# Field Calibrations of a Long – Term UV Dosimeter for Aquatic UVB Exposures

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## ABSTRACT

Various methodologies using a wide range of measurement systems have been employed previously in order to determine the amount of UV that could be incident upon various aquatic organisms in a number of different aquatic locales. Broadband meters and spectroradiometers have been employed extensively to take underwater measurements. However, these measurement campaigns are limited by the fact that radiometric equipment requires a human controller, constant power supply and regular calibrations and corrections 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, and the second type based on a biological matter, such as a DNA sample. 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 no more than a day. Previous research has shown that Poly (2,6-dimethyl-1, 4-phenylene oxide) (PPO) has excellent potential for use as a long - term underwater solar UVB dosimeter. However, there is no documented methodology on how to properly calibrate the PPO dosimeter for water based measurements and it has yet to be trialled in an outdoors marine environment, either real or simulated. This manuscript shows that calibrations obtained in air can not be transferred to calibrations made in water, calibrations made in one type of water can be employed for another type of water, but only within a certain range of spectral transmission and calibrations made at different depths in the same water type are interchangeable. It was also discovered that changing solar zenith angle had an effect upon calibration data. This research addressed these issues by formulating and developing a calibration methodology required for accurate underwater long – term UVB measurements in the field using the PPO film dosimeter.

## INTRODUCTION

The sizeable reduction in the protective ozone layer over recent decades has coincided with an increase in the amount of biologically damaging 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 a wide and varied number of 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<sub>BE</sub> than was once present.

Several studies have analysed the behaviour of the solar UV underwater with varying degrees of success. One recent notable investigation was made by Frost et al. [1] where spectral data was obtained over a range of different depths in order to calculate attenuation factor values in the UV waveband for a variety of different streams each with their own particular dissolved organic matter (DOM) levels. Some other notable similar investigations detailing underwater solar UV spectral irradiance and its relationship with DOM and other marine constituents have been published by: Bracchini et al. [2] in shallow lake water; Conde, Aubriot & Sommaruga [3] in lagoon waters within the Southern Atlantic Ocean; Crump et al. [4] in shallow pond water; Vincent et al. [5] in Antarctic ice covered lakes; and Sommaruga & Psenner [6] in a high altitude mountain lake in Austria. Most recently, Belmont et al. [7] analysed diffuse attenuation factors for river water in both the laboratory and field environments using radiometric instrumentation set to multiple wavelength channels.

All of these measurement campaigns have been limited by the fact that the spectroradiometric equipment used required a constant power supply, a human

controller and regular calibrations in order to operate correctly. Also, due to the high cost of spectroradiometric equipment, usually only one spectroradiometer can be employed during a series of measurements. This greatly reduces the amount of measurement data available for analysis and also does not allow for precise same-time comparisons to be made with the data, for example comparisons between measurements made at different angles and at different depths.

These problems can be alleviated with the use of a high exposure UV dosimeter applicable underwater, as many dosimeters can be deployed at different angles and depths at the same time at a cost far less than that of a conventional spectroradiometer. Also, no human operator is required apart from their initial calibration, setting-up and collection and they require no external power source to operate.

However, despite their usefulness, it is important to note that dosimetric measurements are not a complete replacement for spectroradiometric measurements in the underwater environment. Spectroradiometers and radiometers are still necessary to record short term changes in underwater UV irradiance levels, such as those brought on by rapidly evolving systems, such as cloud coverage.

Dosimetric measurements have been made underwater using two distinct types of dosimeter. The first type based on a synthetic chemical, such as the commonly used polysulphone, and the second type based on a biological composition, such as a particular DNA sample. One example of this DNA dosimeter technique is seen in Regan et al. [8]. Out of these two dosimetric techniques, the biological dosimeters (most often those based on DNA) have been the most commonly used in marine applications.

Boelen et al. [9] has delivered one of the most extensive underwater biological dosimeter investigations to date. Using DNA dosimeters fabricated out of calf thymus DNA, the authors developed distributions of DNA damaging UV irradiance as a function of depth with good accuracy when compared against spectroradiometeric measurements. Other notable examinations have been carried out by Koussoulaki et al. [10] using *Euglena gracilis* cultures and Li et al. [11] by calibrating tobacco cells against UVB related DNA damaging effects. These studies have all shown good results, however the time and skill necessary to make biologically active dosimeters appear to outweigh their usefulness.

Only three chemical dosimeter types have been deployed in the underwater environment. The first and most commonly used is polysulphone. Dunne [12] evaluated UVB radiation with polysulphone dosimeters in a variety of different types of seawater at tropical latitudes. The author found that polysulphone had a practical depth range of between 2.2 and 7.0 m, dependent upon seawater turbidity with a 5% error margin. However, exposures of between 1.5 to 40.0 kJ m<sup>-2</sup> could only be measured. Polysulphone was also successfully employed by Frost et al. [13] to estimate diffuse attenuation coefficient values in shaded water bodies in the Northeast region of the United States. The second type of chemical dosimeter used for underwater UV measurements has been the o-nitrobenzaldehyde dosimeter, which was used in one study carried out by Fleischmann [14] at Discovery Bay in Jamaica. This dosimeter only measures UV exposures over a period of the order of a day and this study measured UV exposures with the o-nitrobenzaldehyde dosimeter to calculate the typical depth distribution and variation of solar UV throughout a single day. The third and final dosimeter to be tested underwater was the PPO film dosimeter by Schouten et al. [15]. This investigation analysed various optical and physical properties of PPO film, such as the cosine response, reproducibility after exposure, dose rate independence, watermarking effects, dark reaction, UVA and visible wavelength response and exposure additivity.

Currently, it is not known if: calibrations measured in air can be reassigned to calibrations made in water; calibrations obtained in one water type can be used for another water type; and calibrations made at separate depths in the same water type are interchangeable. Also unknown at this stage is the effect of solar zenith angle (SZA) upon underwater calibration regimes. This manuscript will extend the previous work presented in this field by answering these important research questions and giving a detailed documentation of the methodology required to calibrate the PPO dosimeter for underwater measurements in the real marine environment.

# MATERIALS AND METHODS

#### **Dosimeter Description and Measurement Technique**

For this investigation, the UV responsive polymer film PPO dosimeter was tested and calibrated in outdoor aquatic environments long – term. In this work, a long – term exposure is defined as an exposure received in an outdoor aquatic environment at a subtropical site over a one week time interval at any time of the year. The physical dosimeter consists of the chemical PPO cast in thin film form at a thickness of approximately 40 µm. The PPO film is placed into a polyvinyl chloride (PVC) holder of size 3.3 cm and an aperture of 1.2 cm - 1.6 cm. The film is secured to the holder with standard electrical tape. The change in optical absorbance caused by UV exposure upon the PPO film is measured by a spectrophotometer (model 1601, Shimadzu Co., Kyoto, Japan) at 320 nm, which is a wavelength where a measurably significant change in optical absorbance is known to occur [15]. The error threshold for optical absorbance measurements in the spectrophotometer has been quoted as  $\pm$ 0.002 by the manufacturer. After each UV exposure, the change in optical absorbance at 320 nm ( $\Delta A_{320}$ ) for each PPO dosimeter used in a measurement campaign is measured to provide a data point, where  $\Delta A_{320}$  is calculated with the following equation:

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

where  $A_{320}^{FINAL}$  is the final optical absorbance measurement taken at the wavelength of the maximum change in optical absorbance at 320 nm as described by Schouten et. al. [15] after exposure to the sun and  $A_{320}^{INITIAL}$  is the initial absorbance measurement taken at the same wavelength of 320 nm before exposure to the sun. After every underwater exposure and before measurement in the spectrophotometer, any residues or particulates remaining on the PPO film surface were removed with a distilled water jet and then left to dry in a dark box.

To better improve the accuracy of the measurements, the  $\Delta A_{320}$  value is measured over four positions across the film surface with the mean of these values used to calculate the UV exposure by means of interpolation from a dose – response calibration.

## **Dose Response Calibrations**

The PPO dosimeter was calibrated on the horizontal plane to solar UV over the time period of approximately 25 hours sunlight spanning 5 to 7 days outdoors to solar UV for the UVB waveband running from 300 nm to 320 nm in four different water types. These were clear tap water, sea water, moderately turbid creek water and highly turbid stagnant dam water. The 320 nm cut – off has been used occasionally in photobiological investigations and was more applicable to our research. The calibrations took place in Toowoomba, Australia (27.5° S, 151.9 ° E, 693 m altitude) over the six month time period between March and August inclusive, representing the autumn (low SZA) and winter (high SZA) seasons. The SZA range over the autumn calibration period was  $20^{\circ}$  to  $70^{\circ}$ . The SZA range over the winter calibration period was  $35^{\circ}$  to  $65^{\circ}$ . The measurement campaign ran over both autumn and winter in order to investigate the effect of changing SZA on the underwater calibrations. The water types were chosen as they represent a good cross section of the different water types and for their own distinct level of turbidity, DOM (dissolved organic matter) level 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). According to the work of Lester et al. [16], the response of the PPO dosimeter is not influenced in any way by fluctuations in local temperature. Therefore, changes in temperature over the different calibration sessions would not have had any effect upon the measured  $\Delta A_{320}$  data.

For each water type, one batch of dosimeters was calibrated just above the water surface (which acted as the control calibration), while another batch was placed below the water surface at a depth of about 1 cm ( $Z_{1CM}$ ). UV exposures during these calibrations were measured using an IL1400 radiometer working at a  $\frac{1}{2}$  second refresh rate (International Light, Newburyport, MA) fitted with an underwater detector with a UVB filter having a response running from 265 to 332 nm (UVB-1, International Light). The IL1400 radiometer was chosen as the primary measurement instrument due to the fact that it is capable of recording the integrated UVB exposure.

Another batch of dosimeters were placed at a depth of 20 cm below the water surface  $(Z_{20CM})$  in order to test for differences in calibration trends at varying depth. As a second IL1400 unit was not available for use, the exposure received at  $Z_{20CM}$  in each water type had to be calculated from that at  $Z_{1CM}$ . A basic methodology using current underwater light attenuation theory was utilised in order to achieve this.

The attenuation of any form of light (including UV) into a water column is dependent upon both absorption and scattering, which are specific optical characteristics of the water type [17]. Absorption removes the incoming light completely, while scattering changes the direction in which the light moves. The characterization of the water column relies upon a single parameter known as the diffuse attenuation coefficient  $K_d$ . This parameter is calculated by the following expression which details the exponential decrease with depth of the underwater downwelling irradiance ( $E_d$ ) which is composed of photons propagating in the downwards direction ([18]; [19]):

$$K_{d}(\lambda, z) = -\frac{1}{E_{d}(\lambda, z)} \frac{dE_{d}(\lambda, z)}{dz}$$

where  $K_d$  ( $\lambda$ , z) is the diffuse attenuation coefficient given in m<sup>-1</sup>,  $E_d$  ( $\lambda$ , z) is the underwater downwelling irradiance in units of W m<sup>-2</sup> and z is the depth of the water column in m.  $K_d$  ( $\lambda$ , z) is dependent on the constituent content of the water column and in turn, the distribution of the underwater light field. Dissolved and particulate matter in the water column, especially dissolved organic matter (DOM) is known to greatly affect the propagation of solar UV in any water column and hence change the value of  $K_d$  ( $\lambda$ , z) ([2]; [20]).  $K_d$  ( $\lambda$ , z), is not affected by any changes in the surface incident light field such as those caused by a change in the sun's elevation angle [21]. The equation detailed above to calculate  $K_d$  ( $\lambda$ , z) can be written in another form, which can then be used as a simple model, based upon the Beer-Lambert-Bouguer relation to describe the exponential decay of the underwater light field with increasing depth, if  $K_d$  ( $\lambda$ , z) has already been calculated [22]:

$$E_{d}(\lambda, z) = E(0, \lambda)e^{-K_{d}(\lambda, z)z}$$

where  $E(0, \lambda)$  is the downwelling irradiance at a depth just below the water surface. In this research, the  $K_d$  value for each water type over the 300 to 320 nm waveband was calculated using spectral data measured using the spectrometer mentioned in the next section over a six month campaign running from March 2007 through to August 2007. Irradiance data was obtained using the spectrometer at three different depths in each water type to create a depth profile. Linear regression techniques were applied to these profiles respectively in order to determine approximate  $K_d$  values. Direct linear comparisons between the irradiances measured by the spectrometer and the IL1400 radiometer in all four particular water types all displayed satisfactory  $R^2$  values of between 0.87 and 0.98.

Column ozone levels above Toowoomba were monitored by accessing OMI satellite information (http://jwocky.gsfc.nasa.gov/ozone/ozone\_v8.html) each day over the duration of the calibration campaign. This data was used in order to deduce if ozone variations had any influence upon the calibration data from season to season. Figure 2 shows a time series of the ozone levels measured by the OMI satellite from March to August 2007 above Toowoomba. Aerosol levels were not analysed as Toowoomba is a high – altitude location with an atmosphere that is relatively low in aerosol concentrations.

# **Immersion Effect**

To ensure the highest levels of accuracy, the IL1400 radiometer was calibrated for underwater use against a standardised immersion effect corrected spectrometer (StellarNet EPP2000 C-UV-VIS, Tampa, Florida). The immersion effect comes into play when an optical meter is submerged underwater to take a light measurement. A larger amount of light is backscattered out of the meter during a water – based measurement in comparison to an air – based measurement. This is due to the discrepancies between the refractive indices for air and water at the collector interface. The methodology employed to calculate these immersion factors was based upon the work of Zibordi [23], Hooker & Zibordi [24] and Zibordi et al. [25].

## Water Tank Description

The water tank used during the calibration campaign had a length of 66 cm, a width of 46 cm and a depth of 35 cm. The tank was made out of tinted plastic. This plastic is opaque to the UV waveband, so any UV wavelengths incident upon the sides of the tank during the calibrations would not have had any effect upon the submerged dosimeters. Any pieces of debris that landed in the tank were removed each day in order the keep the water as close to its natural state as possible. Also, at the end of each daily session, the tanks were sealed off using a lid in order to reduce evaporation and to ensure no debris fragments would fall into the water overnight.

## RESULTS

#### Water Type Spectrophotometry

Figure 1 presents the transmission and absorption spectra over the 300 to 320 nm waveband for the four water types analysed in this research. It can be seen that the clear, creek and sea water all share similar transmission and absorption spectra, within approximately  $\pm$  5% of each other in transmission and within  $\pm$  0.03 arbitrary units of each other in absorption. However, the dam water displayed transmission and absorption spectra far different to the other three water types. The transmission spectrum for the dam water recorded a relatively low transmission value of 61% at 310 nm in comparison to 75% at 310 nm for creek water, 76% at 310 nm for sea water and 79% at 310 nm for clear water. In turn, the absorption spectrum for the dam water recorded a high level of approximately 0.22 at 310 nm. This is compared to 0.13 at 310 nm for the creek water, 0.12 at 310 nm for the sea water and 0.10 at 310 nm for the clear water.

## **Immersion Effect**

The immersion factors calculated for the spectrometer can be seen in Figure 3. It is clear from this graph that the immersion factor remains relatively static across the 300 to 320 nm waveband. There is a slight fluctuation in the immersion factor value from 300 nm to 305 nm. This can be attributed to the lower response of the spectrometer at in this region.

#### **Dose Response Calibrations**

Figure 4 and Figure 6 display the in-air and underwater PPO dosimeter calibrations for each water type as measured at  $Z_{1CM}$  in autumn and winter respectively with the cumulative UVB exposures as measured by the IL1400 broadband meter. Figure 5 and Figure 7 displays the in – air and underwater PPO dosimeter calibrations for each water type as measured at  $Z_{20CM}$  in autumn and winter respectively with the cumulative UVB exposure derived from the Beer-Lambert-Bouguer relation. A second-order polynomial equation normalised to zero (as no change in optical absorbance represents no exposure time) was employed to model each particular calibration data set in the following form:

$$UVB_{Z} = -\alpha (\Delta A_{320})^{2} + \beta (\Delta A_{320})$$

where  $UVB_Z$  is the UVB exposure received at the depth z in units of kJ m<sup>-2</sup>. Table 1 displays the different  $\alpha$ ,  $\beta$  and  $R^2$  values obtained for each particular calibration.

In Figures 4 to 7, 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. [15]. 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 estimated average interdosimeter variation found to exist across the batch of dosimeters used for the in – air calibration.

Figure 8 displays the master calibration equations derived from the data measured over the autumn and winter months of 2007. The autumn underwater calibration data was merged together and compared to the combined winter underwater calibration data in order to see if SZA had any influence over calibration trends. The master

calibration equations featured for autumn and winter do not include the calibration data obtained for the dam water at  $Z_{20CM}$ . As in Figures 3, 4, 5, and 6, the x-axis error bars for each data point in the underwater calibrations shown an error of  $\pm$  9%, which was the calculated in – water dosimeter variation for PPO as determined by Schouten et al. [15]. A polynomial trend equation was applied to both the autumn and winter master calibration data sets. For autumn the equation took on the following form:

$$UVB = -43.422(\Delta A_{320})^2 + 221.8(\Delta A_{320})$$

with an  $R^2$  value of 0.96 where UVB is the UVB exposure received in units of kJ m<sup>-2</sup> across the 300 nm to 320 nm waveband. For winter the following equation emerged:

$$UVB = -203.09(\Delta A_{320})^2 + 544.51(\Delta A_{320})$$

with an  $R^2$  value of 0.97 where again UVB is the UVB exposure received in units of kJ m<sup>-2</sup> across the 300 nm to 320 nm waveband.

#### DISCUSSION

For each season, 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 the dosimeters. Based on this result, 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 50 kJ at a  $\Delta A_{320}$  value of 1.2. So it is not appropriate to apply an air based calibration equation to dosimetric measurements made underwater, without incurring substantial errors in the measured exposures.

Over autumn and winter, the calibrations measured at  $Z_{20CM}$  in each water type were also all found to be in close proximity to each other, apart from the dam water calibration, which presented a regime completely different to the three other water types. From the spectrophotometry data shown in Figure 1 it is clear to see that the dam water has the lowest level of UV transmission and in turn the highest amount of UV absorption across the 300 to 320 nm waveband when compared to the other three water types due to having a high concentration of DOM constituents. So it appears that calibrations made at deeper depths (lower than  $Z_{1CM}$ ) are transferable from one water type to another, but only within a certain spectral transmission (or absorption) range. In this research it appears that this range is approximately  $\pm$  5% UV transmission difference (or  $\pm$  0.03 UV absorption difference) between each water type for calibrations to be completely transferable with minimal error. Researchers would have to keep this in mind when calibrating dosimeters to measure exposures deeper than just below the water surface.

The direct comparison between the master calibration equations for autumn and winter show that there is a definite difference between the calibration regimes obtained over the autumn months when compared to those obtained in the winter months. This discrepancy between the calibration sets could be attributed not only to the change in the sun's position between the two seasons, but also to a progressive increase in column ozone levels over the measurement site. Figure 8 displays this significant increase in column ozone levels above Toowoomba that began in late autumn (May) and continued towards the end of winter (August). It is well known that the shorter UV wavelengths, especially those in the UVB are blocked by a much greater amount when there are increased levels of ozone present in the atmosphere. This has a direct effect on the UV spectrum present here on the Earth. The UVB spectra received by the dosimeters during the winter calibration campaign would have had a different cut - off point, and in turn, have had a different composition in comparison to the spectra received by the dosimeters during the autumn calibration campaign. Consequently, when calibrating the PPO film for underwater usage, researchers should obtain calibration data for the season in which they will be recording measurements. Similar results to this have been discovered by other researchers investigating the effect of fluctuations in column ozone upon the response of broadband UV meters. In particular, Bodhaine et. al. [26] found that if the influence of ozone is ignored during calibration, UV measurements made with broadband meters can produce errors of 10% or greater.

The total UVB energy received after the 25 hour exposure period was measured to be approximately 200 kJ m<sup>-2</sup> for each water type. This is significantly greater than the 40 kJ m<sup>-2</sup> maximum reached by Dunne [12] when 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. This additional dosage is estimated to approximately another 200 kJ m<sup>-2</sup> before complete optical saturation is achieved. These results show that the PPO dosimeter can be calibrated and employed to measure UVB exposures in aquatic environments under a variety of atmospheric conditions in a number of distinct water types.

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## FIGURE AND TABLE LEGENDS

**Table 1** –  $\alpha$ ,  $\beta$  and R<sup>2</sup> values obtained for each particular calibration over autumn and winter.

**Figure 1** – Transmission and absorption distributions for tap water, creek water, sea water and water taken from a stagnant water reserve.

**Figure 2** – Time series of OMI measured column ozone levels present over Toowoomba from March 2007 to August 2007 where day 1 is 1 March 2007.

**Figure 3** – Immersion effect coefficients across the modified UVB waveband as measured for the StellarNet EPP2000 spectrometer in a controlled environment.

**Figure 4** – Calibration curves as made against the solar UVB exposures over autumn for tap water, creek water, sea water and water taken from a stagnant water reserve at  $Z_{1CM}$ . The surface (in – air) calibration curve acts as the control.

Figure 5 – Calibration curves as made against the solar UVB exposures over autumn for tap water, creek water, sea water and water taken from a stagnant water reserve at  $Z_{20CM}$ .

Figure 6 – Calibration curves as made against the solar UVB exposures over winter for tap water, creek water, sea water and water taken from a stagnant water reserve at  $Z_{1CM}$ .

Figure 7 – Calibration curves as made against the solar UVB exposures over winter for tap water, creek water, sea water and water taken from a stagnant water reserve at  $Z_{20CM}$ .

**Figure 8** – Comparison between underwater master calibrations obtained over autumn and winter.

CALIBRATION TYPE	α	β	$\mathbf{R}^2$
Control	86.78	322.39	0.99
Clear Water Autumn Z <sub>1CM</sub>	63.77	249.68	0.99
Creek Water AutumnZ <sub>1CM</sub>	68.6	248.9	0.99
Sea Water Autumn Z <sub>1CM</sub>	52.48	236.93	0.99
Dam Water Autumn Z <sub>1CM</sub>	99.21	296.12	0.99
Clear Water Autumn Z <sub>20CM</sub>	73.37	235.11	0.99
Creek Water Autumn Z <sub>20CM</sub>	15.28	171.35	0.99
Sea Water Autumn Z <sub>20CM</sub>	37.56	190.74	0.98
Dam Water Autumn Z <sub>20CM</sub>	2.64	29.93	0.99
Clear Water Winter Z <sub>1CM</sub>	254.96	595.5	0.96
Creek Water Winter Z <sub>1CM</sub>	188.96	542.93	0.99
Sea Water Winter Z <sub>1CM</sub>	182.76	530.56	0.99
Dam Water Winter Z <sub>1CM</sub>	299.31	643.08	0.98
Clear Water Winter Z <sub>20CM</sub>	223.53	498.58	0.99
Creek Water Winter Z <sub>20CM</sub>	379.98	666.83	0.99
Sea Water Winter Z <sub>20CM</sub>	269.89	527.54	0.99
Dam Water Winter Z <sub>20CM</sub>	251.78	357.77	0.99

**Table 1** –  $\alpha$ ,  $\beta$  and R<sup>2</sup> values obtained for each particular calibration over autumn and

winter.



**Figure 1** – Transmission and absorption distributions for tap water, creek water, sea water and water taken from a stagnant water reserve.



**Figure 2** – Time series of OMI measured column ozone levels present over Toowoomba from March 2007 to August 2007 where day 1 is 1 March 2007.



**Figure 3** – Immersion effect coefficients across the modified UVB waveband as measured for the StellarNet EPP2000 spectrometer in a controlled environment.



**Figure 4** – Calibration curves as made against the solar UVB exposures over autumn for tap water, creek water, sea water and water taken from a stagnant water reserve at  $Z_{1CM}$ . The surface (in – air) calibration curve acts as the control.



Figure 5 – Calibration curves as made against the solar UVB exposures over autumn for tap water, creek water, sea water and water taken from a stagnant water reserve at  $Z_{20CM}$ .



Figure 6 – Calibration curves as made against the solar UVB exposures over winter for tap water, creek water, sea water and water taken from a stagnant water reserve at  $Z_{1CM}$ .



Figure 7 – Calibration curves as made against the solar UVB exposures over winter for tap water, creek water, sea water and water taken from a stagnant water reserve at  $Z_{20CM}$ .



**Figure 8** – Comparison between underwater master calibrations obtained over autumn and winter.