Calibration Of PPO Film For Use As An Underwater Dosimeter

Peter Schouten
Alfio Parisi

Objectives

- Describe the effect of solar ultraviolet radiation (UV) upon aquatic organisms
- Detail the science of underwater UV dosimetry and the poly(2,6-dimethyl-1,4-phenylene oxide) film (PPO) dosimeter
- Describe the calibration technique required for reliable underwater measurements with the PPO dosimeter
- Present PPO dosimeter calibration data obtained during Autumn (Southern Hemisphere)
- Discuss some future directions for this research

Introduction

Underwater UV

- The UV waveband runs from 280 – 400 nm ~ highly capable of causing biological damage, especially UVB (280 – 315 nm)

- A great deal of research has been performed linking the effect of UVB exposure to aquatic life forms

- UVB causes damage to organisms living in aquatic environments such as (Hader, 1997):
  - Plankton (bacterio, pico, phyto)
  - Seagrass
  - Cyanobacteria
  - Corals and sea urchins (Some species *may* have adapted to the UVB)

Photo Credit: *http://www.clark.wa.gov/water-resources/images/monitoring/VanLake-sunset-May05.jpg*

Introduction

Underwater Dosimetry

- Several difficulties arise when UV measurements are made underwater with spectrometers and radiometers

- These devices are expensive to purchase and require routine calibration and corrections for the immersion effect

- *However* dosimeters (such as the PPO dosimeter) are:
  - Relatively inexpensive to fabricate
  - Light and compact
  - Require no power to run
  - Can take multiple measurements at different alignments simultaneously

Introduction

Underwater Dosimetry

- A small variety of UV chemical dosimeters have been tested in the underwater environment (Dunne, 1999)

- These dosimeters only had the capability to record a response over less than two days

- To take measurements over a long time frame these dosimeters have to be repeatedly replaced by the researcher

- So there is a need for a dosimeter that can be deployed underwater and can handle large amounts of exposure over extended intervals without replacement

- PPO is an ideal candidate for this task

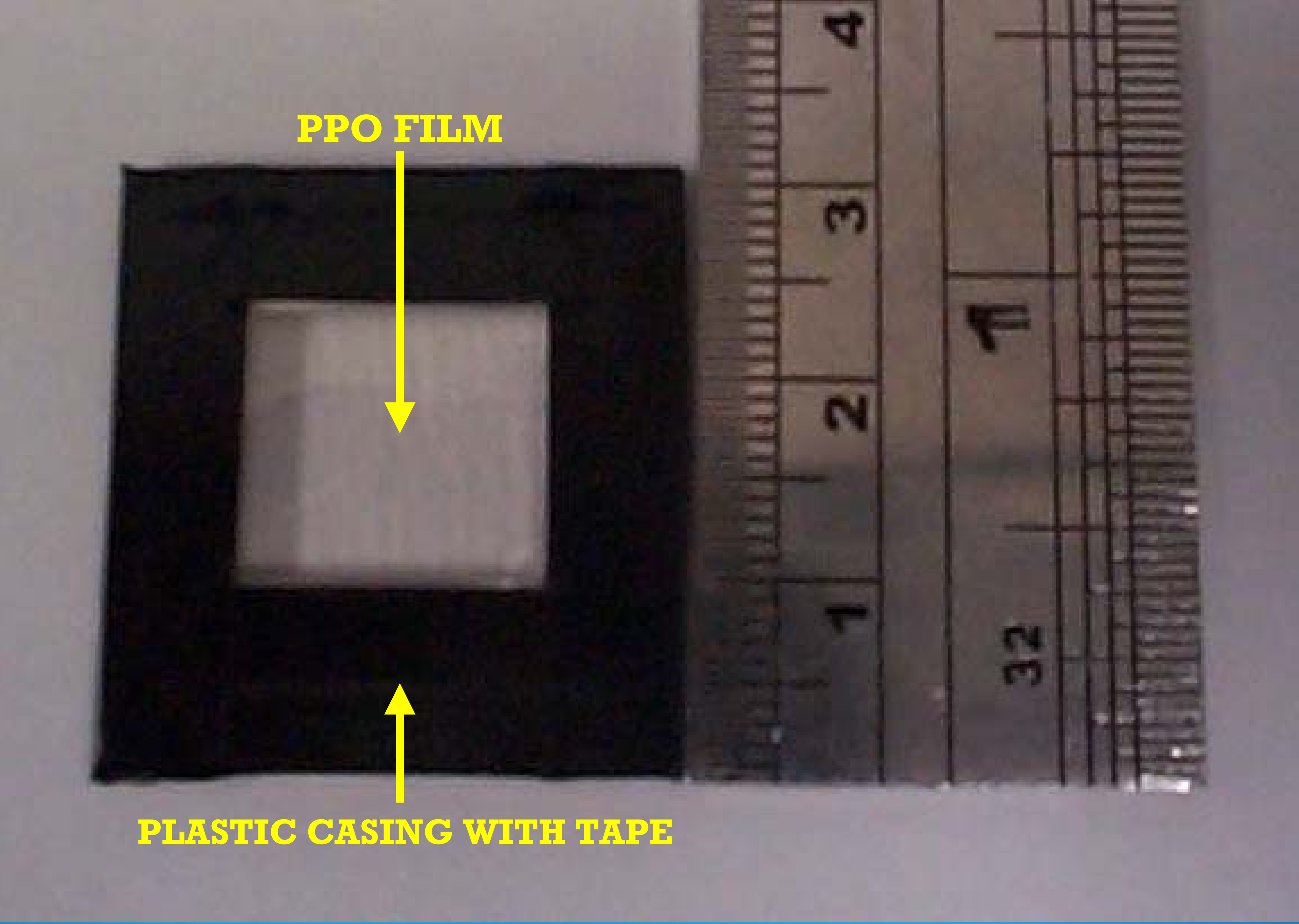


Figure 1: The PPO dosimeter in a plastic holder

Methodology

PPO Dosimeter Preparation

- PPO and chloroform are mixed together at a certain ratio
- The mixture is cast and dried on an automated casting table
- PPO film is cast at an optimal thickness of 40 μm
- The PPO film is then attached to a 3 cm x 3 cm plastic holder with electrical tape
- This results in the PPO film having an effective area of 1.2 cm x 1.6 cm
- This process is carried out at the University of Southern Queensland chemistry labs
- Sheets can be ordered

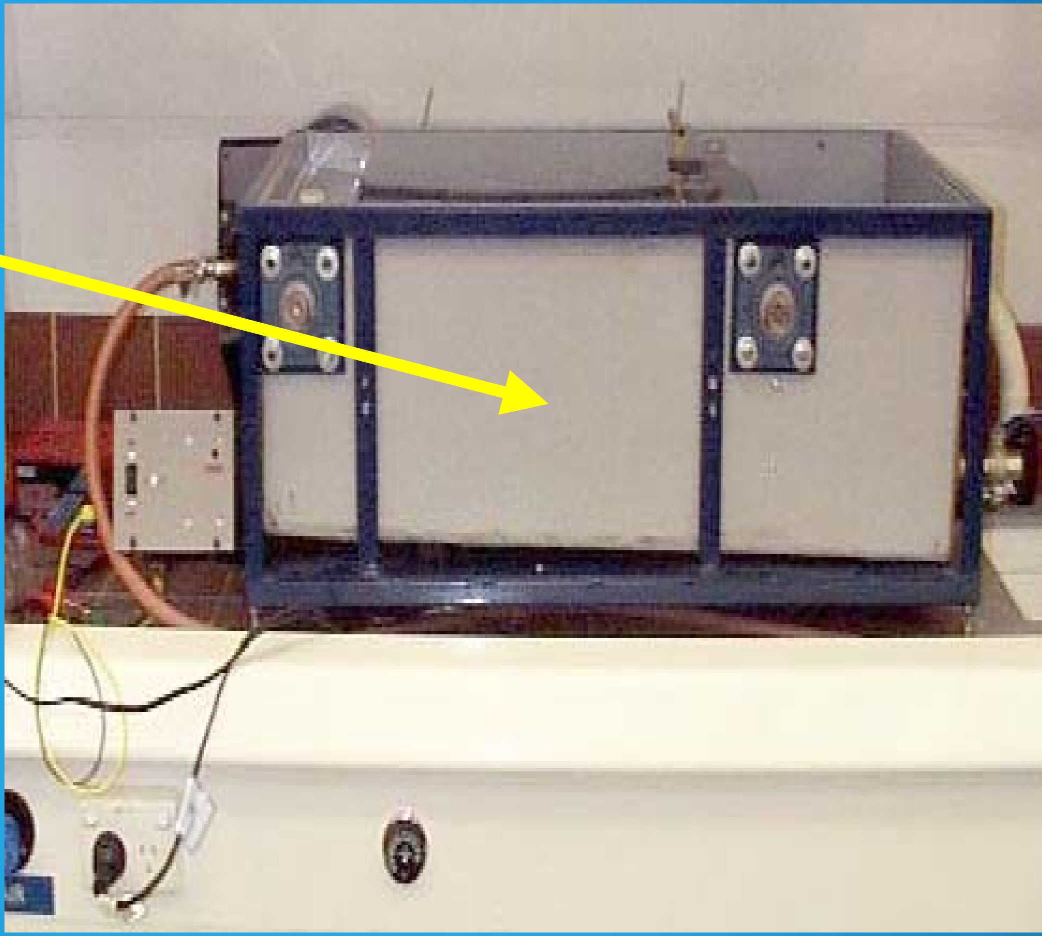


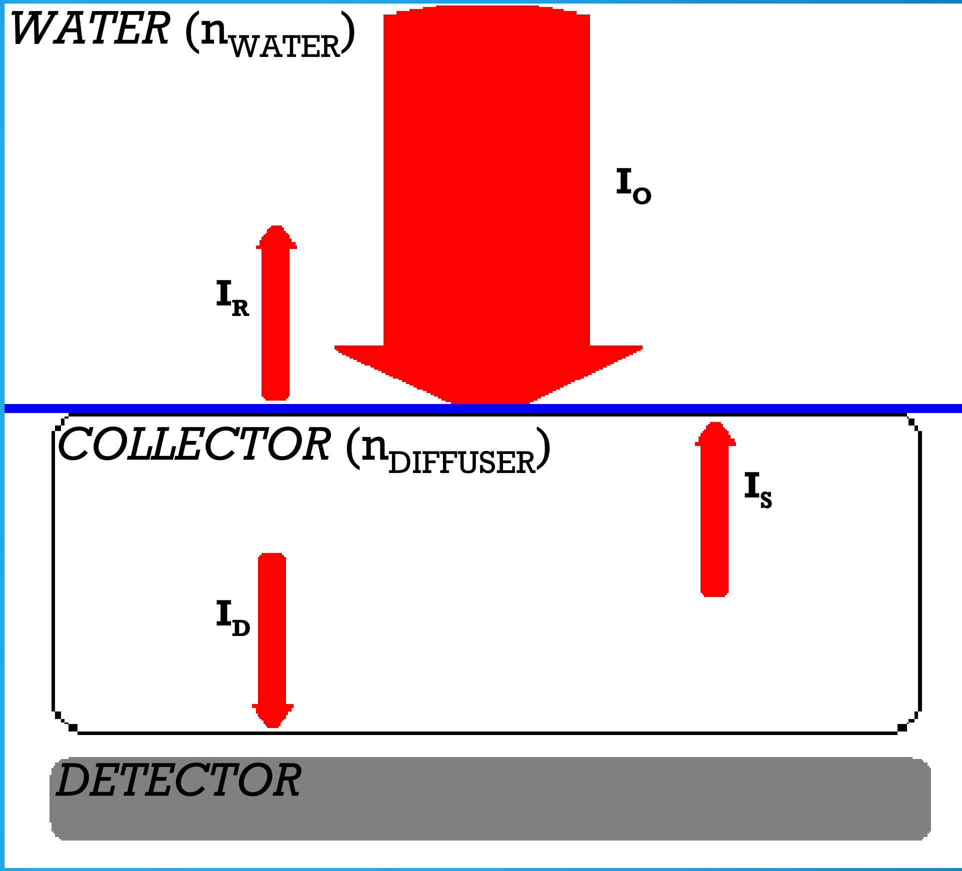
Photo Credit: *A.V. Parisi.*

Methodology

The Immersion Effect

- The immersion effect occurs when an optical meter is submerged in water for a measurement
- During a water-based measurement a greater amount of light is backscattered out of the meter in comparison to a similar air-based measurement
- Caused by the difference between the refractive indices (n) at the meter interface
- Calculated directly with experimental data
- The original irradiance measurement is multiplied by the immersion factor for each wavelength

Reference: Zibordi et al. 2004



I_O = Incoming irradiance

I_R = Reflected irradiance

I_S = Backscattered irradiance

I_D = Irradiance intercepted by detector

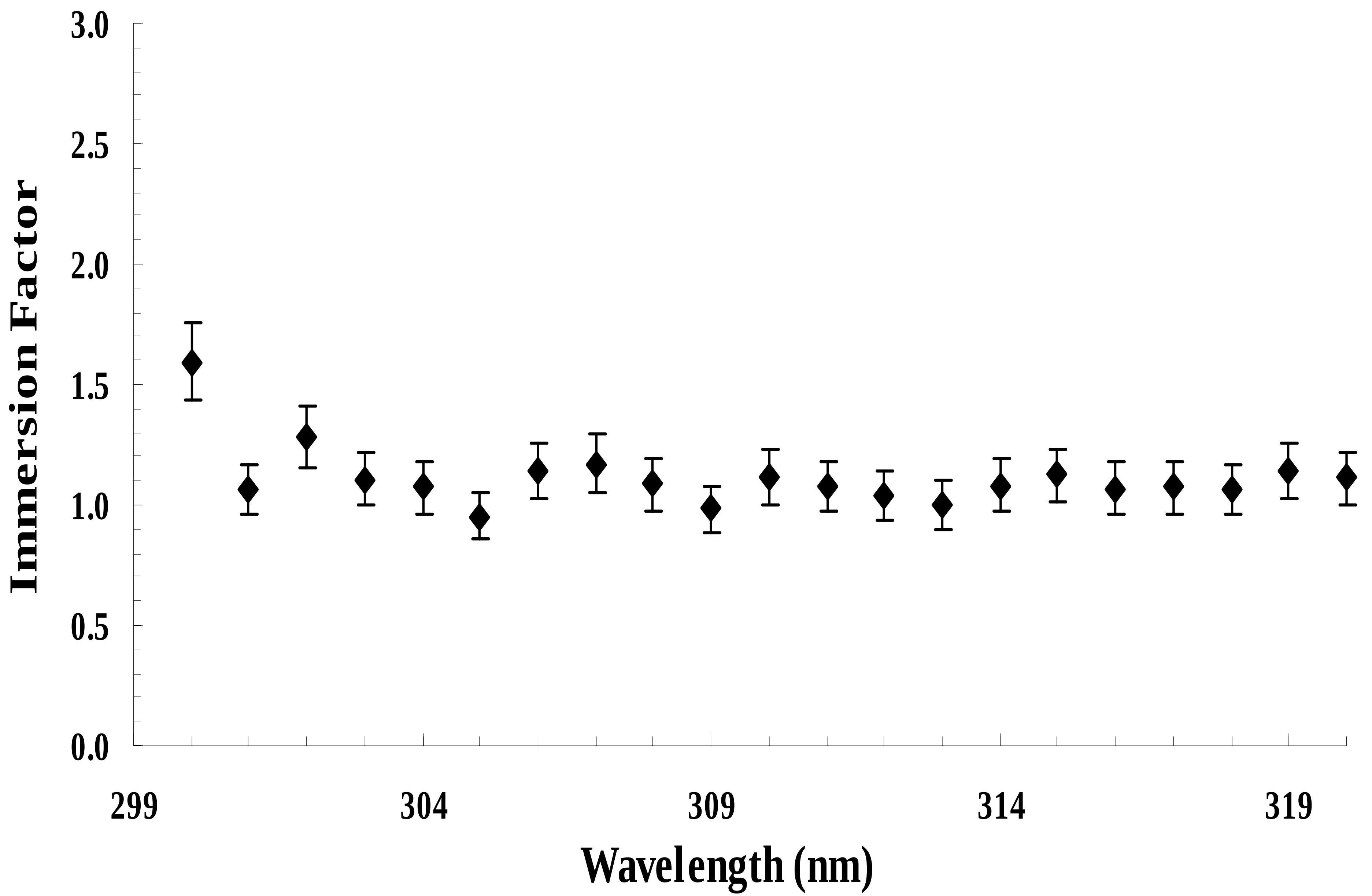


Figure 2: Clear water immersion factors in the UVB for the StellarNet EPP2000 Spectrometer (y - error bars represent ± 5% error estimation)

Methodology

Underwater Dosimeter Calibration

- Only UV exposure changes the chemical structure of the PPO film
- This change is measured by analysing the optical absorbance of the PPO using a spectrophotometer
- A significant change in optical absorbance is seen at 320 nm (ΔA320)
- A series of ΔA320 values was calibrated against the solar UVB spectrum at one shallow (Z_{1CM}) and one deep depth (Z_{20CM}) in a 100 litre tank holding four water types for over the space of four weeks
- Any differences between shallow and deep calibrations between each water type could be determined from this data

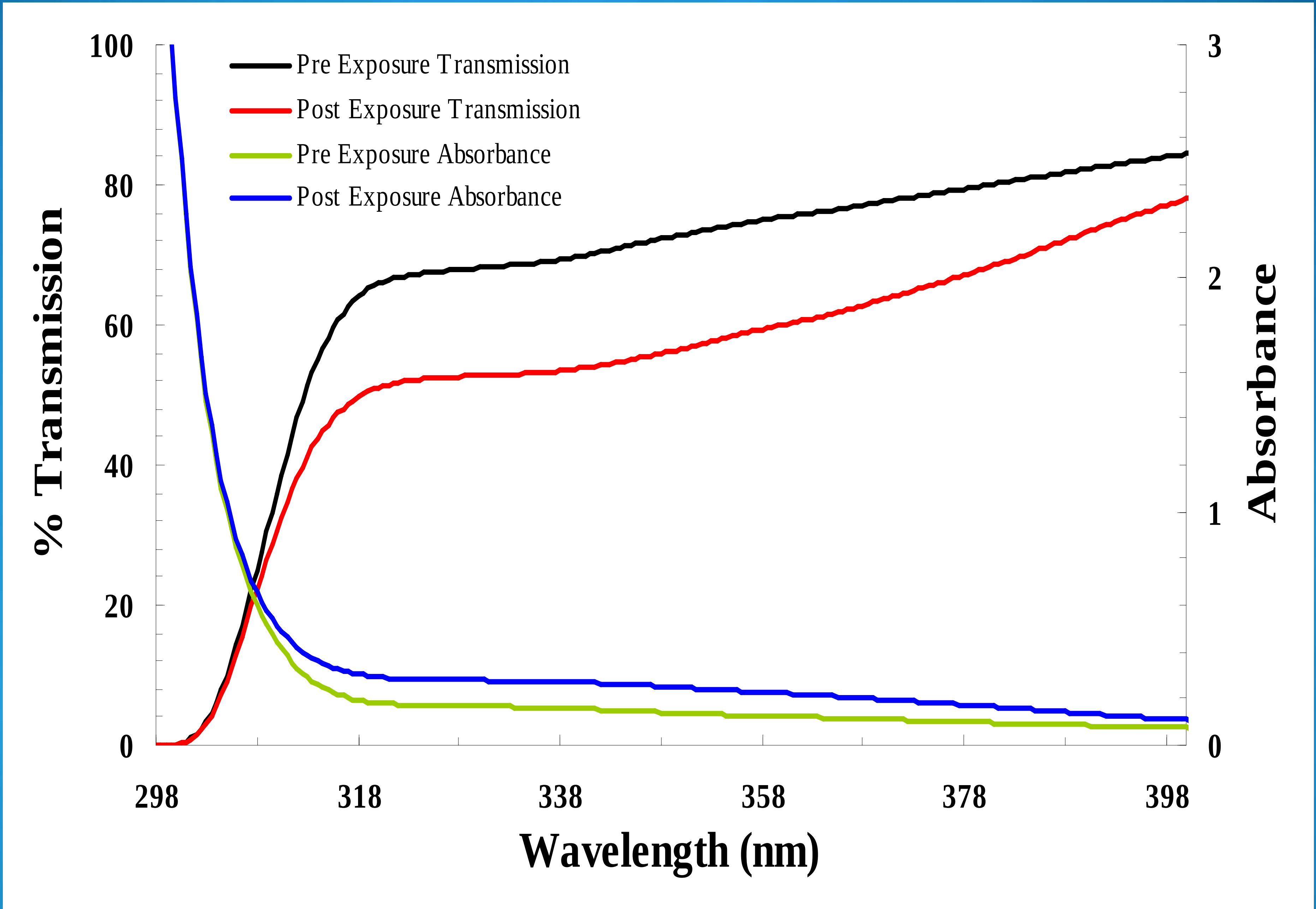


Figure 3: Change in PPO transmission and absorbance – post minus pre exposure (after 18.4 kJ m^{-2} exposure).

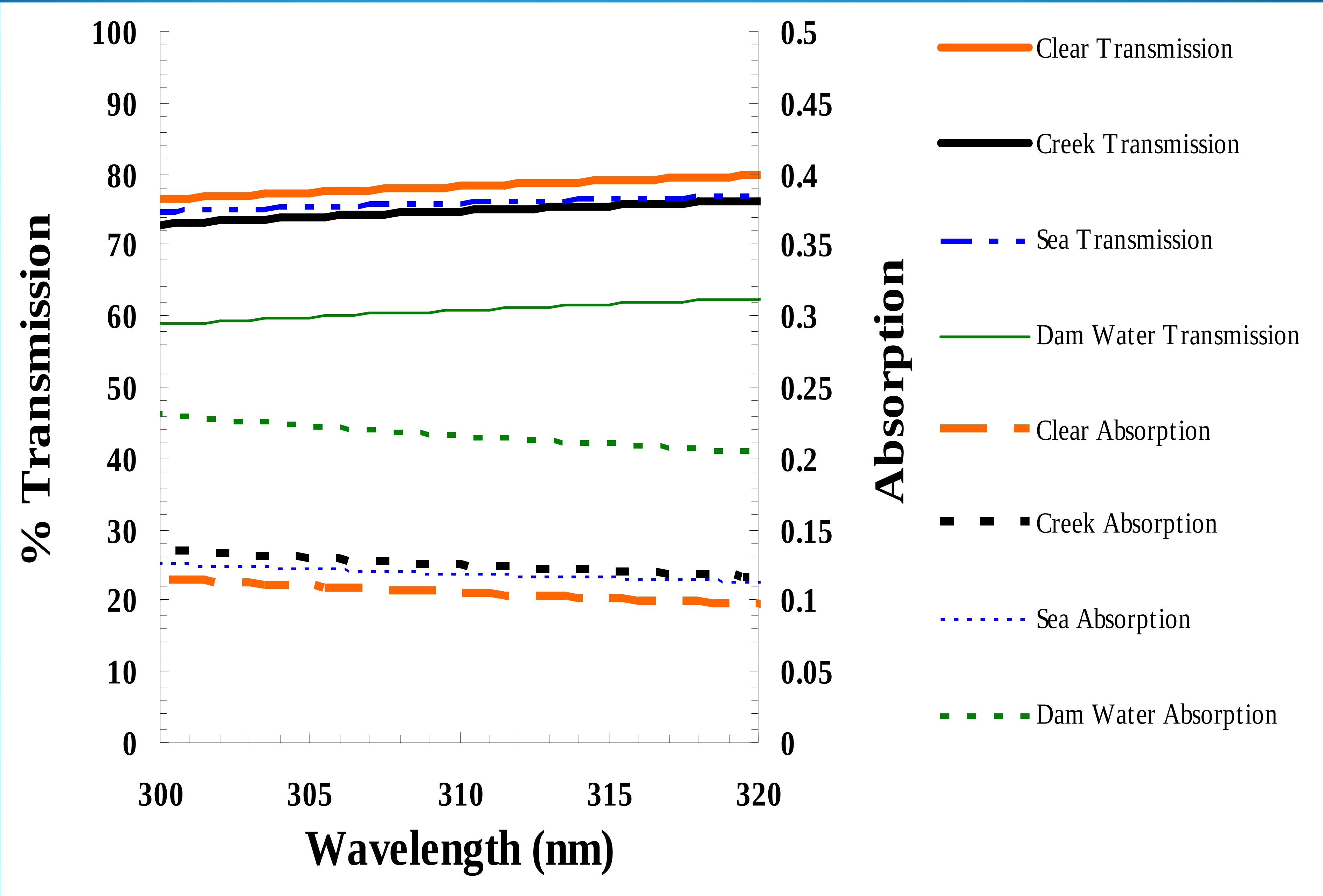


Figure 4: Transmission and absorption spectra for each water type used in the PPO calibrations

Methodology

Underwater Dosimeter Calibration

- For the PPO dosimeter calibrations, the solar exposure was measured each day (Southern Hemisphere Autumn – SZA from 20° to 70°) underwater by an IL1400 broadband UVB meter at Z_{1CM}

- Before this, the IL1400 was calibrated underwater for the UVB spectrum to a standardised and immersion effect corrected StellarNet EPP2000 spectrometer for each particular water type

- These calibrations were measured for each particular water type

- To calculate the exposures received at Z_{20CM} the following equation was used

$$E_d(\lambda, z) = E(0, \lambda) e^{-K_d(\lambda, z) z}$$

Results – PPO Underwater Calibration @ Z_{1CM}

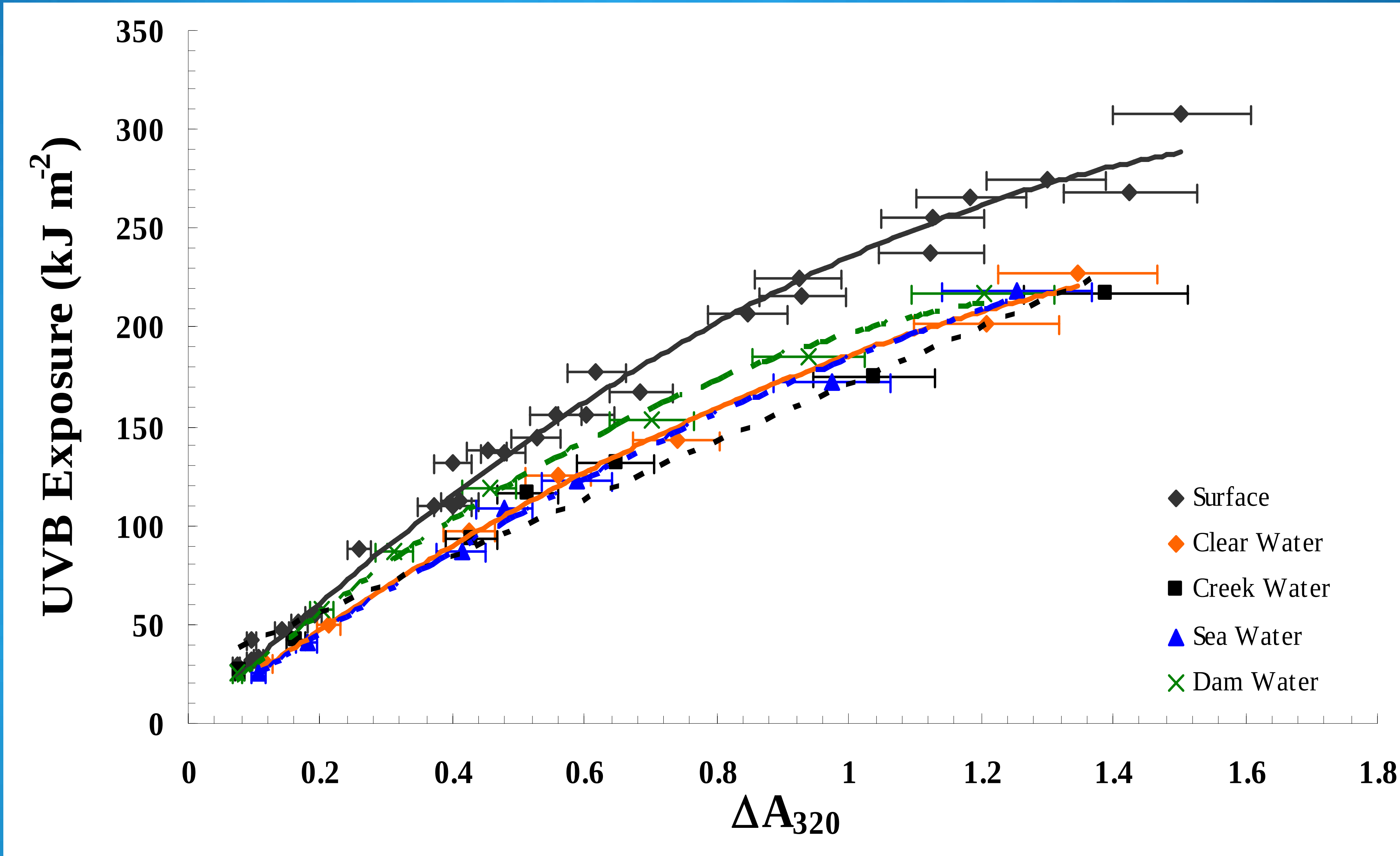


Figure 6: UVB Calibrations between the IL1400 UVB meter PPO Dosimeter at a depth of 1 cm for each water type (x - error bars represent ± 9% interdosimeter variation)

Results – PPO Underwater Calibration @ Z_{20CM}

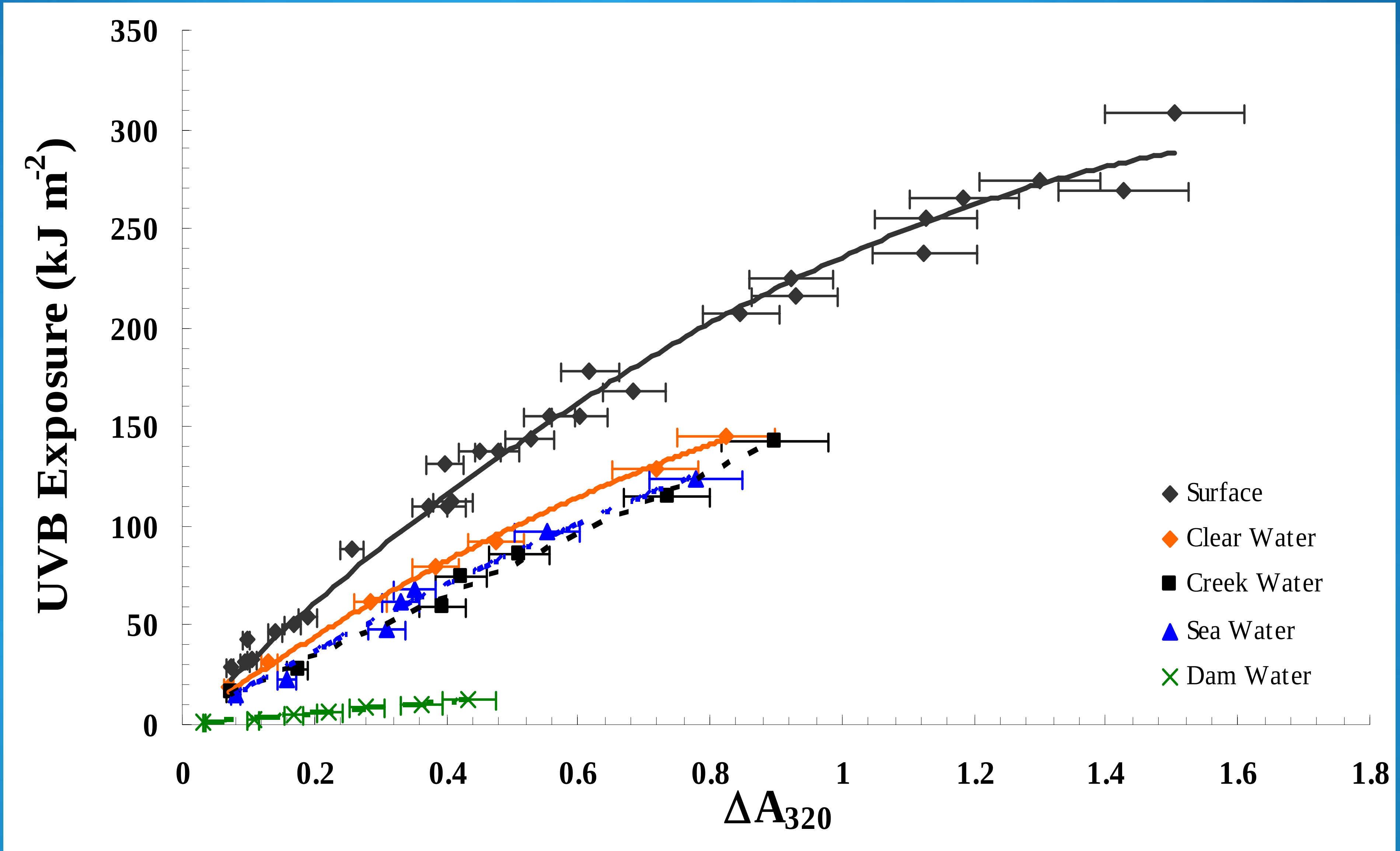


Figure 7: UVB Calibrations between the IL1400 UVB meter PPO Dosimeter at a depth of 20 cm for each water type (x - error bars represent ± 9% interdosimeter variation)

Results – All Underwater Calibrations Combined

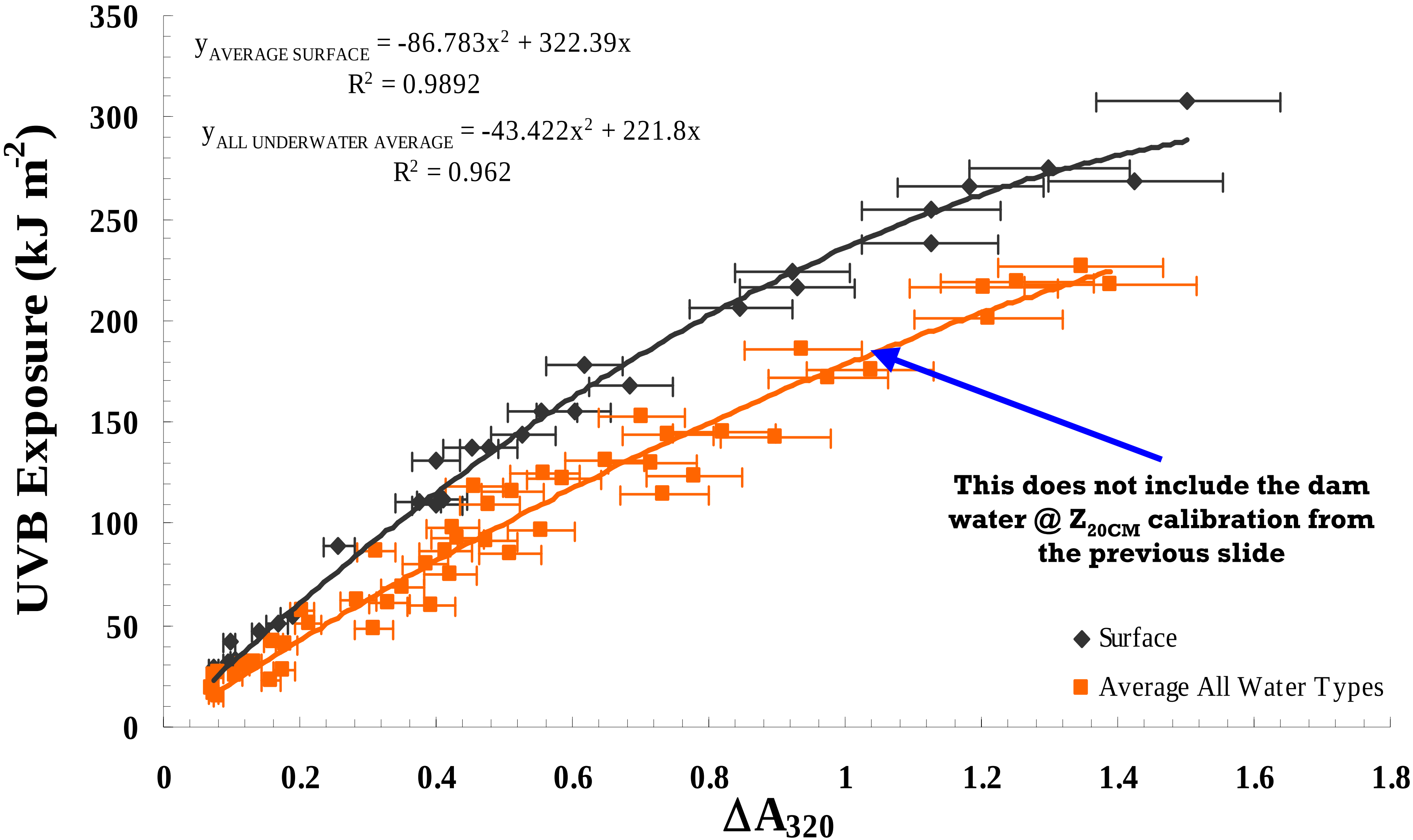


Figure 8: UVB Calibrations between the IL1400 UVB meter PPO Dosimeter combined for all depths for each water type (x - error bars represent ± 9% interdosimeter variation)

Conclusions

- At Z_{1CM} 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

- At the final measurement point, the PPO film dosimeters had yet to fully degrade and would be able to accept another substantial UVB dosage

- The underwater calibrations differed significantly from the surface calibration, hence they are not interchangeable

Conclusions

- The calibrations obtained at Z_{1CM} in each water type were all measured to be in close proximity to each other, within the 9% error estimated to exist for each ΔA320 measurement
- The calibrations obtained at Z_{20CM} in each water type were also all measured to be in close proximity to each other, apart from the dam water calibration
- So it appears that calibrations are transferable from one water type to another within a certain spectral transmission range

Further Research

- Over the next year, the PPO dosimeter will be deployed into various real world aquatic environments

- The PPO dosimeter's capabilities will be tested in a range of different water bodies including creeks, stagnant dams and the ocean

- The dosimeters will be attached to a custom built submersible float to a deepest depth of approximately 1 metre

- The exposures received by the dosimeters will be compared to exposures measured by a spectrometer

Thanks

Mr. Oliver Kinder

Mr. Graham Holmes

Dr. David Turnbull

USQ for the APA Scholarship

Background Photo Credit: *www.greengeek.ca/wpcontent/uploads/2006/08/underwater.jpg*