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Abstract Minimization of solar UV exposures is necessary to reduce the risks of detrimental sun-related effects caused by overexposure to sunlight and vitamin D deficiency related diseases. Furthermore, agricultural production can be influenced by changes in solar UV and visible radiation due to atmospheric variability. Consequently, there is a requirement for a full understanding of the solar radiation environment. This chapter describes the development of dosimetric techniques for the measurement of solar UV exposures in different conditions in order to provide an improved characterization of the solar radiation environment for humans and plants. The erythemal exposures during normal daily activities and the effectiveness of UV protective strategies have been measured with polysulphone dosimeters. These dosimeters have also been miniaturized in order to increase the number of environments in which they can be used. Additionally, polysulphone dosimeters have been employed with appropriate calibration to evaluate the pre-vitamin D_3 effective UV exposure on humans, along with the UVB $(280 \text{ nm} - 320 \text{ nm})$ exposures to plant leaves. The dynamic range of polysulphone has been extended by the development of a dosimeter that is based on polyphenylene oxide with a dynamic range that is approximately four times longer than that of polysulphone.

Keywords UV, dosimeter, polysulphone, PPO, erythema, plants

7.1 Introduction

The costs of excessive solar UV exposures are high with over 1 million nonmelanoma cases and 59,940 melanoma cases in the USA during 2007 (American

Cancer Society, 2008). In 2007, there were 2,740 deaths from nonmelanoma and 8,110 deaths from melanoma in the USA. Additionally, there is the incalculable cost of the associated human suffering and disfigurement. The risk of the detrimental sun-related effects can be lowered by the reduction of human exposures to solar UV radiation. On the positive side, exposures to UVB wavelengths (280 nm 320 nm) are required for the production of vitamin D (Holick, 2004a). The solar UVB waveband acts as an initiator of the synthesis of vitamin D_3 by the photolysis of 7-dehydrocholesterol in the human skin, to pre-vitamin D_3 . This vitamin plays an important role in calcium metabolism and is essential for good bone development, prevention of rickets in children, and prevention of osteoporosis, osteomalacia, and fractures in the elderly (Holick, 2004b). Vitamin D can also be obtained through vitamin D supplements and a small number of foods; however, the simplest way to obtain vitamin D is from moderate exposure to sunlight (Holick, 2004a). Exposures of 1 MED (minimum erythemal dose) to the entire body produce serum vitamin D that is equivalent to 10,000 IU to 25,000 IU of vitamin D (Holick, 2004b). Furthermore, optimisation of adequate sun exposure to maintain adequate serum vitamin D levels, while avoiding excessive exposures that increase the risk of skin cancer, is also the most cost effective way of maintaining adequate vitamin D levels without the additional burden of vitamin D supplements. Adequate levels of vitamin D can be maintained by exposures of 1/6 to 1/3 MED to 15% of the body (Samanek et al., 2006). It is estimated that $90\% - 95\%$ of the vitamin D levels required in the human body are obtained from exposure to sunlight (Holick, 2004a).

Agricultural production and natural vegetation can be influenced by changed levels of solar UV and visible radiation due to atmospheric change. The UVB has been shown to produce biological damage in higher plants (Caldwell, 1971). The wavelengths extending into the UVA $(320 \text{ nm} - 400 \text{ nm})$ waveband have also been found to produce a response in plants with an action spectrum for plant growth inhibition in higher plants that extends to 366 nm being recently developed (Flint and Caldwell, 2003). The action spectrum for a biological reaction provides the effectiveness of each wavelength for producing that reaction (Ambach and Blumthaler, 1993).

In order to optimize the UV exposure of humans and to reduce the influence of UV exposures on both agricultural crops and natural vegetation, a complete understanding of the solar radiation environment is necessary. As recommended by the World Health Organization (WHO, 1994), monitoring of personal UV exposures is important in order to establish the percentage of the ambient solar UV received by the population. Solar UV dosimeters are an important tool in this research. Dosimeters that have been developed for UV research fall into two categories; namely, the thin film type and the spore or biofilm type. The latter types are based on spores or biological specimens that are UV sensitive (e.g., Quintern et al., 1992; Quintern et al., 1997; Munakata et al., 1998). For the thin film type, dosimeters fabricated from a polysulphone thickness of 30 μ m -45μ m possess a

spectral response that approximates the erythemal action spectrum (CIE, 1992). This chapter reports on the use of thin film dosimeters in different environments in order to provide an improved characterization of the solar radiation environment for humans and plants.

7.2 UV Dosimetry and Minimization Strategies

UV radiation incident on the earth's surface is comprised of both a direct component and a diffuse component. The combination of the diffuse and direct UV is termed the global UV. As the direct component is incident directly from the sun, it is easier to minimize by simply blocking its path. However, the diffuse UV component is incident from all directions due to atmospheric and environmental scattering and can constitute a significant proportion of the UV exposure to the human body. The relative amounts of direct and diffuse UV compared to global UV depend on the solar zenith angle (SZA). For example, the ratio of the diffuse UV to global UV increases with increasing SZA (Blumthaler and Ambach, 1991). This is due to the longer path through the atmosphere. Furthermore, the ratio of diffuse UV to global UV is higher at the shorter wavelengths due to the higher degree of scattering at the shorter wavelengths.

Numerous studies have employed UV dosimeters to investigate the efficacy of different strategies utilized to minimize exposures to diffuse UV and direct UV. Tree shade is widely employed and Parisi et al. (2000a, 2000b) utilized manikin forms with dosimeters placed at specific anatomical sites in tree shade to measure the UV exposure ratios under Australian gum trees. The exposure ratios of global UV radiation in a shaded environment to an unshaded environment ranged from 0.16 to 0.49 for the different anatomical sites. It was also found that exposure ratios for the legs ranged from 0 to 0.75 for the different anatomical sites for a sitting posture in summer compared to 0.14 to 0.39 for a standing posture. Furthermore, tree shade provided reductions in personal annual erythemal UV exposures by a factor of 2 to 3 and 4 to 6 in the contribution to the risk of basal cell carcinomas and squamous cell carcinomas, respectively, compared to not employing the protection of tree shade.

Erythemal UV exposures to the faces of school children wearing hats while playing sports were measured with polysulphone dosimeters over the period of an hour. The mean facial exposures of unprotected students (no hat) to protected students (hat) varied from 140 ± 82 Jm⁻² to 99 ± 33 Jm⁻², respectively (Downs and Parisi, 2008). The cosine response of the polysulphone film used in these dosimeters has been found to be within approximately 20% of the cosine function for angles of incidence up to 70° (Krins et al., 2000). Parisi and Wilson (2005) measured erythemal UV exposures beneath different types of clothing with dosimeters and found that the highest exposure under a high ultraviolet protection factor (UPF) knitted garment was only 1.5% of that of full sun exposure. Parisi et al. (1999)

employed dosimeters to measure the solar UPF for different stocking thicknesses and colors and found that the highest UPF of 4.6 was provided by 50 denier stockings with the lowest UPF of 1.4 provided by 15 denier stockings. Dosimetric measurements behind different thicknesses of glass (Parisi et al., 2007) found that the glass filtered solar UV ranged from 59% to 70% compared to the unfiltered UV and was only influenced to a small extent by the thickness of the glass and the solar zenith angle. It was also found that laminated window glass only transmitted 12% of incident UV radiation and that windscreen laminated glass transmitted approximately 2.6%. All new cars use laminated windscreen glass that transmits minimal UV. Turnbull and Parisi (2005) measured exposures to the human form while using shade structures. An example of polysulphone dosimeters employed on a human form manikin to measure the UV protection of a shade device is provided in Fig. 7.1. This research found that during summer and winter, significant decreases in exposure of up to 65% for summer and 57% for winter can be attained when comparing the use and non-use of polycarbonate sheeting for side-on UV protection.

Figure 7.1 A human form manikin with dosimeters placed at various anatomical sites measuring the UV protection provided by a shade umbrella

7.3 Miniaturization of Polysulphone Dosimeters

Miniaturized polysulphone dosimeters were employed to take high density measurements on living and manikin subjects under various environmental conditions to facilitate detailed mapping of the erythemal UV exposure to unprotected skin (Downs and Parisi, 2007; 2008). These dosimeters are cost-effective and provide accurate short-term UV exposure measurements for personal and environmental applications that may require a large number of dosimeters. Such applications may include UV exposure measurements to humans, animals, and plants.

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Polysulphone film employed in the manufacturing of miniaturized dosimeters is adhered to flexible cardboard frames measuring approximately $1.5 \text{ cm} \times 1 \text{ cm}$ having a clear circular aperture of 6 mm. The smaller flexible, lightweight dosimeter can be placed along curved surfaces and attached to complex surface topography not readily accessible to conventionally sized dosimeters, including the eyes, ears, and fingers of life-sized manikin models. The miniaturized dosimeter can also be conveniently attached to human subjects with the use of medical tape. An example of the application of miniaturized dosimeters used to measure UV exposures on the hand is given in Fig. 7.2.

Figure 7.2 UV exposure measured by application of miniaturized polysulphone dosimeters placed on the hand of a life-sized manikin

Miniaturized polysulphone dosimeters undergo the same UV induced photodegradation as conventional polysulphone film dosimeters and can be calibrated on a horizontal plane in proximity to a calibrated spectroradiometer or radiometer. Typically this involves the measurement of pre- and post-exposure polysulphone film absorbance at 330 nm $(∆A₃₃₀)$ taken at four different dosimeter film sites which are averaged to account for a variation in film absorbance and plotted with respect to the cumulative UV exposure measured by a spectroradiometer or radiometer. The change in absorbance is measured at 330 nm as this is approximately the wavelength at which the maximum change occurs (Davis et al., 1976a). Polysulphone film calibrated in this manner is typically weighted to the erythemally effective UV, but alternative action spectra, including the vitamin D action spectrum, can also be used. The dose response calibration of polysulphone dosimeters is related to the total atmospheric ozone amount and the solar zenith angle (Casale et al., 2006). This requires the calibration curve to be determined under the same atmospheric conditions of the field study.

The calibrated UV exposure measured using conventional polysulphone dosimeters is accurate to within 10% for a ΔA_{330} less than 0.3 and 30% for a ΔA_{330} less than 0.4 (Diffey, 1987). Comparative measurements made using miniaturized

polysulphone dosimeters give the uncertainty in calibrated UV exposure at 24% for a ΔA_{330} less than 0.35 (Downs and Parisi, 2008), the approximate equivalent of $1,500 \text{ Jm}^{-2}$ of erythemally effective UV. Increases in calibrated uncertainty with greater periods of exposure are due to the dynamic saturation of the polysulphone. Figure 7.3 illustrates the increasing calibrated uncertainty with increasing exposure. In this figure, sets of three miniaturized polysulphone dosimeters were removed at predetermined time intervals extending up to nine hours of exposure during a clear summer day, and measured at a subtropical latitude. Greater variability in the change of absorbance can be observed for dosimeters removed after longer periods of exposure.

Figure 7.3 Calibration of miniaturized polysulphone dosimeters measured over a nine-hour period in summer

7.4 Measurements on Plants

UVB radiation can be damaging to plant physiology and plant growth (Teramura and Sullivan, 1994), but solar visible radiation is important to the photosynthesis process in plants. This radiation $(400 \text{ nm} - 700 \text{ nm})$ is referred to as photosynthetically active radiation (PAR). Both PAR and UV radiation within the solar spectrum have to be accounted for as the plant response to UVB depends on solar visible radiation exposure (Caldwell et al., 1995). PAR can have a direct influence on plant response to UVB radiation. Plant response to UVB radiation during growth can be a function of PAR levels. There may be an observed reduction in plant growth and mass with reduced PAR and increasing UV radiation, and different plant species may not respond in the same way. Rather than relying on large equipment that is too bulky for measuring solar spectral irradiance or broadband UV within a plant canopy, a combination of dosimeters can be used to evaluate the UVB and PAR incident on a plant canopy. A UVB and PAR dosimeter package allows the measurement of exposure at different locations within the canopy, or locations on the plant itself (Parisi et al., 2003). This is important as

leaf angle, leaf reflectance, and shading will affect the UVB and PAR exposures on plants, as well as the relative proportions of UVB to PAR.

The dosimeter package consists of two sensors: a polysulphone dosimeter to measure the UVB and a second dosimeter material to extend the wavelength range to measure the PAR (Parisi et al., 1998; 2003). The second dosimeter material, made from 35 mm AGFA 25 APX photographic film, responds to visible radiation which is easy to obtain, simple to process, responds to visible wavelengths. Additionally, the optical density (absorbance) can be measured using appropriate equipment, such as a dual beam spectrophotometer (Shimadzu, model UV-160, Kyoto, Japan) with maximum absorbance measured at a wavelength of 800 nm. The PAR dosimeter is constructed by cutting the unexposed film into 30 mm lengths in total darkness and mounting it in a black plastic holder with an opening of $10 \text{ mm} \times 20 \text{ mm}$. This opening is covered with cardboard when not exposed and also acts as a shutter. The exposure time of the PAR dosimeter can be adjusted using filters made of exposed and developed AGFA 25 APX film. Once the dosimeter has been exposed, the film is processed using a standardized procedure (Parisi et al., 2003), and the absorbance is measured. Calibration of the PAR dosimeter (Fig. 7.4) is used to determine photosynthetic photon flux by exposing a number of PAR dosimeters for varying periods of time and then comparing them to simultaneously measured visible spectral irradiance using a scanning spectroradiometer recording at 1 nm increments. The PAR dosimeter is dose rate independent, has a very small dark reaction (within $1\% - 2\%$ of original measured values after periods of one and seven days), is temperature stable from 20° C to 45° C and has a cosine response agreement of 13% or better for solar zenith angles smaller than 20° and up to 21% for solar zenith angles up to 60° (Parisi et al., 1998). The overall error of the PAR dosimeter is 20%.

Figure 7.4 Calibration of the photosynthetically active radiation dosimeter for photosynthetically active photons or PAP (Parisi et al., 1998)

7.5 Long-Term UV Dosimeters

One of the main dosimetric materials for UV exposures has been the polymer polysulphone, which was first employed in the 1970s by Davis et al. (1976a). Despite its immense usefulness, the polysulphone dosimeter is restricted as it is only capable of measuring solar exposures approximately less than ten hours during a clear summer day at a subtropical location before reaching the maximum optical saturation point. Furthermore, the uncertainty of polysulphone increases to 30% for a ΔA_{330} between 0.3 and 0.4 (Diffey, 1987). This makes the long-term measurement of UV a difficult task logistically as polysulphone dosimeters would have to be continually replaced on location in order to achieve a continuous stream of measurements. Another dosimeter was formulated in the 1970s, again by Davis et al. (1976b), this time using a polymer called poly 2,6-dimethyl-1,4-phenylene oxide, or just PPO in short. The PPO dosimeter was fabricated using similar methods to polysulphone and was just as easy to use, however instead of having a short responsive lifetime, PPO was capable of receiving a subtropical UV exposure over a period of time no less than five to ten days before complete saturation at the same level of accuracy as its polysulphone counterpart. It can be seen that the potential of the PPO dosimeter was far more substantial than the polysulphone dosimeter; however, in recent years most solar radiation researchers have chosen to use polysulphone.

The PPO dosimeter has recently experienced a revival with a varied amount of research being performed both on it and with it. The optical properties of PPO have been trialled for in-air use and calibrated to the erythemal action spectrum (Lester et al., 2003) and also to short UVA wavelengths $(320 \text{ nm} - 340 \text{ nm})$ by implementation of a Mylar filter (Turnbull and Schouten, 2008), similar to the methodology used by Parisi et al. (2005) when calibrating the prototype phenothiazine dosimeter to the UVA waveband. Figure 7.5 graphically shows how much more erythemal UV solar exposure the PPO dosimeter can handle in comparison to the polysulphone dosimeter. It demonstrates that on a typical summer's day, polysulphone can receive an approximate dosage of 2,500 J/m² before reaching its exposure limit at its characteristic sampling wavelength of 330 nm $(∆A₃₃₀)$. Comparatively, the PPO dosimeter can accept close to a further $25,000$ J/m² before optical saturation at its own particular sampling wavelength of 320 nm $(∆A₃₂₀)$. This is a ten-fold increase in exposure capability during summertime (low solar zenith angle conditions).

The high exposure capability of the PPO dosimeter means that it is also ideal for underwater measurements that would usually be awkward to achieve by using traditional spectroradiometric and radiometric instrumentation. Schouten et al. (2007) tested the PPO dosimeter in a controlled underwater environment using solar UVB simulation focusing on dose response calibration trends, cosine response, interdosimeter variability, dark reaction, UVA/visible wavelength responsivity, and additionally, exposure additivity. The information gathered from this investigation

Figure 7.5 PPO dosimeter (\triangleleft) and polysulphone dosimeter $(+)$ calibration to the erythemal action spectrum (CIE, 1987). Polysulphone dosimeter calibration data obtained from Turnbull and Parisi (2005)

showed that PPO was viable for underwater measurements with only a slight decrease in accuracy introduced when compared with in-air measurements, which was caused by watermarking on the PPO film surface. This research also made the important finding that calibrations made in-air could not be used as proxies to calculate underwater exposures.

This initial trial research has since been extended (Schouten et al., 2008) by obtaining calibration regimes at different depths to the real solar UVB spectrum for the PPO dosimeter in four different water types (clear water, sea water, dam water, and creek water) over a wide range of solar zenith angles and under fluctuating ozone conditions. This work found that at shallow depths, calibrations could be transferred from one water type to another with only a relatively small reduction in total uncertainty on the condition that each water type was within a certain spectral transmission (or absorption) range. It was also discovered that PPO calibrations are sensitive to atmospheric ozone variations. This means that if researchers wish to measure UVB with the PPO dosimeter, calibrations would have to be made just before, after, or during the measurement campaign to reduce the response error brought on by ozone attenuation causing changes in the solar spectrum of the UVB wavelengths.

7.6 Vitamin D Effective UV Dosimetry

The action spectrum for the synthesis of pre-vitamin D_3 shows that only the short wavelength UV is effective (CIE, 2006) for this process. This action spectrum can be approximated by the spectral response of polysulphone (CIE, 1992). Using polysulphone dosimeters, the transmission of pre-vitamin D_3 effective UV through clothing has been investigated (Hutchinson and Hall, 1984; Parisi and Wilson, 2005). Many factors influence the UV exposure to an individual, and therefore,

the synthesis of pre-vitamin D_3 , including clothing, use of sunscreen, pigmentation of the skin, age, and latitude of residence (Matsuoka et al., 1990; 1992; Webb, 2006). The face, arms, and hands contain approximately 15% of the skin area of the human body. UV exposure of 1 MED to these parts would produce serum vitamin D equivalent to $1,500$ IU $-3,750$ IU (Samanek et al., 2006). Most research conducted on UV transmission through clothes is generally from the perspective of protection from UV; however, some of the incident UV can transmit through clothing and has been measured at various body sites under garments with polysulphone dosimeters for pre-vitamin D_3 effective UV (Parisi and Wilson, 2005).

This work can be extended for the quantification with polysulphone dosimeters of pre-vitamin D_3 effective UV to humans in different environments. Figure 7.6 shows a typical calibration curve for pre-vitamin D_3 effective UV in winter at a sub-tropical site.

Figure 7.6 Calibration of polysulphone dosimeters for pre-vitamin D_3 effective UV exposures on a winter's day (Parisi and Turnbull, 2006)

7.7 Discussion and Conclusions

The use of UV polysulphone dosimeters to quantify erythemal exposures to humans during normal daily activities in different environments and to determine the effectiveness of UV minimization strategies has been reported. Miniaturization of these dosimeters to a diameter of 6 mm has allowed an increase in the density of the UV exposure measurements, along with an increase in the potential number of environments in which they can be used. Additionally, polysulphone dosimeters employed in conjunction with a dosimeter sensitive to the visible waveband have been employed to measure the UVB exposures and the photosynthetically active radiation to plant leaves. With appropriate calibration, polysulphone dosimeters have measured the pre-vitamin D_3 effective UV to humans in order to quantify the amount of UV producing this vitamin that is essential for the well being of humans. The dynamic range of polysulphone at a

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sub-tropical site is approximately one day in summer. For periods of exposure longer than this, the polysulphone dosimeters have to be replaced on a daily basis or alternatively a dosimeter based on polyphenylene oxide with a dynamic range that is approximately ten times longer than that of polysulphone has been employed for erythemal and UVB exposures.

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