



### Supplement of

# Concerted measurements of lipids in seawater and on submicrometer aerosol particles at the Cabo Verde islands: biogenic sources, selective transfer and high enrichments

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Figure S1: Overview of the sampling stations during the campaign: Cape Verde Atmospheric Observatory (CVAO) and seawater sampling site



Figure S2: TLC-FID chromatogram of an aerosol sample (red) and the corresponding standards (black): lipid classes are numbered as follows: 1 HC, 2 WE, 3 ME, 4 KET (IS), 5 TG, 6 FFA, 7 ALC, 8 1,3 DG, 9 ST, 10 1.2 DG, 11 PIG, 12 MG, 13 MGDG, 14 DGDG, 15 SQDG, 16 PG, 17 PE, 18 PC

Chemical parameters	In SML and ULW samples Dissolved and particulate lipid classes as listed in section 2.2.1: HC, WE, ME, TG, FFA, ALC, ST, 1,2 DG, PIG, MG, MGDG, DGDG, SQDG, PE, PG, total lipids (TL), Lipolysis Index (LI)	
(Micro)biological parameters	<i>In SML and ULW samples</i> : TCN, <i>Synechococcus-like cells</i> (Synecho), <i>Nanoeucaryotes</i> (Nanoeuc) <i>In bulk samples</i> <sup>*</sup> : pigments as listed in section 2.2.1: chl- <i>a</i> , chl- <i>b</i> , chl-c3, fucoxanthin, pheophorbide, pheophytin a/b, zeaxanthin, diadinoxanthin, lutein, chlorophyllide (Chl-ide_a), violaxanthin, peridinin, β-carotene (beta-carotene)	Correlation analysis with chemical, (micro)biological and physical parameters
Physical parameters	<i>In SML and ULW samples</i> : INP at -10°C (INP_10), INP at -15°C (INP_15), INP at -20°C (INP_20)	

## Figure S3: Overview of the chemical, (micro)biological and physical parameters and their availability in the investigated seawater samples used for the correlation analysis

5 \* the pigments were analyzed in bulk surface water samples. These bulk surface water samples were only compared with the ULW samples in the correlation matrix. No pigment data were available for the SML samples.



Figure S4: Statistical analysis as screening of the correlation coefficient (R) of the ULW samples focusing on the dissolved fraction of lipids; color scale of R from red (R = -1) to blue (R = 1)



Figure S5: Statistical analysis as screening of the correlation coefficient (R) of the SML samples focusing on the dissolved fraction of lipids; color scale of R from red (R = -1) to blue (R = 1)



Figure S6: Statistical analysis as screening of the correlation coefficient (R) of the ULW samples focusing on the particulate fraction of lipids; color scale of R from red (R = -1) to blue (R = 1)



Figure S7: Statistical analysis as screening of the correlation coefficient (R) of the SML samples focusing on the particulate fraction of lipids; color scale of R from red (R = -1) to blue (R = 1)



Figure S8: Correlation plot between the particulate PE concentration and the concentration of (a) Zeaxanthin and (b) Fucoxanthin as proxy for autotrophic organisms in the ULW samples



Figure S9: Correlation plot between (a) the concentration of dissolved PE and TCN in the ULW samples, between (b) the concentration of particulate PE and TCN in the ULW (black) and SML (blue) samples and between (c) the Lipolysis index of the total particulate lipids ( $LI_{\Sigma PL}$ ) and the TCN concentration in the ULW (black) and SML (blue) samples



Figure S10: Boxplot explanation related to Fig. 4



Figure S11: Correlation plot of the EF<sub>aer</sub> and the corresponding log K<sub>OW</sub> of the individual lipid classes: HC, TG, FFA, ALC, ST, 1,2DG, MGDG, DGDG, SQDG, PG, PE; with p=0.028



Figure S12: Concerted measurements of the individual lipid classes in the (a) particulate and (b) dissolved fraction in seawater (differentiation between ULW and SML) and on (c) PM<sub>1</sub> aerosol particles at the CVAO; the lipid concentrations in seawater are in µg L<sup>-1</sup> and on aerosol particles as atmospheric concentration in ng m<sup>-3</sup>



Figure S13: Correlation plot between (a) the concentration of the total particulate lipids in µg L<sup>-1</sup> and INP at -10 °C in L<sup>-1</sup> in the SML samples, between (b) the concentration of the total dissolved lipids in µg L<sup>-1</sup> and INP at -10 °C in L<sup>-1</sup> in the SML samples and between (c) the concentration of the particulate PE in µg L<sup>-1</sup> and INP at -10 °C in L<sup>-1</sup> in the SML samples



Figure S14: Correlation plot between (a) the concentration of the particulate FFA in μg L<sup>-1</sup> and INP at -10 °C in L<sup>-1</sup> in the SML samples, between (b) the concentration of the dissolved FFA in μg L<sup>-1</sup> and INP at -10 °C in L<sup>-1</sup> in the SML samples and between (c) the concentration of the particulate FFA in μg L<sup>-1</sup> and INP at -15 °C in L<sup>-1</sup> in the ULW samples



Figure S15: number of active INP in seawater distinguished between SML (above) and ULW (below) for non-heated and heated (95 °C) samples



5 Figure S16: Comparison of the saturation vapor pressure (p) of the individual standards calculated with EVAPORATION (x-axis) and with SIMPOL.1 (y-axis); values displayed as log values

In addition to SIMPOL.1 (Pankow and Asher, 2008), the EVAPORATION model (Compernolle et al., 2011) was used to calculate the saturation vapor pressure (p) for comparison (Fig. S17). Comparing both calculation methods (Fig. S18) of p, SIMPOL.1 and EVAPORATION, showed that their values for the saturation vapor pressure of the individual standards as representatives of the lipid classes were in good agreement ( $R^2$ =0.989).

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Figure S17: Overview of possible distributions of the analyte between interface, water and air: a) K<sub>aq</sub>>>K<sub>a</sub>, the analyte is preferably distributed (from water) into air; b) K<sub>a</sub>>>K<sub>aq</sub>, the analyte is preferably distributed (from air) into water; c) K<sub>aq</sub>~ K<sub>a</sub>, the analyte is preferably distributed at the interface



Figure S18: Scheme of a bubble during the process of bubble rising through the water column, distinguished between 'air' (inside the bubble), 'water' (surrounding the bubble), the 'interface' (bubble surface) and the distribution of the lipid classes MGDG, TG and ALC related to their K<sub>a</sub> and K<sub>aq</sub> values

Table S1: Investigated nutrients during the campaign in the ULW and the SML samples and as an averaged value in  $\mu$ mol L<sup>-1</sup>; dinitrogen trioxide (N<sub>2</sub>O<sub>3</sub>), nitrogen dioxide (NO<sub>2</sub>), nitrate (NO<sub>3</sub><sup>-</sup>), phosphate (PO<sub>4</sub><sup>3-</sup>) and silicates (SiO<sub>4</sub><sup>4-</sup>); LOQ: limit of quantification; NA: not available

		$\mu$ mol L <sup>-1</sup>										
Sampling	$N_2$	O <sub>3</sub>	NO	2	NO	D <sub>3</sub> -	PC	SiO4 <sup>4-</sup>		O4 <sup>4-</sup>		
date	ULW	SML	ULW	SML	ULW	SML	ULW	SML	ULW	SML		
20/09/2017	0.36	0.50	<loq< td=""><td>0.02</td><td>0.36</td><td>0.49</td><td>0.09</td><td>0.19</td><td>0.60</td><td>1.25</td></loq<>	0.02	0.36	0.49	0.09	0.19	0.60	1.25		
25/09/2017	0.28	0.66	0.01	0.02	0.28	0.64	0.06	0.15	1.00	1.40		
26/09/2017	0.52	0.47	0.03	0.03	0.49	0.44	0.05	0.08	1.00	1.40		
27/09/2017	0.24	0.32	0.02	0.01	0.22	0.31	0.12	0.07	2.20	1.20		
28/09/2017	0.25	0.38	0.00	0.03	0.25	0.35	0.07	0.13	1.10	0.90		
2/10/2017	0.91	NA	0.03	NA	0.89	NA	0.07	NA	1.90	NA		
3/10/2017	0.22	NA	0.01	NA	0.21	NA	0.10	NA	1.45	NA		
4/10/2017	0.31	NA	0.01	NA	0.30	NA	0.10	NA	0.50	NA		
5/10/2017	0.35	NA	0.02	NA	0.33	NA	0.09	NA	1.00	NA		
6/10/2017	0.18	0.23	0.03	0.03	0.16	0.20	0.06	0.02	0.50	0.50		
7/10/2017	0.28	0.26	0.07	0.04	0.22	0.22	0.23	0.04	0.35	0.10		
averaged	0.35	0.40	0.02	0.02	0.33	0.38	0.09	0.09	1.05	0.96		

pigments	18/09	20/09	25/09	27/09	28/09	02/10	03/10	05/10	07/10	09/10	10/10
chlorophyll c2	1.63E-02	2.56E-02	3.05E-02	4.13E-02	2.30E-02	2.88E-02	2.81E-02	2.46E-02	3.85E-02	3.88E-02	6.16E-02
19-butyl	4.79E-04	1.75E-02	1.94E-03	1.80E-02	4.01E-03	1.85E-02	1.24E-02	1.32E-02	2.57E-02	3.11E-02	5.79E-02
fucoxanthin											
19-hexanoyl	1.46E-02	4.41E-02	1.81E-02	4.53E-02	2.70E-02	4.48E-02	3.32E-02	3.10E-02	6.25E-02	6.87E-02	1.10E-01
fucoxanthin											
chlorophyll-b	2.10E-02	4.22E-02	5.48E-02	3.81E-02	3.18E-02	5.00E-02	6.15E-02	3.50E-02	6.27E-02	6.53E-02	1.09E-01
chlorophyll-a	1.12E-01	2.16E-01	3.23E-01	3.35E-01	1.84E-01	2.64E-01	2.98E-01	1.92E-01	3.46E-01	4.37E-01	6.04E-01
fucoxanthin	1.45E-02	4.37E-02	9.35E-02	1.71E-01	3.97E-02	4.54E-02	6.04E-02	3.68E-02	1.05E-01	1.53E-01	2.23E-01
pheophorbide a	3.13E-02	3.23E-02	4.70E-02	4.13E-02	3.73E-02	3.37E-02	3.57E-02	3.27E-02	3.65E-02	3.88E-02	3.79E-02
pheophytin a	1.71E-02	1.78E-02	2.69E-02	2.28E-02	2.29E-02	2.64E-02	2.92E-02	2.05E-02	2.51E-02	2.64E-02	2.74E-02
chlorophyllide a	0.00E+00	1.00E-02	1.00E-02	1.00E-02	0.00E+00	0.00E+00	1.00E-02	0.00E+00	1.00E-02	1.00E-02	*
violaxanthin	*	3.49E-03	4.67E-03	3.08E-03	2.60E-03	4.29E-03	5.54E-03	3.19E-03	5.36E-03	6.40E-03	7.03E-03
diadinoxanthin	9.16E-03	1.81E-02	1.63E-02	2.07E-02	1.44E-02	1.74E-02	1.75E-02	1.25E-02	2.31E-02	2.99E-02	3.41E-02
lutein	1.38E-03	1.83E-03	5.09E-03	*	2.78E-03	1.85E-03	2.75E-03	1.90E-03	2.78E-03	3.33E-03	*
chlorophyll c3	1.40E-02	2.20E-02	2.66E-02	3.80E-02	1.72E-02	2.53E-02	2.49E-02	2.15E-02	3.52E-02	3.42E-02	5.93E-02
peridinin	2.62E-03	4.69E-03	7.31E-03	5.92E-03	2.75E-03	6.50E-03	4.80E-03	6.48E-03	5.16E-03	4.83E-03	7.69E-03
zeaxanthin	1.08E-01	1.06E-01	1.34E-01	8.91E-02	1.36E-01	1.41E-01	2.06E-01	1.65E-01	1.85E-01	1.48E-01	1.29E-01
ß-carotene	6.19E-03	8.72E-03	1.70E-02	1.05E-02	1.02E-02	1.33E-02	1.81E-02	1.00E-02	1.41E-02	1.46E-02	1.54E-02

Table S2: Pigment concentration in the bulk surface water in µg L<sup>-1</sup> along the campaign in 2017; \* investigated pigment was not measured

	Syne	chococcus-like	e cells	1	Nanoeucaryote	25	TCN			
	ULW	SML	EF <sub>SML</sub>	ULW	SML	EF <sub>SML</sub>	ULW	SML	EF <sub>SML</sub>	
20/09/2017	1.6E+04	2.0E+04	1.2	1.5E+03	2.6E+03	1.8	1.0E+06	1.1E+06	1.1	
25/09/2017	2.6E+04	3.1E+04	1.2	3.2E+03	3.4E+03	1.1	1.4E+06	1.6E+06	1.2	
26/09/2017	8.0E+03	9.7E+03	1.2	6.5E+02	8.5E+02	1.3	1.1E+06	9.9E+05	0.9	
27/09/2017	1.4E+04	1.3E+04	0.9	1.1E+03	9.6E+02	0.9	1.2E+06	1.2E+06	1.0	
28/09/2017	1.1E+04	1.2E+04	1.1	1.3E+03	1.2E+03	0.9	1.1E+06	1.3E+06	1.2	
02/10/2017	4.5E+04	2.4E+04	0.5	2.1E+03	1.4E+03	0.7	1.1E+06	1.3E+06	1.1	
03/10/2017	3.2E+04	3.6E+04	1.1	2.2E+03	1.7E+03	0.8	1.5E+06	1.4E+06	0.9	
04/10/2017	1.6E+04	1.9E+04	1.1	1.2E+03	1.1E+03	0.9	1.3E+06	1.2E+06	1.0	
05/10/2017	1.4E+04	NA	NA	1.1E+03	NA	NA	1.3E+06	NA	NA	
06/10/2017	9.9E+03	1.1E+04	1.1	4.8E+02	3.1E+02	0.7	1.3E+06	1.2E+06	0.9	
averaged	1.9E+04	1.9E+04	1.1	1.5E+03	1.5E+03	1.0	1.2E+06	1.3E+06	1.0	

Table S3: Abundances of autotrophic organisms (*Nanoeucaryotes* and *Synechococcus-like cells*) and of bacteria (TCN) in cells  $mL^{-1}$  in the ULW and the SML samples and the calculated EF<sub>SML</sub> (Eq. 2) along the campaign; NA – not available

#### Pigments, nutrients and microbiological investigations in seawater

- 5 The pigment measurements of bulk surface water (Table S2) indicated temporal changes in the composition of the community with total pigment concentrations between 0.4  $\mu$ g L<sup>-1</sup> and 1.5  $\mu$ g L<sup>-1</sup> during the campaign and an increasing trend in pigment concentration towards the end of the campaign. A nutrient limitation (Table S1), especially for phosphate (averaged concentration of 0.09  $\mu$ mol L<sup>-1</sup> in each the ULW and the SML) could explain the low total abundance of autotrophic organisms, which is also reflected in low chl-*a* concentrations.
- Nanoeucaryotes, Synechococcus-like cells and TCN are presented in Table S3. The mean TCN value was 1.2·10<sup>6</sup>±1.3·10<sup>5</sup> cells mL<sup>-1</sup> in the ULW
  and 1.3·10<sup>6</sup>±1.9·10<sup>5</sup> cells mL<sup>-1</sup> in the SML samples, which is consistent with previous reports for surface water of subtropical regions (Zäncker et al., 2018). The abundance of Synechococcus-like cells was 1.9·10<sup>4</sup>±1.2·10<sup>4</sup> cells mL<sup>-1</sup> (ULW), 1.9·10<sup>4</sup>±9.1·10<sup>3</sup> cells mL<sup>-1</sup> (SML) and for Nanoeucaryotes 1.5·10<sup>3</sup>±8.2·10<sup>2</sup> cells mL<sup>-1</sup> (ULW), 1.5·10<sup>3</sup>±9.6·10<sup>2</sup> cells mL<sup>-1</sup> (SML). Duhamel et al. (2019) reported a Synechococcus cell abundance of 2.5-9.2·10<sup>3</sup> cells mL<sup>-1</sup> for seawater samples (20 m depth) taken in the western subtropical Atlantic Ocean. Although comparable data are lacking, the low cell abundances in the present study are indicative of an oligotrophic system. Synechococcus-like cells and Nanoeucaryotes

showed a similar trend as chl-*a* (two slight increases, followed by depression), indicating that autotrophic organisms followed a similar temporal pattern.

Table S4: PE/PG ratio of the particulate fraction in the ULW and the SML samples along the campaign; NA - not avai
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sampling	PE/PG ratio						
date	ULW	SML					
20/09/2017	0.6	1.9					
25/09/2017	1.5	2.8					
26/09/2017	0.9	NA					
27/09/2017	1.2	1.8					
28/09/2017	1.4	NA					
2/10/2017	1.7	NA					
3/10/2017	4.8	NA					
4/10/2017	3.3	NA					
5/10/2017	1.5	NA					
6/10/2017	0.9	1.3					
7/10/2017	0.5	0.8					
9/10/2017	0.7	NA					
10/10/2017	0.5	0.7					
averaged	1.3	1.4					

sampling	dissolved	l fraction	particulate fraction		
date	LI <sub>ULW</sub>	LI <sub>SML</sub>	LI <sub>ULW</sub>	LI <sub>SML</sub>	
20/09/2017	0.53	0.48	0.21	0.51	
25/09/2017	0.26	0.24	0.13	0.37	
26/09/2017	0.25	NA	0.18	NA	
27/09/2017	0.25	0.28	0.27	0.61	
28/09/2017	0.21	NA	0.27	NA	
2/10/2017	0.23	NA	0.21	NA	
3/10/2017	0.28	NA	0.13	NA	
4/10/2017	0.34	NA	0.20	NA	
5/10/2017	0.27	NA	0.15	NA	
6/10/2017	0.13	0.20	0.12	0.66	
7/10/2017	0.38	0.35	0.27	0.46	
9/10/2017	0.18	NA	0.31	NA	
10/10/2017	0.25	0.23	0.29	0.38	
averaged	0.27	0.30	0.21	0.50	

Table S5: The Lipolysis Index (LI) in the ULW and in the SML samples for the dissolved and the particulate fraction of lipids; NA: not available

Lipid	20/09	9/2017	25/09	9/2017	27/09	/2017	06/10	/2017	07/10	/2017	10/10	/2017	avera	aged
classes	PF	DF	PF	DF	PF	DF	PF	DF	PF	DF	PF	DF	PF	DF
НС	1.4	0.9	2.0	0.7	2.3	1.4	1.4	0.7	2.0	1.0	1.0	1.0	1.7	0.9
WE	2.7	0.6	2.4	4.4	2.3	1.1	0.6	NA	NA	3.4	NA	1.2	1.3	1.8
ME	NA	0.7	2.8	3.5	1.3	NA	0.7	0.7						
TG	3.2	0.9	2.5	1.0	4.4	0.5	0.3	1.5	2.3	1.0	0.9	1.1	2.3	1.0
FFA	3.6	1.8	4.2	1.5	3.2	1.5	4.6	2.1	1.9	1.1	1.1	1.2	3.1	1.5
ALC	1.1	1.5	2.2	2.8	1.7	1.3	0.9	1.8	2.1	1.6	2.5	1.4	1.7	1.7
ST	2.5	1.9	2.4	2.9	1.7	1.4	2.9	3.3	3.0	0.9	2.4	1.3	2.5	1.9
1,2 DG	1.5	1.4	2.0	1.8	1.4	NA	NA	3.0	2.9	NA	NA	NA	1.3	1.0
PIG	0.9	1.0	0.9	0.4	0.8	0.3	0.6	0.9	0.9	0.9	0.7	0.5	0.8	0.7
MG	NA	NA	NA	0.8	NA	NA	NA	NA	NA	NA	1.8	NA	0.3	0.1
MGDG	1.0	2.1	1.6	2.3	1.4	1.2	0.9	0.9	1.2	1.2	0.9	1.2	1.2	1.5
DGDG	2.5	2.8	3.2	1.7	NA	NA	1.1	NA	NA	4.3	NA	NA	1.1	1.5
SQDG	0.7	1.8	0.9	1.0	1.2	NA	0.8	0.7	1.0	0.7	0.9	0.7	0.9	0.8
PE	2.9	4.7	1.6	2.1	1.4	1.6	1.1	1.8	1.4	1.1	1.1	1.6	1.6	2.1
PG	0.9	1.6	0.8	1.1	0.9	1.5	0.7	1.6	0.9	0.9	0.9	1.0	0.8	1.3
PC	NA	NA	2.9	1.5	1.5	NA	1.2	NA	1.5	NA	1.0	NA	1.3	0.3
total lipids	1.7	1.3	1.7	1.4	1.7	1.4	1.2	1.3	1.4	1.1	1.0	1.2	1.4	1.3
PP*	1.9	2.4	1.4	1.7	1.2	1.6	0.9	1.7	1.1	1.1	0.9	1.3	1.2	1.6
GL**	0.9	2.1	1.3	1.8	1.4	1.4	0.9	1.1	1.2	1.4	0.9	1.4	1.1	1.5

Table S6: Enrichment factor in the SML ( $EF_{SML}$ ) of the individual lipid classes in the particulate fraction (PF) and in the dissolved fraction (DF) along the campaign and as an average; NA - not available

PP\* - Phospholipids, including PE, PG and PC. In order to determine the enrichment factor, the sum of the concentrations of the individual lipid classes (PE, PG, PC) in the SML was determined in relation to the sum of the concentrations of the individual lipid classes (PE, PG, PC) in the ULW and is called EF<sub>SML</sub> of phospholipids (EF<sub>SML(PP)</sub>) in the following

5

GL\* - Glycolipids, including MGDG, DGDG, SQDG. The same calculation as for PP is applied, except that the individual lipid classes MGDG, DGDG, SQDG were considered for the glycolipids and are referred to as EF<sub>SML</sub> of glycolipids (EF<sub>SML(GL)</sub>)

Table S7: Estimation of the surfactant activity of the individual lipid classes based on the parameter density, XLogP3-AA and topological polar surface area; NA – not available

Standards	Lipid class	Density	log K <sub>OW</sub> *	Topological Polar Surface Area/Å2
nonadecane	НС	0.7774	9.9	0
cetyl alcohol	ALC	0.8187	7.3	20.2
stearyl palmitate	WE	0.935	16.3	26.3
methyl palmitate	ME	NA	7.9	26.3
stearic acid	FFA	0.86	7.4	37.3
cholesterol	ST	1.067	8.7	20.2
1-stearoyl-rac-glycerol	MG	0.894-0.906	7.4	66.8
glyceryl 1, 3 distearate	1,3 DG	0.894-0.906	16.2	72.8
D, L-α,β distearin	1,2 DG	0.894-0.906	16.2	72.8
tristearin	TG	0.8559	25.2	78.9
chlorophyll-a	PIG	NA	NA	96.4
Phosphatydilgycerol (18:1/16:0)	PG	NA	12.3	149
1,2-diacyl-sn-glycero-3-	PC	NA	12.9	111
phosphocholine				
phosphatidylethanolamine	PE	1.0±0.1	-4.4	134
sulfoquinovosyldiacylglycerol	SQDG	NA	10	195
galactosyldiglyceride	MGDG	NA	-3.5	203
digalactosyldiglyceride	DGDG	NA	-3.8	208

\* The calculation of the octanol-water partition coefficient (Kow) is based on the XLOGP3-AA method, which predicts the log Kow as XLogP3-AA value of compound by using the known log Kow of a reference compound as a starting point (Cheng et al., 2007). For each compound we also used the PubChem database (<u>https://pubchem.ncbi.nlm.nih.gov/</u>), an open chemistry database at the National Institutes of Health (NIH), to extract chemical and physical properties.

#### Surfactant activity of investigated individual lipid classes:

To estimate the surface activity of the individual lipid classes based on their physico-chemical properties, individual parameters, namely the density, the partitioning coefficient between octanol and water (log K<sub>OW</sub>) and the topological polar surface area were considered. One physical parameter which shows a superficial correlation with bubble and/or currenttransport susceptibility is specific gravity, also called relative density. An inverse relationship of this function with increased rates of surface accumulation by current seems logical since substances with lower densities would probably resist remixing into the water column once they have been dissolved and concentrated at the air-water interface (Brown et al., 1992). Based

15 on available density data from the literature presented within Table S7, we may roughly estimate that more nonpolar lipids

such as FFA and ALC should have higher susceptibility for the air-water surface (surface accumulation) in comparison to GL and PP. In fact, FFA and ALC have lower molecular masses and densities compared to GL and PP. The octanol-water partition ratio, in turn, is the most common way of expressing the lipophilicity of compounds in logarithmic form. Referred to as log Kow or log P it is obtained either through experimental procedures (Rothwell et al., 2005) or prediction approaches (Mannhold

- 5 et al., 2009). In general, the positive values for log K<sub>OW</sub> indicate some hydrophobic character, whereas larger values lead to an increased hydrophobicity. Molecules with low or negative values for K<sub>OW</sub>, however, are often defined as polar, although no direct link between K<sub>OW</sub> and the charge distribution in the molecule exists. Based on the ranking of XLogP3-AA data presented in Table S7, the most hydrophobic lipid would be TG. Another important factor which affects the adsorption is the solubility. According to the Lundelius, 1920), the extent of the adsorption of a surfactant could be assumed to be inversely
- 10 proportional to its solubility in water. An increase of polar moiety contribution in a molecule heightens its hydrophilicity which leads to an enhanced solubility in water. As the topological polar surface area (TPSA) of a molecule is defined as the surface sum over all polar atoms or molecules, primarily oxygen and nitrogen, also including their attached hydrogen atoms, it can serve as suitable measure to get a rough estimate of the magnitude of the surfactant activity of investigated lipids as illustrated in Table S5. It becomes apparent that the lower the TSPA, the higher is the surfactant activity. Consequently, the higher polar
- 15 surface area of GL and PP shows a larger hydrophilicity in comparison with FFA and ALC. Since PP is indeed more soluble than FFA or ALC, we expect less surface activity.

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Table S8: The enrichment factor on the aerosol particles ( $EF_{aer}$ ) of the total lipids ( $\sum$ lipids) of individual sampling days with corresponding SML and PM<sub>1</sub> aerosol particles samples (CVAO) and as an average and the measured solar radiation; NA – not available

	total lipid con	ncentration in	atmospheric	concentration	EFae	$r(\sum lipids)^{1}$	average
	SML		on PM <sub>1</sub> aero	osol particles			solar
							radiation <sup>4</sup>
date	dissolved	particulate	total lipids	sodium	dissolved <sup>2</sup>	particulate <sup>3</sup>	W m <sup>-2</sup>
	μg	μg L <sup>-1</sup> ng m <sup>-3</sup>					
20/09/2017	121.5	118.1	133.6	150.6	9E+04	9E+04	NA
25/09/2017	75.5	110.1	182.1	110.5	3E+05	2E+05	676.2
27/09/2017	55.7	61.0	173.1	52.9	7E+05	7E+05	581.7
6/10/2017	99.7	114.9	94.0	103.8	1E+05	1E+05	371.2
7/10/2017	78.6	81.6	97.7	109.8	1E+05	1E+05	551.4
10/10/2017	65.2	84.4	75.2	79.5	2E+05	1E+05	243.3
averaged	82.7	95.0	126.0	101.2	3E+05	2E+05	484.8

<sup>1</sup>For the calculation of EF<sub>aer(∑lipids)</sub>, Eq. (3) was used. For the analysis of sodium in the SML n=5 samples were investigated. In the SML the
 sodium concentration was 12.53 ± 0.53 g L<sup>-1</sup>. Due to small relative standard deviation (4.2 % for SML), the mean value of the sodium concentration in the SML samples (12.53 g L<sup>-1</sup>) was used for the calculation of EF<sub>aer</sub>.

 ${}^{2}$  EF<sub>aer( $\sum$ lipids) dissolved is based on the total lipid concentration in the dissolved fraction of the SML and the atmospheric concentration of total lipids and of sodium on PM<sub>1</sub> aerosol particles.</sub>

 ${}^{3}$  EF<sub>aer( $\Sigma$ lipids) particulate is based on the total lipid concentration in the particulate fraction of the SML and the atmospheric concentration of total lipids and of sodium on PM<sub>1</sub> aerosol particles.</sub>

Considering the sample preparation, the averaged  $\text{EF}_{aer(\sum lipids) \text{ dissolved}}(3\cdot10^5)$  is considered in the following, since the filtration (sample preparation, section 2.2.1) of the particles in the dissolved fraction of seawater samples ( $\leq 0.7 \,\mu\text{m}$ ) are in the size-range of PM<sub>1</sub> aerosol particles ( $\leq 1 \,\mu\text{m}$ ). The particulate fraction in seawater covers the particle size-range 0.7-200  $\mu$ m. The averaged  $\text{EF}_{aer(\sum lipids) \text{ particulate}}$  with 2·10<sup>5</sup> is similar to the  $\text{EF}_{aer(\sum lipids) \text{ dissolved}}(3\cdot10^5)$ .

<sup>4</sup> The solar radiation was measured during the campaign with a 'Pyranometer SKS 1110' (Skye Instruments Ltd, Powys, United Kingdom) installed on the 10 m high tower of the CVAO. The average solar radiation shown here includes the averaged solar radiation data over the sampling period of the SML samples (listed in detail in van Pinxteren et al. (2020)).

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Lipid classes	20/09/2017	25/09/2017	27/09/2017	06/10/2017	07/10/2017	10/10/2017	averaged
НС	6E+04	4E+05	4E+05	5E+05	1E+05	3E+05	3E+05
TG	7E+05	2E+06	1E+07	2E+05	1E+06	1E+06	3E+06
FFA	1E+05	3E+05	6E+05	9E+04	2E+05	1E+05	2E+05
ALC	1E+05	7E+05	4E+06	8E+05	7E+05	3E+06	1E+06
ST	8E+04	6E+05	8E+05	2E+05	5E+05	1E+06	5E+05
1,2 DG	1E+05	8E+05	1E+05	3E+05	8E+05	NA	4E+05
MG	3E+04	NA	NA	NA	NA	NA	NA
MGDG	1E+04	5E+04	1E+05	1E+04	1E+04	2E+04	4E+04
DGDG	5E+05	4E+05	1E+06	7E+02	6E+02	NA	4E+05
SQDG	3E+05	8E+05	NA	2E+05	6E+05	5E+05	5E+05
PE	2E+05	6E+04	4E+05	8E+04	8E+04	8E+04	1E+05
PG	NA	NA	1E+06	NA	1E+04	6E+03	5E+05
total lipids	9E+04	3E+05	7E+05	1E+05	1E+05	2E+05	3E+05
PP*	2E+05	6E+04	9E+05	8E+04	4E+04	4E+04	2E+05
GL**	3E+05	4E+05	7E+05	6E+04	2E+05	2E+05	3E+05

Table S9: The enrichment factor on the aerosol particles (EFaer) of the individual lipid classes along the campaign and as an average

For the calculation of  $EF_{aer}$ , Eq. (3) was used. For the analysis of sodium in the SML n=5 samples were investigated. In the SML, the sodium 5 concentration was  $12.53 \pm 0.53$  g L<sup>-1</sup>. Due to small relative standard deviation (4.2 % for SML), the mean value of sodium concentration in SML samples (12.53 g L<sup>-1</sup>) was used for the calculation of  $EF_{aer}$ . For the sodium concentration on PM<sub>1</sub> aerosol particles, the measured atmospheric concentrations, listed in Table S8, were used. Moreover, for *c* (*analyte*)<sub>*SML*</sub> in Eq. (3) the measured concentration of the respective lipid class of the dissolved fraction in the SML was used for the calculation as shown in Table S8. PP\* - Phospholipids, including PE, PG and PC

10 GL\* - Glycolipids, including MGDG, DGDG, SQDG

lipid	standard	saturation	Henry's law	adsorption	adsorption
classes		vapor	constants	coefficient in	coefficient in air <sup>3</sup>
		pressure <sup>1</sup> (p)	( <b>H</b> )	water <sup>2</sup> (K <sub>aq</sub> )	(Ka)
		Ра	mol m <sup>-3</sup> Pa <sup>-1</sup>	m <sup>-1</sup>	m <sup>-1</sup>
НС	nonadecane	6.1E-02	1.45E-07 <sup>a</sup>	8.17E+03	2.94E+00
WE	stearyl palmitate	1.74E-09	8.62E-06 <sup>a</sup>	1.50E+08	3.21E+06
ME	methyl palmitate	2.82E-02	1.80E-03 <sup>b</sup>	6.15E-02	2.74E-01
TG	tristearine	1.3175E-21	7.00E-03 <sup>c</sup>	2.96E+17	5.14E+18
FFA	stearic acid	4.99E-05	8.40E-01 <sup>b</sup>	9.64E-01	2.01E+03
ALC	cetyl alcohol	7.49E-03	3.90E-02 <sup>b</sup>	1.81E-02	1.75E+00
ST	cholesterol	1.024E-07	5.80E-02 <sup>c</sup>	4.79E+02	6.88E+04
MG	1-stearoyl-rac-glycerol	6.99E-06	8.13E-01 <sup>a</sup>	1.75E-01	3.52E+02
PG	phosphatidylglycerol	9.94E-17	1.92E+11 <sup>a</sup>	5.43E-01	2.59E+14
	(18:1/16:0)				
PC	1,2-diacyl-sn-glycero-3-	9.05E-15	6.17E+16 <sup>a</sup>	6.20E-10	9.4916E+10
	phosphocholine				
1,2 DG	diacyl-glycerol	5.69E-15	4.24E+01 <sup>a</sup>	2.51E+06	2.6409E+11
1,3 DG	glyceryl 1, 3 distearate	5.69E-15	4.24E+01 <sup>a</sup>	3.27E+05	3.4391E+10
DGDG	digalactosyl diglyceride	1.53E-22	5.18E+19 <sup>a</sup>	1.03E-03	1.3251E+20
MGDG	monogalactosyldiglyceride	7.34E-18	8.62E+13 <sup>a</sup>	2.98E-02	6.3667E+15
SQDG	sulfoquinovosyldiacylglycerol	7.46E-24	2.98E+15 <sup>a</sup>	2.10E+02	1.5497E+21
PE	phosphatidylethanolamine	5.02E-14	2.64E+16 <sup>a</sup>	1.50E-08	9.7974E+11

Table S10: Calculation of the adsorption coefficient in water  $(K_{aq})$  and in air  $(K_a)$  of the individual lipid classes based on the saturation vapor pressure p and the Henry's law constants (H)

<sup>1</sup> the saturation vapor pressure at 298.15 K was calculated with SIMPOL.1 (Pankow and Asher, 2008)

<sup>a</sup> Henry's Law Constants at 298.15 K were calculated by HENRYWIN by US EPA. [2011]. Estimation Programs Interface Suite<sup>™</sup> for Microsoft® Windows, v 3.20. United States Environmental Protection Agency, Washington, DC, USA.

<sup>b</sup> Henry's Law Constants were calculated by Hilal et al. (2008) as mentioned in Sander (2015)

<sup>c</sup> Henry's Law Constants were calculated based on the method by Meylan and Howard (1991) as mentioned in Sander (2015)

 $^2$  The adsorption coefficient in water (Kaq) was calculated using equation (4):

$$K_{aq} = \frac{\frac{c(analyte)_{SML}}{1\cdot 10^{-6}}}{H_{A(analyte)} \cdot p_{analyte}}$$
(4)

with  $c(analyte)_{SML}$  as the mean concentration of the analyte in the dissolved fraction of the SML (in mol m<sup>-3</sup>), the mean thickness of the SML  $(1 \cdot 10^{-6} m)$ , the Henry's law constants of the analyte  $H_{A(analyte)}$  (in mol m<sup>-3</sup> Pa<sup>-1</sup>) and  $p_{analyte}$  (saturation vapor pressure at 298.15 K in Pa).

#### 5 <sup>3</sup> The adsorption coefficient in air ( $K_a$ ) was calculated using equation (5):

$$K_a = \frac{\frac{c(analyte)_{SML}}{\frac{1\cdot10^{-6}}{p_{analyte}}}}{\frac{p_{analyte}}{RT}}$$
(5)

with  $c(analyte)_{SML}$  as the mean concentration of the analyte in the dissolved fraction of the SML (in mol m<sup>-3</sup>), the mean thickness of SML  $(1 \cdot 10^{-6} m)$ ,  $p_{analyte}$  (saturation vapor pressure at 298.15 K in Pa=N m<sup>-2</sup>= kg m<sup>-1</sup> s<sup>-2</sup>), the gas constant *R* (8.314 kg m<sup>2</sup> s<sup>-2</sup> mol<sup>-1</sup> K<sup>-1</sup>) and the temperature *T* (298.15 K).

#### Adsorption of the individual lipid classes at the bubble air-water interface:

To estimate the adsorption of the individual lipid classes at the air-water interface, both the adsorption coefficient in water  $(K_{aq})$  and the one in air  $(K_a)$  were calculated, as shown in Table S10. Considering the concentration of the adsorbed solute at the air-water interface as well as the equilibrium concentration of the solute, the principle of  $K_a$  was based on the approach of

- 15 Kelly et al. (2004). According to it, the concentration in the SML and the saturation vapor pressure (p) of the analyte describe the distribution of the analyte between the interface and the air, namely K<sub>a</sub>. K<sub>a</sub> expresses the maximum gas-phase concentration of the analyte before the condensation on the surface occurs. Also, another new adsorption coefficient, K<sub>aq</sub>, was introduced in this context. It takes into account the concentration of the adsorbed solute at the air-water interface, but uses the saturation concentration of the solute in water instead of air. K<sub>aq</sub> expresses the maximum amount of the analyte that can be dissolved. If
- 20 this value is exceeded (K<sub>a</sub>>K<sub>aq</sub>), enrichment takes place in this medium. The saturation concentration of the solute in water was calculated by multiplying p with the Henry's Law (H<sub>A</sub>) constant of the analyte. As for most analytes no H<sub>A</sub> constants has been determined, however, which is also the case for p, estimation programs had been applied to calculate these values shown by Table S10. The parameters p and H<sub>A</sub> for the standards of the individual lipid classes were calculated. A comparison of p by using different models (SIMPOL.1 vs. EVAPORATION) is further discussed in Fig. S16.
- Overall, the results in Table S10 help evaluating the possible adsorption of the individual lipid classes at the bubble air-water interface. Assuming that the differences between both adsorption coefficients,  $K_{aq}$  and  $K_a$ , were between 10<sup>1</sup> and 10<sup>2</sup>,  $K_{aq} \sim K_a$ was defined. For example, this was applied to TG with  $K_{aq(TG)}$ :2.96·10<sup>17</sup>,  $K_{a(TG)}$ :5.14·10<sup>18</sup> and ALC with  $K_{aq(ALC)}$ :1.81·10<sup>-2</sup>,  $K_{a(ALC)}$ :1.75·10<sup>0</sup>. Based on the ratio of the two adsorption coefficients to each other ( $K_{aq} \sim K_a$ ), we conclude that the lipid classes TG and ALC are preferably distributed at the interface, the bubble surface. As regards the EF<sub>aer</sub> (Table S9), TG and ALC
- 30 showed the comparatively highest  $EF_{aer}$  with  $3 \cdot 10^6$  and with  $1 \cdot 10^6$ , respectively. In contrast, if we look at the lipid class which had the comparatively lowest  $EF_{aer}$  ( $4 \cdot 10^4$ ), the ratio of the adsorption coefficients was  $K_a >> K_{aq}$  for MGDG, meaning that it was preferably distributed into water.

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