Supplementary Information

Time-resolved intermediate-volatility and semivolatile organic compound emissions from household coal combustion in northern

China

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Туре	Source region	Mad (%)	Aad (%)	Ad (%)	Vad (%)	Vd (%)	Vdaf (%)	FCd (%)
Anthracite coal 1 (AC1)	NingXia	0.3	7.8	7.8	7.6	7.6	8.3	84.6
Anthracite coal 2 (AC2)	GuiZhou	0.8	14.9	15.0	7.1	7.1	8.4	77.9
Bituminous coal 1 (BC1)	ShenMu	4.1	5.3	5.5	31.4	32.7	34.6	61.8
Bituminous coal 2 (BC2)	Inner Mongolia	6.4	3.1	3.3	30.1	32.1	33.2	64.6
Bituminous coal 3 (BC3)	Unknown	5.6	8.0	8.5	32.0	33.9	37.0	57.6

Table S1. Compositions and properties of coal used.

Note: Mad, Aad, Ad, Vad, Vd, Vdaf and FCd stand for the moisture content on a dry air basis, ash content on a dry air basis, ash content on a dry basis, volatile matter content on a dry air basis, volatile matter content on a dry basis, volatile matter content on a dry-and ash-free basis, and fixed carbon content on a dry basis, respectively.

	Calibration factor under dry
	conditions (ncps/ppbV)
formaldehyde	3.9
acetonitrile	28.3
propene	9.7
acetaldehyde	31.2
acetone	29.2
benzene	19.4
toluene	22.3
xylene	23.3
trimethylbenzene	24.3

Table S2. Results of calibration measurements.

Substance quantification without external calibrants proceeds as follows:

$$\frac{CF_x}{CF_{Acetone}} = \frac{Kx}{K_{Acetone}} \times \frac{\Gamma_x}{\Gamma_{Acetone}}$$

where CF_x , $CF_{Acetone}$, K_x , K_{Actone} , Γ_x and $\Gamma_{Acetone}$ stand for the calibration factor of molecule x, calibration factor of acetone, reaction rate coefficient of molecule x, reaction rate coefficient of acetone, mass transmission efficiency of molecule x, and mass transmission efficiency of acetone, respectively. Acetone can also be replaced with any calibrant present in the calibration cylinder. Acetone was the preferred choice due to its humidity independence.

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Table	\$3.	Peak	assignment.

MW	Exact m/z	Measured	$\Delta m/z \times 10^3 a$	С	Н	0	N	RDBE ^b	Group	Species	GCxGC-ToF-
17	18.033	18.033	-0.5							Ammonia	
27	28.019	28.019	-0.6	1	1		1	2	N-containing VOC	Hydrogen cyanide	-
30	31.018	31.018	1	1	2	1		1	Carbonyls	Formaldehyde	
32	33.033	33.033	0.2	1	4	1		0	Alcohols	Methanol	
40	41.038	41.038	0.2	3	4			2	HC fragments		
41	42.033	42.033	-0.2	2	3		1	2	N-containing VOC	Acetonitrile	
42	43.054	43.054	-0.2	3	6			1	Aliphatics	Propene	
43	44.013	44.013	-1	1	1	1	1	2	N-containing VOC	Isocyanic acid	
44	45.033	45.033	0.1	2	4	1		1	Carbonyls	Acetaldehyde	
46	47.013	47.013	0.6	1	2	2		1	Acids	Formic acid	
52	53.038	53.038	0.7	4	4			3	Aliphatics	Vinylacetylene	
54	55.054	55.054	-0.1	4	6			2	Aliphatics	Buta-1,3-diene	
56	57.033	57.034	1	3	4	1		2	Carbonyls	Acrolein	Yes
56	57.069	57.069	-0.1	4	8			1	Aliphatics	Butene	Yes
58	59.05	59.05	0.3	3	6	1		1	Carbonyls	Acetone/propanal	
60	61.028	61.028	0.5	2	4	2		1	Acids	Acetic acid	
61	62.024	62.024	0.6	1	3	2	1	1	N-containing VOC	Nitromethane	Yes
66	67.054	67.054	1	5	6			3	Aliphatics	Cyclopentadiene	

MW	Exact m/z	Measured m/z	$\Delta m/z \times 10^3 a$	С	Н	0	N	RDBE ^b	Group	Species	GCxGC-ToF- MS detected ^c
68	69.07	69.07	1	5	8			2	Aliphatics	Cyclopentene/Isoprene	Yes
70	71.049	71.049	1.1	4	6	1		2	Carbonyls	Methacrolein	
70	71.085	71.085	-0.6	5	10			1	Aliphatics	Cyclopentane/2-methylbut-1-ene	
72	73.064	73.064	0.2	4	8	1		1	Carbonyls	Butanal/butan-2-one	Yes
74	75.044	75.044	0.6	3	6	2		1	Acids	Propanoic acid	
78	79.053	79.053	0.3	6	6			4	Aromatics	Benzene	Yes
80	81.07	81.07	0.9	6	8			3	Aliphatics	Cyclohexadiene	
82	83.085	83.085	0.4	6	10			2	Aliphatics	Cyclohexene	
84	85.065	85.065	1	5	8	1		2	Carbonyls	Cyclopentanone	
84	85.1	85.1	-0.1	6	12			1	Aliphatics	Cyclohexane	
88	89.059	89.059	0.4	4	8	2		1	Acids	Butanoic acid	Yes
92	93.07	93.07	0.5	7	8			4	Aromatics	Toluene	Yes
94	95.049	95.049	0.3	6	6	1		4	Oxygenated aromatics	Phenol	Yes
96	97.1	97.1	-0.5	7	12			2	Aliphatics	Methylcyclohexene	Yes
102	103.053	103.056	2.5	8	6			6	Aliphatics	Ethylcyclohexane	
104	105.07	105.071	1.6	8	8			5	Aromatics	Styrene	Yes
106	107.05	107.052	2	7	6	1		5	Oxygenated aromatics	Benzaldehyde	Yes
106	107.085	107.085	-0.1	8	10			4	Aromatics	Xylene	Yes
108	109.063	109.063	0.1	7	8	1		4	Oxygenated aromatics	Cresol	Yes
110	111.044	111.044	-0.2	6	6	2		4	Oxygenated	Benzenediol/2-methylfuraldehyde	Yes

MW	Exact m/z	Measured m/z	$\Delta m/z \times 10^3 a$	С	Н	0	N	RDBE ^b	Group	Species	GCxGC-ToF- MS detected ^c
									aromatics		
110	111.08	111.078	-2.7	7	10	1		3	Carbonyls		Yes
110	111.115	111.116	1.4	8	14			2	Aliphatics	Ethylcyclohexene	Yes
116	117.075	117.073	-1.5	9	8			6	Aromatics	Indene	Yes
118	119.049	119.052	2.8	8	6	1		6	Oxygenated aromatics	Benzofuran	Yes
118	119.086	119.086	0.5	9	10			5	Aromatics	Indane	Yes
120	121.065	121.067	2.5	8	8	1		5	Oxygenated aromatics	1-Phenylethanone 3-/4- methylbenzaldehyde	Yes
120	121.101	121.1	-1	9	12			4	Aromatics	C3-benzene	Yes
122	123.08	123.08	0.1	8	10	1		4	Oxygenated aromatics	C2-phenol	Yes
124	125.06	125.06	0.1	7	8	2		4	Oxygenated aromatic	2- Methoxyphenol/methylbenzenediol s	Yes
128	129.07	129.072	1.8	10	8			7	Aromatics	Naphthalene	Yes
130	131.049	131.053	3.8	9	6	1		7	Oxygenated aromatics		
130	131.086	131.087	2	10	10			6	Aromatics	Dihydronaphthalene	Yes
132	133.065	133.067	2.4	9	8	1		6	Oxygenated aromatics		Yes
132	133.101	133.098	-2.7	10	12			5	Aromatics	Cymenene	Yes
134	135.08	135.083	2.5	9	10	1		5	Oxygenated aromatics	Methylacetophenone	Yes

MW	Exact m/z	Measured m/z	$\Delta m/z \times 10^3 a$	С	Н	0	N	RDBE ^b	Group	Species	GCxGC-ToF- MS detected ^c
134	135.116	135.113	-3.4	10	14			4	Aromatics	Cymene	Yes
136	137.06	137.062	1.9	8	8	2		5	Oxygenated aromatics	Phenylacetic acid	Yes
136	137.096	137.096	0.3	9	12	1		4	Oxygenated aromatics	Trimethylphenol	Yes
142	143.085	143.087	2.3	11	10			7	Aromatics	C1-Naphthalene	Yes
144	145.101	145.1	-1.5	11	12			6	Aromatics		Yes
144	145.065	145.068	2.5	10	8	1		7	Oxygenated aromatics	2-Naphthol	Yes
146	147.083	147.08	-2.1	10	10	1		6	Oxygenated aromatics		Yes
148	149.096	149.096	0.6	10	12	1		5	Oxygenated aromatics		Yes
152	153.07	153.072	2.3	12	8			9	Aromatics	Acenaphthylene	Yes
154	155.086	155.088	2.5	12	10			8	Aromatics	1,1'-Biphenyl/1,2- dihydroacenaphthylene	Yes
156	157.101	157.103	2	12	12			7	Aromatics	C2-Naphthalene	Yes
158	159.08	159.083	2.3	11	10	1		7	Oxygenated aromatics	C1-Naphthol	Yes
160	161.096	161.097	1.3	11	12	1		6	Oxygenated aromatics		Yes
166	167.085	167.088	3.1	13	10			9	Aromatics	Fluorene	Yes
168	169.101	169.097	-4.4	13	12			8	Aromatics		Yes
170	171.117	171.118	1.5	13	14			7	Aromatics	C3-Naphthalene	Yes

MW	Exact m/z	Measured m/z	$\Delta m/z \times 10^3 a$	С	Н	0	N	RDBE ^b	Group	Species	GCxGC-ToF- MS detected ^c
172	173.096	173.099	3.1	12	12	1		7	Oxygenated aromatics	C2-Naphthol	Yes
174	175.117	175.118	0.5	12	14	1		6	Oxygenated aromatics		Yes
178	179.085	179.089	3.5	14	10			10	Aromatics	Anthracene/Phenanthrene	Yes
180	181.101	181.102	1.2	14	12			9	Aromatics	Dihydroanthracene/c1-fluorene	Yes
182	183.08	183.083	3.7	13	10	1		9	Oxygenated aromatics	Benzophenone	Yes
184	185.132	185.13	-2.5	14	16			7	Aromatics	C4-Naphthalene	Yes
192	193.101	193.104	3.1	15	12			10	Aromatics	C1-Phenanthrene/c1-anthracene	Yes
194	195.116	195.111	-4.9	15	14			9	Aromatics	C2-Fluorene	Yes
196	197.096	197.099	2.9	14	12	1		9	Oxygenated aromatics	C1-Benzophenone	Yes
206	207.117	207.119	2.1	16	14			10	Aromatics	C2-Phenanthrene	Yes
210	211.112	211.113	1.4	15	14	1		9	Oxygenated aromatics	C2-Benzophenone	Yes
216	217.101	217.105	3.9	17	12			12	Aromatics	Benzo(b)fluorene/Benzo[a]fluorene	Yes
218	219.117	219.114	-3.1	17	14			11	Aromatics		Yes
220	221.133	221.133	0.9	17	16			10	Aromatics	C3-Phenanthrene	Yes
224	225.127	225.127	0.6	16	16	1		9	Oxygenated aromatics	C3-Benzophenone	Yes
228	229.101	229.106	4.6	18	12			13	Aromatics	Benz[a]anthracene	Yes
230	231.117	231.12	2.6	18	14			12	Aromatics		Yes
234	235.148	235.149	0.7	18	18			10	Aromatics	Retene	Yes

MW	Exact m/z	Measured m/z	$\Delta m/z \times 10^3 a$	С	Н	0	N	RDBE ^b	Group	Species	GCxGC-ToF- MS detected ^c
244	245.133	245.135	1.9	19	16			12	Aromatics	Benzylbiphenyl	Yes
246	247.112	247.116	4.3	18	14	1		12	Oxygenated aromatics		Yes
248	249.164	249.159	-4.6	19	20			10	Aromatics	C1-Retene	Yes
256	257.132	257.129	-2.6	20	16			13	Aromatics		Yes

^{a)} The difference between the measured and exact m/z values.

^{b)} Ring double-bond equivalent.

^{c)} GCxGC-ToF-MS: A LECO Pegasus 4D GCxGC-ToF-MS (LECO Instrument GmbH., Germany) was used to analyze the organic compounds collected on quartz filter.

Exp.	Batch#	NMOC	I/SVOCs	Aliphatics	Aromatics	Oxygenated aromatics	Alcohols	Acids	Carbonyls	N-containing VOC
	One cycle 1	128.2	18.0	15.6	29.3	7.9	4.0	8.1	21.1	42.3
	One cycle 2	99.0	9.7	8.0	16.5	4.1	2.7	5.6	15.4	46.7
	Batch 1	94.2	12.6	2.4	14.0	5.8	2.7	6.2	13.8	49.5
	Batch 2	57.7	2.3	1.2	12.8	0.9	3.0	2.7	10.7	26.3
AC1 ^a	Batch 3	39.1	1.3	1.2	13.0	0.5	1.9	2.2	4.7	15.8
	Batch 4	135.3	5.6	3.1	36.8	2.3	8.3	5.0	15.6	64.3
	Batch 5	140.8	6.2	3.8	42.7	2.2	6.3	6.2	12.2	67.4
	Batch 6	108.1	3.3	3.7	45.1	2.2	3.3	5.8	8.7	39.2
	Batch 7	94.3	3.1	9.1	23.1	6.5	2.6	10.2	20.5	22.2
1	One cycle	<i>113.6</i> ±20.7	13.8±5.9	11.8±5.4	22.9±9.0	6.0±2.7	3.4±0.9	6.9±1.7	18.2±4.0	44.5±3.1
Average	Consecutive	95.7±37.4	4.9±3.8	3.5±2.7	26.8±14.4	2.9±2.3	4.0±2.3	5.5±2.7	12.3±5.1	40.7±20.5
	One cycle 1	101.9	17.2	7.2	8.8	21.0	2.7	37.2	13.5	11.5
AC2 ^a	One cycle 2	162.8	11.0	10.9	12.0	18.9	0.0	36.5	21.8	62.7
	One cycle 3	122.3	5.4	8.8	10.8	8.5	1.4	18.9	18.0	55.8
Average	One cycle	129.0±31.0	11.2±5.9	9.0±1.9	10.5±1.6	<i>16.1</i> ± <i>6</i> .7	1.4±1.4	30.9±10.3	17.8±4.2	43.3±27.8
	One cycle 1	3,894.8	1,284.8	765.2	1,304.1	1,087.1	14.2	117.7	264.5	341.9
	One cycle 2	3,050.7	1,035.9	506.1	938.3	970.2	7.8	92.6	215.8	319.8
	Batch 1	3,083.1	999.5	632.2	1,004.4	888.6	13.2	63.3	284.3	197.3
BC1	Batch 2	3,141.7	1,061.8	444.1	935.2	897.4	18.4	136.2	393.5	317.1
	Batch 3	1,319.7	459.2	100.2	380.9	325.7	6.5	75.0	152.2	279.1
	Batch 4	2,620.2	816.9	359.3	724.5	790.5	8.9	65.7	285.3	385.9
	Batch 5	3,557.9	1,208.7	523.5	1,096.9	1,158.7	12.9	83.2	329.1	353.7

Table S4. Batchwise emission factors for NMOC (mg/kg).

Exp.	Batch#	NMOC	I/SVOCs	Aliphatics	Aromatics	Oxygenated aromatics	Alcohols	Acids	Carbonyls	N-containing VOC
	Batch 6	4,301.3	1,495.1	561.2	1,315.9	1,371.3	9.2	95.3	349.0	599.5
Auguaga	One cycle	3,472.7±596.9	1,160.4±176.0	635.7±183.2	1,121.2±258.7	1,028.7±82.7	11.0±4.5	105.1±17.7	240.2±34.4	330.9±15.6
Average	Consecutive	<i>3,004.0</i> ±999.9	1,006.9±351.6	436.7±190.0	909.6±323.6	905.4±355.2	11.5±4.2	86.4±27.1	298.9±82.8	355.4±136.2
DCap	One cycle 1	4,089.8	1,468.8	619.4	1,413.4	1,285.6	15.7	102.9	353.8	299.1
DC2~	One cycle 2	3,404.9	1,111.3	536.6	1,232.7	1,051.0	9.1	66.6	231.4	277.5
Average	One cycle	3,747.3±484.3	1,290.0±252.8	578.0±58.5	<i>1,323.0</i> ± <i>127.7</i>	1,168.3±165.9	12.4±4.7	84.8±25.6	292.6±86.6	288.3±15.3
	One cycle 1	4,154.2	1,523.3	739.4	1,342.7	1,460.3	11.9	133.0	287.3	179.7
DC2	One cycle 2	4,133.7	1,539.7	691.2	1,475.4	1,365.6	9.7	143.8	222.7	225.3
DCJ	One cycle 3	4,411.0	1,879.1	556.9	1,560.0	1,582.9	11.4	142.8	233.2	323.6
	One cycle 4	4,533.0	1,505.1	596.5	1,328.9	1,555.4	19.0	120.0	305.7	607.3
Average	One cycle	<i>4,308.0</i> ± <i>196.0</i>	1,611.8±178.8	646.0±84.0	1,426.8±110.7	1,491.1±98.8	13.0±4.1	134.9±11.1	262.2±40.5	334.0±191.8

a) Difficulties with sustaining the flame post coal addition have been observed during experiments with both anthracite coals. Therefore, *EF*s of complete combustion cycles of both anthracite coals are used.

b) Coal stoking measurements of BC2 were interrupted due to failure of the PTR-ToF-MS between measurements.

		Α	C1	Α	C2	B	C1	B	C 2	BC	C 3
MW	Species	EFs	%	EFs	%	EFs	%	EFs	%	EFs	%
17	Ammonia	27.5		22.1		282.3		147.2		31.9	
27	HCN	13.1	11.6%	0.0	0.0%	88.9	3.0%	69.1	1.8%	108.6	2.5%
30	Formaldehyde	10.7	9.4%	10.2	7.9%	133.8	4.5%	123.9	3.3%	91.5	2.1%
32	Methanol	3.4	3.0%	1.4	1.1%	11.5	0.4%	12.4	0.3%	13.0	0.3%
41	Acetonitrile	0.5	0.5%	1.0	0.8%	15.6	0.5%	18.7	0.5%	13.6	0.3%
42	C3H6	4.8	4.2%	5.7	4.4%	143.5	4.8%	172.1	4.6%	188.4	4.4%
43	HNCO	22.4	19.7%	40.0	31.0%	217.5	7.2%	179.8	4.8%	198.5	4.6%
44	Acetaldehyde	4.2	3.7%	3.1	2.4%	49.6	1.7%	40.4	1.1%	41.1	1.0%
46	Formic acid	3.5	3.1%	3.2	2.4%	16.0	0.5%	7.0	0.2%	17.2	0.4%
52	C4H4					3.9	0.1%	5.9	0.2%	4.9	0.1%
54	C4H6					46.4	1.5%	54.3	1.4%	54.1	1.3%
56	C3H4O	0.5	0.4%	2.0	1.5%	30.2	1.0%	24.1	0.6%	24.4	0.6%
56	C4H8	3.4	3.0%	1.4	1.1%	89.4	3.0%	116.3	3.1%	126.1	2.9%
58	Acetone	2.7	2.4%	1.9	1.5%	37.5	1.2%	43.9	1.2%	46.1	1.1%
60	Acetic acid	3.1	2.7%	19.9	15.4%	62.4	2.1%	69.0	1.8%	103.4	2.4%
61	CH3NO2	8.5	7.5%	2.4	1.8%	33.4	1.1%	20.7	0.6%	13.4	0.3%
66	C5H6	0.0	0.0%	0.0	0.0%	19.2	0.6%	27.8	0.7%	26.5	0.6%
68	C5H8	1.6	1.4%	0.0	0.0%	32.8	1.1%	50.5	1.3%	60.7	1.4%
70	C4H6O			0.3	0.2%	17.0	0.6%	13.9	0.4%	13.8	0.3%
70	C5H10			0.3	0.2%	28.2	0.9%	34.8	0.9%	39.0	0.9%
72	C4H8O	0.1	0.1%	0.0	0.0%	10.5	0.3%	18.0	0.5%	17.0	0.4%
74	C3H6O2	0.2	0.2%	7.5	5.8%	5.7	0.2%	5.8	0.2%	10.0	0.2%

Table S5. *EF*s for NMOC species (mg/kg) and the proportion of total NMOC.

		A	C1	A	C2	BO	C1	B	C 2	BC	C 3
MW	Species	EFs	%	EFs	%	EFs	%	EFs	%	EFs	%
78	Benzene	2.0	1.7%	4.8	3.7%	110.0	3.7%	156.0	4.2%	94.3	2.2%
80	C6H8	0.1	0.1%	0.4	0.3%	13.8	0.5%	27.2	0.7%	32.0	0.7%
82	C6H10	1.5	1.3%	0.4	0.3%	15.0	0.5%	29.6	0.8%	37.5	0.9%
84	C5H8O			0.3	0.2%	10.8	0.4%	13.5	0.4%	14.5	0.3%
84	C6H12					18.0	0.6%	22.6	0.6%	24.1	0.6%
88	C4H8O2	0.0	0.0%	0.3	0.2%	2.3	0.1%	2.9	0.1%	4.3	0.1%
92	Toluene	0.8	0.7%	1.3	1.0%	70.0	2.3%	110.1	2.9%	106.0	2.5%
94	C6H6O	0.9	0.8%	3.6	2.8%	116.0	3.9%	146.4	3.9%	161.1	3.7%
96	C7H12	0.5	0.4%	0.4	0.3%	14.3	0.5%	19.8	0.5%	27.6	0.6%
102	C8H6					5.8	0.2%	8.3	0.2%	11.1	0.3%
104	C8H8	8.5	7.5%			25.4	0.8%	33.2	0.9%	35.2	0.8%
106	C7H6O			0.8	0.6%	19.6	0.7%	20.2	0.5%	19.6	0.5%
106	Xylene	0.4	0.4%	0.3	0.2%	52.0	1.7%	91.6	2.4%	106.0	2.5%
108	C7H8O	0.8	0.7%	2.9	2.3%	146.1	4.9%	198.9	5.3%	268.4	6.2%
110	C6H6O2			2.6	2.0%	25.1	0.8%	24.2	0.6%	43.6	1.0%
110	C7H10O					9.5	0.3%	14.7	0.4%	13.9	0.3%
110	C8H14			0.4	0.3%	6.4	0.2%	8.8	0.2%	14.0	0.3%
116	C9H8			0.1	0.1%	17.8	0.6%	26.3	0.7%	27.8	0.6%
118	C8H6O					8.2	0.3%	11.7	0.3%	8.4	0.2%
118	C9H10					14.9	0.5%	24.3	0.6%	27.5	0.6%
120	C8H8O	0.3	0.3%	0.5	0.4%	22.3	0.7%	25.1	0.7%	30.3	0.7%
120	C9H12	0.1	0.1%		0.0%	28.2	0.9%	65.9	1.8%	86.2	2.0%
122	C8H10O	1.4	1.2%	1.8	1.4%	115.4	3.8%	154.1	4.1%	219.7	5.1%

		A	AC1		AC2		BC1		BC2		BC3	
MW	Species	EFs	%	EFs	%	EF s	%	EFs	%	EFs	%	
124	C7H8O2			1.4	1.1%	22.0	0.7%	27.1	0.7%	51.0	1.2%	
128	C10H8	0.3	0.2%			40.7	1.4%	62.3	1.7%	59.5	1.4%	
130	C9H6O					5.4	0.2%	6.1	0.2%	4.8	0.1%	
130	C10H10			0.1	0.1%	17.5	0.6%	28.5	0.8%	30.8	0.7%	
132	C9H8O			0.3	0.2%	18.9	0.6%	25.7	0.7%	26.6	0.6%	
132	C10H12					11.2	0.4%	18.4	0.5%	23.9	0.6%	
134	C9H10O	0.3	0.3%	0.6	0.5%	15.5	0.5%	29.9	0.8%	41.6	1.0%	
134	C10H14	0.3	0.3%			15.5	0.5%	29.9	0.8%	41.6	1.0%	
136	C8H8O2	0.1	0.1%			20.3	0.7%	17.2	0.5%	17.1	0.4%	
136	C9H12O	0.9	0.8%	0.2	0.2%	34.9	1.2%	56.4	1.5%	93.3	2.2%	
142	C11H10	0.2	0.2%			38.2	1.3%	66.3	1.8%	77.7	1.8%	
144	C10H8O					22.7	0.8%	23.4	0.6%	23.0	0.5%	
144	C11H12			0.2	0.2%	14.7	0.5%	24.6	0.7%	28.5	0.7%	
146	C10H10O			0.4	0.3%	37.5	1.2%	50.2	1.3%	59.2	1.4%	
148	C10H12O	0.5	0.4%	0.4	0.3%	15.3	0.5%	20.2	0.5%	32.0	0.7%	
152	C12H8	7.4	6.5%	1.6	1.2%	19.4	0.6%	25.4	0.7%	40.9	0.9%	
154	C12H10			0.3	0.2%	14.0	0.5%	20.2	0.5%	31.3	0.7%	
156	C12H12	1.0	0.9%	0.4	0.3%	42.9	1.4%	75.2	2.0%	86.5	2.0%	
158	C11H10O					40.0	1.3%	47.6	1.3%	49.6	1.2%	
160	C11H12O	0.0	0.0%			31.0	1.0%	41.8	1.1%	54.2	1.3%	
166	C13H10	0.4	0.4%	0.1	0.1%	20.4	0.7%	24.5	0.7%	33.8	0.8%	
168	C13H12					27.7	0.9%	36.1	1.0%	43.3	1.0%	
170	C13H14	0.8	0.7%	0.9	0.7%	41.4	1.4%	62.4	1.7%	71.3	1.7%	

		A	C1	A	C2	BC	C1	BC	22	BC	3
MW	Species	EFs	%	EFs	%	EFs	%	EFs	%	EFs	%
172	C12H12O	0.0	0.0%			30.3	1.0%	37.0	1.0%	41.1	1.0%
174	C12H14O					23.4	0.8%	30.4	0.8%	45.3	1.1%
178	C14H10	0.5	0.4%	0.1	0.0%	28.4	0.9%	30.9	0.8%	44.2	1.0%
180	C14H12			0.2	0.1%	27.1	0.9%	29.5	0.8%	38.6	0.9%
182	C13H10O	0.3	0.3%	0.1	0.1%	36.7	1.2%	45.9	1.2%	53.5	1.2%
184	C14H16			0.4	0.3%	35.0	1.2%	43.1	1.1%	51.6	1.2%
192	C15H12	0.2	0.1%			27.5	0.9%	28.8	0.8%	33.4	0.8%
194	C15H14					24.8	0.8%	28.1	0.8%	32.6	0.8%
196	C14H12O	0.4	0.3%	0.3	0.2%	40.3	1.3%	47.6	1.3%	51.5	1.2%
206	C16H14					22.8	0.8%	24.8	0.7%	25.6	0.6%
210	C15H14O					30.7	1.0%	36.6	1.0%	41.3	1.0%
216	C17H12					19.9	0.7%	26.9	0.7%	27.4	0.6%
218	C17H14					4.8	0.2%	23.7	0.6%	24.1	0.6%
220	C17H16					18.5	0.6%	20.6	0.6%	19.4	0.5%
224	C16H16O					20.9	0.7%	25.0	0.7%	31.3	0.7%
228	C18H12					15.0	0.5%	17.8	0.5%	22.4	0.5%
230	C18H14					17.5	0.6%	24.1	0.6%	23.4	0.5%
234	C18H18					5.3	0.2%	5.6	0.1%	4.9	0.1%
244	C19H16					11.9	0.4%	15.8	0.4%	17.1	0.4%
246	C18H14O					14.7	0.5%	18.6	0.5%	17.6	0.4%
248	C19H20					12.0	0.4%	12.7	0.3%	1.1	0.0%
256	C20H16					9.1	0.3%	10.6	0.3%	14.5	0.3%
	NMOCs	113.6		129.0		3004.0		3747.3		4308.0	

Coal	Benzene	Toluene	References		
Ningxia AC1	2.0	0.8	This study		
Guizhou AC2	4.8	1.3	This study		
Honeycomb	Approximately	Approximately	Tsai et al. 2003 ¹		
Briquette	7.4	3.7	Tsai et al. 2003 ¹		
Anthracite and bituminous coal	21.5	7.4	Wang et al. 2013 ²		
Shenmu BC1	110	70	This study		
Neimeng BC2	156	110	This study		
Unknown BC3	94	106	This study		
Washed coal	440	67.5	Tsai et al. 2003 ¹		
Pulverized coal	Approximately 25.8-1,050	Approximately 7.2-161	Tsai et al. 2003 ¹		
Bituminous coal (flaming and smoldering stage)	58.2-622.2	30.5-551.7	Liu et al. 2017 ³		
Bituminous coal (flaming and smoldering stage)	71-724	47-849	Liu et al. 2015 ⁴		

Table S6. The comparison of benzene and toluene EFs with values from other studies (mg/kg).

Provinces	Residential coal consumption (kt) ⁵	NMOCs (kt)	I/SVOC (kt)
Beijing	2,730	5.6	2.0
Tianjin	780	2.6	0.9
Hebei	16,960	60.6	21.4
Shanxi	9,310	31.0	10.9
Shandong	6,210	20.7	7.3
Henan	6,670	22.2	7.8
Inner Mongolia	3,090	10.3	3.6
Total	45,750	153.0	53.9

Table S7. Emissions of I/SVOCs in northern China in 2015 (kt).

The emissions of NMOCs and I/SVOCs from residential coal combustion in northern China were calculated by the following equation:

$$E_i = \sum_j E_{i,j} = \sum_j (A_j \times EF_i)$$

where E is the emission level, A is the activity level (the amount of residential coal consumption), and *EF* is the emission factor. Additionally, i, and j are parameters that represent the type of pollutant (NMOCs or I/SVOCs) and province. *EF* data for the NMOCs and I/SVOCs were obtained from the experimental results of this study (**Table S4**). Activity data A (residential coal consumption) for the provinces are presented in **Table S7**.

Commoned	SOA yield used in this	Reported in the		
Compound	study	literature		
acrolein	0.026	0.022-0.035 8,14		
cyclopentene	0.079	0.05-0.092 7		
methacrolein	0.02	0.019-0.194 8,14		
benzene	0.33	0.28-0.37 9		
toluene	0.26	0.08-0.66 9,10		
phenol	0.38	0.13-0.54 8,11		
styrene	0.22	0.04-0.4 6		
benzaldehyde	0.38	0.27-0.49 ⁶		
m-xylene	0.22	0.04-0.4 8,9		
m-/o-cresol	0.38	0.27-0.49 12		
o-benzenediol	0.53	0.39-0.53 12,13		
2,4-/2,6-/3,5-dimethylphenol	0.52	0.13-0.9 12		
2-methoxyphenol	0.4	0.35-0.5 11		
naphthalene	0.36	0.11-0.74 14,15		
1-/2-methylnaphthalene	0.45	0.19-0.71 14		
acenaphthylene	0.03	0.03-0.04 15		
acenaphthene	0.05	0.04-0.05 15		
1,2-dimethylnaphthalene	0.31	0.31 14		
other I/SVOCs (oxygenated)	0.43 ^a			
other I/SVOCs (nonoxygenated)	0.22 ^b			

Table S8. SOA yields used in this study.

a) Average of oxygenated PAHs

b) Average of PAHs

We used the following equation to estimate the SOA formation potential:

SOAFP=
$$\sum EF_i \times Y_i$$

where SOAFP is the SOA formation potential, EFi is the emission factor for species i, and Yi is SOA yield for species i. *EF*i data for the I/SVOC species were obtained in this study (**Table S5**). Yi data for I/SVOC species are provided in **Table S8**.



Figure S1. Measurement range and temporal/chemical resolution of common technologies for the analysis of organic compounds.



Figure S2. Schematic of the combustion facility and sampling setup.



Figure S3. A photo of the residential coal combustion measurement system.



Figure S4. (a) Averaged mass spectra of anthracite 1 (AC1) and bituminous coal 1 (BC1). Signals of instrument-intrinsic ions, ¹³C isotopes and mass calibrant are omitted. (b) Double-bond equivalent plot against the carbon number for BC1. (c) Double-bond equivalent plot against the carbon number for AC1. The sphere size indicates the absolute intensity of respective peaks.



Figure S5. Comparison between the total NMOCs detected by the PTR-ToF-MS and the portable analyzer with a PID module (JK40). Both series showed quite similar temporal profiles. The difference between NMOCs and NMOCs-PID is attributed to the lower responses towards oxygenated organic compounds when using the portable analyzer (JiShunAn JK40).



12:01 12:51 13:41 14:31 15:21 16:11 17:01 17:51 18:41

7

Local time 5 -N-containing VOC

S24

0

8:41

1

9:31 10:21 11:11

2

3 4







(e) BC3 single cycle combustion



Figure S6. Time-resolved profile of the emission composition of the five coals. (a) BC1 consecutive stoking. (b) AC1 consecutive stoking. (c) AC2 single cycle combustion. (d) BC2 single cycle combustion. (e) BC3 single cycle combustion.

Difficulties with sustaining the flame post coal addition have been observed during experiments with both anthracite coals. The difficulties explain the noisy AC1 profile and why only complete a combustion cycle of AC2 was performed. In terms of BC2, the coal stoking measurements were interrupted due to failure of the PTR-ToF-MS.



Figure S7. Changes in the composition of NMOCs with time. (a) One complete coal combustion cycle. (b) Consecutive stoking coal combustion.



Figure S8. EFs for three bituminous coals.



Figure S9. Estimated emissions of VOC and I/SVOC in northern China (kt). The percentages of bituminous coal in Beijing, Baoding and Hebei Provinces were obtained from the literature. It was assumed that most of the raw coal was bituminous coal, and honeycomb coal was considered anthracite.

REFERENCES

- Tsai, S. M.; Zhang, J. F.; Smith, K. R.; Ma, Y. Q.; Rasmussen, R. A.; Khalil, M. A. K. Characterization of non-methane hydrocarbons emitted from various cookstoves use. *Environ. Sci. Technol.* 2003, 37, 2869-2877.
- Wang, Q.; Geng, C.; Lu, S.; Chen, W.; Shao, M. Emission factors of gaseous carbonaceous species from residential combustion of coal and crop residue briquettes. *Front. Environ. Sci. Eng.* 2013, 7(1), 66–76.
- 3. Liu, C.; Zhang, C.; Mu, Y.; Liu, J.; Zhang, Y. Emission of volatile organic compounds from domestic coal stove with the actual alternation of flaming and smoldering combustion processes. *Environ. Pollut.* **2017**, 221, 385-391.
- Liu, C.; Zhang, C.; Zhang, Y.; Mu, Y. Preliminary study on volatile organic compounds emission from domestic cooking stoves under different coal combustion modes. *Journal of Jilin University (Earth Science Edition)*. 2015, 45, S1, 1508-1509. (in Chinese)
- National Bureau of Statistics of China, China Energy Statistical Yearbook 2016. Beijing, 2017. http://www.stats.gov.cn/tjsj/ndsj/2016/indexch.htm.
- Fang, Z.; Deng, W.; Zhang, Y.; Ding, X.; Tang, M.; Liu, T.; Hu, Q.; et al. Open burning of rice, corn and wheat straws: primary emissions, photochemical aging, and secondary organic aerosol formation. *Atmos. Chem. Phys.* 2017, 17, 14821-14839.
- Keywood, M. D.; Varutbangkul, V.; Bahreini, R.; Flagan, R. C.; Seinfeld, J. H. Secondary organic aerosol formation from the ozonolysis of cycloalkenes and related compounds. *Environ. Sci. Technol.* 2004, 38(15): 4157-4164.
- Chhabra, P. S.; Ng, N. L.; Canagaratna, M. R.; Corrigan, A. L.; Russell, L. M.; Worsnop, D. R.; Flagan, R. C.; Seinfeld, J. H. Elemental composition and oxidation of chamber organic aerosol. *Atmos. Chem. Phys.* 2011, 11, 8827–8845.
- Ng, N. L.; Kroll, J. H.; Chan, A. W. H.; Chhabra, P. S.; Flagan, R. C.; Seinfeld, J. H. Secondary organic aerosol formation from m-xylene, toluene, and benzene. *Atmos. Chem. Phys.* 2007, 7, 3909–3922.
- Hildebrandt, L.; Donahue, N. M.; Pandis, S. N. High formation of secondary organic aerosol from the photo-oxidation of toluene. *Atmos. Chem. Phys.* 2009, 9, 2973–2986.
- Yee, L. D.; Kautzman, K. E.; Loza, C. L.; Schilling, K. A.; Coggon, M. M.; Chhabra, P. S.; Chan, M. N.; Chan, A. W. H.; Hersey, S. P.; Crounse, J. D.; Wennberg, P. O.; Flagan, R. C.; Seinfeld, J. H. Secondary organic aerosol formation from biomass burning intermediates: phenol and methoxyphenols. *Atmos. Chem. Phys.* 2013, 13, 8019–8043.
- Nakao, S.; Clark, C.; Tang, P.; Sato, K.; Cocker III, D. Secondary organic aerosol formation from phenolic compounds in the absence of NOx. *Atmos. Chem. Phys.* 2011, 11, 10649–10660.
- 13. Borras, E.; Tortajada-Genaro, L.A. Secondary organic aerosol formation from the photo-oxidation of benzene, *Atmos. Environ.* **2012**, 47, 154-163.
- 14. Chan, A. W. H.; Kautzman, K. E.; Chhabra, P. S.; Surratt, J. D.; Chan, M. N.;

Crounse, J. D.; Kuerten, A.; Wennberg, P. O.; Flagan, R. C.; Seinfeld, J. H. Secondary organic aerosol formation from photooxidation of naphthalene and alkylnaphthalenes: implications for oxidation of intermediate volatility organic compounds (IVOCs). *Atmos. Chem. Phys.* **2009**, *9*, 3049–3060.

- 15. Shakya, K. M.; Griffin, R. J. Secondary organic aerosol from photooxidation of polycyclic aromatic hydrocarbons. *Environ. Sci. Technol.* **2010**, 44, 8134–8139.
- Zhao, W.; Xu, Q.; Li, L.; Jiang, L.; Zhang, D.; Chen, T. Estimation of air pollutant emissions from coal burning in the semi-rural areas of Beijing Plain. *Res. Environ. Sci.* 2015, 28, 869–876. (in Chinese)
- Zhi, G.R.; Zhang, Y.; Sun, J.; Cheng, M.; Dang, H.; Liu, S.; Yang, J.; Zhang, Y.; Xue, Z.; Li, S.; Meng, F. Village energy survey reveals missing rural raw coal in northern China-Significance in science and policy. *Environ. Pollut.* 2017, 223, 705-712.
- Zhi, G.R.; Yang, J.C.; Tao, Z.; Jian, G.; Du, J.H.; Xue, Z.G.; et al. Rural household coal use survey, emission estimation and policy implications. *Res. Environ. Sci.* 2015, 28, 1179–1185. (in Chinese)