

Table 1. Overview of experiments performed in this study. Sample volumes are the targeted volumes. Gas chromatography–mass spectrometry is abbreviated as GC–MS. The treatments with artificial seawater were prepared with either of two salts, depending on their availability. Details about composition are only available for the medium with Tropic Marin® Pro-Reef Sea Salt. Research objectives: (1) pure sampling efficiency (2) effect of surfactants on sampling efficiency. * Not addressed further in main text, instead see Sect. S1.

Treatments	Medium	Analysis Sample volume	Research objectives	Additional measurements
TS1 Experiment A* (GEOMAR) 13–15 March – tank: incubation bath				
fresh water	ultrapure water	GC–MS 10 mL	(1)	
Experiment B (ICBM) 18–20 April – tank: aquarium				
fresh water	ultrapure water	GC–MS 10 mL	(1)	occasional T_{water} , $T_{\text{air}} \approx 12.7^\circ\text{C}$
artificial seawater	Tropic Marin® Pro-Reef Sea Salt 74 L, $S_p = 34.5$, 7.5°dKH	GC–MS 10 mL	(1)	
Experiment C (GEOMAR) 28 July–31 August – tank: “AZ crate”				
fresh water	ultrapure water 78 L, $\text{pH} = 6.3$	GC–MS 10 mL	(1), (2)	T_{water} , $T_{\text{air}} \approx 23.1^\circ\text{C}$ ($\Delta T_{\text{air}} = 4^\circ\text{C}$)
artificial seawater	ultrapure water with ordinary aquarium salt 78–81 L, $S_p = 29.1$, $\text{pH} = 8.06\text{--}7.84$	GC–MS 10 mL	(1), (2)	
artificial seawater with an artificial surfactant (3 levels)	ultrapure water with ordinary aquarium salt 78–81 L, $S_p = 33.9$, $\text{pH} = 8.06\text{--}7.84$	GC–MS, voltammetry 15 mL	(2)	

wards the air side due to the oversaturation and waited for 2 min for the turbulent motion to subside. We sampled the SML, ULW (10–13 cm) and surface (1–6.5 cm). All samples were collected in amber borosilicate glass bottles (20 mL). SML samples were taken with the glass plate technique (Harvey and Burzell, 1972). Following the recommendation by Cunliffe and Wurl (2014) and examples from recent studies (e.g., Adenaya et al., 2021), we reduced the speed of extracting the glass plate to 5 cm s^{-1} . The glass plate (borosilicate glass, $30\text{ cm} \times 25\text{ cm} \times 0.5\text{ cm}$ in experiment B, $40\text{ cm} \times 30\text{ cm} \times 0.5\text{ cm}$ in experiment C) was immersed to a depth of about 20 or 25 cm. Both sides of the glass plate were wiped with a regular silicone or rubber wiper and the runoff was collected into a sample bottle with a plastic funnel. A single dip provided between 1.8–4.0 mL of medium when no surfactants were present, and 3.4–6.3 mL when an artificial surfactant was added. To collect sufficient sample volume for analysis, two to five dips were required for analysis with gas chromatography–mass spectrometer (GC–MS) and voltammetry samples. The thickness of the sampled layer is determined by Eq. (1) (Cunliffe and Wurl, 2014).

$$h_{\text{SML}} \approx h_{\text{sampled}} = \frac{V_{\text{sample}}}{n_{\text{dips}} A} \quad (1)$$

where h_{SML} is the true thickness of the SML, h_{sampled} is the thickness that was actually sampled in cm, V_{sample} is the total volume of the glass plate sample in mL, A is the wetted

surface area of the glass plate in cm^2 and n_{dips} is the number of dips that were needed to collect V_{sample} .

Each SML sample is always associated with a reference ULW sample and sometimes with additional ULW or surface samples. All samples taken together after the same mixing event are referred to as a sample set. The reference ULW sample was taken immediately after the first dip of the SML sample was collected, interrupting the SML sampling for less than a minute (overall SML sampling took 90–235 s). All additional ULW or surface samples were taken after the SML sample had been finished (exception from this order is 19 April in experiment B). ULW samples were taken with a pipette (5 and 10 mL, Eppendorf SE, Hamburg, Germany) set to the required sample volume by inserting the tip of the pipette vertically and carefully into the water. For sample volumes of 15 mL, a pipette was immersed twice in the same location. ULW samples were taken from a water depth below surface of $\sim 10\text{ cm}$ in experiment B and $\sim 13\text{ cm}$ in experiment C. Surface samples were sampled the same way as ULW samples, with the only difference that we were aiming for a depth below surface of less than 1 cm in experiment B and $\sim 4.5\text{ cm}$ in experiment C (with exception of 31 August: $\sim 6.5\text{ cm}$). Additional ULW and surface samples were collected once or twice daily to confirm that the tank was well mixed. These tests were necessary, as the concentration difference between the oversaturated water and the near-zero air is large and might re-establish gradients in the SML quickly.