

Characterisation and evaluation of a miniaturised polyphenylene oxide dosimeter

A dissertation submitted by

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Abstract

In light of the ever changing composition of the Earth's atmosphere and the consequences of ultraviolet (UV) radiation for the biological environment, it is important to be able to determine the specific ultraviolet radiation levels that reach plants and humans on the Earth's surface. Dosimetry is a technique that is commonly employed to measure UV exposures to an object or subject. Miniaturised dosimeters using polysulphone have previously been used to measure received surface exposures by plants and humans, for exposure periods of up to one day. Larger dosimeters using polyphenylene oxide (PPO) as the photoactive material have successfully recorded UV exposures for up to seven days. A combination of a miniaturised dosimeter with PPO as the photoactive material has been developed in this research. An examination of the miniaturised PPO dosimeter for: the dark reaction, repeatability of measurement, dose response and the cosine response was completed. Two field tests comparing change in absorbance measurements for both large and miniaturised dosimeters were also undertaken. The results show the miniaturised PPO dosimeter to have the same dosimeter characteristics as the larger dosimeter and to provide results in the field consistent with those of the larger dosimeters. Consequently the miniaturised PPO dosimeters can be employed to evaluate the biologically effective UV to plants and humans. Successfully characterising the miniaturised PPO dosimeters allows greater number of measurements and increased potential for a wide range of environments to be tested in a cheaper and more time and measurement efficient way. Current research indicates that the financial cost of damage caused by UVB is extensive. Costs are incurred due to skin cancer in humans and reduced crop yields. Development of methods that allow for greater accuracy in

recording specific radiation exposures will benefit society by providing information that enables action to be taken to reduce the future impact of UV radiation.

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Chapter 1

Literature Review

1.1 Introduction

The Sun is the major energy supplier for the Earth. The energy provided supplies food, warmth and power. The type of energy that actually reaches the Earth's surface can have both positive and negative impacts. Positive impacts for humans include its role in the Vitamin D production required for good health and for plants, and the important function it has in photosynthesis. Negative impacts include causing melanoma and eye problems in humans and retarding growth in plants.

The specific type of radiation known to cause these damaging effects is ultraviolet (UV) radiation, in particular UVB. There are a number of different factors that have an effect on the amount of UVB radiation that actually reaches the Earth's surface, among these are the compounds that occur in the atmosphere, a key component being ozone. Studies have shown that UVB radiation increases when there is a reduction in the level of atmospheric ozone. Monitoring of UV exposures is important in gaining a full understanding of the relation of UV to the biological environment.

A number of experts agree that stratospheric ozone depletion will have an impact on the level of UV that reaches the earth's surface (Bigelow et al. 1998; Cancer Council Australia 2007 - 09B; Horneck et al. 2006).

As stated previously UVB is seen as a major cause of skin cancer. The Cancer Council Australia (2007 - 2009B) reports that skin cancer accounts for 81% of all new cancers

diagnosed each year and that non melanoma skin cancer (NMSC) is the most common cancer in Australia. NMSC is also the most expensive in terms of diagnosis and treatment. Studies have shown that there is an increasing trend in Vitamin D deficiency among humans at present (Scragg et al. 2010; Vu et al. 2010). This could be a consequence of the fear of skin cancer and subsequent over prevention or avoidance of sun exposure (Holick & Jenkins 2003). At present it has been suggested that sufficient exposure for Vitamin D production can be received if the face, hair and hands of a moderately fair person are exposed for 5 minutes three times a week (Lucas & Ponsonby 2002).

UVB is only a small fraction (0.5%) of total solar radiation, (Reddy, Prasad & Singh 2010) however all living organisms are known to respond to UVB exposure. Plants are known to be very sensitive to UVB. Qi et al. (2010) states that, 'Nearly two-thirds of the 400 plant species and cultivars tested to date appear to be UV-B sensitive'. However photosynthetically active radiation (400 nm - 700 nm) is required for healthy plant physiology and growth (Teramura & Sullivan 1994). Biological weighting functions are key in determining the implications of ozone reduction. They can be used to calculate the increase in biological surface UV due to ozone reduction (Flint & Caldwell 2003).

The discussion that follows will give a general overview of solar UV and its divisions according to wavelength, followed by both the positive and negative effects of UV radiation for both humans and plants. A range of factors that influence surface UV levels will be discussed followed by a brief examination of the methods currently used for measuring these levels. Particular attention is given to the area of dosimetry as it is a method for localized measurement of UV exposures. Types and sizes of dosimeters will be covered, including the suitability of various dosimeters for different environments.

This project will investigate whether miniaturised dosimeters using polyphenylene oxide as the photo-active material can successfully be used as replacements for larger dosimeters, by testing the cosine response, dose response, reproducibility and comparison of UV measured in the field. Miniaturised dosimeters would allow an increase in the number of environments where dosimetry can be utilised.

1.2 Solar Ultraviolet Radiation

The main source of ultraviolet radiation is the sun, although UV radiation can also be produced from lamps or welders. UV radiation forms only a small part of the electromagnetic spectrum (EM) approximately 9.3% and of this only a portion will reach the Earth's surface (Webb 1998). The electromagnetic spectrum can be divided into sections that are usually defined by their respective wavelengths (Knight 2004). For our purposes the EM spectrum can be divided into ultraviolet radiation, visible radiation and infrared radiation as well as other areas (Figure 1).

Normal visible light falls between wavelengths of 400 nm and 700 nm. The UV wavelengths are in the region between 400 nm and 100 nm and can be further divided into three sections UVA (320 – 400 nm), UVB (280 – 320 nm) and UVC (100 – 280 nm). Wavelengths that are above 700 nm belong to the infrared section of the spectrum, however this is 'a rather loose definition, and there is no universality in the nomenclature' (Hecht 2002).

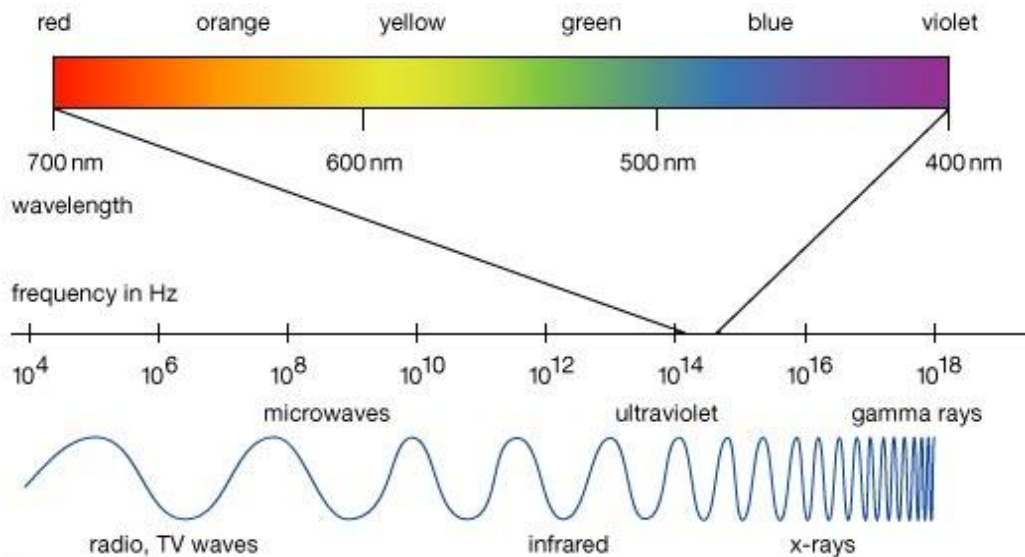


Figure 1 Electromagnetic spectrum (Merriam-Webster, Inc. 2006)

Definitions of the demarcation between UVA, UVB and UVC differ. The CIE (1999) report concluded that 'the upper limit of UV-B should remain at 315 nm', whereas Diffey (2002), while including this limit, states that the subdivisions are arbitrary and can differ depending on the discipline involved. As an example, environmental and dermatological photobiologists utilise a UVB range of 320 - 290 nm as in McKenzie et al. (2002) and Rafanelli et al. (2010).

The UV radiation that actually reaches the Earth's surface is made up of two types: direct and diffuse radiation. Direct radiation comes in a single direction straight from the sun. Diffuse radiation can come from a range of directions and is caused by the scattering that occurs as the radiation is dispersed as it travels through the atmosphere. The level of diffuse radiation increases as the wavelengths get shorter (Parisi & Kimlin 1997).

1.2.1 UVC

All three of the wavelength bands are present outside the earth's atmosphere. However the UV radiation with wavelengths below 290 - 295 nm does not actually reach the Earth's

surface. This part is usually absorbed by oxygen (O₂), ozone (O₃) and other atmospheric particles in the upper atmosphere. The variable components of the atmosphere influence the threshold wavelength that actually reaches the Earth's surface (Parisi, Sabburg & Kimlin 2004).

1.2.2 UVB

The shortest wavelength UV to reach the Earth is UVB. This high energy contributes to the fact that UVB elicits the greatest degree of biological response, although it accounts for approximately 1% of the UV emitted by the sun (Bohren & Clothiaux 2006). It takes only a few minutes for a response to occur, and this response can have important biological and chemical reactions. Biological responses include erythema in humans which can be linked to melanoma (Cancer Council Australia 2007 - 09A) and retarded plant height growth (Flint & Caldwell 2003).

1.2.3 UVA

UVA is at the edge of the visible spectrum. UVA is of a longer wavelength than UVB, and therefore a greater proportion of UVA (6 - 7%) compared to UVB (1%) reaches the earth's surface (Webb 1998). It has been established that UVA contributes to biological damage (Sicora et al. 2006; Sun Protection Programs Working Party 1996), although the damage caused is produced differently to that from UVB.

1.2.4 Biological Action Spectra

Action spectra are biological weighting functions (Horneck et al. 2006). An action spectrum is a method of showing the variation with wavelength of the biological response from a UV source. Various action spectra have been developed, and a selection of these are: the erythemal action spectrum (CIE 1987); the DNA damage action spectrum (Caldwell et al. 1983); and the plant damage action spectrum (Coohill 1989) (Figures 2 - 4). Each of these action spectra shows the relative effectiveness for producing a specific response (Flint, Searles & Caldwell 2004).

The action spectrum uses a comparative value between 0 and 1 to express its effectiveness. For the erythemal action spectrum wavelengths below 298 nm are assigned an effective value of 1 while other wavelengths up to 400 nm are assigned a relative value in comparison to this (Herman 2010).

The effects of solar UV irradiance can be estimated by combining the known amount of UV radiation reaching an object with the specific action spectrum for the object being tested. For a given action spectrum it can be seen that the longer the wavelength, the lower the sensitivity of the organism and the degree of biological effect. Given that UVA is some six times more prevalent than UVB (Webb 1998), it is possible that a larger dose of UVA than UVB may be received, thereby enhancing the biological effect.

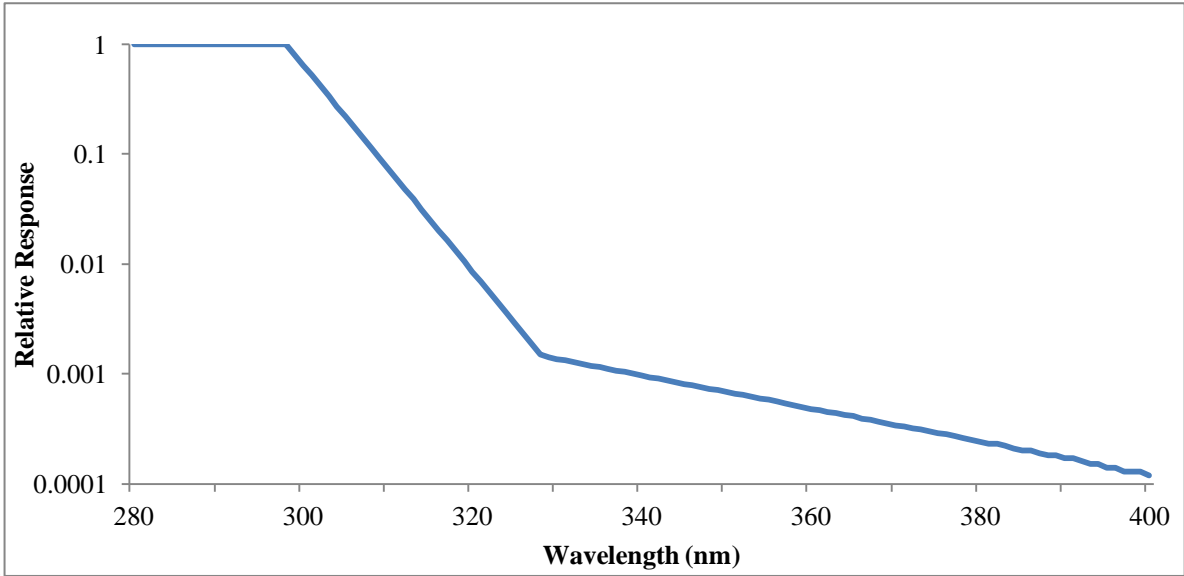


Figure 2 Erythral action spectrum (CIE, 1987)

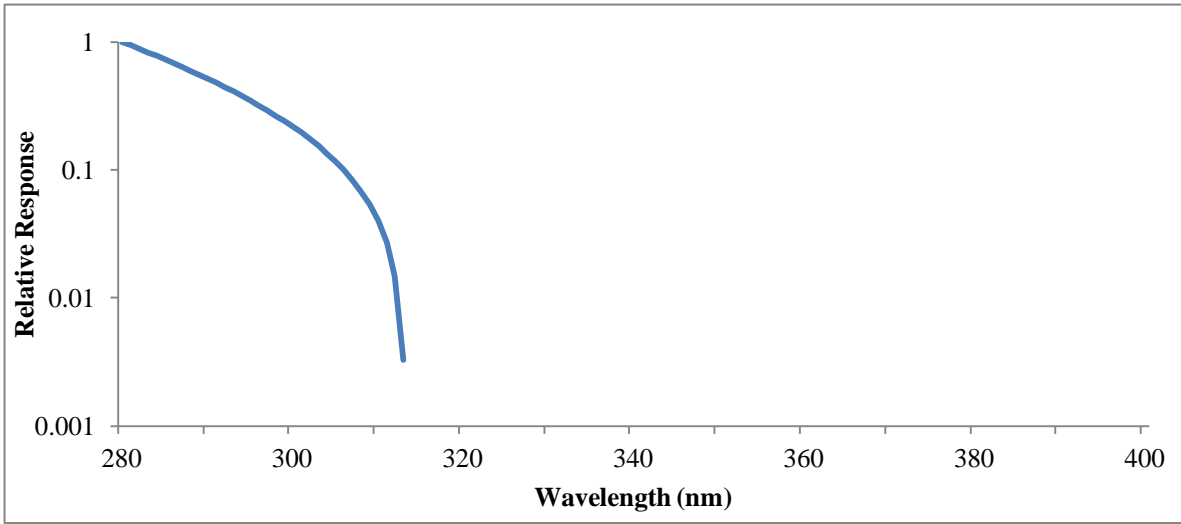


Figure 3 Plant damage action spectrum (Coohill, 1989)

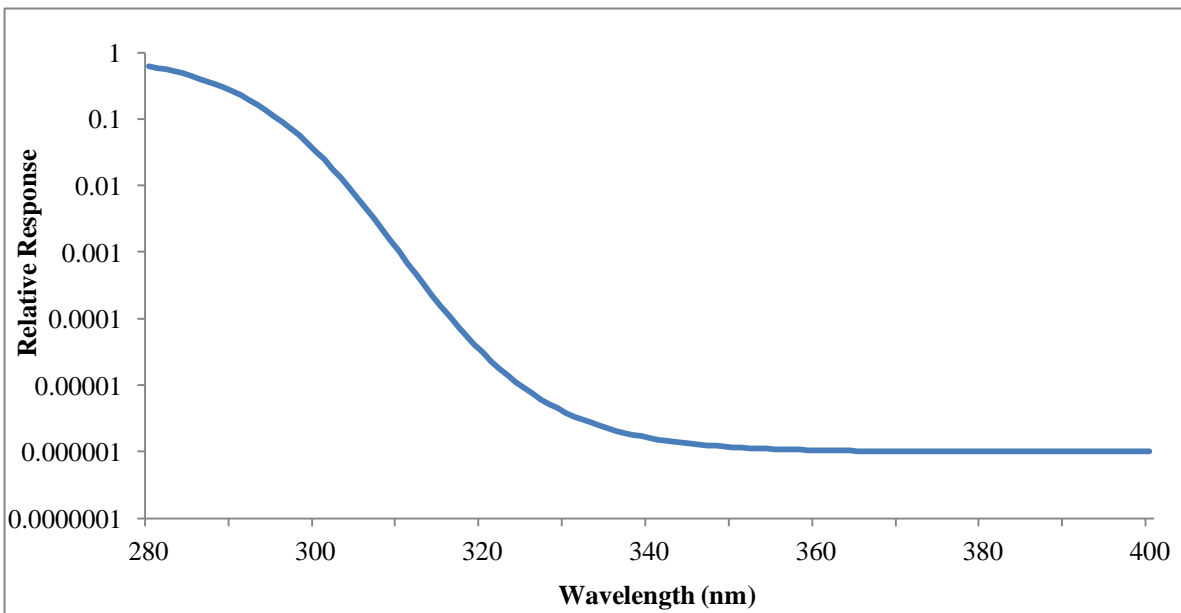


Figure 4 DNA damage action spectrum (Caldwell et al. 1983)

1.3 Effects of Solar UV Radiation

1.3.1 Hazards

It is well established that UV radiation exposure is the major factor in causing the development of melanoma and NMSC (Sun Protection Programs Working Party 1996). NMSC's include basal cell carcinoma and squamous cell carcinoma. UV radiation has also been shown to contribute to cataract formation and other eye damage. Other effects of UV exposure include photo aging, which includes damage such as loss of elasticity, mottled pigmentation, wrinkling and sagging of the skin (Webb 1998).

Australia has the world's highest rate of diagnosed skin cancer (Cancer Council Australia, 2007 - 2009B) with Queensland producing the highest incidence rate within Australia (McCarthy 2004).

The length of an individual exposure and long-term repeated exposures play different roles in each of the damaging effects. Melanomas are due to short severe UVB exposures while non-malignant damage is due to long term repeated exposures, possibly with UVA as a greater contributing factor (Sun Protection Programs Working Party 1996). The occurrence of non-melanoma skin cancers is thought to be associated with long-term cumulative exposure to UV radiation, while 'melanoma mutational subtypes are associated with UV radiation exposure at different life stages' (Lee-Taylor et al. 2010).

The use of UVB barrier sunscreen has been shown to prevent erythema but at this time has not been shown to prevent melanoma. The current recommendation for avoiding melanoma is to avoid exposure to the sun (Cancer Council Australia, 2007 - 2009B).

UVB is also known to cause biological damage to plants. One observed effect of UVB radiation in plants is the inhibition of height growth (Flint & Caldwell 2003). Another is 'brown sunburn spotting' (Hofman et al. 2010) on grapes. Harm caused to plants that is not easily observed includes damage to cell membranes, the organelles within the cells as well as the DNA within the cell nucleus. As a consequence of this UV exposure, crop yields and quality are negatively affected (Reddy, Prasad & Singh 2010).

1.3.2 Benefits

Although much has been stated about the known hazards of UV radiation as listed above there is far less research available on the positive benefits of UV, in particular to humans. The most important positive known effect of solar UV for humans is the production of Vitamin D. Up to 90% of Vitamin D created is produced as a consequence of the action of UVB on the skin (Lucas & Ponsonby 2002). The skin contains certain precursors which when stimulated by UVB undergo a number of processes resulting in the production of Vitamin D.

Healthy production and maintenance of the skeletal structure rely on the availability of Vitamin D (Holick, 2001). Vitamin D in sufficient quantities has been identified as preventing diseases such as rickets and osteoporosis and other bone disorders and may help some forms of cancer. Holick and Jenkins (2003) state that the benefits of sunlight include improved bone, cellular, organ, autoimmune and mood-related health.

Recent research by Vu et al. (2010) has shown that up to 51% of office workers tested have insufficient Vitamin D by the end of winter. Levels of Vitamin D were shown to have a

significant seasonal variation within individuals (Kimlin 2010) that however did not show a relationship to the individuals' reported sun exposure.

UVB radiation has been shown to have some positive effects on plants; Holmes (2006) has found indirect effects to include a reduction of certain fungal pests and a reduction of insect attacks. Direct effects found are the development of phytoprotective screening pigments and antioxidants which can give the plant an adaptive advantage to increasing UVB.

1.4 Main Influences on Levels of Surface UV Radiation

1.4.1 Absorption and Scattering due to Atmospheric Molecules

Ozone (O₃) is a natural stratospheric component of the earth's atmosphere, and plays an important role in protecting the earth from damaging solar radiation. No UVC penetrates the Earth's atmosphere to finally reach its surface; it is all absorbed by stratospheric ozone and oxygen (Barnard & Wenny 2010). Some UVB is also absorbed by ozone. There is a link between the wavelength of the incoming radiation and the absorption level that the ozone achieves.

The introduction of artificial manmade chemicals into the atmosphere influences ozone production. Any introduced chemicals may preferentially combine with the elements or particles at any stage in the process, thus preventing either the ozone formation or the absorption of UVC. Known examples of chemicals which do this damage are CFC's or bromine compounds (Mettlin 2001). Studies have shown that for each 1% drop in ozone there is a 2% increase in surface UVB (Mettlin 2001), and a localised increase in UVB of

14.6% occurs when there was a 4.6% decrease in ozone levels (Kimlin, Parisi & Mainstone 2000).

Rayleigh scattering is the type of scattering that occurs when the molecules in the atmosphere are smaller than the wavelength of the incident light. This means there is more scattering of shorter wavelengths than the longer wavelengths (Barnard & Wenny 2010), and consequently more UVB scattered than UVA.

1.4.2 Absorption and Scattering due to Aerosols

Aerosols are small particles suspended in air. Some examples of aerosols are sulfate haze, soot, dust and seasalt (Madronich et al. 1998). Aerosols contribute to a type of scattering known as Mie scattering. This occurs when the particles are equal to or larger than the wavelength of the incident light (Barnard & Wenny 2010).

The interaction between a particle and incoming light/photon can result in a number of outcomes. '...particles can absorb it completely, absorb and reradiate it at a lower, longer wavelength, or completely reflect it' (Barnard & Wenny 2010). Thus the photon's energy, direction or both can be altered significantly which would change the amount and type of energy reaching the earth's surface.

1.4.3 Albedo from the Surface and Surroundings

Albedo is the term given to the proportion of light that is reflected away after it hits a surface. Albedo can be given as a ratio between the upwelling irradiance and the downwelling irradiance (Bohren & Clothiaux 2006).

$$A = I_r/I_i \quad (1.1)$$

where A is albedo, I_r is the reflected irradiance and I_i is the incident irradiance.

A surface of albedo $A = 1$ would *reflect* all incoming radiation and a surface of albedo $A = 0$ would *absorb* all incoming radiation. Most of the Earth's albedo is caused by clouds reflecting energy away from the Earth. The main albedo categories for the earth's surface are vegetated areas, bare soil, human constructions and these same surfaces covered by ice/snow (Lenoble 1993). UVB exposures can change with these differing geographical areas (McKenzie, Kotcamp & Ireland 1996) and (McKenzie et al. 2002).

1.4.4 Altitude above Sea Level

Higher altitude sites generally have higher UV levels than lower altitude sites, in part due to the decreased atmospheric pressure and lower levels of scattering that occur at higher altitudes. At some high altitude sites the UV levels may be further increased due to the high albedo of snow.

The effect on UV levels due to altitude can be expressed as follows and is known as the altitude effect (AE) (Blumthaler, Ambach & Ellinger 1997).

$$AE = \left[\frac{I_H}{I_L} - 1 \right] \times \frac{\Delta A}{1000} \times 100\% \quad (1.2)$$

where AE = Altitude Effect

I_H = irradiance at high altitude

I_L = irradiance at low altitude

ΔA = difference in altitudes in metres

1.4.5 Clouds

Clouds generally cause a decrease in surface UV levels from those recorded under clear sky conditions. However, under some cloud conditions the surface UV can actually increase, due to scattering and reflectance from the lower sections of the cloud back to the Earth's surface (Parisi, Sabburg & Kimlin 2004). The optical depth of the clouds and the amount of sky covered are factors that alter the surface UV levels (Parisi, Turnbull & Turner 2007). The type of cloud cover is also an important influence, with cumulus cloud having been shown to increase UVB levels by up to 25% (Roy, Gies & Toomey, 1995).

1.4.6 Solar Zenith Angle

Solar Zenith Angle (SZA) is the angle between the local vertical and the angle of the sun when measured at the object. As there is less atmosphere and possibly less pollution to travel through at smaller SZA's, there may be increased levels of UV radiation at smaller SZA's.

The solar noon hour will have the lowest SZA's and, given clear skies, the daily peak surface UV irradiance values due to the minimum atmospheric path length for any particular day (Wenny, Saxena & Frederick 2001).

1.4.7 Solar Irradiance at the Top of the Atmosphere

The Earth has an elliptical orbit around the sun, resulting in a regular seasonal change of distance between the Earth and Sun. This changing distance can result in a variation of the

amount of UV that actually reaches the Earth's atmosphere by $\pm 7\%$ (Seidlitz & Krins 2006). Top of atmosphere measurements are important in determining the base point for calculating the attenuation of UV as it travels to the Earth's surface.

1.5 Methods for Measuring UV

Irradiance is the term used to identify the intensity of the radiant power on a unit area of a surface. This is normally measured in Watts per square metre (W/m^2). Erythemal exposure can be determined in units defined as the amount of UV radiation that is required to produce a barely perceptible reddening of the skin (erythema), apparent 24 hours after exposure, in people with a skin type that always burns and never tans (Diffey 1992). This erythemal exposure is the minimum erythemal dose (MED), approximately $200 \text{ J}/\text{m}^2$. However, due to differences in skin types a standard erythemal dose (SED) is used, which is $100 \text{ J}/\text{m}^2$ of radiant erythemal exposure (Diffey 2002).

The instruments used for measuring irradiances and exposures include sunphotometers, spectroradiometers, broadband radiometers and UV dosimetry.

1.5.1 Sunphotometer

A sun photometer is an electronic device that measures direct sunlight over a narrow range of wavelengths. Some sun photometers use 'interference filters' with a narrow passband of several nanometres to limit the amount of light reaching a photosensitive detector (Herman 2010).

As sun photometers are supposed to measure only *direct* sunlight, the detectors are housed inside a case so that sunlight can enter only through a small hole. With a larger aperture the

detectors would see both direct sunlight and diffuse light. The measurement of direct UV in narrow wavebands allows determination of the atmospheric O₃ and aerosols (Herman 2010).

1.5.2 Spectroradiometer

A spectroradiometer is used to measure the distribution of UV energy with wavelength. The apparatus consists of entrance optics, monochromator, detector, amplifier and a control and data acquisition unit (Seidlitz & Krins 2006). The input optics depolarise the incoming radiation and should also have a good cosine response, where the receptor takes into account the angular distribution of the incident radiation. Radiation is prevented from moving straight to the diffuser by a baffle (Webb 1998). The diffuser within the input optics scatters the radiation before it exits to the monochromator. A monochromator eliminates light outside the wavelength band being measured by employing gratings. The detector samples the light over the waveband for each of the wavelengths being measured. Calibration of spectroradiometers is very important and they need to be recalibrated both for wavelength and irradiance before each measurement session. The advantage of spectroradiometers is that they allow specific selection of the wavelength bands of interest.

1.5.3 Broadband Radiometer

A radiometer is an instrument that measures the intensity of electromagnetic energy sources in radiometric units such as Watts/m² or Watts/cm². Broadband refers to the ability to measure over a broad spectrum of wavelengths (Seidlitz & Krins 2006). A sensor produces a measurable electric current when electromagnetic radiation at any frequency is absorbed.

The Multi-Filter Rotating Shadowband Radiometer is a field instrument that simultaneously measures global, diffuse and direct normal components of spectral solar irradiance (Yankee Environmental Systems Inc 1996). An automated shadowband is used to alternately shade and then expose the entrance aperture of the instrument which allows for the measurement of the three components. The global and diffuse measurements can be determined directly from measured data with the direct component being calculated by subtracting the diffuse from the global components (Harrison, Michalsky & Bernd 1994).

Some shadowband radiometers can make spectral measurements at selected wavelengths. Wavelengths are usually chosen to optimise the determination of optical depths of water vapour, aerosols and ozone. The broadband channel measures the total solar irradiance.

1.5.4 UV Dosimetry

Diffey (1987) stated the importance of obtaining accurate and reliable dosimetry of solar UV radiation, particularly in the UVB region, to help obtain an understanding of the relationship between sunlight exposure and the photobiological effects it causes.

Dosimeters are small portable devices capable of recording UV exposures and they enable the measurement of exposures to plants and humans. In order to do this, dosimeters have to be much smaller than spectroradiometers and sunphotometers. Their small size allows for a number of different locations on the subject to be measured at the same time (Webb 1998). The dosimeters should be made in such a way that they do not interfere with the normal activity of the subject being tested when they are in place, but still be able to record UV exposures in a way that is relevant to the actual UV that is experienced by the plants or

humans. Different types of dosimeters currently in use are biological, chemical and electronic.

1.5.4.1 Chemical Types

A number of different chemicals have been used in the manufacture of UV dosimeters, some respond only to UVA wavelengths, others only to UVB, and some materials respond to both the UVA and UVB wavelengths. Chemical dosimeters mimic a specific biological response that is similar to the action spectrum required for the specific research project.

One of the most common active materials used is polysulphone (PS) (Diffey 1987). It is a photo-active chemical and has been used because there is 'an approximation of the spectral response to the erythral action spectrum' (Parisi, Sabburg & Kimlin 2004). Polysulphone dosimeters have been very useful for short term exposures but polysulphone appears to reach saturation levels, a maximum change in absorbance, at about one day. At certain times of the year it may reach saturation before the end of the day.

Another chemical used for UV dosimetry is polyphenylene oxide (PPO) formulated by Davis et al. (1976). Like PS, PPO has a response spectrum in accord with the erythral action spectrum for wavelengths in the UV range between 290 and 340 nm, and with a minimal response to UVA at 340 nm (Lester et al. 2003).

In contrast to PS however, the exposure level required for PPO to reach saturation is much higher (Schouten, Parisi & Turnbull 2010). This allows PPO dosimeters to be used to measure exposures for more than one day, with up to 7 days measurement recorded on one

dosimeter (Parisi, Schouten & Turnbull 2010), depending on seasonal and geographical conditions.

The dosimeters consist of a frame supporting a layer of PPO or PS film of 40 µm thickness. This thickness has the greatest change in optical density at 330 nm for PS (Diffey 1989) and at 320 nm for PPO, it is also the most robust and easiest to cast (Lester et al. 2003). Using a spectrophotometer with a special mounting, the change in absorbance of the film can be determined, by measuring the absorbance both before and after exposure.

1.5.4.2 Biological Types

Biological dosimeters are made of micro organisms, which if exposed to UV should respond in a way that reflects the action spectrum that is being tested. Examples of the biological active components in the dosimeters are, *E. coli* in suspension or spores of *B. subtilis* in suspension or in a biofilm (Horneck et al. 2006). Biological dosimeters are likely to incur changes through atmospheric conditions as well as UV exposure when used in an uncontrolled environment.

1.5.4.3 Electrical Types

Electronic dosimeters have been developed recently. The dosimeters used in studies in New Zealand (Allen & McKenzie 2010) measured 35 mm diameter x 10 mm and weighed approximately 20 g, being worn with a velcro wrist strap. These electronic dosimeters recorded measurements at 8 second intervals and stored up to 12 days of data. The sensor used has a spectral response matching the erythemal action spectrum. Although electronic

dosimeters can be reused they are more costly than the other forms and the large amount of data collected can make meaningful interpretation difficult (Liley et al. 2010). A study by Seckmeyer et al. (2011) found that each electrical UV sensor had to be calibrated separately to a reference instrument which was a time consuming and costly process.

1.5.4.4 Sizes

Dosimeters are necessarily of a small size so they can be easily attached to objects such as plants, clothing etc. and at a variety of angles so that true and relevant exposures can be measured. The small size and light weight of the dosimeters means there is no gravitational effect on plants to disorient the location of the leaves (Parisi et al. 2010b). Small sizes also mean that they are easily worn by people and multiples can be placed on the same object.

A standard size dosimeter used in previous work measures 30 x 30 mm with an average weight of 0.7 g (Parisi et al. 2010a). Even this small size was found to be too heavy for some plants or too large to sit flat against some measurable surfaces for example; angles around a human face (Downs & Parisi 2007).

A dosimeter of smaller size has recently been developed for PS dosimeters that measure 15 x 10 mm and these miniaturised dosimeters have an average weight of 0.03 g (Parisi et al. 2010a).

The miniaturised dosimeters are made of lightweight cardboard frames with an aperture of 6 mm diameter. This aperture is covered with a layer of PS film of approximately 40 μm thickness. Miniaturised dosimeters can increase the number of environments in which they

can be used (Parisi et al. 2008). Miniaturisation of PPO dosimeters has not been completed at this time.

1.6 Current Situation and Future Directions

The known effects of solar UV and its growing effects due to climate change emphasises the importance of a complete understanding of the solar radiation environment in order to be able to accurately record UV levels received by biological specimens but also to be able to predict expected UV levels accurately. This would allow appropriate recommendations to be made for UV exposures to humans with regard to the risks and benefits. Additionally plants with UVB exposure tolerance could be identified more easily.

Miniaturising dosimeters can increase the number of environments in which dosimeters can be used (Parisi et al. 2008). Miniaturisation of PPO dosimeters needs to be done to assist in this data gathering. The smaller dosimeters would be light weight, cheaper to make than the present size, allow for more sites to be tested concurrently, can remain in-situ longer and with PPO as the photo-active material it is an ideal media for testing of the plant damage action spectrum and the erythemal response spectrum.

Once the miniaturisation has been achieved, the cosine response, dose response and reproducibility need to be tested to ensure the miniaturised dosimeters give the same quality of results as the larger dosimeters.

1.7 Conclusion

It has been shown from the literature that UVB exposure is harmful to both human and plant biology. The level of this biologically effective radiation that reaches the Earth's surface can change according to various climatic or atmospheric conditions. UVB exposure can be measured in a number of ways, from the permanently fixed devices such as spectroradiometers to the small and portable such as dosimeters.

Dosimetry can be used to measure dosages received by individuals, or plants in their natural environment without impacting on the orientation or actions of the subject being measured. Small measuring devices such as the miniaturised dosimeters have a place in recording biological changes which now appear to be more prevalent during a time of accelerating climate change. The PPO material in the miniaturised dosimeter to be developed with its relatively long life span means that exposures can be measured for up to a week without concern that the material will reach saturation. Longer exposures and smaller dosimeters also allow for less material to be used, a cost saving that could permit more studies to be done. As PPO has a response spectrum in line with the plant damage action spectrum and the erythemal response spectrum it is an ideal material for use in these miniaturised dosimeters.

1.7.1 Research Project

1.7.1.1 Research Hypothesis

The miniaturised PPO dosimeters display the same characteristics as the large PPO dosimeters when measuring erythemal and plant damaging UV exposures.

1.7.1.2 Research Objectives

The object of this project is to investigate whether miniaturised polyphenylene oxide dosimeters can measure erythemal exposures and plant damage effective UV exposures and have a cosine response and a reproducibility which are in line with those found previously for larger dosimeters.

The objectives of the project are:

- To characterize the properties of the miniaturised dosimeters and compare these with the properties of the current size dosimeters. Properties being measured are cosine response, dose response and reproducibility;
- To evaluate the miniaturised dosimeters for measurement of erythemal UV in the field; and
- To evaluate the miniaturised dosimeters for measurement of plant damage UV in the field.

Chapter 2

Methodology

2.1 Overview

Miniaturised PPO dosimeters were tested in this research to see if they have the same properties and perform in the same way under various conditions as the larger PPO dosimeters. PPO has been used in dosimeters previously (Davis et al. 1976, Lester et al. 2003, Berre & Lala 1989) and it has been established that using PPO as the photoactive material allows for long term exposures (Schouten, Parisi & Turnbull 2007, 2009) when compared to polysulphone. PPO can be used for five to seven times as long which would be around seven days of exposure on a horizontal plane at a sub-tropical site (Parisi, Schouten & Turnbull 2010).

Studies have been done using dosimeters to determine the UV exposure received by a human, but there is a limitation due to the restricted number of measurements that can be obtained using large dosimeters placed on unprotected skin surfaces (Siani et al. 2009, Stanton et al. 2003).

The miniaturised size of the dosimeter is desirable as it is flexible enough to fit over curved surfaces, such as the contours on the face, it is lighter than conventional dosimeters, thus not changing the orientation of plant leaves being tested (Parisi et al. 2010a) and the size also allows for a greater density to be used on the test subject or object (Downs & Parisi 2012).

To determine if the miniaturised dosimeter would be an appropriate replacement for the large dosimeter, tests were carried out to compare the properties of both sizes of dosimeters under

the same conditions. This was done by testing the variation in absorbance at a wavelength of 320 nm. This is the wavelength at which the maximum change in optical absorbance has been shown to occur for PPO (Schouten, Parisi & Turnbull 2007). The two sizes of dosimeters were tested concurrently for:

- The dark reaction which is a measure of the change of absorbance after exposure when the post exposure measurement is delayed for a varying number of hours. This determines whether any change occurs in the PPO if it is stored before being measured.
- Repeatability to ensure that dosimeters given the same exposure would return similar changes in absorbance.
- Dose response which shows how the change in absorbance of the dosimeters varies with increasing exposure levels.
- Comparability in field tests to ensure that the miniaturised dosimeters show a change in absorbance comparable to the large dosimeters when placed in the same physical location and exposed for the same time period.

Additionally, the cosine response was tested for the miniaturised dosimeters, to show how the change in absorbance levels varied when the angle of incidence of the radiation was changed.

All measurements were performed in Toowoomba, Queensland (27° 33' S 151° 55' E, elevation of 691 m).

2.2 Materials and Equipment

2.2.1 Construction of Dosimeters

Previous work has been done with miniaturised dosimeters using PS as the photoactive material (Downs & Parisi 2007). Although PS has been the predominant photoactive chemical used in dosimetry research, PPO film has been recognised as an appropriate material for long term solar exposure (Lester et al. 2003, Berre & Lala 1989), long term meaning cumulative exposure of a period up to seven days (Parisi, Schouten & Turnbull 2010). Work has also been done using the large size dosimeters with PPO as the photoactive material (Schouten, Parisi & Turnbull 2008, 2009).

This project used both large and miniaturised dosimeters made with PPO. Lester et al (2003) have shown that the PPO can be used successfully as an erythemal UV dosimeter. It has also been shown that PPO can be weighted against the plant damage action spectrum as there is a similar response sensitivity within the UVB waveband, thus making PPO an acceptable choice for a dosimeter to measure plant damage effective UV (Parisi et al. 2010a).

The PPO film was cast at the University of Southern Queensland, Toowoomba using a mix of PPO in powder form (General Electric Plastics, USA) with chloroform as a solvent. The PPO sheets had a thickness of 40 microns as this was shown to be the thickness with the best level of tensile durability in previous studies (Lester et al. 2003).

In making the large dosimeters, a PVC holder was used with an area of 3 cm x 3 cm, the central opening measuring 1.2 cm x 1.6 cm. The PPO sheet was cut into 2 cm x 2 cm squares

that were attached to the holder with electrical tape. The dosimeters weighed an average of 0.6 g.

Initially the miniaturised dosimeters were made with a flexible cardboard frame measuring 1 cm x 1.5 cm with a circular hole of 0.6 cm diameter (Downs & Parisi 2007). The thin cardboard was found to be not robust enough for repeated use, so the frame material was changed to a thin flexible plastic and new dosimeters made to the same dimensions (Figure 5). The PPO was cut into sections 1.0 cm x 0.8 cm and attached to the frame using waterproof scotch tape as this is thinner than electrical tape. These dosimeters have a significantly reduced weight of 0.05 g.

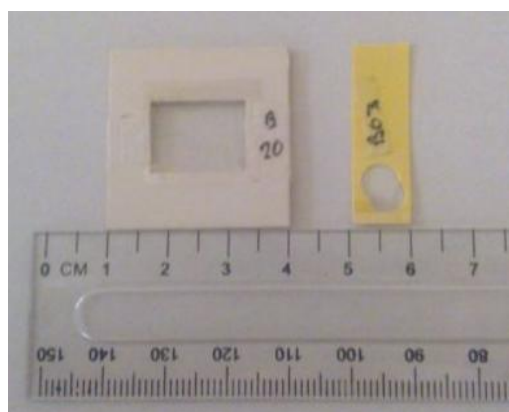


Figure 5 Comparative size of large and miniaturised dosimeters

2.2.2 Other Equipment

2.2.2.1 Spectrophotometer

Once the dosimeters were made and numbered the optical absorbance was measured using a spectrophotometer (UV-1601, Shimadzu & Co, Kyoto, Japan) (Figure 6). The spectrophotometer measures the intensity of the transmitted UV radiation by comparing the

transmitted irradiance to a reference beam of the same wavelength that has not passed through the PPO film. The spectrophotometer has an error of 0.004% (Shimadzu 1997). The spectrophotometer has a rotating mount (Figure 7) to hold the larger dosimeters and using this, each large dosimeter was measured at four points. Using four separate points improves the accuracy of the measurements as it allows for any variations in thickness of the photoactive material or changes that may have occurred on the surface. The mean of these four measured values is used for all subsequent calculations to determine UV exposure through calibration. This procedure is followed for all the subsequent testing for both sizes of dosimeters.



Figure 6 Spectrophotometer for measuring the absorbance of the dosimeter

A special holder was manufactured for the miniaturised dosimeters; this holder can be attached to the mount for the large dosimeters (Figures 8 and 9). The holder has a thin slot that the dosimeter is inserted into to keep it in place, if electrical tape was used to hold the PPO in place the miniaturised dosimeters were too thick to fit in the slot, so instead scotch tape was used. The miniaturised dosimeters were also measured at four separate points to ascertain the average absorbance for each dosimeter. To provide relevant information on the photodegradation of the PPO the dosimeters were measured for the optical absorbance both

before and after exposure. At the time of reading the absorbance in the spectrophotometer each dosimeter was inspected to ensure the film was free of marks before measurement.

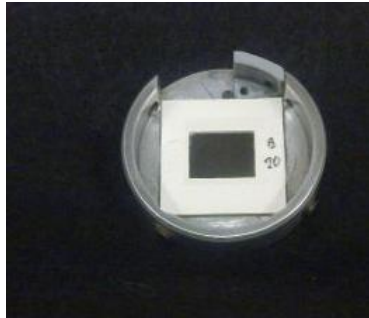


Figure 7 Large dosimeter in mount



Figure 8 Miniaturised dosimeter in holder attached to mount



Figure 9 A miniaturised dosimeter in the spectrophotometer prior to being measured

2.2.2.2 Scanning Spectroradiometer

Two different Spectroradiometers were used in the research as follows:

Fixed Spectroradiometer

The data collected by a scanning spectroradiometer (Model DM300, Bentham Instruments, Ltd., Reading, UK) was used in calibrating the PPO dosimeters by comparing the change in

optical absorbance of the dosimeter with the spectral measurements. This instrument is permanently located in an environment controlled box on the G block roof at the University of Southern Queensland (USQ). This spectroradiometer is programmed to scan the global UV every 10 minutes from dawn until dusk.

Transportable Spectroradiometer

The other spectroradiometer (Model DMc150, Bentham Instruments Ltd., Reading, UK) is a transportable instrument which was used in the laboratory to check the irradiance emitted by the solar simulator. The irradiance scans can be done with a range of different parameters as required using a sensor with a fibre optic link attached that is connected to the spectroradiometer.

Both instruments are double grating scanning spectroradiometers, which are regularly calibrated for wavelength and irradiance to a mercury lamp spectral lines and a quartz tungsten halogen lamp calibrated to the standard at the National Physical Laboratory, UK.

2.2.2.3 Solar Simulator

The UV solar simulator (model 15S, Solar Light Co., PA, USA) (Figure 10) provides an artificial source of UV radiation, that approximates the solar UV spectrum and was used as an approximately collimated UV source during the cosine response test. The diameter of the beam emitted can be adjusted so that it matches the size of the dosimeter aperture. The irradiance output was measured using a transportable spectroradiometer (details above).



Figure 10 Solar simulator that provides an artificial source of UV radiation.

2.2.2.4 Biometer

A Biometer located at USQ was used to measure solar erythemal UV exposures. The Biometer (model 501 UV-Biometer, Solar Light Co., PA, USA) has a spectral response that approximates the erythemal action spectrum and measures the erythemal exposure in units of MED. The Biometer is set to automatically record the erythemal UV exposure for every five minutes.

2.2.2.5 IL1400 Broadband Meter

The primary on site UV radiation measurement instrument used in these tests was the IL1400 broadband meter ('A' Series, International Light, Newburyport, MA, USA). This instrument is able to integrate UVB exposures over time thus allowing the calibration of the PPO dosimeters over extended time periods. The meter was fitted with a waterproof detector (SUD240, International Light) with a UVB filter (UVB1 phototherapy filter, International Light Inc.). This restricts the IL1400 broadband meter to only respond to UVB wavelengths.

2.3 Characteristics of Dosimeter

2.3.1 Cosine Response

Two components of solar UV reach the surface of the object being tested; (in this case dosimeters) these are the direct and diffuse components. Direct being the straight path from the sun and diffuse being the scattered component, approaching from many different angles. The dosimeter needs to be tested for its response to different incident angles of irradiance, the cosine response. It is important that the cosine response of the miniaturised PPO dosimeter is tested as variations in cosine response have been shown to add errors of up to 15% in the recorded irradiance (Webb 1998). Ideally the cosine response of the dosimeter should follow the curve of the normal cosine function, with the difference between the two being the degree of error in the cosine response.

The cosine response allows for the difference in recorded levels of irradiance if the incident beam is not normal to the surface. For angles other than normal the correction formula is $I \cdot \cos\theta$, where θ is the angle measured between the incident beam and the normal and I is the irradiance (Parisi, Sabburg & Kimlin 2004).

In order to check the cosine response of the miniaturised PPO dosimeters, dosimeters were exposed to a collimated UV source in a controlled environment with constant temperature of 21° C. Incident angles tested ranged from 0° to 70° in 10° increments. The source used was the solar simulator (as specified above). The irradiance of the emitted beam at the dosimeter location was measured from 280 nm to 400 nm using the transportable scanning spectroradiometer both before and after exposure of the dosimeter and the change in absorbance of each dosimeter was determined in the spectrophotometer. An initial test over

a five hour period with one dosimeter measured every hour at an incident angle of 0° was used to determine a minimum exposure time. This test established that the dosimeters used to measure angular response for angles greater than 0° degrees needed to be each exposed for a period of three hours. A plane mirror was used in place of the dosimeter in order to determine 0° by aligning the reflected beam with the incident beam. Subsequent angles were measured from this path.

A dose response equation for the solar simulator was determined by plotting cumulative exposure versus time at an incident angle of 0° . A trend curve for this plot gives the exposure equation of:

$$UV_{Tot} = 79920x^3 - 13008x^2 + 16509x \text{ J/m}^2 \quad (2.1)$$

where x is the change in dosimeter absorbance and UV_{Tot} is the UV exposure from 280 nm to 400 nm.

Normalisation of the response of the dosimeters at each angle was calculated by using the following equation:

$$R_N = \frac{UV_{Tot}(\theta)}{UV_{Tot}(0)} \quad (2.2)$$

where $UV_{Tot}(0)$ is the exposure measured at an angle of 0° and $UV_{Tot}(\theta)$ is the exposure measured for the angle being measured.

The cosine error was determined by comparing the normalised response to the cosine function.

2.3.2 Dark Reaction

Chemical film dosimeters such as PS and PPO are known to continue to change in optical absorbance when stored after exposure (Davis et al 1976). The dark reaction looks at this post exposure behaviour of the dosimeters. This is done by measuring the pre exposure absorbance for each dosimeter and then measuring the post exposure absorbance after differing periods of time.

Fifteen dosimeters of each size were made and their pre exposure absorbances (A_b) were measured. All the dosimeters were exposed to solar UV for six hours at the same time and under the same conditions.

These dosimeters were then removed from the irradiance source and the post exposure absorbance was measured straight away to allow calculation of the change in absorbance after no storage time (ΔA_0). The dosimeters were then stored in a UV light free environment for one hour before being measured again. They were then returned to the light free environment and only removed to be measured again after 24 hours following the initial removal from the irradiance and finally measured again seven days after being removed from

the UV source. For each time (t), the change in absorbance (ΔA_t) was calculated as:

$$\Delta A_t = A_t - A_b. \quad (2.3)$$

where A_t is the absorbance following storage for a given time. The amount of dark reaction after a given time was calculated as:

$$\frac{(\Delta A_t - \Delta A_0)}{\Delta A_0} \times 100 \% \quad (2.4)$$

2.3.3 Reproducibility

A specific test was done to determine the variance in the change of absorbance (ΔA) for each size of dosimeter. Fifteen dosimeters of each size were employed. Variance in the change of absorbance can be ascribed to the composition of the PPO itself as the manufacture of PPO can result in variations in thickness of the material and in distribution of the photoactive materials.

The dosimeters were exposed to solar UV for an eight hour period at the same time and under the same conditions. Each of the dosimeters was measured at four points before exposure and after exposure. The average of each of the four points was taken to determine the average change in absorbance for each dosimeter.

2.3.4 Calibration

A calibration curve is required that links the gradual changes in the optical absorbance of the PPO dosimeter to the measured exposure. As the response spectra of the IL1400, the PPO

and the Biometer are different; the calibrations against each other have relevance only for the source spectrum and the season in which the calibration is done (Turnbull & Parisi 2010, Schouten, Parisi & Turnbull 2010).

Before UV dosimeters are able to be used in the field independently they still require calibration to the UV spectrum. In this case separate calibrations are required for the erythemal action spectrum and the plant damage action spectrum.

Two different calibrations are required, one which calibrates to the erythemal action spectrum and another which calibrates to the plant damage action spectrum. Therefore the dosimeters used in this research were calibrated as per the process in Figure 11:

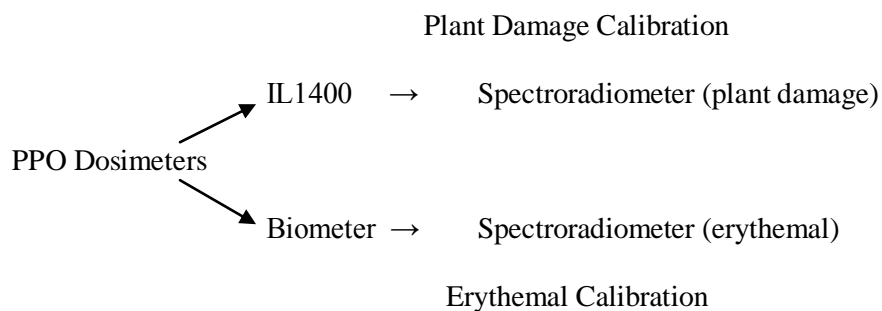


Figure 11 Diagram outlining the calibration process

For solar erythemal UV calibrations of the PPO dosimeters, the fixed scanning spectroradiometer was used in conjunction with the continuously operating Biometer. Both pieces of equipment are located on the G block roof (USQ). The software for the spectroradiometer allowed integrations of total UV, UVB and erythemal irradiances to be

calculated, in the appropriate units, for the dates and times required. The Biometer software is set up so that it can produce integrated erythemal UV exposure information at each five minute interval.

The Biometer was calibrated directly to the spectroradiometer for erythemal exposures on a cloud free day in each season. For the pilot study carried out in winter this calibration had previously been done (N Downs 2012, pers. comm., 5 Jan.). The summer and autumn plant damage and erythemal calibrations were carried out as part of this research project.

The plant damage action spectrum covers the wavelength range 280 nm to 313 nm and the spectroradiometer data has to be weighted to this spectrum before calibration using the formula:

$$UV_{plant} = \sum_{280}^{313} S(\lambda)A(\lambda)\Delta\lambda \quad W/m^2 \quad (2.5)$$

where $A(\lambda)$ is the plant damage action spectrum, $S(\lambda)$ is the spectral irradiance recorded by the spectroradiometer and $\Delta\lambda$ is the wavelength interval, in this case 0.5 nm. The weighted spectroradiometer data were then integrated for the wavelength range of 280 nm to 313 nm for each 10 minute interval and multiplied by the time interval for conversion to J/m^2 .

Data from the IL1400 were manually recorded at 10 minute intervals corresponding to those automatically used by the spectroradiometer to give cumulative irradiance in J/m^2 . These values were recorded at the same G block roof location as the spectroradiometer.

The IL1400 data were calibrated to the weighted spectroradiometer data for the plant damage exposures for both the summer and autumn seasons. Plotting the cumulative value of the spectroradiometer weighted data against the recorded values of the IL1400 for the same time intervals gives a calibration function that can be used when checking the PPO dosimeters for plant damage action spectrum relevance.

Table 1 shows the specific information at the time of recording the data required for the calibration. All data for erythemal and plant damage calibrations were collected at the same time. The SZA's were retrieved online from the US Naval Observatory (US Naval Observatory 2012), the ozone measurements were retrieved from OMI (NASA 2012). Cloud cover was recorded as personal observations.

Table 1 Dates, times and atmospheric conditions at time of calibration data collection

	Date	Time	SZA	Cloud Cover	Ozone (DU)
Summer Calibration	06/01/2012	8.20 am - 12.20 pm	49.1° - 7.1°	Zero - 2 octa	246
Autumn Calibration	24/03/2012	11.10 am - 3.10 pm	31.4° - 54.4°	Zero	275

2.3.5 Dose Response

The dose response of a UV dosimeter refers to the rate of change of the absorbance of the dosimeter as exposure time increases. To ensure that a varying range of atmospheric conditions were experienced, dose response was measured for both the summer and autumn seasons for both plant damage and erythemal responses. An additional winter dose response

test was carried out for the erythemal response only as part of a pilot study. The winter pilot study was done with miniaturised dosimeters only, which were made with a cardboard frame. All other miniaturised dosimeters were made with a plastic frame.

The determination of the dose response was carried out by exposing a series of dosimeters to solar UV on a horizontal plane for a specific range of time intervals. These time intervals being; 4 hours, 8 hours, 12 hours, 16 hours, 24 hours, 32 hours and 40 hours. The same time intervals were used in each season. A minimum of three dosimeters of each size were exposed concurrently for each time interval. After exposure the dosimeters were placed in an envelope and stored away from any natural light. After the final dosimeters were removed all were stored for a week before the absorbance was measured again in the spectrophotometer. Then after the post exposure measurement, the average change in absorbance and the standard deviation was determined for each time interval.

The erythemal exposure was determined by multiplying the recorded Biometer data by the erythemal calibration value for the appropriate season. The erythemal dose response was then expressed as the erythemal exposure versus the ΔA . The plant damage exposure was determined by multiplying the manually recorded IL1400 data by the plant damage calibration value for the appropriate season. The plant damage dose response can then be expressed as plant damage exposure versus the ΔA . A calibration equation in polynomial form was fitted to the calibration data for each dosimeter size in each season and for each spectrum being tested.

Tables 2, 3 and 4 show the atmospheric conditions recorded when the winter, summer and autumn dose response data collections occurred. The SZA's were retrieved from the US

Naval Observatory online (US Naval Observatory 2012, the ozone measurements were also retrieved online from OMI (NASA 2012). Cloud cover was estimated from personal observations.

From Table 3 it can be seen that all the dosimeters were removed at 2.30 pm on the 31/12/2011 due to full cloud cover and moderate rainfall occurring. Where possible the Aerosol Optical Thickness (AOT) was recorded using a sunphotometer (Microtops II, Sunphotometer version 5.6, Solar Light Co., PA, USA). This instrument was only available during the summer data collection period and the last three days of the autumn collection period. Measurements can only be made when there is no cloud in the direct path between the instrument and the sun, hence readings have not been given for all dates and times.

During day one (25/03/2012) for the autumn data collection there was intermittent full cloud cover for the whole day. After four hours had elapsed the IL1400 had recorded an exposure of less than 2.00 J/m^2 . During the cosine response preliminary investigation it was determined that a minimum of 3.00 J/m^2 is required for ΔA measurements to be higher than the noise or inherent dosimeter error of the PPO. As a result six dosimeters were removed after eight hours.

Table 2 Winter dose response data collection

Date	Time	Exposure Time	SZA	Cloud Cover (octa)	Daily Ozone (DU)
19/08/2011	7.50 am	0	72°	zero	269
	12.00 noon	4 h 10 min	40.5°	4	
	4.00 pm	8 h 10 min	71.5°	6	
20/08/2011	8.00 am		69.8°	zero	267
	12.00 noon	12 h 10 min	40.2°	5	
	4.00 pm	16 h 10 min	71.4°	7	
21/08/2011	8.00 am		69.6°	2	269
	4.00 pm	24 h 10 min	71.3°	7	
22/08/2011	8.00 am		69.3°	3	281
	4.00 pm	32 h 10 min	71.1°	5	
23/08/2011	8.00 am		69.1°	zero	281
	4.00 pm	40 h 10 min	71°	6	

Table 3 Summer dose response data collection

Date	Time	Exposure Time (hrs)	SZA	AOT (340 nm)	Cloud Cover (octa)	Daily Ozone (DU)
28/12/2011	7.30 am	0	58.9°	0.111	zero	245
	11.30 am	4	6.8°	0.133	zero	
	3.30 pm	8	48.7°		7	
29/12/2011	7.30 am		59°		7	248
	11.30 am	12	6.9°	0.252	3	
	3.30 pm	16	48.6°	0.503	zero	
30/12/2011	7.30 am		59.1°		7	238
	3.30 pm	24	48.5°		2	
31/12/2011	7.30 am		59.3°		zero	244
	2.30 pm	32	35.1°		full (rain)	
01/01/2012	7.30 am		59.4°	0.132	zero	not available
	3.30 pm	40	43.3°	0.130	zero	

Table 4 Autumn dose response data collection

Date	Time	Exposure Time (hrs)	SZA	AOT (340 nm)	Cloud Cover (octa)	Daily Ozone (DU)
25/03/2012	8.30 am	0	58°		full	263
	4.30 pm	8	71.5°		zero	
26/03/2012	8.30 am		58.2°		2	245
	12.30 noon	12	30.9°		zero	
	4.30 pm	16	71.8°		1	
27/03/2012	8.30 am		58.3°	0.248	full	260
	4.30 pm	24	72°		4	
28/03/2012	8.30 am		58.5°	0.090	2	not available
	4.30 pm	32	72.3°		5	
29/03/2012	8.30 am		58.7°	0.117	2	not available
	4.30 pm	40	72.5°		1	

2.3.6 Field Tests

In order to test the miniaturised dosimeters for the evaluation of the biologically effective UV in the field, 28 dosimeters of each size were manufactured and their absorbance measured. The dosimeters were deployed in pairs with one miniaturised dosimeter being placed on the frame of the large dosimeter so that the PPO apertures would be as close as possible to the same position and alignment when in situ (Figure 12).



Figure 12 Paired large and miniaturised dosimeters prior to placement on plants or head forms

2.3.6.1 Field Test on Head Forms

Dosimeters used to test the erythemally effective UV were attached with blu tac at specific locations on manikin head forms (Figure 13). These were then deployed on a turntable rotating at approximately 1 revolution per minute (Figure 14) which is designed to mimic the

movement of an individual in the sun as employed by other researchers (Downs & Parisi 2007, Parisi et al. 2008). Two head forms were used with matched pairs of dosimeters being placed on the; top of the head, forehead, nose, left cheek, chin and above the left ear. Placing the two size dosimeters so close allows for comparisons to be made of the change in the absorbance of each size when subject to the same irradiance. A matched pair was also placed on a board in a horizontal position away from the rotating turntable.

The complete turntable was placed outside at 8.00 am and operated for approximately seven hours each day, after which time the head forms were covered from the sunlight and taken indoors. This process was repeated at these times for three consecutive days. Table 5 shows the dates, times, SZA's and the ozone values recorded for these days.

Table 5 Dates, times, SZA and ozone details for the field test on the head forms

Date	Time	Exposure Time (hrs)	SZA range	Cloud Cover (octa)	Daily Ozone (DU)
11/5/2012	8.00 am	0	44.5° - 71.6°	2	292
	2.50 pm	6.83		5	
12/05/2012	8.00 am		45.7° - 71.8°	4	311
	3.00 pm	13.83		5	
13/05/2012	8.00 am		46° - 71.9°	2	329
	2.40 pm	20.50		6	



Figure 13 Head form with matched dosimeters located at specific anatomical sites, prior to being exposed to solar UV.



Figure 14 Head forms on the rotating turntable

2.3.6.2 Field Test on Plants

Matched pairs of dosimeters were placed on leaves at a variety of angles (Figure 15). The test was designed to measure the plant damage effective solar UV by comparing the change of absorbance for each pair. The positions were selected to represent a reasonable range of angles and directions which, when left in situ, would be exposed to the full directional changes of the sun over three days as UV on the receiving plane of the plant leaves is different to that on a horizontal plane (Parisi, Wong & Galea 1998). This test was carried out on the same dates as the head form field test. The dosimeters remained on the leaves for the full time period of 8.00 am 11/05/2012 until 2.40 pm on 13/05/2012. This means that these dosimeters were exposed to the full range of SZA for this period and that the exposure time extended from first light until last light of the day.

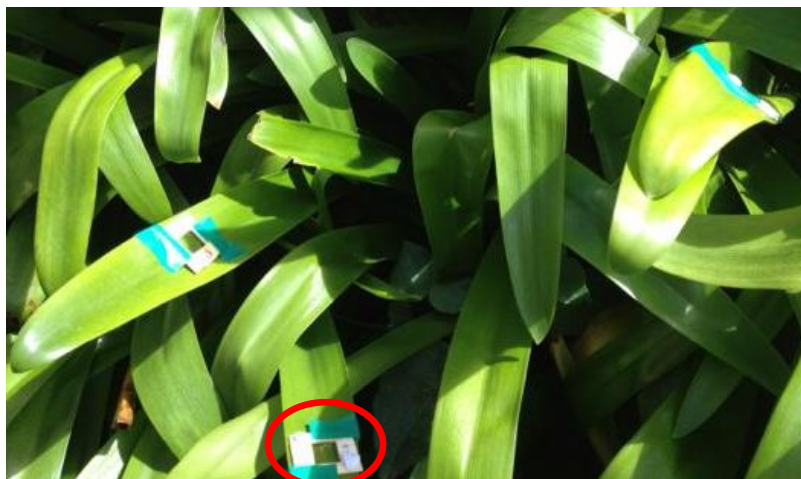


Figure 15 Matched dosimeters on plant leaves

Chapter 3

Results

3.1 Calibration

3.1.1 Erythral Calibration

Figures 16 and 17 show the erythral calibration performed for the summer and autumn seasons of the Biometer data to the spectroradiometer data.

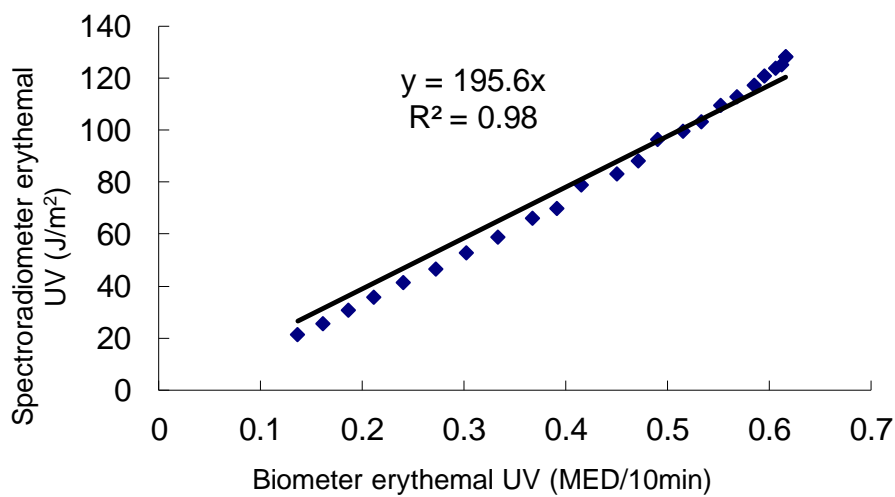


Figure 16 Autumn erythral calibration of the Biometer to the calibrated spectroradiometer

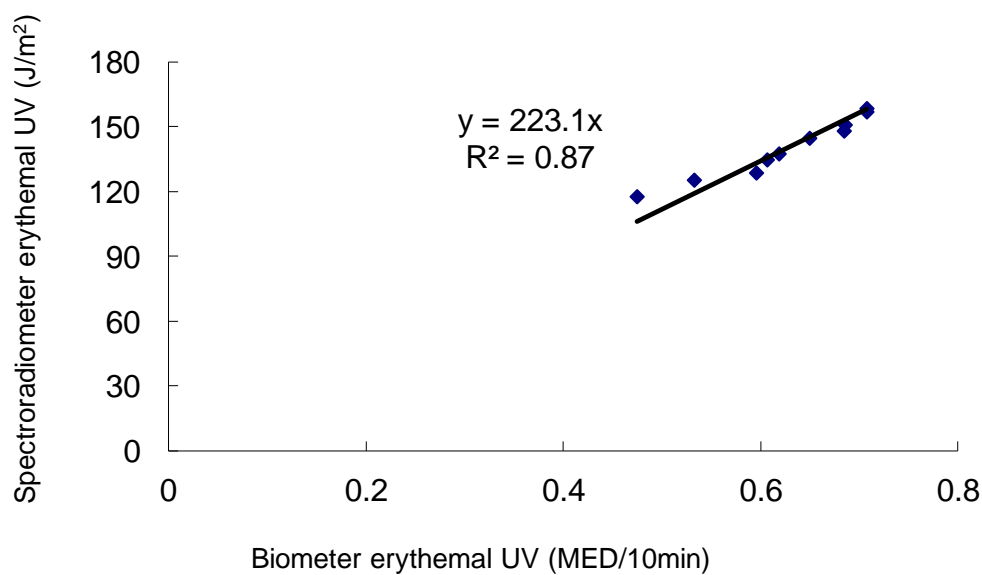


Figure 17 Summer erythral calibration of the Biometer to the calibrated spectroradiometer

3.1.2 Plant Damage Calibration

Figures 18 and 19 show the plant damage calibration of the IL1400 for the summer and autumn seasons.

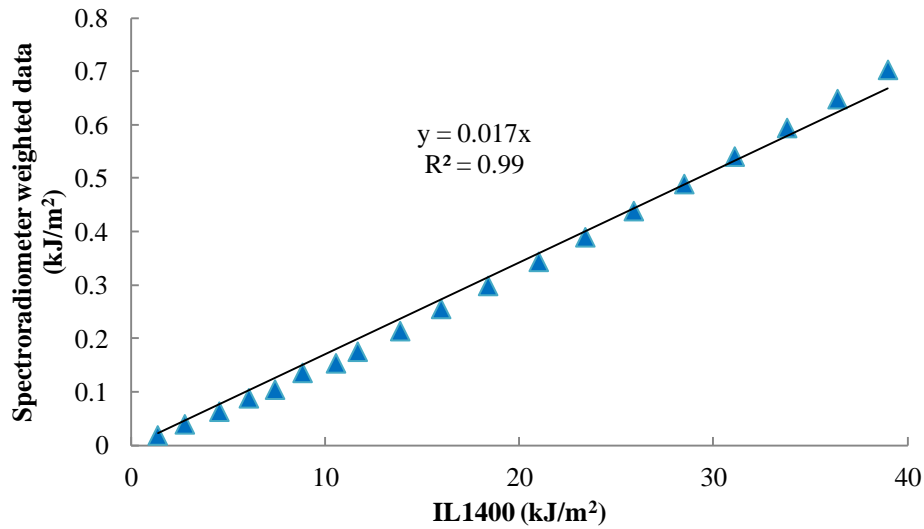


Figure 18 Summer plant damage calibration of the IL1400 to the weighted spectroradiometer

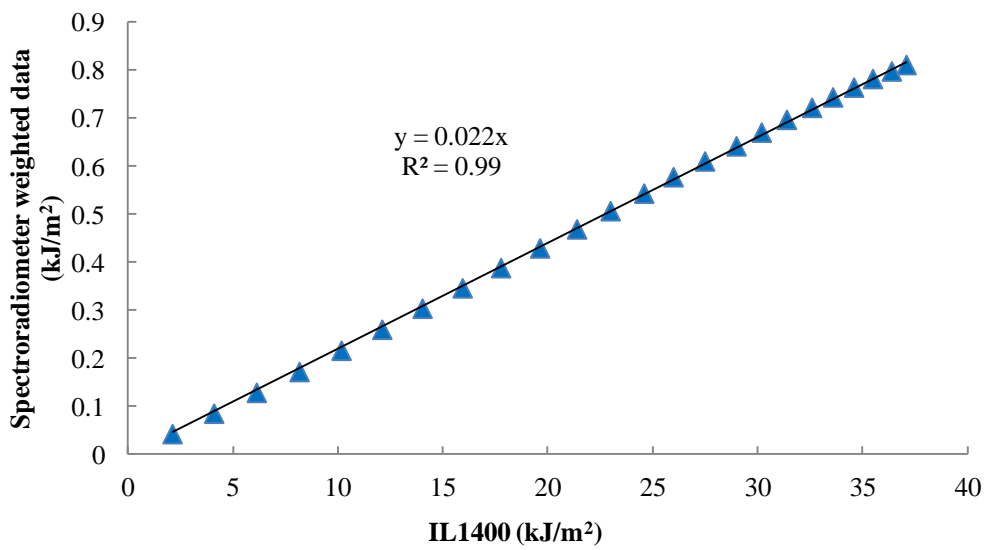


Figure 19 Autumn plant damage calibration of the IL1400 to the weighted spectroradiometer

3.2 Quantitative Tests

3.2.1 Cosine Response

The cosine response of the miniaturised PPO dosimeter is shown in Figure 20. The error bars represent the error calculated using the following equation:

$$\text{Absolute error} = \pm \left(\frac{\delta(\theta)}{\Delta A(\theta)} + \frac{\delta(0)}{\Delta A(0)} \right) R_N \quad (3.1)$$

for the ΔA measurements, where $\delta(\theta)$ and $\delta(0)$ are the standard deviations at each angle and $\Delta A(\theta)$ and $\Delta A(0)$ are the change in absorbance at each angle. The cosine response of the miniaturised PPO dosimeter is within 14% of the cosine curve for the range up to 60° .

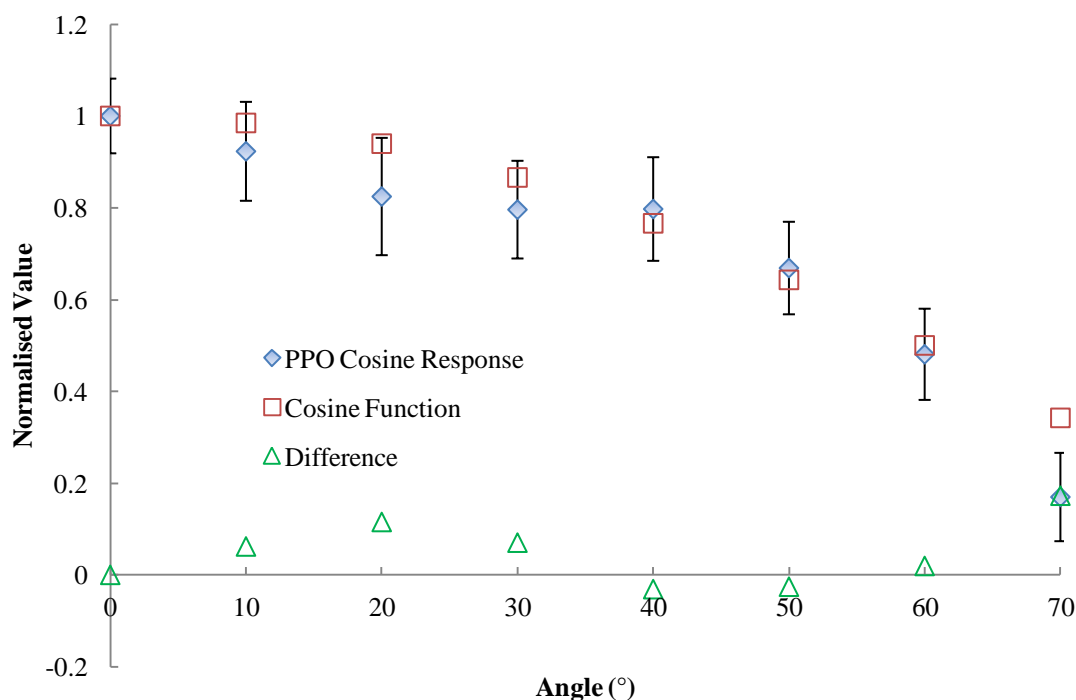


Figure 20 Cosine response for miniaturised PPO dosimeters

3.2.2 Dark Reaction

The dark reaction of both the large and miniaturised PPO dosimeters is shown in Table 6 for the periods of one hour, 24 hours and seven days after exposure.

Table 6 Dark reaction results showing the change in absorbance for the three different time periods measured

Period of Time	Large		Miniaturised	
	Change in absorbance	% Change	Change in absorbance	% Change
1 Hour	0.001	0.2	0.013	4.5
24 Hours	0.012	4.2	0.023	7.9
7 days	0.025	8.7	0.035	12.1

3.2.3 Reproducibility

The miniaturised PPO dosimeters produced a mean change in absorbance of 0.151 with a variance of 5.8% and the large PPO dosimeters returned a mean change in absorbance of 0.139 with a variance of 11.5% as shown in Table 7.

Table 7 Reproducibility results showing the mean change in absorbance and the variance for both dosimeter sizes

	Mean (change in absorbance)	Standard Deviation (change in absorbance)	% Variance
Miniaturised Dosimeters	0.151	0.008	5.8
Large Dosimeters	0.139	0.016	11.5

3.2.4 Dose Response

All dose response curves were done on a horizontal plane using PPO film. A second-order polynomial equation that went through the origin was used to describe the trend of each set of erythemal or plant damage measurement data. Figures 21 to 25 provide the relationship for

each case. The x-axis error bars represent one standard deviation in ΔA and where the error bars are not seen they are contained within the marker on the graph.

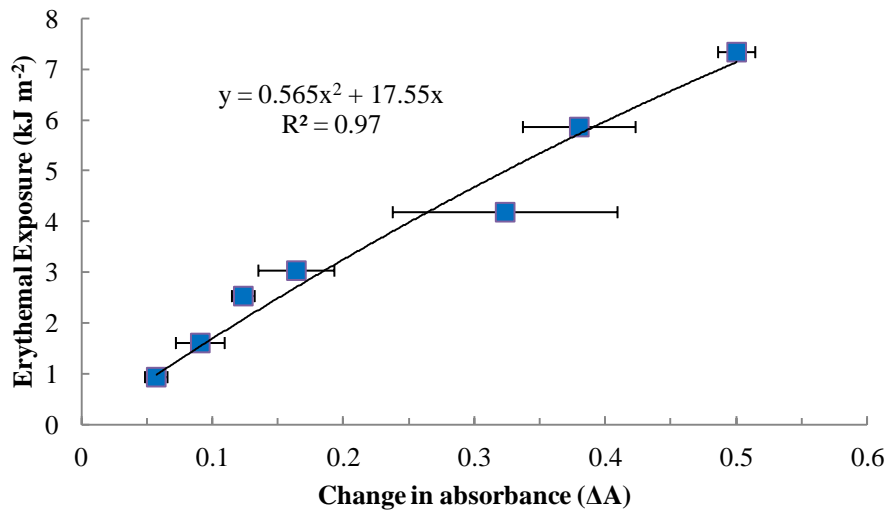


Figure 21 Winter erythemal dose response using miniaturised dosimeters

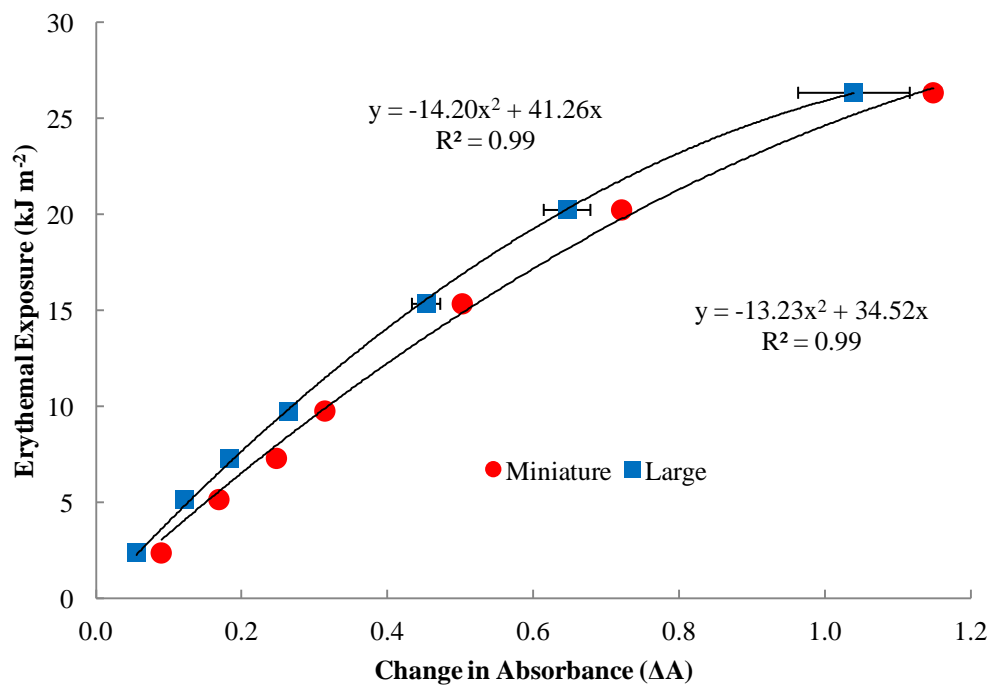


Figure 22 Summer erythemal dose response

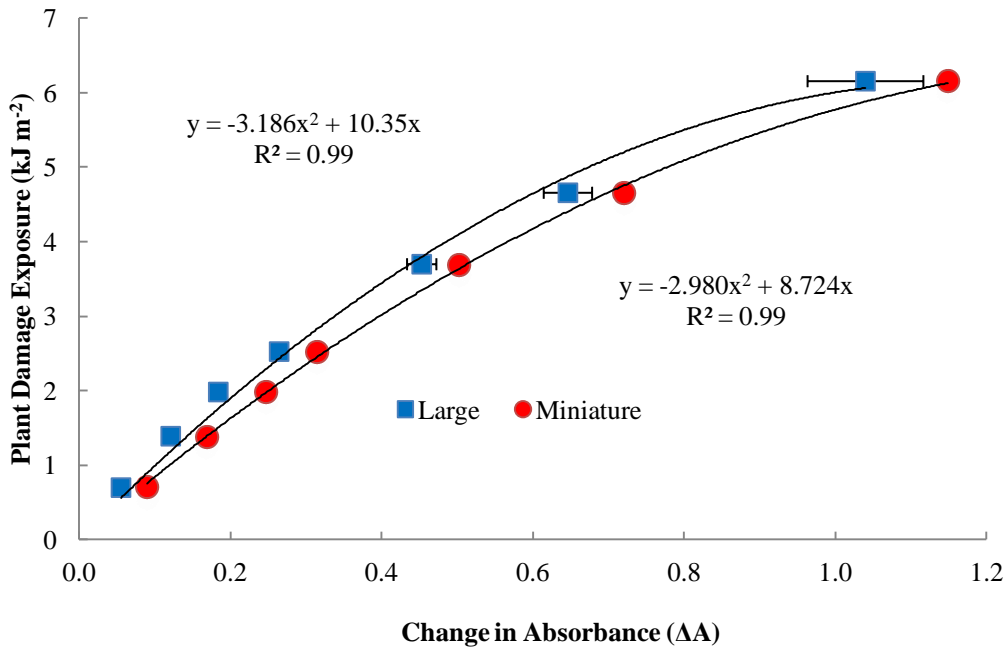


Figure 23 Summer plant damage dose response

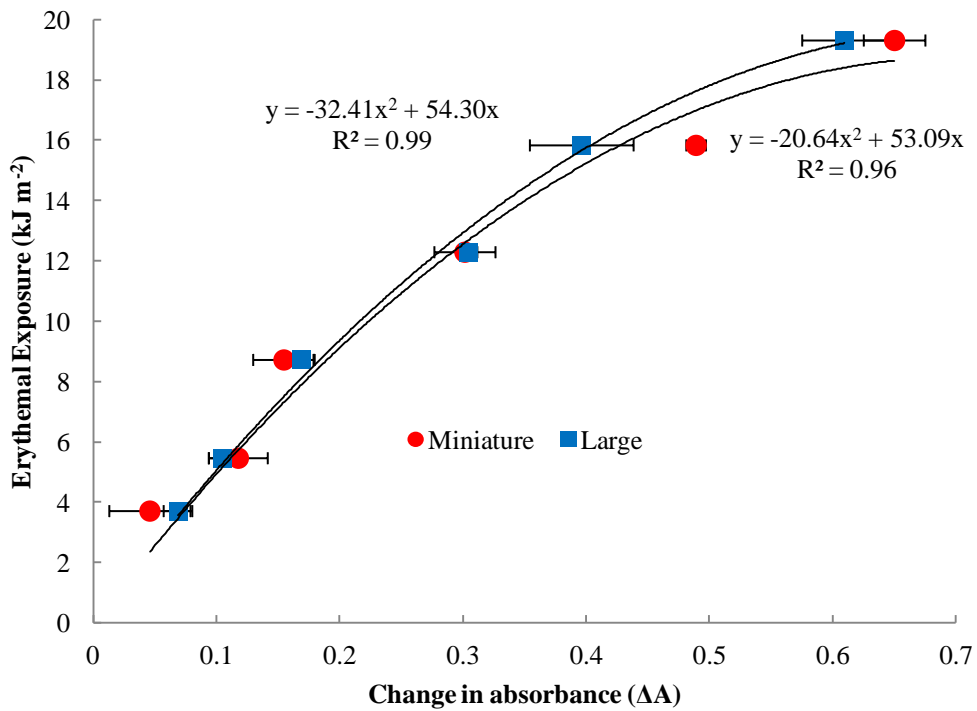


Figure 24 Autumn erythema dose response

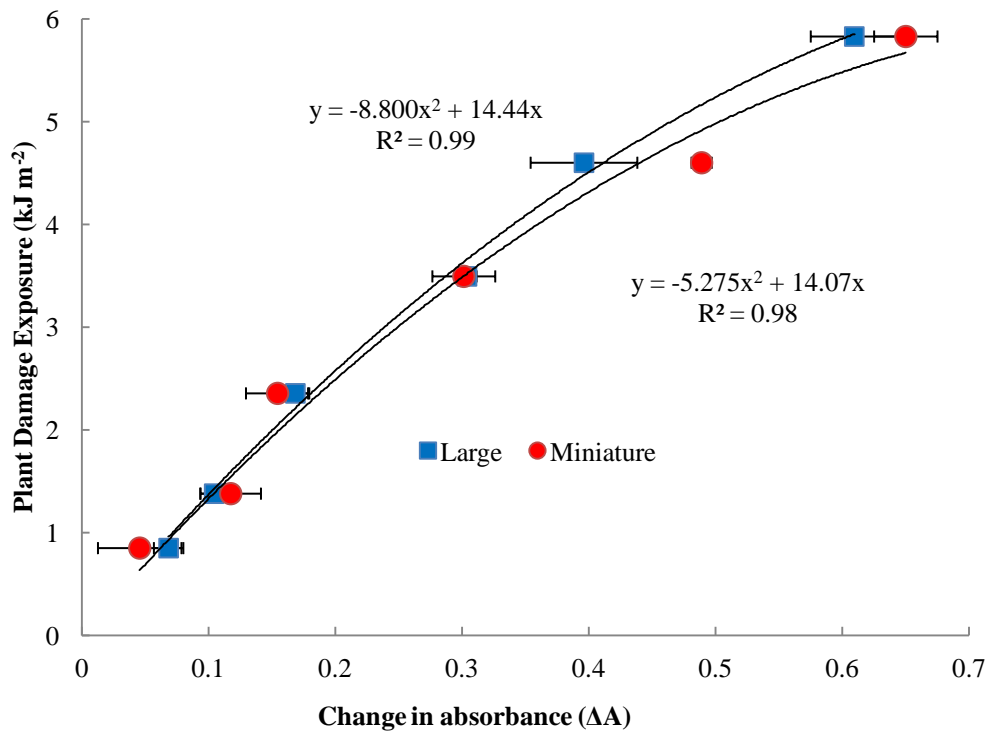


Figure 25 Autumn plant damage dose response

Figure 26 shows the relationship of the ΔA when comparing the same exposure to both large and miniaturised dosimeters. A linear equation that goes through the origin has been used to describe the relationship.

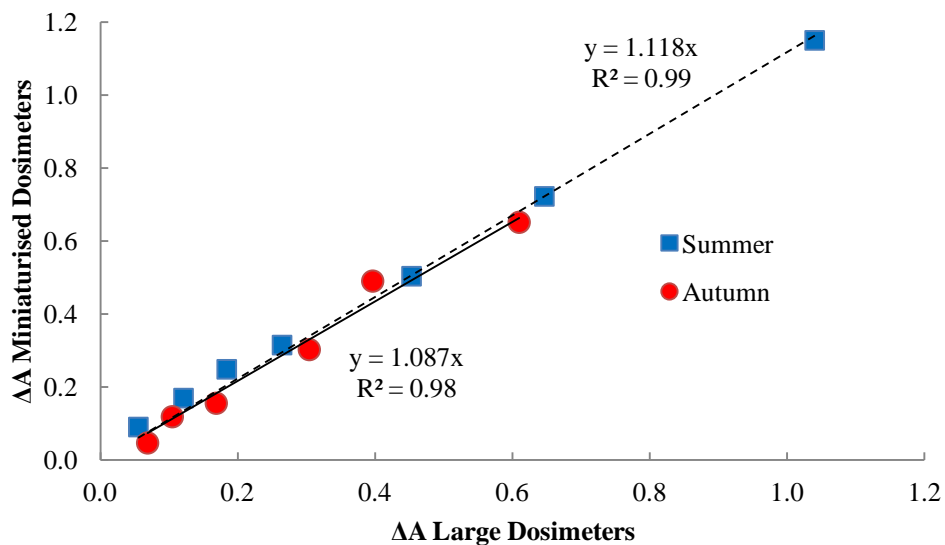


Figure 26 Direct change of absorbance comparison between sizes of dosimeters with same exposure

3.2.5 Field Tests

3.2.5.1 Field Test on Head forms

Figure 27 shows the change of absorbance between the matched pairs of dosimeters that were placed on the specific sites on each of the two head forms and exposed to solar UV over three days. The error bars show the $\pm 5.8\%$ variance for the miniaturised dosimeter and the $\pm 11.5\%$ variance for the large dosimeter. The IL1400 recorded UVB irradiance was 3.16 J/m^2 , 3.61 J/m^2 and 3.23 J/m^2 on each respective day. The total irradiance recorded on a horizontal plane over the exposure time was 10 J/m^2 .

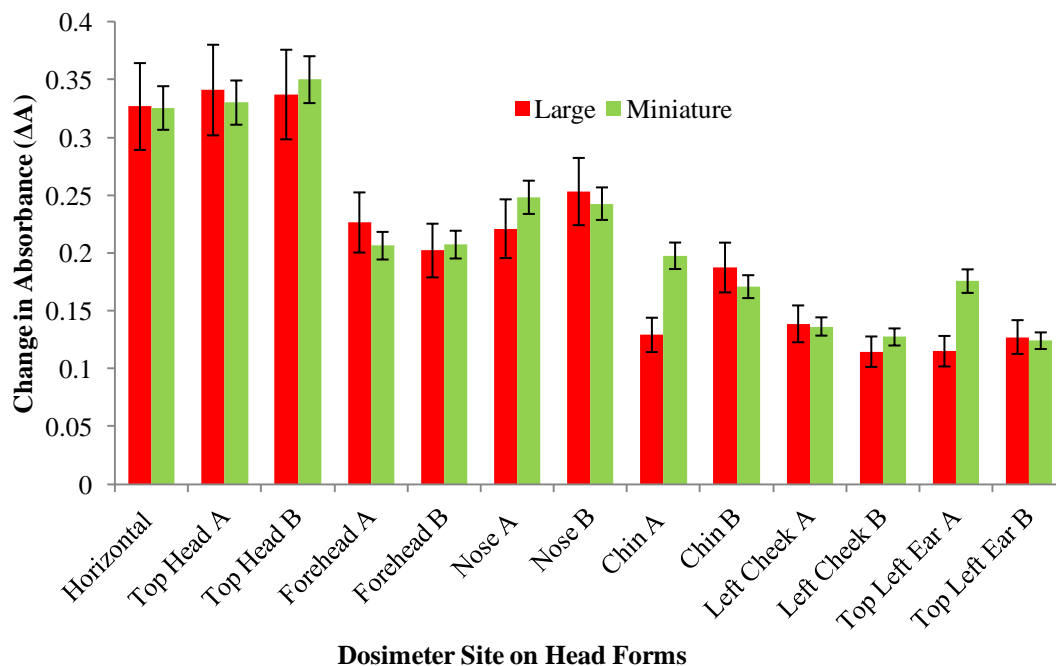


Figure 27 Head form change of absorbance comparisons by anatomical site and specific head form

3.2.5.2 Field Test on Plants

Figure 28 shows the change of absorbance between the matched pairs of dosimeters that were placed on plant leaves at a variety of different orientations. The error bars show the $\pm 5.8\%$ dosimeter error for the miniaturised dosimeter and the $\pm 11.5\%$ error for the large dosimeter.

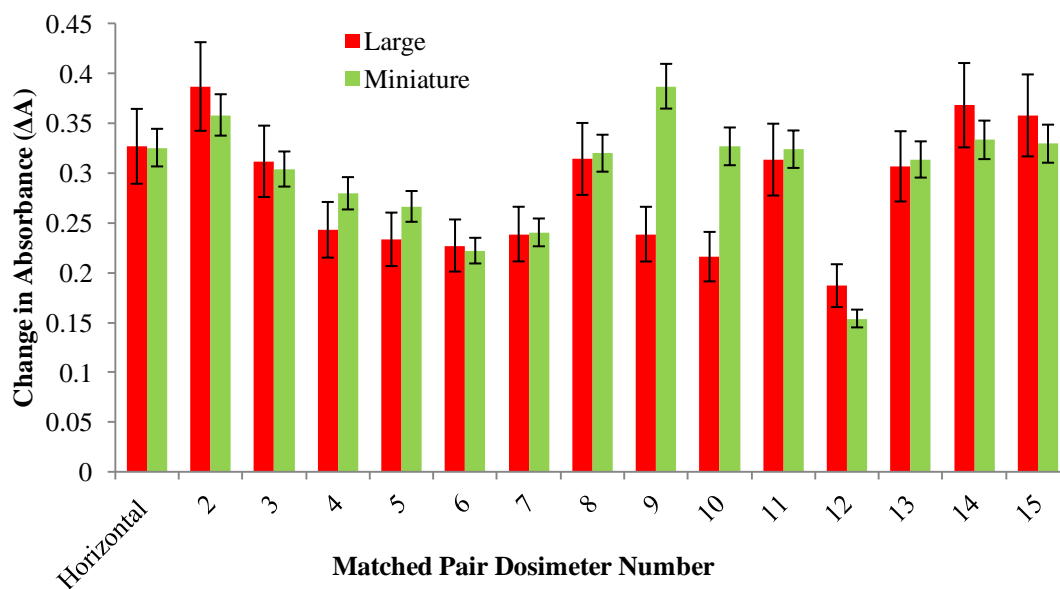


Figure 28 Change of absorbance comparisons of matched pairs of dosimeters on plants

Chapter 4

Discussion

4.1 Overview

Pre-made sheets of PPO were used to construct both sizes of dosimeters. Variation in the surface and in the thickness of the PPO film was taken into consideration by measuring the change in absorbance at four different points on the dosimeter. A wavelength of 320 nm was used for all absorbance measurements. Unless otherwise stated all post exposure measurements were made one week after removal from the irradiance source.

4.1.1 Calibration

Figures 16 and 17 show the erythemal calibration of the Biometer to the spectroradiometer for both the summer and autumn seasons. The calibration constants determined here are 195.6 and 223.1 J/m² for an MED for autumn and summer respectively. The winter value used was 184.4 J/m²/MED. These constants are then used to convert the Biometer information to an erythemally weighted irradiance for use when determining the dose response. The autumn calibration data was collected on a cloud free day but although the day of the summer data collection was initially cloud free, there was intermittent cloud cover during 50 minutes of the collection time which may have contributed to the R² value of 0.87 in summer.

A similar method was used to determine the plant damage calibration values. In this case the information from the IL1400 was calibrated to the spectroradiometer. The calibration constant for the plant damage in autumn is 0.022 and for summer it is 0.017. The differences

in the calibration constants between seasons for both erythemal UV and plant damage UV, is due to the differences between the spectral responses of the meters and the respective action spectrum resulting in a different calibration as the incident UV spectrum changes (Wong & Parisi 1999)

4.2 Quantitative Tests

4.2.1 Cosine Response

A normalised cosine response of the miniaturised PPO dosimeter was determined once the dose response to the solar simulator radiation was established. The cosine response was established by recording the change in absorbance of the dosimeter after a three hour exposure period at angles from 0° to 70° at 10° increments. As can be seen from Figure 20, the cosine response of the dosimeter is within 14% of the cosine function for angles up to 60° . For angles greater than 60° , this corresponds to SZA greater than 60° where the irradiances are less and the influence of the cosine error of these larger angles is not as significant. Previously PPO in the large dosimeters has been shown to have a cosine error of less than 10% for angles below 50° (Lester et al 2003). Similarly Schouten, Parisi and Turnbull (2007) found a cosine error of 4% - 22% for angles smaller than 50° .

The solar simulator used in this test was noted to have fluctuations of up to 220% in the emitted irradiance when checked with a scanning spectroradiometer. This may have contributed to the size of the error; however the variance in the irradiance level emitted from the solar simulator can be reduced in future tests as a solar simulator with an exposure controller, which will be available in the near future, can be used.

4.2.2 Dark Reaction

From Table 1 it can be seen that the large PPO dosimeter changed on average by 4.2% after 24 hours and 8.7% after seven days. The miniaturised PPO dosimeter changed on average by 7.9% after 24 hours and by 12.1% after seven days. Davis et al. (1976) has shown that PS has a dark reaction of 4% after 24 hours and 5% after one week. A UV_{Mel} dosimeter was found to have a dark reaction of 8.2% and 13.1% respectively (Turnbull & Parisi 2010).

The effect of the dark reaction on the PPO dosimeter can be minimised if both the measurement dosimeters and the calibration dosimeters are measured after the same time post exposure. Consequently, the effects of the dark reaction of the miniaturised dosimeters are taken into account within the dose response calibration.

4.2.3 Reproducibility

The reproducibility test showed that the miniaturised PPO dosimeter has a variance of $\pm 5.8\%$ while the large dosimeter has a variance of $\pm 11.5\%$. The smaller variance is possibly due to the smaller surface area which may have less variation in film thickness. In the use of dosimeters this error is added to the error in the spectroradiometer which has been reported as 6% (Parisi & Downs 2004) giving a dosimeter error of the order of $\pm 11.8\%$ for the miniaturised dosimeters. This is an acceptable error and is comparable to the variances found for PS of $\pm 17.7\%$ (Downs & Parisi 2008).

4.2.4 Dose Response

Both the large and miniaturised dosimeters were exposed and calibrated for erythema and plant damage exposure in summer and autumn. A winter calibration was carried out for the

miniaturised dosimeters for erythematous exposure only. The Figures 21 - 25 in section 3.2.4 show the dose responses over the three seasons. The graphs show a similarity in shape and position for the season and spectrum of calibration. In summer the miniaturised dosimeters have consistently recorded a marginally higher ΔA for the same exposure than the large dosimeters. The standard deviation of the absorbance of the miniaturised dosimeters is markedly lower as the error bars indicate. In autumn the overall exposures were lower and there was less difference in ΔA for the same exposure levels. In both the winter and autumn measurements an outlier appears within the results. In the winter this point is quite noticeable as the error bar is very wide as well, possibly indicating a flaw in the PPO film of a particular dosimeter. The autumn outlier is one of the large dosimeter data points; this data point also has the largest standard deviation. Once again this could be indicative of a fault within the film used in the dosimeter.

Analysis of the dose response calibrations shows that there is a seasonal difference in the response of the dosimeters. This has previously been reported for the large dosimeters (Schouten, Parisi & Turnbull 2010) and is taken into account by doing a calibration for the season and condition of the field research. Similarly this approach needs to be used for the miniaturised dosimeters. The calibrations account for the appropriate season and spectrum.

Figure 26 shows a linear relationship between the change in absorbance for large and miniaturised dosimeters receiving the same exposure. However in both cases the difference is within the combined variance of the two types of dosimeter found in section 3.2.3.

The dose response examination has shown that the miniaturised dosimeters perform in a similar way to the large dosimeters under the same exposure conditions as long as the appropriate calibration is carried out.

4.2.5 Field Tests

During the field tests both the plants and the head forms experienced periodic episodes of shading. The head forms were shaded during the turntable rotation and the plants were shaded depending on the SZA. Two matched pairs of dosimeters were exposed on a horizontal surface so that the change in absorbance for an unshaded site on a horizontal plane could be recorded. The average of these readings is used for comparison only.

As dosimeters have been left out over the whole period of three days, there is the possibility of them becoming wet either through light rain showers or heavy dew. The result of this is there may be watermarks being left on the film. This was overcome by flushing the dosimeters with distilled water and then allowing the dosimeters to dry (Schouten, Parisi & Turnbull 2007).

4.2.5.1 Field Test on Head forms

The comparative results for the head form test are shown in Figure 27. There is less than 1% difference in the change of absorbance recorded for the large and miniaturised horizontal dosimeters. The dosimeters on the head forms have a larger difference although all are within 12% with two exceptions. This is within the combined error of the two types of dosimeters. The two exceptions were two sites on head form A; the chin and the top of the ear. These exceptions were only on one head form and the difference was within 12% for the other head form. This may be due to some difficulties experienced in locating the dosimeters on the

head forms to ensure that both the apertures were situated as centrally as possible to the site. A combination of blu tac and electrical tape was used to maintain the alignment. The large dosimeters were difficult to attach, particularly to the curved area of the cheek. Contributing factors for the differences may include, contact with the PPO film during the covering and moving process or during the original placement on the head forms. It should be noted that the two miniaturised dosimeters that showed the major differences were both made from adjacent sections of the same sheet of PPO.

4.2.5.2 Field Test on Plants

The placement of the dosimeters on the plants was less difficult. The leaves chosen were robust enough not to change orientation due to the weight of the dosimeters. Figure 28 shows the comparisons between the changes in absorbance for the matched pairs used here. The differences are much greater than those shown for the head forms. However it is worth noting that there was no significant difference for the horizontal dosimeters. The SZA and solar azimuth were important factors in the results in this test. During the day it was possible to see that certain sections of each dosimeter received a greater exposure due to shading and the orientation of the miniaturised dosimeter on the large dosimeter. The circled dosimeter on Figure 15 shows shade covering the central aperture but not the edge where the miniaturised dosimeter was located. There were cases when the miniaturised dosimeter was placed at the bottom of the large dosimeter and this section received a higher direct exposure as the SZA decreased and the large top portion of the combined dosimeter remained in shade. This explains some of the differences in the ΔA between the large and miniaturised dosimeters.

4.3 PPO Dosimeters Miniaturised versus Large

The miniaturised PPO dosimeters allow for more measurements over the exposed area and the PPO film allows for measurements to be made for periods longer than one day. The combination of size and photoactive material allows for more flexibility in future research. This results in an increase in the potential number of environments where they can be deployed.

4.3.1 Significance

UVB damage impacts on a wide range of living organisms; costs related to these impacts are high. These costs are particularly associated with skin cancer in humans and the reduction in quality of crops and crop yields in plants. Any development of improved methods to measure the surface UV radiation, or refinement of existing measurement methods can only be to society's benefit through providing more reliable levels of UVB exposure. The development of the miniaturised PPO dosimeter through its reduction in size can lead to more research being undertaken for less cost. It would also enable a wider range of subjects and objects to be researched and increase the scope of field locations.

4.4 Future Directions

Miniaturisation of the PPO dosimeters would allow an increase in the density of the measurements taken and an increase in the environments they can be employed in. Future directions of research where the use of miniaturised dosimeters would be beneficial include:

- An examination of the dose response of the PPO dosimeter over a range of angles; this would determine if the calibration that is done on a horizontal plane is valid for

exposures at a variety of angles. This could also be extended to include the examination of the dose response in shade and sun.

- Long term studies to quantify the effects of changing atmospheric conditions such as ozone and aerosols. This would allow appropriate corrections to be made for these atmospheric conditions in further studies. Previous research has shown that the addition of a neutral density filter can extend the time frame for long term exposures (Schouten, Parisi & Turnbull 2010). A neutral density filter needs to be tested on miniaturised dosimeters.
- Use of the miniaturised dosimeter would allow more reliable evaluation of long term erythemal UV exposures on humans in a variety of activities, occupational, sporting and recreational. The miniaturised dosimeters will allow determination of UV exposures to humans in a wider range of environments due to the less invasive nature of these miniaturised dosimeters. Furthermore, they will enable an improved measure in terms of relationship between actual exposure and the Vitamin D levels of test subjects (previous studies have anecdotal exposure statements). The previous work on skin surface area calculations using polysulphone (Downs & Parisi 2012) can be extended for long term high density measurements. This would contribute information to studies into determining the required UV dose that is optimal for the production of Vitamin D, whilst avoiding overexposure (Seckmeyer et al. 2011).
- An investigation into the influence of body posture and the effects of shading during various outdoor activities.

- Monitoring UV radiation to the whole plant and not just the leaves for crop plants as suggested by Kakani et al. (2003). The non invasive nature of these miniaturised dosimeters allows deployment on a wide range and size of plants compared to the larger dosimeters. These smaller dosimeters will provide less interference to the inclination and orientation of the leaves and reduce the blockage of photosynthetically active radiation to the plant. Work has recently been done underwater (Schouten & Parisi 2012) and following on from this on corals (Downs, Schouten & Parisi 2012). Similar benefits could be obtained in this area of research as well.

Chapter 5

Conclusion

UVB radiation can be harmful to both humans and plants. The monitoring of individual UV radiation exposures is important in light of the potential damaging consequences. To date large PPO dosimeters have been used to measure exposures lasting longer than one day and miniaturised PS dosimeters have been used to take multiple personal measurements for exposures lasting up to day. This study aimed to establish whether combining the two key features into a miniaturised PPO dosimeter would be beneficial. The objective being to confirm that the miniaturised PPO dosimeter would have the same important characteristics as the dosimeters currently in use. This was done by quantifying the characteristics of the dosimeter including; dose response (erythemal and plant damage), dark reaction, cosine response and reproducibility along with comparison in the field.

The dose response for both sizes of dosimeter was measured in summer and autumn for both erythemal and plant damage action spectra and was consistent for the season and the action spectrum of calibration.

The dark reaction of the miniaturised dosimeter did vary with respect to the large dosimeter; however it was similar to the magnitude of the dark reaction that had been found for other chemical dosimeters. The cosine response of the miniaturised dosimeter was found to approximate the cosine function, with errors of less than 14% for angles up to 60° from the normal. The reproducibility was shown to be a variance of $\pm 5.8\%$ for the miniaturised PPO dosimeter while the large dosimeter had a variance of $\pm 11.5\%$. This combined with the

spectroradiometer error gave a dosimeter error of the order of $\pm 11.8\%$ for the miniaturised dosimeters which is acceptable in research with dosimeters.

The field tests on the head forms showed a similarity in the change of absorbance between the matched pairs of dosimeters. The ΔA within the horizontal matched pairs was less than 1%. This is the only matched pair where no shade covered any part of the dosimeters at any time and where the orientation of the dosimeters was not changed. These two factors will have influenced the ΔA shown by all other matched pairs in both the plant and head form field tests.

This research has concluded that the miniaturised PPO dosimeters have the same dosimeter characteristics as the larger dosimeter and provide results in the field consistent with those of the larger dosimeters. In summary, the miniaturised dosimeters can be employed in research to determine biologically effective UV in plant and human studies.

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Appendix 1 - Abbreviations

AE Altitude effect

EM Electromagnetic

MED Minimum erythematous dose

NMSC Non melanoma skin cancer

O₂ Oxygen

O₃ Ozone

PPO Polyphenylene oxide

PS Polysulphone

SED Standard erythematous dose

SZA Solar zenith angle

UV Ultraviolet

UVA Ultraviolet A (320 - 400 nm)

UVB Ultraviolet B (280 – 320 nm)

UVC Ultraviolet C (< 280 nm)

UVR Ultraviolet radiation

ΔA Change in absorbance