Supplement of Atmos. Chem. Phys., 23, 6571–6590, 2023
https://doi.org/10.5194/acp-23-6571-2023-supplement

Atmospheric Chemistry and Physics
Open Access
EGU

Supplement of

Amino acids, carbohydrates, and lipids in the tropical oligotrophic Atlantic Ocean: sea-to-air transfer and atmospheric in situ formation

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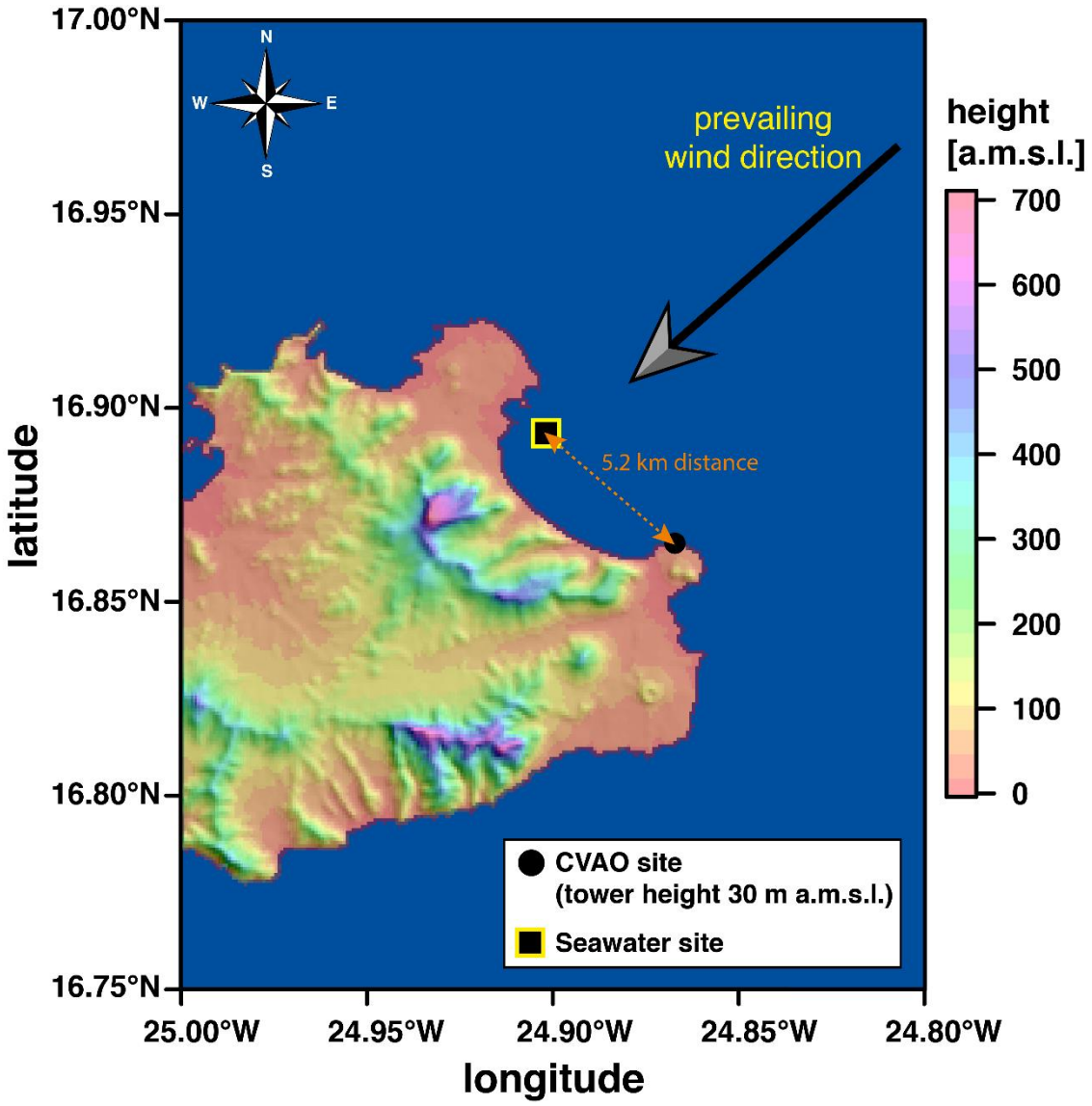

Figure S1: Sampling stations of the MarParCloud: Cape Verde Atmospheric Observatory (CVAO) and seawater sampling site (adopted from Triesch et al. 2021b)

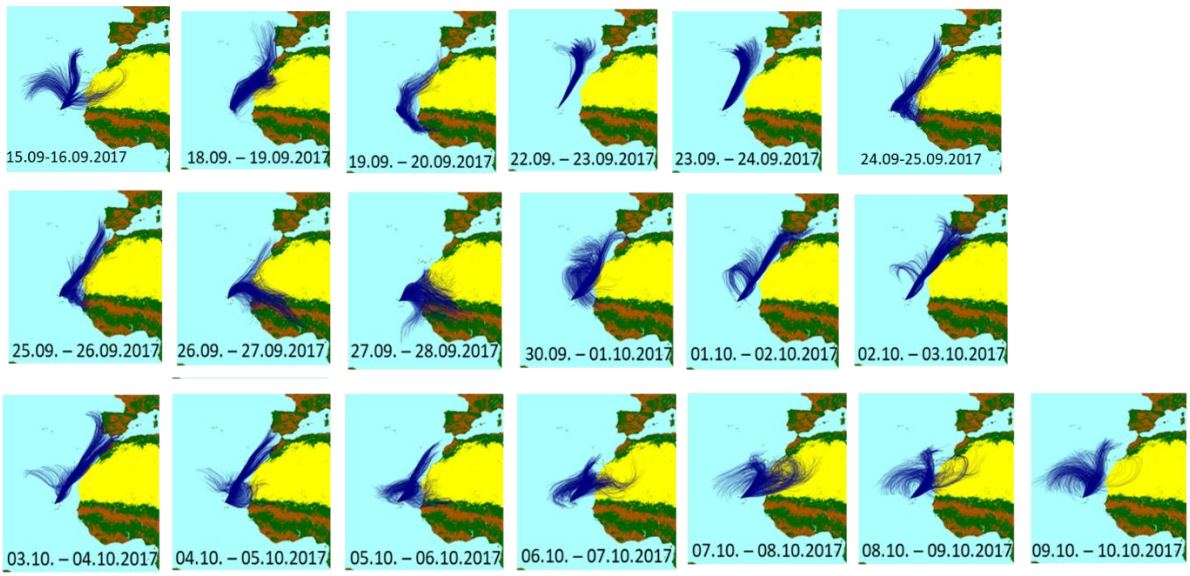

Figure S2: 96 hour back trajectories calculated on an hourly basis within the intervals of the aerosol particle filter sampling at the CVAO for selected time periods, using the NOAA HYSPLIT model (HYbrid Single-Particle Lagrangian Integrated Trajectory, http://www.arl.noaa.gov/ready/hysplit4.html, 26.07.19) in the ensemble mode at an arrival height of 500 m ± 200 m (van Pinxteren et al., 2010), adopted from van Pinxteren et al. (2020). The meteorological conditions observed during the campaign were typical for this site with strong north-easterly wind (30 to 60 °) and are reported in van Pinxteren et al. (2020).

Tab. S1: Overview of the sampling details. The MarParCloud campaign took place from 13 September 2017 – 13 October 2017 and details are given in van Pinxteren et al. (2020). Selected samples from the campaign were analysed for the OC groups. Further details are given in van Pinxteren et al. (2020), and (Triesch et al., 2021a;Triesch et al., 2021b).

Type of sample	**Sampling location**	**Types of samples**	**Type of analysis / number of samples**	**Sample treatment and analysis**
SML 	Bahia das Gatas: 16°53ˈ17ˈN, 24°54ˈ25ˈE	Water samples, Spot samples	DL: n = 6 DAA: n = 6 DCHO: n = 3	DL: extract in dichloromethane, filtration (GF-F); analysis: TLC-FID[*1] DAA, DCHO: desalination, filtration (0.2 µm), hydrolysis; analysis: UHPLC/ESI-Orbitrap-MS[*2] (DAA), HPAEC-PAD[*3] (DCHO)
Bulk water 	Bahia das Gatas: 16°53ˈ17ˈN, 24°54ˈ25ˈE	Water samples, Spot samples	DL: n = 13 DAA: n = 3 DCHO: n = 3	DL: extract in dichloromethane, filtration (GF-F); analysis: TLC-FID[*1] DAA, DCHO: desalination, filtration (0.2 µm), hydrolysis; analysis: UHPLC/ESI-Orbitrap-MS[*2] (DAA), HPAEC-PAD[*3] (DCHO)
PM_1 	CVAO: 16°51ˈˈ49ˈN, 24°52ˈ02ˈE sampler installed on a tower: 30 m height	Quartz fiber filters samples, comprise a 24 h intervall	DL: n = 14 AA_{aer}: n = 7 CHO_{aer}: n = 8 Na^+: n = 14 OC: n = 8 EC: n = 8	$Lipids_{aer}$: extract in dichloromethane, filtration (GF-F); analysis: TLC-FID[*1] AA_{aer} , CHO_{aer}: aqueous extract, filtration (0.2 µm), hydrolysis; analysis: UHPLC/ESI-Orbitrap-MS[*2] (AA_{aer}), HPAEC-PAD[*3] (CHO_{ae}) OC/EC: filter piece directly measured; analysis: Sunset Analyzer Na^+: aqueous extract, filtration (0.45 µm); analysis: ion chromatography

[*1] Thin-layer chromatography -flame ionisation detector, [*2] Ultra-high performance liquid chromatography with electrospray ionization and Orbitrap mass spectrometry (UHPLC/ESI-Orbitrap-MS), [*3] High-Performance Anion-Exchange Chromatography coupled with Pulsed Amperometric Detection

Table S2: Concentration of individual monosaccharides, after hydrolysis step, (µg L^{-1}) in the SML and bulk water samples. For the calculation of the EF_{SML} ($EF_{SML} = c_{SML} / c_{bulkwater}$) the SML sample was related to the bulk water sample from the same day.

Sample ID	Sampling date	Fuc	GalN	Rha	Ara	GlcN	Gal	Glc	Xyl+Man	MurAc	GalAc	GlcAc
SML 7	27.09. 2017	9.9	3.9	8.7	7.6	5.2	18.1	35.0	10.3	2.1	7.2	*1.0*
SML 7 (2)	27.09. 2017	10.5	4.4	9.1	7.5	5.2	19.2	30.6	9.4	2.4	7.4	*1.0*
SML 10	03.10. 2017	8.2	3.0	6.7	6.9	4.2	17.5	17.6	10.0	2.1	8.3	1.9
SML 10 (2)	03.10. 2017	9.1	3.5	7.4	7.5	4.8	18.6	23.5	10.5	2.5	7.3	3.3
SML 14	07.10. 2017	5.3	2.1	5.0	4.0	2.6	8.8	14.3	4.9	3.2	1.7	1.5
SML 14 (2)	07.10. 2017	6.1	2.4	5.0	4.1	2.6	8.4	13.0	4.6	3.9	1.8	1.9
ULW 7	27.09. 2017	4.6	1.6	4.1	3.8	2.4	9.0	24.9	5.4	*1.0*	8.9	2.7
ULW 7 (2)	27.09. 2017	4.6	1.4	4.3	3.6	2.3	8.7	30.1	4.5	*1.0*	7.3	1.8
ULW 10	03.10. 2017	7.2	2.8	7.1	5.8	3.5	14.3	16.0	4.8	*1.0*	7.5	4.2
ULW 10 (2)	03.10. 2017	6.9	3.0	7.5	6.5	3.8	13.9	13.9	5.3	*1.0*	8.2	0.4
ULW 14	07.10. 2017	7.9	3.0	7.3	7.7	3.9	14.4	30.5	7.3	2.0	6.9	3.5
ULW 14 (2)	07.10. 2017	7.5	3.4	8.1	6.7	4.5	13.1	28.2	7.4	1.8	5.5	3.9

Table S3: Concentration of individual amino acids, after hydrolysis step, (µg L^{-1}) in the SML and bulk water samples. For the calculation of the EF_{SML} ($EF_{SML} = c_{SML} / c_{bulkwater}$) two groups were constructed. The sum of amino acids from SML 16 and ULW 16 were related to each other (group 1), all other SML values were summed up and averaged and divided by all other (summed up and averaged) bulk water values. The final EF SML was calculated as the average between these two values.

Sample ID	Sampling date	Gly	Ala	Ser	Glu	Thr	Pro	Tyr	Val	Phe	Asp	Iso	Leu
SML 8	28.09. 2017	50.8	39.9	70.4	0.2	17.1	12.2	2.9	15.6	2.2	19.3	7.5	11.1
SML 10	03.10. 2017	22.6	7.4	16.3	0.2	1.3	2.5	0.1	2.5	0.4	0.2	0.3	0.9
ULW 11	04.10. 2017	5.7	0.2	0.2	0.2	38.2	0.2	0.1	25.8	4.0	38.3	0.2	0.2
ULW 12	05.10. 2017	33.6	12.9	38.9	0.2	4.7	3.5	0.1	5.1	1.0	3.9	0.2	3.7
SML 13	06.10. 2017	24.3	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.2	0.2	0.2	0.1
SML 14	07.10. 2017	38.1	14.1	30.0	0.2	3.1	3.9	0.1	5.6	1.7	9.1	1.9	9.9

SML 16	10.10. 2017	36.5	1.2	5.0	0.2	0.8	1.5	0.1	2.4	0.2	0.2	0.2	0.2
ULW 16	10.10. 2017	17.4	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.2	0.2	0.2	0.2
SML 3	20.09. 2017	163.2	93.4	156.9	54.9	28.1	25.4	0.7	28.5	5.4	54.9	9.7	25.7

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85 Table S4: Concentration of individual monosaccharides, after hydrolysis step, (pg m^{-3}) in the
86 PM_1 (detection limit = 5 pg m^{-3}).

Sample ID	Start sampling (UTC)	Stop sampling (UTC)	Fuc	GalN	Rha	Ara	GlcN	Gal	Glc	Xyl+Man	MurAc	GalAc	GlcAc
PM1 924	19.09.2017 20:00	20.09.2017 20:00	44	21	5	113	5	112	422	95	187	193	5
PM1 926	22.09.2017 15:00	23.09.2017 15:00	22	13	5	5	5	28	128	138	5	103	5
PM1 927	23.09.2017 15:00	24.09.2017 15:00	27	5	5	5	5	66	917	18	5	454	5
PM1 928	24.09.2017 15:00	25.09.2017 15:00	49	31	5	345	504	107	553	82	5	1147	5
PM1 934	30.09.2017 15:00	01.10.2017 15:00	27	5	5	5	32	35	5	18	5	84	5
PM1 937	02.10.2017 15:00	03.10.2017 15:00	5	5	5	54	5	131	141	71	112	66	5
PM1 945	08.10.2017 15:00	09.10.2017 15:00	5	5	5	5	5	5	50	5	5	5	5
PM1 946	09.10.2017 15:00	10.10.2017 15:00	22	5	5	5	5	5	77	45	5	5	5

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90 Table S5: Concentration of individual amino acids, after hydrolysis step, (pg m^{-3}) in the PM_1
91 (detection limit = 2 pg m^{-3}).

Sample ID	Start sampling (UTC)	Stop sampling (UTC)	Gly	Ala	Ser	Glu	Thr	Pro	Tyr	Val	Phe	Asp	Iso	Leu
PM1 920	15.09.2017 15:00	16.09.2017 15:00	1208	794	136	236	562	118	144	51	5	32	30	1208
PM1 923	18.09.2017 20:00	19.09.2017 20:00	318	528	7	84	148	58	46	3	1143	6	4	318
PM1 927	23.09.2017 15:00	24.09.2017 15:00	571	811	1039	302	462	420	325	45	5	61	172	571
PM1 930	26.09.2017 15:00	27.09.2017 15:00	82	387	5	24	45	7	17	5	388	5	5	82
PM1 932	28.09.2017 15:00	29.09.2017 15:00	668	604	108	149	204	119	111	37	5	22	29	668
PM1 940	05.10.2017 15:00	06.10.2017 15:00	124	458	199	45	128	69	70	12	5	20	38	124
PM1 942	07.10.2017 15:00	08.10.2017 15:00	275	805	5	38	170	26	3	-	1168	5	5	275

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Table S6: Relative composition (mol%) of the individual compounds in the bulk water, the SML and the aerosol particles. Italic values correspond to half the detection limit. Classification of the lipids after (Parrish, 1988;Parrish and Wells, 2021).

	bulk water	SML	aerosol	classification
amino acids				
Phe	2.15	0.88	0.66	neutral/polar
Gly	23.68	29.37	35.33	neutral/polar
Ser	16.39	24.42	18.68	neutral/polar
Tyr	*0.14*	0.36	0.23	neutral/polar
Thr	17.94	4.43	4.45	neutral/non-polar
Ala	5.56	13.67	11.67	neutral/non-polar
Pro	1.59	3.98	4.79	neutral/non-polar
Val	12.87	4.77	3.70	neutral/non-polar
Leu	1.65	4.19	1.33	neutral/non-polar
Iso	*0.19*	1.73	0.63	neutral/non-polar
Asp	17.66	7.33	12.35	acidic
Glu	*0.19*	4.87	6.16	acidic
carbohydrates				
GlcN	4.29	4.77	7.99	basic
GalN	3.23	3.76	1.84	basic
Fuc	8.88	10.46	3.08	neutral
Rha	8.82	8.91	1.76	neutral
Ara	8.56	8.73	8.75	neutral
Gal	15.39	17.56	6.04	neutral
Glc	30.07	25.96	28.98	neutral
Xyl+Man	7.24	9.63	5.52	neutral
MurAc	1.73	2.25	19.03	acidic (bacterial tracer)
GalAc	8.59	6.06	7.15	acidic
GlcAc	3.21	1.91	9.87	acidic
lipids				
HC	44.07	30.89	39.00	hydrocarbon
ST	0.28	0.53	0.94	sterol
PIG	2.09	1.28	0.50	pigments
ME	0.36	1.34	no data	methyl ester
WE	0.61	0.80	no data	membrane component
TG	0.91	1.17	8.03	metbolic reserve
FFA	13.65	17.32	21.27	degradation lipids
ALC	1.22	2.26	8.49	degradation lipids
1,3DG	no data	0.29	0.17	degradation lipids
1,2 DG	0.07	0.42	0.46	degradation lipids
MG	0.19	0.19	0.43	degradation lipids

MGDG	16.77	18.44	3.42	glycolipids
DGDG	0.35	3.49	2.84	glycolipids
SQDG	2.11	2.01	5.55	glycolipids
PE	6.17	8.40	4.74	polar lipids
PG	11.12	11.04	4.17	polar lipids
PC	0.03	0.15	no data	polar lipids

Table S7: Concentration of organic carbon (OC) and elemental carbon (EC) in µg m^{-3}) in the PM_1.

Sample ID	Start sampling (UTC)	Stop sampling (UTC)	OC	EC
PM1 922	17.09.2017 20:00	18.09.2017 20:00	0.310	0.127
PM1 923	18.09.2017 20:00	19.09.2017 20:00	0.274	0.131
PM1 924	19.09.2017 20:00	20.09.2017 20:00	0.201	0.136
PM1 927	23.09.2017 15:00	24.09.2017 15:00	0.169	0.053
PM1 929	25.09.2017 15:00	26.09.2017 15:00	0.202	0.115
PM1 932	28.09.2017 15:00	29.09.2017 15:00	0.130	0.091
PM1 933	30.09.2017 15:00	29.09.2017 15:00	0.13	0.054
PM1 934	30.09.2017 15:00	01.10.2017 15:00	0.150	0.069

Tab. S8: Average concentration and respective carbon contribution of the OC groups

OC group	ng m^{-3}	ng C m^{-3}	% OC	Reference
carbohydrates				
DCHO	1.5	0.6	0.30	this work
amino acids				
DAA	2.4	0.8	0.41	this work
lipids (DL)				
HC	32.1	27.25	13.56	(Triesch et al., 2021b)
TG	21.9	16.83	8.38	(Triesch et al., 2021b)
FFA	18.5	14.08	7.00	(Triesch et al., 2021b)
ALC	6.3	5.00	2.49	(Triesch et al., 2021b)
1,3DG	0.2	0.19	0.09	(Triesch et al., 2021b)
ST	2.6	1.74	0.87	(Triesch et al., 2021b)
1,2DG	0.5	0.41	0.20	(Triesch et al., 2021b)
PIG	0.9	0.55	0.27	(Triesch et al., 2021b)
MG	0.8	0.61	0.30	(Triesch et al., 2021b)
MGDG	3.4	1.51	0.75	(Triesch et al., 2021b)
DGDG	4.0	1.88	0.94	(Triesch et al., 2021b)
SQDG	14.2	8.77	4.36	(Triesch et al., 2021b)
PG	3.8	1.38	0.69	(Triesch et al., 2021b)

PE	10.5	6.62	3.29	(Triesch et al., 2021b)
others				
oxalic acid*	2.0	0.55	0.27	(van Pinxteren et al., 2015)
amine	17.0	8.84	4.40	(van Pinxteren et al., 2015)
MSA	14.0	1.76	0.88	(van Pinxteren et al., 2015)
carbonyls	0.1	0.02	0.01	(van Pinxteren et al., 2015)

**Oxalic acid was the dominant dicarboxylic acid and all other dicarboxylic acids were below LOD.*

References:

Parrish, C. C.: Dissolved and particulate marine lipid classes - a review, Marine Chemistry, 23, 17-40, 10.1016/0304-4203(88)90020-5, 1988.

Parrish, C. C., and Wells, J. S.: Determination of Total Lipid and Lipid Classes in Marine Samples, Jove-Journal of Visualized Experiments, 10.3791/62315, 2021.

Triesch, N., van Pinxteren, M., Engel, A., and Herrmann, H.: Concerted measurements of free amino acids at the Cape Verde Islands: High enrichments in submicron sea spray aerosol particles and cloud droplets, Atmos. Chem. Phys., 21, 163–181, 2021a.

Triesch, N., van Pinxteren, M., Frka, S., Stolle, C., Spranger, T., Hoffmann, E. H., Gong, X., Wex, H., Schulz-Bull, D., Gašparović, B., and Herrmann, H.: Concerted measurements of lipids in seawater and on submicrometer aerosol particles at the Cabo Verde islands: biogenic sources, selective transfer and high enrichments, Atmos. Chem. Phys., 21, 4267-4283, 10.5194/acp-21-4267-2021, 2021b.

van Pinxteren, D., Brueggemann, E., Gnauk, T., Mueller, K., Thiel, C., and Herrmann, H.: A GIS based approach to back trajectory analysis for the source apportionment of aerosol constituents and its first application, Journal of Atmospheric Chemistry, 67, 1-28, 10.1007/s10874-011-9199-9, 2010.

van Pinxteren, M., Fiedler, B., van Pinxteren, D., Iinuma, Y., Koertzinger, A., and Herrmann, H.: Chemical characterization of sub-micrometer aerosol particles in the tropical Atlantic Ocean: marine and biomass burning influences, Journal of Atmospheric Chemistry, 72, 105-125, 10.1007/s10874-015-9307-3, 2015.

van Pinxteren, M., Fomba, K. W., Triesch, N., Stolle, C., Wurl, O., Bahlmann, E., Gong, X. D., Voigtlander, J., Wex, H., Robinson, T. B., Barthel, S., Zeppenfeld, S., Hoffmann, E. H., Roveretto, M., Li, C. L., Grosselin, B., Daele, V., Senf, F., van Pinxteren, D., Manzi, M., Zabalegui, N., Frka, S., Gasparovic, B., Pereira, R., Li, T., Wen, L., Li, J. R., Zhu, C., Chen, H., Chen, J. M., Fiedler, B., Von Tumpling, W., Read, K. A., Punjabi, S., Lewis, A. C., Hopkins, J. R., Carpenter, L. J., Peeken, I., Rixen, T., Schulz-Bull, D., Monge, M. E., Mellouki, A., George, C., Stratmann, F., and Herrmann, H.: Marine organic matter in the remote environment of the Cape Verde islands - an introduction and overview to the MarParCloud campaign, Atmospheric Chemistry and Physics, 20, 6921-6951, 10.5194/acp-20-6921-2020, 2020.