

SUPPLEMENTARY INFORMATION

Free amino acids quantification in cloud water at the puy de Dôme station (France)

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Table S1. Characteristics and Concentrations of AAs for each cloud samples expressed in various units and cloud bio-physico-chemical characterization.

	Sampling characteristics			
Label	Sampling date	Sampling Start	Sampling end	Category Renard et al. (2020)
22 Mar	22-Mar-14	07:35	11:00	Marine
3 May	3-May-18	09:30	14:00	Marine
13 Jun	13-Jun-18	10:30	12:30	Marine
24 Aug	24-Aug-18	10:50	15:15	Marine
24 Sep	24-Sep-18	08:30	16:00	Marine
1 Oct	1-Oct-18	11:00	12:45	Marine
8 Oct	8-Oct-18	13:15	16:45	Marine
25 Sep	25-Sep-19	08:45	12:38	Marine
2 Oct	2-Oct-19	14:35	16:45	Marine
22 Oct Am	22-Oct-19	10:10	13:37	Marine
22 Oct Pm	22-Oct-19	13:40	16:30	Marine
11 Mar	11-Mar-20	08:40	13:40	Marine
17 Jul	17-Jul-20	11:36	14:40	Continental

Table S1. Continued.

	Amino acids ($\mu\text{g L}^{-1}$) diluted (9:1)*																	
Label	<i>Ala</i>	<i>Arg</i>	<i>Asn</i>	<i>Asp</i>	<i>Gln</i>	<i>Glu</i>	<i>Gly</i>	<i>His</i>	<i>Leu</i> / <i>I</i>	<i>Lys</i>	<i>Met</i>	<i>Phe</i>	<i>Pro</i>	<i>Ser</i>	<i>Thr</i>	<i>Trp</i>	<i>Tyr</i>	<i>SUM</i>
22 Mar	17	8	< LOQ	12	< LOQ	32	8	12	26	16	4	1	8	22	11	4	7	188
3 May	19	< LOQ	2	11	1	6	16	3	10	0	1	5	18	34	13	< LOQ	5	143
13 Jun	8	< LOQ	102	4	< LOQ	2	10	< LOQ	12	< LOQ	< LOQ	< LOQ	10	8	2	< LOQ	< LOQ	158
24 Aug	26	5	131	15	15	17	21	6	17	2	< LOQ	11	15	33	28	4	5	352
24 Sep	11	4	11	4	1	7	14	5	7	3	0	3	8	17	21	1	2	122
1 Oct	69	1	31	45	3	22	42	22	41	9	< LOQ	10	30	157	42	2	21	547
8 Oct	27	< LOQ	2	14	0	8	18	3	22	< LOQ	< LOQ	5	14	36	15	1	5	169
25 Sep	ND	8	21	ND	6	10	87	ND	ND	8	< LOQ	18	ND	155	25	5	ND	343
2 Oct	ND	3	67	65	2	22	121	26	68	19	< LOQ	20	ND	282	49	1	27	772
22 Oct Am	ND	< LOQ	2	22	< LOQ	10	48	9	22	6	< LOQ	6	ND	78	18	< LOQ	7	228
22 Oct Pm	ND	2	1	6	< LOQ	3	57	3	17	1	< LOQ	4	ND	42	8	4	< LOQ	150
11 Mar	54	3	2	< LOQ	< LOQ	1	33	2	16	< LOQ	< LOQ	9	ND	0	3	< LOQ	2	126
17 Jul	ND	2	4	< LOQ	6	8	72	< LOQ	19	2	< LOQ	10	9	22	9	< LOQ	8	171

*: See Figure S3

ND: Not determined

LOQ: Limit of Quantification ($\approx$ standard deviation, see Figure S3, Table S3 and Section 3.1)

Unlike Table S3, negative values are considered as below the LOQ.

Table S1. Continued.

	Amino acids (nM)																	
Label	<i>Ala</i>	<i>Arg</i>	<i>Asn</i>	<i>Asp</i>	<i>Gln</i>	<i>Glu</i>	<i>Gly</i>	<i>His</i>	<i>Leu</i> / <i>I</i>	<i>Lys</i>	<i>Met</i>	<i>Phe</i>	<i>Pro</i>	<i>Ser</i>	<i>Thr</i>	<i>Trp</i>	<i>Tyr</i>	<i>SUM</i>
22 Mar	215	52	< LOQ	97	< LOQ	244	123	85	218	119	27	6	76	237	107	22	42	1670
3 May	239	< LOQ	17	92	8	44	234	22	83	0	4	34	177	358	121	< LOQ	29	1462
13 Jun	96	< LOQ	859	33	< LOQ	19	144	< LOQ	103	< LOQ	< LOQ	< LOQ	92	81	23	< LOQ	< LOQ	1450
24 Aug	320	33	1105	125	111	129	309	40	145	16	< LOQ	77	149	351	261	20	32	3223
24 Sep	134	27	95	37	7	52	210	38	60	26	3	22	81	183	193	5	13	1187
1 Oct	862	4	257	372	25	168	627	159	345	70	< LOQ	67	290	1663	393	10	129	5441
8 Oct	341	< LOQ	13	114	2	63	267	18	183	< LOQ	< LOQ	33	137	379	142	3	33	1729
25 Sep	ND	51	174	ND	49	79	1281	ND	ND	62	< LOQ	123	ND	1637	232	26	ND	3714
2 Oct	ND	17	566	543	18	167	1787	185	577	141	< LOQ	133	ND	2983	462	5	165	7749
22 Oct Am	ND	< LOQ	19	182	< LOQ	74	706	62	182	48	< LOQ	42	ND	822	169	< LOQ	46	2352
22 Oct Pm	ND	14	8	53	< LOQ	21	849	24	147	9	< LOQ	29	ND	439	74	23	< LOQ	1691
11 Mar	676	18	19	< LOQ	< LOQ	6	491	16	132	< LOQ	< LOQ	58	ND	4	32	< LOQ	13	1465
17 Jul	ND	10	36	< LOQ	44	64	1065	< LOQ	158	12	< LOQ	66	91	237	84	< LOQ	50	1917

ND: Not determined

LOQ: Limit of Quantification ($\approx$ standard deviation, see Figure S3, Table S3 and Section 3.1)

Unlike Table S3, negative values are considered as below the LOQ.

Table S1. Continued.

	Amino acids (ng m ⁻³)*																	
Label	<i>Ala</i>	<i>Arg</i>	<i>Asn</i>	<i>Asp</i>	<i>Gln</i>	<i>Glu</i>	<i>Gly</i>	<i>His</i>	<i>Leu</i> / <i>I</i>	<i>Lys</i>	<i>Met</i>	<i>Phe</i>	<i>Pro</i>	<i>Ser</i>	<i>Thr</i>	<i>Trp</i>	<i>Tyr</i>	<i>SUM</i>
22 Mar	5	3	< LOQ	4	< LOQ	10	3	4	8	5	1	0	2	7	4	1	2	60
3 May	6	< LOQ	1	4	0	2	5	1	3	0	0	2	6	11	4	< LOQ	1	45
13 Jun	2	< LOQ	32	1	< LOQ	1	3	< LOQ	4	< LOQ	< LOQ	< LOQ	3	2	1	< LOQ	< LOQ	50
24 Aug	8	2	42	5	5	5	7	2	5	1	< LOQ	4	5	11	9	1	2	111
24 Sep	3	1	4	1	0	2	4	2	2	1	0	1	3	5	7	0	1	39
1 Oct	22	0	10	14	1	7	13	7	13	3	< LOQ	3	10	50	13	1	7	173
8 Oct	9	< LOQ	0	4	0	3	6	1	7	< LOQ	< LOQ	2	4	11	5	0	2	54
25 Sep	ND	3	7	ND	2	3	27	ND	ND	3	< LOQ	6	ND	49	8	2	ND	109
2 Oct	ND	1	21	21	1	7	38	8	22	6	< LOQ	6	ND	89	16	0	9	244
22 Oct Am	ND	< LOQ	1	7	< LOQ	3	15	3	7	2	< LOQ	2	ND	25	6	< LOQ	2	72
22 Oct Pm	ND	1	0	2	< LOQ	1	18	1	5	0	< LOQ	1	ND	13	3	1	< LOQ	47
11 Mar	17	1	1	< LOQ	< LOQ	0	10	1	5	< LOQ	< LOQ	3	ND	0	1	< LOQ	1	40
17 Jul	ND	1	1	< LOQ	2	3	23	< LOQ	6	0	< LOQ	3	3	7	3	< LOQ	3	54

* When LWC is not available, we consider mean LWC at PUY: 0.285 g m⁻³

ND: Not determined

LOQ: Limit of Quantification ($\approx$ standard deviation, see Figure S3, Table S3 and Section 3.1)

Unlike Table S3, negative values are considered as below the LOQ.

Table S1. Continued.

	Amino acids ($\mu\text{gC L}^{-1}$)																	
Label	<i>Ala</i>	<i>Arg</i>	<i>Asn</i>	<i>Asp</i>	<i>Gln</i>	<i>Glu</i>	<i>Gly</i>	<i>His</i>	<i>Leu</i> / <i>I</i>	<i>Lys</i>	<i>Met</i>	<i>Phe</i>	<i>Pro</i>	<i>Ser</i>	<i>Thr</i>	<i>Trp</i>	<i>Tyr</i>	<i>SUM</i>
22 Mar	7	3	< LOQ	4	< LOQ	13	3	5	14	8	1	1	4	8	5	3	4	83
3 May	8	< LOQ	1	4	0	2	5	1	5	0	0	3	10	12	5	< LOQ	3	60
13 Jun	3	< LOQ	37	1	< LOQ	1	3	< LOQ	7	< LOQ	< LOQ	< LOQ	5	3	1	< LOQ	< LOQ	61
24 Aug	10	2	48	5	6	7	7	3	9	1	< LOQ	7	8	11	11	2	3	142
24 Sep	4	2	4	2	0	3	5	2	4	2	0	2	4	6	8	1	1	50
1 Oct	28	0	11	16	1	9	14	10	22	5	< LOQ	7	16	54	17	1	13	223
8 Oct	11	< LOQ	1	5	0	3	6	1	12	< LOQ	< LOQ	3	7	12	6	0	3	71
25 Sep	ND	3	7	ND	3	4	28	ND	ND	4	< LOQ	12	ND	53	10	3	ND	128
2 Oct	ND	1	24	23	1	9	39	12	37	9	< LOQ	13	ND	97	20	1	16	302
22 Oct Am	ND	< LOQ	1	8	< LOQ	4	15	4	12	3	< LOQ	4	ND	27	7	< LOQ	4	89
22 Oct Pm	ND	1	0	2	< LOQ	1	18	2	10	1	< LOQ	3	ND	14	3	3	< LOQ	58
11 Mar	22	1	1	< LOQ	< LOQ	0	11	1	9	< LOQ	< LOQ	6	ND	0	1	< LOQ	1	53
17 Jul	ND	1	2	< LOQ	2	3	23	< LOQ	10	1	< LOQ	6	5	8	4	< LOQ	5	70

ND: Not determined

LOQ: Limit of Quantification ($\approx$ standard deviation, see Figure S3, Table S3 and Section 3.1)

Unlike Table S3, negative values are considered as below the LOQ.

Table S1. Continued.

	Amino acids (relative abundance, % nM)																
Label	<i>Ala</i>	<i>Arg</i>	<i>Asn</i>	<i>Asp</i>	<i>Gln</i>	<i>Glu</i>	<i>Gly</i>	<i>His</i>	<i>Leu</i> / <i>I</i>	<i>Lys</i>	<i>Met</i>	<i>Phe</i>	<i>Pro</i>	<i>Ser</i>	<i>Thr</i>	<i>Trp</i>	<i>Tyr</i>
22 Mar	13%	3%	< LOQ	6%	< LOQ	15%	7%	5%	13%	7%	2%	0%	5%	14%	6%	1%	3%
3 May	16%	< LOQ	1%	6%	1%	3%	16%	2%	6%	0%	0%	2%	12%	24%	8%	< LOQ	2%
13 Jun	7%	< LOQ	59%	2%	< LOQ	1%	10%	< LOQ	7%	< LOQ	< LOQ	< LOQ	6%	6%	2%	< LOQ	< LOQ
24 Aug	10%	1%	34%	4%	3%	4%	10%	1%	5%	0%	< LOQ	2%	5%	11%	8%	1%	1%
24 Sep	11%	2%	8%	3%	1%	4%	18%	3%	5%	2%	0%	2%	7%	15%	16%	0%	1%
1 Oct	16%	0%	5%	7%	0%	3%	12%	3%	6%	1%	< LOQ	1%	5%	31%	7%	0%	2%
8 Oct	20%	< LOQ	1%	7%	0%	4%	15%	1%	11%	< LOQ	< LOQ	2%	8%	22%	8%	0%	2%
25 Sep	ND	1%	5%	ND	1%	2%	35%	ND	ND	2%	< LOQ	3%	ND	44%	6%	1%	ND
2 Oct	ND	0%	7%	7%	0%	2%	23%	2%	7%	2%	< LOQ	2%	ND	38%	6%	0%	2%
22 Oct Am	ND	< LOQ	1%	8%	< LOQ	3%	30%	3%	8%	2%	< LOQ	2%	ND	35%	7%	< LOQ	2%
22 Oct Pm	ND	1%	0%	3%	< LOQ	1%	50%	1%	9%	1%	< LOQ	2%	ND	26%	4%	1%	< LOQ
11 Mar	46%	1%	1%	< LOQ	< LOQ	0%	33%	1%	9%	< LOQ	< LOQ	4%	ND	0%	2%	< LOQ	1%
17 Jul	ND	1%	2%	< LOQ	2%	3%	56%	< LOQ	8%	1%	< LOQ	3%	5%	12%	4%	< LOQ	3%

ND: Not determined

LOQ: Limit of Quantification ($\approx$ standard deviation, see Figure S3, Table S3 and Section 3.1)

Unlike Table S3, negative values are considered as below the LOQ.

Table S1. Continued.

	Air mass history calculated with the CAT model*												
	Zone matrix				Sector matrix								
Label	Sea surface (<ABLH) [□]	Sea surface (>ABLH)	Continental surface (<ABLH)	Continental surface (>ABLH)	SSW	WSW	WNW	NNW	NNE	ENE	ESE	SSE	NEAR
22 Mar	11.99%	76.38%	0.81%	10.82%	0.00%	77.37%	21.18%	0.00%	0.00%	0.00%	0.00%	0.00%	1.44%
3 May	10.74%	46.87%	0.88%	41.51%	0.00%	49.24%	26.28%	12.16%	9.71%	0.00%	0.00%	0.00%	2.61%
13 Jun	0.02%	40.33%	1.53%	58.13%	0.00%	0.00%	11.50%	56.40%	29.34%	0.00%	0.00%	0.00%	2.77%
24 Aug	27.26%	40.96%	6.63%	25.16%	0.00%	0.91%	96.68%	0.00%	0.00%	0.00%	0.00%	0.00%	2.41%
24 Sep	0.00%	55.88%	0.80%	43.31%	0.00%	0.00%	27.61%	30.30%	25.13%	15.02%	0.00%	0.00%	1.94%
1 Oct	27.41%	32.81%	11.21%	28.56%	0.00%	0.00%	60.44%	37.65%	0.00%	0.00%	0.00%	0.00%	1.91%
8 Oct	0.00%	7.44%	1.07%	91.50%	0.00%	0.00%	0.00%	0.00%	0.00%	55.94%	34.12%	5.73%	4.21%
25 Sep	48.82%	41.32%	0.00%	9.86%	0.00%	19.16%	79.53%	0.00%	0.00%	0.00%	0.00%	0.00%	1.31%
2 Oct	62.87%	4.55%	8.43%	24.15%	0.00%	7.57%	10.40%	55.43%	24.24%	0.00%	0.00%	0.00%	2.36%
22 Oct Am	1.06%	35.76%	6.25%	56.94%	12.76%	5.88%	0.00%	0.00%	0.00%	0.00%	22.50%	56.69%	2.17%
22 Oct Pm	0.00%	26.00%	8.95%	65.05%	4.50%	0.00%	0.00%	0.00%	0.00%	0.00%	20.25%	73.63%	1.62%
11 Mar	0.00%	86.48%	0.00%	13.52%	0.00%	67.70%	29.22%	0.00%	0.00%	0.00%	0.00%	0.00%	3.08%
17 Jul	0.00%	46.50%	0.00%	53.50%	0.00%	0.00%	51.20%	35.10%	10.50%	0.00%	0.00%	0.00%	3.20%

* Computing Atmospheric Trajectory Tool

□ ABLH: Atmosphere Boundary Layer Height

Table S1. Continued.

	Physical characterization			Chemical characterization											Biological characterization	
Label	LWC (g m ⁻³)	Effective Radius (μm)	Temp. (°C)	pH	Na ⁺ (μM)	NH ₄ ⁺ (μM)	Mg ²⁺ (μM)	K ⁺ (μM)	Ca ²⁺ (μM)	SO ₄ ²⁻ (μM)	NO ₃ ⁻ (μM)	Cl ⁻ (μM)	TOC (mgC L ⁻¹)	H ₂ O ₂ (μM)	Bacteria (17°C) CFU mL ⁻¹ *	ATP conc. (nM)
22 Mar	0.38	9.03	0	6.67	20.92	87.56	12.38	2.33	4.72	34.77	24.68	65.73	2.90	18.00	ND	ND
3 May	0.08	3.49	3	5.50	32.90	51.70	10.50	11.10	38.40	10.70	36.00	10.60	6.80	13.89	20	0.06
13 Jun	ND	ND	6.9	5.00	22.70	125.60	10.60	4.10	49.30	6.20	30.60	15.40	10.60	29.26	150	0.12
24 Aug	ND	ND	10.3	5.00	22.80	17.30	6.50	11.70	42.50	13.60	76.10	13.20	7.20	6.28	235	0.21
24 Sep	ND	ND	2.4	4.70	14.20	21.40	5.70	6.20	40.50	9.60	32.80	4.50	3.00	2.95	216	0.01
1 Oct	0.06	2.94	0.8	5.00	30.20	21.30	14.20	7.40	61.00	26.60	37.20	11.80	6.70	0.72	340	0.03
8 Oct	0.17	2.75	8	4.50	21.40	78.90	8.60	7.10	52.40	15.30	132.00	26.40	9.80	14.64	277	0.05
25 Sep	ND	ND	6.8	5.21	105.26	3.00	7.56	15.42	10.59	14.34	6.14	114.18	6.90	19.20	179	0.68
2 Oct	ND	ND	6.1	5.15	120.38	4.18	7.48	39.01	19.35	13.23	42.60	108.97	6.80	5.75	212	0.84
22 Oct Am	ND	ND	5.8	5.80	68.66	0.00	3.90	14.17	7.44	11.69	10.04	52.01	3.20	34.65	134	0.40
22 Oct Pm	ND	ND	6.3	5.80	46.09	0.00	4.23	13.85	9.61	19.67	0.10	35.12	11.20	31.64	120	0.34
11 Mar	ND	ND	5.7	5.13	53.02	61.75	4.13	16.48	6.03	21.51	12.83	37.78	4.00	0.50	186	0.30
17 Jul	0.07	11.20	10.3	5.44	54.66	339.76	13.25	12.61	36.23	39.99	162.06	39.62	ND	ND	196	2.25

*CFU:
Colony-Forming Unit

Table S2. Retention times and exact mass of the AA measured by UPLC-HRMS in cloud samples.

Amino Acid	Abbrev.	Molecular formula	Monoisotopic mass (Da)	m/z [M+H]⁺	Mean retention time (min)
Alanine	Ala	C ₃ H ₇ NO ₂	89.0477	90.0557	3.66
Arginine	Arg	C ₆ H ₁₄ N ₄ O ₂	174.1117	175.1194	6.84
Asparagine	Asn	C ₄ H ₈ N ₂ O ₃	132.0535	133.0612	5.3
Aspartic acid	Asp	C ₄ H ₇ NO ₄	133.0375	134.0452	4.92
Glutamine	Gln	C ₅ H ₁₀ N ₂ O ₃	146.0691	147.0768	5.13
Glutamic acid	Glu	C ₅ H ₈ NO ₄	147.0532	148.0608	4.47
Glycine	Gly	C ₂ H ₅ NO ₂	75.0320	76.0401	4.14
Histidine	His	C ₆ H ₉ N ₃ O ₂	155.0695	156.0772	6.95
Isoleucine	Ile	C ₆ H ₁₃ NO ₂	131.0946	132.1023	1.66
Leucine	Leu	C ₆ H ₁₃ NO ₂	131.0946	132.1023	1.66
Lysine	Lys	C ₆ H ₁₄ N ₂ O ₂	146.1055	147.1127	6.77
Methionine	Met	C ₅ H ₁₁ NO ₂ S	149.0511	150.0588	2.79
Phenylalanine	Phe	C ₉ H ₁₁ NO ₂	165.0790	166.0867	2.33
Proline	Pro	C ₅ H ₉ NO ₂	115.0633	116.0711	4.19
Serine	Ser	C ₃ H ₇ NO ₃	105.0426	106.0504	5.14
Threonine	Thr	C ₄ H ₉ NO ₃	119.0582	120.0660	4.43
Tryptophan	Trp	C ₁₁ H ₁₂ N ₂ O ₂	204.0899	205.0978	2.00
Tyrosine	Tyr	C ₉ H ₁₁ NO ₃	181.0739	182.0815	3.65
Valine	Val	C ₅ H ₁₁ NO ₂	117.0790	118.0868	2.85

Table S3. Concentration ($\mu\text{g L}^{-1}$ with dilution 9:1, detailed in Figure S3), calibration curve and R^2 data for the 18 amino acids (AA) analyzed in the 13 clouds sampled at PUY. The calculation method (detailed in Figure S3) might mathematically provide negative values for the concentration. However, if the concentration (Conc) may turn out to be positive due to a higher STD ($\text{STD} > |\text{Conc}|$), the values are left as is (e.g., Asn -1 ± 4). Otherwise ($\text{STD} < |\text{Conc}|$), we assume to be below the limit of quantification ($< \text{LOQ}$). ND: Not Determined.

22 Mar						
AA	Concentration ($\mu\text{g L}^{-1}$)			Eq. of calibration curve	R ²	
Ala	17	±	4	y = 9.6E+4 x + 1.7E+6	0.9984	
Arg	8	±	1	y = 3.7E+5 x + 3.0E+6	0.9999	
Asn	-1	±	4	y = 8.0E+4 x - 9.8E+4	0.9977	
Asp	12	±	3	y = 5.2E+4 x + 6.1E+5	0.9989	
Gln	-4	±	4	y = 1.1E+5 x - 4.8E+5	0.9984	
Glu	32	±	9	y = 1.7E+5 x + 5.4E+6	0.9916	
Gly	8	±	2	y = 1.2E+5 x + 9.6E+5	0.9997	
His	12	±	4	y = 3.4E+5 x + 4.1E+6	0.9985	
Leu/I	26	±	7	y = 3.3E+5 x + 8.4E+6	0.9943	
Lys	16	±	7	y = 7.7E+4 x + 1.2E+6	0.9970	
Met	4	±	3	y = 2.8E+5 x + 1.0E+6	0.9989	
Phe	0.9	±	0.8	y = 4.8E+5 x + 4.6E+5	0.9999	
Pro	8	±	2	y = 4.6E+5 x + 3.6E+6	0.9993	
Ser	22	±	9	y = 1.1E+5 x + 2.5E+6	0.9911	
Thr	11	±	4	y = 8.6E+4 x + 9.8E+5	0.9983	
Trp	4	±	3	y = 1.5E+5 x + 6.1E+5	0.9984	
Tyr	7	±	3	y = 2.0E+5 x + 1.4E+6	0.9985	

13 Jun					
AA	Concentration ($\mu\text{g L}^{-1}$)			Eq. of calibration curve	R ²
Ala	8	±	5	y = 1.9E+4 x + 1.5E+5	0.9981
Arg	-2	±	7	y = 4.1E+5 x - 1.0E+6	0.9954
Asn	102	±	4	y = 4.5E+4 x + 4.6E+6	0.9995
Asp	4	±	5	y = 2.1E+4 x + 8.3E+4	0.9977
Gln	-1	±	5	y = 9.9E+4 x - 1.3E+5	0.9975
Glu	2	±	5	y = 7.9E+4 x + 1.9E+5	0.9971
Gly	10	±	6	y = 4.5E+4 x + 4.3E+5	0.9949
His	-4	±	6	y = 3.8E+5 x - 1.6E+6	0.9976
Leu/I	12	±	4	y = 1.8E+5 x + 2.2E+6	0.9983
Lys	-5	±	6	y = 5.6E+4 x - 2.8E+5	0.9965
Met	< LOQ			y = 1.7E+5 x - 1.1E+6	0.9977
Phe	-2	±	4	y = 3.6E+5 x - 8.7E+5	0.9982
Pro	10	±	5	y = 3.3E+5 x + 3.2E+6	0.9980
Ser	8	±	5	y = 5.5E+4 x + 4.2E+5	0.9979
Thr	2	±	4	y = 4.6E+4 x + 1.2E+5	0.9983
Trp	-4	±	5	y = 1.1E+5 x - 4.7E+5	0.9977
Tyr	-4	±	5	y = 1.3E+5 x - 4.7E+5	0.9975

3 May					
AA	Concentration (µg L ⁻¹)			Eq. of calibration curve	R ²
Ala	19	±	1	y = 7.6E+4 x + 1.5E+6	0.9998
Arg	< LOQ			y = 3.8E+5 x - 1.4E+6	0.9974
Asn	2.0	±	0.4	y = 9.0E+4 x + 1.8E+5	1.0000
Asp	11	±	2	y = 4.6E+4 x + 5.1E+5	0.9994
Gln	1.0	±	0.7	y = 1.6E+5 x + 1.6E+5	0.9999
Glu	6	±	1	y = 1.2E+5 x + 7.2E+5	0.9998
Gly	16	±	2	y = 1.1E+5 x + 1.8E+6	0.9996
His	3	±	1	y = 3.7E+5 x + 1.2E+6	0.9998
Leu/I	10	±	1	y = 3.4E+5 x + 3.3E+6	0.9998
Lys	0	±	2	y = 8.0E+4 x + 1.9E+3	0.9996
Met	0.5	±	0.6	y = 2.6E+5 x + 1.5E+5	1.0000
Phe	5	±	2	y = 4.3E+5 x + 2.2E+6	0.9995
Pro	18	±	2	y = 3.6E+5 x + 6.5E+6	0.9995
Ser	34	±	5	y = 1.1E+5 x + 3.9E+6	0.9982
Thr	13	±	2	y = 8.5E+4 x + 1.1E+6	0.9996
Trp	< LOQ			y = 1.7E+5 x - 1.4E+5	1.0000
Tyr	5	±	1	y = 1.7E+5 x + 8.0E+5	0.9998

24 Aug					
AA	Concentration ($\mu\text{g L}^{-1}$)			Eq. of calibration curve	R ²
Ala	26	±	2	y = 2.4E+4 x + 6.2E+5	0.9994
Arg	5	±	3	y = 2.8E+5 x + 1.5E+6	0.9992
Asn	130	±	17	y = 5.8E+4 x + 7.6E+6	0.9899
Asp	15	±	4	y = 1.5E+4 x + 2.3E+5	0.9979
Gln	15	±	5	y = 5.9E+4 x + 8.7E+5	0.9964
Glu	17	±	11	y = 5.6E+4 x + 9.6E+5	0.9894
Gly	21	±	4	y = 3.4E+4 x + 7.2E+5	0.9978
His	6	±	1	y = 2.3E+5 x + 1.3E+6	0.9999
Leu/I	17	±	3	y = 1.4E+5 x + 2.4E+6	0.9990
Lys	2	±	1	y = 3.3E+4 x + 7.0E+4	0.9999
Met	-1	±	4	y = 1.2E+5 x - 1.8E+5	0.9978
Phe	11	±	5	y = 2.2E+5 x + 2.5E+6	0.9968
Pro	15	±	3	y = 2.5E+5 x + 3.9E+6	0.9987
Ser	33	±	5	y = 4.0E+4 x + 1.3E+6	0.9975
Thr	28	±	4	y = 3.3E+4 x + 9.3E+5	0.9981
Trp	3.7	±	0.9	y = 6.3E+4 x + 2.3E+5	0.9999
Tyr	5	±	4	y = 7.9E+4 x + 4.1E+5	0.9979

24 Sep					
AA	Concentration ($\mu\text{g L}^{-1}$)			Eq. of calibration curve	R ²
Ala	10.7	±	0.6	y = 2.8E+4 x + 3.0E+5	0.9987
Arg	4.3	±	0.8	y = 2.2E+5 x + 9.5E+5	0.9985
Asn	11	±	2	y = 4.2E+4 x + 4.7E+5	0.9994
Asp	4.4	±	0.6	y = 1.9E+4 x + 8.3E+4	0.9988
Gln	1.0	±	0.6	y = 6.7E+4 x + 6.5E+4	0.9989
Glu	6.8	±	0.8	y = 6.4E+4 x + 4.4E+5	0.9977
Gly	14.2	±	0.6	y = 3.8E+4 x + 5.4E+5	0.9989
His	5	±	1	y = 2.6E+5 x + 1.4E+6	0.9964
Leu/I	7.1	±	0.8	y = 1.6E+5 x + 1.1E+6	0.9978
Lys	3.4	±	0.8	y = 3.4E+4 x + 1.2E+5	0.9981
Met	0.4	±	0.7	y = 1.5E+5 x + 5.9E+4	0.9983
Phe	3	±	1.1	y = 3.0E+5 x + 9.9E+5	0.9953
Pro	8.4	±	1.0	y = 3.2E+5 x + 2.7E+6	0.9968
Ser	17.3	±	0.8	y = 4.9E+4 x + 8.5E+5	0.9976
Thr	20.7	±	1.0	y = 4.0E+4 x + 8.2E+5	0.9970
Trp	0.9	±	0.6	y = 7.7E+4 x + 7.3E+4	0.9986
Tyr	2.2	±	0.8	y = 1.1E+5 x + 2.4E+5	0.9975

8 Oct					
AA	Concentration ($\mu\text{g L}^{-1}$)			Eq. of calibration curve	R ²
Ala	27	±	2	y = 7.5E+4 x + 2.1E+6	0.9996
Arg	-4	±	6	y = 4.0E+5 x - 1.6E+6	0.9952
Asn	1.5	±	1.0	y = 9.7E+4 x + 1.5E+5	0.9999
Asp	13.7	±	0.3	y = 5.2E+4 x + 7.1E+5	1.0000
Gln	0	±	2	y = 1.7E+5 x + 4.7E+4	0.9994
Glu	8	±	3	y = 1.3E+5 x + 1.1E+6	0.9988
Gly	18.0	±	0.6	y = 1.2E+5 x + 2.2E+6	1.0000
His	3	±	2	y = 4.0E+5 x + 1.0E+6	0.9996
Leu/I	21.6	±	0.7	y = 3.5E+5 x + 7.6E+6	0.9999
Lys	-1	±	3	y = 8.3E+4 x - 8.8E+4	0.9988
Met	-0.7	±	0.6	y = 2.9E+5 x - 2.2E+5	1.0000
Phe	5	±	1	y = 4.6E+5 x + 2.3E+6	0.9998
Pro	14.2	±	0.9	y = 3.9E+5 x + 5.6E+6	0.9999
Ser	36	±	1	y = 1.3E+5 x + 4.6E+6	0.9999
Thr	15	±	1	y = 8.9E+4 x + 1.4E+6	0.9998
Trp	0.6	±	0.5	y = 1.7E+5 x + 9.5E+4	1.0000
Tyr	5	±	3	y = 1.9E+5 x + 1.0E+6	0.9984

1 Oct					
AA	Concentration ($\mu\text{g L}^{-1}$)			Eq. of calibration curve	R ²
Ala	69	±	5	y = 3.0E+4 x + 2.1E+6	0.9978
Arg	1	±	6	y = 4.1E+5 x + 2.5E+5	0.9952
Asn	31	±	7	y = 4.2E+4 x + 1.3E+6	0.9960
Asp	45	±	7	y = 2.1E+4 x + 9.4E+5	0.9950
Gln	3	±	1	y = 7.9E+4 x + 2.6E+5	0.9998
Glu	22	±	3	y = 7.4E+4 x + 1.6E+6	0.9988
Gly	42	±	2	y = 4.3E+4 x + 1.8E+6	0.9993
His	22	±	4	y = 3.0E+5 x + 6.7E+6	0.9980
Leu/I	41	±	4	y = 1.6E+5 x + 6.3E+6	0.9983
Lys	9	±	4	y = 4.9E+4 x + 4.5E+5	0.9981
Met	-0	±	1	y = 1.7E+5 x - 6.5E+4	0.9998
Phe	10	±	3	y = 3.5E+5 x + 3.5E+6	0.9989
Pro	30	±	3	y = 3.3E+5 x + 9.9E+6	0.9991
Ser	157	±	8	y = 5.4E+4 x + 8.5E+6	0.9974
Thr	42	±	2	y = 4.5E+4 x + 1.9E+6	0.9995
Trp	2	±	1	y = 8.4E+4 x + 1.5E+5	0.9998
Tyr	21	±	5	y = 1.1E+5 x + 2.2E+6	0.9972

25 Sep					
AA	Concentration ($\mu\text{g L}^{-1}$)			Eq. of calibration curve	R ²
Ala				ND	
Arg	8	±	4	y = 2.5E+4 x + 2.0E+5	0.9831
Asn	21	±	3	y = 6.2E+3 x + 1.3E+5	0.9778
Asp				ND	
Gln	6	±	2	y = 9.7E+3 x + 6.2E+4	0.9965
Glu	10	±	1	y = 9.2E+3 x + 9.6E+4	0.9957
Gly	87	±	8	y = 1.6E+3 x + 1.4E+5	0.9781
His				ND	
Leu/I				ND	
Lys	8	±	1	y = 7.6E+3 x + 6.2E+4	0.9978
Met	< LOQ			y = 4.1E+3 x - 2.8E+4	0.9566
Phe	18	±	5	y = 2.3E+4 x + 4.2E+5	0.9783
Pro				ND	
Ser	150	±	22	y = 4.1E+3 x + 6.3E+5	0.9384
Thr	25	±	3	y = 6.0E+3 x + 1.5E+5	0.9918
Trp	5	±	2	y = 3.7E+3 x + 1.8E+4	0.9488
Tyr				ND	

2 Oct						
AA	Concentration (µg L ⁻¹)			Eq. of calibration curve	R ²	
Ala	ND					
Arg	3	±	4	y = 2.7E+5 x + 7.4E+5	0.9978	
Asn	67.3	±	0.9	y = 1.5E+4 x + 1.0E+6	0.9999	
Asp	65	±	2	y = 7.2E+3 x + 4.7E+5	0.9994	
Gln	2.43	±	2	y = 2.4E+4 x + 5.9E+4	0.9994	
Glu	22.0	±	0.9	y = 2.5E+4 x + 5.6E+5	0.9999	
Gly	121	±	3	y = 4.6E+3 x + 5.5E+5	0.9994	
His	25.9	±	0.7	y = 1.5E+5 x + 3.8E+6	0.9999	
Leu/I	68	±	1	y = 5.3E+4 x + 3.6E+6	0.9998	
Lys	19	±	1	y = 3.8E+4 x + 7.1E+5	0.9997	
Met	-0	±	1	y = 3.5E+4 x - 6.4E+3	0.9998	
Phe	19.7	±	0.3	y = 1.2E+5 x + 2.3E+6	0.9999	
Pro	ND					
Ser	282	±	6	y = 1.5E+4 x + 4.3E+6	0.9985	
Thr	49	±	1	y = 1.3E+4 x + 6.5E+5	0.9998	
Trp	1.0	±	0.2	y = 4.1E+4 x + 4.1E+4	0.9999	
Tyr	27	±	3	y = 3.3E+4 x + 8.9E+5	0.9984	

22 Oct Pm						
AA	Concentration (µg L ⁻¹)			Eq. of calibration curve	R ²	
Ala	ND					
Arg	2.2	±	0.6	y = 1.8E+5 x + 4.0E+5	0.9992	
Asn	1.0	±	0.4	y = 1.4E+4 x + 1.3E+4	1.0000	
Asp	6	±	1	y = 6.6E+3 x + 4.2E+4	0.9998	
Gln	< LOQ			y = 2.1E+4 x - 4.6E+4	0.9994	
Glu	2.8	±	0.5	y = 2.4E+4 x + 6.6E+4	1.0000	
Gly	57	±	5	y = 3.5E+3 x + 2.0E+5	0.9966	
His	3.4	±	1.0	y = 1.3E+5 x + 4.4E+5	0.9998	
Leu/I	17	±	3	y = 6.9E+4 x + 1.2E+6	0.9983	
Lys	1	±	2	y = 3.3E+4 x + 3.8E+4	0.9995	
Met	< LOQ			y = 4.0E+4 x - 5.2E+4	1.0000	
Phe	4	±	1	y = 1.5E+5 x + 6.4E+5	0.9961	
Pro	ND					
Ser	42	±	1	y = 1.5E+4 x + 6.3E+5	0.9998	
Thr	8.0	±	0.5	y = 1.2E+4 x + 9.5E+4	1.0000	
Trp	4	±	3	y = 4.3E+4 x + 1.8E+5	0.9985	
Tyr	-1	±	3	y = 3.2E+4 x - 1.7E+4	0.9983	

22 Oct Am						
AA	Concentration (µg L ⁻¹)			Eq. of calibration curve	R ²	
Ala	ND					
Arg	-2	±	4	y = 2.6E+5 x - 4.7E+5	0.9973	
Asn	2.3	±	0.6	y = 1.4E+4 x + 3.2E+4	0.9999	
Asp	21.8	±	1.0	y = 6.4E+3 x + 1.4E+5	0.9998	
Gln	< LOQ			y = 2.1E+4 x - 4.0E+4	0.9992	
Glu	9.7	±	0.7	y = 2.4E+4 x + 2.3E+5	0.9999	
Gly	48	±	2	y = 4.0E+3 x + 1.9E+5	0.9994	
His	8.7	±	0.5	y = 1.3E+5 x + 1.1E+6	0.9999	
Leu/I	21.5	±	0.5	y = 6.9E+4 x + 1.5E+6	1.0000	
Lys	6	±	1	y = 3.4E+4 x + 2.2E+5	0.9996	
Met	< LOQ			y = 3.6E+4 x - 7.2E+4	1.0000	
Phe	6.19	±	0.37	y = 1.4E+5 x + 8.4E+5	0.9997	
Pro	ND					
Ser	78	±	2	y = 1.5E+4 x + 1.2E+6	0.9995	
Thr	18.1	±	0.7	y = 1.2E+4 x + 2.2E+5	0.9999	
Trp	-0.2	±	0.3	y = 4.4E+4 x - 9.0E+3	1.0000	
Tyr	7	±	2	y = 3.2E+4 x + 2.4E+5	0.9996	

3 Mar						
AA	Concentration (µg L ⁻¹)			Eq. of calibration curve	R ²	
Ala	54	±	10	y = 1.5E+3 x + 8.0E+4	0.9906	
Arg	3	±	3	y = 1.4E+5 x + 3.9E+5	0.9894	
Asn	2.3	±	0.9	y = 1.0E+4 x + 2.3E+4	0.9998	
Asp	< LOQ			y = 1.8E+3 x - 4.4E+3	0.9996	
Gln	-0.5	±	0.6	y = 1.8E+4 x - 9.1E+3	0.9995	
Glu	1	±	2	y = 1.4E+4 x + 1.1E+4	0.9993	
Gly	33	±	3	y = 4.1E+2 x + 1.4E+4	0.9986	
His	2	±	4	y = 1.1E+5 x + 2.6E+5	0.9970	
Leu/I	15.6	±	0.7	y = 4.4E+4 x + 6.8E+5	0.9999	
Lys	-1	±	2	y = 3.8E+4 x - 5.1E+4	0.9994	
Met	< LOQ			y = 2.3E+4 x - 2.3E+5	0.9995	
Phe	9	±	2	y = 5.3E+4 x + 4.6E+5	0.9995	
Pro	ND					
Ser	0	±	3	y = 5.1E+3 x + 1.8E+3	0.9989	
Thr	3	±	3	y = 6.9E+3 x + 2.4E+4	0.9983	
Trp	< LOQ			y = 3.5E+4 x - 1.8E+4	0.9996	
Tyr	2	±	2	y = 1.7E+4 x + 3.6E+4	0.9990	

17 Jul					
AA	Concentration (µg L ⁻¹)			Eq. of calibration curve	R ²
Ala	ND				
Arg	2	±	2	y = 1.8E+4 x + 2.9E+4	0.9971
Asn	4	±	1	y = 2.6E+3 x + 1.1E+4	0.9991
Asp	-1	±	2	y = 8.6E+2 x - 8.4E+2	0.9983
Gln	6	±	1	y = 4.8E+3 x + 2.8E+4	0.9988
Glu	8	±	1	y = 4.5E+3 x + 3.8E+4	0.9987
Gly	72	±	8	y = 3.8E+2 x + 2.7E+4	0.9829
His	< LOQ			y = 1.5E+4 x - 3.8E+4	0.9979
Leu/I	19	±	1	y = 5.6E+3 x + 1.1E+5	0.9985
Lys	2	±	1	y = 4.4E+3 x + 6.7E+3	0.9985
Met	< LOQ			y = 5.8E+3 x - 1.0E+4	0.9991
Phe	9.8	±	0.9	y = 1.3E+4 x + 1.2E+5	0.9994
Pro	9.4	±	0.6	y = 3.4E+4 x + 3.1E+5	0.9997
Ser	22	±	3	y = 1.9E+3 x + 4.3E+4	0.9960
Thr	9	±	1	y = 3.0E+3 x + 2.7E+4	0.9989
Trp	< LOQ			y = 6.3E+3 x - 2.9E+4	0.9980
Tyr	8	±	2	y = 4.2E+3 x + 3.5E+4	0.9981

Table S4. FAAs concentrations in atmospheric samples: Cloud, fog, rain and aerosol particles (non-exhaustive).

Localization	Environment	Period / Samples	Method Separation	Concentration range FAAs	Distribution (major FAAs)	Reference
Cloud, fog, rain						
Puy de Dôme Mountain, France (1465 m)	Rural + marine influence (Cloud)	03/2014 05-10/2018 09, 10/2019 03, 07/2020 13 samples	HPLC-MS/MS Standard addition	Range: 39 - 244 ng m ⁻³	Ser > Gly > Ala > Asn > Leu/I	This work
Puy de Dôme Mountain, France (1465 m)	Rural + marine influence (Cloud)	03-04/2014 (spring) 11/2014 (winter) 25 samples	HPLC-Fluorescence OPA-Derivatization	Mean: 118.6 ± 97.6 ng m ⁻³	Trp > Ile/Leu > Phe > Ser	Bianco et al. (2016)
Cabo Verde islands (744 m)	Marine (Cloud)	09-10/2017 (winter) 10 samples	HPLC-MS OPA-Derivatization	Range: 11.2 - 489.9 ng m ⁻³	Ser > Asp > Ala > Gly > Thr	Triesch et al. (2021)
Davis, CA, US (10 m)	Rural (Fog)	1997 - 1999 (winter) 11 samples	HPLC-Fluorescence OPA-Derivatization	Mean: 40.8 ± 38.0 ng m ⁻³ (FAAs, protein type)	Ser > Gly > Leu > Ala > Val	Zhang and Anastasio (2003)
Atlantic Ocean, Gulf Mexico (Cruise)	Marine (Rain)	09-10/1985 02, 06, 09/1986 7 samples	HPLC-Fluorescence OPA-Derivatization	Mean: 604 ± 585 µg L ⁻¹	Gly > Ser > Ala > acidic AAs	Mopper and Zika (1987)
Seoul, South Korea (17 m)	Urban (Rain)	03/2012 - 04/2014 36 samples	HPLC-Fluorescence OPA-Derivatization	Mean: 21.0 ± 17.9 µg L ⁻¹ (Seoul)	Gly > Glu > Asp > Ser	Yan et al. (2015)
Uljin, South Korea (30 m)	Marine (Rain)	02/2011 - 01/2012 31 samples		Mean: 100.9 ± 110.2 µg L ⁻¹ (Uljin)		
Guiyang, China (1300 m)	Suburban (Rain)	05/2017 - 04/2018 Summer (n = 29) Autumn (n = 9) Winter (n = 14) Spring (n = 13) 65 samples	HPLC-Fluorescence OPA-Derivatization	Total: 1.1 - 10.1 µM Mean: 3.7 µM Range Summer: 1.3 - 6.6 µM Mean Summer: 2.9 µM Range Autumn: 1.1 - 8.8 µM Mean Autumn: 4.4 µM Range Winter: 1.5 - 9.9 µM Mean Winter: 3.4 µM Range Spring: 2.6 - 10.1 µM Mean Spring: 5.2 µM	Glu + Gln, Gly, Pro > Asp, Ala	Xu et al. (2019)

Aerosol						
Erdemli, Eastern Mediterranean coast, Turkey (21m)	Marine (Aerosol)	03-05/2000 (spring) 39 samples	HPLC-UV-Vis DABS-Cl- Derivatization	Mean: 33.8 ng m ⁻³ Range: 3.65 - 102 ng m ⁻³	Gly > Arg > Val > Pro	Mace et al. (2003a)
Cape Grim Baseline Air, Tasmania (94 m)	Marine (Aerosol)	11/2000 (winter) 13 samples	HPLC-UV-Vis DABS-Cl- Derivatization	Mean: 8.74 ng m ⁻³ Range: 1.83 - 20 ng m ⁻³	Arg > Gly > Pro > Ala > Val	Mace et al. (2003b)
Davis, CA, US (10 m)	Rural (Aerosol)	08/1997 - 07/1998 41 PM _{2.5} samples	HPLC-Fluorescence OPA-Derivatization	Mean: 58.5 ng m ⁻³ Range: 8.62 - 236 ng m ⁻³	Ornithine > Gly > Thr > Ser > Ala	Zhang and Anastasio (2003)
Western Pacific Ocean (Cruise)	Marine (Aerosol)	05-06/2000 (spring) 06-07/2000 (summer) Fine p. d < 2.5 µm Coarse p. d > 2.5 µm 15 samples	HPLC-Fluorescence OPA-Derivatization	Mean: 0.98 ng m ⁻³ Range: 0.14 - 2.81 ng m ⁻³	Gly > Ser > Asp > Ala	Matsumoto and Uematsu (2005)
Atlantic (Cruise)	Marine (Aerosol)	05-06/2003 (spring) Total suspended particles	HPLC-Fluorescence OPA-Derivatization	Mean: 1.83 ng m ⁻³ Range: 0.27 - 9.13 ng m ⁻³	Gly > Ala > Ser > Leu	Wedyan and Preston (2008)
Finokalia, Crete Island, Greece (250 m)	Marine (Aerosol)	7/2007-8/2010 (summer/autumn) 47 daily PM ₁ samples	HPLC-UV/Vis DABS-Cl- Derivatization	Mean: 45.6 ng m ⁻³	Gly > Ser > Arg + Ala > Lys > His	Violaki and Mihalopoulos (2010)
Finokalia, Crete Island, Greece (250 m)	Marine (Aerosol)	06-08/2007 (summer) 46 samples Total suspended particles	GC-MS MTBSTFA- Derivatization	Mean: 16.01 ng m ⁻³ Range: 0.7 - 76.9 ng m ⁻³	Gly > Gln > Ala > Asp ~ Glu	Mandalakis et al. (2011)
CVAO (0 m) Mt Verde (744m) Island of São Vicente, Cape Verde	Marine (Aerosol)	09-10/2017 (autumn) 8 samples 5 size segregated aerosol particles (0.05 - 10 µm)	HPLC-MS/MS	CVAO: Range PM _{1.2} : 1.3 - 6.3 ng m ⁻³ Range PM _{>1.2} : 0.2 - 1.4 ng m ⁻³ MV: Range PM _{1.2} : 0.8 - 1.9 ng m ⁻³ Range PM _{>1.2} : 0.2 - 2.9 ng m ⁻³	Gly > Ala > Ser CVAO & MV	Triesch et al. (2021)

Gosan, Jeju Island, South Korea (10 m)	Rural (Aerosol)	03-04/2001 (spring) PM _{2.5} 36 samples 4 composites (9 samples grouped together)	HPLC-Fluorescence OPA-Derivatization	Range TAAs: 77 - 255 ng m ⁻³ FAA ~ 19% TAA	Gly > Glu > Val	Yang et al. (2004)
Duke Forest Research Facility NC, USA (150 m)	Rural (Aerosol)	07-08/2010 (summer) PM _{2.5} 13 samples	HPLC-MS	Range: 11 - 40 ng m ⁻³	Gly > Arg > Ala > Asp > Glu	Samy et al. (2011)
SMEAR II station, Hyytiälä, Finland (148 m)	Rural (Aerosol)	02-10/2014 Dekati PM ₁₀ cascade impactor (<1.0, 1-2.5, 2.5-10 and >10 µm) 69 samples	HPLC-MS/MS	Mean: PM ₁ : 5.22 ng m ⁻³ PM _{2.5} : 10.95 ng m ⁻³ PM ₁₀ : 18.45 ng m ⁻³ PM _{>10} : 27.62 ng m ⁻³	PM ₁ : Arg > Gly > Pro PM _{2.5} : Arg > Pro > Gln PM ₁₀ : Arg > Pro > Gln PM _{>10} : Pro > Arg > Gly	Helin et al. (2017)
Tianhu, Guangzhou, China (170 m)	Rural (Aerosol)	03/2012 - 02/2013 PM _{2.5} 52 samples	HPLC-Fluorescence OPA-Derivatization	Mean: Annual: 133 ± 48 ng m ⁻³ Spring: 107 ± 26 ng m ⁻³ Summer: 115 ± 35 ng m ⁻³ Autumn: 186 ± 56 ng m ⁻³ Winter: 123 ± 31 ng m ⁻³	Gly > Val > Met > Phe	Song et al. (2017)
Col Margherita Atmospheric Observatory, Eastern Alps, Italy (2543 m)	Remote (Aerosol)	04, 08/2018 (spring/summer) PM ₁₀ 7 samples	HPLC-MS/MS	Mean spring: 6 ± 5 ng m ⁻³ Mean summer 7 ± 2 ng m ⁻³	Spring: Gly > Glu > Arg Summer: Gly > Glu > Ala	Barbaro et al. (2020)
SMEAR II station, Hyytiälä, Finland (148 m)	Rural (Aerosol)	09-11/2017 Cascade impactor (PM ₁ to PM ₁₀) 84 samples	HPLC-MS/MS	Range PM ₁ : 2.1 - 5.4 ng m ⁻³ Range PM _{2.5} : 1.8 - 5.7 ng m ⁻³ Range PM ₁₀ : 11.4 - 36.9 ng m ⁻³ Range PM _{>10} : 7.1 - 46.6 ng m ⁻³	PM ₁ : Gly > Ala > Glu PM _{2.5} : Gln > Arg > Glu PM ₁₀ : Leu > Arg > Gln PM _{>10} : Leu > Asp > Arg	Ruiz-Jimenez et al. (2021)

Nanjing University, China (10 m)	Urban (Aerosol)	02/2001 (winter) - 09/2001 (autumn) PM _{2.5} 10 samples (winter) 14 samples (autumn)	HPLC-Fluorescence AQC-Derivatization	Mean: 129 ng m ⁻³ (winter) Range: 81.9 - 188 ng m ⁻³ Mean: 84.9 ng m ⁻³ (autumn) Range: 39.3 - 162 ng m ⁻³	Gly > Cys > Val	Yang et al. (2005)
Purple Mountain Observatory, Nanjing, China (267 m)	Suburban (Aerosol)	02/2001 (winter) PM _{2.5} 12 samples		Mean: 189 ng m ⁻³ (winter) Range: 58.5 - 396 ng m ⁻³		
Sacca San Biagio Island, Venice, Italy (0 m)	Urban (Aerosol)	04-10/2007 Total suspended particles 10 samples	HPLC-MS/MS	Mean: 38 ng m ⁻³ Range FAAs: 7 - 146 ng m ⁻³	Gly > Gln > Pro > Ala Asn > Glu > Asp > Ser	Barbaro et al. (2011)
Research Triangle Park NC, US (90 m)	Suburban (Aerosol)	09-10/2010 PM _{2.5} (30 samples)	HPLC-MS/MS	Mean: 11 ± 6 ng m ⁻³	Gly > Ala = Asp = Arg > Glu > Ser	Samy et al. (2013)
University of Rome, Italy (40 m)	Urban (Aerosol)	01/2013 (winter) - 09/2013 (summer) PM _{0.1} , PM ₁ , PM _{2.5} , PM ₁₀ 13 samples (winter) 13 samples (summer)	HPLC-MS/MS	Mean: PM ₁₀ : 195 ng m ⁻³ (winter) 272 ng m ⁻³ (summer) PM _{2.5} : 167 ng m ⁻³ (winter) 193 ng m ⁻³ (summer) PM ₁ : 129 ng m ⁻³ (winter) 145 ng m ⁻³ (summer) PM _{0.1} : 48 ng m ⁻³ (winter) 94 ng m ⁻³ (summer)	Gly > Ser > His > Asp	Di Filippo et al. (2014)
Institute of Atmospheric, Physics, Beijing, China (50 m)	Urban (Aerosol)	04-05/2013 (spring) Total suspended particles 29 samples	HPLC-Fluorescence OPA-Derivatization	Range TAAs: Whole year: 72 - 3820 ng m ⁻³ Spring: 374 - 3195 ng m ⁻³ Summer: 154 - 2262 ng m ⁻³ Fall: 161 - 2067 ng m ⁻³ Winter: 340 - 2405 ng m ⁻³ FAA ~ 25 % TAA	Gly > Ala > Val	Ren et al. (2018)
Nanchang, China (37 m)	Urban Town Suburban Airport Forested site (Aerosol)	04-05/2019 PM _{2.5} 14 samples / site	GC-MS tBDMS- Derivatization	Range total FAAs: 57 - 1238 pmol m ⁻³ Mean: Airport: 321 ± 200 pmol m ⁻³ Town: 350 ± 267 pmol m ⁻³ Urban: 307 ± 131 pmol m ⁻³ Suburban: 264 ± 113 pmol m ⁻³ Forest: 220 ± 132 pmol m ⁻³	Gly > Ala = Pro	Zhu et al. (2021)

Gruvenbadet observatory, Svalbard, Arctic (8 m)	Polar (Aerosol)	04-09/2010 (boreal summer) Cascade impactor 9 samples	HPLC-MS/MS	Mean PM _{0.5} : 102.42 ng m ⁻³ Range: 15.66 - 308.65 ng m ⁻³	Gly > Ser > Ala	Scalabrin et al. (2012)
Faraglione Camp, MZS, Antarctica (57 m)	Polar coastal area (Aerosol)	11/2010-01/2011 (summer) PM ₁₀ and cascade impactor 5 samples	HPLC-MS/MS	Mean: PM ₁₀ : 1.51 ng m ⁻³ Mean: PM ₁ : 1.5 ng m ⁻³	Arg > Gly	Barbaro et al. (2015)
Dome C station, Antarctic (3233m)	Polar (Aerosol)	11/2011-01/2012 (summer) PM ₁₀ and cascade impactor 4 samples		Mean: PM ₁₀ : 0.11 ng m ⁻³	Gly > Asp > Ala	
Dome C station, Antarctic (3233m)	Polar (Aerosol)	12/2012-01/2013 (summer) PM ₁₀ and cascade impactor 5 samples		Mean: PM ₁₀ : 0.1 ng m ⁻³	Gly > Asp > Ala	
Rose Sea (Cruise)	Marine (Aerosol)	11-12/2011 TSP 5 samples		Mean: TSP: 0.48 ng m ⁻³	Gly > Pro = Glu	
Gruvebadet observatory, Svalbard, Arctic (8 m)	Polar (Aerosol)	04-06/2015 Cascade impactor 7 samples	HPLC-MS/MS	Mean: 6.1 ± 3.4 pmol m ⁻³ Mean Gly: 0.27 ng m ⁻³ Range PM ₁₀ : 2.0-10.8 pmol m ⁻³	Gly > Ala > Asp	Feltracco et al. (2019)
Zeppelin observatory Svalbard, Arctic (420 m)	Polar (Aerosol)	09-12/2015 (winter) Coarse (2 - 10 µm) Fine (< 2 µm) 40 samples	HPLC (MS/MS) C ₄ -NA-NHS- Derivatization	Range TAA: Fine: 6 - 2914 pmol m ⁻³ Coarse: 0.02 - 1417 pmol m ⁻³	Leu > Ala > Val	Mashayekhy Rad et al. (2019)

Lists of acronyms

- AQC: Molecular composition of the water-soluble fraction of atmospheric carbonaceous
- C₄-NA-NHS: N-butyl nicotinic acid Nhydroxysuccinimide ester
- DABS-Cl: 4-dimethylaminoazobenzene-40-sulfonyl chloride
- MTBSTFA: N-(t-butyltrimethylsilyl)-N-methyltrifluoroacetamide
- OPA: ortho-phthalaldehyde
- tBDMS : Gly-tert-butyl dimethylsilyl
- TSP: Total suspended particles
- GC: Gas chromatography
- HPLC: high performance liquid chromatography
- IRMS: Isotope Ratio Mass Spectrometry

Estimated lifetimes of AAs : Description of the calculations performed in Table 4.

1- Calculations of the lifetimes considering theoretical HO•, O₃ and ¹O₂* concentrations (column (A) in Table 4)

Aqueous concentrations of HO•, O₃ and ¹O₂* are respectively equal to 10⁻¹⁴, 5.0 10⁻¹⁰ and 1.0 10⁻¹² M. The concentration of HO• derives from the study of Arakaki et al. (2013); the concentration of O₃ is calculated considering a 50 ppb concentration of gaseous O₃ and its Henry's law constant (H(O₃) = 10⁻³ M atm⁻¹). ¹O₂* concentration is estimated to be 2 orders of magnitude more concentrated than HO•. All the kinetic constants derive from the Jaber et al. (2021) study (considering T and pH-dependency when necessary and available). The lifetimes for individual AA are calculated as following:

$$\tau = \frac{1}{k_{HO} \times [HO^\bullet] + k_{O_3} \times [O_3] + k_{1O_2^*} \times [^1O_2^*]}$$

2- Calculations of the lifetimes using irradiation experiments in artificial cloud medium (column (D) in Table 4)

Experimental irradiation of 19 amino acids at a concentration of 1 μM each in an artificial cloud medium were conducted in Jaber et al. (2021). HO• production was performed using Fe-Ethylenediamine-N,N'-disuccinic acid (EDDS) complex solution. HO• concentration of 8.3 10⁻¹³ M was estimated during the experiment. Abiotic transformation rates ($R_{photo,exp}$) are evaluated during the experiment in mol L⁻¹ h⁻¹ (see Table 2 in Jaber et al., 2021). For Arg, Asn, Asp, Gln, Gly, Lys and Pro, lifetimes cannot be calculated since a production is observed during the experiment.

The lifetimes for individual AA are calculated as follows:

$$\tau = \frac{[AA]}{R_{photo,exp} \cdot \frac{[HO^\bullet]_{photo.exp}}{[HO^\bullet]_{cloud}}}$$

[AA] represents the initial AA concentration in the experiment, i.e., 1 μM.

Since the experiments were conducted with HO• concentrations likely higher than ambient ones in cloud water, we correct these abiotic rates to HO• concentrations in clouds by $[HO^\bullet]_{photo.exp} = 8.3 \times 10^{-13}$ M and $[HO^\bullet]_{cloud} = 10^{-14}$ M. This correction has been considered as in Jaber et al. (2021) to fit the abiotic rates to an HO• concentration of 10⁻¹⁴M.

3- Calculations of the lifetimes using biodegradation experiments in artificial cloud medium (column (F) in Table 4)

Biodegradation experiments of 19 amino acids were performed by Jaber et al. (2021) using 4 microbial strains (*Rhodococcus enclensis* PDD-23b-28, *Pseudomonas graminis* PDD-13b-3, *Pseudomonas syringae* PDD-32b-74 and *Sphingomonas sp.* PDD-32b-11) in artificial cloud water. Biodegradation rates are evaluated experimentally in mol cell⁻¹ h⁻¹ (see Table 1 in Jaber et al., 2021). These values are multiplied by 6.8 10⁷ cells L⁻¹ which corresponds to the average concentration of microorganisms in cloud water reported at PUY (Vařtilingom et al., 2012). This leads to the values R_{23b-28} , R_{13b-3} , R_{32b-74} , R_{32b-11} in mol L⁻¹ h⁻¹. *Rhodococcus enclensis* PDD-23b-28, *Pseudomonas graminis* PDD-13b-3, *Pseudomonas syringae* PDD-32b-74 and *Sphingomonas sp.* PDD-32b-11 contributes respectively to 6.3 %, 14.9 %, 14.9 % and 16.2% of the total cell concentration. The remaining 47.7 % belongs to other phyla or classes. We scale up each contribution by a factor 1.91 (=100/52.3), implying that the four bacteria types are representative for the remainder (47.7 %) of the bacteria population.

Therefore, we calculate the atmospheric lifetimes for individual AA as following:

$$\tau = \frac{[AA]}{0.063 R_{23b-28} \cdot 1.91 - 0.149 R_{13b-3} \cdot 1.91 - 0.149 R_{32b-74} \cdot 1.91 - 0.162 R_{32b-11} \cdot 1.91}$$

[AA] represents the initial AA concentration in the experiment, i.e., 1 μM.

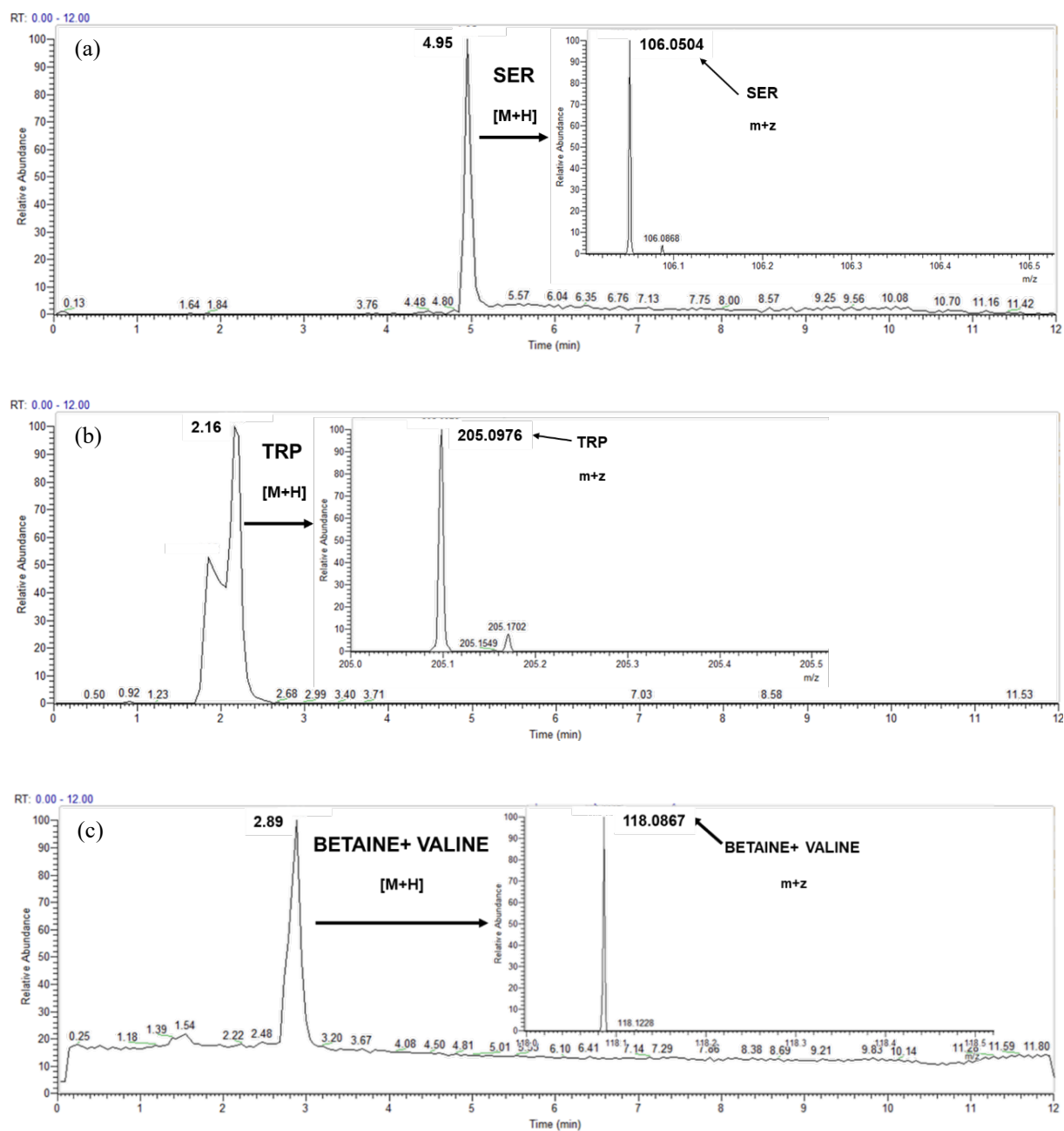


Figure S1. Chromatograms and MS spectra of: (a) Ser, (b) Trp and (c) Val (+ Betaine) measured by UPLC-HRMS (11 Mar Cloud).

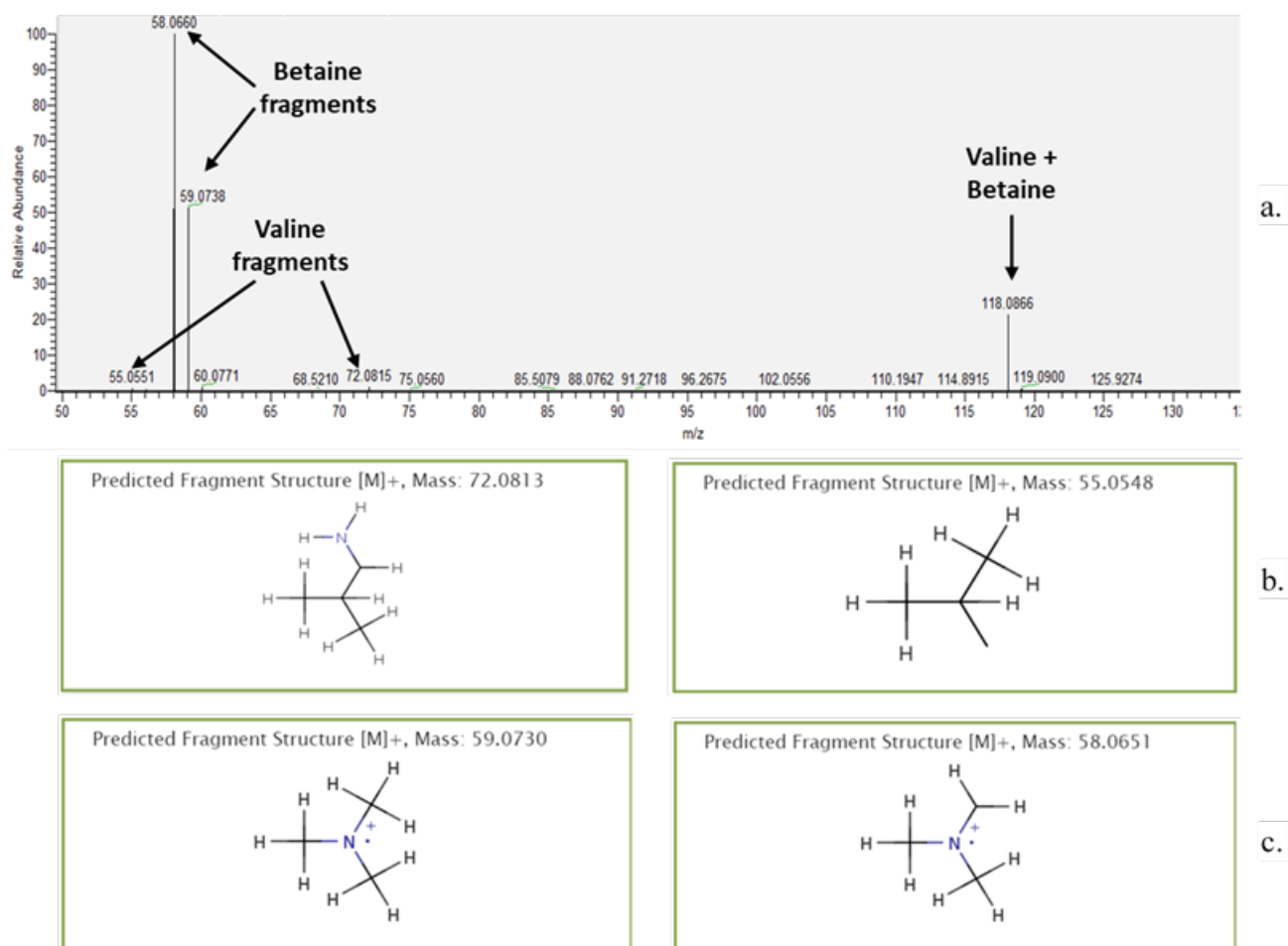


Figure S2. a. MS/MS of the compounds at m/z 118.0866 $[M+H]^+$ detected on 11 Mar cloud, and the characteristic product ions: **b.** Predicted structures and values of Betaine fragments $m/z = 58.0651$ and 59.0730 $[M+H]^+$; **c.** Predicted structures and values of Valine fragments $m/z = 55.0548$ and 72.0813 $[M+H]^+$. Predicted values and structures are issued from MetLIN Mass Spectral Database.

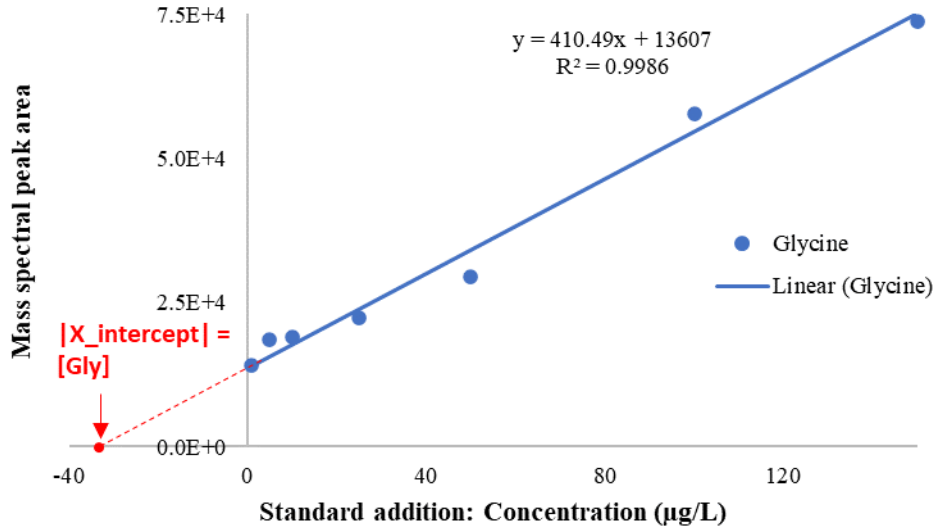


Figure S3. Quantification of amino acid concentrations (11 Mar cloud sample) using the addition standard method: case study of glycine (Gly).

Quantification and uncertainty (Figure S3)

In standard addition, known quantities of analyte (AA) are added to the unknown quantity in the sample. From the increase in signal, we deduce how much analyte was originally in the sample. This method requires a linear response to analyte (Broekaert, 2015).

The magnitude of the intercept on the x-axis is the original concentration of Gly. The equation of the trendline is $y = a x + b$. The $x_{\text{intercept}}$ is obtained by setting $y = 0$: $x = -b / a$, with $a = \text{slope of the curve}$, $b = y_{\text{intercept}}$, $x = \text{the concentration of the AA}$, $y = \text{the mass spectral area}$:

$$\text{Gly: } a = 410.49; b = 13607 \quad \rightarrow \quad |x_{\text{intercept}}| = [\text{Gly}] = 33.1 \mu\text{g L}^{-1} \text{ (negative value)}$$

The obtained values are then corrected by the dilution factor of 10 % (due to the ratio 9:1 volume cloud: volume added standard). Final value is: $[\text{Gly}] = 33.1 \times \frac{10}{9} = 36.8 \mu\text{g L}^{-1}$.

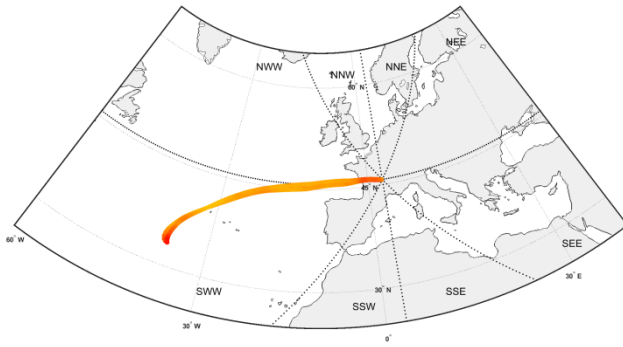
The uncertainty in the $x_{\text{intercept}}$ is s_x :

$$s_x = \frac{s_y}{|a|} \sqrt{\frac{1}{n} + \frac{\bar{y}^2}{a^2 \times \sum (x_i - \bar{x})^2}}$$

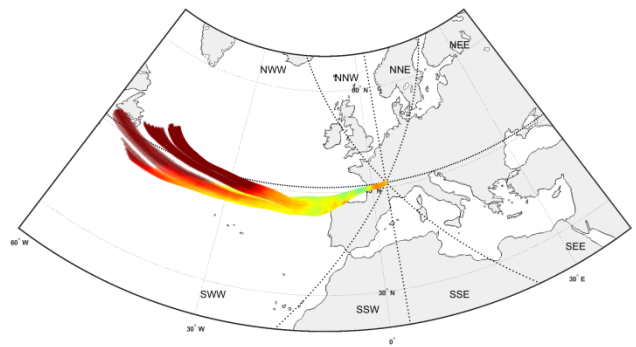
where a is the absolute value of the slope of the trendline, n is the number of data points, $\bar{y}$ is the mean value of y for the points, x_i are the individual values of x , $\bar{x}$ is the mean value of x for the points, and s_y is the standard deviation for y :

$$s_y = \sqrt{\frac{1}{(n-2)} \times \left[\sum ((y - \bar{y})^2 - \frac{[\sum (x - \bar{x})(y - \bar{y})]^2}{\sum (x - \bar{x})^2}) \right]}$$

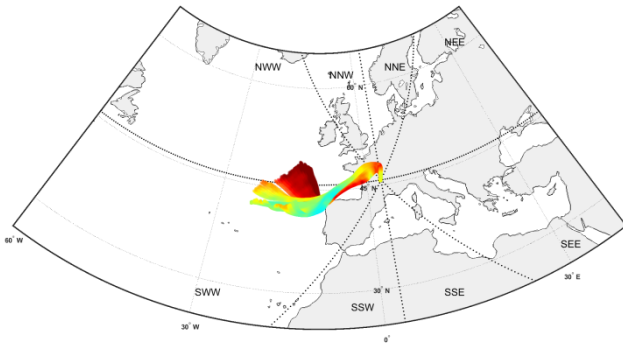
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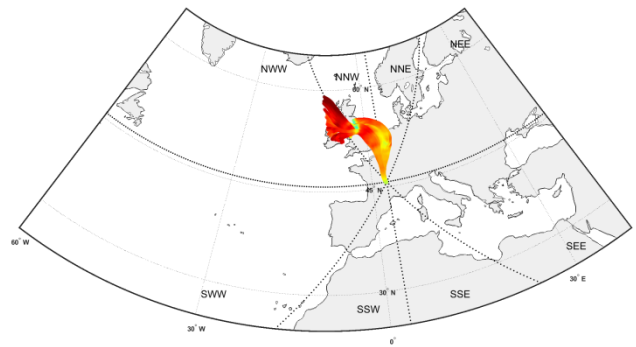
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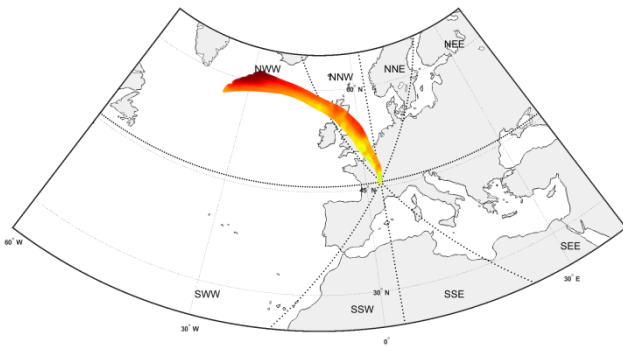
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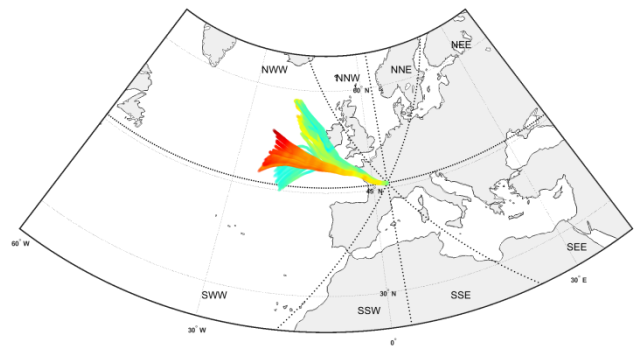
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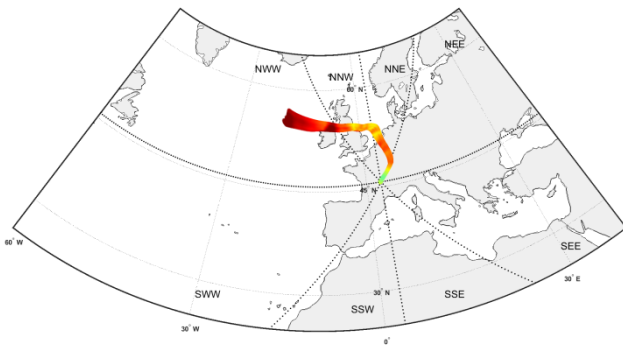
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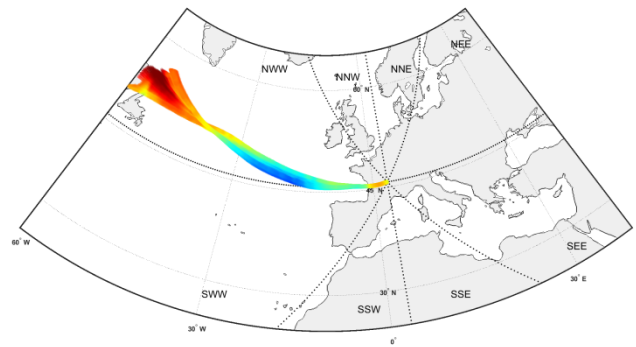
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CAT ECMWF ERA5 - 24 Sep



CAT ECMWF ERA5 - 25 Sep



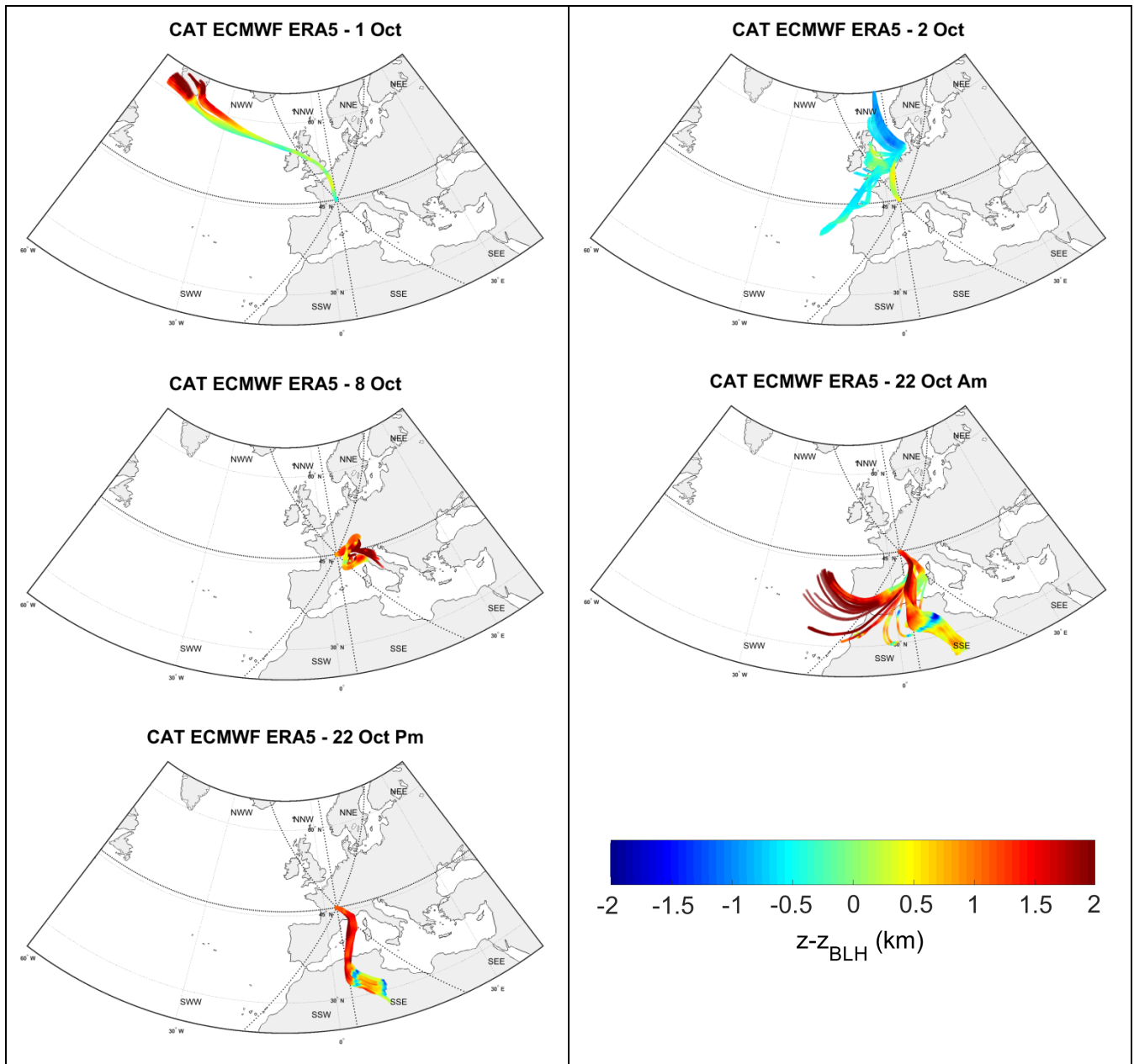


Figure S4. Individual CAT model back trajectories of each of the 13 cloud events reaching PUY. Colors correspond to the air mass height minus the atmospheric boundary layer height (ABLH). Positive values ($> ABLH$, red) indicate the air mass is in the free troposphere. Negative values ($< ABLH$, blue) indicate the air mass is in the boundary layer.

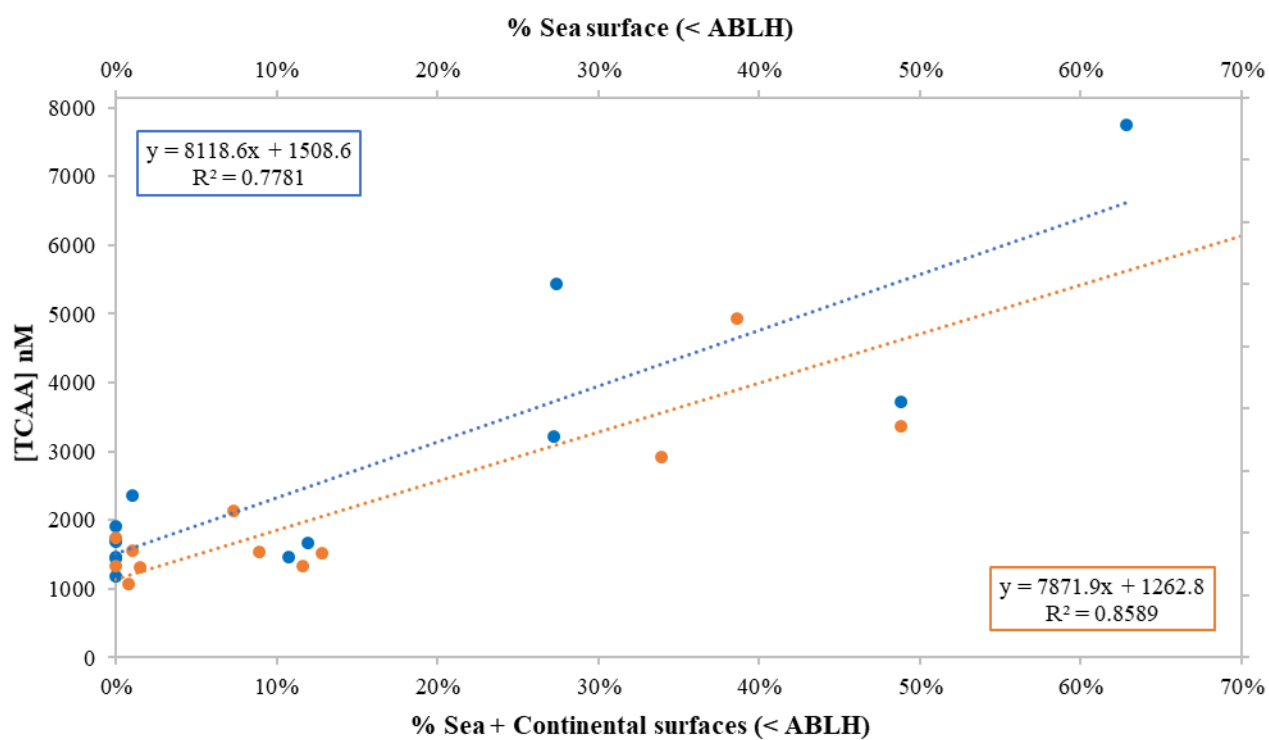


Figure S5. Correlation between total concentration of 18 AAs (TCAA) and the percentage of time spent above: in blue, the Sea surface (< ABLH); and in orange, the Sea plus the Continental surfaces (< ABLH).

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