University of Southern Queensland

Seasonal erythemal UV, UVA and vitamin D effective UV exposures of office workers.

A Thesis submitted by

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ABSTRACT

In light of the ever changing composition of the Earth's atmosphere and the consequences of ultraviolet radiation (UVR) for the biological environment, it is important to be able to determine the specific ultraviolet radiation levels that reach humans living on the Earth's surface. Optimal human health requires a balanced amount of UV exposure as both too much and too little have different but serious potential health consequences. Sun damage can be caused by both UVB (280 – 320 nm) and UVA (320 – 400 nm) with melanoma and keratinocyte cancers being linked to UVB and UVA exposures. Humans need vitamin D to maintain good health and the best natural source of vitamin D is UVB from the Sun. Vitamin D deficiency, or insufficiency, is increasingly reported as people avoid potentially damaging UV exposure.

Miniaturized dosimeters using polyphenylene oxide (PPO) as a photoactive material have been used to measure erythemal UV exposures received by humans for exposure periods of between one to seven days. In order to broaden the range of the PPO dosimeter, research was undertaken for the dual calibration of PPO dosimeters to both the erythemal and vitamin D action spectra. Through this dual calibration PPO dosimeters were able to record both types of biologically effective exposure as both are active within the UVB waveband. The calibration provided an R^2 of 0.86 – 0.99 for erythemal UV and an R^2 of 0.92 – 0.99 for vitamin D effective UV.

A new miniaturized dosimeter using 8-methoxypsoralen (8-MOP) as the photoactive material was characterized and a technique developed for the calibration of UVA exposures. Using Mylar as a filter to remove the UVB, the spectral response showed that 8-MOP reacts only to wavelengths between 320 – 400 nm. The measured cosine response had an error of less than 14% for angles between 0° and 50°. Seasonal dose response tests indicated that these UVA dosimeters are able to measure exposures greater than 21.5 kJ/m^2 for a continuous period of up to seven days.

These two dosimeters were combined into one dosimeter badge; these combined badges were worn in research to record concurrently the personal erythemal UV, UVA

and vitamin D effective UV exposures received by office workers in their occupational and recreational environments over a minimum period of a week in each season of the year. The amount of time spent outdoors, general UV protection strategies employed and the ambient UV both outdoors and within the office environment were recorded. Participants were all indoor office workers located at two sites at the sub-tropical location of Toowoomba (27°33'S 151°55'E, elevation 691 m). The participants wore a combined dosimeter badge horizontally on the shoulder for a minimum of one week in each season. The median erythemal exposure was highest during the spring and lowest during winter, as was the median vitamin D effective exposure. Median UVA exposures were at a similar level in winter and summer, autumn was higher and spring at a lower level. The behaviour of participants changed in each season; in winter 45% of the time spent outdoors was between the hours of 10:00 – 14:00 h compared to 27% in summer. The daily UVA/UVB ratio is also lowest between 10:00 – 14:00 h and also changes with the season, resulting in the differences between the distributions of exposures for each of the wavebands. Each category of exposures must be assessed individually as no association was found between any of the wavebands over the whole year, indicating that each season and each waveband had different distributions.

Use of sunscreen, wearing of hats and type of clothing worn were analysed as part of the UV protection aspect of the study. Over 50% (n=128) of participants reported not using any sunscreen or wearing a hat at any time. Autumn rather than summer had the highest reported use of sunscreen and the highest proportion of people wearing hats. Clothing was separated into leg covering and arm covering. In all seasons, apart from winter, more than 25% (n=99) of participants always had short sleeves when outdoors. In winter 80% (n=29) of people had full leg cover and 30% (n=29) had full arm cover. These results indicate that the majority of people are not using UV protection on a regular basis.

The results also demonstrate that, the dual film dosimeter developed and characterized with a calibration to three different biological responses, is an effective device for the concurrent measurement of the erythemal UV, UVA and vitamin D effective UV exposures for periods of a week before needing to change the dosimeters.

CERTIFICATION OF THESIS

This thesis is entirely the work of Lisa Wainwright except where otherwise acknowledged. The work is original and has not previously been submitted for any other award, except where acknowledged.

Student and supervisors signatures of endorsement are held at USQ.

Professor Alfio Parisi

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Principal Supervisor

Dr Nathan Downs

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Associate Supervisor

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When I started the process Dr Christine McDonald told me that a PhD was less about researching and exploring an original idea and more about continuing on despite changes and setbacks until you reach completion. This insight proved very true.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

8-MOP	8-methoxypsoralen
MED	Minimum erythemal dose
NMSC	Non-melanoma skin cancer
O_3	Ozone
PPO	Polyphenylene oxide
PS	Polysulphone
PVC	Polyvinyl chloride
SED	Standard erythemal dose
SZA	Solar zenith angle
THF	Tetrahydrofuran
TSI	Total sky imager
USQ	University of Southern Queensland
UVA	Ultraviolet A (320 – 400 nm)
UVB	Ultraviolet B (280 – 320 nm)
UVC	Ultraviolet C (< 280 nm)
UVI	Ultraviolet index
UVR	Ultraviolet radiation
ΔA	Change in absorbance

1. INTRODUCTION

1.1 RATIONALE

Solar radiation is the predominant source of power for the Earth, sustaining life through the energy it provides. The wavelength of the energy that reaches the Earth's surface is important as it is related to the type of damage or benefits that occur to human health. The particular type of non-ionizing solar radiation most associated with damaging effects to humans is ultraviolet radiation (UVR).

The reality that UVR exposure is the foremost known cause in the development of melanoma and non-melanoma skin cancer (NMSC) or keratinocyte cancers (Sun Protection Programs Working Party 1996) has been acknowledged for at least the last 50 years (Movshovitz & Modan 1973). Keratinocytes include basal cell carcinomas and squamous cell carcinomas. Australia has one of the world's highest rates of diagnosed skin cancer (Cancer Council Australia 2016) second only to New Zealand, with Queensland producing one of the two highest incidence rates in Australia (McCarthy 2004; Cancer Council Australia 2016). Exposure to the Sun can also cause damage to the eyes and accelerate the process of skin ageing (Webb 1998).

The type of damage is related to the specific waveband within the ultraviolet (UV) wavelengths of 100 nm to 400 nm and the time of exposure. The most severe consequences such as melanoma can be linked to short very intense UVB (280 – 300 nm) exposures such as a serious sunburn experienced in childhood. Frequent, recurrent UV exposure over a longer time frame, such as that experienced by outdoor workers has been connected with non-malignant damage and the accelerated ageing of the skin and may be caused more by UVA (320 – 400 nm) than UVB (Sun Protection Programs Working Party 1996).

Exposure to UVB wavelengths is necessary for humans to initiate vitamin D production, however low levels of vitamin D have been reported in various studies (Azizi et al. 2009; Vu et al. 2010; Cinar et al. 2013) undertaken in different locations around the world. Avoiding sun exposure through fear of the negative effects (Holick & Jenkins 2003) could be contributing to the increase in vitamin D deficiency.

As the lag time for disease onset after UV exposure is highly variable (Lucas et al. 2013), recording the level of human UV exposures in different wavebands is necessary in order to develop a complete picture of the effects of UV exposure to humans and other biological organisms. Measuring this UV exposure can be performed in a variety of ways using large permanently located instruments such as spectroradiometers which have a high degree of accuracy, through to single use small, portable dosimeters (Webb 1998) which have less accuracy but can be used for multiple situational measurements.

The benefits of dosimeters for recording biologically effective UV exposure include: being able to use them at the site of the required measurement, flexibility in measuring angled non-flat surfaces and having low to no impact on the lifestyle of the wearer during normal daily functions. They are small, relatively cheap to manufacture and can be used to measure multiple sites on an individual.

Changes in ozone concentrations and other atmospheric elements and conditions can affect the amount of atmospheric UVR absorption and potentially increase the amount of damaging solar UV that reaches the Earth's surface (Bigelow et al. 1998). This potential increase underlines the need to develop a total awareness of the solar radiation environment. Accurate recording of UV levels received by humans would also eventually enable UV levels to be predicted accurately. This would then enable some pertinent guidance to be given regarding acceptable UV exposures to humans.

The objectives of the research are:

1. To design, manufacture and fully characterize the properties of a long term UVA dosimeter and evaluate its suitability for exposure periods of one week before saturation.

2. To extend the range of the polyphenylene oxide (PPO) dosimeter through testing and calibration to determine its suitability for use as a vitamin D effective UV dosimeter in conjunction with its current use as an erythemal UV dosimeter: a dual calibration.

3. To devise and construct a method of combining the two dosimeters into a compact package capable of simultaneously measuring, erythemal UV, UVA and vitamin D effective UV, exposures for up to a week before the dosimeters reach saturation levels.

4. To design and conduct field tests to validate the use of these dosimeters for the concurrent measurement of erythemal UV, UVA and vitamin D effective UV to simultaneously determine the level of the beneficial and the damaging exposure received by office workers.

5. Evaluate the reported use of UV protection factors by participants in the field tests specifically; sunscreen, hats and clothing.

1.2 HYPOTHESIS

Dosimetry can be used successfully to simultaneously record the erythemal UV, UVA and vitamin D effective UV radiation exposures received by office workers in their occupational and recreational environments, thus characterizing exposure patterns which can be related to potential health outcomes.

1.3 DISSERTATION OUTLINE

- Chapter 1 – Provides an overview of UV radiation including both damaging and beneficial effects to humans

- Chapter 2 – Presents information on the methods, and equipment used in the manufacture of dosimeters and the measurement of received UVR, atmospheric and climate conditions

- Chapter 3 – Details the process of fabrication and full characterization of the UVA dosimeter

- Chapter 4 – Describes the method of the dual calibration of the PPO dosimeter

- Chapter 5 – Analyses data from the field study to assess the received exposures of erythemal UV, UVA and vitamin D effective UV by study participants
- Chapter 6 – Explores the reported use of UV protection such as sunscreen, hats and clothing type
- Chapter 7 – Conclusions and future research

1.4 OVERVIEW

Solar UVR is damaging to human health and there is a sound research evidence base linking sun exposure to skin and eye damage. Solar UV exposure also has beneficial effects, related to vitamin D production, bone health and recovery times post-surgery. Changes to the world's climate have the potential to increase these damaging effects to human health. It is important to develop a complete awareness of the solar radiation environment; maintaining a balanced view of both the positive and negative effects of exposure to the sun. The ability to document the UV exposures received by humans is imperative in order to be able to predict, with confidence, expected UV exposures and the effects on humans. Accurate measurement and thus prediction will allow appropriate exposure recommendations to be developed with regard to the recognized risks and benefits. The discussion in this chapter is a review of the solar UV environment including the circumstances that affect the levels of surface UV and the relative amounts of UV within the electromagnetic spectrum. The chapter will also review both the positive and negative effects of UVR exposure on humans and then consider the methods used to measure these levels. Attention is given to the area of dosimetry which is a technique used to measure localized UV exposures.

1.5 ULTRAVIOLET RADIATION (UVR)

The majority of UVR is generated from the sun, although it can also be produced from man-made sources such as lamps or welders. The electromagnetic spectrum covers a wide range of wavelengths and the UVR waveband is only 9.3% of this range. Not all of the UVR waveband reaches the Earth's surface (Webb 1998). Wavelength determines the divisions within the spectrum (Knight 2004). Divisions include ultraviolet radiation, visible radiation and infrared radiation. An overview of the electromagnetic spectrum highlighting the UV region can be seen in Figure 1.1.

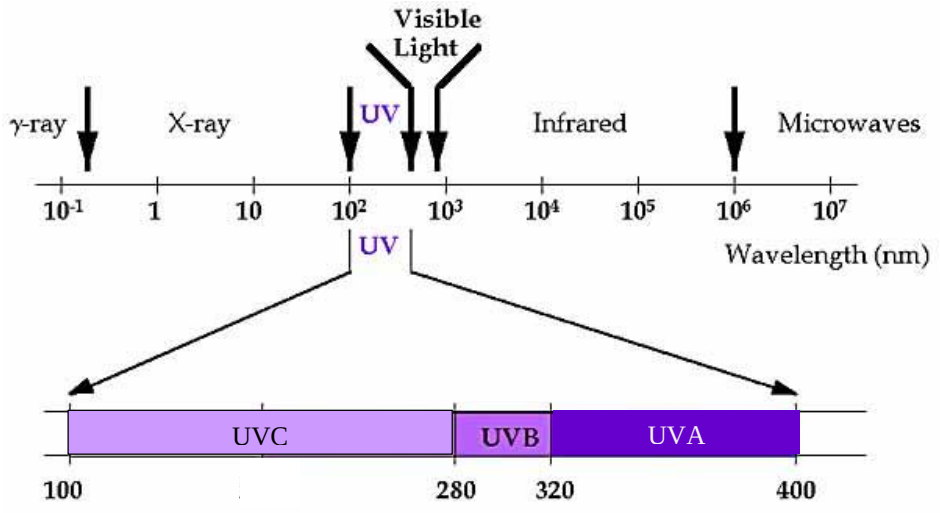

Figure 1.1 Ultraviolet radiation as part of the electromagnetic spectrum (Soehnge, Ouhtit & Ananthaswamy 1997).

Wavelengths of 400 nm to 700 nm encompass visible light. UV wavelengths lie between 100 nm and 400 nm and the UV section is divided into three areas UVA (320 – 400 nm), UVB (280 – 320 nm) and UVC (100 – 280 nm). Wavelengths over 700 nm are part of the infrared section of the spectrum however, this is "a rather loose definition, and there is no universality in the nomenclature" (Hecht 2002).

The standardization of UV definitions concluded that "the upper limit of UV-B should remain at 315 nm" (CIE 1999b, 2014). Diffey (2002), states that the subdivisions are arbitrary and can differ depending on the discipline involved. People researching UV in various scientific fields use different wavelengths to distinguish the UV regions. Environmental and dermatological photobiologists use a UVB range of 290 – 320 nm, as in McKenzie et al. (2002) and Rafanelli et al. (2010), largely due to the biological significance of wavelengths between 315 and 320 nm (Cole 2001; Lavker et al. 1995).

1.5.1 UVC

UVR with wavelengths below 290 – 295 nm are usually absorbed by oxygen (O_2), ozone (O_3) and other atmospheric particles in the upper atmosphere. Consequently, no solar UVC reaches the Earth. Depending on the atmospheric components at any given time, the threshold wavelength that actually reaches the Earth's surface may change (Parisi, Sabburg & Kimlin 2004).

1.5.2 UVB

UVB has the shortest wavelength of the UV that reaches the Earth. It has a high energy level and causes the greatest amount of biological response, although it accounts for approximately 1% of the UV emitted by the Sun (Bohren & Clothiaux 2006). Only a few minutes of skin exposure is required for biological and/or chemical reactions to occur in sensitive skin. Ultraviolet radiation, particularly UVB, is the main cause of a range of melanoma and keratinocyte cancers as well as eye damage and skin photoageing. UVB wavelengths are the cause of sunburn which, in turn, causes 95 – 99% of skin cancers (Cancer Council Australia 2016).

1.5.3 UVA

UVA wavelengths are closest to one end of the visible spectrum. UVA has a longer wavelength than the UVB. This longer wavelength means that UVA is not affected by atmospheric (Rayleigh) scattering to the same degree as UVB. Additionally, ozone absorption is minimal in the UVA waveband; with absorption falling significantly from 315 to 320 nm (Barnard & Wenny 2010). UVA does cause some biological damage (Sicora et al. 2006; Sun Protection Programs Working Party 1996), although the damage caused is produced differently to that from UVB as UVA penetrates further into the skin, and reaches the dermal skin layers (Agar et al. 2004). As a contributing factor to skin damage, UVA is also associated with skin photoageing, melanoma and keratinocyte cancers (Krutmann 2000). Figure 1.2 shows a UV spectral scan taken on a clear summer day at the University of Southern Queensland (USQ). This scan clearly shows the actual irradiances in both the UVA and UVB regions.

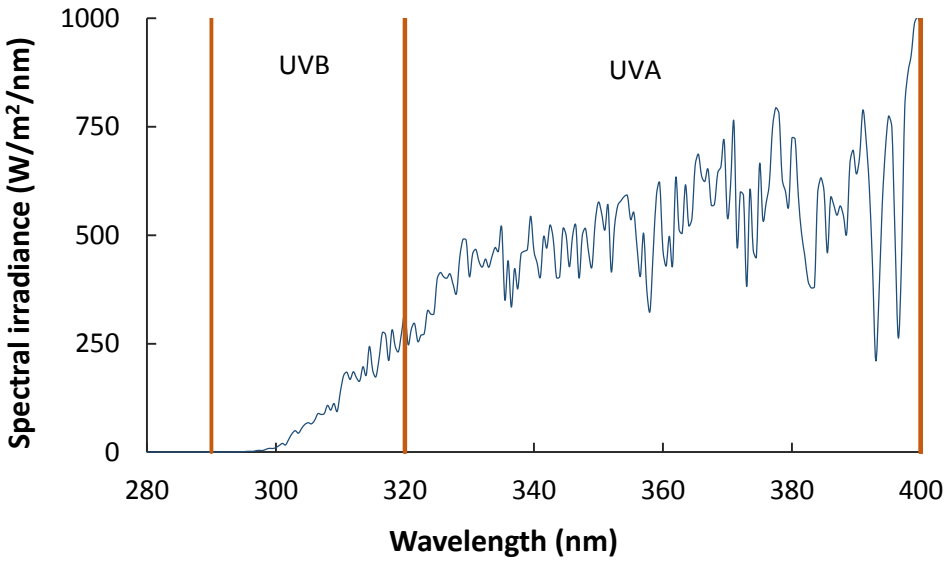

Figure 1.2 Ultraviolet irradiance recorded on a clear day at the University of Southern Queensland.

1.5.4 UV Index

The UV Index (UVI) is a linear scale used for measuring the level of UV radiation. The scale ranges from zero (night time) to 11+. Each point on the scale is equivalent to 25 mW/m^2 with 11+ representing the presence of extreme levels of UV. The higher the UVI, the higher the likelihood of damage occurring to the skin and eyes. Higher UVI also indicates that it takes less time for this damage to occur (WHO 2016), thus motivating the inclusion of UVI predictions in weather reports to remind people of the level of sun protection required.

Only erythemal UV wavelengths are used in determining UVI and these are wavelengths between 280 nm and 400 nm. UVI is a unit-less quantity that is obtained by dividing the integrated erythemal UV (mW/m^2) by 25 (mW/m^2) to give the UVI range within each exposure period (WHO 2002). The integrated erythemal UV is used as shorter UV wavelengths cause more erythemal damage.

1.5.5 Absorption and Scattering due to Aerosols

Aerosols are minute particles that are suspended in the air. Desert dust, sulfate caused by burning coal and oil and particles from volcanic eruptions are examples of the three main types of atmospheric aerosol (Madronich et al. 1998). These small particles contribute to a type of scattering known as Mie scattering which occurs when the particles themselves are equal to, or larger than, the wavelength of the incident light (Barnard & Wenny 2010). A visible haze occurs when aerosols scatter and absorb sunlight.

Mie scattering can involve the particle completely absorbing the UVR which heats the atmosphere, absorbing and reradiating it at a lower, longer wavelength, or completely reflecting it (Barnard & Wenny 2010). These interactions change the energy, direction or both of the UVR which would change the level reaching the Earth's surface.

1.5.6 Direct/Diffuse

To reach the Earth, UV can travel one of two paths. The first is the direct path that is coming in a straight line from the Sun. This is known as direct radiation. UV not travelling the direct route is called diffuse radiation. Global UV radiation refers to the combination of the diffuse and direct components. Diffuse radiation can contribute 50% of the global irradiance under clear skies. The relative percentage of diffuse radiation can increase significantly under overcast conditions (Grant, Heisler & Gao 1997). The path taken in this case may have many changes of direction due to scattering when travelling through the atmosphere. Increasing amounts of scattering are caused by increasing volumes of atmospheric aerosols. Diffuse radiation may also be reflected from the Earth’s surface or from the underside of clouds before arriving at the location where it is measured. As UVR wavelengths decrease, the amount of diffuse radiation increases (Parisi & Kimlin 1997). There is a need to measure, with dosimeters, global UVR as diffuse and direct components of both UVA and UVB can change under varying atmospheric conditions as well as time of day.

1.5.7 Albedo

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

$$A = {}^{I_r}/_{I_i} \tag{1.1}$$

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. Categories of albedo for different surface types on Earth include: vegetated areas, bare soil, human constructions and these same surfaces covered by ice/snow (Lenoble 1993). Albedo levels for specific wavebands can change according to different surface types (McKenzie, Kotcamp & Ireland 1996; McKenzie et al. 2002).

1.5.8 Altitude

Locations at higher altitudes usually record higher UV levels than locations at lower altitudes. Higher altitude locations have lower atmospheric pressure and can have fewer atmospheric particles due to less pollution. As a result less scattering occurs. Albedo levels due to snow and ice can also contribute to higher UV levels being recorded.

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

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

where AE = Altitude Effect, I_H = irradiance at high altitude, I_L = irradiance at low altitude and ΔA = difference in altitude in metres. As the difference in altitude increases the AE increases.

1.5.9 Clouds

The presence of clouds has been shown to decrease surface UV levels from those experienced in cloud free conditions (Grant & Heisler 2000). Some specific cloud conditions can increase the surface UV as UV is scattered and reflected from the lower sections of cloud back to the Earth's surface (Parisi, Sabburg & Kimlin 2004). Cumulus cloud has been shown to increase UVB levels by up to 25% (Roy, Gies & Toomey 1995) when not directly covering the Sun. Cumulus clouds are low altitude clouds that do not cover the whole sky thus allowing UVB to reach the surface through gaps. A greater surface area of the clouds (sides as well as base) increases the refraction and scattering of UVB. Variations in the optical depth of the clouds and the proportion of cloud covering the sky will also change surface UV levels (Parisi, Turnbull & Turner 2007).

1.5.10 Solar Zenith Angle

The Solar Zenith Angle (SZA) is the angle between the local vertical or zenith and the angle of the Sun when measured at the object at any given time. SZAs are measured from the vertical so when the Sun is directly overhead the SZA is 0°. A SZA of 0° only occurs when the Earth's surface is perpendicular to the centre of the solar disc. Under clear sky conditions, the daily peak surface UV irradiance values occur when the SZAs are lowest. This occurs at solar noon. At this time, for any particular day, the UV travels the minimum path through the atmosphere (Wenny, Saxena & Frederick 2001). Smaller SZAs result in higher UVR levels being recorded as the optical path is minimized and there are less atmospheric interactions to disperse the UV.

1.5.11 Season

The distance between the Earth and the Sun changes in a regular cycle due to the Earth's elliptical orbit, resulting in a ±7% variation of the amount of UV that actually reaches the Earth's atmosphere (Seidlitz & Krins 2006). The axial tilt of the Earth also means that the intensity of surface UV changes with the seasons. The solar constant is approximately 1.368 kW/m^2. This is the amount of solar energy (all wavelengths) that reaches the top of the Earth's atmosphere at a point perpendicular to the Sun's rays. This value can vary by ±3% as the 11 year solar sunspot cycle progresses and

the Earth's orbital path changes (NASA 2016) the magnetic activity that accompanies the sunspots can produce dramatic changes in UV emission levels. Consequently, the level of UV that reaches the Earth's surface changes with the seasons.

1.6 ACTION SPECTRA

An action spectrum is used to show how a particular wavelength of UV relates to a specific biological response (Flint, Searles & Caldwell 2004). Action spectras are known as biological weighting functions (Horneck et al. 2006) and use a comparative value between 0 and 1 to express effectiveness. As an example: 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) to account for the diminishing effectiveness of erythema associated with increasing wavelength. Action spectra have been developed for a range of biological functions for plants, fish and humans. Two examples are shown in Figure 1.3: the erythemal action spectrum (CIE 1988) and the vitamin D effective action spectrum (CIE 2006).

The effects of solar UV irradiance can be estimated by combining the known amount of spectral UVR reaching an object with the specific action spectrum for the effect being tested. Figure 1.3 shows that longer wavelengths indicate lower sensitivity of the biological specimen and therefore a lower relative degree of biological effect.

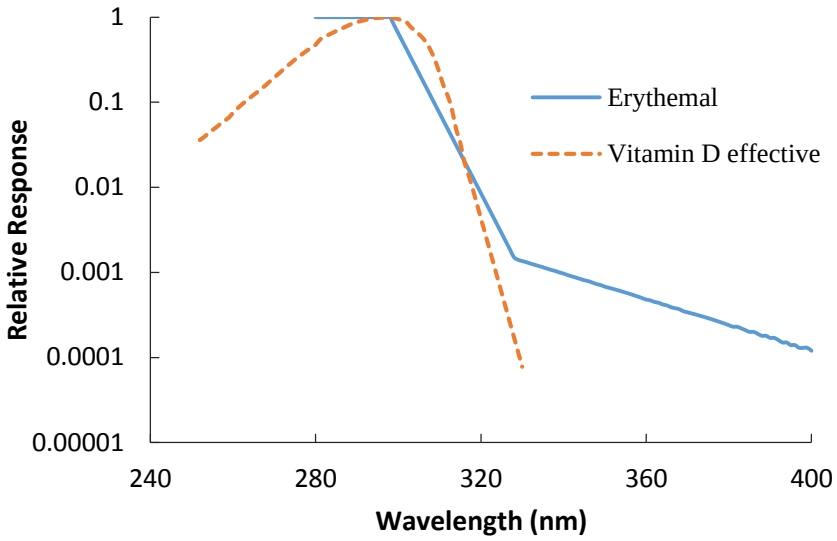

Figure 1.3 Erythemal (CIE 1988) and vitamin D effective (CIE 2006) action spectra.

1.7 POSITIVE AND NEGATIVE EFFECTS

The Sun as the major energy supplier for the Earth plays an important role in the provision of food, warmth and power. For humans the type of energy that actually reaches the Earth's surface can have both positive and negative impacts. People need exposure to UV, particularly UVB in order to manufacture vitamin D; a necessity for good health (Grant 2009). Too much exposure to the Sun's UVR has been linked definitively to a range of diseases and sun damage that can have long term or life threatening effects. A balanced amount of exposure to UVR from the Sun gives the best health outcome.

1.7.1 Negative Impacts on Human Health

UVB elicits the greatest degree of human biological response (Bohren & Clothiaux 2006), and the fastest, most visible biological response in humans is erythema which is associated with the occurrence of melanoma (Cancer Council Australia 2007–2009A).

1.7.1.1 Erythema

Erythema or sunburn is the most immediately obvious consequence of sun exposure. Erythemal exposure is measured in units that relate to the level of UVR that is required to produce a barely perceptible reddening of the skin (erythema). In people with a skin

type that always burns and never tans (Diffey 1992) this reddening is apparent 24 hours after exposure. The amount of erythemal exposure required for this to occur is defined as the minimum erythemal dose (MED), which is approximately 200 J/m^2 of biologically effective exposure (CIE 2014). A standard erythemal dose (SED), which is 100 J/m^2 of radiant erythemal exposure (CIE 1999a; Diffey et al. 1997; Diffey 2002) is more often used, to describe the amount of erythemal exposure, due to the different skin types that exist. Biological effective (UV_{BE}) exposure is:

$$UV_{BE} = \int_0^t \int_{280}^{400} A(\lambda)\, S(\lambda) d\lambda dt \qquad (1.3)$$

where $A(\lambda)$ is the action spectrum, $S(\lambda)$ is the spectral irradiance recorded by the spectroradiometer and $d\lambda$ is the wavelength interval.

Skin type has been classified into six different categories according to the degree of erythemal reaction observed after exposure (Fitzpatrick 1975). These categories (Diffey 1991) are listed in Table 1.1.

Table 1-1 Categories of skin type according to the degree of erythemal reaction (Diffey 1991).

Skin Type	Biologically Effective UV (J/m^2)	Effect	Description
I	200	Always burns, never tans.	Very fair, freckles. Green eyes, red hair.
II	250	Usually burns and peels, tans very lightly.	Fair skin, red or blonde hair, eyes of any colour, white unexposed skin.
III	300	Burns moderately, tans to some degree.	White unexposed skin, any hair or eye colour.
IV	450	Burns to a minimal degree, always tans, increased tanning with increased exposure.	White or light brown unexposed skin, dark hair and dark eyes.
V	600	Rarely burns, tans very easily, immediate skin darkening.	Unexposed skin is brown.
VI	1000	Never burns, always tans, immediate skin darkening.	Unexposed skin is black.

1.7.1.2 Skin Damage

Research into the skin damage caused by UVB (de Gruijl 1999) and to a lesser degree UVA (Agar et al. 2004) has been undertaken for many years and the relationship between cause and effect is well documented. In 2009, 81% of all new cancers diagnosed each year were skin cancers (Cancer Council Australia 2007–2009B). In 2016, the level remains high with 80% of all new cancers diagnosed being skin cancers (Cancer Council Australia 2016). The financial and social cost of the diagnosis and treatment of UV damage, such as melanoma caused by UVB, is extensive. Keratinocytes include basal cell carcinomas and squamous cell carcinomas and occur most frequently. In 2010 the total cost of diagnosis, treatment and pathology of these type of cancers in Australia was AUD $511 million (Cancer Council Australia 2015A).

The time and type of sun exposure have different cancer outcomes. Australia has one of the world's highest rates of diagnosed skin cancer (Cancer Council Australia, 2007–2009B) with two in three Australians being diagnosed with skin cancer before age 70. Sunburn (severe UVB exposure) has been linked to 95% of melanoma cases in Australia (Cancer Council Australia 2016) and "melanoma mutational subtypes are associated with UVR exposure at different life stages" (Lee-Taylor et al. 2010). Non-malignant damage can be linked to long-term repeated exposures with UVA having a greater effect in these cases (Sun Protection Programs Working Party 1996).

There has been less research in the area of UVA damage to humans than that caused by UVB though it has been established that UVA contributes to biological damage (Sicora et al. 2006; Sun Protection Programs Working Party 1996; Agar et al. 2004). Damage caused by UVA is produced differently to that caused by UVB. UVA penetrates further into the human skin, with impacts being less acute but taking longer to show (Webb 1998). The effects of UV exposure include photoageing, which includes damage such as loss of elasticity, mottled pigmentation, wrinkling and sagging of the skin (Webb 1998) as well as cataract formation and other eye damage.

1.7.2 Positive Impacts on Human Health

The benefits of UVR exposure to humans have been much less researched than the damaging effects. The most important known positive effect of solar UV for humans is the production of vitamin D. The amount of time spent in the Sun can be used to predict personal vitamin D levels (Cinar et al. 2013).

UVA exposure can also be beneficial. Phototherapy, using doses of UVA, can improve the condition of patients with skin conditions such as psoriasis and atopic eczema (El-Mofty et al. 2010; York & Jacobe 2010).

1.7.2.1 Vitamin D

The skin contains certain precursors which when stimulated by UVB undergo a number of processes resulting in the production of vitamin D. For humans living at most latitudes, this process of UVB stimulation to the skin produces up to 90% of the vitamin D created within the body (Lucas & Ponsonby 2002). The healthy production and maintenance of the skeletal structure rely on the availability of vitamin D (Holick

2001). Increasingly, research is showing that the contribution of sufficient quantities of vitamin D within the body extends beyond the commonly and long known function of preventing rickets and other musculoskeletal problems. Holick and Jenkins (2003) state that the benefits of sunlight include improved bone, cellular, organ, autoimmune and mood-related health.

The positive benefits of exposure to UV radiation is a rapidly expanding area of research, particularly research into the benefits of vitamin D which is produced as a consequence of exposure to specific wavelengths of UVB. The significant role that vitamin D has as a preventative and cure for rickets has been known since 1923 (Dent & Stamp 1977) and the existence of an association between vitamin D levels and reduced mortality in diagnosed cases of colon cancer since 1980 (Garland & Garland 1980). More recently, studies have indicated that avoidance of the Sun can contribute to mortality from melanoma even when the initial cause could be attributed to UVB exposure (Brondum-Jacobsen et al. 2013; Lindqvist et al. 2014). More research into this inverse relationship between cancer, sunlight and vitamin D is required (van der Rhee, Coebergh & de Vries 2013; Grant 2012).

Vitamin D deficiency or insufficiency is becoming more prevalent (Scragg et al. 2010; Vu et al. 2010) in recent times. This could be a consequence of avoiding sun exposure (Holick & Jenkins 2003) or using excessive prevention methods in order to protect against UV damage. Up to 51% of office workers tested in an Australian study had insufficient vitamin D levels by the end of winter (Vu et al. 2010). Levels of vitamin D had a significant seasonal variation within individuals that could not be related to the individual's reported sun exposure (Kimlin 2010).

1.7.2.2 Previous Studies

The interest in vitamin D studies is increasing, with a substantial rise in the level of vitamin D testing in Australia from 2000 to 2010 (Lucas & Neale 2014). Research into the benefits and delivery methods of vitamin D has also shown much potential in areas such as protecting against colon cancers and improved recovery time following cancer. However, consensus on the optimal levels of vitamin D has not yet been reached (Webb et al. 2010; Lucas & Neale 2014; de Gruijl 2011; Osmancevic et al. 2015). Achieving a sufficient level requires optimization of the type and duration of

exposure. A seasonal cycle of vitamin D production is recognised and for latitudes higher than 51°N, studies indicate that in winter there is not enough appropriate ambient UV to allow for any vitamin D production (Engelsen et al. 2005). Studies from other nations, not just those located in high latitudes are reporting deficient and insufficient vitamin D levels. These nations include Israel (Azizi et al. 2009), Australia (McGrath et al. 2001) and Turkey (Cinar et al. 2013). Webb et al. (2010) has shown that weekly exposures of around 3.7 times the SED can significantly improve vitamin D levels within adults of fair skin type. One SED is equivalent to 100 J/m^2 of erythemal UV. Potential positive benefits are continuing to be identified (Knippenberg et al. 2014; Le et al. 2015), but have yet to be fully researched or documented. It is accepted that the majority of vitamin D is generated through exposure to sunlight and, in ideal circumstances, such exposure would be sufficient to create enough vitamin D in humans (de Gruijl 2011; Osteoporosis Australia 2015).

1.8 SUN EXPOSURE RECOMMENDATIONS

Vitamin D production through sun exposure is recognized as the ideal production method (de Gruijl 2011) and is, at present, how the majority of vitamin D is generated. The current recommendation for avoiding melanoma is to use sunscreen which provides broad-spectrum (UVB and UVA) protection, and to avoid exposure to the Sun when the UVI is 3 or above (Cancer Council Australia 2015B).

These two statements highlight the difficulty in presenting an overview of the effects of UV exposure. The effects of casual sun exposure on a specific individual cannot be predicted due to the large number of factors influencing UV exposure (Webb 2006). These factors range from the personal, such as area of skin exposed and personal baseline vitamin D levels (Bogh et al. 2010), to the general which include time of day, season and geographic location (Webb et al. 2010).

1.9 METHODS AND TERMINOLOGY USED IN UV MEASUREMENT

The term irradiance specifically relates to the intensity of the radiant power on a unit area of a surface. Irradiance is normally measured in watts per square metre (W/m^2). Exposure is calculated by multiplying irradiance by a period of exposure in seconds.

The units of exposure are joules per square meter (J/m^2). A variety of methods and equipment is used in the measurement of the UV levels. These may range from expensive permanently located equipment to small portable devices that are single use and relatively cheap to produce.

1.9.1 Portable and Fixed Equipment

1.9.1.1 Radiometer

Radiometers are used to measure the intensity of electromagnetic energy in radiometric units such as W/m^2 or W/cm^2. A broadband radiometer measures over a broad spectrum of wavelengths (Seidlitz & Krins 2006). The measurements are made via a sensor which produces a measurable electric current whenever any frequency within a given waveband of electromagnetic radiation is absorbed.

A multi-filter rotating shadowband radiometer is an instrument capable of measuring the total, diffuse and the direct components of spectral solar irradiance (Yankee Environmental Systems Inc. 1996). A 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 total and diffuse values can be determined directly from the recorded measurements, the direct component is calculated by subtracting the diffuse measurement from the total measurement (Harrison, Michalsky & Berndt 1994).

Shadowband radiometers can be configured to take measurements at specific selected wavelengths. These wavelengths are usually chosen in order to help determine the optical depths of water vapour, aerosols and ozone. A broadband channel measures the total solar irradiance.

1.9.1.2 Spectroradiometer

A spectroradiometer measures the distribution of UV energy with wavelength. Spectroradiometers are able to measure the irradiances within specific selected wavelength limits. The apparatus consists of entrance optics, a monochromator, detector, amplifier and a control and data acquisition unit (Seidlitz & Krins 2006). Input optics depolarise the incoming radiation and the receptor should take into

account the angular distribution of the incident radiation. A baffle prevents radiation from moving straight to the diffuser (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. Before each measurement session spectroradiometers need to be calibrated to known irradiance sources both for wavelength and irradiance.

1.9.1.3 Sun Photometer

Sun photometers are used to measure direct sunlight over a specified 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).

For sun photometers to measure only the *direct* sunlight, the light passes through a small hole in the casing to reach the detectors inside. A large aperture would permit some diffuse light to enter as well as the direct. Measuring the direct UV in narrow wavebands also enables the measurement of atmospheric ozone and aerosols (Herman 2010).

1.10 SOLAR UV DOSIMETRY

Dosimetry is an established method for measuring specific UV exposures received by an object or subject. Dosimeters are small enough to be attached to any surface being measured; such as skin or clothing. They can be placed at multiple locations (Webb 1998) and are flexible enough to be used at a range of angles. This allows for many measurements to be made simultaneously. Dosimeters should be constructed so that they have no effect on the participant's usual daily activity. This allows exposures to be measured during normal daily activities. Types of dosimeters include: biological, electrical and chemical.

1.10.1 Biological Dosimeters

Biological dosimeters measure changes induced by UV radiation. They usually contain microorganisms that change in a way similar to the action spectrum of interest. Yagura et al. (2011) tested DNA, bacteria and mammalian cells for use as biological dosimeters. Horneck et al. (2006) described biological dosimeters including *E. coli* in suspension or spores of *B. subtilis* in suspension or in a biofilm. Biological dosimeters can be difficult to handle and may undergo changes due to environmental conditions other than UV exposure.

1.10.2 Electrical Dosimeters

Electronic dosimeters are being used more frequently. Examples include the dosimeters used in studies in New Zealand (Allen & McKenzie 2010) which measure 35 mm diameter × 10 mm and weigh approximately 20 g, being worn with a Velcro wrist strap. Thieden et al. (2004) developed a personal electronic UVR dosimeter in a wristwatch comprising a sensor, a data logger, and a battery. The data were calibrated to a stationery UV Biometer. Electronic dosimeters were used in a comprehensive study of the UVR exposure of school children in New Zealand (Wright et al. 2007). In this study the received exposure was weighted to the erythemal action response and the children were asked to complete an activity diary to record clothing and the type and location of the activity. Electronic dosimeters can record a large amount of data as they can take measurements every few seconds over a number of days. The sensor used has a spectral response matching the required action spectrum. Electronic dosimeters are costly but they can be reused. The large amount of data collected can make meaningful interpretation difficult (Liley et al. 2010). 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.

1.10.3 Chemical Dosimeters

Chemical dosimeters measure UV exposures by utilizing a photoactive chemical film that mimics a specific biological response. This biological response would be similar to that of the action spectrum of the area under investigation. Various chemicals have been used in the manufacture of polymer film UV dosimeters. Their use depends on the required UV measurements. A range of chemicals can be used that respond to

specific wavelengths such as only UVA wavelengths, only to UVB, or across both the UVA and UVB wavelength ranges.

The standard size dosimeters used in previous research measure approximately 30 × 30 mm with an average weight of 0.7 g (Parisi, Schouten & Turnbull 2010) and have a rigid PVC frame supporting an area of 12 × 16 mm of exposed photoactive film (Lester et al. 2003). Even though this type of dosimeter is quite small, it is too large and the frame too rigid to lie parallel to some measurable surfaces such as the angles around a human face (Downs & Parisi 2007). A dosimeter of smaller size has recently been developed. It measures 10 × 30 mm and has an average weight of 0.03 g (Parisi, Schouten & Turnbull 2010).

1.11 DOSIMETRY STUDIES

Polysulphone (PS) is a photoactive chemical often used in manufacturing chemical dosimeters (Diffey 1987). When exposed to UV, PS has "an approximation of the spectral response to the erythemal action spectrum" (Parisi, Sabburg & Kimlin 2004). Saturation of a chemical dosimeter occurs when no further change is possible despite further UV exposure. Davis, Deane & Diffey (1976) have determined that the saturation level of PS occurs at about one day's exposure. The amount of time actually taken would depend on the season. At peak exposure times saturation may occur well below one day in tropical climates. PS dosimeters are very useful where short term or daily exposure measurements are required.

Polyphenylene oxide (PPO) is also a photoactive chemical used in dosimeters that was identified by Davis et al. (1976). PPO has a low response to UVA at 340 nm and a response spectrum in line with the erythemal action spectrum for wavelengths in the UV range between 290 and 340 nm (Lester et al. 2003). The time to reach saturation due to exposure for PPO is much higher than for PS (Schouten, Parisi & Turnbull 2010).

Dosimeters have been employed in a number of studies (Downs & Parisi 2012; Schouten, Parisi & Turnbull 2010; Siani et al. 2009) that have successfully measured personal UVR exposures under varying conditions, particularly UVB exposures and

more specifically the erythemal UV. Dosimetry studies have used either PS (Guy et al. 2003; Downs & Parisi 2008; Downs et al. 2009; Siani et al. 2009, 2011) or PPO (Schouten, Parisi & Turnbull 2010; Wainwright, Parisi & Schouten 2013; Casale et al. 2015) as the photoactive material for measuring the exposure. Usually PS film is used in studies requiring exposure times up to eight hours, and PPO film is used for studies of one to seven days duration.

Dosimeters have also been used to measure UVA exposures for specified wavelengths and limited times (Jia, Parisi & Kimlin 2010; Turnbull & Parisi 2010). A short wavelength UVA dosimeter has been employed in measuring the shorter UVA wavelengths of 320 to 340 nm (Turnbull & Schouten 2008). There are other dosimetric systems capable of measuring the full UV spectrum and ionising radiation (Kozicki & Sasiadek 2011, 2013).

Dosimetry can contribute to developing an understanding of the personal photobiological effects caused by exposure to the Sun through accurate measurement and reliable recording of these measurements (Diffey 1987). Predominantly, research using dosimeters has measured individual wavebands. Parisi & Wilson (2005) used PS dosimeters to record vitamin D effective UV levels through clothing as well as recording the erythemal exposures over a three hour period. A dual calibrated combined dosimeter able to measure three wavebands concurrently is necessary because of the interactions of beneficial and damaging UV.

1.12 CHAPTER SUMMARY

This chapter looked at UV radiation; the separate wavebands of UV, the atmospheric conditions that influence surface UV levels, the positive and negative effects that UV exposure has for humans, and some methods of measuring levels of UV. The following chapter gives more detail on the equipment and methods involved for the testing and calibration of dosimeters in this research to develop and characterize a dual calibrated combined dosimeter for measuring three wavebands concurrently.

2. MATERIALS AND METHODS

2.1 OVERVIEW

This chapter gives details of the various items of equipment and the methods used in this research, both in the laboratory and in the field. Descriptions of the instrumentation used in recording atmospheric conditions are also included. In this chapter the word dosimeter applies to any type of chemical film dosimeter. Details of the manufacturing process of the specific dosimeters used in this study will be covered in Chapters 3 and 4.

2.2 EQUIPMENT

In order to establish a base level by which the dosimeters can be calibrated, it is necessary to record the ambient UV and the atmospheric conditions under which this UV was measured. The equipment used to record this information includes the following items:

- Biometers
- Spectroradiometer
- Total Sky Imager
- IL1400 Broadband Meter
- Sunphotometer
- Portable UV Meter
- Solar Simulator
- Irradiation Monochromator
- Portable Scanning Spectroradiometer
- Spectrophotometer

2.2.1 External Equipment

The following items of equipment are located in a shade free position on a rooftop at USQ Toowoomba, Queensland (27°33'S 151°55'E, elevation of 691 m) Australia. This location offers a full hemispherical sky view, has many cloud free days and has low pollution.

2.2.1.1 Biometers

There are two Biometers in use at USQ. The first of these (model 501 UV-Biometer, Solar Light Co., PA, USA) was used to measure the erythemal exposure in units of MED as it has a spectral response that approximates the erythemal action spectrum. The erythemal Biometer automatically records the integrated erythemal UV exposure for every five minute period during the day. The second Biometer (UVA Biometer model 501A, Solar Light Co., PA, USA) was used specifically for UVA measurements. It records the integrated UVA exposures over each five minute period of the day. Figure 2.1 shows the two Biometers on their rooftop location at USQ. The biometers can also be seen in the background of Figure 2.2. The angular response of the Biometer detector is in the order of ±5% from an ideal cosine response for incident zenith angles less than 60º (Morys & Berger 1993). The Biometers are regularly calibrated against the Bentham spectroradiometer (Section 2.2.1.2) and are set to record the cumulative erythemal UV exposures each five minutes. The accuracy of the Biometer is ±10% of the daily total (Lester et al. 2003).

Figure 2.1 The erythemal and UVA Biometers located on a rooftop at the University of Southern Queensland.

2.2.1.2 Spectroradiometer

A double grating scanning UV spectroradiometer (model DTM300, Bentham Instruments, Ltd., Reading, UK) was used to record the complete spectral range of UV measurements. The global spectral UV was recorded in 0.5 nm increments between 280 and 400 nm at ten minute intervals. An automated shadowband was used so that diffuse levels could be measured five minutes after each global measurement. Each scan lasts a maximum of three minutes during which time integrals for the total UV and for the erythemal UV are calculated. Both sets of these measurements were

recorded from 05:00 – 19:00 h daily. The spectroradiometer is wavelength calibrated to the UV mercury spectral lines and irradiance calibrated to a quartz tungsten halogen lamp with a calibration traceable to the primary standard located at the National Physical Laboratory (NPL) United Kingdom (UK) in summer and winter of each year. The software for the spectroradiometer allows integrations of total UV, UVA, UVB, vitamin D effective UV and erythemal irradiances to be calculated in the appropriate units, for the dates and times required. Figure 2.2 shows the spectroradiometer in the foreground with the shadowband obscuring the sensor. Figure 2.3 is another view of the spectroradiometer which is housed in a climate controlled Envirobox to protect it against the elements. A separate air-conditioning unit maintains a stable temperature of 25 ºC. Bentham has estimated that the cosine error of the diffuser is in the order of ±0.8% for a SZA less than or equal to 70° and is approximately 3.3% at a SZA of 80°. Parisi & Downs (2004) determined that the overall absolute irradiance accuracy of the Bentham spectroradiometer was of the order of ±9%.

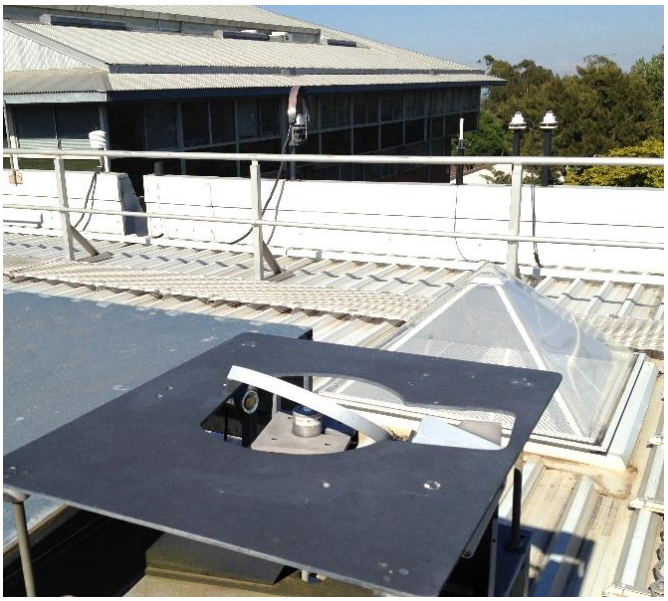

Figure 2.2 Bentham spectroradiometer showing shadowband over the sensor in the foreground and the Biometers in the background.

Figure 2.3 Bentham spectroradiometer in the Envirobox (Schouten 2009).

2.2.1.3 Total Sky Imager

A Total Sky Imager (TSI) (TSI440, Yankee Environmental Systems, PA, USA) captures images from the sky every minute of the day via a CCD camera that looks down towards a heated hemispherical mirror as shown in Figure 2.4 (USQ 2016). The mirror has a solar-ephemeris guided shadowband which blocks reflected solar radiation and prevents CCD saturation. The saved images are analysed to determine the percentage of cloud cover which is displayed on the USQ Solar UV data website (USQ 2016), as shown in Figure 2.5.

Figure 2.4 Total Sky Imager used to record cloud cover (USQ 2016).

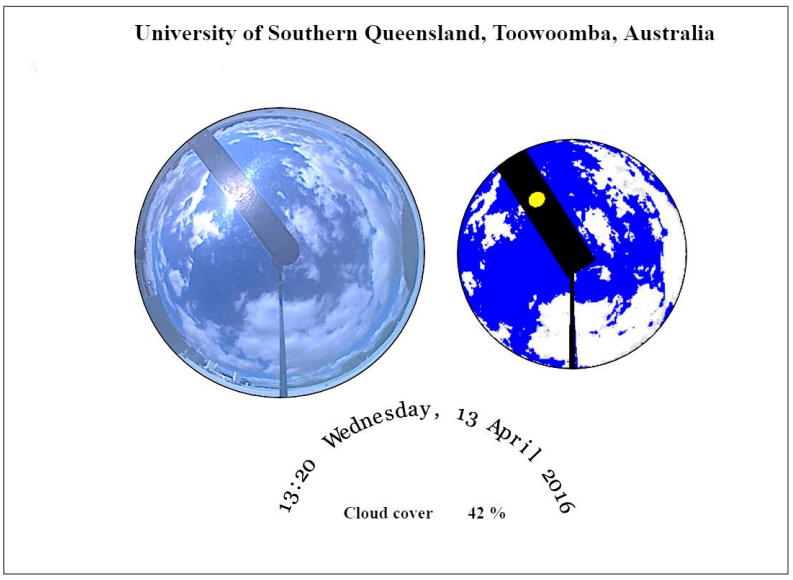

Figure 2.5 A cloud percentage calculation based on data from the Total Sky Imager as shown on the USQ website (USQ 2016).

2.2.2 Portable Equipment

2.2.2.1 IL1400 Broadband Meter

In order to specifically calibrate the vitamin D effective UV, an IL1400 broadband meter ("A" Series, International Light Inc., Newburyport, MA, USA) was used. It had a waterproof detector attached responsive to the 265–332 nm waveband (SUD240, International Light Inc., Newburyport, MA, USA) with a UVB filter (UVB1 phototherapy filter, International Light Inc., Newburyport, MA, USA). For the purpose of this thesis these items will be referred to collectively as the IL1400. The IL1400 broadband meter is completely portable and was used as an onsite UVR measurement instrument. Figure 2.6 shows the IL1400 being used to measure exposure. Although the sensor is waterproof the instrument itself needs to be protected from both water and excessive heat and is shown here inside part of a weatherproof container. The response of the IL1400 broadband meter with the detector and filter was restricted to UVB wavelengths and it is able to integrate UVB exposures over time, allowing calibration of the dosimeters to be done over extended time periods. The IL1400 was calibrated to the weighted spectroradiometer data for vitamin D effective UV. International Light Inc. (1998) states that the IL1400 has 0.2% linearity and has a level of repeatability no greater than ±3% when compared to the National Institute of Standards and Technology (NIST) transfer standards.

Figure 2.6 IL1400 broadband meter recording UVB exposure.

2.2.2.2 Sunphotometer

Where possible, Aerosol Optical Thickness (AOT) was recorded using a sunphotometer (Microtops II, sunphotometer version 5.6, Solar Light Co. Inc., PA, USA). This instrument was only available for a limited time during the initial development phases of data collection and testing. As measurements can only be made when there is no cloud in the direct path between the instrument and the sun, readings could not be made for all dates and times. This instrument was calibrated by the manufacturer at the Mauna Loa Observatory, Hawaii (Morys et al. 2001).

2.2.2.3 Portable UV Meter

A portable UV meter (model 3D, Solar Light Co., PA, USA) was used to detect the presence of any ambient UVA and erythemal UV irradiances at indoor locations. This meter measures irradiance in units of mW/cm^2, and has been calibrated to the Bentham spectroradiometer.

2.2.3 Laboratory Equipment

Prior to field testing, the dosimeters were tested in a climate and light controlled laboratory using the equipment described in this section.

2.2.3.1 Solar Simulator

A solar simulator (1000 W, model 19160–1000, Newport Co., CA, USA) combined with a digital exposure controller (model 68945, Newport Co., CA, USA) was used to test the dosimeters in the laboratory (Figure 2.7). The solar simulator provides a stable artificial source of UVR that approximates the solar UV spectrum. The emitted beam is collimated and is uniform over an area 5.1 cm × 5.1 cm (Amar 2014). Figure 2.8 shows dosimeters being exposed well within the collimated field area of the solar simulator.

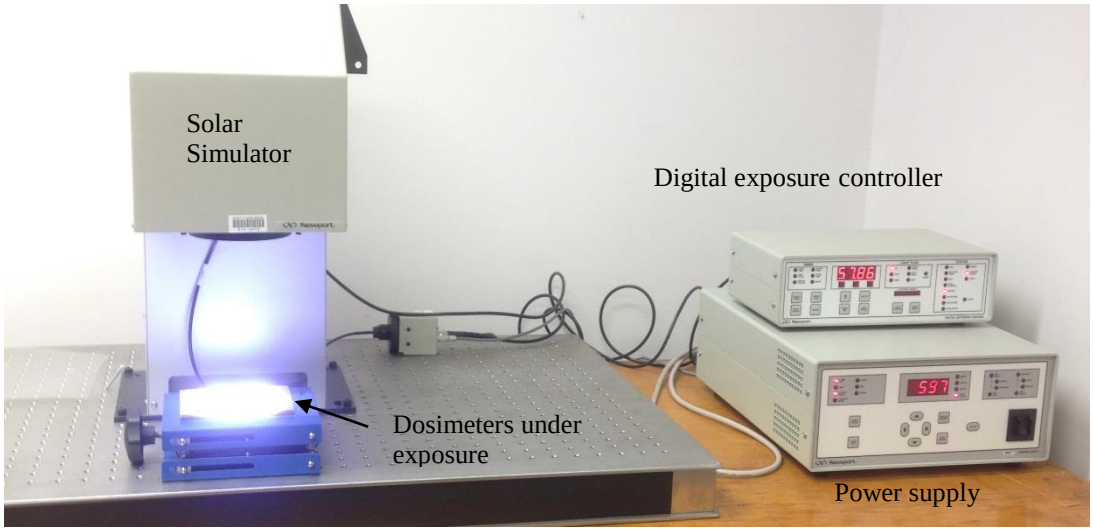

Figure 2.7 The solar simulator being used to expose dosimeters.

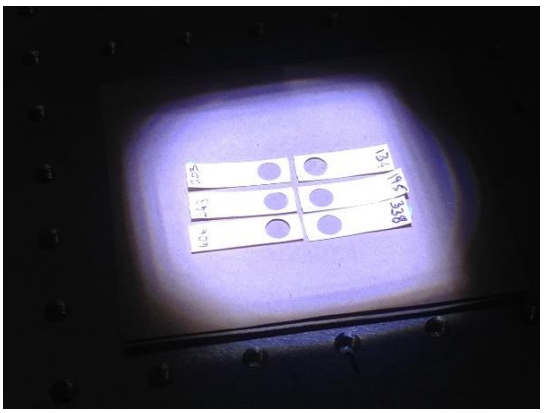

Figure 2.8 Dosimeters being exposed within the collimated beam of the solar simulator.

2.2.3.2 Irradiation Monochromator

An irradiation monochromator (Cornerstone™ 260 ¼ m motorized monochromator Oriel Instruments, USA) (Figure 2.9) was used to investigate the degree of effectiveness of different wavelengths for producing measurable change in the dosimeter. The radiation source was a 1600 W xenon mercury arc lamp (model 66870, Oriel Instruments, USA). The lamp was powered by a digital arc lamp power supply (model 69922, Oriel Instruments, USA) with an exposure controller (model 68945, Newport Co., CA, USA) used to stabilize the lamp output. The width of the input and output slits of the monochromator can be adjusted to control the full width at half maximum (FWHM) of the output beam. The slits were set to produce a beam with a FWHM of approximately 5 nm.

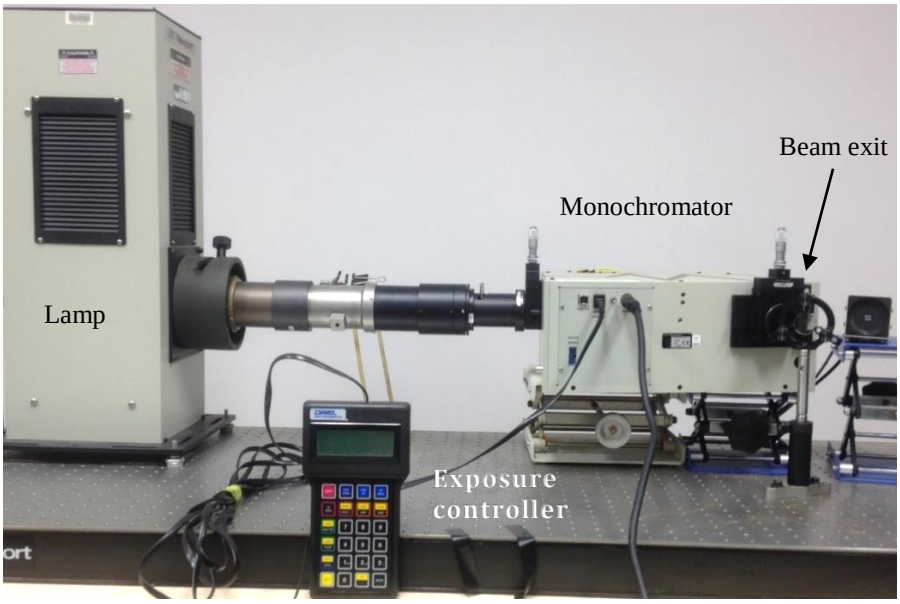

Figure 2.9 The equipment arrangement for the irradiation monochromator.

2.2.3.3 Portable Scanning Spectroradiometer

A double grating scanning spectroradiometer (model DMc150, Bentham Instruments Ltd., Reading, UK) was used to obtain spectral irradiance measurements of the artificial sources of UVR that were used in the laboratory (Figure 2.10). A five metre fibre optic cable links the spectroradiometer to the input diffuser (model D7, Bentham Instruments Ltd., Reading, UK). This spectroradiometer is also regularly calibrated as described in Section 2.2.1.2.

Figure 2.10 Portable scanning spectroradiometer used for irradiance measurements in the laboratory.

2.2.3.4 Spectrophotometer

A UV-Vis double beam spectrophotometer (UV-2700, Shimadzu Co., Kyoto, Japan) together with UV-Probe software was used to measure the changes in the UV absorbance of the photoactive film in each dosimeter (Figure 2.11). This spectrophotometer measures the intensity of the transmitted UVR by comparing the irradiance transmitted through the dosimeter film to a reference beam of the same wavelength that has not passed through the film. Absorbance is a unit-less quantity that represents the amount of photons that are absorbed. The radiation sources of the instrument are halogen and deuterium lamps with an on-board automatic light source positioning mechanism. The spectrophotometer is characterized by a photometric range of −5 to 5 ABS for the absorbance mode, and 0 to 100000% for the transmittance mode (Shimadzu 2011).

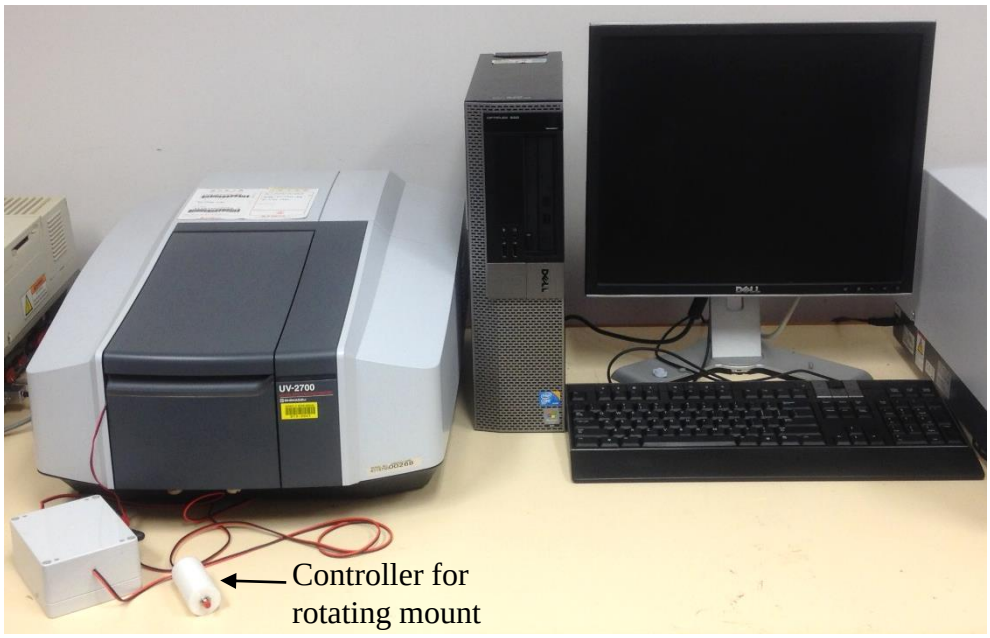

Figure 2.11 Spectrophotometer used to measure absorbance of the dosimeters. The controller used to spin the rotating mount is at the front.

The spectrophotometer has a purpose built rotating mount to which a specially manufactured dosimeter holder can be attached. Figure 2.11 shows the spectrophotometer with the controller and motor used to activate the rotating mount in front. Figure 2.12 shows a dosimeter in the holder, and Figure 2.13 shows the rotating mount and dosimeter in position within the spectrophotometer. Dosimeters were inserted into the holder and secured in place during measurement.

The absorbance of each dosimeter was measured at four points with the rotating mount turning through 90° between each measurement. Using four separate points improves the accuracy of the individual measurements as it takes into account any variations in thickness of the photoactive material or disturbances that may have occurred on the surface during deployment. The arithmetic mean of these four measured absorbance values was used for all subsequent calculations to determine UV exposure through calibration and characterization of the dosimeter. This procedure was followed for all exposure testing of the dosimeters. During absorbance measurements with the spectrophotometer, each dosimeter was visually inspected to ensure that the film was free of aberrations and breakages before insertion into the holder. Tests of the spectrophotometer showed that the variability of absorbance measurements due to the

equipment was within the range of 0.000 – 0.008. Values above this can be attributed to changes due to external exposure.

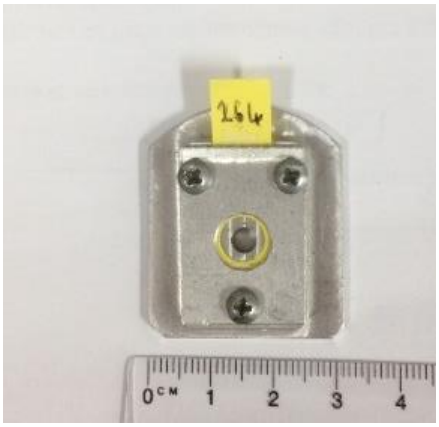

Figure 2.12 Dosimeter in the holder used for spectrophotometer measurements.

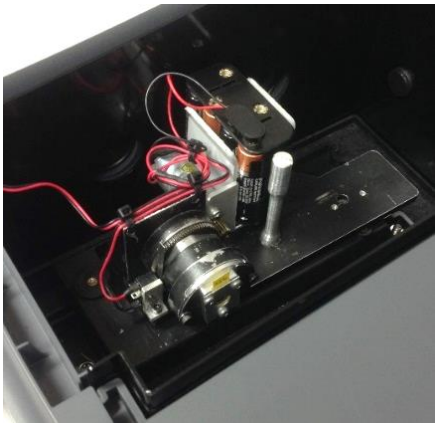

Figure 2.13 Dosimeter in position in the spectrophotometer prior to being measured.

2.3 METHOD

2.3.1 Dosimeter Selection

There is no current dosimetric method for measuring damaging and beneficial UV at the same time over a long exposure period. In developing a methodology that could achieve both measurements, dosimeters were investigated in several ways. All the testing reported here was done using miniaturized dosimeters of 10 × 30 mm with a 7 mm diameter area of exposed film. These smaller dosimeters have a flexible plastic frame which enables a smooth fit over curved surfaces. The smaller size also allows "a greater density of dosimeters to be deployed across the test subject or object" (Downs & Parisi 2012). Approximately three times as many miniaturized dosimeters can be constructed for the same cost and in the same production time per sheet of film as the larger-sized dosimeters.

2.3.1.1 Dosimeter for Measuring Erythemal and Vitamin D Effective UV

In selecting a dosimeter suitable for measuring both erythemal and vitamin D effective UV, two different photoactive chemicals were investigated:

1. PS has been the predominant photoactive chemical used in dosimetry research for exposure times of up to eight hours (Guy et al. 2003; Downs & Parisi 2007; Downs et al. 2009; Siani et al. 2011). PS was not chosen due to the relatively low time of exposure before the saturation point is reached

2. PPO film, on the other hand, has been recognized as an appropriate material for long term solar exposure (Lester et al. 2003; Berre & Lala 1989; Schouten et al. 2010; Casale et al. 2015), where long term means cumulative exposure of a period up to seven days (Parisi, Schouten & Turnbull 2010).

In performing a full characterization of PPO, Lester et al. (2003) showed that PPO can be used successfully as an erythemal UV dosimeter. As PPO has a response within the UVB waveband and the vitamin D effective UV action spectrum is in the UVB range, it is expected that a calibration can be performed to weight the PPO against the vitamin D effective action spectrum. As PPO can be exposed for up to one week and has a response within the UVB range PPO was chosen as the photoactive material to be used for the erythemal and vitamin D effective UV dosimeter.

2.3.1.2 Dosimeter for Measuring UVA

After eliminating electrical dosimeters due to high cost and limited availability, and eliminating biological dosimeters as they are not robust enough for field work, investigation into the selection of a thin film dosimeter for measuring UVA found that a dosimeter suitable for long term use had not been developed. A phenothiazine dosimeter was found to have too short an exposure time at up to three hours (Parisi et al. 2005). The exposure time of PS was also too short. PPO has been investigated for use as a UVA dosimeter (Turnbull & Schouten 2008); it has minimal response to UVA at wavelengths longer than 340 nm (Lester et al. 2003), therefore it was deemed unsuitable for this research as it was not able to respond to the longer UVA wavelengths to a significant degree.

Diffey & Davis (1978) identified, but only partially characterized, a potential UVA dosimeter using 8-methoxypsoralen (8-MOP). It was decided to investigate and fully characterize this dosimeter to see if it was appropriate for long term (seven days) UVA exposure measurements.

2.3.2 Population Field Study

All field studies were performed in Toowoomba, Queensland. The study followed the method outlined below. All experimentation was approved by the Human Research Ethics Committee of the University of Southern Queensland (approval H12REA191) under the guidelines of the National Health and Medical Research Council of Australia.

In the field study, participants at two separate sites were tested concurrently. Volunteer participants were required to wear a dosimeter badge during daylight hours for one to two week periods and record the time spent on daylight outdoor activities on a daily activity list (Appendix A), as well as noting the type of clothing worn and if any sunscreen was used. The participants were asked to remain within the Toowoomba area whilst participating in the study. As the amount of UVB and UVA that reaches the Earth changes throughout the year, and levels of vitamin D have been shown to have a significant seasonal variation within individuals (Engelsen et al. 2005; Kimlin 2010), this procedure was repeated four times: with one study being carried out in each season. Each seasonal study was self-contained so it was not necessary to have the same participants in all four seasons. Each participant was required to ensure that the dosimeters were worn each day, and was instructed in the use of an activity list.

2.3.3 Calibration

UV dosimeters require calibration to the UV spectrum at the Earth's surface before they are able to be used in the field independently (Casale et al. 2006). The relationship between the changes in absorbance of the dosimeters and the recorded exposure is defined in each season and used for calibration purposes. Detailed explanations of specific calibrations will be given in Chapters 3 and 4.

2.3.3.1 Instrument Calibration

The Biometers and the IL1400 were calibrated directly to the spectroradiometer for exposures on a cloud free day in each season. The studies were performed in winter, spring, summer and autumn. The dates selected for the studies fall within the definition of each season, whether the season is determined as starting on the first of the month (meteorological seasons) or the twenty first of the month (astronomical seasons).

The recorded irradiances were multiplied by the time in seconds to provide the respective exposures over four-hourly periods of the day to calibrate the UVA Biometer, the erythemal UV Biometer and the IL1400 broadband meter.

The measured spectroradiometer UV spectra for the calibration period were weighted separately with the erythemal action spectrum (CIE 1988) and the vitamin D effective action spectrum (CIE 2006). These two sets of biologically effective UV were employed to calibrate the UV Biometer for erythemal UV and the IL1400 for vitamin D effective UV.

2.3.3.2 Dosimeter Calibration

Separate calibrations for the erythemal action spectrum, the vitamin D action spectrum and broadband UVA were conducted over a period of up to one week in each season. This was done by establishing a calibration equation which linked the gradual changes in the optical absorbance of each dosimeter type to the measured exposure in the respective UV wavebands. As the response spectra of each photoactive film, the IL1400 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).

The UVA dosimeters were calibrated to the UVA Biometer which records the UVA exposures over each five minute period of the day. The PPO dosimeters were calibrated for erythemal UV to the UVB Biometer. The vitamin D effective UV was calibrated against the IL1400 radiometer with a detector responsive to the waveband 265 – 332 nm. The IL1400 provided the integrated exposures over a given time period.

2.3.4 Atmospheric Considerations

As a number of factors influence surface UVR, the following parameters were monitored and the details recorded during both field tests and seasonal calibrations:

- The Aerosol optical thickness and the ozone levels were recorded using the Microtops II sunphotometer where possible, or were otherwise retrieved online from Giovanni, Goddard Earth Sciences Data and Information Services Center (GES DISC)

- The solar zenith angle data was recorded by the TSI or was retrieved online from Geoscience Australia (2016)

- The ultraviolet index was calculated from the on-site Biometer measurements these results were displayed on the USQ website as shown in Figure 2.14

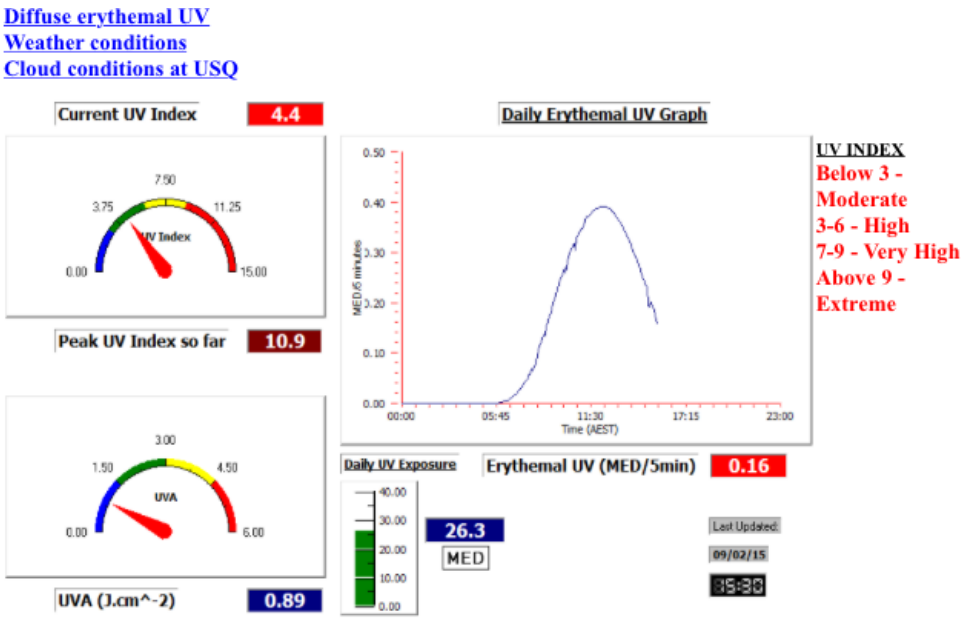

Figure 2.14 Ultraviolet Index (UVI) calculations as displayed on the USQ website (USQ 2016).

2.4 CHAPTER SUMMARY

This chapter provided information on the equipment used both in the field and in the laboratory during the testing and calibration of dosimeters. The structure of the field test was outlined and the atmospheric considerations were addressed. The next chapter will give more detail of how some of these items were used when researching the suitability of 8-MOP as a UVA dosimeter.

3. UVA DOSIMETER

3.1 OVERVIEW

Using equipment and methods outlined in the previous chapter, this chapter details the process of fabrication, testing and calibration of a dosimeter used to measure UVA wavelengths. The photoactive chemical being investigated is 8-MOP. This chemical was previously identified by Diffey & Davis (1978) for use in a UVA dosimeter but was not fully evaluated at that time. In this and following chapters where mean values are given in the analysis of dosimeters this is always the arithmetic mean.

3.2 INTRODUCTION

3.2.1 UVA Effects

Current research indicates that the financial and social cost of damage such as melanoma, caused by UVB is extensive (Cancer Council Australia 2016) and that UVA is a contributing factor in skin cancers (Agar et al. 2004). Although UVA damage to humans has been less researched than that caused by UVB, it has been established that UVA contributes to biological damage (Lavker & Kaidbey 1997; Sun Protection Programs Working Party 1996), and that the damage it causes is produced differently to that caused by UVB. Given that there is greater than six times more measurable UVA than UVB (Webb 1998) in terrestrial surface spectra, there is more potential for larger doses of UVA compared to UVB to enhance the biological effects.

3.2.2 Measuring UVA with Dosimeters

Dosimeters using either PPO or PS have been used to measure received erythemal UV exposures by humans for exposure periods of half a day up to seven days depending on the season and latitude (Wainwright, Parisi & Schouten 2013; Davis, Deane & Diffey 1976). PS dosimeters can measure erythemal UV exposures over a shorter time of up to one day. A PPO dosimeter has a larger dynamic range and can record exposures of five to seven days subject to seasonal and atmospheric conditions (Casale et al. 2012).

An extension of this type of dosimeter is the polyvinyl chloride (PVC) based dosimeter (Amar & Parisi 2012, 2013B) that allows erythemal UV measurements over periods of up to three weeks before requiring replacement due to saturation. A dosimeter based on phenothiazine has been reported for the measurement of UVA exposures. The phenothiazine dosimeter is useable for periods up to approximately half a day at subtropical southern latitudes (Jia, Parisi & Kimlin 2010). Further UVA dosimeters employ the use of radiochromic film for measurement over shorter periods (Butson et al. 2000; Abukassam & Bero 2013) however, these would require frequent changes to record measurement periods greater than one day, making them impractical for some applications. A short wavelength UVA dosimeter based on PPO has also been employed in measuring the shorter UVA2 wavelengths of 320 to 340 nm (Turnbull & Schouten 2008). There is however, a research need for a dosimeter sensitive to both the UVA1 (340 – 400 nm) and UVA2 (320 – 340 nm) wavebands that allows for measurement over longer time frames. This research reports on the characterization and evaluation of a UVA dosimeter sensitive to wavelengths between 320 to 400 nm, and which is capable of longer periods of measured exposure than is possible with the dosimeters currently in use.

3.3 DEVELOPMENT OF THE 8-MOP DOSIMETER

Diffey & Davis (1978) identified, but only partially characterized and evaluated, a potential UVA dosimeter using 8-methoxypsoralen. The following tests were undertaken to assess the capability of 8-MOP for use as a long term UVA dosimeter: the dark reaction, repeatability of measurement, seasonal dose response, cosine response, spectral response, temperature independence and dose rate independence. This procedure has been used previously in dosimeter development for other types of dosimeters (Davis, Deane & Diffey 1976; Diffey 1989; Lester et al. 2003).

3.3.1 Dosimeter Fabrication

3.3.1.1 Making the Solution

The 8-MOP film used for the UVA dosimeter was manufactured by the author at USQ. The film was made from a solution of 8-MOP crystals (Sigma, Saint Louis, USA) and polyvinyl chloride (PVC) powder dissolved in tetrahydrofuran (THF) as outlined by

Diffey & Davis (1978). The spectral response of the PVC dosimeter developed by Amar & Parisi (2013A) determined that the PVC dosimeter did not react to the UVA waveband. The 8-MOP solution was mixed for 12 – 18 hours to ensure the 8-MOP was fully dissolved. When ready, the solution was completely clear, colourless and slightly viscous. Figure 3.1 shows a container of the 8-MOP solution just prior to being used for casting.

3.3.1.2 Casting the Film

The film sheets were cast on a specifically constructed casting table employing a glass slab smooth to one micron (Figure 3.2). The casting table was located within a fume cupboard and the surrounding lights did not emit any UV wavelengths. The solution was poured at one end of the glass slab and a motor driven blade passed over the glass to distribute the solution evenly. The height of the blade above the glass could be adjusted by the micrometer shown in Figure 3.2. After the blade had stopped moving the casting table was covered and the sheet left to dry. Figure 3.3 shows a sheet of film being removed from the casting table after several hours of drying. Each sheet was then set aside in a light free cupboard for further drying before being ready for use.

3.3.1.3 Measuring Film Thickness

A predetermined blade height gives the cast sheets a mean thickness of 26 μm as measured using a dial thickness gauge (Logitech, UK) shown in Figure 3.4. To determine the correct blade height that produced the required thickness, several sheets were cast at various blade to glass distances. Once the sheets were dry they were divided into quarters, the thickness of a small section from each piece was measured using the dial thickness gauge which also assessed the evenness of the poured solution. The thickness gauge measures thicknesses within the range of 0 – 10 mm. All thickness measurements had to be made with the film placed between feeler gauges of known thickness. Measuring the film by itself, without placing it between the feeler gauges, gave false readings as the pressure applied by the anvil during measurement compressed the film.

Figure 3.1 A container of 8-methoxypsoralen (8-MOP) solution prior to being used for casting.

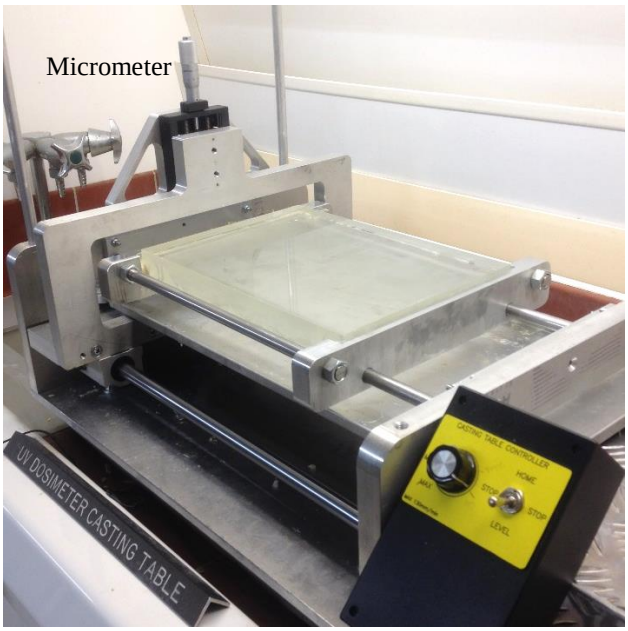

Figure 3.2 The purpose built thin film casting table.

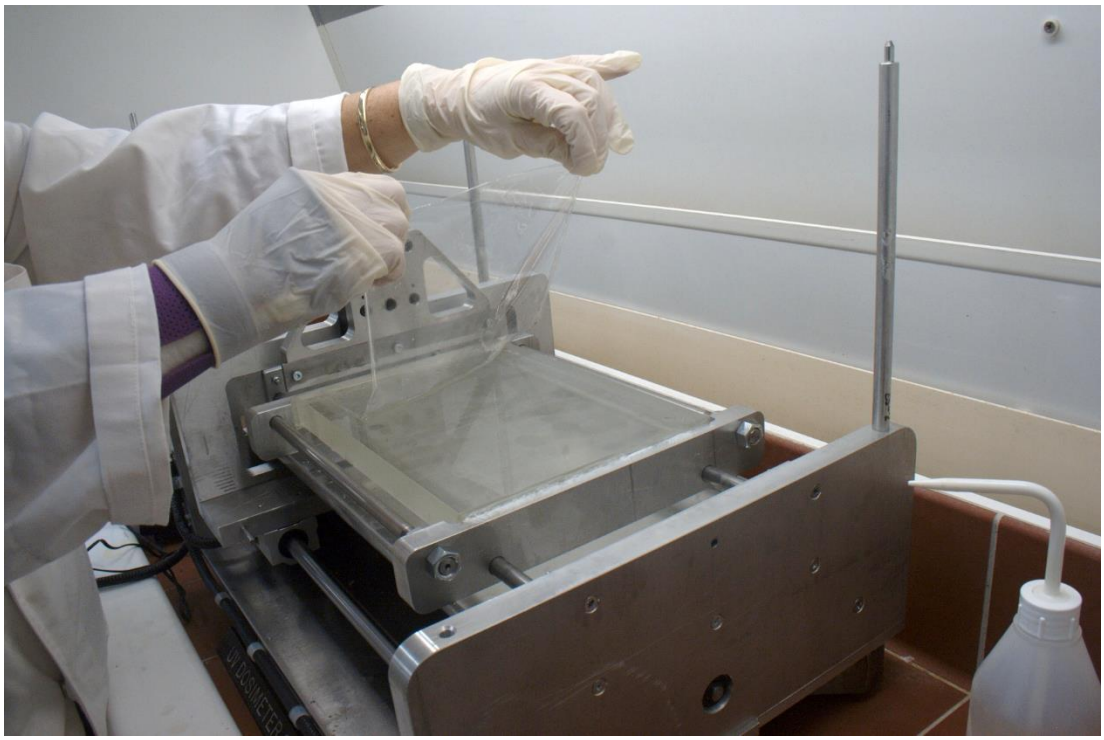

Figure 3.3 A sheet of 8-methoxypsoralen (8-MOP) film being removed from the casting table.

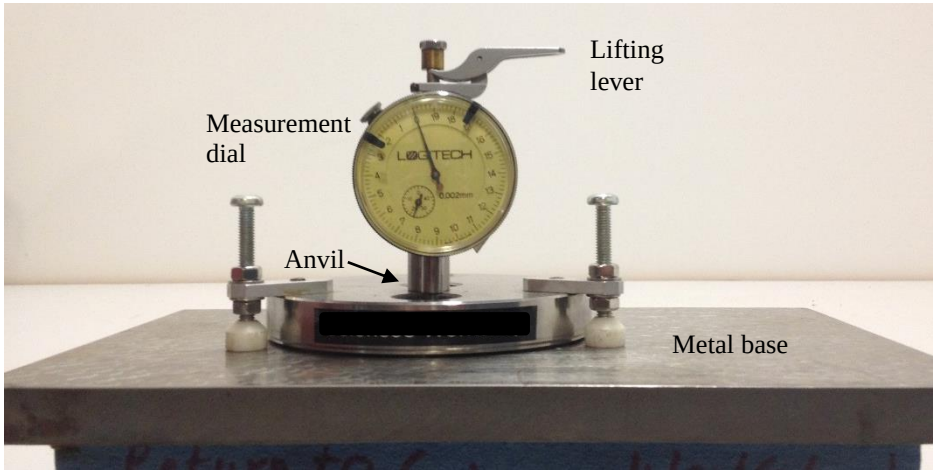

Figure 3.4 Logitech dial thickness gauge used to measure the thickness of sheets of film placed between the anvil and the metal base.

3.3.1.4 Assembling the Dosimeters

The cast film was attached to dosimeter holders made with a thin flexible plastic frame measuring 1.0 cm × 3.0 cm, with a 0.7 cm diameter aperture at one end. This miniaturized size provides a dosimeter that is smaller and less obtrusive than the 3 cm × 3 cm size dosimeter used with previous long-term film dosimeters (Schouten, Parisi & Turnbull 2007; Amar & Parisi 2013B). The sheets of film were cut into 1.0 cm × 0.9 cm sections and attached to the frame using waterproof tape (Figure 3.5).

Figure 3.5 shows some dosimeters during solar exposure. Three different types of plastic frames were tested simultaneously to see if the colour or type of plastic had any effect on the absorbance. The polypropylene (yellow) was selected as it did not affect the absorbance of the dosimeter, it was thicker than the other two and did not retain heat, or soften or deform when heated.

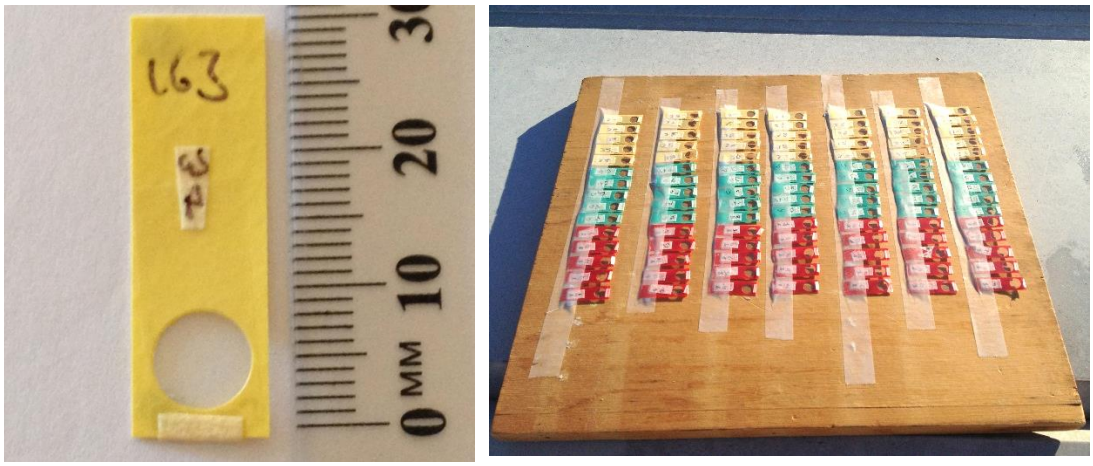

Figure 3.5 A photograph of a fabricated miniaturized UVA dosimeter is on the left and the photo on the right shows an array of dosimeters being exposed during testing of the types of plastic holders.

3.3.1.5 Absorbance Measurements

To ensure that 8-MOP only reacted to the UVA waveband when exposed, all initial testing was done with two sets of dosimeters. In one set, the dosimeter film was covered with a piece of 120 μm thick Mylar (Cadillac Plastics, Australia) that does not transmit the majority of the UVB wavelengths (McLeod 1997; Parisi, Sabburg & Kimlin 2004). The other set was left uncovered. To determine the degree of photodegradation of the film, the dosimeters were measured for optical absorbance both before and after exposure. Using the spectrophotometer discussed in Section 2.2.3.4 with a rotating mount specifically constructed to hold the miniaturized dosimeters, each dosimeter was measured at four different sites over the dosimeter film surface by rotating the dosimeter and mount in increments of 90^{o} and measuring the absorbance at each increment. The testing of the dosimeters was carried out by measuring the variation in absorbance at the specific wavelength of 305 nm. This wavelength corresponds to the maximum change in optical absorbance for 8-MOP (Diffey & Davis 1978).

3.3.2 Dosimeter Characterization

3.3.2.1 Reproducibility

It is essential that dosimeters react in a reproducible and consistent way when exposed to the same UV source under exactly the same conditions. To ensure that the dosimeters yielded consistent results, the reproducibility of the UV induced change of

the measured mean dosimeter absorbance was assessed. Thirty 8-MOP dosimeters were exposed concurrently to five hours of solar UV in the same location and under identical conditions. The SZA range was 71.4° – 41.8°. Unless otherwise stated it can be assumed that the dosimeters for this and the research in the following sections were exposed on a horizontal plane in an unshaded site at USQ. To evaluate the consistency of the change in the absorbance of the dosimeter set, absorbance measurements were taken immediately before and immediately following exposure.

3.3.2.2 Dark Reaction

After being removed from exposure chemical film dosimeters such as PS and PPO continue to change in optical absorbance (Schouten, Parisi & Turnbull 2010). This post exposure behaviour of the dosimeters is known as the dark reaction. To limit the effect of the dark reaction dosimeters are stored for a predetermined time before measuring the post exposure absorbance. In this research, thirty dosimeters were exposed to five hours' solar UV simultaneously under the same conditions. This was done on a relatively cloud free day with the solar disc unobscured by cloud. The SZA range was 71.4° – 41.8°. The absorbance of the dosimeters was measured immediately after removal from the source and the dosimeters were then placed in a light proof box, the dosimeters were removed and the absorbance measured again at varying time intervals. The dark reaction was quantified by measuring the pre exposure absorbance (A_i) of each dosimeter and measuring the post exposure absorbance immediately following exposure to give the change in absorbance at nil storage time (ΔA_0). The dosimeters were removed from storage at different time intervals to determine subsequent absorbance changes (ΔA_t). In this way any change in absorbance from ΔA_0 can be attributed to a dark reaction. For each time (t), ΔA_t was calculated as:

$$\Delta A_t = A_t - A_i \tag{3.1}$$

where A_t is the absorbance following storage for a given time and A_i is the absorbance prior to exposure.

The dark reaction (*D*) after a given time was expressed as a percentage and calculated as:

$$D = \frac{(\Delta A_t - \Delta A_0)}{\Delta A_0} \times 100 \qquad (3.2)$$

3.3.2.3 Spectral Response

To ensure that the 8-MOP dosimeter was only reacting to the UVA part of the spectrum, a spectral response was determined for the dosimeter. Sets of two dosimeters were simultaneously exposed to a specific wavelength (band) from 300 to 400 nm in 10 nm increments. The discrete irradiances were produced using the irradiation monochromator described in Section 2.2.3.2. This produced a beam with a FWHM of 5.0 nm for an exposure at each wavelength of 39 kJ/m^2. This exposure was used as it resulted in a measurable change in absorbance (ΔA) within a reasonable time frame. For each wavelength, one of the dosimeters in the exposed set of two had a Mylar filter and the other was unfiltered. Spectral irradiance measurements of the irradiation monochromator beam were taken at each discrete wavelength both before and after exposure using the calibrated portable spectroradiometer described in Section 2.2.3.3, with calibration traceable to the NPL UK standard. Spectral irradiance measurements were performed to include 10 nm either side of the specified discrete wavelength in 0.1 nm intervals to ensure there was no unexpected exposure outside the required monochromator wavelength. All the following exposure tests were performed with a Mylar filter in place.

3.3.2.4 Cosine Response

The cosine response of the 8-MOP dosimeters was determined in a controlled environment using the UV source described in Section 2.2.3.1. This source provides a collimated beam of 5 cm × 5 cm. Batches of four 8-MOP (Mylar filtered) dosimeters were irradiated sequentially at incidence angles ranging from 0º to 80º in intervals of 10º. The ambient temperature was maintained at 21 °C during exposure and the laboratory lights were filtered and tested to eliminate stray UV emissions. To confirm that the simulated UV irradiance was uniform to within 5%, various positions within the beam area were tested with the calibrated portable Bentham spectroradiometer

measuring from 320 to 400 nm in 0.5 nm increments. This uniformity of the beam allowed for up to four dosimeters to be tested simultaneously at each of the angles. The ΔA was found by measuring each dosimeter both before and immediately after exposure to the simulated UV source.

The exposure time required was ascertained using an incidence angle of 0°, exposing the dosimeters for a total of 90 minutes and measuring the dosimeters after each 10 minute exposure in the 90 minute interval before replacing them beneath the source. This test showed that 60 minutes exposure was required at each of the angles for a measurable photochemical change to take place. Plotting the cumulative exposure versus time at 0° allowed a dose response equation for the film to be determined for the solar simulator.

3.3.2.5 Dose Rate Independence

Groups of five dosimeters were placed at different distances from a fluorescent lamp UV source (Philips 40/12, supplier Lawrence & Hansen, Toowoomba, Australia). Three distances 5, 10 and 15 cm from the source were employed. To ensure that the total exposure received was the same for all dosimeters, the irradiance was measured for each distance before the exposure and after one hour of exposure. For the three distances the UVA irradiances measured were 1.6, 2.2 and 3.7 W/m^2. The pre-exposure absorbance for all dosimeters within the groups measured was the same to ensure a uniform starting position. Using this information and knowing the exposure required to affect a measurable change in the absorbance (from the cosine zero test), the calculated UVA exposure required for all three groups was 40 kJ/m^2. This UVA exposure was reached for the closest dosimeters in 3 hours, for the next group in 5 hours and, for the group with the largest distance, after 7.1 hours. The post exposure absorbance of the dosimeters was measured immediately after removal from the source for each group.

3.3.2.6 Temperature Independence

Two separate tests relating to temperature were performed on the 8-MOP dosimeters. The first investigated the temperature used during the drying phase of the film manufacture. The second test investigated the reaction of the film when exposed to a

UV source at different temperatures. After the dosimeter film was cast and removed from the glass, further drying time was required before use to ensure that all the remaining THF was removed from the film. Diffey & Davis (1978) recommend drying at 55 °C for 24 hours in a vacuum even though their testing showed no change in reactivity when the film was dried at different temperatures. To test the drying temperature a sheet of freshly cast 8-MOP was cut into sections and placed in separate drying ovens set at different temperatures for 24 hours. The oven temperatures employed were 25 °C, 35 °C, 45 °C and 55 °C. A separate section of film was allowed to dry in a light free cupboard at room temperature between 19 °C to 21 °C.

The second test examined the temperature independence of the film exposure. Temperature independence requires that dosimeters return similar responses despite the exposure being undertaken at different temperatures. Using the UV fluorescent lamp as the exposure source, three sets of dosimeters were exposed at different temperatures. The temperatures were controlled using an ice bath and a heated water bath, with additional dosimeters placed at room temperature. The temperatures tested ranged from 10 – 40 °C. Dosimeters received the same exposure time of four hours with the irradiance at the dosimeter surface being measured by the portable spectroradiometer before and after exposure. To ensure that the distances between the UV source and the dosimeters remained the same throughout the test, and were consistent for all sets of dosimeters, they were measured prior to exposure and post exposure.

3.3.2.7 Dose Response

A UVA Biometer, described in Section 2.2.1.1, sensitive to the UVA wavelengths between 320 and 400 nm was employed for the calibration of the dosimeters in each season. This instrument was calibrated, on a cloud free day in each season, to a scanning double grating spectroradiometer, described in Section 2.2.1.2, measuring the terrestrial solar spectrum in each of the relevant seasons. This spectroradiometer scanned the global UV in 0.5 nm wavelength increments every 10 minutes from 05:00 – 19:00 h daily.

The dosimeter dose response was carried out by exposing a series of dosimeters to solar UV on a horizontal plane in close proximity to the rooftop UVA Biometer for a

specific range of time intervals, with all of the dosimeters having a Mylar filter in place. These time intervals were 4, 8, 12, 16, 24, 32 and 40 hours. The same time intervals were used each season. A minimum of five dosimeters were exposed concurrently for each time interval. Following exposure, the dosimeters were placed in an envelope and stored away from any ambient light. After the final dosimeters were removed, all were stored for eight more days before the mean change in absorbance and the standard deviation was determined for each time interval

3.3.3 Results

3.3.3.1 Reproducibility

The results of twenty eight of the dosimeters were used due to two being damaged during the absorbance reading. The mean change in absorbance for the five hour solar UV exposure interval was 0.362. Sixty seven percent of the dosimeters were within one standard deviation of the mean, with 89% within 1.5 standard deviations. The variance of these dosimeters was ±4.6%. This variance is in line with the reproducibility of other dosimeters. PPO has a variance of up to 6.5% dependent on exposure levels (Lester et al. 2003) and PVC has a variance of 5% (Amar & Parisi 2013B). Reproducibility was also assessed in other non-specific tests such as the seasonal dose response. These tests showed that the dosimeters had a variance of ±2.6% when exposed under the same conditions. Some variation in dosimeter measurements is to be expected due to the very small differences in dosimeter thickness.

3.3.3.2 Dark Reaction

The dark reaction of the 8-MOP dosimeters is shown in Figure 3.6 for the periods of storage of one hour, twenty four, forty eight, ninety six, one hundred and ninety two, eight and nine hundred and thirty six hours following exposure. The majority of the dark reaction (87%), as calculated with Equation 3.2, occurred within the first two days. The change between four and thirty nine days represents 2% of the total observed change. To avoid delays that may arise from an eight day wait period, a researcher can choose to read the dosimeters immediately after exposure or at another time selected by the researcher as long as the selected time remains consistent. To

minimize dark reaction impact, all dosimeters in this research were measured eight days after exposure unless otherwise stated.

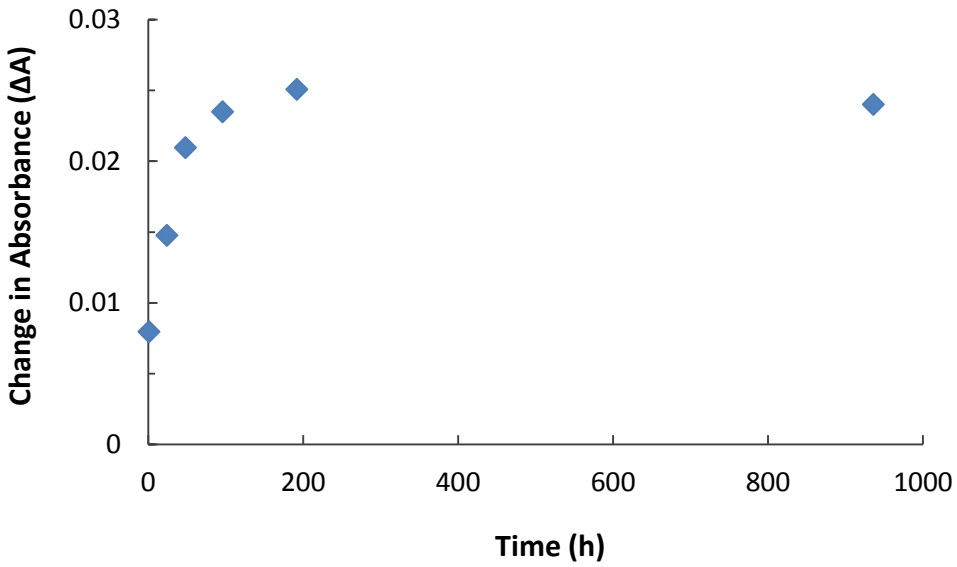

Figure 3.6 Post exposure change in absorbance showing the dark reaction of the UVA dosimeter.

3.3.3.3 Spectral Response

Figure 3.7 shows the results when two dosimeters were exposed simultaneously to the same wavelength; one dosimeter being uncovered and one using Mylar as a UVB filter. The exposure used in each case was 39.1 kJ/m^2. The dosimeters using the filter showed no response until a wavelength of 320 nm was reached. This was the boundary used in this research to define the UVA waveband although the wavelength boundary between the UVB and UVA is defined at both 315 nm and 320 nm.

Figure 3.7 shows that the dosimeters with the Mylar filter respond predominantly to wavelengths within the UVA range. The error bars show the standard deviation of the change in absorbance of the dosimeters. With Mylar the standard deviation was 1.2%, and the standard deviation for unfiltered dosimeters was 2.2%.

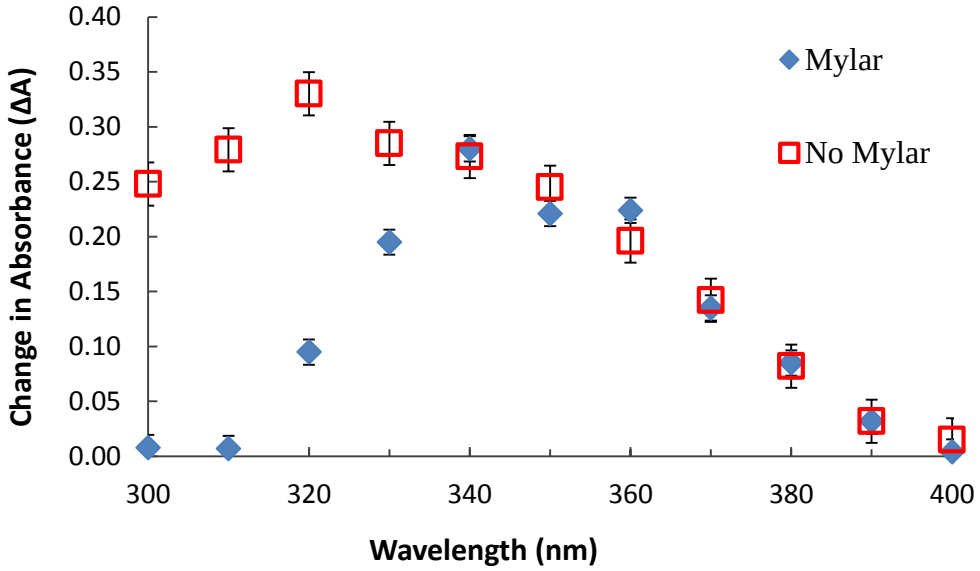

Figure 3.7 Spectral response of the UVA dosimeter covered with the Mylar filter and with no Mylar filter for an exposure of 39.1 kJ/m^2. The error bars represent the standard deviation of the absorbance of the dosimeters.

3.3.3.4 Cosine Response

A dose response equation for the solar simulator was determined by plotting cumulative exposure versus time at an incident angle of 0^o. A trend curve for this plot gives the exposure equation. The equation employed for the calibration to the solar simulator UV source, with an R^2 of 0.99 was:

$$UVA = 238772 \times \Delta A^{1.6697} \tag{3.3}$$

where *UVA* is the UV exposure from 320 nm to 400 nm in J/m^2.

Normalization of the response of the dosimeters at each angle of incidence to the solar source was calculated using:

$$R_N = \frac{UVA\ (\theta)}{UVA\ (0)} \tag{3.4}$$

where $UVA(0)$ is the exposure measured at an angle of 0° and $UVA\ (\theta)$ is the exposure measured for the respective incidence angle.

Figure 3.8 shows a normalized cosine response of the 8-MOP UVA dosimeters. The error bars reflect the standard deviation of each of the absorbance measurements. The dosimeters showed a very uniform change in absorbance when exposed under the same conditions, hence the small range in the error calculations. The cosine response of the 8-MOP dosimeter was within 14% of the cosine curve up to 50°. At angles of 70° and 80°, there was a noticeable reflection from the Mylar which may have contributed to the larger deviation from the cosine curve at these angles.

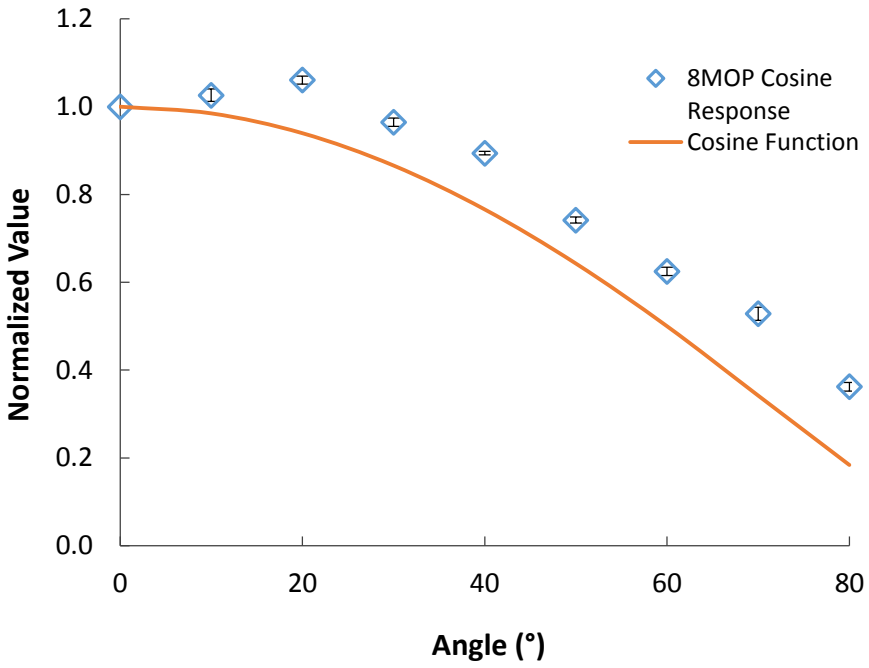

Figure 3.8 Cosine response of the UVA dosimeter error bars representing one standard deviation are contained within the symbol.

3.3.3.5 Dose Rate Independence

The dose rate independence test was designed to show that, for dosages derived from an irradiating UV source, there was an equal response in change of dosimeter absorbance that was unrelated to the exposure time taken or dose rate used. Figure 3.9 shows the normalized change in dosimeter absorbance against irradiance for each of the distances tested. The post exposure measurement was expressed as a percentage of the initial absorbance due to the range of initial absorbance values of the dosimeters. The error bars show the standard deviation of the measured post exposure absorbance

which was between 2.2 – 3.2%. The results show that for UVA irradiances between 1.6 and 3.7 W/m^2 the response of the 8-MOP dosimeters was dose rate independent. These irradiance rates approximate an 8 hour exposure in spring 2014 and autumn 2015 and a 12 hour exposure in winter 2014.

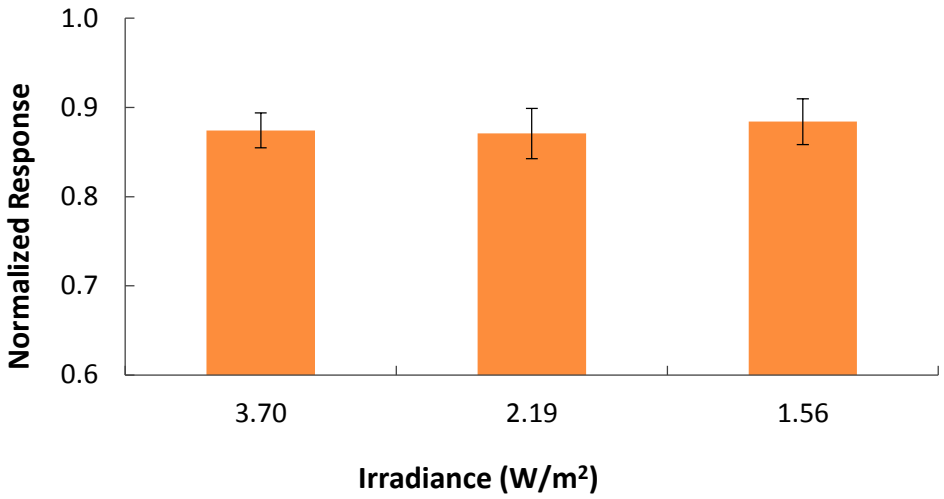

Figure 3.9 Dose rate independence of the UVA dosimeters for each irradiance, with the error bars representing one standard deviation of the change in absorbance measurements.

3.3.3.6 Temperature Independence

Absorbance was measured for the various drying temperatures and the result expressed as a percentage of the absorbance measured for the section of film dried at room temperature. Both 25 °C and 35 °C are within 5% of the air dried absorbance however, with the higher temperatures the difference was 30%. Based on these results, all films produced for calibration to the solar UVA exposure were air dried in a light secure cupboard at temperatures between 18 °C – 22 °C.

In the second test for temperature independence, absorbance readings were taken before and immediately after exposure. The post exposure measurements were calculated as a percentage of the initial measurements. For the low (10 – 20 °C) and medium (20 – 30 °C) temperature ranges the variation was less than 2% in the initial absorbance. For the higher (30 – 40 °C) temperature range, the difference in absorbance was less than 6%. The variance within the dosimeter measurements in each instance was less than ±2%. These results show that the dosimeter response was independent of temperature in the 10 – 40 °C temperature range ±6%.

3.3.3.7 Dose Response

Figures 3.10 – 3.13 provide the dose response calibration for each of the four seasons with the *y* axis providing the UVA exposure in kJ/m^2. In winter, the overall exposures were lower and there was less change in absorbance for the same exposure time. Correspondingly, the higher exposures in the other three seasons means that the change in absorbance occurred at a faster rate than in winter. The actual change in absorbance cannot be compared between seasons, differences occur in the solar spectrum and SZA's between seasons. The significant difference in the dose response of the dosimeters that occurs between seasons can be taken into account by doing a calibration in the season and under the atmospheric conditions in which the dosimeters will be used.

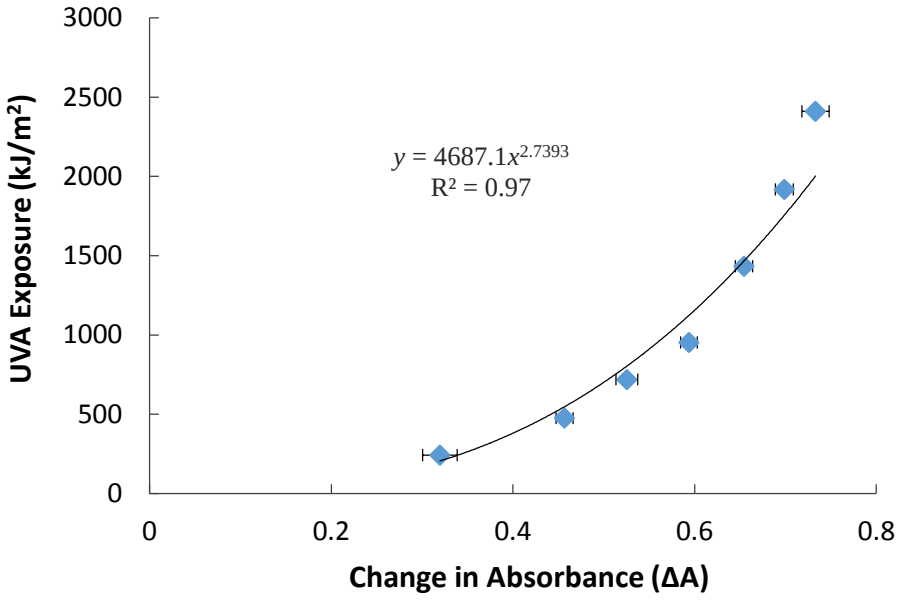

Figure 3.10 Winter dose response of the UVA dosimeter. The error bars represent the mean standard deviation of the UVA dosimeters.

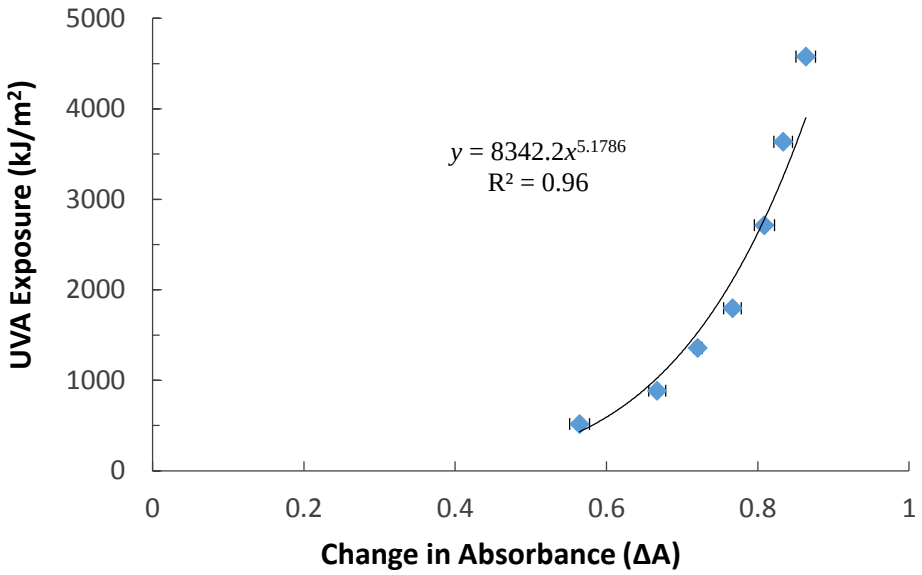

Figure 3.11 Spring dose response of the UVA dosimeter. The error bars represent the mean standard deviation of the UVA dosimeters.

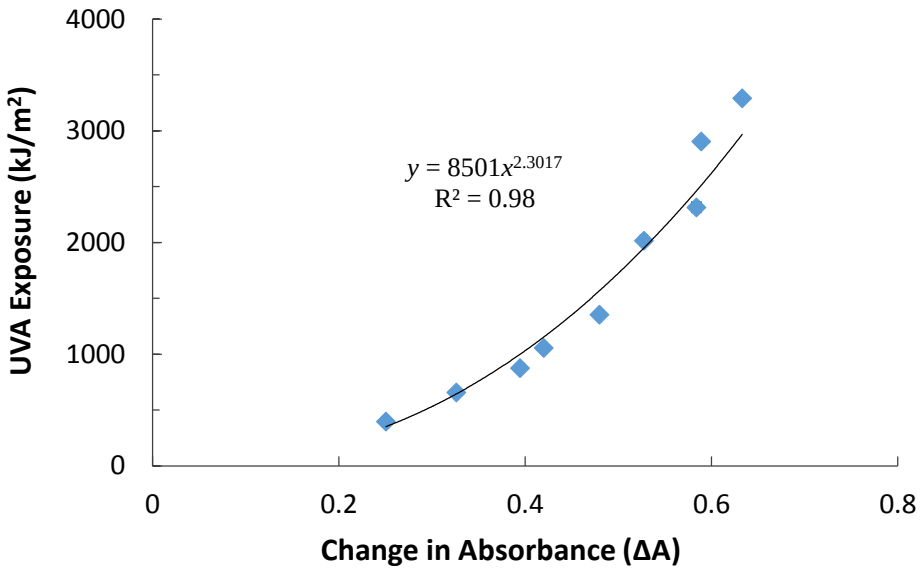

Figure 3.12 Summer dose response of the UVA dosimeter. The error bars (which may be contained within the symbol) represent the mean standard deviation of the UVA dosimeters.

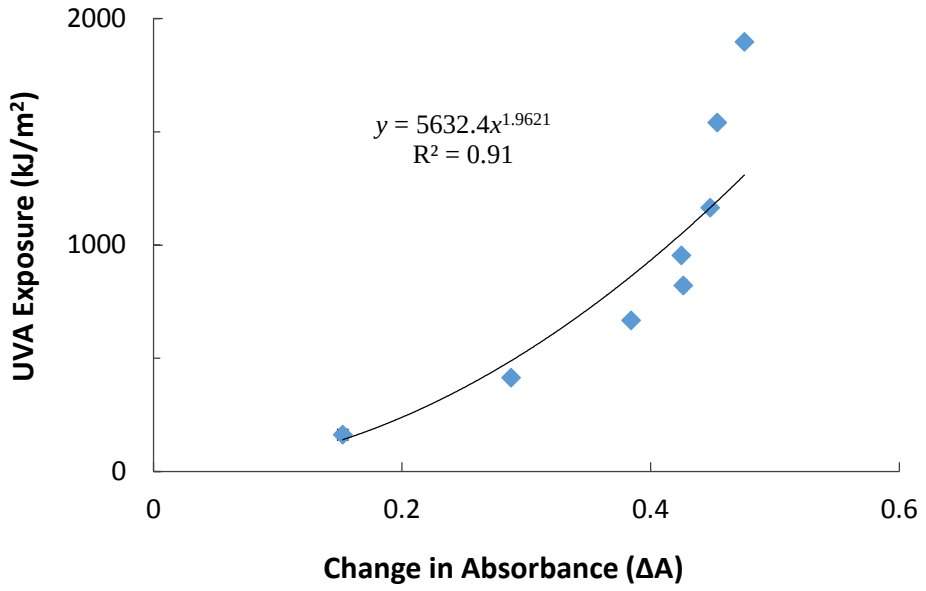

Figure 3.13 Autumn dose response of the UVA dosimeter. The error bars (which may be contained within the symbol) represent the mean standard deviation of the UVA dosimeters.

3.3.3.8 Exposure Thresholds

Two separate tests were performed to look at the changes occurring at low levels of exposure. The first test involved outdoor solar exposure where a series of dosimeters was exposed for a maximum of 135 minutes with dosimeters being removed from exposure after fifteen minute intervals. The test was done on the roof at USQ on the same cloud free day as the autumn 2015 calibration. A change in absorbance of 0.304 was recorded in the dosimeters after fifteen minutes exposure. This change was well outside the equipment sensitivity range of these dosimeters which is between 0.000 – 0.008. Increasing changes in absorbance occurred for every subsequent fifteen minute exposure time (Figure 3.14). The fifteen minute exposure equated to approximately 21.5 kJ/m^2. Based on this level of irradiance and with this result, the UVA dosimeter can be used for exposures of fifteen minutes or longer.

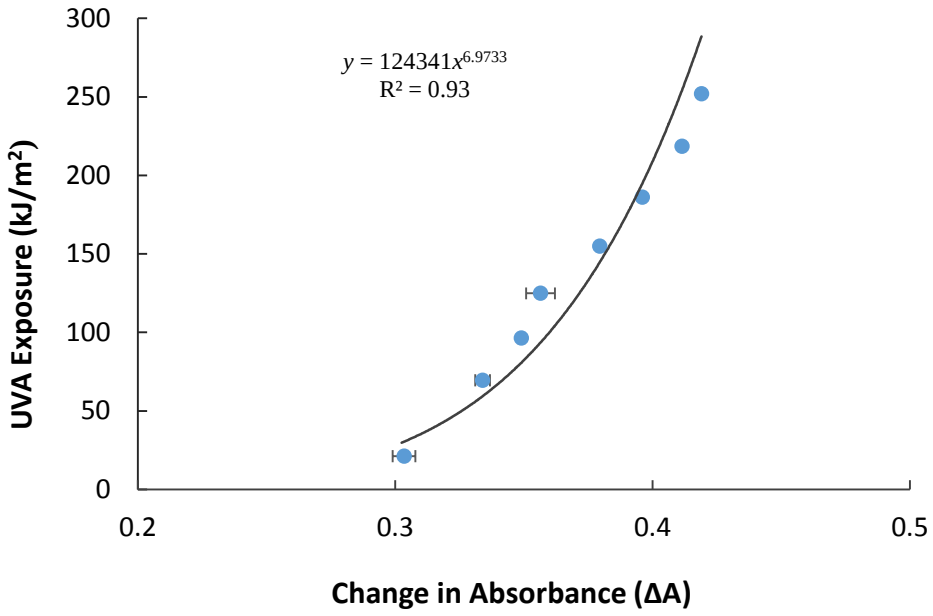

Figure 3.14 UVA exposure versus change in absorbance for fifteen minutes exposure up to 135 minutes total exposure in the field. The error bars represent the mean standard deviation of the UVA dosimeters.

Another test was conducted in the laboratory. A solar simulator was used for the exposure with spectral scans conducted at 0, 10, 20 and 30 minutes of dosimeter exposure. Four dosimeters were simultaneously exposed for one minute at a time from 1 – 10 minutes total exposure, for two minutes at a time for 10 – 20 minutes exposure and five minutes at a time for 20 – 30 minutes total exposure. To assess only the UVA section of the spectrum, a Mylar filter was placed over the dosimeters. The exposed Mylar was changed for unexposed Mylar after each ten minutes of cumulative exposure.

In normal circumstances the change in absorbance measurements of the UVA dosimeter decreases with increased exposure and this is what occurred during the test. To avoid the constant use of negative values, calculations were done based on the magnitude of the difference.

Figure 3.15 shows the UVA effective exposure in kJ/m^2 versus change in absorbance measurement. The equation that best fits the relationship of the recorded changes has an R^2 of 0.99. This relationship includes all measured values from one minute of exposure to thirty minutes total exposure. The one minute solar simulator exposure showed a 3.2% difference in the absorbance measurement, the mean ΔA value recorded

was 0.030 which is outside the equipment sensitivity range of these dosimeters which is between 0.000 – 0.008. The two minute exposure shows a 5% change in absorbance. The one minute exposure was 14.0 kJ/m^2 of UVA. A one hour outdoor exposure between 10:00 and 11:00 h on 19 March 2015 (autumn) had a total exposure of 121.9 kJ/m^2. A dosimeter placed outside at this time would have recorded a measurable change in absorbance after nine minutes.

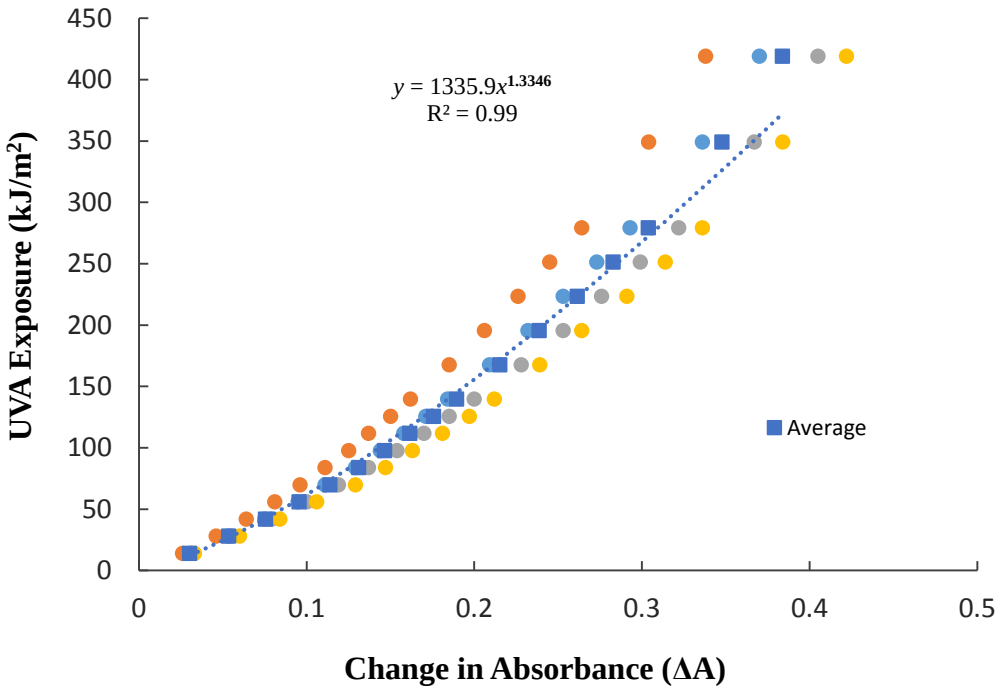

Figure 3.15 UVA exposure versus change in absorbance for one minute to thirty minutes exposure using a solar simulator. The dashed curve plots the mean of the four dosimeters.

3.4 CHAPTER SUMMARY

This chapter looked at the suitability of measuring UVA exposures with a dosimeter manufactured from 8-MOP in conjunction with a Mylar filter. A total error in UVA dose measurements of up to 14.6% should be expected when dosimeter error and instrument error are combined. As the objective was to measure the UVA exposure concurrently with erythemal and vitamin D effective UV, the PPO dosimeter will be further investigated in the next chapter before combining the two dosimeters together.

4. DUAL CALIBRATION

4.1 OVERVIEW

The previous chapter found that dosimeters made from 8-MOP were suitable for measuring the UVA component of the combined dosimeter intended to be used for concurrent UV measurements. The PPO dosimeter has previously been used to measure the erythemal UV exposure. This chapter reports on the research to extend this use by calibrating the PPO dosimeter to enable measurement of vitamin D effective exposures in addition to erythemal exposures, giving a dual calibrated PPO dosimeter.

4.2 INTRODUCTION

Ultraviolet radiation, particularly UVB, is widely acknowledged for its role in increasing the risk of sun related diseases in humans, but it is also widely acknowledged that some sun exposure is essential for good health. One of the beneficial effects is that it initiates the process of vitamin D production (Webb 2006; Grant 2009; Caini et al. 2014). For healthy living, it is important to find a balance in the received UV that minimizes chronic exposure risks while optimising potential exposure benefits. There is, therefore, an optimal UV exposure that minimizes the risk of disease (Lucas & Ponsonby 2002). Being able to predict with confidence expected UV exposures and being able to record accurately the UV received by biological specimens and humans, would allow the development of appropriate recommendations to be made for UV exposures, to humans, with regard to the recognized risks and benefits.

4.2.1 Vitamin D

The most important known positive effect of solar UV for humans is the initiation of the production of vitamin D. Sunlight exposure time is one of the major predictors of vitamin D levels (Cinar et al. 2013). The accepted measurement of serum vitamin D in humans is done by measuring 25-hydroxyvitamin D [25(OH)D], a precursor to vitamin D (Webb et al. 2010). Up to 90% of vitamin D production comes from unprotected skin being exposed to UVB radiation (Lucas & Ponsonby 2002). UVB wavelengths initiate the process of vitamin D_3 production which, after a time, is

converted to a measurable form of serum 25(OH)D_3 the specific section of serum 25(OH)D related to UVB exposure. There is no consensus on the various levels that are required to meet given thresholds. Webb et al. (2010) used the following levels: Deficient < 5 ng/mL (12.5 nmol/L), Insufficient < 20 ng/mL (50 nmol/L), Sufficient ≥ 20 ng/mL (50 nmol/L), Suboptimal < 32 ng/mL (80 nmol/L) and Optimal ≥ 32 ng/mL (80 nmol/L) to determine that the majority of the UK population will become vitamin D insufficient in the winter. Gill et al. (2014) cite a range of sources with different thresholds: Deficient < (25 nmol/L) or (< 27.5 nmol/L), Insufficient (25 – 50 nmol/L) or (27.5 – 49.9 nmol/L), Sufficient > (50 nmol/L) or (25 nmol/L), Suboptimal (50 – < 75 nmol/L) and Optimal (60 – 160 nmol/L). Based on these thresholds Gill et al. (2014) found 22.7% of a sampled population in South Australia having serum 25(OH)D below 50 nmol/L. Another Australian study by Vu et al. (2010) in Australian office workers showed 51% of the tested participants were vitamin D insufficient in winter, highlighting the significance of personal exposure habits in establishing sufficient vitamin D health in climates which experience typically high ambient UV levels.

4.2.2 Sun Exposure:- Recommendations and Optimization

Osteoporosis Australia (OA) (2015) has released new recommendations regarding sun exposure for vitamin D production but still include qualifier statements that recommendations depend on skin type and geographic location. OA also recommends a level of at least 50 nmol/L at the end of winter with an additional 10 – 20 nmol/L required during summer. The guidelines in Australia from September to April (spring through autumn) are that sufficient UV exposure for vitamin D production can be received if the face, arms and hands of a moderately fair skinned person are exposed for a few minutes in mid-morning or mid-afternoon on most days of the week (Cancer Council Victoria 2014).

There are plenty of preventative measures for erythemal exposure ranging from the extreme of complete sun avoidance or complete cover up to utilising sunscreen application, clothing, wrap-around sunglasses and appropriate head wear. Vitamin D insufficiency or deficiency may be treated by taking supplements (Nowson et al. 2004; Diamond et al. 2005). Recommendations for specific or timed amounts of UV exposure are complicated and can potentially be dangerous as levels of exposure vary

according to factors such as skin type, age, clothing, geographic location and seasonal conditions (Webb 2006; Holick 2004). Finding an optimum level of exposure that allows for vitamin D production before erythemal effects begin, would improve the health of the population. This requires information on the erythemal UV and the vitamin D effective UV to which the population is exposed. Samanek et al. (2006) provided an estimate, for seven Australian cities, of the exposure times required for recommended vitamin D production and for erythema. Downs et al. (2014) have determined optimal exposures weighted to the occupationally effective solar radiation. Other research (Engelsen et al. 2005) has produced a web page (https://fastrt.nilu.no/VitD.html) for the evaluation of vitamin D production for different conditions. Grobner, Grobner & Hulsen (2014) have used electronic dosimeters to measure personal UV exposure and then used blood samples from the participants to establish the increase in serum $25(OH)D_3$. However, there is no dosimeter-based system for the simultaneous measurement of personal erythemal UV and vitamin D effective UV.

4.2.3 Studies on the Biological Response to UVB

A range of methods have been used to determine specific biological UV responses within measured received personal exposure times by humans. In some studies, self-reporting of sun exposure time via a diary have been used (Cargill et al. 2013). Direct solar measurements have been achieved through studies which have used PS or PPO dosimeters which have been calibrated to erythemal exposure (Webb et al. 2010; Brodie et al. 2013; Schouten, Parisi & Turnbull 2010; Wainwright, Parisi & Schouten 2013). Also, electronic dosimeters have been used in several studies with the dosimeters worn at various sites on the body for example, chest, forehead and wrist (Wright et al. 2007, Schmalwieser et al. 2010; Feister, Meyer & Kirst 2013; Idorn et al. 2013). With any dosimetry research, there are some limitations (Siani et al. 2014) including multiple calibrations which are required for the season of testing, the relative action spectrum and the position of the dosimeters used with respect to a horizontal plane.

Controlled artificial UV exposures in a laboratory environment are often employed for studies investigating vitamin D production response. Osmancevic et al. (2015) used exposures from a broadband UV lamp and the UVB exposures measured with a

portable UV light meter. Bogh et al. (2012) compared narrow band UVB (311 ±2 nm) exposure with oral vitamin D supplements equivalent to 1600 International Units (IU) = 40 μg. The artificial UV exposure was not measured at the skin but from the settings of the lamp. Modelling has also been used to try to determine vitamin D effective exposures. Webb & Engelsen (2006) devised a solar spectral model which was tested with dosimeters. Cargill et al. (2013) highlighted the difficulty of accurately measuring personal sun exposure as electronic UV dosimeters are not feasible for large study populations or for long time periods. Cargill et al. (2013) also highlighted how self-reported sun exposure data via questionnaire compared with the recorded dosimeter results.

4.2.4 Benefits of Dual Calibration

The research currently presented will cover the dual calibration of miniaturized PPO dosimeters to both the erythemal action spectrum and the vitamin D effective action spectrum. Employing only one set of dual calibrated measurements and dosimeter processing, the exposures of both erythemal UV and vitamin D effective UV can be established. The dual calibration of the miniaturized PPO dosimeter has the advantage of allowing two sets of measurements to be conducted over a longer time interval. The presented technique also enables the measurement of multiple locations of UV exposure that are incident on a subject as well as multiple subjects. These measurements can be evaluated non-invasively and more cost effectively than with the use of electronic dosimeters.

4.3 MATERIALS AND METHODS

4.3.1 Dosimeter Description

Investigations of erythemal UV have used PS for measurements of up to one day (Downs & Parisi 2012; Siani et al. 2011; Gies et al. 2013) and PPO for longer investigations (Wainwright, Parisi & Schouten 2013; Schouten, Parisi & Turnbull 2010) as PPO has been established to have a dynamic range of approximately five days in summer and longer in winter in subtropical conditions. Figure 4.1 shows that the erythemal action spectrum has a significantly higher response in the UVB (CIE 1988) as has the vitamin D effective UV action spectrum (CIE 2006). Figure 4.1 also shows

that PPO has a strong response within the UVB waveband (Lester et al. 2003; Parisi, Schouten & Turnbull 2010). Consequently PPO was selected as the UV dosimeter material to be used for the dual purpose of measuring erythemal UV and vitamin D effective UV. Vitamin D effective UV has a higher relative response than erythemal UV between the wavelengths of 298 to 328 nm. Therefore, there may be times when the vitamin D effective UV exposure is higher than the erythemal UV exposure.

4.3.1.1 Dosimeter Production

The PPO film was cast at USQ, Toowoomba using a mix of PPO in powder form (General Electric Plastics, USA) with chloroform as a solvent in a similar way to the UVA dosimeters described in Section 3.3.1. An adjustment was made to the blade height of the casting table which meant that the PPO film sheets had a thickness of 40 μm. This has been shown to be the thickness with the best level of tensile durability in previous studies (Lester et al. 2003). The dosimeters were manufactured from small flexible plastic frames 1.5 cm × 3 cm with a 0.7 cm circular aperture at one end over which a 40 μm thickness of PPO film was attached.

Measurements of the optical absorbance of this film were undertaken prior to and after UV exposure in a spectrophotometer using a wavelength of 320 nm, which has previously been established as the wavelength that shows the maximum change in absorbance (Schouten, Parisi & Turnbull 2007). All post exposure measurements were taken at more than eight days after removal from exposure in order to allow for the dark reaction as previously determined (Wainwright, Parisi & Schouten 2013). The difference in the pre and post absorbance measurements (ΔA), measured at 320 nm, was used to establish the UV exposure by being calibrated to solar UV exposures weighted with the relevant action spectrum. The vitamin D effective action spectrum as provided by CIE (2006) was employed in this research.

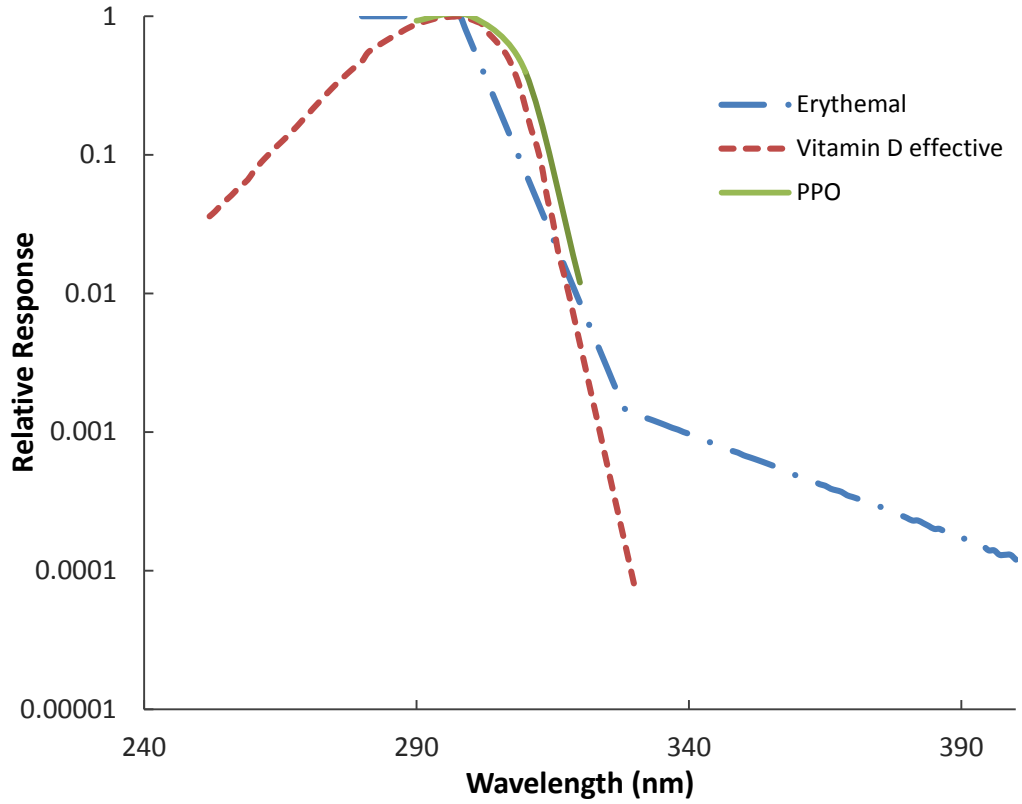

Figure 4.1 Erythemal (CIE 1988) and vitamin D effective (CIE 2006) action spectra and PPO spectral response (Parisi, Schouten & Turnbull 2010).

4.3.2 Instrument Calibration

In order for UV dosimeters to be used independently in the field, they require calibration to the UV spectrum at the Earth's surface (Casale et al. 2006). This was done by establishing a calibration equation which links the gradual changes in the optical absorbance of the dosimeter to the measured UV exposure. Separate calibrations were required for the erythemal action spectrum and the vitamin D effective action spectrum in order to provide a dual calibration of the dosimeter.

Solar UV calibrations of the dosimeters were carried out by using the calibrated scanning spectroradiometer (described in Section 2.2.1.2), measuring the global solar spectrum in 10 minute intervals in conjunction with the continuously operating (integrated) erythemal UV Biometer (Solar Light Co., PA., USA) and a broadband meter using a UVB filter with a response from 265 – 332 nm, the IL1400 discussed in Section 2.2.2.1. Figure 4.2 provides a flow chart showing the calibration process for the dual calibration of the dosimeters enabling measurement of erythemal UV and

vitamin D effective UV. All equipment and the dosimeters were located on a rooftop at USQ, Toowoomba, Australia at the time of calibration. In each season on a cloud free day, the erythemal Biometer and broadband meter were calibrated directly to the spectroradiometer. As the spectral response of the broadband meter, the photoactive film 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 (Schouten, Parisi & Turnbull 2010; Turnbull & Parisi 2010). The measured spectroradiometer UV spectra for the calibration period were weighted separately with the erythemal action spectrum (CIE 1988) and the vitamin D effective action spectrum (CIE 2006). These two sets of biologically effective UV were employed to calibrate the UV Biometer and the IL1400 for erythemal UV and vitamin D effective UV respectively. To provide a dual calibration for the dosimeters the dosimeters were then calibrated to the exposures measured by each of these two instruments.

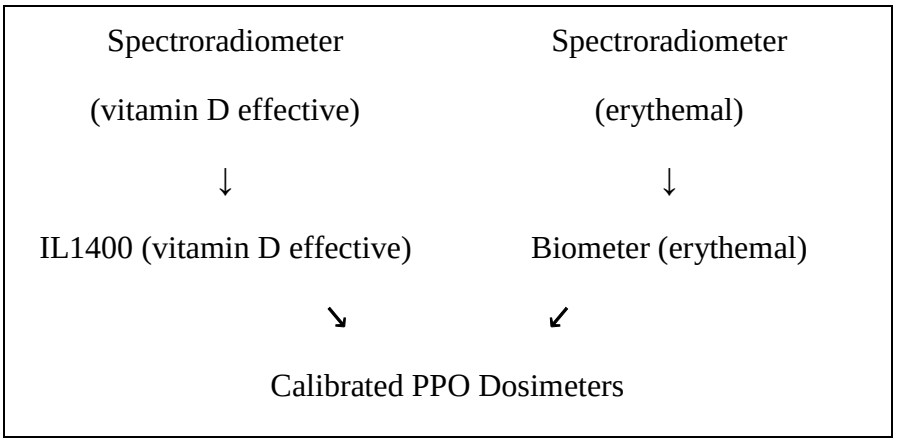

Figure 4.2 Calibration flow chart for the dual calibrated polyphenylene oxide (PPO) dosimeters.

4.4 DOSIMETER DUAL CALIBRATION

Between 28 and 35 dosimeters were exposed to solar UV for a maximum of forty hours over five days while concurrently measuring the erythemal UV and the vitamin D effective UV exposures. The exposures were done in an unshaded location at the USQ rooftop site on a horizontal plane. Table 4.1 gives details of the cumulative exposure times of the dosimeters during the seasonal tests. Using spring as an example, a total of 35 dosimeters were exposed. In the morning of Day 1 all the dosimeters were placed outside in the test location. After four hours 5 dosimeters were removed from exposure and stored in a light free environment, after another four hours, 5 more dosimeters

were removed and similarly stored. The remaining 25 dosimeters were placed in a light secure environment overnight, then all 25 were re-exposed the following morning. Batches of five dosimeters were removed and stored periodically, as outlined in Table 4.1, until only 5 dosimeters were exposed on Day 5. At the times the dosimeters were removed, the readings of the erythemal Biometer and the IL1400 were noted. The dosimeters were also removed from exposure during heavy rain and strong winds. This meant that only the spring dosimeters were exposed for the full 40 hours. After the final batch of dosimeters was removed from exposure, all the dosimeters were stored in a light secure environment for a minimum of eight days to allow for the post exposure dark reaction of the PPO film before measuring the absorbance.

Table 4.2 gives details of the dates and times of the exposures as well as various atmospheric conditions. The cloud cover was recorded on site via a Total Sky Imager which also recorded the SZA. The Aerosol Optical Thickness (AOT) and the ozone levels were both retrieved online from Giovanni, Goddard Earth Sciences Data and Information Services Center (GES DISC). The UVI was obtained from the USQ website as outlined in Section 2.2.4.

Table 4-1 Cumulative exposure time for the dual calibrated polyphenylene oxide (PPO) dosimeters in each of the seasons.

	Cumulative Exposure Time						
Season	Day 1 Cumulative exposure per batch (hours)	Day 2 Cumulative exposure per batch (hours)	Day 3 Cumulative exposure per batch (hours)	Day 4 Cumulative exposure per batch (hours)	Day 5 Cumulative exposure per batch (hours)	Number of dosimeters in batch	Total Number of Dosimeters used
Winter	4, 7.5	11.5, 15.5	22.83	Nil	Nil	5	35
Spring	4, 8	12, 16	24	32	40	5	35
Summer	4, 8	12, 16	24	32	37	4	28
Autumn	2, 4, 6, 8	12, 16	24	32	Nil	4	32

Table 4-2 Dates, times, solar zenith angle (SZA) and atmospheric conditions at the time of dose response data collection in each of the seasons.

Season	Date	Time	SZA range	Cloud Cover Average (%)	Daily Ozone max (DU)	UVI (min – max)	Aerosol Optical Thickness (AOT) λ 342.5 nm (mean)
Winter	12/07/2014 –16/07/2014	7:50 – 16:00	77.4° – 46.3°	Not Available	299	0.4 – 3.7	0.18
Spring	05/11/2014 –09/11/2014	7:0 – 15:50	59.6° – 11.7°	< 6	319	1.3 – 9.4	0.17
Summer	07/02/2015 –11/02/2015	7:30 – 15:30	64.6° – 12.2°	< 12 46 on 11/02/2015	273	0.6 – 11.6	Not available
Autumn	27/03/2015 –30/03/2015	8:00 – 16:00	64.7° – 30.4°	< 11 58 on 30/03/2015	270	0.9 – 8.2	0.16

4.5 RESULTS AND DISCUSSION

4.5.1 Calibration

In each of the seasons, a clear relationship was obtained between the relevant weighted spectrum and the measured ΔA of the dosimeters (Figures 4.3 – 4.10). The figures show a similarity in shape and position for the season and spectrum of calibration. The first season tested was winter; the R^2 for the erythemal UV was 0.86 and 0.92 for the vitamin D effective UV. After the winter test, where the error bars were significant refinements were made to the equipment used to manufacture and measure the dosimeters. These refinements were: a complete overhaul of the casting table including replacing the blade and resurfacing the glass slab, the rotating mount for the spectrophotometer was reconstructed and a new dosimeter holder was designed and built which held the dosimeters firmly in place. Making these changes improved the R^2 values in subsequent seasons of testing. The relationships for both erythemal UV and vitamin D effective UV provided an R^2 value of 0.97 or better in spring, summer and autumn. Previous research has shown that the reproducibility of miniaturized PPO dosimeters has a variance of ±5.8% (Wainwright, Parisi & Schouten 2013). The dynamic range of the dosimeters was five days with a maximum measured exposure time of 40 hours. This range can be extended if seasonal variations are considered. As can be seen from Figures 4.4, 4.6, 4.8 and 4.10, the erythemal seasonal exposures show an approximately linear relationship at lower levels of exposure which decreases as the dosimeters near saturation level; saturation being the point at which no further ΔA can be measured. An exposure time of 24 hours in summer and 32 hours in autumn still fell within the linear region indicating that a longer exposure time was possible in these seasons.

Figures 4.3, 4.5, 4.7 and 4.9 show that there was also a clear relationship between ΔA and the vitamin D effective exposure however, there was no obvious tapering off of the exposure as was seen with the erythemal dose responses. It was possible that this difference was due to the specific vitamin D spectral weighting and should not be taken as an indication that the dosimeters had not approached a saturation point. PPO dosimeters require a minimum exposure before any measurable ΔA can be observed at 320 nm. Previously polynomial functions have been used to provide these calibrations.

When a polynomial relationship was used: the fit was better at higher exposures, but at very small exposures the fit was less accurate as the polynomials tended to have a minimum occurring in these areas, also the same order of polynomial was not suitable for all three exposure types. As no participant had a ΔA (x axis) of more than 0.30 in any season, the exponent fit was appropriate for this study.

The Cancer Council Australia (2015A) highlights the need for balanced solar exposure. The presented calibration technique was therefore valuable in being able to measure both erythemal and vitamin D effective exposure simultaneously.

Lester et al. (2003) have shown that PPO can be used successfully as an extended range erythemal UV dosimeter. All the dosimeters were exposed on a horizontal plane. Casale et al. (2006) has shown that horizontal calibrations can apply to PS dosimeters for incidence angles up to 70° and it is reasonable to expect a similar relationship with PPO dosimeters. This research shows that PPO can also be weighted against the vitamin D effective action spectrum as there is a similar response sensitivity within the UVB waveband, thus making PPO an acceptable choice for a dosimeter to measure erythemal and vitamin D effective UV simultaneously. Using only the PPO dosimeter, and with only one set of pre and post exposure processing and analysis, two sets of biologically effective exposure data can be produced.

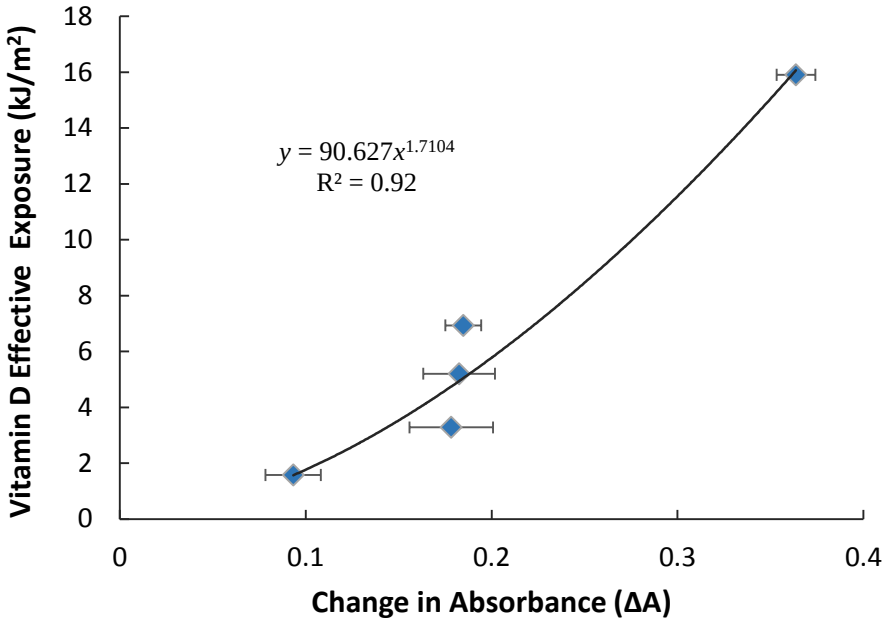

Figure 4.3 Winter solar vitamin D effective dose response curve. The error bars represent the standard deviation of the polyphenylene oxide (PPO) dosimeter batches.

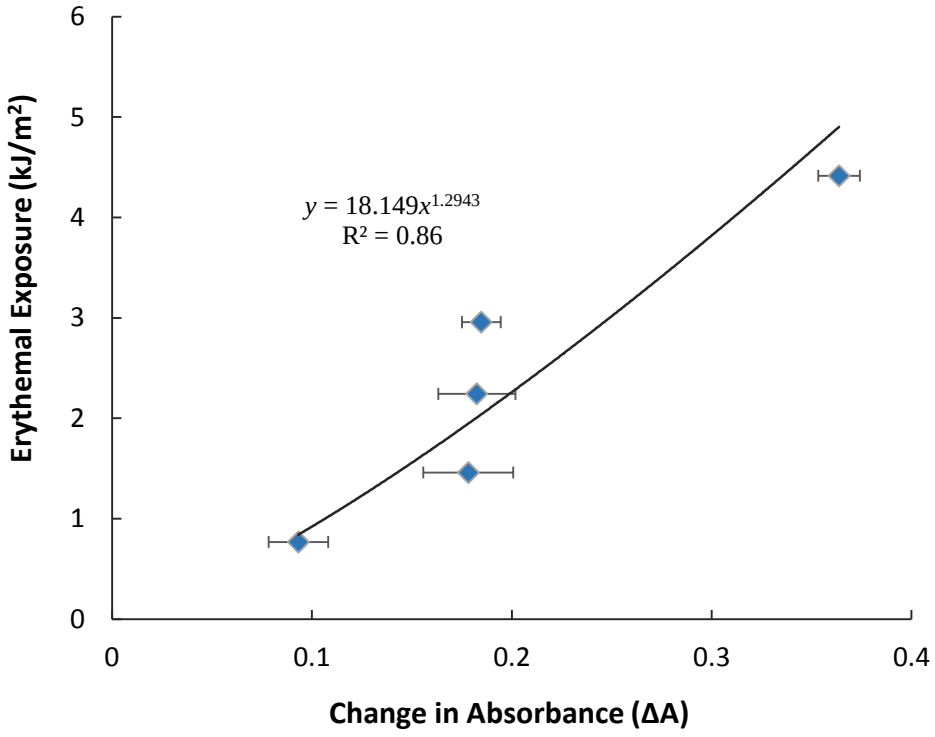

Figure 4.4 Winter solar erythemal dose response curve. The error bars represent the standard deviation of the polyphenylene oxide (PPO) dosimeter batches.

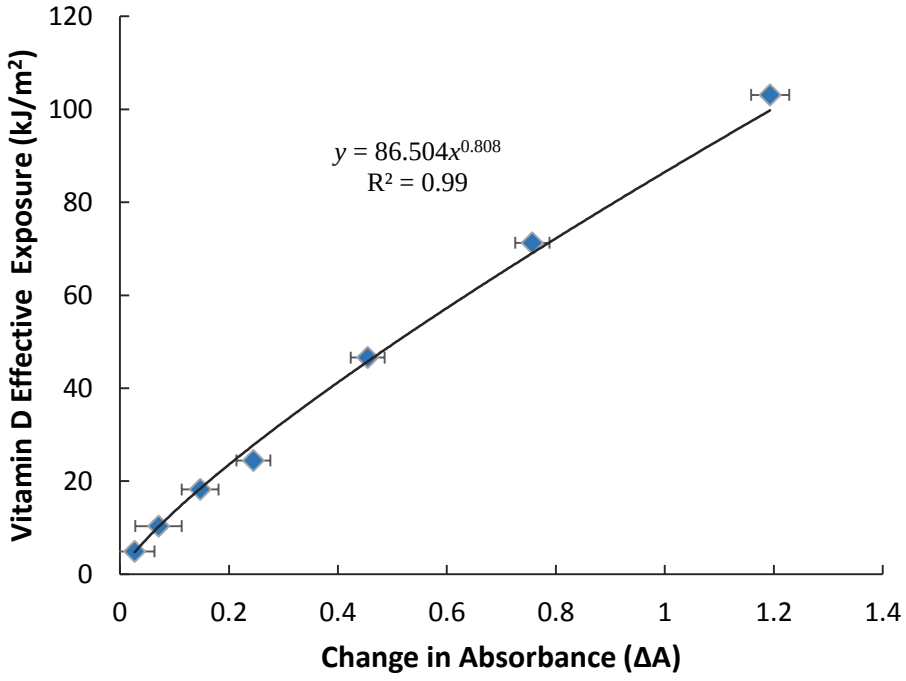

Figure 4.5 Spring solar vitamin D effective dose response curve. The error bars represent the standard deviation of the polyphenylene oxide (PPO) dosimeter batches.

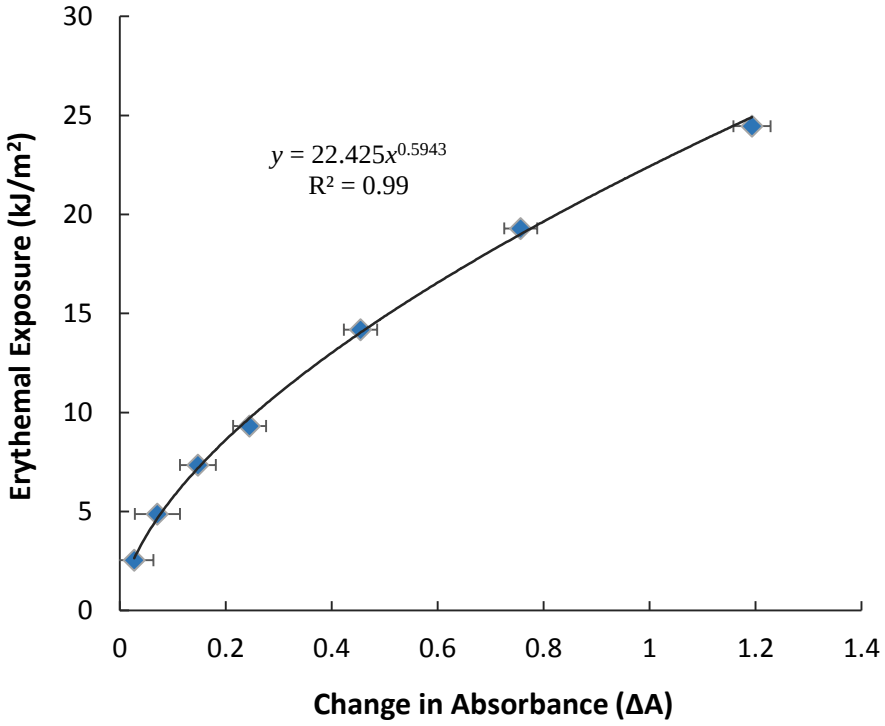

Figure 4.6 Spring solar erythemal dose response curve. The error bars represent the standard deviation of the polyphenylene oxide (PPO) dosimeter batches.

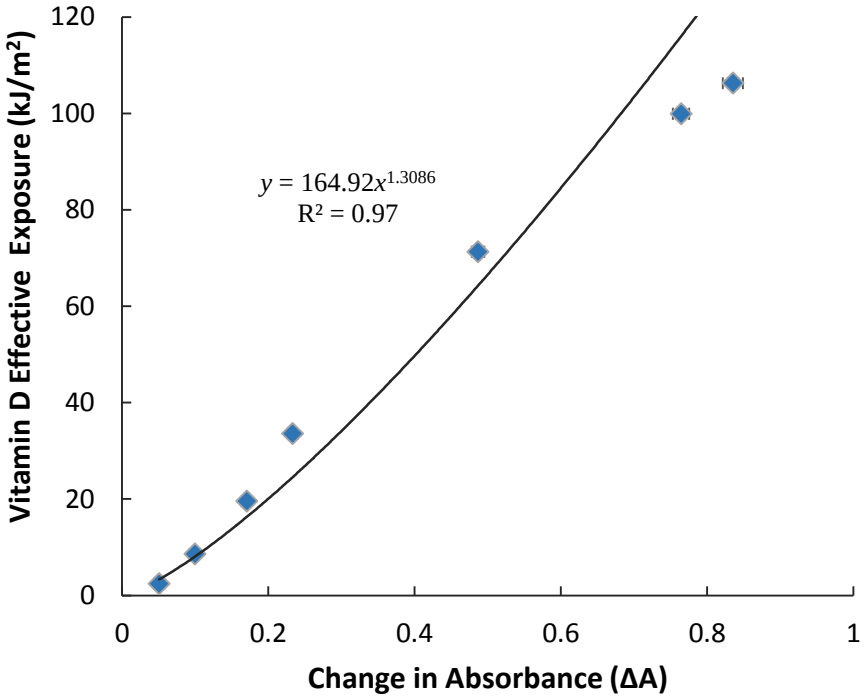

Figure 4.7 Summer solar vitamin D effective dose response curve. The error bars (which may be contained within the symbol) represent the standard deviation of the polyphenylene oxide (PPO) dosimeter batches.

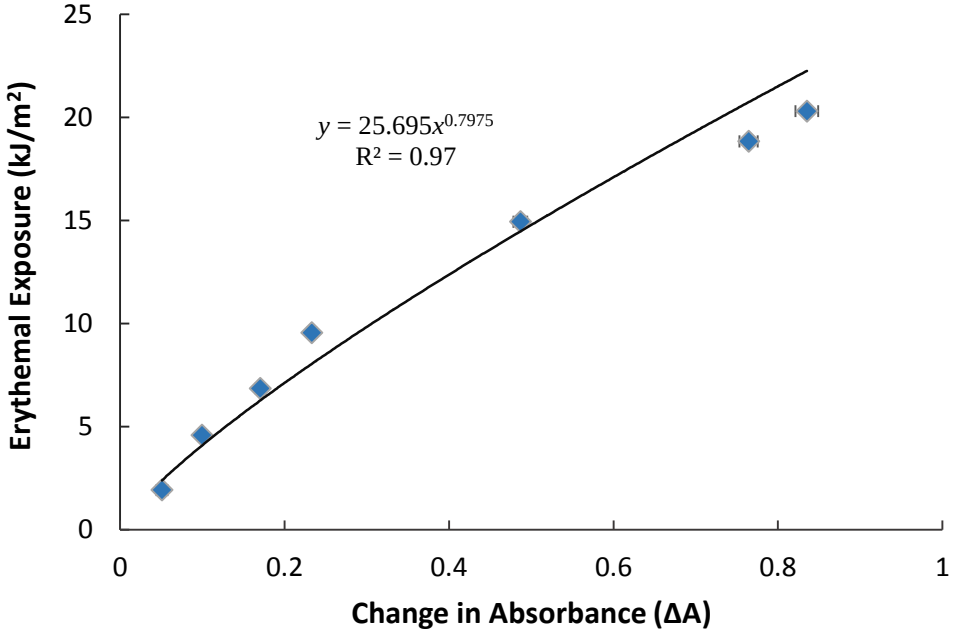

Figure 4.8 Summer solar erythemal dose response curve. The error bars (which may be contained within the symbol) represent the standard deviation of the polyphenylene oxide (PPO) dosimeter batches.

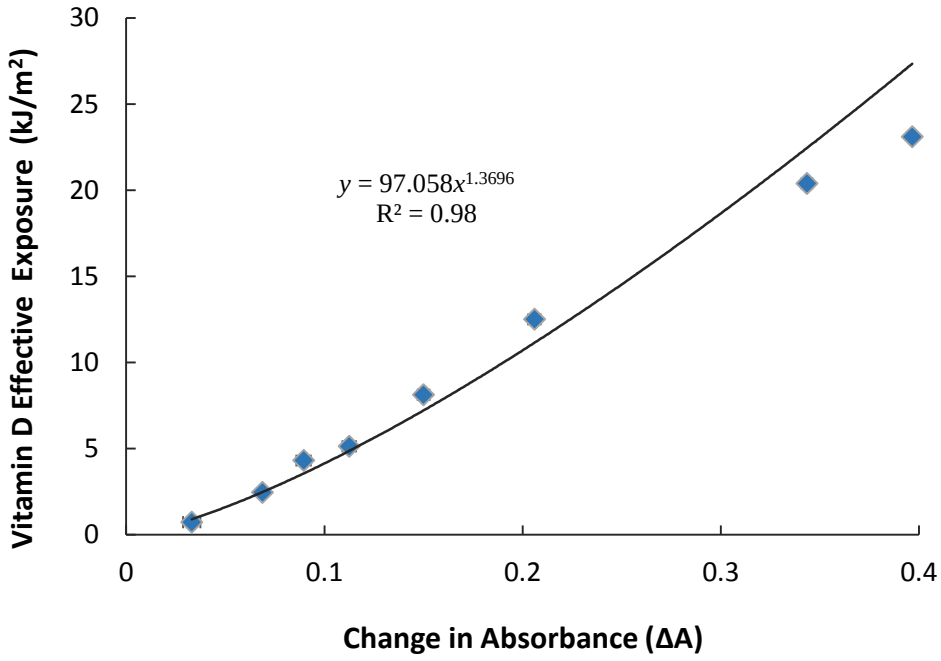

Figure 4.9 Autumn solar vitamin D effective dose response curve. The error bars (which may be contained within the symbol) represent the standard deviation of the polyphenylene oxide (PPO) dosimeter batches.

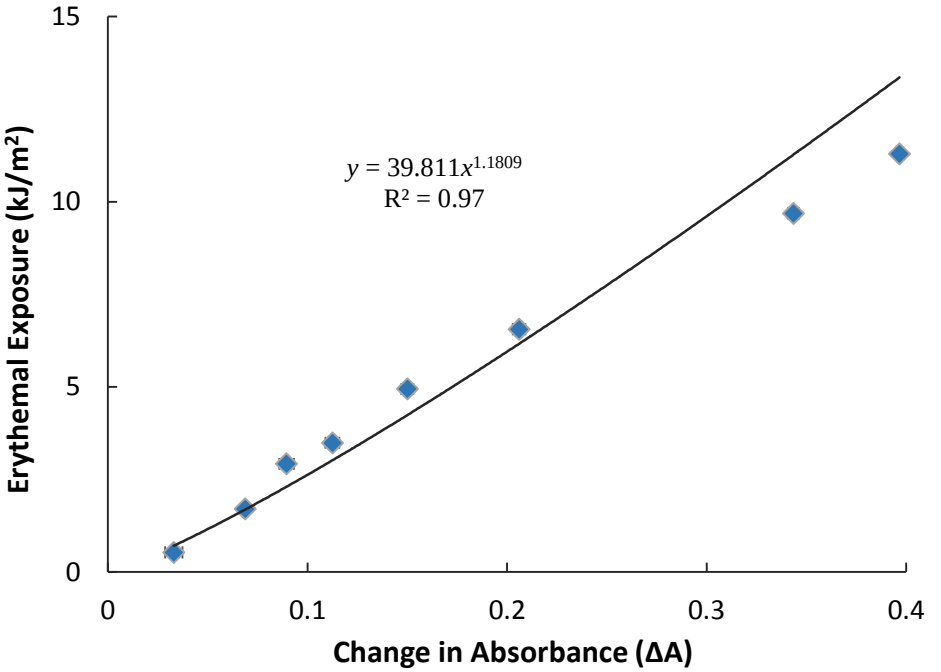

Figure 4.10 Autumn solar erythemal dose response curve. The error bars (which may be contained within the symbol) represent the standard deviation of the polyphenylene oxide (PPO) dosimeter batches.

4.5.2 Seasonal Differences

A comparison of Figures 4.3 and 4.4 (winter) with Figures 4.7 and 4.8 (summer) shows the significant difference in the dose response of the dosimeters that occurs between seasons. The differences between summer and the other seasons (Figures 4.5, 4.6, 4.9 and 4.10) were less pronounced, these seasonal differences have been identified previously (Schouten, Parisi & Turnbull 2010; Wainwright, Parisi & Schouten 2013). The solar UV spectrum is not constant and changes with each season (Schouten, Parisi & Turnbull 2010), which can be attributed to changes in total ozone and SZA (Casale et al. 2006). These seasonal changes necessitate that a separate calibration be conducted for each season, and under the same atmospheric conditions in which the dosimeters will be used. As a result, the dosimeters were calibrated in each of the four seasons. For the calibration of the instruments, the ten minute values recorded by the erythemal UV Biometer and the IL1400 were recorded to coincide with the ten minute spectral data from the Bentham spectroradiometer over a minimum period of four hours in order to get a full range of SZA's. The essential aspect of the seasonal calibrations of the instruments is that the calibrations were done at a time that was completely cloud free. The resulting vitamin D effective calibrations provided an R^2 of above 0.92 for each instrument in each season.

Error bars are included in Figures 4.3 – 4.10. Where the error bars are not obvious they have been included but are contained within the symbol used in the figure. These error bars reflect the standard deviation of the change in absorbance for each dosimeter which was then averaged for each exposure time. The change in absorbance of each dosimeter is measured four times and there are either four or five dosimeters used for each exposure time. The size of the error bars reduces from winter to summer. After winter, refinements were made to the spinner used in the spectrophotometer as described in Section 4.5.1. A further adjustment was made after the spring test. This meant that, in summer and autumn, the batches of dosimeters showed a uniform change in absorbance when exposed under the same conditions hence, the small size of the error bars in these seasons.

4.6 LOW EXPOSURES

PPO dosimeters have been used successfully in many tests that extend over more than one day (Schouten, Parisi & Turnbull 2010). When the PPO dosimeters were analysed after conducting the field tests, some of the dosimeters had a ΔA that was negative (See Chapter 5). The range of the negative absorbance values was −0.002 to −0.039. In ensuring that the PPO dosimeter was able to meet the higher exposure levels, there may have been a problem recording the lower exposure levels. Further testing of the PPO dosimeter was performed to determine what happened at low exposure levels.

The tests were carried out in a laboratory using a solar simulator. In this way the ΔA could be measured immediately after the exposure. The solar simulator was allowed to warm up and a spectral scan was made prior to commencing exposures using the portable scanning spectroradiometer.

Due to the size of the collimated beam from the solar simulator, six miniaturized dosimeters could be exposed simultaneously. The dosimeters were exposed for one minute at a time from 1 – 10 minutes total exposure. After each minute the dosimeters' absorbance were measured in the spectrophotometer. Dosimeters were exposed for two minutes at a time from 10 – 20 minutes total exposure, and for five minutes at a time from 20 – 30 minutes total exposure. The dosimeter absorbance was measured after each time interval. Spectral scans were performed at ten, twenty and thirty minutes total exposure. These subsequent scans showed the irradiance over the thirty minutes to be within ±2.7% of the initial scan.

Normally after exposure the change in absorbance of the PPO dosimeters is positive, i.e. the dosimeter starts with an absorbance measurement of 0.160 and after exposure has a higher absorbance value e.g. 0.180 giving a positive difference of 0.020. The change in absorbance of PPO for the first one minute exposure showed that initially the absorbance decreased and the ΔA was a negative value for all the dosimeters measured. With each additional one minute exposure, the ΔA continued to be a negative value although the magnitude of this value decreased each time. After eight minutes of exposure all but one of the dosimeters recorded a positive ΔA (Test a). As

the negative values were unexpected the procedure was repeated with another set of six dosimeters. This set of dosimeters also gave negative ΔA values initially (Test b).

Figure 4.11 (a & b) shows a definite linear relationship between the time of exposure and the change of absorbance for both tests. This relationship extends from the negative differences at one minute exposure through to 30 minutes of exposure which had positive differences. All the individual dosimeter readings are shown, the linear relationship was based on the mean taken from all six dosimeters in the test. The R^2 values were 0.99 in both cases.

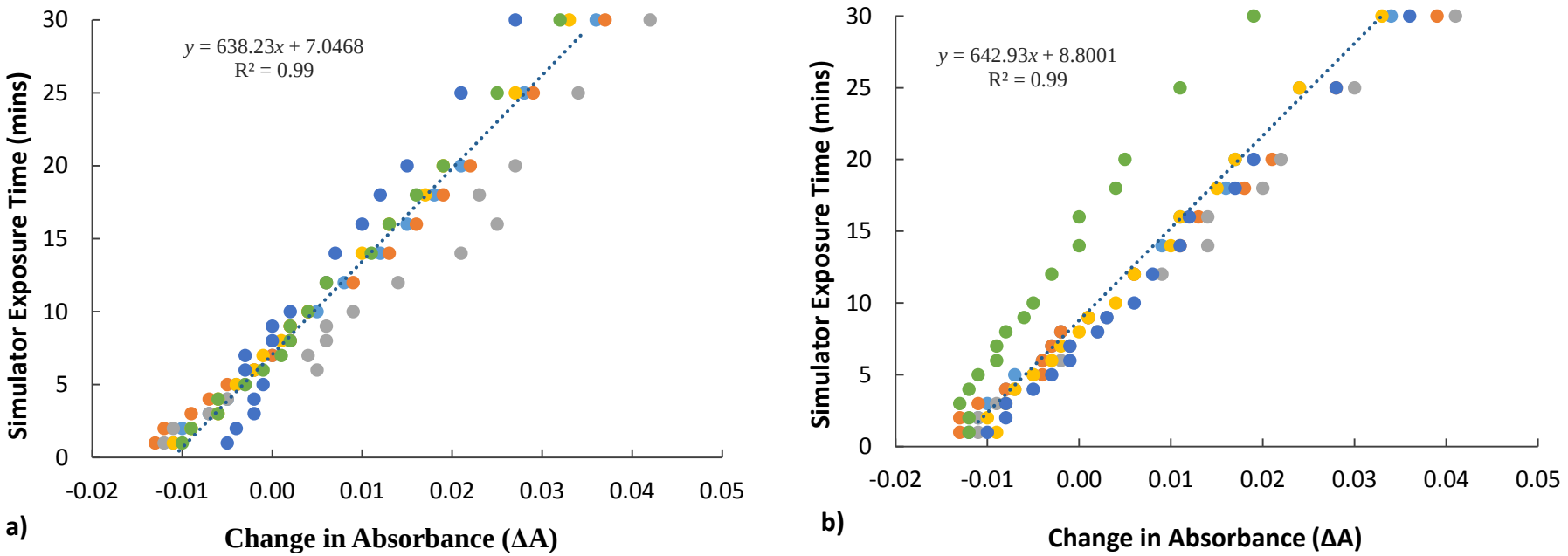

Figure 4.11 Plots a and b show two different trials of the exposure time versus change in absorbance for low time exposure of PPO dosimeters. The linear relationship was taken from the mean of the six dosimeters measured in each of the tests.

In Test (a) the initial absorbance values were not measured on the day of exposure. This is in line with normal practice. In Test (b) the initial absorbance measurements were taken both immediately prior to exposure as well as having been measured some days earlier. These two sets of pre exposure measurements for the second test were similar but not the same, there was a maximum of ±0.25% difference. The set of dosimeters used for both tests had exactly the same initial absorbance measurements to establish a consistent starting point. The green data in Test (b) relates to one dosimeter. The measurements start off in a similar pattern to the other dosimeters, as the measured differences are quite small this change could be due to some dust etc. that was not identified and removed at the time of measurement.

The mean change in absorbance was positive in both tests after nine minutes of exposure. The results clearly show that there was an initial negative change in the dosimeters at low exposure levels. It was not until fourteen minutes of exposure had occurred that the change in absorbance of all dosimeters could be considered to be outside the 0.008 absorbance error margin. Dosimeters with exposures of less than fourteen minutes may not accurately reflect the exposure level that was received by the dosimeter. It is possible that some dosimeters record a negative or zero change in absorbance for exposures below a threshold exposure. This may be something to do with the specific photochemical reaction (as it only occurred in the PPO dosimeter) which can be investigated in future work.

4.7 CHAPTER SUMMARY

This chapter investigated using one PPO dosimeter to measure both erythemal and vitamin D effective UV exposures. This was conducted over periods of five days through seasonal calibration and weighting with the erythemal action spectrum and the vitamin D effective action spectrum. A UVA dosimeter was discussed in Chapter 3. Having now run tests on the two separate dosimeters the two can now be combined into one compact package which is able to measure three biologically effective wavebands at the same time. Field trials using this combined dosimeter were conducted, and the details of the trials are given in the following chapters.

5. FIELD TRIALS

5.1 OVERVIEW

Having now tested the PPO and the UVA dosimeters individually, as discussed in previous chapters, the two dosimeters are now combined into one compact package. This combined dosimeter was used in a field study carried out over four seasons. The results of the field study were assessed in two parts and this chapter will look at the irradiance and exposure measurements recorded by the dosimeters.

5.2 INTRODUCTION

It is widely accepted that ultraviolet radiation, particularly UVB, is the main cause of a range of melanoma and keratinocyte cancers as well as causing eye damage and skin photoageing. UVA penetrates further into the skin than UVB (Webb 1998) and causes skin damage such skin photoageing, melanoma and keratinocyte cancers (Runger 2003.

Understanding the balance of the damaging and beneficial UV exposures requires concurrent measurement of the damaging erythemal UV, UVA and the beneficial vitamin D effective UV for human participants going about their normal daily activities. The focus of this study was to determine concurrently the erythemal UV, the vitamin D effective UV and the UVA radiation exposures received by indoor workers in their occupational and recreational environments over a minimum period of one week in each season. Prior to field testing, a UVA dosimeter was developed, characterized and described in Chapter 3 (Wainwright, Parisi & Downs 2015). The PPO dosimeter, previously characterized as a UVB dosimeter (Lester et al. 2003) was further developed in the research in Chapter 4 through dual calibration for both vitamin D effective UV and erythemal UV exposures (Wainwright, Parisi & Downs 2016). The outcome of the research conducted and examined in this chapter will be the concurrent determination of the levels of erythemal UV, UVA and vitamin D effective UV exposure received by indoor workers, during their outdoor activities, over an extended period.

5.3 PARTICIPANTS

The University's Ethics Committee approval (H12REA191) was granted to measure personal solar radiation exposure at two field sites located in subtropical Australia (Toowoomba, Queensland). A dual film dosimeter calibrated to three different biological responses was worn by the study participants during normal daylight activities for a period of one week in spring (2014), summer (2015) and autumn (2015) and two weeks in winter (2014). Participants were asked to remain within the Toowoomba region during the specific weeks of the study. Those who were travelling outside the area were excluded from the study. Participants were required to complete an activity list (Appendix A) to record time spent outdoors. 'Outdoors' was classified as any area that had at least one surface open to the elements. A car with the windows up was classified as indoors. Participants were recruited via email and were able to take part in any or all of the four seasonal trials. A portable UV meter (Section 2.2.2.3) was used to measure the ambient UVA and erythemal UV irradiances at all indoor locations occupied by participants during their normal working hours. These measurements were performed in each season at various times of the day, including mid and early morning, around the middle of the day and both mid and late afternoon.

Participants at two sites were included in the study, as follows:

- Site 1– was chosen as it is a restricted access building with controlled climate and little natural sunlight. During the working day the employees have limited ability to go outside as they have specific schedules regarding start, finish and break times.

- Site 2– was chosen as it consists of a large number of buildings with open spaces in between. Participants have more access to natural sunlight and greater flexibility of outdoor movement than those at site 1. Figure 5.1 shows photos of both sites.

Figure 5.1 Photos of the buildings where participants of the field study worked. Site 1, a single large building, is on the left and site 2, multiple buildings, is on the right (Google Maps 2016).

5.4 DOSIMETER DETAILS

The UV exposures were measured with two miniaturized UV dosimeters. These dosimeters were seasonally calibrated to measure the erythemal UV, UVA and vitamin D effective UV as outlined in Chapter 3 for UVA and in Chapter 4 for the dual calibration of erythemal UV and vitamin D effective UV.

All films used in the dosimeters were manufactured at USQ. The PPO film, which was used for the erythemal and vitamin D effective exposures, was made using PPO in powder form (General Electric Plastics, USA). The film used for the UVA dosimeters was made using 8-MOP crystals (Sigma, Saint Louis, USA).

A technique has been developed to make the two dosimeters into a compact package. After making the separate dosimeter films, each type of dosimeter was made with a thin flexible plastic frame measuring 1.0 cm × 3.0 cm, with a 0.7 cm diameter aperture at one end as explained in the dosimeter fabrication Sections, 3.3.1 and 4.3.1. Figure 5.2 shows the construction of the combined dual film dosimeter calibrated to three different biological responses. This was done in three layers; on the bottom is the PPO dosimeter, then the UVA dosimeter is placed on top in such a way as not to obscure the aperture containing the PPO below. A Mylar filter was then placed over the entire UVA dosimeter including the aperture (Wainwright, Parisi & Downs 2015) but not obscuring the PPO. This was then secured to the baseplate of a badge using waterproof tape. The dosimeters used in this research were routinely calibrated to horizontal control dosimeters, Casale et al. (2012) has shown that horizontal calibrations can

apply to dosimeters angled at up to 70° for dosimeters manufactured using PS. The purpose built combined dosimeter badges of dimensions 2.0 cm × 4.5 cm employed in this study were worn on the shoulder to provide the most consistent horizontal aspect as shown in Figure 5.3.

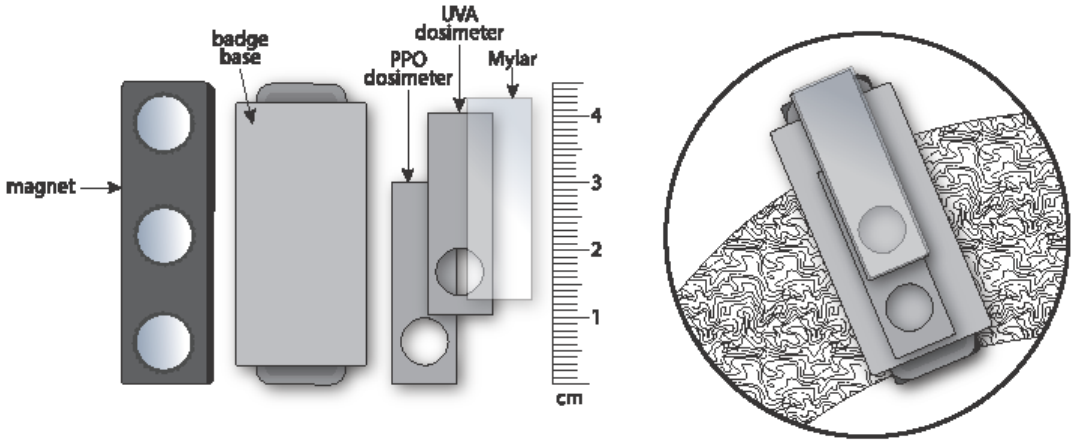

Figure 5.2 Example dosimeter package for simultaneous measurement of the UVA, the erythemal UV and the vitamin D effective UV exposures. The result was a dual film dosimeter calibrated to three different biological responses.

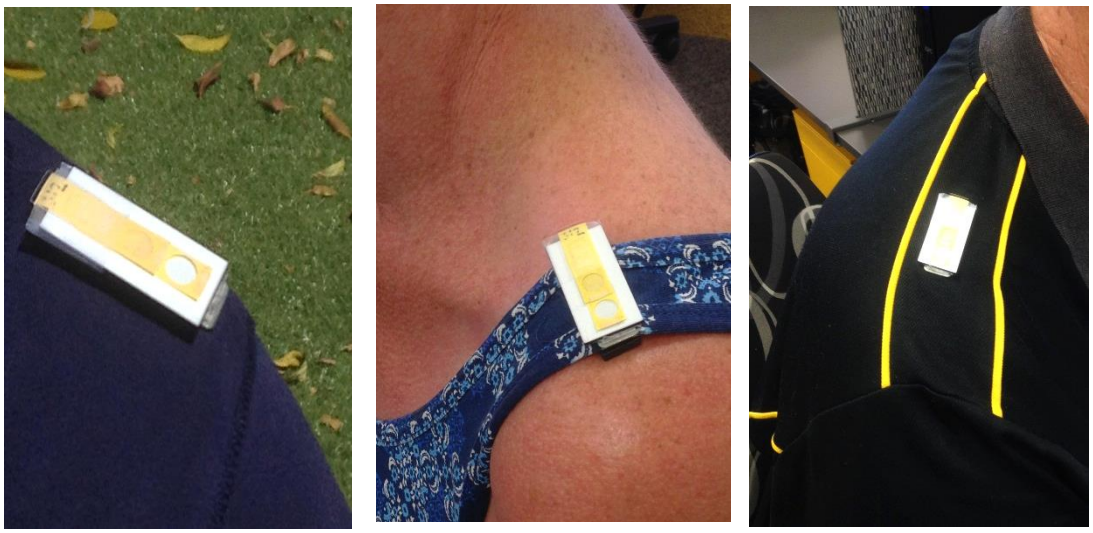

Figure 5.3 Examples of participants wearing the combined dosimeter.

Analysis of the dosimeters was carried out by measuring the variation in absorbance at a specific wavelength: 320 nm for PPO and 305 nm for 8-MOP. These are the wavelengths at which the maximum change in optical absorbance has been shown to

occur by Schouten, Parisi & Turnbull (2007) for PPO and by Diffey & Davis (1978) for 8-MOP.

Both types of dosimeters were measured collectively for optical absorbance both before and eight days after exposure. This was done using a spectrophotometer with a rotating mount as described in Sections 3.3.1.5 and 4.3.1.1. The mean of the measured values was used for all subsequent calculations to determine the UV exposure through calibration in each of the erythemal UV, UVA and vitamin D effective UV wavebands.

5.4.1 Calibration

Before field use (UV dosimeters are able to be used in the field independently), they require calibration to the UV spectrum at the Earth's surface (Casale et al. 2006). A calibration relationship that linked the gradual changes in the optical absorbance of each dosimeter type to the measured exposure in the respective wavebands (as outlined in Chapters 3 and 4) was made.

5.5 RESULTS AND DISCUSSION

The results of each season were assessed individually. Although some people did take part in each season, others did not. Table 5.1 shows the number of dosimeters assessed for UV exposures in each season. The response rate was very good for all four exposure periods, being 97% as only four dosimeters were not handed back over the whole period of the field study. Some dosimeters were completely unusable due to damage, for example two dosimeters were washed after being left on clothing. In other cases only one section of the dosimeter was usable, either the PPO or the UVA section. One participant had completely taped over the UVA aperture making the UVA section unusable and on another dosimeter the PPO film was accidently torn. Of the dosimeters returned, only those dosimeters where the film was not marked or damaged were used in the analysis. Incidents of this type resulted in 85% of the total dosimeters being assessed.

Table 5-1 Number and types of dosimeters assessed in each season for the evaluation of the erythemal UV, UVA and vitamin D effective UV exposures.

Season	Winter		Spring		Summer		Autumn	
Total number of dosimeters issued	30		36		36		27	
Dosimeter Type	PPO	UVA	PPO	UVA	PPO	UVA	PPO	UVA
Assessable Dosimeters	25	25	34	32	27	27	25	23

During analysis, the total exposure was measured as one value per participant and compared against the calibrated control seasonal response therefore giving a personal UV exposure for a week. Erythemal UV and UVA irradiances were measured with the portable UV meter at the location of the office work stations of all participants located at both sites 1 and 2. All indoor locations recorded zero indoor erythemal UV irradiance in all seasons and at all times when the measurements were taken. The UVA irradiances were predominantly zero. The desks of three participants who sat near north facing windows (southern hemisphere) recorded a UVA irradiance of 0.1 mW/cm^2 when measured after 10:30 h. Two of these participants explained that when the Sun became too bright they closed the window blinds for the remainder of the day. These minimal to zero irradiances recorded at indoor work stations show that the changes recorded by the dosimeters were due to exposures received while participants were outdoors on breaks or travelling to and from work.

Table 5.2 shows the maximum and minimum temperatures, the mean maximum temperature (Bureau of Meteorology 2016) and the maximum UVI (USQ 2016), recorded during the dates the dosimeters were worn in each season.

Table 5-2 The study dates including the range and mean maximum daily temperatures (Bureau of Meteorology 2016), and the maximum ultraviolet index (UVI) (USQ 2016) during the time of testing in each of the seasons in the 2014 to 2015 study period.

Season	Dates	Daily Maximum Range (°C)	Mean Maximum (°C)	Daily Minimum Range (°C)	UVI Maximum
Winter	16/07/2014 – 29/07/2014	12.0 – 18.8	16.9	−0.2 – 9.8	3.7
Spring	05/11/2014 – 11/11/2014	27.3 – 31.0	30.3	13.3 – 15.9	9.4
Summer	11/02/2015 – 17/02/2015	24.1 – 27.7	27.0	15.8 – 17.0	11.6
Autumn	25/03/2015 – 31/03/2015	23.0 – 31.2	28.0	16.2 – 19.4	8.2

Control dosimeters were placed at key work station locations at each site and on the roof at USQ. An example is shown in Figure 5.4. These dosimeters were left uncovered for the full length of the trial in each season (two weeks in winter, one week in the other seasons). The mean percentage change in absorbance of the UVA control dosimeters was 0.4% at site 1 and 0.6% at site 2. UVA control dosimeters on the roof experienced a mean measured exposure change in absorbance of 82%. The change in absorbance of all the PPO indoor control dosimeters at both sites was in the negative region indicating very low exposure levels as discussed in Section 4.6. The PPO control dosimeters located on the roof at USQ all reached saturation within the time (one or two weeks) of testing. This equated to a measured change of absorbance of over 12 times the initial reading.

Figure 5.4 Control dosimeters in position indoors at site 1, UVA dosimeters are on the left and PPO dosimeters are on the right.

5.6 SEASONAL EXPOSURE RESULTS

Figures 5.5 – 5.7 show the seasonal UV exposures measured concurrently with the combined dosimeter over the periods of exposure in each of the erythemal UV, UVA and vitamin D effective UV wavebands. The winter exposures over the two week period were divided by 2 in order to be consistent with the exposure periods of one week in the other seasons. Each point in the figures represent the exposure of an

individual over the period of exposure in each season. Each horizontal bar represents the median of the respective exposures in each season. These figures show the distribution of individual exposures, and the variations of the exposure, throughout the year. A logarithmic *y*-axis scale for the exposures has been used to highlight the differences observed. High exposure variability occurred in winter this is due to the behaviour of the individual participants. Some people did not go outside during the time of the study and others were outside for extended periods.

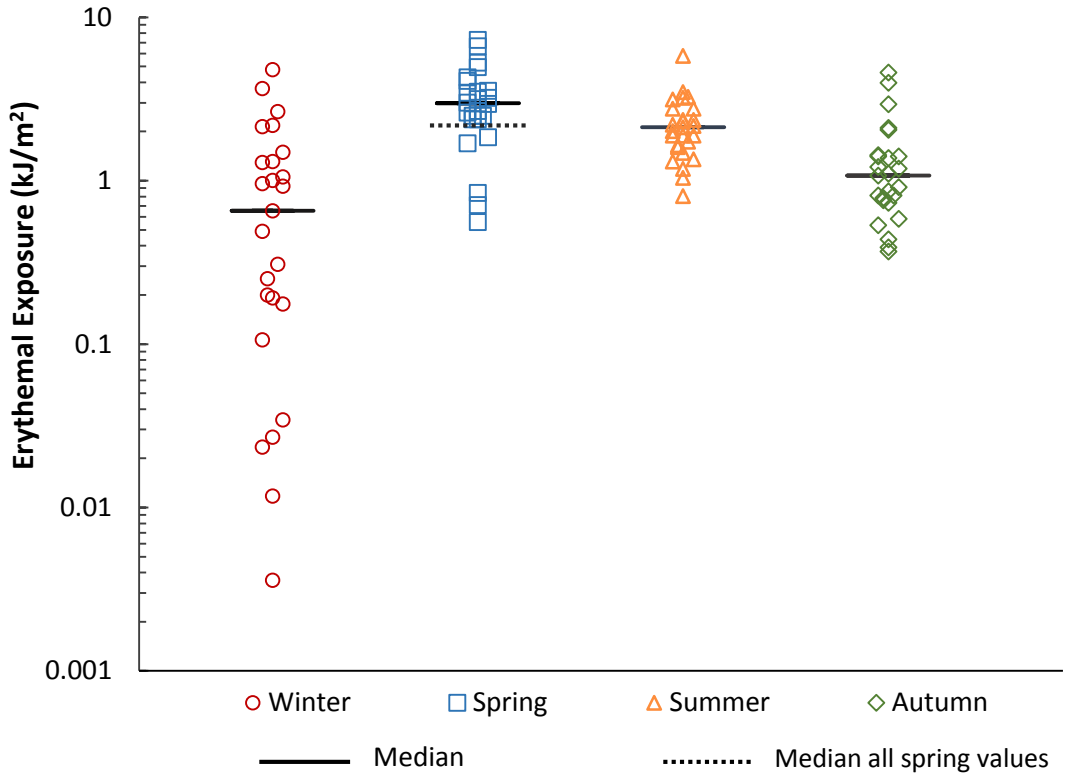

Figure 5.5 Total erythemal exposures per participant over a period of one week in each season, each marker represents one person.

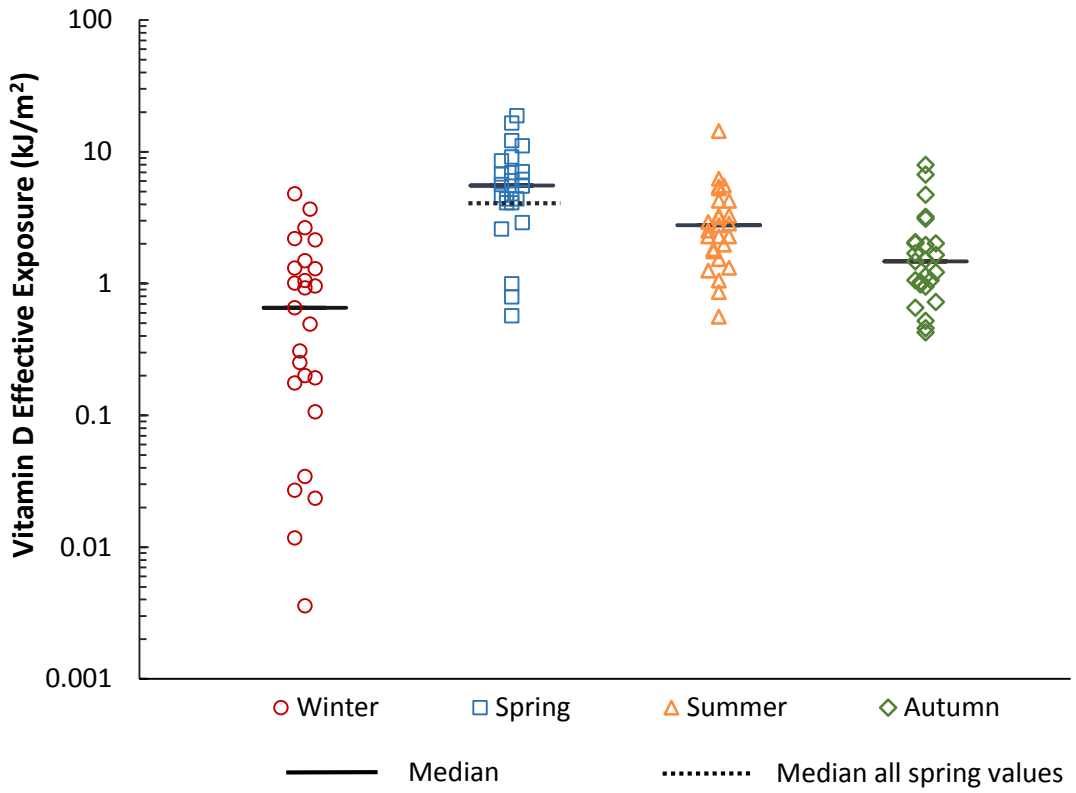

Figure 5.6 Total vitamin D effective UV exposures per participant over a period of one week in each season, each marker represents one person.

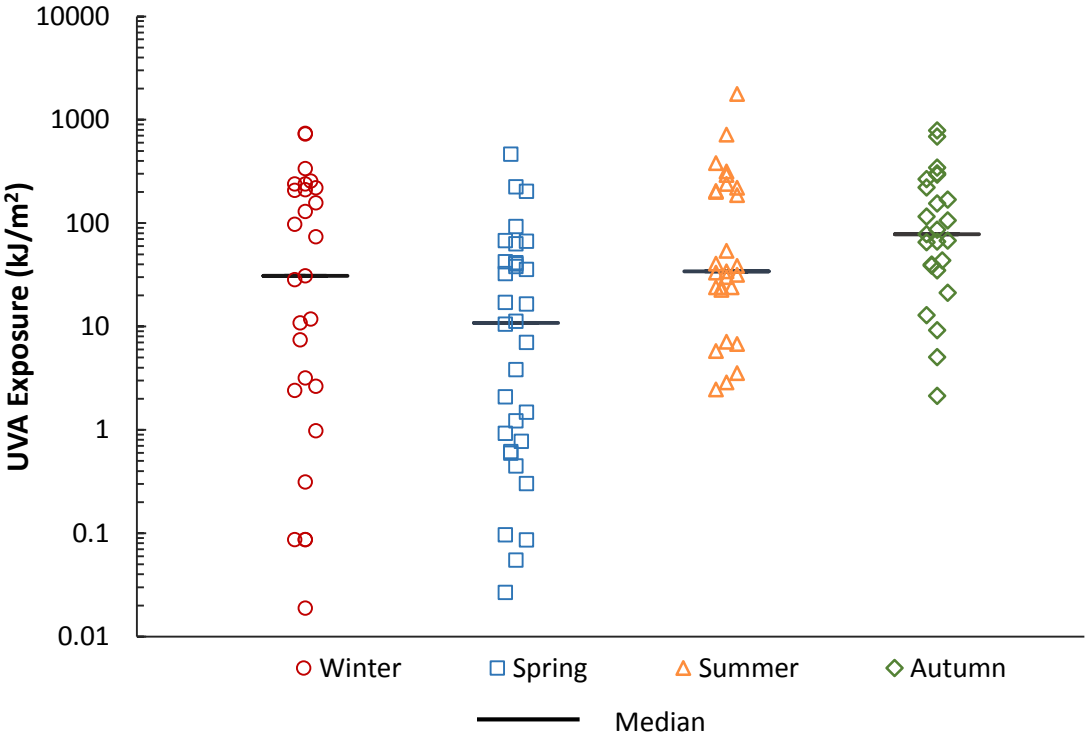

Figure 5.7 Total UVA exposures per participant over a period of one week in each season, each marker represents one person.

In spring, the change in absorbance of ten of the PPO dosimeters was at or below the measureable threshold (see Section 4.6). With the exception of one participant, all of these people were either in the lowest quartile for total time outdoors or for time outdoors between 10:00 – 14:00 h these participants had a mean time outdoors of twenty one minutes per day. The mean time outdoors for all participants in spring was fifty three minutes per day. Figures 5.5 and 5.6 do not have the individual erythemal UV and vitamin D effective UV plotted for these ten participants. Two medians have been calculated for spring and both are shown on Figures 5.5 and 5.6. The higher, solid-line median includes only those participants with measureable dosimeters: the lower, dashed-line median includes all participants; a zero exposure was ascribed to the ten dosimeters below the measureable threshold for these calculations. Even using the lowest median the spring erythemal UV and vitamin D effective UV exposure levels are the highest of all the seasons. All of the UVA dosimeters worn in spring were measureable and the lowest median value for UVA occurred in spring with the median being lower than the other seasons. The range of UVA exposures in spring was similar to the spread in winter.

The week the dosimeters were worn in spring was part of a month of unseasonably warm weather with maximum temperatures being an average 4 °C higher than usual resulting in the spring time mean maximum temperature exceeding the summer maximum (Bureau of Meteorology 2016) as shown in Table 5.2. This unusually hot weather in spring may have resulted in some of the participants modifying their behaviour. Studies of school children (Moise et al. 1999; Guy et al. 2003; Downs & Parisi 2009) noted that activity patterns were the most important factor affecting individual UV exposure. Activity has also been highlighted as a significant factor in Queensland school teachers (Downs et al. 2016). It is probable that changes in activity patterns by adults in the current working environments of this study would also affect their measured exposure levels.

The received erythemal UV exposures are further illustrated in Table 5.3 where the exposures have been converted to units of SED. Both the arithmetic mean and the range have been included for the total weekly exposure in each season. Daily average values were calculated by dividing the weekly values by 7. The Australian Radiation Protection and Nuclear Safety Agency (ARPANSA) advise that one SED per day is

considered to be a safe exposure level for most people (ARPANSA 2016). Table 5.3 shows that the mean of all participants was more than two SED per day in summer, autumn and spring, and one SED in winter. Over 50% of the participants averaged more than one SED per day in winter.

Table 5-3 The weekly and the daily erythemal exposures in units of standard erythemal dose (SED) for each of the seasons, the number of participants used to calculate the mean is shown in brackets.

Season	Weekly erythemal UV (SED)		Mean daily erythemal UV (SED)	
	Mean (n)	Range	Mean	Range
Winter	10 (24)	0 – 48	1	0 – 7
Spring	32 (27)	6 – 53	5	1 – 8
Summer	24 (25)	8 – 63	3	1 – 9
Autumn	11 (26)	4 – 46	2	1 – 7

As expected, the mean of the erythemal UV exposures in winter was lower compared to the erythemal UV exposure means in the other seasons. Differences in the mean could relate to the time of day the participants were outdoors in each of the seasons. In winter, 45% of the recorded time outdoors was between 10:00 – 14:00 h, whereas in summer this reduced to 27%. Corresponding with this, there is also a significant change in the ratio of UVA/UVB irradiances throughout the day (Kimlin et al. 2002). This ratio is lowest between 10:00 – 14:00 h. The recorded 45% time outdoors between these hours corresponds to the lower UVA/UVB irradiance ratios, people outdoors in the middle of the day will record higher UVB levels. The vitamin D effective action spectrum is zero above 330 nm, this results in higher vitamin D effective UV exposure being recorded compared to erythemal UV exposure when different times of the day are spent outdoors particularly during winter. Figure 5.8 shows the change in UVA/UVB ratios for a clear sky day in winter and a day in summer. The ratios were calculated using spectral irradiance values recorded by the UV spectroradiometer in Toowoomba.

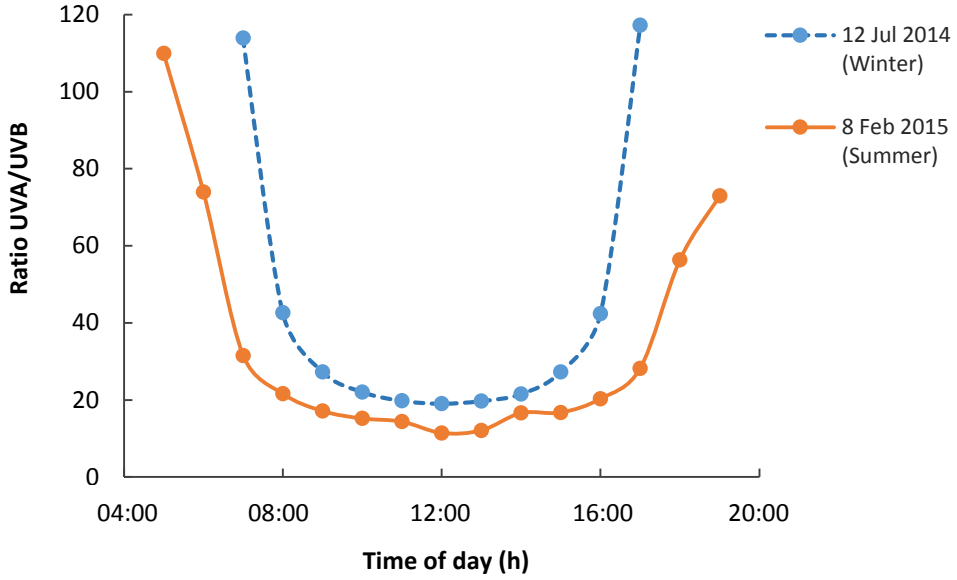

Figure 5.8 UVA/UVB ratios for a clear day in winter and a day in summer using spectral irradiances recorded by the Bentham spectroradiometer.

5.6.1 Distribution of Personal UV

Figures 5.9 – 5.11 show the distribution of the personal exposures in each season for each site. Figure 5.9 showing the erythemal UV exposures, has an expected pattern with more participants having higher exposures in summer and lower exposures in winter. The autumn distribution showed a greater number of lower exposures. The spring distribution shows very few people in the low exposure range (due to the change in absorbance of ten of the dosimeters being below the measureable threshold and these ten participants not being shown) and a shift towards higher exposures similar to those shown for summer which could be related to the unseasonably warm weather at the time, with only those compelled to go outside doing so. Taking all the seasons combined, the vitamin D effective exposures in Figure 5.10 tend to be at the lower end with over half of the participants having vitamin D effective UV exposures of less than 4 kJ/m^2. Spring has the greatest distribution of exposures with more people being above 6 kJ/m^2 (the median) than below. This is probably a consequence of the timing of the daily exposure with those participants going outside at or near solar noon receiving a higher relative UVB effective exposure. As expected, noon time exposures

would result in a lower relative UVA dose. This is reflected in the UVA exposure distribution during spring.

The charts showing the distribution of the UVA exposures (Figure 5.11) indicate most participants in summer and winter had exposures either at the low end or the high end of the recorded levels in these seasons. The larger number of participants with low levels of UVA exposure in spring compared to the other seasons ties in with the ten participants that had erythemal UV and vitamin D effective UV exposures below the measurement threshold in spring. These same participants had very low levels of UVA exposure recorded. In winter, summer and autumn the high number of people with a UVA exposure of more than 200 kJ/m^2 appears to indicate that UVA levels are more responsive to personal behaviour patterns. This is possibly caused by participants going outdoors before and after working hours when UVA/UVB ratios are high. These high UVA levels do not correspond to a similar distribution in Figures 5.9 and 5.10. This is a significant result that would not have been identified without using the combined dosimeter to measure the three concurrent exposures, and shows that the extra dosimeter can track other patterns in UVA exposure.

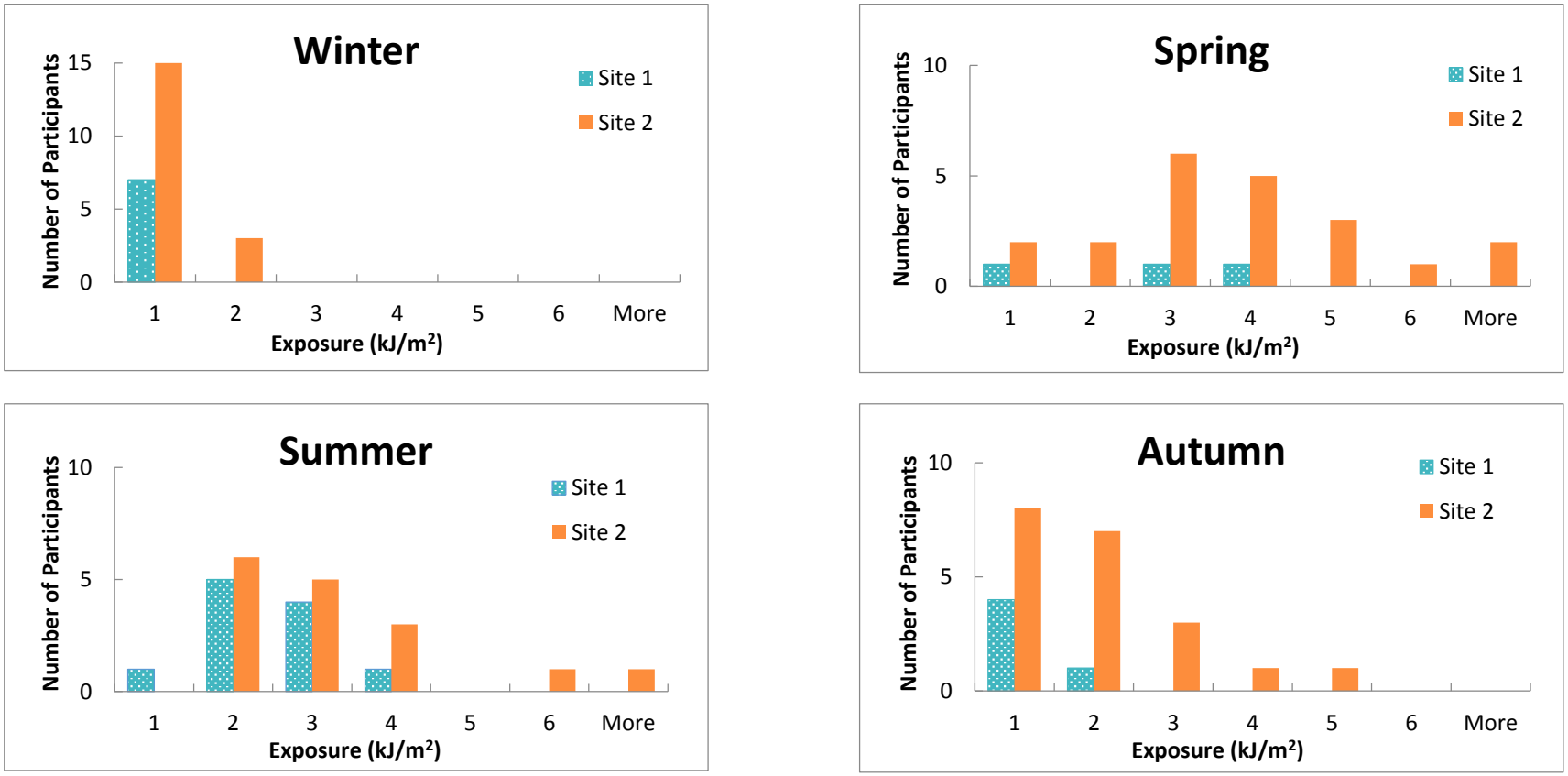

Figure 5.9 Distribution of erythemal exposures over a period of one week in each season.

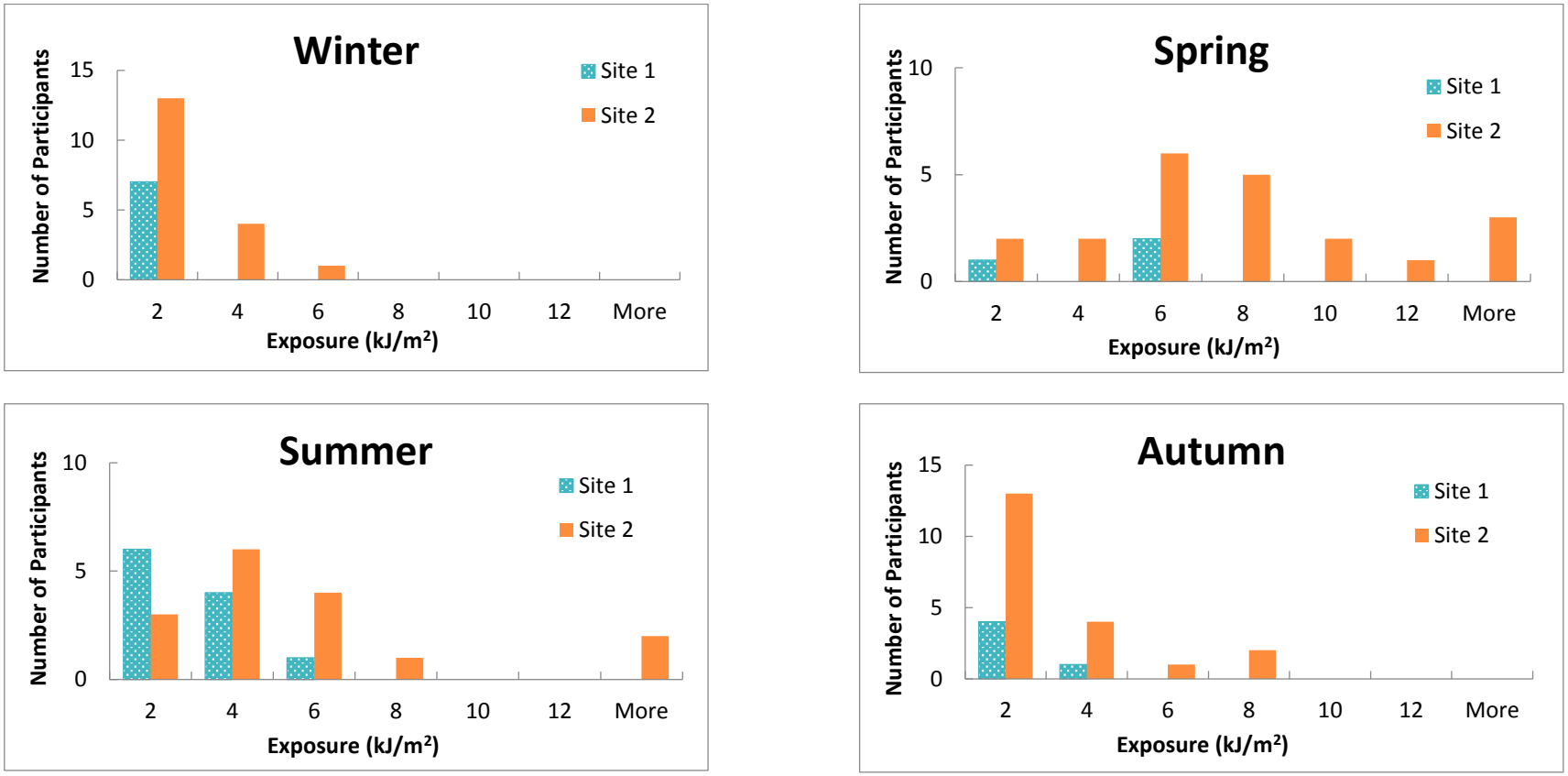

Figure 5.10 Distribution of vitamin D effective exposures over a period of one week in each season.

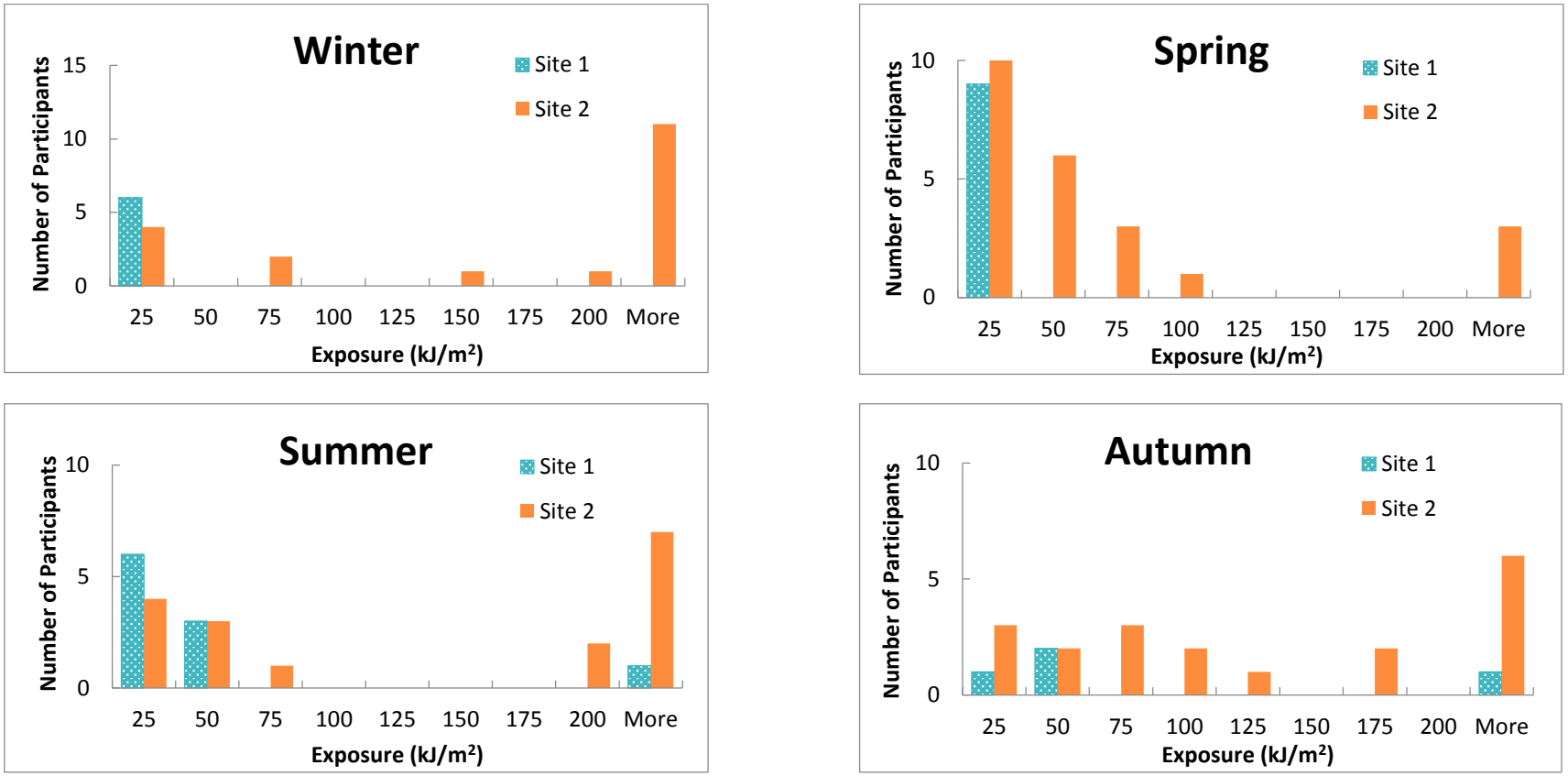

Figure 5.11 Distribution of UVA exposures over a period of one week in each season.

5.7 SITE DIFFERENCES

Fewer participants came from site 1 than from site 2. Figures 5.9 – 5.11 show that participants from site 1 tended to be at the lower end of the distribution, this was most noticeable in all the winter charts. It is important to record exposures to workers who spend a great deal of time indoors. Even between two sets of indoor workers the exposures are very different; compare the low exposure levels of the site 1 workers with the closed/restricted work environment to the people at site 2 that had a more open environment. Of the ten PPO dosimeters that did not reach measureable thresholds in spring, seven came from participants located at site 1. In order to see a clearer comparison, the mean and median values for each type of exposure were determined for each season by site (Table 5.4). When doing the UVA calculations the exposures that were greater than five standard deviations from the normal of the total sample were not included (one value in summer and one value in autumn) as these values skewed the results significantly. As an example, using the autumn UVA data and removing one value greater than five standard deviations changed the mean from 195 to 32 kJ/m^2 for UVA at site 1 and from 164 to 130 kJ/m^2 for UVA at site 2. Table 5.4 shows that the means at site 1 were always lower than those at site 2. This relates to the behaviour of the individual participants, with those from site 2 being outside more than those from site 1. The UVA exposure is a probable consequence of difference in working behaviour, where participants at site 1 were restricted to indoor environments compared to site 2 which had more open environments.

Kitchener (2001), in a study of Naval personnel, highlighted the importance of intermittent exposure during a person's lifetime and the importance of good vitamin D levels in avoiding skin cancer. Using the combined dosimeter could allow for the examination of a range of different workplaces where employees have different opportunities for sun exposure.

McKenzie et al. (2009) was able to show a relationship between vitamin D effective UV and erythemal UV under cloud free conditions for each of summer and winter. Figure 5.12 shows the ratio of vitamin D effective UV/erythemal UV for one day in winter and one day in summer. The irradiances were recorded by the Bentham spectroradiometer. These irradiances were weighted by the vitamin D effective action

spectrum (CIE 2006) and the erythemal action spectrum (CIE 1988) before calculating the ratios. The relative proportions of vitamin D effective UV are shown to increase during the day, reaching a peak around local noon in both winter and summer (Figure 5.12). As mentioned in Section 4.3.1, some of this proportional increase may be due to the higher relative response of vitamin D effective UV at certain wavelengths. The change in ratio of erythemal UV to vitamin D effective UV from less than one to more than one does not occur until around 08:00 h in winter. In winter people may not receive enough vitamin D effective UV but can still be in danger from damaging UVA. Although this was not the focus of the study it highlights the relevance of the work in using the combined dosimeter.

Determining such a ratio for vitamin D effective UV/erythemal UV for each day of this study without going through this process would be difficult due to the many variables that have to be accounted for, such as shade, cloud and SZA. Therefore, each season and each waveband show different distributions, indicating that each category of exposures must be assessed individually. Three factors appear to influence the exposures received: the seasonal changes in the UV spectrum; the seasonal changes in the behaviour of participants; the variability of the UVA/UVB and vitamin D effective UV/erythemal UV ratios throughout the day. Weather conditions also played a part here and were similar to the results of a UK study (Webb et al. 2010) where comparable values of SED were recorded in (northern hemisphere) spring and summer of 3.7 SED per week, the personal SED levels then decreased in autumn, and a further decrease occurred in winter due to inclement, cooler outdoor conditions. There are significant changes in erythemal UVB levels throughout the year in Australia at subtropical latitudes and this, coupled with a strong advertising campaign that promotes avoiding going out between 10:00 – 14:00 h in the hotter months (Cancer Council Australia 2015A) in order to prevent skin damage, may have also influenced the seasonal outdoor sun exposure behaviour of the participants.

These results reinforce the need to know the exposure in all three wavebands as the different biological effects cannot be found if the wavebands are not monitored at the same time. One waveband cannot be used to presume the exposure of another waveband.

Table 5-4 The mean and median erythemal UV, UVA and vitamin D effective UV exposures by site for one week in each season.

	Winter Mean (median)	Spring Mean (median)	Summer Mean (median)	Autumn Mean (median)
Erythemal UV (kJ/m^2) site 1	0.073 (0.040)	2.023 (2.504)	1.870 (1.733)	0.806 (0.760)
Erythemal UV (kJ/m^2) site 2	0.612 (0.518)	3.337 (3.161)	2.723 (2.243)	1.492 (1.144)
Vitamin D effective UV (kJ/m^2) site 1	0.178 (0.069)	3.530 (4.391)	2.373 (1.975)	1.070 (0.984)
Vitamin D effective UV (kJ/m^2) site 2	2.816 (2.062)	6.863 (6.024)	4.716 (3.018)	2.247 (1.582)
UVA (kJ/m^2) Site 1	0.609 (0.087)	2.457 (0.593)	40.99 (23.26)	32.05 (39.67)
UVA (kJ/m^2) Site 2	165.6 (157.2)	63.67 (35.60)	170.6 (53.96)	129.8 (82.29)

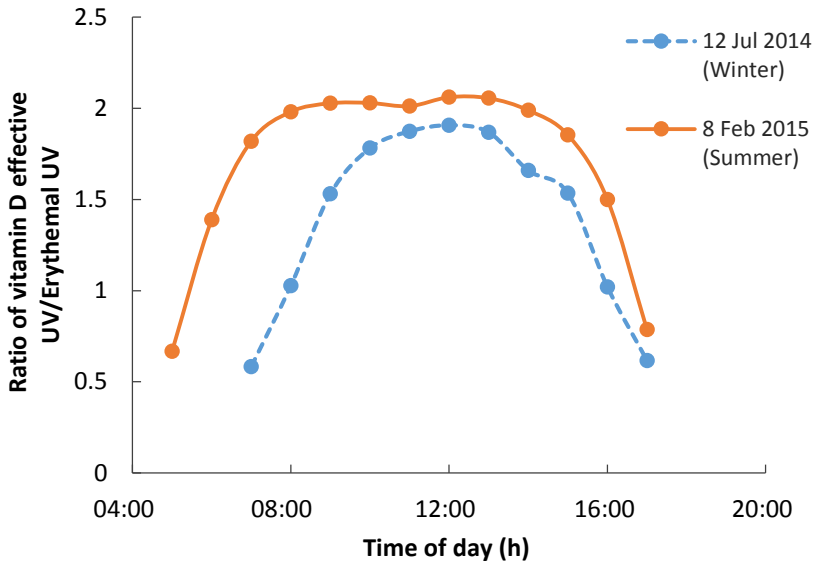

Figure 5.12 Ratios of vitamin D effective UV to erythemal UV for a clear day in winter and a day in summer using irradiances recorded by the Bentham spectroradiometer. The irradiances were weighted using the vitamin D effective (CIE 2006) and erythemal (CIE 1988) action spectra.

5.8 CHAPTER SUMMARY

The combined dosimeter successfully recorded the personal erythemal UV, UVA and vitamin D effective UV exposures concurrently for indoor workers over a minimum of one week in each of four seasons over one year (2014 to 2015). Different patterns of UV biological exposures were identified that could not be found without recording the exposures simultaneously. The exposures received by the dosimeters were measured but, this was not necessarily the exposure received by the individual as sun protection behaviours were not taken into consideration. The next chapter will investigate sun protection behaviour.

6. SUN PROTECTION BEHAVIOUR

6.1 OVERVIEW

The previous chapter dealt with how the combined dosimeter was successful in measuring concurrently the erythemal UV, UVA and vitamin D effective UV irradiances to which participants were exposed during normal daily activities over the four trial periods in the course of one year. The irradiances measured were those received by the combined dosimeter being worn on the shoulder, but may not represent the actual exposure level of the participant due to clothing and sunscreen. Many of the participants used some form of sun protection when they were outdoors.

This chapter focuses on the protective measures used and the type of clothing that was worn by participants when wearing the dosimeters. Four sections will be looked at: sunscreen, hats, clothing that covers the arms and clothing that covers the legs.

6.1.1 Activity List

Although not all dosimeters were usable in terms of reading exposures, the information recorded in the activity list was still usable. Across all seasons only one activity list was not returned. This occurred in winter and the corresponding dosimeter badge was not returned either. The participants who had washed or damaged their dosimeter badges continued with the activity sheets for the remaining term of the trial. Table 6.1 shows the number of participant activity lists assessed in each season.

Table 6-1 The number of participant activity sheets assessed by season.

Season	Winter	Spring	Summer	Autumn
Number of activity lists assessed	29	36	36	27

Participants were asked to record, on the activity list (Appendix A), the sun protection used and the clothing worn when outdoors as well as recording the time spent outside which was referred to in the previous chapter. This would also record any change of

information during a continuous period outside by marking two or more of the relevant sections for that time period. For example, taking off a jacket or applying sunscreen.

6.2 INTRODUCTION

In 1981, a SunSmart campaign was launched in Victoria Australia to help combat rising melanoma rates linked to solar UVR exposure. This was known as the Slip! Slop! Slap! Campaign (SunSmart 2016). The message was very simple slip on a shirt, slop on sunscreen and slap on a hat in order to stop skin cancer.

The campaign has been used constantly throughout Australia, particularly in the warmer months, since its introduction. The slogan has been extended from the original and now includes the additional words Seek and Slide which relate to seeking shade and sliding on sunglasses particularly between 11:00 – 15:00 h (SunSmart 2016).

There are five recommended sun protection factors: sunscreen, hat, clothing (shirt), sunglasses and shade. Since this public awareness message about the sun protection measures has been around for at least 30 years, it was reasonable to expect that the participants in the study had some awareness of sun safe practices. Three of the five recommendations will be covered in this chapter: sunscreen; hat; clothing; as these items were recorded by participants on the activity lists. The use of sunglasses was not recorded and the participants' interpretation of the shade categories was not consistent enough for analysis, with some participants recording cloudy days as being shade. The reported results were analysed without any overlap; each season was assessed separately even though some people were participants in all four seasons. This was done to possibly link patterns in sun protection with patterns of exposure.

A small number of people who had completed the time outdoors and arm covering sections of the activity list did not complete the remainder of the activity list. Therefore a "no response" category appears for sunscreen, hats and leg coverings.

6.3 SUNSCREEN

Sunscreen was the main consideration for people concerned with sun safety. The sunscreen categories that were used in the study were based on sun protection factors (SPF), the categories were: no sunscreen, 15+, 30+ and 50+. Figure 6.1 shows that more than 52% of participants did not wear any sunscreen at any time during winter, spring or summer. In autumn that level changed to 37% of participants who did not wear sunscreen at any time. A small number of participants reported that they always wore sunscreen when they were outdoors but, of the people reporting this, 75% indicated that the sunscreen was worn only on the face. The SPF of the sunscreen used was either 15+ or 30+ in these cases. This may not be sunscreen as such but might be the SPF that was included in moisturiser or makeup used on a daily basis. The remaining participants used sunscreen on an irregular basis either for a certain portion of the day or on specific days when an outdoor activity was planned. Participants in this category may have very low sunscreen use as those who reported a single use of sunscreen for a short time were still included here.

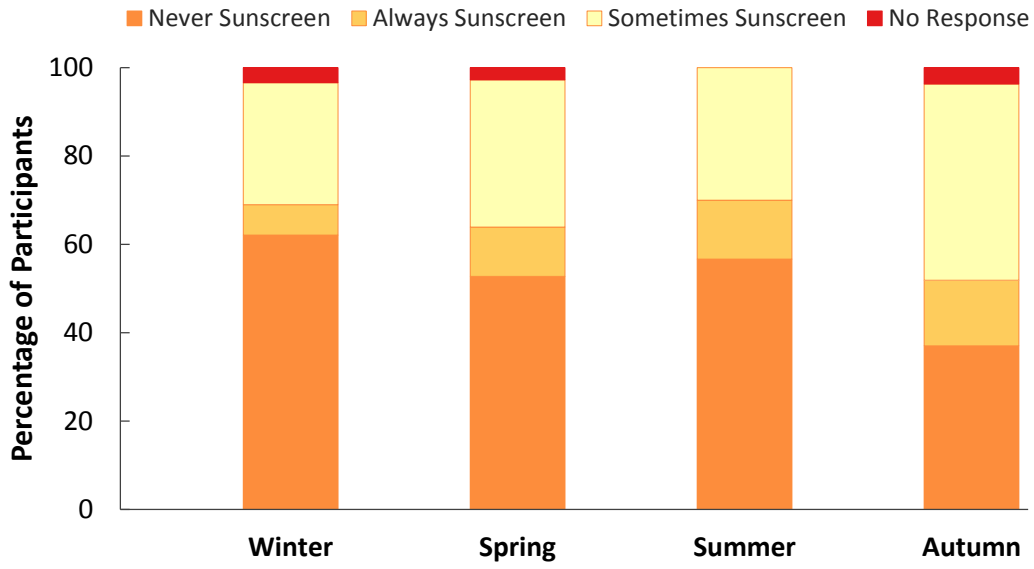

Figure 6.1 Sunscreen use as reported by the participants in each season.

Figure 6.2 shows the SPF of the sunscreen used. The majority of people used the same SPF of sunscreen for all outdoor activities. One person changed from lower to higher SPF in winter and one person in spring, two people changed from lower to higher SPF in both summer and autumn. The 50+ sunscreen was the least used, with only one

person using this SPF in winter and one in spring, and two people using it in summer and two in autumn.

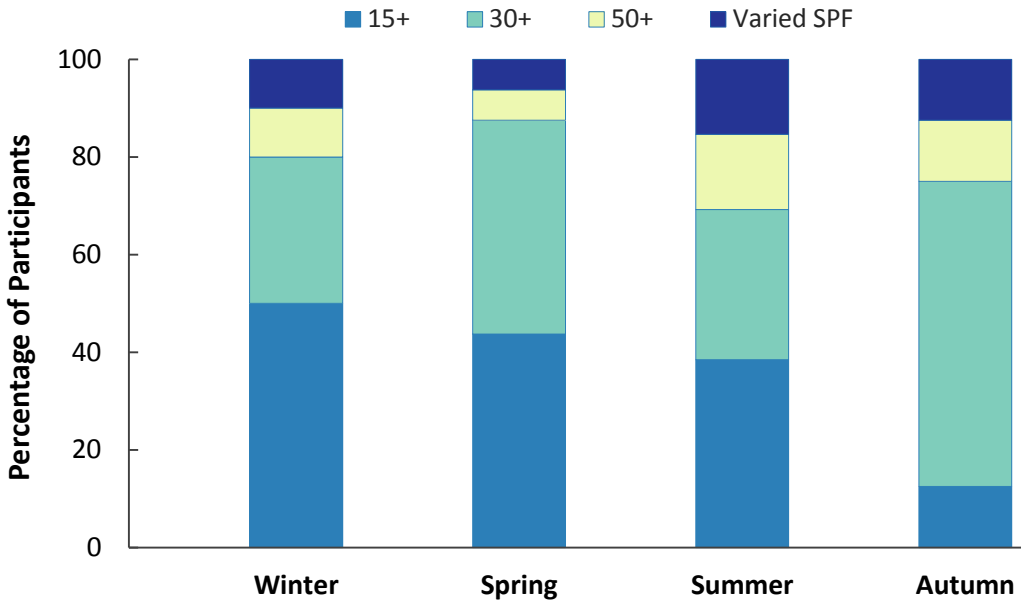

Figure 6.2 The SPF of sunscreen used in each season as recorded by the participants using sunscreen. All participants who reported using sunscreen at any time were included in the percentage calculation.

6.4 HATS

Hats do provide some UV protection but it is advisable that they be worn in conjunction with other protection methods. Studies have shown that a close weave broad brim hat provides the best protection of hats overall when compared with caps, bucket hats and legionnaires hats (Gies et al. 2006). Bucket hats provide only slightly less protection than broad brimmed hats but other hat types may provide better protection to specific areas such as the back of the neck (Gies, McLennan & Javorniczky 2014). Head wear or hats were separated into three categories: caps; narrow brim hats; broad brim hats. Figure 6.3 shows the hat wearing response of participants for each season. Two participants always wore a hat when outdoors in any season. These two also wore the dosimeter badges on the top of the hat rather than on the shoulder. Both these people were unable to take part in all four seasons of testing so the "always worn" section of Figure 6.3 does not always include two participants. More than 55% of participants never wore a hat at any time in winter, spring or summer. The summer season had the highest percentage of people who never

wore hats, at 63%. Autumn had the best hat usage with only 37% reporting never wearing a hat although this season had the fewest participants. Figure 6.4 shows more detail of the type of hat that was worn. Caps were the most popular headwear, although they offer the lowest level of protection, followed by broad brimmed hats. People in the various category, where different types of hat were worn, always included wearing a broad brimmed hat for some time outdoors.

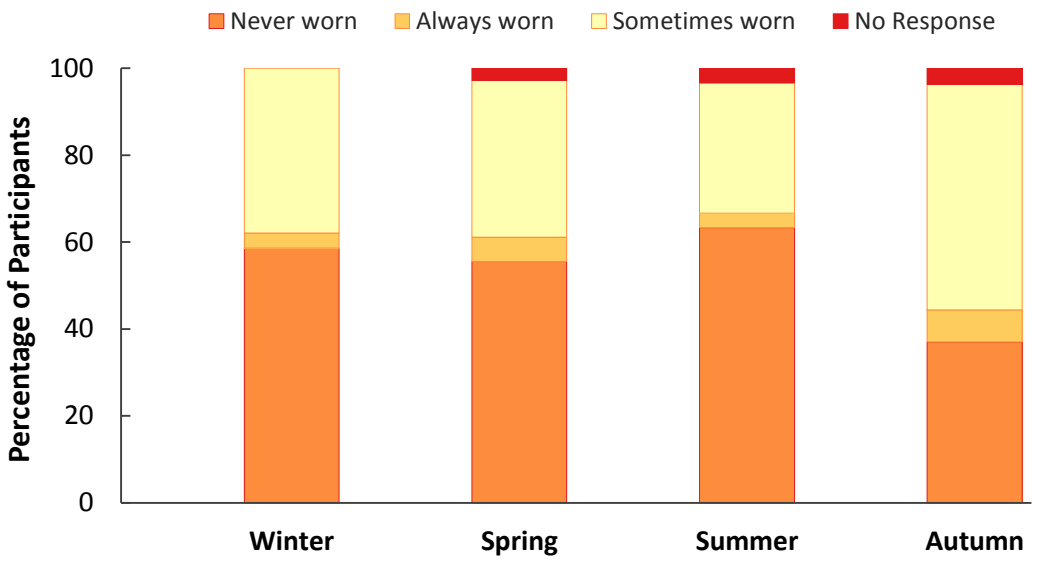

Figure 6.3 Hat use as reported by the participants in each season.

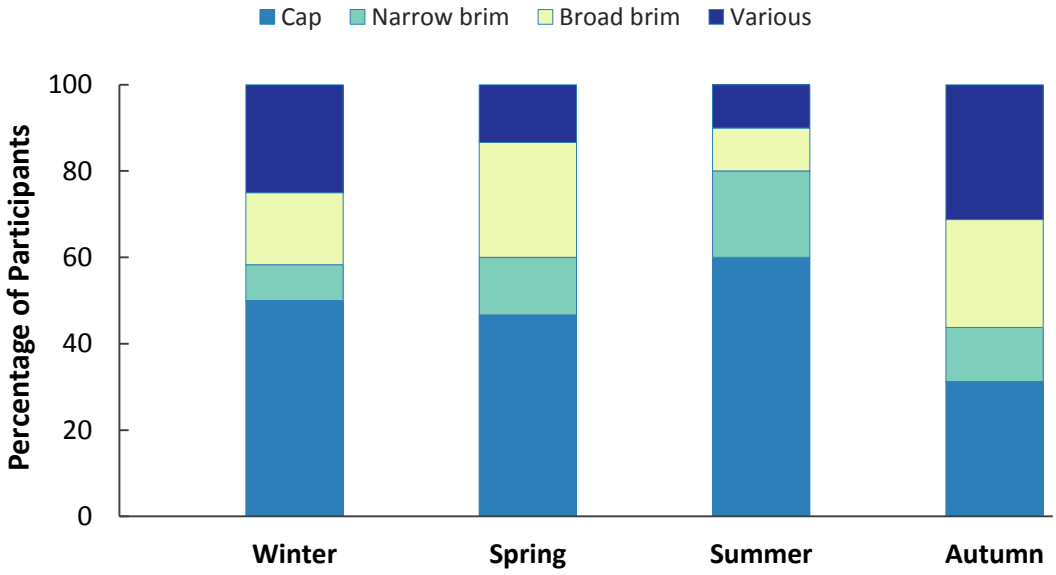

Figure 6.4 Type of hat worn in each season as reported by the hat wearing participants.

Figure 6.5 gives information on the percentage of people who never wore any sunscreen and never wore a hat at any time during a particular season. This number was between 33 – 43% in winter, spring and summer but there was a noticeable change to 18% in autumn. The other category displayed in Figure 6.5 shows the number of people who wore a hat at some time and who also used sunscreen at some time but not necessarily both at the same time. People who wore a hat once and used sunscreen only once in the season were included in this category. Once again the autumn season was very different from the other three seasons with 44% of participants reporting using both hat and sunscreen at some time during the autumn study. This is more than double the level in any other season. Autumn was the last season of the field trial and had the lowest number of participants. It is possible that the participants who continued the study until this point had a greater awareness of sun risks and were more likely to take precautions when going outdoors.

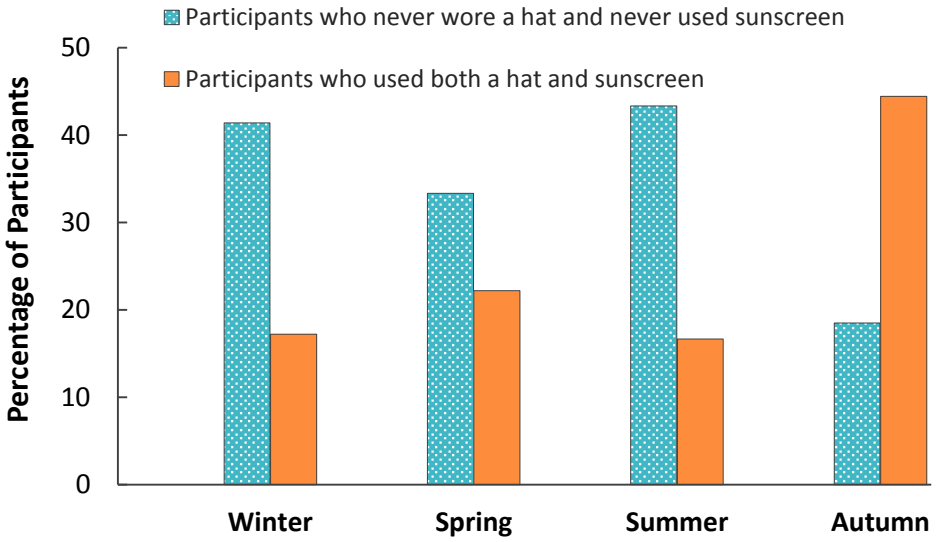

Figure 6.5 Percentage of participants who never used sunscreen and never wore a hat at any time and the percentage of participants who used both a hat and sunscreen at some time in the season although not necessarily at the same time.

Table 5.3 in the previous chapter showed the range of exposures of participants in SED per season. The analysed dosimeters showed that all participants would receive a mean exposure at or above the safe erythemal UV exposure level (one SED) during winter, spring, summer and autumn, so the number of people choosing not to wear sunscreen and/or hats is a concern. These people would be at risk of incurring skin damage and

potential health problems. More people used sunscreen than wore hats but as sunscreen needs to be applied regularly and hats provide limited cover, the best protection comes from using them together. It is impossible to know why so many people in the study chose not to use UV protection, further studies should include additional questions to explore the reasons for this.

6.5 CLOTHING

Clothing information was also recorded and was separated into two areas: arm covering and leg covering

The three categories used for arm covering were: long sleeves that covered the arm to the wrist, short sleeves which covered some part of the arm and singlet which provided no cover of the arm itself, just shoulder cover. The leg categories were: ankle length (this included stockings if worn with shorter skirts), knee length some lower leg exposed and shorts some upper leg exposed. An additional space was included to allow for other items; three clothing items listed here by participants were: gloves (in winter), a strapless full length dress and bathing suits.

Covering up, particularly the arms and upper body with clothing is one of the recommended sun protection factors. The best clothing protection is provided by clothes which have good body coverage, meaning longer shorts, shirts or tops with collars and sleeves longer than ¾ length (Gies, McLennan & Javorniczky 2014) and where the fabric meets the Australian/New Zealand Sun Protective Clothing Standard AS/NZS 4399 (1996) which is used to rate the UV protection of clothing. The rating categories are Good Protection (UPF 15, 20), Very Good Protection (25, 30, 35) or Excellent Protection (40, 45, 50, 50+) wherever the skin is covered by such material.

It was difficult to determine whether covering up of either the arms or legs by the participants was for sun protection reasons or not. Reasons for changing clothing can include: temperature control (for example putting on a jacket) and comfort (for example changing from a uniform or other work standard attire) and functional (clothing for sport and other reasons).

The type of clothing used for arm covering that people reported wearing during each season is shown in Figure 6.6. Very few people wore long sleeves at all times when outdoors even in winter. The largest proportion of people changed their clothing as required.

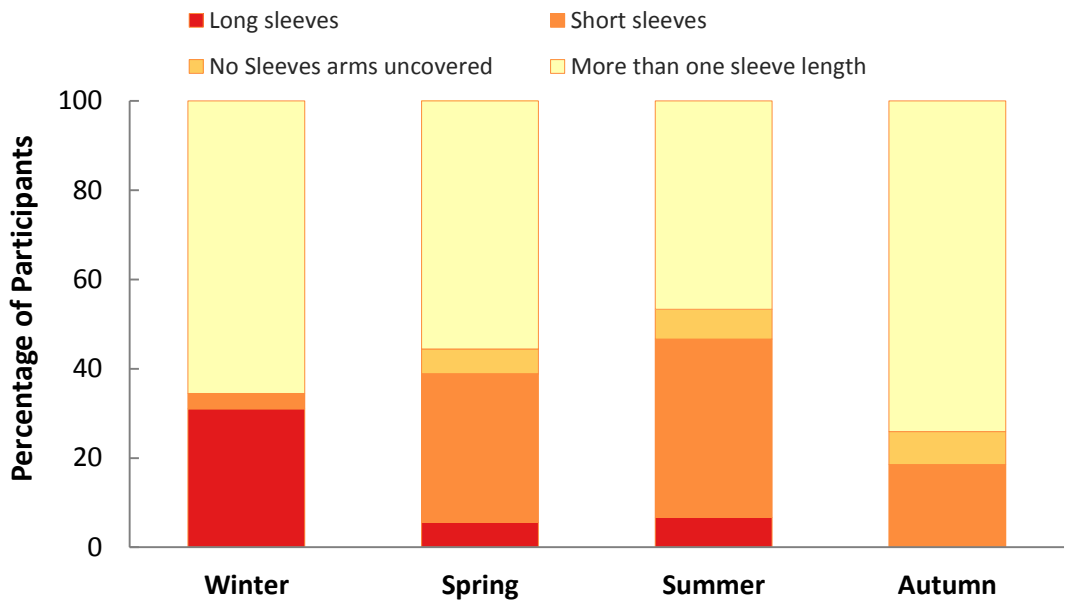

Figure 6.6 Sleeve length as reported by participants in each season. Percentages for long sleeves, short sleeves and no sleeves are for participants who wore the same sleeve length at all times in the season.

The choices participants made for leg covering were more consistent than for arm covering. Figure 6.7 shows that in each season there was always a portion of participants who had their legs completely covered when outdoors. Once again the biggest category involved more than one length with people changing between any of the three lengths of leg covering.

There is very little difference in temperature in three of the seasons of the study. Givoni et al. (2003) found that for people working in air-conditioned environments the clothing worn was often the same in all seasons regardless of the climatic conditions outdoors. De Carli et al. (2007) also found no correlation between clothing worn and outdoor temperature. It takes a large temperature difference to change the type of clothing that is worn in sub-tropical locations.

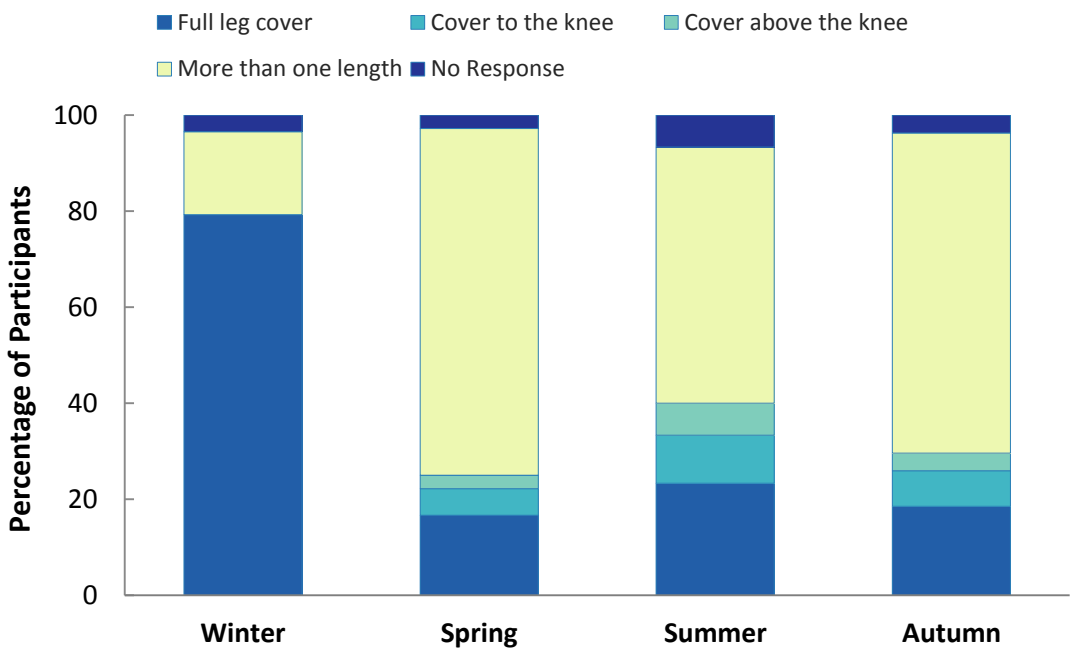

Figure 6.7 Length of clothing used to cover the legs of participants in each season. Percentages for full leg cover, cover to the knee and cover above the knee are for participants who wore the same length at all times in the season.

6.6 CHAPTER SUMMARY

This chapter investigated the use of three sun protection factors, these were: sunscreen, hats and clothing. Identifying and classifying which of these items were used by participants during the field study and how often. In Chapter 5, Table 5.4 shows that there were higher mean levels of vitamin D effective UV received to the dosimeters in winter than in autumn for participants at site 2. This could be viewed as a positive as vitamin D levels are known to decrease in winter (Engelsen et al. 2005; Kimlin 2010). However, as the majority of people reported being clothed to the ankle and in long sleeves during winter, there may not be enough exposed skin to utilise the vitamin D effective UV. More than 50% of participants reported not using sunscreen and not wearing a hat at any time during winter, spring and summer. These people would be at risk of UV damage as mean SED levels were at or above safe levels in these months, and UVA exposures were high for more than 25% of participants in winter and summer.

7. CONCLUSION

7.1 OVERVIEW

Personal exposure to solar UVB is acknowledged as having both positive and negative effects on human health. UVA has also been linked to sun damage and skin cancer. High incidence of skin damage causes a burden within the medical sector of society both in terms of time and financial costs. The associated financial cost across both wavebands of UVR damage is significant and is estimated to be AUD $703 million for NMSC in 2015 (Cancer Council Australia 2016). The monitoring of individual UVR exposures under different lifestyles is important in order to optimize exposure levels so that erythema and other damage is avoided but vitamin D production and the associated health benefits are enabled. To date, no single photochemical dosimeter has successfully measured simultaneously both erythemal and vitamin D effective UV for periods of a week. Similarly, no photochemical dosimeter has successfully measured UVA in isolation for a period of several days.

Due to the different levels of damage various UV wavelengths cause, combined dosimeters were made to measure simultaneously the three different biologically effective wavebands; these being erythemal UV, UVA and vitamin D effective UV.

7.1.1 UVA Dosimeter

Dosimetry has been used to measure received UVB exposures and a dosimeter using PPO has been used to measure received erythemal UV exposures. A new miniaturized dosimeter using 8-MOP as the photoactive material has been characterized and a technique developed for the calibration of UVA exposures. The properties of a dosimeter using 8-MOP as the photoactive chemical in conjunction with a Mylar filter were investigated specifically for measuring UVA over extended periods longer than one day. The results of the dark reaction showed no ongoing change within the dosimeters after eight days post exposure. The spectral response results showed 8-MOP only reacting to wavelengths of 320 – 400 nm as it did not record any UVB at 300 nm or 310 nm indicating that Mylar is an effective UVB filter. The cosine response results showed an error of less than 15% for angles between 0° and 50°. Dose rate independence had a difference of 0.013 in the normalized response for the irradiances tested indicating that the 8-MOP/Mylar dosimeter is suitable for extended

UVA measurement provided the film is seasonally calibrated. Temperature testing showed that the cast sheets could be air dried at room temperature and that the dosimeters were temperature independent in the range 10 – 40 °C ± 6%. Seasonal dose response tests conducted over all four seasons at a subtropical latitude show the UVA dosimeters were able to measure exposures greater than 21.5 kJ/m^2. The successful outcome of this range of testing has established that 8-MOP, in conjunction with a Mylar filter can measure UVA exposures over extended periods longer than one day and can be calibrated to determine seasonal UVA exposure. Therefore, it is suitable for use as a long term UVA dosimeter.

7.1.2 Dual Calibrated PPO Dosimeter

The use of miniaturized PPO dosimeters for measuring both erythemal and vitamin D effective UV exposures over periods of five days was investigated. This was done by calibrating the PPO dosimeter to both the erythemal and the vitamin D effective action spectra as the PPO spectral response approximates the erythemal and the vitamin D effective action spectra. A dual calibration was undertaken in each season of the year with a separate instrument calibration also performed in each season under optimum cloud free conditions.

Seasonal dose response tests conducted over four seasons at a subtropical latitude show that the erythemal and vitamin D effective UV dosimeters were able to measure exposures up to five days. With one set of PPO dosimeters and one set of pre and post exposure processing, both erythemal and vitamin D effective UV exposures could be determined. The successful outcome of this testing has established that PPO is suitable for use as a long term, dual calibrated dosimeter provided the film is seasonally calibrated. The calibration equations showed that the approach was successful with an R^2 of 0.92 – 0.99 for vitamin D effective UV and between 0.86 – 0.99 for the erythemal. Whilst acknowledging that the beneficial effect of UVR is related to the exposure time, time of day and area of skin exposure (McKenzie, Liley & Bjorn 2009) and other considerations, the use of miniaturized PPO dosimeters can enable measurements to be taken at multiple body sites and would enable the dual UV exposure of a large cohort of study participants to be evaluated non-invasively; thus increasing the number of measurements obtained.

The successful outcome of this testing has established that PPO is suitable for use as a long term, dual calibrated dosimeter provided the film is seasonally calibrated. This enables one dosimeter to provide two sets of exposure results. The combination of dual calibration and the long term exposure potential of PPO makes the PPO dosimeter more versatile and increases the scope for UV field research on erythemal UV and vitamin D effective UV in the future.

7.1.3 Combined Dosimeter Field Study

7.1.3.1 Irradiance

Ratios of UV wavebands change throughout the day and from season to season, with each waveband having a specific biological effect that can damage or benefit the health of individuals. The combined dosimeter was designed to determine the personal erythemal UV, UVA and vitamin D effective UV exposures concurrently.

Through using the combined dosimeter badge, which was made from the PPO dosimeter and the UVA dosimeter, and which was worn by volunteer participants; this study measured the personal erythemal UV, UVA and vitamin D effective UV exposures concurrently of indoor workers, over a minimum of one week in each of four seasons for a period of one year (2014 to 2015). Measuring the three wavebands of UV exposure concurrently allowed the comparative assessment of three biologically significant wavebands of UV exposure. Analysis confirmed that variations in the relative amounts of each of the three wavebands exist across all seasons for samples of office worker populations. High levels of UVA were recorded that did not have corresponding high levels of erythemal and vitamin D effective UV for the same participants. This means that each waveband has to be assessed individually in each season.

The personal UV exposure received in each week was measured as one total weekly value for each of the office worker participants, and assessed against the calibrated seasonal response control. The mean of the erythemal UV exposures in winter was lower than the erythemal UV exposure means in the other seasons. UVA exposure medians varied with the seasons. The lowest median occurred in spring, with winter and summer having similar values. The individual vitamin D effective exposures were

lowest in winter, and spring recorded higher values than the other seasons. This can be attributed to the change in the UVA/UVB ratio that occurs throughout the day and with the seasons, combined with the fact that as the seasons grew cooler, participants increased the time spent outdoors during the hours of 10:00 – 14:00 h from 27% in summer to 45% in winter.

More people had higher erythemal UV exposures in summer and lower exposures in winter. Over half of the participants had vitamin D effective UV exposures of more than 2 kJ/m^2 over the week for each of the seasons. Although mean SED levels were highest in spring, this was due to having no measureable responses for ten participants combined with unseasonal warm weather. Median exposures for both erythemal UV and vitamin D effective UV, which included zero values for these ten participants, were highest in spring. UVA exposures tended to concentrate towards the ends of the distribution range, with the exception of autumn, this tendency was most noticeable in summer indicating the study population was probably divided into two distinct behaviour types. Even for indoor workers, there is a significant difference in exposure related to the type of working environment. Site 1 (a single large building) participants always had lower mean exposure levels in each season and for each waveband. These participants were over represented in the lower ends of the distribution. Showing that for the category of office workers the type of office environment influences the exposures of the workers.

Three factors appear to influence the measured personal exposures: the variability of the UVA/UVB ratios throughout the day, the seasonal changes in the UV spectrum and the seasonal changes in behaviour of the participants. These results indicate that studies on the effects of UV exposure require the concurrent measurement of the relevant biologically weighted response. The dual film dosimeter calibrated to three different biological responses is an effective and necessary device for concurrent measurement of erythemal UV, UVA and vitamin D effective UV exposures. The technique extends research on the beneficial and damaging effects of UV.

7.1.3.2 Sun Protection

Considering that the awareness levels of solar UV protection methods is high in Australia, the limited level of protection employed by study participants was

surprising. More than 50% of participants reported never using sunscreen at any time during the study and similarly more than 50% of people reported never wearing a hat at any time. Very few people wore sunscreen or a hat at all times when outdoors. Sunscreen was generally worn on an "as required" basis with 50+ being the least used (only 2 – 6% of people in each season) and only 2 – 6% of people in each season reported changing SPF levels during the day. Hats were also more likely to be worn on an "as required" basis with caps, which offer the lowest sun protection, being the most popular with 18 – 20% of participants wearing caps at some time. The season with the highest reported use of sunscreen and hats was autumn, but this may be due to the type of participants in the research that continued through all four seasons of testing. In winter 80% of people had full leg cover and 30% had full arm cover. In all other seasons, apart from winter, more than 25% of participants always wore short sleeves when outdoors. This study shows that the sun protection message needs to be stronger, particularly with regards to UVA exposure levels.

7.1.4 Research Outcomes

The objectives of this research project have been fulfilled; specifically:

1. A long term UVA dosimeter suitable for exposure periods of a week before saturation has been successfully designed, manufactured and fully characterized.

2. The range of use of the PPO dosimeter has been extended effectively through the calibration and validation of its use as a vitamin D effective UV dosimeter in conjunction with its current use as an erythemal UV dosimeter: a dual calibration.

3. A method of combining the two dosimeters into a compact, robust package has been devised, developed and field tested: the combined package is capable of measuring the erythemal UV, UVA and vitamin D effective UV for exposures of a week before saturation occurs.

4. Field tests have been designed and conducted using the combined dosimeter, analysis of the data established that the combined dosimeter was successful in concurrently measuring the erythemal UV, UVA and vitamin D effective UV

received by office workers and simultaneously determining the level of the beneficial and the damaging exposure.

5. The recorded use of sun protection factors as reported by participants in the field tests has been successfully evaluated, specifically the use of sunscreen, hats and clothing.

7.2 CONCLUSION

The analysis of the field study data shows that the dual film dosimeter calibrated to three different biological responses is an effective and necessary device for use in concurrently measuring the erythemal UV, UVA and vitamin D effective UV biologically effective exposures. Use of this dosimeter in research on the beneficial and damaging effects of solar UV radiation is new and innovative, and will provide an important new methodology that can be extended to other population groups. To provide accurate records of individual UV exposure, studies of damaging and beneficial UV require both measurement of personal UV levels and information on the type and amount of sun protection used.

7.3 FUTURE RESEARCH

Further investigations in this area, such as those detailed below, could be undertaken to extend the understanding and applications of the combined erythemal UV, UVA and vitamin D effective UV dosimeter:

- Conduct further calibrations and field trials in different latitudes where winter and summer UV levels vary more widely than those of the sub-tropical location initially tested
- Use the combined dosimeters in a large scale field survey combined with testing blood samples for vitamin D precursor
- Extend the research to a variety of population groups with different lifestyles

- Through further analysis of the existing data, develop a model to obtain more precise erythemal UV UVA and vitamin D effective UV exposure levels by weighting the individual exposures to known time of day levels and the surface area of skin exposed

- To eventually have sufficient analysed data to assist in developing a predictive model to help forecast the length of sun exposure required for indoor workers to prevent vitamin D deficiency whilst minimizing the harmful effects of erythemal UV and UVA exposure

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APPENDIX A: Outdoor activity list

Date _____ Outdoor Activity List _____

Please record any time you spend outdoors that lasts longer than 5 mins, some examples would include: mowing the lawn, watching or playing sport or hanging the washing.

		Clothing							Hat				Sunscreen				Sun		
Time	Duration (mins)	long sleeves	short sleeves	singlet	long pants	knee length	shorts	other	nil	cap	narrow brim	broad brim	nil	15+	30+	50+	Nil (indoors, in car)	Full	Mixed verandah, sunshade
6.00 - 7.00 am																			
7.00 - 8.00 am																			
8.00 - 9.00 am																			
10.00 – 11.00 am																			
11.00 am – 12.00 noon																			
12.00 noon – 1.00 pm																			
1.00 – 2.00 pm																			
2.00 – 3.00 pm																			
3.00 – 4.00 pm																			
4.00 – 5.00 pm																			
5.00 – 6.00 pm																			

APPENDIX B: Published refereed papers

Wainwright, L, Parisi, AV and Downs, N 2015, 'Dosimeter based on 8-methoxypsoralen for UVA exposures over extended periods', *Journal of Photochemistry and Photobiology B: Biology*, vol. 148, pp. 246–251.

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