



Supplement of

Underestimation of anthropogenic organosulfates in atmospheric aerosols in urban regions

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S1. The UHPLC-HRMS² analysis

The UHPLC-HRMS system was used for sample extraction analysis with full scan and higher-energy collisional dissociation (HCD). Chromatographic separation was performed on a reversed-phase column (Accucore C18, 150×2.1 mm, 2.6 μm particle size, Thermo Scientific) with a flow rate of 0.33 mL/min and an injection volume of 2.5 μL. Mobile phase A consisted of ultrapure water with 0.05% acetic acid, while mobile phase B was a mixture of methanol and 0.05% acetic acid. The HPLC gradient program was as follows: from 0 to 1.5 minutes, the composition was held at 5% B; then, from 1.5 to 8 minutes, it linearly increased to 54% B; subsequently, from 8 to 11 minutes, it linearly changed to 95% B; next, from 11 to 12 minutes, it linearly reached 100% B, holding for 2 minutes, and then, from 14 to 14.5 minutes, it linearly returned to 5% B with a 1.5 minutes hold before the next injection. The settings were as follows: capillary voltage -3.5 kV, capillary temperature 320 °C, vaporizer temperature 35 °C, and sheath, auxiliary, and sweep gas at 2, 1, and 1 arbitrary unit, respectively.

The HRMS operated in negative ESI mode, employing data-dependent acquisition (DDA). Full scan (MS1, m/z = 70–700, resolving power 120000) and fragmentation scan (MS2) for the top ten ions (m/z = 50–500, resolving power 30,000, collision energies 30, 40, and 50 eV, intensity threshold 50000) were collected. The HRMS peaks with more than 2 charges were excluded. The other settings were kept the same as in the full scan mode. An instrumental blank (methanol) was injected every 10 samples to monitor any instrumental background.

S2. PM_{2.5} Source apportionment using PMF

USEPA-PMF 5.0 software was performed on PM_{2.5} for the entire sampling period. The input data for the PMF consists of a concentration matrix and an uncertainty matrix for chemically speciated concentrations of components of PM_{2.5} (carbonaceous fractions, WSIs or the water-soluble inorganic species, and trace elements), where the rows correspond to the time series, and the columns to the species.

The chemical species included were carbonaceous fractions namely organic carbon, and elemental carbon (EC); water-soluble inorganic species namely SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, K⁺, Ca²⁺, Na⁺, K⁺; trace elements namely Al, Si, Ti, Cr, Mn, Fe, Se, Co, Ni, Cu, Zn, As, Br, Sr, Pb, V and K. Species with a S/N ratio > 1 were designated as strong, while S/N ratios < 0.5 were designated as bad. The best solution for the base run was obtained using seven factors: biomass burning, fireworks and crackers, coal combustion, traffic emissions, road dust, secondary inorganics, industry combustion.

S3. Calculations of ALWC, aerosol pH with thermodynamic modeling

The aerosol liquid water content (ALWC) was calculated using the ISORROPIA II thermodynamic model. The model input data mainly include the mass concentration of water-soluble ions (chloride, sulfate, nitrate, and ammonium, in μg/m³), temperature (in Kelvin), and ambient RH (ranging from 0 to 1). We employed ISORROPIA-II in “forward” mode, and the model assumes aerosol was in a “metastable” state with internally mixed and in thermodynamic equilibrium with the gas phase. The calculated ALWC was lower than the actual ALWC because the aerosol liquid water associated with water-soluble organic species was not included (Fountoukis and Nenes, 2007). The pH was calculated by the using eq.(S1):

$$pH = -\log_{10} \frac{1000H_{air}^{+}}{ALWC} \quad (S1)$$

where H_{air}^{+} is H^{+} loading per volume air (μg/m³).

67 **Table S1.** Details of collected samples.

Sampling ID*	Sampling period	Average PM _{2.5} (µg/m ³)	Average RH (%)
TY1211H	23.0 h	114.63	79.61
TY1212H	23.0 h	59.89	79.88
TY1213H	23.0 h	32.83	79.25
TY1214H	15.0 h	22.63	91.07
TY1214M	8.0 h	17.59	57.99
TY1217M	23.0 h	46.82	45.81
TY1218H	6.8 h	193.38	71.49
TY1218L	6.8 h	35.74	30.34
TY1218M	9.4 h	168.33	45.95
TY1220L	23.0 h	10.58	31.34
TY1221L	9.2 h	39.87	30.64
TY1221M	13.8 h	28.70	47.44
TY1222H	6.6 h	70.07	62.81
TY1222L	6.5 h	86.49	36.99
TY1222M	9.9 h	95.72	50.06
TY1223L	9.5 h	40.97	37.64
TY1223M	13.5 h	40.46	55.08
TY1224H	3.5 h	60.89	62.27
TY1224L	6.5 h	64.85	33.91
TY1224M	13.0 h	66.47	52.43
TY1225H	9.0 h	54.50	64.82
TY1225L	8.0 h	48.57	31.30
TY1225M	6.0 h	84.01	52.48
TY1226H	4.5 h	64.47	65.85
TY1226L	6.4 h	82.40	33.37
TY1226M	12.1 h	48.49	50.49
TY1227H	10.5 h	102.23	70.51
TY1227L	3.8 h	80.45	36.76
TY1227M	8.7 h	101.14	51.31
TY1228H	13.9 h	137.82	70.13
TY1228L	3.4 h	97.64	35.22
TY1228M	5.7 h	155.63	48.82
TY1229H	16.6 h	246.03	76.81
TY1229M	6.4 h	247.11	56.38
TY1230H	23.0 h	34.05	67.95
TY1231M	16.4 h	74.79	59.05
TY1231L	6.6 h	20.37	36.19
TY0101H	13.6 h	133.94	71.40
TY0101M	9.4 h	138.30	51.48
TY0102L	8.7 h	23.80	32.56
TY0102M	14.3 h	24.69	53.91
TY0103H	6.0 h	45.26	61.92

Table S1 Continued

Sampling ID*	Sampling period	Average PM _{2.5} (µg/m ³)	Average RH (%)
TY0103L	8.4 h	39.07	32.81
TY0103M	8.6 h	60.97	54.97
TY0104L	15.1 h	38.52	30.19
TY0104M	7.9 h	29.48	48.30
TY0106L	16.2 h	16.22	29.59
TY0106M	6.8 h	17.94	43.27
TY0107L	8.7 h	36.26	22.63
TY0107M	14.3 h	47.55	48.34
TY0108H	14.3 h	109.21	61.37
TY0108L	6.2 h	103.28	34.61
TY0108M	2.5 h	76.61	49.75
TY0109H	7.8 h	44.57	65.18
TY0109L	3.5 h	48.94	38.17
TY0109M	11.7 h	49.84	48.90
TY0110H	8.3 h	70.48	66.80
TY0110L	5.1 h	64.41	38.37
TY0110M	9.6 h	69.07	44.51
TY0111H	5.9 h	95.34	63.55
TY0111L	6.9 h	81.94	34.07
TY0111M	10.2	89.66	53.17
TY0113L	8.9 h	81.32	32.63
TY0113M	14.1 h	68.30	45.10
BJ1203L	13.0 h	41.97	26.06
BJ1203M	10.0 h	52.61	45.80
BJ1208L	6.0 h	90.98	23.39
BJ1208M	17.0 h	59.02	42.40
BJ1209L	3.2 h	36.43	27.27
BJ1209M	19.8 h	28.11	43.65
BJ1210L	5.5 h	31.61	37.28
BJ1210H	17.5 h	24.17	82.23
BJ1211H	23.0 h	28.44	82.41
BJ1212H	23.0 h	59.76	85.39
BJ1213H	23.0 h	82.85	84.82
BJ1215L	23.0 h	6.15	33.01
BJ1216L	23.0 h	7.65	28.00
BJ1217L	9.0 h	16.99	27.52
BJ1217M	14.0 h	30.27	56.72
BJ1218H	5.2 h	79.38	63.45
BJ1218L	7.6 h	33.86	29.21
BJ1218M	10.2 h	74.80	53.15
BJ1222M	12.7 h	29.53	48.35
BJ1222L	10.3 h	19.87	25.09

Table S1 Continued

Sampling ID*	Sampling period	Average PM _{2.5} (µg/m ³)	Average RH (%)
BJ1224H	6.6 h	35.68	64.80
BJ1224L	5.9 h	30.02	21.95
BJ1224M	10.5 h	35.38	47.11
BJ1225H	3.7 h	79.82	64.16
BJ1225L	6.7 h	36.29	27.30
BJ1225M	12.6 h	58.16	51.90
BJ1226H	8.3 h	24.48	66.41
BJ1226L	2.8 h	20.30	30.58
BJ1226M	11.9 h	25.74	53.09
BJ1227H	11.5 h	31.91	71.11
BJ1227L	5.8 h	24.02	31.57
BJ1227M	5.7 h	25.75	50.03
BJ1228H	11.9 h	57.99	72.07
BJ1228L	5.6 h	50.83	31.71
BJ1228M	5.5 h	52.15	50.38
BJ1229H	15.2 h	155.75	75.91
BJ1229L	5.3 h	67.75	34.60
BJ1229M	2.5 h	93.97	45.40
BJ1230L	7.3 h	19.84	37.22
BJ1230M	15.7 h	105.58	46.27
CS1211	23.0 h	12.15	89.30
CS1212	23.0 h	30.34	78.37
CS1213	23.0 h	29.52	84.29
CS1214	23.0 h	32.04	91.23
CS1215	23.0 h	16.10	85.37
CS1216	23.0 h	18.67	53.45
CS1217	23.0 h	20.93	48.84
CS1218	23.0 h	27.36	87.01
CS1219	23.0 h	41.75	74.37
CS1220	23.0 h	34.38	76.16
CS1221	23.0 h	51.23	63.41
CS1222	23.0 h	31.67	41.99
CS1223	23.0 h	39.62	53.17
CS1224	23.0 h	54.91	57.05
CS1225	23.0 h	73.04	56.77
CS1226	23.0 h	60.96	43.26
CS1227	23.0 h	97.74	63.02
CS1228	23.0 h	159.01	73.79
CS1229	23.0 h	216.33	75.10
CS1230	23.0 h	180.26	83.05
CS1231	23.0 h	132.52	80.59
CS0101	23.0 h	86.49	67.63

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Table S1 Continued

Sampling ID*	Sampling period	Average PM _{2.5} (µg/m ³)	Average RH (%)
CS0102	23.0 h	80.91	85.15
CS0103	23.0 h	45.99	76.24
CS0104	23.0 h	57.02	70.55
CS0105	23.0 h	56.16	71.98
CS0106	23.0 h	61.91	72.81
CS0107	23.0 h	82.71	75.75
CS0108	23.0 h	74.73	83.14
CS0109	23.0 h	75.18	80.60

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* TY is short for Taiyuan, BJ for Beijing, and CS for Changsha. In the Beijing and Taiyuan samples, the labels H, M, and L represent high (RH > 60 %), moderate (40 % < RH ≤ 60 %), and low (RH ≤ 40 %) RH regimes, respectively.

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75 **Table S2.** The monitoring instruments in different sites.

Sample site	Instruments	Measured Parameters
Changsha	Ion Chromatography (IC) (DIONEX ICS2000)	water-soluble inorganic ions
	Gas Chromatography - Mass Spectrometry (GC-MS) (Agilent 7890B-5977A)	VOCs
	OC-EC aerosol analyzer (Sunset Lab Model 5L)	EC, OC
	Automatic gas analyzers (Thermo scientific Model 42i, 43i, 48i, 49i)	NO _x , SO ₂ , CO, O ₃
	X-ray Fluorescence (XRF) (Panalytical Zetium)	trace elements
Taiyuan	Monitor for AeRosols and Gases in ambient Air (MARGA) (Metrohm 2060)	water-soluble inorganic ions
	GC-MS (Shimadzu QP2010SE)	VOCs
	Carbon Aerosol Speciation System (CASS) (Aerosol Magee Scientific)	EC, OC
	Three-arm impactor (Home-made)	the particle rebound fraction
	Automatic gas analyzers (Thermo scientific Model 42i, 43i, 48i, 49i)	NO _x , SO ₂ , CO, O ₃
	XRF (Panalytical Zetium)	trace elements
Beijing	MARGA (Metrohm 2060)	water-soluble inorganic ions
	Automatic gas analyzers (Thermo scientific Model 42i, 43i, 48i, 49i)	NO _x , SO ₂ , CO, O ₃
	GC-MS (Shimadzu QP2010SE)	VOCs
	OC-EC aerosol analyzer (Sunset Lab Model 5L)	EC, OC
	XRF (Panalytical Zetium)	trace elements

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77 **Table S3.** CD workflow

Select Spectra		
Spectrum	Lower RT Limit	0
Properties Filter	Upper RT Limit	0
Scan Event Filters	Polarity Mode	Negative
Align Retention Times		
	Alignment Model	Adaptive curve
General Settings	Maximum Shift [min]	2
	Mass Tolerance	5 ppm
Detect Compounds		
	Mass Tolerance [ppm]	5 ppm
General Settings	Min. Peak Intensity	10000
	Use Most Intense Isotope Only	True
Peak Detection	Chromatographic S/N Threshold	3
	Remove Baseline	False
Isotope Pattern	Group Isotopes for	Br; Cl
Detection		
Compound	Ions	[M-H]-1; [M-H-H ₂ O]-1; [2M-H]-1
Detection		
Group Compounds		
	Mass Tolerance	5 ppm
	RT Tolerance [min]	0.5
General Settings	Align Peaks	False
	Preferred Ions	[M-H]-1; [M-H-H ₂ O]-1; [2M-H]-1
	Area Integration	Most Common Ion
	Area Contribution	3
	CV Contribution	10
Peak Rating	FWHM to Base Contribution	5
Contributions	Jaggedness Contribution	5
	Modality Contribution	5
	Zig-Zag Index Contribution	5
Peak Rating Filter	Peak Rating Threshold	0
	Number of Files	0
Merge Features		
Peak	Mass Tolerance	5 ppm
Consolidation	RT Tolerance [min]	0.5
Search mzCloud		
	Compound Classes	All
General Settings	Library	Autoprocessed; Reference
	Search MSn Tree	False

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81 **Table S3** Continued

Search mzCloud		
DDA Search	Identity Search	Cosine
	Match Activation Type	False
	Match Activation Energy	Any
	Activation Energy Tolerance	20
	Apply Intensity Threshold	True
DIA Search	Similarity Search	Confidence Reverse
	Match Factor Threshold	30
	Use DIA Scans for Search	True
	Max. Isolation Width [Da]	500
	Match Activation Type	False
	Match Activation Energy	Any
	Activation Energy Tolerance	100
	Apply Intensity Threshold	True
	Match Factor Threshold	20
Predict Compositions		
Prediction Settings	Mass Tolerance	5 ppm
	Min. Element Counts	C H
	Max. Element Counts	C90 H200 N5 O20 S2
	Min. RDBE	0
	Max. RDBE	40
	Min. H/C	0.3
	Max. H/C	3.5
	Max. # Candidates	10
	Intensity Tolerance [%]	30
	Intensity Threshold [%]	0.1
Pattern Matching	S/N Threshold	3
	Use Dynamic Recalibration	True
	Use Fragments Matching	True
Fragments Matching	Mass Tolerance	5 ppm
	S/N Threshold	3
Assign Compound Annotations		
General Settings Scoring Rules	Mass Tolerance	5 ppm
	Use mzLogic	True
	Use Spectral Distance	True
	SFit Threshold	20
	SFit Range	20
Data Sources	Data Source #1	mzCloud Search
	Data Source #2	mzVault Search
	Data Source #3	Predicted Compositions
	Data Source #4	ChemSpider Search
Reprocessing	Clear Names	False

82 **Table S3** Continued

Search ChemSpider		
Search Settings	Database(s)	ACToR: Aggregated Computational Toxicology Resource; DrugBank; EAWAG Biocatalysis/Biodegradation Database; EPA DSSTox; EPA Toxcast; FDA UNII-NLM; Nature Chemistry; Sigma-Aldrich
	Search Mode	By Formula or Mass
	Mass Tolerance	5 ppm
	Max. # of results per compound	20
	Max. # of Predicted Compositions to be searched per Compound	3
	Fill Gaps	
	General Settings	Mass Tolerance
	S/N Threshold	1.5
Mark Background Compounds		
General Settings	Max. Sample/Blank	5
	Max. Blank/Sample	0
	Hide Background	True
Apply Spectral Distance		
Pattern Matching	Mass Tolerance	5 ppm
	Intensity Tolerance [%]	30
	Intensity Threshold [%]	0.1
	S/N Threshold	3
	Use Dynamic Recalibration	True
Apply mzLogic		
Search Settings	Max. # Compounds	0
	Max. # mzCloud Similarity Results to consider per Compound	10
	Match Factor Threshold	30

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Table S4. Overview of detected OSs compounds in this work that were also identified in previous studies.

Formula	m/z ([M-H] ⁻)	RT (min)	Previous studies
Aromatic OSs			
C ₈ H ₆ O ₅ S	212.98532	0.88	(Yang et al., 2024)
C ₈ H ₁₄ O ₁₀ S	301.02349	0.99	(Yang et al., 2024)
C ₉ H ₁₂ O ₅ S	231.03327	0.90	(Riva et al., 2015)
C ₉ H ₁₄ O ₇ S	265.03875	1.01	(Yang et al., 2020)
C ₉ H ₁₈ O ₈ S	285.06496	1.03	(Riva et al., 2016)
C ₉ H ₁₄ O ₈ S	281.03366	0.99	(Yang et al., 2020)
C ₁₀ H ₁₂ O ₇ S	275.02310	0.99	(Riva et al., 2015)
C ₁₁ H ₁₂ O ₇ S	287.02310	1.00	(Le Breton et al., 2018)
C ₁₁ H ₂₀ O ₁₁ S	359.06536	1.12	(Yang et al., 2024)
C ₁₀ H ₁₀ O ₇ S	273.00745	1.01	(Riva et al., 2015)
C ₁₁ H ₁₄ O ₇ S	289.03875	1.04	(Riva et al., 2015)
C ₉ H ₁₃ O ₉ NS	310.02383	0.94	(Yang et al., 2020)
Aliphatic OSs			
C ₈ H ₁₈ O ₄ S	209.08530	10.06	(Huang et al., 2023)
C ₉ H ₁₈ O ₄ S	221.08530	10.62	(Yang et al., 2024)
C ₉ H ₁₈ O ₅ S	237.08022	10.65	(Riva et al., 2016)
C ₉ H ₂₀ O ₄ S	223.10095	10.71	(Riva et al., 2016; Meade et al., 2016)
C ₁₀ H ₂₂ O ₄ S	237.11660	10.75	(Huang et al., 2023)
C ₁₁ H ₂₂ O ₅ S	265.11152	10.79	(Yang et al., 2024)
C ₁₃ H ₂₆ O ₅ S	293.14282	10.99	(Yang et al., 2024)
C ₁₄ H ₂₈ O ₅ S	308.16629	11.06	(Yang et al., 2024)
Monoterpene OSs			
C ₈ H ₁₄ O ₇ S	253.03875	1.00	(Hettiyadura et al., 2019; Xu et al., 2015)
C ₉ H ₁₂ O ₇ S	263.02310	1.03	(Br üggemann et al., 2019; Xu et al., 2021)
C ₉ H ₁₆ O ₆ S	251.05948	1.04	(Hettiyadura et al., 2019; Xu et al., 2015)
C ₉ H ₁₆ O ₇ S	267.05440	1.02	(Xu et al., 2015; Meade et al., 2016)
C ₉ H ₁₆ O ₈ S	283.04931	1.01	(Br üggemann et al., 2019; Meade et al., 2016)
C ₉ H ₁₆ O ₉ S	299.04423	1.00	(Br üggemann et al., 2019)
C ₁₀ H ₁₄ O ₉ S	309.02858	0.99	(Br üggemann et al., 2019)
C ₁₀ H ₁₆ O ₅ S	247.06457	1.01	(Xu et al., 2015; Ma et al., 2014)

Table S4 Continued

C ₉ H ₁₈ O ₇ S	269.07005	1.03	(Riva et al., 2016; Brüggenmann et al., 2019)
C ₁₀ H ₁₆ O ₆ S	263.05948	1.02	(Ma et al., 2014)
C ₁₀ H ₁₆ O ₇ S	279.05440	1.00	(Ma et al., 2014; Xu et al., 2015; Meade et al., 2016; Hettiyadura et al., 2019)
C ₁₀ H ₁₆ O ₈ S	295.04931	1.01	(Riva et al., 2016; Brüggenmann et al., 2019)
C ₁₀ H ₁₈ O ₅ S	249.0806	1.02	(Xu et al., 2015; Ma et al., 2014; Xu et al., 2021; Wang et al., 2017; Hansen et al., 2014)
C ₁₀ H ₁₈ O ₆ S	265.07513	1.02	(Brüggenmann et al., 2019; Ma et al., 2014)
C ₁₀ H ₁₈ O ₇ S	281.07005	1.01	(Hettiyadura et al., 2019; Ma et al., 2014)
C ₁₀ H ₁₈ O ₈ S	297.06496	1.02	(Xu et al., 2015; Meade et al., 2016)
C ₁₀ H ₂₀ O ₅ S	251.09587	1.03	(Riva et al., 2016; Brüggenmann et al., 2019)
C ₁₀ H ₂₀ O ₆ S	267.09078	1.05	(Brüggenmann et al., 2019)
C ₁₀ H ₂₀ O ₇ S	283.08570	1.03	(Brüggenmann et al., 2019; Ma et al., 2014)
C ₉ H ₁₅ O ₈ NS	296.04456	5.61	(Hettiyadura et al., 2019; Xu et al., 2015; Xu et al., 2021)
C ₁₀ H ₁₇ O ₇ NS	294.06530	9.26	(Hettiyadura et al., 2019; Meade et al., 2016; Xu et al., 2021; Le Breton et al., 2018)
C ₁₀ H ₁₇ O ₈ NS	310.06021	8.27	(Xu et al., 2015; Ma et al., 2014)
C ₁₀ H ₁₇ O ₉ NS	326.05513	8.50	(Xu et al., 2015; Meade et al., 2016)
C ₁₀ H ₁₇ O ₁₀ NS	342.05004	5.01	(Xu et al., 2015; Meade et al., 2016; Hettiyadura et al., 2019)
C ₁₀ H ₁₉ O ₈ NS	312.07586	7.59	(Stone et al., 2012)
C ₁₀ H ₁₉ O ₉ NS	328.07078	5.37	(Xu et al., 2015)
Sesquiterpene OSs			
C ₁₄ H ₂₆ O ₆ S	321.13773	10.76	(Chan et al., 2011)
C ₁₄ H ₂₈ O ₆ S	323.15338	10.85	(Tao et al., 2014)
C ₁₄ H ₃₀ O ₄ S	293.17920	11.88	(Tao et al., 2014)
C ₁₅ H ₂₆ O ₇ S	349.13265	8.98	(Chan et al., 2011)
C ₁₄ H ₂₂ O ₇ S	333.10135	9.01	(Chan et al., 2011)
C ₁₅ H ₂₅ O ₇ NS	362.12790	11.55	(Chan et al., 2011)

91 **Table S5** The formula, classification, and MS² fragments of Unknown OSs

Formula	Classification	<i>m/z</i>	MS ² fragments			
		([M-H] ⁻)	[C _n H _{2n+1}] ⁻	[C _n H _{2n-1}] ⁻	[C _n H _{2n-3}] ⁻	[C ₆ H ₅ R-H] ⁻
C ₁₂ H ₂₆ O ₄ S	Aliphatic OSs	265.14790	√			
C ₁₃ H ₂₈ O ₄ S		279.16355	√			
C ₁₅ H ₃₂ O ₄ S		307.19485	√			
C ₁₆ H ₃₄ O ₄ S		321.21050	√			
C ₁₈ H ₃₈ O ₄ S		349.24180	√			
C ₂₀ H ₄₂ O ₄ S		377.27310	√			
C ₂₂ H ₄₆ O ₄ S		405.30440	√			
C ₂₃ H ₄₆ O ₄ S		417.30440	√			
C ₂₃ H ₄₈ O ₄ S		419.32005	√			
C ₂₄ H ₅₀ O ₄ S		433.33570	√			
C ₂₅ H ₅₂ O ₄ S		447.35135	√			
C ₂₆ H ₅₄ O ₄ S		461.36700	√			
C ₁₂ H ₂₆ O ₅ S		281.14282	√			
C ₁₃ H ₂₈ O ₅ S		295.15847	√			
C ₁₄ H ₃₀ O ₅ S		309.17412	√			
C ₁₆ H ₃₂ O ₅ S		335.18977	√			
C ₁₆ H ₃₄ O ₅ S		337.20542	√			
C ₁₈ H ₃₆ O ₅ S		363.22107	√			
C ₁₉ H ₃₈ O ₅ S		377.23672	√			
C ₂₀ H ₄₀ O ₅ S		391.25237	√			
C ₁₀ H ₂₂ O ₆ S		269.10643	√			
C ₁₁ H ₂₂ O ₆ S		281.10643	√			
C ₁₁ H ₂₄ O ₆ S		283.12208	√			
C ₁₂ H ₂₄ O ₆ S		295.12208	√			
C ₁₆ H ₃₂ O ₆ S		351.18468	√			
C ₁₇ H ₃₄ O ₆ S		365.20033	√			
C ₁₈ H ₃₄ O ₆ S		377.20033	√			
C ₁₈ H ₃₆ O ₆ S		379.21598	√			
C ₂₄ H ₄₄ O ₆ S		459.27858			√	
C ₁₁ H ₂₀ O ₇ S		295.08570				
C ₁₂ H ₂₀ O ₇ S		307.08570		√		
C ₁₆ H ₃₂ O ₇ S		367.17960	√			
C ₁₈ H ₃₄ O ₇ S		393.19525	√			
C ₁₉ H ₃₈ O ₇ S		409.22655	√			
C ₂₀ H ₃₈ O ₇ S		421.22655	√			
C ₂₁ H ₄₀ O ₇ S		435.24220	√			
C ₂₁ H ₄₂ O ₇ S		437.25785	√			
C ₈ H ₁₆ O ₈ S		271.04931				
C ₁₈ H ₃₄ O ₈ S		409.19016	√			
C ₁₉ H ₃₈ O ₈ S		425.22146	√			
C ₂₅ H ₄₈ O ₈ S		507.29971	√			

Table S5 Continued

C ₁₀ H ₂₁ NO ₇ S	298.09660	√	
C ₁₁ H ₂₃ NO ₇ S	312.11225	√	
C ₁₂ H ₂₅ NO ₇ S	326.12790	√	
C ₁₃ H ₂₇ NO ₇ S	340.14355	√	
C ₁₄ H ₂₉ NO ₇ S	354.15920	√	
C ₁₅ H ₃₁ NO ₇ S	368.17485	√	
C ₁₆ H ₃₃ NO ₇ S	382.19050	√	
C ₁₇ H ₃₅ NO ₇ S	396.20615	√	
C ₁₈ H ₃₇ NO ₇ S	410.22180	√	
C ₁₉ H ₃₉ NO ₇ S	422.22180		√
C ₁₉ H ₃₉ NO ₇ S	424.23745	√	
C ₂₁ H ₄₃ NO ₇ S	452.26875	√	
C ₈ H ₁₇ NO ₈ S	286.06021	√	
C ₉ H ₁₉ NO ₈ S	300.07586	√	
C ₁₂ H ₂₅ NO ₈ S	342.12281	√	
C ₁₉ H ₃₉ NO ₈ S	440.23236	√	
C ₂₁ H ₄₁ NO ₈ S	466.24801		√
C ₁₈ H ₃₅ NO ₉ S	440.19598		√
C ₈ H ₁₂ O ₈ S	267.01801		√
C ₈ H ₁₄ O ₈ S	269.03366		
C ₁₀ H ₁₄ O ₈ S	293.03366		
C ₈ H ₁₂ O ₉ S	283.01293		√
C ₈ H ₁₄ O ₉ S	285.02858		
C ₁₀ H ₁₈ O ₉ S	313.05988		
C ₉ H ₁₂ O ₁₀ S	311.00784		√
C ₉ H ₁₄ O ₁₀ S	313.02349		
C ₈ H ₁₃ NO ₇ S	266.03400		√
C ₉ H ₁₅ NO ₇ S	280.04965		√
C ₈ H ₁₃ NO ₈ S	282.02891		
C ₁₀ H ₁₅ NO ₈ S	308.04456		√
C ₈ H ₁₃ NO ₉ S	298.24255		
C ₁₀ H ₁₉ NO ₁₀ S	344.06569		
C ₈ H ₁₃ NO ₁₁ S	330.01365		
C ₁₀ H ₈ O ₈ S	286.98671		√
C ₈ H ₁₀ O ₈ S	265.00236		√
C ₈ H ₁₀ O ₉ S	280.99728		√
C ₁₀ H ₁₀ O ₈ S	289.00236		√
C ₁₀ H ₁₂ O ₈ S	291.01801		√
C ₁₁ H ₁₂ O ₆ S	271.02818		√
C ₁₄ H ₁₂ O ₅ S	291.29755		√
C ₁₆ H ₂₂ O ₈ S	374.10409		√
C ₂₁ H ₃₀ O ₅ S	393.17412		√

94 **Table S5** Continued

$C_{22}H_{32}O_5S$	Aromatic OSs	407.18977	√
$C_{30}H_{48}O_4S$		503.32005	√
$C_8H_{11}NO_7S$		265.02617	√
$C_8H_{11}NO_8S$		281.02109	
$C_{10}H_{11}NO_7S$		288.01835	√
$C_{16}H_{27}NO_8S$		392.13846	√

95 *: common fragments, including $[HSO_4]^-$ (m/z 96.96010) and $[ONO_2]^-$ (m/z 61.98837) were not
 96 listed in Table S5

97

98 **Table S6.** The mass concentrations of PM_{2.5} and its chemical composition, gaseous pollutants
99 concentrations, and the mean values of the meteorological parameters.

Species (unit)	Beijing	Taiyuan	Changsha
PM _{2.5} (μg/m ³)	46.65 ± 30.43	73.15 ± 49.73	66.05 ± 49.20
NO ₃ ⁻ (μg/m ³)	11.96 ± 12.40	14.36 ± 9.75	34.86 ± 30.02
SO ₄ ²⁻ (μg/m ³)	5.34 ± 5.91	11.50 ± 9.84	9.84 ± 6.00
NH ₄ ⁺ (μg/m ³)	5.66 ± 6.06	9.00 ± 6.75	10.68 ± 8.04
OC (μg/m ³)	4.53 ± 2.40	9.05 ± 4.86	9.75 ± 5.46
SO ₂ (μg/m ³)	3.10 ± 1.19	18.23 ± 8.86	6.60 ± 2.07
NO ₂ (μg/m ³)	44.98 ± 19.36	62.21 ± 23.85	46.60 ± 17.73
CO (mg/m ³)	0.73 ± 0.32	1.34 ± 0.59	1.08 ± 0.42
O ₃ (μg/m ³)	22.58 ± 15.80	24.71 ± 19.69	26.12 ± 12.88
OS (ng/m ³)	41.11 ± 34.47	57.39 ± 39.23	102.06 ± 80.54
RH (%)	47.97 ± 19.04	50.73 ± 15.62	71.45 ± 13.75
Temperature (°C)	0.62 ± 6.58	-2.58 ± 4.82	7.79 ± 3.52

100

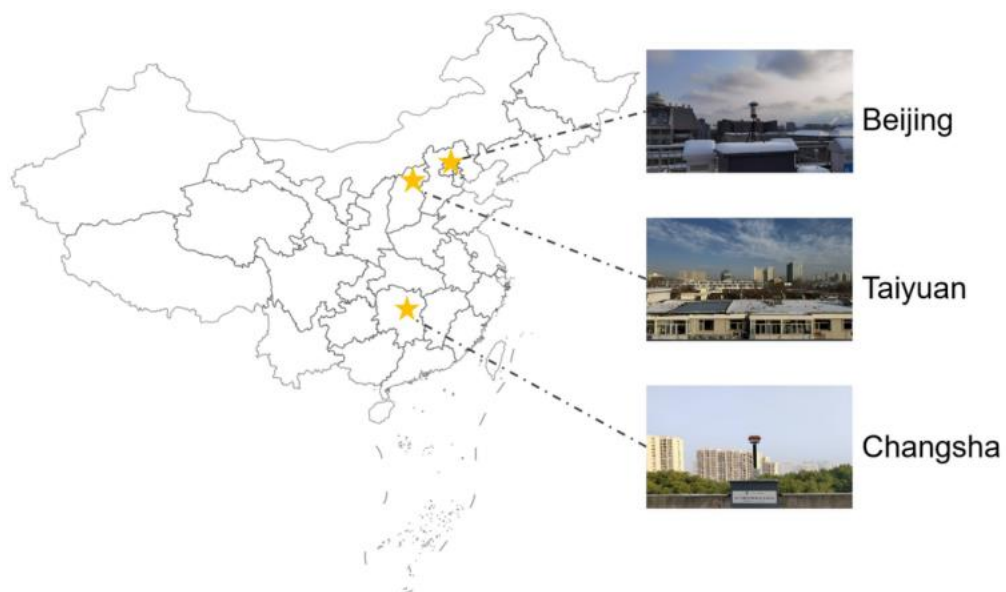


Figure S1. The geographical locations of the sample sites in this study. All photos were entirely created by the authors, there are no copyright issues.

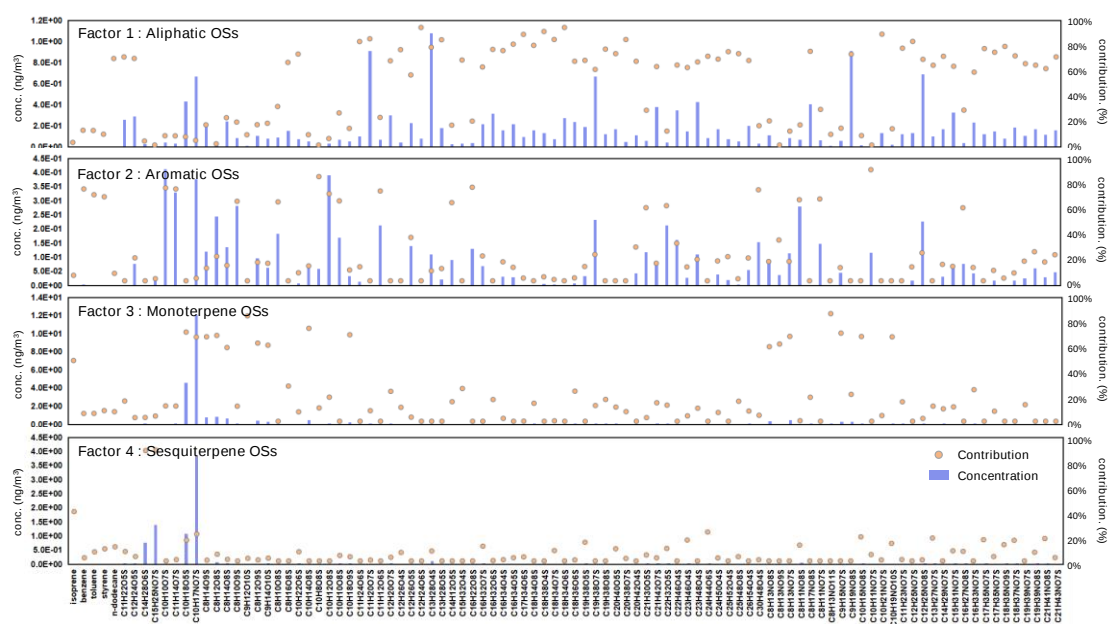


Figure S2 The factor profile of the precursor-constrained PMF model

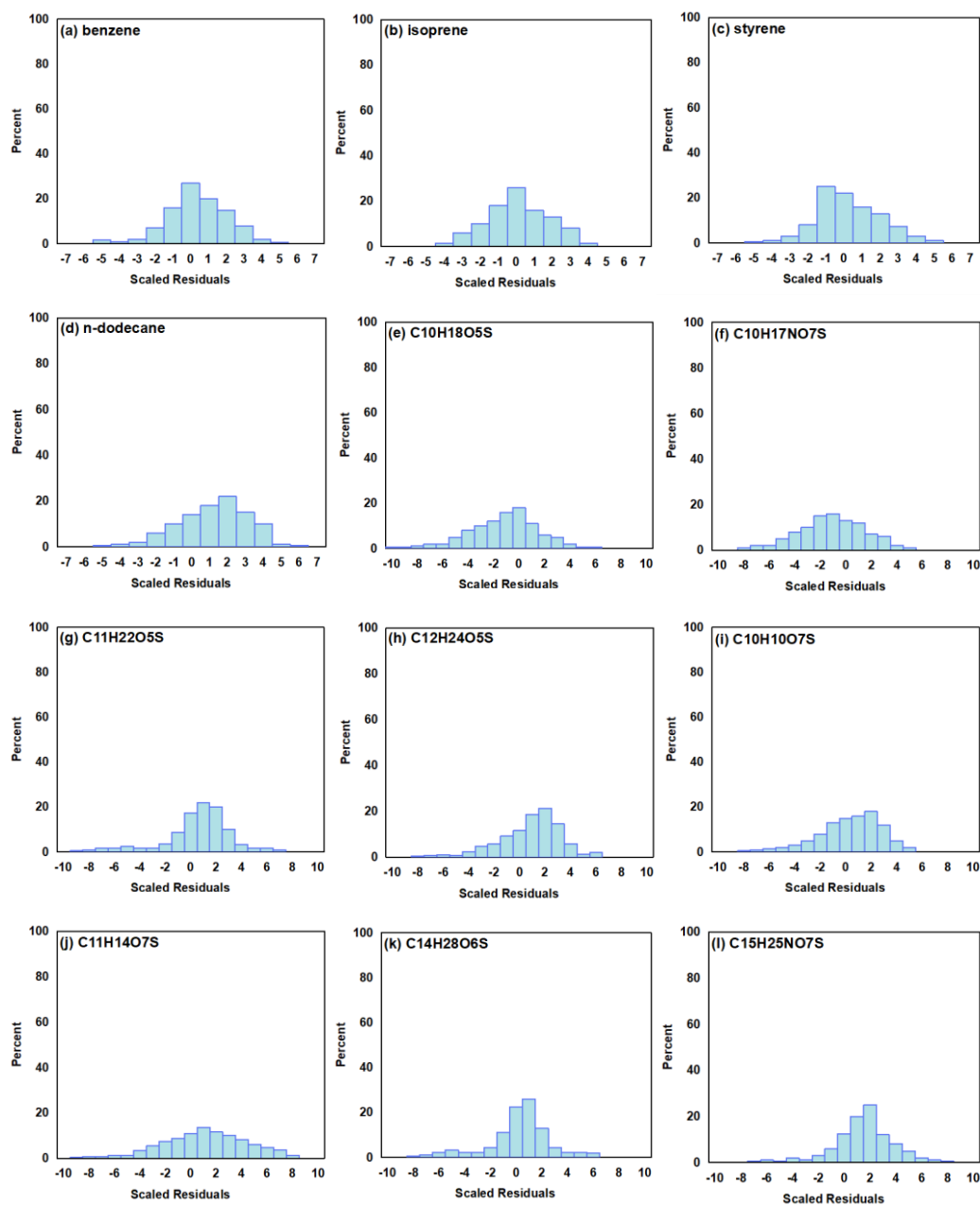


Figure S3 The scaled residual matrix of precursor-constrained PMF model

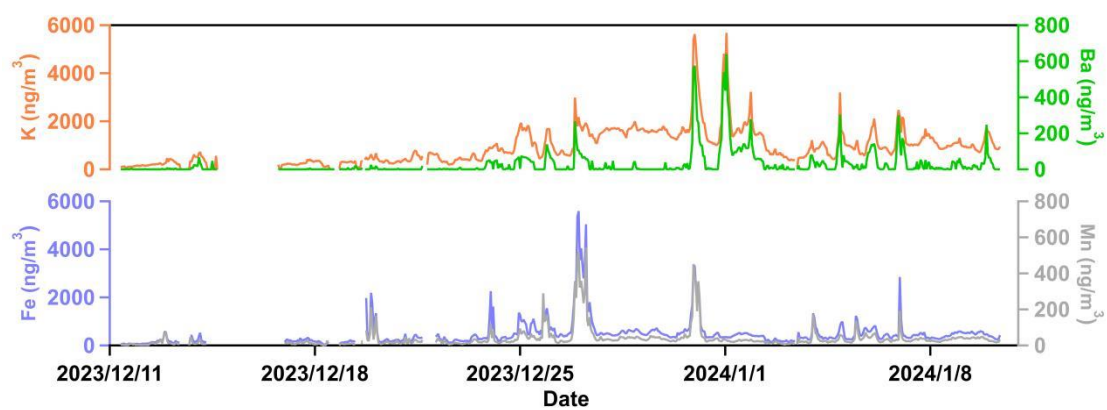


Figure S4. Time series of Ba, K, Fe and Mn concentrations in Changsha.

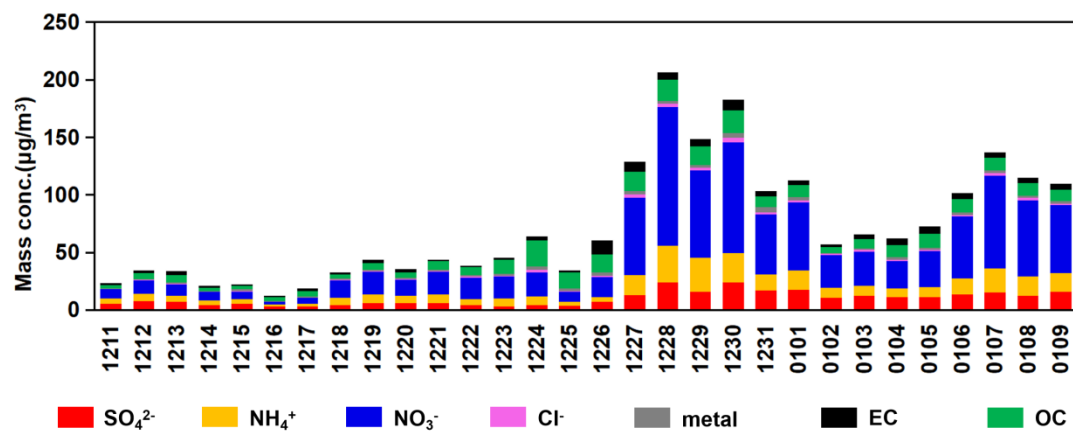


Figure S5. Time series of chemical components concentrations in Changsha.

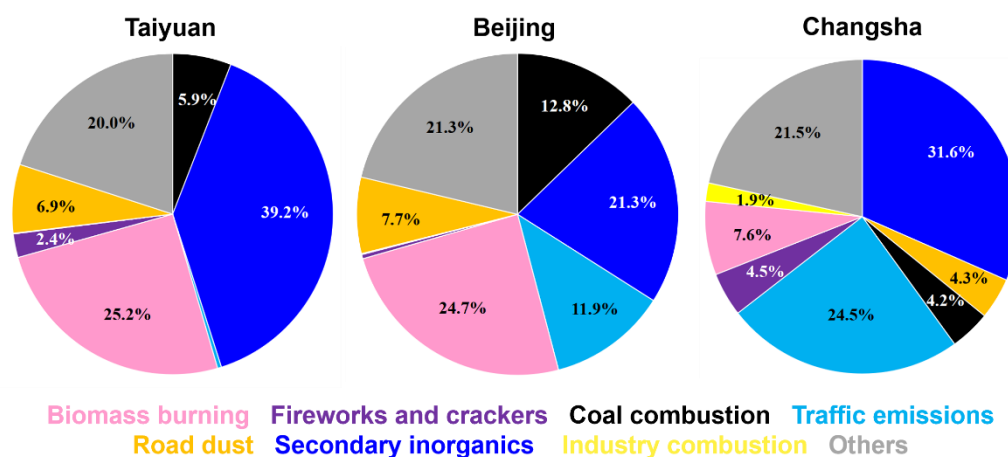


Figure S6. Contribution of different sources to PM_{2.5} mass in three sites.

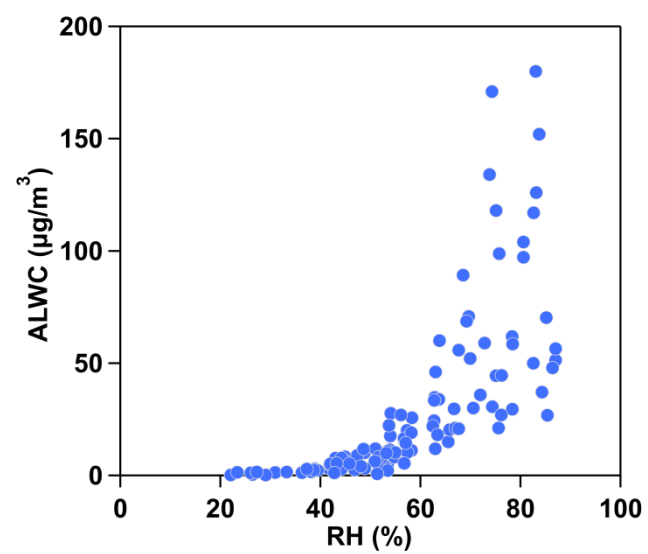


Figure S7. ALWC as a function of the RH.

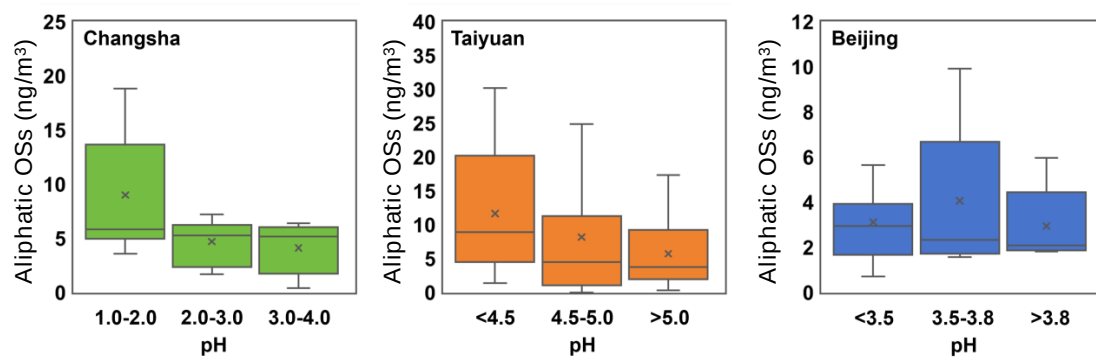


Figure S8. The mass concentrations of Aliphatic OSs under different pH levels.

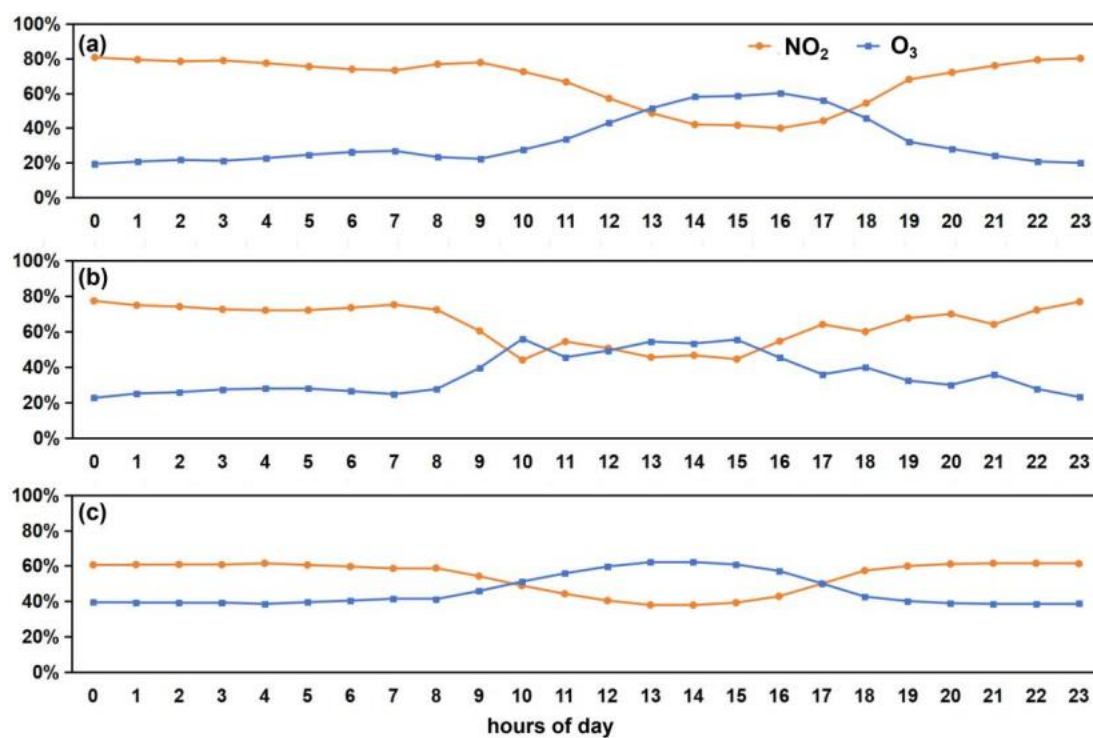


Figure S9. Diurnal variations of the distribution of NO_2 , and O_3 on O_x in (a) Changsha, (b) Taiyuan, and (c) Beijing.

References

- Brüggemann, M., van Pinxteren, D., Wang, Y. C., Yu, J. Z., and Herrmann, H.: Quantification of known and unknown terpenoid organosulfates in PM10 using untargeted LC-HRMS/MS: contrasting summertime rural Germany and the North China Plain, *Environmental International*, 16, 333-346, <https://doi.org/10.1071/EN19089>, 2019.
- Chan, M. N., Surratt, J. D., Chan, A. W. H., Schilling, K., Offenberg, J. H., Lewandowski, M., Edney, E. O., Kleindienst, T. E., Jaoui, M., Edgerton, E. S., Tanner, R. L., Shaw, S. L., Zheng, M., Knipping, E. M., and Seinfeld, J. H.: Influence of aerosol acidity on the chemical composition of secondary organic aerosol from β -caryophyllene. *Atmospheric Chemistry and Physics*, 11, 1735-1751, <https://doi.org/10.5194/acp-11-1735-2011>, 2011.
- Fountoukis, C., and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K⁺; Ca²⁺; Mg²⁺; NH₄⁺; Na⁺; SO₄²⁻; NO₃⁻; Cl⁻; H₂O aerosols, *Atmospheric Chemistry and Physics*, 7, 4639-4659, <https://doi.org/10.5194/acp-7-4639-2007>, 2007.
- Hansen, A. M. K., Kristensen, K., Nguyen, Q. T., Zare, A., Cozzi, F., Nøjgaard, J. K., Skov, H., Brandt, J., Christensen, J. H., Ström, J., Tunved, P., Krejci, R., and Glasius, M.: Organosulfates and organic acids in Arctic aerosols: speciation, annual variation and concentration levels, *Atmospheric Chemistry and Physics*, 14, 7807-7823, <https://doi.org/10.5194/acp-14-7807-2014>, 2014.
- Hettiyadura, A. P. S., Al-Naiema, I. M., Hughes, D. D., Fang, T., and Stone, E. A.: Organosulfates in Atlanta, Georgia: anthropogenic influences on biogenic secondary organic aerosol formation, *Atmospheric Chemistry and Physics*, 19, 3191-3206, <https://doi.org/10.5194/acp-19-3191-2019>, 2019.
- Huang, L., Wang, Y., Zhao, Y., Hu, H., Yang, Y., Wang, Y., Yu, J.-Z., Chen, T., Cheng, Z., Li, C., Li, Z., and Xiao, H.: Biogenic and Anthropogenic Contributions to Atmospheric Organosulfates in a Typical Megacity in Eastern China, *Journal of Geophysical Research: Atmosphere*, 128, e2023JD038848, <https://doi.org/10.1029/2023JD038848>, 2023.
- Le Breton, M., Wang, Y., Hallquist, Å. M., Pathak, R. K., Zheng, J., Yang, Y., Shang, D., Glasius, M., Bannan, T. J., Liu, Q., Chan, C. K., Percival, C. J., Zhu, W., Lou, S., Topping, D., Wang, Y., Yu, J., Lu, K., Guo, S., Hu, M., and Hallquist, M.: Online gas- and particle-phase measurements of organosulfates, organosulfonates and nitrooxy organosulfates in Beijing utilizing a FIGAERO ToF-CIMS, *Atmospheric Chemistry and Physics*, 18, 10355-10371, <https://doi.org/10.5194/acp-18-10355-2018>, 2018.
- Ma, Y., Xu, X., Song, W., Geng, F., and Wang, L.: Seasonal and diurnal variations of particulate organosulfates in urban Shanghai, China. *Atmospheric Environment*, 85, 152-160, <https://doi.org/10.1016/j.atmosenv.2013.12.017>, 2014.
- Meade, L. E., Riva, M., Blomberg, M. Z., Brock, A. K., Qualters, E. M., Siejack, R. A., Ramakrishnan, K., Surratt, J. D., and Kautzman, K. E.: Seasonal variations of fine particulate organosulfates derived from biogenic and anthropogenic hydrocarbons in the mid-Atlantic United States, *Atmospheric Environment*, 145, 405-414, <https://doi.org/10.1016/j.atmosenv.2016.09.028>, 2016.
- Riva, M., Tomaz, S., Cui, T., Lin, Y.-H., Perraudin, E., Gold, A., Stone, E. A., Villenave, E., and Surratt, J. D.: Evidence for an Unrecognized Secondary Anthropogenic Source of Organosulfates and Sulfonates: Gas-Phase Oxidation of Polycyclic Aromatic Hydrocarbons in the Presence of Sulfate Aerosol, *Environmental Science & Technology*, 49, 6654-6664, <https://doi.org/10.1021/acs.est.5b00836>, 2015.
- Riva, M., Da Silva Barbosa, T., Lin, Y. H., Stone, E. A., Gold, A., and Surratt, J. D.: Chemical

- characterization of organosulfates in secondary organic aerosol derived from the photooxidation of alkanes, *Atmospheric Chemistry and Physics*, 16, 11001-11018. <https://doi.org/10.5194/acp-16-11001-2016>, 2016.
- Stone, E. A., Yang, L., Yu, L. E., and Rupakheti, M.: Characterization of organosulfates in atmospheric aerosols at Four Asian locations, *Atmospheric Environment*, 47, 323-329. <https://doi.org/10.1016/j.atmosenv.2011.10.058>, 2012.
- Tao, S., Lu, X., Levac, N., Bateman, A. P., Nguyen, T. B., Bones, D. L., Nizkorodov, S. A., Laskin, J., Laskin, A., and Yang, X.: Molecular Characterization of Organosulfates in Organic Aerosols from Shanghai and Los Angeles Urban Areas by Nanospray-Desorption Electrospray Ionization High-Resolution Mass Spectrometry, *Environmental Science & Technology*, 48, 10993-11001. <https://doi.org/10.1021/es5024674>, 2014.
- Wang, Y., Ren, J., Huang, X. H. H., Tong, R., and Yu, J. Z.: Synthesis of Four Monoterpene-Derived Organosulfates and Their Quantification in Atmospheric Aerosol Samples, *Environmental Science & Technology*, 51, 6791-6801, <https://doi.org/10.1021/acs.est.7b01179>, 2017.
- Xu, L., Guo, H., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R., Isaacman-VanWertz, G., Kreisberg, N. M., Knote, C., Olson, K., Koss, A., Goldstein, A. H., Hering, S. V., de Gouw, J., Baumann, K., Lee, S.-H., Nenes, A., Weber, R. J., and Ng, N. L.: Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States, *Proceedings of the National Academy of Sciences of the United States of America*, 112, 37-42, <https://doi.org/10.1073/pnas.1417609112>, 2015.
- Xu, L., Yang, Z., Tsona, N. T., Wang, X., George, C., and Du, L.: Anthropogenic–Biogenic Interactions at Night: Enhanced Formation of Secondary Aerosols and Particulate Nitrogen- and Sulfur-Containing Organics from β -Pinene Oxidation, *Environmental Science & Technology*, 55, 7794-7807, <https://doi.org/10.1021/acs.est.0c07879>, 2021.
- Yang, T., Xu, Y., Ma, Y.-J., Wang, Y.-C., Yu, J. Z., Sun, Q.-B., Xiao, H.-W., Xiao, H.-Y., and Liu, C.-Q.: Field Evidence for Constraints of Nearly Dry and Weakly Acidic Aerosol Conditions on the Formation of Organosulfates, *Environmental Science & Technology Letters*, 11, 981-987, <https://doi.org/10.1021/acs.estlett.4c00522>, 2024.
- Yang, Z., Tsona, N. T., Li, J., Wang, S., Xu, L., You, B., and Du, L.: Effects of NO_x and SO₂ on the secondary organic aerosol formation from the photooxidation of 1,3,5-trimethylbenzene: A new source of organosulfates, *Environmental Pollution*, 264, 114742, <https://doi.org/10.1016/j.envpol.2020.114742>, 2020.