

Supplementary Materials:

Detection of atmospheric gaseous amines and amides by a high resolution time-of-flight chemical ionization mass spectrometer with protonated ethanol reagent ions

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Table S1 Tentative formula assignment of MS peaks with m/z values less than 163 Th.

ID	Ion formula	Molecular weight	Potential identity
1	$\text{NH}_3\cdot\text{H}^+$	18.0338	
2	$\text{H}_2\text{O}\cdot\text{H}^+$	19.0178	
3	$\text{HCN}\cdot\text{H}^+$	28.0182	Hydrogen cyanide
4	$\text{C}_2\text{H}_4\cdot\text{H}^+$	29.0386	
5	$\text{CH}_3\text{N}\cdot\text{H}^+$	30.0338	
6	$\text{CH}_2\text{O}\cdot\text{H}^+$	31.0178	
7	O_2^+	31.9893	
8	$\text{CH}_5\text{N}\cdot\text{H}^+$	32.0495	Methylamine
9	$\text{CH}_4\text{O}\cdot\text{H}^+$	33.0335	
10	$\text{NH}_3\cdot\text{H}_2\text{O}\cdot\text{H}^+$	36.0444	
11	$(\text{H}_2\text{O})_2\cdot\text{H}^+$	37.0284	
12	$\text{C}_2\text{H}_3\text{N}\cdot\text{H}^+$	42.0338	Acetonitrile
13	$\text{C}_2\text{H}_2\text{O}\cdot\text{H}^+$	43.0178	
14	$\text{C}_2\text{H}_5\text{N}\cdot\text{H}^+$	44.0495	
15	$\text{C}_2\text{H}_4\text{O}\cdot\text{H}^+$	45.0335	
16	NO_2^+	45.9924	
17	$\text{CH}_3\text{NO}\cdot\text{H}^+$	46.0287	Formamide
18	$\text{C}_2\text{H}_7\text{N}\cdot\text{H}^+$	46.0651	$\text{C}_2\text{-Amine}$
19	$\text{C}_2\text{N}_2\cdot\text{H}^+$	53.0134	Cyanogen
20	$(\text{H}_2\text{O})_3\cdot\text{H}^+$	55.0389	
21	$\text{C}_3\text{H}_4\text{O}\cdot\text{H}^+$	57.0335	
22	$\text{C}_4\text{H}_8\cdot\text{H}^+$	57.0699	
23	$\text{C}_3\text{H}_7\text{N}\cdot\text{H}^+$	58.0651	
24	$\text{C}_3\text{H}_6\text{O}\cdot\text{H}^+$	59.0491	
25	$\text{C}_2\text{H}_5\text{NO}\cdot\text{H}^+$	60.0444	$\text{C}_2\text{-Amide}$
26	$\text{C}_3\text{H}_9\text{N}\cdot\text{H}^+$	60.0808	$\text{C}_3\text{-Amine}$
27	$\text{CH}_4\text{N}_2\text{O}\cdot\text{H}^+$	61.0396	
28	$\text{C}_2\text{H}_7\text{NO}\cdot\text{H}^+$	62.0600	2-Aminoethanol
29	$\text{C}_2\text{H}_6\text{O}_2\cdot\text{H}^+$	63.0441	
30	$(\text{C}_2\text{H}_5\text{OH})\cdot\text{NH}_3\cdot\text{H}^+$	64.0757	
31	$(\text{C}_2\text{H}_5\text{OH})\cdot\text{H}_2\text{O}\cdot\text{H}^+$	65.0597	
32	$\text{C}_4\text{H}_5\text{N}\cdot\text{H}^+$	68.0495	Pyrrole
33	$\text{C}_4\text{H}_4\text{O}\cdot\text{H}^+$	69.0335	
34	$\text{C}_5\text{H}_8\cdot\text{H}^+$	69.0699	
35	$\text{C}_3\text{H}_3\text{NO}\cdot\text{H}^+$	70.0287	
36	$\text{C}_4\text{H}_7\text{N}\cdot\text{H}^+$	70.0651	3-Pyrroline
37	$\text{C}_3\text{H}_2\text{O}_2\cdot\text{H}^+$	71.0128	
38	$\text{C}_4\text{H}_6\text{O}\cdot\text{H}^+$	71.0491	
39	$\text{C}_3\text{H}_5\text{NO}\cdot\text{H}^+$	72.0444	
40	$\text{C}_4\text{H}_9\text{N}\cdot\text{H}^+$	72.0808	Pyrrolidine
41	$\text{C}_3\text{H}_4\text{O}_2\cdot\text{H}^+$	73.0284	
42	$\text{C}_4\text{H}_8\text{O}\cdot\text{H}^+$	73.0648	
43	$\text{C}_3\text{H}_7\text{NO}\cdot\text{H}^+$	74.0600	$\text{C}_3\text{-Amide}$
44	$\text{C}_4\text{H}_{11}\text{N}\cdot\text{H}^+$	74.0964	$\text{C}_4\text{-Amine}$
45	$\text{C}_4\text{H}_{10}\text{O}\cdot\text{H}^+$	75.0804	
46	$\text{C}_2\text{H}_5\text{NO}_2\cdot\text{H}^+$	76.0393	Glycine
47	$\text{C}_3\text{H}_8\text{O}_2\cdot\text{H}^+$	77.0597	

48	C ₂ H ₇ NO ₂ ·H ⁺	78.0549	
49	CH ₃ NH ₂ ·(C ₂ H ₅ OH)·H ⁺	78.0913	
50	C ₂ H ₆ OS·H ⁺	79.0212	
51	C ₆ H ₆ ·H ⁺	79.0542	
52	C ₃ H ₈ O·H ₂ O·H ⁺	79.0753	
53	C ₅ H ₅ N·H ⁺	80.0495	Pyridine
54	C ₄ H ₄ N ₂ ·H ⁺	81.0447	Pyrimidine
55	C ₂ H ₆ O ₂ ·H ₂ O·H ⁺	81.0546	
56	C ₆ H ₈ ·H ⁺	81.0699	
57	C ₅ H ₇ N·H ⁺	82.0651	N-Methylpyrrole
58	C ₂ H ₆ O·(H ₂ O) ₂ ·H ⁺	83.0703	
59	C ₄ H ₅ NO·H ⁺	84.0444	
60	C ₄ H ₄ O ₂ ·H ⁺	85.0284	
61	C ₅ H ₈ O·H ⁺	85.0648	
62	C ₄ H ₇ NO·H ⁺	86.0600	
63	C ₄ H ₆ O ₂ ·H ⁺	87.0441	
64	C ₅ H ₁₀ O·H ⁺	87.0804	
65	C ₃ H ₅ NO ₂ ·H ⁺	88.0393	C ₃ -Oxoamide
66	C ₄ H ₉ NO·H ⁺	88.0757	C ₄ -Amide
67	C ₅ H ₁₃ N·H ⁺	88.1121	C ₅ -Amine
68	C ₃ H ₄ O ₃ ·H ⁺	89.0233	
69	C ₄ H ₈ O ₂ ·H ⁺	89.0597	
70	C ₅ H ₁₂ O·H ⁺	89.0961	
71	C ₂ H ₇ N ₃ O·H ⁺	90.0662	
72	C ₄ H ₁₀ O ₂ ·H ⁺	91.0754	
73	CH ₄ NO·(C ₂ H ₅ OH)·H ⁺	92.0706	
74	C ₂ H ₇ N·(C ₂ H ₅ OH)·H ⁺	92.1070	
75	C ₅ H ₅ NO·H ⁺	96.0444	
76	C ₅ H ₄ O ₂ ·H ⁺	97.0284	
77	C ₆ H ₈ O·H ⁺	97.0648	
78	C ₅ H ₇ NO·H ⁺	98.0600	
79	C ₆ H ₁₁ N·H ⁺	98.0964	2,5-Dimethyl-3-pyrroline
80	C ₅ H ₆ O ₂ ·H ⁺	99.0441	
81	C ₆ H ₁₀ O·H ⁺	99.0804	
82	C ₅ H ₉ NO·H ⁺	100.0757	
83	C ₅ H ₈ O ₂ ·H ⁺	101.0597	
84	C ₆ H ₁₂ O·H ⁺	101.0961	
85	C ₄ H ₇ NO ₂ ·H ⁺	102.0550	C ₄ -Oxoamide
86	C ₅ H ₁₁ NO·H ⁺	102.0913	C ₅ -Amide
87	C ₆ H ₁₅ N·H ⁺	102.1277	C ₆ -Amine
88	C ₅ H ₁₀ O ₂ ·H ⁺	103.0754	
89	C ₆ H ₁₄ O·H ⁺	103.1117	
90	C ₄ H ₉ NO ₂ ·H ⁺	104.0706	4-Aminobutyric acid
91	C ₅ H ₁₂ O ₂ ·H ⁺	105.0910	
92	C ₂ H ₆ NO·(C ₂ H ₅ OH)·H ⁺	106.0863	
93	C ₃ H ₉ N·(C ₂ H ₅ OH)·H ⁺	106.1226	
94	C ₆ H ₅ NO·H ⁺	108.0444	
95	C ₈ H ₁₂ ·H ⁺	109.1012	

96	C ₆ H ₇ NO·H ⁺	110.0600	
97	C ₆ H ₆ O ₂ ·H ⁺	111.0441	
98	C ₆ H ₈ O ₂ ·H ⁺	113.0597	
99	C ₆ H ₁₁ NO·H ⁺	114.0913	
100	C ₅ H ₆ O ₃ ·H ⁺	115.0390	
101	C ₆ H ₁₀ O ₂ ·H ⁺	115.0754	
102	C ₆ H ₁₄ N ₂ ·H ⁺	115.1230	2,5-Dimethylpiperazine
103	C ₅ H ₉ NO ₂ ·H ⁺	116.0760	C ₅ -Oxoamide
104	C ₆ H ₁₃ NO·H ⁺	116.1070	C ₆ -Amide
105	C ₅ H ₈ O ₃ ·H ⁺	117.0546	
106	C ₆ H ₁₂ O ₂ ·H ⁺	117.0910	
107	C ₅ H ₁₂ N ₂ O·H ⁺	117.1022	
108	C ₅ H ₁₁ NO ₂ ·H ⁺	118.0863	L-Valine
109	C ₄ H ₁₀ N ₂ O ₂ ·H ⁺	119.0815	
110	C ₆ H ₁₄ O ₂ ·H ⁺	119.1067	
111	C ₅ H ₁₁ OS·H ⁺	120.0570	
112	C ₃ H ₇ NO·(C ₂ H ₅ OH)·H ⁺	120.1019	
113	C ₄ H ₁₂ N·(C ₂ H ₅ OH)·H ⁺	120.1383	
114	C ₈ H ₈ O·H ⁺	121.0648	
115	C ₆ H ₁₄ O·H ₂ O·H ⁺	121.1210	
116	C ₄ H ₁₁ NOS·H ⁺	122.0634	
117	C ₈ H ₁₁ N·H ⁺	122.0964	Phenethylamine
118	C ₄ H ₁₀ O ₂ S·H ⁺	123.0474	
119	C ₈ H ₁₀ O·H ⁺	123.0804	
120	C ₉ H ₁₄ ·H ⁺	123.1168	
121	C ₃ H ₉ NO ₂ S·H ⁺	124.0995	
122	C ₇ H ₈ O ₂ ·H ⁺	125.0597	
123	C ₈ H ₁₂ O·H ⁺	125.0961	
124	C ₆ H ₆ O ₃ ·H ⁺	127.0390	
125	C ₇ H ₁₀ O ₂ ·H ⁺	127.0753	
126	C ₈ H ₁₄ O·H ⁺	127.1117	
127	C ₅ H ₅ NO ₃ ·H ⁺	128.0342	
128	C ₆ H ₉ NO ₂ ·H ⁺	128.0706	
129	C ₇ H ₁₃ NO·H ⁺	128.1070	
130	C ₇ H ₁₂ O ₂ ·H ⁺	129.0910	
131	C ₉ H ₇ N·H ⁺	130.0651	Quinoline
132	C ₆ H ₁₀ O ₃ ·H ⁺	131.0702	
133	C ₇ H ₁₄ O ₂ ·H ⁺	131.1067	
134	C ₆ H ₁₃ NO ₂ ·H ⁺	132.1019	L-Leucine
135	C ₆ H ₁₂ O ₃ ·H ⁺	133.0859	
136	C ₃ H ₅ NO ₂ ·(C ₂ H ₅ OH)·H ⁺	134.0812	
137	C ₄ H ₉ NO·(C ₂ H ₅ OH)·H ⁺	134.1176	
138	C ₅ H ₁₃ N·(C ₂ H ₅ OH)·H ⁺	134.1539	
139	C ₈ H ₆ O ₂ ·H ⁺	135.0441	
140	C ₄ H ₁₀ N ₂ O ₃ ·H ⁺	135.0764	
141	C ₆ H ₁₄ O ₃ ·H ⁺	135.1016	
142	C ₇ H ₅ NS·H ⁺	136.0215	
143	C ₄ H ₉ NO ₄ ·H ⁺	136.0604	

144	C ₅ H ₁₃ NO ₃ ·H ⁺	136.0968	
145	C ₇ H ₈ N ₂ O·H ⁺	137.0709	
146	C ₉ H ₁₂ O·H ⁺	137.0961	
147	C ₆ H ₁₄ O ₂ ·H ₂ O·H ⁺	137.1172	
148	C ₄ H ₁₁ NO ₂ S·H ⁺	138.1039	
149	C ₇ H ₈ O ₃ ·H ⁺	141.0546	
150	C ₈ H ₁₂ O ₂ ·H ⁺	141.0910	
151	C ₉ H ₁₆ O·H ⁺	141.1308	
152	C ₆ H ₇ NO ₃ ·H ⁺	142.0499	
153	C ₈ H ₁₅ NO·H ⁺	142.1226	
154	C ₇ H ₁₀ O ₃ ·H ⁺	143.0703	
155	C ₈ H ₁₄ O ₂ ·H ⁺	143.1067	
156	C ₈ H ₁₈ N ₂ ·H ⁺	143.1542	1-Butylpiperazine
157	C ₅ H ₉ N ₃ O ₂ ·H ⁺	144.0768	
158	C ₇ H ₁₃ NO ₂ ·H ⁺	144.1019	
159	C ₈ H ₁₇ NO·H ⁺	144.1383	
160	C ₆ H ₈ O ₄ ·H ⁺	145.0495	
161	C ₇ H ₁₂ O ₃ ·H ⁺	145.0859	
162	C ₈ H ₁₆ O ₂ ·H ⁺	145.1223	
163	C ₆ H ₁₁ NO ₃ ·H ⁺	146.0811	
164	C ₇ H ₁₅ NO ₂ ·H ⁺	146.1176	7-Aminoheptanoic acid
165	C ₆ H ₁₀ O ₄ ·H ⁺	147.0652	
166	C ₇ H ₁₄ O ₃ ·H ⁺	147.1016	
167	C ₈ H ₁₈ O ₂ ·H ⁺	147.1379	
168	C ₄ H ₇ NO ₂ ·(C ₂ H ₅ OH)·H ⁺	148.0968	
169	C ₅ H ₁₁ NO·(C ₂ H ₅ OH)·H ⁺	148.1332	
170	C ₆ H ₁₅ N·(C ₂ H ₅ OH)·H ⁺	148.1696	
171	C ₅ H ₈ O ₃ S·H ⁺	149.0267	
172	C ₉ H ₈ O ₂ ·H ⁺	149.0597	
173	C ₆ H ₁₂ O ₄ ·H ⁺	149.0808	
174	C ₈ H ₇ NS·H ⁺	150.0372	
175	C ₅ H ₁₁ NO ₄ ·H ⁺	150.0761	
176	C ₅ H ₁₅ N ₃ O ₂ ·H ⁺	150.1237	
177	C ₅ H ₁₄ N ₂ OS·H ⁺	151.0899	
178	C ₁₀ H ₁₄ O·H ⁺	151.1117	
179	C ₇ H ₅ NOS·H ⁺	152.0165	
180	C ₁₀ H ₁₅ O·H ⁺	152.1196	
181	C ₆ H ₁₄ O ₃ ·H ₂ O·H ⁺	153.1121	
182	C ₉ H ₁₄ O ₂ ·H ⁺	155.1067	
183	C ₉ H ₁₈ N ₂ ·H ⁺	155.1543	4-Pyrrolidinopiperidine
184	C ₈ H ₁₂ O ₃ ·H ⁺	157.0859	
185	C ₉ H ₁₆ O ₂ ·H ⁺	157.1223	
186	C ₉ H ₂₀ N ₂ ·H ⁺	157.1699	Triacetonediamine
187	C ₁₁ H ₁₁ N·H ⁺	158.0964	2,8-Dimethylquinoline
188	C ₉ H ₁₉ NO·H ⁺	158.1539	
189	C ₇ H ₁₀ O ₄ ·H ⁺	159.0652	
190	C ₈ H ₁₄ O ₃ ·H ⁺	159.1016	
191	C ₁₀ H ₉ NO·H ⁺	160.0757	

192	C ₁₁ H ₁₃ N·H ⁺	160.1121	2,3,3-Trimethylindolenine
193	C ₈ H ₁₇ NO ₂ ·H ⁺	160.1332	8-Aminooctanoic acid
194	C ₇ H ₁₂ O ₄ ·H ⁺	161.0808	
195	C ₈ H ₁₆ O ₃ ·H ⁺	161.1172	
196	C ₉ H ₂₀ O ₂ ·H ⁺	161.1536	
197	C ₄ H ₅ NO ₃ ·(C ₂ H ₅ OH)·H ⁺	162.0761	
198	C ₅ H ₉ NO ₂ ·(C ₂ H ₅ OH)·H ⁺	162.1125	
199	C ₆ H ₁₃ NO·(C ₂ H ₅ OH)·H ⁺	162.1489	
200	C ₈ H ₁₈ O ₃ ·H ⁺	163.1329	

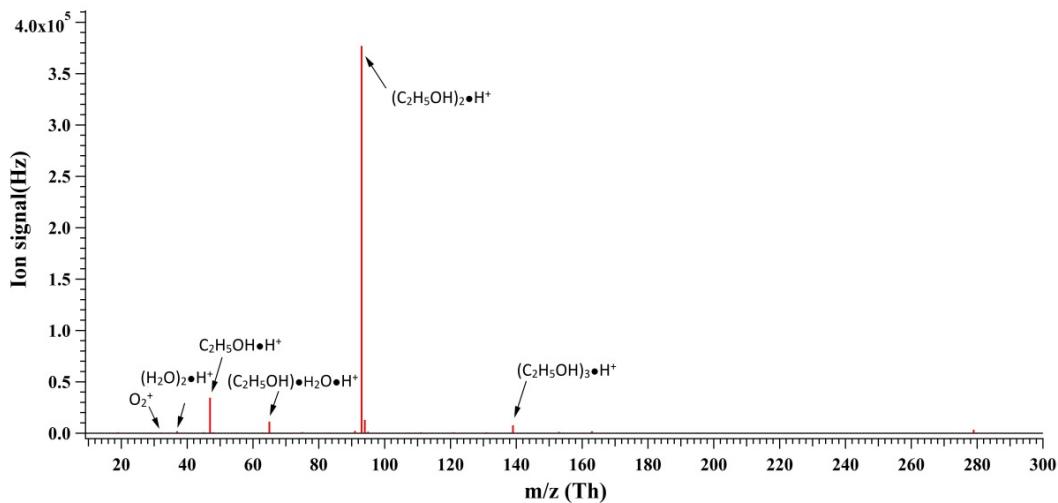


Figure S1. A typical mass spectrum with RH<20%. The dominant reagent ions are protonated ethanol dimer ($(\text{C}_2\text{H}_5\text{OH})_2\cdot\text{H}^+$), monomer ($(\text{C}_2\text{H}_5\text{OH})\cdot\text{H}^+$), and trimer ($(\text{C}_2\text{H}_5\text{OH})_3\cdot\text{H}^+$). The ratio of the clusters of protonated ethanol with water ($\text{C}_2\text{H}_5\text{OH}\cdot\text{H}_2\text{O}\cdot\text{H}^+$) to the sum of $(\text{C}_2\text{H}_5\text{OH})\cdot\text{H}^+$, $(\text{C}_2\text{H}_5\text{OH})_2\cdot\text{H}^+$, and $(\text{C}_2\text{H}_5\text{OH})_3\cdot\text{H}^+$ is ~0.026.

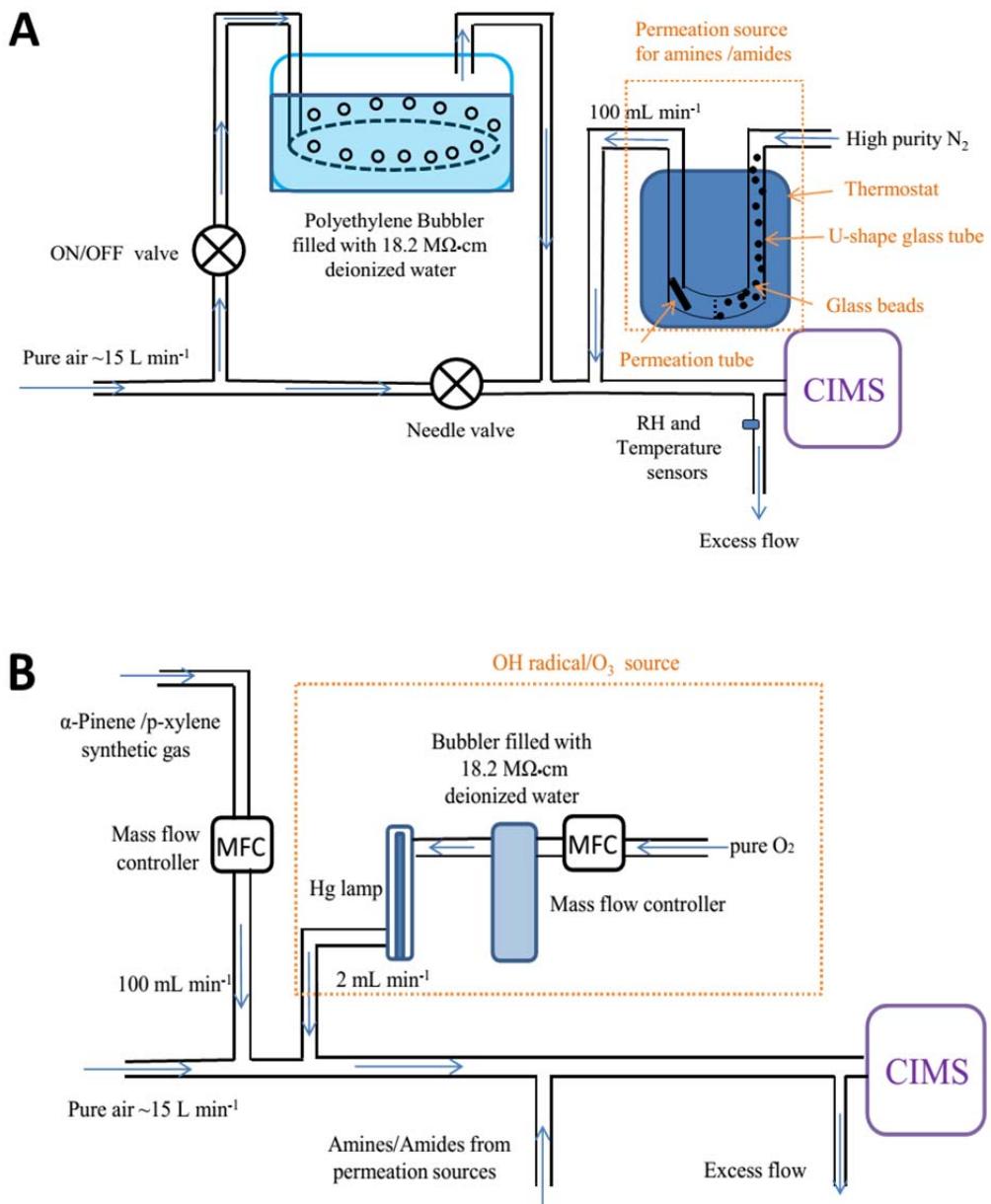


Figure S2. Schematics for laboratory tests of effects of (A) RH and (B) organics. All sampling lines are made of PFA or PTFE material.

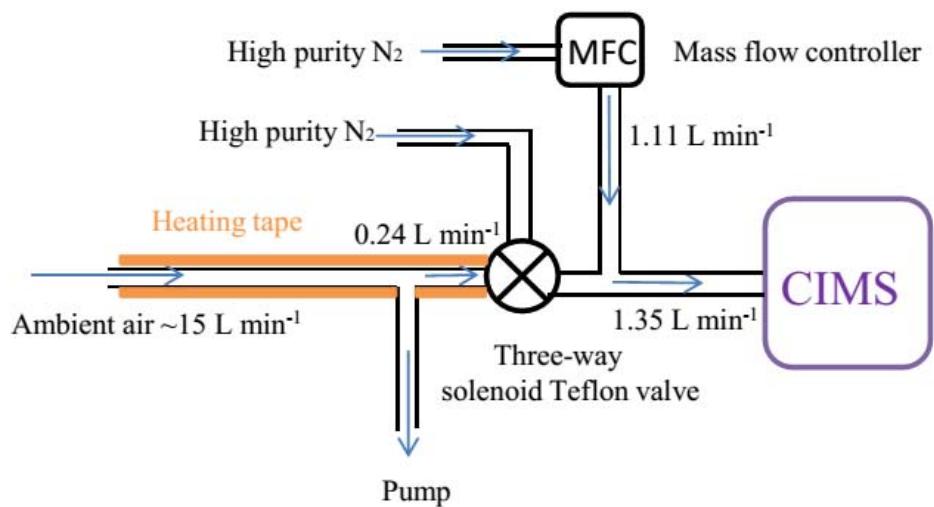


Figure S3. Schematic of CIMS setup during the field measurements.

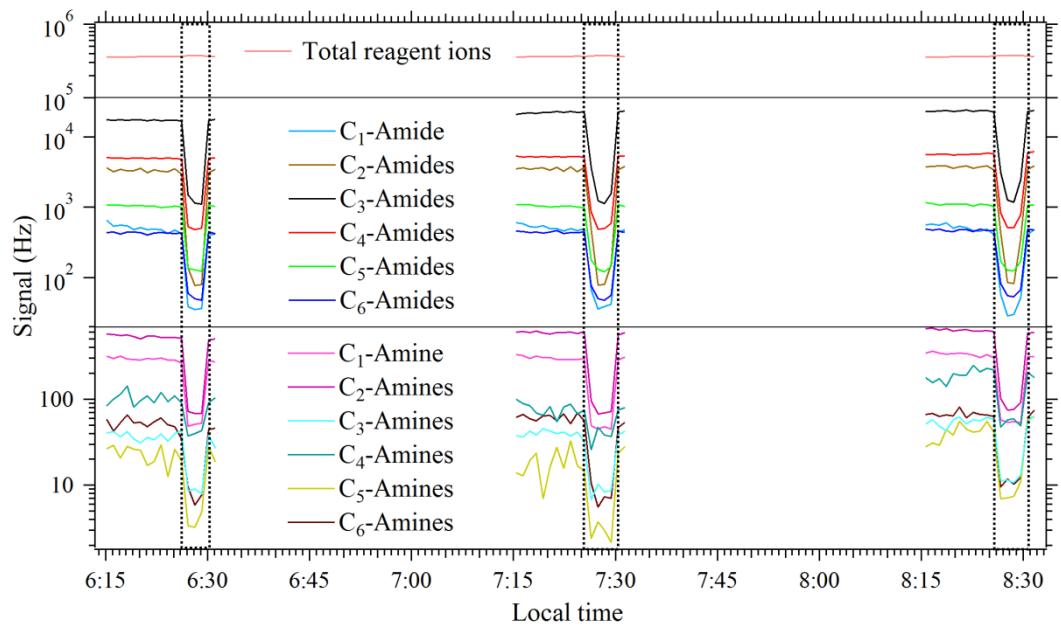


Figure S4. Background check for amines and amides during a 3 h ambient sampling period.

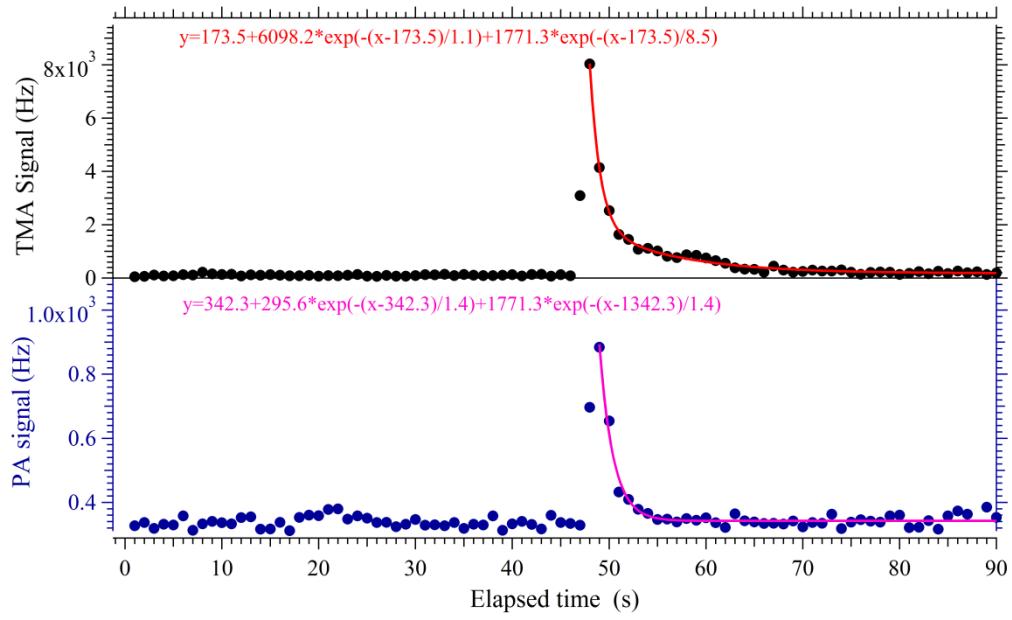


Figure S5. Inlet memory of TMA and PA by inlet spike tests. The red and pink curves are fittings by the sum of two decaying exponentials. The characteristic decaying times of two exponentials, which are displacement of amines and amides inside the inlet by pumping and removing amines and amides adsorbed on the inlet surface, were 1.1 s and 8.5 s for TMA, and 1.4 s and 1.4 s for PA, respectively.

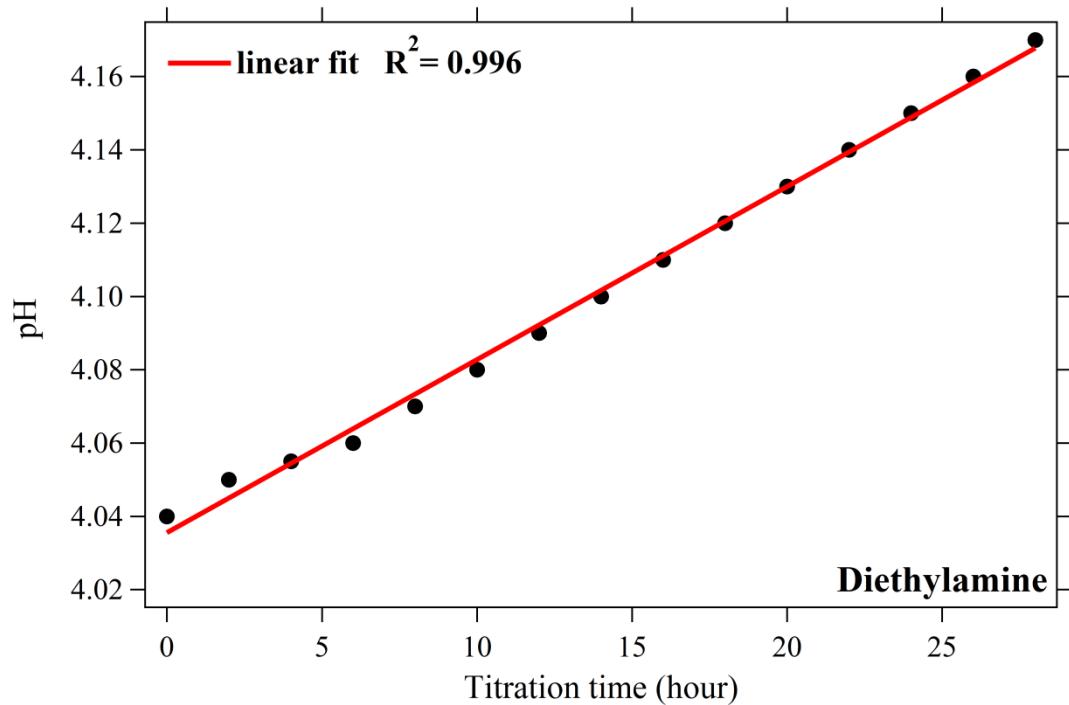


Figure S6. Changes in pH values of HNO_3 solution as titration by diethylamine proceeds.
Note that pH values in this plot are 2-h averages

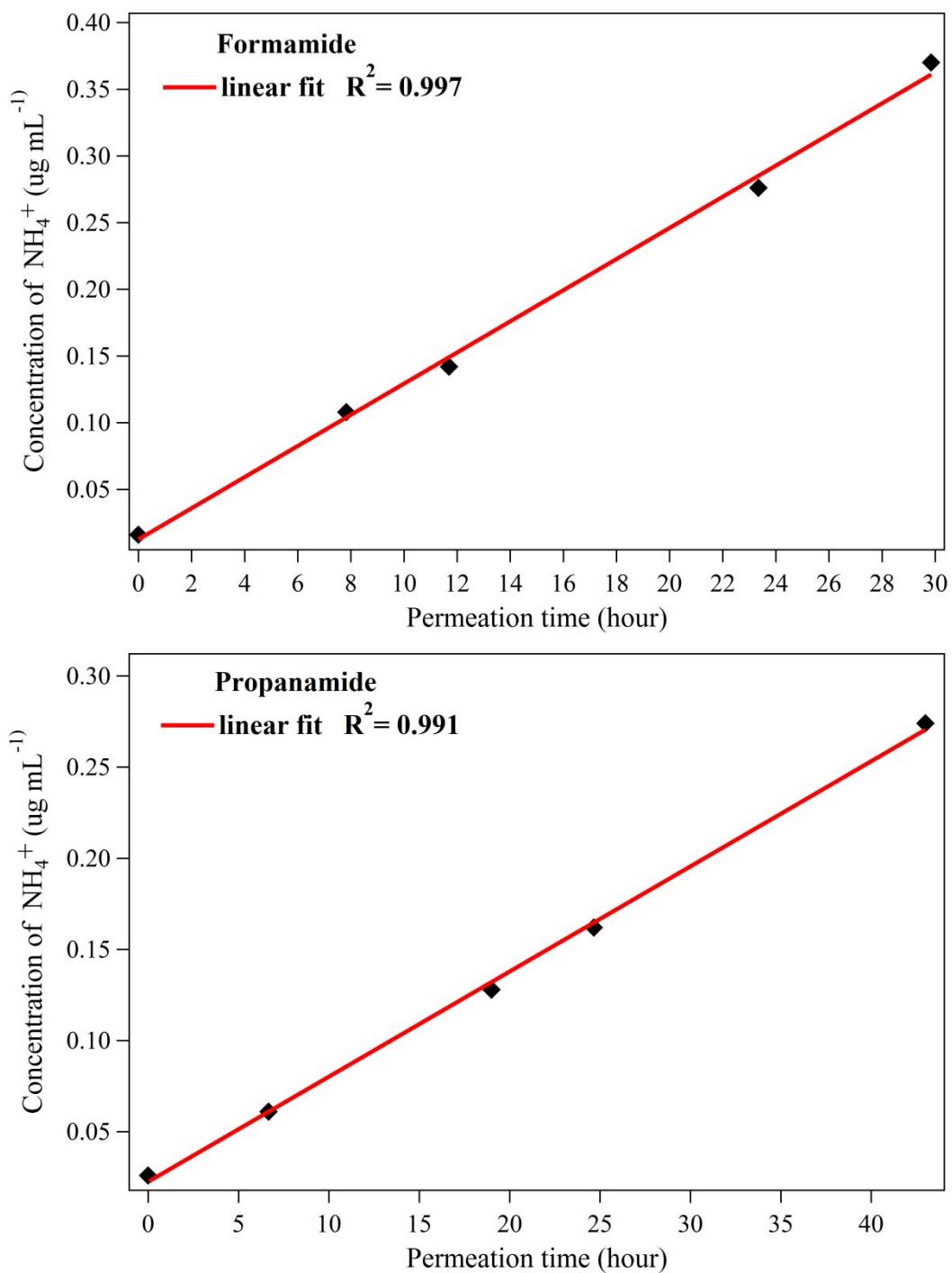
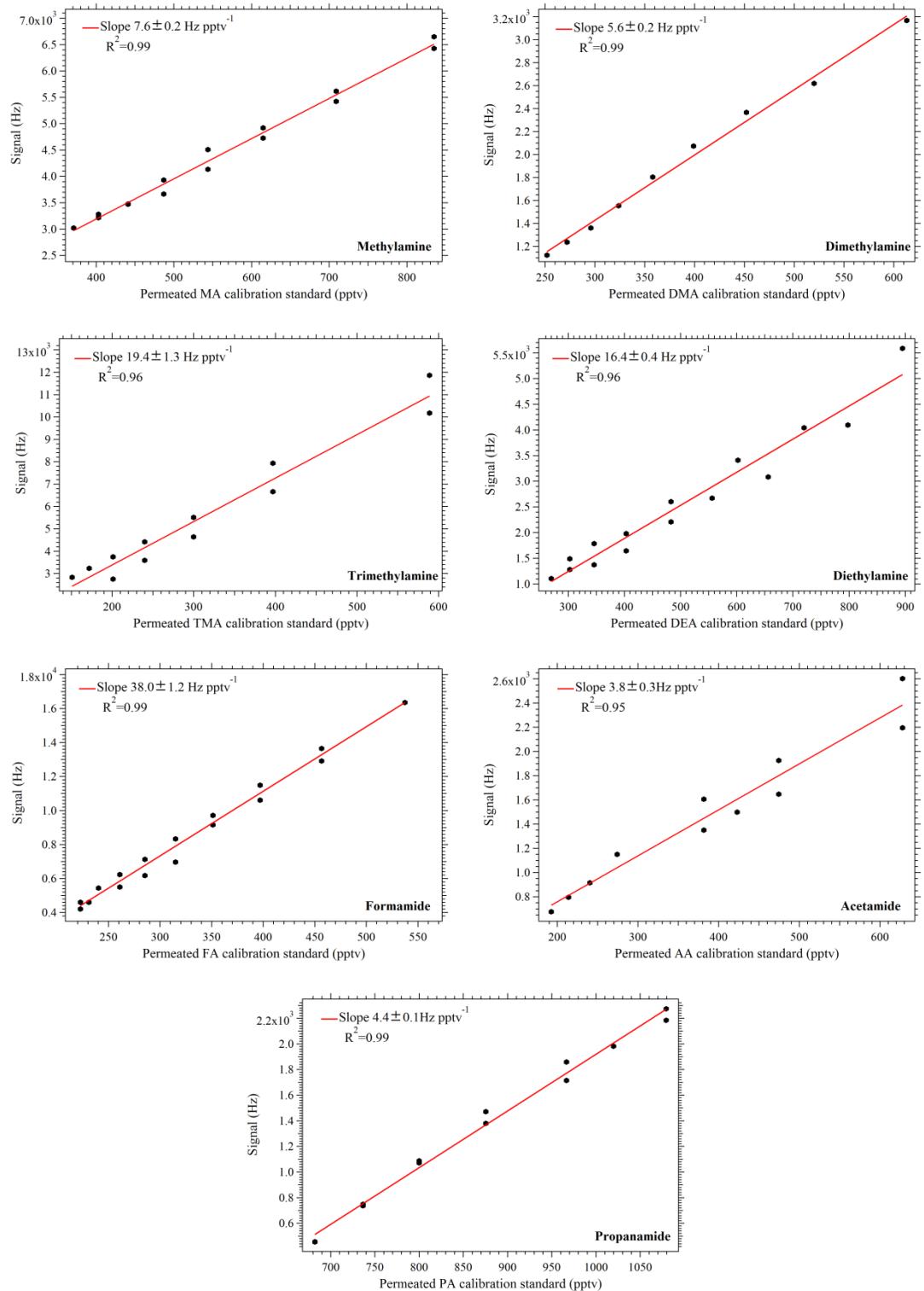


Figure S7. Changes in NH_4^+ concentration as hydrolysis of formamide and propanamide proceeds.



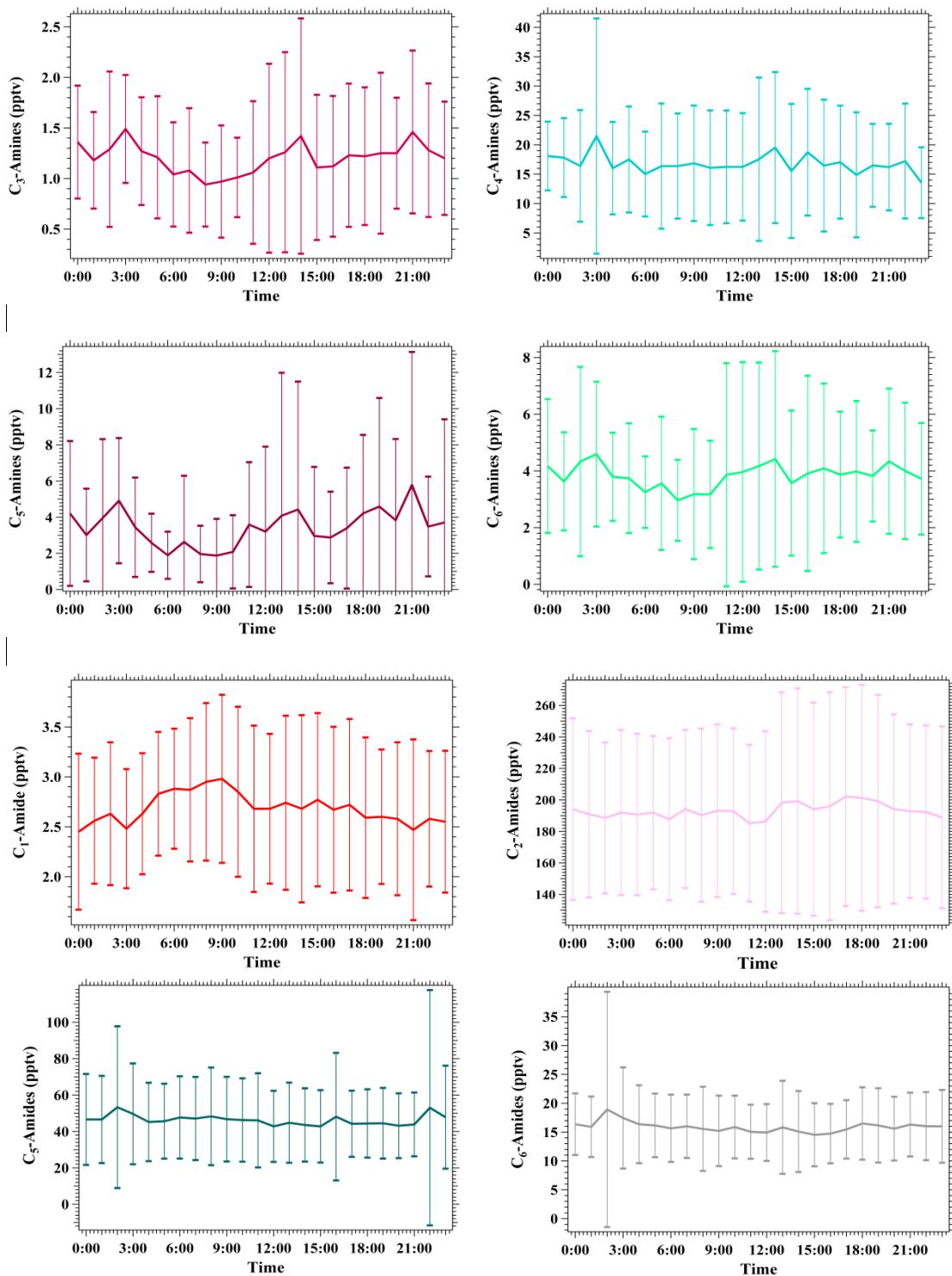


Figure S9. Diurnal variations of amines and amides with less variation.

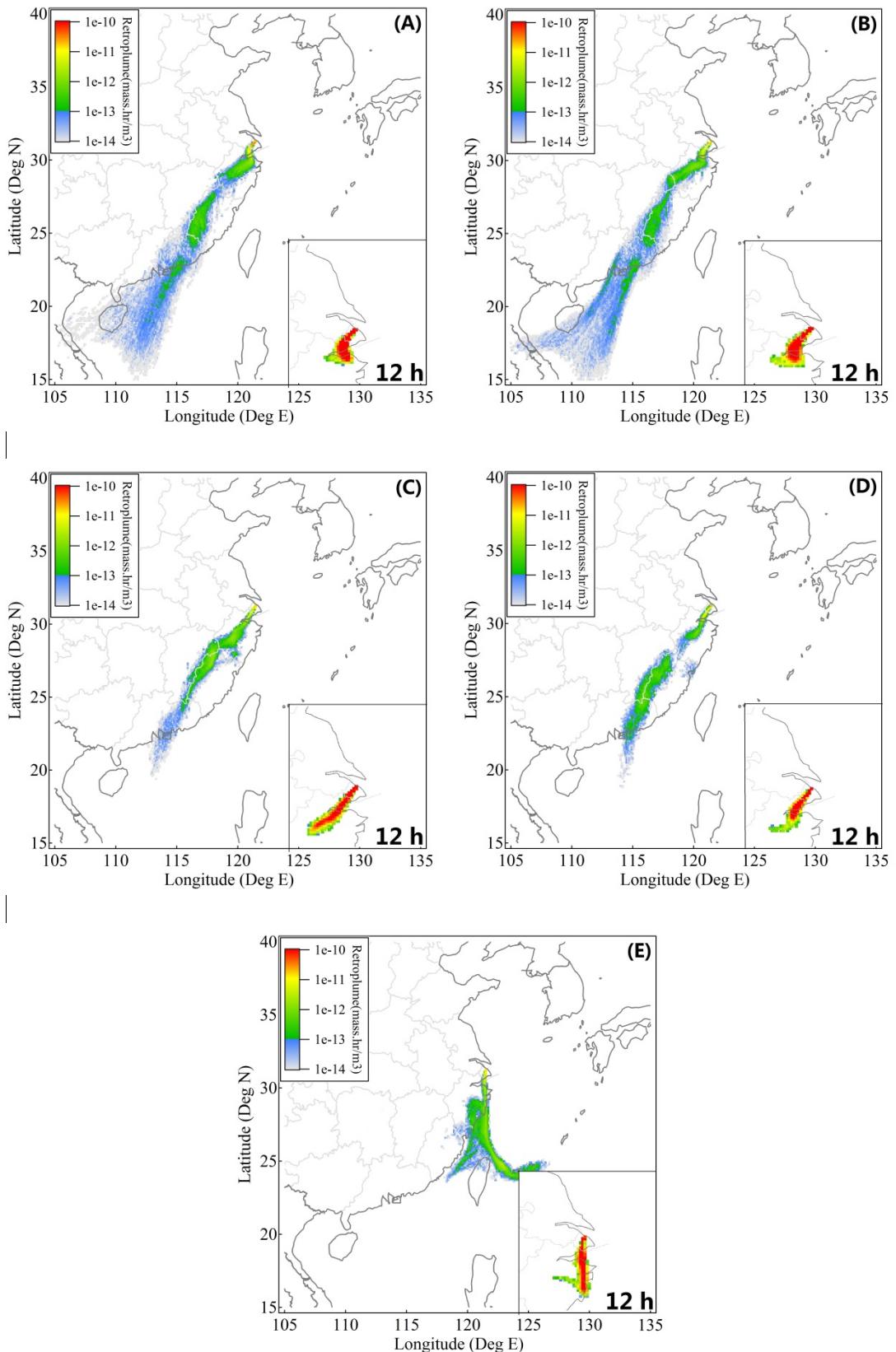


Figure S10. Three-day backward retroplumes (100 m above the ground level) from the sampling location at (A) 07:00, 27 July 2015; (B) 07:00, 28 July 2015; (C) 07:00, 30 July 2015; (D) 07:00, 31 July 2015; and (E) 07:00, 4 August 2015. The embedded boxes show 12h backward trajectories.