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Sources, concentrations, and seasonal variations of VOC and aerosol particles in downtown Munich in 2023/2024

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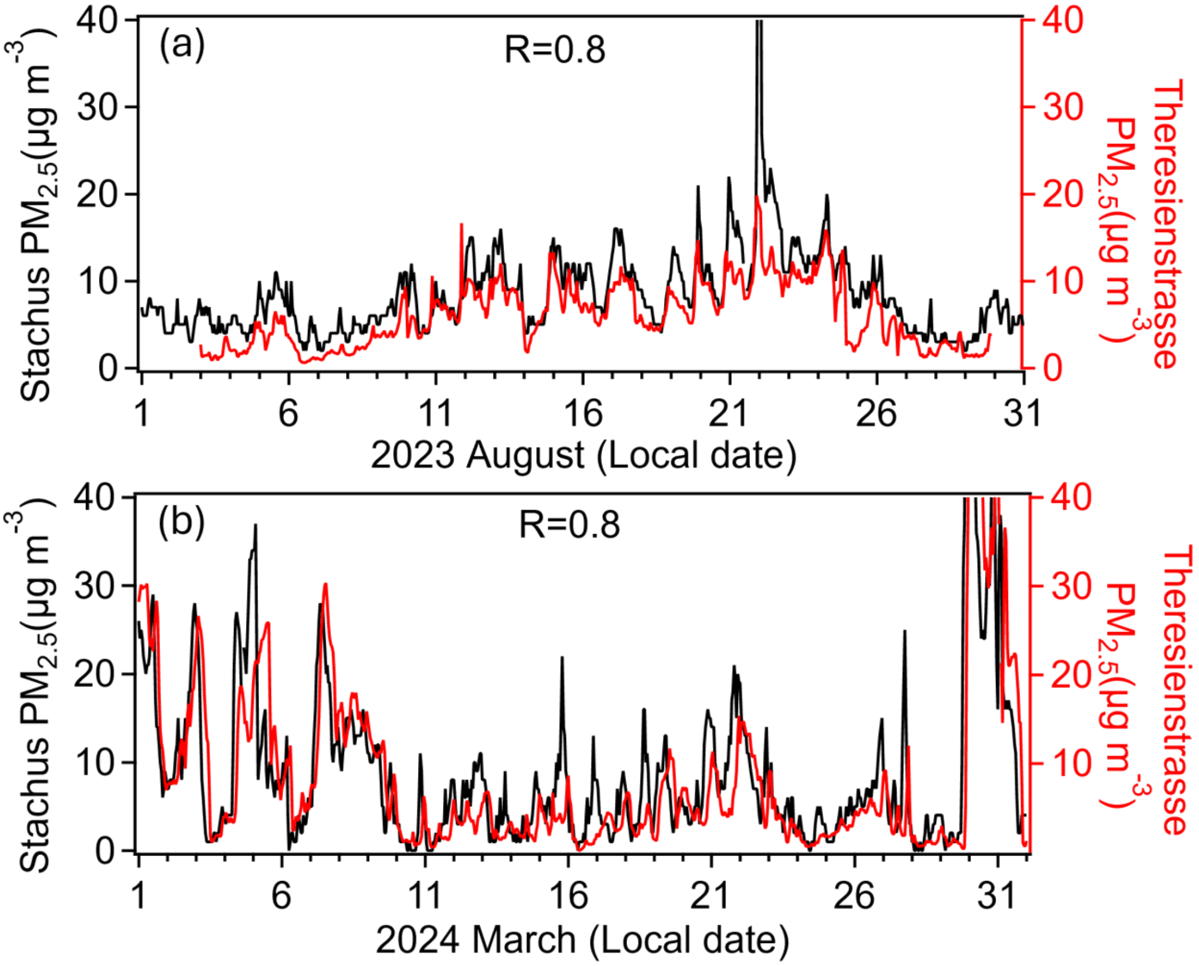

Figure S1: The time series and correlations of $PM_{2.5}$ mass concentrations at Landesamt fur Umwelt Munich/Stachus station and our measurement container in Theresienstrasse in August 2023 (a) and the time series and correlations of $PM_{2.5}$ mass concentrations at Landesamt fur Umwelt Munich/Stachus station and our measurement container in Theresienstrasse in March 2024 (b).

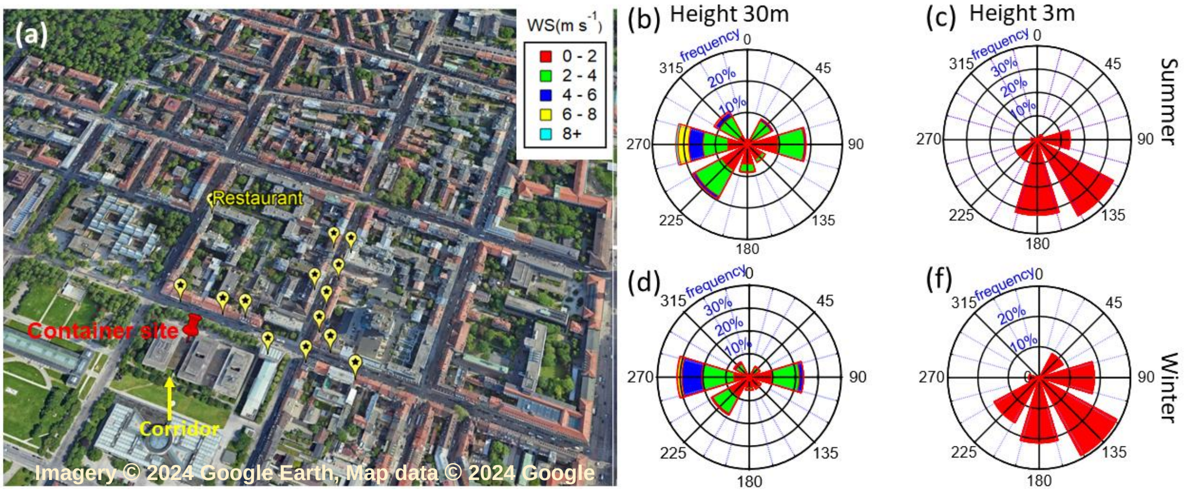

Figure S2. (a) Map of the measurement location at Theresienstrasse 39 in downtown Munich (red pin, LMU) and surrounding restaurants (yellow markers, © is copyright). (b) and (d) Wind direction and wind speed measured by the Institute of Meteorology of LMU at the rooftop (30 meters above ground level) adjacent to the measurement container in summer and winter, respectively. (c) and (f) Wind direction and wind speed measured at 3 meters above the street level on the measurement container in summer and winter, respectively. The tall building redirects the supra-regional wind (30 m) into a very local wind (direction) (3 m). Hence, potential emissions of restaurant west of the measurement location may have a stronger influence on the observations.

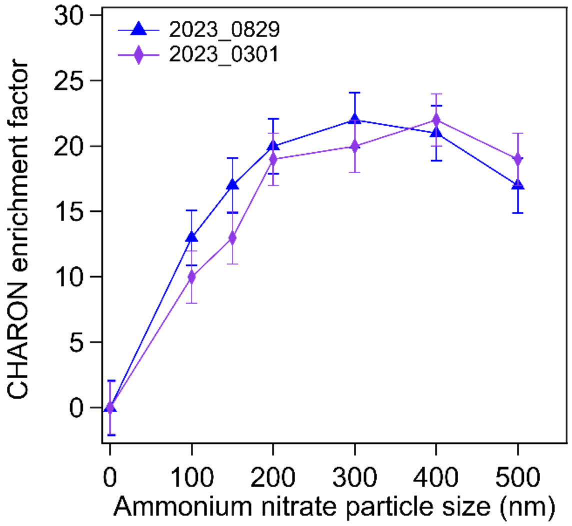

Figure S3 Enrichment factor of CHARON inlet determined by the size-selected ammonium nitrate particles in summer and winter

Instrumental background measurements were performed for all detected ions. For clarity, Fig. S4 presents selected representative ions with relatively high ambient signal intensities, including m/z 59 (acetone-related ions), m/z 93 (toluene-related ions), m/z 121 (trimethylbenzene-related ions), and m/z 137 (monoterpene-related ions). These ions were chosen to illustrate background stability across different chemical classes commonly observed during the campaign.

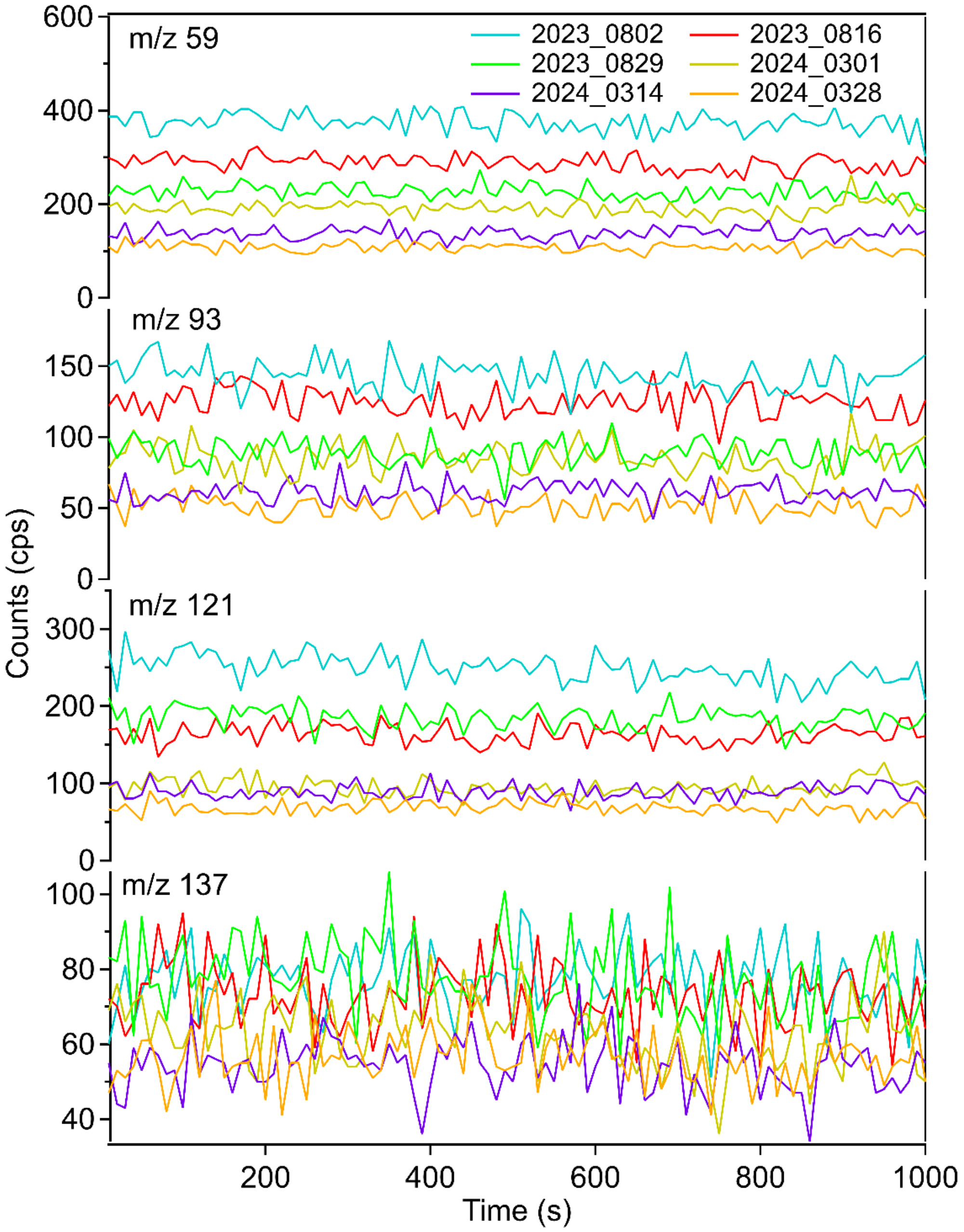

Figure S4. Instrumental background signals measured during weekly nitrogen background tests for selected representative ions. Background measurements were conducted for all detected ions; ions shown here (m/z 59, 93, 121, and 137) were selected as examples due to their relatively high ambient signal intensities and representation of different chemical classes. The small variability demonstrates stable instrumental baseline conditions throughout the campaign.

Calibrations were performed using a gas cylinder (Ionicon Analytik GmbH) containing toluene, 1,2,4-trimethylbenzene, o-xylene, α-pinene, 1,2,4-trichlorobenzene, 3-hexanone, acetaldehyde, acetone, acetonitrile, benzene, 1,2-(O-)-dichlorobenzene, isoprene, and methanol, each at ~1 ppm (10% accuracy), as well as decamethylcyclopentasiloxane and hexamethylcyclotrisiloxane, each at ~0.5 ppm (10% accuracy). Two calibrated mass flow controllers (Bronkhorst, Netherlands) with maximum flow rates of 10 L/min and 0.1 L/min (±5% accuracy) were used to dilute the gas standard to 1 ppb.

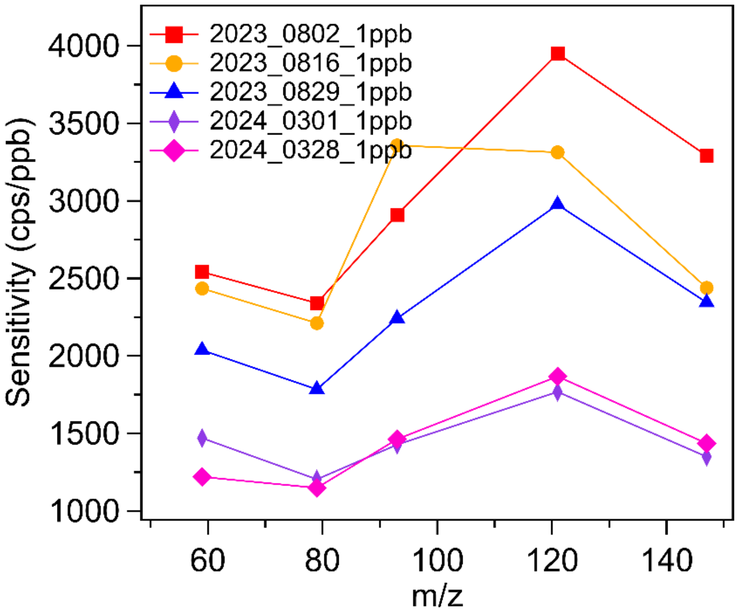

Figure S5 Comparison of sensitivities for calibrated species during summer and winter campaign. The calibrations were conducted before and after the campaigns. The variability is mainly caused by contamination of the instrument inlet throughout the campaign durations.

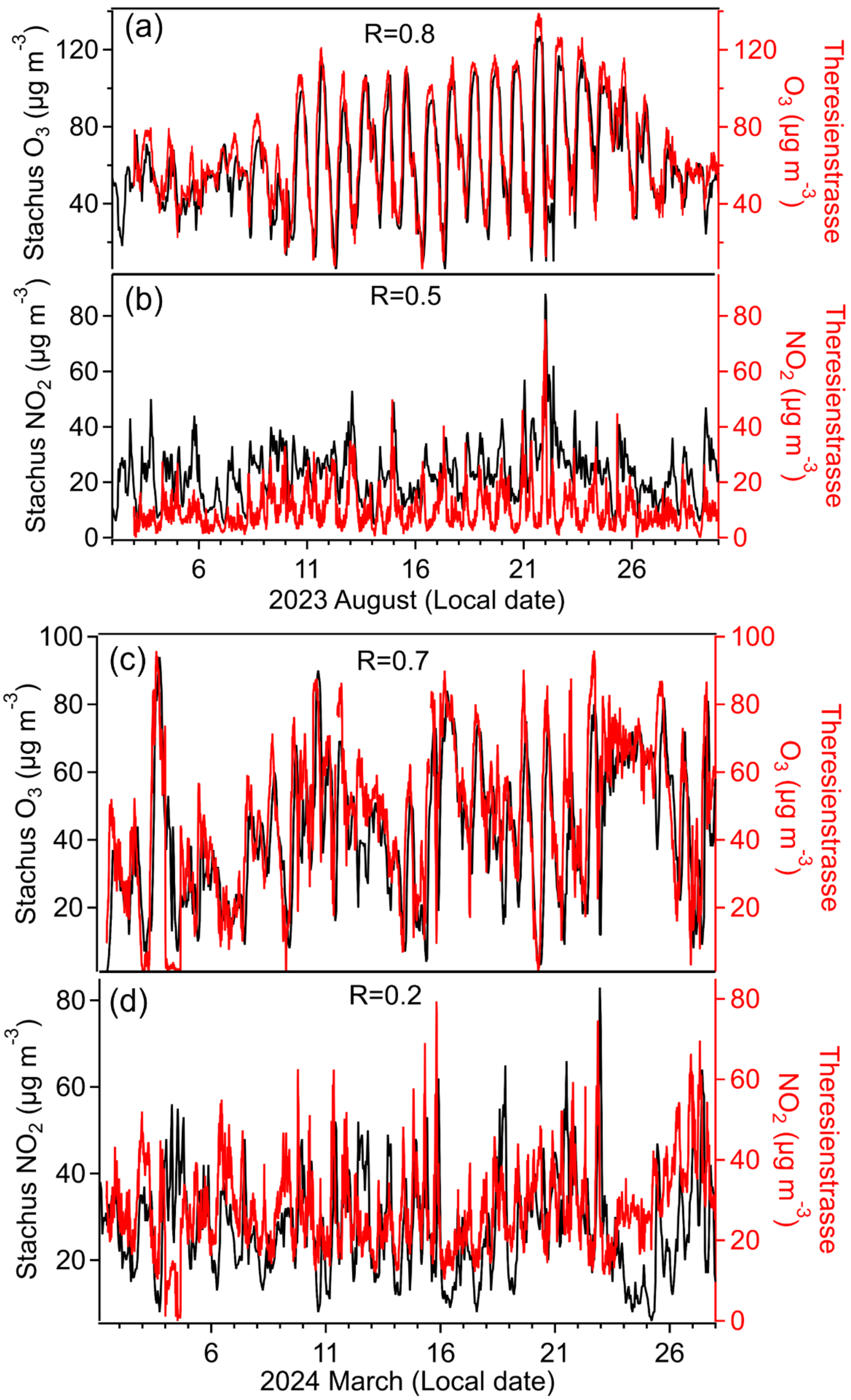

Figure S6. Time series and correlations between LFU and Theresienstrasse stations: (a) O_3 in summer, (b) NO_2 in summer, (c) O_3 in winter, and (d) NO_2 in winter

Table S1: Main instruments used in the different field campaigns

Parameter	Instrument (Manufacturer)	Time resolution	Munich 23	Munich 24
VOCs/semi-volatile particles	CHARON-PTR-MS (IONICON Analytik GmbH)	1 s	×	×
Particle mass composition (0.07-2.5 µm)	HR-ToF-AMS (Aerodyne Research)	1 min	×	×
PM_1, $PM_{2.5}$ and PM_{10} mass	FIDAS200 (Palas GmbH)	1 s	×	×
Black Carbon	AE33 (Magee Scientific)	1 min	×	×
Particle number concentration (>7 nm)	CPC3022A (TSI Inc.)	1 s		×
Particle number concentration (>2.5 nm)	CPC3756 (TSI Inc.)	1 s	×	
Particle number concentration (>2.5 nm)	CPC3776 (TSI Inc.)	1 s	×	×
Particle size distribution (14 -763.5 nm)	SMPS (DMA 3081, TSI Inc.)	6 min		×
Particle size distribution (7-763.5 nm)	U-SMPS (1050, PALAS)	4 min	×	
Formaldehyde (HCHO)	KASCALFiber laser-induced fluorescence (FILIF)	1 s	×	×
Meteorological parameters	WS700 (Lufft GmbH)	1 s	×	×
NO_2	AS32M (Environment SA.)	1 min	×	×
O_3	O341M (Environment SA.)	1 min	×	×
NH_3	G2103 (Picarro)	2 min	×	×

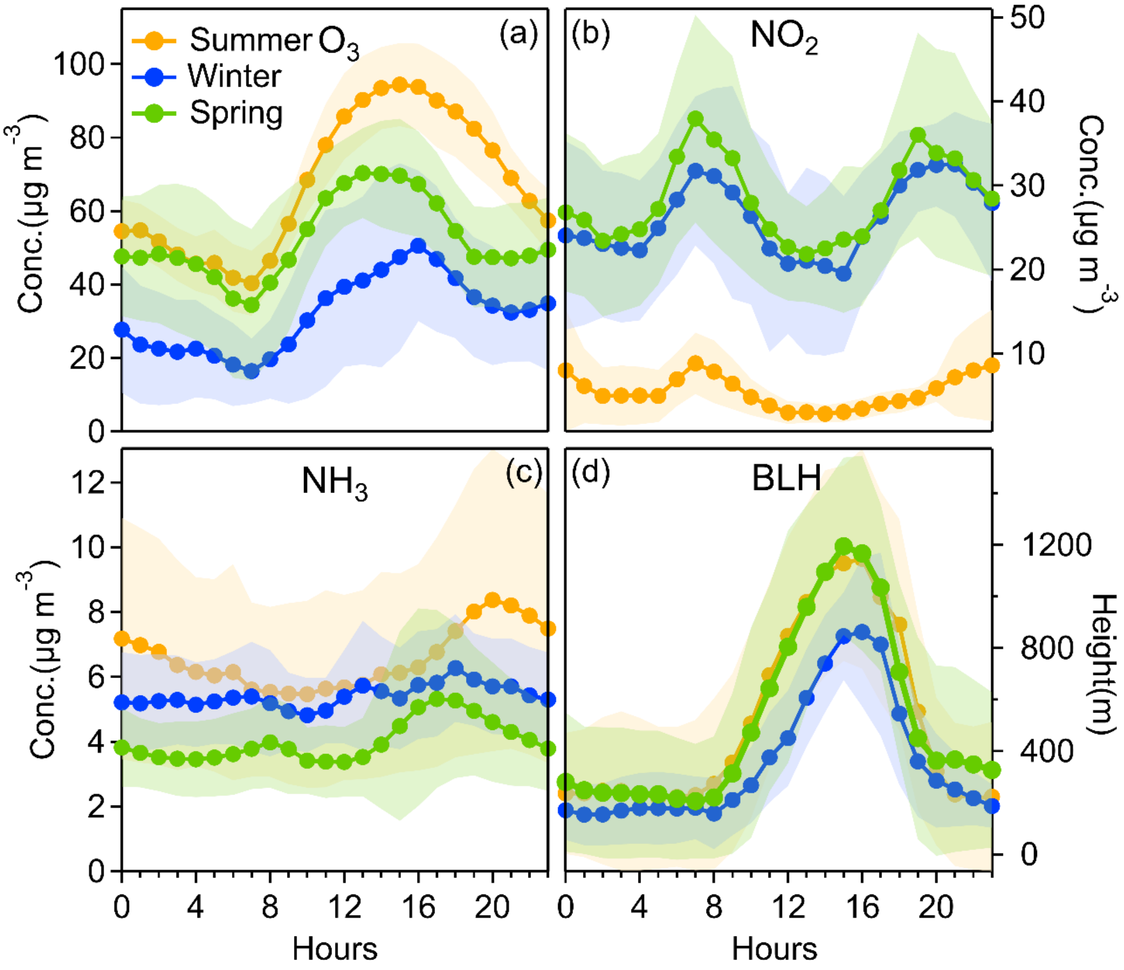

Figure S7. Seasonal mean diurnal cycles of O_3 (a), NO_2 (b), NH_3 (c), and boundary layer height (BLH) (d). Shaded areas represent ±1 standard deviation.

Table S2: List of 117 VOC ions from PTR-MS analysis and average (Ave) mixing ratios with standard deviation (Std) as well as measurement detection limit (MDL) included in the summer time gas PMF analysis.

m/z	**Tentative ion**	**Tentative compound**	**Ave (ppb)**	**Std (ppb)**	**MDL (ppb)**
62.027	$C_1H_4N_1O_2^+$	nitromethane	0.012	0.007	0.006
67.051	$C_5H_7^+$	fragment	0.029	0.021	0.012
69.030	$C_4H_5O_1^+$	furan	0.016	0.006	0.011
69.067	$C_5H_9^+$	Isoprene	0.138	0.075	0.056
71.046	$C_4H_7O_1^+$	methyl vinyl ketone + methacrolein	0.090	0.056	0.014
71.083	$C_5H_{11}^+$	pentenes	0.048	0.025	0.038
73.025	$C_3H_5O_2^+$	methylglyoxal/acrylic acid	0.046	0.017	0.018
73.062	$C_4H_9O_1^+$	methyl ethyl ketone/butanals	0.116	0.074	0.017
74.060	$C_3H_8N_1O_1^+$	n,n-Dimethylformamide	0.009	0.005	0.006
75.042	$C_3H_7O_2^+$	propanonic acid/hydroxyacetone	0.137	0.078	0.035
77.022	$C_2H_5O_3^+$	glycolic acid	0.031	0.022	0.003
77.057	$C_3H_9O_2^+$	propylene glycol	0.120	0.088	0.005
79.037	$C_2H_7O_3^+$	orthoacetic acid	0.116	0.106	0.017
79.052	$C_6H_7^+$	benzene	0.054	0.035	0.010
80.053	$C_5H_6N_1^+$	Pyridine	0.004	0.003	0.003
81.067	$C_6H_9^+$	fragment of monoterpenes	0.093	0.069	0.017
82.070	$C_5H_8N_1^+$	1-methylpyrrole, 4-pentenenitrile	0.007	0.005	0.001
83.047	$C_5H_7O_1^+$	methylfuran	0.026	0.017	0.008
83.083	$C_6H_{11}^+$	fragments of hexenol/hexanal	0.092	0.073	0.042
85.026	$C_4H_5O_2^+$	furanone	0.046	0.013	0.021
85.063	$C_5H_9O_1^+$	cyclopentanone	0.021	0.010	0.010
87.042	$C_4H_7O_2^+$	2,3-butanedione	0.066	0.026	0.025
87.079	$C_5H_{11}O_1^+$	2-pentanone	0.017	0.009	0.006
89.021	$C_3H_5O_3^+$	butyric acid	0.024	0.005	0.010
89.057	$C_4H_9O_2^+$	methyl propanoate	0.045	0.027	0.028
91.036	$C_3H_7O_3^+$	Dimethyl ester carbonic acid	0.014	0.006	0.018
91.051	$C_7H_7^+$	thujone and linalool fragment	0.040	0.038	0.012
93.068	$C_7H_9^+$	toluene	0.190	0.162	0.017
95.046	$C_6H_7O_1^+$	phenol	0.017	0.007	0.012
95.083	$C_7H_{11}^+$	fragment of monoterpenes	0.029	0.017	0.013
97.026	$C_5H_5O_2^+$	furfural	0.044	0.018	0.031
97.062	$C_6H_9O_1^+$	2-ethylfuran/2,5-dimethylfuran	0.016	0.008	0.007
97.099	$C_7H_{13}^+$	methylcyclohexene	0.032	0.013	0.025
99.006	$C_4H_3O_3^+$	Maleic anhydride	0.012	0.002	0.012
99.042	$C_5H_7O_2^+$	furanone	0.055	0.025	0.021
99.079	$C_6H_{11}O_1^+$	cyclohexanone	0.017	0.008	0.011
100.074	$C_5H_{10}N_1O_1^+$	2-Piperidinone	0.009	0.002	0.007
101.021	$C_4H_5O_3^+$	pentanedione	0.026	0.005	0.015
101.058	$C_5H_9O_2^+$	C_5-hydroxy carbonyl (ISOPOOH conversion product)	0.077	0.037	0.020
103.037	$C_4H_7O_3^+$	acetic anhydride	0.021	0.009	0.008
103.074	$C_5H_{11}O_2^+$	oxidized molecules of Isoprene	0.009	0.004	0.012
105.058	$C_4H_9O_3^+$	oxidized molecules of Isoprene	0.009	0.006	0.005
105.074	$C_8H_9^+$	styrene	0.010	0.009	0.011
105.097	$C_5H_{13}O_2^+$	oxidized molecules of Isoprene	0.002	0.001	0.003
107.045	$C_7H_7O_1^+$	Benzaldehyde	0.019	0.012	0.009
107.083	$C_8H_{11}^+$	C_8 aromatics (xylenes)	0.184	0.166	0.012
108.087	$C_7H_{10}N_1^+$	3-ethyl-pyridine	0.011	0.009	0.002
109.099	$C_8H_{13}^+$	fragment of sesquiterpenes	0.030	0.023	0.016
111.044	$C_6H_7O_2^+$	1,2-benzenediol; resorcinol	0.033	0.015	0.012
111.079	$C_7H_{11}O_1^+$	heptadienal	0.010	0.005	0.006
111.114	$C_8H_{15}^+$	oxidized molecules of monoterpenes	0.020	0.008	0.019
113.024	$C_5H_5O_3^+$	furoic acid	0.024	0.006	0.015
113.057	$C_6H_9O_2^+$	hexendione	0.029	0.014	0.013
115.036	$C_5H_7O_3^+$	pentanetrione	0.019	0.005	0.011
115.074	$C_6H_{11}O_2^+$	2,5-hexanedione/ethyl-2-butenoate	0.030	0.015	0.012

117.017	$C_4H_5O_4^+$	maleic acid	0.014	0.003	0.009
117.051	$C_5H_9O_3^+$	oxidized molecules of Isoprene	0.010	0.005	0.005
119.033	$C_4H_7O_4^+$	oxidized molecules of Isoprene	0.027	0.011	0.008
119.073	$C_5H_{11}O_3^+$	oxidized molecules of Isoprene	0.004	0.004	0.006
121.059	$C_8H_9O_1^+$	acetophenone; 2-phenylacetaldehyde	0.012	0.006	0.019
121.098	$C_9H_{13}^+$	C9 aromatics (trimethylbenzene)	0.068	0.065	0.012
123.077	$C_8H_{11}O_1^+$	phenethyl alcohol; ethylphenol	0.004	0.002	0.004
123.115	$C_9H_{15}^+$	fragment of sesquiterpenes	0.025	0.035	0.009
125.059	$C_7H_9O_2^+$	guaiacol + dihydroxy toluene	0.014	0.008	0.007
125.095	$C_8H_{13}O_1^+$	oxidized molecules of monoterpenes	0.008	0.004	0.006
125.131	$C_9H_{17}^+$	3,3,5-trimethylcyclohexene	0.011	0.009	0.011
127.077	$C_7H_{11}O_2^+$	oxidized molecules of monoterpene (a-terpinene)	0.015	0.008	0.010
127.114	$C_8H_{15}O_1^+$	oxidized molecules of monoterpenes	0.008	0.003	0.022
129.054	$C_6H_9O_3^+$	sotolone; 2,5-di-(hydroxymethyl)furan	0.011	0.004	0.008
129.089	$C_7H_{13}O_2^+$	cyclohexanecarboxylic acid	0.012	0.005	0.007
129.126	$C_8H_{17}O_1^+$	octanal; octanone	0.006	0.004	0.006
131.033	$C_5H_7O_4^+$	methylene butanedioic acid	0.017	0.010	0.012
131.071	$C_6H_{11}O_3^+$	ethyl acetoacetate; (e)-3-methoxy-2-butenoic	0.005	0.002	0.003
131.106	$C_7H_{15}O_2^+$	ethyl pentanoate; propyl butanoate	0.004	0.002	0.002
133.049	$C_5H_9O_4^+$	oxidized molecules of Isoprene	0.009	0.004	0.004
133.098	$C_{10}H_{13}^+$	cymenene	0.007	0.005	0.004
135.112	$C_{10}H_{15}^+$	C10 aromatics/p-cymene	0.026	0.020	0.006
137.092	$C_9H_{13}O_1^+$	p-cumenol	0.003	0.003	0.005
137.131	$C_{10}H_{17}^+$	monoterpenes	0.038	0.036	0.010
138.133	$C_9H_{16}N_1^+$	triallylamine	0.004	0.005	0.001
139.037	$C_7H_7O_3^+$	salicylic acid	0.010	0.004	0.009
139.073	$C_8H_{11}O_2^+$	oxidation products of ethylbenzene	0.008	0.004	0.008
139.111	$C_9H_{15}O_1^+$	nopinone	0.022	0.016	0.006
141.053	$C_7H_9O_3^+$	dicarbonyl epoxide	0.012	0.008	0.006
141.090	$C_8H_{13}O_2^+$	oxidized molecules of monoterpenes	0.009	0.005	0.007
141.126	$C_9H_{17}O_1^+$	3,6-nonadienol	0.010	0.013	0.009
143.042	$C_6H_7O_4^+$	hydroxy maltol	0.007	0.003	0.006
143.075	$C_7H_{11}O_3^+$	oxidized molecules of monoterpene (Terpinolene)	0.007	0.003	0.004
143.106	$C_8H_{15}O_2^+$	oxidized molecules of monoterpenes	0.008	0.003	0.007
143.141	$C_9H_{19}O_1^+$	nonanal	0.010	0.009	0.010
145.049	$C_6H_9O_4^+$	acetate furanol; dehydrated levoglucosan	0.010	0.006	0.007
149.098	$C_{10}H_{13}O_1^+$	estragole; anethole; isoestragole	0.003	0.002	0.004
151.111	$C_{10}H_{15}O_1^+$	oxidized molecules of monoterpenes	0.013	0.013	0.003
152.115	$C_9H_{14}N_1O_1^+$	3-dimethylaminoanisole; 4-aminophenol	0.004	0.005	0.001
153.052	$C_8H_9O_3^+$	methyl salicylate; vanillin	0.007	0.004	0.004
153.089	$C_9H_{13}O_2^+$	4-ethyl guiacol	0.007	0.004	0.004
153.126	$C_{10}H_{17}O_1^+$	oxidized molecules of monoterpenes	0.010	0.007	0.004
155.071	$C_8H_{11}O_3^+$	syringol	0.006	0.004	0.005
155.106	$C_9H_{15}O_2^+$	oxidized molecules of monoterpenes	0.007	0.005	0.004
155.142	$C_{10}H_{19}O_1^+$	oxidized molecules of monoterpenes	0.003	0.001	0.012
157.049	$C_7H_9O_4^+$	1-(5-methyl-2-furanyl)-2-	0.011	0.008	0.005
157.120	$C_9H_{17}O_2^+$	oxidized molecules of monoterpene(a-terpinene)	0.006	0.004	0.007
157.157	$C_{10}H_{21}O_1^+$	decanone; decanal	0.005	0.002	0.009
159.067	$C_7H_{11}O_4^+$	dimethyl 2-	0.005	0.003	0.003
161.044	$C_6H_9O_5^+$	2-oxoadipic acid	0.005	0.002	0.003
163.132	$C_8H_{19}O_3^+$	diethyl carbitol	0.006	0.002	0.010
165.089	$C_{10}H_{13}O_2^+$	methyl phenylpropionate; β-phenethyl acetate	0.003	0.002	0.003
167.105	$C_{10}H_{15}O_2^+$	oxidized molecules of monoterpenes	0.006	0.004	0.001

169.090	$C_9H_{13}O_3^+$	1,2,4-trimethoxybenzene; methylsyringol	0.005	0.003	0.001
169.124	$C_{10}H_{17}O_2^+$	oxidized molecules of monoterpenes	0.005	0.004	0.001
171.068	$C_8H_{11}O_4^+$	oxidation products of ethylbenzene	0.007	0.005	0.004
171.110	$C_9H_{15}O_3^+$	oxidized molecules of monoterpenes	0.004	0.002	0.002
171.142	$C_{10}H_{19}O_2^+$	oxidized molecules of monoterpenes	0.002	0.001	0.001
177.148	$C_9H_{21}O_3^+$	1,3,3-triethoxypropane	0.006	0.003	0.002
183.108	$C_{10}H_{15}O_3^+$	oxidized molecules of monoterpenes	0.003	0.002	0.001
185.114	$C_{10}H_{17}O_3^+$	oxidized molecules of monoterpenes	0.002	0.001	0.001
205.190	$C_{15}H_{25}^+$	sesquiterpenes	0.002	0.002	0.001

Table S3: List of 97 VOC ions from Charon-PTR-MS and average (Ave) mixing ratios with standard deviation (Std) as well as measurement detection limit (MDL) included in the winter time gas PMF analysis.

m/z	Tentative ion	Tentative compound	Ave (ppb)	Std (ppb)	MDL (ppb)
57.031	$C_3H_5O_1^+$	propionic acid fragment	0.098	0.044	0.0447
60.046	$C_2H_6N_1O_1^+$	acetamide; n-methyl-formamide	0.037	0.013	0.0095
62.027	$C_1H_4N_1O_2^+$	nitromethane	0.021	0.009	0.0133
67.051	$C_5H_7^+$	fragment	0.019	0.009	0.0132
69.030	$C_4H_5O_1^+$	furan	0.018	0.007	0.0117
69.067	$C_5H_9^+$	Isoprene	0.097	0.050	0.0718
71.046	$C_4H_7O_1^+$	methyl vinyl ketone + methacrolein	0.037	0.017	0.0171
71.083	$C_5H_{11}^+$	pentenes	0.044	0.027	0.0410
73.025	$C_3H_5O_2^+$	methylglyoxal/acrylic acid	0.040	0.011	0.0196
73.062	$C_4H_9O_1^+$	methyl ethyl ketone/butanals	0.141	0.086	0.0201
74.060	$C_3H_8N_1O_1^+$	n,n-Dimethylformamide	0.009	0.004	0.0052
75.042	$C_3H_7O_2^+$	propanonic acid/hydroxyacetone	0.086	0.043	0.0427
77.022	$C_2H_5O_3^+$	glycolic acid	0.016	0.008	0.0032
77.057	$C_3H_9O_2^+$	propylene glycol	0.066	0.052	0.0059
79.052	$C_6H_7^+$	benzene	0.133	0.056	0.0100
80.053	$C_5H_6N_1^+$	Pyridine	0.006	0.003	0.0027
81.067	$C_6H_9^+$	fragment of monoterpenes	0.070	0.050	0.0229
83.047	$C_5H_7O_1^+$	methylfuran	0.015	0.007	0.0098
83.083	$C_6H_{11}^+$	fragments of hexenol/hexanal	0.071	0.036	0.0518
85.026	$C_4H_5O_2^+$	furanone	0.044	0.010	0.0242
85.063	$C_5H_9O_1^+$	cyclopentanone	0.015	0.006	0.0130
85.098	$C_6H_{13}^+$	methylcyclopentane	0.016	0.010	0.0194
87.042	$C_4H_7O_2^+$	2,3-butanedione	0.056	0.020	0.0280
87.079	$C_5H_{11}O_1^+$	2-pentanone	0.017	0.007	0.0061
89.021	$C_3H_5O_3^+$	butyric acid	0.017	0.005	0.0112
89.057	$C_4H_9O_2^+$	methyl propanoate	0.041	0.023	0.0342
90.017	$C_2H_4N_1O_3^+$	oxamic acid	0.009	0.002	0.0064
91.036	$C_3H_7O_3^+$	dimethyl ester carbonic acid	0.019	0.008	0.0177
91.051	$C_7H_7^+$	thujone and linalool fragment	0.030	0.022	0.0152
91.073	$C_4H_{11}O_2^+$	butanediol	0.013	0.011	0.0046
93.068	$C_7H_9^+$	toluene	0.226	0.158	0.0187
95.046	$C_6H_7O_1^+$	phenol	0.019	0.009	0.0140
95.083	$C_7H_{11}^+$	fragment of monoterpenes	0.025	0.015	0.0165
97.026	$C_5H_5O_2^+$	furfural	0.048	0.019	0.0323
97.062	$C_6H_9O_1^+$	2-ethylfuran/2,5-dimethylfuran	0.010	0.005	0.0089
97.099	$C_7H_{13}^+$	methylcyclohexene	0.033	0.016	0.0293
99.006	$C_4H_3O_3^+$	Maleic anhydride	0.019	0.003	0.0120
99.042	$C_5H_7O_2^+$	furanone	0.036	0.010	0.0279
99.079	$C_6H_{11}O_1^+$	cyclohexanone	0.012	0.006	0.0123
100.074	$C_5H_{10}N_1O_1^+$	2-Piperidinone	0.008	0.002	0.0076
101.021	$C_4H_5O_3^+$	pentanedione	0.028	0.005	0.0175
101.058	$C_5H_9O_2^+$	C_5-hydroxy carbonyl (ISOPOOH conversion product)	0.063	0.034	0.0230
103.037	$C_4H_7O_3^+$	acetic anhydride	0.015	0.005	0.0085

103.074	$C_5H_{11}O_2^+$	oxidized molecules of Isoprene	0.009	0.004	0.0139
105.074	$C_8H_9^+$	styrene	0.027	0.018	0.0143
107.045	$C_7H_7O_1^+$	Benzaldehyde	0.017	0.013	0.0095
107.083	$C_8H_{11}^+$	C8 aromatics (xylenes)	0.257	0.208	0.0158
108.087	$C_7H_{10}N_1^+$	3-ethyl-pyridine	0.013	0.010	0.0018
109.099	$C_8H_{13}^+$	fragment of sesquiterpenes	0.024	0.013	0.0245
111.044	$C_6H_7O_2^+$	1,2-benzenediol; resorcinol	0.030	0.012	0.0129
111.079	$C_7H_{11}O_1^+$	heptadienal	0.008	0.005	0.0070
111.114	$C_8H_{15}^+$	oxidized molecules of monoterpenes	0.019	0.009	0.0209
113.024	$C_5H_5O_3^+$	furoic acid	0.021	0.005	0.0162
113.057	$C_6H_9O_2^+$	hexendione	0.018	0.007	0.0156
115.036	$C_5H_7O_3^+$	pentanetrione	0.017	0.004	0.0129
115.074	$C_6H_{11}O_2^+$	2,5-hexanedione/ethyl-2-butenoate	0.017	0.007	0.0131
117.017	$C_4H_5O_4^+$	maleic acid	0.016	0.009	0.0095
117.051	$C_5H_9O_3^+$	oxidized molecules of Isoprene	0.009	0.004	0.0053
119.033	$C_4H_7O_4^+$	oxidized molecules of Isoprene	0.018	0.010	0.0090
121.059	$C_8H_9O_1^+$	acetophenone; 2-phenylacetaldehyde	0.009	0.005	0.0192
121.098	$C_9H_{13}^+$	C9 aromatics (trimethylbenzene)	0.113	0.079	0.0151
122.101	$C_8H_{12}N_1^+$	2-(1-methylethyl)-pyridine	0.006	0.004	0.0015
123.043	$C_7H_7O_2^+$	benzoic acid; o-hydroxybenzaldehyde	0.012	0.004	0.0012
123.115	$C_9H_{15}^+$	fragment of sesquiterpenes	0.013	0.007	0.0106
125.059	$C_7H_9O_2^+$	guaiacol + dihydroxy toluene	0.011	0.005	0.0075
125.095	$C_8H_{13}O_1^+$	oxidized molecules of monoterpenes	0.005	0.002	0.0134
125.131	$C_9H_{17}^+$	3,3,5-trimethylcyclohexene	0.010	0.005	0.0141
127.077	$C_7H_{11}O_2^+$	oxidized molecules of monoterpene (a-terpinene)	0.008	0.003	0.0106
127.114	$C_8H_{15}O_1^+$	oxidized molecules of monoterpenes	0.006	0.003	0.0623
129.054	$C_6H_9O_3^+$	sotolone; 2,5-di-(hydroxymethyl)furan	0.012	0.005	0.0073
129.089	$C_7H_{13}O_2^+$	cyclohexanecarboxylic acid	0.008	0.004	0.0072
129.126	$C_8H_{17}O_1^+$	octanal; octanone	0.004	0.001	0.0065
131.033	$C_5H_7O_4^+$	methylene butanedioic acid	0.010	0.004	0.0097
131.071	$C_6H_{11}O_3^+$	ethyl acetoacetate; (e)-3-methoxy-2-butenoic	0.003	0.001	0.0096
131.106	$C_7H_{15}O_2^+$	ethyl pentanoate; propyl butanoate	0.003	0.001	0.0088
133.049	$C_5H_9O_4^+$	oxidized molecules of Isoprene	0.006	0.003	0.0046
133.098	$C_{10}H_{13}^+$	cymenene	0.008	0.005	0.0044
135.112	$C_{10}H_{15}^+$	C10 aromatics/p-cymene	0.035	0.019	0.0069
137.131	$C_{10}H_{17}^+$	monoterpenes	0.039	0.033	0.0131
138.133	$C_9H_{16}N_1^+$	triallylamine	0.003	0.004	0.0009
139.037	$C_7H_7O_3^+$	salicylic acid	0.014	0.004	0.0089
139.073	$C_8H_{11}O_2^+$	oxidation products of ethylbenzene	0.006	0.002	0.0095
139.111	$C_9H_{15}O_1^+$	nopinone	0.008	0.005	0.0074
141.053	$C_7H_9O_3^+$	dicarbonyl epoxide	0.006	0.002	0.0061
141.090	$C_8H_{13}O_2^+$	oxidized molecules of monoterpenes	0.005	0.002	0.0088
141.126	$C_9H_{17}O_1^+$	3,6-nonadienol	0.004	0.002	0.0112
143.042	$C_6H_7O_4^+$	hydroxy maltol	0.008	0.002	0.0068
143.075	$C_7H_{11}O_3^+$	oxidized molecules of monoterpene (Terpinolene)	0.005	0.002	0.0051
143.141	$C_9H_{19}O_1^+$	nonanal	0.007	0.004	0.0118
145.049	$C_6H_9O_4^+$	acetate furanol; dehydrated levoglucosan	0.008	0.003	0.0086
149.098	$C_{10}H_{13}O_1^+$	estragole; anethole; isoestragole	0.003	0.001	0.0040
151.111	$C_{10}H_{15}O_1^+$	oxidized molecules of monoterpenes	0.011	0.009	0.0035
153.052	$C_8H_9O_3^+$	methyl salicylate; vanillin	0.004	0.001	0.0046
153.089	$C_9H_{13}O_2^+$	4-ethyl guiacol	0.004	0.002	0.0048
153.126	$C_{10}H_{17}O_1^+$	oxidized molecules of monoterpenes	0.008	0.005	0.0055
177.148	$C_9H_{21}O_3^+$	1,3,3-triethoxypropane	0.006	0.002	0.0007
205.190	$C_{15}H_{25}^+$	sesquiterpenes	0.003	0.002	0.0001

For PMF analysis, Temporal measurements of variables, such as m/z intensities from mass spectrometers, can be represented as a data matrix X_{ij}, where columns (j) are variables, and rows (i) are individual time scans. A widely applied approach is the bilinear model, which decomposes X_{ij} into two matrices, G and F, with a residual matrix E:

$$X_{ij}=GF+E$$

Here, G represents the time series of the p factors (columns), while F captures their corresponding profiles or fingerprints (rows). The residual matrix E accounts for deviations between observed and modeled data. In this framework, factor profiles remain constant over time, and their temporal variability is represented solely by G.

The fpeak approach, represented by ϕ, is employed to globally regulate matrix rotations. When ϕ takes positive values, the process involves elementary or successive rotations that amplify the elements in the columns of matrix G while reducing those in the rows of matrix F, maintaining mass balance throughout. In contrast, negative ϕ values reverse this effect, diminishing G’s columns and enhancing F’s rows. In PMF analysis using fpeak, initial and final values, along with the step interval, must be specified. The fpeak range should ensure environmentally interpretable solutions with similar mathematical quality (i.e., comparable Q values). The entries in G and F are determined using a least-squares algorithm that minimizes Q, the weighted sum of squared residuals eij divided by uncertainties σij for all data points:

$$Q=\sum_{i=1}^{m}\sum_{j=1}^{n}\left(\frac{e_{ij}}{\sigma_{ij}}\right)^2$$

Here, σ_{ij} typically represents the measurement uncertainty. Data points with e_{ij}/σ_{ij} »1 dominate Q and heavily influence the model. While this emphasizes data with high signal-to-noise ratios, such outliers can also result from local events or instrument noise, which the model should exclude. Monitoring total Q across PMF runs is often not meaningful, as its value depends on the data matrix size and the number of factors. Instead, Q is normalized by the degrees of freedom, yielding Q_{exp}:

$$Q_{exp}=m\cdot n-p\cdot(m+n)$$

In an ideal PMF run, Q/Q_{exp} approaches ~1 if uncertainties account for both measurement and modeling errors. However, modeling uncertainty is often unknown, especially for ambient data. For AMS, typical Q/Q_{exp} values range from 1 to 5. Environmental conditions and factor overlap must be considered, as increasing the number of factors often reduces Q/Q_{exp} without significant improvement and may lead to overlapping factors. In such cases, fewer factors should be selected. For PTR gas and Charon data, limited studies report Q/Q_{exp} values. Factors should be screened based on their correlation with tracers (e.g., toluene for traffic, levoglucosan and vanillin acid for biomass burning). Select runs with high correlations ($R > 0.8$) with tracers for suitable PMF results.

The optimal number of factors was determined by considering both statistical diagnostics and physical interpretability. Increasing the number of factors leads to a reduction in Q/Qexp, as expected for PMF solutions; however, the improvement becomes marginal beyond five factors (Fig. S8a). Solutions with fewer factors failed to resolve key source-related features, whereas higher-factor solutions resulted in overlapping or non-distinct factors.

Therefore, a five-factor solution was selected as the best compromise between statistical performance and physically interpretable source separation. The robustness of the selected solution is further supported by the distribution of scaled residuals (Fig. S8b), which are centered near zero and show no pronounced systematic structure.

The same evaluation procedure was applied consistently to both PTR-MS VOC and CHARON-PTR-MS datasets.

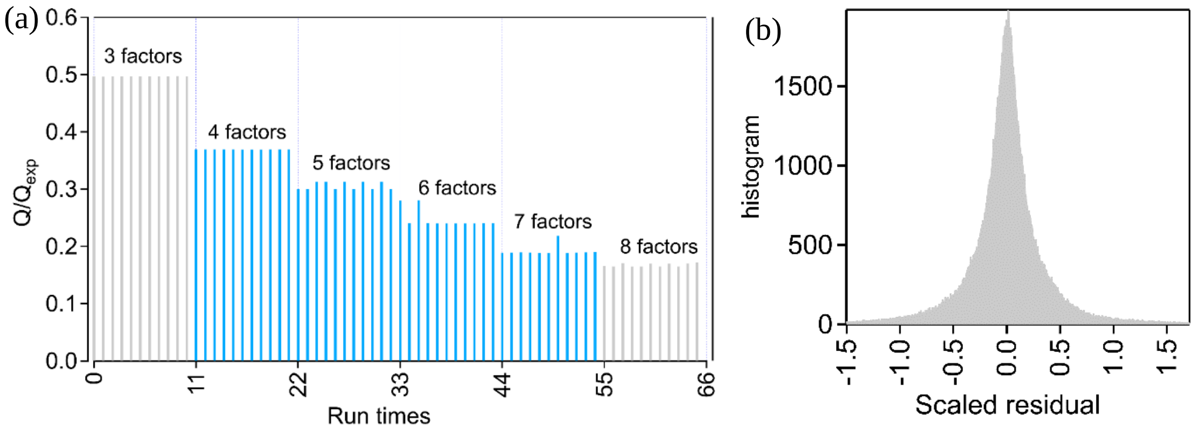

Figure S8 (a) Q/Qexp values obtained from multiple PMF runs for different factor numbers for summertime VOC measurements. The decrease in Q/Qexp becomes gradual beyond five factors, indicating diminishing improvement in model performance. (b) Histogram of scaled residuals (eij/σij) for the selected PMF solution (five factors). The residual distribution is centered near zero and approximately symmetric, indicating an adequate representation of the data and uncertainty structure.

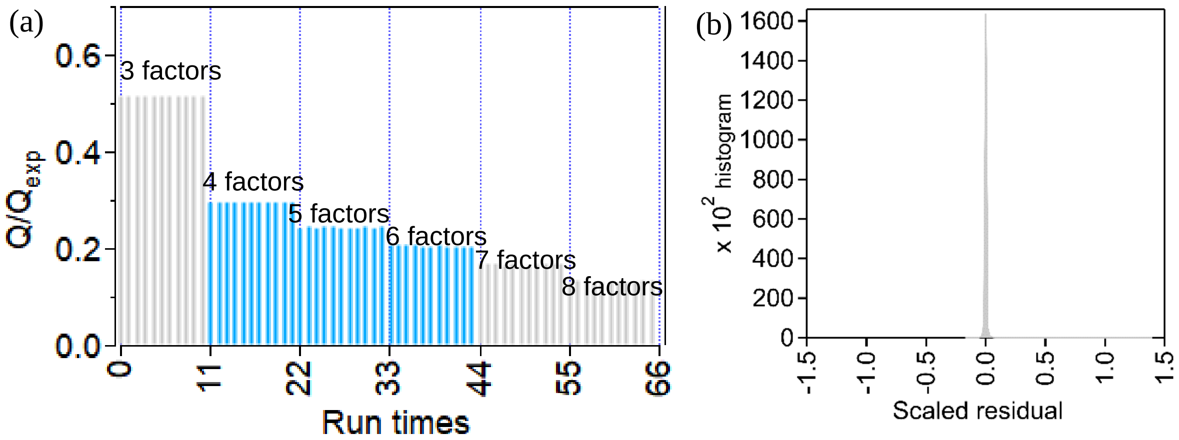

Figure S9. (a) Q/Qexp values obtained from multiple PMF runs for March VOC measurements. (b) Histogram of scaled residuals (eij/σij) for the selected PMF solution (five factors), showing a distribution centered near zero and indicating an adequate model fit.

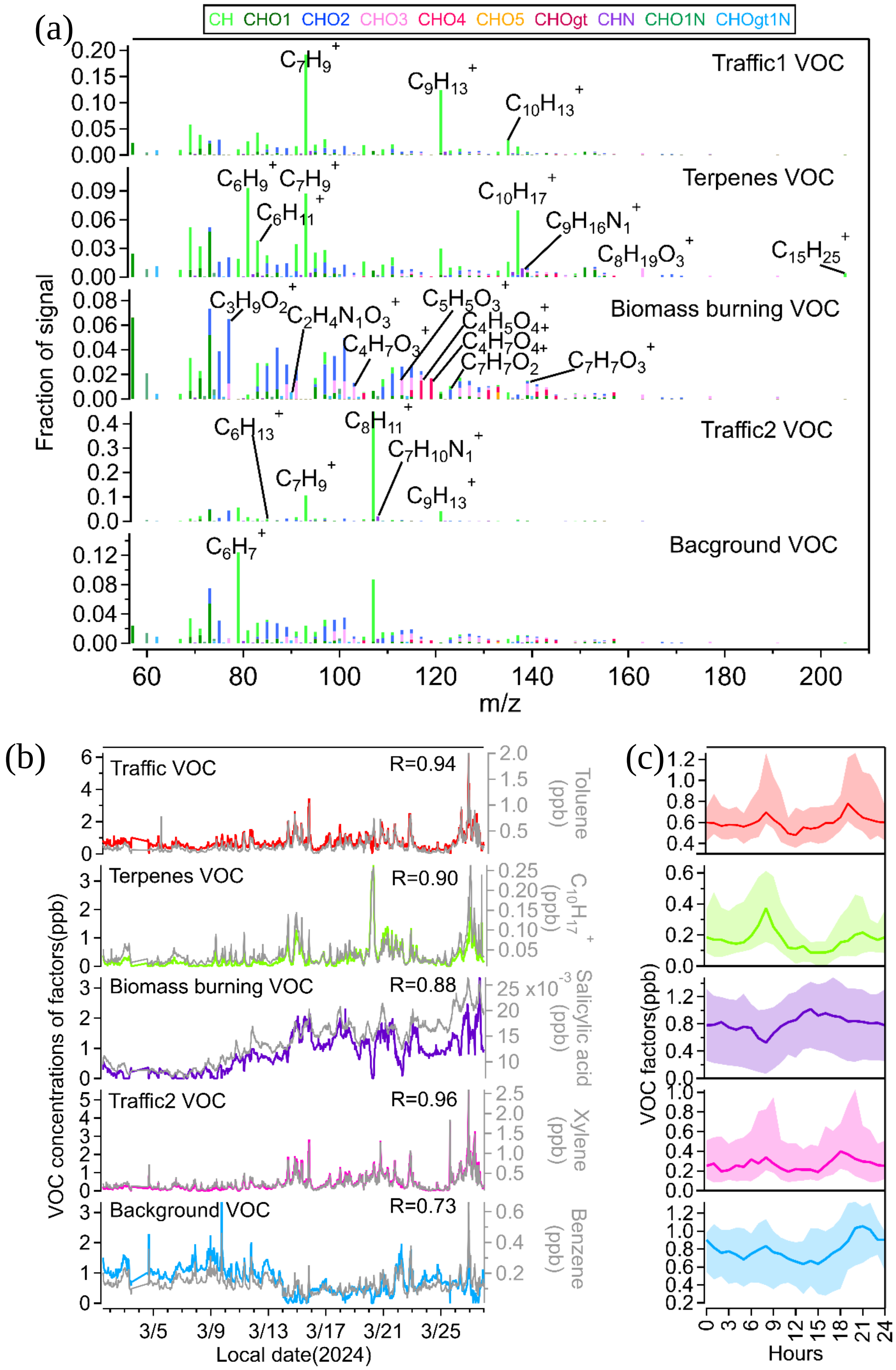

Figure S10 (a) Normalized VOC factor spectra from PMF analysis and characteristic mass /z peaks in winter/spring; (b) Time series of VOC factors including traffic, terpenes, biomass burning, traffic2, and background VOCs; and (c) Median diurnal variations in VOC factors during winter/spring time.

Table S4: Major VOC mass peaks from PTR-MS analysis correlated to the five related gas source factors in summer

Mass peak (m/z)	**Tentative ion**	**Tentative compound**	**PMF factor related**	**Correlation to PMF factor**
121.10	$C_9H_{13}^+$	C_9 aromatics trimethylbenzene	Traffic	0.95
107.09	$C_8H_{11}^+$	xylene		0.93
93.07	$C_7H_9^+$	toluene		0.92
152.11	$C_9H_{14}N_1O_1^+$	alcohols or aldehydes with nitrogen groups	Oxidized BVOC	0.97
167.11	$C_{10}H_{15}O_2^+$	oxidized molecules of monoterpenes		0.93
149.10	$C_{10}H_{13}O_1^+$	carvone		0.93
151.11	$C_{10}H_{15}O_1^+$	oxidized molecules of monoterpenes		0.93
153.13	$C_{10}H_{17}O_1^+$	oxidized molecules of monoterpenes		0.91
139.11	$C_9H_{15}O_1^+$	myrcenol		0.87
137.13	$C_{10}H_{17}^+$	monoterpene	BVOC	0.98
138.13	$C_9H_{16}N_1^+$	unknown		0.90
81.07	$C_6H_9^+$	fragment of monoterpenes		0.86
82.07	$C_5H_8N_1^+$	unknown		0.81
205.20	$C_{15}H_{25}^+$	sesquiterpenes		0.80
89.02	$C_3H_5O_3^+$	butryic acid	Aged VOC	0.75
101.02	$C_4H_5O_3^+$	pentanedione		0.72
	O_3			0.51
131.03	$C_5H_7O_4^+$	fragment of oxidized guaiacol molecules	Biomass burning VOC	0.92
95.01	$C_5H_3O_2^+$	fragment of oxidized guaiacol molecules		0.91
119.03	$C_4H_7O_4^+$	fragment of oxidized guaiacol molecules		0.90
103.04	$C_4H_7O_3^+$	fragment of oxidized guaiacol molecules		0.86
77.06	$C_3H_9O_2^+$	1,3-propanediol		0.85
79.04	$C_2H_7O_3^+$	orthoacetic acid		0.83

Table S5: Major VOC mass peaks from PTR-MS analysis correlated to the five related gas source factors in winter

Mass peak (m/z)	**Tentative ion**	**Tentative compound**	**PMF factor related**	**Correlation to PMF factor**
121.10	$C_9H_{13}^+$	C_9 aromatics trimethylbenzene	Traffic1 VOC	0.96
93.07	$C_7H_9^+$	toluene		0.94
133.10	$C_{10}H_{13}^+$	cymenene		0.86
138.13	$C_9H_{16}N_1^+$	triallylamine	Monoterpenes VOC	0.98
205.2	$C_{15}H_{25}^+$	sesquiterpenes		0.92
137.13	$C_{10}H_{17}^+$	monoterpene		0.90
81.07	$C_6H_9^+$	fragment of monoterpenes		0.89
163.13	$C_8H_{19}O_3^+$	diethyl carbitol		0.76
103.0	$C_4H_7O_3^+$	acetic anhydride	Biomass burning VOC	0.89
139.04	$C_7H_7O_3^+$	salicylic acid		0.88
77.06	$C_3H_9O_2^+$	1,3-propanediol		0.87
113.02	$C_5H_5O_3^+$	furoic acid		0.86
90.02	$C_2H_4N_1O_3^+$	oxamic acid		0.86
123.04	$C_7H_7O_2^+$	benzoic acid		0.86
117.02	$C_4H_5O_4^+$	maleic acid		0.85
119.03	$C_4H_7O_4^+$	butanedioic acid		0.85
108.08	$C_7H_{10}N_1^+$	3-ethyl-pyridine	Traffic2 VOC	0.98
107.09	$C_8H_{11}^+$	C8 aromatics xylenes		0.96
121.10	$C_9H_{13}^+$	C_9 aromatics trimethylbenzene		0.91
93.07	$C_7H_9^+$	toluene		0.91
85.10	$C_6H_{13}^+$	methyl cyclopentane		0.90
79.0	$C_6H_7^+$	benzene	Regional background VOC	0.73

Table S6: List of 153 SVOC ions from Charon-PTR-MS analysis and average (Ave) mixing ratios with standard deviation (Std) as well as measurement detection limit (MDL) included in the summer time semi volatile organic aerosol PMF analysis.

m/z	**Tentative ion**	**Tentative compound**	**Ave (μg m^{-3})**	**Std (μg m^{-3})**	**MDL (μg m^{-3})**
69.031	$C_4H_5O_1^+$	furan	0.0034	0.0026	0.0011
71.046	$C_4H_7O_1^+$	methyl vinyl ketone + methacrolein	0.0055	0.0039	0.0021
73.025	$C_3H_5O_2^+$	methylglyoxal/acrylic acid	0.0030	0.0025	0.0029
75.042	$C_3H_7O_2^+$	propanoic acid/hydroxyacetone	0.0080	0.0066	0.0189
77.022	$C_2H_5O_3^+$	glycolic acid	0.0006	0.0007	0.0008
81.035	$C_5H_5O_1^+$	2,4-cyclopentadiene-1-one	0.0009	0.0008	0.0005
83.047	$C_5H_7O_1^+$	methyl furan	0.0062	0.0057	0.0013
84.047	$C_4H_6N_1O_1^+$	5-methyl-isoxazole	0.0007	0.0007	0.0002
85.026	$C_4H_5O_2^+$	furanone	0.0093	0.0079	0.0040
85.063	$C_5H_9O_1^+$	cyclopentanone	0.0018	0.0013	0.0012
86.030	$C_3H_4N_1O_2^+$	cyano acetic acid	0.0004	0.0004	0.0002
87.042	$C_4H_7O_2^+$	2,3-butanedione	0.0058	0.0049	0.0043
89.021	$C_3H_5O_3^+$	butyric acid	0.0040	0.0041	0.0021
89.057	$C_4H_9O_2^+$	methyl propanoate	0.0007	0.0005	0.0016
90.018	$C_2H_4N_1O_3^+$	oxamic acid	0.0007	0.0007	0.0008
91.036	$C_3H_7O_3^+$	lactic acid	0.0008	0.0007	0.0011
93.060	$C_3H_9O_3^+$	ethanol cluster; 1,2,3-propanetriol	0.0022	0.0029	0.0018
95.046	$C_6H_7O_1^+$	phenol	0.0046	0.0043	0.0018
95.083	$C_7H_{11}^+$	fragment of monoterpenes	0.0014	0.0013	0.0010
96.049	$C_5H_6N_1O_1^+$	4-pyridinol;	0.0006	0.0005	0.0002
97.026	$C_5H_5O_2^+$	furfural	0.0047	0.0035	0.0049
97.062	$C_6H_9O_1^+$	2-ethylfuran/2,5-dimethylfuran	0.0025	0.0020	0.0010
99.042	$C_5H_7O_2^+$	furanone	0.0103	0.0077	0.0039
99.079	$C_6H_{11}O_1^+$	cyclohexanone	0.0009	0.0007	0.0011
100.040	$C_4H_6N_1O_2^+$	succinimide	0.0009	0.0008	0.0007
101.021	$C_4H_5O_3^+$	pentanedione	0.0035	0.0030	0.0031
101.058	$C_5H_9O_2^+$	C_5-hydroxy carbonyl (ISOPOOH conversion product)	0.0053	0.0044	0.0031
105.018	$C_3H_5O_4^+$	propanedioic acid	0.0071	0.0061	0.0019
105.056	$C_4H_9O_3^+$	isobutyric acid	0.0005	0.0006	0.0004
107.038	$C_3H_7O_4^+$	glyceric acid	0.0009	0.0009	0.0004
107.083	$C_4H_{11}O_3^+$	trimethoxy methane	0.0028	0.0033	0.0008
108.086	$C_7H_{10}N_1^+$	3-ethyl-pyridine; 2,3-dimethyl-pyridine	0.0007	0.0013	0.0001
109.059	$C_7H_9O_1^+$	cresol, anisole	0.0023	0.0022	0.0027
109.099	$C_8H_{13}^+$	fragment of sesquiterpenes	0.0017	0.0020	0.0011
111.044	$C_6H_7O_2^+$	1,2-benzenediol; resorcinol	0.0050	0.0037	0.0096
111.079	$C_7H_{11}O_1^+$	heptadienal	0.0010	0.0009	0.0004
112.045	$C_5H_6N_1O_2$+	2,3-pyridinediol	0.0006	0.0005	0.0007
113.024	$C_5H_5O_3^+$	furoic acid	0.0041	0.0034	0.0041
113.057	$C_6H_9O_2^+$	hexendione	0.0044	0.0033	0.0028
113.094	$C_7H_{13}O_1^+$	cycloheptanone	0.0007	0.0005	0.0005
114.056	$C_5H_8N_1O_2$+	ethyl cyanoacetate	0.0005	0.0004	0.0004
115.036	$C_5H_7O_3^+$	pentanetrione	0.0037	0.0030	0.0023
115.074	$C_6H_{11}O_2^+$	2,5-hexanedione/ethyl-2-butenoate	0.0030	0.0024	0.0019
117.017	$C_4H_5O_4^+$	maleic acid	0.0014	0.0013	0.0019
117.051	$C_5H_9O_3^+$	oxidized molecules of Isoprene	0.0022	0.0019	0.0009
119.033	$C_4H_7O_4^+$	oxidized molecules of Isoprene	0.0035	0.0032	0.0028
121.032	$C_4H_8O_2S^+$	s-ethyl o-methyl	0.0007	0.0008	0.0004
121.065	$C_8H_9O_1^+$	acetophenone	0.0004	0.0004	0.0005
121.095	$C_9H_{13}^+$	C_9-aromatics trimethylbenzene	0.0005	0.0006	0.0004
123.051	$C_7H_7O_2^+$	benzoic acid	0.0027	0.0029	0.0009
123.077	$C_8H_{11}O_1^+$	phenethyl alcohol; ethylphenol	0.0010	0.0009	0.0003
125.024	$C_6H_5O_3^+$	2,5-furandicarboxaldehyde	0.0008	0.0006	0.0012

125.059	$C_7H_9O_2^+$	guaiacol + dihydroxy toluene	0.0044	0.0037	0.0011
125.095	$C_8H_{13}O_1^+$	oxidized molecules of monoterpenes	0.0008	0.0007	0.0005
127.038	$C_6H_7O_3^+$	methyl 2-furoate	0.0047	0.0035	0.0027
127.077	$C_7H_{11}O_2^+$	oxidized molecules of monoterpene (a-terpinene)	0.0035	0.0029	0.0011
128.037	$C_5H_6N_1O_3^+$	n-methylolmaleimide	0.0006	0.0005	0.0004
129.017	$C_5H_5O_4^+$	methanetetracarbaldehyde	0.0015	0.0014	0.0011
129.054	$C_6H_9O_3^+$	sotolone; 2,5-di-(hydroxymethyl)furan	0.0031	0.0026	0.0014
129.089	$C_7H_{13}O_2^+$	cyclohexanecarboxylic acid	0.0006	0.0005	0.0009
130.054	$C_5H_8N_1O_3^+$	dimethadione	0.0006	0.0005	0.0003
131.033	$C_5H_7O_4^+$	methylene butanedioic acid	0.0032	0.0029	0.0020
131.071	$C_6H_{11}O_3^+$	ethyl acetoacetate; (e)-3-methoxy-2-butenoic	0.0009	0.0007	0.0004
133.016	$C_4H_5O_5^+$	oxalacetic acid	0.0012	0.0011	0.0008
133.049	$C_5H_9O_4^+$	oxidized molecules of Isoprene	0.0031	0.0031	0.0012
133.098	$C_{10}H_{13}^+$	cymenene	0.0005	0.0005	0.0003
135.032	$C_4H_7O_5^+$	malic acid	0.0008	0.0008	0.0004
135.076	$C_9H_{11}O_1^+$	1-phenyl-1-propanone	0.0003	0.0004	0.0004
135.109	$C_6H_{15}O_3^+$	dimethyl carbitol	0.0022	0.0036	0.0010
137.057	$C_8H_9O_2^+$	methylbenzoic acid	0.0012	0.0010	0.0006
137.092	$C_9H_{13}O_1^+$	p-cumenol	0.0007	0.0007	0.0002
139.037	$C_7H_7O_3^+$	salicylic acid	0.0028	0.0026	0.0011
139.073	$C_8H_{11}O_2^+$	oxidation products of ethylbenzene	0.0019	0.0016	0.0007
139.111	$C_9H_{15}O_1^+$	nopinone	0.0003	0.0004	0.0005
140.038	$C_6H_6N_1O_3^+$	2-nitrophenol	0.0004	0.0004	0.0003
141.053	$C_7H_9O_3^+$	dicarbonyl epoxide	0.0074	0.0063	0.0014
141.090	$C_8H_{13}O_2^+$	oxidized molecules of monoterpenes	0.0012	0.0010	0.0006
142.059	$C_6H_8N_1O_3^+$	methyl acetylcyanoacetate	0.0007	0.0006	0.0002
143.042	$C_6H_7O_4^+$	hydroxy maltol	0.0018	0.0015	0.0013
143.075	$C_7H_{11}O_3^+$	oxidized molecules of Terpinolene	0.0024	0.0023	0.0008
143.106	$C_8H_{15}O_2^+$	oxidized molecules of monoterpenes	0.0005	0.0004	0.0006
144.033	$C_5H_6N_1O_4^+$	5-nitro-2-furanmethanol	0.0003	0.0003	0.0003
145.049	$C_6H_9O_4^+$	acetate furanol; dehydrated levoglucosan	0.0085	0.0080	0.0024
146.051	$C_5H_8N_1O_4^+$	pyruvylglycine	0.0007	0.0007	0.0003
147.028	$C_5H_7O_5^+$	2-oxopentanedioic acid	0.0012	0.0012	0.0007
147.064	$C_6H_{11}O_4^+$	hexanedioic acid	0.0008	0.0007	0.0004
149.038	$C_5H_9O_5^+$	oxidized molecules of isoprene	0.0019	0.0020	0.0012
149.063	$C_9H_9O_2^+$	trans-cinnamic acid	0.0006	0.0005	0.0003
151.034	$C_8H_7O_3^+$	piperonal	0.0005	0.0005	0.0003
151.070	$C_9H_{11}O_2^+$	benzyl acetate	0.0016	0.0014	0.0004
151.111	$C_{10}H_{15}O_1^+$	oxidized molecules of monoterpenes	0.0014	0.0016	0.0004
152.115	$C_9H_{14}N_1O_1^+$	3-dimethylaminoanisole	0.0005	0.0008	0.0001
153.052	$C_8H_9O_3^+$	methyl salicylate; vanillin	0.0017	0.0015	0.0006
153.089	$C_9H_{13}O_2^+$	4-ethyl guiacol	0.0027	0.0026	0.0006
153.126	$C_{10}H_{17}O_1^+$	oxidized molecules of monoterpenes	0.0004	0.0006	0.0004
155.032	$C_7H_7O_4^+$	β-resorcylic acid	0.0013	0.0013	0.0008
155.071	$C_8H_{11}O_3^+$	syringol	0.0050	0.0045	0.0009
155.106	$C_9H_{15}O_2^+$	oxidized molecules of monoterpenes	0.0005	0.0005	0.0006
156.033	$C_6H_6N_1O_4^+$	4-nitrocatechol	0.0004	0.0006	0.0002
156.073	$C_7H_{10}N_1O_3^+$	ethyl 2-cyanoacetoacetate	0.0006	0.0006	0.0002
157.049	$C_7H_9O_4^+$	1-(5-methyl-2-furanyl)-2-	0.0077	0.0076	0.0020
157.096	$C_8H_{13}O_3^+$	oxidized molecules of monoterpenes	0.0011	0.0009	0.0004
158.051	$C_6H_8N_1O_4^+$	1-(acetoxy)pyrrolidine-2,5-	0.0009	0.0009	0.0003
159.028	$C_6H_7O_5^+$	tricarballylic anhydride	0.0016	0.0016	0.0012
159.067	$C_7H_{11}O_4^+$	dimethyl 2-	0.0032	0.0029	0.0009
160.069	$C_{10}H_{10}N_1O_1^+$	acetylindole	0.0003	0.0003	0.0001
161.044	$C_6H_9O_5^+$	2-oxoadipic acid	0.0025	0.0027	0.0011
163.039	$C_9H_7O_3^+$	7-hydroxycoumarin	0.0009	0.0011	0.0005

163.058	$C_6H_{11}O_5^+$	levoglucosan	0.0014	0.0012	0.0005
165.039	$C_5H_9O_6^+$	oxidized molecules of Isoprene	0.0012	0.0013	0.0006
165.089	$C_{10}H_{13}O_2^+$	methyl phenylpropionate; β-phenethyl acetate	0.0012	0.0011	0.0004
166.086	$C_9H_{12}N_1O_2^+$	benzocaine	0.0004	0.0005	0.0001
167.035	$C_8H_7O_4^+$	isophthalic acid	0.0044	0.0062	0.0013
167.065	$C_9H_{11}O_3^+$	acetoguaiacon	0.0013	0.0011	0.0007
167.105	$C_{10}H_{15}O_2^+$	oxidized molecules of monoterpenes	0.0016	0.0015	0.0005
169.040	$C_8H_9O_4^+$	vanillic acid	0.0010	0.0011	0.0008
169.090	$C_9H_{13}O_3^+$	1,2,4-trimethoxybenzene; methylsyringol	0.0031	0.0027	0.0006
169.124	$C_{10}H_{17}O_2^+$	oxidized molecules of monoterpenes	0.0008	0.0010	0.0004
170.083	$C_8H_{12}N_1O_3^+$	dl-noradrenaline	0.0004	0.0004	0.0001
171.068	$C_8H_{11}O_4^+$	oxidation products of ethylbenzene	0.0062	0.0064	0.0016
171.110	$C_9H_{15}O_3^+$	oxidized molecules of monoterpenes	0.0007	0.0006	0.0003
173.041	$C_7H_9O_5^+$	oxidation products of guaiacol	0.0028	0.0031	0.0012
173.077	$C_8H_{13}O_4^+$	oxidized molecules of monoterpenes	0.0020	0.0019	0.0006
174.045	$C_6H_8N_1O_5^+$	succinimidoglycolic acid	0.0004	0.0005	0.0002
175.060	$C_7H_{11}O_5^+$	shikimic acid	0.0036	0.0035	0.0009
176.062	$C_6H_{10}N_1O_5^+$	n-acetyl-l-aspartic acid	0.0004	0.0004	0.0001
177.075	$C_7H_{13}O_5^+$	diacetin	0.0005	0.0004	0.0002
181.083	$C_{10}H_{13}O_3^+$	anisyl acetate	0.0012	0.0010	0.0003
183.063	$C_9H_{11}O_4^+$	unknown	0.0016	0.0018	0.0005
183.100	$C_{10}H_{15}O_3^+$	oxidized molecules of monoterpenes	0.0015	0.0014	0.0004
185.080	$C_9H_{13}O_4^+$	fragments of the $C_9H_{14}O_n$ series	0.0033	0.0031	0.0008
186.086	$C_{12}H_{12}N_1O_1^+$	unknown	0.0004	0.0004	0.0001
187.059	$C_8H_{11}O_5^+$	oxidation products of ethylbenzene	0.0040	0.0041	0.0016
187.095	$C_9H_{15}O_4^+$	oxidized molecules of monoterpenes	0.0005	0.0005	0.0001
188.062	$C_{11}H_{10}N_1O_2^+$	unknown	0.0006	0.0006	0.0002
189.039	$C_7H_9O_6^+$	fragment of $C_7H_{11}O_6^+$	0.0006	0.0007	0.0005
189.076	$C_8H_{13}O_5^+$	oxidized molecules of monoterpenes	0.0026	0.0028	0.0007
191.053	$C_7H_{11}O_6^+$	oxidation product of benzene	0.0013	0.0015	0.0006
193.083	$C_{11}H_{13}O_3^+$	unknown	0.0004	0.0004	0.0001
195.068	$C_{10}H_{11}O_4^+$	dimethyl 1,3-benzenedicarboxylate	0.0004	0.0004	0.0002
197.080	$C_{10}H_{13}O_4^+$	fragments of $C_{10}H_{15}O_4^+$	0.0013	0.0012	0.0004
199.051	$C_9H_{11}O_5^+$	unknown	0.0008	0.0009	0.0005
199.089	$C_{10}H_{15}O_4^+$	oxidized molecules of monoterpenes	0.0016	0.0015	0.0004
200.093	$C_9H_{14}N_1O_4^+$	fragments of monoterpene-derived organic nitrates $C_9H_{15}N_1O_{5\text{–}7}$	0.0004	0.0004	0.0001
201.077	$C_9H_{13}O_5^+$	unknown	0.0018	0.0018	0.0006
202.084	$C_{12}H_{12}N_1O_2^+$	unknown	0.0004	0.0004	0.0001
205.074	$C_8H_{13}O_6^+$	oxidized molecules of monoterpenes	0.0006	0.0007	0.0004
213.076	$C_{10}H_{13}O_5^+$	fragments of $C_{10}H_{15}O_5^+$	0.0008	0.0008	0.0004
215.051	$C_9H_{11}O_6^+$	unknown	0.0004	0.0005	0.0003
215.094	$C_{10}H_{15}O_5^+$	oxidized molecules of monoterpenes	0.0009	0.0009	0.0004
216.088	$C_9H_{14}N_1O_5^+$	fragments of monoterpene-derived organic nitrates $C_9H_{15}N_1O_{5\text{–}7}$	0.0005	0.0006	0.0001
217.071	$C_9H_{13}O_6^+$	unknown	0.0008	0.0009	0.0004
229.074	$C_{10}H_{13}O_6^+$	unknown	0.0004	0.0004	0.0002

Table S7: List of 171 SVOC ions and average (Ave) mixing ratios with standard deviation (Std) as well as measurement detection limit (MDL) included in the winter time semi volatile organic aerosol PMF analysis.

m/z	**Tentative ion**	**Tentative compound**	**Ave (µg m^{-3})**	**Std (µg m^{-3})**	**MDL (µg m^{-3})**
69.031	$C_4H_5O_1^+$	furan	0.0013	0.0012	0.0007
71.046	$C_4H_7O_1^+$	methyl vinyl ketone + methacrolein	0.0005	0.0005	0.0003
73.025	$C_3H_5O_2^+$	methylglyoxal/acrylic acid	0.0008	0.0008	0.0006
83.047	$C_5H_7O_1^+$	methyl furan	0.0005	0.0004	0.0002
84.047	$C_4H_6N_1O_1^+$	5-methyl-isoxazole	0.0002	0.0002	0.0002
85.026	$C_4H_5O_2^+$	furanone	0.0041	0.0037	0.0027
86.030	$C_3H_4N_1O_2^+$	cyano acetic acid	0.0003	0.0002	0.0002
87.042	$C_4H_7O_2^+$	2,3-butanedione	0.0014	0.0016	0.0010
89.021	$C_3H_5O_3^+$	butyric acid	0.0004	0.0004	0.0001
90.018	$C_2H_4N_1O_3^+$	oxamic acid	0.0006	0.0006	0.0005
93.070	$C_7H_9^+$	toluene	0.0005	0.0006	0.0003
95.046	$C_6H_7O_1^+$	phenol	0.0005	0.0004	0.0003
95.083	$C_7H_{11}^+$	fragment of monoterpenes	0.0003	0.0003	0.0002
96.049	$C_5H_6N_1O_1^+$	4-pyridinol;	0.0001	0.0001	0.0001
97.026	$C_5H_5O_2^+$	furfural	0.0023	0.0017	0.0014
97.062	$C_6H_9O_1^+$	2-ethylfuran/2,5-dimethylfuran	0.0003	0.0003	0.0002
98.024	$C_4H_4N_1O_2^+$	1h-pyrrole-2,5-dione	0.0002	0.0002	0.0001
98.060	$C_5H_8N_1O_1^+$	4,5-dimethyl- oxazole	0.0001	0.0001	0.0002
99.042	$C_5H_7O_2^+$	furanone	0.0015	0.0012	0.0009
99.079	$C_6H_{11}O_1^+$	cyclohexanone	0.0002	0.0002	0.0001
100.040	$C_4H_6N_1O_2^+$	succinimide	0.0002	0.0002	0.0001
100.076	$C_5H_{10}N_1O_1^+$	2-piperidinone	0.0002	0.0001	0.0001
101.021	$C_4H_5O_3^+$	pentanedione	0.0022	0.0025	0.0018
101.058	$C_5H_9O_2^+$	C_5-hydroxy carbonyl (ISOPOOH conversion product)	0.0006	0.0006	0.0004
102.019	$C_3H_4N_1O_3^+$	methyl isocyanatoformate	0.0002	0.0002	0.0001
103.039	$C_4H_7O_3^+$	propylene carbonate	0.0007	0.0006	0.0002
104.035	$C_3H_6N_1O_3^+$	1-nitro-2-propanone	0.0002	0.0001	0.0001
105.018	$C_3H_5O_4^+$	propanedioic acid	0.0015	0.0015	0.0005
107.074	$C_4H_{11}O_3^+$	trimethoxy methane	0.0007	0.0012	0.0006
108.086	$C_7H_{10}N_1^+$	3-ethyl-pyridine; 2,3-dimethyl-pyridine	0.0002	0.0003	0.0001
109.099	$C_8H_{13}^+$	fragment of sesquiterpenes	0.0005	0.0006	0.0002
111.079	$C_7H_{11}O_1^+$	heptadienal	0.0002	0.0002	0.0001
113.024	$C_5H_5O_3^+$	furoic acid	0.0012	0.0013	0.0003
113.057	$C_6H_9O_2^+$	hexendione	0.0007	0.0006	0.0003
114.056	$C_5H_8N_1O_2$+	ethyl cyanoacetate	0.0001	0.0001	0.0001
115.036	$C_5H_7O_3^+$	pentanetrione	0.0015	0.0014	0.0010
115.074	$C_6H_{11}O_2^+$	2,5-hexanedione/ethyl-2-butenoate	0.0005	0.0005	0.0002
116.035	$C_4H_6N_1O_3^+$	3-methyl-2,5-oxazolidine-dione	0.0002	0.0002	0.0002
117.017	$C_4H_5O_4^+$	maleic acid	0.0007	0.0004	0.0005
117.051	$C_5H_9O_3^+$	oxidized molecules of Isoprene	0.0005	0.0004	0.0006
119.033	$C_4H_7O_4^+$	oxidized molecules of Isoprene	0.0009	0.0008	0.0004
123.051	$C_7H_7O_2^+$	benzoic acid	0.0006	0.0005	0.0017
123.077	$C_8H_{11}O_1^+$	phenethyl alcohol; ethylphenol	0.0002	0.0002	0.0003
125.024	$C_6H_5O_3^+$	2,5-furandicarboxaldehyde	0.0007	0.0005	0.0007
125.059	$C_7H_9O_2^+$	guaiacol + dihydroxy toluene	0.0009	0.0008	0.0009
125.095	$C_8H_{13}O_1^+$	oxidized molecules of monoterpenes	0.0002	0.0002	0.0001
127.038	$C_6H_7O_3^+$	methyl 2-furoate	0.0024	0.0019	0.0010
127.077	$C_7H_{11}O_2^+$	oxidized molecules of monoterpene (a-terpinene)	0.0006	0.0005	0.0013
128.037	$C_5H_6N_1O_3^+$	n-methylolmaleimide	0.0003	0.0002	0.0002
129.017	$C_5H_5O_4^+$	methanetetracarbaldehyde	0.0006	0.0005	0.0005
129.054	$C_6H_9O_3^+$	sotolone; 2,5-di-(hydroxymethyl)furan	0.0008	0.0007	0.0008

130.054	$C_5H_8N_1O_3^+$	dimethadione	0.0002	0.0002	0.0001
131.033	$C_5H_7O_4^+$	methylene butanedioic acid	0.0012	0.0010	0.0005
131.071	$C_6H_{11}O_3^+$	ethyl acetoacetate; (e)-3-methoxy-2-butenoic	0.0002	0.0001	0.0003
132.029	$C_4H_6N_1O_4^+$	iminoaspartic acid	0.0001	0.0001	0.0001
133.016	$C_4H_5O_5^+$	oxalacetic acid	0.0002	0.0002	0.0002
133.049	$C_5H_9O_4^+$	oxidized molecules of Isoprene	0.0008	0.0007	0.0004
133.098	$C_{10}H_{13}^+$	cymenene	0.0001	0.0002	0.0003
135.029	$C_8H_7O_2^+$	malic acid	0.0002	0.0002	0.0002
135.109	$C_6H_{15}O_3^+$	dimethyl carbitol	0.0006	0.0008	0.0002
137.057	$C_8H_9O_2^+$	methylbenzoic acid	0.0004	0.0004	0.0004
137.092	$C_9H_{13}O_1^+$	p-cumenol	0.0002	0.0002	0.0002
139.037	$C_7H_7O_3^+$	salicylic acid	0.0006	0.0006	0.0019
139.073	$C_8H_{11}O_2^+$	oxidation products of ethylbenzene	0.0004	0.0004	0.0006
139.111	$C_9H_{15}O_1^+$	nopinone	0.0001	0.0001	0.0003
140.038	$C_6H_6N_1O_3^+$	2-nitrophenol	0.0002	0.0002	0.0002
141.053	$C_7H_9O_3^+$	dicarbonyl epoxide	0.0015	0.0012	0.0009
141.090	$C_8H_{13}O_2^+$	oxidized molecules of monoterpenes	0.0002	0.0003	0.0007
142.059	$C_6H_8N_1O_3^+$	methyl acetylcyanoacetate	0.0002	0.0002	0.0001
143.042	$C_6H_7O_4^+$	hydroxy maltol	0.0008	0.0007	0.0004
143.075	$C_7H_{11}O_3^+$	oxidized molecules of monoterpene (Terpinolene)	0.0005	0.0004	0.0006
144.033	$C_5H_6N_1O_4^+$	5-nitro-2-furanmethanol	0.0002	0.0001	0.0001
145.049	$C_6H_9O_4^+$	acetate furanol; dehydrated levoglucosan	0.0024	0.0020	0.0006
146.051	$C_5H_8N_1O_4^+$	pyruvylglycine	0.0002	0.0002	0.0001
147.028	$C_5H_7O_5^+$	2-oxopentanedioic acid	0.0004	0.0003	0.0002
147.064	$C_6H_{11}O_4^+$	hexanedioic acid	0.0003	0.0003	0.0002
149.024	$C_8H_5O_3^+$	phthalic anhydride	0.0004	0.0004	0.0002
149.063	$C_9H_9O_2^+$	trans-cinnamic acid	0.0005	0.0004	0.0002
149.096	$C10H13O1^+$	estragole; anethole	0.0001	0.0001	0.0002
151.034	$C_8H_7O_3^+$	piperonal	0.0002	0.0002	0.0002
151.070	$C_9H_{11}O_2^+$	benzyl acetate	0.0004	0.0003	0.0004
151.111	$C_{10}H_{15}O_1^+$	oxidized molecules of monoterpenes	0.0008	0.0011	0.0001
152.115	$C_9H_{14}N_1O_1^+$	3-dimethylaminoanisole	0.0001	0.0002	0.0001
153.052	$C_8H_9O_3^+$	methyl salicylate; vanillin	0.0005	0.0004	0.0003
153.089	$C_9H_{13}O_2^+$	4-ethyl guiacol	0.0008	0.0008	0.0010
153.126	$C_{10}H_{17}O_1^+$	oxidized molecules of monoterpenes	0.0002	0.0003	0.0002
154.050	$C_7H_8N_1O_3^+$	4-nitroanisole; 2-nitrobenzyl alcohol	0.0001	0.0001	0.0001
155.032	$C_7H_7O_4^+$	β-resorcylic acid	0.0004	0.0003	0.0002
155.071	$C_8H_{11}O_3^+$	syringol	0.0008	0.0006	0.0008
155.106	$C_9H_{15}O_2^+$	oxidized molecules of monoterpenes	0.0002	0.0002	0.0006
156.033	$C_6H_6N_1O_4^+$	4-nitrocatechol	0.0008	0.0012	0.0001
157.049	$C_7H_9O_4^+$	1-(5-methyl-2-furanyl)-2-	0.0010	0.0009	0.0007
157.096	$C_8H_{13}O_3^+$	oxidized molecules of monoterpenes	0.0003	0.0002	0.0004
158.051	$C_6H_8N_1O_4^+$	1-(acetoxy)pyrrolidine-2,5-	0.0002	0.0002	0.0001
159.028	$C_6H_7O_5^+$	tricarballylic anhydride	0.0004	0.0004	0.0002
159.067	$C_7H_{11}O_4^+$	dimethyl 2-	0.0005	0.0004	0.0001
161.044	$C_6H_9O_5^+$	2-oxoadipic acid	0.0006	0.0006	0.0002
163.039	$C_9H_7O_3^+$	7-hydroxycoumarin	0.0003	0.0003	0.0003
163.058	$C_6H_{11}O_5^+$	levoglucosan	0.0005	0.0005	0.0003
165.089	$C_{10}H_{13}O_2^+$	methyl phenylpropionate; β-phenethyl acetate	0.0005	0.0005	0.0002
166.050	$C_8H_8N_1O_3^+$	3-nitroacetophenone	0.0001	0.0001	0.0000
166.086	$C_9H_{12}N_1O_2^+$	benzocaine	0.0001	0.0001	0.0000
167.035	$C_8H_7O_4^+$	isophthalic acid	0.0003	0.0003	0.0002
167.065	$C_9H_{11}O_3^+$	acetoguaiacon	0.0004	0.0003	0.0004
167.105	$C_{10}H_{15}O_2^+$	oxidized molecules of monoterpenes	0.0006	0.0006	0.0005
169.040	$C_8H_9O_4^+$	vanillic acid	0.0004	0.0004	0.0004

169.090	$C_9H_{13}O_3^+$	1,2,4-trimethoxybenzene; methylsyringol	0.0008	0.0006	0.0006
169.124	$C_{10}H_{17}O_2^+$	oxidized molecules of monoterpenes	0.0005	0.0007	0.0003
170.045	$C_7H_8N_1O_4^+$	4-nitroguaiacol	0.0005	0.0008	0.0001
171.068	$C_8H_{11}O_4^+$	oxidation products of ethylbenzene	0.0008	0.0006	0.0005
171.110	$C_9H_{15}O_3^+$	oxidized molecules of monoterpenes	0.0004	0.0003	0.0003
173.041	$C_7H_9O_5^+$	oxidation products of guaiacol	0.0005	0.0005	0.0003
173.077	$C_8H_{13}O_4^+$	oxidized molecules of monoterpenes	0.0004	0.0003	0.0003
174.045	$C_6H_8N_1O_5^+$	succinimide glycolic acid	0.0001	0.0001	0.0001
175.060	$C_7H_{11}O_5^+$	shikimic acid	0.0006	0.0005	0.0001
177.039	$C_6H_8O_6^+$	vitamin C	0.0004	0.0003	0.0002
178.050	$C_9H_8N_1O_3^+$	4-nitrocinnamaldehyde	0.0001	0.0001	0.0001
179.034	$C_9H_7O_4^+$	ninhydrin	0.0003	0.0003	0.0002
179.092	$C_7H_{15}O_5^+$	bis(2-methoxyethyl)	0.0003	0.0003	0.0001
181.083	$C_{10}H_{13}O_3^+$	anisyl acetate	0.0005	0.0004	0.0003
182.045	$C_8H_8N_1O_4^+$	methyl 3-nitrobenzoate	0.0001	0.0001	0.0001
183.063	$C_9H_{11}O_4^+$	unknown	0.0006	0.0005	0.0004
183.100	$C_{10}H_{15}O_3^+$	oxidized molecules of monoterpenes	0.0004	0.0004	0.0003
184.061	$C_7H_6N_1O_5^+$	unknown	0.0002	0.0003	0.0001
185.045	$C_8H_9O_5^+$	unknown	0.0003	0.0003	0.0002
185.080	$C_9H_{13}O_4^+$	fragments of the $C_9H_{14}O_n$ series	0.0007	0.0006	0.0004
185.117	$C_{10}H_{17}O_3^+$	oxidized molecules of monoterpenes	0.0002	0.0003	0.0003
186.040	$C_7H_8N_1O_5^+$	unknown	0.0002	0.0002	0.0001
186.086	$C_{12}H_{12}N_1O_1^+$	unknown	0.0001	0.0001	0.0001
187.059	$C_8H_{11}O_5^+$	oxidation products of ethylbenzene	0.0007	0.0007	0.0003
187.097	$C_9H_{15}O_4^+$	pinic acid	0.0003	0.0002	0.0002
188.055	$C_7H_{10}N_1O_5^+$	unknown	0.0001	0.0001	0.0000
189.055	$C_{11}H_9O_3^+$	unknown	0.0003	0.0002	0.0002
189.076	$C_8H_{13}O_5^+$	oxidized molecules of monoterpenes	0.0003	0.0002	0.0002
190.050	$C_{10}H_8N_1O_3^+$	unknown	0.0001	0.0001	0.0000
191.092	$C_{10}H_{23}O_3^+$	unknown	0.0003	0.0003	0.0003
193.034	$C_6H_9O_7^+$	citric cid	0.0002	0.0002	0.0001
194.045	$C_9H_8N_1O_4^+$	unknown	0.0002	0.0002	0.0001
195.068	$C_{10}H_{11}O_4^+$	dimethyl 1,3-benzenedicarboxylate	0.0001	0.0001	0.0001
197.080	$C_{10}H_{13}O_4^+$	fragments of $C_{10}H_{15}O_4^+$	0.0002	0.0002	0.0003
199.051	$C_9H_{11}O_5^+$	unknown	0.0001	0.0002	0.0001
199.089	$C_{10}H_{15}O_4^+$	oxidized molecules of monoterpenes	0.0005	0.0004	0.0002
200.055	$C_8H_{10}N_1O_5^+$	unknown	0.0004	0.0004	0.0001
200.093	$C_9H_{14}N_1O_4^+$	fragments of monoterpene-derived organic nitrates $C_9H_{15}N_1O_{5\text{–}7}$	0.0004	0.0003	0.0001
201.055	$C_8H_9O_6^+$	unknown	0.0001	0.0002	0.0002
201.112	$C_{10}H_{17}O_4^+$	oxidized molecules of monoterpenes	0.0001	0.0001	0.0004
207.050	$C_7H_{11}O_7^+$	unknown	0.0003	0.0003	0.0001
207.102	$C_{16}H_{15}^+$	unknown	0.0003	0.0003	0.0001
213.076	$C_{10}H_{13}O_5^+$	fragments of $C_{10}H_{15}O_5^+$	0.0002	0.0002	0.0002
215.092	$C_{14}H_{15}O_2^+$	unknown	0.0002	0.0002	0.0001
216.088	$C_9H_{14}N_1O_5^+$	fragments of monoterpene-derived organic nitrates $C_9H_{15}N_1O_{5\text{–}7}$	0.0003	0.0003	0.0001
217.071	$C_9H_{13}O_6^+$	unknown	0.0002	0.0002	0.0001
217.107	$C_{14}H_{17}O_2^+$	unknown	0.0003	0.0003	0.0001
219.081	$C_{16}H_{11}O_1^+$	unknown	0.0002	0.0002	0.0001
224.071	$C_{14}H_{10}N_1O_2^+$	unknown	0.0002	0.0002	0.0003
225.149	$C_{16}H_{17}O_1^+$	unknown	0.0003	0.0003	0.0001
231.102	$C_{14}H_{15}O_3^+$	unknown	0.0002	0.0001	0.0001
233.133	$C_{17}H_{13}O_1^+$	unknown	0.0003	0.0004	0.0001
235.076	$C_{16}H_{11}O_2^+$	unknown	0.0003	0.0003	0.0001
239.092	$C_{12}H_{15}O_5^+$	unknown	0.0001	0.0001	0.0003
239.237	$C_{16}H_{31}O_1^+$	fragments of $C_{16}H_{33}O_2^+$	0.0001	0.0001	0.0002
243.065	$C_{14}H_{11}O_4^+$	unknown	0.0002	0.0001	0.0001
247.112	$C_{18}H_{15}O_1^+$	unknown	0.0003	0.0004	0.0000

255.232	$C_{16}H_{31}O_2^+$	fragments of $C_{16}H_{33}O_2^+$	0.0001	0.0001	0.0004
257.248	$C_{16}H_{33}O_2^+$	corresponding to palmitic acid	0.0004	0.0006	0.0004
259.112	$C_{19}H_{15}O_1^+$	unknown	0.0001	0.0002	0.0001
275.258	$C_{16}H_{35}O_3^+$	$C_{16}H_{33}O_2(H_2O)^+$	0.0004	0.0006	0.0005
281.248	$C_{18}H_{33}O_2^+$	fragments of $C_{18}H_{35}O_2^+$	0.0001	0.0001	0.0001
283.263	$C_{18}H_{35}O_2^+$	oleic acid; fragment of stearic acid (fatty acid)	0.0007	0.0010	0.0002
285.279	$C_{18}H_{37}O_2^+$	stearic acid (fatty acid)	0.0002	0.0003	0.0002

The PMF factor selection for summertime semi-volatile organic aerosol (SVOA) measurements followed the same evaluation procedure as described for the VOC datasets. The decrease in Q/Qexp becomes gradual beyond five factors (Fig. S11a), indicating limited additional improvement with increasing factor number. The selected five-factor solution provides a stable and physically interpretable representation of the dataset, supported by scaled residuals centered near zero (Fig. S11b).

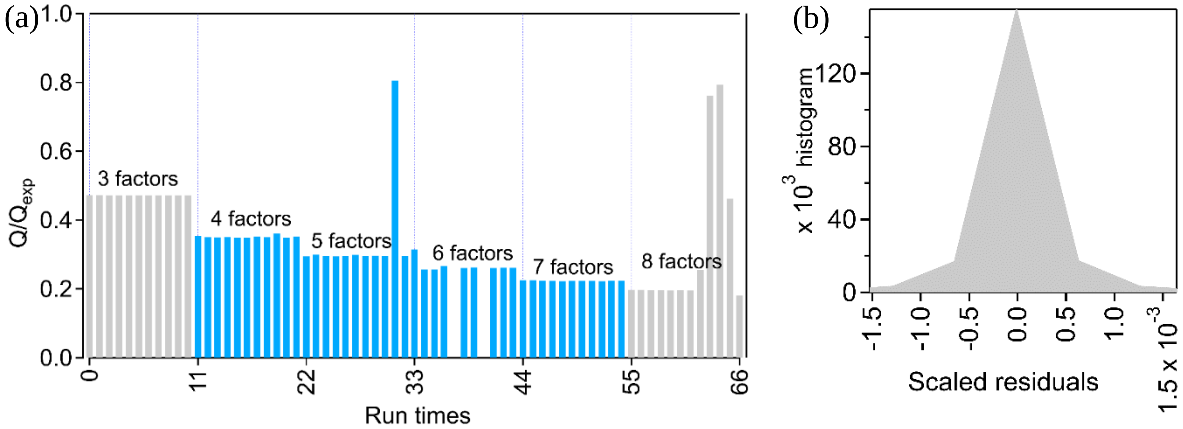

Figure S11. (a) Q/Qexp values obtained from multiple PMF runs for Summer semi-volatile organic aerosol measurements. (b) Histogram of scaled residuals (eij/σij) for the selected PMF solution (five factors), showing a distribution centered near zero and indicating an adequate model fit.

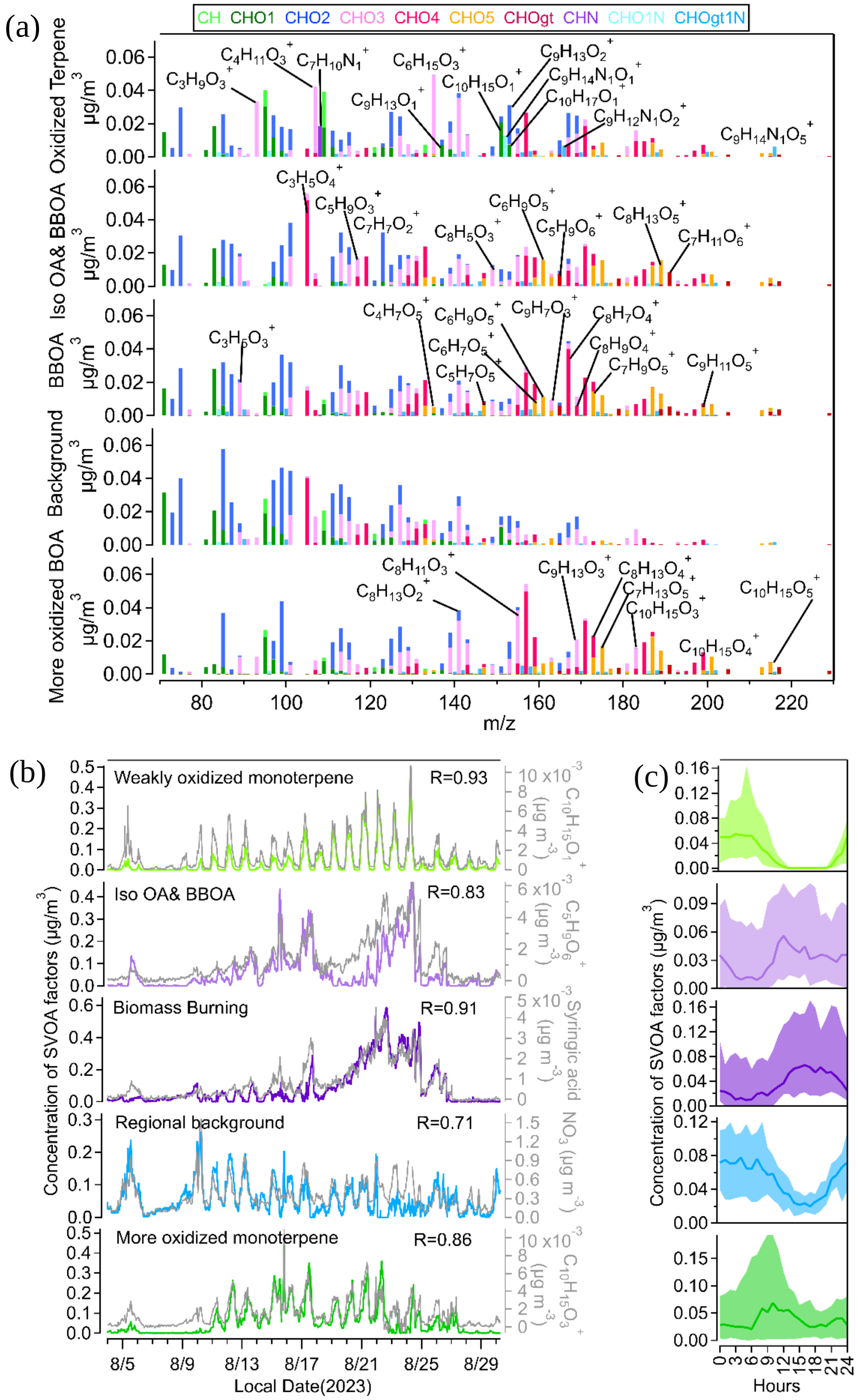

Figure S12 Semi-volatile OA (SVOA) apportionment in summer. (a) Normalized SVOA factor spectra from PMF analysis on the m/z peaks in summer time; (b) Time series of SVOA factors including oxidized terpene, iso OA & BBOA, BBOA, background, and more oxidized BOA; (c) Median diurnal variations in SVOA factors during summer.

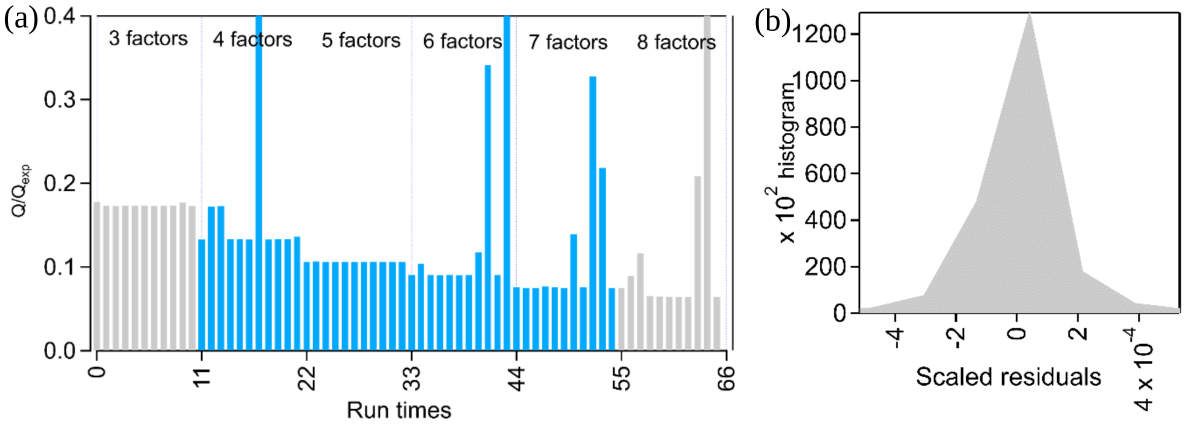

Figure S13. (a) Q/Qexp values obtained from multiple PMF runs for March semi-volatile organic aerosol measurements. (b) Histogram of scaled residuals (eij/σij) for the selected PMF solution (five factors), showing a distribution centered near zero and indicating an adequate model fit.

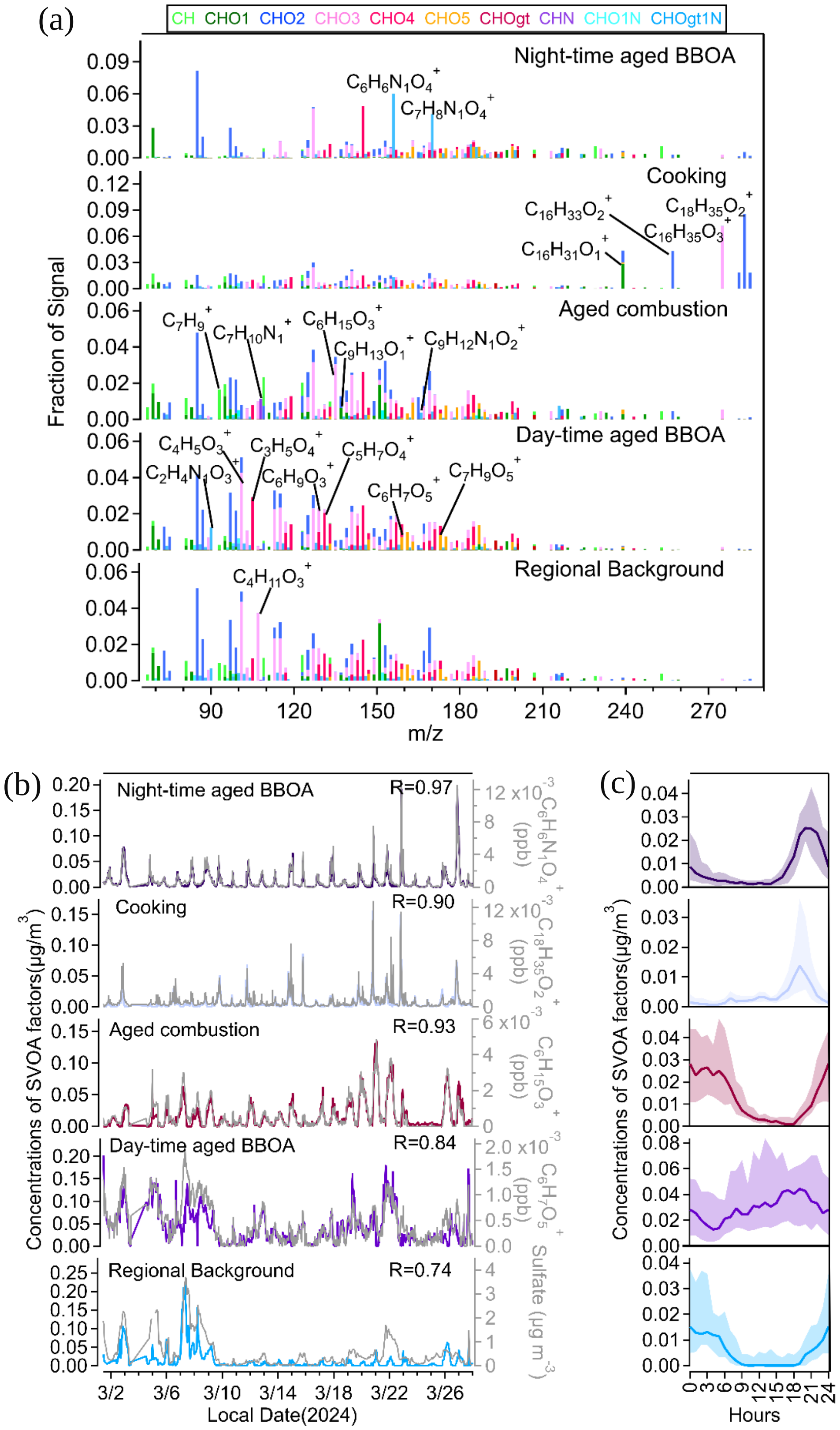

Figure S14 (a) Normalized SVOA factor spectra from PMF analysis on the m/z peaks in winter time; (b) Time series of SVOA factors including night-time aged BBOA, cooking, aged combustion, day-time aged BBOA, and regional background OA; and (c) Median diurnal variations in SVOA factors during winter time

Table S8: Major SVOC mass peaks from Charon-PTR-MS correlated to the five semi volatile organic aerosol related source factors in summer

Mass peak (m/z)	**Tentative ion**	**Tentative compound**	**PMF factor related**	**Correlation to PMF factor**
108.08	$C_7H_{10}N_1^+$	3-ethyl-pyridine	Weakly oxidized monoterpene	0.99
152.11	$C_9H_{14}N_1O_1^+$	alcohols or aldehydes with nitrogen groups		0.98
166.09	$C_9H_{12}N_1O_2^+$	alcohols or aldehydes with nitrogen groups		0.93
135.10	$C_6H_{15}O_3^+$	dimethyl carbitol		0.93
107.07	$C_4H_{11}O_3^+$	trimethoxy methane		0.93
151.11	$C_{10}H_{15}O_1^+$	oxidized molecules of monoterpenes		0.93
216.09	$C_9H_{14}N_1O_5^+$	fragments of monoterpene-derived organic nitrates		0.91
137.10	$C_9H_{13}O_1^+$	p-cumenol		0.91
93.06	$C_3H_9O_3^+$	1,2,3-propanetriol		0.90
153.13	$C_{10}H_{17}O_1^+$	oxidized molecules of monoterpenes		0.89
153.09	$C_9H_{13}O_2^+$	4-ethyl guiacol		0.85
123.04	$C_7H_7O_2^+$	benzoic acid	Oxidized Isoprene & BBOA	0.95
105.02	$C_3H_5O_4^+$	originates from the oxidation of ISOPOOH		0.85
191.06	$C_7H_{11}O_6^+$	oxidation of o-cresol		0.84
161.05	$C_6H_9O_5^+$	oxidation product of benzene		0.84
165.04	$C_5H_9O_6^+$	oxidized molecules of isoprene		0.83
189.08	$C_8H_{13}O_5^+$	oxidized molecules of monoterpenes		0.83
149.02	$C_8H_5O_3^+$	phthalic anhydride		0.83
117.06	$C_5H_9O_3^+$	oxidized molecules of isoprene		0.82
167.03	$C_8H_7O_4^+$	fragment of vanillic acid	BBOA	0.96
163.04	$C_9H_7O_3^+$	fragment of syringic acid		0.95
199.06	$C_9H_{11}O_5^+$	syringic acid		0.91
159.03	$C_6H_7O_5^+$	oxidation products of guaiacol		0.90
147.03	$C_5H_7O_5^+$	2-oxopentanedioic acid		0.89
189.04	$C_7H_9O_6^+$	oxidation of o-cresol		0.88
169.05	$C_8H_9O_4^+$	vanillic acid		0.88
89.02	$C_3H_5O_3^+$	pyruvic acid		0.87
173.05	$C_7H_9O_5^+$	oxidation products of guaiacol		0.86
135.03	$C_4H_7O_5^+$	pentanedioic acid		0.86
161.04	$C_6H_9O_5^+$	2-oxoadipic acid		0.85
	AMS-NO_3	Nitrate	Regional background	0.71
183.10	$C_{10}H_{15}O_3^+$	oxidized molecules of monoterpenes	More oxidized monoterpene	0.86
199.10	$C_{10}H_{15}O_4^+$	oxidized molecules of monoterpenes		0.85

215.09	$C_{10}H_{15}O_5^+$	oxidized molecules of monoterpenes	0.84
155.07	$C_8H_{11}O_3^+$	syringol	0.83
169.09	$C_9H_{13}O_3^+$	Methylsyringol	0.81
141.09	$C_8H_{13}O_2^+$	oxidized molecules of monoterpenes	0.81
173.08	$C_8H_{13}O_4^+$	oxidized molecules of monoterpenes	0.80
177.08	$C_7H_{13}O_5^+$	diacetin	0.79

Table S9 Major SVOC mass peaks from Charon-PTR-MS correlated with the five semi volatile organic aerosol factors in winter time

Mass peak (m/z)	Tentative ion	Tentative compound	PMF factor related	Correlation to PMF factor
156.03	$C_6H_6N_1O_4^+$	4-nitrocatechol	Night-time aged BBOA	0.97
170.05	$C_7H_8N_1O_4^+$	4-nitroguaiacol		0.97
186.04	$C_7H_8N_1O_5^+$	unknown		0.87
184.02	$C_7H_6N_1O_5^+$	fragments of $C_7H_8N_1O_5^+$		0.85
201.04	$C_8H_9O_6^+$	unknown		0.75
198.05	$C_9H_{10}O_5^+$	syringic acid		0.70
283.26	$C_{18}H_{35}O_2^+$	oleic acid	Cooking	0.90
247.11	$C_{18}H_{15}O_1^+$	unknown		0.88
275.26	$C_{16}H_{35}O_3^+$	$C_{16}H_{33}O_2(H_2O)^+$		0.88
285.28	$C_{18}H_{37}O_2^+$	stearic acid (fatty acid)		0.73
257.25	$C_{16}H_{33}O_2^+$	corresponding to palmitic acid		0.54
239.24	$C_{16}H_{31}O_1^+$	fragments of $C_{16}H_{33}O_2^+$		0.54
108.08	$C_7H_{10}N_1^+$	3-ethyl-pyridine; 2,3-dimethyl-pyridine	Aged combustion	0.94
135.10	$C_6H_{15}O_3^+$	dimethyl carbitol		0.93
153.13	$C_{10}H_{17}O_1^+$	oxidized molecules of monoterpenes		0.86
137.10	$C_9H_{13}O_1^+$	p-cumenol		0.82
166.09	$C_9H_{12}N_1O_2^+$	benzocaine		0.80
93.07	$C_7H_9^+$	toluene		0.79
105.02	$C_3H_5O_4^+$	propanedioic acid	Day-time aged BBOA	0.88
131.03	$C_5H_7O_4^+$	methylene butanedioic acid		0.87
90.02	$C_2H_4N_1O_3^+$	oxamic acid		0.86
132.03	$C_4H_6N_1O_4^+$	iminoaspartic acid		0.85
129.06	$C_6H_9O_3^+$	sotolone; 2,5-di-(hydroxymethyl)furan		0.84
89.02	$C_3H_5O_3^+$	butyric acid		0.84
101.02	$C_4H_5O_3^+$	pentanedione		0.84
143.03	$C_6H_7O_4^+$	hydroxy maltol		0.84
147.03	$C_5H_7O_5^+$	2-oxopentanedioic acid		0.83
102.02	$C_3H_4N_1O_3^+$	methyl isocyanatoformate		0.83
116.03	$C_4H_6N_1O_3^+$	3-methyl-2,5-oxazolidine-dione		0.83
159.03	$C_6H_7O_5^+$	tricarballylic anhydride		0.83
129.02	$C_5H_5O_4^+$	methanetetracarbaldehyde		0.83
173.05	$C_7H_9O_5^+$	oxidation products of guaiacol		0.83
103.04	$C_4H_7O_3^+$	propylene carbonate		0.82

161.04	$C_6H_9O_5^+$	2-oxoadipic acid		0.82
285.28	$C_{18}H_{37}O_2^+$	stearic acid (fatty acid)	Regional background	0.95
275.26	$C_{16}H_{35}O_3^+$	$C_{16}H_{33}O_2(H_2O)^+$		0.91
247.11	$C_{18}H_{15}O_1^+$	unknown		0.90
259.11	$C_{19}H_{15}O_1^+$	unknown		0.88
283.26	$C_{18}H_{35}O_2^+$	oleic acid; fragment of stearic acid (fatty acid)		0.88
107.07	$C_4H_{11}O_3^+$	trimethoxy methane		0.82
	AMS-SO_4^{2-}	sulfate		0.74
	AMS-NH_4^+	Ammonium		0.54

The selection of five OA factors was based on a combination of statistical diagnostics and physical interpretability. The Q/Qexp value decreased progressively with increasing factor number; however, the reduction became marginal after five factors, indicating limited additional improvement in model performance. To evaluate solution stability, we examined solutions with one fewer and one additional factor. When fewer factors were used, at least one factor lacked clear correlations with characteristic compound markers and did not exhibit a physically interpretable composition, suggesting factor merging and insufficient separation of sources. In contrast, solutions with more factors resulted in two factors showing highly similar time series and mass spectral profiles, indicating factor splitting. Furthermore, correlations between factor time series and individual compounds were evaluated for all tested solutions. The five-factor solution showed consistent associations between factors and representative marker compounds, supporting meaningful source attribution. Based on these combined criteria, five factors were selected as the optimal interpretable solution.

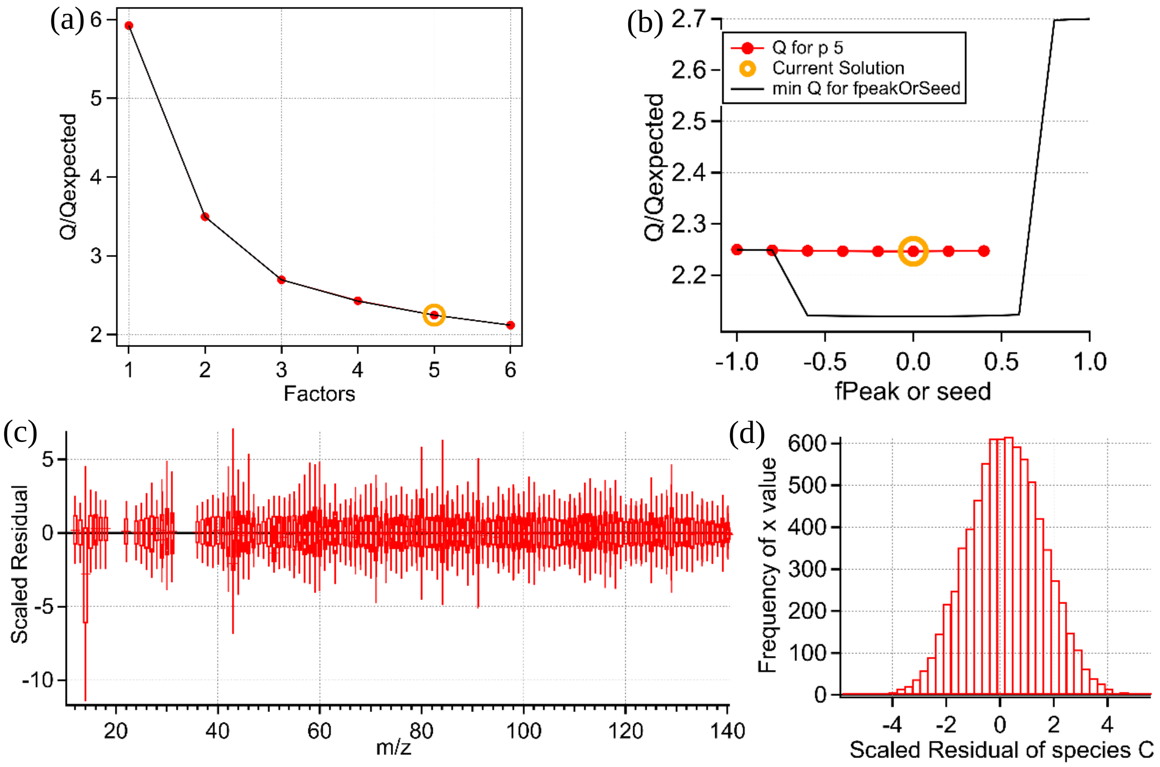

Figure S15 PMF diagnostic evaluation for the selected five-factor solution for summer OA measurements. (a) Q/Qexp as a function of factor number, showing diminishing improvement beyond five factors. (b) Sensitivity of Q/Qexp to the rotational parameter (fpeak), indicating a stable solution with minimal dependence on rotation. (c) Scaled residuals (eij/σij) for all species, demonstrating the absence of systematic structure across m/z values. (d) Histogram of scaled residuals for a representative species, showing an approximately symmetric distribution centered near zero and supporting an adequate model fit and uncertainty representation.

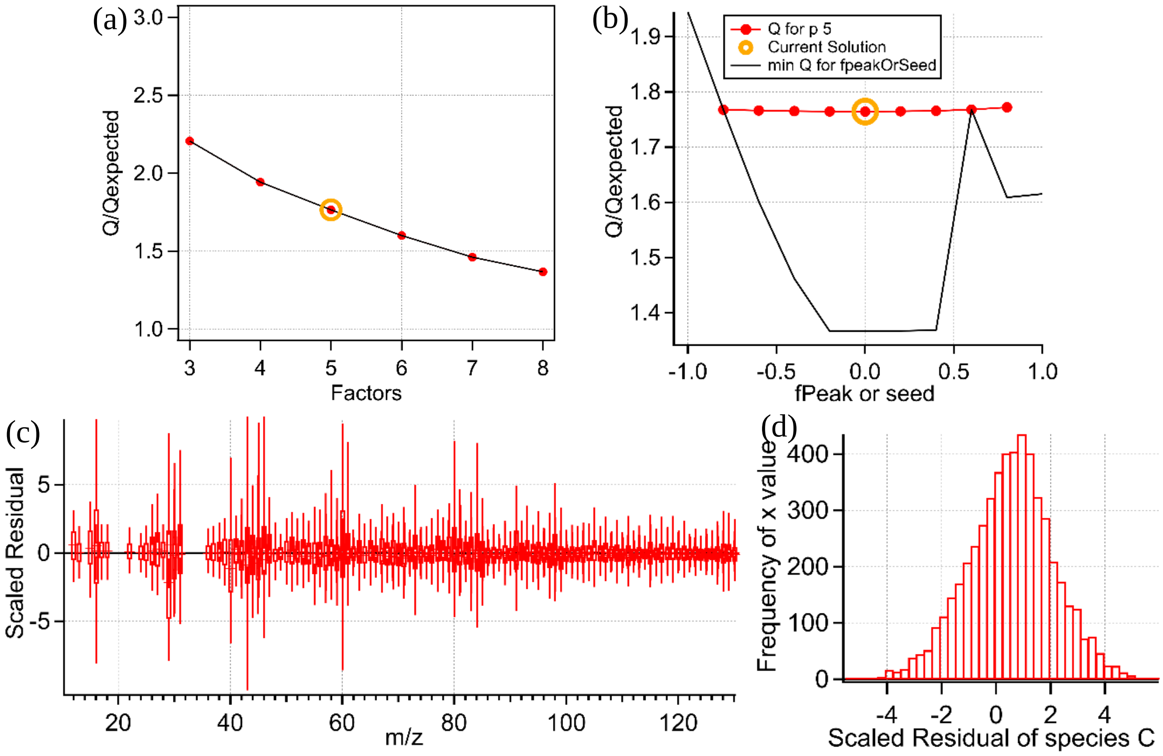

Figure S16. PMF diagnostic evaluation for the selected five-factor solution for March OA measurements. (a) Q/Qexp as a function of factor number. (b) Sensitivity of Q/Qexp to the rotational parameter (fpeak). (c) Scaled residuals (eij/σij) for all species. (d) Histogram of scaled residuals for a representative species, showing a distribution centered near zero and indicating an adequate model fit.

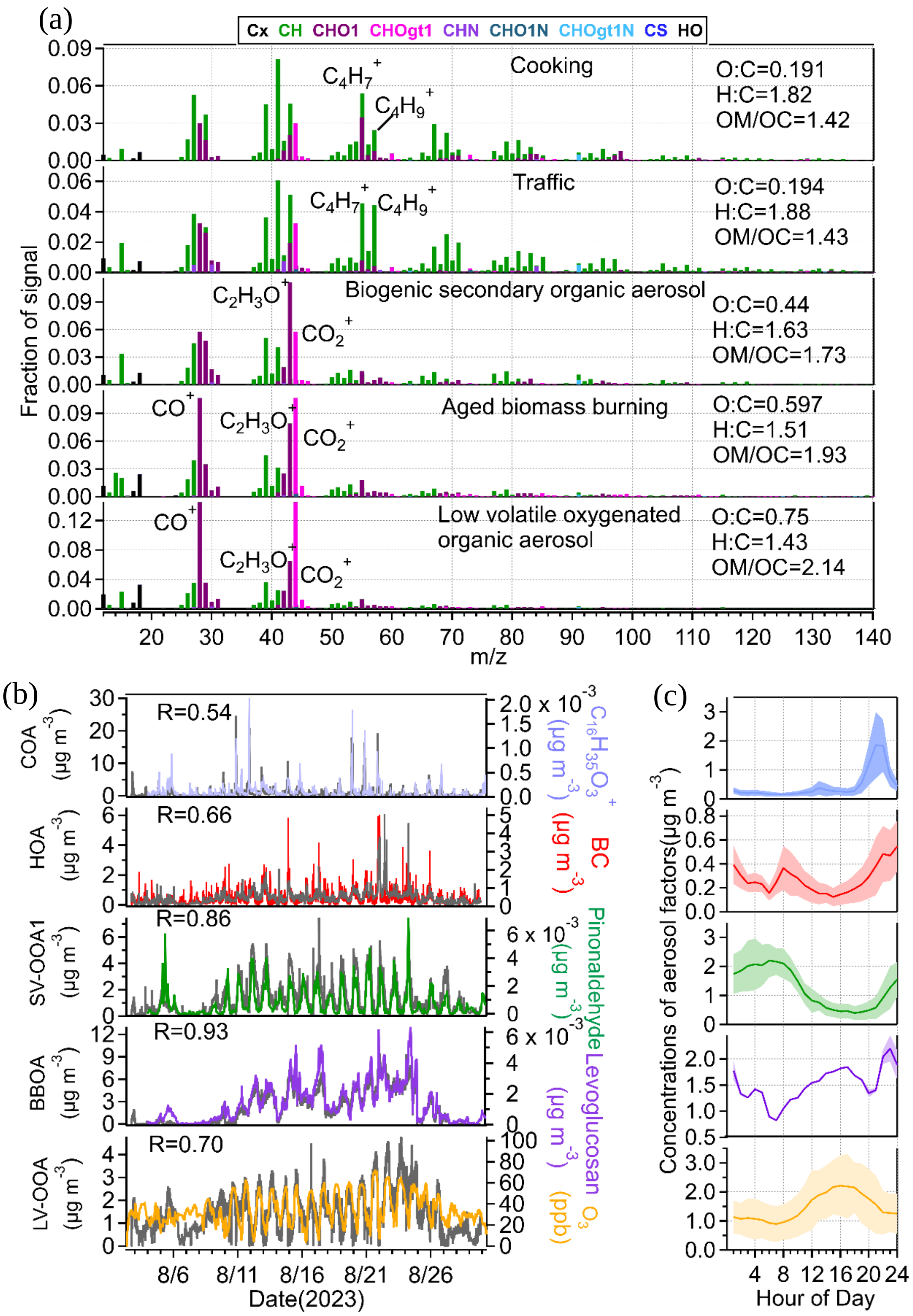

Figure S17 Source apportionment of OA in summer measured by the AMS. (a) Mass spectra of OA factors – cooking OA(COA), hydrocarbon-like OA (HOA), biogenic secondary OA(BOA), aged biomass burning aerosol (BBOA), and low-volatility oxygenated OA (LV-OOA). (b) Time series of OA factors and external tracer species (fatty acid, pinon aldehyde and levoglucosan measured by the PTR-MS, BC measured by the AE33, and O_3 measured by $O_3$41M). (c) Median diurnal variations in OA factors.

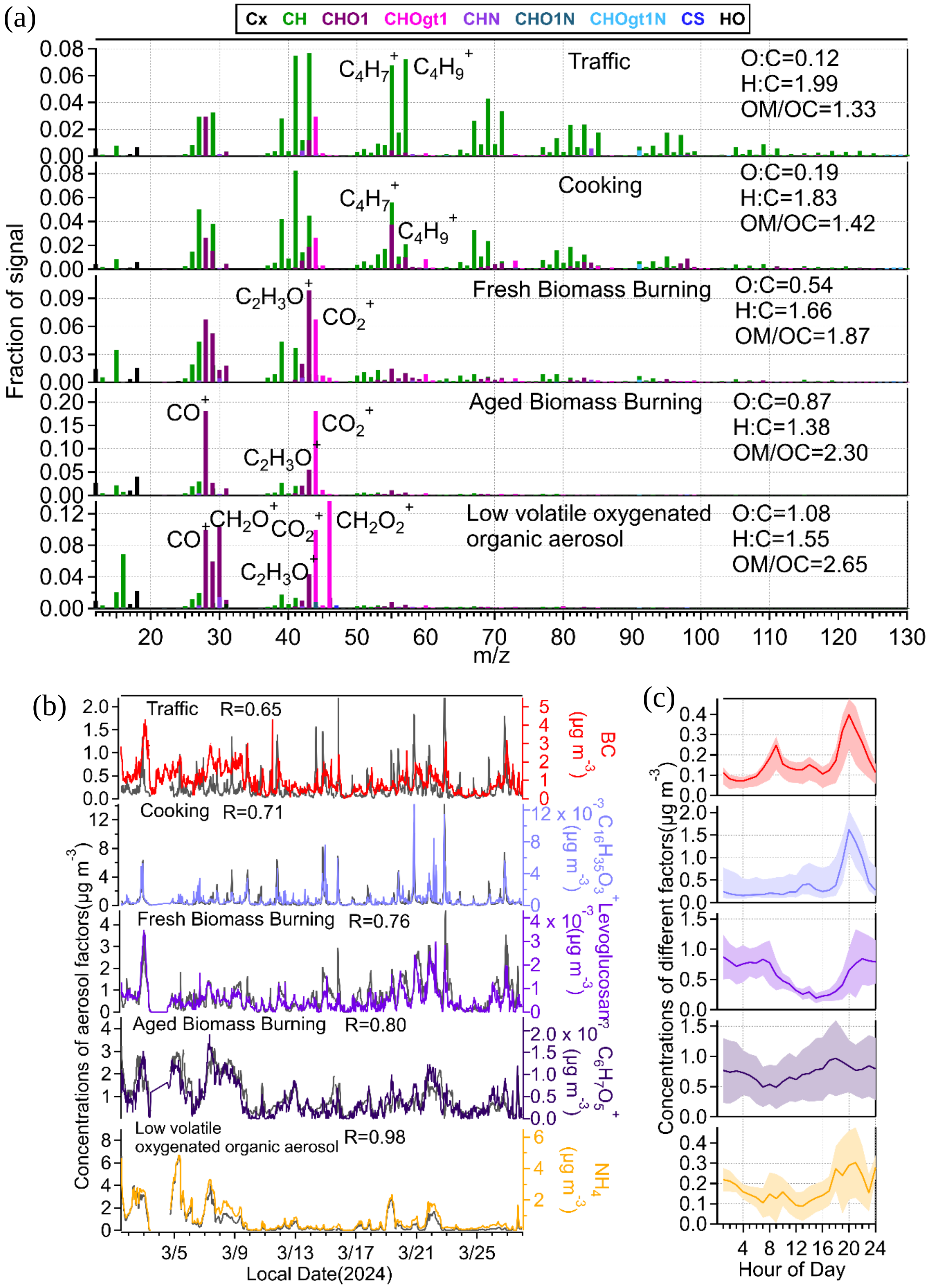

Figure S18 (a) Mass spectra of OA factors in winter– HOA, COA, fresh BBOA, aged BBOA, and LV-OOA. (b) Time series of OA factors and external tracer species (xylene, fatty acid, and $C_6H_7O_5^+$ measured by the PTR-MS, ammonia aerosol measured by AMS. (c) Median diurnal variations in OA factors.

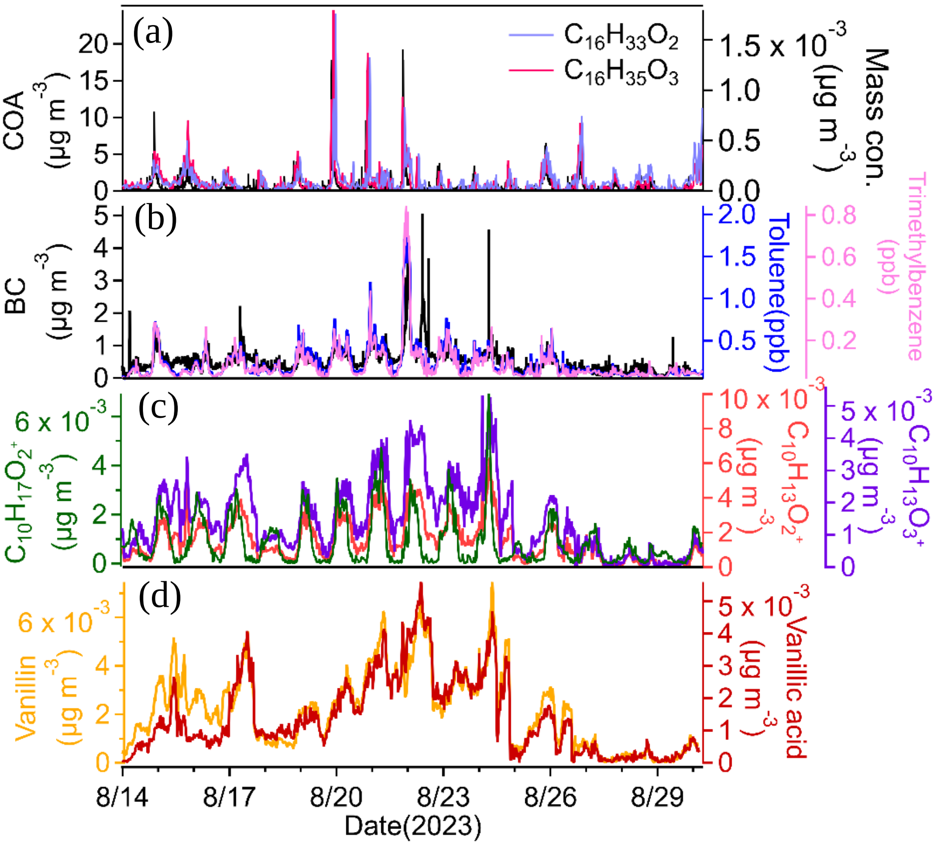

Figure S19 illustrates the time-series correlation of various tracers with the respective AMS factors: (a) COA tracers, including fatty acids ($C_{16}H_{33}O_2^+$ and $C_{16}H_{35}O_3^+$); (b) HOA tracers such as BC, toluene, and trimethylbenzene; (c) monoterpene oxidation products, including $C_{10}H_{17}O_2^+$, $C_{10}H_{13}O_2^+$, and $C_{10}H_{13}O_3^+$; and (d) BBOA tracers like vanillin and vanillic acid.

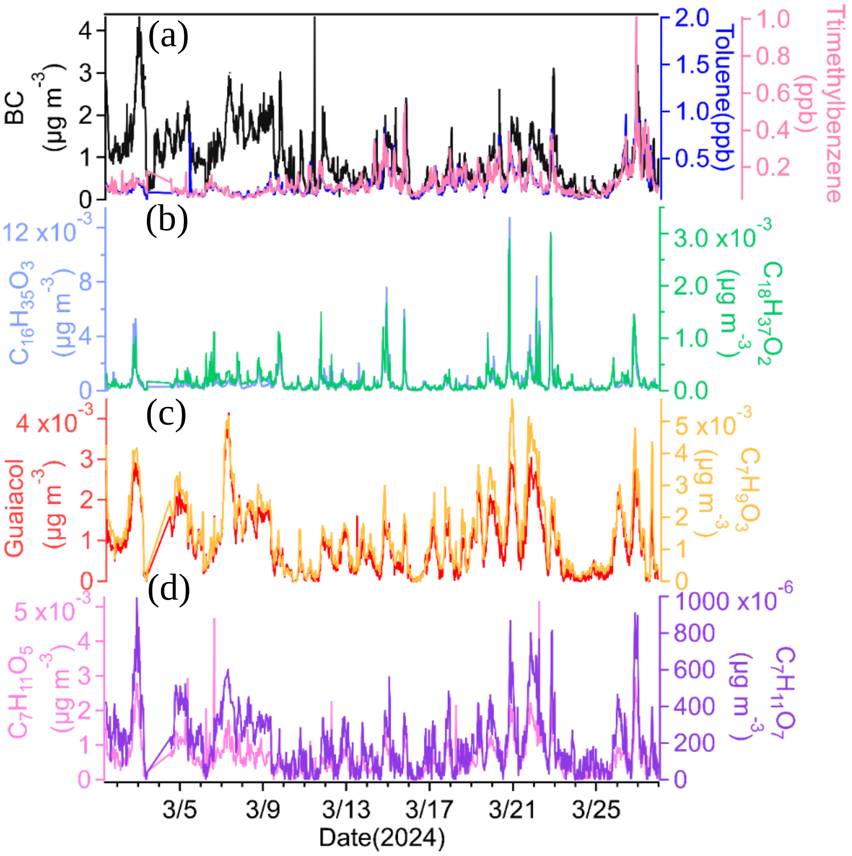

Figure S20 illustrates the time-series correlation of various tracers with the respective AMS factors: (a) HOA tracers such as BC, toluene, and trimethylbenzene; (b) COA tracers, including fatty acids ($C_{18}H_{37}O_2^+$ and $C_{16}H_{35}O_3^+$); (c) fresh BBOA tracers, including Guaiacol ($C_7H_9O_2^+$), $C_7H_9O_3^+$; and (d) aged BBOA compounds like $C_7H_{11}O_5^+$ and $C_7H_{11}O_7^+$.

Table S10 The correlation between aged BBOA with black carbon, formaldehyde, barbecue tracers ($C_{10}H_{13}O_3^+$, $C_9H_{15}O_4^+$, $C_9H_{11}O_4^+$), fresh biomass burning tracers ($C_6H_{11}O_5^+$, $C_9H_{11}O_5^+$, $C_9H_7O_3^+$), and oxidized guaiacol products ($C_6H_7O_5^+$, $C_7H_9O_5^+$)

	August	22nd-24th August	March	7-9th March	Fresh BBOA in March	Fresh BBOA in 7-9th March
BC	0.75	0.64	0.39	-0.13	0.15	-0.17
Formaldehyde	0.80	-0.20	0.14	0.20	0.38	-0.35
Coniferyl alcohol ($C_{10}H_{13}O_3^+$)	0.90	0.82	0.47	0.44	0.69	0.65
Pinic acid $C_9H_{15}O_4^+$	0.76	0.65	0.41	0.54	0.68	0.42
Homovanilic acid $C_9H_{11}O_4^+$	0.83	0.83	0.51	0.42	0.67	0.56
Levoglucosan	0.93	0.76	0.30	0.28	0.72	0.62
syringic acid ($C_9H_{11}O_5^+$)	0.84	0.81	0.24	0.06	0.62	0.50
$C_6H_7O_5^+$	0.88	0.74	0.80	0.79	0.36	0.25
$C_7H_9O_5^+$	0.87	0.86	0.74	0.70	0.50	0.35

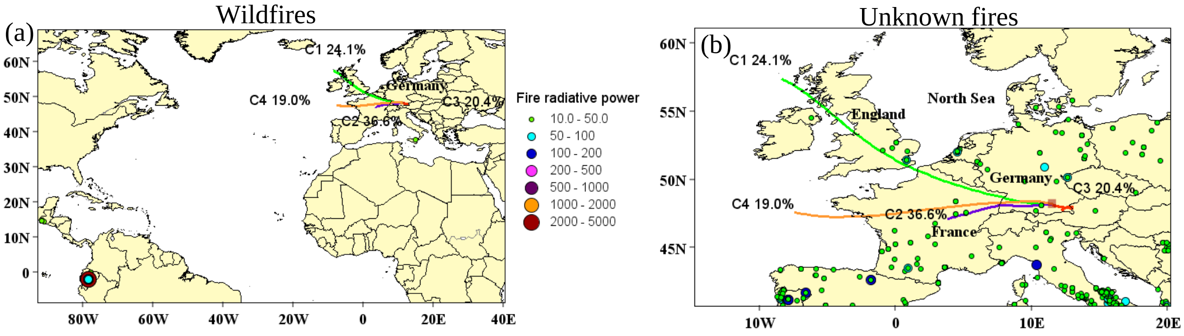

Figure S21. VIIRS satellite fire detections (https://firms.modaps.eosdis.nasa.gov/map/#d:2024-03-03;@11.9,47.3,5.7z) during August overlaid with clustered backward trajectories arriving in Munich. (a) All classified wildfires during August, colored by fire radiative power (FRP). (b) All unknown (unclassified) fire type during August, colored by FRP. The trajectory clusters (C1–C4; percentages indicate cluster frequency) illustrate the main transport pathways during the summer campaign and enable assessment of potential influence from fire activity along the air-mass histories.

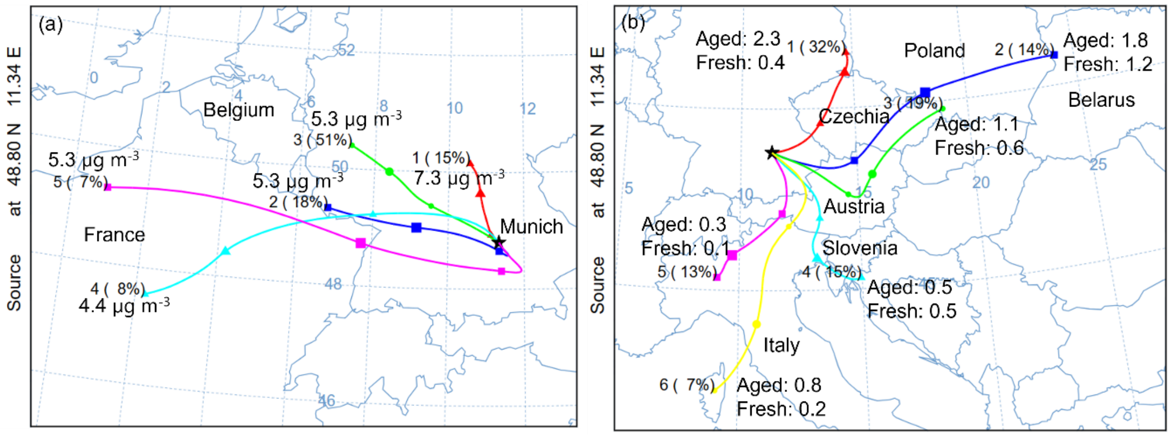

Figure S22: 72-hour back trajectories calculated at 500 m above ground level colored by (a) aged BBOA mass concentrations during the summer episode (22nd – 24th August 2023) and (b) fresh BBOA and aged BBOA mass concentrations during the winter episode (7th -9th March 2024)