



Supplement of

Unveiling the formation of atmospheric oxygenated organic molecules under anthropogenic–biogenic interactions: insights from binned positive matrix factorization on multi-subrange mass spectra

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Supplement

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S1 Additional details for the instruments

S1.1 Flow settings of the instruments

For the CI-API-TOF measurements, ambient air was drawn into a laminar flow reactor through a stainless-steel tube (100 cm long, 3/4 in. diameter) at a flow rate of 10 L/min. A sheath flow of 25 L/min of purified airflow was used to maintain laminar flow conditions within the reactor. Nitrate reagent ions were generated in the sheath flow by exposing air-conditioning nitric acid to a photoionizer X-ray (Model L9491, Hamamatsu, Japan). The PTR-MS sampled air at a flow rate of 200 mL/min and was connected to an external pump operating at 1.5 L/min to assist in flow control. Flow settings and additional details for other instruments used in this study are summarized in Table S1.

Table S1. Settings for instrumentations used in this study

Measurement	Instruments	Manufacturer	Sample flow	Resolution
OOMs	CI-API-TOF	Aerodyne Research, USA/ Tofwerk AG, Switzerland	10 L/min	30 min/1s
VOCs	PTR-TOF	Ion-icon Analytik, Austria	0.2 L/min	10 min/1min
PM _{2.5}	SHARP-5030	Thermo Fisher Scientific, USA	16.7 L/min	5 min
O ₃	TEI-49i	Thermo Fisher Scientific, USA	0.7 L/min	5 min/1 min
NO _x	TEI-42i	Thermo Fisher Scientific, USA	1.285 L/min	5 min/1 min
SO ₂	TEI-43C	Thermo Fisher Scientific, USA	0.5 L/min	5 min/1 min
CO	TEI-48C	Thermo Fisher Scientific, USA	1 L/min	5 min/1 min

S1.2 Sulfuric acid calibration and transmission test

The sulfuric acid calibration factor used in this study was obtained following the method described by Kürten et al. (2012), and the results are shown in Fig. S1. The transmission efficiency of the CI-API-TOF as a function of mass was evaluated using perfluorinated organic acids, including Propanoic acid, Pentanoic acid, and Heptanoic acid. The outcome of the transmission test is also presented in Fig. S1.

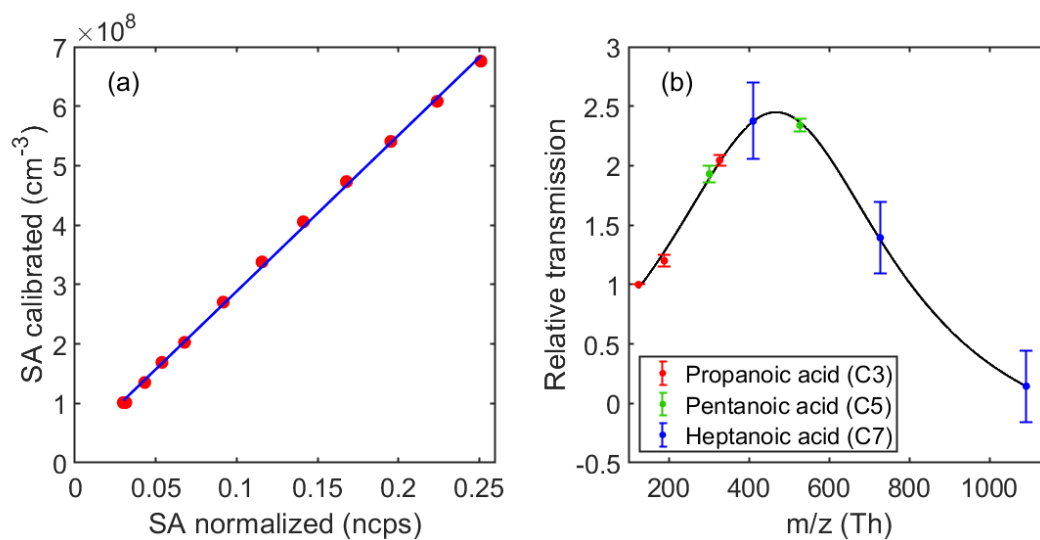


Figure S1. (a) Calibration of sulfuric acid (SA) using the method described by Kürten et al. (2012). (b) Mass-dependent transmission efficiency of the CI-APi-TOF.

S2 Related Calculation of OOMs

Carbon oxidation state (OS_c). The OS_c of each non-nitro OOM was calculated based on Eq. S1 modified from that in Kroll et al. (2011) include organic nitrate contributions, by assuming that all nitrogen come from the nitrate group (-ONO₂).

$$OS_c = \frac{2(n_O - 3n_N)}{n_C} - \frac{n_H}{n_C} + \frac{n_N}{n_C}. \quad (S1)$$

Double bond equivalent (DBE). The DBE of each OOM was calculated using Eq.S2, based on the assumption that all nitrogen come from the nitrate group (-ONO₂) or nitro group (-NO₂). DBE represents the combined effect of double or triple bonds, as well as the ring structure in the molecule, helping to identify the class of precursors of OOM (Nie et al., 2022).

$$DBE = n_C + 1 - \frac{n_H + n_N}{2}. \quad (S2)$$

Effective Oxygen Number (no_{eff}). The effective oxygen number was calculated using Eq.S3, by assuming that all nitrogen of non-nitro OOM come from the nitrate group (-ONO₂):

$$n_{O_{eff}} = n_O - 2 \times n_N. \quad (S3)$$

Volatility Basis Set (VBS). The saturation concentration at 300K of OOMs can be used as a characterization of volatility and was calculated using Eq.S4 based on the group-contribution method proposed by Donahue et al. (2011):

$$\log_{10} C^*(300K) = (25 - n_C) \cdot b_C - (n_O - 2n_N) \cdot b_O - 2b_{CO} \left[\frac{(n_O - 2n_N) \cdot n_C}{n_C + n_O - 2n_N} \right]. \quad (S4)$$

where $b_C=0.475$, $b_O=2.3$, $b_{CO}=-0.3$. The effect of nitrate group (-ONO₂) on volatility is similar to hydroxyl group (-OH).

Furthermore, since monoterpene-derived OOMs primarily contain hydroperoxide groups (-OOH) and nitrate groups (-ONO₂), their saturation concentrations were estimated using methods reported by Mohr et al. (2019):

$$\log_{10} C^*(300K) = (25 - n_C) \cdot b_C - (n_O - 3n_N) \cdot b_O - 2b_{CO} \left[\frac{(n_O - 3n_N) \cdot n_C}{n_C + n_O - 3n_N} \right] - n_N \cdot b_N. \quad (S5)$$

where $b_C=0.475$, $b_O=0.2$, $b_{CO}=0.9$, $b_N=2.5$. In this study, the identification of monoterpene-related compounds was based on the approach proposed by Nie et al. (2022), where OOMs with DBE=2 that appeared in the PMF monoterpene-related factors were classified as monoterpene OOMs.

The temperature dependence of volatilities is described by Eq.S6, according to Stolzenburg et al. (2018):

$$\log_{10}C_i^*(T) = \log_{10}C_i^*(300K) + \frac{\Delta H_{vap}}{R \cdot \ln(10)} \left(\frac{1}{300} - \frac{1}{T} \right) \quad (S6)$$

The evaporation enthalpy (ΔH_{vap}) can be linked to the saturation mass concentration at 300K, $\log_{10}C^*(300K)$, based on Donahue et al. (2011) and combined with Epstein et al. (2010):

$$\Delta H_{vap}[kJ \text{ mol}^{-1}] = 129 - 5.7 \cdot \log_{10}C_i^*(300K) \quad (S7)$$

Hydroxyl radical (OH) estimate. The concentration of OH radical was calculated by applying Eq.S8, based on the assumption that gaseous SA is produced primarily by the oxidation of SO_2 by OH and is lost mainly through condensation on particles.

$$[OH] = \frac{[H_2SO_4] \cdot CS}{k_{OH+SO_2} \cdot [SO_2]}. \quad (S8)$$

where the constant k_{OH+SO_2} is a termolecular reaction constant for the rate-limiting step of the formation pathway of SA in the atmosphere (Finlayson-Pitts and Pitts, 2000). The condensation sink (CS) is the loss rate of SA by condensation of the aerosol surface, which is calculated by the following Eq. S9 (Kulmala et al., 2012):

$$CS = 2\pi D \sum_i \beta_{m_i} d_{p_i} N_i. \quad (S9)$$

where D is the diffusion coefficient of gaseous SA, β_m is a transition-regime correction factor dependent on the Knudsen number (Fuchs and Sutugin, 1971), and d_{p_i} and N_i are the diameter and number concentration of particles in size bin i .

S3 PMF input and diagnostics for each range

S3.1 binPMF inputs

Consistent with previous studies employing the binPMF methodology (Liu et al., 2021, 2023), the mass spectrometry data were divided into narrow bins with a width of 0.004 Th after mass axis calibration to construct the input data matrix for PMF analysis. Data quality control measures were implemented by excluding periods of instrumental instability and retaining only signal regions with meaningful signals in the mass spectra between $N-0.1$ and $N+0.4$ Th. The three ranges contained 17280, 18105, 18812 bins. The data were averaged into 30 min time resolution, and finally we got 1679 time points in the data matrix. The error matrix was calculated according to Zhang et al. (2019). To minimize the potential influence of nitrophenols and fluorinated contaminants on the final PMF results, these compounds were systematically down-weighted in the analysis.

S3.2 Diagnosis of binPMF solutions

As established in previous works applying PMF (Ulbrich et al., 2009; Yan et al., 2016), determining the optimal number of factors represents a critical step in the interpretation of PMF results. Accordingly, we systematically evaluated and diagnostically examined solutions encompassing a comprehensive range of factor numbers from 1 to 20 to ensure robust factor resolution. The Q/Q_{exp} ratio exhibited a decreasing trend with increasing factor numbers, albeit with a diminishing rate of reduction (Fig. S1). When the number of PMF factors exceeded eight across all mass ranges, the Q/Q_{exp} ratio stabilized at relatively low levels, accompanied by an explanation ratio exceeding 90% for the original dataset. While higher factor numbers facilitate the resolution of more subtle details within the data, excessive factor decomposition may lead to physically meaningful factors being artificially fragmented into less interpretable ones. In the Range 1, significant influence from nitrophenols was observed. The 10-factor solution successfully isolated and removed the nitrophenol-dominated factors without compromising subsequent analytical interpretations. The N2-MT-I factor was only resolved in the 12-factor solution. Further increasing the number of factors did not yield additional meaningful factors but rather resulted in excessive decomposition of existing factors, thereby compromising the analytical utility of the solution. Consequently, we conducted rotational ambiguity analysis on the 12-factor solution, systematically varying the f_{peak} parameter from -1 to 1 with an increment of 0.1. Notably, for R1, the f_{peak} range was extended to 1.5 to identify potentially more optimal solutions. Through this rotational analysis, we selected solutions that maximized the separation between contamination factors and NP-dominated factors. These specifically separated factors were subsequently excluded from further analytical consideration. Similarly, we performed this analytical framework to both R2 and R3, ultimately identifying 11-factor solutions as the optimal configurations for each respective dataset.

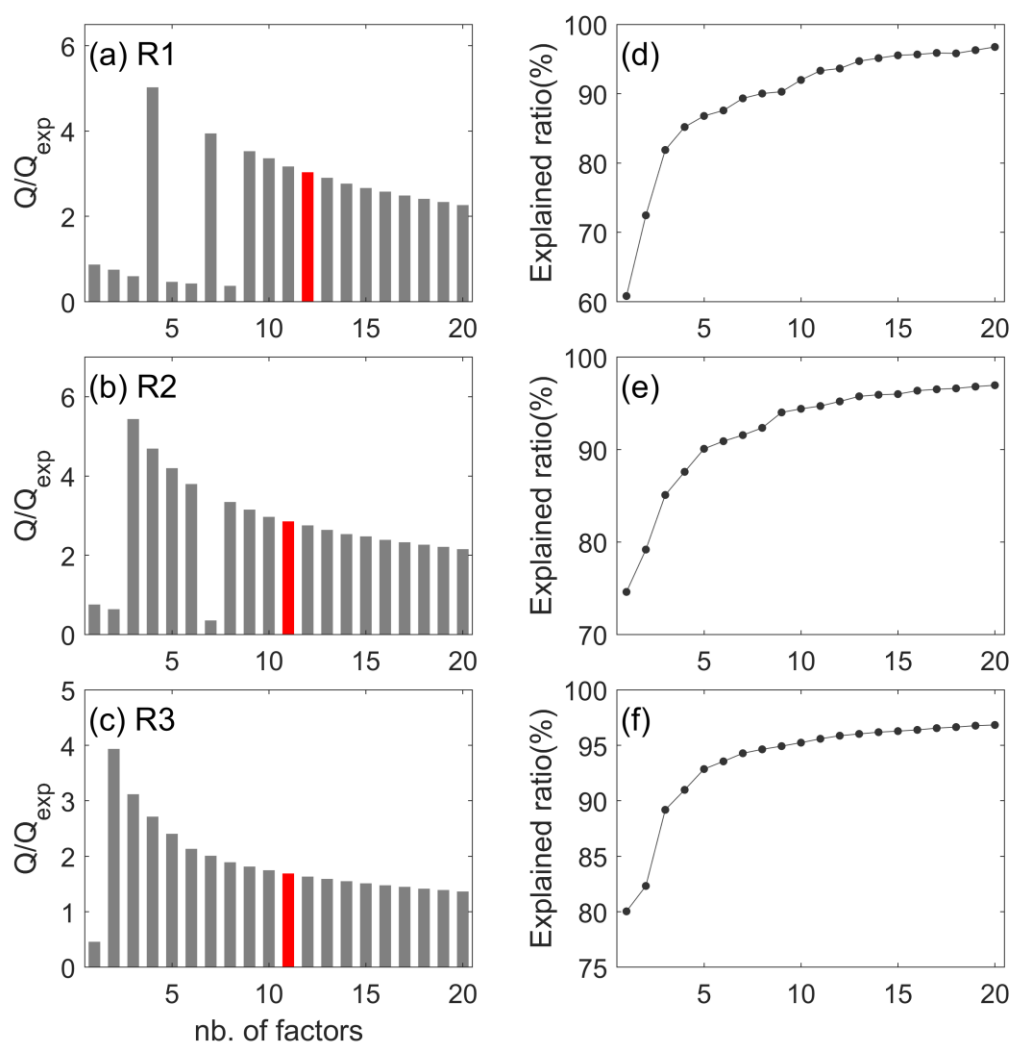


Figure S2. Diagnostics of PMF solutions, including (a)-(c) the variation of Q/Q_{exp} and (d)-(f) explained ratio of PMF factors relative to the number of factors in three range. The red bars indicate the selected PMF solution.

S4 Selected PMF solution for each range

The final PMF solutions selected for each range are presented in Fig. S2-S4. Notably, Range 3 exhibited two closely related factors (D3-AVOC-III-1, D3-AVOC-III-2) that demonstrated strong correlation with corresponding factors in the first two ranges only after factor merging. Therefore, these two factors were consolidated into a single composite factor (D3-AVOC-III) for subsequent analytical interpretation. The merging was performed as follows:

First, the time series of the two factors were summed to create the time series (ts) of the new merged factor. Then, the original time series and profiles of each factor were used to reconstruct their respective data matrices (A1 and A2) by matrix multiplication. These two matrices were then added to obtain the data matrix A of the combined factor:

$$A = A_1 + A_2 = (ts_1 \cdot pr_1) + (ts_2 \cdot pr_2) \quad (S10)$$

Finally, the new profile (pr) of the merged factor was derived by solving the equation:

$$ts \cdot pr = A \quad (S11)$$

This approach preserved both the temporal and spectral information of the original two factors and ensured consistency in subsequent correlation analysis across subranges.

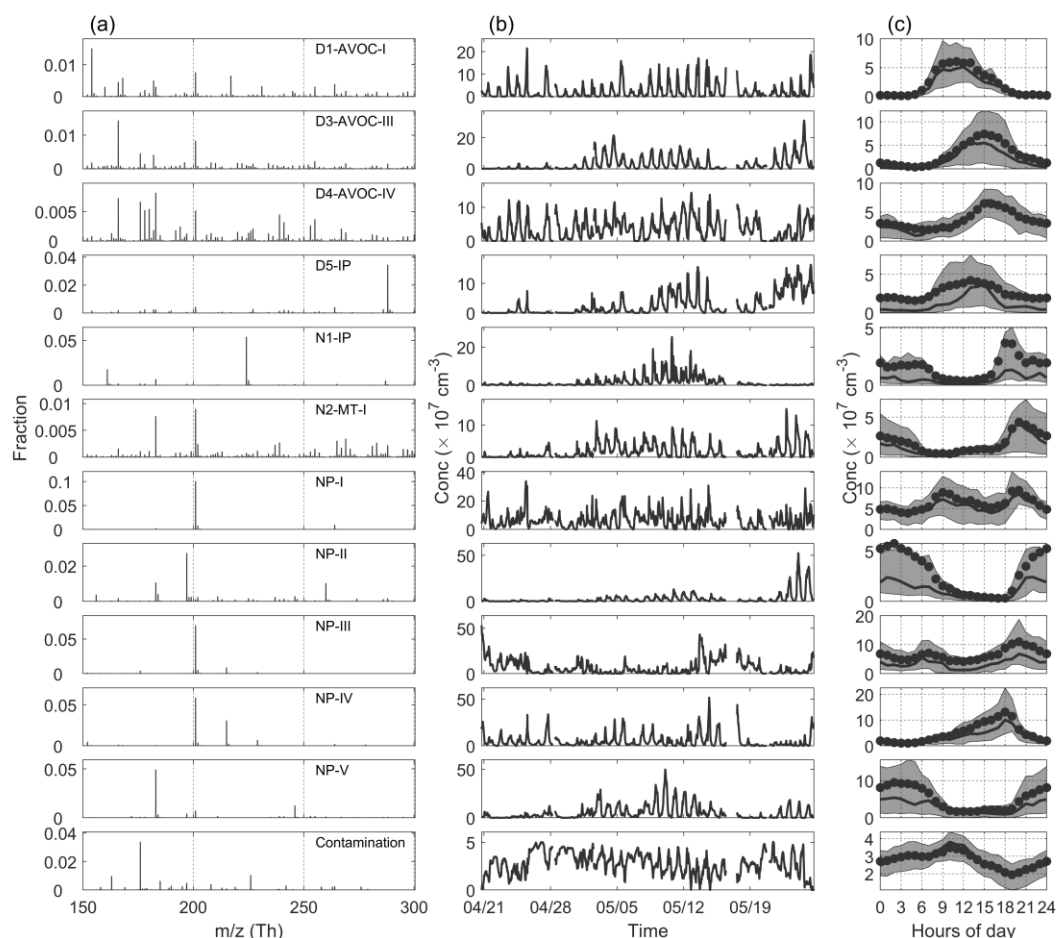


Figure S3. Selected PMF solution for Range 1. (a) PMF factor profiles. (b) Time series of these factors. (c) Diurnal variations in PMF factors.

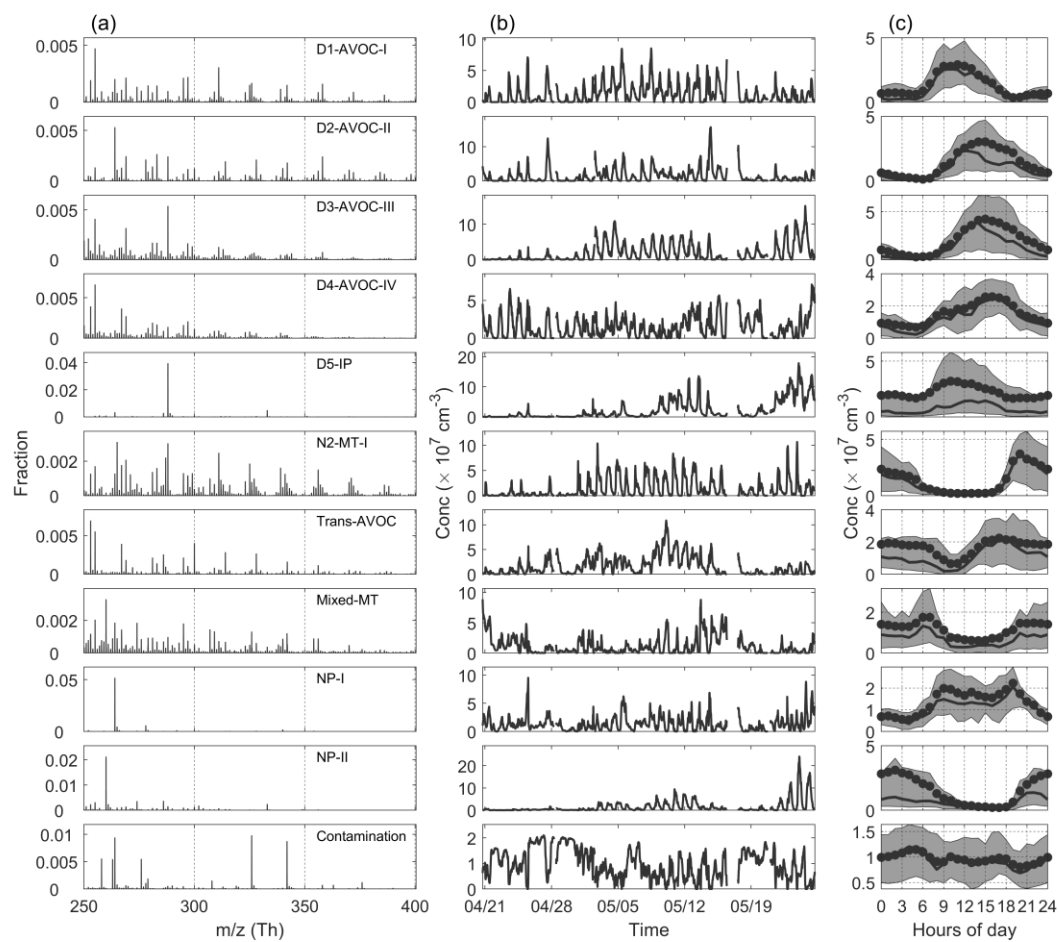


Figure S4. Selected PMF solution for Range 2. (a) PMF factor profiles. (b) Time series of these factors. (c) Diurnal variations in PMF factors.

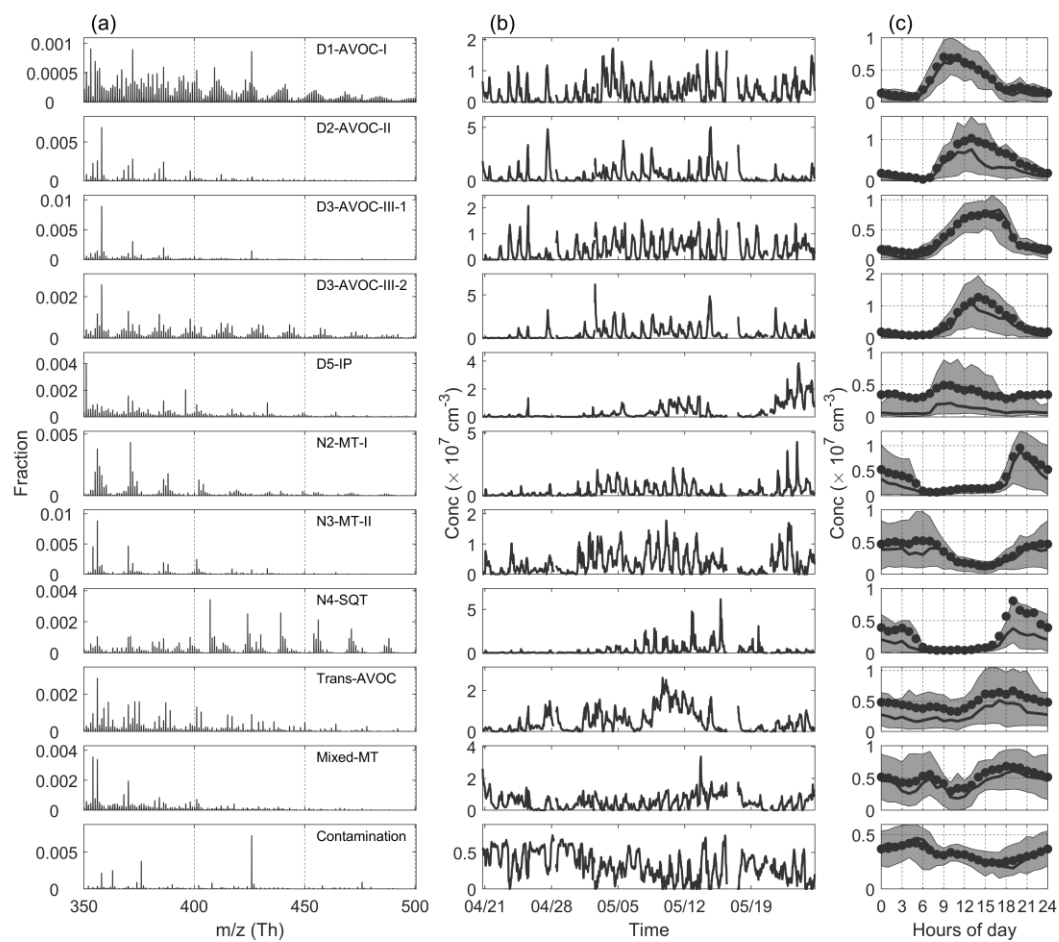


Figure S5. Selected PMF solution for Range 3. (a) PMF factor profiles. (b) Time series of these factors. (c) Diurnal variations in PMF factors.

S5 Contributions of factors to total concentration

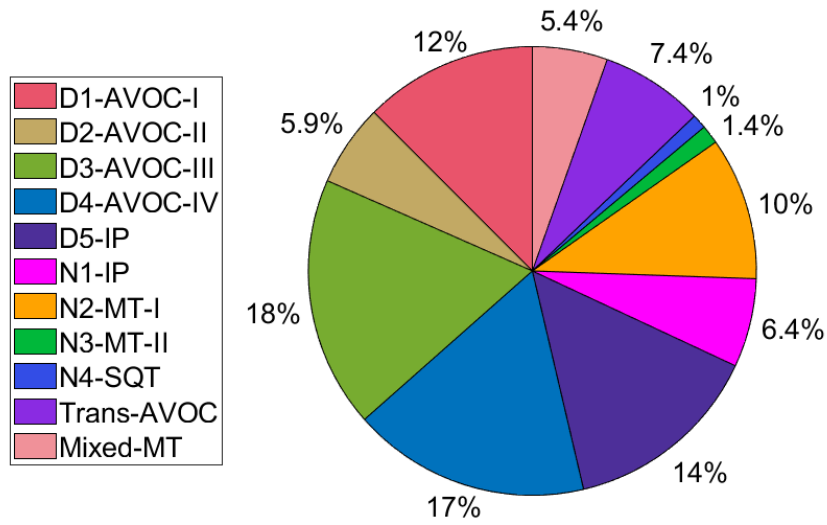


Figure S6. Relative contributions of the 11 factors to the total concentration of measured OOMs.

S6 Correlation of binPMF factors with other data

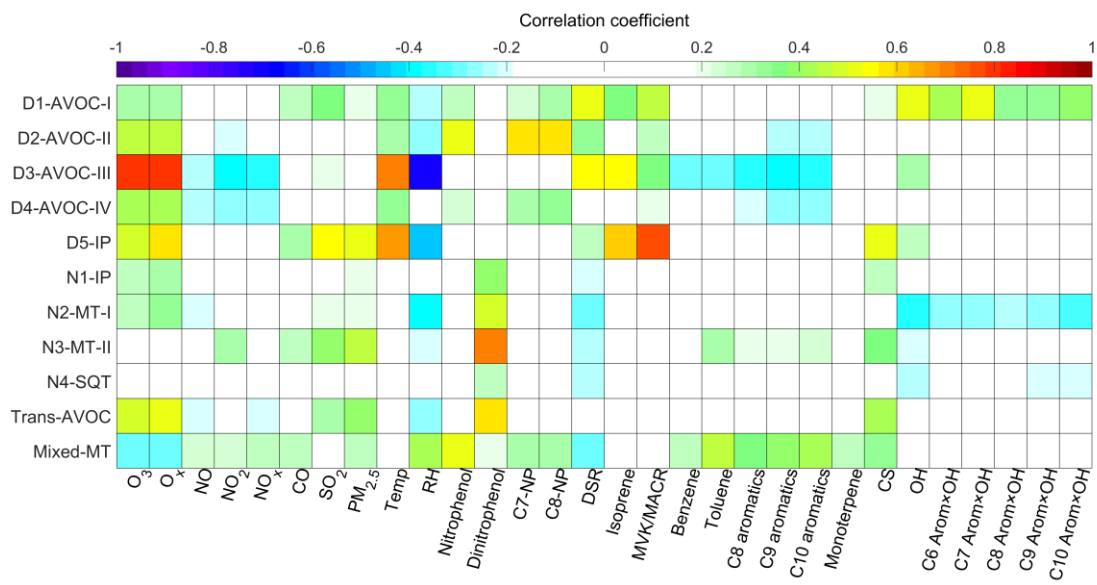


Figure S7. Correlations of factors with external gas-phase and particulate tracers. The colors are differentiated by Pearson correlation coefficients.

S7 Reactivity of nighttime oxidants with BVOCs

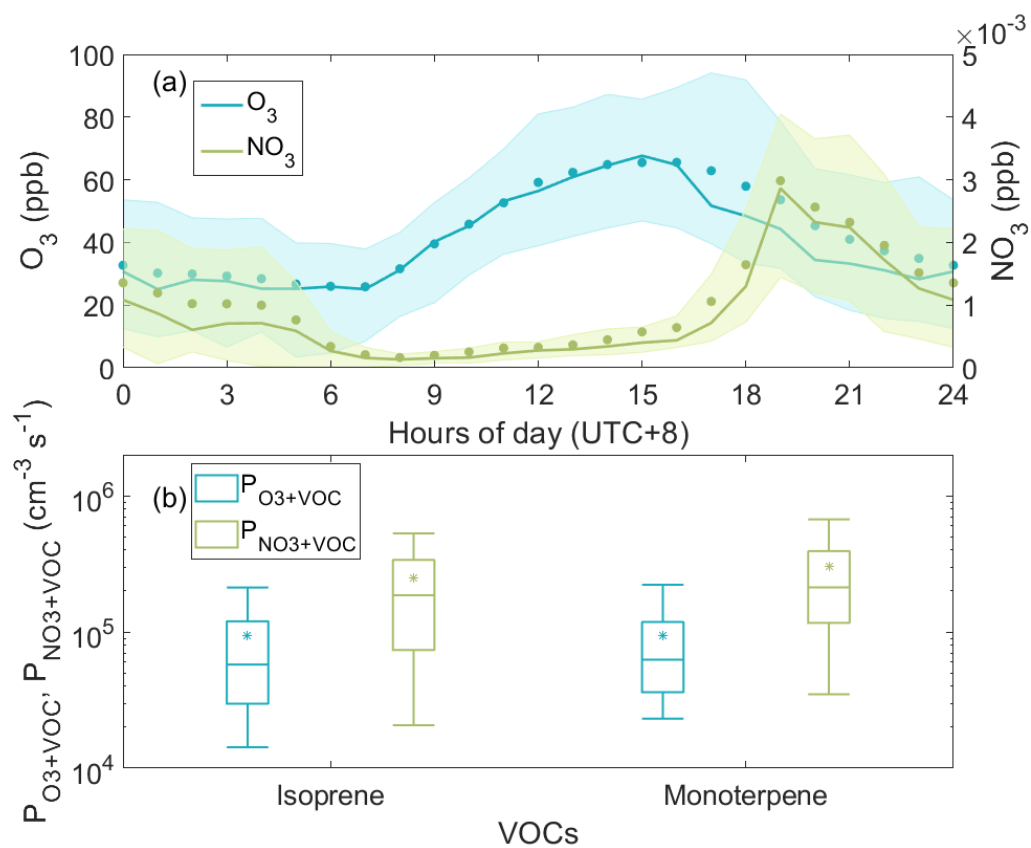


Figure S8. (a) Diurnal variations of O_3 and NO_3 radical. (b) Box plot of the oxidation reaction rates of isoprene and monoterpenes by O_3 and NO_3 radical at nighttime.

S8 Time series of N1-IP factor and $C_5H_8O_5N$

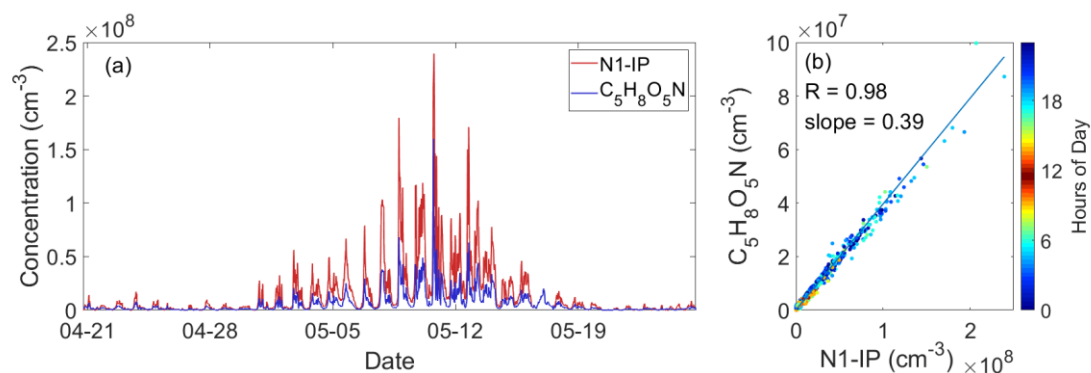


Figure S9. Time series and correlation analysis between the N1-IP factor and $C_5H_8O_5N$. (a) Temporal evolution of the N1-IP factor (red) and $C_5H_8O_5N$ (blue) obtained from direct peak fitting. (b) Correlation between $C_5H_8O_5N$ and the N1-IP factor, colored by hours of day.

S9 Dynamic chemical analysis of specific factors

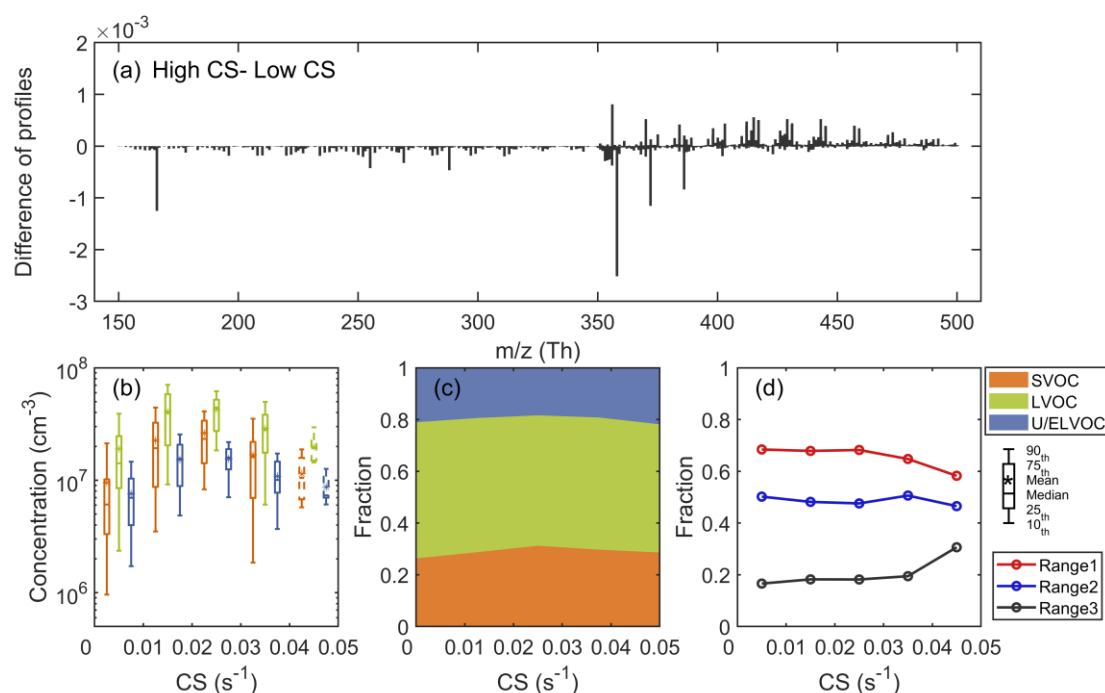


Figure S10. Characteristics of the D3-AVOC-III factor under varying condensation sink (CS) conditions. (a) Difference between the average mass spectra of D3-AVOC-III under high CS (above the upper quartile) and low CS (below the lower quartile) conditions. (b) Boxplots of the concentrations of SVOC, LVOC, and U/ELVOC species binned by CS in each 0.01 s^{-1} interval. Data for $\text{CS} > 0.04 \text{ s}^{-1}$ are represented by dashed box plots owing too few data points. (c) Fractional contributions of SVOC, LVOC, and U/ELVOC species across different CS conditions. (d) Evolution of fractional contributions of three sub-ranges as a function of CS.

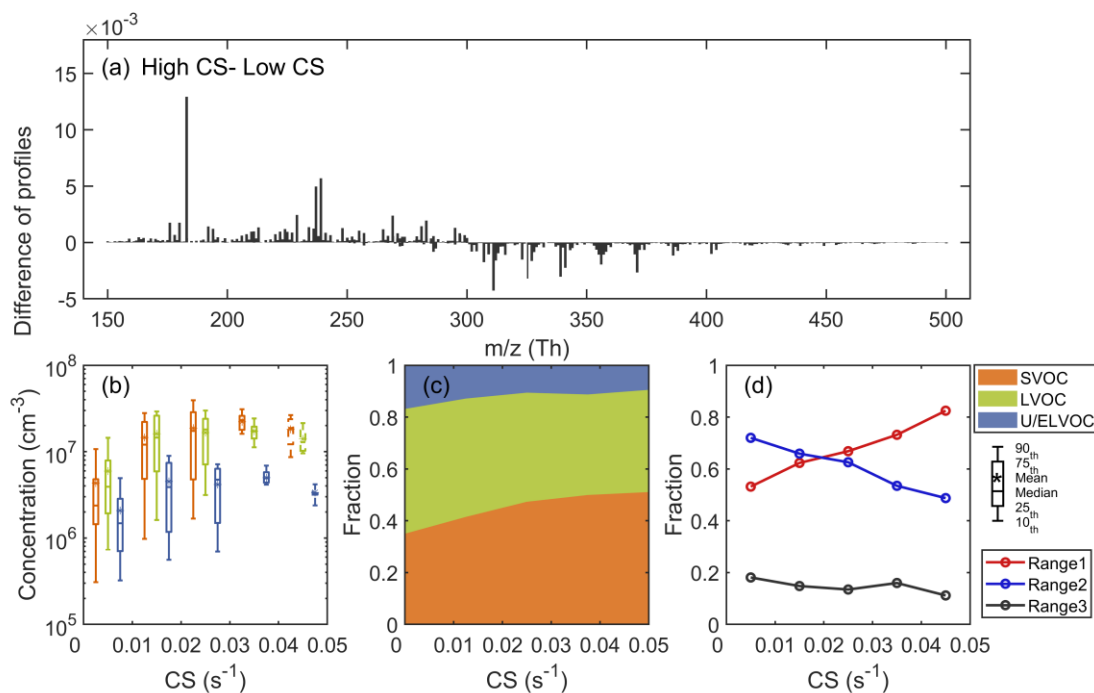


Figure S11. Characteristics of the N2-MT-I factor under varying condensation sink (CS) conditions. (a) Difference between the average mass spectra of N2-MT-I under high CS (above the upper quartile) and low CS (below the lower quartile) conditions. (b) Boxplots of the concentrations of SVOC, LVOC, and U/ELVOC species binned by CS in each 0.01 s^{-1} interval. Data for $\text{CS} > 0.04 \text{ s}^{-1}$ are represented by dashed box plots owing too few data points. (c) Fractional contributions of SVOC, LVOC, and U/ELVOC species across different CS conditions. (d) Evolution of fractional contributions of three sub-ranges as a function of CS.

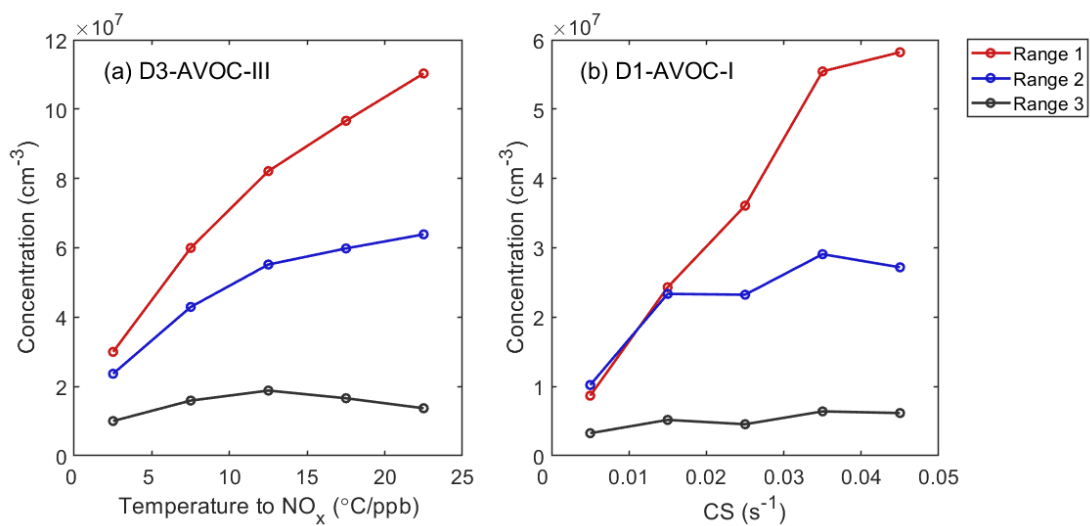


Figure S12. Evolution of concentrations of three sub-ranges of (a) D3-AVOC-III with T/ NO_x ratio, and (b) D1-AVOC-I with CS.

S10 Main peaks of binPMF factors

Table S2. Molecular characteristics of D1-AVOC-I factor. The reagent ion has been omitted from the formulas.

Range	No.	Formulas	Contribution to the Range (%)	DBE	n_O	n_N
R1	1	$C_xH_{2x-1}O_6N$, $x = [3, 9]$	18.6	1	6	1
	2	$C_xH_{2x-2}O_4$, $x = [3, 10]$	9.6	2	4	0
	3	$C_xH_{2x-3}O_7N$, $x = [4, 8]$	8.3	2	7	1
	4	$C_xH_{2x-3}O_6N$, $x = [4, 9]$	6.7	2	6	1
	5	$C_xH_{2x-5}O_7N$, $x = [5, 8]$	5.1	3	7	1
R2	1	$C_xH_{2x-1}O_6N$, $x = [6, 13]$	13.1	1	6	1
	2	$C_xH_{2x-5}O_8N$, $x = [5, 14]$	9.9	3	8	1
	3	$C_xH_{2x-3}O_7N$, $x = [5, 15]$	8.8	2	7	1
	4	$C_xH_{2x-5}O_7N$, $x = [5, 14]$	7.5	3	7	1
	5	$C_xH_{2x-3}O_6N$, $x = [6, 14]$	6.1	2	6	1
R3	1	$C_xH_{2x-5}O_8N$, $x = [11, 18]$	4.3	3	8	1
	2	$C_xH_{2x-5}O_9N$, $x = [10, 17]$	3.5	3	9	1
	3	$C_xH_{2x-4}O_{10}N_2$, $x = [9, 16]$	3.3	2	10	2
	4	$C_xH_{2x-3}O_8N$, $x = [11, 18]$	3.0	2	8	1
	5	$C_xH_{2x-3}O_7N$, $x = [12, 18]$	2.8	2	7	1

Table S3. Molecular characteristics of D2-AVOC-II factor. The reagent ion has been omitted from the formulas.

Range	No.	Formulas	Contribution to the Range (%)	DBE	n_O	n_N
R2	1	$C_xH_{2x-2}O_8N_2$, $x = [6, 13]$	14.8	1	8	2
	2	$C_xH_{2x-3}O_7N$, $x = [5, 14]$	9.3	2	7	1
	3	$C_xH_{2x-1}O_6N$, $x = [6, 14]$	9.3	1	6	1
	4	$C_xH_{2x-4}O_{10}N_2$, $x = [7, 11]$	6.7	2	10	2
	5	$C_xH_{2x}O_8N_2$, $x = [5, 13]$	6.5	0	8	2
R3	1	$C_xH_{2x-4}O_{10}N_2$, $x = [8, 12]$	18.3	2	10	2
	2	$C_xH_{2x-2}O_8N_2$, $x = [10, 18]$	12.3	1	8	2
	3	$C_xH_{2x}O_7N_2$, $x = [11, 19]$	8.5	0	7	2
	4	$C_xH_{2x-4}O_8N_2$, $x = [10, 17]$	6.2	2	8	2
	5	$C_xH_{2x}O_8N_2$, $x = [10, 15]$	4.1	0	8	2

Table S4. Molecular characteristics of D3-AVOC-III factor. The reagent ion has been omitted from the formulas.

Range	No.	Formulas	Contribution to the Range (%)	DBE	n_O	n_N
R1	1	$C_xH_{2x-2}O_4$, $x = [3]$	12.4	2	4	0
	2	$C_xH_{2x-3}O_7N$, $x = [4, 8]$	7.6	2	7	1
	3	$C_xH_{2x-4}O_5$, $x = [4, 10]$	7.3	3	5	0
	4	$C_xH_{2x-6}O_5$, $x = [5, 10]$	6.1	4	5	0
	5	$C_xH_{2x-2}O_5$, $x = [4, 9]$	6.0	2	5	0
R2	1	$C_xH_{2x-3}O_7N$, $x = [5, 11]$	11.1	2	7	1
	2	$C_xH_{2x-5}O_7N$, $x = [5, 11]$	6.1	3	7	1
	3	$C_xH_{2x-5}O_8N$, $x = [5, 12]$	6.1	3	8	1
	4	$C_xH_{2x-3}O_8N$, $x = [5, 11]$	6.0	2	8	1
	5	$C_xH_{2x}O_8N_2$, $x = [5]$	5.7	0	8	2
R3	1	$C_xH_{2x-4}O_{10}N_2$, $x = [8, 15]$	13.0	2	10	2
	2	$C_xH_{2x-4}O_9N_2$, $x = [9, 16]$	5.7	2	9	2
	3	$C_xH_{2x-2}O_9N_2$, $x = [9, 16]$	4.1	1	9	2
	4	$C_xH_{2x-2}O_8N_2$, $x = [10, 16]$	4.1	1	8	2
	5	$C_xH_{2x-1}O_{10}N_3$, $x = [7, 15]$	3.4	0	10	3

Table S5. Molecular characteristics of D4-AVOC-IV factor. The reagent ion has been omitted from the formulas.

Range	No.	Formulas	Contribution to the Range (%)	DBE	n_O	n_N
R1	1	$C_xH_{2x-2}O_4$, $x = [3, 9]$	16.8	2	4	0
	2	$C_xH_{2x-3}O_6N$, $x = [4, 9]$	15.4	2	6	1
	3	$C_xH_{2x-1}O_6N$, $x = [3, 9]$	15.2	1	6	1
	4	$C_xH_{2x-1}O_5N$, $x = [2, 5]$	9.1	1	5	1
	5	$C_xH_{2x-4}O_4$, $x = [5, 10]$	6.6	3	4	0
R2	1	$C_xH_{2x-1}O_6N$, $x = [6, 12]$	14.8	1	6	1
	2	$C_xH_{2x-3}O_6N$, $x = [6, 14]$	13.9	2	6	1
	3	$C_xH_{2x-3}O_7N$, $x = [5, 12]$	6.5	2	7	1
	4	$C_xH_{2x-2}O_8N_2$, $x = [4, 9]$	4.8	1	8	2
	5	$C_xH_{2x-5}O_7N$, $x = [7, 13]$	4.2	3	7	1

Table S6. Molecular characteristics of D5-IP factor. The reagent ion has been omitted from the formulas.

Range	No.	Formulas	Contribution to the Range (%)	DBE	n_C	n_N
R1	1	$C_5H_{10}O_xN_2$, $x = [8]$	45.7	0	5	2
	2	$C_5H_9O_xN$, $x = [4, 9]$	4.6	1	5	1
	3	$C_5H_8O_xN_2$, $x = [7, 8]$	3.8	1	5	2
	4	$C_4H_7O_xN$, $x = [5, 6]$	3.6	1	4	1
	5	$C_5H_7O_xN$, $x = [3, 8]$	3.4	2	5	1
R2	1	$C_5H_{10}O_xN_2$, $x = [8, 9]$	45.4	0	5	2
	2	$C_5H_9O_xN_3$, $x = [10, 11]$	6.9	0	5	3
	3	$C_5H_8O_xN_2$, $x = [8, 9]$	4.0	1	5	2
	4	$C_6H_{10}O_xN_2$, $x = [8, 9]$	1.8	1	6	2
	5	$C_7H_{10}O_xN_2$, $x = [8, 10]$	1.6	2	7	2
R3	1	$C_{10}H_{16}O_xN_2$, $x = [8, 14]$	5.6	2	10	2
	2	$C_5H_{10}O_xN_2$, $x = [8]$	5.6	0	5	2
	3	$C_{10}H_{17}O_xN_3$, $x = [10, 14]$	4.3	1	10	3
	4	$C_9H_{14}O_xN_2$, $x = [9, 14]$	3.9	2	9	2
	5	$C_5H_9O_xN_3$, $x = [10]$	3.1	0	5	3

Table S7. Molecular characteristics of N1-IP factor. The reagent ion has been omitted from the formulas.

Range	No.	Formulas	Contribution to the Range (%)	DBE	n_C	n_N
R3	1	$C_5H_8O_xN$, $x = [5]$	57.4	1.5	5	1
	2	$C_6H_{10}O_x$, $x = [5]$	8.7	2	6	0
	3	$C_6H_{11}O_xN$, $x = [6, 8]$	3.8	1	6	1
	4	$C_5H_9O_xN$, $x = [5, 6]$	2.9	1	5	1
	5	$C_7H_9O_xN$, $x = [6, 8]$	2.6	3	7	1

Table S8. Molecular characteristics of N2-MT-I factor. The reagent ion has been omitted from the formulas.

Range	No.	Formulas	Contribution to the Range (%)	DBE	n_C	n_N
R1	1	$C_7H_9O_xN$, $x = [6, 8]$	8.5	3	7	1
	2	$C_2H_3O_xN$, $x = [5]$	7.0	1	2	1
	3	$C_7H_{11}O_xN$, $x = [6, 8]$	6.8	2	7	1
	4	$C_6H_9O_xN$, $x = [5, 8]$	6.4	2	6	1
	5	$C_5H_7O_xN$, $x = [5, 8]$	5.1	2	5	1
R2	1	$C_7H_9O_xN$, $x = [6, 9]$	6.7	3	7	1
	2	$C_{10}H_{15}O_xN$, $x = [6, 10]$	6.6	3	10	1
	3	$C_9H_{15}O_xN$, $x = [6, 9]$	6.2	2	9	1
	4	$C_{10}H_{17}O_xN$, $x = [6, 10]$	5.5	2	10	1
	5	$C_6H_{11}O_xN$, $x = [6, 9]$	5.1	1	6	1
R3	1	$C_{10}H_{15}O_xN$, $x = [9, 12]$	9.0	3	10	1
	2	$C_{10}H_{16}O_xN_2$, $x = [8, 13]$	6.3	2	10	2
	3	$C_{10}H_{16}O_xN$, $x = [9, 11]$	6.1	2.5	10	1
	4	$C_{10}H_{18}O_xN_2$, $x = [8, 12]$	5.1	1	10	2
	5	$C_9H_{16}O_xN_2$, $x = [9, 13]$	4.0	1	9	2

Table S9. Molecular characteristics of N3-MT-II factor. The reagent ion has been omitted from the formulas.

Range	No.	Formulas	Contribution to the Range (%)	DBE	n_C	n_N
R3	1	$C_{10}H_{16}O_xN_2$, $x = [8, 13]$	17.7	2	10	2
	2	$C_{10}H_{18}O_xN_2$, $x = [8, 13]$	16.7	1	10	2
	3	$C_{10}H_{17}O_xN_3$, $x = [10, 13]$	7.4	1	10	3
	4	$C_{10}H_{16}O_xN$, $x = [9, 11]$	3.0	2.5	10	1
	5	$C_9H_{16}O_xN_2$, $x = [9, 13]$	2.9	1	9	2

Table S10. Molecular characteristics of N4-SQT factor. The reagent ion has been omitted from the formulas.

Range	No.	Formulas	Contribution to the Range (%)	DBE	n_C	n_N
R3	1	$C_{15}H_{23}O_xN$, $x = [6, 12]$	14.3	4	15	1
	2	$C_{15}H_{24}O_xN$, $x = [7, 13]$	7.6	3.5	15	1
	3	$C_{15}H_{25}O_xN$, $x = [6, 13]$	5.8	3	15	1
	4	$C_{15}H_{24}O_xN_2$, $x = [8, 12]$	5.3	3	15	2
	5	$C_{11}H_{16}O_xN_2$, $x = [9, 13]$	3.9	3	11	2

Table S11. Molecular characteristics of Trans-AVOC factor. The reagent ion has been omitted from the formulas.

Range	No.	Formulas	Contribution to the Range (%)	DBE	n_O	n_N
R2	1	$C_xH_{2x-2}O_8N_2$, $x = [4, 12]$	20.2	1	8	2
	2	$C_xH_{2x-3}O_6N$, $x = [6, 11]$	18.0	2	6	1
	3	$C_xH_{2x-1}O_6N$, $x = [6, 10]$	10.4	1	6	1
	4	$C_xH_{2x-3}O_{10}N$, $x = [5, 11]$	5.6	2	10	1
	5	$C_xH_{2x}O_7N_2$, $x = [5, 11]$	4.5	0	7	2
R3	1	$C_xH_{2x-3}O_{10}N_3$, $x = [7, 14]$	11.0	1	10	3
	2	$C_xH_{2x-1}O_{10}N_3$, $x = [7, 13]$	8.0	0	10	3
	3	$C_xH_{2x-3}O_{11}N_3$, $x = [6, 14]$	7.6	1	11	3
	4	$C_xH_{2x-2}O_8N_2$, $x = [10, 14]$	7.2	1	8	2
	5	$C_xH_{2x-4}O_9N_2$, $x = [9, 14]$	5.2	2	9	2

Table S12. Molecular characteristics of Mixed-MT factor. The reagent ion has been omitted from the formulas.

Range	No.	Formulas	Contribution to the Range (%)	DBE	n_O	n_N
R2	1	$C_xH_{2x-3}O_6N$, $x = [6, 14]$	10.2	2	6	1
	2	$C_xH_{2x-5}O_6N$, $x = [6, 15]$	7.2	3	6	1
	3	$C_xH_{2x-1}O_6N$, $x = [6, 12]$	6.6	1	6	1
	4	$C_xH_{2x}O_7N_2$, $x = [5, 14]$	6.0	0	7	2
	5	$C_xH_{2x-1}O_5N$, $x = [7, 13]$	5.0	1	5	1
R3	1	$C_xH_{2x-2}O_8N_2$, $x = [10, 15]$	9.3	1	8	2
	2	$C_xH_{2x-4}O_8N_2$, $x = [10, 15]$	7.9	2	8	2
	3	$C_xH_{2x-4}O_9N_2$, $x = [9, 15]$	5.9	2	9	2
	4	$C_xH_{2x}O_7N_2$, $x = [11, 16]$	5.4	0	7	2
	5	$C_xH_{2x-3}O_{10}N_3$, $x = [7, 13]$	3.2	1	10	3

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