The presence of selected UV filters in a freshwater recreational reservoir and fate in controlled experiments

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Abstract

UV filters present in sunscreen and other cosmetics are directly released into the environment during aquatic recreational activities. The extent to which the wide range of UV filters pose a risk to the environment remains unclear. This study investigated the occurrence and dissipation of selected organic UV filters at a recreational site (Enoggera Reservoir, Queensland, Australia) over 12 hours. Furthermore, different possible degradation processes were investigated in a controlled off-site experiment with surface water exposed to natural light. Half-lives were estimated for ten UV filters. In Enoggera Reservoir, seven UV filters were detected, of which the most prevalent were octocrylene, avobenzone (BMDBM) and enzacamene (4-MBC). Summed concentrations of the seven UV filters ranged from 7330 ng L^{-1} at 13:00 h to 2550 ng L^{-1} at 21:00 h. In the degradation experiment, four UV filters showed no significant change over time. The fate of these compounds in the environment is likely to be mainly influenced by dispersion. Half-lives of the remaining UV filters were 6.6 h for amiloxate (IMC), 20 h for benzophenone 1, 23 h for octinoxate (EHMC), 30 h for 3-benzylidene camphor, 34 h for 4-MBC and 140 h for dioxybenzone (BP8). The degree of susceptibility to photodegradation and biodegradation was generally consistent within a structural class. The fate and half-lives of UV filters are variable and should be considered on a per site basis when assessing environmental risk.

Keywords: sunscreen agents, personal care products, degradation, environmental half-life

1. Introduction

The use of sunscreen and other personal care products containing UV filters is recommended worldwide and particularly in Australia to combat high rates of skin cancer (Koch et al. 2017; Whiteman et al. 2019). According to a 2016 survey, over 2.5 million Australians purchase sunscreen within a given four week period (Roy Morgan Research 2016). In Australia, there are 28 organic and two mineral UV filters permitted for use in sunscreen (Therapeutic Goods Administration 2016). Of the organic UV filters, only a handful are frequently used, including avobenzone (BMDBM), octocrylene (OC), homosalate and enzacamene (4-MBC). Some UV filters show endocrine activity and there is evidence that some UV filters may be toxic to coral and other aquatic organisms (McCoshum, Schlarb, and Baum 2016; Kunz, Galicia, and Fent 2006; Paredes et al. 2014; Downs et al. 2016; Park et al. 2017; Lozano et al. 2020). This has led to concern, which is heightened by the direct release of these compounds into the environment during water based recreational activities.

Organic UV filters have been detected in both marine and freshwater systems around the world, with recreational activities and the release of wastewater effluent mentioned as key sources (Ramos et al. 2015). Some of the highest concentrations found at recreational sites have been reported in Germany, the U.S.A and Hong Kong (Rodil, Schrader, and Moeder 2009; Downs et al. 2016; Tsui et al. 2014). At a lake in Germany, summer samples showed high concentrations of OC (4380 ng L^{-1}), octinoxate (EHMC) (3010 ng L^{-1}), BMDBM (2430 ng L^{-1}) and 4-MBC (1140 ng L^{-1}) (Rodil, Schrader, and Moeder 2009). Samples collected within popular reef sites in the U.S Virgin Islands showed concentrations of oxybenzone (BP3) ranging from 75 – 1400 µg L^{-1} (Downs et al. 2016). In Australia, only one study has reported UV filter concentrations in the environment, where seven UV filters were detected at concentrations up to 640 ng L^{-1} (for 4-MBC and EHMC) (Allinson et al. 2018). Most studies report individual snapshot samples and have only few have investigated spatial or short-term temporal trends. A study led by Tovar-Sánchez *et al.* (2013) found that concentrations of BP3 and 4-MBC at densely populated beaches varied together throughout the day and were highest between 14:00 and 18:00, shortly after the number of beachgoers peaked and sunscreen application was expected to be the highest. The diurnal variation of EHMC was investigated at a beach in Japan where concentrations were found to correlate with the number of bathers. EHMC concentrations gradually decreased during the night, although full attenuation did not occur, indicating persistence into the next day (Sankoda et al. 2015). Yet, these studies did not investigate or discuss the specific mechanisms that resulted in the decrease and associated fate of the UV filters over time.

Due to the potential environmental risk that UV filters present, it is important to understand their fate and behaviour in the environment. Photodegradation is suspected to be a primary process affecting the fate of many UV filters. Several studies have investigated the photostability of UV filters using photoreactor experiments (Rodil et al. 2009; Zhang et al. 2012; Semones et al. 2017; Sayre et al. 2005). Research on the photostability of UV filters originally focused on the stability of UV filters in sunscreen formulation to assess the effectiveness of the commercial products. More recently, there has been greater focus on studying the degradation of UV filters in an environmental context. A review by Ahmed *et al.* (2017) describes the photodegradation of BP3, BMDBM, EHMC and ensulizole (PBSA). The findings summarized therein indicate that photolysis of UV filters is accelerated by the presence of photosensitisers and nutrients but inhibited by dissolved organic matter (DOM) and divalent cations. However, other studies have shown photosensitisation of UV filters by DOM and indicate the importance of indirect photolysis for the degradation of some UV filters (Li *et al.*, 2016; Semones *et al.*, 2017). Hence, we have some understanding of the photodegradation of UV filters, but there is still little known about the biodegradation or overall fate of UV filters in the environment.

Using an Australian freshwater reservoir popular for water-based recreational activities as a case study, our work aimed to investigate the occurrence and daily trend of eleven UV filters. Furthermore, we conducted a controlled experiment to gain insight into the key attenuation processes for the studied UV filters including estimates of environmental half-lives.

2. Materials and methods

2.1 Chemicals and materials

High purity native standards (purity >98%) including 2,4-dihydroxybenzophenone (benzophenone 1, BP1), 2-hydroxy-4-methoxybenzophenone (BP3), 2-ethylhexyl 4-methoxycinnamate (EHMC), and 3-4-methylbenzylidene camphor (4-MBC) were purchased from AccuStandard (Connecticut, USA). 2,2-dihydroxy-4-methoxybenzophenone (BP8), 2-phenylbenzimidazole-5-sulfonic acid (PBSA) and 3-benzylidene camphor (3-BC) were purchased from Sigma Aldrich (Steinheim, Germany). 2-hydroxy-4-methoxybenzophenone-5 sulfonic acid (BP4), 2-ethylhexyl 2-cyano-3,3-diphenylacrylate (OC) and 4-tert-butyl-4'methoxydibenzoylmethane (BMDBM) were purchased from Dr. Ehrenstorfer (Augsburg, Germany). Isoamyl 4-methoxycinnamate (IMC) was purchased from Sapphire Bioscience (Redfern, Australia). Isotopically labelled internal standards included BP3-d_3 and BP1-$^{13}C_{12}$ (Sapphire Bioscience, Australia), and 4-MBC-d_4 (CDN Isotopes, Canada). Analytical grade methanol, dichloromethane, acetonitrile and hydrochloric acid were purchased from Merck Pty Ltd. (Bayswater, Australia). Water was purified using a MilliQ system, 0.22 µm filtered at 18.2 MΩ cm^{-1} (Millipore, Bedford, USA). 1000 mL Pyrex borosilicate glass beakers were sourced from Thermoline Scientific (NSW, Australia) to be used as vessels in the degradation experiment. Strata X 200 mg, 6 mL, solid phase extraction (SPE) cartridges were purchased from Phenomenex (NSW, Australia) and were used for sample extraction.

2.2 Study site and sampling

Sampling was conducted at Enoggera Reservoir, located 16 km north west of Brisbane, Australia. The site was built in 1866 as a water storage dam for Brisbane. It is no longer used for water supply and in 2014 the site was opened to recreational use. Permitted recreational activities include swimming, fishing and non-motorized watercraft use. Enoggera Reservoir has a capacity of 4 500 ML and is supplied by a 33 km^2 catchment area (Seqwater 2020). The surrounding catchment is predominately forestry and residential land with no direct input from wastewater treatment plants or septic systems.

Surface water samples were collected from Enoggera Reservoir every two hours between 9:00 and 21:00 h and additionally at noon during a warm summer day on the 12th of January 2018. During sampling and laboratory procedures, personnel avoided the use of products containing organic UV filters. Duplicate samples were collected at 9:00 and 11:00 h to account for variability in sample processing. Samples were collected within the designated swimming area several meters from the shore at a depth of approximately 30 cm (Figure S1). Swimmers and bathers were at least 1.5 m away at the time of sampling. Approximately 500 mL of water was collected in rinsed amber glass bottles. Samples were kept in a cooler for a maximum of six hours prior to being stored at 4°C in the dark prior to extraction. The number of people in the water (at any depth) within the designated swimming area at the time of each sample collection was counted and recorded as the number of swimmers.

The surface water used in the degradation experiment was collected from Enoggera Reservoir outside the swimming area in 4 L amber glass bottles. The surface water for autoclaved treatments was collected several days prior to allow time for autoclaving. Two 2 L bottles of water were autoclaved by a Tuttnauer 5075EL-D benchtop autoclave at 121 °C and 210 Kpa for 15 minutes, then cooled and stored at 4 °C. The surface water for other treatments was collected the day before the experiment and stored at room temperature.

2.3 Degradation experiment

This experiment was conducted from the 23rd - 29th of September 2019 in Brisbane, Australia (27° 29’ 12” South, 153° 1’ 52” East). The experiment consisted of four exposure variants, each conducted in duplicate. The All treatment consisted of spiked surface water accounting for all loss processes (photodegradation, biodegradation, hydrolysis and sorption). The Light treatment was filled with autoclaved water to limit the process of biodegradation (bacteria would have re-entered the system during the experiment, but they were expected to be comparatively low in numbers). The Biological treatment was fully sheltered with black plastic to limit photodegradation (headspace was provided above the beakers). Control beakers were in the dark and filled with autoclaved water to limit both photodegradation and biodegradation, accounting for losses due to sorption or volatilisation. Each beaker was filled with 800 mL of surface water set-up on plate shakers at 50 RPM outdoors exposed to full sunlight. Replicate beakers containing 800 mL of MilliQ water were placed next to the experimental setup for the whole duration to account for possible contamination (experimental set-up shown in Supplementary Information Figure S2).

Before the beakers were spiked with UV filters, replicate samples were taken from an All and a Control beaker to measure background concentrations of UV filters in Enoggera Reservoir water. Background concentrations were detected at low levels for IMC, PBSA, BMDBM, 4-MBC and BP3 ($<$ 0.2 µg L^{-1}), and OC (mean 0.7 µg L^{-1}). Each beaker was then spiked with a mixture of UV filters to reach a final concentration of 5 µg L^{-1} above residual levels. Samples were collected from each treatment at t = 2, 4, 8, 24, 48, 72 and 144 hours and from the Control and blank beakers at t = 2, 24 and 144 hours. Duplicate samples were collected from each beaker at 24 h. 5 mL aliquots were collected from the centre of the beaker using a pipette and were transferred to 7 mL amber glass vials. During sample collection, exposure of Biological and Control treatments to light was minimised. Samples were stored at -20 °C in the dark within five minutes.

The surface water used had a pH of 6.6 and a total organic carbon content of 11 mg L^{-1} at the beginning of the experimental period. Water temperature and light intensity were measured throughout the experiment and were recorded along with measurements of air temperature, sunlight hours and rainfall, provided by the Australian Bureau of Meteorology (Table S1). Any minor loss of water due to evaporation was replaced daily with the matching water using post-sampling water level markings. The volume of water added was weighed and recorded.

2.4 Sample preparation

All samples were brought to room temperature and acidified to pH 2 using 2M hydrochloric acid and spiked with labelled internal standards to achieve a concentration of 5 µg L^{-1} in the final extracts. A non-extracted side spike was made by spiking the labelled internal standards into the same volume of methanol/MilliQ water (20/80) as the final sample extracts. Enoggera Reservoir samples were weighed prior to extraction to determine sample volumes. Samples collected from Enoggera Reservoir (approximately 500 mL) and sample aliquots from the degradation study (5 mL) were extracted using the same solid phase extraction (SPE) method. Strata X 200 mg cartridges were conditioned with 6 mL of dichloromethane, 6 mL of methanol, and 12 mL of MilliQ water. Full sample volumes were loaded and passed through the cartridges at a drop wise rate assisted by pressure where needed. Cartridges were then dried and eluted with 6 mL of methanol and 6 mL of dichloromethane into glass tubes. Combined extracts were then evaporated using nitrogen to 1 mL before being transferred into 2 mL amber glass vials. Each extract was further evaporated to 100 µl of methanol and adjusted to a final volume of 500 µl, 20% methanol : 80% MilliQ water.

2.5 Analytical method

Samples were analysed on a Sciex 6500+ QTrap mass spectrometer (Sciex, Ontario, Canada) coupled to a Shimadzu Nexera 2 high performance liquid chromatography system (Shimadzu Corp., Kyoto, Japan). Analyte separation was achieved on a Phenomenex Kinetex EVO C18 column (2.6 µm, 50 × 2.1 mm). Eluents used were A = MilliQ water containing 0.1 % formic acid, and B = 99 % acetonitrile : 1 % MilliQ water containing 0.1 % formic acid. Scheduled multiple reaction monitoring was performed in positive ion mode as outlined in previous work (O'Malley et al.

2019). The isotope dilution method was employed for quantification using calibration standards prepared in 20% methanol : 80% MilliQ water. An 8-point calibration curve was used in which the concentrations of the native standards ranged from 0.1 to 100 μg L^{-1}, while the concentration of the labelled (internal) standards was constant at 5 μg L^{-1}. Instrumental detection limits ranged from 0.10 (BP1) to 0.66 (BMDBM) μg L^{-1} (Table S2). Homosalate and octisalate were included in the suite of UV filters analysed, however, due to poor sensitivity (LOD > 10 μg L^{-1}) and the resulting weak external calibration these compounds are not reported. Based on reasonable availability of internal standards, BP1-$^{13}C_{12}$ was the internal standard used to quantify BP1, PBSA and BP4, BP3-d_3 was used to quantify BP3, BP8 and IMC, and 4-MBC-d_4 was used to quantify 4-MBC, 3-BC, EHMC, OC and BMDBM. The matching of internal standard to analyte was based on similarity in absolute recovery as measured in spiked recovery tests (see section 2.7) and similarity in LC retention time. The geometrical isomers of 4-MBC, IMC and EHMC were quantified together and reported as a total.

2.6 Calculations and statistics

Calculated concentrations were log transformed and half-lives were estimated using the equation provided in the supplementary information. We observed highly variable UV filter concentrations in samples collected within the first 2 hours of the experiment. This is possibly due to incomplete mixing within the system that may have taken some time to homogenise. Because of this, these time points were not included in the calculated half-lives. Under the experimental conditions, there was natural daily sunlight variability. Despite this variability, these calculations are based on the assumption that the reaction rate is constant over time.

The half-lives from each treatment group were tested for significant differences. This was performed using a one-way analysis of variance (ANOVA) with pairwise comparison of the mean slope of each treatment group. The confidence level of the test was .05.

2.7 Quality assurance and quality control

500 mL water samples from Enoggera Reservoir were spiked with the analytes at concentrations of 0.5, 1, and 10 ng L^{-1} and the internal standards at a concentration of 5 ng L^{-1}, and were extracted by SPE to calculate method detection limits (MDL) and spiked recoveries (Table S2). MDLs were calculated at either 0.5 or 1 ng L^{-1} as the mean of seven replicates plus three times the standard deviation and ranged from 0.31 to 1.8 ng L^{-1}. Spike recoveries were calculated by comparing the mean measured signal in spiked samples (n = 7) against a matrix-free standard solution in methanol : water (20/80). The spike recoveries ranged from 33 % (BMDBM) to 120 % (PBSA). Internal standard recovery rates in the analysed samples were on average 49% for 4-MBC-d_4, 70% for BP3-d_3 and 87% for BP1-$^{13}C_{12}$, as quantified using a matrix-free standard solution in methanol : water (20/80) (non-extracted side spike) (detailed in section 2.4).

Two method blanks were extracted alongside the Enoggera Reservoir samples. Five UV filters were detected in blank samples (OC, 4-MBC, BP3, BMDBM and EHMC) at concentrations < 1 ng L^{-1}. All UV filter concentrations detected in blanks were at least three times lower than sample concentrations and no blank correction was performed.

Two method blanks and six experimental blanks were analysed as part of the degradation experiment. OC and 4-MBC were detected in blank samples at average concentrations of 0.6 and 0.5 µg L^{-1}, respectively. The relative difference between sample replicates of the degradation experiment was on average less than 20 % for BP8, PBSA, 4-MBC, BP1, BP3, 3-BC and BP4. For the more hydrophobic compounds, BMDBM, IMC, EHMC and OC, replicate variability was on average 29, 33, 55 and 61 %, respectively (Table S3). Using one-way ANOVA, we found no significant difference between the slopes of replicate experiments for any analyte. Therefore, the data from the two replicate beakers for each exposure variant were combined to estimate half-lives.

3. Results and discussion

3.1 Presence of UV filters in Enoggera Reservoir over 12 hours

Seven of eleven analysed UV filters were detected in Enoggera Reservoir water during the 12-hour time trend study (Figure 1). OC was the most dominant with concentrations ranging from 1380 – 4660 ng L^{-1}, followed by 4-MBC (436 – 1240 ng L^{-1}) and BMDBM (424 – 1130 ng L^{-1}). At least six UV filters were detected in each sample, producing summed UV filter concentrations ranging from 2550 - 7830 ng L^{-1}. The coefficient of variation of replicate samples (collected at 9:00 and 11:00) was < 15% for BP8, OC, BMDBM, 4-MBC and BP3. BP1 and EHMC were both detected at low concentrations and had a higher coefficient of variation between replicate samples (BP1: 8 and 21%, EHMC: 86 and 95%). In a German recreational lake OC was detected at the highest concentration (4380 ng L^{-1}) of nine analysed UV filters and BMDBM was also prominent at a concentration of 2430 ng L^{-1} (Rodil et al. 2009). In a recent study conducted at beaches along the French Mediterranean coast, OC and BMDBM were found in the highest concentrations of the investigated organic UV filters (Labille *et al.*, 2020). BMDBM is present within the environment although, to our knowledge, it has not often been a compound of interest in other studies. We recommend the consideration of BMDBM as a compound of interest in future UV filter studies. Labille et al. (2020) also found concentrations of mineral UV filters that were more than 100 times higher than organic UV filters in marine water. The investigation of mineral UV filters was not within the scope of this study, but we recommend investigation of mineral UV filters at recreational sites in Australia.

We identified the most commonly used organic UV filters in sunscreen in Australia through the Australian Register of Therapeutic Goods and found that the UV filters most prevalent in sunscreen products were also the most commonly detected in Enoggera Reservoir (Table S4) (Therapeutic Goods Administration 2020). IMC, BP4 and PBSA were below detection limits. This may be due to their less frequent use in Australian sunscreen. Of 100 randomly selected sunscreen products, IMC and BP4 were not used in any, and PBSA was used in 11%. 3-BC was not detected and is not permitted for use in sunscreen in Australia. BP1 is also not permitted for use in sunscreens in Australia but was detected at concentrations of 13 - 51 ng L^{-1}. It is a known metabolite of BP3 and its presence may have been due to formation from the breakdown of BP3, which was present at 17 – 26 times higher concentrations. The profile of UV filters detected contrasts with other countries, suggesting different preferences in the use of UV filters in sunscreen. For example, Tsui et al. (2014) measured 12 UV filters in seawater from various countries and found the highest concentrations of OC > BP3 > EHMC in Hong Kong. In Los Angeles, BP3 was found at the highest concentrations and OC and EHMC concentrations were 1.6 and 4.4 times lower. This suggests that the most abundant UV filters and the UV filters posing the highest risk may vary from country to country.

The summed UV filter concentrations ranged from 6170 – 7830 ng L^{-1} during daylight hours while swimmers were present (Figure 1). At 19:00 h when it is assumed sunscreen was no longer being applied, summed concentrations dropped to 3370 ng L^{-1}, and even further to 2700 ng L^{-1} at 21:00 h. Concentrations were between 29 % (BP1) and 85 % (IMC) lower at 21:00 h compared to 17:00 h. Six UV filters were still detectable at 21:00 h. The number of swimmers was 25 at 9:00 h and ranged up to 70 at 17:00 h. Sampling was conducted on a Friday, so the peak observed at 17:00 h is likely attributable to swimmers arriving after business hours. However, we did not observe an increase in concentrations at this time point, likely because sunscreen application is low or negligible at this time of the day. The greatest cumulative concentrations were observed at 9:00 and 13:00 h. We suspect that these were the times of greatest sunscreen application and reapplication. However, in this study we have no record of how many swimmers recently entered the water or are continuing swimmers from a previous time point.

We see relatively consistent concentrations during the day. This is in line with consistent sunscreen inputs that counteract attenuation by dispersion, sorption and degradation. The more variable trend in EHMC concentrations may be due to its less frequent use in sunscreen in Australia (Therapeutic Goods Administration 2020) resulting in emissions being linked to the activities of just one or several individuals. During the evening, we observed a substantial decrease in UV filter concentrations within several hours once inputs from swimmers decreased. A similar trend was observed for BP3 and 4-MBC in samples collected around Majorca Island, Spain (Tovar-Sánchez et al. 2013). The concentration decrease during the evening may be due to dispersion, degradation or sorption. However, the available information on the fate of UV filters is not sufficient to determine the specific cause of the observed decreases. To better understand the fate of UV filters in the reservoir, we carried out a semi-controlled experiment to measure the fate of UV filters in reservoir water under natural sunlight.

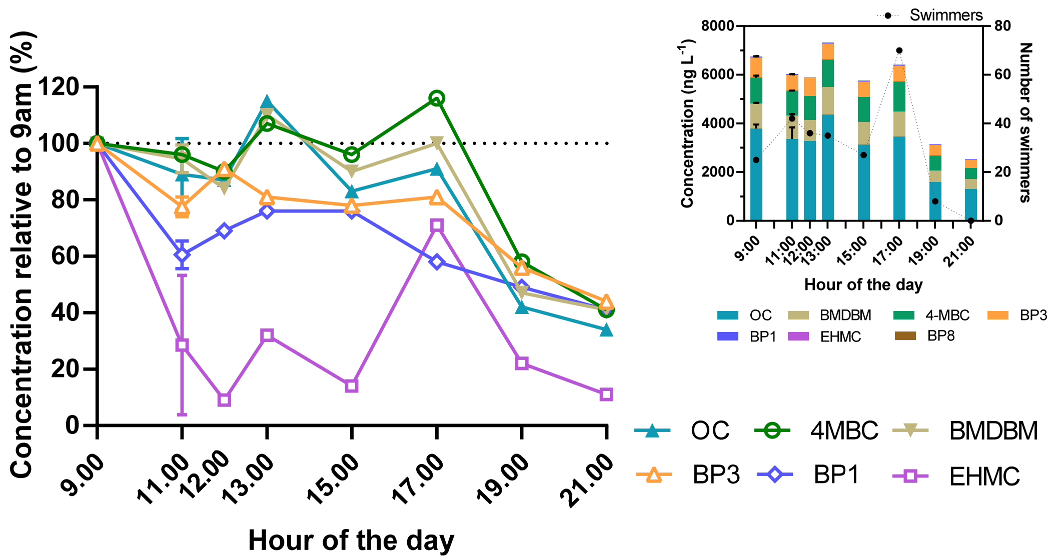

Figure 1: Trend of UV filter concentrations at Enoggera Reservoir from 9:00 to 21:00 as a percentage of the concentration measured at 9:00. Trend shown for the six UV filters detected at every time point. Insert: Cumulative concentrations of seven UV filters detected over a 12 hour period at Enoggera Reservoir swimming site. Number of swimmers shown includes all people in the water, within the marked swimming area at the time of sampling.

3.2 Degradation of selected UV filters in surface water

Initial concentrations of the test substances in the treatment beakers at T = 2 h varied across the investigated UV filters. Lower initial concentrations were observed for the hydrophobic UV filters indicating the likelihood of sorption to the beaker or potentially as a result of floatation at the water's surface. However, measurements taken after 2 hours from the control beakers (accounting for sorption losses) showed no further losses.

Of the eleven UV filters investigated, BMDBM did not show first order dissipation kinetics in the controlled experiments (graph shown in Figure S3). This may be a result of persistent background interferences or unknown mixture effects. As a result, half-lives have not been calculated for this compound. All other compounds did show first order dissipation kinetics (Figure 2). The estimated half-lives of ten UV filters under the four different treatment conditions are shown in Table 1. In the All treatment, four UV filters (BP3, BP4, PBSA and OC) showed no statistically significant dissipation, i.e. the half-life was not significantly different than infinity. BP3 is known to break down into the metabolites BP1 and BP8. However, since degradation of BP3 in this experiment was slow, any formation of BP1 and BP8 was negligible compared to the amount initially spiked into the water. The results from the All treatment indicate that BP3, BP4, PBSA and OC were not subject to measurable attenuation during the 144 h period of the experiment (Figure 2). The half-life of these chemicals in the other treatments was also not significantly different than infinity, which is consistent with this conclusion.

The half-lives of the remaining UV filters in the All treatment ranged from 6.6 h (IMC) to 140 h (BP8) (Table 1). In contrast, their half-lives in the Control treatment were not significantly different than infinity. The Control treatment accounted for potential losses due to sorption, volatilisation or hydrolysis. Since there was no significant attenuation in the Control treatment for any compound, these processes did not significantly contribute to chemical attenuation during the experiment. Further conclusions are drawn through comparison of other treatments to the Control.

In the Light treatment, the estimated half-lives for BP1, 4-MBC and 3-BC were between 21 and 37 h. For these UV filters, the half-life in the Light treatment was significantly different to the Control. Therefore, photodegradation was a significant attenuation process for BP1, 4-MBC and 3-BC. In the Biological treatment, half-lives were significantly different than infinity for six compounds. These half-lives ranged from 20 h to 180 h. IMC and EHMC show the shortest half-lives in the Biological treatment. However, no half-life in the Biological treatment was significantly different than the Control treatment.

Exploring the relative importance of the different attenuation processes, we observed three different situations. Firstly, BP8 and EHMC showed no significant differences between any treatment group and the Control. Therefore, it is not possible to conclude which process dominated attenuation. Secondly, for BP1, 3-BC and 4-MBC the half-lives in the All and Light treatments were significantly shorter than the Biological and Control treatments. There is no significant difference between the All and Light treatment for these compounds. These results indicate that photodegradation dominated the attenuation of BP1, 3-BC and 4-MBC. Finally, IMC had half-lives of 6.6 h in the All treatment, 28 h in the Light treatment and 20 h in the Biological treatment. The half-life in the All treatment was significantly shorter than all other treatment types including the Control treatment. The Light and Biological treatments were significantly different than infinity but were not significantly different to one another or the Control treatment. Therefore, the attenuation observed in the All treatment for IMC was likely due to a combination of biodegradation and photodegradation.

There is consistency between the dominant degradation processes and the molecular structure of the UV filters. The majority of the benzophenones were stable except for the metabolite BP1. BP1 was transformed by photodegradation along with the camphor derivatives, 4-MBC and 3-BC. Degradation of the cinnamate derivative IMC occurred by a combination of photodegradation and biodegradation. The observations for the other cinnamate derivative, EHMC, are also consistent with this interpretation even though no significant differences with respect to the Control treatment were observed.

Studies investigating the transformation of UV filters have usually measured the photostability of these compounds in aqueous solution under artificial sunlight. Previous studies have focused on compounds such as BP3, BP4, PBSA and BMDBM (Ahmed et al. 2017). A study of BP3 photodegradation in river water estimated a near surface average half-life of three days (Semones et al. 2017). A longer half-life was modelled by Vione *et al.* (2013), who estimated summer-time half-lives of BP3 to range from 2 to 3 weeks. They noted that the range of the half-life would increase with increasing surface water depth and dissolved organic carbon content. For BP3, our lower limit (5th percentile) estimate of the half-life was 260 h (10.8 days), which lies within the range of the previous studies. There is a limited number of studies investigating other UV filters, such as BP4 or PBSA. Photodegradation half-lives for BP4 and PBSA have been estimated to be 4 days and from 3 to 35 days in natural water, respectively (Semones et al. 2017; Zhang et al. 2012). To our knowledge, the photostability of BMDBM has only been tested in sunscreen films and solvent solutions (Huong et al. 2008; Sayre et al. 2005). As such, there is no information on the half-life or dominant attenuation processes of BMDBM in the environment. OC has been shown to be stable in pure water under artificial sunlight (Rodil et al. 2009). However, the stability of OC in natural water has not been tested to our knowledge.

The biodegradation of UV filters in water has also been rarely investigated. A study of the biodegradation of BP3 under various redox conditions found that BP3 was well degraded by microorganisms (Liu et al. 2012). Biodegradation half-lives ranged from 4.3 - 10.7 days with anaerobic biodegradation being the more favourable attenuation mechanism for BP3. These half-lives are similar to photodegradation half-lives found in other studies. However, generally there is little published about the dominant attenuation processes of UV filters.

Table 1: Half-lives of the UV filters in the four different treatments. The mean, 5% confidence interval and 95% confidence interval are shown. Statically significant differences of the mean half-life between the treatments are labelled as follows: P value <.01 (**), < .001 (***). na indicates a slope not significantly different from zero.

	Half-life (hours)

	All ^{A}			Light ^{B}			Biological ^{C}			Control ^{D}		
	5% CI	**Mean**	95% CI	5% CI	**Mean**	95% CI	5% CI	**Mean**	95% CI	5% CI	**Mean**	95% CI
BP3	260	na	na	400	na	na	330	na	na	130	na	na
BP4	200	**450**	na	130	**1400**	na	149	**390**	na	50	**4400**	na
OC	79	na	na	110	**790**	na	150	na	na	69	**7000**	na
PBSA	480	na	na	610	na	na	250	**1000**	na	40	na	na
BP8	92	**140**	330	120	**220**	990	170	**630**	na	39	na	na
EHMC	14	**23**	55	20	**29**	49	14	**20**	37	10	**430**	na
BP1	18	**20** $^{**C, D}$	22	17	**21** $^{**C, D}$	29	97	**180**	1400	47	**140**	na
3-BC	25	**30** $^{**C, D}$	38	26	**30** ^{**C,D}	36	100	**180**	969	79	**160**	na
4-MBC	31	**34** $^{***C, D}$	38	33	**37** $^{**C, D}$	42	110	**170**	480	43	**290**	na
IMC	5	**6.6** $^{**B, C, D}$	9.6	19	**28**	52	13	**20**	39	12	**33**	na

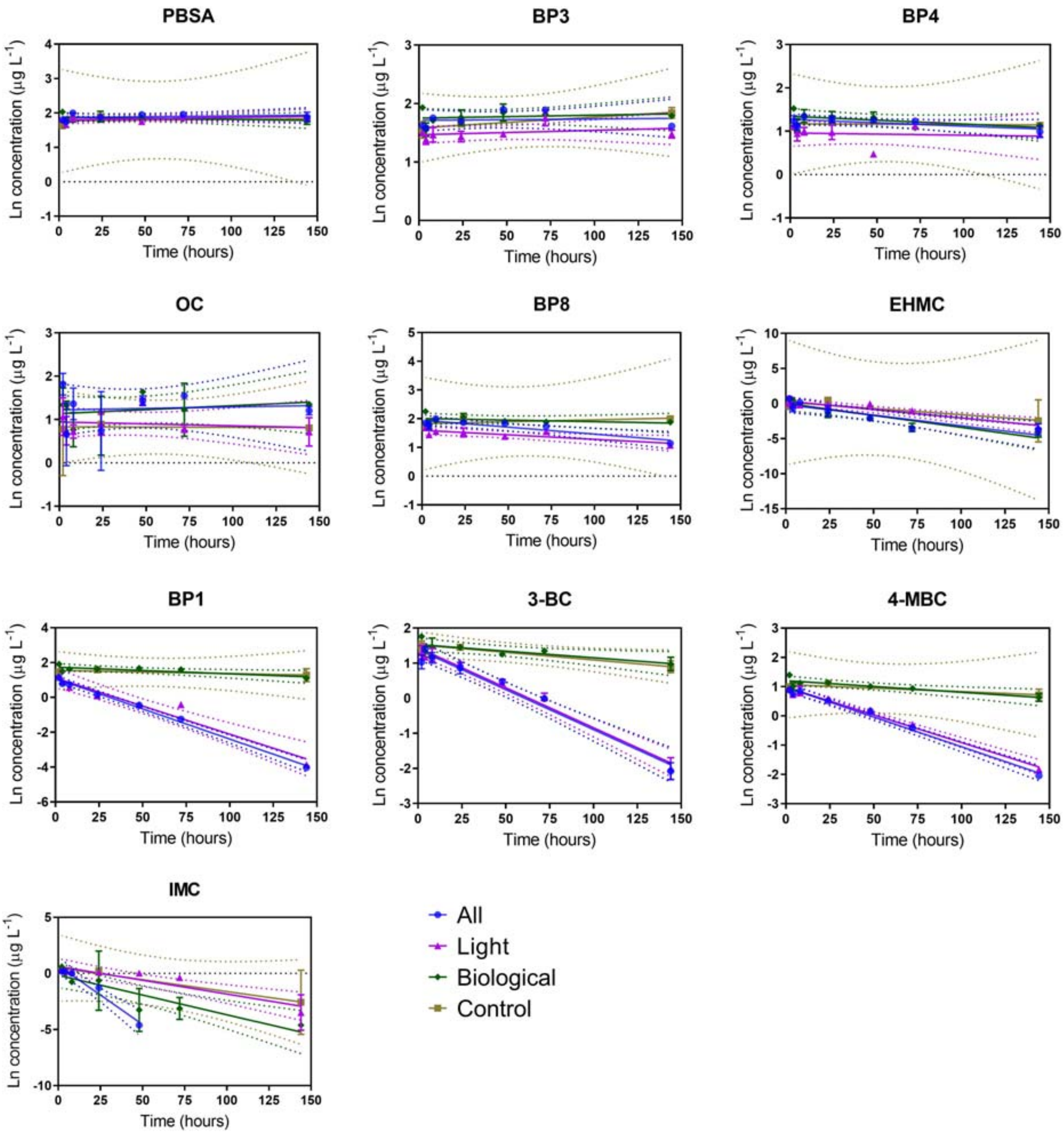

Figure 2 Linear regressions showing the attenuation of the investigated UV filters over 144 hours across four different treatments. Each point is the average of two replicate experiments while the error bars show the 95% confidence interval.

3.3 Limitations and environmental significance

The degradation experiment in this study represents a near surface high irradiation situation under natural sunlight. A strength of the experiment is that it used natural sunlight conditions and incorporated the day/night cycle. However, the test water was not exposed to the full spectrum of light due to filtering by the glass beaker. UVA light will have passed through the beakers while almost all UVB light will have been blocked. We calculated that at noon, the angle of the sun allowed direct light exposure to at least 20% of the water surface. For compounds that undergo photodegradation, half-lives in a deep water column are expected to be longer than the estimated half-lives. In addition, during times of recreation within Enoggera Reservoir there is likely to be sediment disturbance causing increased mixing and resuspension of particulate matter that may reduce photodegradation rapidly with increasing depth. There may also be differences in the environmental fate of UV filters from sunscreen products compared to the pure compounds. We recommend future degradation studies also investigate UV filter fate and degradation in the environment after skin application.

We observed biodegradation within the study, indicating the presence of a microbial community that facilitated degradation of some of the UV filters. However, due to periodically high water temperatures in the beakers we do not expect the microbial community to have remained the same as was originally present in Enoggera Reservoir. Therefore, the observed biodegradation may not have been fully representative of conditions in Enoggera Reservoir. These results provide an indication of the potential for these compounds to be biodegraded in natural freshwater.

The degradation of UV filters observed in the controlled experiments does not account for the rapid loss that we observed in the field. Furthermore, in the field, almost all compounds show the same trend of loss, while the behaviour of chemicals in the degradation experiment is varied. The observed daily trends are therefore likely to be largely a result of dilution. The effect of dilution will vary across sites, where greater dissipation is likely at open beach sites with increased currents and lower dissipation via dilution is likely in shallow bays or pools. As a result, the hydrology and flow rate of an area is an important factor in determining the potential risk of UV filters in the aquatic environment.

At sites with limited flow, degradation is likely to play a role and, given regular inputs, accumulation of UV filters is possible. Enoggera Reservoir receives daily input of UV filters providing a possibility for long term accumulation of persistent UV filters. The estimated half-lives are sufficiently long to exceed the typical time between inputs suggesting that there may be potential for these UV filters to accumulate. IMC may be an exception to this because of its shorter half-life (6.6 h).

UV filters are also widely present in the marine environment. Chemical attenuation can differ between freshwater and seawater (Li *et al.* 2016). It has been shown that salinity and high DOM reduce direct photolysis, while the presence of nutrients can increase the photolysis of some benzophenones (eg BP1, BP3, BP8) (Kotnik et al. 2016).

4. Conclusion

Over the 12-hour sampling period at Enoggera Reservoir, seven detected UV filters showed similar concentration time trends. The highest concentrations were found for OC followed by 4-MBC, BMDBM and BP3. These most prevalent compounds are consistent with the most prevalent compounds used in Australian sunscreens. For the studied UV filters under a controlled experiment, we identified class dependent attenuation processes. Four UV filters had half-lives significantly different to the control treatment and all UV filters except for IMC had half-lives greater than 18 hours. We observed that dispersion played a large role in the fate of UV filters within the recreational area at Enoggera Reservoir. Nevertheless, the persistence of UV filters can be important when assessing their environmental risk, particularly at sites with still water or low DOM concentrations. Future research into the degradation mechanisms of UV filters in freshwater and the marine environment is recommended.

Conflicts of Interest

There are no conflicts of interest to declare.

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