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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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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 (Wang et al., 2018). 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 (Wang et al., 2015). 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 S2, 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 were 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. There were no strong correlations ($R \geq 0.7$) between the resolved factors, as shown in Table S2, indicating that overall the 18 factors were independent of each other and represented 18 distinct sources. Consequently, the 18-factor solution was selected to do subsequent analysis. Figure S3 displays the profiles of the 18 resolved factors while Figure S4 shows the time series and diel variation patterns of each factor contribution, respectively. Figure S5 presents comparisons of modelled and observed ON and OC concentrations. The source compositions of OC resolved from PMF analysis are shown in Figure S6 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 S3.

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, αβ-norhopane, αβ-hopane, αβ-22S-homohopane, αβ-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. Correlation (R) matrix between the PMF-resolved factors.

	β-caryophyllene SOA formation	Nitrocatechol formation	Phthalic acid formation	Nitrophenol formation	Vehicle emission	Dicarboxylic acid formation	Cooking emission	Residue oil combustion	Photochemical formation	Sea salt emission	Biomass burning	Coal combustion	Industrial emission	Nitrate formation	Sulfate formation	Soil dust	Isoprene&α-pinene SOA formation	Oxygenated cooking OA
β-caryophyllene SOA formation	1.00																	
Nitrocatechol formation	0.29	1.00																
Phthalic acid formation	0.24	0.30	1.00															
Nitrophenol formation	0.07	0.65	0.21	1.00														
Vehicle emission	0.43	0.58	0.12	0.47	1.00													
Dicarboxylic acid formation	0.37	-0.10	0.23	-0.22	-0.08	1.00												
Cooking emission	0.27	0.43	0.16	0.28	0.59	-0.08	1.00											
Residue oil combustion	0.26	0.20	0.01	0.23	0.32	0.26	0.01	1.00										
Photochemical formation	-0.17	-0.41	-0.06	-0.45	-0.63	0.21	-0.37	-0.37	1.00									
Sea salt emission	-0.18	0.12	-0.08	0.32	0.07	-0.26	0.06	-0.06	-0.14	1.00								
Biomass burning	0.35	0.20	0.23	0.03	0.23	0.26	0.06	0.13	-0.40	-0.13	1.00							
Coal combustion	0.22	0.54	0.14	0.50	0.42	-0.01	0.14	0.30	-0.43	0.05	0.37	1.00						
Industrial emission	0.29	0.43	0.12	0.34	0.56	0.03	0.33	0.24	-0.21	0.13	0.00	0.40	1.00					
Nitrate formation	0.32	0.48	0.42	0.32	0.37	0.15	0.23	0.21	-0.22	0.05	0.23	0.44	0.33	1.00				
Sulfate formation	-0.19	0.03	0.19	0.18	-0.16	0.04	-0.18	-0.07	0.07	0.06	-0.02	0.17	-0.02	0.41	1.00			
Soil dust	0.21	0.26	-0.08	-0.02	0.39	-0.05	0.28	-0.01	0.03	-0.16	-0.07	0.10	0.42	0.18	-0.10	1.00		
Isoprene&α-pinene SOA formation	0.46	0.10	0.54	0.00	0.06	0.69	0.06	0.25	0.00	-0.09	0.34	0.08	0.05	0.31	0.07	-0.16	1.00	
Oxygenated cooking OA	0.24	0.14	0.32	0.06	0.23	0.07	0.29	0.06	-0.25	-0.14	0.23	-0.04	0.01	0.21	-0.25	0.21	0.24	1.00

Table S3. 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 μgN m^{-3}	Percent contribution %	Mass contribution μgC 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 processes	0.11±0.09	14±9	0.29±0.23	5±4
Sulfate formation processes	/	/	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

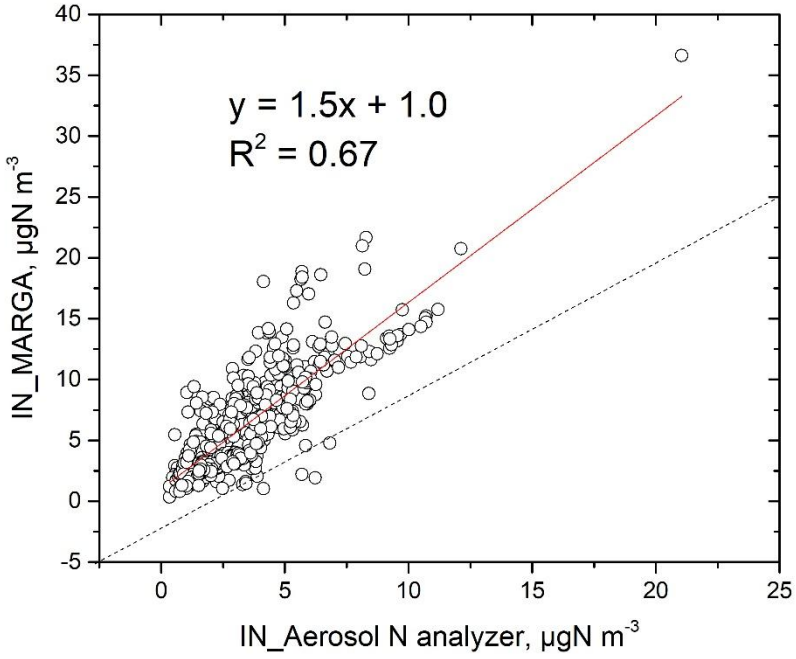

Figure S1. The comparison of aerosol IN concentrations determined by the new method and Monitor for AeRosols and GAses (MARGA) system. The gap between the two measurements was attributed to the differences in sampling, measurement approach, and calibrations of the two methods.

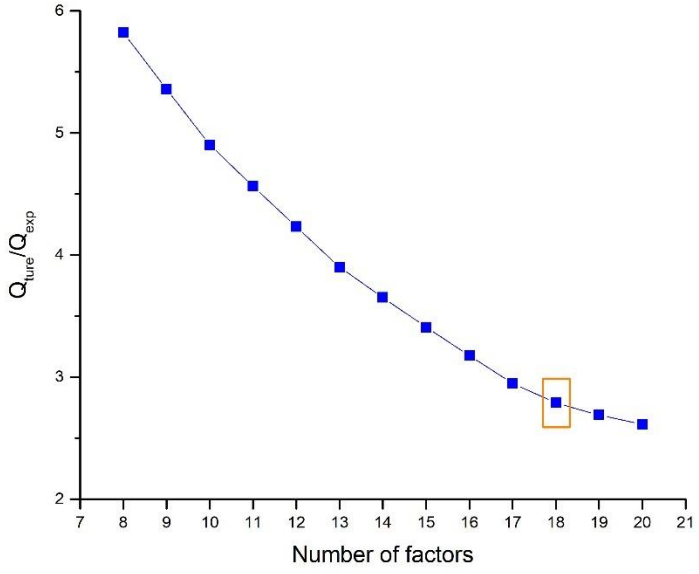

Figure S2. Variation of Q/Qexp with the increasing of factor numbers in PMF analysis. 18-factor solution was selected as indicated by a yellow box.

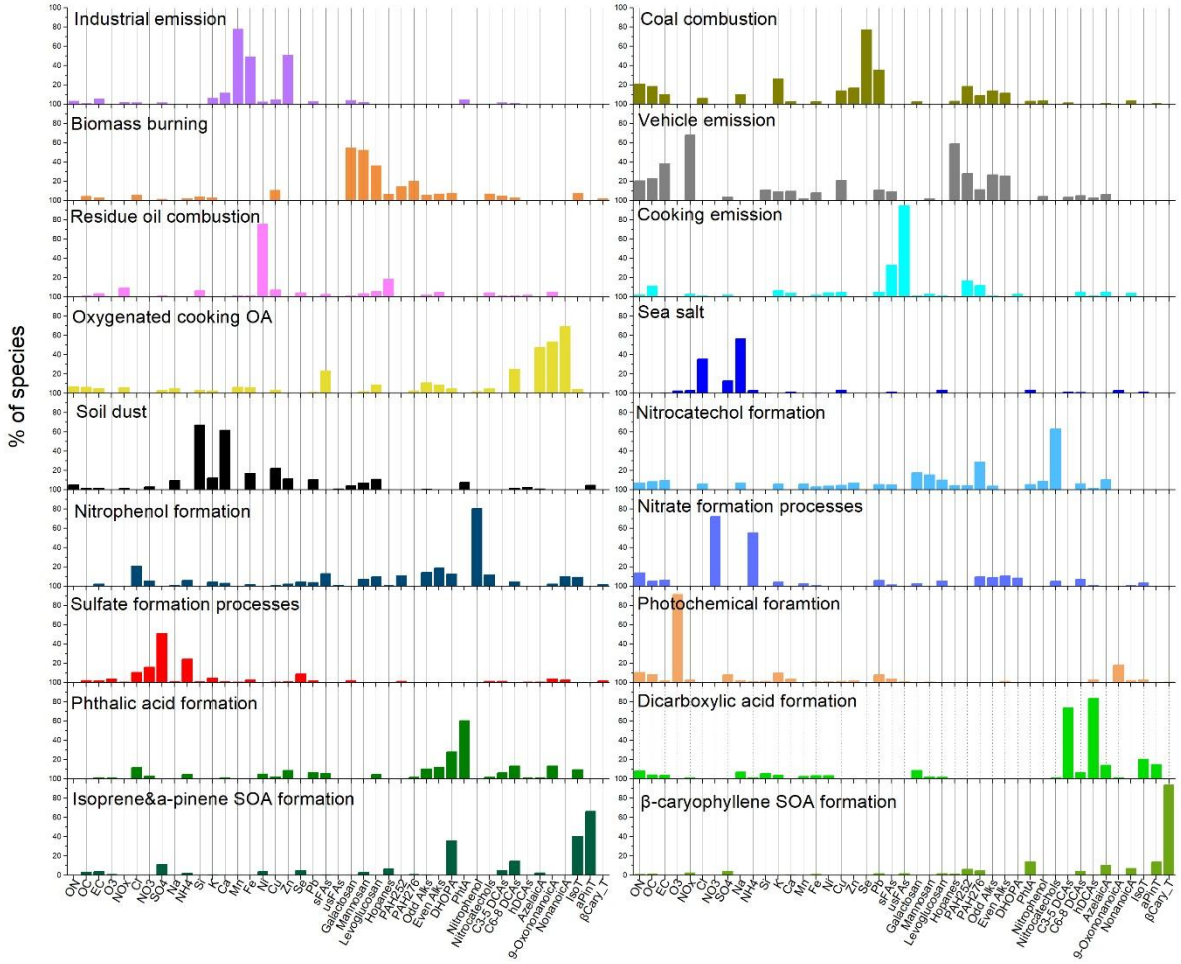

Figure S3. Source profiles for the 18-factor solution from PMF analysis. Detailed descriptions of organic species can be found in Table S1.

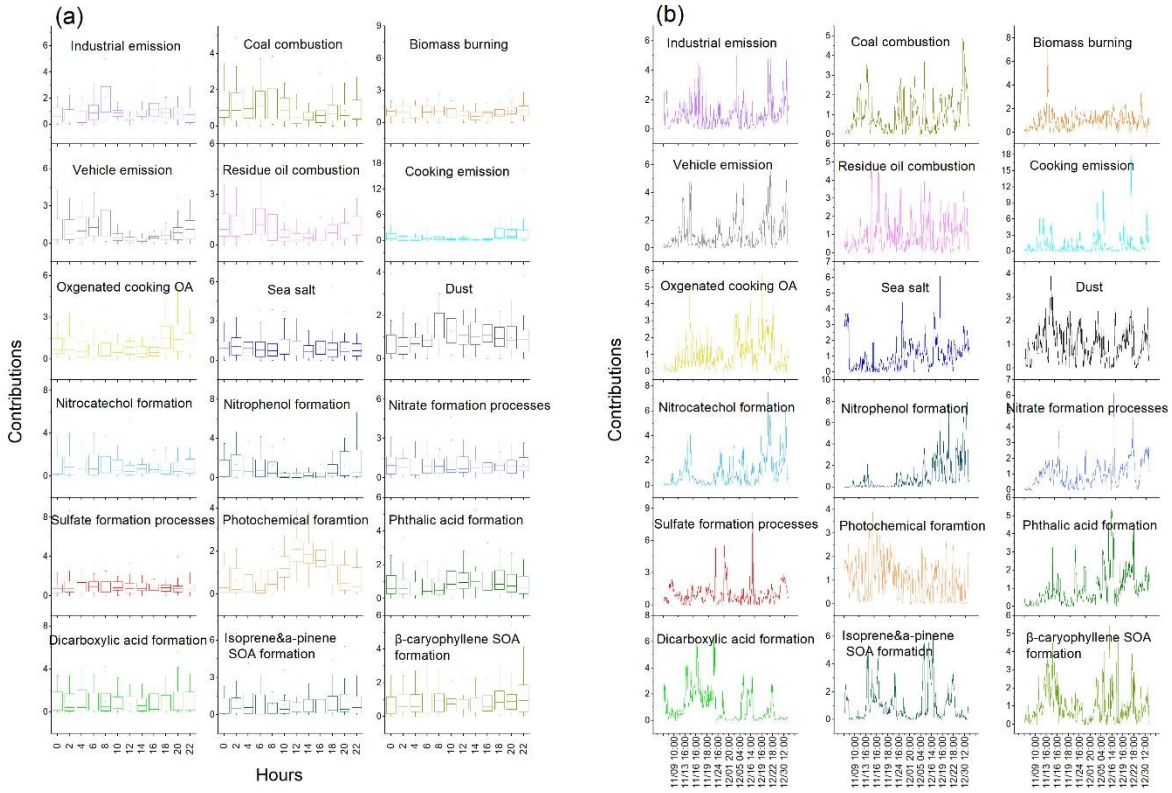

Figure S4. Diel variation patterns (a) and time series (b) of source contributions for the 18 factor-PMF solution.

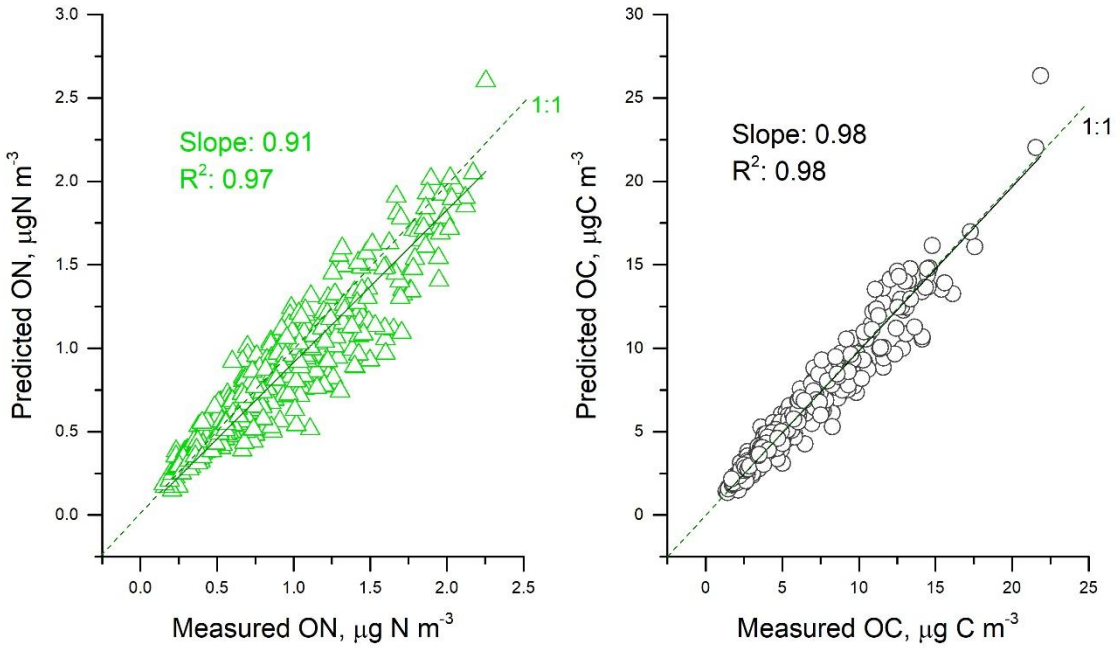

Figure S5. Comparisons between measured and PMF-predicted ON and OC concentrations.

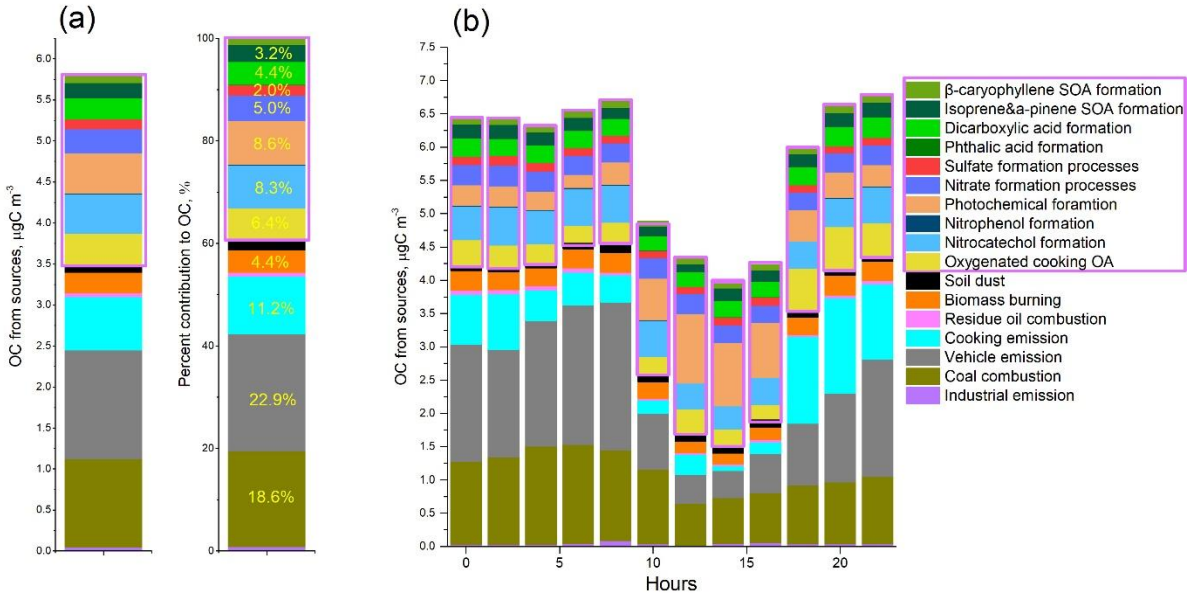

Figure S6. Source apportionment results for aerosol OC by PMF analysis. (a) Overall mass and percent contributions of resolved sources to OC. Numerical results of percent contribution to OC from industrial emission (0.8%), residual oil combustion (0.8%), soil dust (2%), nitrophenol formation (0.2%), 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.

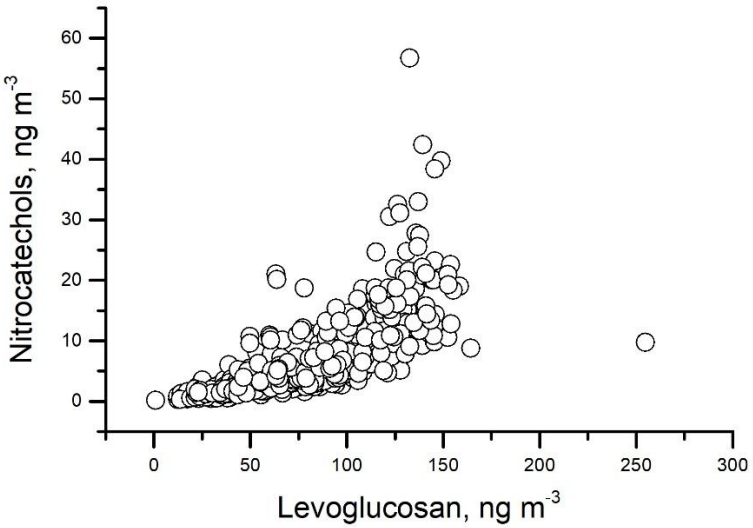

Figure S7. Relationship between levoglucosan and nitrocatechols. Nitrocatechols represent the summation of 4-nitrocatechol, 3-Methyl-5-Nitrocatechol, 4-Methyl-5-Nitrocatechol.

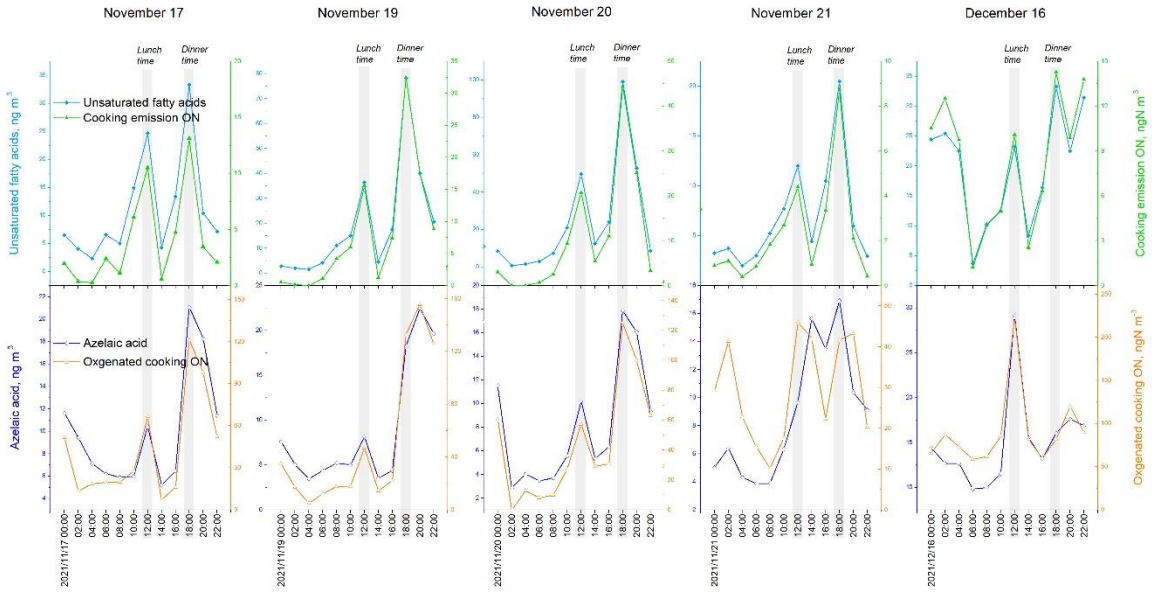

Figure S8. Five representative cases in which the concentrations of cooking emission tracers (unsaturated fatty acids) and oxygenated cooking OA (Azelaic acid) and their associated ON were peaked both at lunchtime and dinnertime.

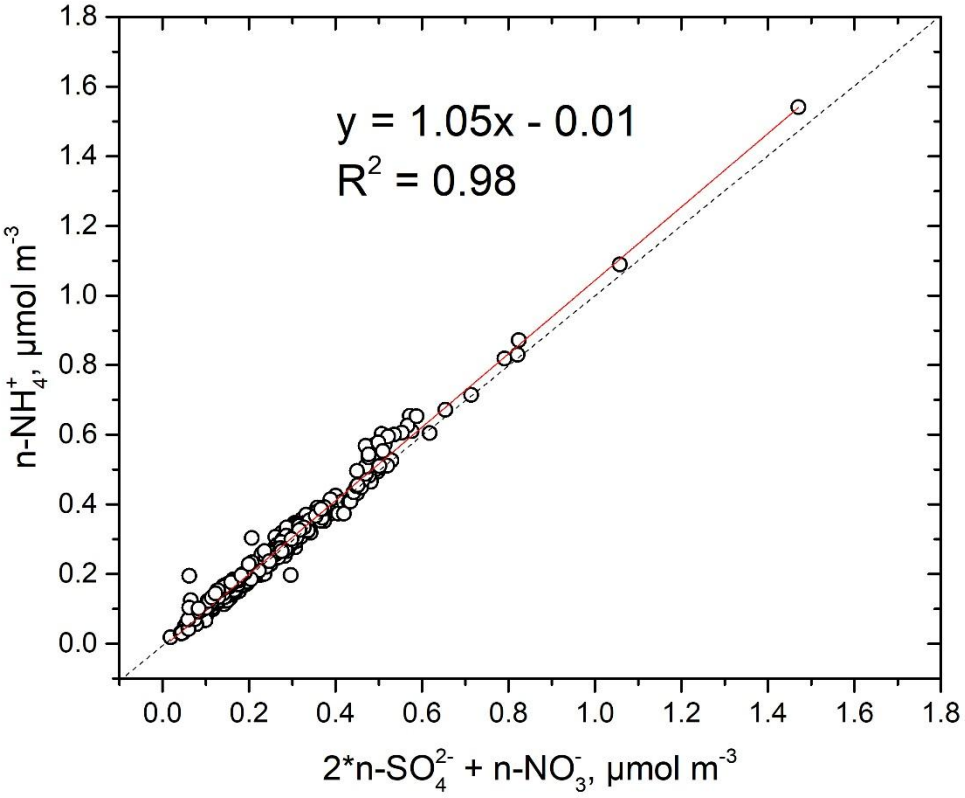

Figure S9. Charge balance between ammonium, sulfate and nitrate during the observation.

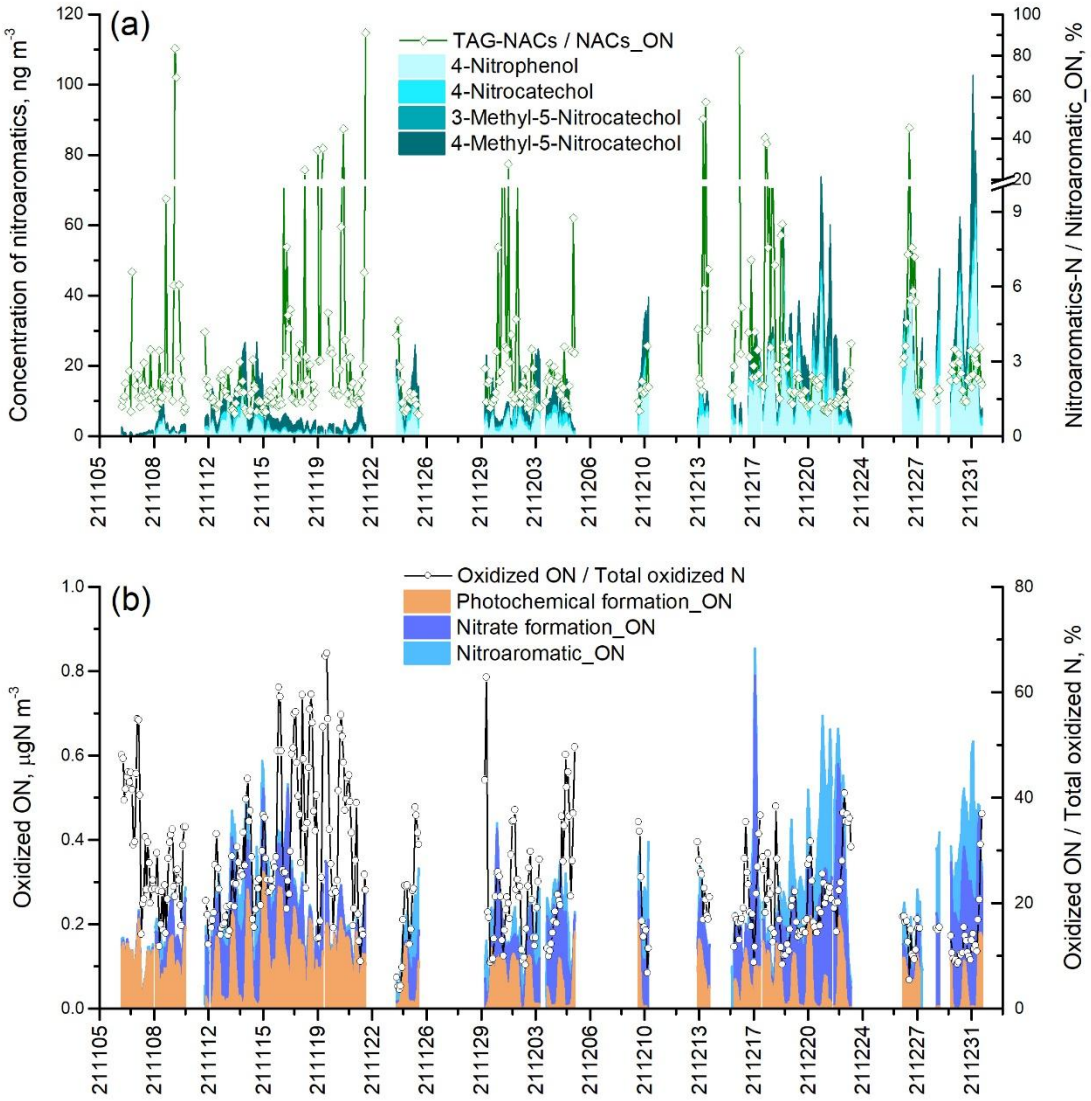

Figure S10. (a) Concentrations of the four nitroaromatic compounds determined by TAG system and the ratio of nitroaromatics-N over the nitroaromatic_ON. The nitroaromatics-N is the summation of N in the four individual nitroaromatic compounds determined by TAG system, and the nitroaromatic_ON is ON mass 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.

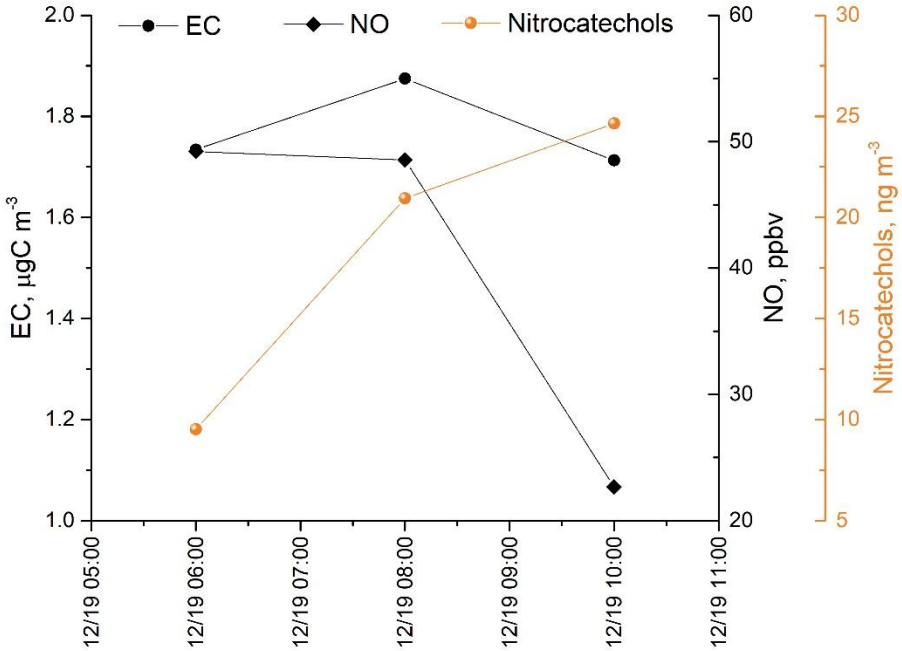

Figure S11. Variations of the concentrations of elemental carbon (EC), nitric oxide (NO), and nitrocatechols during the Type 4 case shown in Figure 4 in the main text.

References

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