Supporting Information

Molecular characteristics and formation pathways of organosulfur compounds: a comparative field study across contrasting atmospheric environments

Dongmei Cai[1,2,3], Xianda Gong[1,2]*, Runqi Zhang[3], Shenyan Zhang[4], Yuhan Cheng[1,2,], Saidur Rahaman[1,2,], Yin Fang[4], Jianmin Chen[3]*

[1]*Key Laboratory of Coastal Environment and Resources of Zhejiang Province, School of Engineering, Westlake University, Hangzhou, Zhejiang 310030, China*

[2]*Research Center for Industries of the Future, Westlake University, Hangzhou, Zhejiang 310030, China*

[3] *Shanghai Key Laboratory of Atmospheric Particle Pollution and Prevention (LAP3), IRDR ICoE on Risk Interconnectivity and Governance on Weather/Climate Extremes Impact and Public Health, Department of Environmental Science and Engineering, Fudan University, Shanghai 200438, China*

[4]*State Key Laboratory of Estuarine and Coastal Research, Institute of Eco-Chongming, Blue Carbon Science and Technology Centre, East China Normal University, Shanghai, 200241, China*

Correspondence: Xianda Gong (gongxianda@westlake.edu.cn) and Jianmin Chen (jmchen@fudan.edu.cn)

*Corresponding author.

Number of Page	22
Number of Figures	4
Number of Tables	11

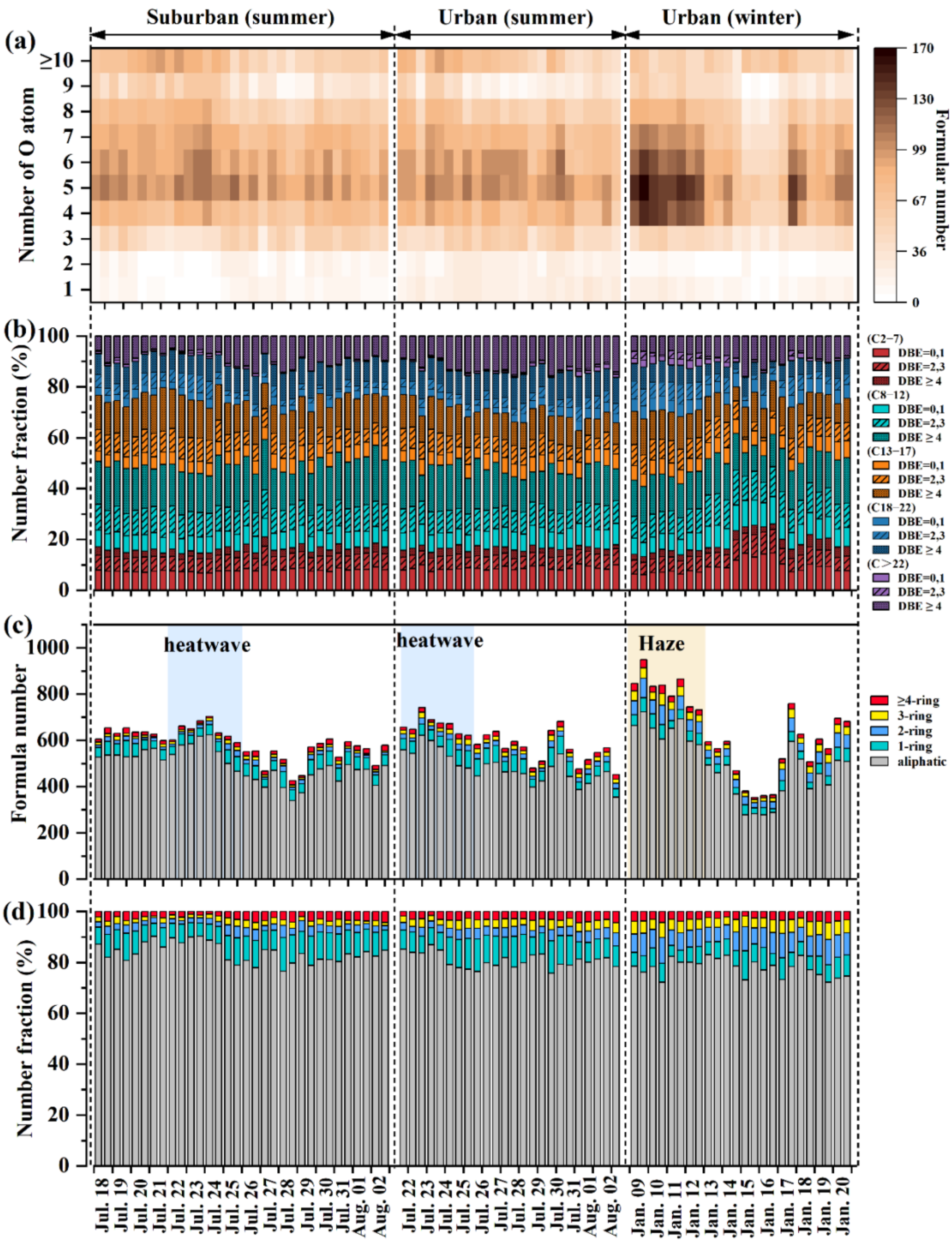

Figure S1 (a) Number distribution of the total CHOS species sorted by the oxygen atom number in the molecular formulas across the three field campaigns. (b) Formular number percentages of each subgroup which were divided based on the DBE value and the length of carbon skeleton in the CHOS formulas; (c) Formular number and (d) number percentages of each subgroup which were divided based on the Xc value of formulas.

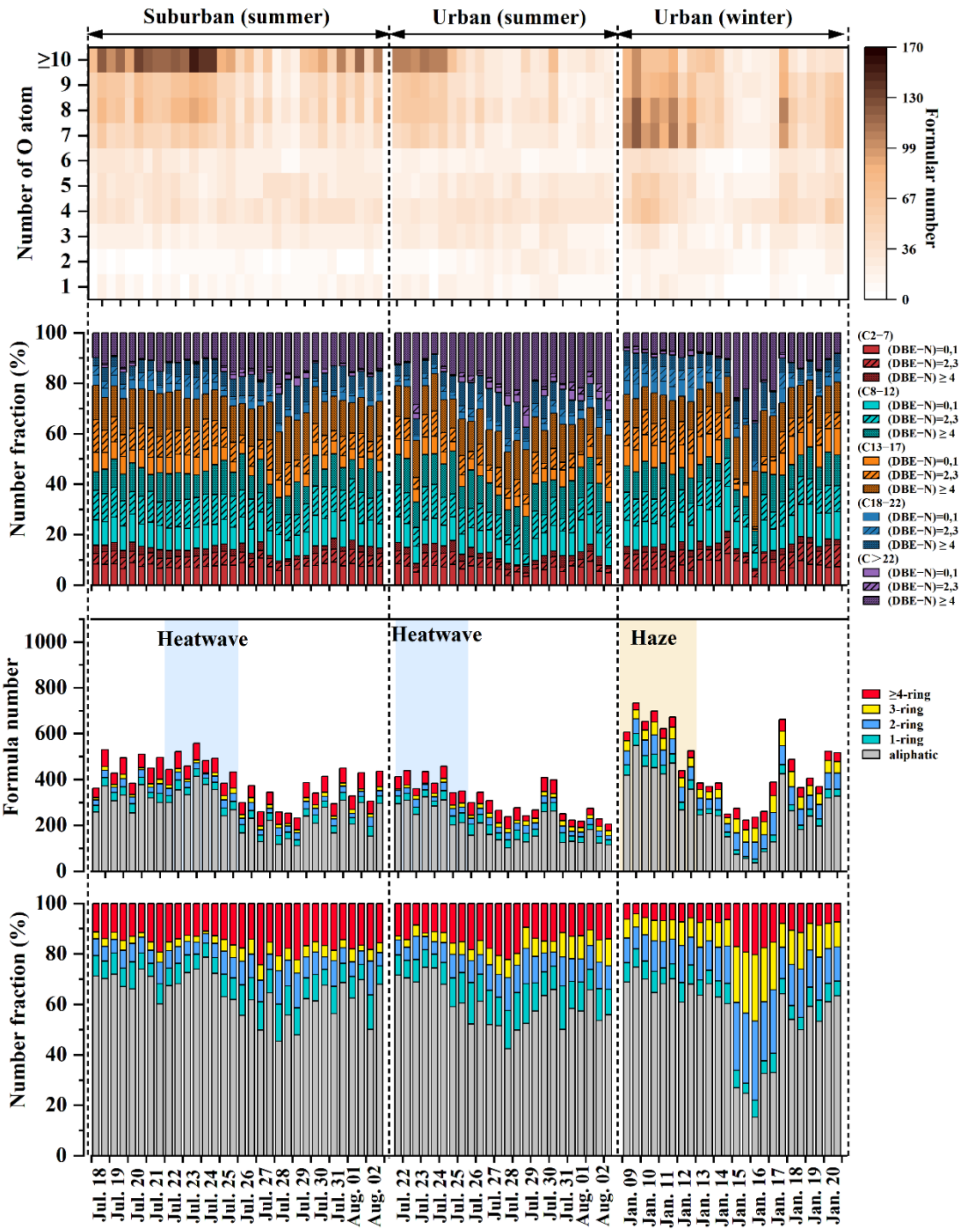

Figure S2 (a) Number distribution of the total CHONS species sorted by the oxygen atom number in the molecular formulas across the three field campaigns. (b) Formular number percentages of each subgroup which were divided based on the (DBE−N) value and the length of carbon skeleton in the CHONS formulas; (c) Formular number and (d) number percentages of each subgroup which were divided based on the Xc value of formulas.

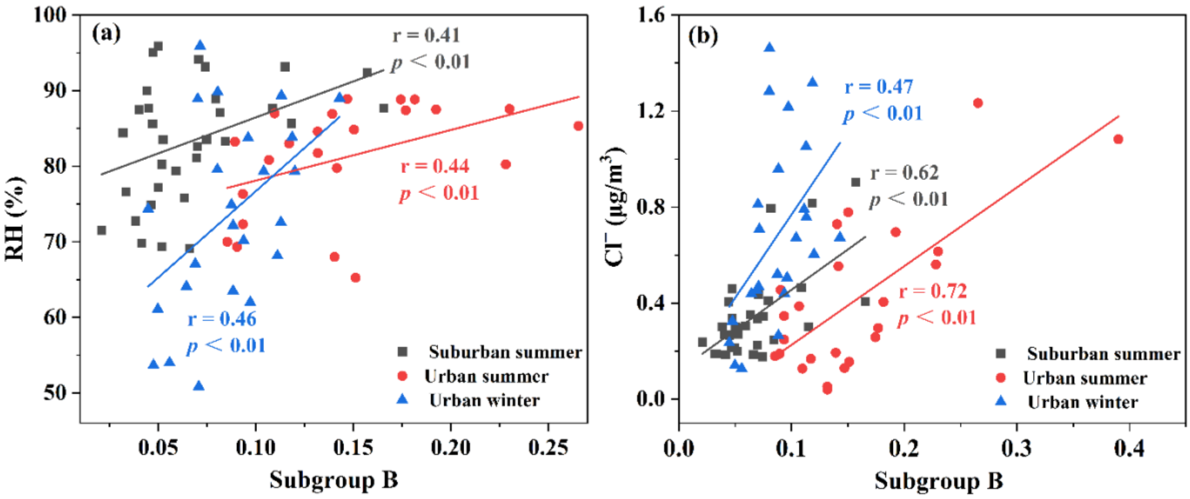

Figure S3. Significant correlations of the sum-normalized peak areas of OSs classified into subgroup B (with DBE≤2, C>8, 3<O<7 for CHOS) with RH (a) and Cl^- (b).

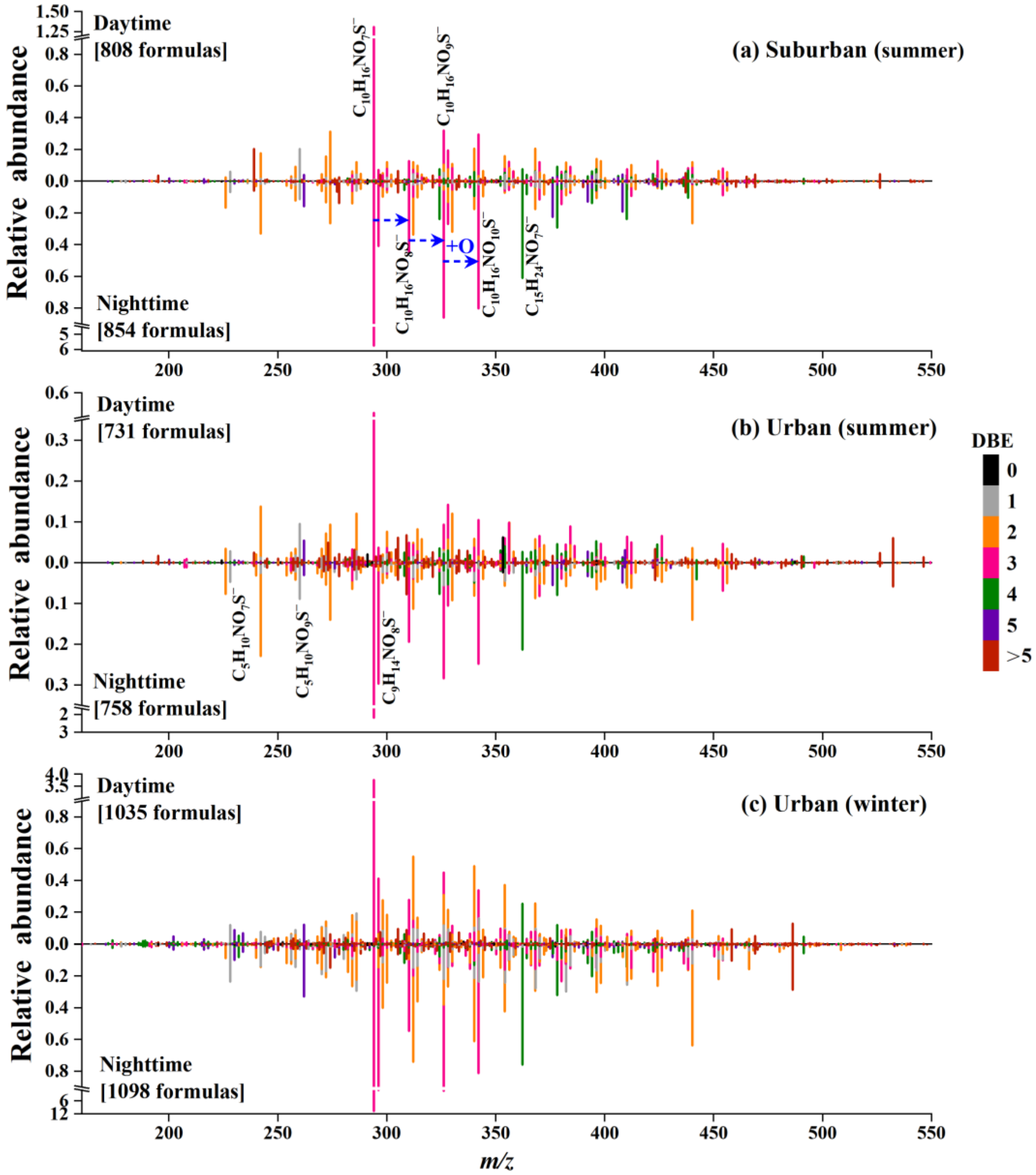

Figure S4 The relative abundance distribution of detected CHONS compounds in the suburban (a, summer) and urban (b, summer; c, winter). The color bar denotes the DBE of CHONS compounds. Note that the abundances of IS in each sample were set arbitrarily to 100%.

Table S1. The concentrations of $PM_{2.5}$, gaseous pollutants, and meteorological parameters in the suburban (summer) and urban (summer, winter) of Shanghai. The involved abbreviations included temperature (T), relative humidity (RH), and wind speed (WS).

	Suburban summer	**Daytime**	**Nighttime**	**Urban summer**	**Daytime**	**Nighttime**	**Urban winter**	**Daytime**	**Nighttime**
I. $PM_{2.5}$ and gaseous pollutants ($\mu g\ m^{-3}$)									
$PM_{2.5}$	14.6 ± 7.67	16.7 ± 8.15	12.5 ± 6.50	17.9 ± 9.44	20.5 ± 9.41	15.4 ± 8.76	50.8 ± 34.0	50.1 ± 31.4	51.6 ± 36.4
SO_2	2.21 ± 0.61	2.05 ± 0.60	2.16 ± 0.60	4.56 ± 1.15	5.05 ± 1.37	4.06 ± 0.90	8.08 ± 2.18	8.34 ± 2.29	7.81 ± 2.03
NO_x	17.7 ± 8.91	13.1 ± 5.80	22.9 ± 9.11	25.7 ± 8.22	23.7 ± 7.35	27.6 ± 9.26	56.5 ± 26.5	53.8 ± 21.8	59.2 ± 30.4
CO	456 ± 88.7	477 ± 70.7	435 ± 99.2	779 ± 80.1	785 ± 76.2	774 ± 83.3	1174 ± 271	1108 ± 266	1239 ± 282
O_3	78.5 ± 25.2	95.3 ± 33.7	61.7 ± 13.8	61.3 ± 17.3	75.9 ± 24.3	46.7 ± 11.7	42.8 ± 22.5	50.9 ± 21.4	34.6 ± 23.2
OC	2.51 ±5.59	3.49 ± 2.82	1.52 ± 1.87	3.46 ± 2.55	4.09 ± 3.04	2.87 ± 1.82	6.60 ± 5.47	6.36 ± 4.08	6.84 ± 6.55
EC	0.49 ± 0.48	0.66 ± 0.54	0.31 ± 0.32	1.03 ± 0.90	1.23 ± 1.07	0.83 ± 0.62	2.77 ± 1.77	2.73 ± 1.31	2.80 ±2.13
II. Meteorological parameters									
T (°C)	28.7 ± 1.70	29.9 ± 1.39	27.4 ± 0.83	30.8 ± 1.54	32.4± 1.38	29.1 ± 0.59	7.64 ± 3.28	9.43 ± 3.44	5.84 ± 3.13
RH (%)	83.3 ± 7.78	78.1 ± 6.95	88.6± 4.29	80.8 ± 7.60	76.0 ± 7.94	85.5 ± 2.78	75.7 ± 13.9	67.6 ± 14.3	83.7 ± 7.26
WS ($m\ s^{-1}$)	2.45 ± 1.14	2.85 ± 0.98	2.05 ± 1.16	4.70 ± 1.13	5.07 ± 1.21	4.33 ± 0.91	3.39 ± 1.60	3.90 ± 1.16	2.88 ± 1.81

Table S2. Summary of molecular characteristics of CHOS and CHONS compounds detected in suburban and urban $PM_{2.5}$ samples from Shanghai.

Sample ID	Group	Subgroup	Number of formulas	% of total OrgS number	% of total OrgS Intensity	% of formulas number with $(4s+3n)/o \leq 1$	% of formulas intensity with $(4s+3n)/o \leq 1$	MW_w	H/C_w	O/C_w	DBE_w	Xc_w
Suburban Summer	CHOS	$CHOS_1$	418−688	58.4±3.33	64.8±16.0	88.2±3.80	86.1±13.9	300±16.2	1.87±0.06	0.58±0.15	2.05±0.46	0.37±0.24
		Total	**425−703 (1069)**	**59.8±3.41**	**65.2±16.1**	**86.6±3.71**	**86.2±13.8**	**300±16.0**	**1.88±0.06**	**0.58±0.14**	**2.06±0.46**	**0.37±0.24**
Urban Summer	CHOS	$CHOS_1$	439−677	64.8±3.36	76.7±12.4	84.4±2.38	85.3±11.6	301±16.4	1.82±0.04	0.53±0.11	2.11±0.43	0.42±0.26
		Total	**452−689 (1127)**	**66.4±3.56**	**77.1±12.6**	**83.2±2.53**	**85.2±11.5**	**302±16.5**	**1.81±0.04**	**0.53±0.11**	**2.18±0.44**	**0.43±0.27**
Urban Winter	CHOS	$CHOS_1$	324−846	59.5±4.07	73.8±8.44	89.2±2.13	91.7±7.37	285±15.4	1.62±0.03	0.45±0.06	2.48±0.46	0.58±0.31
		Total	**330−949 (1412)**	**60.8±4.11**	**73.9±8.44**	**87.5±2.25**	**91.6±7.36**	**285±15.4**	**1.62±0.03**	**0.45±0.06**	**2.56±0.47**	**0.60±0.31**
Suburban Summer	CHONS	$CHON_1S_1$	139−438	29.0±4.30	31.9±16.4	62.3±11.3	88.2±12.4	321±10.2	1.71±0.06	0.83±0.09	3.20±0.50	0.17±0.21
		$CHON_2S_1$	60−111	8.37±1.31	2.29±1.59	8.45±3.55	5.36±3.39	332±29.4	0.76±0.15	0.37±0.09	12.6±2.41	2.50±0.17
		Total	**231−558 (895)**	**40.2±3.41**	**34.8±16.1**	**56.3±9.21**	**73.0±10.2**	**325±14.9**	**1.60±0.17**	**0.77±0.11**	**4.27±1.73**	**0.43±0.47**
Urban Summer	CHONS	$CHON_1S_1$	132−359	23.1±4.38	18.4±13.6	74.2±9.76	93.5±9.36	336±30.2	1.67±0.06	0.74±0.06	3.59±1.56	0.29±0.47
		$CHON_2S_1$	53−114	9.67±1.84	4.30±3.81	3.85±3.53	8.13±3.03	335±16.5	0.75±0.13	0.32±0.15	13.6±3.47	2.59±0.61
		Total	**206−458 (787)**	**33.6±3.56**	**22.9±12.6**	**59.7±7.54**	**89.4±9.89**	**332±19.2**	**1.53±0.26**	**0.69±0.12**	**4.89±2.64**	**0.54±0.55**
Urban Winter	CHONS	$CHON_1S_1$	54−578	29.2±7.24	23.2±9.81	68.8±4.50	94.4±3.18	318±9.72	1.63±0.05	0.68±0.07	4.49±1.16	0.59±0.58
		$CHON_2S_1$	37−87	7.41±2.91	1.99±2.57	12.4±9.35	21.3±16.0	358±12.5	0.74±0.10	0.31±0.09	12.1±1.09	2.49±0.13
		Total	**144−694 (1277)**	**39.2±4.11**	**26.1±8.44**	**56.5±6.70**	**92.0±6.54**	**322±9.08**	**1.44±0.24**	**0.65±0.17**	**6.02±2.60**	**0.88±0.70**

Table S3. Comparison of H/C$_w$ and O/C$_w$ ratios of CHOS compounds in this study and other studies.

Sample	Location	Season	Extraction solution	H/C$_w$	O/C$_w$	Instrument	References
$PM_{2.5}$	Shanghai (suburb)	Summer	Methanol	**1.88±0.06**	**0.58±0.14**	Orbitrap MS	This study
	Shanghai (urban)	Summer		**1.81±0.04**	**0.53±0.11**		
		Winter		**1.62±0.03**	**0.45±0.06**		
$PM_{2.5}$	Pearl River Delta		Water	1.67±0.31	0.55 ± 0.17	Orbitrap MS	(Lin et al., 2012)
$PM_{2.5}$	Cambridge	winter	Water and acetonitrile	1.47	0.47	Orbitrap MS	(Rincón et al., 2012)
		summer		1.50	0.66		
$PM_{0.18-1.8}$	California	after midnight		1.7±0.05	0.87±0.09	Orbitrap MS	(O'Brien et al., 2014)
		morning		1.8±0.1	0.93±0.1		
		afternoon		1.8±0.05	0.82±0.09		
		before midnight		1.8±0.0	0.88±0.05		
TSP	Virginia		Water	1.46±0.35	0.47±0.23	FT-ICR MS	(Willoughby et al., 2014)
			Pyridine	1.54±0.38	0.49±0.31		
			Acetonitrile	1.42±0.36	0.49±0.32		
$PM_{2.5}$	Beijing	Hazy	DCM	1.55±0.41	0.49±0.26	FT-ICR MS	(Jiang et al., 2016)
		Clear		1.74±0.34	0.62±0.34		
		Hazy	Water	1.64±0.37	0.65±0.28		
		Clear		1.82±0.26	0.75±0.37		
$PM_{2.5}$	Wuhan	Winter	Methanol	1.68±0.44	0.37±0.25	Orbitrap MS	(Wang et al., 2016)
		Summer		1.75±0.36	0.39±0.23		
	Nanjing	Summer		1.68±0.41	0.43±0.32		
	Shanghai	Winter		1.68±0.46	0.40±0.29		
		Summer		1.68±0.42	0.47±0.31		
$PM_{2.5}$	Shanghai	Spring	Acetonitrile	1	0.2	Orbitrap MS	(Wang et al., 2017)
		Summer		1.1	0.6		
		Fall		1.2	0.4		
		Winter		1.3	0.2		
$PM_{2.5}$	Mainz	low-pollution	Acetonitrile /water	1.66	0.78	Orbitrap MS	(Wang et al., 2018)
	Beijing	low-pollution		1.81	0.63		
		high-pollution		1.74	0.51		
$PM_{2.5}$	Changchun		Acetonitrile /water	1.56±0.11	1.17±0.13	Orbitrap MS	(Wang et al., 2021)
	Shanghai			1.85±0.04	1.41±0.19		
	Guangzhou			1.85±0.02	1.48±0.05		
$PM_{2.5}$	Guangzhou	Whole year	Methanol	1.77±0.03	0.52±0.07	FT-ICR MS	(Jiang et al., 2022)
$PM_{2.5}$	Beijing	Winter	Methanol	1.17	0.76	Orbitrap MS	(Wang et al., 2024)
		Summer		1.37	0.60		
	Harbin	Winter		1.20	0.73		
		Summer		1.35	0.60		
	Xi'an	Winter		1.29	0.74		
		Summer		1.45	0.63		
	Chengdu	Winter		1.23	0.76		
		Summer		1.33	0.60		
	Guangzhou	Winter		1.27	0.74		
		Summer		1.43	0.65		
	Wuhan	Winter		1.16	0.77		
		Summer		1.40	0.63		
$PM_{2.5}$	Anshan	Winter	Water	1.42±0.07	0.45±0.05	FT-ICR MS	(Ning et al., 2025)

Table S4. Comparison of H/C_w and O/C_w ratios of CHONS compounds in this study and other studies.

Sample	Location	Season	Extraction solution	H/C_w	O/C_w	Instrument	References
$PM_{2.5}$	Shanghai (suburb)	Summer	Methanol	**1.60±0.17**	**0.77±0.11**	Orbitrap MS	This study
	Shanghai (urban)	Summer		**1.53±0.26**	**0.69±0.12**		
		Winter		**1.44±0.24**	**0.65±0.17**		
$PM_{2.5}$	Pearl River Delta		Water	1.73±0.29	0.81±0.22	Orbitrap MS	(Lin et al., 2012)
$PM_{2.5}$	Cambridge	Winter	Water and acetonitrile	1.99	0.73	Orbitrap MS	(Rincón et al., 2012)
		Summer		1.65	0.80		
$PM_{0.18-1.8}$	California	after midnight		1.7±0.0	0.99±0.02	Orbitrap MS	(O'Brien et al., 2014)
		morning		1.7±0.0	1.0±0.005		
		afternoon		1.7±0.05	0.92±0.03		
		before midnight		1.7±0.05	0.89±0.09		
TSP	Virginia		Water	1.65±0.20	0.71±0.21	FT-ICR MS	(Willoughby et al., 2014)
			Pyridine	1.52±0.28	0.64±0.23		
			Acetonitrile	1.27±0.29	0.45±0.25		
$PM_{2.5}$	Beijing	Hazy	DCM	1.57±0.37	0.69±0.31	FT-ICR MS	(Jiang et al., 2016)
		Clear		1.75±0.31	0.76±0.27		
		Hazy	Water	1.51±0.37	0.70±0.32		
		Clear		-	-		
$PM_{2.5}$	Wuhan	Winter	Methanol	1.58±0.46	0.35±0.13	Orbitrap MS	(Wang et al., 2016)
		Summer		1.69±0.34	0.40±0.17		
	Nanjing	Summer		1.69±0.35	0.44±0.21		
	Shanghai	Winter		1.64±0.52	0.42±0.27		
		Summer		1.64±0.47	0.53±0.38		
$PM_{2.5}$	Shanghai	Spring	Acetonitrile	1.5	0.2	Orbitrap MS	(Wang et al., 2017)
		Summer		1.5	0.4		
		Fall		1.6	0.3		
		Winter		1.5	0.4		
$PM_{2.5}$	Mainz	Low pollution	Acetonitrile/water	1.54	0.91	Orbitrap MS	(Wang et al., 2018)
	Beijing	Low pollution		1.57	0.81		
		High pollution		1.56	0.59		
$PM_{2.5}$	Changchun		Acetonitrile/water	1.35±0.02	1.07±0.11	Orbitrap MS	(Wang et al., 2021)
	Shanghai			1.56±0.03	1.00±0.13		
	Guangzhou			1.56±0.04	0.82±0.03		
$PM_{2.5}$	Guangzhou	Whole year	Methanol	1.72±0.03	0.72±0.06	FT-ICR MS	(Jiang et al., 2022)
$PM_{2.5}$	Beijing	Winter	Methanol	1.15	1.02	Orbitrap MS	(Wang et al., 2024)
		Summer		1.28	0.96		
	Harbin	Winter		1.30	1.08		
		Summer		1.26	0.98		
	Xi'an	Winter		1.26	1.04		
		Summer		1.39	0.99		
	Chengdu	Winter		1.17	1.02		
		Summer		1.34	0.91		
	Guangzhou	Winter		1.20	1.02		
		Summer		1.51	0.82		
	Wuhan	Winter		1.12	1.06		
		Summer		1.49	1.00		
$PM_{2.5}$	Anshan	Winter	Water	1.43±0.09	0.55±0.07	FT-ICR MS	(Ning et al., 2025)

Table S5. Molecular information and their relative abundance of isoprene-derived organosulfates detected at Shanghai. Noted the formulas in the Table S5−S10 were from the summarization of recent studies and the reference in (Bruggemann et al., 2020; Wang et al., 2019; Ye et al., 2020; Zhu et al., 2019).

Molecular formula	*m/z* [M-H]⁻	DBE	Relative peak area (%)		
			Suburban Summer	Urban Summer	Urban Winter
$C_2H_6O_5S$	140.9863	0	3.05	3.67	3.62
$C_3H_4O_8S$	198.9554	2	0.53	0.47	1.35
$C_3H_6O_6S$	168.9812	1	6.93	5.14	12.58
$C_3H_6O_7S$	184.9761	1	0.18	0.49	2.64
$C_3H_6O_8S$	200.9711	1	0.74	0.25	1.07
$C_3H_6O_9S$	216.9660	1	1.25	0.88	3.00
$C_3H_8O_6S$	170.9969	0	0.08	0.02	0.21
$C_4H_6O_5S$	164.9863	2	3.27	2.73	2.68
$C_4H_6O_6S$	180.9812	2	3.32	1.53	3.80
$C_4H_8O_5S$	167.0020	1	4.22	2.44	6.01
$C_4H_8O_6S$	182.9969	1	16.51	11.79	12.95
$C_4H_8O_7S$	198.9918	1	2.62	3.52	0.30
$C_4H_8O_8S$	214.9867	1	0.06	0.07	0.55
$C_4H_8O_9S$	230.9816	1	0.21	0.13	0.82
$C_5H_8O_6S$	194.9969	2	8.06	6.02	9.75
$C_5H_8O_7S$	210.9918	2	4.48	1.14	6.63
$C_5H_8O_8S$	226.9867	2	1.63	2.87	1.63
$C_5H_8O_{11}S$	274.9715	2	1.23	0.89	2.35
$C_5H_{10}O_5S$	181.0176	1	5.72	5.69	20.68
$C_5H_10O_6S$	197.0125	1	10.57	9.76	17.33
$C_5H_{10}O_7S$	213.0074	1	2.94	1.88	3.10
$C_5H_{10}O_8S$	229.0024	1	5.63	0.13	0.44
$C_5H_{12}O_6S$	199.0282	0	0.31	0.25	0.66
$C_5H_{12}O_7S$	215.0231	0	16.41	7.75	10.32
$C_5H_{12}O_8S$	231.0180	0	1.32	0.98	2.45
$C_7H_{10}O_6S$	221.0125	3	1.62	1.09	3.80
$C_7H_{10}O_7S$	237.0074	3	5.42	3.17	5.66
$C_8H_{12}O_6S$	235.0282	3	0.56	0.46	2.36
$C_8H_{12}O_7S$	251.0231	3	8.20	4.66	13.64
$C_8H_{14}O_5S$	221.0489	2	3.52	2.42	11.83
$C_8H_{14}O_6S$	237.0438	2	13.77	9.04	21.72
$C_8H_{14}O_7S$	253.0387	2	33.92	17.88	20.05
$C_8H_{14}O_8S$	269.0337	2	6.85	1.49	6.20
$C_8H_{14}O_{10}S$	301.0235	2	0.10	0.24	0.61
$C_9H_{16}O_7S$	267.0544	2	50.43	25.62	35.43

$C_{10}H_{20}O_{10}S$	331.0704	1	0.04	0.05	0.05
$C_{10}H_{22}O_{10}S$	333.0861	0	0.23	0.14	0.19
$C_{12}H_{18}O_8S$	321.0650	4	3.48	2.60	2.80
$C_{12}H_{20}O_6S$	291.0908	3	1.96	1.58	5.50
$C_{15}H_{32}O_{13}S$	451.1491	0	0.49	0.23	1.76
$C_5H_{11}NO_7S$	228.0183	1	6.49	3.88	13.11
$C_5H_{11}NO_8S$	244.0133	1	1.22	0.81	3.78
$C_5H_{11}NO_9S$	260.0082	1	15.82	9.21	2.20
$C_5H_9NO_{10}S$	273.9874	2	29.00	11.79	0.96
$C_5H_{10}N_2O_{11}S$	304.9933	2	0.43	0.09	0.78
$C_8H_{13}NO_{12}S$	346.0086	3	0.18	0.11	1.32

Table S6. Molecular information and their relative abundance of monoterpene-derived organosulfates detected at Shanghai.

Precursor group	Molecular formula	*m/z* [M-H]$^-$	DBE	Relative peak area (%)		
				Suburban Summer	Urban Summer	Urban Winter
Monoterpene	$C_3H_6O_8S$	200.9711	1	0.76	0.42	1.36
	$C_5H_8O_8S$	226.9867	2	1.63	2.87	1.63
	$C_5H_{10}O_8S$	229.0024	1	0.27	0.13	0.44
	$C_5H_{12}O_6S$	199.0282	0	0.36	0.25	0.66
	$C_5H_{12}O_7S$	215.0231	0	0.27	0.18	0.72
	$C_6H_{12}O_4S$	179.0384	1	1.77	2.05	18.69
	$C_6H_{12}O_6S$	211.0282	1	20.30	14.53	45.85
	$C_6H_{12}O_8S$	243.0180	1	0.66	0.67	0.28
	$C_7H_8O_8S$	250.9867	4	0.60	0.64	0.36
	$C_7H_{10}O_8S$	253.0024	3	5.13	1.45	2.13
	$C_7H_{12}O_6S$	223.0282	2	7.69	7.49	17.66
	$C_7H_{12}O_9S$	271.0129	2	0.71	0.60	1.12
	$C_7H_{14}O_6S$	225.0438	1	16.39	10.65	37.45
	$C_8H_{10}O_8S$	265.0024	4	0.54	0.76	1.25
	$C_8H_{12}O_7S$	251.0231	3	8.20	4.66	13.64
	$C_8H_{12}O_8S$	267.0180	3	14.90	11.52	3.32
	$C_8H_{14}O_6S$	237.0438	2	13.77	9.04	21.72
	$C_8H_{14}O_7S$	253.0387	2	33.92	17.88	20.05
	$C_8H_{14}O_9S$	285.0286	2	0.45	0.07	0.29
	$C_8H_{18}O_6S$	241.0751	0	0.86	0.42	6.28
	$C_8H_{18}O_8S$	273.0650	0	0.85	0.57	3.42
	$C_9H_8O_7S$	258.9918	6	0.66	0.42	5.70
	$C_9H_{10}O_5S$	229.0176	5	1.87	1.59	6.47
	$C_9H_{10}O_6S$	245.0125	5	1.06	0.90	7.25
	$C_9H_{12}O_7S$	263.0231	4	2.04	1.49	1.71
	$C_9H_{12}O_9S$	295.0129	4	0.60	1.17	0.56
	$C_9H_{14}O_6S$	249.0438	3	2.84	2.91	6.79
	$C_9H_{14}O_7S$	265.0387	3	17.95	6.82	15.11
	$C_9H_{14}O_8S$	281.0337	3	13.86	6.20	9.50
	$C_9H_{14}O_9S$	297.0286	3	3.25	0.22	1.43
	$C_9H_{16}O_4S$	219.0697	2	0.58	0.54	4.01
	$C_9H_{16}O_5S$	235.0646	2	15.59	11.36	38.59
	$C_9H_{16}O_6S$	251.0595	2	26.01	17.22	49.34
	$C_9H_{16}O_7S$	267.0544	2	50.43	25.62	35.43
	$C_9H_{16}O_8S$	283.0493	2	9.53	5.02	17.32
	$C_9H_{16}O_9S$	299.0442	2	0.72	0.34	0.41
	$C_9H_{18}O_4S$	221.0853	1	3.14	2.32	15.43

	$C_9H_{18}O_6S$	253.0751	1	20.61	15.06	36.02
	$C_9H_{18}O_7S$	269.0700	1	10.32	3.59	13.60
	$C_9H_{20}O_4S$	223.1010	0	8.85	15.47	24.86
	$C_{10}H_{10}O_5S$	241.0176	6	0.52	0.43	2.51
	$C_{10}H_{10}O_7S$	273.0074	6	0.64	0.63	7.89
	$C_{10}H_{12}O_6S$	259.0282	5	2.24	1.77	3.61
	$C_{10}H_{14}O_4S$	229.0540	4	2.60	1.36	2.74
	$C_{10}H_{14}O_6S$	261.0438	4	2.03	1.06	1.93
	$C_{10}H_{14}O_{11}S$	341.0184	4	0.02	0.01	0.07
	$C_{10}H_{16}O_4S$	231.0697	3	4.41	2.37	7.80
	$C_{10}H_{16}O_5S$	247.0646	3	6.46	4.07	16.45
	$C_{10}H_{16}O_6S$	263.0595	3	12.82	6.54	18.43
	$C_{10}H_{16}O_7S$	279.0544	3	47.47	23.30	67.24
	$C_{10}H_{16}O_8S$	295.0493	3	14.38	4.44	13.00
	$C_{10}H_{16}O_9S$	311.0442	3	5.90	0.87	1.02
	$C_{10}H_{16}O_{10}S$	327.0391	3	2.37	2.09	1.34
	$C_{10}H_{18}O_5S$	249.0802	2	11.99	8.76	25.14
	$C_{10}H_{18}O_6S$	265.0751	2	17.15	9.58	31.55
	$C_{10}H_{18}O_7S$	281.0700	2	52.91	25.09	31.85
	$C_{10}H_{18}O_8S$	297.0650	2	13.43	5.27	14.93
	$C_{10}H_{18}O_9S$	313.0599	2	5.11	2.04	1.52
	$C_{10}H_{20}O_5S$	251.0959	1	56.42	29.99	118.32
	$C_{10}H_{20}O_6S$	267.0908	1	11.76	6.89	23.91
	$C_{10}H_{20}O_7S$	283.0857	1	6.66	2.38	13.58
	$C_{10}H_{22}O_4S$	237.1166	0	4.85	7.18	24.18
	$C_{10}H_{22}O_5S$	253.1115	0	0.89	0.77	7.12
	$C_{11}H_{16}O_7S$	291.0544	4	1.23	1.21	1.80
	$C_{11}H_{18}O_8S$	309.0650	3	7.95	2.27	8.40
	$C_{12}H_{12}O_6S$	283.0282	7	0.34	0.21	0.39
Sesquiterpene	$C_{14}H_{22}O_7S$	333.1013	4	2.74	1.63	2.41
	$C_{14}H_{22}O_8S$	349.0963	4	1.85	1.77	2.12
	$C_{14}H_{24}O_5S$	303.1272	3	2.09	0.84	4.99
	$C_{14}H_{24}O_6S$	319.1221	3	3.10	1.59	3.43
	$C_{14}H_{24}O_8S$	351.1119	3	3.15	2.78	6.31
	$C_{15}H_{24}O_7S$	347.1170	4	7.90	3.96	4.85
	$C_{15}H_{24}O_8S$	363.1119	4	1.62	1.17	3.38
	$C_{15}H_{26}O_5S$	317.1428	3	1.33	0.34	6.19
	$C_{15}H_{26}O_6S$	333.1377	3	1.93	0.84	3.48
	$C_{16}H_{28}O_7S$	363.1483	3	2.28	1.28	2.86
	$C_{16}H_{28}O_8S$	379.1432	3	6.96	2.19	4.10
	$C_{20}H_{32}O_5S$	383.1898	5	3.66	1.48	1.96
	$C_{20}H_{34}O_5S$	385.2054	4	0.67	0.23	1.06

	$C_{20}H_{34}O_9S_2$	481.1571	4	0.14	0.01	0.23
Terpene	$C_{10}H_{17}NO_7S$	294.0653	3	352.88	158.71	531.63
	$C_9H_{15}NO_8S$	296.0446	3	24.04	19.32	55.92
	$C_{10}H_{17}NO_8S$	310.0602	3	28.79	13.28	30.43
	$C_9H_{15}NO_9S$	312.0395	3	8.53	4.14	12.81
	$C_{10}H_{17}NO_9S$	326.0551	3	59.04	19.53	21.00
	$C_{10}H_{19}NO_9S$	328.0708	2	10.60	5.05	17.91
	$C_9H_{17}NO_{10}S$	330.0500	2	22.12	9.87	6.22
	$C_{10}H_{17}NO_{10}S$	342.0500	3	54.93	18.18	42.47
	$C_{10}H_{16}N_2O_{10}S$	355.0453	4	1.03	0.67	2.14
	$C_{15}H_{25}NO_7S$	362.1279	4	34.29	12.63	37.31
	$C_{10}H_{18}N_2O_{11}S$	373.0559	3	1.15	0.64	1.73
	$C_{14}H_{25}NO_9S$	382.1177	3	2.88	2.01	6.77
	$C_{10}H_{18}N_2O_{12}S$	389.0508	3	1.03	0.23	1.45

Table S7. Molecular information and their relative abundance of other biogenic VOCs-derived organosulfates (2-Methyl-3-Buten-2-ol; 2-E-pentenal, 2-E-hexenal, 3-Z-hexenal, cis-3-hexen-1-ol, and β-caryophyllene) detected at Shanghai.

Molecular formula	*m/z* [M-H]$^-$	DBE	Relative peak area (%)		
			Suburban Summer	Urban Summer	Urban Winter
$C_3H_6O_6S$	168.9812	1	6.93	5.14	12.58
$C_3H_6O_7S$	184.9761	1	0.18	0.49	2.64
$C_4H_{10}O_5S$	169.0176	0	3.84	5.57	4.77
$C_5H_{12}O_6S$	199.0282	0	0.36	0.25	0.66
$C_5H_{10}O_7S$	213.0074	1	2.94	1.88	3.1
$C_5H_{10}O_8S$	229.0024	1	0.23	0.13	0.44
$C_6H_{10}O_6S$	209.0125	2	11.25	5.78	14.19
$C_6H_{12}O_6S$	211.0282	1	20.3	14.53	45.85
$C_9H_{16}O_6S$	251.0595	2	26.01	17.22	49.34
$C_9H_{18}O_7S$	269.0700	1	10.32	3.59	13.6
$C_{14}H_{24}O_5S$	303.1272	3	2.09	0.84	4.99
$C_{14}H_{24}O_6S$	319.1221	3	3.1	1.59	3.43
$C_{14}H_{22}O_7S$	333.1013	4	2.74	1.63	2.41
$C_{14}H_{22}O_8S$	349.0963	4	1.85	1.77	2.12
$C_{14}H_{24}O_8S$	351.1119	3	3.15	2.78	6.31
$C_{15}H_{26}O_5S$	317.1428	3	1.33	0.34	6.19
$C_{15}H_{26}O_6S$	333.1377	3	1.93	0.84	3.48
$C_{15}H_{24}O_7S$	347.117	4	7.9	3.96	4.85
$C_{15}H_{24}O_8S$	363.1119	4	1.62	1.17	3.38
$C_{16}H_{28}O_7S$	363.1483	3	2.28	1.28	2.86
$C_{16}H_{28}O_8S$	379.1432	3	6.96	2.19	4.1
$C_{14}H_{25}NO_9S$	382.1177	3	2.88	2.01	6.77
$C_{15}H_{25}NO_7S$	362.1279	4	34.29	12.63	37.31

Table S8. Molecular information and their relative abundance of aromatic-derived organosulfates detected at Shanghai.

Molecular formula	*m/z* [M-H]⁻	DBE	Relative peak area (%)		
			Suburban Summer	Urban Summer	Urban Winter
$C_6H_6O_4S$	172.9914	4	0.56	0.31	1.18
$C_7H_6O_4S$	184.9914	5	0.23	0.28	1.18
$C_7H_6O_5S$	200.9863	5	2.26	1.70	8.29
$C_7H_8O_4S$	187.0071	4	0.55	0.71	3.01
$C_8H_6O_6S$	228.9812	6	0.51	0.35	5.74
$C_8H_8O_4S$	199.0071	5	0.71	0.43	1.37
$C_8H_8O_5S$	215.0020	5	3.22	2.61	7.46
$C_8H_{10}O_4S$	201.0227	4	1.01	2.73	4.73
$C_9H_8O_5S$	227.0020	6	0.22	0.06	1.89
$C_9H_{10}O_5S$	229.0176	5	1.87	1.59	6.47
$C_9H_{12}O_4S$	215.0384	4	0.62	0.75	1.70
$C_9H_{12}O_5S$	231.0333	4	0.67	0.65	2.24
$C_{10}H_{10}O_6S$	257.0125	6	0.19	0.26	7.13
$C_{10}H_{10}O_7S$	273.0074	6	0.64	0.63	7.89
$C_{10}H_{12}O_7S$	275.0231	5	0.10	0.05	0.57
$C_{11}H_{12}O_7S$	287.0231	6	1.04	0.58	3.75
$C_{11}H_{14}O_7S$	289.0387	5	0.13	0.19	0.28
$C_6H_5NO_6S$	217.9765	5	0.07	0.13	0.45
$C_{10}H_{11}NO_7S$	288.0183	6	0.54	0.59	3.30
$C_{10}H_{11}NO_8S$	304.0133	6	0.01	0.07	0.38
$C_{10}H_{11}NO_9S$	320.0082	6	0.17	#DIV/0!	0.59
$C_{10}H_{17}NO_9S$	326.0551	3	59.04	19.53	21.00
$C_{11}H_{13}NO_8S$	318.0289	6	0.08	0.09	0.23
$C_{11}H_{13}NO_9S$	334.0238	6	0.11	0.07	0.14
$C_{12}H_{15}NO_8S$	332.0446	6	0.02	0.06	0.19
$C_{12}H_{15}NO_{10}S$	364.0344	6	0.04	0.09	0.18

Table S9. Molecular information and their relative abundance of long-chain alkanes-derived organosulfates detected at Shanghai.

Molecular formula	*m/z* [M-H]$^-$	DBE	Relative peak area (%)		
			Suburban Summer	Urban Summer	Urban Winter
$C_7H_{14}O_5S$	209.0489	1	22.41	18.24	76.35
$C_7H_{16}O_4S$	195.0697	0	2.42	4.03	35.49
$C_8H_{18}O_4S$	209.0853	0	11.64	16.55	95.01
$C_9H_{16}O_7S$	267.0544	2	50.43	25.62	35.43
$C_9H_{18}O_5S$	237.0802	1	18.64	17.03	62.95
$C_9H_{18}O_7S$	269.0700	1	10.32	3.59	13.60
$C_9H_{18}O_8S$	285.0650	1	0.31	0.15	0.29
$C_9H_{20}O_8S$	287.0806	0	0.23	0.09	0.98
$C_{10}H_{16}O_8S$	295.0493	3	14.38	4.44	13.00
$C_{10}H_{18}O_6S$	265.0751	2	17.15	9.58	31.55
$C_{10}H_{18}O_7S$	281.0700	2	52.91	25.09	31.85
$C_{10}H_{18}O_8S$	297.0650	2	13.43	5.27	14.93
$C_{10}H_{20}O_5S$	251.0959	1	56.42	29.99	118.32
$C_{10}H_{20}O_6S$	267.0908	1	11.76	6.89	23.91
$C_{10}H_{20}O_8S$	299.0806	1	0.32	0.15	0.33
$C_{12}H_{20}O_7S$	307.0857	3	6.37	1.44	10.26
$C_{12}H_{24}O_5S$	279.1272	1	88.32	47.93	201.25
$C_{12}H_{26}O_4S$	265.1479	0	64.32	98.49	59.52
$C_7H_{15}NO_8S$	272.0446	1	2.85	1.92	10.07
$C_8H_{15}NO_9S$	300.0395	2	9.38	5.00	15.91
$C_9H_{17}NO_7S$	282.0653	2	1.49	1.36	9.15
$C_9H_{17}NO_8S$	298.0602	2	7.46	3.68	24.95
$C_9H_{17}NO_9S$	314.0551	2	10.14	5.80	19.40
$C_9H_{17}NO_{10}S$	330.0500	2	22.12	9.87	6.22
$C_{10}H_{19}NO_8S$	312.0759	2	22.81	8.72	47.88
$C_{10}H_{19}NO_9S$	328.0708	2	10.60	5.05	17.91
$C_{10}H_{19}NO_{10}S$	344.0657	2	8.11	3.58	11.03
$C_{10}H_{19}NO_{11}S$	360.0606	2	0.79	0.45	1.81

Table S10. Summary of molecular characteristics of CHOS compounds detected in our field samples and source samples, as the MS data are obtained from Cui et al. (2019) and Tang et al. (2020).

Source samples	Formula number	MW_W	H/C_W	O/C_W	O/S_w	DBE_w	% of Xc≥2.5	% of (4*s*+3*n*)/*o* ≤1
BBOA1(Musa)	444	360	1.52	0.47	6.21	4.76	43	88
BBOA2(Hevea)	174	396	1.35	0.40	5.97	7.68	59	86
CCOA1(Anthracite)	549	323	1.01	0.40	5.40	8.55	82	95
CCOA2(Bituminous coal)	463	340	0.99	0.31	4.64	9.90	94	85
Tunnel aerosol	635	325	1.74	0.59	6.79	2.75	23	96
Vehicle emission	112	441	1.31	0.25	4.47	9.54	71	75
Excavator-idling(diesel)	1004	353	1.61	0.38	5.81	4.18	58	96
Excavator-moving(diesel)	334	326	1.51	0.46	5.20	3.58	49	98
Excavator-working(diesel)	631	342	1.63	0.36	5.44	4.00	55	93
Diesel-vessel	334	306	1.66	0.40	5.14	3.47	50	95
Heavy-fuel-oil-vessel	1110	311	1.48	0.36	4.77	4.85	71	83
Suburban summer	1069	300	1.88	0.58	5.21	2.06	7	86
Urban summer	1127	302	1.81	0.53	5.12	2.18	10	85
Urban winter	1412	285	1.62	0.45	4.98	2.56	18	92

Table S11. Summary of molecular characteristics of CHONS compounds detected in our field samples and source samples, as the MS data are obtained from Cui et al. (2019) and Tang et al. (2020).

Source samples	Formula number	MW_W	H/C_W	O/C_W	O/S_w	DBE_w	% of Xc≥2.5	% of (4*s*+3*n*)/*o* ≤1
BBOA1(Musa)	371	379	1.55	0.50	7.21	4.98	64	64
BBOA2(Hevea)	65	411	1.56	0.50	7.51	4.79	69	63
CCOA1(Anthracite)	767	340	0.98	0.52	6.49	8.99	97	47
CCOA2(Bituminous coal)	293	308	0.97	0.49	5.82	8.04	93	29
Tunnel aerosol	410	340	1.81	0.90	8.73	2.78	29	91
Vehicle emission	17	400	1.17	0.72	8.59	6.92	59	47
Excavator-idling(diesel)	310	325	1.47	0. 41	5.59	5.18	65	42
Excavator-moving(diesel)	117	298	1.62	0.48	5.17	5.55	64	9
Excavator-working(diesel)	260	323	1.47	0.40	5.41	5.26	69	27
Diesel-vessel	13	461	1.50	0.36	6.74	9.38	38	46
Heavy-fuel-oil-vessel	398	343	1.35	0.39	5.68	6.35	86	28
Suburban summer	895	325	1.60	0.77	7.54	4.27	11	73
Urban summer	787	332	1.53	0.69	6.98	4.89	15	89
Urban winter	1277	322	1.44	0.65	6.44	6.02	21	92

References

Bruggemann, M., Xu, R., Tilgner, A., Kwong, K. C., Mutzel, A., Poon, H. Y., et al. (2020). Organosulfates in Ambient Aerosol: State of Knowledge and Future Research Directions on Formation, Abundance, Fate, and Importance, *Environ. Sci. Technol.*, 54(7), 3767-3782, https://doi.org/10.1021/acs.est.9b06751

Cui, M., Li, C., Chen, Y., Zhang, F., Li, J., Jiang, B., et al. (2019). Molecular characterization of polar organic aerosol constituents in off-road engine emissions using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS): implications for source apportionment, *Atmos. Chem. Phys.*, 19(22), 13945-13956, https://doi.org/10.5194/acp-19-13945-2019

Jiang, B., Kuang, B. Y., Liang, Y., Zhang, J., Huang, X. H. H., Xu, C., et al. (2016). Molecular composition of urban organic aerosols on clear and hazy days in Beijing: a comparative study using FT-ICR MS, *Environ. Chem.*, 13(5), 888-901, https://doi.org/10.1071/en15230

Jiang, H., Li, J., Tang, J., Cui, M., Zhao, S., Mo, Y., et al. (2022). Molecular characteristics, sources, and formation pathways of organosulfur compounds in ambient aerosol in Guangzhou, South China, *Atmospheric Chemistry and Physics*, 22(10), 6919-6935, https://doi.org/10.5194/acp-22-6919-2022

Lin, P., Rincon, A. G., Kalberer, M., &Yu, J. Z. (2012). Elemental Composition of HULIS in the Pearl River Delta Region, China: Results Inferred from Positive and Negative Electrospray High Resolution Mass Spectrometric Data, *Environmental Science & Technology*, 46(14), 7454-7462, https://doi.org/10.1021/es300285d

Ning, C., Tang, Y., Sun, H., Wang, D., Sun, S., &Gao, Y. (2025). Molecular characteristics and formation pathways of organosulfates in atmospheric fine particles: A case study in steel industrial city during winter heating period, *Journal of Hazardous Materials*, 495(138882, https://doi.org/https://doi.org/10.1016/j.jhazmat.2025.138882

O'Brien, R. E., Laskin, A., Laskin, J., Rubitschun, C. L., Surratt, J. D., &Goldstein, A. H. (2014). Molecular characterization of S- and N-containing organic constituents in ambient aerosols by negative ion mode high-resolution Nanospray Desorption Electrospray Ionization Mass Spectrometry: CalNex 2010 field study, *J. Geophys. Res. Atmos.*, 119(22), 12706-12720, https://doi.org/10.1002/2014jd021955

Rincón, A. G., Calvo, A. I., Dietzel, M., &and Kalberer, M. (2012). Seasonal differences of urban organic aerosol composition – an ultra-high resolution mass spectrometry study, *Environmental Chemistry*, 9(298-319, https://doi.org/10.1071/EN12016_AC

Tang, J., Li, J., Su, T., Han, Y., Mo, Y., Jiang, H., et al. (2020). Molecular compositions and optical properties of dissolved brown carbon in biomass burning, coal combustion, and vehicle emission aerosols illuminated by excitation–emission matrix spectroscopy and Fourier transform ion cyclotron resonance mass spectrometry analysis, *Atmos. Chem. Phys.*, 20(4), 2513-2532, https://doi.org/10.5194/acp-20-2513-2020

Wang, D., Shen, Z., Yang, X., Huang, S., Luo, Y., Bai, G., et al. (2024). Insight into the Role of NH_3/NH_4^+ and NO_x/NO_3^- in the Formation of Nitrogen-Containing Brown Carbon in Chinese Megacities, *Environmental Science & Technology*, 58(9), 4281-4290, https://doi.org/10.1021/acs.est.3c10374

Wang, K., Huang, R.-J., Brüggemann, M., Zhang, Y., Yang, L., Ni, H., et al. (2021). Urban organic aerosol composition in eastern China differs from north to south: molecular insight from a liquid chromatography–mass spectrometry (Orbitrap) study, *Atmos. Chem. Phys.*, 21(11), 9089-9104, https://doi.org/10.5194/acp-21-9089-2021

Wang, K., Zhang, Y., Huang, R.-J., Cao, J., &Hoffman, T. (2018). UHPLC-Orbitrap mass spectrometric characterization of organic aerosol from a central European city (Mainz, Germany) and a Chinese megacity (Beijing), *Atmospheric Environment*, 189(22-29, https://doi.org/10.1016/j.atmosenv.2018.06.036

Wang, K., Zhang, Y., Huang, R. J., Wang, M., Ni, H., Kampf, C. J., et al. (2019). Molecular Characterization and Source Identification of Atmospheric Particulate

Organosulfates Using Ultrahigh Resolution Mass Spectrometry, *Environ. Sci. Technol.*, 53(11), 6192-6202, https://doi.org/10.1021/acs.est.9b02628

Wang, X., Hayeck, N., Brüggemann, M., Yao, L., Chen, H., Zhang, C., et al. (2017). Chemical Characteristics of Organic Aerosols in Shanghai: A Study by Ultrahigh-Performance Liquid Chromatography Coupled With Orbitrap Mass Spectrometry, *J. Geophys. Res. Atmos.*, 122(21), 11703-11722, https://doi.org/10.1002/2017jd026930

Wang, X. K., Rossignol, S., Ma, Y., Yao, L., Wang, M. Y., Chen, J. M., et al. (2016). Molecular characterization of atmospheric particulate organosulfates in three megacities at the middle and lower reaches of the Yangtze River, *Atmos. Chem. Phys.*, 16(2285–2298, https://doi.org/10.5194/acp-16-2285-2016

Willoughby, A. S., Wozniak, A. S., &Hatcher, P. G. (2014). A molecular-level approach for characterizing water-insoluble components of ambient organic aerosol particulates using ultrahigh-resolution mass spectrometry, *Atmos. Chem. Phys.*, 14(18), 10299-10314, https://doi.org/10.5194/acp-14-10299-2014

Ye, Y., Zhan, H., Yu, X., Li, J., Wang, X., &Xie, Z. (2020). Detection of organosulfates and nitrooxy-organosulfates in Arctic and Antarctic atmospheric aerosols, using ultra-high resolution FT-ICR mass spectrometry, *Sci. Total Environ.*, 767(144339, https://doi.org/10.1016/j.scitotenv.2020.144339

Zhu, M., Jiang, B., Li, S., Yu, Q., Yu, X., Zhang, Y., et al. (2019). Organosulfur Compounds Formed from Heterogeneous Reaction between SO2 and Particulate-Bound Unsaturated Fatty Acids in Ambient Air, *Environ. Sci. Technol. Lett.*, 6(6), 318-322, https://doi.org/10.1021/acs.estlett.9b00218