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Supplement of

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	$NH_3 \cdot H^+$	18.0338	
2	$H_2O \cdot H^+$	19.0178	
3	$HCN \cdot H^+$	28.0182	Hydrogen cyanide
4	$C_2H_4 \cdot H^+$	29.0386	
5	$CH_3N \cdot H^+$	30.0338	
6	$CH_2O \cdot H^+$	31.0178	
7	O_2^+	31.9893	
8	$CH_5N \cdot H^+$	32.0495	Methylamine
9	$CH_4O \cdot H^+$	33.0335	
10	$NH_3 \cdot H_2O \cdot H^+$	36.0444	
11	$(H_2O)_2 \cdot H^+$	37.0284	
12	$C_2H_3N \cdot H^+$	42.0338	Acetonitrile
13	$C_2H_2O \cdot H^+$	43.0178	
14	$C_2H_5N \cdot H^+$	44.0495	
15	$C_2H_4O \cdot H^+$	45.0335	
16	NO_2^+	45.9924	
17	$CH_3NO \cdot H^+$	46.0287	Formamide
18	$C_2H_7N \cdot H^+$	46.0651	C_2-Amine
19	$C_2N_2 \cdot H^+$	53.0134	Cyanogen
20	$(H_2O)_3 \cdot H^+$	55.0389	
21	$C_3H_4O \cdot H^+$	57.0335	
22	$C_4H_8 \cdot H^+$	57.0699	
23	$C_3H_7N \cdot H^+$	58.0651	
24	$C_3H_6O \cdot H^+$	59.0491	
25	$C_2H_3O_2 \cdot H^+$	60.0206	
26	$C_2H_5NO \cdot H^+$	60.0444	C_2-Amide
27	$C_3H_9N \cdot H^+$	60.0808	C_3-Amine
28	$CH_4N_2O \cdot H^+$	61.0396	
29	$C_2H_7NO \cdot H^+$	62.0600	2-Aminoethanol
30	$C_2H_6O_2 \cdot H^+$	63.0441	
31	$(C_2H_5OH) \cdot NH_3 \cdot H^+$	64.0757	
32	$(C_2H_5OH) \cdot H_2O \cdot H^+$	65.0597	
33	$C_4H_5N \cdot H^+$	68.0495	Pyrrole
34	$C_4H_4O \cdot H^+$	69.0335	
35	$C_5H_8 \cdot H^+$	69.0699	
36	$C_3H_3NO \cdot H^+$	70.0287	
37	$C_4H_7N \cdot H^+$	70.0651	3-Pyrroline
38	$C_3H_2O_2 \cdot H^+$	71.0128	
39	$C_4H_6O \cdot H^+$	71.0491	
40	$C_3H_5NO \cdot H^+$	72.0444	
41	$C_4H_9N \cdot H^+$	72.0808	Pyrrolidine
42	$C_3H_4O_2 \cdot H^+$	73.0284	
43	$C_4H_8O \cdot H^+$	73.0648	
44	$C_3H_7NO \cdot H^+$	74.0600	C_3-Amide

45	$C_4H_{11}N \cdot H^+$	74.0964	C_4-Amine
46	$C_4H_{10}O \cdot H^+$	75.0804	
47	$C_2H_5NO_2 \cdot H^+$	76.0393	Glycine
48	$C_3H_8O_2 \cdot H^+$	77.0597	
49	$C_2H_7NO_2 \cdot H^+$	78.0549	
50	$CH_3NH_2 \cdot (C_2H_5OH) \cdot H^+$	78.0913	
51	$C_2H_6OS \cdot H^+$	79.0212	
52	$C_6H_6 \cdot H^+$	79.0542	
53	$C_3H_8O \cdot H_2O \cdot H^+$	79.0753	
54	$C_5H_5N \cdot H^+$	80.0495	Pyridine
55	$C_4H_4N_2 \cdot H^+$	81.0447	Pyrimidine
56	$C_2H_6O_2 \cdot H_2O \cdot H^+$	81.0546	
57	$C_6H_8 \cdot H^+$	81.0699	
58	$C_5H_7N \cdot H^+$	82.0651	*N*-Methylpyrrole
59	$C_2H_6O \cdot (H_2O)_2 \cdot H^+$	83.0703	
60	$C_4H_5NO \cdot H^+$	84.0444	
61	$C_4H_4O_2 \cdot H^+$	85.0284	
62	$C_5H_8O \cdot H^+$	85.0648	
63	$C_4H_7NO \cdot H^+$	86.0600	
64	$C_4H_6O_2 \cdot H^+$	87.0441	
65	$C_5H_{10}O \cdot H^+$	87.0804	
66	$C_3H_5NO_2 \cdot H^+$	88.0393	C_3-Oxoamide
67	$C_4H_9NO \cdot H^+$	88.0757	C_4-Amide
68	$C_5H_{13}N \cdot H^+$	88.1121	C_5-Amine
69	$C_3H_4O_3 \cdot H^+$	89.0233	
70	$C_4H_8O_2 \cdot H^+$	89.0597	
71	$C_5H_{12}O \cdot H^+$	89.0961	
72	$C_2H_7N_3O \cdot H^+$	90.0662	
73	$C_4H_{10}O_2 \cdot H^+$	91.0754	
74	$CH_4NO \cdot (C_2H_5OH) \cdot H^+$	92.0706	
75	$C_2H_7N \cdot (C_2H_5OH) \cdot H^+$	92.1070	
76	$C_5H_5NO \cdot H^+$	96.0444	
77	$C_5H_4O_2 \cdot H^+$	97.0284	
78	$C_6H_8O \cdot H^+$	97.0648	
79	$C_5H_7NO \cdot H^+$	98.0600	
80	$C_6H_{11}N \cdot H^+$	98.0964	2,5-Dimethyl-3-pyrroline
81	$C_5H_6O_2 \cdot H^+$	99.0441	
82	$C_6H_{10}O \cdot H^+$	99.0804	
83	$C_5H_9NO \cdot H^+$	100.0757	
84	$C_5H_8O_2 \cdot H^+$	101.0597	
85	$C_6H_{12}O \cdot H^+$	101.0961	
86	$C_4H_7NO_2 \cdot H^+$	102.0550	C_4-Oxoamide
87	$C_5H_{11}NO \cdot H^+$	102.0913	C_5-Amide
88	$C_6H_{15}N \cdot H^+$	102.1277	C_6-Amine
89	$C_5H_{10}O_2 \cdot H^+$	103.0754	
90	$C_6H_{14}O \cdot H^+$	103.1117	
91	$C_4H_9NO_2 \cdot H^+$	104.0706	4-Aminobutyric acid
92	$C_5H_{12}O_2 \cdot H^+$	105.0910	

93	$C_2H_6NO \cdot (C_2H_5OH) \cdot H^+$	106.0863	
94	$C_3H_9N \cdot (C_2H_5OH) \cdot H^+$	106.1226	
95	$C_6H_5NO \cdot H^+$	108.0444	
96	$C_8H_{12} \cdot H^+$	109.1012	
97	$C_6H_7NO \cdot H^+$	110.0600	
98	$C_6H_6O_2 \cdot H^+$	111.0441	
99	$C_6H_8O_2 \cdot H^+$	113.0597	
100	$C_6H_{11}NO \cdot H^+$	114.0913	
101	$C_5H_6O_3 \cdot H^+$	115.0390	
102	$C_6H_{10}O_2 \cdot H^+$	115.0754	
103	$C_6H_{14}N_2 \cdot H^+$	115.1230	2,5-Dimethylpiperazine
104	$C_4H_5NOS \cdot H^+$	116.0165	
105	$C_5H_9NO_2 \cdot H^+$	116.0760	C_5-Oxoamide
106	$C_6H_{13}NO \cdot H^+$	116.1070	C_6-Amide
107	$C_5H_8O_3 \cdot H^+$	117.0546	
108	$C_6H_{12}O_2 \cdot H^+$	117.0910	
109	$C_5H_{12}N_2O \cdot H^+$	117.1022	
110	$C_5H_{11}NO_2 \cdot H^+$	118.0863	L-Valine
111	$C_4H_{10}N_2O_2 \cdot H^+$	119.0815	
112	$C_6H_{14}O_2 \cdot H^+$	119.1067	
113	$C_5H_{11}OS \cdot H^+$	120.0570	
114	$C_3H_7NO \cdot (C_2H_5OH) \cdot H^+$	120.1019	
115	$C_4H_{12}N \cdot (C_2H_5OH) \cdot H^+$	120.1383	
116	$C_8H_8O \cdot H^+$	121.0648	
117	$C_6H_{14}O \cdot H_2O \cdot H^+$	121.1210	
118	$C_4H_{11}NOS \cdot H^+$	122.0634	
119	$C_8H_{11}N \cdot H^+$	122.0964	Phenethylamine
120	$C_4H_{10}O_2S \cdot H^+$	123.0474	
121	$C_8H_{10}O \cdot H^+$	123.0804	
122	$C_9H_{14} \cdot H^+$	123.1168	
123	$C_3H_9NO_2S \cdot H^+$	124.0995	
124	$C_7H_8O_2 \cdot H^+$	125.0597	
125	$C_8H_{12}O \cdot H^+$	125.0961	
126	$C_6H_6O_3 \cdot H^+$	127.0390	
127	$C_7H_{10}O_2 \cdot H^+$	127.0753	
128	$C_8H_{14}O \cdot H^+$	127.1117	
129	$C_5H_5NO_3 \cdot H^+$	128.0342	
130	$C_6H_9NO_2 \cdot H^+$	128.0706	
131	$C_7H_{13}NO \cdot H^+$	128.1070	
132	$C_7H_{12}O_2 \cdot H^+$	129.0910	
133	$C_9H_7N \cdot H^+$	130.0651	Quinoline
134	$C_6H_{10}O_3 \cdot H^+$	131.0702	
135	$C_7H_{14}O_2 \cdot H^+$	131.1067	
136	$C_6H_{13}NO_2 \cdot H^+$	132.1019	L-Leucine
137	$C_6H_{12}O_3 \cdot H^+$	133.0859	
138	$C_3H_5NO_2 \cdot (C_2H_5OH) \cdot H^+$	134.0812	
139	$C_4H_9NO \cdot (C_2H_5OH) \cdot H^+$	134.1176	
140	$C_5H_{13}N \cdot (C_2H_5OH) \cdot H^+$	134.1539	

141	$C_8H_6O_2 \cdot H^+$	135.0441	
142	$C_4H_{10}N_2O_3 \cdot H^+$	135.0764	
143	$C_6H_{14}O_3 \cdot H^+$	135.1016	
144	$C_7H_5NS \cdot H^+$	136.0215	
145	$C_4H_9NO_4 \cdot H^+$	136.0604	
146	$C_5H_{13}NO_3 \cdot H^+$	136.0968	
147	$C_7H_8N_2O \cdot H^+$	137.0709	
148	$C_9H_{12}O \cdot H^+$	137.0961	
149	$C_6H_{14}O_2 \cdot H_2O \cdot H^+$	137.1172	
150	$C_4H_{11}NO_2S \cdot H^+$	138.1039	
151	$C_7H_8O_3 \cdot H^+$	141.0546	
152	$C_8H_{12}O_2 \cdot H^+$	141.0910	
153	$C_9H_{16}O \cdot H^+$	141.1308	
154	$C_6H_7NO_3 \cdot H^+$	142.0499	
155	$C_8H_{15}NO \cdot H^+$	142.1226	
156	$C_7H_{10}O_3 \cdot H^+$	143.0703	
157	$C_8H_{14}O_2 \cdot H^+$	143.1067	
158	$C_8H_{18}N_2 \cdot H^+$	143.1542	1-Butylpiperazine
159	$C_5H_9N_3O_2 \cdot H^+$	144.0768	
160	$C_7H_{13}NO_2 \cdot H^+$	144.1019	
161	$C_8H_{17}NO \cdot H^+$	144.1383	
162	$C_6H_8O_4 \cdot H^+$	145.0495	
163	$C_7H_{12}O_3 \cdot H^+$	145.0859	
164	$C_8H_{16}O_2 \cdot H^+$	145.1223	
165	$C_6H_{11}NO_3 \cdot H^+$	146.0811	
166	$C_7H_{15}NO_2 \cdot H^+$	146.1176	7-Aminoheptanoic acid
167	$C_6H_{10}O_4 \cdot H^+$	147.0652	
168	$C_7H_{14}O_3 \cdot H^+$	147.1016	
169	$C_8H_{18}O_2 \cdot H^+$	147.1379	
170	$C_4H_7NO_2 \cdot (C_2H_5OH) \cdot H^+$	148.0968	
171	$C_5H_{11}NO \cdot (C_2H_5OH) \cdot H^+$	148.1332	
172	$C_6H_{15}N \cdot (C_2H_5OH) \cdot H^+$	148.1696	
173	$C_5H_8O_3S \cdot H^+$	149.0267	
174	$C_9H_8O_2 \cdot H^+$	149.0597	
175	$C_6H_{12}O_4 \cdot H^+$	149.0808	
176	$C_8H_7NS \cdot H^+$	150.0372	
177	$C_5H_{11}NO_4 \cdot H^+$	150.0761	
178	$C_5H_{15}N_3O_2 \cdot H^+$	150.1237	
179	$C_5H_{14}N_2OS \cdot H^+$	151.0899	
180	$C_{10}H_{14}O \cdot H^+$	151.1117	
181	$C_7H_5NOS \cdot H^+$	152.0165	
182	$C_{10}H_{15}O \cdot H^+$	152.1196	
183	$C_6H_{14}O_3 \cdot H_2O \cdot H^+$	153.1121	
184	$C_9H_{14}O_2 \cdot H^+$	155.1067	
185	$C_9H_{18}N_2 \cdot H^+$	155.1543	4-Pyrrolidinopiperidine
186	$C_8H_{12}O_3 \cdot H^+$	157.0859	
187	$C_9H_{16}O_2 \cdot H^+$	157.1223	
188	$C_9H_{20}N_2 \cdot H^+$	157.1699	Triacetonediamine

189	$C_{11}H_{11}N \cdot H^+$	158.0964	2,8-Dimethylquinoline
190	$C_9H_{19}NO \cdot H^+$	158.1539	
191	$C_7H_{10}O_4 \cdot H^+$	159.0652	
192	$C_8H_{14}O_3 \cdot H^+$	159.1016	
193	$C_{10}H_9NO \cdot H^+$	160.0757	
194	$C_{11}H_{13}N \cdot H^+$	160.1121	2,3,3-Trimethylindolenine
195	$C_8H_{17}NO_2 \cdot H^+$	160.1332	8-Aminooctanoic acid
196	$C_7H_{12}O_4 \cdot H^+$	161.0808	
197	$C_8H_{16}O_3 \cdot H^+$	161.1172	
198	$C_9H_{20}O_2 \cdot H^+$	161.1536	
199	$C_4H_5NO_3 \cdot (C_2H_5OH) \cdot H^+$	162.0761	
200	$C_5H_9NO_2 \cdot (C_2H_5OH) \cdot H^+$	162.1125	
201	$C_6H_{13}NO \cdot (C_2H_5OH) \cdot H^+$	162.1489	
202	$C_8H_{18}O_3 \cdot H^+$	163.1329	

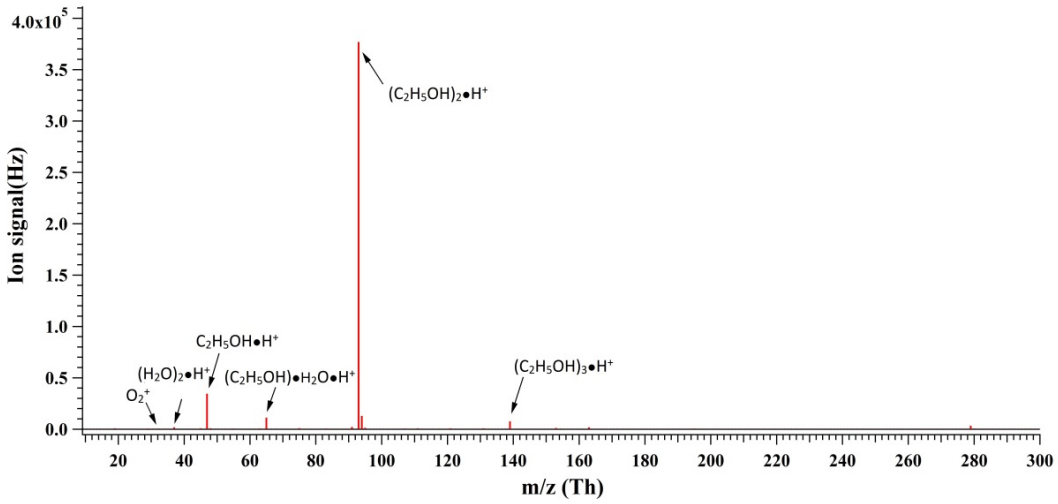

Figure S1. A typical mass spectrum with RH＜20%. The dominant reagent ions are protonated ethanol dimer ($(C_2H_5OH)_2 \cdot H^+$), monomer ($(C_2H_5OH) \cdot H^+$), and trimer ($(C_2H_5OH)_3 \cdot H^+$). The ratio of the clusters of protonated ethanol with water ($C_2H_5OH \cdot H_2O \cdot H^+$) to the sum of $(C_2H_5OH) \cdot H^+$, $(C_2H_5OH)_2 \cdot H^+$, and $(C_2H_5OH)_3 \cdot H^+$ is ~0.026.

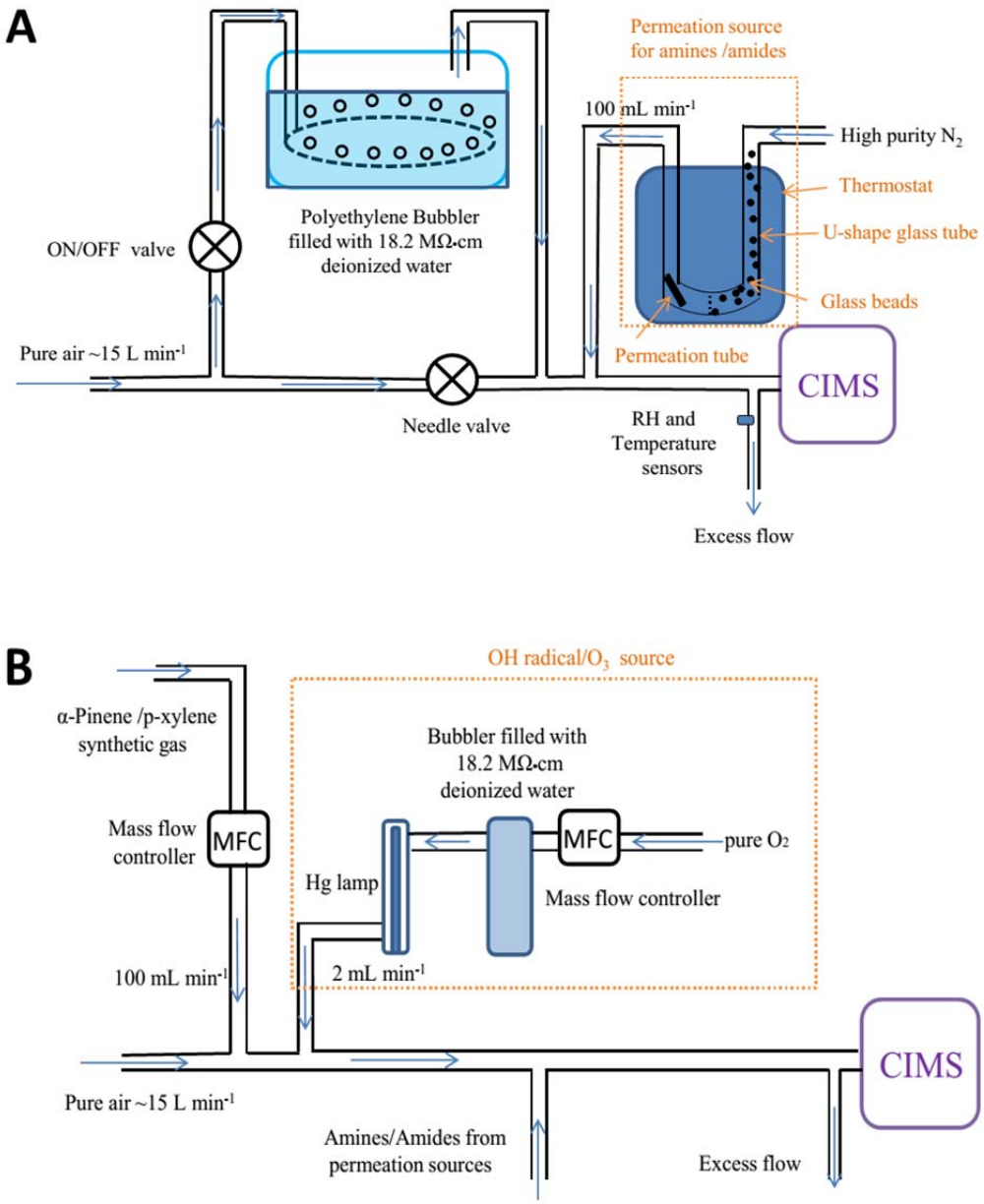

Figure S2. Schematics for laboratory tests of effects of (**A**) RH and (**B**) organics. All sampling lines are made of PFA or PTFE material.

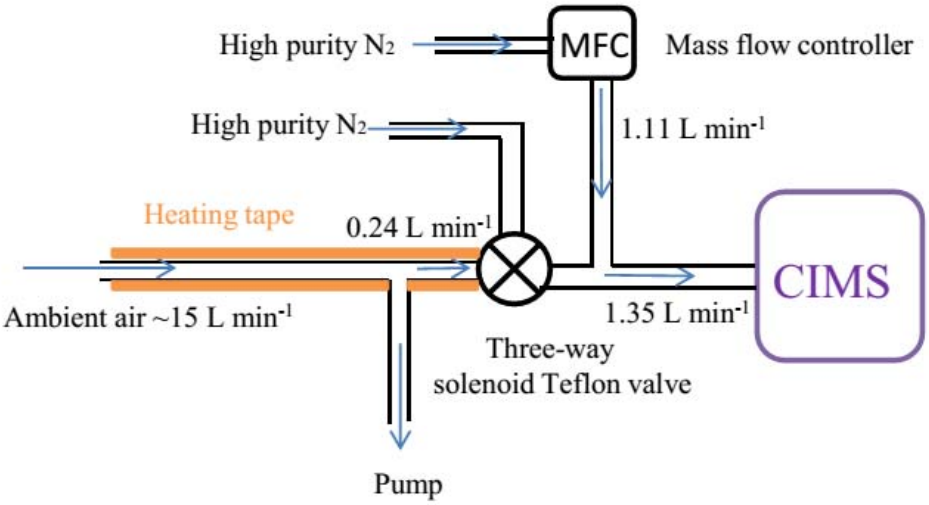

Figure S3. Schematic of CIMS setup during the field measurements.

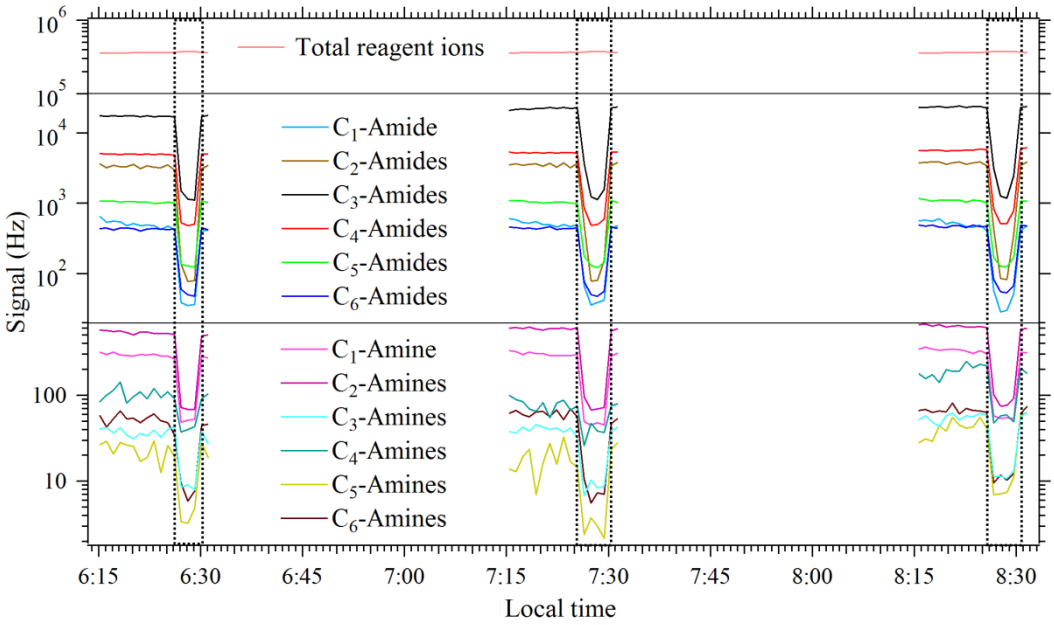

Figure S4. Background check for amines and amides during a 3 h ambient sampling period.

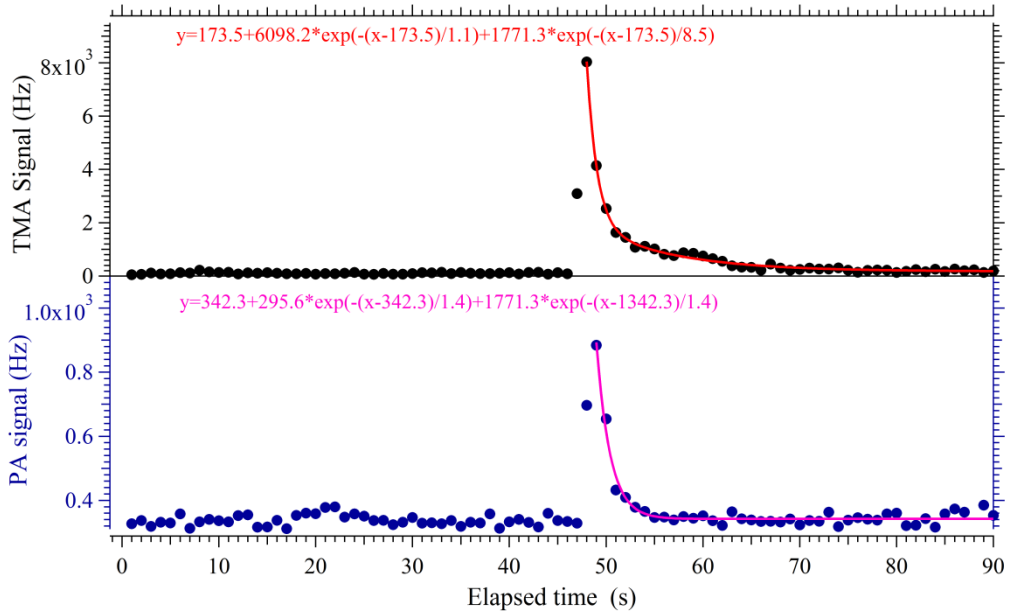

Figure S5. Inlet memory of TMA and PA by inlet spike tests. The red and pink curves are fittings by the sum of two decaying exponentials. The characteristic decaying times of two exponentials, which are displacement of amines and amides inside the inlet by pumping and removing amines and amides adsorbed 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.

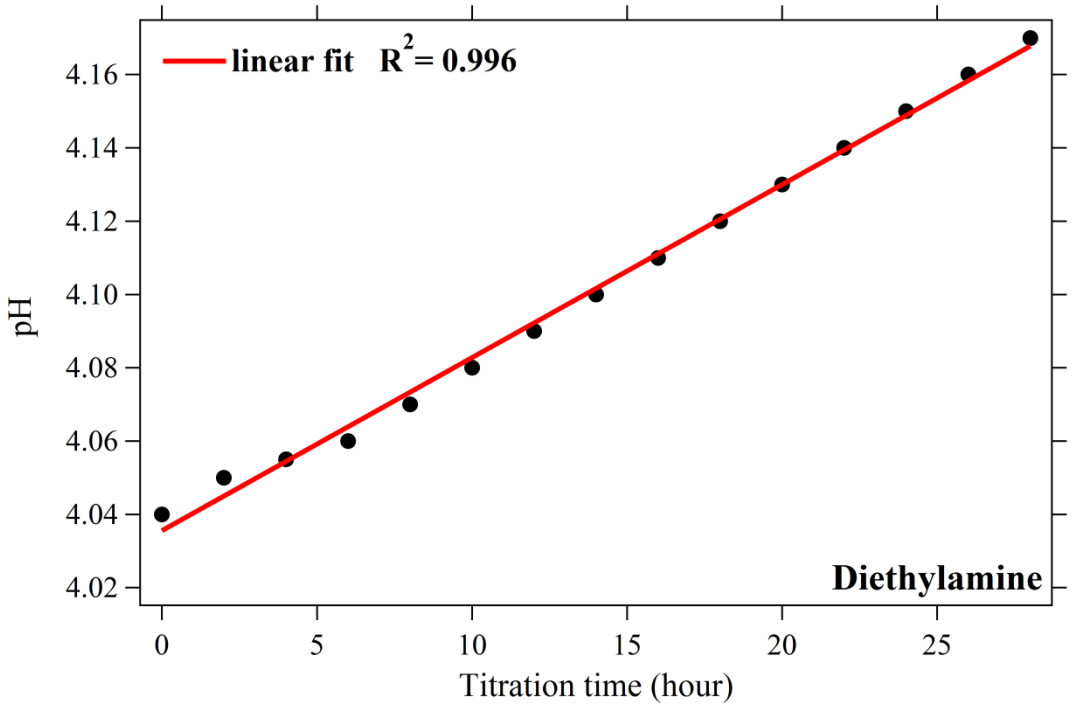

Figure S6. Changes in pH values of HNO_3 solution as titration by diethylamine proceeds. Note that pH values in this plot are 2-h averages

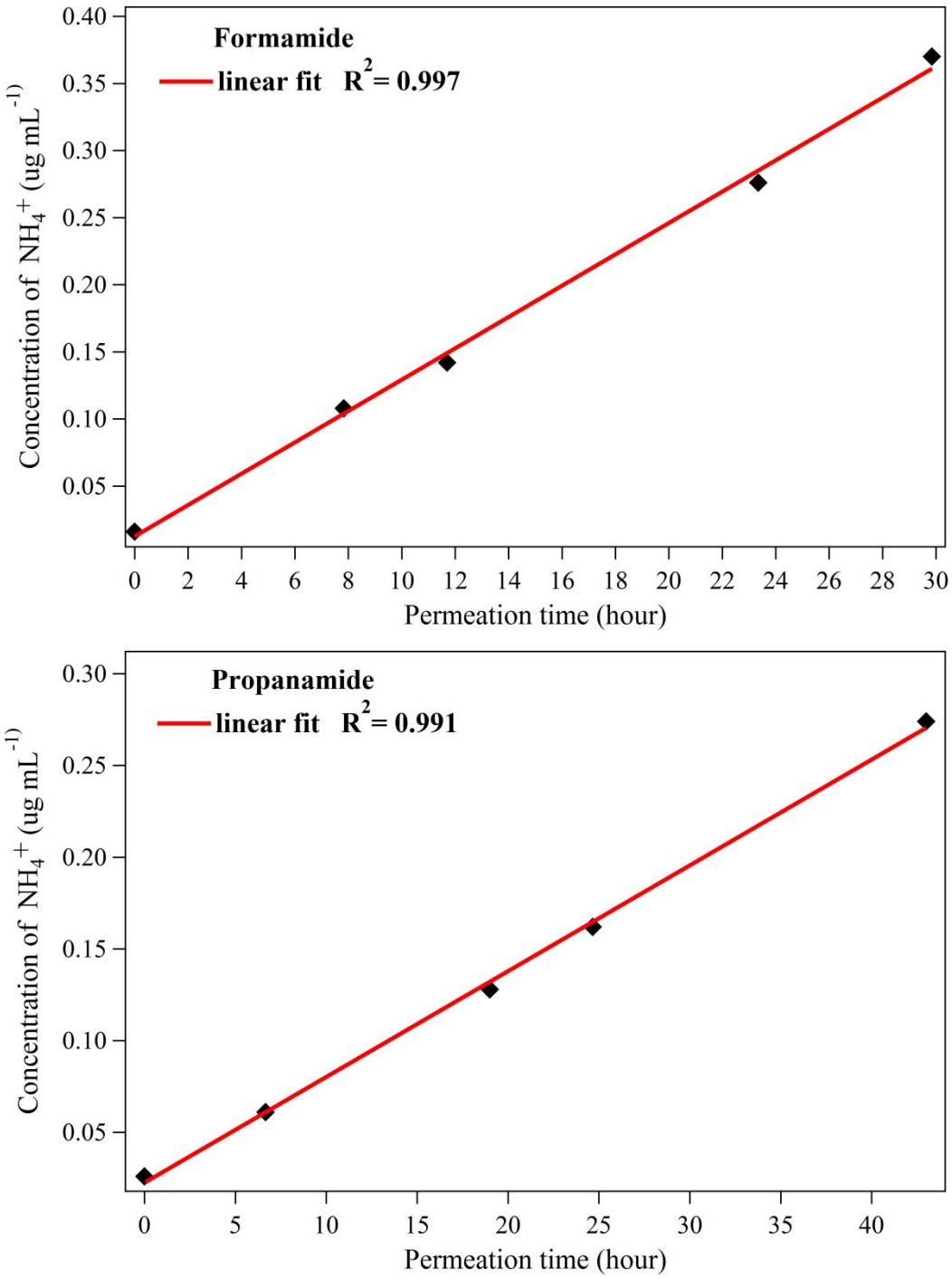

Figure S7. Changes in NH_4^+ concentration as hydrolysis of formamide and propanamide proceeds.

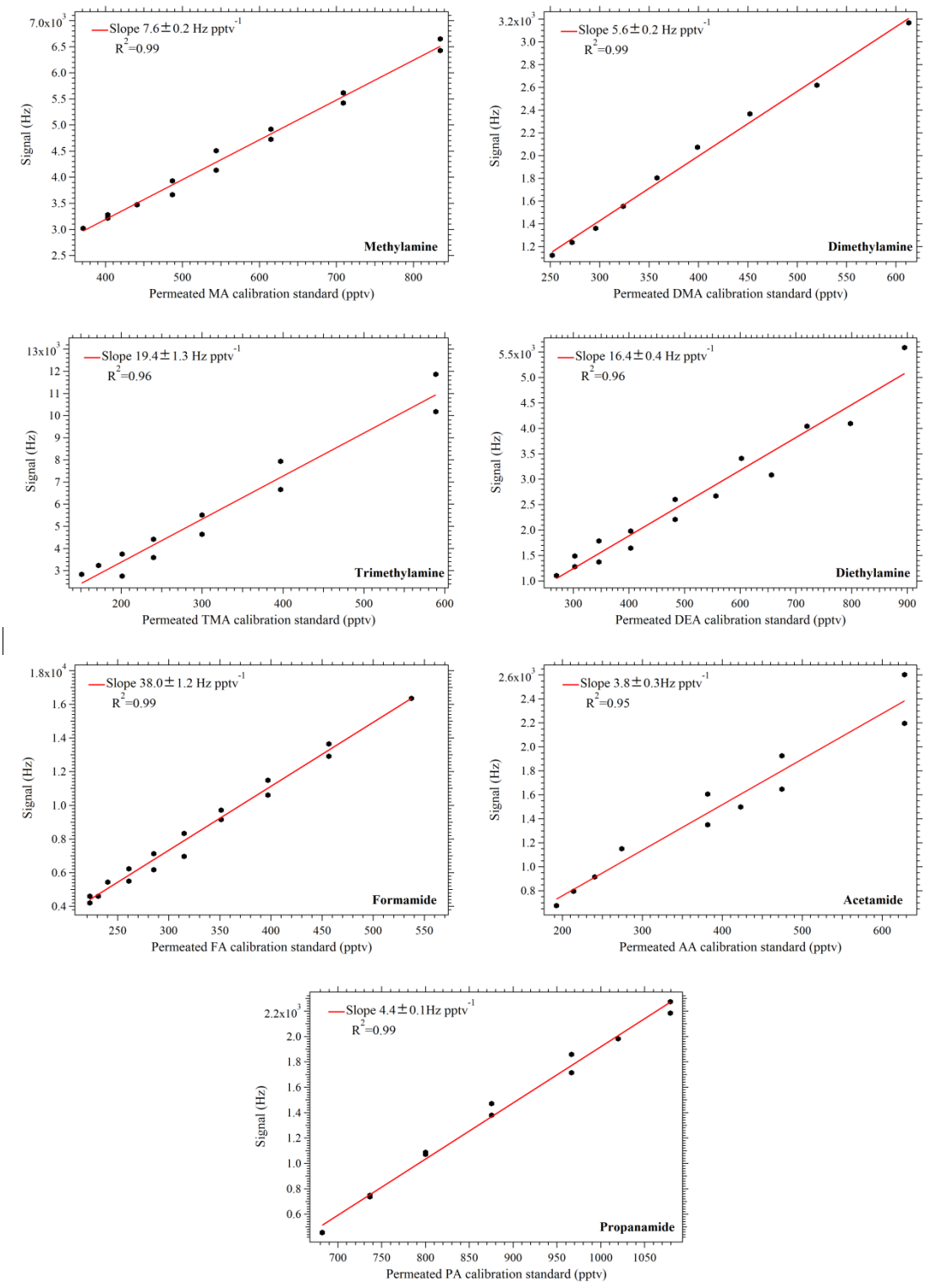

Figure S8. Calibration curves of C_1- to C_4-amines (MA, DMA, TMA, and DEA) and C_1- to C_3-amides (FA, AA, and PA). The red solid lines are linear fittings to guide the eye and the slopes are sensitivities for detection.

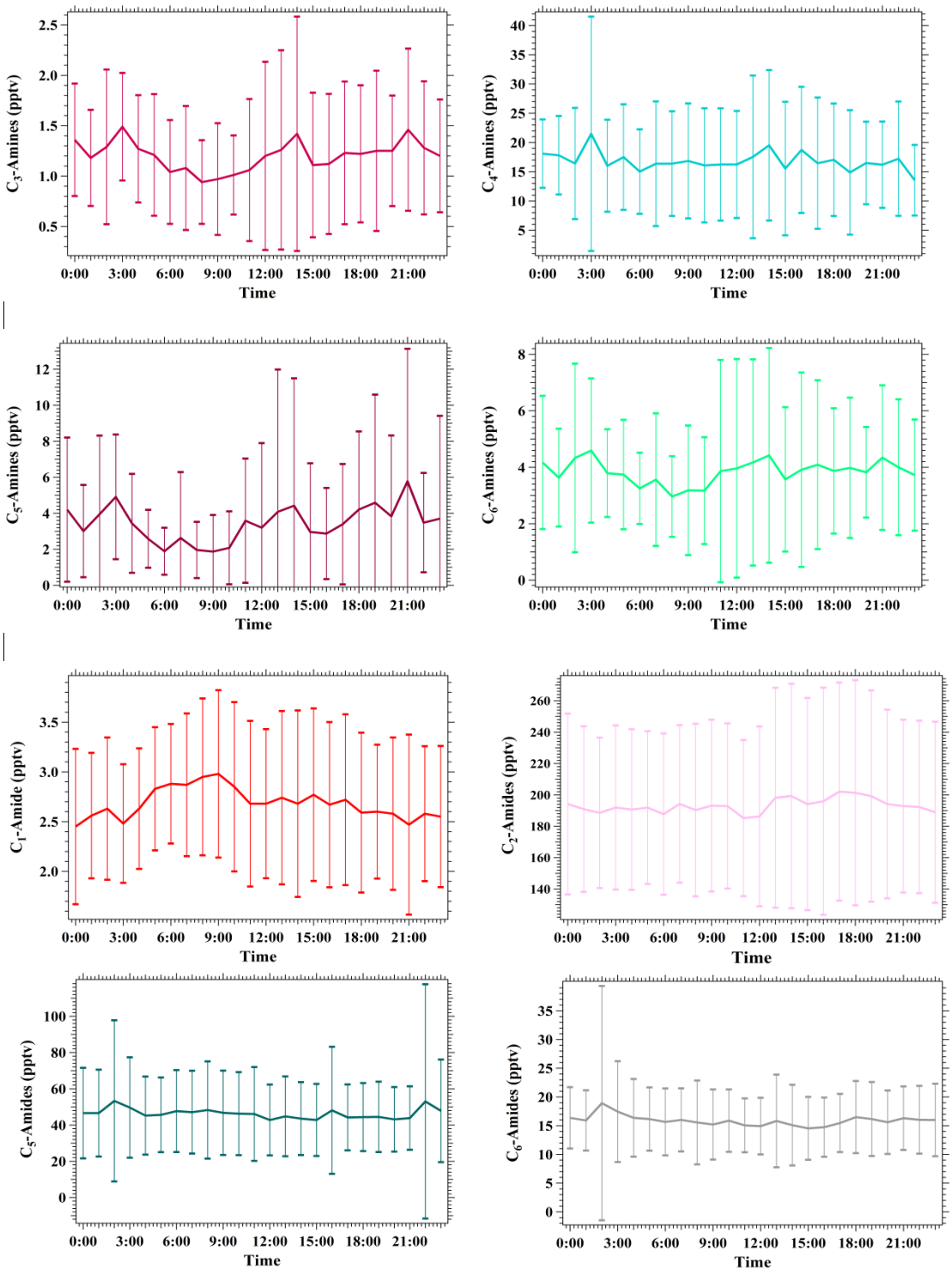

Figure S9. Diurnal variations of amines and amides with less variations.

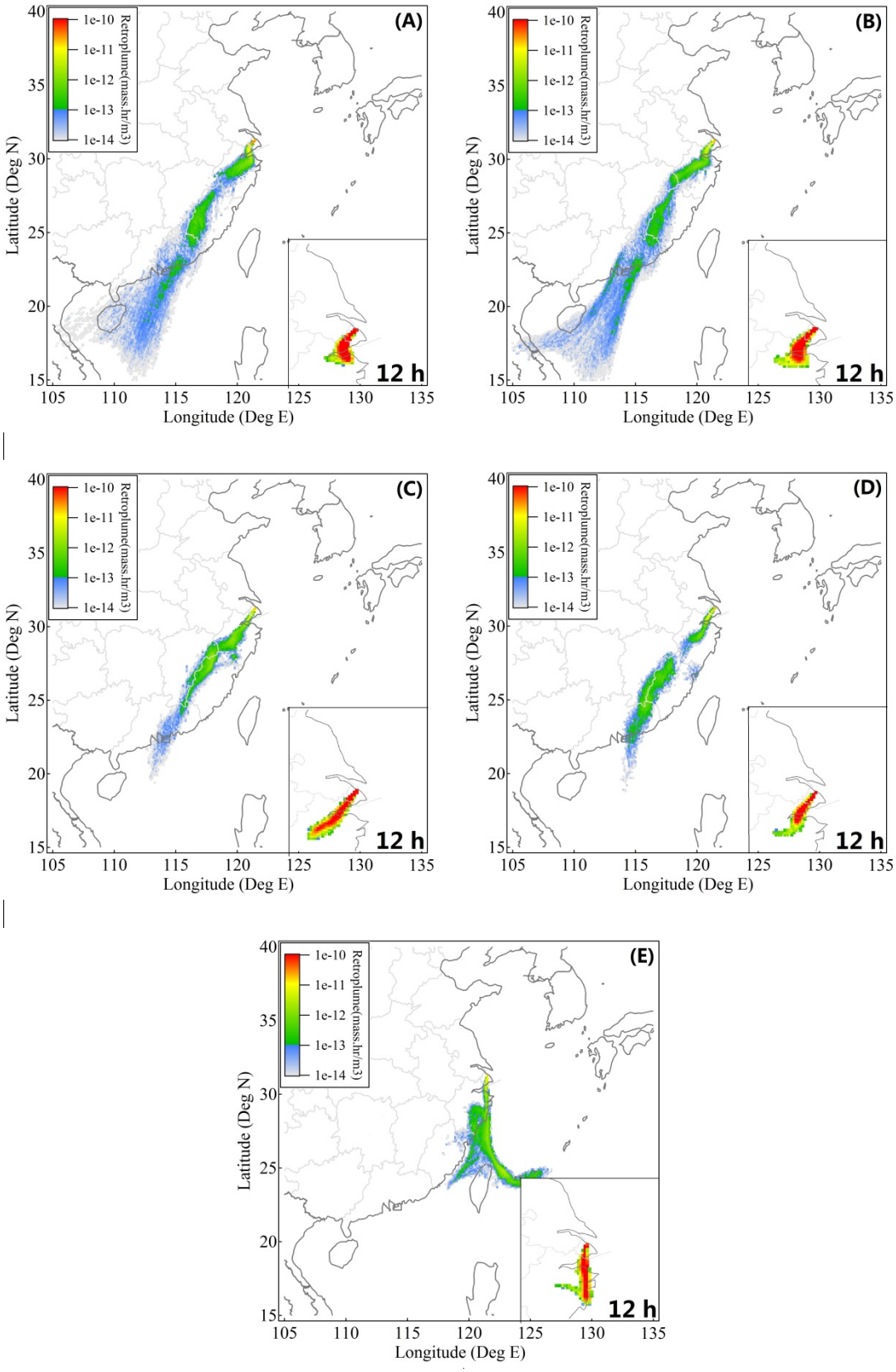

Figure S10. Three-day backward retroplumes (100 m above the ground level) from the sampling location at (**A**) 07:00, 27 July 2015; (**B**) 07:00, 28 July 2015; (**C**) 07:00, 30 July 2015; (**D**) 07:00, 31 July 2015; and (**E**) 07:00, 4 August 2015. The embedded boxes show 12h backward trajectories.