

Photo-reactivity of surfactants in the sea-surface microlayer and subsurface water of the Tyne estuary, UK

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Introduction

The supporting data presented here details the Tyne estuary (UK) sampling locations, conditions, and respective sample treatments (Table S1 and Figure S1), and shows chromophoric dissolved organic matter (CDOM) changes recorded during irradiation experiments (Figures S2-S5), correlations between in situ salinity (0.3-32.0), CDOM and total surfactant activity (SA; T-X-100 eq. mg l⁻¹) (Figure S6) and the correlation between in situ CDOM and surfactant production due to irradiation (SA_{irr}) (Figure S7). The CDOM indices presented are: the absorption coefficient at 300 nm (a_{300}), 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), and the spectral slope ratio ($S_R = S_{275-295}/S_{350-400}$) (Helms et al., 2008).

Site ID	Site name	Longitude	Latitude	Date(s) sampled	Depth sampled	F/UF	Salinity	Sunrise (hh:mm)	Sunset (hh:mm)
TE1	Newburn	1°44'42.6"W	54°58'53.8"N	27 June 2016	SML	UF	3.2	04:29	21:49
					SSW	UF	3.0		
				18 July 2016	SML	UF	5.4		
					SSW	UF	5.5		
				29 August 2016	SML	UF	0.3		20:05
					SSW	UF	0.3		
				30 January 2017	SML	UF	1.3		16:39
TE2	Millennium Bridge	1°35'39.1"W	54°58'22.5"N	14 October 2016	SML	UF	20.7	07:34	18:09
					SSW	UF	19.6		
TE3	Walker	1°31'99.8"W	54°58'66.1"N	25 November 2016	SML	UF	9.1	07:57	15:48
					SSW	UF	9.8		
TE4	Herd Sands	1°25'21.1"W	55°00'36.6"N	2 December 2016	SML	UF	30.5	08:09	15:42
					SSW	UF	32.0		

Table S1. Details of Tyne estuary, UK, sampling sites (TE1-TE4): 1 L of sea-surface microlayer (SML) and 1 L of subsurface water (SSW) were collected in each case, except at TE1 in January 2017 where only SML (2 L) was sampled and split into 0.22 μm filtered (F) (Millex-GP polyethersulfone (PES) membrane) and unfiltered (UF) subsamples.

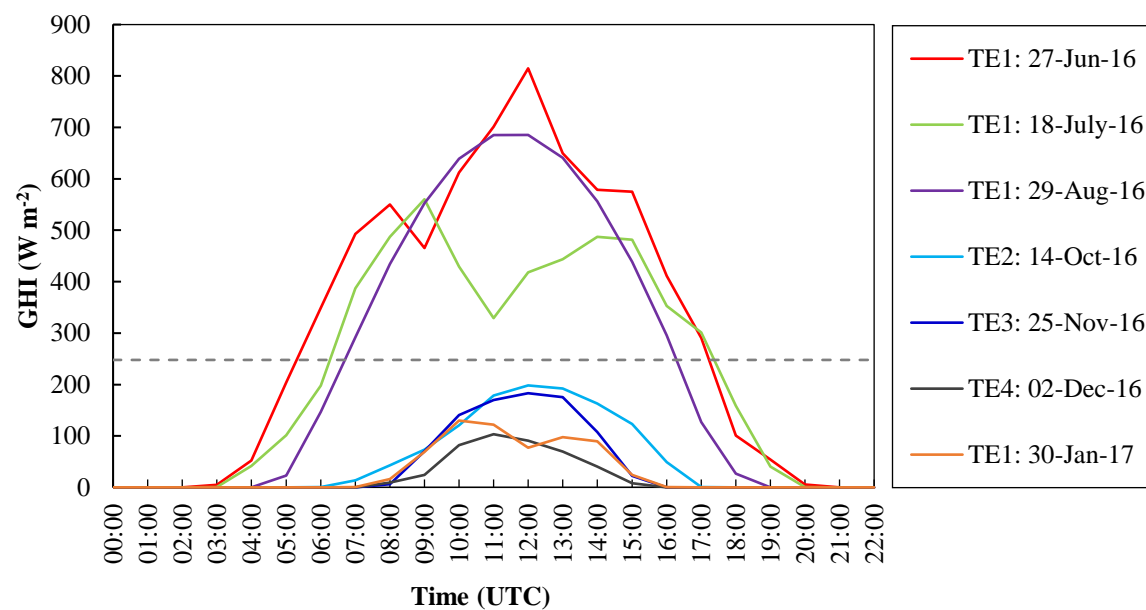


Figure S1. Global irradiation on horizontal plane at ground level (GHI, W m⁻²) in the Tyne estuary (sites TE1-TE4), UK, for all sampling dates, from Copernicus Atmosphere Monitoring Service (CAMS; copernicus.eu/; 240-4606 nm; Qu et al., 2017). The dotted grey line is the integrated spectral irradiance (247.8 W m⁻²; 250-1050 nm; ILT950, LOT Quantum Design) of the Xe-arc light source used in all irradiation experiments.

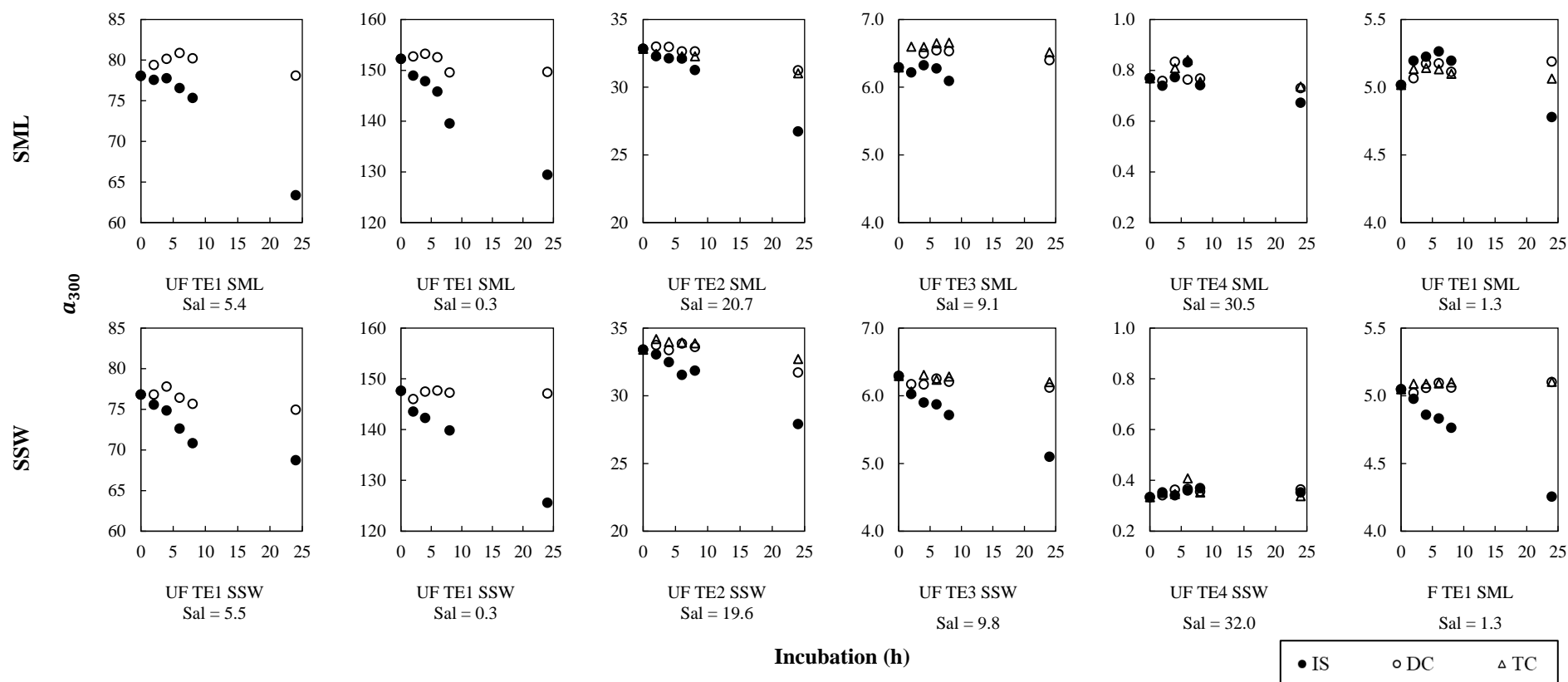


Figure S2. Changes in α_{300} during 24-hour incubations of Tyne estuary (sites TE1-TE4), UK, sea-surface microlayer (SML) and subsurface water (SSW) samples in the solar simulator, for sample treatments: irradiated samples (IS), dark controls (DC) and temperature controls (TC); unfiltered (UF) and 0.22 μm filtered (F) (Millex-GP polyethersulfone (PES) membrane). The salinity (Sal) of each sample is indicated.

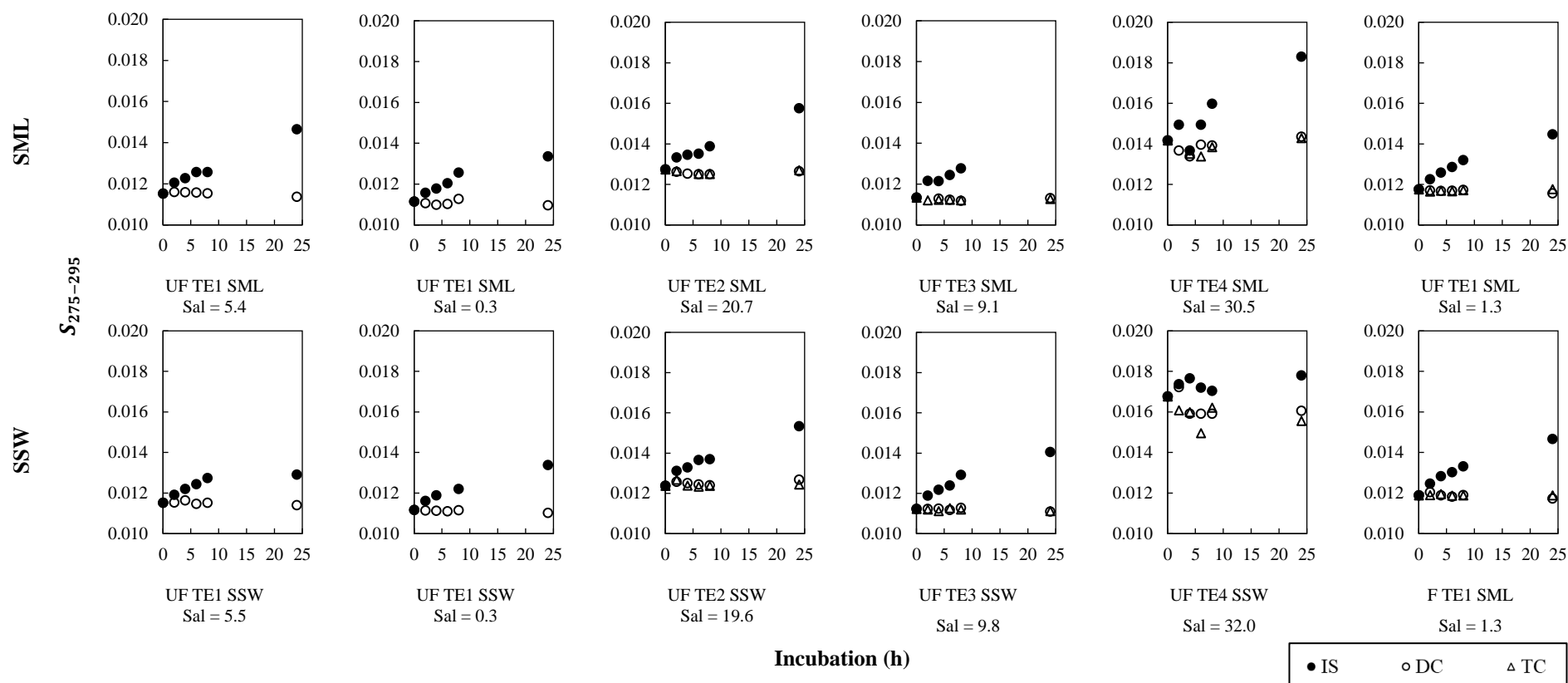


Figure S3. Changes in $S_{275-295}$ during 24-hour incubations of Tyne estuary (sites TE1-TE4), UK, sea-surface microlayer (SML) and subsurface water (SSW) samples in the solar simulator, for sample treatments: irradiated samples (IS), dark controls (DC) and temperature controls (TC); unfiltered (UF) and 0.22 μm filtered (F) (Millex-GP polyethersulfone (PES) membrane). The salinity (Sal) of each sample is indicated.

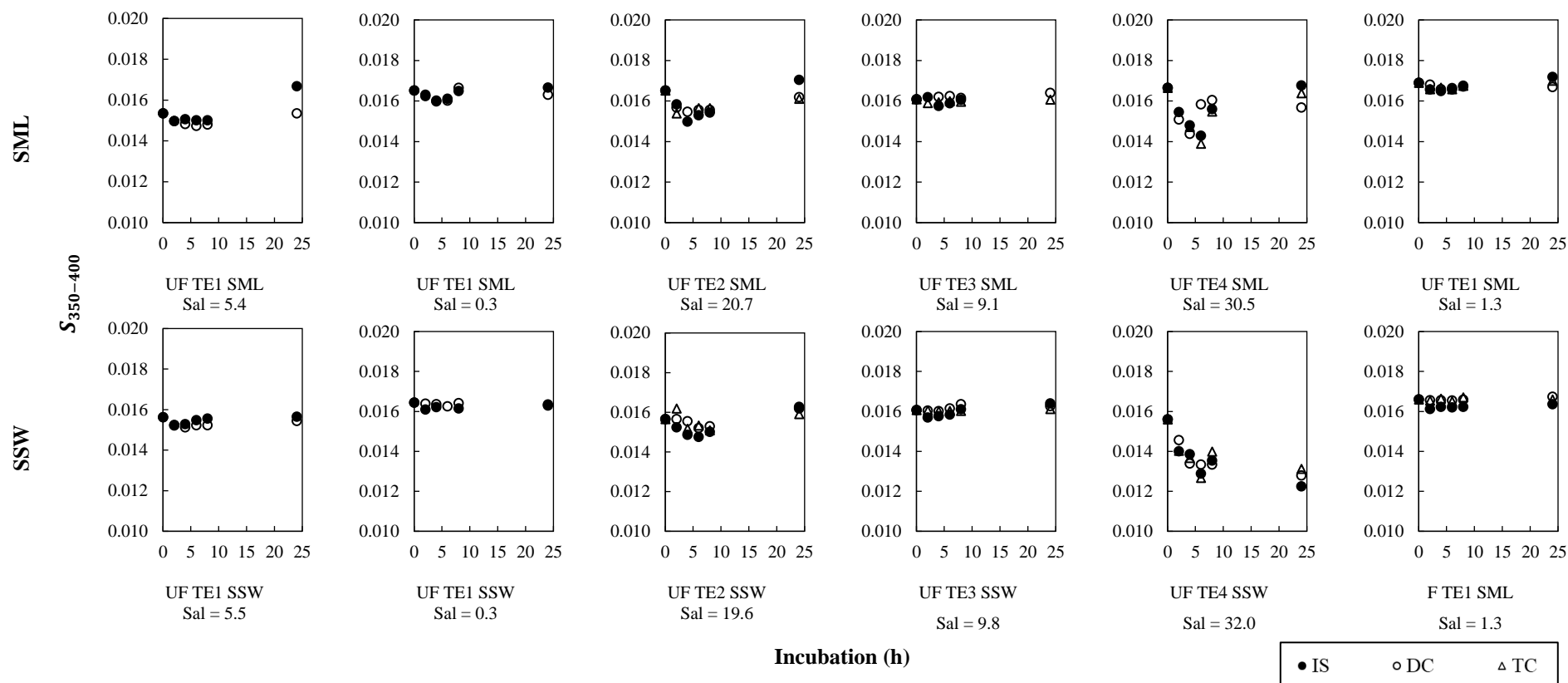


Figure S4. Changes in $S_{350-400}$ during 24-hour incubations of Tyne estuary (sites TE1-TE4), UK, sea-surface microlayer (SML) and subsurface water (SSW) samples in the solar simulator, for sample treatments: irradiated samples (IS), dark controls (DC) and temperature controls (TC); unfiltered (UF) and 0.22 μm filtered (F) (Millex-GP polyethersulfone (PES) membrane). The salinity (Sal) of each sample is indicated.

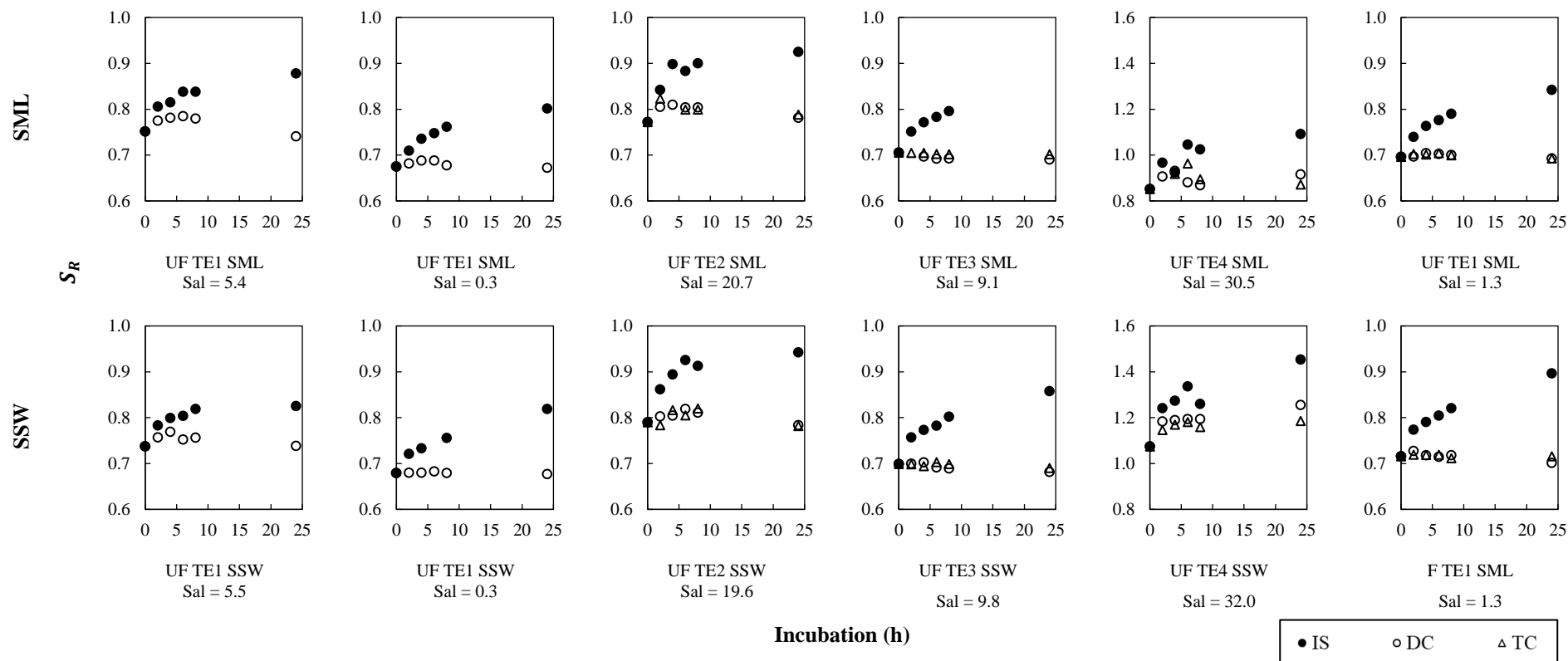


Figure S5. Changes in S_R during 24-hour incubations of Tyne estuary (sites TE1-TE4), UK, sea-surface microlayer (SML) and subsurface water (SSW) samples in the solar simulator, for sample treatments: irradiated samples (IS), dark controls (DC) and temperature controls (TC); unfiltered (UF) and 0.22 μm filtered (F) (Millex-GP polyethersulfone (PES) membrane). The salinity (Sal) of each sample is indicated.

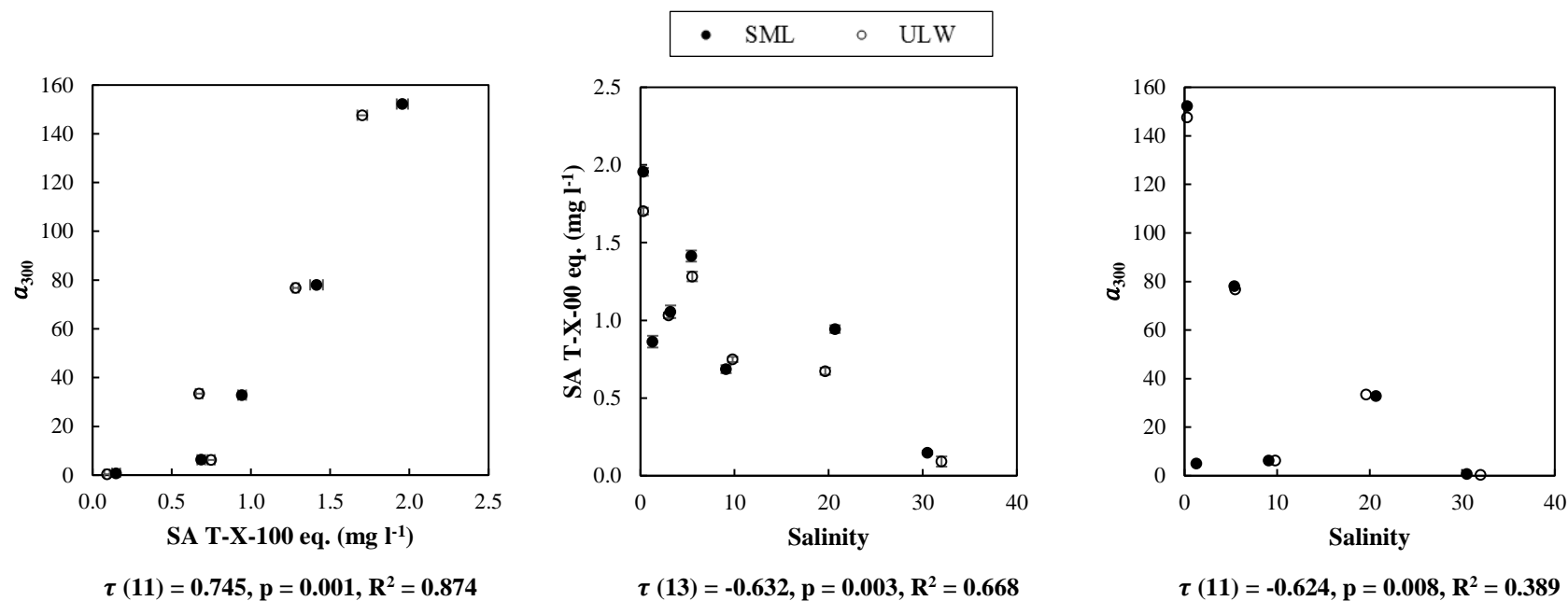
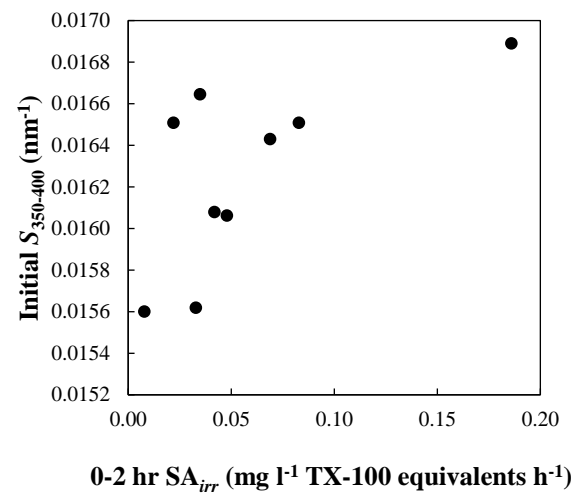


Figure S6. Correlations between in situ total surfactant activity (SA; T-X-100 eq. mg l⁻¹) with chromophoric dissolved organic matter (CDOM) absorption coefficient at 300 nm (a_{300}), and SA and a_{300} with salinity, in Tyne estuary, UK, sea-surface microlayer (SML) and subsurface water (SSW) samples over the salinity gradient 0.3-32.0. Error bars show one standard deviation on SA measurements.



$$\tau(11) = 0.585, p = 0.015, R^2 = 0.546$$

Figure S7. Initial CDOM spectral slope over the wavelength range 350-400 nm ($S_{350-400}$) vs SA due to irradiation (SA_{irr}) calculated for the initial 0-2 hours for unfiltered samples where $SA_{IS} > SA_{DC}$.