

Application of Poly (2,6-dimethyl-1, 4-phenylene oxide) Film for the Long –

Term Measurement of Underwater Solar UVB

P.W. Schouten, A.V. Parisi, and D.J. Turnbull

Department of Biological and Physical Sciences, University of Southern Queensland, Toowoomba, Queensland, Australia.

Abstract For underwater ultraviolet radiation (UV) measurements, the usage of chemical dosimeters has been relatively low in comparison to measurements made with optical meters. However, dosimeters such as the Poly (2,6-dimethyl-1, 4-phenylene oxide) film (PPO) offer an inexpensive, easy to deploy and accurate alternative to the optical meters, and could prove to be an invaluable tool for researchers investigating the underwater effects of solar UV. To date, no literature has been produced detailing how to adequately calibrate and deploy chemical dosimeters for long-term underwater usage. The following paper details a basic methodology on how to calibrate the PPO dosimeter for underwater use and also demonstrates how in-air and in-water dosimetric calibrations cannot be transferred while shallow calibrations for different water types can be with only a small reduction in accuracy.

Introduction

The sizeable reduction in the protective ozone layer over recent decades has coincided with an increase in the amount of biologically effective solar ultraviolet radiation (UV_{BE}) reaching the Earth's surface. Not only does this intensification of the UV_{BE} affect terrestrial life forms, but it also has a negative influence upon numerous organisms inhabiting marine environments such as rivers and dams. Coupled with the enhanced evaporative effect of global warming, these organisms living underwater have even less protection against the UV_{BE} than was once present.

Various methodologies using a wide range of measurement systems have been employed previously in order to determine the amount of UV_{BE} incident upon various aquatic organisms in a number of different water bodies. Optical meters (such as radiometers and spectrometers) have been employed to take underwater measurements, for example the recent investigations made by Hargreaves et al. (2007) and Bracchini et al. (2004). Measurement campaigns employing optical meters as the primary measurement tool produce accurate results, however they are limited by the fact that this type of equipment requires a human controller, some kind of power supply, can be logistically cumbersome and require regular calibrations in order to function properly. Dosimetric measurements have also been made underwater using two distinct types of dosimeter. The first type based on a synthetic chemical, like polysulphone (Dunne, 1999), and the second type based on a biological matter, such as a DNA sample (Boelen et al., 1999). The studies made using biological dosimeters have displayed very good results, however the time and skill necessary to make these types of dosimeters can outweigh their usefulness. The chemical dosimeters are easier to make and have also provided useable data, but

only for short periods of exposure, usually less than a day.

Previous laboratory research has shown that PPO has the potential for use as a long-term underwater solar UV dosimeter (Schouten et al., 2007). However, there is no documented methodology on how to properly calibrate the PPO dosimeter for outdoors aquatic-based measurements and it has yet to be trialed in a real aquatic environment. This paper will detail the calibration methodology required for accurate underwater dosimetry and will investigate the differences between in-air calibrations and underwater based PPO dosimeter calibrations in different water types.

Methodology

The PPO dosimeter was calibrated over the time period of approximately 25 hours over 5 days to solar UV for the UVB waveband running from 300 nm to 320 nm in four different water types, these being: clear tap water, sea water, moderately turbid creek water and highly turbid stagnant dam water. These calibrations took place over the months of March and April in Toowoomba, Australia (27.5° S, 151.9 ° E, 693 m altitude). For each water type, one batch of dosimeters was calibrated just above the water surface, while another batch was placed below the water surface at a depth of about 1 cm (Z_{1cm}). Each water type was selected for its own distinct level of turbidity, DOM (dissolved organic matter) and salinity. Figure 1 shows the respective UV transmission and absorption distributions from 300 nm to 320 nm for each water type, measured using a spectrophotometer (model 1601, Shimadzu Co., Kyoto, Japan). UV exposures during these calibrations were measured using an IL1400 radiometer (International Light, Newburyport, MA) with a UVB filter (UVB-1, International Light). This radiometer was calibrated for underwater use against an immersion effect corrected spectrometer (StellarNet EPP2000 C-UV-VIS, Tampa, Florida). The immersion factors calculated for the spectrometer can be seen in Figure 2.

After each UV exposure, the change in optical absorbance at 320 nm (ΔA_{320}) for each PPO dosimeter used was measured to give a data point, where ΔA_{320} is calculated as:

$$\Delta A_{320} = A_{320}^{AFTER} - A_{320}^{INITIAL}$$

where A_{320}^{AFTER} is the optical absorbance measurement after exposure at 320 nm and $A_{320}^{INITIAL}$ is the initial absorbance measurement before exposure at 320 nm.

To increase the accuracy of the measurements, each ΔA_{320} value was measured over four positions across the film to produce a mean ΔA_{320} value to be used in the calibration data set.

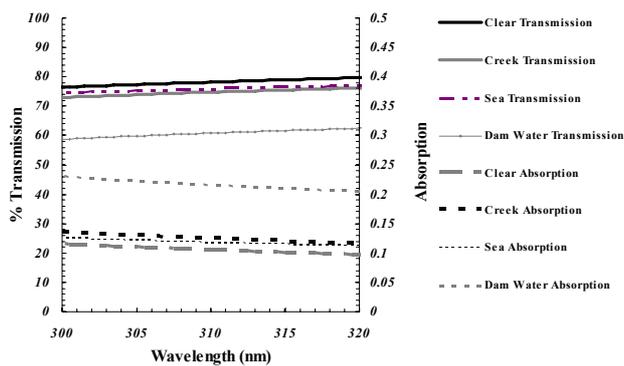


Figure 1. Transmission and absorption distributions for each particular water type in the UVB waveband.

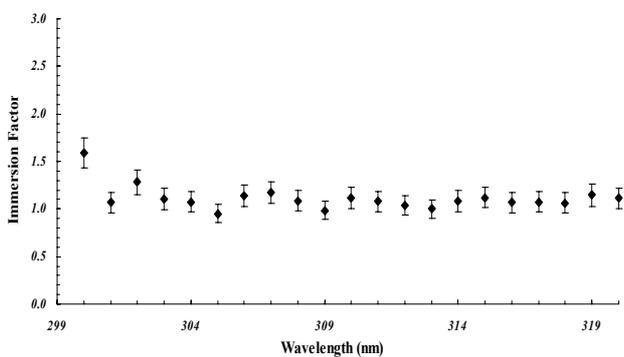


Figure 2. Immersion factors as calculated in the waveband running from 300 nm to 320 nm for the spectrometer. The y-axis error bars represent a $\pm 10\%$ uncertainty approximation.

Results

Figure 3 displays the in-air and underwater PPO dosimeter calibrations for each water type. A second-order polynomial equation was employed to model each particular calibration data set. The x-axis error bars for each data point in the underwater calibrations represent an uncertainty margin of $\pm 9\%$, which was the calculated in-water dosimeter variation for PPO as found by Schouten et al. (2007). The x-axis error bars on the data points for the in-air calibration series represent a calculated error margin of approximately $\pm 7\%$, which was the average interdosimeter variation found to exist across the batch of dosimeters used in the in-air calibration.

The total UVB energy received after the 25 hour exposure period was measured to be approximately 200 kJ m^{-2} for each water type. This is significantly greater than the 40 kJ m^{-2} maximum reached by Dunne (1999) using polysulphone as an underwater dosimeter. Additionally, at the final measurement point, the PPO film dosimeters had yet to fully degrade and would be able to accept another substantial UVB dosage.

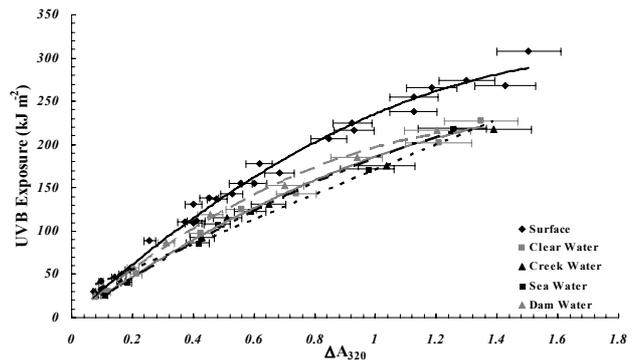


Figure 3. UVB PPO dosimeter calibration curves at the water surface and at $Z_{1\text{cm}}$ for each water type.

Discussion and Conclusions

The calibrations obtained at a depth of approximately 1 cm in each water type were all measured to be in close proximity to each other, mostly within the 9% error estimated to exist for each ΔA_{320} measurement. Based on this outcome, it can be assumed that a single shallow calibration in clear water should be transferable to measurements made in different water types that have a percentage transmission in the range of 40% to 80% as encountered in the water types employed in this research. However these calibrations do differ to the calibration made in air, with the difference becoming more pronounced with increasing cumulative exposure, reaching a discrepancy of as much as approximately 500 kJ at a ΔA_{320} value of 1.2. So it is not sufficient to apply an air based calibration equation to dosimetric measurements made underwater.

Acknowledgments The authors would like to thank Graham Holmes and Oliver Kinder from the Faculty of Sciences at the University of Southern Queensland for their technical assistance over the duration of this project.

References

- Boelen, P., Obernosterer, I., Vink, A.A., Buma, A.G.J., Attenuation of biologically effective UV radiation in tropical Atlantic waters measured with a biochemical DNA dosimeter, *Photochem. Photobiol.*, 69(1), 34-40, 1999
- Bracchini, L., Loiselle, S., Dattilo, A.M., Mazzuoli, S., Cozar, A., Rossi, C., The spatial distribution of optical properties in the ultraviolet and visible in an aquatic ecosystem, *Photochem. Photobiol.*, 80, 139-149, 2004.
- Dunne, R.P., Polysulphone film as an underwater dosimeter for solar ultraviolet-B radiation in tropical latitudes, *Mar. Ecol. Prog. Ser.*, 189, 53-63, 1999.
- Hargreaves, B.R., Girdner, S.F., Buktenica, M.W., Collier, R.W., Urbach, E., Larson, G.L., Ultraviolet radiation and bio-optics in Crater Lake, Oregon, *Hydrobiologia*, 574, 107-140, 2007.
- Schouten, P.W., Parisi, A.V., Turnbull, D.J., Evaluation of a high exposure solar UV dosimeter for underwater use, *Photochem. Photobiol.*, 83, 1-7, 2007.