Chemical films and monolayers on the water surface and their

interactions with ultraviolet radiation: A pilot investigation

Peter Schouten^{1,2*}, Charles Lemckert¹, David Turnbull², Alfio Parisi², Nathan

Downs², Ian Underhill¹ and Geoff Turner¹.

¹ School of Engineering, Griffith University, Gold Coast, Australia.

² Centre for Rural and Remote Area Health, University of Southern Queensland,

Toowoomba, Australia.

to whom correspondence should be addressed

email p.schouten@griffith.edu.au

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Abstract

Over the past fifty years numerous types of chemical films and monolayers have been deployed on top of a wide variety of water reserves in an endeavour to reduce evaporation. To date very little knowledge has been assimilated on how these chemical films and monolayers, once applied to a water surface, influence the underwater UV light field and, in turn, the delicate ecosystems that exist in aquatic environments. This manuscript presents underwater UV exposure profiles weighted to the DNA damage action spectrum measured under an octadecanol/hexadecanol/lime chemical film mixture, a silicone-based chemical film and an octadecanol monolayer applied to the water surface. UV transmission and absorption properties were also evaluated for each of these chemical films and monolayers. From this it was found that when chemical films/monolayers are applied to surface water they can reduce the penetration of biologically effective UV into the water column by up to 85% at a depth as small as 1 cm. This could have a positive influence on the aquatic ecosystem, as harmful UV radiation may be prevented from reaching and consequently damaging a variety of life forms or it could have a negative effect by potentially stopping aquatic organisms from adapting to solar ultraviolet radiation over extended application intervals. Additionally, there is currently no readily applicable system or technique available to readily detect or visualise chemical films and monolayers on the water surface. To overcome this problem a new method of monolayer and chemical film visualisation, using a UV camera system, is detailed and tested and its applicability for usage in both laboratory based trials and real-world operations is evaluated.

Introduction

Long-term drought conditions alongside excess water wastage continue to be a major problem for many countries around the world. From this, several technologies have been developed to help reduce sizeable losses in both potable and non-potable water storages in both the agricultural and government sectors. Some of these technologies have included land-anchored shade sails, wind breaks, hard and floating water surface covers, along with destratification and mixing systems. However, all of these particular evaporation reduction mechanisms have a number of disadvantages that greatly reduce or even prohibit their use. Some of these disadvantages are that they are generally expensive and difficult to install and maintain, pose a physical threat to the health of local environments and the successful propagation of ecosystems, and they can ruin the usability and aesthetic appeal of publically accessible water basins. However, over the past fifty years several cost-effective and easily deployed chemical films and monolayers have been produced, tested and deployed by a range of end users from the agricultural, commercial and government sectors.

Chemical monolayers are long chain molecules that contain a single hydrophilic end and a single corresponding hydrophobic end. This particular molecular composition enables the monolayer to anchor itself on top of a water surface and rapidly disperse and reassemble in a closely packed regime usually only a few nanometres thick. This effectively traps a high percentage of volatilising water vapour beneath it. The successful application of chemical monolayers is highly dependent on local atmospheric, environmental and water quality conditions as they are very vulnerable to wind and wave action which causes them to stretch and break up on the water surface and are also affected by biological degradation caused by interactions with a

wide variety of microbes on the water surface. Chemical films many times thicker than monolayers have also been deployed across water storages in order to reduce evaporation. Previously employed chemical films have been based on combinations of both stearyl alcohol (hexadecanol) and cetyl alcohol (octadecanol) along with other substances with water repelling qualities such as silicone. The operating principle of these thick chemical films is similar to the monolayers as they exert a high pressure upon the water surface effectively stopping escaping water molecules from leaving the water-air interface.

Various studies have sought to ascertain a general idea of how biologically weighted UVB radiation (280 nm to 320 nm) is distributed with depth to give a general prediction on how solar UVB could affect certain aquatic organisms. The most commonly employed action spectrum in these investigations is the DNA damaging action spectrum as initially presented by Setlow (1). One such study looking at the basic depth distribution for DNA damaging UV was presented by Dunne and Brown (2) in which DNA damaging irradiances were measured at different depths at an atoll, an inshore reef and a coastal island within the Indian Ocean and the Andaman Sea using a spectroradiometer. It was discovered that the attenuation of the DNA damaging UVB irradiance was amplified with increasing depth with 1% incident surface UV radiation ($z_{1\%}$) values being calculated as 9 metres for the ocean atoll, 2.6 metres for the inshore reef and 4.7 metres for the coastal island compared to $z_{1\%}$ values estimated for unweighted UVB irradiance measurements of 11 metres for the ocean atoll, 3 metres for the inshore reef and 6 metres for the coastal island.

Most studies have taken a different approach to the study by Dunne and Brown (2) in measuring and quantifying the actual damage caused by biologically effective UVB radiation to marine life forms by using various types of biological sampling procedures performed either in the field or in the laboratory in combination with the measurement of UV radiation by the usual systems such as radiometers, spectrometers and spectroradiometers. These kinds of investigations are now more important than ever, with current global warming conditions modulating an increased level of stratification in natural waters, thus leading to conditions in which UVB can penetrate to deeper depths and thus cause more biological harm (3).

Very few studies have been performed detailing the effect of either solar UV or artificial UV on evaporation minimising chemical films and monolayers and the influence of monolayer presence on the underwater penetration of biologically effective UV. Craig et al (4) has provided a preliminary test describing the influence of a long-term substantial exposure to an artificial UV source on a commercially available hexadecanol/octadecanol/lime thin film mixture spread out on a water surface at a coverage rate several times greater than the rate recommended by the manufacturer. Specifically, this test evaluated the ability of both hexadecanol and octadecanol to stop evaporation occurring before, during and after an uninterrupted intensive UV exposure. The results from this experiment indicated that there was no discernable difference between the evaporation rates measured for both hexadecanol and octadecanol with or without a sustained UV exposure.

There is a need to supplement these initial results in order to better detail how both ultra thin monolayers and thicker chemical films, once deployed on a given water surface, will influence the underwater UV distribution and in turn quantify how they could affect the short and long term health and sustainability of an aquatic ecosystem. This manuscript addresses this gap in the literature by detailing a series of laboratory tests investigating the UV transmitting and absorbing capabilities of one commonly used monolayer (octadecanol suspension) and two chemical film products (a hexadecanol/octadecanol/lime mixture and a silicone film) and also describes how the monolayer and the chemical films modulate the penetration and distribution of incoming biologically weighted UV wavelengths.

If a change in the penetration of UV through and within a water column can be detected in comparison to a baseline case in which no monolayer or chemical film is present on the water surface, it follows that UV sensitive cameras positioned above the water level can be used to passively sense the altered reflected UV component and in turn monitor the time evolution of the spread and distribution of a monolayer or chemical film over a given surface area of water. UV imaging with UV cameras and UV recording systems have been used previously by law enforcement agencies, medical professionals and government departments around the world for many years using both reflected UV photography and UV fluorescence photography, which are the two specific types of UV imaging currently utilised (5). Some applications of UV photography and imaging have included the detection of blood stains and other organic fluids along with artificial trace chemicals that may have faded, evaporated or blended into their surrounds, fingerprint analysis, detection of document forgeries and erasures and also the visualisation of long-term skin damage caused by exposure to UV radiation (6).

Despite the widespread use of UV photography and UV cameras to visualise numerous types of fluids and substances in a wide variety of different environments, the application of UV reflection to detect evaporation suppressing monolayers and chemical films has not been attempted or evaluated in any previous literature. This is a considerable issue as in order to effectively and comprehensibly measure and model the evaporation reducing efficiency, spreading velocity and recovery ability of any monolayer or chemical film it must be completely visible at all times. By utilising UV reflection photography and a UV camera system, this manuscript attempts to detail a possible solution to this problem by presenting a new and improved method for remotely visualising both monolayers and chemical films in real-time on a water surface in ideal conditions using a UV camera capable of recording wavelengths across the majority of the terrestrial UV waveband.

Materials and Methods

Chemical film and monolayer descriptions

Three distinctive chemical films and monolayers were chosen for analysis in each stage of this investigation. The first chemical film tested was a fine powdered dry substance capable of rapid self spreading based upon a mixture of hydrated lime powder combined with cetyl alcohol (hexadecanol) and stearyl alcohol (octadecanol) (referred to as octadecanol/hexadecanol/lime chemical film for the remainder of this paper). This mixture is currently a commercially available product and is patented so the exact mixing ratio of each of the chemical ingredients within its composition is not available. The second chemical film evaluated was a self-spreading film based on silicone (specifically polydimethylsiloxane) mixed in with other unnamed assorted surfactants and additives (referred to as silicone film for the remainder of this paper). Again, this film is available to be purchased by private end users and as a result the manufacturers have not publically detailed the exact chemical constituents or mixture ratios comprising the mixture in order to maintain intellectual property against possible competition. The final substance tested in this investigation was an ultra thin monolayer based on an octadecanol (chemical formula: CH₃(CH₂)₁₇OH) suspension formulation. Specifically, this mixture contained 5% octadecanol and was combined with 1% Brij 78 in distilled water. Brij 78 is a surfactant that was added to the octadecanol suspension in order to improve its spreading ability. A detailed study into how the molecular structure of octadecanol behaves across a water surface in accordance to changing temperatures and surface densities has been measured and modelled previously in depth by Henry et al (7).

Measurement of UV transmission and absorption properties of the chemical films and monolayers

Before exposure to any UV radiation, both pure hexadecanol and octadecanol were dissolved in a solution of one part monolayer to 20 parts petroleum spirit (95% Hexane). Each solution was then spread across one side of a quartz cuvette, being optically transparent in the UV region. The monolayer solutions were left to dry for ten minutes to allow the petroleum spirit to evaporate completely in order to leave a hexadecanol or octadecanol layer approximately 45±25 µm thick on the quartz cuvette surface. Immediately after this the cuvettes were positioned 0.16 m from the output aperture of a solar UV simulator (model 15S solar UV simulator, Solar Light Co., Philadelphia, USA) and exposed to an artificial solar UV beam imitating the terrestrial solar UV output from 298 nm to 400 nm for a total duration of thirteen hours. Total UV output from the solar simulator was calculated to be 1.5 MJ m⁻² over the exposure time. This exposure equates to approximately three days of cloud free unshaded solar UV exposure during summer in the southern hemisphere at a subtropical site.

The solar simulator was also used to determine the effect of UV exposure upon the silicone film. In this trial two quartz cuvettes were filled completely with the silicone film and exposed directly to the artificial UV spectrum delivered by the solar simulator. The total UV exposure supplied to the silicone film was approximately 0.4 MJ m⁻² over a time interval of three hours. This exposure period was shorter than that given to the hexadecanol and octadecanol films as the silicone film deteriorated quickly from being optically transparent to taking on a deep yellow appearance during the course of the artificial UV exposures.

The change in optical transmission and absorbance across the entire UV waveband for the two chemical films and the octadecanol monolayer after the extended UV exposures was measured and quantified in a spectrophotometer (model 1601, Shimadzu Co., Kyoto, Japan). 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 a given wavelength (ΔA_{λ}) for each type of chemical film and monolayer was measured to provide a data point, where ΔA_{λ} was calculated with the following equation:

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

where A_{λ}^{FINAL} is the final optical absorbance measurement after exposure, taken at a given wavelength in the UV waveband and $A_{\lambda}^{INITIAL}$ is the initial absorbance measurement before exposure, also taken at a given wavelength in the UV waveband. Both A_{λ}^{FINAL} and $A_{\lambda}^{INITIAL}$ were measured by the spectrophotometer with the following logarithmic functions:

$$A_{\lambda}^{FINAL} = -\log_{10}\left(\frac{I_{\lambda}^{FINAL}}{I_{\lambda}^{REF}}\right)$$

$$A_{\lambda}^{INITIAL} = -\log_{10}\left(\frac{I_{\lambda}^{INITIAL}}{I_{\lambda}^{REF}}\right)$$

where I_{λ}^{FINAL} and $I_{\lambda}^{INITIAL}$ are measurements of the transmitted UV radiation intensity at a given UV wavelength passing through either an exposed or unexposed chemical film or monolayer and I_{λ}^{REF} is the intensity of a reference beam that has not passed through a chemical film or monolayer. To convert the absorbance measurements to their equivalent percentage transmission (%T) values the following expressions were used:

$$\Delta\%T_{\lambda} = \%T_{\lambda}^{\mathit{FINAL}} - \%T_{\lambda}^{\mathit{INITIAL}}$$

where:

$$\%T_{\lambda}^{FINAL} = 100 \left(10^{-A_{\lambda}^{INITIAL}}\right)$$

$$\%T_{\lambda}^{INITIAL} = 100 \left(10^{-A_{\lambda}^{FINAL}}\right)$$

UV Penetration through chemical films and monolayers

To supplement and extend the initial investigations performed by Craig et al (4) the underwater distribution of artificial UVB radiation weighted to the DNA damaging action spectrum as evaluated by Setlow (1) underneath octadecanol suspension, silicone film and the octadecanol/hexadecanol/lime chemical film was performed in a small water tank over a 72 hour trial period. The UV source employed was a fluorescent UV lamp (model FS40/12, Philips, Lawrence & Hanson, Toowoomba, Australia) covered by a section of cellulose acetate. This material was used to block out the UVC wavelengths emitted by the lamp. The cellulose acetate covering was replaced at the beginning of each new trial. The lamp was suspended in place over the top of the tank at a constant distance of approximately 20 cm from the water surface. Both in-air and underwater spectra measured for this UV source has been presented previously by Schouten et al (8). The primary UV radiation measurement instrument employed throughout this component of the research was the IL1400 broadband meter ('A' Series, International Light, Newburyport, MA) positioned at 1 cm below the water surface. The reasoning for choosing the IL1400 was that it has the capability to integrate subsurface UV exposures over an extended interval of time. Also, the IL1400 has excellent power economy, only requiring four AA sized batteries to operate consistently over 72 hours working time. UV exposures at deeper depths

 $(E_d(z, \lambda))$ were modelled by employing the Beer-Lambert-Bouguer law that is given in the following form:

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

where $E(0, \lambda)$ is the downwelling exposure at a depth of 1 cm below the water surface, $K_d(z, \lambda)$ is the attenuation coefficient given in m⁻¹ or cm⁻¹ and z is the depth of the water column in m or cm.

Before measurements began, a waterproof detector (SUD240, International Light) with a working spectral response in the UV running from 265 nm to 332 nm (9) was attached to the meter. International Light (10) has stated that the IL1400 has 0.2% linearity and has a level of repeatability no greater than \pm 3% when compared to the National Institute of Standards and Technology (NIST, United States) transfer standards. Output from the IL1400 meter was calibrated to a spectroradiometer system corrected for the immersion effect using a similar methodology to that previously detailed by Schouten *et al* (8), Hooker and Zibordi (11), Zibordi (12) and Zibordi *et al* (13). The specifications of the spectroradiometer system have been described before by Schouten *et al* (8). A picture of the waterproof detector with the UVB fluorescent lamp housed inside a felt covered measurement enclosure custom built for the trial series is shown in Figure 1.

FIGURE 1

The water tank used in the experiments had a length of 51 cm, a width of 37 cm and a depth of 30 cm. The rigid sides of the water tank were painted with blue paint to stop any diffuse radiation entering the water through the sides. Additionally, the tank was

covered over completely by black felt in order to stop any outside stray light from penetrating the water. The water used was clear tap water, kept free of any floating particulates. For all of the experiments UVB was defined as the waveband running from 280 to 320 nm. The 320 nm cut-off has sometimes been employed by photobiologists and was more applicable to our investigation (8). Transmission and absorption spectra for clear tap water along with characteristic diffuse attenuation coefficients have already been detailed by Schouten *et al* (8), Schouten *et al* (14) and Schouten *et al* (15). The water remained completely stable, with no mixing or surface disturbance occurring during the duration of each experiment. The measurement enclosure and tank were kept inside an air-conditioned room. As such, temperatures remained relatively consistent between trials. Ambient temperatures were measured using a generic digital thermometer around the measurement enclosure and tank environment during each of the experiments and are shown in Figure 2. Negligible amounts of evaporation were measured to occur in the tank throughout each trial, so refilling was not necessary.

FIGURE 2

Visualisation of chemical films and monolayers on the water surface using a UV camera system

A change in the penetration of UV through the water column was detected for octadecanol suspension, silicone film and the octadecanol/hexadecanol/lime chemical film, meaning that UV radiation must be absorbed, reflected or transmitted by the films. From this, it was assumed that it could be possible to use a UV sensitive camera positioned above the water surface to passively sense the reflected UV component

from the films over time in ideal conditions with negligible wind and wave action on the water surface. To follow through on this idea, a series of experiments were performed employing a specialised digital UV camera system (UVCorder, Oculus Photonics, USA) in order to conclusively determine if UV reflections could be used to passively monitor the spreading evolution of both chemical films and monolayers over time. The UVCorder system consists of a regular camcorder (Vixia HV40 HD, Canon, Japan) attached directly to a custom built silicon CCD based UV detector unit fitted with a TV lens (16 mm, Pentax, Japan) with a 22.6° x 17.1° field of view. The UV detector has a working spectral response of between 330 nm to 420 nm (with a maximal spectral response at 370 nm). This response allows the UVCorder system to effectively detect close to the entirety of the terrestrial UVA spectrum. The UV detector also has an inbuilt filter that blocks the influence of both infrared and visible radiation down to less than 1% in regular outdoor lighting conditions (16). Additionally, the UVCorder system has its own 396 nm UV point source attached above its UV detector housing.

Separate scenarios in a small tank (40 cm x 20 cm x 20 cm) filled with clear tap water were investigated both outdoors and indoors with incident radiation from the Sun (during cloud free conditions coinciding with an experimental time frame running within \pm 30 minutes of solar noon and minimum solar zenith angle) and incident radiation from the manufacturer provided 396 nm point source illuminating the octadecanol/hexadecanol/lime chemical film, silicone film and octadecanol suspension applied to the water surface. The UV exposures to the chemical films and monolayer were recorded for approximately 1 minute each and compared directly to a baseline case with no chemical film/monolayer applied to the water surface in order to

determine if the UVCorder system did detect any visible differences at the water surface. UV imagery was also compared to visible spectrum photos taken by a standard digital camera (µ Tough-8000, Olympus, Japan). The UV images were collected in real-time, recorded and backed up to a mini DV cassette tape and were sent through to a computer system via a high-speed firewire connection for post analysis. Post analysis consisted of the capture of screenshots from the raw footage followed by simple colour correction performed with the Microsoft Office Picture Manager. Figure 3 (A) and Figure 3 (B) show the setup and components of the camera system retrofitted to the same felt covered measurement enclosure used in the UVB radiation under chemical films/monolayers study. The UVB fluorescent lamp visible in Figure 3 (A) was removed from within the enclosure before trials began.

FIGURE 3

Results

UV transmission and absorbance of chemical films and monolayers

Figure 4 (A) and Figure 4 (B) displays single UV transmission and UV absorbance measurements at a wavelength within the UVB waveband (300 nm) and a wavelength within the UVA waveband (360 nm) for hexadecanol and octadecanol before and after an artificial solar UV exposure of 1.5 MJ m⁻² delivered over a time span of 13 hours. From this data it is clear that following a substantial UV exposure, the levels of UV transmission (and absorbance) occurring within both the UVB and UVA wavebands for both hexadecanol and octadecanol are relatively similar and only increased very slightly (with absorbance decreasing) by no more than 1% to 2% of their initial values. This indicates that the optical characteristics of both hexadecanol and octadecanol are well protected against degradation by UV radiation for the given exposure periods.

FIGURE 4

Figure 4 (C) and Figure 4 (D) show UV transmission and UV absorbance measurements at two specific wavelengths within the UVB waveband (360 nm and 400 nm) for the silicone film before and after an artificial solar UV exposure of 0.4 MJ m⁻² delivered over 3 hours. Unlike hexadecanol and octadecanol, the silicone film did not allow any UV transmission to occur up until the 320 nm to 330 nm range during both pre and post exposure scans, meaning that the silicone film essentially either absorbed and/or reflected almost all of the UVB waveband. At the 400 nm wavelength the drop off in UV transmission was the most substantial in comparison to the rest of the UV waveband, with a decrease of close to 75% taking place after the

0.4 MJ m⁻² UV exposure. The UV wavelengths below 400 nm also exhibited significant reductions in UV transmission after exposure, with a large drop off of approximately 48% occurring at 360 nm. These results suggest that silicone film is a very efficient absorber or reflector of UVB radiation and its absorbing and reflecting capabilities are enhanced across the entire UV waveband with increasing UV exposure.

The chemical alteration driving the enhancement of the UV absorbing capabilities of the silicone film has yet to be fully investigated, as the film is only relatively new. However, throughout the testing the silicone film did display a progressive discolouration from clear to white to deep yellow over the duration of the broadband UV exposures. This result was similar to that seen by Rasmussen et al (17), in which solid silicone samples were seen to change colour after being irradiated with UV over a short exposure time. This UV induced discolouration could be a link to the chemical change occurring within the silicone film that provides the increase in UV absorption. To better ascertain what is occurring within the chemical structure of the silicone film before and after UV exposure, nuclear magnetic resonance spectroscopy will need to be performed.

Measured and modelled distributions of water column UV exposure beneath the chemical films and monolayer

Figure 5 (A) displays DNA damaging irradiances averaged over the 72 hour exposure time recorded at a depth of 1 cm for octadecanol, the octadecanol/hexadecanol/lime mixture and the silicone film applied to the water surface. The y-axis error bars represent the \pm 3% repeatability margin estimated for the IL1400 radiometer

previously detailed in the Materials and Methods section. In this figure these averaged irradiances are compared to average DNA damaging irradiances measured above the water surface and just below the water surface at a depth of 1 cm with no monolayer or chemical films applied. From this it can be seen that the average irradiances measured 1 cm below each of the chemical films and monolayers were lower in comparison to the average irradiances measured above the waterline and 1 cm below the waterline without any chemical films or monolayer on the water surface. The average DNA damaging irradiance measured beneath the silicone film was the lowest for all of the chemical films and monolayers at just 2.4 x 10⁻⁴ W m⁻² in comparison to 4.1 x 10⁻⁴ W m⁻² and 5.7 x 10⁻⁴ W m⁻² for the octadecanol/hexadecanol/lime mixture and octadecanol monolayer respectively. This result was entirely expected as, from the UV absorbance and transmission testing, the silicone film was shown to be a much better absorber/reflector of UV radiation in comparison to octadecanol and hexadecanol.

FIGURE 5

The modelled DNA damaging UV exposure underwater depth distributions as shown in Figure 5 (B) clearly depict that chemical films/monolayers when applied to surface water can reduce the penetration of UV into the water column by a substantial amount even down to a depth as shallow as 50 cm. From this testing it is clear that silicone film, when compared to the octadecanol/hexadecanol/lime chemical film and octadecanol is the most effective attenuator of incoming UV. For example, at a depth of just 30 cm it was calculated that an exposure of as little as 0.26 J m⁻² hour⁻¹ would occur beneath a silicon film covered water surface in comparison to exposures of 0.67

J m⁻² hour⁻¹ and 0.85 J m⁻² hour⁻¹ for the octadecanol/hexadecanol/lime mixture and octadecanol suspension respectively.

More specifically, from Figure 6 (A) it becomes clearer that each of the tested chemical films/monolayers can either absorb or reflect biologically weighted UV at the water surface and reduce its underwater presence. For example, after 72 hours exposure time, when compared to the scenario with no chemical film/monolayer on the water surface, UV irradiance was reduced by at much as 70%, 43% and 28% for the silicone film, the octadecanol/hexadecanol/lime mixture and the octadecanol suspension respectively at a depth of only 1 cm. In addition, Figure 6 (B) shows that with the application of a chemical film/monolayer, underwater UV irradiance at 1 cm depth can drop by up to 85%, 72% and 65% for the silicone film, the octadecanol/hexadecanol/lime mixture and the octadecanol suspension in comparison to a UV exposure measured just above the water surface after a 72 hour time interval. These results could mean that the application of these chemical films and monolayers could have a positive influence on the aquatic ecosystem, as harmful UV radiation may be prevented from reaching and consequently damaging a variety of organisms. Conversely, the long-term deployment of these chemical films/monolayers could also have a detrimental effect on the health of various aquatic life forms and on the delicate underwater chemistry balance.

FIGURE 6

Visualisation of chemical films and monolayers on the water surface using UV and infrared cameras

From the UV transmission/absorbance tests and exposure measurements/modelling results it appears that a relatively low amount of UV radiation is actually transmitted by the chemical films/monolayers when spread across a water surface. This implies that the films/monolayers must be either absorbing or reflecting a substantial amount of UV radiation. From this it is a logical progression to try to intercept the reflected UV component as a potential technique to visually monitor the spread and positioning of the monolayers/chemical films on the water surface.

Figure 7 (A) Figure 7 (B1), Figure 7 (C1) and Figure 7 (D1) provide separate stills captured by the UVCorder system of a baseline case with no chemical film or monolayer present on the water surface, the octadecanol/hexadecanol/lime mixture, the silicone film and octadecanol suspension each spread randomly over a still water surface. UV illumination in these stills was provided by the 396 nm UV point source fixed to the top of the UVCorder system. Comparison images taken by the visible spectrum camera with illumination provided by standard indoor lighting are shown in Figure 7 (B2) for the octadecanol/hexadecanol/lime mixture, Figure 7 (C2) for the silicone film and Figure 7 (D2) for the octadecanol suspension. From these images it is clear that the stills produced by the UVCorder extract much more detail of the spread and distribution of the chemical films/monolayers, especially the silicone film and the octadecanol suspension. The visible spectrum camera did detect the presence of the silicone film and the octadecanol suspension on the water surface as can be seen by the disappearance of the crosshairs in Figure 7 (C2) and Figure 7 (D2). However, the visible spectrum camera could not pick up any fine detail of the thin film spread distribution, namely the spreading patterns, clusters and streaks (around which surface water was exposed) that are depicted in Figure 7 (C1) and Figure 7 (D1). Due to its particulate based composition, the octadecanol/hexadecanol/lime mixture was readily visualised by both the UVCorder system and the visible spectrum camera. However, the UVCorder managed to better detail the spreading pattern of the octadecanol/hexadecanol/lime mixture and provide an improved perspective on the height and overall size of the octadecanol/hexadecanol/lime clusters conglomerating following the initial film deployment.

FIGURE 7

Figure 8 (A) Figure 8 (B1), Figure 8 (C1) and Figure 8 (D1) depict separate images captured by the UVCorder system of a baseline case with no chemical film or monolayer present on the water surface, the octadecanol/hexadecanol/lime mixture, the silicone film and octadecanol suspension all spread randomly over a still water surface. UV illumination in these images was provided by the Sun over a \pm 30 minute time interval close to solar noon during cloud free conditions. Comparison pictures obtained by the visible spectrum camera with illumination also provided by Sun are provided in Figure 8 (B2) for the octadecanol/hexadecanol/lime mixture, Figure 8 (C2) for the silicone film and Figure 8 (D2) for the octadecanol suspension. The increase in UV intensity produced by the completely unshaded and cloud free conditions made it difficult for the UVCorder to clearly visualise larger clusters of the chemical films/monolayers without picking up lens flare, hazing and saturation artefacts. This effect could be clearly seen in the UVCorder image taken for the octadecanol/hexadecanol/lime mixture (Figure 8 D2). The full sun images recorded outdoors by the UVCorder system did not reveal as much information on the spreading distribution as the UV images recorded indoors with the 396 nm UV point source. However, they did provide more detail than the visible photography, especially for octadecanol suspension (Figure 8 D1). Finer surface spread details were also more clearly deduced with the UVCorder system for the silicone film with several thin silicone streaks and patches apparent in the UV image which did not appear at all in the visible spectrum image.

FIGURE 8

Discussion

Monolayers and chemical films do provide a relatively good level of evaporation mitigation at a price generally much lower than other evaporation prevention methods such as hard or floating covers, shade sails and destratification. The logistical and physical effort required to deploy and maintain monolayers and chemical films is also much lower than the aforementioned alternatives which makes their use a very appealing evaporation mitigation strategy for end users, particularly those in the agricultural sector. Specifically, the silicone film costs approximately \$16 per litre with a spreading ratio of 2 litres per hectare and an estimated reapplication time of 10 days. Also, the octadecanol/hexadecanol/lime chemical film is priced at \$10 per kilogram with a spreading ratio of 0.35 kilograms per hectare and an approximate reapplication time of 24 hours (18). From these figures it is clear that over both short and extended time intervals, the continuous application of these chemical films do represent good value for money, especially considering that they have no associated start up costs. However, there are several critical environmental issues and impacts surrounding the ongoing use of these monolayers and chemical films in real-world

water reserves that need to be either eliminated or sufficiently addressed and minimised before they can be extensively employed.

Question marks exist over how the octadecanol/hexadecanol/lime chemical film, silicone film and octadecanol will influence the aquatic ecosystem over short and long time intervals. Interestingly, a sizeable number of field and laboratory investigations have shown that both hexadecanol and octadecanol pose a very minimal toxicological threat to both aquatic and terrestrial life forms such as ducks, fish, insects and plants (19, 20, 21). In addition to this, silicone film has been determined to have a negligible effect on aquatic species health and potable water quality over short time periods of no more than two weeks (22). However, as they are alcohol based, it is known that hexadecanol and octadecanol are initially broken down by solar radiation into acids and eventually down into both carbon dioxide and water. The breakdown of hexadecanol and octadecanol into an acid may affect pH levels, and in turn may have a detrimental influence upon the health of aquatic organisms living both on the water surface and in the water column (18).

The results displayed in Figure 4, Figure 5 and Figure 6 clearly show that the octadecanol/hexadecanol/lime chemical film, silicone film and octadecanol all effectively block or absorb biologically effective UV from entering the water column which may be helpful in protecting some aquatic life forms short-term. For instance, the application of chemical films/monolayers to the aquatic habitat of Bufo genus amphibians may be extremely helpful in ensuring their survival. Solar UV has been found to inhibit the development of Bufo embryos, which makes them far more susceptible to an aggressive fungal disease known as Saprolgenia ferax, which is a

worldwide amphibian killer. In water bodies less than 50 cm deep, up to 12% of a given tadpole cluster will die from the fungus, while in water bodies less than 20 cm deep, with more solar UV reaching the tadpoles, as much as 80% of a cluster will be killed (23, 24). Blaustein and Kiesecker (25) have also found that the embryo hatching rate of the mountain dwelling Cascades frog can decrease after being irradiated by solar UV radiation over an extended amount of time. Just these examples show that terrestrial solar UV has a detrimental impact upon marine organisms along with other reported reductions in reproduction, growth and development rates and an increase in DNA damage in species such as phytoplankton, zooplankton, bacterioplankton, picoplankton, fish eggs, fish larvae, seagrasses and also macroalgae (26) and as a result short term protection provided by chemical films/monolayers may be an effective means of aiding the recovery and protecting the life cycle of numerous forms of aquatic biota.

On the other hand, extended chemical film/monolayer deployment periods may gradually cause serious ecological problems as some organisms may not progressively adapt to the UV and as a result may be highly vulnerable once the chemical films/monolayers are completely removed. Also, the natural balance and breakdown of dissolved organic matter (DOM) may be disturbed and as a result may have a detrimental influence on the aquatic food chain and life cycle. A vast number of investigations including Thomas and Lara (27), Reitner *et al* (28) and Tranvik and Kokalj (29) have analysed the complex biochemical balance between solar UVB, DOM and other trace marine chemicals. From these studies it has become clear that microbial activity is enhanced by the decomposition of polymeric components of DOM down to biologically available organic compounds and other types of mineral

nutrients after intensive solar UV exposure. Additionally, the photodegradation of DOM into carbon dioxide by means of solar UV exposure is known to be a highly important source of decomposition in numerous types of marine locations (30). As the chemical films/monolayers are so effective at either absorbing or reflecting UV, it is also possible that the films will block and absorb photosynthetically active radiation (PAR) which could have a negative effect on water chemistry and may also reduce the ability of underwater plant life to perform photosynthesis. At the very least, chemical films/monolayers will influence the stratification of solar energy in a given water column, affecting the biology of underwater inhabitants, and perhaps influencing in the distribution of subsurface habitable zones.

The use of a UV camera to intercept UV reflections from chemical films and monolayers on the water surface appears to be a viable technique as it offers a higher level of visualisation capable of interpreting greater levels of surface spread detail than that offered by visible spectrum photography. Using UV photography to detect chemical films/monolayers also has the advantage against other visualisation methods such as using fine powders and indicator oils (such as talc, dodecanol and mineral oils) as it is performed remotely and does not interfere physically with the chemical films/monolayers in any way.

The UVCorder system detected more spreading distribution detail in a darkened indoors environment with just a single intense monochromatic point source in comparison to an outdoors environment with the full solar spectrum available. For the visualisation of a chemical film/monolayer inside an enclosed laboratory environment it is recommended that an evenly spaced grid of monochromatic UV point sources are

placed over the top of the water surface in order to achieve full scale illumination and to avoid any occurrence of far edge darkening, which can be seen around the edges of the UV images displayed in Figure 7 (B1), Figure 7 (C1) and Figure 7 (D1). It is also recommended that the UV photography device employed for visualisation has a peak response wavelength the same as or close to the wavelength of the monochromatic radiation source/s and that an appropriate lens is chosen with an adequate field of view so that the entirety of the illuminated water basin surface area can be seen.

From the pictures displayed in Figure 8 (B1), Figure 8 (C1) and Figure 8 (D1) it appears that a rudimentary visualisation of the chemical films/monolayers using the terrestrially available solar spectrum is possible, but is much more difficult to achieve in comparison to indoors visualisation using a less intense artificial UV source. This difficulty arises due to the incidence of inherent camera related issues such as lens flare and picture hazing arising from the oversaturation of the CCD detector caused by signal saturated pixels bleeding into neighbouring pixels, which occurs especially during cloud free conditions combined with a low solar zenith angle when solar radiative output is at is peak. For visualisation at real-world water reserves one way to reduce or possibly overcome these flare and saturation issues could be to attach a lens hood to the UV camera.

A variable proportion of UV energy hits the water and is immediately reflected back into the atmosphere towards the UV camera. The amount of reflection at the water surface is dependent primarily upon the solar zenith angle, which varies with the time of day, the season and the latitude. However, the solar zenith angle becomes less of a factor in surface reflection when cloudy skies are prominent over the water body as

the ratio of diffuse to direct solar UV increases in these conditions. As such, it is suggested that outdoors chemical film/monolayer UV visualisation be performed during periods when diffuse radiation is prevalent in the atmosphere in order to reduce the probability of the interception of intensive direct UV beams or flashes that could cause lens flare and/or saturation effects. It is also recommended that in outdoors environments UV photography should be tested for applicability at a relatively high altitude above the water reserve, either from a jetty, a tower or even from a low flying aircraft in order to effectively average out the influence of capillary wave effects on the water surface.

At this stage it is unclear which UV wavelengths are the most effective for the visualisation of each particular chemical film/monolayer. In this investigation the 396 nm point source worked well and provided a good level of surface spread detail. Further studies are required to separately test each wavelength within both the UVB and UVA wavebands to determine which wavelengths are the most readily reflected by evaporation suppressing chemical films/monolayers. Also, experiments are required to quantify if the UV reflection visualisation technique can be applied during the occurrence of low to high energy capillary wave action generated by winds in both laboratory based and real-world environments.

Conclusion

This manuscript has detailed the influence of UV radiation on evaporation suppressing chemical film monolayers and has also tested a novel method of visualising these films once they are deployed on the water surface. From viewing the results it is clear that octadecanol, hexadecanol and silicone, when applied on a given

water body, can all inhibit the propagation of UV radiation in the water column. This could have both a positive and negative influence on water chemistry and the aquatic ecosystem over an extended time period. Further studies are required to accurately quantify the extent of this influence in real-world water reserves and to deduce the potential for each of these chemical films to become a pollutant if they are not properly managed. The use of UV reflection to visualise the basic distribution of octadecanol, hexadecanol and silicone on the water surface has proven to be successful, with UV images providing far more detail in comparison to visible spectrum photography. The next logical stage in this research will be to develop an algorithm to process the raw UV images in order to calculate the total percentage spread of the films across a given surface area.

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List of Figures



Figure 1: The waterproof IL1400 detector with the UVB fluorescent lamp housed inside the felt covered measurement enclosure custom built for the chemical film and monolayer UV exposure trial series.

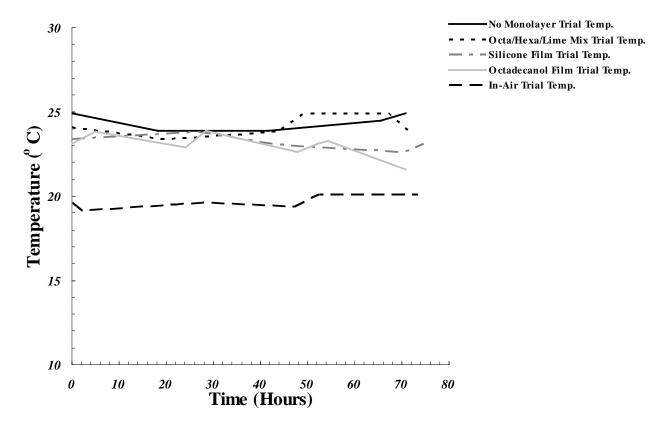


Figure 2: Evolution of ambient temperature measurements as recorded around the measurement enclosure and tank environment throughout each chemical film/monolayer underwater UV exposure trial.

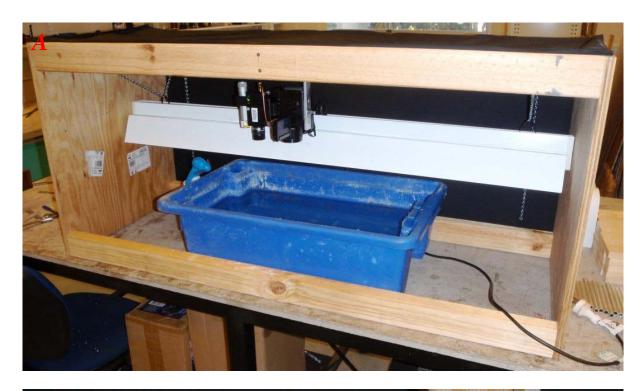
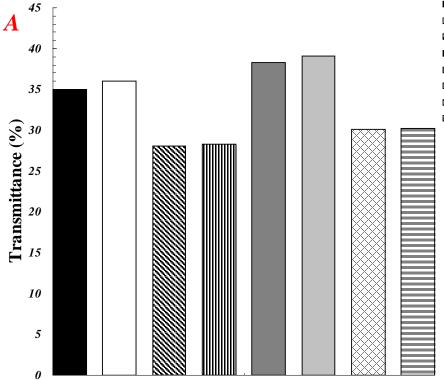
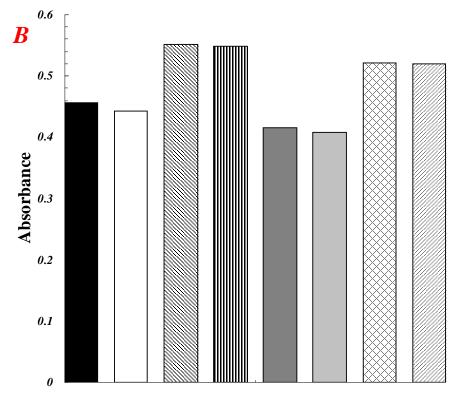




Figure 3: (A) The UVCorder UV camera system inserted inside the felt covered tank enclosure. (B) A close up of the UVCorder UV camera system with the 396 nm UV source tube, the CCD UV detector and the camcorder connected from left to right.



■ Hexa. Trans. 300 nm Before Exposure
□ Hexa. Trans. 300 nm After Exposure
□ Octa. Trans. 300 nm Before Exposure
□ Octa. Trans. 300 nm After Exposure
□ Hexa. Trans. 360 nm Before Exposure
□ Hexa. Trans. 360 nm Before Exposure
□ Octa. Trans. 360 nm Before Exposure
□ Octa. Trans. 360 nm After Exposure



■ Hexa. Abs. 300 nm Before Exposure
□ Hexa. Abs. 300 nm After Exposure
☑ Octa. Abs. 300 nm Before Exposure
Ⅲ Octa. Abs. 300 nm Before Exposure
Ⅲ Hexa. Abs. 360 nm Before Exposure
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□ Octa. Abs. 360 nm After Exposure
□ Octa. Abs. 360 nm After Exposure

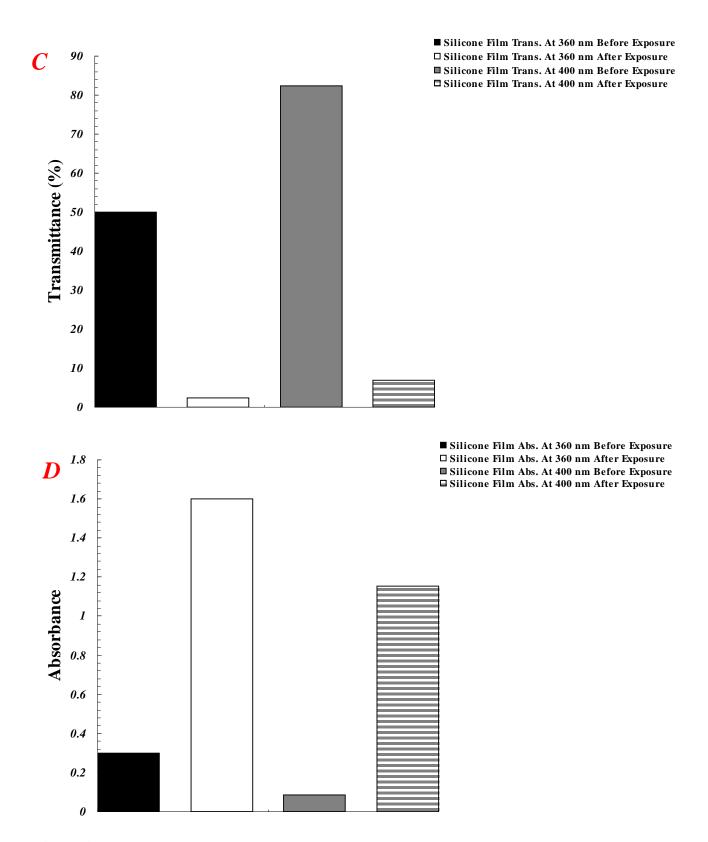


Figure 4: (A) UV transmission measurements at 300 nm and 360 nm for hexadecanol and octadecanol before and after an artificial solar UV exposure of 1.5 MJ m⁻² delivered over 13 hours. (B) UV absorbance measurements at 300 nm and 360 nm for

hexadecanol and octadecanol before and after an artificial solar UV exposure of 1.5 MJ m⁻² delivered over 13 hours. (C) UV transmission measurements at 360 nm and 400 nm for the silicone film before and after an artificial solar UV exposure of 0.4 MJ m⁻² delivered over 3 hours. (D) UV absorbance measurements at 360 nm and 400 nm for the silicone film before and after an artificial solar UV exposure of 0.4 MJ m⁻² delivered over 3 hours.

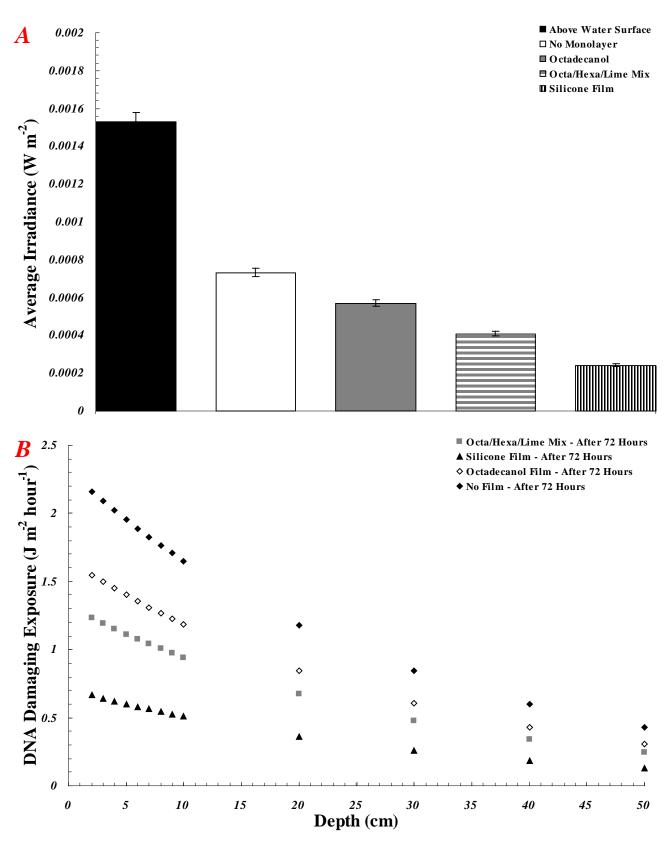


Figure 5: (A) DNA damaging irradiances averaged over an approximate 72 hour exposure time recorded at a depth of 1 cm with octadecanol, the octadecanol/hexadecanol/lime mixture and the silicone film applied to the water

surface. Also included for comparison are the average DNA damaging irradiances recorded just above the water surface and just below the water surface at a depth of 1 cm with no monolayer applied. (B) Modelled distributions of clean water column DNA damage action spectrum weighted UV exposure down to a depth of 50 cm beneath the octadecanol/hexadecanol/lime chemical film mixture, the silicone chemical film and the octadecanol monolayer after an approximate 72 hour time interval. An underwater exposure distribution for a scenario where no chemical film/monolayer was present on the water surface is also included.

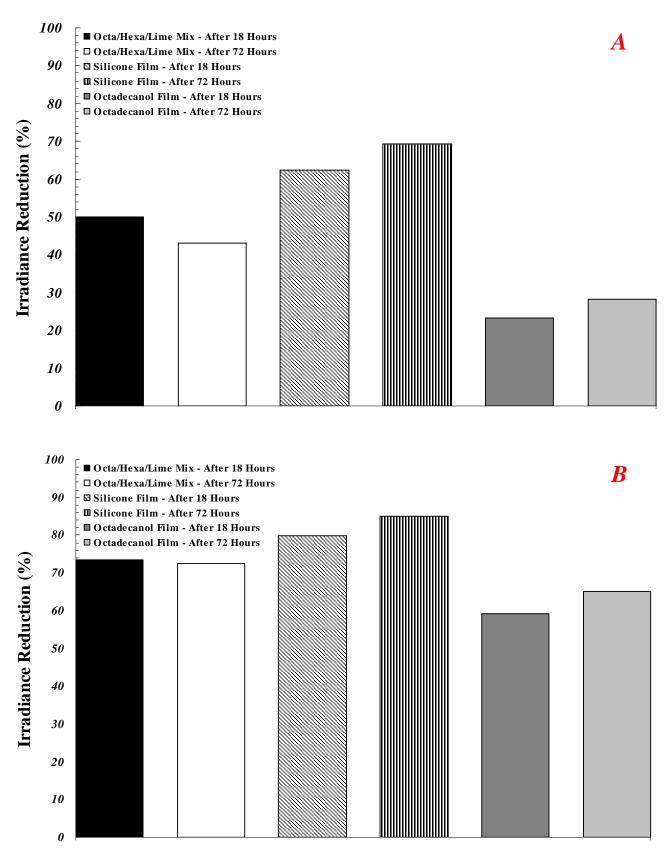
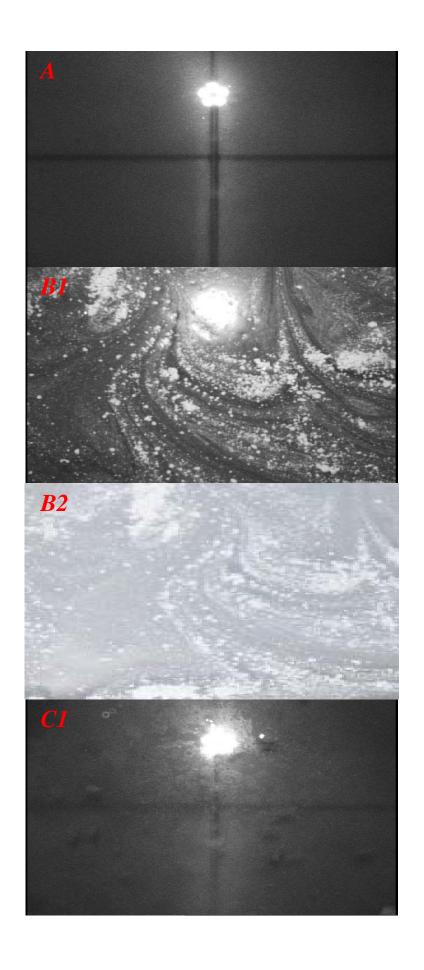


Figure 6: (A) Irradiance reduction percentage values calculated at a 1 cm depth between total subsurface DNA damaging UV exposures for the

octadecanol/hexadecanol/lime chemical film mixture, the silicone chemical film and the octadecanol monolayer and the total subsurface DNA damaging UV exposure measured without a monolayer present on the water surface after time intervals of approximately 18 hours and 72 hours. (B) Irradiance reduction percentages between the total subsurface DNA damaging UV exposures measured at a depth of 1 cm for the octadecanol/hexadecanol/lime chemical film mixture, the silicone chemical film and the octadecanol monolayer and the total DNA damaging UV exposure measured above the water surface after time intervals of approximately 18 hours and 72 hours.



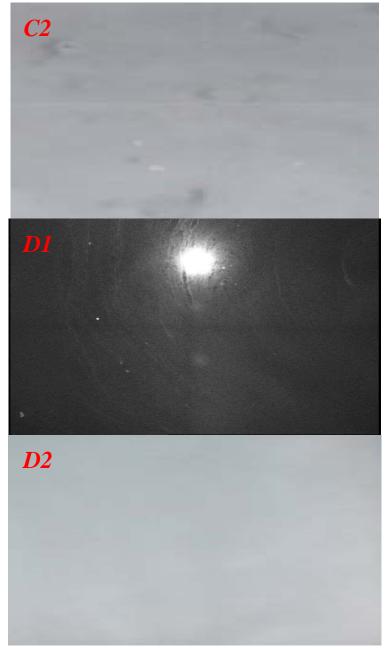
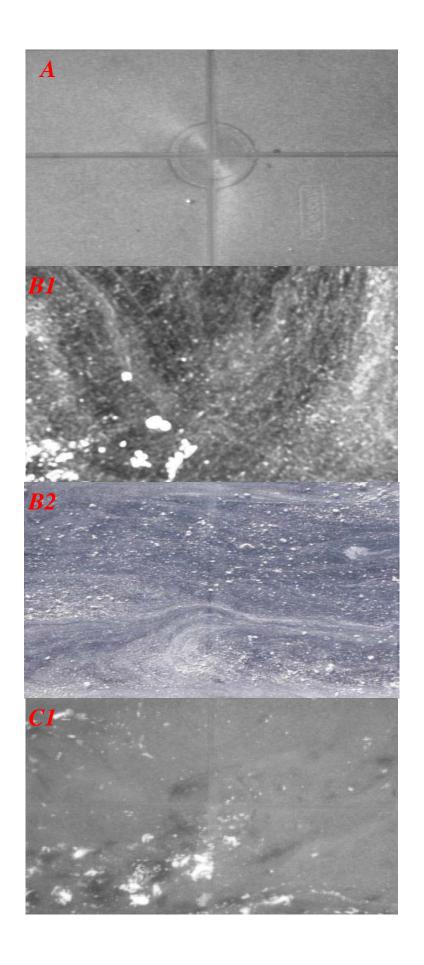


Figure 7: Example images captured by the UVCorder system: (A) A baseline case with no chemical film or monolayer present on the water surface. (B1) The octadecanol/hexadecanol/lime mixture. (C1) The silicone film. (D1) Octadecanol suspension. Illumination in these stills was provided by the 396 nm UV point source fixed to the top of the UVCorder system. The UV illuminated stills are compared to photographs taken using a visible spectrum camera with illumination provided by indoor lighting: (B2) The octadecanol/hexadecanol/lime mixture. (C2) The silicone film. (D2) Octadecanol suspension.



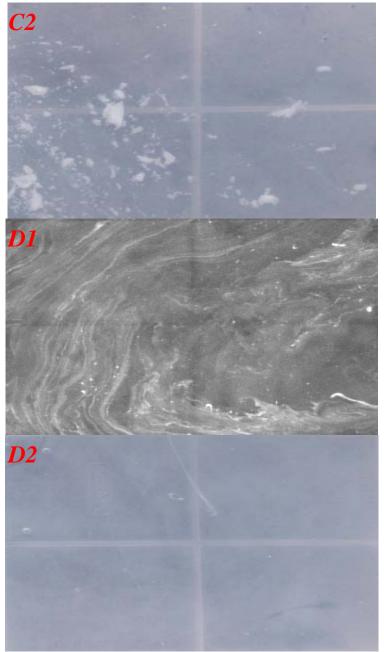


Figure 8: Example images captured by the UVCorder system: (A) A baseline case with no chemical film or monolayer present on the water surface. (B1) The octadecanol/hexadecanol/lime mixture. (C1) The silicone film. (D1) Octadecanol suspension. Illumination in these stills was provided by the Sun close to solar noon during cloud free conditions. The solar UV illuminated stills are compared to photographs taken using a visible spectrum camera with illumination provided by the Sun: (B2) The octadecanol/hexadecanol/lime mixture. (C2) The silicone film. (D2) Octadecanol suspension.