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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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Key Points:

- Irradiation results in increased surfactant activity in the sea-surface microlayer and in subsurface water in the Tyne estuary (UK)
- Surfactant activity increased in parallel to photodegradation of chromophoric dissolved organic matter
- Insolation driven increases in sea-surface microlayer surfactant activity may have global implications for air-sea trace gas exchange

Supporting Information:

Supporting Information may be found in the online version of this article.

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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 ± 0.062 mg l⁻¹ T-X-100 equivalents h⁻¹ in the SML and 0.031 ± 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 ~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 CO₂) 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 (Sabbaghzadeh et al., 2017; Wurl et al., 2011) via their adherence to the surfaces of rising bubbles that are generated during wave breaking (Robinson et al., 2019; Tseng et al., 1992), and which burst at the sea surface. This reduces the air-sea gas transfer velocity (k_w) of CO₂ and other gases by up to 50% (Calleja et al., 2009; Frew, 2005; Mustafa et al., 2020; Pereira et al., 2016, 2018; Salter et al., 2011), and following wind entrainment, impacts the MBL aerosol inventory (Kroflíč et al., 2018; Leck & Bigg, 1999; Ovadnevaite et al., 2011).

High UV irradiance promotes high SML photo-reactivity. Correlations of SML total surfactant activity (SA) with chromophoric 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 photodegradation (e.g., Kieber et al., 1997; Ortega-Retuerta et al., 2009; Swan et al., 2012), but photochemical formation of amphiphilic substances (= 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

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of trace gases (e.g., CO₂, CH₄, N₂O, 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_w . 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 m³ 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 cm²) 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 (Ćosović, 2005; Ćosović & 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 cm³). 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; Schneider-Zapp et al. (2013) established that this protocol ensures sample integrity for periods in excess of this.

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 Oriol; 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

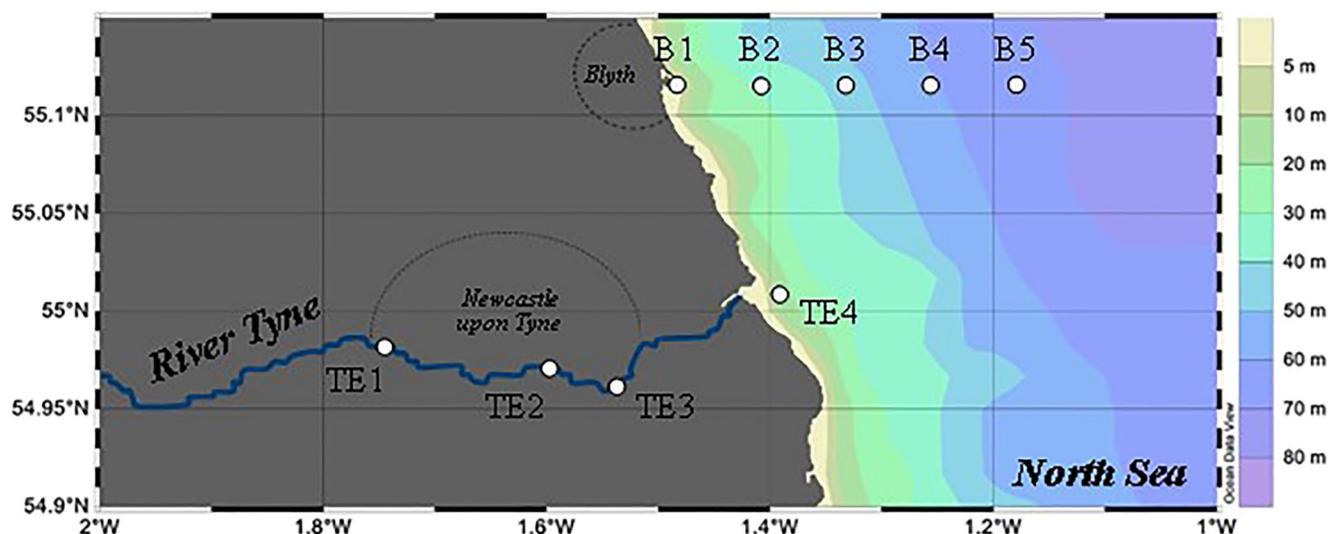


Figure 1. Tyne estuary (UK) sampling locations: TE4 (salinity 32.0) to TE1 (28 km upstream, salinity 0.3). Data from sites B1–B5 (Pereira et al., 2016) support our subsequent data interpretation. Color bar indicates water depth (m). Map created with Ocean Data View: Schlitzer, R., <https://odv.awi.de> (2018).

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 $\pm 5\%$. 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: $a = 2.303 A/L$ (Kitidis et al., 2006), where A is the offset corrected wavelength-dependent absorbance (dimensionless) and L is optical pathlength (m). We adopted a_{300} (absorption coefficient at 300 nm) as a CDOM concentration proxy (Bricaud et al., 1981; Hu et al., 2002), as in previous studies of coastal and oceanic waters (Helms et al., 2013; Kitidis et al., 2006; Sabbaghzadeh et al., 2017).

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_{IS}) and dark controls (SA_{DC}) over time (T ; 2 or 24 hr): $SA_{irr} = SA_{IS} - SA_{DC}/T$. 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 ; nm⁻¹) for the wavelength ranges 275–295 nm ($S_{275-295}$; nm⁻¹) and 350–400 nm ($S_{350-400}$; nm⁻¹), using: $a(\lambda) = a(\lambda_r)e^{-S(\lambda-\lambda_r)}$ (Helms et al., 2008), where $a(\lambda)$ is the absorption coefficient (m⁻¹) at wavelength λ (nm) and λ_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).

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 (τ_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 l⁻¹ T-X-100 eq. (SML) and 0.09 to 1.70 mg l⁻¹ T-X-100 eq. (SSW), with associated enrichment factors (EF = SA_{SML}/SA_{SSW}) of 0.9–1.6; in situ CDOM a_{300} 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 ($\tau_b(11) = 0.745, p = 0.001$; 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_{300} 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).

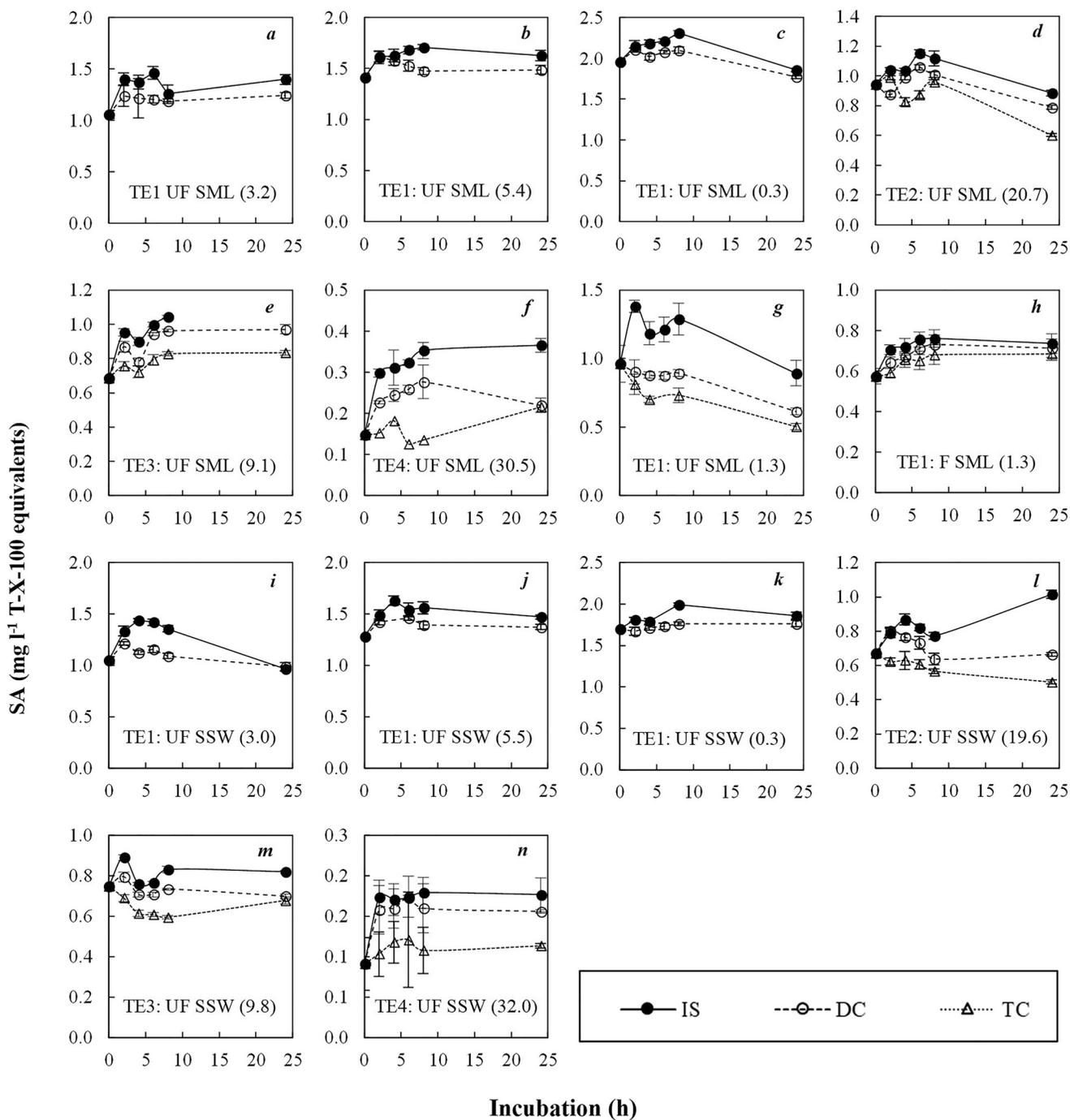
SA changes during irradiations indicated both photochemical and temperature effects in the SML and in SSW (Figure 2). For 64 of 67 time-points SA_{IS} exceeded SA_{DC}, for all time-points (39) SA_{IS} exceeded SA_{TC}, and for 38 of 39 time-points SA_{DC} exceeded SA_{TC}. The data thus confirm a photochemical SA source in the Tyne estuary. The largest changes in SA_{IS} consistently occurred 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 2i). 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}) and temperature (SA_{temp}) estimated over 0–2 hr (Table 1), the interval for which the greatest SA changes were consistently observed. These estimates are reasonable for our study area, for which total daylight ranged from ~7.5 hr (2 December 2016) to ~17.3 hr (27 June 2016) (Supporting Information S1). Although we also calculated SA_{irr} and SA_{temp} over 0–24 hr (Table 1), these do not represent conditions in situ.

Mean SA_{irr} (Table 1) was greater in the unfiltered SML than unfiltered SSW (0.064 ± 0.062 vs. 0.031 ± 0.027 mg L⁻¹ T-X-100 eq. h⁻¹ respectively), whereas mean SA_{temp} was greater in SSW than in the SML (0.056 ± 0.031 vs. 0.024 ± 0.054 mg L⁻¹ T-X-100 eq. h⁻¹ respectively). 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_{300} and SA in initial (T_0) samples ($\tau_b(11) = 0.745, p = 0.001$; 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., Tilstone 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 $S_{275-295}$ ($\tau_b(10-15) = 0.529-0.740, p = 0.003-0.027$), implying increased SA during irradiation to be consistent with decreasing CDOM



Incubation (h)

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.

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.

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	SA (mg l^{-1} T-X-100 equivalents h^{-1})			
		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 $\pm \sigma$		$0.064 \pm 0.062^{\text{a}}$	-	$0.006 \pm 0.002^{\text{a}}$	-
		$0.087 \pm 0.070^{\text{b}}$	$0.024 \pm 0.054^{\text{b}}$	$0.007 \pm 0.003^{\text{b}}$	$0.005 \pm 0.003^{\text{b}}$
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 $\pm \sigma$		$0.031 \pm 0.025^{\text{a}}$	-	$0.008 \pm 0.009^{\text{a}}$
		$0.017 \pm 0.028^{\text{b}}$	$0.056 \pm 0.031^{\text{b}}$	$0.007 \pm 0.007^{\text{b}}$	$0.003 \pm 0.003^{\text{b}}$

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.

^aMean and one standard deviation calculated using all available data. ^bMean and one standard deviation calculated using only experimental data where temperature controls were included as a sample treatment.

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 SA_{temp} data showed no concomitant changes in CDOM a_{300} or S_R . Nonetheless, microbial processing, adsorption and photodissolution 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 2
Projected k_{660} (cm H^{-1}) Values, Based on Pereira et al. (2016), for Tyne Estuary Sea-Surface Microlayer (SML) and Subsurface Water (SSW) Surfactant Activity at 0 and 2 hr Irradiation (Irradiated Samples Only), Over a Salinity Gradient of 0.3 (TE1) to 32.0 (TE4)

Site	SML projected k_{660} (cm h^{-1}):			SSW projected k_{660} (cm h^{-1}):		
	0 hr	2 hr	Δ (%)	0 hr	2 hr	Δ (%)
TE1	0.59	1.48	44.1	0.90	2.24	18.9
TE1	1.45	1.05	28.1	1.81	1.28	29.2
TE1	2.65	0.43	27.3	2.76	0.75	16.7
TE1	3.66	1.87	48.9	-	-	-
TE1 ^a	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

^a0.22 μm filtered SML sample.

A noteworthy feature was that irradiation per se was an independent driver of SA production, where SA_{irr} in the unfiltered SML ($0.064 \pm 0.062 \text{ mg L}^{-1} \text{ T-X-100 equivalents h}^{-1}$) generally exceeded that in unfiltered SSW ($0.031 \pm 0.027 \text{ mg L}^{-1} \text{ T-X-100 equivalents h}^{-1}$). 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 hr^{-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 $0.15 \text{ mg L}^{-1} \text{ T-X-100 eq.}$; Figures 1 and 2f) was closest to the salinity range (33.1–34.6) given by Pereira et al. (2016) and within the respective SA range ($0.08\text{--}0.38 \text{ mg L}^{-1} \text{ T-X-100 eq.}$), we extended the Pereira et al. (2016) analysis to our 2 hr SA_{IS} data for TE4, which gives k_{660} suppressions of 22.2% (9.4 cm hr^{-1} at 2 hr; SML) and 12.9% (11.6 cm hr^{-1} at 2 hr; SSW) relative to $T_0 k_{660}$ (12.1 cm hr^{-1} and 13.4 cm hr^{-1} , respectively) in coastal North Sea water. Overall, unfiltered samples gave k_{660} suppressions of 15.2%–48.9% ($0.4\text{--}9.4 \text{ cm hr}^{-1}$ at 2 hr) in the SML and 12.9%–29.3% ($0.8\text{--}11.6 \text{ cm hr}^{-1}$ 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

Adequate 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; 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 via ads.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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