Supporting information for "Probing the impact of a phytoplankton bloom on the chemistry of nascent sea spray aerosol using high-resolution mass spectrometry"

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Table S1: Overview of the sea spray chamber experiments conducted during the campaign

Exp.	Start time	End time	Duration	Mean seawater properties		
				Temp. (std. dev.)	Sal. (std. dev.)	Chl-a (min - max)
			(hours)	(C)	(g kg-1)	(µg l-1)
1	04/06/2019 16:00	05/06/2019 12:00	20	N/A	N/A	1.08 (1.00 - 1.12)
2	06/06/2019 10:00	07/06/2019 10:00	24	N/A	N/A	1.51 (1.04 - 1.99)
3	09/06/2019 09:00	10/06/2019 09:00	24	8.14 (0.016)	35.07 (0.005)	1.45 (1.35 - 1.53)
4	12/06/2019 09:00	13/06/2019 09:00	24	8.22 (0.025)	35.08 (0.003)	1.76 (1.38 - 2.11)
5	16/06/2019 21:00	18/06/2019 09:00	36	8.35 (0.042)	35.08 (0.004)	1.89 (1.78 - 2.07)
6	20/06/2019 21:00	22/06/2019 09:00	36	8.49 (0.022)	35.07 (0.005)	2.67 (2.57 - 2.87)

Table S2: List of SS and SML samples

SS/SML sample	Date	Chl-a (µg l^{-1})
1	05/06/2019	1.1
2	06/06/2019	1.975
3	07/06/2019	1.04
4	08/06/2019	1.47
5	09/06/2019	1.44
6	10/06/2019	1.455
7	12/06/2019	1.455
8	17/06/2019	1.795
9	18/06/2019	1.885
10	20/06/2019	2.68
11	21/06/2019	2.665

Table S3: Mobile-phase gradient used

Retention time (min)	Mobile phase A (%)	Mobile phase B (%)	Flow rate (ml/min)
0	100	0	0.3
0.7	100	0	0.3
2.5	90	10	0.3
5	90	10	0.3
5.1	80	20	0.3
9	60	40	0.3
13	0	100	0.3
16	0	100	0.3
16.3	100	0	0.3
23	100	0	0.3

Table S4: Description of replicate injections for the different experiments

				Sea spray aerosol ($> 1\mu$m)		Sea spray aerosol ($< 1\mu$m)	
Exp.	Plunging jet flow rate (L min^{-1})	Start time	End time	Number of replicates	Injection volumes (μL)	Number of replicates	Injection volumes (μL)
1	5	04/06/2019 16:00	05/06/2019 12:00	1	18	1	20
2	5	06/06/2019 10:00	07/06/2019 10:00	3	10, 15, 20	1	20
3	4	09/06/2019 09:00	10/06/2019 09:00	3	10, 15, 20	1	20
4	4	12/06/2019 09:00	13/06/2019 09:00	3	10, 15, 20	1	20
5	4	16/06/2019 21:00	18/06/2019 09:00	4	5, 10, 15, 20	1	20
6	4	20/06/2019 21:00	22/06/2019 09:00	4	5, 10, 15, 20	1	20

Table S5: Summary of the variability of replicate injections

		SS	SSA
Total number of samples		11	6
Number of samples used to estimate reproducibility		1	5
Total number of replicate measurements		5	17
Injection volumes (μL)		20	5-20
Bray-Curtis dissimilarity between replicates (mean ± SD)	Fraction A	1.1 ± 0.1%	5 ± 1.1%
	Fraction B	1.9 ± 0.6%	2.7 ± 1.5%
	Fraction C	4.6 ± 1.6%	3.1 ± 0.5%

Table S6: Overview of number and atomic composition of identified molecular formulas

		No. of compounds identified:		No of compounds identified in:		Percentage of tot. intensity identified in:		Formula fractions			Percentage of compounds whose relative intensity correlates with chl-a* (%)
		Total	On example day (21-06-2019)	10/11 samples	5/6 samples	10/11 samples (%)	5/6 samples (%)	CHO (%)	CHON (%)	CHOS (%)	
SS	Fraction A	2796	2350	1946		99		53.1	36.8	10.1	48
	Fraction B	3437	2929	2394		99		58	34.7	7.3	41
	Fraction C	2029	1455	814		92		87.4	11	1.6	37
SML	Fraction A	3357	2278	2007		99		50.7	35.1	14.2	39
	Fraction B	3549	2723	2316		98		55.1	33.2	11.7	55
	Fraction C	2386	1603	943		90		86.09	10.21	3.7	85
Foam	Fraction A		2310					52.7	33.7	13.6	
	Fraction B		2819					54.2	33.5	12.3	
	Fraction C		2642					57.6	22.3	20.1	
SSA ($> 1\mu$m)	Fraction A	2040	1651		670		85	64.1	27	8.9	60
	Fraction B	2997	2472		683		82	64.47	27.33	8.2	62
	Fraction C	3497	2764		1677		91	61.2	26.4	12.4	78
SSA ($< 1\mu$m)	Fraction C	765	573		349		90	82.2	6.2	11.6	78

*(Spearman correlation rank > 0.3 or < -0.3)

Table S7: Weighted average molecular element ratios (mean ± SD) of hydrogen to carbon (H/C) and oxygen to carbon (O/C) as well as the weighted average molecular weight (MW) for each polarity fraction of each sample type.

	Weighted average H/C			Weighted average O/C			Weighted average MW		
Sample type	Fraction A	Fraction B	Fraction C	Fraction A	Fraction B	Fraction C	Fraction A	Fraction B	Fraction C
SS	1.225 ± 0.002	1.292 ± 0.002	1.377 ± 0.002	0.564 ± 0.002	0.461 ± 0.001	0.347 ± 0.001	399.68 ± 0.49	427.5 ± 1.3	439.2 ± 4.6
SML	1.227 ± 0.002	1.295 ± 0.002	1.426 ± 0.016	0.565 ± 0.001	0.459 ± 0.001	0.331 ± 0.007	397.84 ± 0.65	425 ± 2.2	458.4 ± 7.2
Foam	1.309	1.411	1.509	0.556	0.447	0.281	373.13	420.69	498.21
SSA ($> 1\mu\mu$)	1.405 ± 0.02	1.408 ± 0.010	1.514 ±0.033	0.537 ± 0.003	0.399 ± 0.011	0.298 ± 0.042	325.43 ± 5.5	429.4 ± 11	502.25 ± 37.5
SSA ($< 1\mu\mu$)	-	-	1.508 ± 0.008	-	-	0.331 ± 0.007			420.7 ± 5.6

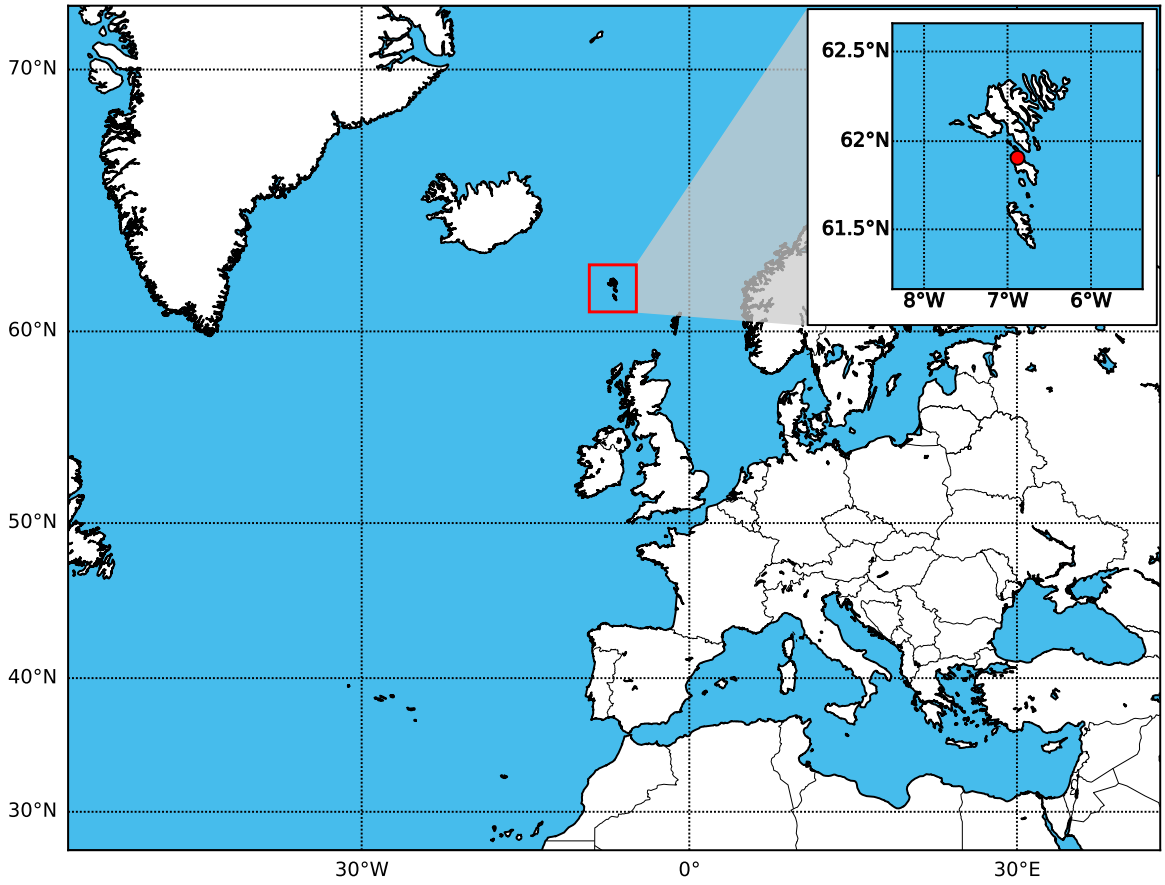

Figure S1: The location of the campaign (Skopun, Faroe Islands).

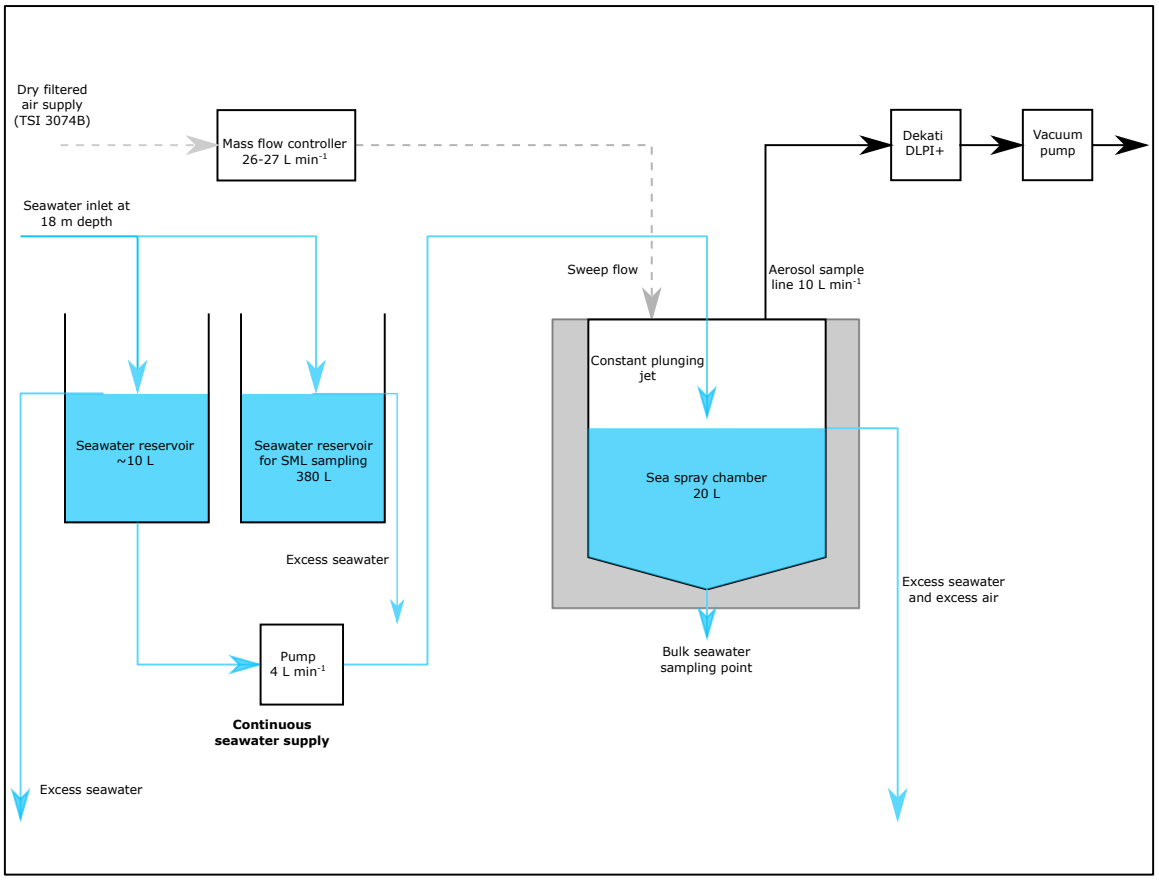

Figure S2: Schematic setup of the sampling. The sea spray chamber is continuously supplied by seawater. Nascent SSA is generated used a plunging jet and directed towards the DLPI+ for offline analysis.

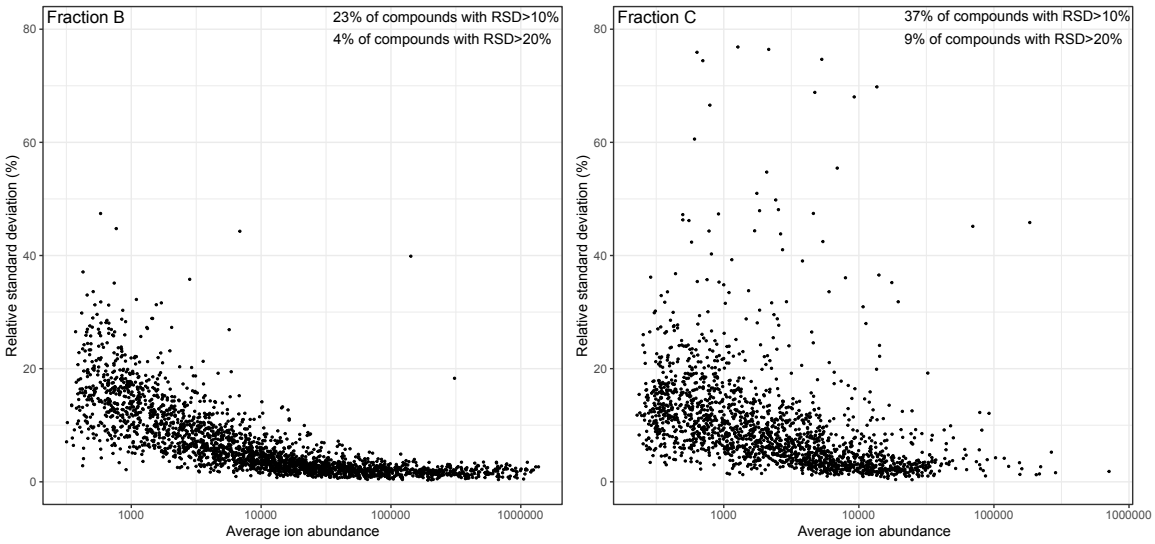

Figure S3: Relative standard deviation of ion intensities from 5 replicate measurements of subsurface seawater samples as a function of average ion intensity for each identified ion.

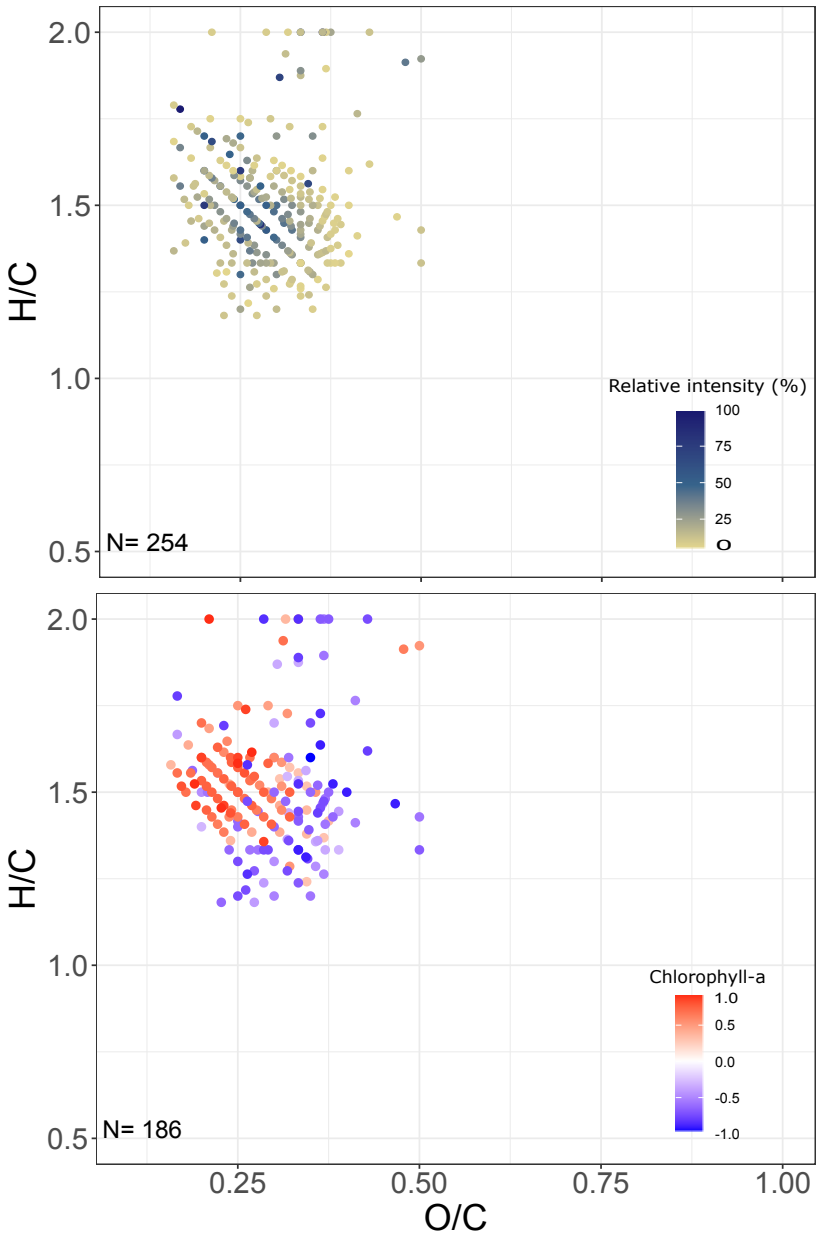

Figure S4: Top plot shows compounds identified in 5 or 6 submicron SSA samples which are also identified in 5 or 6 supermicron SSA samples. Bottom plot shows the correlation (Spearman's coefficient) between their sum-normalised intensities with chl-a concentrations. Only compounds that show Spearman's coefficient > 0.3 or < -0.3 were plotted.

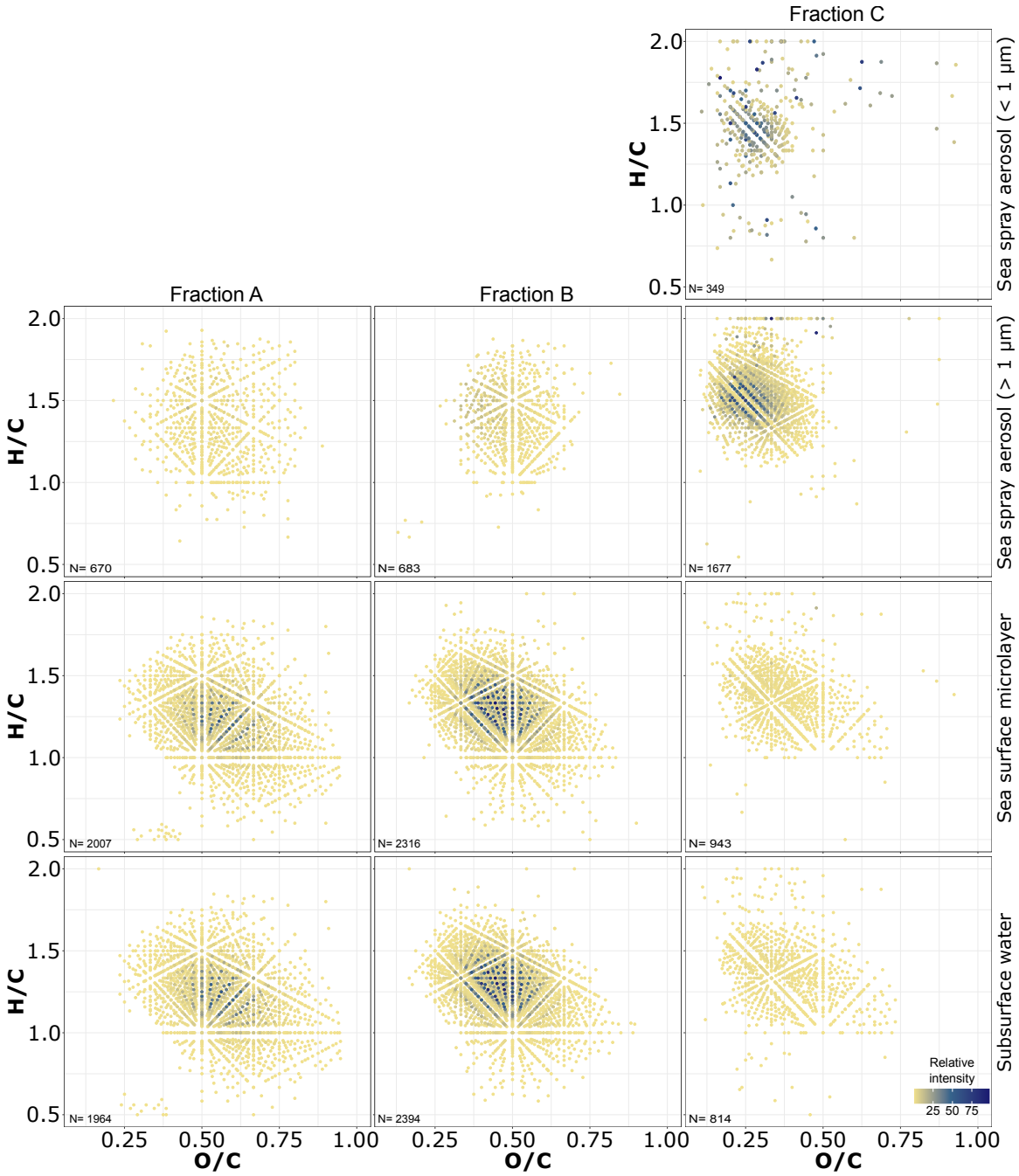

Figure S5: Compounds identified in 10 or 11 SS and SML samples and in 5 or 6 submicron and supermicron SSA samples plotted in Van Krevelen diagrams by their H/C and O/C atomic ratios. Colour scale represents average ion intensities of all samples that were then normalised to the sum of the identified ions from all 3 polarity fractions. "N" represents total number of compounds plotted for each fraction.

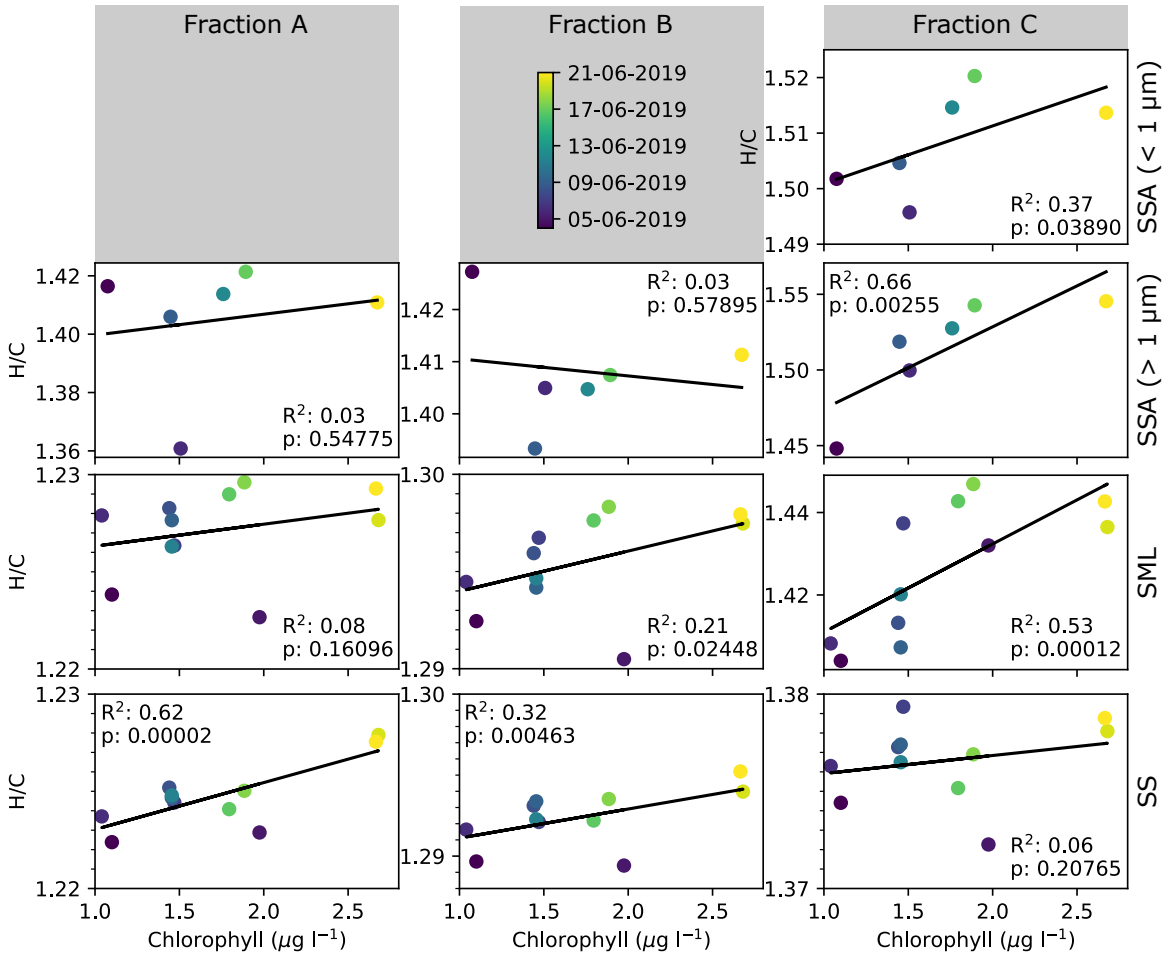

Figure S6: Correlation of weighted average H/C values for each samples vs. chl-a concentrations.

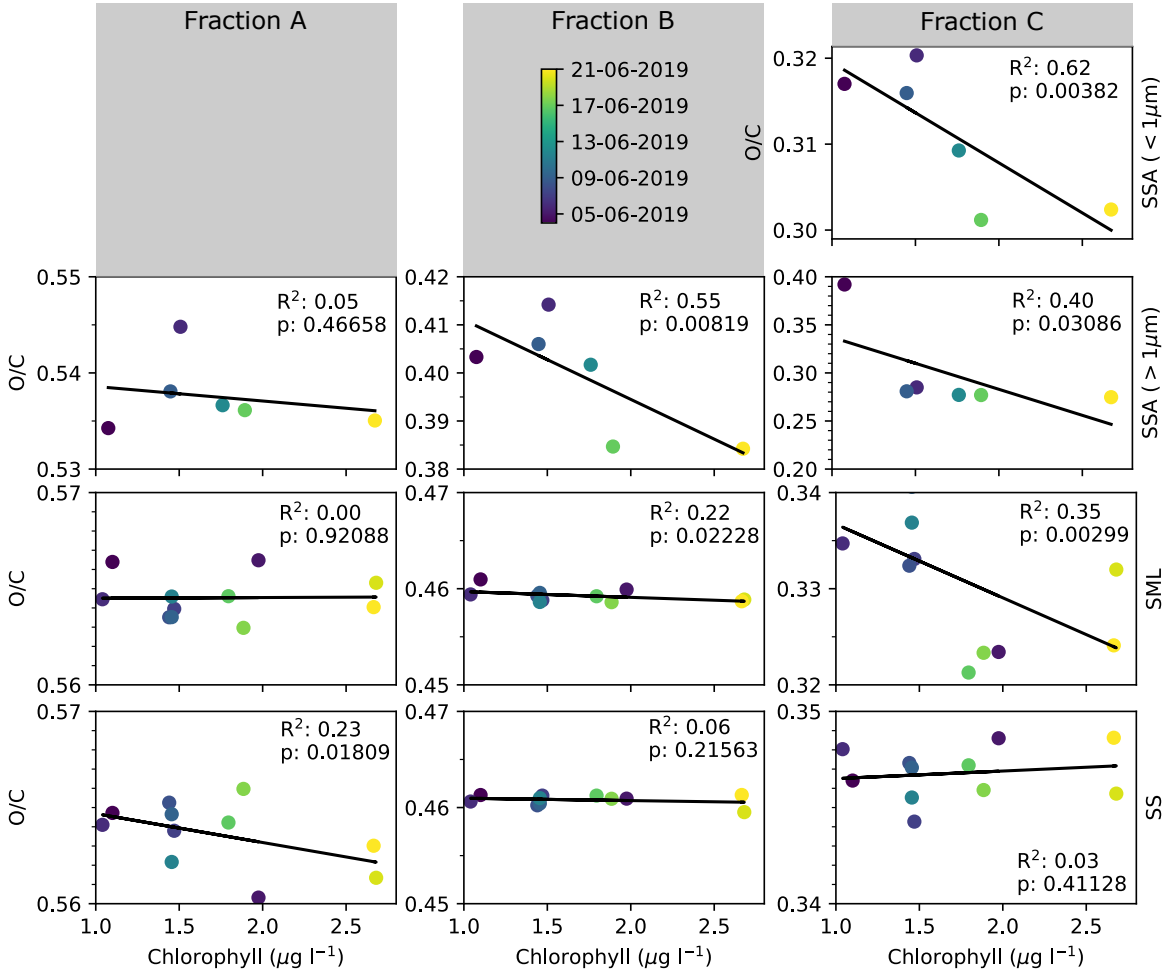

Figure S7: Correlation of weighted average O/C values for each samples vs. chl-a concentrations.

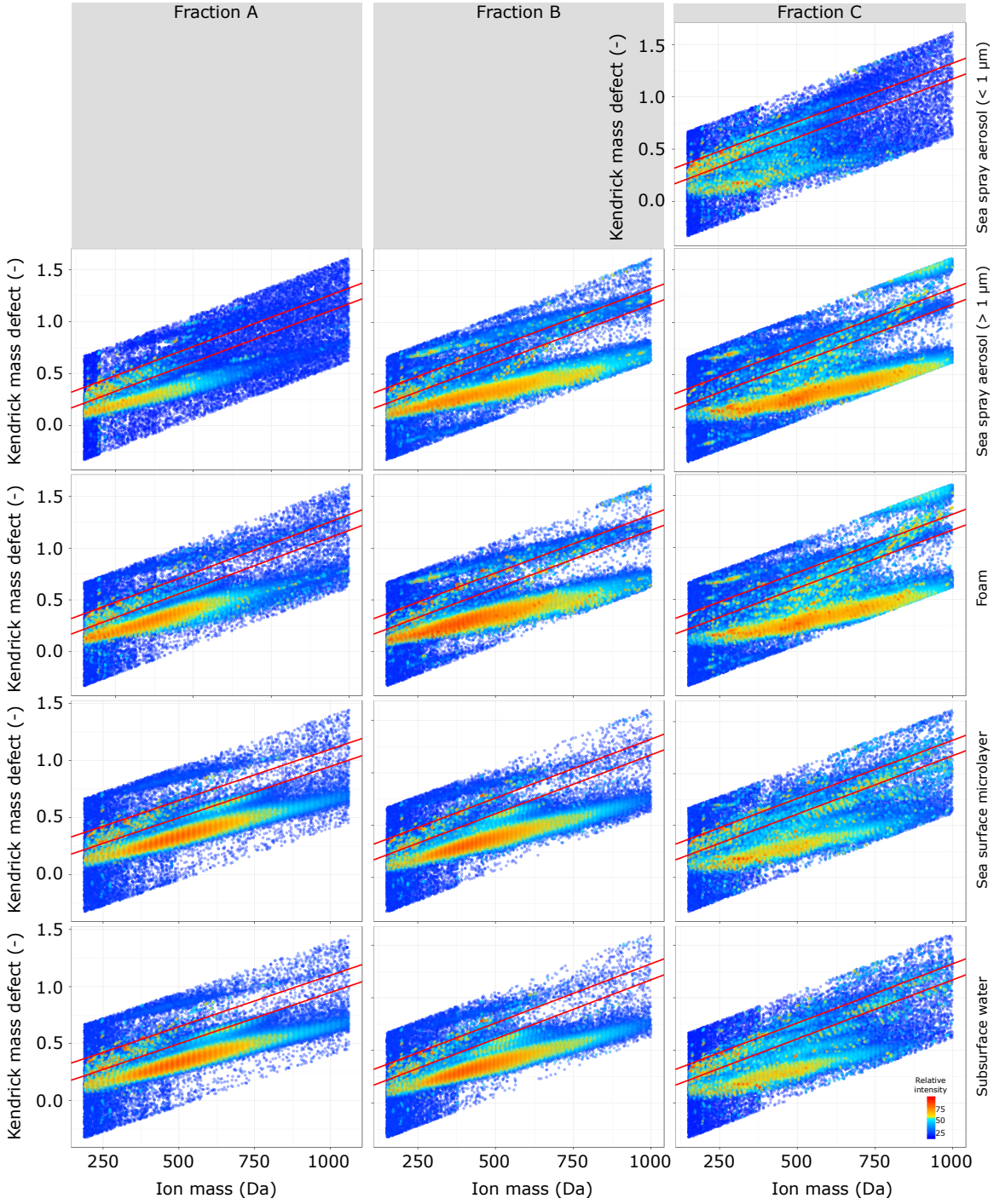

Figure S8: Kendrick mass defects (KMD) of all detected ions before noise removal. Figure shows SS, SML, foam and SSA samples collected on the 21st of June 2019. Colour scale shows relative intensities for each polar fraction individually. Areas between red lines represent KMD dependent region used to estimate noise levels with KMDNoise function[1].

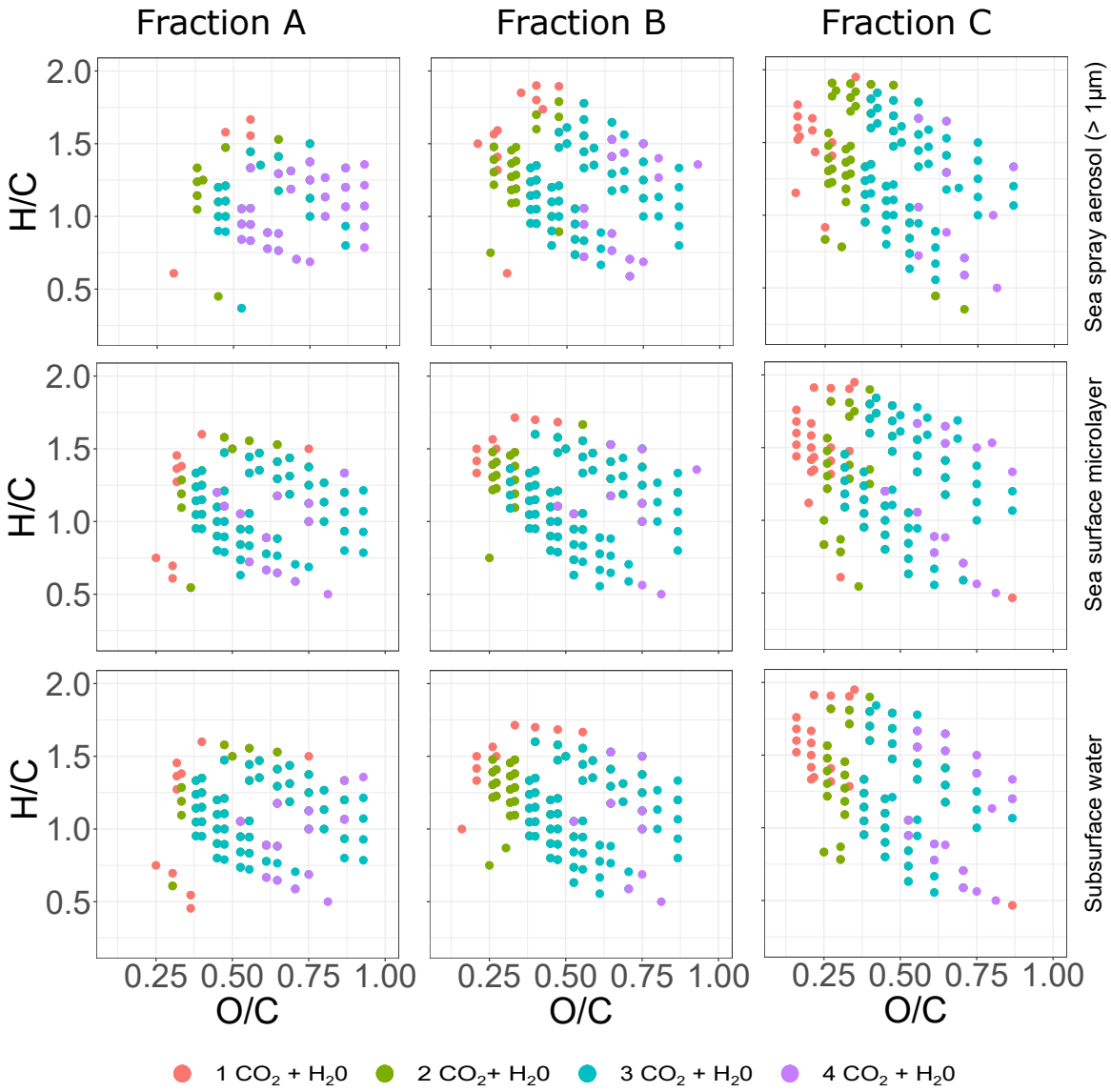

Figure S9: Van Krevelen diagrams (H/C vs O/C of identified molecular formulas) of DOM compounds assigned based on their detected fragment ions. The colours represent different types of neutral losses (1-4 CO_2 + 1 H_20 neutral loss). When a molecular formula showed more than one type of neutral loss, data points were overlapped so that the colour shows the highest number of CO_2 losses observed. Results are based on the fragmentation of compounds in the mass range of m/z 398.343-409.005.

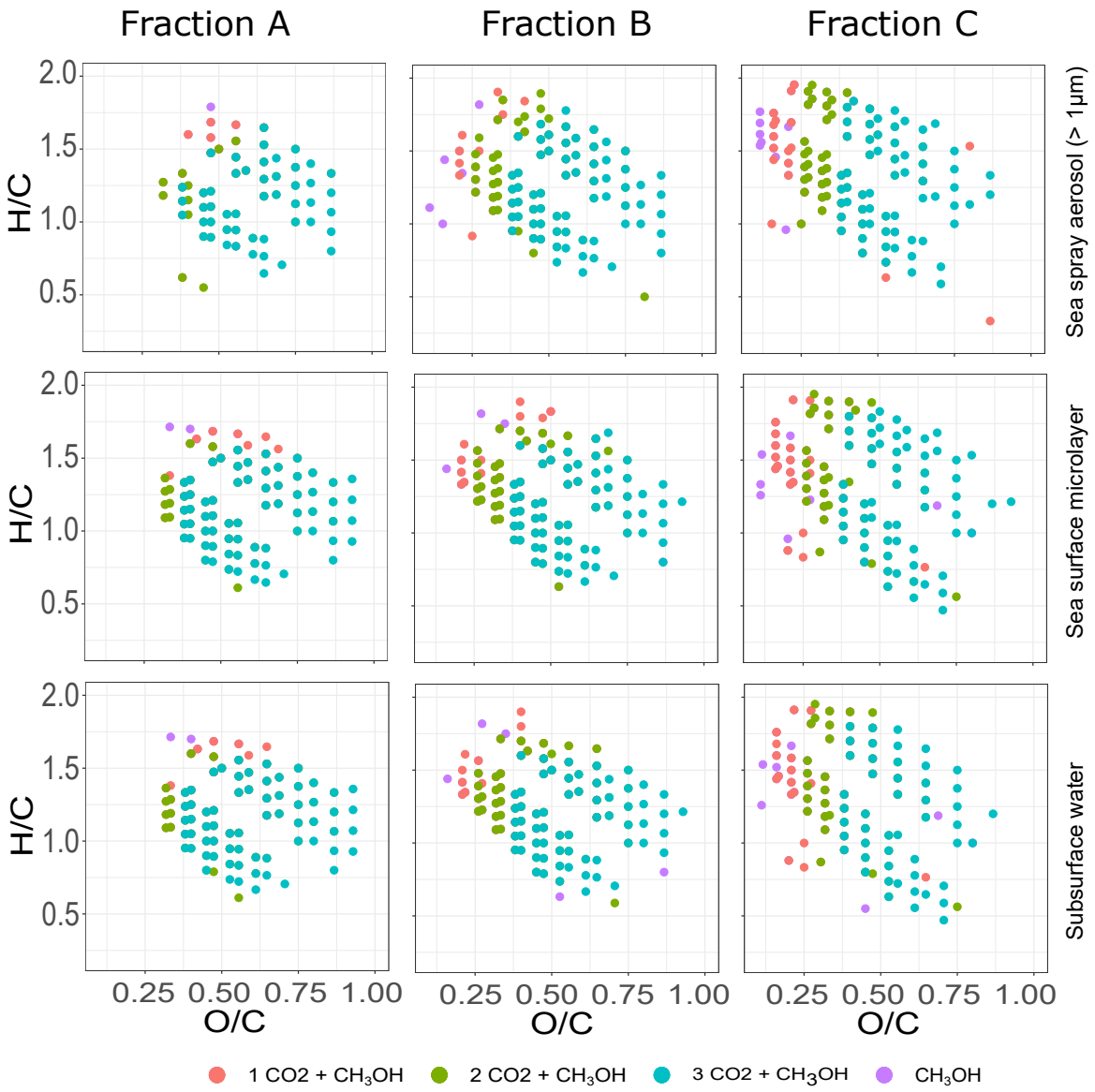

Figure S10: Van Krevelen diagrams (H/C vs O/C of identified molecular formulas) of DOM compounds assigned based on their detected fragment ions. The colours represent different types of neutral losses (0-3 CO_2 + 1 CH_3OH neutral loss). When a molecular formula showed more than one type of neutral loss, data points were overlapped so that the colour shows the highest number of CO_2 losses observed. Results are based on the fragmentation of compounds in the mass range of m/z 398.343-409.005.

References

[1]Simeon K Schum, Laura E Brown, and Lynn R Mazzoleni. Mfassignr: Molecular formula assignment software for ultrahigh resolution mass spectrometry analysis of environmental complex mixtures. Environmental Research, 191: 110114, 2020