Supplementary Information for

Molecular-level analysis of atmospheric particulate organic compounds using HPLC-Orbitrap MS/MS: effects of solvents

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Figure S2. Extraction efficiency of OC using different solvents.

Figure S3. Superimposed and averaged measurement results from three different solvents. (a)Venn diagram illustrating differences in chemical species across three solvents; (b) Average superimposed measurement plot of chemical species using three solvents.

Figure S4. Line plots of carbon numbers frequency distributions for three solvents across seasonal samples.

Text S1. Measurement methods for carbonaceous species.

A quartz filter sample of 0.518 cm^2 was analyzed using a thermal/optical reflectance carbon analyzer (DRI Model 2001A). In a pure helium atmosphere, a stepwise temperature program was executed at 140°C (OC1), 280°C (OC2), 480°C (OC3), and 580°C (OC4), with each stage maintained for 150 seconds. Subsequently, the atmosphere was switched to a mixture of 2% oxygen and 98% helium, and the temperature was stepped at 580°C (EC1), 740°C (EC2), and 840°C (EC3), again holding for 150 seconds at each stage. The concentrations of organic carbon (OC), elemental carbon (EC), and total carbon (TC) were calculated according to the IMPROVE-A protocol using the following formulas. In the formulas, OPC refers to pyrolytic organic carbon.

$$OC = OC1 + OC2 + OC3 + OC4 + OPC$$

$$EC = EC1 + EC2 + EC3 - OPC$$

$$TC = OC + EC$$

Text S2. Chromatographic methods and ionisation source parameters.

The Thermo Hypersil column (C18, 100 mm×2.1 mm, 1.9 μm) was used. The mobile phases were A: 0.1% formic acid in water, B: 0.1% formic acid in acetonitrile, and the gradient elution was performed using a mixture of A and B phases at a flow rate of 300 μl/min. The elution protocol was as follows: 5% B (0–4 min), linearly increased to 98% B (4–35 min), held at 98% B (35–50 min), decreased to 5% B (50–51 min), and held at 5% B (51–60 min).

The ionisation source parameters were set as follows: sheath gas flow rate, 40; aux gas flow rate, 10; sweep gas flow rate, 0; spray voltage, +3.8 kV for ESI+ and –3.2 kV for ESI– mode; capillary temperature, 320 °C; S-lens RF level, 50%; and aux gas heater temperature, 350 °C.

Table S1. Solvent applications in LC-MS analysis of organic aerosols.

Composition to be analyzed	Extraction solvents	MS	Reference
NTS	MeOH	Orbitrap MS	(Li et al., 2024; Evans et al., 2025; He et al., 2025; Tang et al., 2025b)
		qTOF MS	(Ditto et al., 2020)
	ACN	Orbitrap MS	(Wang et al., 2017; Wan et al., 2022; Thomas et al., 2025)
	ACN/H_2O (8:2, v/v)	Orbitrap MS	(Wang et al., 2018; Wang et al., 2021)
	ACN/H_2O (95:5, v/v)	QQQ MS	(Liu et al., 2025)
	MeOH:dichloromethane:n-hexane (2:2:1, v/v/v)	Orbitrap MS	(Wang et al., 2022)
Organosulfates	MeOH/H_2O (1:1, v/v)	Orbitrap MS	(Wang et al., 2023; Ma et al., 2025)
		qTOF MS	(Glasius et al., 2018)
	ACN/H_2O (95:5, v/v)	QQQ MS	(Hettiyadura et al., 2019)
	ACN/H_2O (8:2)	Orbitrap MS	(Wang et al., 2019)
	MeOH	Orbitrap MS	(Gómez-González et al., 2008; Gómez-González et al., 2012)
Nitroaromatics	MeOH	QQQ MS	(Cao et al., 2023; Huang et al., 2024; Tang et al., 2025a)
	sequential extraction utilize MeOH and ACN	qTOF MS	(Yin et al., 2025)
Sulfonates	H_2O	Orbitrap MS	(Wei et al., 2020)
Nitrates	MeOH	LIT MS	(Li et al., 2018)

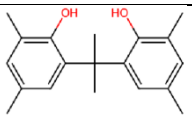
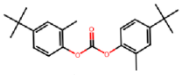
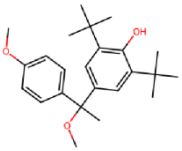
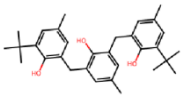
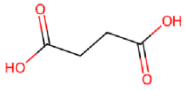
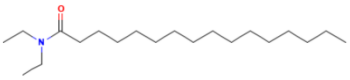
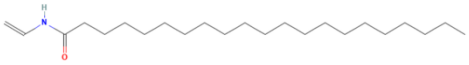
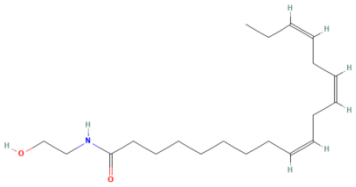
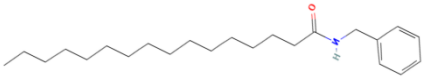
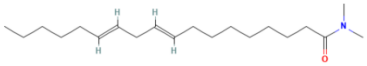
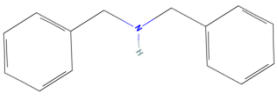
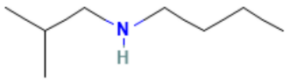
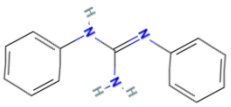
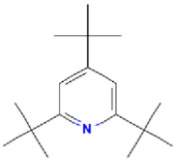
Table S2. Samples information and $PM_{2.5}$ concentrations.

Season	Sampling Date	$PM_{2.5}$ concentration ($\mu g/m^3$)	OC ($\mu g/m^3$)
Spring	2023.03.30 - 2023.04.11	35.8±14.2	8.5±2.4
Summer	2023.07.05 - 2023.08.09	21.3±6.2	5.8±2.0
Autumn	2023.10.01 - 2023.11.06	52.2±47.2	9.3±5.3
Winter	2023.12.16 - 2024.01.11	101.8±69.0	12.0±4.8

Table S3. Detection of Internal Standards in Mass Spectrometric Analysis.The retention times, m/z values, and peak areas of the internal standard in 15 samples were calculated, and their means and standard deviations were determined.

Formula (Ionisation mode)	Average retention time (min)	Average m/z	Average peak area
$C_{12}H_{11}D_3N_4O_4S$ (+)	11.37±0.02	314.09951±0.00010	(2.28±0.54) × 10^7
$C_{12}H_8D_6N_4O_4S$ (+)	13.51±0.01	317.11838±0.00007	(2.91±0.98) × 10^7
$C_6H_7D_2N_3O_4$ (+)	2.28±0.03	190.07912±0.00005	(1.81±0.86) × 10^7
$C_6H_5D_4N_3O_3$ (+)	2.99±0.03	176.09675±0.00004	(5.43±1.44) × 10^7
$C_6D_3H_5N_4O_4$ (+)	4.00±0.02	204.08067±0.00004	(1.29±0.28) × 10^7
$C_5H_4D_3N_3O_2$ (+)	3.61±0.03	145.07993±0.00004	(9.77±3.80) × 10^7
$C_6HD_4NO_3$ (–)	11.73±0.01	142.04457±0.00003	(1.13±0.26) × 10^8
$C_{12}H_{11}D_3N_4O_4S$ (–)	11.36±0.02	312.08482±0.00018	(2.97±1.09) × 10^5
$C_{12}H_8D_6N_4O_4S$ (–)	13.51±0.01	315.10387±0.00010	(8.22±2.59) × 10^5
$C_6H_7D_2N_3O_4$ (–)	2.29±0.03	188.06446±0.00005	(4.65±2.25) × 10^5

Table S4. Homologous series for CHO–, CHON+, CHN+ contaminants and representative structures.

Composition	Homologous series	Area fraction(%)			Structure
		MeOH	ACN	ACN/H_2O	
CHO	$C_nH_{2n-14}O_2$	73.7	81.0	5.2	
	$C_nH_{2n-16}O_3$	3.8	4.5	14.5	
	$C_nH_{2n-14}O_3$	6.8	1.2	2.0	
	$C_nH_{2n-22}O_3$	2.1	2.4	0	
	$C_nH_{2n-2}O_4$	1.1	0	23.3	
	$C_nH_{2n+1}NO$	45.6	42.6	10.7	
	$C_nH_{2n-1}NO$	21.2	22.2	7.8	
CHON	$C_nH_{2n-5}NO_2$	5.3	5.3	0.4	
	$C_nH_{2n-7}NO$	4.6	4.5	0.6	
	$C_nH_{2n-3}NO$	3.6	4.5	0.4	
CHN	$C_nH_{2n-13}N$	36.2	47.8	12.3	
	$C_nH_{2n+3}N$	38.8	36.3	0.5	
	$C_nH_{2n-13}N_3$	9.5	1.7	62.6	
	$C_nH_{2n-5}N$	6.8	6.5	1.2	

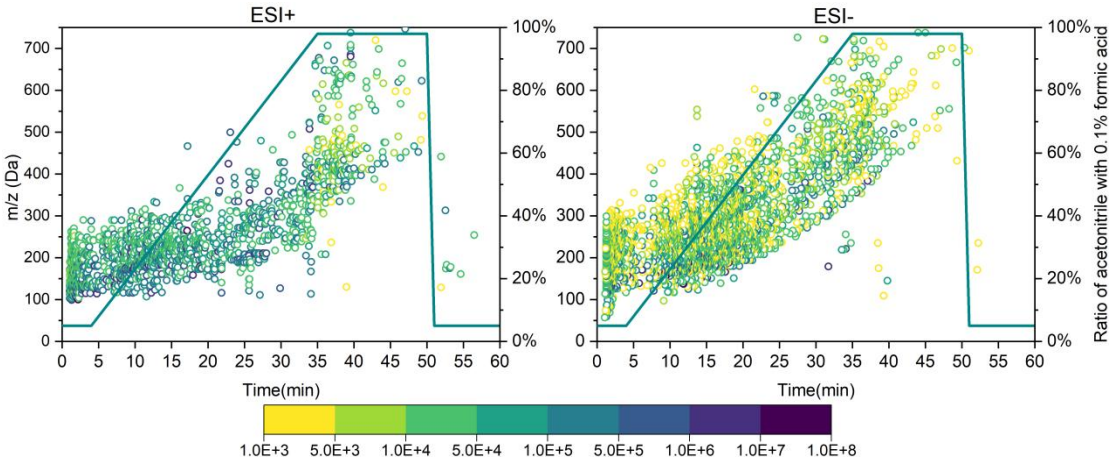


Figure S1. Separation of substances under chromatographic gradient elution program for winter methanol extract.

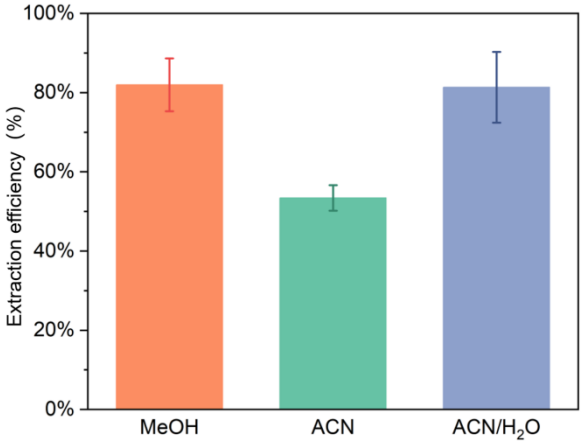


Figure S2. Extraction efficiency of OC using different solvents.

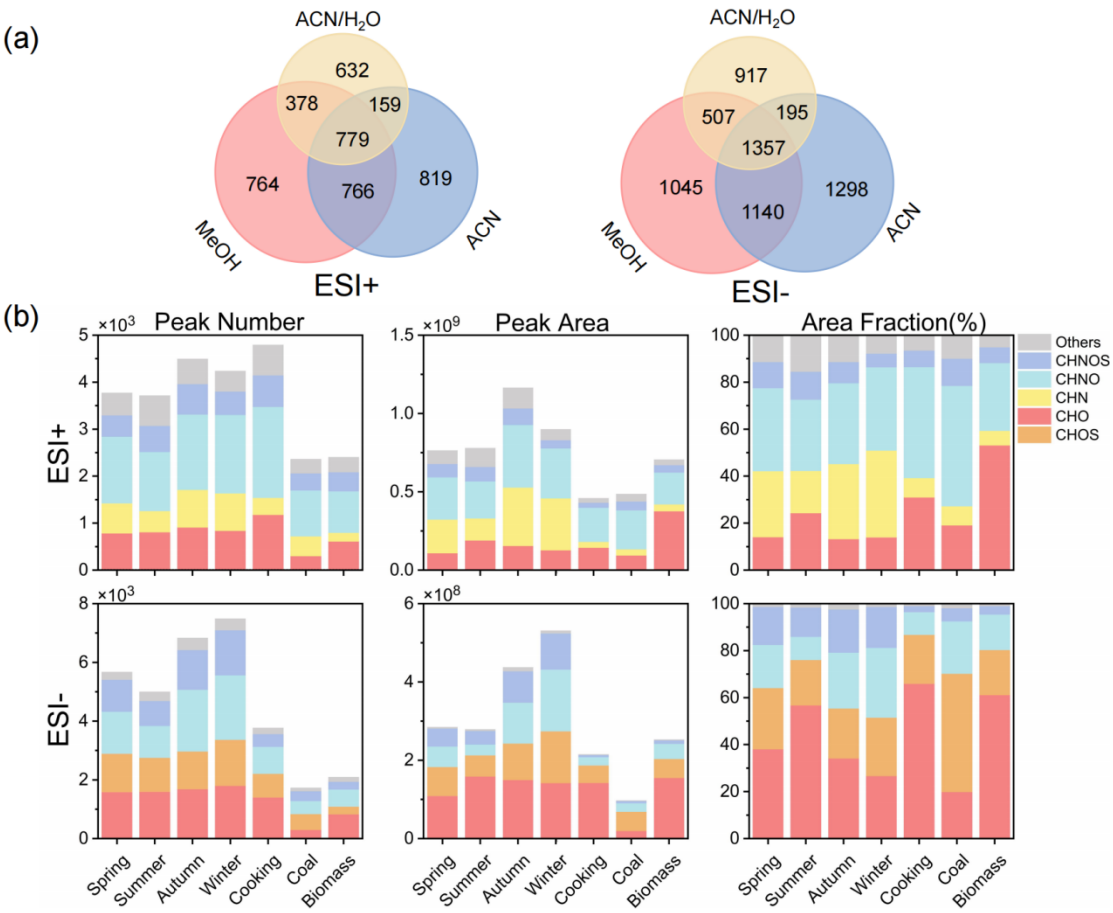


Figure S3. Superimposed and averaged measurement results from three different solvents. (a)Venn diagram illustrating differences in chemical species across three solvents; (b) Average superimposed measurement plot of chemical species using three solvents.

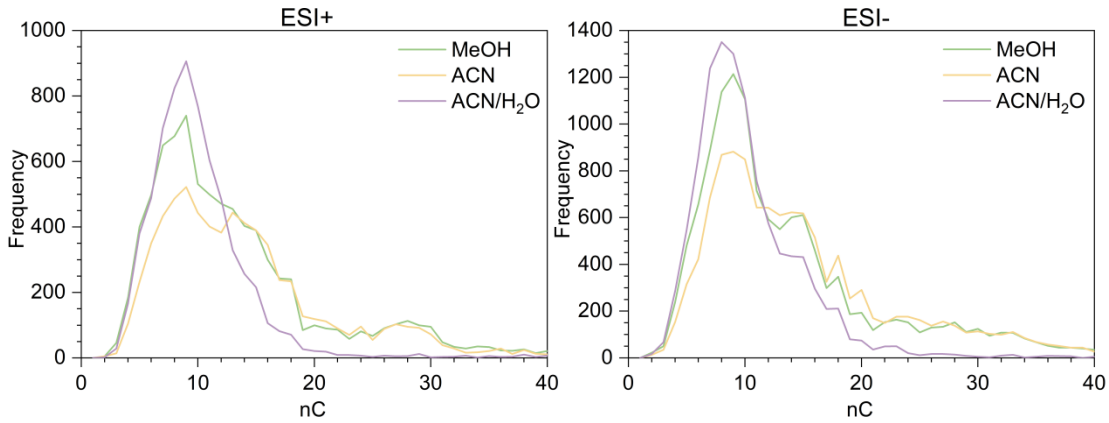


Figure S4. Line plots of carbon numbers frequency distributions for three solvents across seasonal samples.

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