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**Photoreactivity of
TEP**

E. Ortega-Retuerta

Effects of ultraviolet B radiation on (not so) transparent exopolymer particles

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Abstract

Transparent exopolymer particles (TEP) are the most ubiquitous gel particles in the ocean and form abiotically from dissolved precursors. Although these particles can accumulate at the ocean surface, being thus exposed to intense sunlight, the role of solar radiation on the assembly and degradation of TEP is unknown. In this study, we experimentally determined the effects of visible and ultraviolet B (UVB) radiation on (1) TEP degradation (photolysis experiments), (2) TEP assembly from dissolved polymers (photoinhibition experiments) and (3) TEP release by microorganisms. Solar radiation, particularly in the UVB range, caused significant TEP photolysis, with loss rates from 27 to 34% per day. Dissolved polysaccharides did not increase in parallel. No TEP were formed under UVB, visible or dark conditions, indicating that light does not promote TEP assembly. UVB radiation enhanced TEP release by microorganisms, possibly due to cell deaths, or as a protective measure. Increases in UVB may lead to enhanced TEP photolysis in the ocean, with further consequences for TEP dynamics and, ultimately, sea-air gas exchange.

1 Introduction

Transparent exopolymer particles (TEP), defined as large, sticky particles, stainable with alcian blue (Alldredge et al., 1993), are the most ubiquitous gel particles in the ocean (Passow, 2002a; Verdugo et al., 2004). TEP are predominantly formed by spontaneous self-assembly of dissolved precursors, mostly acidic polysaccharides that are released by microorganisms (Passow and Alldredge, 1994). TEP facilitate aggregation and carbon export from the surface to deep waters acting as the matrix of large aggregates (Passow et al., 2001; Engel et al., 2004). However, the density of TEP is low and, unballasted, TEP move upward (Azetsu-Scott and Passow, 2004; Mari, 2008), accumulating in the surface microlayer (SML) (Wurl and Holmes, 2008). This microlayer, about 100 μm thick, is located at the air-ocean interface, and is enriched in organic and

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inorganic matter, especially in surface-active compounds (Sieburth et al., 1976). The SML can severely affect exchange processes between the ocean and atmosphere, including the retardation of air–sea gas exchange (Frew, 1997). Relative partitioning of TEP between the aggregated fraction that sediments and the fraction that accumulates at the sea surface may determine carbon flux.

To date, the effects of solar radiation on organic matter dynamics have been mostly focused on chromophoric and humic substances. These organic compounds are susceptible to photodegradation to lower molecular weight compounds and inorganic forms (dissolved inorganic carbon, carbon monoxide and dioxide) (Kieber et al., 1990; Mopper et al., 1991; Miller and Zepp, 1995; Reche et al., 1999). In turn, humic-like compounds can be generated by sunlight-mediated condensation of dissolved fatty acids derived from phytoplankton (Kieber et al., 1997). Despite the potential for phototransformations of TEP, to our knowledge there is no specific information of the effect of solar radiation, both in the ultraviolet (UV) and visible ranges, on TEP assembly from their dissolved precursors or vice versa. The polysaccharide content and gel character of TEP confer high transparency to these particles in the visible range (Alldredge et al., 1993; Passow, 2002a) and suggest low photoreactivity in this range (i.e. chemical changes associated with photon absorption).

However, Orellana & Verdugo (2003) found that ultraviolet B (UVB) radiation can block the abiotic self-assembly of dissolved organic polymers into gels, and may completely disperse preexisting gels. The proposed mechanism for this breakage is a loss of anionic charge, which would lead to a decline in polymer network stability. Moreover, polysaccharides such as alginic acid, pullulan and laminarin can also be photolysed at high UVB levels (Kovac et al., 2000; Akhlaq et al., 1990). We hypothesized that UVB radiation will decrease TEP concentration, both by photolytic dispersion of existing TEP and by inhibiting TEP assembly. High UVB radiation at the surface of the ocean makes this effect especially important for TEP standing stock in the SML, where a reduction in TEP would presumably have significant effects on the gas exchange between the atmosphere and ocean.

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In this study, we experimentally tested three hypotheses: First, UVB radiation can disperse pre-assembled TEP into their dissolved precursors (photolysis). Second, UVB radiation can block the self-assembly of dissolved precursors to form TEP (photoinhibition). Third, TEP generation rate by microorganisms is a function of the light exposure.

2 Material and methods

2.1 Experimental set-up

Different types of experiments were performed to test the three hypotheses (Table 1). North Sea water (collected from two locations at the German Bight, between 53° and 54° N and 7° and 8° E), was used in four of the experiments, and three were conducted with water from a batch culture of *Chaetoceros affinis*, a diatom species known to produce large amounts of TEP and their dissolved precursors (Passow and Alldredge, 1994). The culture was grown in f/2 media based on North Sea water, with a photoperiod of 12 hours light-12 hours dark at an irradiance of $150 \mu\text{mol photon m}^{-2} \text{s}^{-1}$ and harvested in the exponential growth phase.

Two experiments were conducted with natural solar radiation by incubating outdoors on the laboratory roof in a water bath (Table 1) with a mean light dose of 0.05 W m^{-2} at UVB, 3.52 W m^{-2} at UVA, and $660 \mu\text{mol photon m}^{-2} \text{s}^{-1}$ at photosynthetically active radiation (PAR). Five experiments were conducted indoors inside a culture room at constant temperature (15°C) under regulated, artificial light regimes with 18:6 hrs light: dark under UVB and PAR lamps, yielding a light dose of 0.15 W m^{-2} at UVB, 5.86 W m^{-2} at UVA, and $10 \mu\text{mol photon m}^{-2} \text{s}^{-1}$ at PAR.

2.1.1 TEP photolysis experiments

A total of three experiments to determine if TEP photolysis is significant were conducted. All three experiments were conducted inside culture rooms. Experiment 1 was

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performed with natural North Sea water and experiments 2 and 3 with the filtrate of *C. affinis* culture. North Sea water or water from the batch culture of *C. affinis* culture were sequentially filtered: first through a 40 μm mesh, then through precombusted GF/C and GF/F glass fiber filters ($\approx 1.2 \mu\text{m}$ and $\approx 0.7 \mu\text{m}$, Whatman) and then by 0.2 μm polycarbonate filters (Poretics). This procedure removed all particles, but filtrates contained (dissolved) TEP-precursors. This filtrate was subsequently incubated in a Couette flocculator for 24 h at a shear rate of 33.3 s^{-1} to promote the formation of TEP from precursors. A Couette flocculator consists of a fixed inner and a rotating outer cylinder which provide a quantifiable 2-dimensional laminar shear in the annular space between them (Duuren, 1968). Incubation in a flocculator under these conditions enhances TEP formation from dissolved precursors (Passow, 2000). The resultant TEP-enriched, but organism-free water was used in the experiments on TEP photolysis. Each experiment consisted of three treatments in triplicate: (1) **+UVB** (water incubated in 50 mL quartz bottles, transparent to UVB, UVA and PAR light), (2) **-UVB** (water incubated in 50 mL borosilicate bottles, opaque to UVB light and transparent to UVA and PAR light), and (3) **dark** (water incubated in aluminium-covered borosilicate 50 mL bottles).

Samples were collected initially, after 1.5 and after 3 days to measure concentrations of TEP, dissolved mono- and polysaccharides (DTCHO) and bacterial abundance. Bacteria concentration had to be monitored because bacteria generate and utilize TEP (Passow, 2002b; Stoderegger and Herndl, 1999) and may pass throughout 0.2 μm filters (Hahn, 2004).

Normalized TEP photolysis rates were calculated after the following expression:

$$-\Delta\text{TEP}(\text{d}^{-1}) = \frac{(\text{TEP}_{t_f} - \text{TEP}_{t_0})/t}{\text{TEP}_{t_0}} \times 100$$

where t_f and t_0 are final and initial times respectively and t is incubation time in days.

2.1.2 TEP photoinhibition

A total of 3 experiments were conducted to assess the role of solar radiation on the self-assembly of dissolved polymers to form TEP. We used natural (experiment 4) or artificial light (experiments 5 and 6), and water from either the North Sea (experiments 4 and 5) or from the *C.affinis* culture (experiment 6). The water was filtered through 0.2 μm to eliminate phytoplankton, bacteria and TEP. This $<0.2 \mu\text{m}$ filtrate was used directly to initiate the experiments. Each experiment consisted of the same three treatments (+UVB, -UVB, dark, each in triplicate) as described above, in this case using 250 mL quartz or borosilicate bottles for all treatments. Samples were collected initially, and after 1.5 and 3 days to determine TEP and DTCHO concentration as well as bacterial abundance. We confirmed the presence of dissolved TEP-precursors in the water used for experiments by incubating an aliquot of the $<0.2 \mu\text{m}$ filtered water in a Couette flocculator for 1 day in the dark and determining TEP formation rate.

2.1.3 Influence of solar radiation on TEP generation in the presence of microorganisms

Experiment 7 was conducted with unfiltered (whole planktonic community) North Sea water. The experiment consisted of the same three treatments as the prior experiments using 250 mL bottles, with 3 replicates each, and was conducted under natural solar radiation. Samples were collected initially, and after 4.5 and 9 days for the determination of TEP and DTCHO concentrations.

2.1.4 Methodological tests

Three types of methodological experiments were conducted to test our experimental set-up.

The light transmission through the borosilicate and quartz bottles, respectively, was measured by placing quartz and borosilicate pieces inside a spectrophotometer. The

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transmission through the quartz bottles was around 90% in the whole spectra, whereas through the borosilicate bottles it was zero in the UVB range and over 60% in the UVA and PAR ranges (Fig. 1a).

The presence of chromophoric groups (e.g. double bonds, rings, etc.) is indicative of the susceptibility of an organic compound to react with solar radiation, and absorption in the UV range suggests photoreactivity under UV light. We measured absorbance spectra (250 to 500 nm) of the acidic polysaccharides xanthan gum (3.4 mg L⁻¹) and alginic acid (5.5 mg L⁻¹) to determine if TEP-like substances absorb in the UV range. Absorbance was converted to Napierian absorption coefficients in m⁻¹ (Miller, 1998). Xanthan gum and alginic acid have been used as model substances for TEP in the past. Although they are transparent in the visible range, both compounds exhibited significant absorption in the UV range (Fig. 1b).

Given the surface-active character of TEP, loss due to TEP sticking to bottle walls was a concern. This potential loss to the bottle walls could possibly differ as a function of light regime. We incubated in duplicate the model substances xanthan gum and alginic acid (same concentrations as above) in quartz bottles that were covered with aluminium foil (dark treatments) or not (+UV), under natural solar radiation (laboratory roof) for three days. We measured the xanthan gum and alginic acid concentration before and after vigorously shaking the bottles to remove attached polysaccharides from bottle walls. In dark treatments, concentration of both polysaccharides did not change significantly (t-test, $p > 0.05$) during the incubation, suggesting loss processes, including those to bottle walls, to be unimportant. Moreover, no significant difference was observed in the concentration of polysaccharides before compared to after vigorous shaking (Fig. 1c), emphasizing that loss due to adhesion to bottle walls must have been insignificant. A significant decrease in both xanthan gum and alginic acid was observed in +UV treatments compared to the dark treatments or compared to initial concentrations (Fig. 1c), suggesting loss due to UV-irradiation as the only loss process of significance.

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3 Chemical and biological analyses

3.0.5 Transparent Exopolymer Particles (TEP)

TEP was determined following the colorimetric method of (Passow and Alldredge, 1995). Briefly, TEP were filtered onto 0.4 μm polycarbonate filters, stained with Alcian Blue solution, the filters soaked in 80% sulphuric acid for 3 h and measured spectrophotometrically at 787 nm, using empty but stained filters as blanks. Alcian Blue absorption was calibrated using a xanthan gum solution. TEP concentration was expressed in μg of Xanthan Gum equivalents per litre. The detection limit of the method was 2.2 μg XG eq L^{-1} and the coefficient of variation was 13%.

3.0.6 Dissolved Mono (DMCHO) and polysaccharide (DPCHO)

Samples were filtered through pre-combusted (Whatman GF/F) glassfiber filters and stored in pre-combusted glass scintillation vials at -20°C until analysis. DMCHO and DPCHO were analyzed following the ferricyanide reaction before (DMCHO) or after (DPCHO) hydrolysis by oxidation of the free reduced sugars (Myklestad et al., 1997). The reagents and standard solutions were made up in MilliQ water. Reagents were calibrated using a standard curve made of d-glucose, and triplicate reagent blanks in MilliQ water were subtracted. Concentrations were expressed in μmol of glucose carbon equivalents per liter (μmol gluc-C L^{-1}). The detection limit of the method was 0.4 μmol gluc-C L^{-1} , and the coefficient of variation between samples was 7%.

3.0.7 Xanthan gum/Alginate acid

Xanthan gum and alginate acid concentrations were measured by filtering known volumes onto preweighted 0.4 μm polycarbonate filters that were subsequently dried for 2 h, and weighed again. Xanthan gum and alginate acid concentrations (μg L^{-1}) were calculated from the difference of weigh before and after filtration divided per filtered volume.

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3.0.8 Bacterial abundance

Bacterial abundance was determined by enumeration using an epifluorescence microscope. Samples of 4–10 mL were filtered onto a black 0.2 μm polycarbonate Filter (Poretics) and stained with DAPI (4,6-diamidino-2 phenylindole) to a final concentration of 1 $\mu\text{g mL}^{-1}$. Slides were stored frozen. At least 350 cells in 15 random fields were counted (Porter and Feig, 1980).

4 Statistical analyses

To test for significant differences between treatments over time in each experiment, repeated measures ANOVA tests were applied. This analysis is useful for experiments where there may be a within-treatment effect (incubation time) and a between-treatment effect (+UVB, –UVB or dark) (Sokal and Rohlf, 1995). The analysis tests three types of effects allowing to set out three hypotheses: within-treatment effect (does TEP or DTCHO change through incubation time?), between-treatment effect (are TEP or DTCHO different in +UVB, –UVB or dark treatments at every incubation time?), and between-treatment by within-treatment interactions (does the difference between TEP in +UVB, –UVB and dark treatments increase through incubation time?).

5 Results

5.1 TEP photolysis experiments

TEP concentration decreased markedly in the +UVB treatments of all the photolysis experiments. TEP concentrations were very low or undetectable after 1.5 days and at the end of each experiment (3 days). When UVB was excluded (–UVB) TEP decreased at lower rates in experiment 2 and no significant changes were observed in experiments 2 and 3. No changes (exp 1) or increases in TEP (exp 2 and 3) were

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detected in the dark treatments (Fig. 2). Repeated measures ANOVA confirmed differences between +UVB and -UVB or dark treatments to be statistically significant (Table 2).

Bacterial growth was low in +UVB and -UVB treatments, ranging from undetectable to 0.02×10^9 cells L^{-1} in +UVB treatments and to 0.3×10^9 cells L^{-1} in -UVB treatments. However, high bacterial growth was detected in the dark treatments, particularly in those experiments performed with culture filtrate (experiments 2 and 3) with bacterial concentrations reaching up to 11.4×10^9 cells L^{-1} in three days (experiment 3 dark treatment). As bacteria are able to generate TEP (Passow, 2002b), we estimated the potential contribution of bacteria to TEP production using an equation empirically obtained from incubation experiments on the production of TEP by bacteria (Ortega-Retuerta, 2008):

$$\Delta TEP (\mu g \text{ XG eq } L^{-1} \text{ d}^{-1}) = 5.73 + 5.37 \times 10^{-8} \Delta BA (\text{cell } L^{-1} \text{ d}^{-1})$$

Correction for the potential bacterial production of TEP did not change the main results: the net decrease in TEP was appreciable in +UVB treatments of photolysis experiments (1-3) and in -UVB treatments of experiments 1 and 2, with no changes in TEP in experiment 3. In the dark treatments, after the correction for bacterial contributions, no significant changes were detected in TEP concentration, suggesting that the increase in TEP in dark treatments was due to bacterial activity.

Bacteria are also able to utilize TEP, but no correction was deemed necessary for loss due to bacteria, as bacteria concentrations increased in dark treatments, where TEP concentrations increased, rather than decreased. Thus loss of TEP in +UVB and -UVB treatments may be interpreted as the result of photolysis.

In our experiments, time averaged TEP photolysis rates ranged from 27 to 34% d^{-1} in the +UVB treatments. However, photolysis rates in experiments 1 and 2 were 69 to 71% during the first 1.5 days, leading to almost undetectable TEP concentrations, whereas this rate was constant (32%) during the whole 3 days in experiment 3 (Table 3) In the -UVB treatments TEP photolysis rates ranged from negligible ($8 \pm 8\% \text{ d}^{-1}$) to $18 \pm 2\% \text{ d}^{-1}$.

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Dissolved mono- and polysaccharide (DTCHO) concentrations also decreased in the +UVB treatments of all experiments, but statistically significant only for +UVB treatment of experiments 2 ($p < 0.001$) and 3 ($p < 0.05$) (Fig. 3). In contrast, there was no consistent pattern in the -UVB and dark treatments. DTCHO photolysis rates in the +UVB treatments ranged from 2.3 ± 0.5 to $17 \pm 0.2\% d^{-1}$.

5.2 TEP photoinhibition experiments

TEP formation was low or not detectable in all treatments of experiments 4, 5 and 6 leading to non-significant differences in concentrations between treatments or over time ($p > 0.05$, Fig. 4). The flocculator test confirmed the presence of dissolved TEP precursors in the samples, as a significant amount of TEP (between 100 and 1100 $\mu g XG eq L^{-1}$, $p < 0.001$) was formed within 24 h in the water used for experiments 4 and 5. This test was not performed in experiment 6 due to the low volume of water available.

DTCHO generally decreased in all photoinhibition experiments and treatments, except for the +UVB treatment of experiment 4. The differences between treatments, like for TEP concentration, were not statistically significant ($p > 0.05$). Bacteria did not show measurable growth in any treatment of experiments 4, 5 or 6, except for the dark treatment of experiment 6, where bacteria reached an abundance of 32×10^6 cells L^{-1} .

5.3 Influence of solar radiation on TEP generation in the presence of microorganisms

In experiment 7, high increases in TEP and DTCHO (Fig. 5) were observed over the incubation period, particularly in +UVB and -UVB treatments. TEP exhibited formation rates of 17% and 11% d^{-1} in +UVB and -UVB treatments, respectively. Increases in TEP were significantly higher in the +UVB treatments, while increases in DTCHO were higher in the -UVB treatments (Table 4).

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6 Discussion

In this study, we report the first evidence of photolysis of TEP due to UVB light. The particular role of UVB radiation on TEP fragmentation or loss of integrity is consistent with the only published work on the effects of UV radiation on micro-gels (Orellana and Verdugo, 2003). Inhibition of gel assembly likely results from the destabilization of polymer networks caused by a loss of net charge. In that study, full dispersion of self-assembled gels was detected in less than 12 hours when exposed to UVB radiation at 0.5 W m^{-2} that is, a light dose 70% higher than those in our study (0.15 W m^{-2}). We obtained an average TEP photolysis rate of $31\% \text{ d}^{-1}$, which would yield complete TEP photolysis in ca. 3 days under UVB radiation. However, TEP photolysis rates were even faster, at least 69–71% per day in 2 of our experiments, leading to a complete loss of TEP in around 35 h or less. Although UVB radiation appears to dominate photolysis, UVA and PAR radiation also caused TEP photolysis to some extent, with rates up to 17% per day (Table 3). We argue that photolysis was the main loss process of TEP in our experiments (Fig. 2) as bacteria which can either degrade or generate TEP did not grow noticeably in the +UVB and –UVB treatments. Moreover, our initial tests showed that loss of TEP due to adhesion to bottle walls was insignificant also (Fig. 1). Consequently, our results indicate that photolysis may at times be a potentially significant loss process of TEP, which should be included in future TEP budgets and carbon cycling scenarios. Other known loss processes of TEP include sedimentation (Passow et al., 2001) or uptake of colloidal organic matter by flagellate grazing (Passow and Alldredge, 1994; Tranvik et al., 1993).

DTCHO generally decreased in the +UVB treatments of photolysis experiments, indicating that DTCHO were not the final products of TEP photolysis. TEP photolysis products could be other dissolved organic compounds or, alternatively, dissolved inorganic carbon forms. Photoproduction of inorganic carbon after irradiation of organic matter has been previously reported (Miller and Zepp, 1995; Mopper et al., 1991), and it would imply, therefore, a net loss of organic carbon for the system. Polysaccharides

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can also be photodegraded into monosaccharides or photomineralized into inorganic forms after the cleavage of glycosidic linkages (Kovac et al., 2000). However, the photolysis rates of DTCHO in our experiments (up to 17%) were smaller than those of TEP (27–34%, Table 3), suggesting that the surface active nature of TEP make these particles more susceptible to photolysis compared to the overall pool of polysaccharides.

No significant increases in TEP were observed in any of the treatments of the photoinhibition experiments. As we detected no TEP assembly in dark treatments, we were unable to determine if UVB inhibits the self-assembly of dissolved polymers to TEP. We can state, however, that solar radiation does not promote the abiotic self-assembly of TEP from its precursors, because the lack of TEP assembly in all treatments was not attributable to the absence of a sufficient amount of precursors in the filtered water. TEP were formed abiotically within the same water when submitted to shear. Previous studies (Mopper et al., 1995; Zhou et al., 1998; Passow, 2000) have demonstrated that freshly released precursors abiotically form larger colloids, and ultimately TEP, within hours to days, that is, in shorter incubation times than used in our experiments, in some cases even in the absence of bubbling or shear. However, it seems that in our samples TEP did not form in the absence of shear independent of light regime.

In the experiment testing TEP formation in the presence of microorganisms, TEP increased greatly under UVB radiation suggesting that UV promotes the production of TEP by organisms. The increase in TEP concentration was higher in +UVB than in –UVB treatments. The higher TEP production under UVB observed in our study could be a consequence of cell disintegration, as UVB often inhibits photosynthesis (Cullen et al., 1992; Lesser, 1996) and causes cell mortality and lysis (Agustí and Llabrés, 2007). Alternatively, the increased release of TEP due to UVB could be a protective measure; TEP may reduce penetration depths of UVB acting similar to the UV-absorbing mycosporine-like amino acids (MAAs) synthesised from macroalgae (e.g. Hoyer, 2003). The influence of UVB light on the release of TEP by organisms, suggested for the first time in this study, deserves further attention.

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7 Conclusions

We found TEP photolysis due to UVB radiation to be a significant loss process. Non-ballasted TEP migrate upward (Azetsu-Scott and Passow, 2004; Mari, 2008), accumulating in the surface microlayer (Wurl and Holmes, 2008), where they will be exposed to intense solar radiation. Photolysis of TEP at the sea surface may gain further importance in the future ocean, as increasing atmospheric CO₂ concentrations lead to increased TEP formation but also result in an increase in the fraction of TEP accumulating at the sea surface (Mari, 2008), where, as our new results imply, TEP will be lost rapidly due to photolysis. This scenario conflicts with the postulated future increase in sedimentation rate due to increased TEP production (Riebesell et al., 2007) predicting a much grimmer picture of the future. Our results combined with those of Mari (2008) suggest that sedimentation rates, and thus the efficiency of the biological pump, could decrease, despite additional TEP formation due to elevated CO₂. Ozone depletion (Madronich, 1992) may further magnify this process. Increased loss rates of TEP in the surface layer due to increased UVB radiation could lead to a more rapid decrease in TEP concentration at the sea surface, thus impacting gas exchange between the ocean and atmosphere.

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Table 1. Summary of experiments conducted.

#	Type of experiment	Sample	Incubation location
1	TEP photolysis	North Sea water	Culture room
2	TEP photolysis	<i>C. affinis</i> culture	Culture room
3	TEP photolysis	<i>C. affinis</i> culture	Culture room
4	TEP photoinhibition	North Sea water	Laboratory roof
5	TEP photoinhibition	North Sea water	Culture room
6	TEP photoinhibition	<i>C. affinis</i> culture	Culture room
7	TEP photoreactivity with microorganisms	North Sea water	Laboratory roof

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Table 2. Results of repeated measures ANOVA performed to assess significant differences in TEP concentrations among the different treatments of TEP photolysis experiments (exp. 1 to 3). Ns=not significant. Bold: significant.

Experiment	Effect	F	<i>p</i> level
1	Full solar spectrum (UVB vs. Dark)	6.3	ns
	Full sol. sp.xTime	2.15	ns
	UVB (+UVB vs. -UVB)	32.11	<0.05
2	UVBxTime	1.74	ns
	-UVB (-UVB vs. Dark)	5.44	ns
	-UVBxTime	1.74	ns
	Full solar spectrum (UVB vs. Dark)	23.6	<0.01
	Full sol. sp.xTime	7.3	<0.05
	UVB (+UVB vs. -UVB)	3.7	ns
3	UVBxTime	1.2	ns
	-UVB (-UVB vs. Dark)	7.3	ns
	-UVBxTime	2.9	ns
	Full solar spectrum (UVB vs. Dark)	509.0	<0.01
	Full sol. sp.xTime	108.9	<0.01
	UVB (+UVB vs. -UVB)	367.4	<0.01
	UVBxTime	11.9	<0.05
	-UVB (-UVB vs. Dark)	47.8	ns
	-UVBxTime	23.2	<0.05

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Table 3. TEP photolysis rates (d^{-1}) determined in +UVB and –UVB treatments after corrections by bacterial growth.

Experiment	Photolysis rate (% d^{-1})	
	UVB	–UVB
1	27 ± 5	10 ± 4
2	34	18 ± 2
3	32	8 ± 8

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Table 4. Results of the repeated measures ANOVA for differences in TEP and DTCHO among treatments in experiment 7 (TEP photoreactivity with microorganisms). Ns=not significant. Bold=significant.

Variable	Effect	F	p level
TEP	Full solar spectrum (UVB vs. Dark)	42.9	<0.01
	Full sol. sp.×Time	16.5	<0.01
	UVB (+UVB vs. –UVB)	6.5	ns
	UVB×Time	0.8	ns
	–UVB (–UVB vs. Dark)	17.3	<0.05
	–UVB×Time	1.9	ns
DTCHO	Full solar spectrum (UVB vs. Dark)	719.10	<0.001
	Full sol. sp.×Time	160.2	<0.001
	UVB (+UVB vs. –UVB)	82.7	<0.05
	UVB×Time	7.2	<0.05
	–UVB (–UVB vs. Dark)	613.0	<0.01
	–UVB×Time	124.4	<0.01

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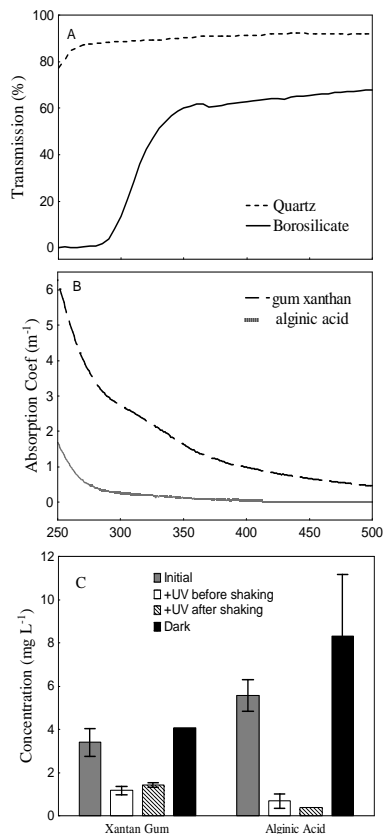


Fig. 1. Results of methodological tests performed: **(A)** Percentage of light transmission through the experimental bottles for UVB and –UVB treatments (quartz and borosilicate) as a function of wavelength measured on a spectrophotometer. **(B)** Absorption spectra from 250 to 500 nm of xanthan gum and alginic acid solutions. **(C)** concentration of xanthan gum (left columns) and alginic acid (right columns) at time 0, in +UVB treatments at final time before and after shaking the experimental bottles, and in dark controls. Whiskers=Standard Error of duplicates.

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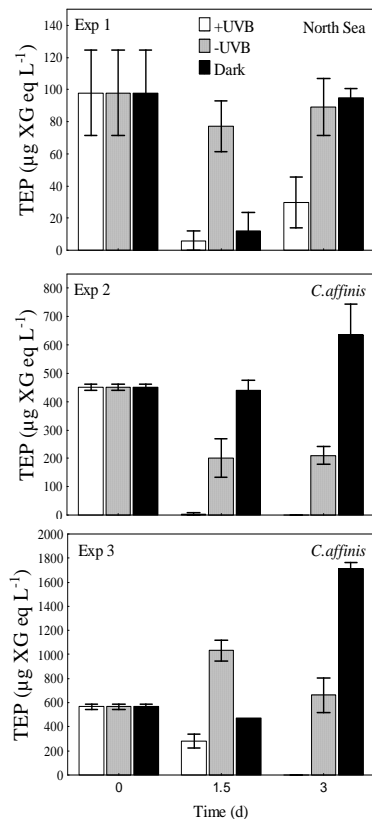



Fig. 2. Changes in TEP concentrations over incubation in the +UVB (white bars), –UVB (grey bars) and dark (black bars) treatments of photolysis experiments (1 to 3) before correcting for bacterial contributions. Whisker=Standard Error of triplicates. Note the different scales in the y axis.

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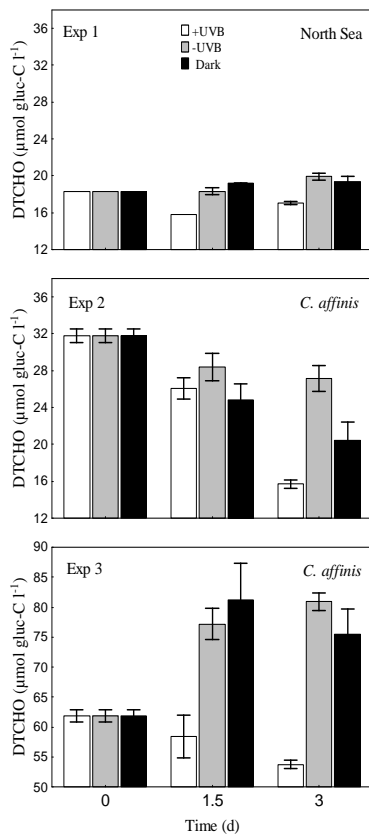


Fig. 3. Changes in DTCHO concentrations over incubation in the +UVB (white bars), -UVB (grey bars) and dark (black bars) treatments of photolysis experiments (1 to 3). Whisker=Standard Error of triplicates.

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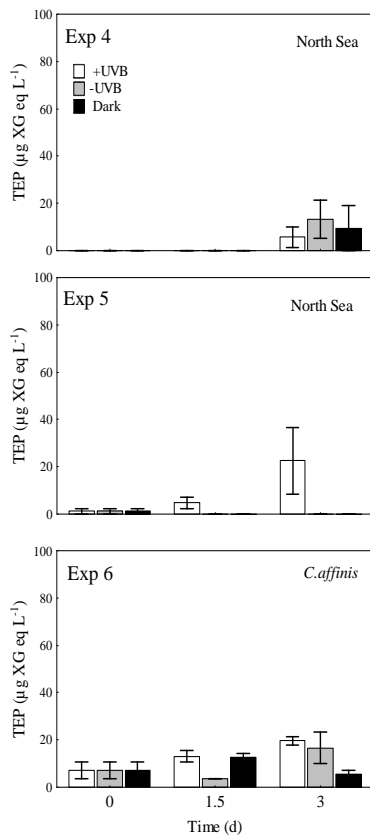


Fig. 4. Changes in TEP concentrations over incubation in the +UVB (white bars), –UVB (grey bars) and dark (black bars) treatments of photoinhibition experiments (4 to 6). Whisker=Standard Error of triplicates.

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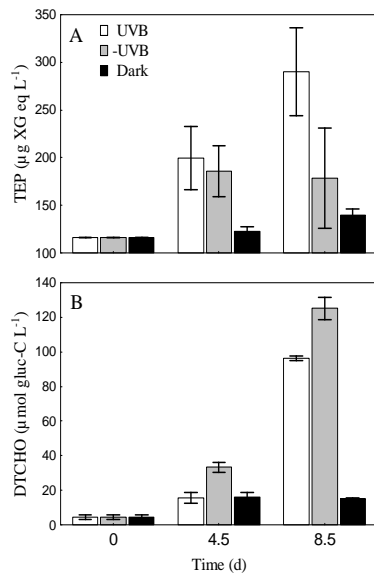


Fig. 5. Changes in TEP (A) and DTCHO (B) concentrations: +UVB (white bars), -UVB (grey bars) and dark (black bars) treatments of the TEP formation experiment with microorganisms (Exp. 7). Whisker=Standard Error of triplicates.

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