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Photo-Reactivity of Surfactants in the Sea-Surface Microlayer and Subsurface Water of the Tyne Estuary, UK

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Abstract We report the first estimates of total surfactant photo-reactivity in the sea-surface microlayer (SML) and in subsurface water (SSW) (Tyne estuary, UK; salinity 0.3–32.0). In addition to temperature, a known driver of surfactant adsorption kinetics, we show that irradiation contributes independently to enhanced interfacial surfactant activity (SA), a notion supported by coincident CDOM photodegradation. We estimate a mean SA production via irradiation of $0.064 \pm 0.062$ mg l$^{-1}$ T-X-100 equivalents h$^{-1}$ in the SML and $0.031 \pm 0.025$ mg l$^{-1}$ T-X-100 equivalents h$^{-1}$ in the SSW. Using these data, we derive first-order estimates of the potential suppression of the gas transfer velocity ($k_w$) by photo-derived surfactants $\sim$12.9%–22.2% in coastal North Sea water. Given the ubiquitous distribution of natural surfactants in the oceans, we contend that surfactant photochemistry could be a hitherto unrecognized additional driver of air-sea gas exchange, with potential implications for global trace gas budgets and climate models.

Plain Language Summary Surface-active substances (surfactants) are ubiquitous in seawater and freshwater. They accumulate in the uppermost <1,000 μm (surface microlayer), where they slow the rate of gas exchange between water and air. Improved knowledge of surfactant distributions and behavior will improve global gas flux estimates (e.g., for CO$_2$) used to inform climate models. While increased temperature is known to enhance the microlayer accumulation of surfactants, further slowing gas exchange, our knowledge of other potentially important processes (e.g., surfactant photo-reactivity) is lacking. In the laboratory, we simulated the natural solar irradiation of estuarine waters (Tyne, UK), and found surfactant enhancement additional to that from increased temperature, presumably reflecting photo-degradation of larger organic molecules. We argue that sunlight induced changes in other coastal waters, in the open ocean, and in freshwater will likely reflect differences in their organic compositions, prompting a need for wider investigation of this process.

1. Introduction

The sea surface microlayer (SML) impacts global element cycling and climate through the production, removal, and air-sea exchange of climate-active gases (Carpenter & Nightingale, 2015; Cunliffe et al., 2013; Engel et al., 2017; Upstill-Goddard et al., 2003), and by generating marine boundary layer (MBL) aerosols (Donaldson & George, 2012; Facchini et al., 1999). Natural surfactants that are ubiquitous in seawater are enriched in the SML and MBL chemistry, photochemical changes to natural SML surfactants have yet to be studied. Natural surfactants that are ubiquitous in seawater are enriched in the SML and MBL chemistry, photochemical changes to natural SML surfactants have yet to be studied. High UV irradiance promotes high SML photo-reactivity. Correlations of SML total surfactant activity (SA) with chromohoric dissolved organic matter (CDOM) absorbance (Sabbaghzadeh et al., 2017) are consistent with surfactant photo-reactivity, by analogy with CDOM photodegradation (Helms et al., 2008). Artificial surfactants produced volatile organics (e.g., isoprene and secondary organic aerosols) during irradiations of laboratory grade water (Alpert et al., 2017; Bernard et al., 2016; Fu et al., 2015), saline solutions (Ciuraru et al., 2015a, 2015b), and artificial biofilms (Brüggemann et al., 2017). CDOM and other surfactant components have been shown to undergo photo-degradation (e.g., Kieber et al., 1997; Ortega-RETuerta et al., 2009; Swan et al., 2012), but photochemical formation of amphiphilic substances (e.g., surfactants) from partial oxidation of predominantly unpolar dissolved organic matter (DOM) is plausible. While photochemistry involving SML surfactants likely modifies $k_w$ (e.g., Pereira et al., 2018) and MBL chemistry, photochemical changes to natural SML surfactants have yet to be unequivocally demonstrated. Quantifying the effect of SML photochemistry on $k_w$ and the biogeochemical cycling...
of trace gases (e.g., CO$_2$, CH$_4$, N$_2$O, and DMS) is of global significance (Cunliffe et al., 2013; Engel et al., 2017; Frka et al., 2009; Wurl et al., 2011) and critical to global climate change research (Donelan & Wanninkhof, 2002). Hence, our hypothesis is that insolation modifies SML SA, which will likely modify $k_{\text{u}}$. We therefore irradiated (solar simulator) samples from the River Tyne estuary (UK), generating the first direct evidence for photochemical changes in SML SA. We compared these data with simultaneous changes in subsurface water (SSW) SA, and with corresponding changes in spectral CDOM characteristics, to evaluate the potential for air-sea gas exchange control by photochemically derived surfactants in the SML.

2. Study Site and Sampling

The River Tyne (mean discharge 45 m$^3$ s$^{-1}$) enters the North Sea via the 35 km long Tyne estuary, which is macrotidal and partially mixed (Stubbins et al., 2011). We collected 13 estuarine samples (seven SML and six SSW: see Supporting Information S1) from four sites (TE1–TE4; Figure 1) spanning 0.3–32.0 salinity between the estuary mouth and 28 km upstream. SML sampling (June 2016–January 2017) used a Garrett Screen (Garrett, 1965) (mesh: 16, wire diameter: 0.36 μm; effective surface area: 2,025 cm$^2$) according to standard procedures (Gašparović et al., 2014) routine in our work (Pereira et al., 2016; Sabbaghzadeh et al., 2017). Visual inspection prior to screen deployment precluded SML contamination by floating debris. TE1 was accessed using waders, sampling upstream of the wader “footprint” to avoid microlayer disruption and entrainment of resuspended sediments. TE2–TE4 required a support vessel (RV Princess Royal; 17 m catamaran). While SML integrity is disrupted by a moving vessel, or when sampling from its stern (Cunliffe & Wurl, 2014; Wurl & Soloviev, 2014), the SML can be successfully sampled from a vessel's bow while on-station (e.g., Sabbaghzadeh et al., 2017; Salter et al., 2011; Kurata et al., 2016) with the ambient waterflow toward the RV (Cunliffe & Wurl, 2014). We therefore adopted this procedure, hand-deploying the Garrett Screen over the bow on the crest of a wave (Cunliffe & Wurl, 2014) and further minimizing potential contamination (engines off, wheelhouse and afterdeck downwind) (Pereira et al., 2016). Sample volumes ~15 ml per dip equated to a 65–80 μm sampling depth. 12 samples were unfiltered (Supporting Information S1) to retain SA associated with suspended particles (Čosović, 2005; Čosović & Vojvodić, 1987; Pereira et al., 2016; Schneider-Zapp et al., 2013). During photo-irradiation experiments SA might potentially be generated by additional processes such as suspended particle degradation, and microbial changes including cell lysis and photoprotection related transformations. To discern these from photochemically mediated changes in SA and CDOM absorbance, one sample (TE1; 30 January 2017) (Supporting Information S1) was split into 0.22 μm filtered (Millex-GP polyethersulfone [PES] membrane) and unfiltered subsamples. For the irradiations we pooled SML samples from ~65 repeat deployments at each site (1,000 cm$^3$). SSW sampling (~20 cm depth) used a clean 12-L steel bucket (Princess Royal) or 1-L polypropylene sample bottle (TE1). Sample storage bottles (1-L polypropylene) were aged (leachable organics-free), pre-washed (10% HCl acid; analytical grade water [milli-Q: ≥ 18.2 MΩ cm, Millipore System Inc., USA]), and filled to overflowing to preclude any headspace. Transport (<3 hr) and storage preirradiation (<48 hr) was at 4°C in the dark.

3. Irradiation Experiments

Irradiation experiments used a custom-designed solar simulator (Kitidis et al., 2008) and established procedures (e.g., Stubbins et al., 2011; Uher et al., 2017). The irradiation source (300 W Xenon-arc lamp: LOT Oriel; 300 nm transmission cut off) was borosilicate glass-sleeved to remove UVC radiation and surrounded by a motorized, 16 flask carousel. Total integrated spectral irradiance (247.8 W m$^{-2}$; 250–1,050 nm; ILT950, LOT Quantum Design) exceeded mean July daily surface shortwave radiation (280–850 nm) for Newcastle upon Tyne (150–200 W m$^{-2}$) (Hatzianastassiou et al., 2005) but was in the range of in situ daily maximum Global Horizontal Irradiance (GHI) during sampling (103.4–814.8 W m$^{-2}$; Supporting Information S1) (copernicus.eu/; 240–4,606 nm) (Qu et al., 2017). Three experimental protocols (Supporting Information S1) used precombusted (450°C; ≥ 4 hr), 50 ml quartz irradiation flasks: (a) irradiated samples (IS: solar simulator, 14 experiments); (b) dark controls (DC: double tin foil insulation, solar simulator, 14 experiments); (c) temperature controls (TC: double tin foil insulation, 4°C storage [Schneider-Zapp et al., 2013], 8 experiments). Sampling was at 0, 2, 4, 6, 8, and 24 hr, with 0 hr samples assumed to represent in situ conditions. Analytical constraints (irradiation duration, carousel spaces) precluded routine sample replication in individual experiments. We therefore replicated each experiment in full. Sample temperatures (unfiltered: IS, 19.1–28.5°C; DC, 17.0–24.6°C; TC, 7.6–17.3°C) were recorded.
Immediately prior to SA analysis, CDOM subsamples were immediately filtered (0.22 μm PES) and equilibrated to ambient temperature for 1 hr prior to analysis.

4. SA and CDOM Analysis

All glassware was precombusted (450°C; ≥ 4 hr), acid washed (10% HCl) and rinsed (Milli-Q) between samples. SA was analyzed by hanging mercury drop, phase sensitive AC voltammetry (797VA Computrace, Metrohm, Switzerland) (Ćosović & Vojvodić, 1998). Calibration was against a nonionic soluble surfactant (Triton T-X-100 [Sigma-Aldrich, UK]; mg L⁻¹ T-X-100 equivalents) in a 0.55 mol L⁻¹ NaCl matrix. Samples were adjusted to the ionic strength of the standards by adding NaCl solution (3 mol L⁻¹) to a maximum of 50 μL. Analytical precision was typically better than ±5%. We recorded CDOM absorbance (250–800 nm, 1 nm increments) on a UV-Visible double beam spectrophotometer (M550: Spectronic Camspec Ltd., UK), using 0.01 m pathlength cuvettes and a Milli-Q reference. We corrected for instrument drift, refractive index effects and light scattering by residual particles by subtracting the mean 650–700 nm sample absorbance (Kitidis et al., 2006). Absorption spectra were derived from:

\[ a(\lambda) = \frac{A}{L} = a(\lambda_r)e^{-S(\lambda-\lambda_r)} \] (Helms et al., 2008),

where \( a(\lambda) \) is the absorption coefficient (m⁻¹) at wavelength \( \lambda \) (nm) and \( \lambda_r \) is a reference wavelength (nm). These spectral slopes and the resulting spectral slope ratios (\( S_R = S_{275-295}/S_{350-400} \)) were used as broad indices of CDOM characteristics, including source, molecular weight, and degradation history (Helms et al., 2008; Kitidis et al., 2006).

5. Derived Quantities and Statistical Analysis

We defined SA production during irradiation (mg L⁻¹ T-X-100 eq. h⁻¹) as the difference between SA in irradiated samples (SA_{irr}) and dark controls (SA_{DC}) over time (T; 2 or 24 hr): \( SA_{irr} = SA_{irr} - SA_{DC}/T \). The SA temperature effect was estimated as the difference between SA in dark controls (SA_{DC}) and temperature controls (SA_{TC}) over time (T; 2 or 24 hr): \( SA_{temp} = SA_{DC} - SA_{TC}/T \). Following Helms et al. (2008), we derived CDOM spectral slopes (\( S; \text{nm}^{-1} \)) for the wavelength ranges 275–295 nm (\( S_{275-295} \), nm⁻¹) and 350–400 nm (\( S_{350-400} \), nm⁻¹), using:

All statistical procedures used SPSS. Data were screened for normality (Shapiro-Wilk tests), and where appropriate, comparison of means were assessed using Independent t-tests (\( d = \text{Cohen's} \ d \)), and correlations assessed.
using Kendall's Tau-b correlation coefficient ($\tau_b$; strong monotonous correlation: $-0.5 \geq \tau_b \geq 0.5$); significance at $p < 0.05$.

6. Results

In situ SA ranged from 0.15 to 1.96 mg $1^{-1}$ T-X-100 eq. (SML) and 0.09 to 1.70 mg $1^{-1}$ T-X-100 eq. (SSW), with associated enrichment factors (EF = SA$_{SML}$/SA$_{SSW}$) of 0.9–1.6; in situ CDOM $a_{350}$ ranged from 0.77 to 152.23 nm$^{-1}$ (SML) and 0.33 to 147.63 nm$^{-1}$ (SSW), with EFs of 1.0–2.3. A significant correlation was found between SA and CDOM ($r_s (11) = 0.745, p = 0.001$; data not shown). Both decreased with increasing salinity, in agreement with previously identified non-conservative mixing of CDOM in the Tyne estuary (Uher et al., 2001).

CDOM behavior over 24 hr irradiation followed established trends of decreasing CDOM with time (e.g., Fichot & Benner, 2012; Helms et al., 2008), with $a_{350}$ pseudo first-order half-lives ($t_{1/2}$) ~0.3–0.9 days. In IS, consistent increases in $S_{275−295}$ (6%–29%) and $S_r$ (12%–35%) (Supporting Information S1) imply irradiation induced decreases in CDOM molecular weight and aromaticity (Helms et al., 2008). Changes in $S_{350−400}$ were negligible over time and between experimental protocols (Supporting Information S1).

SA changes during irradiations indicated both photochemical and temperature effects in the SML and in SSW (Figure 2). For 64 of 67 time-points SA$_{IS}$ exceeded SA$_{TC}$, for all time-points (39) SA$_{IS}$ exceeded SA$_{DC}$, and for 38 of 39 time-points SA$_{DC}$ exceeded SA$_{TC}$. The data thus confirm a photochemical SA source in the Tyne estuary. The largest changes in SA$_{IS}$ occurred consistently during the initial 2 hr of irradiation and changes in both SA$_{IS}$ and SA$_{DC}$ were generally greater in the SML (SA$_{IS}$: 0.236 ± 0.108 mg L$^{-1}$ T-X-100 eq.; SA$_{DC}$: 0.108 ± 0.100 mg L$^{-1}$ T-X-100 eq.) than in SSW (SA$_{IS}$: 0.130 ± 0.042 mg L$^{-1}$ T-X-100 eq.; SA$_{DC}$: 0.068 ± 0.062 mg L$^{-1}$ T-X-100 eq.). Overall SA$_{IS}$ increase during the initial 2 hr was significantly greater in the SML than SSW ($t (8) = 2.374, p = 0.045, d = 1.242$), while no significant difference was found for that of SA$_{DC}$ ($t (11) = 0.854, p = 0.411, d = 0.475$). In general, SA$_{IS}$ increased over 24 hr in both SML and SSW (Figures 2a, 2b, 2e, 2f, 2h, 2j–2n), although some experiments showed overall decreases (Figures 2c and 2d) or no discernible change (Figure 2g and 2l). Comparison of initial SA in unfiltered and 0.22 μm filtered SML subsamples from TE1 (Figure 2g and 2h) indicated a significant particle contribution (40%). Importantly, SA$_{IS}$ increased in both subsamples during irradiation and remained higher than both SA$_{DC}$ and SA$_{TC}$, consistent with photochemical SA production.

As our experimental design precluded SML interaction with SSW or air, the variable changes in SA we observed (Figure 2) must reflect a dynamic balance between production and removal. To clarify the overall extent of SA change we subsequently consider only those production rates due to irradiation (SA$_{irr}$). Table 1 also shows that in SML samples, generally SA$_{irr}$ > SA$_{temp}$ whereas in SSW, SA$_{temp}$ > SA$_{irr}$.

A strong correlation between CDOM $a_{350}$ and SA in initial ($T_0$) samples ($r_s (11) = 0.745, p = 0.001$; Supporting Information S1), corroborates previous SA and CDOM data from estuaries and the open ocean, where SA and CDOM negatively correlate with salinity (e.g., Pereira et al., 2016, 2018; Uher et al., 2001). In many estuaries photochemical SA production could be masked by strong lateral SA gradients from the mixing of high SA river water with low SA coastal water (Pereira et al., 2016).

CDOM photodegradation (SML and SSW) coincided with SA photoproduction across the salinity range sampled (0.3–32.0). CDOM is an important seawater surfactant component (e.g., Trilstone et al., 2010) whose photodegradation in coastal and oceanic waters is widely documented (Mopper et al., 2014). Eight of 12 irradiations where CDOM was quantified showed significant positive correlations between SA and $S_{275−295}$ ($r_s (10–15) = 0.529−0.740, p = 0.003−0.027$), implying increased SA during irradiation to be consistent with decreasing CDOM.
molecular weight. We therefore contend that relatively low molecular weight surfactants are a likely by-product of CDOM photodegradation in marine waters.

We found moderately strong positive correlations between SA$_{irr}$ and initial $S_{350-400}$ ($p = 0.018$, $\tau_b = (11) 0.561$, Supporting Information S1) but not for SA$_{temp}$, or for $a_{300}$, $S_{275-295}$ or $S_R$ at $T_0$ ($p = 0.176–1.000$ and $\tau_b (7–11) = −0.50–0.429$ for all; data not shown). This suggests that the initial chemical composition and hence reactivity of the CDOM pool, rather than CDOM abundance, impacts rates of SA production during irradiation.

Figure 2. Changes in surfactant activity during 24-hr irradiations (sites TE1–TE4; Tyne estuary) for three experimental protocols: irradiated samples, dark controls, and temperature controls. Sample designations are: UF (unfiltered); F (0.2 μm polyethersulfone membrane filtered sea-surface microlayer [SML]); SML; sub-surface water. The salinity of each sample is shown in brackets.
7. Discussion and Implications

We have shown the first evidence of coincident SA photoproduction and CDOM photodegradation in marine (estuarine) waters, although photoreactions implicating specific components of the marine surfactant pool are well established (e.g., Grzybowski, 2009; Kieber et al., 1997; Ortega-Retuerta et al., 2009). Our irradiations showed typical CDOM photobleaching reflected in decreasing $a_{300}$ and increasing $S_R$ with time, indicative of decreases in DOM molecular weight.

Our irradiation data inevitably include a temperature related component due to warming that could cause increases in microbial production (e.g., Kurata et al., 2016) or the interfacial adsorption of surfactants due to entropic effects in the hydration shell (e.g., Gosálvez et al., 2009; Mohajeri & Dehghan Noudeh, 2012; Southall et al., 2002; Tielrooij et al., 2010), or an aggregate of both. At higher temperatures, the hydrogen bond network in the hydration shell is more dynamic (Tielrooij et al., 2010). Hence, an increase in temperature increases hydration shell entropy by breaking hydrogen bonds (Southall et al., 2002). Consequently, the size of the hydration shell diminishes, and surfactant adsorption density increases (Gosálvez et al., 2009). We contend that changes in surfactant adsorption behavior are a plausible driver of temperature-related SA changes because the $S_{temp}$ data showed no concomitant changes in CDOM $a_{350}$ or $S_R$. Nonetheless, microbial processing, adsorption and photo-dissolution cannot be excluded in these unfiltered water samples. Changes in CDOM spectral characteristics may be used to diagnose CDOM processing: increasing $S_{275–295}$ and $S_R$ and decreasing $S_{350–400}$ indicate photobleaching, while opposite trends indicate microbial alteration (Helms et al., 2008). However, $S_{350–400}$ changes during irradiations were negligible between sample treatments, suggesting that microbial activity followed the same trend in each.

Table 1
Surfactant Activity (SA) Production Rates (mg l$^{-1}$ T-X-100 eq. h$^{-1}$) Estimated Over 0–2 hr and 0–24 hr of Irradiation for All Tyne Estuary Samples

| Sample description | Site | 2 hr incubation | 24 hr incubation |
|--------------------|------|----------------|-----------------|
|                    |      | $SA_{irr}$ | $SA_{temp}$ | $SA_{irr}$ | $SA_{temp}$ |
| Unfiltered SML ($n = 7$) | TE1 | 0.083 | - | 0.006 | - |
|                    | TE1 | -0.004 | - | 0.006 | - |
|                    | TE1 | 0.022 | - | 0.004 | - |
|                    | TE2 | 0.083 | -0.056 | 0.004 | 0.008 |
|                    | TE3 | 0.042 | 0.056 | - | 0.006 |
|                    | TE4 | 0.035 | 0.037 | 0.006 | 0.000 |
|                    | TE1 | 0.186 | 0.057 | 0.010 | 0.005 |
| Mean ± σ | 0.064 ± 0.062$^a$ | - | 0.006 ± 0.002$^a$ | - |
| | 0.087 ± 0.070$^b$ | 0.024 ± 0.054$^b$ | 0.007 ± 0.003$^b$ | 0.005 ± 0.003$^b$ |
| 0.22 μm filtered SML ($n = 1$) | TE1 | 0.030 | 0.026 | 0.001 | 0.001 |
| Unfiltered SSW ($n = 6$) | TE1 | 0.036 | - | 0.024 | - |
|                    | TE1 | 0.033 | - | 0.004 | - |
|                    | TE1 | 0.069 | - | 0.004 | - |
|                    | TE2 | -0.006 | 0.089 | 0.015 | 0.007 |
|                    | TE3 | 0.048 | 0.052 | 0.005 | 0.001 |
|                    | TE4 | 0.008 | 0.027 | 0.001 | 0.002 |
| Mean ± σ | 0.031 ± 0.025$^a$ | - | 0.008 ± 0.009$^a$ | - |
| | 0.017 ± 0.028$^b$ | 0.056 ± 0.031$^b$ | 0.007 ± 0.007$^b$ | 0.003 ± 0.003$^b$ |

Note. SA production due to irradiation ($SA_{irr}$) is the difference in SA (mg l$^{-1}$ T-X-100 eq.) between irradiated samples and dark controls (DC) at each timepoint (divided by the appropriate time) and SA production due to temperature ($SA_{temp}$) is the corresponding difference between DC and temperature controls.

$^a$Mean and one standard deviation calculated using all available data. $^b$Mean and one standard deviation calculated using only experimental data where temperature controls were included as a sample treatment.
A noteworthy feature was that irradiation per se was an independent driver of SA production, where $S A_{irr}$ in the unfiltered SML ($0.064 \pm 0.062$ mg L$^{-1}$ T-X-100 equivalents h$^{-1}$) generally exceeded that in unfiltered SSW ($0.31 \pm 0.027$ mg L$^{-1}$ T-X-100 equivalents h$^{-1}$). Overall, SML enrichments in relatively labile DOM compounds are an established feature of coastal systems (e.g., Galgani & Engel, 2016); these compounds transfer to the SML via bubble scavenging (Hardy, 1982; Robinson et al., 2019) and can be produced in situ by microbial processing. Our data support the notion of SA photoproduction, either via the formation of new surface-active substances, or by photochemical transformations of existing surfactants allowing adsorption to the air-sea interface in greater numbers. CDOM photodegradation in parallel with SA photo-production strongly supports this concept.

Our data imply potential contributions of SML photochemistry to $k_w$ suppression by surfactants (e.g., Brockmann et al., 1982; Calleja et al., 2009; Frew et al., 1990; Mustaffa et al., 2020; Pereira et al., 2016, 2018; Ribas-Ribas, Helleis, et al., 2018; Salter et al., 2011) and to marine boundary layer aerosol and trace gas photochemistry (Alpert et al., 2017; Bernard et al., 2016; Brüggemann et al., 2017; Ciuraru et al., 2015a, 2015b; Clifford et al., 2008; Fu et al., 2015; Reeser et al., 2009; Rossignol et al., 2016) that demand further scrutiny. Pereira et al. (2018) applied a positive relationship between sea surface temperature (SST) and $k_w$ suppression at the ocean basin scale, implicating daily insolation as a driver of surfactant production via primary productivity. Our results indicate that irradiation of the SML is a likely important independent driver of SA production in addition to skin layer temperature, and consequently is an important independent control on $k_w$.

It is instructive to estimate the potential scale of such control, by re-examining $k_{660}$ ($k_w$ for CO$_2$ in seawater at 20°C) estimates for the coastal North Sea (B1–B5; Figure 1), made by Pereira et al. (2016) in a gas exchange tank, that showed strong inverse relationships with SA. We applied these to our $T_0$ irradiation data assuming them to represent in situ SA (Table 2). This resulted in $k_{660}$ values of 0.6–13.4 cm h$^{-1}$ spanning TE1–TE4 (salinity 0.3–32.0) that are typical of other coastal sites (e.g., Kremer et al., 2003; Ribas-Ribas, Kilcher, & Wurl, 2018). These are toward the lower range found to be mediated in situ by surfactants in oceanic regimes (e.g., Calleja et al., 2009; Mustaffa et al., 2020), notwithstanding any difference in CDOM and surfactant properties.

Given that our most saline SML sample (TE4: salinity 30.5, SA 0.15 mg L$^{-1}$ T-X-100 eq.; Figures 1 and 2) was closest to the salinity range (33.1–34.6) given by Pereira et al. (2016) and within the respective SA range (0.08–0.38 mg L$^{-1}$ T-X-100 eq.), we extended the Pereira et al. (2016) analysis to our 2 hr $S A_{irr}$ data for TE4, which gives $k_{660}$ suppressions of 22.2% (9.4 cm h$^{-1}$ at 2 hr; SML) and 12.9% (11.6 cm h$^{-1}$ at 2 hr; SSW) relative to $T_0$ $k_{660}$ (12.1 cm h$^{-1}$ and 13.4 cm h$^{-1}$, respectively) in coastal North Sea water. Overall, unfiltered samples gave $k_{660}$ suppressions of 15.2%–48.9% (0.4–9.4 cm h$^{-1}$ at 2 hr) in the SML and 12.9%–29.3% (0.8–11.6 cm h$^{-1}$ at 2 hr) in SSW, relative to respective $T_0$ $k_{660}$. Considering the range of $k_{660}$ suppression by surfactants (Pereira et al., 2016), gas exchange control driven by photochemical changes could be considerable.

Due to the proximity of our samples to those of Pereira et al. (2016) (Figure 1), differences in organic composition between them, even when accounting for potential temporal variability, are likely to be smaller than contrasts with other geographical regions, and we note that SML surfactant photochemistry is yet to be explored at different insolation intensities, in either oceanic waters or indeed in freshwater systems. Given that SML surfactant pool composition is likely to be important in addition to SA in controlling the magnitude of $k_w$ (Pereira et al., 2016), regional to global differences in the composition of the SML surfactant pool and the attendant temporal variability will likely be reflected in a variable photochemical contribution to $k_w$ control that demands further scrutiny.

### 8. Conclusions

Adapted parameterization of the factors controlling air-sea gas exchange is a long-standing scientific goal deemed essential to predicting global climate change. An increasing scientific focus is now on SML surfactant control of $k_w$ (e.g., Brockmann et al., 1982; Frew et al., 1990; Pereira et al., 2016, 2018; Ribas-Ribas, Helleis, et al., 2018).

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**Table 2**

| Site  | SML projected $k_{660}$ (cm h$^{-1}$): | SSW projected $k_{660}$ (cm h$^{-1}$): |
|-------|--------------------------------------|--------------------------------------|
|       | 0 hr 2 hr $\Delta$ (%) | 0 hr 2 hr $\Delta$ (%) |
| TE1   | 0.59 1.48 44.1 | 0.90 2.24 18.9 |
| TE1*  | 5.93 4.78 19.5 | - - - |
| TE2   | 3.20 2.71 15.2 | 5.04 4.14 17.7 |
| TE3   | 4.93 3.15 36.1 | 4.44 3.49 21.3 |
| TE4   | 12.14 9.44 22.2 | 13.36 11.64 12.9 |

*0.22 μm filtered SML sample.*
et al., 2018; Salter et al., 2011). Temperature is a known control of surfactant adsorption kinetics, but we have shown irradiation to be an additional, independent driver, in parallel with CDOM photodegradation. We contend that photoinduced increases in SA will likely impede $k_w$ at the global scale, with implications for the global budgets of climate-active gases. Consequently, studies of surfactant photoreactivity in a range of estuarine, coastal, and oceanic waters will be important, specifically those that examine how differences in total surfactant pool composition might differentially affect photochemistry and hence $k_w$.

Data Availability Statement

Supporting data are available in the in-text data citation references: Rickard et al. (2021), findable and accessible via the Newcastle University data repository http://doi.org/10.25405/data.ncl.17006176; Copernicus Atmosphere Monitoring Service (CAMS) (2021), generated using CAMS information accessible viaads.atmosphere.copernicus.eu/cdsapp#!/dataset/cams-solar-radiation-timeseries?tab=form, using dates and locations listed in Table S1 in Supporting Information S1 for both cloud-free and actual weather conditions in 1-hr time steps. Neither the European Commission nor European Centre for Medium-Range Weather Forecasts (ECMWF) is responsible for any use that may be made of the CAMS information or data it contains.

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References

Alpert, P. A., Csuiraru, R., Rossignol, S., Passananti, M., Tinel, L., & Perrier, S. (2017). Fatty acid surfactant photochemistry results in new particle formation. *Science Reports*, 7, 12693. https://doi.org/10.1038/s41598-017-12601-2

Bernard, F., Csuiraru, R., Boréave, A., & George, C. (2016). Photosensitized formation of secondary aerosol compounds above the air/water interface. *Environmental Science & Technology*, 50(16), 8678–8686. https://doi.org/10.1021/acs.est.6b03520

Bricaud, A., Morel, A., & Prieur, L. (1981). Absorption by dissolved organic matter of the sea (yellow substance) in the UV and visible domains. *Limnology & Oceanography*, 26(1), 43–53. https://doi.org/10.4319/lo.1981.26.1.0043

Brockmann, U. H., Hulme, H., Kattner, G., Broecker, H. C., & Hentschel, G. (1982). Artificial surface films in the sea area near Sylt. *Limnology & Oceanography*, 27(6), 1050–1058. https://doi.org/10.4319/lo.1982.27.6.1050

Brugge, J. B., Hayeck, N., Bonnieux, C., Pesce, S., Alpert, P. A., Perrier, S., et al. (2017). Interfacial photochemistry of biogenic surfactants: A major source of abiotic volatile organic compounds. *Faraday Discussions*, 200, 59–74. https://doi.org/10.1039/c7fd00022g

Caljea, M., Duarte, C. M., Prairie, Y. T., Agusti, S., & Herndl, G. J. (2009). Evidence for surface organic matter modulation of air-sea CO$_2$ gas exchange. *Biogeosciences*, 6, 1105–1114. https://doi.org/10.5194/bg-6-1105-2009

Carpenter, L. J., & Nightingale, P. D. (2015). Chemistry and release of gases from the surface ocean. *Chemical Reviews*, 115(10), 4015–4034. https://doi.org/10.1021/cr5007123

Csuiraru, R., Fine, L., van Pinxteren, M., D’Anna, B., Herrmann, H., & George, C. (2015a). Photosensitized production of functionalized and unsaturated organic compounds at the air-sea interface. *Science Reports*, 5, 12741. https://doi.org/10.1038/srep12741

Csuiraru, R., Fine, L., van Pinxteren, M., D’Anna, B., Herrmann, H., & George, C. (2015b). Unravelling new processes at interfaces: Photochemical isoprene production at the sea surface. *Environmental Science & Technology*, 49(22), 13199–13205. https://doi.org/10.1021/acs.est.5b03288

Clifford, D., Donaldson, D. J., Brigante, M., D’Anna, B., & George, C. (2008). Reactive uptake of ozone by chlorophyll at aqueous surfaces. *Environmental Science & Technology*, 42(4), 1138–1143. https://doi.org/10.1021/es0718220

Copernicus Atmosphere Monitoring Service (CAMS) information. (2021). *CAMS solar radiation time-series*. [Dataset]. Retrieved fromads.atmosphere.copernicus.eu/cdsapp#!/dataset/cams-solar-radiation-timeseries?tab=form

Čosović, B. (2005). Surface-active properties of the sea surface microlayer and consequences for pollution in the Mediterranean sea (pp. 269–296). 5K.

Čosović, B., & Vojvodić, V. (1987). Direct determination of surface active substances in natural waters. *Marine Chemistry*, 22(2–4), 363–373. https://doi.org/10.1016/0304-4203(87)90020-X

Čosović, B., & Vojvodić, V. (1998). Voltammetric analysis of surface active substances in natural seawater. *Electroanalysis*, 10(6), 429–434. https://doi.org/10.1002/(SICI)1521-4109(199805)10:6<429::AID-ELAN429>3.0.CO;2-7

Cunliffe, M., Engel, A., Frka, S., Galpazovic, B., Guitart, C., Murrell, J. C., et al. (2013). Sea surface microlayers: A unified physicochemical understanding of the sea surface microlayer. *Frontiers in Marine Science*, 10, 1–10. https://doi.org/10.3389/fmars.2017.00165

Cunliffe, M., Engel, A., Feki, S., Galpazovic, B., Guitart, C., Murrell, J. C., et al. (2013). Sea surface microlayers: A unified physicochemical and biological perspective of the air–ocean interface. *Progress in Oceanography*, 109, 104–116. https://doi.org/10.1016/j.pocean.2012.08.004

Cunliffe, M., & Wurl, O. (2014). Guide to best practices to study the ocean’s surface. Occasional Publications of the Marine Biological Association of the United Kingdom, 46(19), 10385–10389. https://doi.org/10.1017/S0025315414000071

Donaldson, D. J., & George, C. (2012). Sea-surface chemistry and its impact on the marine boundary layer. *Environmental Science & Technology*, 46(19), 10385–10389. https://doi.org/10.1021/es301651m

Donelan, M. A., & Wanninkhof, R. (2002). Gas transfer at water surfaces—Concepts and issues. *Geophysical Monograph Series*, 127, 1–10. https://doi.org/10.1029/2001GM127p0001

Engel, A., Bange, H. W., Cunliffe, M., Burrows, S. M., Friedrichs, G., Galpazovic, B., et al. (2017). The ocean’s vital skin: Toward an integrated understanding of marine surface microlayer. *Frontiers in Marine Science*, 4(1), 165. https://doi.org/10.3389/fmars.2017.00165

Fucchini, M. C., Mircea, M., Fuzzi, S., & Charlson, R. J. (1999). Cloud albedo enhancement by surface-active organic solutes in growing droplets. *Nature*, 401(6750), 257–259. https://doi.org/10.1038/45758

Fichot, C. G., & Benner, R. (2012). The spectral slope coefficient of chromophoric dissolved organic matter (S275–295) as a tracer of terrigenous dissolved organic carbon in river-influenced ocean margins. *Limnology & Oceanography*, 57(5), 1453–1466. https://doi.org/10.4319/lo.2012.57.5.1453

Frew, N. M. (2005). The role of organic LMS in air-sea gas exchange. In P. S. Liss, & R. A. Duce (Eds.), *The sea surface and global change* (pp. 121–171). Cambridge University Press.
Robinson, T.-B., Wurl, O., Bahlmann, E., Jürgens, K., & Stolle, C. (2019). Rising bubbles enhance the gelatinous nature of the air–sea interface. *Limnology & Oceanography, 64*, 2358–2372. https://doi.org/10.1002/lno.11188

Rossignol, S., Tinel, L., Bianco, A., Passananti, M., Brigante, M., Donaldson, D. J., et al. (2016). Atmospheric photochemistry at a fatty acid-coated air-water interface. *Science, 353*(6300), 699–702. https://doi.org/10.1126/science.aaf3617

Sabbaghzadeh, B., Upstill-Goddard, R. C., Beale, R., Pereira, R., & Nightingale, P. D. (2017). The Atlantic Ocean surface microlayer from 50°N to 50°S is ubiquitously enriched in surfactants at wind speeds up to 13 m s⁻¹. *Geophysical Research Letters, 44*(6), 2852–2858. https://doi.org/10.1002/2017gl072988

Salter, M. E., Upstill-Goddard, R. C., Nightingale, P. D., Archer, S. D., Blomquist, B., Ho, D. T., et al. (2011). Impact of an artificial surfactant release on air-sea gas fluxes during Deep Ocean Gas Exchange Experiment II. *Journal of Geophysical Research, 116*, C11016. https://doi.org/10.1029/2010jc007023

Schneider-Zapp, K., Salter, M. E., Mann, P. J., & Upstill-Goddard, R. C. (2013). Technical Note: Comparison of storage strategies of sea surface microlayer samples. *Biogeosciences, 10*(7), 4927–4936. https://doi.org/10.5194/bg-10-4927-2013

Southall, N. T., Dill, K. A., & Haymet, A. D. J. (2002). A View of the hydrophobic effect. *Journal of Physical Chemistry B, 106*(3), 521–533. https://doi.org/10.1021/ja015514e

Stubbins, A., Law, C. S., Uher, G., & Upstill-Goddard, R. C. (2011). Carbon monoxide apparent quantum yields and photoproduction in the Tyne estuary. *Biogeosciences, 8*(3), 703–713. https://doi.org/10.5194/bg-8-703-2011

Swan, C. M., Nelson, N. B., Siegel, D. A., & Kostadinov, T. S. (2012). The effect of surface irradiance on the absorption spectrum of chromophoric dissolved organic matter in the global ocean. *Deep Sea Research Part I: Oceanographic Research Papers, 63*, 52–64. https://doi.org/10.1016/j.dsr.2012.01.008

Tielrooij, K.-J., Hunger, J., Buchner, R., Bonn, M., & Bakker, H. J. (2010). Influence of concentration and temperature on the dynamics of water in the hydrophobic hydration shell of tetramethylurea. *Journal of the American Chemical Society, 132*(44), 15671–15678. https://doi.org/10.1021/ja106273w

Tilstone, G. H., Ains, R. L., Vicente, V. M., Widdicombe, C., & Llewellyn, C. (2010). High concentrations of mycosporine-like amino acids and colored dissolved organic matter in the sea surface microlayer off the Iberian Peninsula. *Limnology & Oceanography, 55*(5), 1835–1850. https://doi.org/10.4319/lno.2010.55.5.1835

Tseng, R.-S., Viechnicki, J. T., Skop, R. A., & Brown, J. W. (1992). Sea-to-air transfer of surface-active organic compounds by bursting bubbles. *Journal of Geophysical Research, 97*(C4), 5201–5206. https://doi.org/10.1029/91jc00954

Uher, G., Hughes, C., Henry, G., & Upstill-Goddard, R. C. (2001). Non-conservative mixing behavior of colored dissolved organic matter in a humic-rich, turbid estuary. *Geophysical Research Letters, 28*(17), 3309–3312. https://doi.org/10.1029/2000gl012509

Uher, G., Pillans, J. J., Hatton, A. D., & Upstill-Goddard, R. C. (2017). Photochemical oxidation of dimethylsulphide to dimethylsulphoxide in estuarine and coastal waters. *Chemosphere, 186*, 805–816. https://doi.org/10.1016/j.chemosphere.2017.08.050

Upstill-Goddard, R. C., Frost, T., Henry, G. R., Franklin, M., Murrell, J. C., & Owens, N. J. P. (2003). Bacterioneuston control of air-water methane exchange determined with a laboratory gas exchange tank. *Global Biogeochemical Cycles, 17*(4), 1108. https://doi.org/10.1029/2003gb002043

Wurl, O., & Soloviev, A. (2014). Selection of sampling sites and suitable sampling platforms. In M. Cunliffe, & O. Wurl (Eds.), *Guide to best practices to study the ocean’s surface*. Occasional Publications of the Marine Biological Association of the United Kingdom.

Wurl, O., Wurl, E., Miller, L., Johnson, K., & Vagle, S. (2011). Formation and global distribution of sea-surface microlayers. *Biogeosciences, 8*(1), 121–135. https://doi.org/10.5194/bg-8-121-2011