



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

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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 hardness 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., 2009). 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

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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 40°, increasing to 16% at 50° (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 ($UVBE_{\text{plant}}$) (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 $UVBE_{\text{plant}}$ exposures and UVB exposures, PVC dosimeters were fabricated from 16 μm thick PVC film in 3 cm \times 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 $UVBE_{\text{plant}}$ exposures evaluated over the long term exposure period. Forty four PPO dosimeters with a film thickness of 40 μm in a 3 cm \times 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 $UVBE_{\text{plant}}$ 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 $UVBE_{\text{plant}}$ 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 $\pm 6\%$ (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) (Fig. 1) to evaluate the $UVBE_{\text{plant}}$ 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 $UVBE_{\text{plant}}$ 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 (Fig. 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 ($UVBE_{\text{plant}}$) weighted with the plant damage action spectrum ($A_{\text{plant}}(\lambda)$) and the dosimeter effective UV ($UVBE_{\text{PVC}}$) (Krins et al., 2001):

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