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Supplement of

Organosulfates in atmospheric aerosols in Shanghai, China: seasonal and interannual variability, origin, and formation mechanisms

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Table S1. Summary of average (standard deviation) values of meteorological parameters, trace gases, aerosol liquid water content (ALWC), aerosol [H⁺], PM_{2.5} and components of PM_{2.5} in four seasons and throughout the year in 2015/2016 and 2018/2019.

	Spring		Summer		Autumn		Winter		Annual	
	2015	2019	2015	2019	2015	2018	2016	2019	2015-2016	2018-2019
T	16.6 (3.8)	17.2 (3.8)	30.2 (2.3)	30.5 (2.3)	16.4 (3.1)	17.9 (1.9)	7.2 (3.1)	6.2 (1.7)	18.2 (9.2)	18.4 (9.3)
RH	0.6 (0.1)	0.7 (0.1)	0.7 (0.1)	0.7 (0.1)	0.8 (0.1)	0.7 (0.1)	0.7 (0.1)	0.7 (0.1)	0.7 (0.1)	0.7 (0.1)
wind speed	3.8 (1.5)	4.0 (1.2)	4.4 (1.3)	4.4 (1.2)	3.6 (1.0)	3.4 (0.7)	3.3 (1.6)	3.4 (1.0)	3.8 (1.4)	3.8 (1.1)
NO₂	30.4 (11.5)	22.4 (6.1)	14.9 (5.2)	11.7 (4.0)	28.5 (7.4)	20.1 (7.1)	36.2 (14.1)	32.6 (9.9)	27.0 (13.0)	21.3 (10.3)
O₃	35.9 (8.9)	41.2 (11.0)	38.5 (18.9)	30.7 (13.8)	19.2 (8.8)	31.7 (7.8)	21.1 (9.5)	14.9 (6.7)	29.8 (15.2)	29.6 (13.9)
SO₂	6.3 (2.4)	2.2 (0.6)	3.5 (2.1)	1.5 (0.3)	4.8 (1.8)	3.5 (1.3)	8.4 (3.5)	2.8 (1.1)	5.7 (3.1)	2.5 (1.1)
ALWC	14.0 (15.4)	12.0 (8.5)	9.6 (4.5)	5.0 (3.3)	52.7 (43.7)	14.6 (32.4)	31.7 (16.8)	29.2 (19.8)	24.4 (27.0)	14.8 (20.4)
[H⁺]	2.4E-4 (3.5E-4)	7.0E-5 (7.5E-5)	7.3E-3 (6.7E-3)	2.0E-3 (2.4E-3)	1.9E-4 (1.2E-4)	9.7E-5 (9.7E-5)	6.1E-5 (7.2E-5)	3.0E-3 (1.1E-2)	2.3E-3 (4.8E-3)	1.4E-3 (5.7E-3)
OM	15.9 (7.4)	10.6 (5.2)	7.4 (5.5)	6.2 (4.5)	11.5 (6.3)	8.3 (5.4)	16.2 (8.9)	11.1 (6.0)	12.7 (8.0)	9.0 (5.5)
EC	3.9 (1.7)	3.4 (1.2)	2.5 (1.1)	1.5 (0.8)	3.2 (1.2)	1.8 (0.8)	4.0 (1.8)	2.2 (1.0)	3.4 (1.6)	2.2 (1.2)
Cl⁻	0.5 (0.7)	0.4 (0.2)	0.1 (0.1)	0.3 (0.2)	1.1 (0.8)	0.3 (0.2)	1.5 (1.0)	1 (0.6)	0.7 (0.9)	0.5 (0.4)
NO₃⁻	9.4 (5.7)	9.9 (6.3)	1.0 (1.1)	3.4 (3.2)	9.6 (8.2)	6.7 (6.5)	16.6 (10.0)	14.1 (10.0)	8.8 (8.9)	8.4 (7.8)
SO₄²⁻	8.9 (4.2)	5.3 (2.4)	7.4 (3.1)	4.2 (2.0)	9.4 (5.7)	4.0 (1.9)	11.1 (5.1)	9.2 (5.3)	9.1 (4.6)	5.7 (3.8)
NH₄⁺	5.9 (3.1)	4.6 (2.6)	2.7 (1.7)	1.4 (1.1)	7.0 (4.8)	3.1 (2.6)	10.2 (5.1)	6.2 (4.1)	6.2 (4.6)	3.8 (3.3)
PM_{2.5}	59.1 (21.4)	44.6 (20)	30.8 (13.5)	22 (11.1)	59.7 (35.0)	34.2 (17.7)	91 (47.5)	55.9 (29.9)	59.0 (37.9)	38.6 (24.0)

Units: T (°C), wind speed (m s⁻¹), NO₂ (ppb), O₃ (ppb), SO₂ (ppb), ALWC (μg m⁻³), aerosol [H⁺] (mol L⁻¹), and major aerosol components (μg m⁻³).

Table S2. Recoveries of OS standards spiked in the blank filter.

OS standard	Spike concentration (ppm)	Recovery
Limonaketone sulfate	2.50	88.5%
α -Pinene sulfate	2.86	88.7%
Δ -Carene sulfate	3.26	66.4%
β -Caryophyllene sulfate	1.82	84.2%
Octyl sulfate	1.94	82.6%
Methyl sulfate	1.92	88.0%
Phenyl sulfate	1.57	87.7%
Camphorsulfonate	2.27	94.3%
Lactic acid sulfate	5.05	72.5%
Glycolic acid sulfate	4.82	77.8%

Table S3. Dates and concentrations of major components of aerosol samples used for matrix effect evaluation, as well as the ratios of the signal response of OS standards in different sample extracts to that in pure solvent.

	Exp. 1	Exp. 2	Exp. 3	Exp. 4
Date of sample	19/01/2019	19/01/2019	31/07/2019	01/08/2019
OM	22	22	4	4
NO ₃ ⁻	34	34	0.4	0.7
SO ₄ ²⁻	15	15	2	2
OS standard				
Limonaketone sulfate	0.93 (1.3)	0.93 (7.8)	1.09	1.15
α -Pinene sulfate	0.90 (1.4)	0.98 (9.0)	1.02	1.06
Δ -Carene sulfate	0.81 (1.6)	0.91 (10.2)	1.02	1.08
β -Caryophyllene sulfate	0.96 (0.9)	1.08 (5.7)	1.07	1.10
Octyl sulfate	0.87 (1.0)	1.00 (6.1)	1.10	1.14
Methyl sulfate	0.20 (1.0)	0.16 (6.0)	0.51	0.55
Phenyl sulfate	1.01 (0.8)	0.96 (4.9)	1.06	1.12
Camphorsulfonate	0.89 (1.1)	1.07 (7.1)	1.06	1.11
Lactic acid sulfate	0.93 (1.0)	0.86 (6.3)	1.35	1.38
Glycolic acid sulfate	0.17 (1.0)	0.31 (6.0)	0.45	0.53

Units: OM, NO₃⁻ and SO₄²⁻ ($\mu\text{g m}^{-3}$). The values in parentheses are the concentrations (ppm) of the OS standards added to the aerosol sample extracts. The OS standard concentrations in experiments 2-4 are the same.

Table S4. Molecular formulas of high-molecular-weight CHOS species observed during the pollution periods of winter and summer in 2019.

Winter in 2019		Summer in 2019	
Formula	m/z	Formula	m/z
C ₁₈ H ₃₃ O ₈ S ⁻	409.1896	*C ₁₈ H ₁₃ O ₈ S ₂ ⁻	421.0052
C ₂₀ H ₃₇ O ₇ S ⁻	421.226	C ₂₂ H ₂₁ O ₇ S ⁻	429.1008
C ₁₉ H ₃₇ O ₈ S ⁻	425.2209	C ₁₄ H ₁₃ O ₁₄ S ⁻	437.0026
C ₂₂ H ₄₃ O ₆ S ⁻	435.278	C ₁₅ H ₁₅ O ₁₄ S ⁻	451.0183
*C ₁₆ H ₂₃ O ₁₀ S ₂ ⁻	439.0733	C ₁₅ H ₁₇ O ₁₄ S ⁻	453.0339
C ₁₈ H ₃₁ O ₁₀ S ⁻	439.1638	*C ₁₅ H ₁₉ O ₁₂ S ₂ ⁻	455.0318
C ₂₄ H ₃₇ O ₈ S ⁻	485.2209	C ₁₅ H ₁₅ O ₁₅ S ⁻	467.0132
C ₃₀ H ₂₇ O ₁₂ S ⁻	611.1223	C ₂₄ H ₃₇ O ₈ S ⁻	485.2209
C ₃₇ H ₄₉ O ₇ S ⁻	637.3199	C ₃₄ H ₄₉ O ₅ S ⁻	569.3301
C ₃₁ H ₅₇ O ₁₄ S ⁻	685.3469	C ₃₅ H ₅₃ O ₆ S ⁻	601.3563
		C ₃₆ H ₄₇ O ₆ S ⁻	607.3093
		C ₃₇ H ₄₉ O ₇ S ⁻	637.3199
		C ₃₇ H ₅₉ O ₇ S ⁻	647.3981
		C ₄₃ H ₆₃ O ₅ S ⁻	691.4396

*The high-molecular-weight CHOS species with two sulfur atoms may be accretion products of smaller CHOS species.

Table S5. Summary of individual organosulfate concentration (in ng m⁻³) in four seasons in 2015/2016 and 2018/2019.

Category	Formula [M-H] ⁻	Spring		Summer		Autumn		Winter	
		2015	2019	2015	2019	2015	2018	2016	2019
C ₂ /C ₃ OS	C ₃ H ₅ O ₄ S ⁻	0.53	0.35	0.67	0.82	0.59	0.28	0.67	0.48
	C ₂ H ₃ O ₅ S ⁻	0.51	0.57	0.58	0.76	0.62	0.42	0.64	0.50
	C ₃ H ₅ O ₅ S ⁻	1.29	1.15	4.56	3.77	1.50	0.92	1.35	0.93
	C ₂ H ₃ O ₆ S ⁻	2.58	2.55	3.79	3.19	2.43	1.80	2.58	1.33
	C ₃ H ₇ O ₅ S ⁻	0.75	0.53	0.63	1.24	2.59	0.33	1.27	0.63
	C ₃ H ₅ O ₆ S ⁻	2.25	2.32	2.06	1.97	2.15	1.74	2.49	1.72
Anthropogenic OS	C ₄ H ₇ O ₄ S ⁻	2.29	2.18	2.31	1.30	1.75	1.23	1.77	2.33
	C ₅ H ₇ O ₆ S ⁻	0.85	0.63	0.79	1.14	0.69	0.48	0.95	0.69
	C ₆ H ₉ O ₆ S ⁻	0.86	0.46	1.43	1.47	1.24	0.34	2.20	0.25
	C ₈ H ₁₇ O ₄ S ⁻	0.94	0.54	0.37	0.34	0.99	0.54	1.86	1.95
	C ₆ H ₅ O ₄ S ⁻	0.35	0.08	0.37	--	0.41	0.13	0.34	0.12
	C ₇ H ₇ O ₄ S ⁻	0.33	0.11	0.32	0.28	0.43	0.11	0.33	0.16
Unknown source OS	C ₄ H ₅ O ₅ S ⁻	1.06	0.56	1.09	0.47	1.13	0.80	1.49	1.28
	C ₅ H ₈ NO ₈ S ⁻	1.40	1.06	3.34	2.98	0.90	1.04	0.70	0.68
Isoprene OS	C ₄ H ₇ O ₅ S ⁻	1.05	1.41	1.02	1.91	1.09	0.97	1.35	1.50
	C ₄ H ₇ O ₆ S ⁻	1.51	1.96	6.35	4.19	1.68	1.14	1.41	1.06
	C ₅ H ₉ O ₆ S ⁻	1.33	2.34	2.87	1.69	1.60	1.49	1.69	1.35
	C ₄ H ₇ O ₇ S ⁻	1.62	2.16	4.57	4.49	1.03	1.84	1.26	1.16
	C ₅ H ₁₁ O ₆ S ⁻	0.53	0.64	0.74	1.21	0.54	0.42	0.52	0.40
	C ₅ H ₇ O ₇ S ⁻	2.89	3.96	13.14	8.85	2.67	2.55	3.81	3.06
	C ₅ H ₉ O ₇ S ⁻	1.57	2.56	9.66	9.74	1.19	1.40	1.33	1.06
	C ₃ H ₁₁ O ₇ S ⁻	1.26	1.23	35.80	30.52	0.52	0.57	0.48	0.37
	C ₇ H ₉ O ₇ S ⁻	0.48	0.50	0.96	0.87	0.45	0.36	0.45	0.33
	C ₅ H ₁₀ NO ₉ S ⁻	0.82	0.60	2.64	6.82	--	0.40	0.20	0.24
	C ₅ H ₈ NO ₁₀ S ⁻	0.57	0.59	2.14	7.39	--	0.26	--	--
Monoterpene OS	C ₇ H ₁₁ O ₆ S ⁻	1.00	1.01	2.64	2.90	0.81	0.72	0.86	0.49
	C ₇ H ₁₁ O ₇ S ⁻	1.58	2.05	3.35	4.17	1.28	0.95	1.31	0.56
	C ₁₀ H ₁₇ O ₅ S ⁻	0.32	0.04	0.29	0.14	0.31	0.10	0.37	0.27
	C ₉ H ₁₅ O ₆ S ⁻	1.56	1.10	1.47	0.91	0.95	1.06	1.20	0.99
	C ₈ H ₁₃ O ₇ S ⁻	1.11	2.24	2.20	3.90	1.01	1.10	1.07	0.61
	C ₁₀ H ₁₅ O ₇ S ⁻	2.79	4.37	3.35	6.45	1.77	3.12	3.72	3.57
	C ₁₀ H ₁₇ O ₇ S ⁻	0.31	0.22	0.45	0.20	0.31	0.20	0.29	--
	C ₁₀ H ₁₆ NO ₇ S ⁻	11.20	6.57	6.50	4.92	3.00	5.52	3.04	5.39
	C ₉ H ₁₄ NO ₈ S ⁻	2.28	3.00	1.21	1.22	1.36	3.65	1.57	1.53
	C ₁₀ H ₁₆ NO ₁₀ S ⁻	1.70	2.06	1.24	1.60	1.13	1.59	1.11	1.11
SUM		51.04	51.53	114.13	102.09	38.15	37.98	44.48	35.99

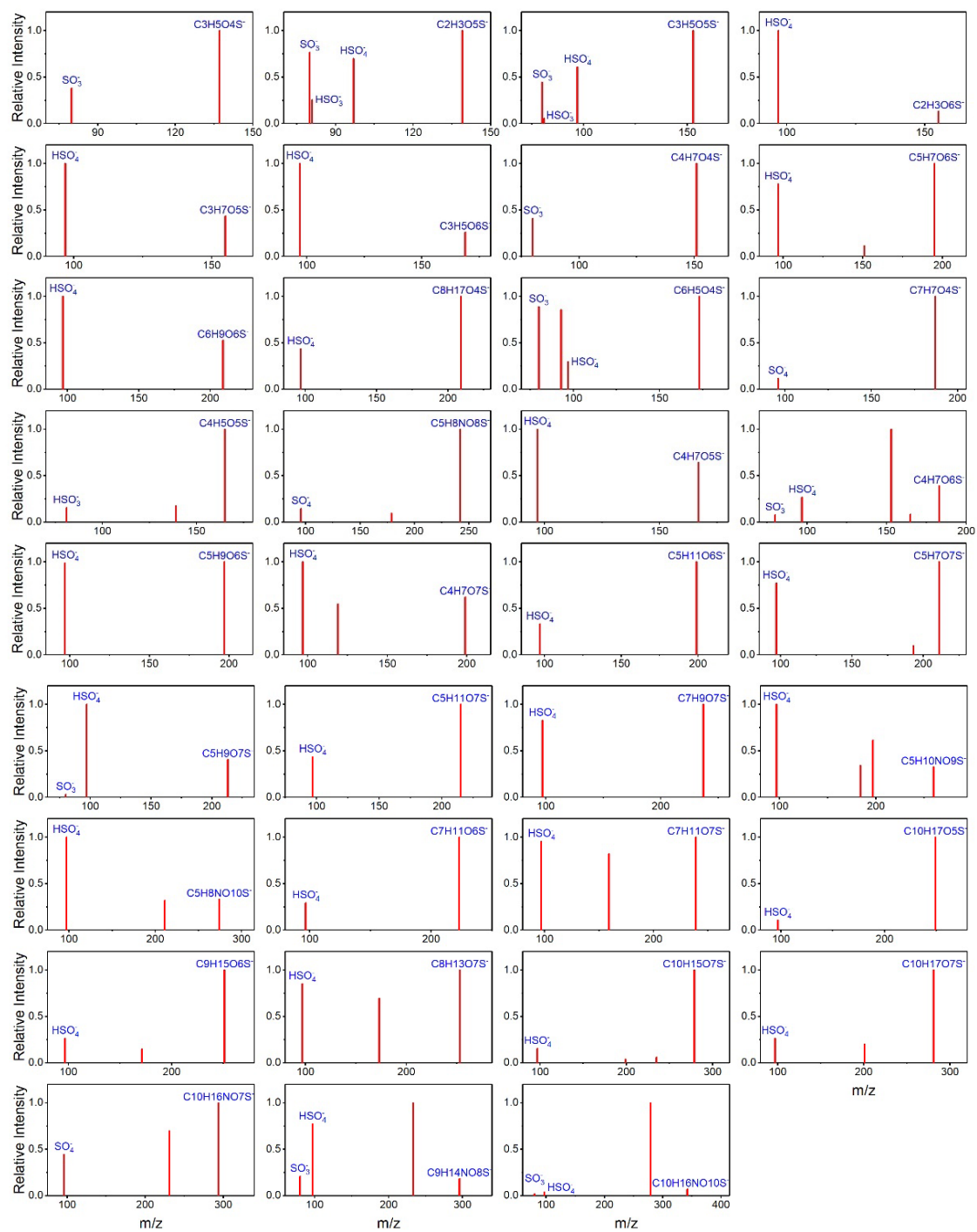


Figure S1. MS² spectra of quantified OS species with S-containing fragments being labeled. The collision energy was 6-10 eV for C₅H₈NO₈S⁻, 12-25 eV for C₃H₅O₄S⁻, C₂H₃O₅S⁻, C₄H₅O₅S⁻, and C₁₀H₁₆NO₁₀S⁻, 20-50 eV for C₆H₅O₄S⁻, and 10-35 eV for the rest.