Supplement of

Concerted measurements of free amino acids at the Cape Verde Islands: High enrichments in submicron sea spray aerosol particles and cloud droplets

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Table S1: Limit of quantification (LOQ) of the individual FAA in the matrices of the marine environment - on aerosol particles as atmospheric concentration in pg m^{-3}, as seawater concentration in nmol L^{-1} and as cloud water concentration in µg L^{-1} and ng m^{-3}

analyte	atmospheric concentration (a)	seawater concentration (b)	cloud water concentration (c)	
	pg m^{-3}	nmol L^{-1}	µg L^{-1}	ng m^{-3}
serine	7.9	4.8	0.2	0.06
glycine	7.9	6.7	0.2	0.06
glutamic acid	7.9	3.4	0.2	0.06
threonine	7.9	4.2	1.0	0.30
alanine	39.5	5.6	0.2	0.06
GABA	39.5	24.2	1.0	0.30
proline	7.9	4.3	0.2	0.06
aspartic acid	39.5	3.8	0.2	0.06
tyrosine	7.9	2.8	1.0	0.30
methionine	39.5	16.8	1.0	0.30
valine	7.9	4.3	1.0	0.30
phenylalanine	7.9	3.0	1.0	0.30
glutamine	39.5	3.4	1.0	0.30
isoleucine	39.5	3.8	1.0	0.30
leucine	39.5	3.8	1.0	0.30

For the LOQ, the concentration of the lowest but still quantifiable calibration stage of the external calibration was used and then extrapolated specifically for the various marine matrices:

(a) The following were taken into account for the calculation of the atmospheric concentration of individual FAA: the enrichment factor caused by the reducing of the extract volume, the proportion of the investigated filter material (92 % of the filter material of each stage for the aqueous extract) and an median of the sampled air flow (110 m^3).

(b) For the calculation of the seawater concentration, the enrichment factor caused by the reducing of the desalinated sample volume was considered.

(c) For the calculation of the cloud water concentration in µg L^{-1}, the enrichment factor caused by the reducing of the cloud water volume was considered. Additionally an averaged liquid water content (LWC) of 0.297 was taken into account to calculate additionally the cloud water concentration in ng m^{-3}.

Table S2: Wind speed, chl-*a* concentration in the seawater samples and the FAA concentration in the size-segregated aerosol particle samples (distinguished between the submicron and the supermicron size range) at the CVAO

sampling stop	wind speed*	chl-*a* concentration**	∑FAA concentration in PM_{10} (B1-5)	∑FAA concentration in submicron size range	∑FAA concentration in supermicron size range
	m s^{-1}	µg L^{-1}	ng m^{-3}	ng m^{-3}	ng m^{-3}
20/09/2017	2.64	0.2	2.37	1.53	0.84
22/09/2017	8.23	-	4.37	3.01	1.36
28/09/2017	4.87	0.2	3.01	2.45	0.56
1/10/2017	8.58	-	1.76	1.28	0.47
4/10/2017	5.88	-	5.41	5.02	0.39
6/10/2017	5.18	-	3.10	2.89	0.21
7/10/2017	7.06	0.3	6.82	6.32	0.50
10/10/2017	7.60	0.6	3.77	3.11	0.66

[*] The mean value of the measured wind speed during the 24 h sampling time of the aerosols was considered

[**] Not on every matching sampling day the chl-*a* concentration in seawater was investigated. The chl-*a* concentration in seawater was generally low but increased during the campaign from 0.1 µg L^{-1} to 0.6 µg L^{-1} and will be discussed in more detail by van Pinxteren et al. (2019a).

Table S3: Concentration of the individual FAA in the ULW and the SML samples in nmol L^{-1} and the calculated enrichment factor (EF_{SML}) (grey background) of the individual sampling days during the campaign

		Gly	Ala	Ser	Glu	Thr	Pro	Tyr	Val	Phe	Asp	Ile	Leu
20/09/2017	ULW	3.3*	n.d.	n.d.	n.d.	n.d.	2.2	n.d.	1.8	n.d.	83.5	n.d.	n.d.
	SML	35.7	n.d.	n.d.	n.d.	n.d.	12.8	n.d.	11.9	n.d.	167.1	n.d.	n.d.
	EF_{SML}	10.8*	-	-	-	-	5.9	-	6.5	-	2.0	-	-
22/09/2017	ULW	3.3*	2.8*	n.d.	n.d.	n.d.	2.2*	n.d.	2.1*	n.d.	67.0	n.d.	1.9*
	SML	137.2	58.4	n.d.	n.d.	n.d.	32.7	n.d.	22.2	n.d.	222.6	n.d.	21.7
	EF_{SML}	41.6*	20.9*	-	-	-	14.9*	-	10.6*	-	3	-	11.4*
27/09/2017	ULW	3.3*	2.8*	2.4*	1.7*	2.1*	2.2*	1.4*	2.1*	1.5*	1.9*	1.9*	1.9*
	SML	323.4	371.2	371.2	34.4	100.3	32.9	2.9	72.4	2.1	184.7	18.8	30.1
	EF_{SML}	98.0*	132.6*	154.7*	20.2*	47.8*	15.0*	2.1*	34.5*	1.4*	97.2*	9.9*	15.8*
28/09/2017	ULW	n.d.	2.8*	2.4*	n.d.	2.1*	2.2*	n.d.	2.1*	n.d.	1.9*	n.d.	1.9*
	SML	n.d.	52.5	33.8	n.d.	12.4	3.4	n.d.	6.9	n.d.	14.1	n.d.	3.3
	EF_{SML}	-	18.7*	14.1*	-	5.9*	1.5*	-	3.3*	-	7.4*	-	1.8*
2/10/2017	ULW	3.3*	2.8*	2.4*	1.7*	2.1*	2.2*	1.4*	2.1*	n.d.	1.9*	1.9*	1.9*
	SML	410.9	260.2	742.2	11.8	111.7	21.1	3.9	39.7	n.d.	69.5	11.9	19.3
	EF_{SML}	124.5*	92.9*	309.2*	6.9*	53.2*	9.6*	2.8*	18.9*	-	36.6*	6.3*	10.1*
3/10/2017	ULW	3.3*	13.6	2.4*	1.7*	2.1*	2.2*	n.d.	2.0	n.d.	1.9*	10.4	1.9*
	SML	123.5	117.0	187.8	3.1	24.4	40.0	n.d.	32.8	n.d.	22.4	15.5	31.7
	EF_{SML}	37.4*	9	78.2*	1.8*	11.6*	18.2*	-	16.2	-	11.8*	1.5	16.7*
4/10/2017	ULW	350.4	169.0	273.1	1.7*	29.8	72.3	1.4*	90.4	1.5*	24.1	1.9*	74.1
	SML	231.0	245.5	274.0	9.7	61.9	53.5	3.1	88.6	3.7	63.0	35.1	53.3
	EF_{SML}	0.7	1.5	1.0	5.7*	2.1	0.7	2.2*	1.0	2.5*	2.6	18.5*	0.7
5/10/2017	ULW	16.4	112.4	54.0	n.d.	1.1	13.4	n.d.	15.6	n.d.	2.7	3.1	11.4
6/10/2017	ULW	3.3*	2.8*	2.4*	1.7*	2.1*	1.4	1.4*	2.6	1.5*	1.9*	1.9*	2.2
	SML	461.0	412.5	736.4	17.5	118.4	91.8	4.8	101.2	2.7	163.3	44.1	71.3

	EF_{SML}	139.7*	147.3*	306.8*	10.3*	56.4*	64.2	3.4*	38.7	1.8*	86.0*	23.2*	32.7
7/10/2017	ULW	120.6	192.5	298.5	16.7	31.2	32.7	1.4*	37.6	1.5*	82.3	10.7	15.7
	SML	359.7	400.6	716.0	59.9	119.5	80.6	20.5	85.3	15.8	191.4	41.4	61.8
	EF_{SML}	3.0	2.1	2.4	3.6	3.8	2.5	14.6*	2.3	10.5*	2.3	3.9	3.9
9/10/2017	ULW	3.3*	2.8*	2.4*	1.7*	2.1*	2.2*	1.4*	2.1*	1.5*	1.9*	1.9*	1.9*
	SML	697.9	635.0	1237.4	66.5	224.0	125.8	26.1	150.6	25.4	285.5	70.7	99.1
	EF_{SML}	211.5*	226.8*	515.6*	39.1*	106.7*	57.2*	18.7*	71.7*	16.9*	150.3*	37.2*	52.1*
10/10/2017	ULW	153.3	166.0	207.5	1.7*	19.6	38.9	n.d.	29.2	n.d.	28.8	3.3	19.5
	SML	537.9	361.3	504.5	12.3	72.2	62.4	n.d.	58.5	n.d.	47.2	12.7	20.5
	EF_{SML}	3.5	2.2	2.4	7.2*	3.7	1.6	-	2.0	-	1.6	3.9	1.0

n.d. – not dected: if the individual FAA was not detected in the SML, the concentration in the ULW was not calculated (LOQ/2) to determine the EF_{SML}

* For this samples, the individual FAA was quantified in the SML but below the LOQ in the ULW samples no quantification was possible. Therefore, the concentration of the analyte in the ULW were assumed to be LOQ/2, (LOQ is listed in Table S1).

Enrichment of FAA in SML

Looking at the individual amino acids (Table S3), Ser with a concentration range of 54-299 nmol L^{-1} (ULW) and 34-1237 nmol L^{-1} (SML) had usually the highest contribution to ∑FAA. Also Ala (ULW: 14-193 nmol L^{-1}, SML: 52-635 nmol L^{-1}), Gly (ULW: 16-350 nmol L^{-1}, SML: 36-698 nmol L^{-1}) and Asp (ULW: 3-83 nmol L^{-1}, SML: 14-286 nmol L^{-1}) were included in higher concentrations as part of ∑FAA. This observed high contribution of Ser, Ala, Gly and Asp to ∑FAA in the ULW and especially in the SML are in accordance with the results of Kuznetsova et al. (2004) and Reinthaler et al. (2008). To compare the concentration of ∑FAA in the SML with the ULW samples, the enrichment factor in SML (EF_{SML}) was calculated using Eq. (1) and is shown in Fig. 1 (stars). Regarding the EF_{SML} of ∑FAA, an enrichment of ∑FAA in SML between 1.1 and 298.4 could be observed (averaged EF_{SML} of ∑FAA: 57.2). Although there is a wide variance in the EF_{SML} for ∑FAA, our results are in good agreement with the literature. In the subtropical Atlantic, EF_{SML} of dissolved FAA between 7.6 and 229.4 (59.3±68.8) and in western Mediterranean Sea between 6.2 and 26.1 (16.5±9.1) were reported by Reinthaler et al. (2008). The EF_{SML} depends on the measured concentration of ∑FAA in the SML and the ULW, and here daily variations could be observed during the campaign. Especially the higher EF_{SML} on e.g. 6/10/2017 with 298.4 resulted from higher concentrations of ∑FAA in the SML (2224.9 nmol L^{-1}) and very low concentration in the ULW (6.23 nmol L^{-1}).

Table S4: Concentration of FAA in a SML sample from 21/11/2013, 2pm (local time), coordinates: 16°84ˈ68ˈN, 24°85ˈ25ˈˈW

analyte*	nmol L^{-1}
aspartic acid	57.8
glutamic acid	18.9
serine	212.4
glycine	168.2
arginine	39.3
threonine	7.2
alanine	60.8
GABA	6.3
tyrosine	13.7
valine	20.3
isoleucine	14.4
phenylalanine	9.5
leucine	13.6
∑FAA	642.4

* analytes were measured with a high performance liquid chromatograph (1260 HPLC system, Aglient Technologies) using a C_{18} column (Phenomex Kinetex) after in line ortho-phthaldialdehyde derivatization with mercaptoethanol after Lindroth and Mopper (1979) and Dittmar (2009).

Table S5: DOC and TDN concentrations in the SML and the ULW samples, their enrichment in the SML (EF_{SML}) calculated using Eq. (1) and the percentage contribution of ∑FAA to DOC and TDN in seawater samples; NA – not available

sampling date	sample type	DOC in µg L^{-1}	EF_{SML} DOC	TDN in µg L^{-1}	EF_{SML} TDN	Percentage of ∑FAA to DOC (**)	Percentage of ∑FAA to TDN (***)
20/09/2017	SML	2779.0	2.5	380.3	0.8	0.4	0.8
	ULW	1095.3		478.2		0.4	0.3
22/09/2017	SML	1674.6	0.7	280.2	1.2	1.3	5.2
	ULW	2368.5		236.7		0.1	0.2
27/09/2017	SML	2020.6	1.9	193.6	1.0	3.4	13.0
	ULW	1073.7		189.6		NA	NA
28/09/2017	SML	2271.0	1.7	248.3	1.1	0.2	0.7
	ULW	1372.5		228.5		NA	NA
2/10/2017(*)	SML	2017.8	1.5	270.4	1.3	3.1	8.8
	ULW	1340.5		206.5		NA	NA
3/10/2017	SML	2196.6	1.6	267.9	1.5	1.1	3.1
	ULW	1366.9		174.4		NA	0.1
4/10/2017	SML	2050.2	1.9	196.7	1.0	2.3	8.0
	ULW	1085.3		196.4		4.0	7.8
5/10/2017	ULW	1143.3		112.4		0.8	2.9
6/10/2017	SML	3327.0	2.6	496.7	1.9	2.6	6.3
	ULW	1291.3		255.7		NA	0.03
7/10/2017	SML	1606.6	1.7	124.7	0.9	5.5	24.2
	ULW	946.9		140.1		3.5	8.4
9/10/2017	SML	1941.0		120.3		7.6	42.4
10/10/2017	SML	1821.0	1.4	128.0	0.8	3.3	18.5
	ULW	1291.3		156.1		2.0	6.0

(*) For interpretation of concerted measurements, the seawater samples, sampled during the 24 h sampling interval of size-segregated aerosol particle samples, were considered. Consequently, the date of the sampling stop of the aerosol particle samples matched with the sampling date of seawater samples, one exception: seawater sampling on 2/10/2017 were considered for the size-segregated aerosol particle sample, collected from 30/09/2017 - 1/10/2017, because on 1/10/2017 no seawater sampling was performed.

(**) For the calculation of the percentage contribution of ∑FAA to DOC, the carbon content of the individual amino acids, listed in Table S6, was considered.

(**) For the calculation of the percentage contribution of ∑FAA to TDN, the nitrogen content of the individual amino acids, listed in Table S6, was considered.

For the analysis of sodium corresponding seawater samples (ULW and SML) with n = 5 was investigated. In the SML the sodium concentration was 12.53 ± 0.53 g L^{-1} and in the ULW the sodium concentration was 12.45 ± 0.37 g L^{-1}. Because of small relative standard deviations (4.2 % for SML and 2.9 % for ULW), the mean value of sodium concentration in SML samples (12.53 g L^{-1}) was used for the calculation of EF_{aer} and EF_{cw}.

Table S6: Overview of the molar mass, molecular formula and the carbon and nitrogen content of the individual FAA

analyte	molar mass in g mol^{-1}	molecular formula	carbon content[*] of the analyte in %	nitrogen content[*] of the analyte in %
serine	105.09	C3H7NO3	34.28	13.33
glycine	75.07	C2H5NO2	32.00	18.66
glutamic acid	147.13	C5H9NO4	40.81	9.52
threonine	119.12	C4H9NO3	40.33	11.76
alanine	89.09	C3H7NO2	40.44	15.73
GABA	103.12	C4H9NO2	46.59	13.59
proline	115.13	C5H9NO2	52.16	12.17
tyrosine	181.19	C9H11NO3	59.66	7.73
methionine	149.21	C5H11NO2S	40.25	9.39
valine	117.15	C5H11NO2S	51.26	11.96
phenylalanine	165.19	C9H11NO2	65.43	8.48
glutamine	146.15	C5H10N2O3	41.09	19.17
aspartic acid	133.10	C4H7NO4	36.09	10.53
isoleucine	131.17	C6H13NO2	54.94	10.68
leucine	131.17	C6H13NO2	54.94	10.68

[*] The carbon and nitrogen content of individual FAA were taken into account for the calculation of the FAA/ ∑FAA contribution to WSOC, TDN and WSON concentration in the size-segregated aerosol particle samples and for the calculation of FAA/ ∑FAA contribution to DOC and TDN concentration in the seawater samples.

Table S7: Percentage contribution of the amino acid groups to ∑FAA on the submicron and the supermicron aerosol particles during the campaign and as an average; hydrophilic (Glu, Asp, GABA), neutral (Ser, Gly, Thr, Pro, Tyr), hydrophobic amino acids (Ala, Val, Phe, Ile, Leu)

	amino acid groups in %		
sampling date	hydrophilic	neutral	hydrophobic
20/09/2017 submicron	0	97	3
20/09/2017 supermicron	0	89	11
22/09/2017 submicron	4	89	7
22/09/2017 supermicron	0	88	12
28/09/2017 submicron	0	93	7
28/09/2017 supermicron	0	99	1
1/10/2017 submicron	0	100	0
1/10/2017 supermicron	0	96	4
4/10/2017 submicron	12	74	14
4/10/2017 supermicron	0	100	0
6/10/2017 submicron	48	52	0
6/10/2017 supermicron	0	100	0
7/10/2017 submicron	55	42	3
7/10/2017 supermicron	0	84	16
10/10/2017 submicron	0	95	5
10/10/2017 supermicron	0	90	10
averaged submicron	15	80	5
averaged supermicron	0	93	7

Table S8: Atmospheric concentration of inorganic ions as sulfate (SO$_4^{2-}$), MSA, MSA/sulfate ratio, sodium (Na$^+$) and of mineral dust tracer as iron (Fe) and titanium (Ti) and the fractional 'residence time over water and ice' calculated from 96 h backward trajectories for the supermicron and submicron aerosol particle samples at the CVAO

sampling stop	**∑FAA**	**MSA**	**sulfate**	**MSA/sulfat ratio**	**sodium**	**Residence time over water & ice**	**Ti**	**Fe**
	ng m^{-3}	**ng m^{-3}**	**µg m^{-3}**		**ng m^{-3}**		**ng m^{-3}**	**ng m^{-3}**
supermicron aerosol particles								
20/09/2017	0.8	18.7	1.9	0.010	3903	0.84	16.3	259.3
22/09/2017	1.4	10.5	1.1	0.021	3445	0.90	19.0	182.8
28/09/2017	0.6	5.2	0.8	0.006	1471	0.85	12.6	404.5
1/10/2017	0.5	4.5	1.1	0.004	3409	0.67	16.8	203.2
4/10/2017	0.4	4.9	0.8	0.006	2379	0.96	9.3	110.2
6/10/2017	0.2	4.6	0.8	0.006	2252	0.97	17.8	160.6
7/10/2017	0.5	3.8	0.9	0.004	2661	0.96	48.5	451.6
10/10/2017	0.7	2.5	0.6	0.004	2002	0.91	11.8	109.4
submicron aerosol particles								
20/09/2017	1.5	12.4	0.6	0.019	339	0.84	0.3	21.2
22/09/2017	3.0	15.8	0.8	0.018	229	0.90	0.6	7.6
28/09/2017	2.4	7.9	0.8	0.013	89	0.85	0.2	19.9
1/10/2017	1.3	10.1	0.9	0.011	224	0.67	1.0	19.1
4/10/2017	5.0	18.4	1.3	0.016	186	0.96	0.1	7.0
6/10/2017	2.9	20.8	1.2	0.017	133	0.97	0.7	12.1
7/10/2017	6.3	14.9	0.9	0.021	139	0.96	3.8	40.4
10/10/2017	3.1	14.4	0.8	0.016	33	0.91	16.3	143.1

Air mass origin: First indications of aerosol particle origin

To obtain a first indication of the particle origin that might help to explain the differences in the particle composition concerning amino acids, the particles were associated with the history of the air masses and with marine and dust tracers. Overall, the CVAO station experienced north-easterly winds during this campaign. The air masses were mainly of marine origin and had no to very low dust influences during the first part of the campaign that is typical for this season in this region (Fomba et al., 2014). During the second part (after 29/09/2017) slightly elevated dust concentrations were observed. A comprehensive classification of the air masses will be given in van Pinxteren et al. (2019a) that provides an overview about air mass origin considering backward trajectories and dust concentrations for PM$_{10}$ particles. It has to be noted, that dust generally influences the supermicron particles to a larger extent than the submicron particles (Fomba et al., 2013), meaning that bigger particles may be affected by dust sources whereas smaller particles may have stronger oceanic influences. Consequently, the submicron particles investigated in the present study might have different sources and might undergo different reactions compared to the supermicron particles. To investigate dust and marine impacts on especially the submicron particles we regarded several indicators specifically for the sub- and supermicron particles, such as MSA concentration, the MSA/sulfate ratio, the fractional residence time of the air masses over water and ice and the size-resolved concentrations of the mineral dust tracer iron (Fe) and titanium (Ti), listed in Table S8. Looking at the 96 h backward trajectories of the investigated air masses, it is obvious that all sampling days showed a very long (≥0.84) or a long (0.67) fractional residence time over water and ice. The sulfate concentration was 0.9±0.2 µg m^{-3} in the submicron size range and 1.0±0.4 µg m^{-3} in the supermicron size range. The measured sulfate concentrations in our study were in good agreement with previous studies at the CVAO (Mueller et al., 2010;van Pinxteren et al., 2015). MSA, originating from the multiphase oxidation of dimethylsulfide (DMS) (Hoffmann et al., 2016), is a tracer for marine aerosol particles to estimate the magnitude of biogenic contributions to local aerosol population (Miyazaki et al., 2011;van Pinxteren et al., 2015). The MSA concentration in the submicron size range varied between 7.9-20.8 ng m^{-3} and between 2.5-18.7 ng m^{-3} in the supermicron size range. These values are again in good agreement with previous studies at the CVAO (Mueller et al., 2010). In our study, the molar ratio of MSA to sulfate was on average 0.02±0.003 in the submicron and 0.01±0.006 in the supermicron aerosol particles. The MSA/sulfate ratio in the submicron size range was within the MSA/sulfate ratios (0.02-0.04), reported for clean marine air over the Pacific Ocean (Nagao et al., 1999;Miyazaki et al., 2011) and consistent with the averaged MSA/sulfate ratio of PM_1 samples (0.022) (van Pinxteren et al., 2015). In order to estimate potential dust influences during the campaign, mineral dust tracer as iron (Fe) and titanium (Ti) were considered. Looking at the time-resolved trend of Fe and Ti values in the size-segregated aerosol particle samples, it could be noticed that the lowest concentration of Fe (7.0 ng m^{-3}, submicron size range) was detected on 4/10/2017 ($Fe_{(PM10)}$: 117.2 ng m^{-3}). The Ti concentration on that day was 0.1 ng m^{-3} in the submicron aerosol particles and 9.4 ng m^{-3} for PM_{10}. Looking at typical marine background concentrations of trace metals at the CVAO for PM_{10} aerosol particles with <25 ng m^{-3} for Fe and <6 ng m^{-3} for Ti (Fomba et al., 2013), especially the submicron aerosol particles on e.g. 4/10/2017 showed very low or no mineral dust influences. The MSA concentrations and the MSA/sulfate ratio were generally higher for the submicron particles showing a higher potential influence of marine sources to the submicron particles. The concentrations of the dust tracers in the submicron particles were low and significantly lower than in the supermicron particles except for the last sampling day (10/10/2017). This indicated that the submicron particles were mainly of marine origin during most of the time of the campaign but exhibit a dust impact to some extend on the last sampling day. Comparing this classification of marine and dust influences to the concentration and composition of the amino acids, two things can be hypothesized. Oceanic sources can provide high concentrations of amino acids to the submicron aerosol particles that exhibit a certain complexity (significant amounts of GABA and Asp). Additional dust sources can contribute to a high amino acid concentration on the submicron aerosol particles, but they are less complex in their composition (no GABA, no Asp). However, as we observe a certain variability in the concentrations of the amino acid on predominant marine influenced days (20/09/2017, 22/09/2017, 28/09/2017, 1/10/2017, 4/10/2017, 6/10/2017, 7/10/2017), the contributions from the ocean are not always constant and can be quite low (e.g. 1/10/2017). At present, it remains unclear under which conditions the ocean provides more or less amino acid concentrations and complexity for the FAA in marine aerosol particles.

Table S9: Atmospheric concentration of water-soluble organic carbon (WSOC), total dissolved nitrogen (TDN) and water-soluble organic nitrogen (WSON) on the submicron and the supermicron aerosol particles and the percentage contribution of ∑FAA to WSOC, TDN and WSON during the campaign and as an average; NA – not available data

	atmospheric concentration in ng m^{-3}			percentage contribution (in %) of ∑FAA to		
	WSOC	TDN [a]	WSON [b]	WSOC [d]	TDN [e]	WSON [f]
20/09/2017 submicron	93.4	58.9	14.7	0.04	0.03	0.11
20/09/2017 supermicron	175.4	367.4	91.8	0.03	0.01	0.03
22/09/2017 submicron	75.6	89.3	22.3	0.26	0.08	0.32
22/09/2017 supermicron	96.0	201.7	50.4	0.15	0.03	0.11
28/09/2017 submicron	26.5	109.0	27.2	0.52	0.05	0.19
28/09/2017 supermicron	100.3	284.1	71.0	NA	NA	NA
1/10/2017 submicron	48.1	124.2	31.1	0.04	0.01	0.02
1/10/2017 supermicron	115.3	236.1	59.0	0.03	0.01	0.02
4/10/2017 submicron	73.4	235.2	58.8	1.22	0.12	0.49
4/10/2017 supermicron	103.0	327.9	82.0	NA	NA	NA
6/10/2017 submicron	50.3	174.8	43.7	1.27	0.11	0.42
6/10/2017 supermicron	105.4	268.5	67.1	NA	NA	NA
7/10/2017 submicron	31.9	111.0	27.8	5.30	0.45	1.79
7/10/2017 supermicron	95.4	219.8	55.0	0.05	0.01	0.04
10/10/2017 submicron	83.7	199.6	49.9	0.12	0.02	0.08
10/10/2017 supermicron	90.9	199.0	49.7	0.04	0.01	0.03
averaged submicron	60.4 [c]	137.7	34.4	1.14	0.11	0.43
averaged supermicron	110.2	263.1	65.8	0.04	0.01	0.05

[a] TDN includes the parameter dissolved inorganic ammonium, nitrite, nitrate and dissolved organic nitrogen-containing compounds and these results are in good agreement with (Mueller et al., 2009)

[b] calculation of the WSON content focusing on measured TDN concentration in each Berner stage under the assumption that 25 % of marine total nitrogen consist of WSON as described in Lesworth et al. (2010); (25 % of TDN = WSON)

[c] averaged WSOC concentration with 0.06±0.02 µg m^{-3} in the submicron size range at the CVAO was in same order of magnitude as the WSOC concentration of the PM_1 samples (0.11±0.03 µg m^{-3}) collected at the same time at the CVAO (van Pinxteren et al., (2019a))

[d] consideration of the carbon content of the individual amino acids (listed in Table S6) to calculate the percentage contribution of ∑FAA to WSOC

[e] consideration of the nitrogen content of the individual amino acids (listed in Table S6) to calculate the percentage contribution of ∑FAA to TDN and WSON

Table S10: Atmospheric concentration (ng m^{-3}) of particulate matter (PM), WSOC, sodium (Na$^+$), MSA and ∑FAA in the size-segregated aerosol particle samples at the CVAO and at the MV station on sampling days (4/10/2017, 6/10/2017, 7/10/2017) and as an average of these three days; NA – not available data

date	Berner stage	atmospheric concentration in ng m^{-3}									
sampling stop		PM		WSOC		Na$^+$		MSA		∑FAA	
		CVAO	MV	CVAO	MV	CVAO	MV	CVAO	MV	CVAO	MV
4/10/2017	1	233	NA	23.1	24.9	22.6	4.1	0.4	0.5	0.9	0.3
	2	1821	302	27.3	2.2	15.3	9.9	11.5	1.9	3.7	0.9
	3	2774	1516	23.0	4.7	148.3	44.3	6.5	4.2	0.4	0.7
	4	12454	5116	52.2	5.5	1101.5	260.4	4.1	3.7	0.2	2.9
	5	1308	*	50.8	*	1277.4	*	0.8	*	0.2	*
6/10/2017	1	124	82	0.0	0.9	0.0	6.8	0.4	0.3	0.1	0.3
	2	1707	260	23.4	0.4	8.7	7.8	14.5	0.9	2.2	0.3
	3	2539	902	26.9	2.0	124.8	6.3	6.0	2.5	0.6	1.3
	4	10466	3269	57.1	3.8	1062.3	72.1	3.9	1.6	NA	0.3
	5	9472	3085	48.3	4.7	1189.3	74.6	0.7	1.5	0.2	0.3
7/10/2017	1	NA	NA	0.0	0.7	1.7	0.0	0.5	0.04	1.9	0.3
	2	1141	235	7.8	3.0	10.5	20.3	9.2	2.3	3.0	NA
	3	5121	1198	24.1	3.0	126.4	53.5	5.1	3.5	1.4	0.5
	4	18294	4057	54.2	5.9	1230.3	105.8	3.3	1.7	0.3	0.2
	5	18240	3291	41.2	8.6	1431.2	78.5	0.6	1.1	0.2	0.1
average of 4/10, 6/10, 7/10/2017	1	178	82	7.7	8.8	8.1	3.6	0.4	0.3	1.0	0.3
	2	1556	266	19.5	1.9	11.5	12.7	11.7	1.7	3.0	0.4
	3	3478	1205	24.7	3.3	133.2	34.7	5.9	3.4	0.8	0.8
	4	13738	4147	54.5	5.1	1131.3	146.1	3.8	2.3	0.2	1.1
	5	13600	3188	46.8	6.6	1299.3	76.6	0.7	1.3	0.2	0.2

* this size segregated aerosol sample (B4 of 4/10/2017 at the MV station) was not investigated

Table S11: Cloud water samples at the MV station: sampling time, measured liquid water content and the atmospheric concentration of sodium, sulfate, MSA and ∑FAA

sampling start	sampling stop	liquid water content	atmospheric concentration of			
			sodium	sulfate	MSA	∑FAA
local time	local time	g m^{-3}	µg m^{-3}	µg m^{-3}	ng m^{-3}	ng m^{-3}
27/09/2017 19:00	28/09/2017 7:30	0.424	1.6	1.8	11.0	34.3
28/09/2017 19:00	29/09/2017 7:30	0.459	6.4	3.6	20.7	45.2
5/10/2017 7:45	5/10/2017 10:35	0.249	5.3	3.6	33.8	30.7
5/10/2017 10:40	5/10/2017 17:38	0.117	5.4	2.8	29.2	37.7
5/10/2017 17:40	5/10/2017 20:10	0.373	5.8	3.2	39.0	351.6
5/10/2017 20:10	5/10/2017 23:30	0.325	5.1	3.3	35.3	63.8
5/10/2017 23:30	6/10/2017 4:00	0.205	4.1	2.4	22.1	11.2
6/10/2017 4:05	6/10/2017 8:00	0.254	3.9	2.1	21.1	443.8
7/10/2017 7:48	7/10/2017 11:48	0.198	5.7	2.6	25.1	409.4
7/10/2017 19:00	8/10/2017 7:00	0.366	7.2	3.6	23.9	489.8

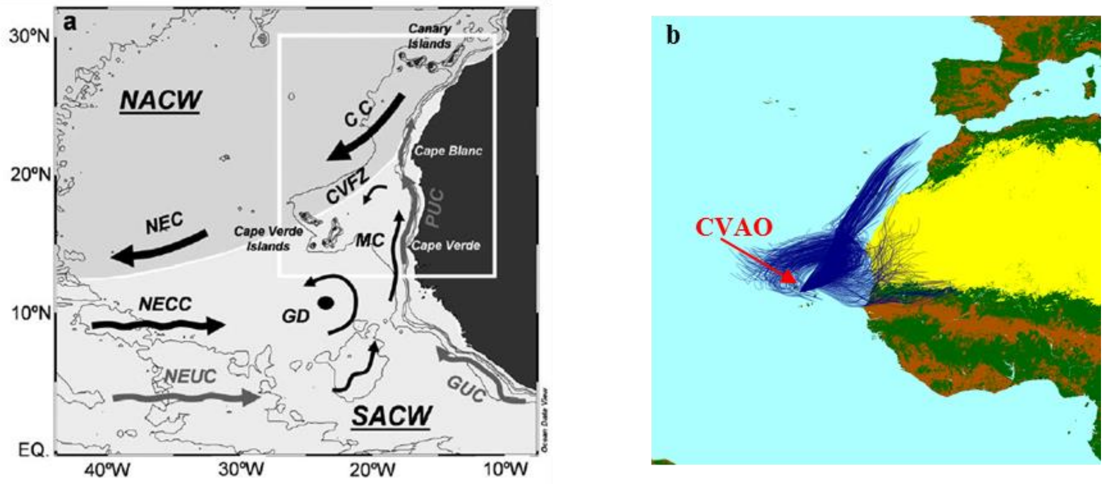

Figure S1: Overview of (a) the water current at the Cape Verde islands (study of Peña-Izquierdo et al., 2012) and (b) the 96 h backward trajectory of an aerosol sample with 'predominant marine' air masses of 5/10/2017 at the CVAO

The comparability of the different marine matrices

Spot measurements in the ocean (ULW, SML) were taken during the sampling time (24 h) of size-segregated aerosol particle samples. As basis for a possible comparison, the origins of the aerosol particles and of the seawater samples had to be investigated in more detail. Due to the origin of the air masses using 96 h backward trajectories, the concentrations of inorganic ions and mineral dust tracers on the aerosol particles the aerosol particles were considered to be mainly of marine origin (section 3.2). Regarding the seawater, it was shown that despite of a strong variability of ∑FAA in seawater samples, the measured ∑FAA concentrations in the ULW and especially in the SML samples are representative for the investigated marine region, the tropical Atlantic Ocean (section 3.1). van Pinxteren et al. (2017) demonstrated that at the CVAO the air masses follow the water current (as described in Peña-Izquierdo et al. (2012)) enhancing the organic carbon link between the SML and the aerosol particles. As mainly winds drive the ocean currents in the upper 100 m of the ocean, a likely connection between DOC on the aerosol particles and in the SML was concluded in van Pinxteren et al. (2017). Regarding the backward trajectories of 'predominant marine' aerosol particles together with the water current of Peña-Izquierdo et al. (2012) (Fig. S1), it could be concluded that there is a likely connection between FAA as part of OM on the aerosol particles and FAA as part of OM in the SML. Moreover, during the campaign additional size-segregated aerosol particle and cloud water samples were simultaneously taken at the mountain station (MV) (744 m a.s.l) to investigate the vertical transport of FAA and their abundance in marine cloud water.

Table S12: Mean lifetime (τ) of investigated amino acids depending on pH-value and different atmospheric scenarios of 'remote cloud case' (for the MV samples) and 'remote aerosol case' (for the CVAO samples) adopted from the study of Herrmann et al., 2010

		remote cloud case[*]		remote aerosol case[**]	
analyte	pH value	τ in d	τ in min	τ in d	τ in min
serine	6	1.64	2361.6	0.01	14.4
glycine	~ 5.9	3.09	4449.6	0.02	28.8
glutamic acid	2	3.29	4737.6	0.02	28.8
threonine	6.6	1.03	1483.2	0.01	14.4
alanine	~ 5.8	6.83	9835.2	0.05	72
GABA	6.7	1.2	1728	0.01	14.4
proline	6.9	1.7	2448	0.01	14.4
tyrosine	7	0.04	57.6	0.0003	0.4
methionine	5.6	0.06	86.4	0.0005	0.7
valine	6.6	8	11520	0.01	14.4
phenylalanine	5.8	0.08	115.2	0.0006	0.9
glutamine	6	0.97	1396.8	0.0071	10.2
isoleucine	6.6	0.29	417.6	0.0021	3.0
leucine	6	0.31	446.4	0.0023	3.3

the mean life time τ of the individual amino acids depends on OH radical concentration, pH value and on the atmospheric scenarios:

[*] the 'remote cloud case' is valid for the size-segregated aerosol particle and cloud water samples, sampled at the mountain station 'Monte Verde' (MV), OH radical concentration of $2.2 \cdot 10^{-14}$ mol L^{-1} (Herrmann et al., 2010) were considered

[**] the 'remote aerosol case' is valid for the size-segregated aerosol particle samples, sampled at the CVAO, OH radical concentration of $3 \cdot 10^{-12}$ mol L^{-1} (Herrmann et al., 2010) were considered

Table S13: Enrichment factor in aerosol particles (EF_{aer}) of ∑FAA and DOC at the CVAO for the case study (4/10/2017, 6/10/2017, 7/10/2017) and averaged results (grey background); NA – not available data

sampling stop	EF_{aer} of ∑FFA					EF_{aer} of DOC				
	B1	B2	B3	B4	B5	B1	B2	B3	B4	B5
4/10/2017	4.E+03	3.E+04	3.E+02	2.E+01	2.E+01	1.E+04	2.E+04	2.E+03	5.E+02	5.E+02
6/10/2017	NA	1.E+04	3.E+02	NA	1E+01	NA	1.E+04	8.E+02	2.E+02	2.E+02
7/10/2017	6.E+04	2.E+04	6.E+02	1.E+01	9E+00	NA	1.E+04	3.E+03	6.E+02	4.E+02
averaged	3E+04	2E+04	4E+02	2E+01	1E+01	1E+04	1E+04	2E+03	4E+02	3E+02

The parameter EF_{aer} regard the transfer from the ocean into the aerosol particles considering the enrichment processes of OM and compounds linked to OM (e.g. FAA) during bubble bursting. Chemcial reaction processes during the transfer process are not taken into account.

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