days over the full exposure period of a month. This is against a physical measurement with calibrated PPO dosimeters that take into account the shading, orientation, inclination, weather conditions and any other conditions of the leaves. The exposures measured with the PVC dosimeter, apart for those at site 3 which had differences in shading, are on average within 11% of those measured with the PPO dosimeter. This is within the estimated error of the PPO dosimeter. The measurements at specified intervals of the irradiance with the radiometer of exposures to the leaves would not be able to take into account the variations in shading, orientation, inclination, weather conditions and any other conditions of the leaves.

This comparison of the cumulative exposures measured with the PPO dosimeters that were changed every four to six days compared to the PVC dosimeter that was exposed for the 30 days shows that there is the potential for the PVC dosimeter to be employed in long-term plant UV exposure measurements, with twelve dosimeters per site fabricated from the same batch of polymer film providing coverage over a year. The dosimeters are rugged and can survive the weather conditions of wind and rain. The situations where there are severe weather conditions such as hail that may damage the dosimeters can be handled by either taking the plants inside for potted plants or for plants in the ground by removing the dosimeters and replacing again on the leaves after the severe weather has subsided.

4. Conclusion

This research has employed a recently developed UV dosimeter based on unstabilized PVC with a large useable range for the measurement of the plant damage UV and the UVB exposures over a period of a month at a sub-tropical site in summer without the need to change dosimeters. This has been validated against the cumulative exposures from six consecutive sets of previously reported dosimeters with a useable range of four to six days. The reported dosimeter can be employed on any other plant canopy that has leaves large enough for the attachment of the dosimeter, providing a means to measure long term UVB and plant damage effective UV exposures to plant leaves. The PVC dosimeter requires calibration for the location, atmospheric conditions and season of the exposures in order to take into account any mismatch between the action spectrum and the spectral response of the dosimeter. This mismatch was quantified as ±12% over the peak exposure times of 10.00 to 14.00. It is the first reported dosimeter with a useable range of a month for measuring the plant damaging UV and the UVB to plant leaves and the exposure period of a month for the PVC dosimeter is an extension by a factor of four on the useable range of dosimeters previously reported for evaluation of UV exposures to plant leaves. The PVC dosimeter allows the measurement of the exposures to each leaf with a dosimeter deployed on it and potentially also for the under canopy exposures. It enables the dosimetric measurement of site specific UVB and plant damage effective UV exposures to plants over extended periods and reduces significantly the expense and time for the changing of dosimeters on a daily or at best a weekly basis.

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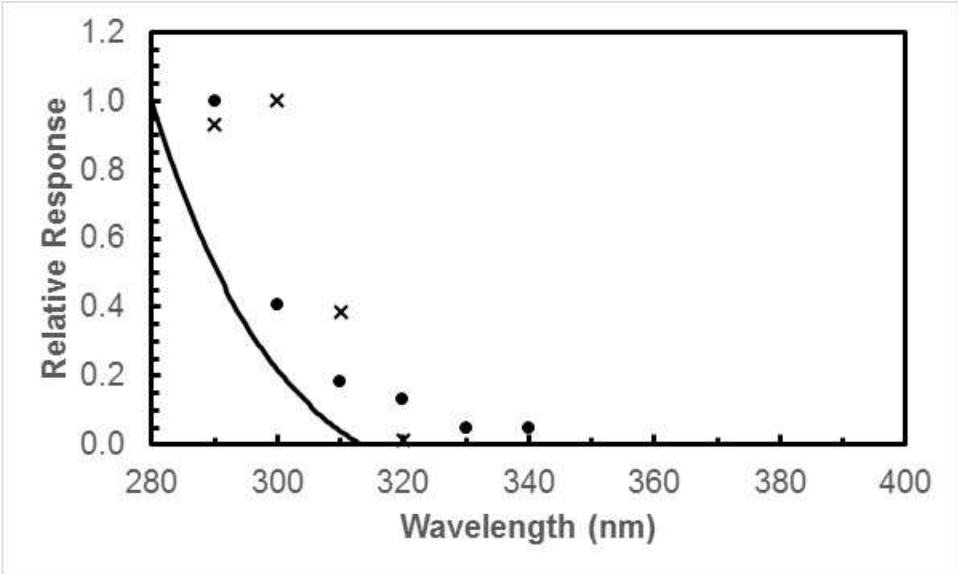

Figure 1: The spectral response of the proposed PVC dosimeter (•) (Amar and Parisi, 2013b) and the spectral response of the PPO dosimeter (x) (Lester et al., 2003) measured at specific wavelength increments. The spectral responses of the dosimeters in this figure are linearly interpolated between the data points to 0.5 nm increments for the processing. The plant damage action spectrum (Caldwell, 1971) is shown as a solid line.

Figure 2: The experimental setup for the plant exposure measurements showing pairs of side by side PVC/PPO dosimeters attached to chosen leaves of the frangipani plant, with the dosimeters to site 3 on a shaded leaf. The dosimeters at location 6 are the PVC/PPO dosimeters measuring the unshaded horizontal plane exposures.

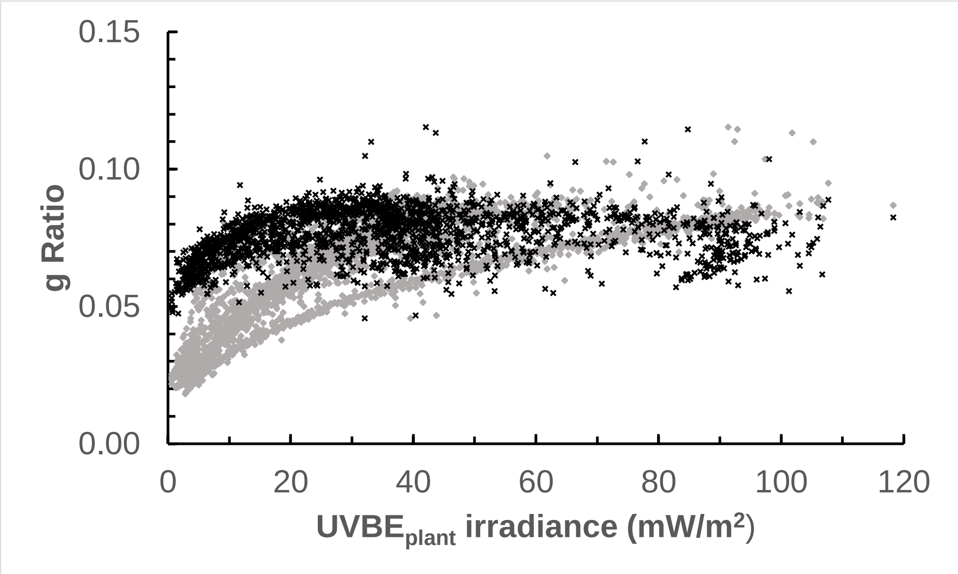

Figure 3: Variation of the g ratio over the month of the measurement with the dosimeters on the plants. The data is for both the global UV at 10 minute intervals and the diffuse UV at ten minute intervals. The dark data points are for the peak UV times of 1000 to 1400 AEST each day and the data points for the remainder of the day are shown by the grey data points.

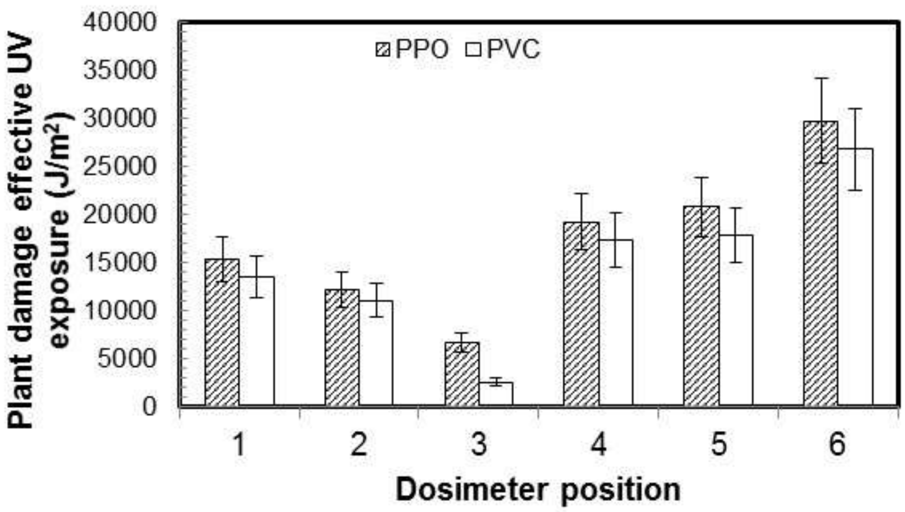

Figure 4: Comparison of the $UVBE_{plant}$ exposures received by five selected plant leaves due to exposure to solar radiation for 30 days as measured by one set of PVC dosimeters and the cumulative exposures from six sets of PPO dosimeters. The sixth position is for the horizontal exposure. The error bars represent the errors associated with the exposure measurements with PPO and PVC dosimeters.

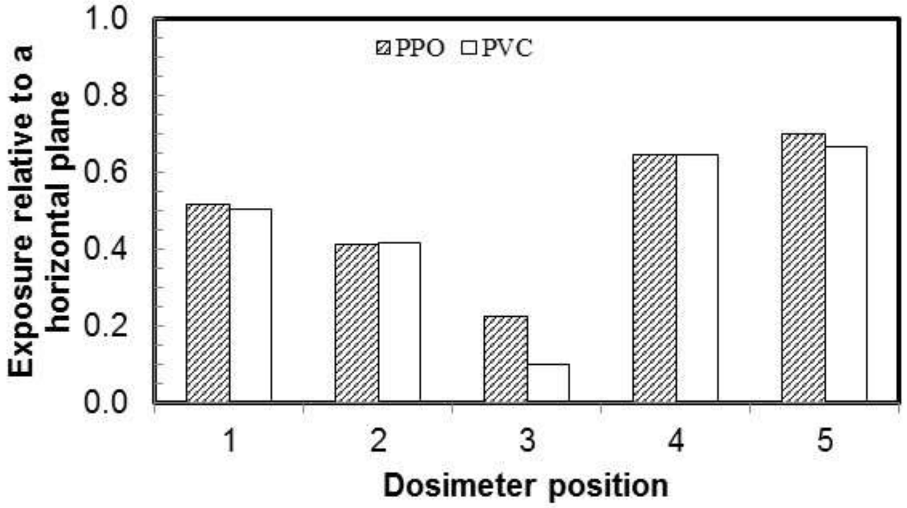

Figure 5: $UVBE_{plant}$ exposures at each leaf relative to that on a horizontal plane for the PVC dosimeters and for the cumulative exposures from six sets of PPO dosimeters.

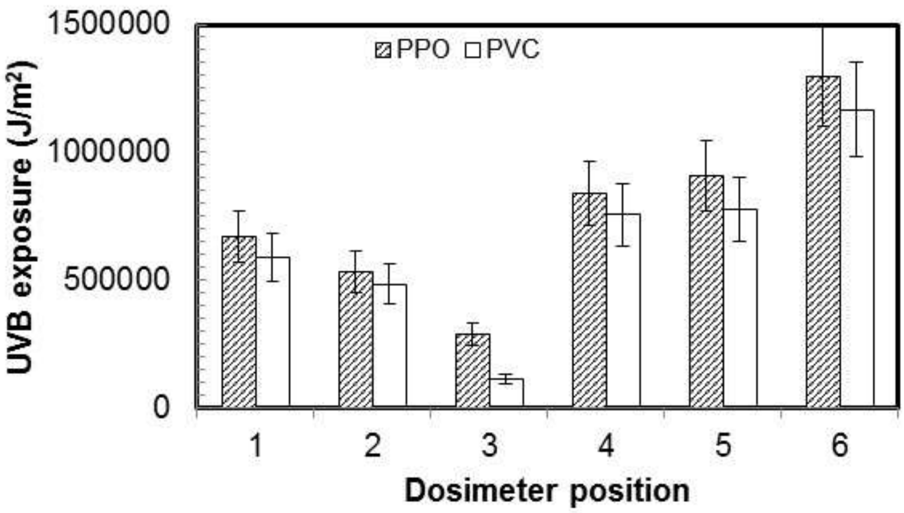

Figure 6: Comparison of the UVB exposures received by five selected plant leaves due to exposure to solar radiation for 30 days as measured by one set of PVC dosimeters and the cumulative exposures from six sets of PPO dosimeters. The sixth position is for the horizontal exposure. The error bars represent the errors associated with the exposure measurements with PPO and PVC dosimeters.