Supplement of

Primary sources and secondary formation of brown carbon in urban Shanghai: Insights from bihourly measurements of brown carbon and organic tracers

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Table S1. Statistics for measured $PM_{2.5}$ component and organic markers during March to August 2020 at SAES site in Shanghai.

	Spring (March-May)		Summer (June to August)		period-avg	
	Avg	Stdev	Avg	Stdev	Avg	Stdev
			$PM_{2.5}$ and its bulk components (μg/m³)			
$PM_{2.5}$	33.01	20.88	25.96	15.31	29.91	18.96
Cl^{-}	0.48	0.38	0.51	0.53	0.49	0.45
NO^{3-}	7.70	8.42	5.62	6.51	6.78	7.71
SO_4^{2-}	3.82	2.93	4.91	3.22	4.30	3.11
NH^{4+}	3.37	3.24	3.64	2.68	3.49	3.01
K^{+}	0.57	3.73	0.16	0.16	0.39	2.80
TC	4.95	2.71	4.65	2.65	4.81	2.68
BC	0.69	0.66	0.69	0.49	0.69	0.59
BrC	1.47	1.23	1.63	1.17	1.54	1.21
WtC	1.66	1.43	1.87	1.37	1.75	1.40
			Trace Elements (ng/m³)			
K	0.503	0.259	0.265	0.210	0.398	0.266
Ca	0.155	0.136	0.091	0.101	0.127	0.126
Cr	0.002	0.003	0.002	0.003	0.002	0.003
Mn	0.033	0.031	0.024	0.030	0.029	0.031
Fe	0.424	0.318	0.283	0.289	0.362	0.313
Ni	0.003	0.003	0.002	0.002	0.003	0.003
Zn	0.078	0.081	0.057	0.073	0.069	0.078
Se	0.001	0.001	0.001	0.001	0.001	0.001
Ba	0.020	0.013	0.011	0.011	0.016	0.013
Pb	0.015	0.010	0.009	0.010	0.013	0.011
			Organic tracers (ng/m³)			
PAHs	1.76	1.26	1.60	0.94	1.69	1.14

Hopanes	0.57	0.46	0.65	0.40	0.60	0.44
Fatty acids	91.61	69.15	83.35	69.45	87.97	69.38
Saccharides	77.2	48.7	73.5	44.2	75.6	46.8
NACs	1.16	1.60	0.74	0.90	0.97	1.35
Aromatic SOA tracers	8.51	7.90	16.77	13.23	12.14	11.34
Isoprene SOA tracers	21.56	67.26	112.57	161.58	61.62	126.72
α-pinene SOA tracers	8.46	9.36	16.51	15.70	12.00	13.16
β-caryophyllinic acid	0.09	0.11	0.14	0.18	0.11	0.15
Azelaic acid	5.39	5.08	9.81	7.30	7.33	6.53
Total organics	216.1	141.1	314.0	216.5	259.2	184.7
Gas pollutants and meteorological parameters						
SO_2 (ppb)	0.28	0.22	0.68	0.69	0.46	0.53
CO (ppm)	0.52	0.15	0.38	0.14	0.45	0.16
O_3 (ppb)	43.2	20.3	36.2	22.7	40.1	21.7
NO_x (ppb)	23.3	15.2	18.1	7.9	21.0	12.8
WS (m/s)	3.94	2.07	3.63	1.57	3.80	1.87
T (°C)	16.81	6.15	27.57	3.79	21.55	7.49
RH (%)	63.6	21.2	76.8	22.5	69.4	22.7

Table S2. Naming and grouping of the organic markers used in this study.

Naming	Grouping	Possible sources
PAHs	benzo[b+k]fluoranthene, benzo[a]fluoranthene, and benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3-cd]pyrene, benzo[ghi]perylene	Coal combustion (Zhu et al., 2021)
Hopanes	αβ-hopane, αβ-norhopane, αβ-22R-homohopane, αβ-22S-homohopane	Vehicle exhaust (Schauer et al., 1999, 2002)
Fatty acids	nonanoic acid, decanoic acid, undecanoic acid, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, heptadecanoic acid, stearic acid, nonadecanoic acid, eicosanoic acid	Cooking emission (Wang et al., 2017)
Saccharides	levoglucosan, mannosan, galactosan	Biomass burning (Simoneit et al., 1999)
NACs	3-methyl-5-nitrocatechol, 3-nitrophenol, 4-nitrocatechol, 4-nitrophenol	Secondary biomass burning (Wang et al., 2022)
Aromatic SOA tracers	2,3-dihydroxy-4-oxopentanoic acid, phthalic acid	Aromatic SOA (Al-Naiema and Stone, 2017; Kleindienst et al., 2012)
Isoprene SOA tracers	2-methylglyceric acid, 2-methylthreitol and 2-methylerythritol, cis-2-methyl-1,3,4-trihydroxy-1-butane, 3-methyl-2,3,4-trihydroxy-1-butane, trans-2-methyl-1,3,4-trihydroxy-1-butane	Isoprene SOA (Claeys et al., 2004)
α-pinene SOA tracers	pinic acid, pinonic acid, 3-hydroxyglutaric acid, 3-hydroxy-4,4-dimethylglutaric acid, 3-methyl-1,2,3-butanetricarboyxlic acid	α-pinene SOA (Claeys et al., 2007)
β-caryophyllinic acid		β-caryophyllene SOA (Jaoui et al., 2007)
Azelaic acid		Secondary cooking emission (Wang and Yu, 2021)

Table S3. Summary of error estimation diagnostics from bootstrap (BS) and displacement (DISP) for PMF run with 15-factor solution for summer data.

BS Mapping (R≥0.6)	vehicle exhaust	cooking emission	biomass burning	secondary cooking	secondary nitrate and sulfate	isoprene SOA	α-pinene SOA	power plant combustion	tire wear	β-caryophyllene SOA	secondary biomass burning	residual oil combustion	re-suspended road dust	coal combustion	aromatic SOA	Unmapped
vehicle exhaust	**100**	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
cooking emission	0	**100**	0	0	0	0	0	0	0	0	0	0	0	0	0	0
biomass burning	0	0	**95**	4	0	0	0	0	0	0	0	1	0	0	0	0
secondary cooking	0	0	0	**95**	0	0	2	0	0	0	0	3	0	0	0	0
secondary nitrate and sulfate	0	0	0	0	**100**	0	0	0	0	0	0	0	0	0	0	0
isoprene SOA	0	0	0	0	0	**100**	0	0	0	0	0	0	0	0	0	0
α-pinene SOA	0	0	0	0	0	0	**100**	0	0	0	0	0	0	0	0	0
power plant combustion	0	0	0	0	0	0	0	**100**	0	0	0	0	0	0	0	0
tire wear	0	0	0	0	0	0	0	0	**100**	0	0	0	0	0	0	0
β-caryophyllene SOA	0	0	0	0	0	0	0	0	0	**100**	0	0	0	0	0	0
secondary biomass burning	0	0	0	0	0	0	0	0	0	0	**100**	0	0	0	0	0
residual oil combustion	0	0	0	0	0	0	0	0	0	0	0	**100**	0	0	0	0
re-suspended road dust	0	0	0	0	0	0	0	0	0	0	0	0	**100**	0	0	0
coal combustion	0	0	0	0	0	0	0	0	0	0	0	0	0	**100**	0	0
aromatic SOA	0	0	0	0	0	0	0	0	0	0	0	0	0	0	**100**	0
DISP Diagnostics	Error Code:0							Largest Decrease in Q: -16.238								
Factor Swaps dQ_{max}=4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
dQ_{max}=8	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
dQ_{max}=15	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
dQ_{max}=25	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	

Table S4. Summary of error estimation diagnostics from bootstrap (BS) and displacement (DISP) for PMF result with 15-factor solution for spring data.

BS Mapping ($R \geq 0.6$)	vehicle exhaust	secondary nitrate and sulfate	biomass burning	aromatic SOA	α-pinene SOA	β-caryophyllene SOA	isoprene SOA	oxygenated cooking OA	secondary biomass burning	coal combustion	residual oil combustion	power plant combustion	re-suspended road dust	tire wear	cooking emission	Unmapped
vehicle exhaust	**100**	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
secondary nitrate and sulfate	0	**94**	0	0	0	0	0	0	0	0	0	0	6	0	0	0
biomass burning	0	0	**100**	0	0	0	0	0	0	0	0	0	0	0	0	0
aromatic SOA	0	0	0	**100**	0	0	2	0	0	0	0	0	0	0	0	0
α-pinene SOA	0	0	0	0	**100**	0	0	0	0	0	0	0	0	0	0	0
β-caryophyllene SOA	0	0	0	0	0	**100**	0	0	0	0	0	0	0	0	0	0
isoprene SOA	0	0	0	0	0	0	**100**	0	0	0	0	0	0	0	0	0
oxygenated cooking OA	0	0	0	0	0	0	0	**100**	0	0	0	0	0	0	0	0
secondary biomass burning	0	0	0	0	0	0	0	0	**100**	0	0	0	0	0	0	0
coal combustion	0	0	0	0	0	0	0	0	0	**100**	0	0	0	0	0	0
residual oil combustion	0	0	0	0	0	0	0	0	0	0	**100**	0	0	0	0	0
power plant combustion	0	0	0	0	0	0	0	0	0	0	0	**100**	0	0	0	0
re-suspended road dust	0	0	0	0	0	0	0	0	0	0	0	0	**100**	0	0	0
tire wear	0	0	0	0	0	0	0	0	0	0	0	0	0	**100**	0	0
cooking emission	0	0	0	0	0	0	0	0	0	0	0	0	0	0	**100**	0
DISP Diagnostics	Error Code:0							Largest Decrease in Q: -14.451								
Factor Swaps $dQ_{max}=4$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Factor Swaps $dQ_{max}=8$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Factor Swaps $dQ_{max}=15$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
Factor Swaps $dQ_{max}=25$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	

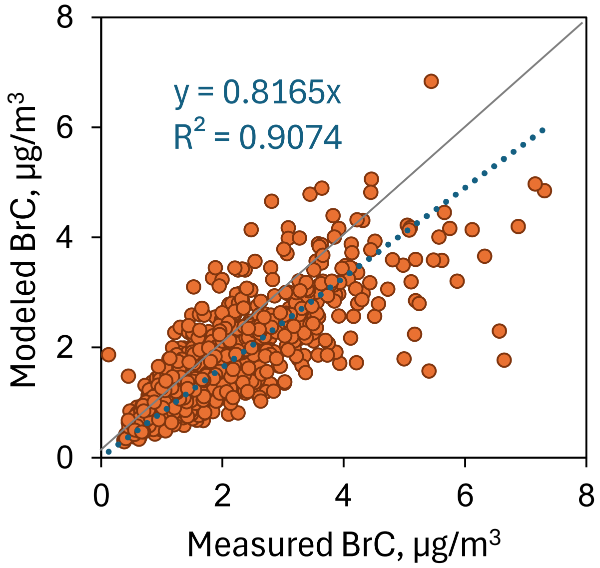

Figure S1. Comparison of PMF predicted versus measured BrC mass.

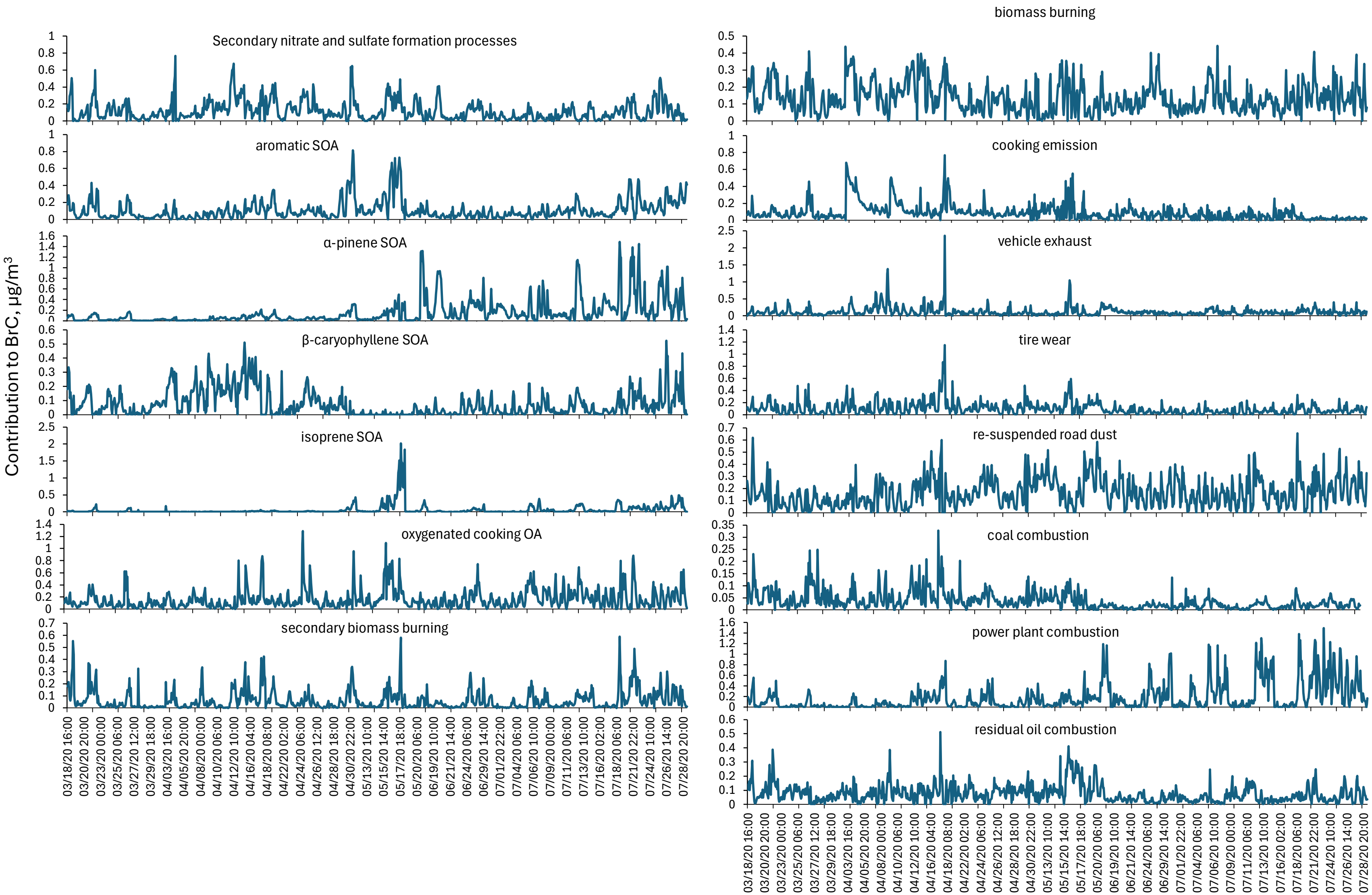

Figure S2. Time series of individual factor contributions to BrC for the 15-factor solution resolved by organic tracer-based PMF model.

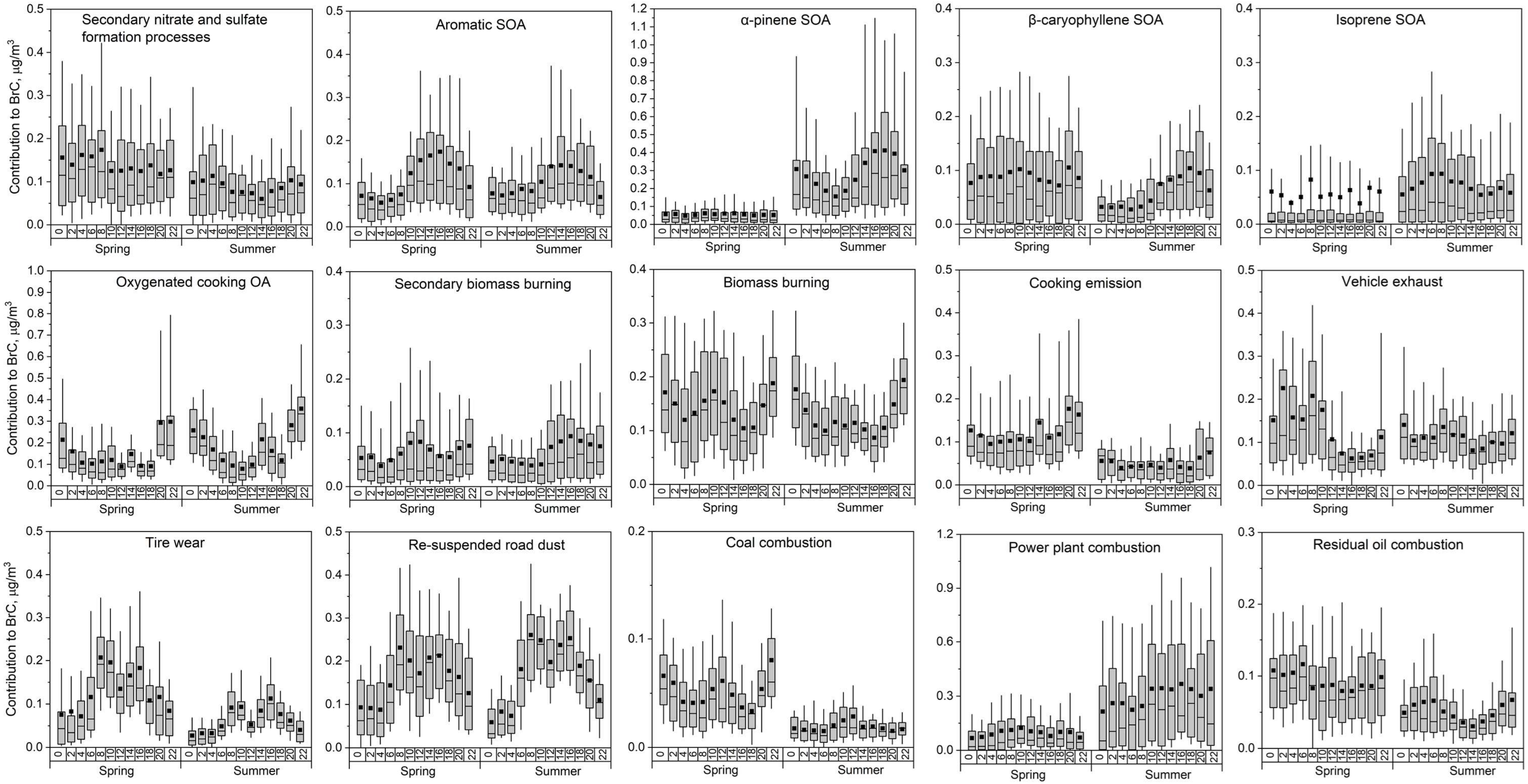

Figure S3. Diurnal variations of individual factor contributions to BrC in spring and summer from PMF results (25th and 75th percentile boxes, 10th and 90th percentile whiskers; the dashed line is the median value, and the solid red line is the mean value).

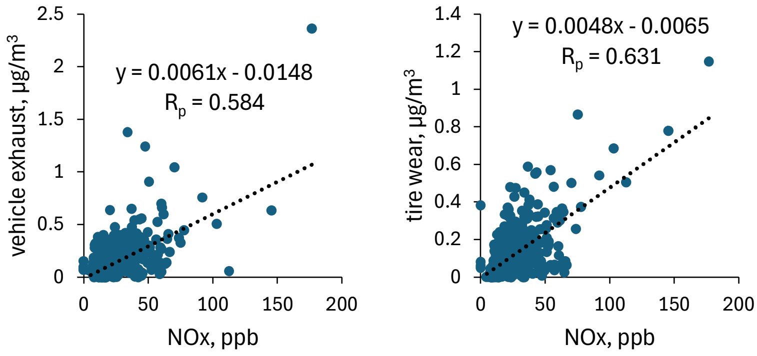

Figure S4. Correlations of the factor contributions of PMF-derived vehicle exhaust and tire wear factors with NO_x.

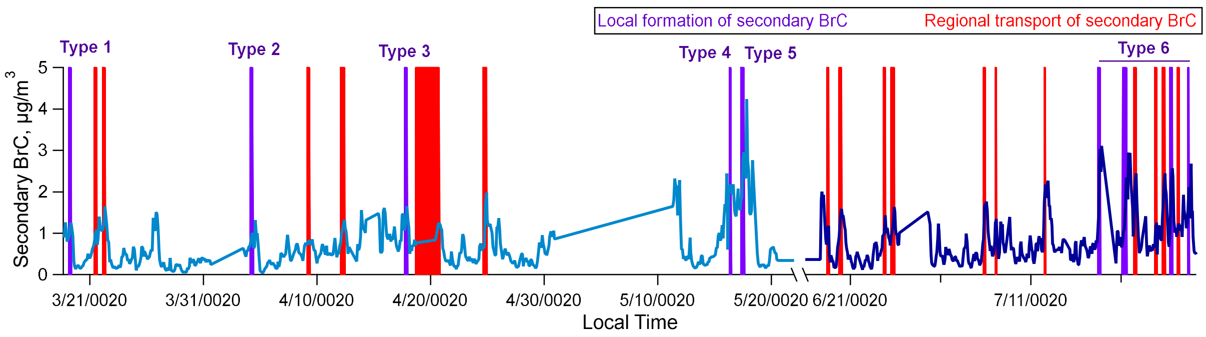

Figure S5. Time series of the total secondary BrC across the campaign period, with identified secondary BrC increment events highlighted in shaded area: local formation events were highlighted in purple and regional transport events were highlighted in red.

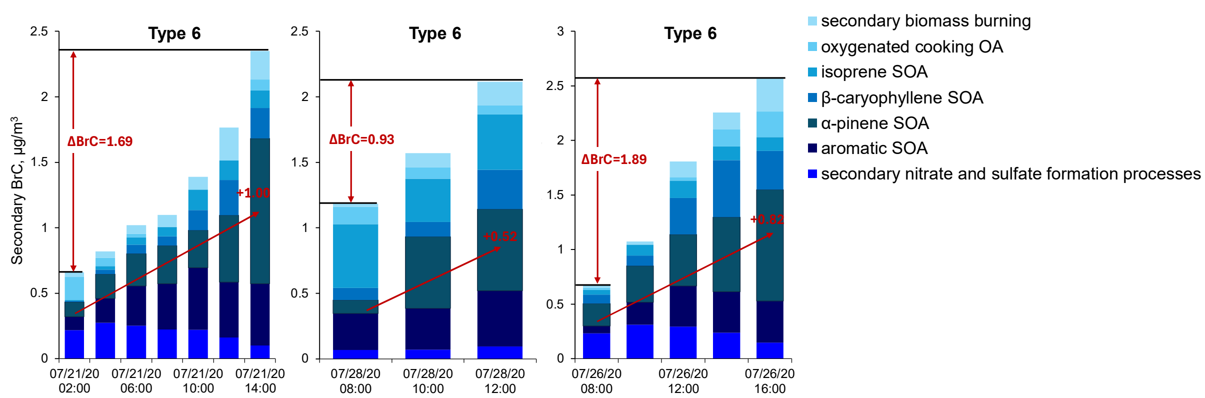

Figure S6. The remaining three cases of type 6 event of secondary BrC increment, driven by α-pinene SOA.

Table S5. Statistical summary of the event of secondary BrC increment across the campaign period.

Season	Date	Duration (h)	Wind speed (m/s)	RH (%)	T (°C)	O_3 (ppb)	NO_x (ppb)	CO (ppm)	Total secondary BrC (μg/m^3)	Type
Spring	3/19/2020 0:00- 3/19/2020 8:00	6	2.12±1.33	77.8 ±10.2	14.3±2.37	25.6±9.3	34.0±14.2	0.61±0.10	1.03±0.18	Type 1
	4/4/2020 2:00- 4/4/2020 8:00	6	1.56±0.45	67±6	12.4±1.15	13.4±13.3	53.3±15.7	0.58±0.03	0.89±0.15	Type 2
	4/17/2020 16:00- 4/17/2020 22:00	6	1.9± 0.92	49.3 ±2.5	19.7 ±2.3	19.8 ±18.7	64.8± 30.5	0.9 ±0.18	1.29±0.27	Type 3
	5/16/2020 6:00- 5/16/2020 10:00	4	1.94± 1.13	92.3± 2.9	23.1 ±0.6	4.47 ±0.71	80.1± 10.9	0.88 ±0.01	2.09 ±0.12	Type 4
	5/17/2020 6:00- 5/17/2020 14:00	8	1.7± 1.91	74.4 ±9.2	27 ±2.8	50.9± 34.6	31.7± 13.5	0.61 ±0.03	2.2± 0.64	Type 5
Summer	7/18/2020 8:00- 7/18/2020 16:00	8	2.59 ±1.24	78.6 ±10.6	30.2 ±2.6	53.9± 40.5	31.3± 18.8	0.49± 0.08	1.77± 0.99	Type 6
	7/21/2020 2:00- 7/21/2020 14:00	12	1.67± 1.06	85.3± 12.2	27.8 ±3.0	49.5 ±37.4	57.9± 8.8	0.46 ±0.06	1.3 ±0.59	
	7/26/2020 8:00- 7/26/2020 16:00	8	2.95 ±1.29	66± 4.9	29.9 ±1.8	91.1 ±32.1	16.8 ±5.10	0.47± 0.05	1.68 ±0.79	
	7/28/2020 8:00- 7/28/2020 12:00	4	1.94 ± 1.13	72.3 ± 10.1	32.2± 2.0	63.5 ± 24.3	17.5± 6.3	0.45 ± 0.03	1.62 ± 0.47	

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