Supporting Information

Significant secondary formation of nitrogenous organic aerosols in an urban atmosphere revealed by bihourly measurements of bulk organic nitrogen and comprehensive molecular markers

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This supplemental information contains 1 text section, 2 table, and 10 figures, totaling 12 pages including the cover page.

Text S1. Source apportionment analysis by PMF receptor model

In this study, the sources of aerosol organic nitrogen (ON) and organic carbon (OC) were quantitatively resolved using the model of positive matrix factorization (PMF) 5.0. ON, organic/elemental carbon (OC/EC), water-soluble ions, metals, selected trace gases such as ozone (O_3) and nitrogen oxides (NO_x), as well as an array of organic markers including primarily emitted species and secondary organic aerosol (SOA) tracers (Table S1) served as the inputs of PMF model. The input uncertainty for each species in this study was calculated as (concentration × error fraction + 1/3 × MDL), where MDL is the method detection limit.[1,2] For concentrations below MDL, the uncertainty was set as 5/6 × MDL. The error fraction was set as 0.12 for ON, OC, EC, major ions, NO_x and O_3, and 0.15 for elements and organic tracers. Given the comprehensive list of source tracers as inputs, PMF model runs were conducted with factors ranging from 8 to 20 factors to determine the optimal number of factors. As shown in Figure S1, the Q/Qexp values decreased significantly when factor number increased from 8 to 18. We found that the 18-factor solution produced distinct factors that represent specific primary emissions and secondary formation sources. There was one or more ambiguous factors when the factor number was less than 18. In addition, through Bootstrap and Displacement error estimations, we confirmed that all resolved factors in the 18-factor solution exhibited >93% mapping and no swaps. Consequently, the 18-factor solution was selected to do subsequent analysis. Figure S2 displays the profiles of the 18 resolved factors while Figure S3a and 3b show the time series and diel variation patterns of each factor contribution, respectively. The source compositions of OC resolved from PMF analysis are shown in Figure S5 while those of ON is presented in the main text (Figure 2). Numerial results of source contributions to ON and OC are presented in Table S2.

Table S1. List of lumped or individual organic species as PMF inputs.

Abbreviation	Lumped species	Potential sources
sFAs	C14-C20 saturated fatty acids	Cooking
usFAs	Oleic, Palmitoleic, Linoleic acid	Cooking
Galactosan	Galactosan	Biomass burning
Mannosan	Mannosan	Biomass burning
Levoglucosan	Levoglucosan	Biomass burning
Hopanes	22,29,30-trisnorhopane, $\alpha\beta$-norhopane, $\alpha\beta$-hopane, $\alpha\beta$-22S-homohopane, $\alpha\beta$-22R-homohopane	Vehicle emissions
PAH252	Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]fluoranthene Benzo[e]pyrene, Benzo[a]pyrene	Combustion sources
PAH276	Indeno[1,2,3-cd]pyrene, Benzo[ghi]perylene	Combustion sources
Odd Alks	C25, C27, C29, C31 n-alkanes	Vegetative detritus, fossil fuel uses
Even Alks	C26, C28, C30, C32 n-alkanes	Fossil fuel uses
DHOPA	2,3-dihydroxy-4-oxopentanoic acid	Oxidation of mono-aromatics
PhtA	Phthalic acid	Oxidation of naphthalene and derivatives
Nitrophenol	4-Nitrophenol	Combustion sources (e.g. biomass burning), oxidation of aromatics in the presence of NOx
Nitrocatechols	4-nitrocatechol, 3-Methyl-5-Nitrocatechol, 4-Methyl-5-Nitrocatechol	Combustion sources (e.g. biomass burning), oxidation of aromatics in the presence of NOx
C3-5 DCAs	Malonic, Succinic, Glutaric acid	Oxidation products of VOCs
C6-8 DCAs	Adipic, Pimelic, Suberic acid	Primary emissions from anthropogenic sources (e.g. industrial emissions), oxidation of aromatic compounds
hDCAs	Glyceric acid, 2-hydroxyglutaric, 3-hydroxyglutaric, 2-hydroxyadipic, 3-hydroxyadipic, hydroxypimelic acid	Oxidation products of VOCs and their parent DCAs
AzelaicA	Azelaic acid	Oxidation products of fatty acids
9-OxononanoicA	9-Oxononanoic acid	Oxidation products of fatty acids
NonanoicA	Nonanoic acid	Oxidation products of fatty acids
Iso_T	2-methylglyceric acid, 2-methylthreitol, 2-methylerythritol, cisMTB1, MTB2, transMTB3	Oxidation products of isoprene
aPin_T	Pinic acid, 3-MBTCA, 3-hydroxy-4-dimethylglutaric, 3-isopropylglutaric acid	Oxidation products of a-pinene
βCary_T	β_caryophyllinic_acid	Oxidation products of β-caryophyllene

Table S2. Numerical results of source contributions to ON and OC based on the 18-factor PMF solution. Both mass contributions and percentage contributions (avg±SD) from the sources are provided.

Sources	ON		OC	
	Mass contribution $\mu gN\ m^{-3}$	Percent contribution %	Mass contribution $\mu gC\ m^{-3}$	Percent contribution %
Industrial emission	0.03±0.03	4±3	0.05±0.04	1±1
Coal combustion	0.17±0.15	21±13	1.08±0.96	19±12
Biomass burning	/	/	0.25±0.19	4±3
Vehicle emission	0.16±0.18	21±12	1.33±1.47	23±13
Residue oil combustion	/	/	0.04±0.04	1±1
Cooking emission	0.02±0.03	2±3	0.65±1.19	11±10
Sea salt	/	/	/	/
Soil dust	0.04±0.03	5±3	0.10±0.07	2±1
Oxygenated cooking OA	0.05±0.05	7±6	0.37±0.36	6±6
Nitrocatechol formation	0.06±0.07	7±5	0.48±0.54	8±6
Nitrophenol formation	0.001±0.002	0.2±0.3	0.01±0.02	0.2±0.3
Nitrate formation	0.11±0.09	14±9	0.29±0.23	5±4
Sulfate formation	/	/	0.12±0.11	2±3
Photochemical foramtion	0.08±0.07	10±14	0.50±0.41	9±13
Phthalic acid formation	/	/	0.002±0.002	0.04±0.05
Dicarboxylic acid formation	0.07±0.08	8±10	0.26±0.31	4±5
Isoprene&a-pinene SOA formation	/	/	0.19±0.23	3±4
β-caryophyllene SOA formation	0.01±0.01	1±1	0.08±0.07	1±1
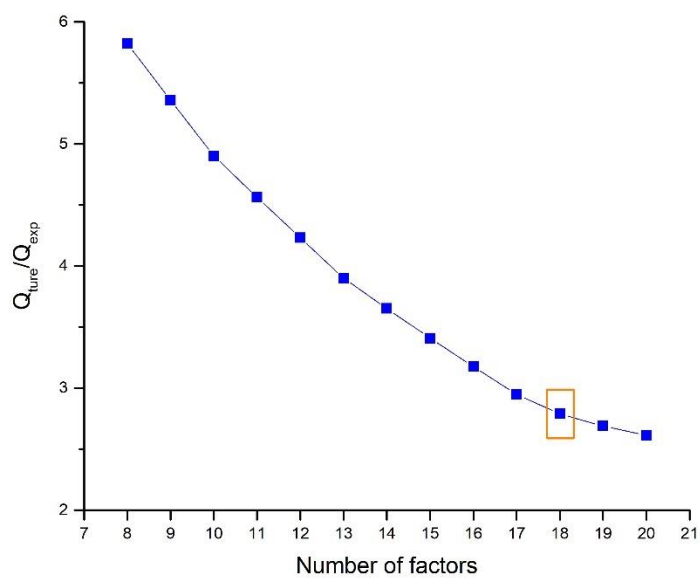
Figure S1. Variation of Q/Qexp with the increasing of factor numbers in PMF analysis. 18-factor solution was selected as indicated by a yellow box.
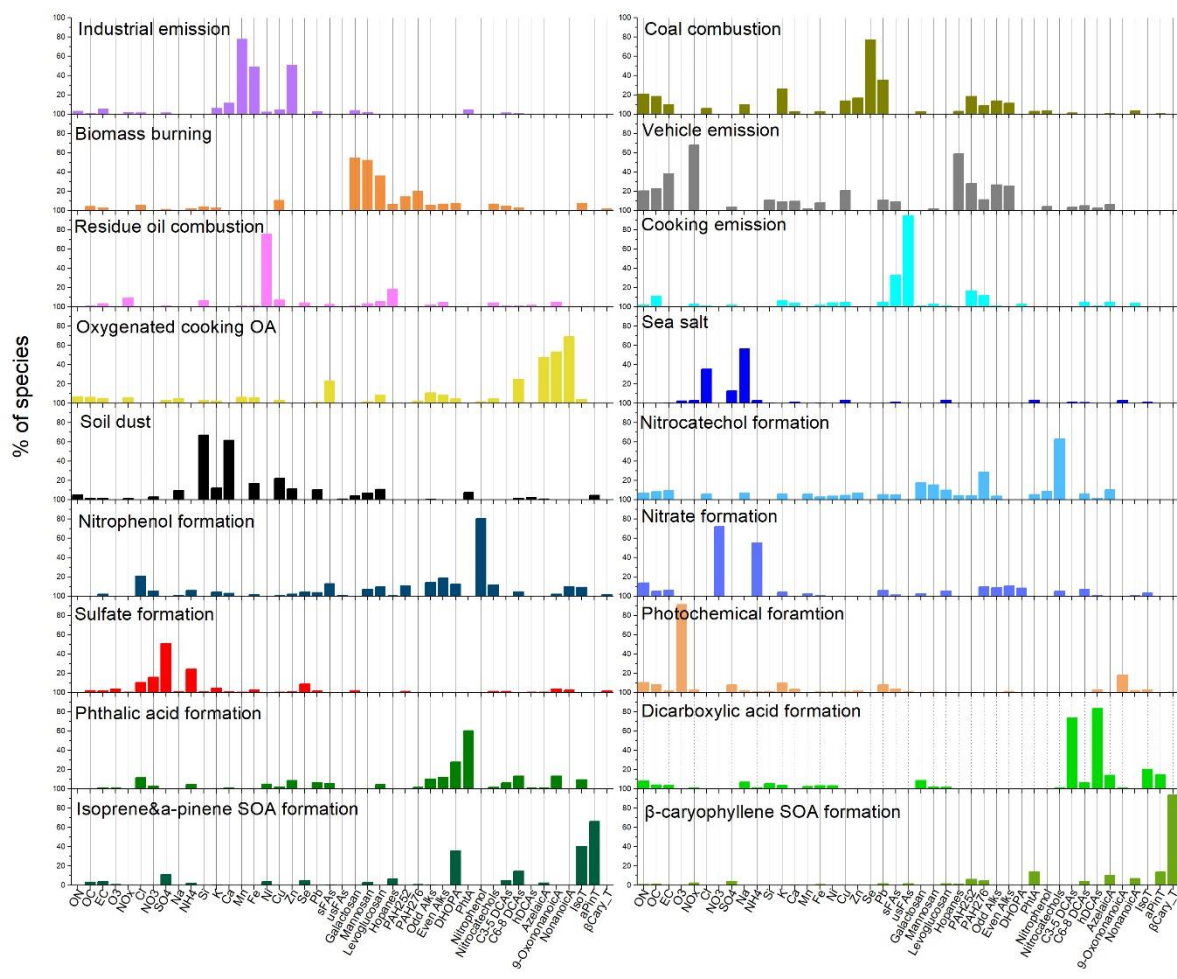
Figure S2. Source profiles for the 18-factor solution from PMF analysis. Detailed descriptions of organic species can be found in Table S1.
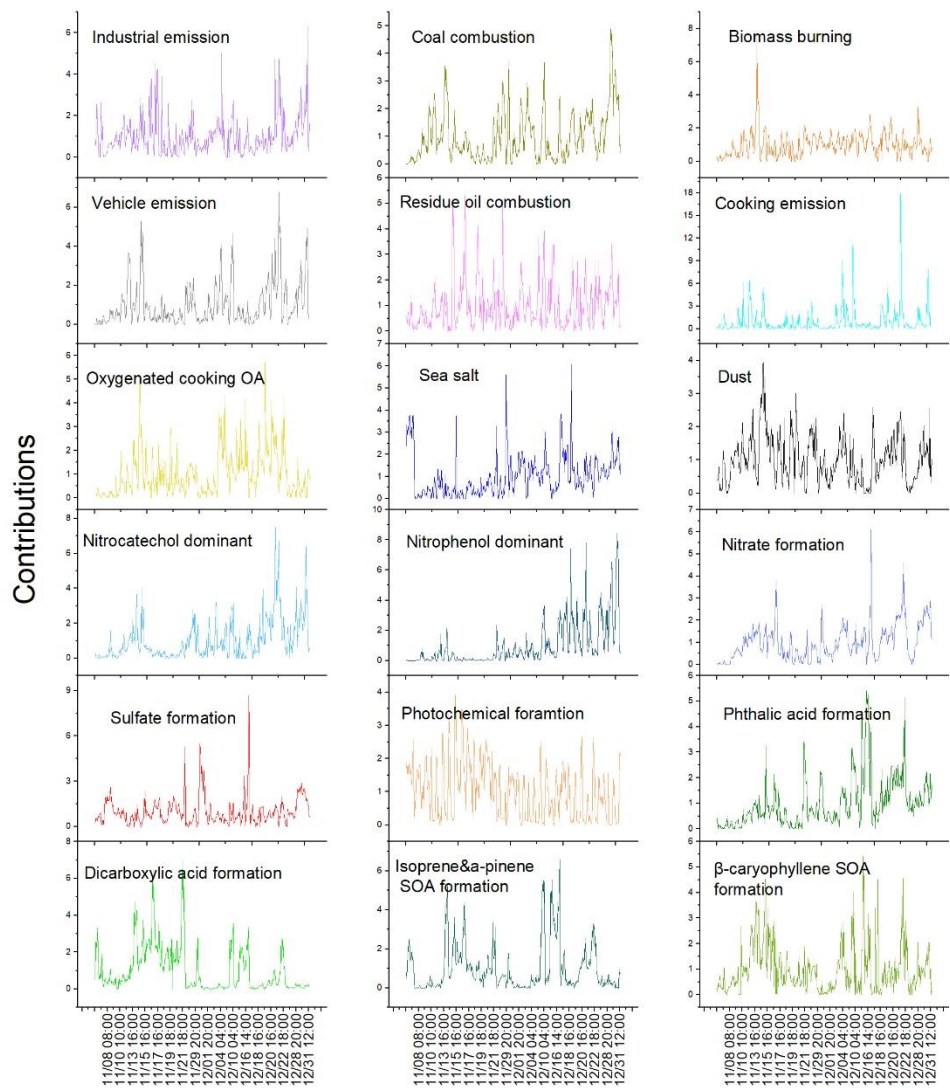
Figure S3a. Time series of source contributions from the 18 factor-PMF solution.
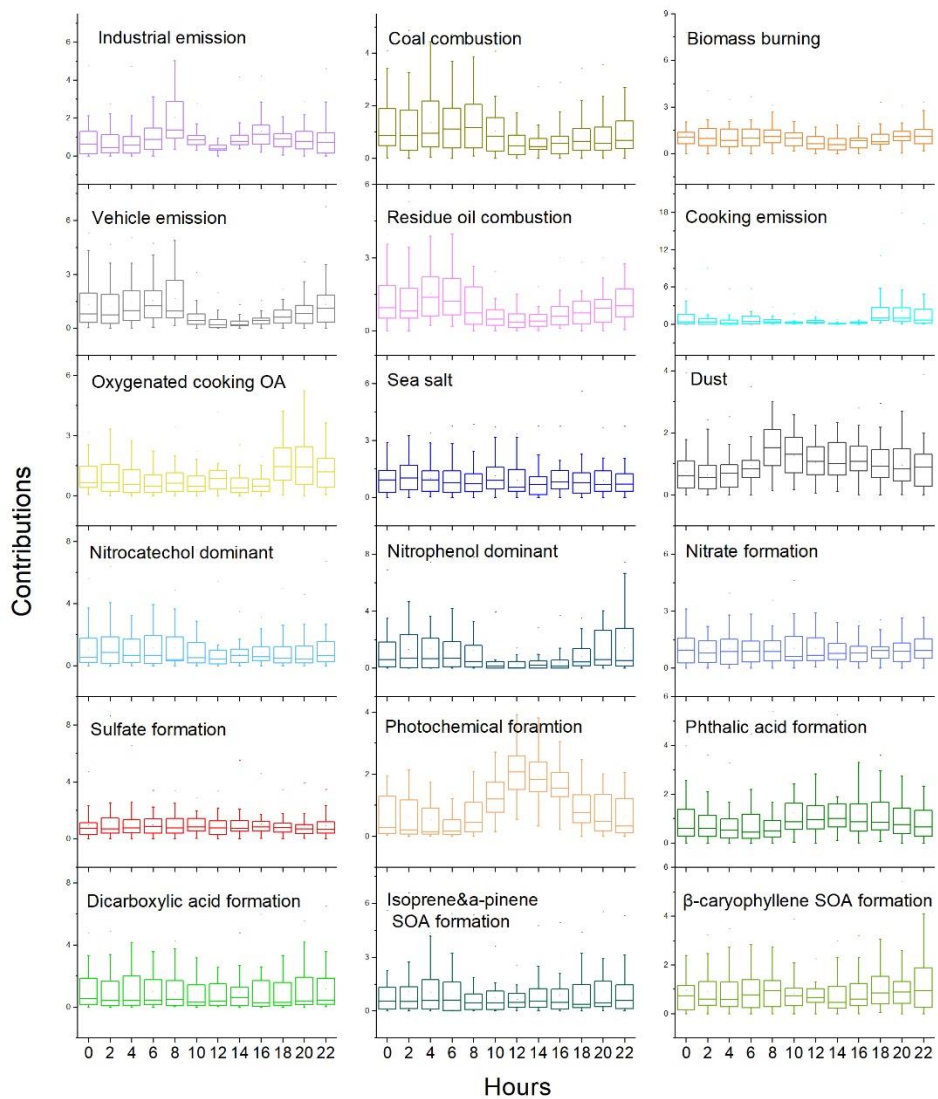
Figure S3b. Diel patterns of source contributions from the 18 factor-PMF solution.
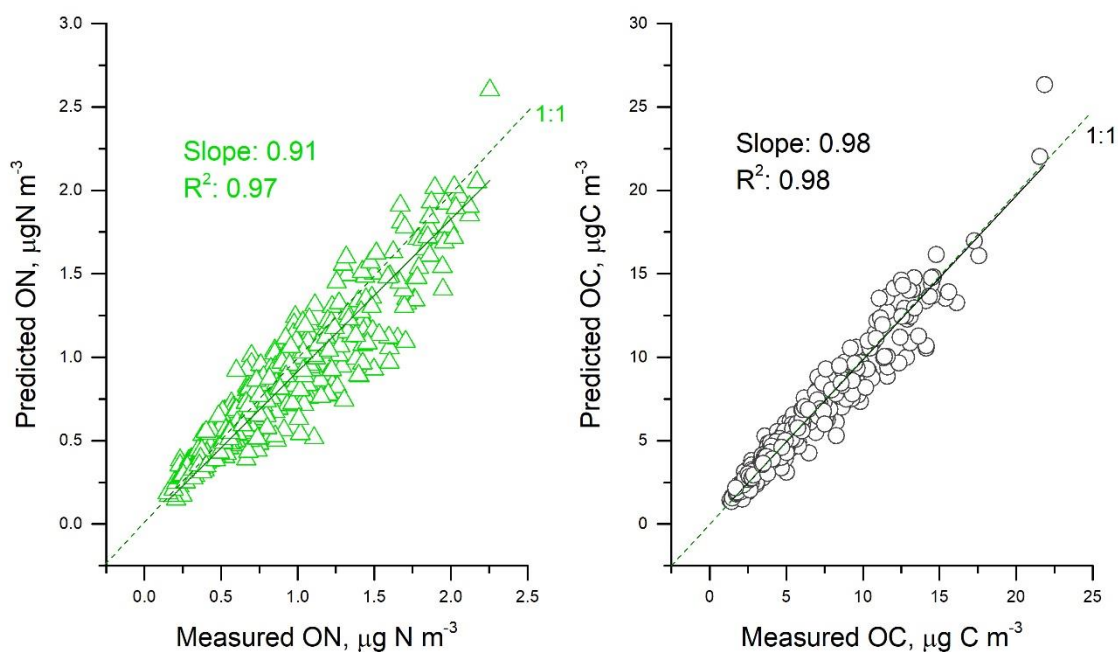
Figure S4. Comparisons between measured and PMF-predicted ON and OC concentrations.
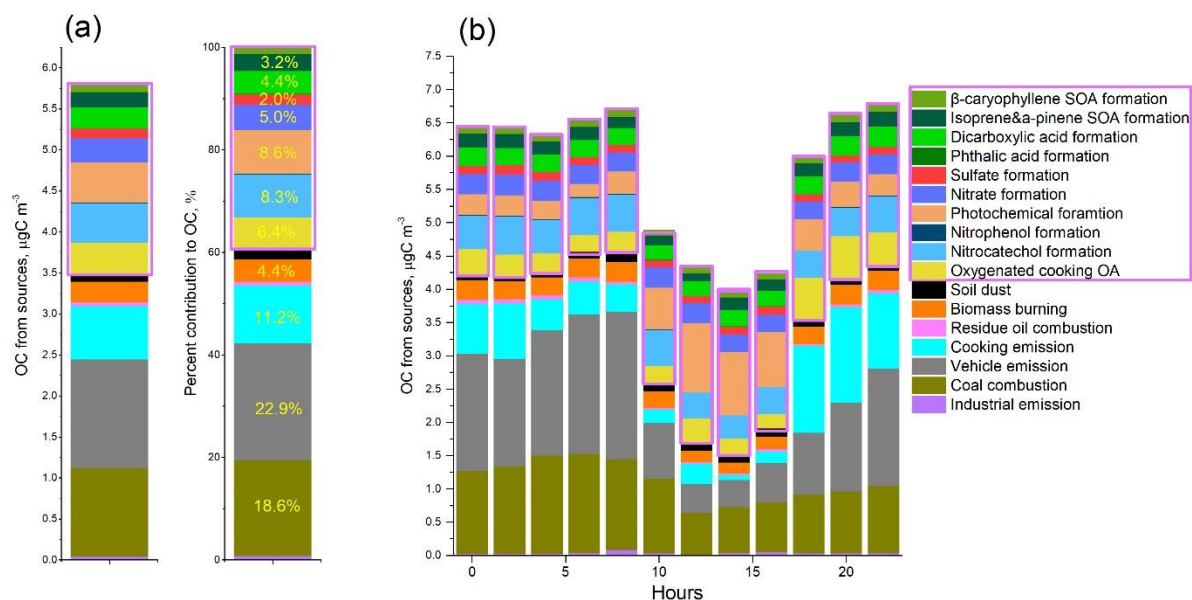
Figure S5. Source apportionment results for aerosol OC by PMF analysis. (a) Overall mass and percent contributions of resolved sources to OC. Numerical results of percent contribution to OC from industrial emission (0.8%), residual oil combustion (0.8%), soil dust (2%), nitrophenol formation (0.2%), phthalic acid formation (0.04%), and β-caryophyllene SOA formation (1%) are very low and not shown. (b) Diel patterns of mass contributions of each source to OC. Secondary sources of OC are highlighted with a purple box. The source compositions of ON can be found in the main text in Figure 2.
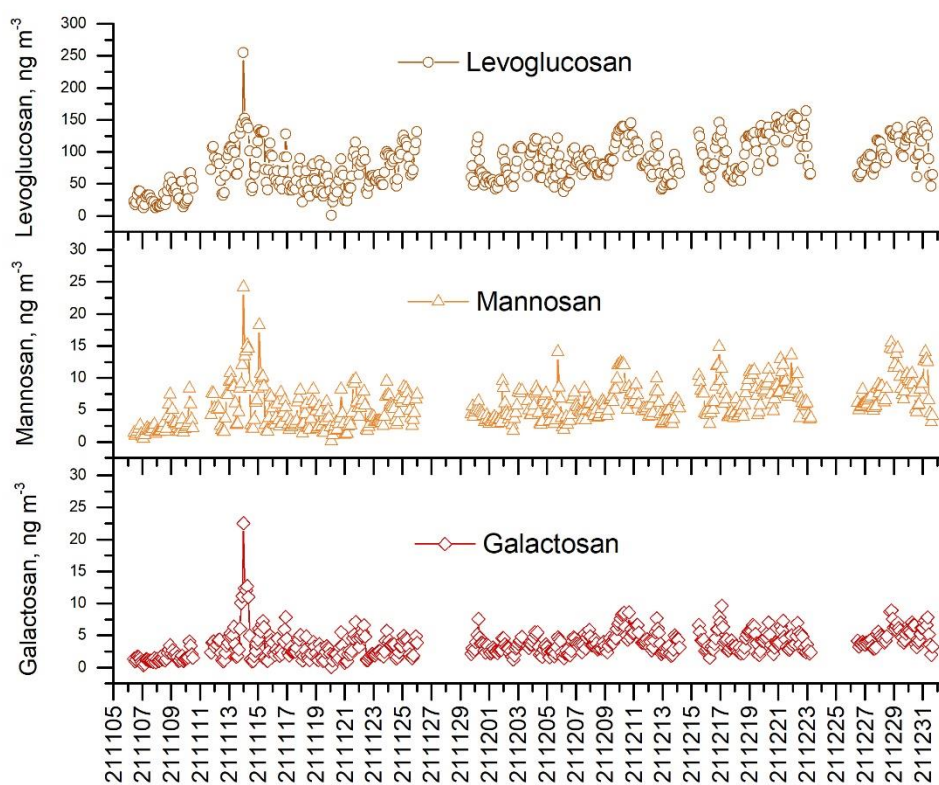
Figure S6. Time series of levoglucosan, mannosan, and galactosan concentrations during the fall-winter observation period.
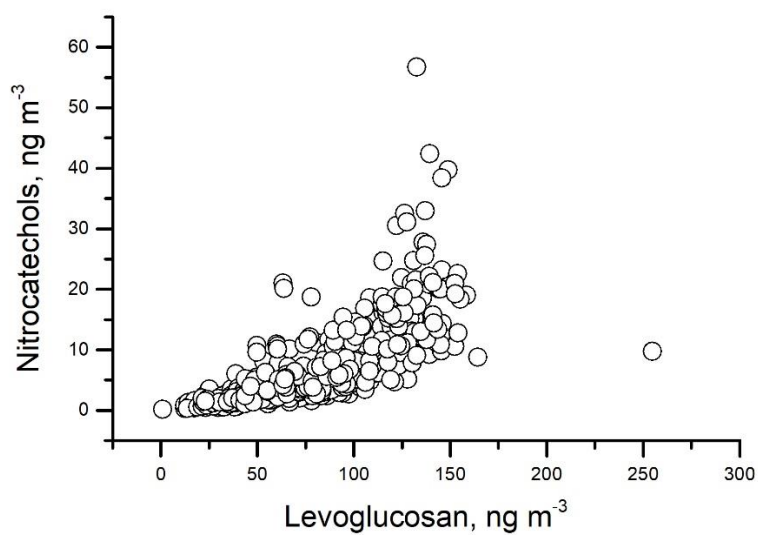
Figure S7. Relationship between levoglucosan and nitrocatechols. Nitrocatechols represent the summation of 4-nitrocatechol, 3-Methyl-5-Nitrocatechol, 4-Methyl-5-Nitrocatechol.
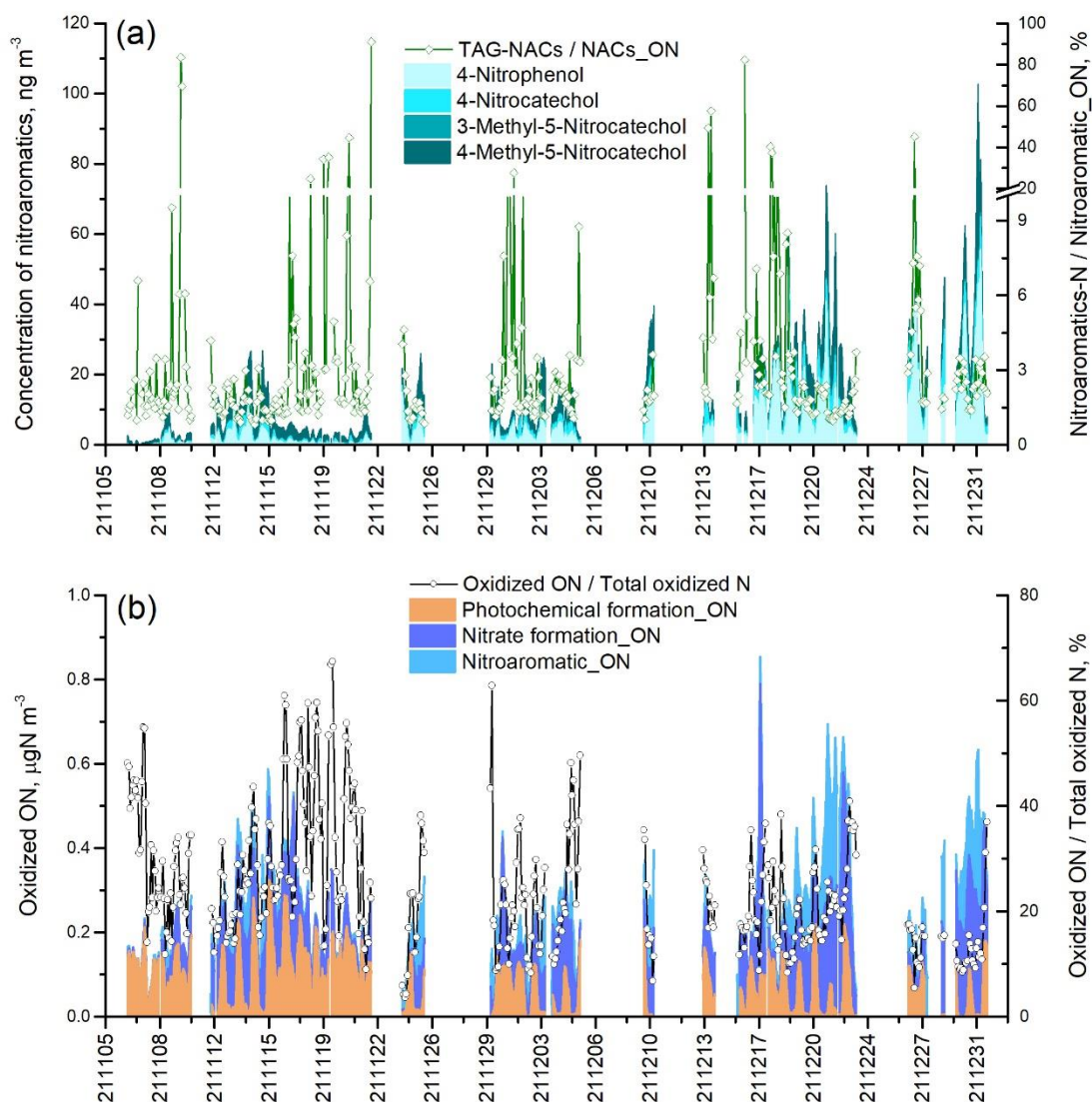
Figure S8. (a) Concentrations of the four nitroaromatic compounds determined by TAG system and the ratio of nitroaromatics-N over the nitroaromatic_ON. The nitroaromatics-N is the summation of N in the four individual nitroaromatic compounds determined by TAG system, and the nitroaromatic_ON is ON mass that distributed in nitrophenol and nitrocatechol formation factors in the PMF analysis. (b) Concentrations of ON fractions associated with photochemical formation, nitrate formation, and nitroaromatic formation processes resolved from the PMF analysis. The ratio of oxidized ON over total oxidized N is also shown. The oxidized ON is the summation of ON fractions associated with photochemical formation, nitrate formation, and nitroaromatic formation processes, while the total oxidized N is the summation of oxidized ON and inorganic nitrate-N.
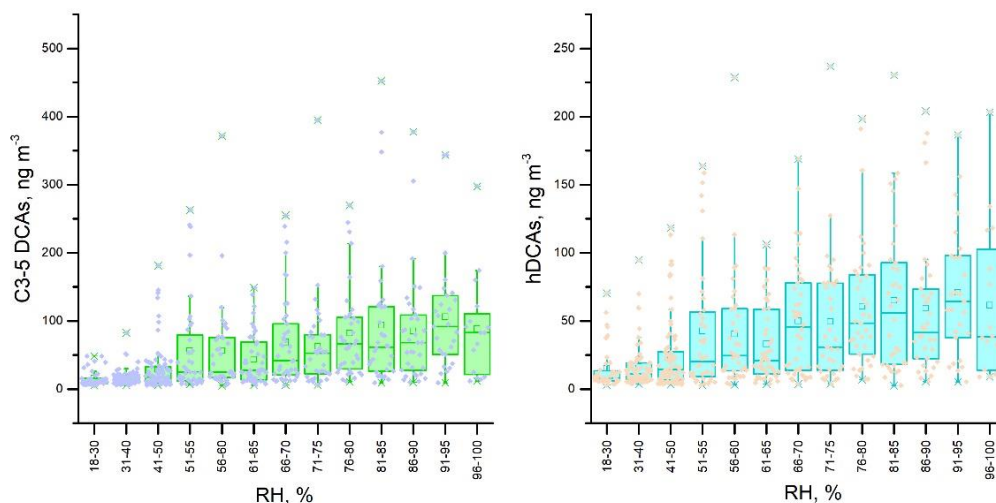
Figure S9. Variations of the concentrations of C3-5 DCAs and hDCAs as a function of relative humidity.
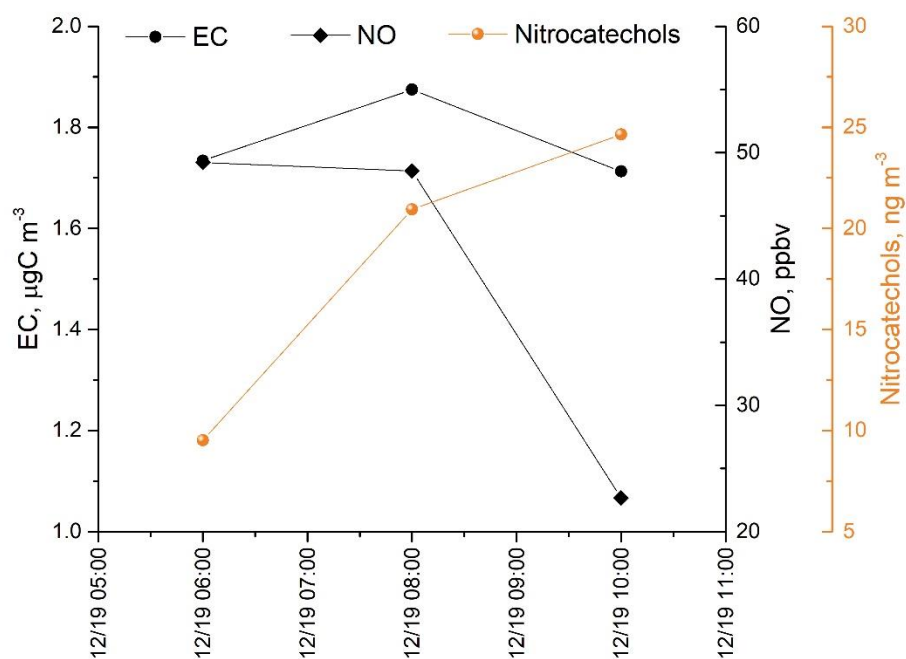
Figure S10. Variations of the concentrations of elemental carbon (EC), nitric oxide (NO), and nitrocatechols during the Type 4 case shown in Figure 4 in the main text.

References

Wang, Q. Q., Huang, X. H. H., Zhang, T., Zhang, Q. Y., Feng, Y. M., Yuan, Z. B., Wu, D., Lau, A. K. H., and Yu, J. Z.: Organic tracer-based source analysis of PM$_{2.5}$ organic and elemental carbon: A case study at Dongguan in the Pearl River Delta, China, Atmos. Environ., 118, 164-175, 2015.

Wang, Q. Q., Qiao, L. P., Zhou, M., Zhu, S. H., Griffith, S., Li, L., and Yu, J. Z.: Source Apportionment of PM$_{2.5}$ Using Hourly Measurements of Elemental Tracers and Major Constituents in an Urban Environment: Investigation of Time-Resolution Influence, J. Geophys. Res. Atmos., 123, 5284–5300, 2018.