

## Supporting Information for Publication: Oxygenated Aromatic Compounds are Important Precursors of Secondary Organic Aerosol in Biomass Burning Emissions

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### Scaling Factor Calculations

For a few select experiments (Fire001, Fire002, Fire003, Fire004, Fire007, and Fire011), we calculated a scaling factor to correct the raw OA mass concentrations measured by the HR-AMS. Only a few experiments were selected because these were the only experiments where data from the scanning mobility particle sizer (SMPS) was found to be sufficient and not influenced by a second number mode at larger sizes (that prevented complete characterization of the volume concentration and also affected corrections for multiple charges) and synchronization issues between the SMPS and the thermodenuder. The scaling factor is expected to account for losses in the aerodynamic lens, collection efficiency, changes in the relative ionization efficiency, and other potential artifacts associated with the HR-AMS.<sup>1</sup> A mass-based scaling factor was calculated as a ratio of the total non-refractory aerosol mass concentration measured by the HR-AMS (organic+inorganic aerosol) to that estimated from subtracting the black carbon (BC) measured by the single particle soot photometer (SP2) from the mass concentration estimated from the SMPS data. Total aerosol mass concentrations were estimated from the SMPS data by multiplying the volume concentrations by a density of 1.42 g cm<sup>-3</sup> based on the work of Tkacik et al.<sup>2</sup> Figure S.1 shows that the scaling factor for these select experiments varied inversely with the oxidation state of the OA. This is consistent with the finding of Lim et al.<sup>3</sup> who found the scaling factor to be a function of the OA volatility where the scaling factor was lower for less volatile OA and vice versa. The scaling factor versus oxidation state trends were fit and the fit was used to correct the OA mass concentrations in all experiments.

Table S.1: Fuel, oxidant, and variables of interest (see column headings) for the eleven chamber experiments performed during FIREX. Note that the table is split into three sections for visual clarity, keeping the first two columns the same.

Fire ID	Fuel	Oxidant and precursor	Dark period (hr)	Lights on (hr)	OH exposure (molecules-h cm <sup>-3</sup> )	Initial surface area (μm <sup>2</sup> cm <sup>-3</sup> )
3	Ponderosa pine	OH/HONO	0.13	0.85	3.85×10 <sup>6</sup>	197
4	Ponderosa pine	OH/H <sub>2</sub> O <sub>2</sub>	0.34	5.78	7.01×10 <sup>6</sup>	859
7	Lodgepole pine	OH/HONO	0.98	4.28	1.40×10 <sup>7</sup>	735
16	Ponderosa pine - litter	UV	0.08	4.13	1.51×10 <sup>6</sup>	345
22	Douglas-fir - litter	O <sub>3</sub>	2.13	2.82	2.27×10 <sup>5</sup>	269
28	Chaparral (manzanita)	OH/H <sub>2</sub> O <sub>2</sub>	0.03	5.47	7.20×10 <sup>6</sup>	306
37	Ponderosa pine	OH/HONO	0.32	3.25	1.22×10 <sup>7</sup>	413
42	Lodgepole pine	OH/HONO	0.10	4.18	6.38×10 <sup>6</sup>	287
54	Engelmann spruce	OH/H <sub>2</sub> O <sub>2</sub>	0.18	2.35	4.14×10 <sup>6</sup>	117
63	Lodgepole pine	OH/HONO	0.47	2.3	6.28×10 <sup>6</sup>	182
67	Subalpine fir	O <sub>3</sub>	2.18	2.57	3.75×10 <sup>5</sup>	149

Fire ID	Fuel	Initial OA (μg m <sup>-3</sup> )	Final OA (μg m <sup>-3</sup> )	OA Mass Enh. Ratio	Initial O:C Ratio	Final O:C Ratio	O:C Enh. Ratio	Final SOA Mass (μg m <sup>-3</sup> )	Final SOA O:C Ratio
3	Ponderosa pine	34.4	42.9	1.18	0.22	0.26	1.14	8.5	0.403
4	Ponderosa pine	34.2	79.8	2.17	0.22	0.43	1.92	45.6	0.648
7	Lodgepole pine	35.1	74.4	1.82	0.24	0.38	1.60	39.3	0.548
16	Ponderosa pine - litter	20.4	30.1	1.30	0.19	0.27	1.41	9.7	0.476
22	Douglas-fir - litter	24.5	26.2	1.05	0.31	0.31	0.99	1.7	0.251
28	Chaparral (manzanita)	20.5	26.8	1.37	0.18	0.26	1.46	6.3	0.663
37	Ponderosa pine	60.3	102.2	1.54	0.24	0.35	1.45	42.0	0.558
42	Lodgepole pine	27.3	42.2	1.41	0.25	0.32	1.30	14.9	0.498
54	Engelmann spruce	10.0	12.3	1.22	0.26	0.33	1.26	2.3	0.948
63	Lodgepole pine	17.2	25.0	1.34	0.26	0.34	1.29	7.8	0.566
67	Subalpine fir	15.0	15.4	1.28	0.35	0.36	1.07	0.4	0.850

Fire ID	Fuel	Initial NO (ppbv)	Initial NO <sub>2</sub> (ppbv)	Initial O <sub>3</sub> (ppbv)	Initial NMVOC (μg m <sup>-3</sup> )	Initial NMVOC (ppbv)	Initial SOA Precursors (μg m <sup>-3</sup> )	Initial SOA Precursors (ppbv)
3	Ponderosa pine	2453.7	BDL	6.5	418.1	183.1	166.3	42.6
4	Ponderosa pine	28.7	BDL	11.1	491.1	215.1	195.3	50.1
7	Lodgepole pine	40.3	BDL	5.7	420.0	184.7	160.0	41.1
16	Ponderosa pine - litter	15.1	37.6	6.8	330.8	143.9	124.6	32.2
22	Douglas-fir - litter	25.1	0.05	504.9	30.4	14.4	10.1	2.6
28	Chaparral (manzanita)	21.7	20.2	3.2	168.8	78.0	60.0	15.9
37	Ponderosa pine	318.6	166.7	3.4	191.5	82.4	79.9	20.4
42	Lodgepole pine	346.1	204.5	3.5	143.9	66.2	52.2	13.6
54	Engelmann spruce	2.1	8.4	2.6	94.6	39.8	36.1	9.2
63	Lodgepole pine	294.1	249.7	4.0	222.3	102.4	80.6	21.1
67	Subalpine fir	0.04	8.8	436.7	217.5	96.0	84.4	21.4

Table S.2: Emissions ratios of SOA precursors with acetonitrile ( $\text{g g}^{-1}$ ) used to calculate SOA precursor concentrations in the 11 chamber experiments.

<b>Emissions Profile</b>	<b>Based on?</b>	<b>Biogenics</b>	<b>Oxygenated Aromatics</b>	<b>Heterocyclics</b>	<b>Reduced Aromatics</b>	<b>Alkanes + Partially Speciated</b>
Fire003 - this study	Average of Fire 001, 002, 037, 059, 072	12.5	19.3	30.1	15.9	15.2
Fire003 - Sekimoto et al.		9.0	20.9	36.4	19.0	1.5
Fire003 - Koss et al.	All Fires	8.3	15.5	24.8	11.9	15.0
Fire004 - this study	Average of fires 001, 002, 037, 059, 072	12.8	19.3	30.1	15.9	15.2
Fire004 - Sekimoto et al.		9.2	20.9	36.4	19.0	1.5
Fire004 - Koss et al.	All Fires	8.4	15.5	24.8	11.9	15.0
Fire007 - this study	Fire007	8.1	22.7	30.7	18.0	19.7
Fire007 - Sekimoto et al.		7.7	25.2	41.6	17.8	2.0
Fire007 - Koss et al.	All Fires	8.3	15.5	24.8	11.9	19.3
Fire016 - this study	Fire038	3.9	18.0	37.6	9.8	16.8
Fire016 - Sekimoto et al.		7.4	28.0	44.9	17.0	2.2
Fire016 - Koss et al.	All Fires	8.8	15.5	24.8	11.9	15.5
Fire022 - this study	Average of fires 014, 018, 031, 043, 057, 064	0.7	19.4	26.6	15.7	13.4
Fire022 - Sekimoto et al.		0.9	23.8	39.9	18.2	1.8
Fire022 - Koss et al.	All Fires	0.6	15.5	24.8	11.9	3.2
Fire028 - this study	Fire028	4.1	23.5	38.8	23.8	18.1
Fire028 - Sekimoto et al.		8.7	24.8	41.1	17.9	1.9
Fire028 - Koss et al.	All Fires	9.0	15.5	24.8	11.9	18.2
Fire037 - this study	Fire037	14.6	24.4	36.0	19.9	15.6
Fire037 - Sekimoto et al.		9.6	20.4	35.9	19.1	1.5
Fire037 - Koss et al.	All Fires	8.6	15.5	24.8	11.9	15.2
Fire042 - this study	Average of Fires 006, 007, 058, 063	9.3	16.6	25.8	16.6	15.1
Fire042 - Sekimoto et al.		9.5	21.7	37.4	18.8	1.6
Fire042 - Koss et al.	All Fires	8.8	15.5	24.8	11.9	15.1
Fire054 - this study	Fire008	2.0	12.5	17.0	6.6	11.4
Fire054 - Sekimoto et al.		8.6	24.1	40.3	18.1	1.8
Fire054 - Koss et al.	All Fires	8.8	15.5	24.8	11.9	11.4
Fire063 - this study	Fire063	8.6	16.8	28.1	16.7	15.9
Fire063 - Sekimoto et al.		8.9	22.3	38.2	18.6	1.7
Fire063 - Koss et al.	All Fires	8.5	15.5	24.8	11.9	15.8
Fire067 - this study	Fire067	1.2	27.4	39.1	25.7	24.7
Fire067 - Sekimoto et al.		0.9	27.1	43.9	17.2	2.2
Fire067 - Koss et al.	All Fires	0.7	15.5	24.8	11.9	24.3

Table S.3: VOC species measured by the PTR-ToF-MS (Koss et al.<sup>10</sup>) and considered as SOA precursors in our model.

Species name	Species formula	$k_{OH}$ [ $cm^3$ molecules <sup>-1</sup> s <sup>-1</sup> ]	$C_{star}$ [ $\mu g\ m^{-3}$ ]	MW [ $g\ mol^{-1}$ ]	Surrogate
Pyrrrole	C4H5N	$1.45 \times 10^{-10}$	$5.74 \times 10^7$	67.0892	Heterocyclics
Furan	C4H4O	$4.00 \times 10^{-11}$	$2.23 \times 10^9$	68.07356	Heterocyclics
Isoprene	C5H8	$1.00 \times 10^{-10}$	$2.05 \times 10^9$	68.11702	Biogenics
Dihydropyrrole	C4H7N	$1.04 \times 10^{-10}$	$5.15 \times 10^7$	69.10508	Heterocyclics
Tetrahydropyrrole	C4H9N	$7.85 \times 10^{-11}$	$2.44 \times 10^8$	71.12096	Heterocyclics
Benzene	C6H6	$1.22 \times 10^{-12}$	$4.05 \times 10^8$	78.11184	Aromatics
Pyridine	C5H5N	$3.70 \times 10^{-13}$	$5.28 \times 10^7$	79.0999	Heterocyclics
Methylpyrrole	C5H7N	$1.10 \times 10^{-10}$	$5.69 \times 10^7$	81.11578	Heterocyclics
MethylFuran	C5H6O	$7.80 \times 10^{-11}$	$7.71 \times 10^8$	82.10014	Heterocyclics
Thiophene	C4H4S	$9.53 \times 10^{-12}$	$3.64 \times 10^8$	84.13956	Heterocyclics
Furanone	C4H4O2	$5.66 \times 10^{-11}$	$1.34 \times 10^7$	84.07256	Heterocyclics
Ethynylpyrrole	C6H5N	$6.45 \times 10^{-11}$	$3.95 \times 10^6$	92.11854	Heterocyclics
Toluene	C7H8	$5.63 \times 10^{-12}$	$1.42 \times 10^8$	92.13842	Aromatics
2-Furancarbonitrile	C5H3NO	$7.15 \times 10^{-12}$	$1.81 \times 10^5$	93.08302	Heterocyclics
MethylPyridine	C6H7N	$1.10 \times 10^{-12}$	$4.36 \times 10^7$	93.12648	Heterocyclics
Phenol	C6H6O	$2.80 \times 10^{-11}$	$2.11 \times 10^6$	94.11084	Oxygenated Aromatics
4-Pyridinol	C5H5NO	$7.65 \times 10^{-11}$	$1.81 \times 10^5$	95.0989	Heterocyclics
C2-pyrroles	C6H9N	$2.00 \times 10^{-10}$	$4.16 \times 10^6$	95.14236	Heterocyclics
Furfural	C5H4O2	$3.56 \times 10^{-11}$	$1.14 \times 10^7$	96.08326	Heterocyclics
Dimethylfuran	C6H8O	$2.00 \times 10^{-10}$	$1.40 \times 10^7$	96.12672	Heterocyclics
Methylthiophene	C5H6S	$9.51 \times 10^{-12}$	$1.28 \times 10^8$	98.16614	Heterocyclics
2Methanolfuran	C5H6O2	$1.04 \times 10^{-10}$	$3.88 \times 10^6$	98.09914	Heterocyclics
Dihydrofurandione	C4H4O3	$8.56 \times 10^{-13}$	$9.00 \times 10^3$	100.0716	Heterocyclics
Phenylacetylene	C8H6	$8.02 \times 10^{-12}$	$2.16 \times 10^6$	102.1332	Aromatics
Benzonitrile	C7H5N	$3.44 \times 10^{-13}$	$4.62 \times 10^6$	103.1213	Aromatics
Styrene	C8H8	$5.80 \times 10^{-11}$	$3.43 \times 10^7$	104.1491	Aromatics
Vinylpyridine	C7H7N	$2.66 \times 10^{-11}$	$1.55 \times 10^6$	105.1372	Heterocyclics
Benzaldehyde	C7H6O	$1.20 \times 10^{-11}$	$7.30 \times 10^6$	106.1215	Aromatics
C8_Aromatics	C8H10	$1.32 \times 10^{-11}$	$4.88 \times 10^7$	106.165	Aromatics
PyridineAldehyde	C6H5NO	$1.71 \times 10^{-11}$	$7.85 \times 10^4$	107.1096	Heterocyclics
Dimethylpyridine	C7H9N	$2.79 \times 10^{-12}$	$2.05 \times 10^7$	107.1531	Heterocyclics
Benzoquinone	C6H4O2	$4.51 \times 10^{-12}$	$8.80 \times 10^5$	108.094	Aromatics
Cresol	C7H8O	$5.30 \times 10^{-11}$	$1.34 \times 10^7$	108.1374	Oxygenated Aromatics
Trimethylpyrrole	C7H11N	$2.00 \times 10^{-10}$	$1.20 \times 10^7$	109.1689	Heterocyclics
Benzenediol	C6H6O2	$1.04 \times 10^{-10}$	$1.10 \times 10^6$	110.1098	Oxygenated Aromatics
Trimethylfuran	C7H10O	$1.59 \times 10^{-10}$	$9.27 \times 10^7$	110.1533	Heterocyclics
Dihydroxypyridine	C5H5NO2	$4.55 \times 10^{-11}$	$3.78 \times 10^4$	111.0979	Heterocyclics
5-Hydroxy 2-furfural	C5H4O3	$4.90 \times 10^{-11}$	$7.36 \times 10^5$	112.0823	Heterocyclics
Nitrofuran	C4H3NO3	$5.06 \times 10^{-12}$	$1.64 \times 10^4$	113.0703	Heterocyclics
5-hydroxymethyl-	C5H6O3	$1.00 \times 10^{-10}$	$2.59 \times 10^5$	114.0981	Heterocyclics

2[3H]-furanone					
5-hydroxy tetrahydro 2-furfural	C5H8O3	$5.00 \times 10^{-12}$	$7.36 \times 10^5$	116.114	Heterocyclics
Indene	C9H8	$7.80 \times 10^{-11}$	$1.06 \times 10^7$	116.1598	Aromatics
Benzeneacetonitrile	C8H7N	$2.07 \times 10^{-12}$	$5.72 \times 10^5$	117.1479	Aromatics
Benzofuran	C8H6O	$3.70 \times 10^{-11}$	$1.13 \times 10^7$	118.1322	Aromatics
Methylstyrene	C9H10	$5.40 \times 10^{-11}$	$1.14 \times 10^7$	118.1757	Aromatics
Isoindoline	C8H9N	$8.00 \times 10^{-11}$	$6.08 \times 10^5$	119.1638	Heterocyclics
Tolualdehyde	C8H8O	$1.60 \times 10^{-11}$	$2.39 \times 10^6$	120.1481	Aromatics
C9_Aromatics	C9H12	$2.20 \times 10^{-11}$	$1.95 \times 10^7$	120.1916	Aromatics
Salicylaldehyde	C7H6O2	$2.80 \times 10^{-11}$	$3.72 \times 10^6$	122.1205	Aromatics
Dimethylphenol	C8H10O	$5.05 \times 10^{-11}$	$5.31 \times 10^6$	122.164	Oxygenated Aromatics
Nitrobenzene	C6H5NO2	$1.40 \times 10^{-13}$	$1.50 \times 10^6$	123.1086	Aromatics
Hydroxy benzoquinone	C6H4O3	$1.30 \times 10^{-11}$	$4.11 \times 10^5$	124.093	Aromatics
Guaiacol	C7H8O2	$7.53 \times 10^{-11}$	$9.16 \times 10^5$	124.1364	Oxygenated Aromatics
Hydroxymethylfurfur al	C6H6O3	$1.00 \times 10^{-10}$	$4.11 \times 10^5$	126.1088	Heterocyclics
Dihydroxymethylfura n	C6H8O3	$1.29 \times 10^{-10}$	$4.11 \times 10^5$	128.1247	Heterocyclics
Naphthalene	C10H8	$2.30 \times 10^{-11}$	$5.73 \times 10^5$	128.1705	Aromatics
dihydronaphthalene	C10H10	$6.42 \times 10^{-11}$	$5.11 \times 10^6$	130.1864	Aromatics
Methylindole	C9H9N	$2.00 \times 10^{-10}$	$3.64 \times 10^4$	131.1745	Aromatics
Methyl benzofuran	C9H8O	$9.75 \times 10^{-11}$	$3.54 \times 10^6$	132.1588	Heterocyclics
Methyl propenyl benzene	C10H12	$3.30 \times 10^{-11}$	$6.76 \times 10^6$	132.2023	Aromatics
3- methylacetophenone	C9H10O	$2.42 \times 10^{-12}$	$1.60 \times 10^6$	134.1747	Aromatics
C10_Aromatics	C10H14	$9.50 \times 10^{-12}$	$1.04 \times 10^7$	134.2182	Aromatics
Methylbenzoicacid	C8H8O2	$1.20 \times 10^{-11}$	$1.66 \times 10^4$	136.1471	Aromatics
Monoterpenes	C10H16	$1.63 \times 10^{-10}$	$2.16 \times 10^7$	136.234	Biogenics
Nitrotoluene	C7H7NO2	$7.72 \times 10^{-13}$	$5.96 \times 10^5$	137.1352	Aromatics
MethylGuaiacol	C8H10O2	$3.98 \times 10^{-11}$	$5.62 \times 10^5$	138.163	Oxygenated Aromatics
Methylnaphthalene	C11H10	$5.65 \times 10^{-11}$	$5.20 \times 10^5$	142.1971	Aromatics
Product of levoglucosan dehydration (pyrolysis)	C6H8O4	$5.28 \times 10^{-11}$	$3.81 \times 10^4$	144.1237	Alkanes
Naphthol	C10H8O	$2.00 \times 10^{-10}$	$2.71 \times 10^5$	144.1695	Aromatics
Ethylindene	C11H12	$6.36 \times 10^{-11}$	$1.67 \times 10^6$	144.213	Aromatics
Dimethylbenzofuran	C10H10O	$1.20 \times 10^{-10}$	$2.71 \times 10^5$	146.1854	Aromatics
Methylchavicol	C10H12O	$5.43 \times 10^{-11}$	$1.13 \times 10^6$	148.2013	Oxygenated Aromatics
C11_aromatics	C11H16	$5.00 \times 10^{-11}$	$4.81 \times 10^6$	148.2447	Aromatics
VinylGuaiacol	C9H10O2	$5.44 \times 10^{-11}$	$2.28 \times 10^5$	150.1737	Oxygenated

					Aromatics
Vanillin	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	$2.73 \times 10^{-11}$	$7.00 \times 10^5$	152.1461	Oxygenated Aromatics
Acenaphthylene	C <sub>12</sub> H <sub>8</sub>	$7.55 \times 10^{-11}$	$6.18 \times 10^4$	152.1919	Aromatics
Camphor	C <sub>10</sub> H <sub>16</sub> O	$4.30 \times 10^{-12}$	$1.98 \times 10^6$	152.233	Biogenics
Syringol	C <sub>8</sub> H <sub>10</sub> O <sub>3</sub>	$9.66 \times 10^{-11}$	$1.00 \times 10^5$	154.162	Oxygenated Aromatics
Cineole	C <sub>10</sub> H <sub>18</sub> O	$2.26 \times 10^{-11}$	$1.63 \times 10^7$	154.2489	Biogenics
1,3-dimethylnaphthalene	C <sub>12</sub> H <sub>12</sub>	$6.94 \times 10^{-11}$	$8.57 \times 10^4$	156.2237	Aromatics
Decanal	C <sub>10</sub> H <sub>20</sub> O	$3.45 \times 10^{-11}$	$1.27 \times 10^6$	156.2648	Alkanes
C <sub>12</sub> _aromatics	C <sub>12</sub> H <sub>18</sub>	$1.13 \times 10^{-10}$	$1.17 \times 10^6$	162.2713	Aromatics
Isoeugenol	C <sub>10</sub> H <sub>12</sub> O <sub>2</sub>	$8.84 \times 10^{-11}$	$1.94 \times 10^5$	188.2217	Oxygenated Aromatics
C <sub>13</sub> _aromatics	C <sub>13</sub> H <sub>20</sub>	$1.13 \times 10^{-10}$	$7.17 \times 10^5$	176.2979	Aromatics
Sesquiterpenes	C <sub>15</sub> H <sub>24</sub>	$3.00 \times 10^{-10}$	$4.58 \times 10^4$	204.3511	Biogenics
5-Methyl furfural	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	$5.18 \times 10^{-11}$	$1.10 \times 10^6$	110.1098	Heterocyclics

Table S.4: SOM grids, surrogates, and parameters used in this work.

<b>Precursor Class</b>	<b>VOC Surrogate</b>	<b><math>\Delta LVP</math></b>	<b><math>m_{frag}</math></b>	<b><math>p_{10}</math></b>	<b><math>p_{20}</math></b>	<b><math>p_{30}</math></b>	<b><math>p_{40}</math></b>	<b>Reference</b>
Long alkanes	<i>n</i> -dodecane	1.4629	0.2627	0.9657	0.0010	0.0020	0.0314	Loza et al. <sup>4</sup>
Benzene	benzene	1.5495	0.7895	0.0743	0.0213	0.8963	0.0081	Ng et al. <sup>5</sup>
Toluene	toluene	1.4169	1.3064	0.5634	0.3413	0.0016	0.0937	Zhang et al. <sup>6</sup>
C <sub>8+</sub> single-ring aromatics	<i>m</i> -xylene	1.4601	0.0736	0.1418	0.2971	0.4571	0.1040	Ng et al. <sup>5</sup>
Polycyclic aromatic hydrocarbons (PAH)	naphthalene	1.4922	0.7673	0.8138	0.0072	0.0635	0.1155	Zhang et al. <sup>6</sup>
Isoprene	isoprene	1.8742	0.5207	0.9924	0.0003	0.0065	0.0009	Chhabra et al. <sup>7</sup>
Terpene	$\alpha$ -pinene	1.9139	0.1312	0.5991	0.2923	0.1079	0.0007	Chhabra et al. <sup>7</sup>
Oxygenated aromatics	phenol, guaiacol	2.023	0.315	0.109	0.048	0.439	0.404	Yee et al. <sup>8</sup>
Oxygenated aromatics	syringol	1.629	0.148	0.394	0.121	0.071	0.414	Yee et al. <sup>8</sup>
Heterocyclic compounds	2-methylfuran, dimethylfuran	1.459	0.449	0.0005	0.0014	0.998	0.0001	He et al. <sup>9</sup>

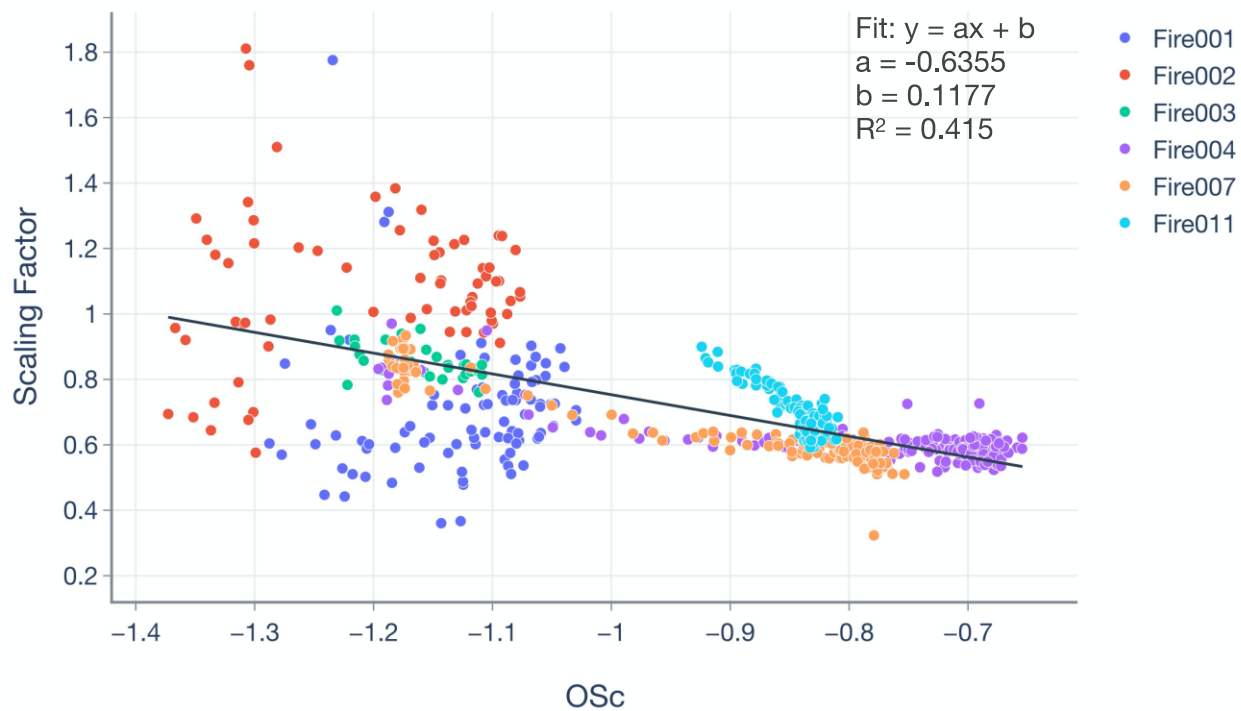


Figure S.1: Scaling factor (SF) as a function of the oxidation state (OSc) for six different experiments. The OSc was approximated as  $2 \times O:C-H:C$ .<sup>11</sup> The relatively larger variability in SF for Fire001 and Fire002 can be attributed to low initial OA mass concentrations in those experiments ( $<4 \mu\text{g m}^{-3}$ ) compared to the rest ( $>20 \mu\text{g m}^{-3}$ ). Gas-phase data were unavailable for Fire001 and Fire002 and hence were not modeled in this study. Fire011 was a nitrate ( $\text{NO}_3$ ) radical experiment performed in the dark and the oxidation results from that experiment will be discussed in a companion paper.



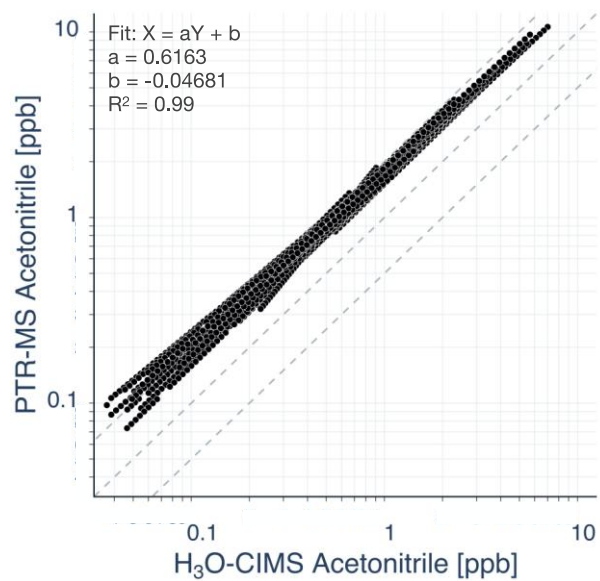


Figure S.2: Scatter plot comparing the acetonitrile concentration measured by the PTR-MS and PTR-ToF-MS in the MIT/UCD mini-chamber over 30 experiments.<sup>2</sup> The slope was used to correct the acetonitrile concentrations in the CSU chamber before being used to determine the initial concentrations of SOA precursors.

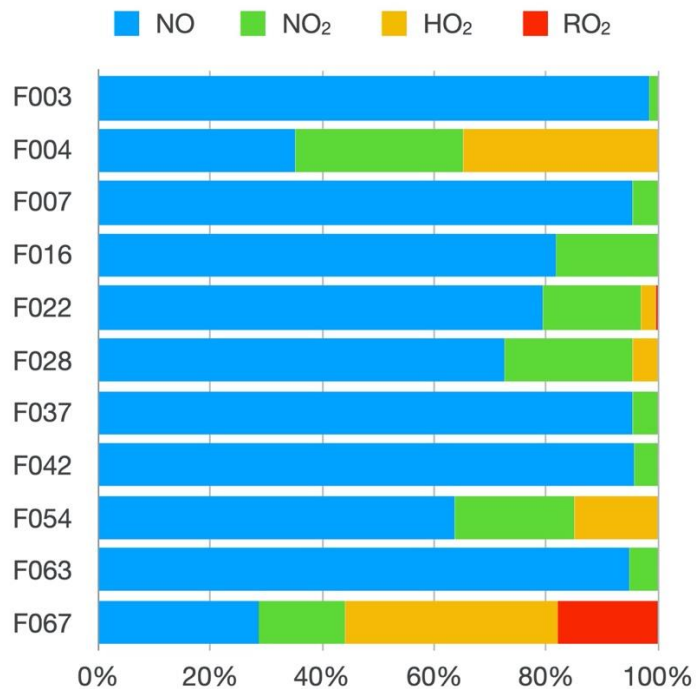


Figure S.3: Averaged fate of the RO<sub>2</sub> radical with reaction with NO, NO<sub>2</sub>, HO<sub>2</sub>, and RO<sub>2</sub>, based on predictions from the Master Chemical Mechanism (MCM) over the entire duration of the chamber experiment.<sup>12</sup> Here, we only calculated the fate of RO<sub>2</sub> radicals with a carbon number larger than or equal to 4.

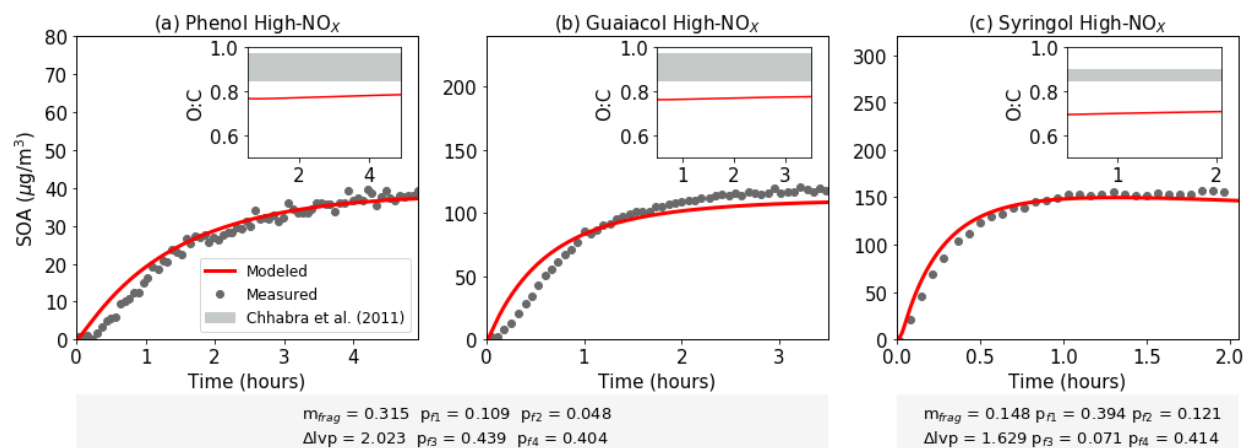


Figure S.4: Model predictions of SOA mass concentrations and O:C ratios for (a) phenol, (b) guaiacol, and (c) syringol compared against measurements from Yee et al.<sup>8</sup> and Chhabra et al.<sup>7</sup>

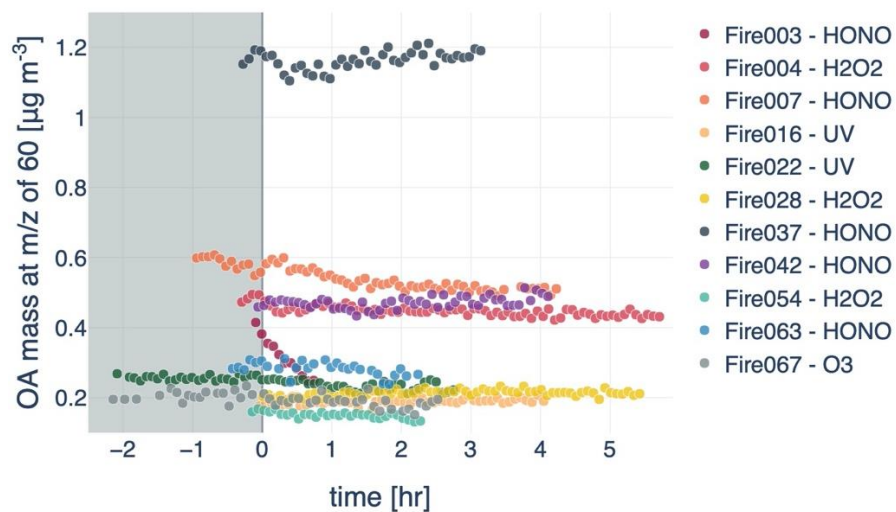


Figure S.5: Particle-wall-loss-corrected OA mass concentrations measured by the HR-AMS at a mass-to-charge ratio of 60.02113 for all eleven chamber experiments. Except for Fire003, the mass was found to be relatively constant during the lights-on period of the experiment, which we concluded as little indication of oxidation of POA.

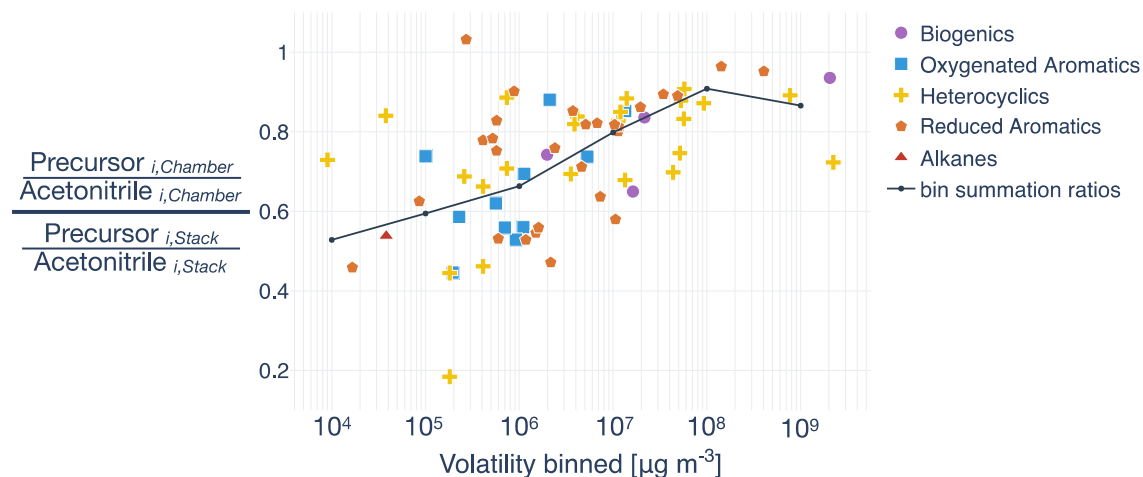


Figure S.6: Emissions ratios of individual SOA precursors to acetonitrile ratioed between those measured in the chamber to those measured in the stack for Fire007. The data are resolved by SOA precursor class. A ratio of 1 indicates no loss in the transfer duct and a ratio of 0 indicates a complete loss in the transfer duct. The time series of these species in the chamber were relatively flat during the dark period indicating that the losses were from those in the transfer duct and not to the walls of the chamber. The solid black line represents the chamber-to-stack ratio if the species were binned by volatility.

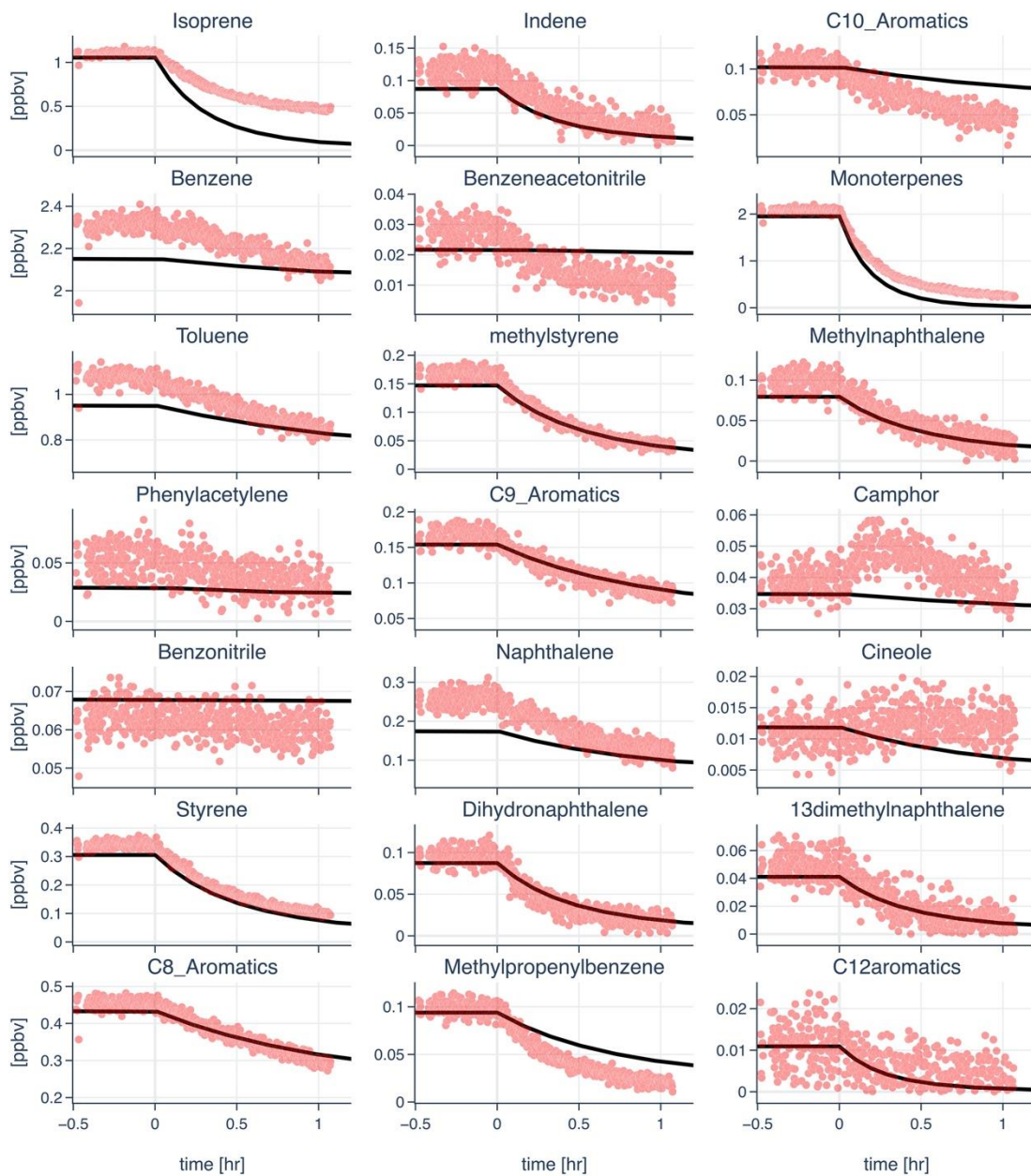


Figure S.7: Modeled (solid black line) and measured (peach circles) decay of reduced hydrocarbons identified by the PTR-ToF-MS for the chamber experiments performed on Fire007.

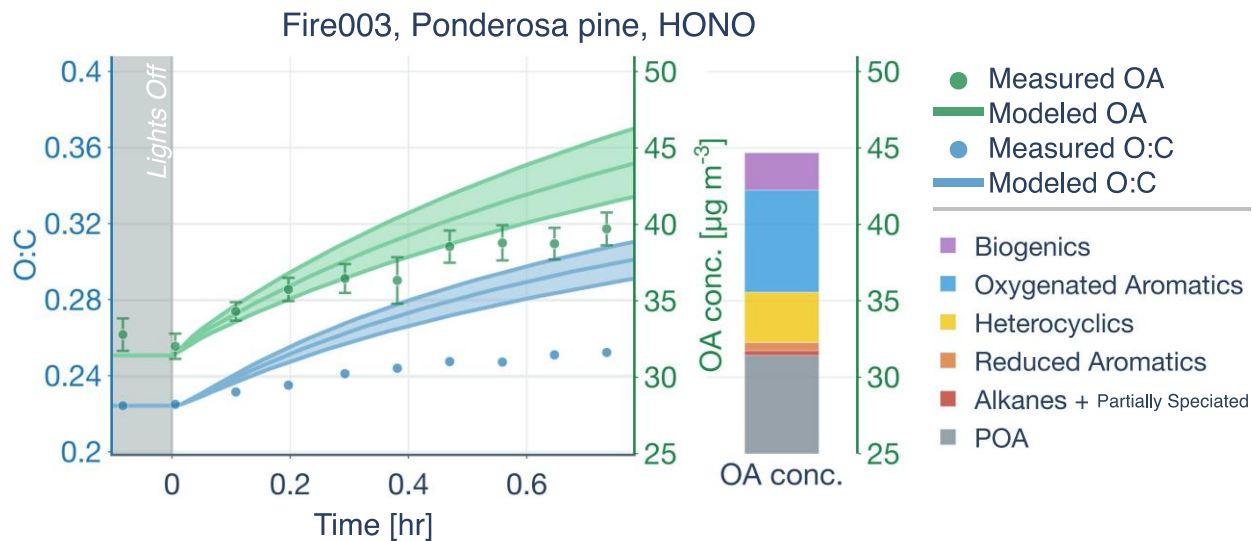


Figure S.8: Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a Ponderosa pine experiment performed at high  $\text{NO}_x$  conditions (Fire003). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.

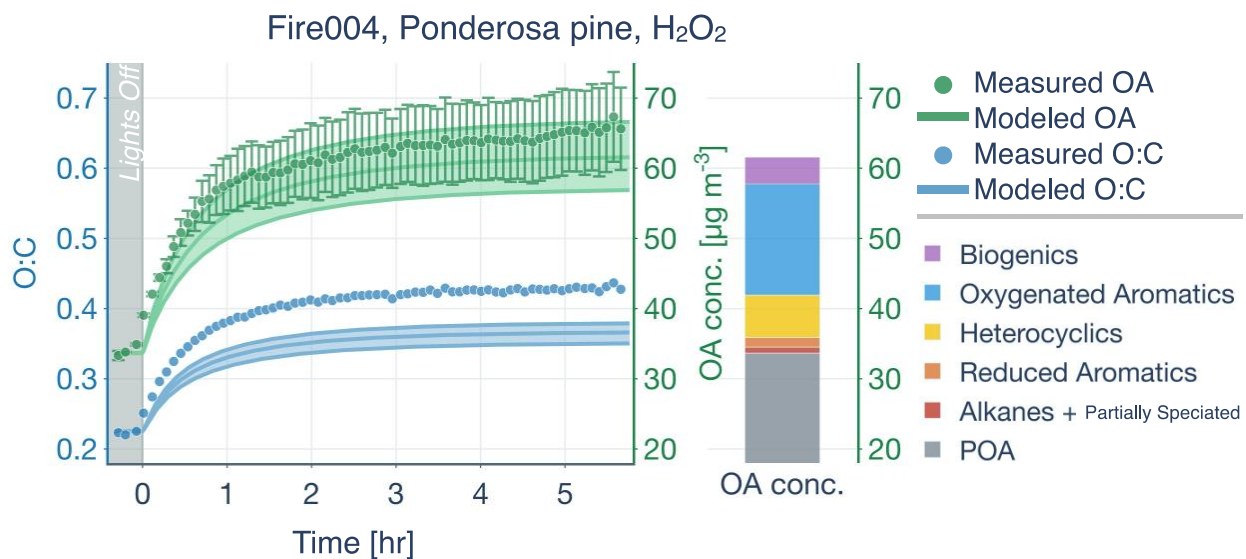


Figure S.9: Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a Ponderosa pine experiment performed at high  $\text{NO}_x$  conditions (Fire004). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.



Fire016, Ponderosa pine - litter, UV

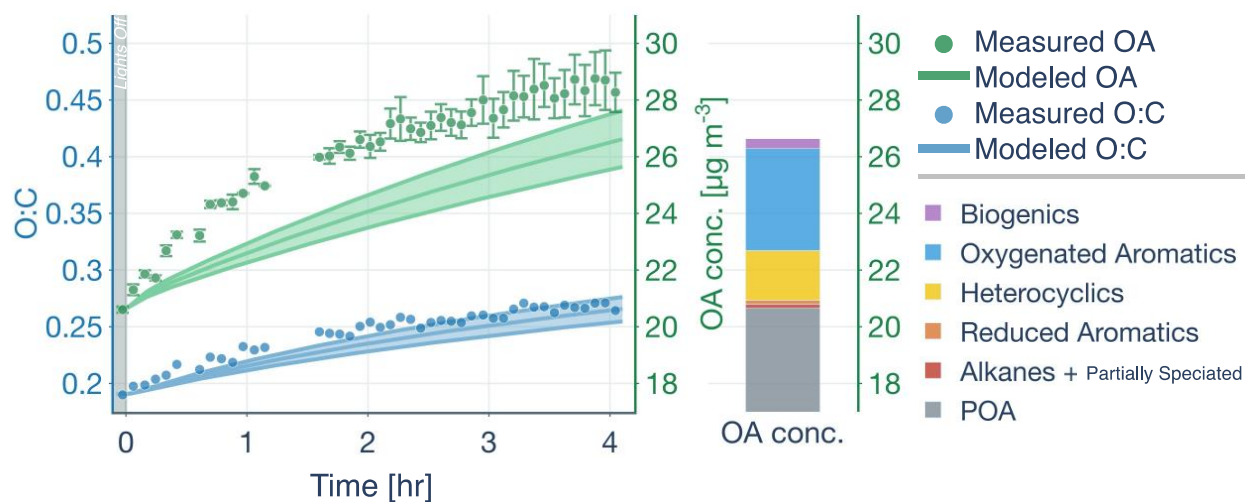


Figure S.10: Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a Ponderosa pine experiment performed without added oxidants (Fire016). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.

Fire022, Douglas-fir - litter, O<sub>3</sub>

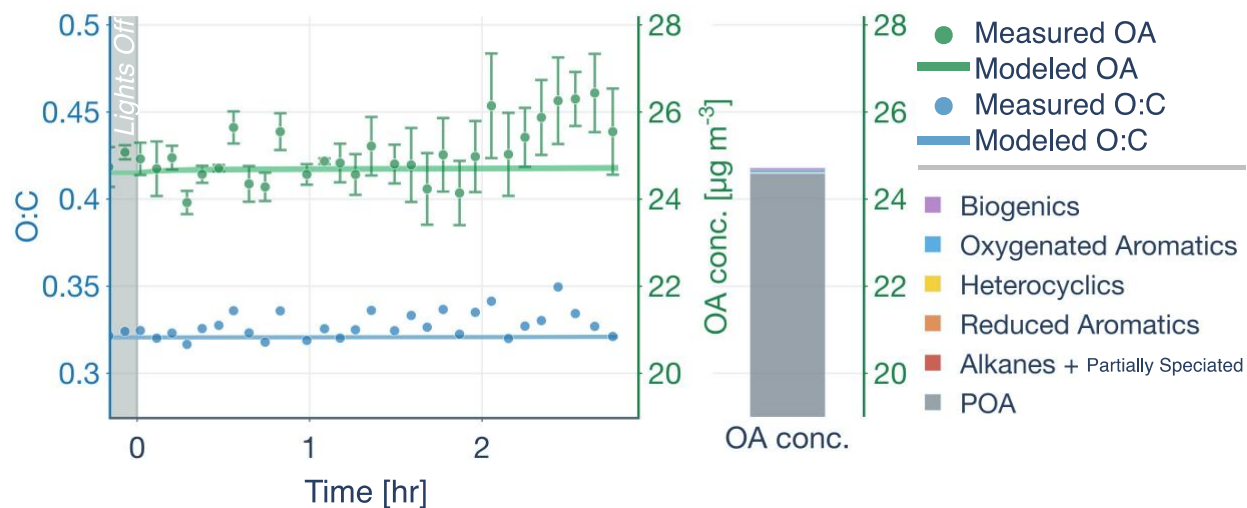


Figure S.11: Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a Douglas fir experiment performed without added oxidants (Fire022). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.

Fire028, Chaparral (manzanita), H<sub>2</sub>O<sub>2</sub>

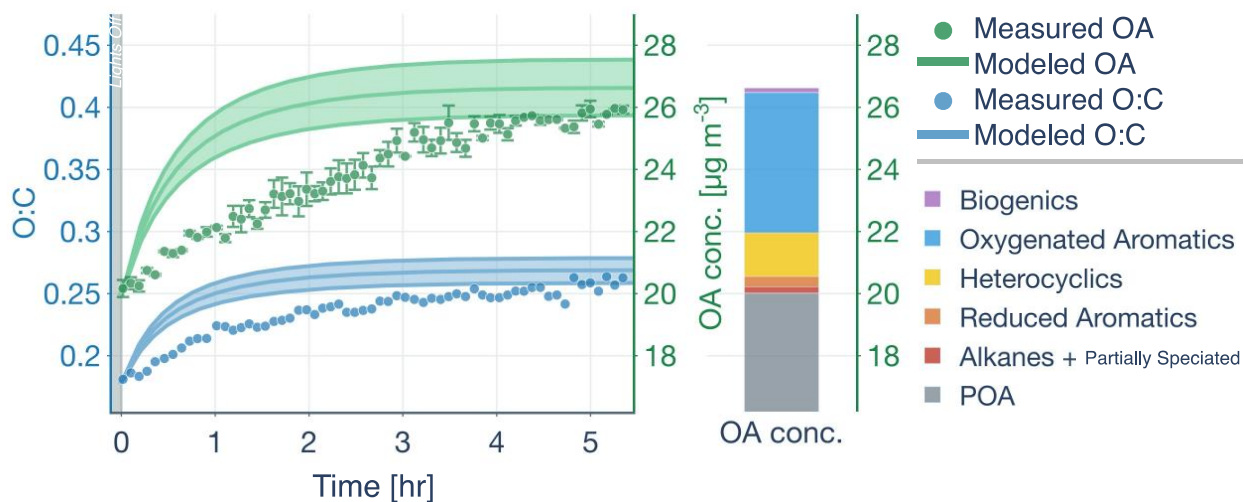


Figure S.12: Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a chaparral (manzanita) experiment performed at high NO<sub>x</sub> conditions (Fire028). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.

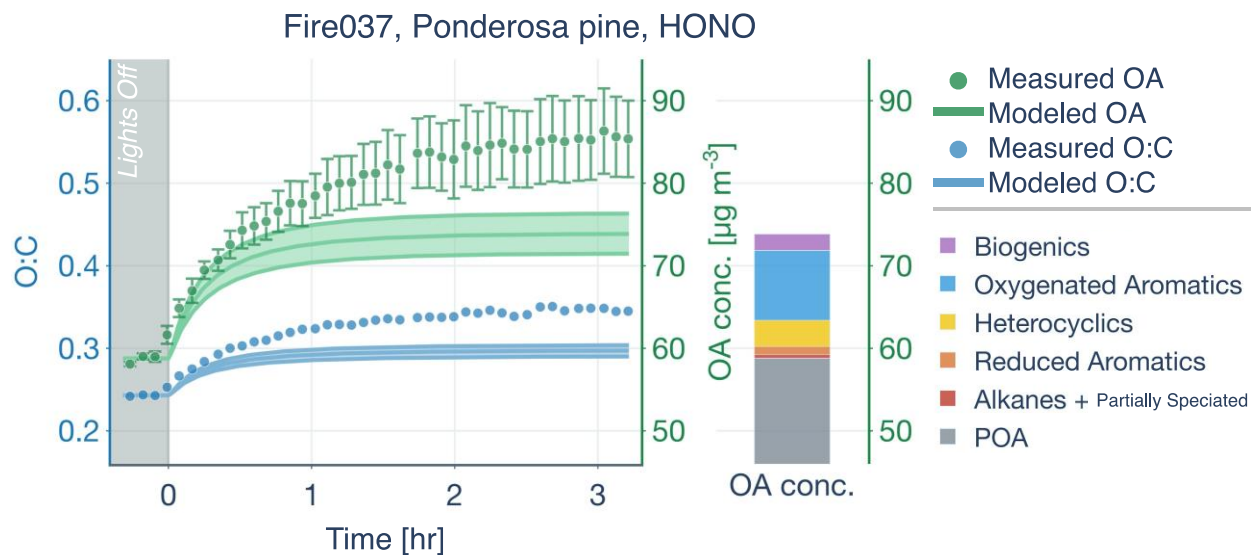


Figure S.13: Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a Ponderosa pine experiment performed at high  $\text{NO}_x$  conditions (Fire037). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.

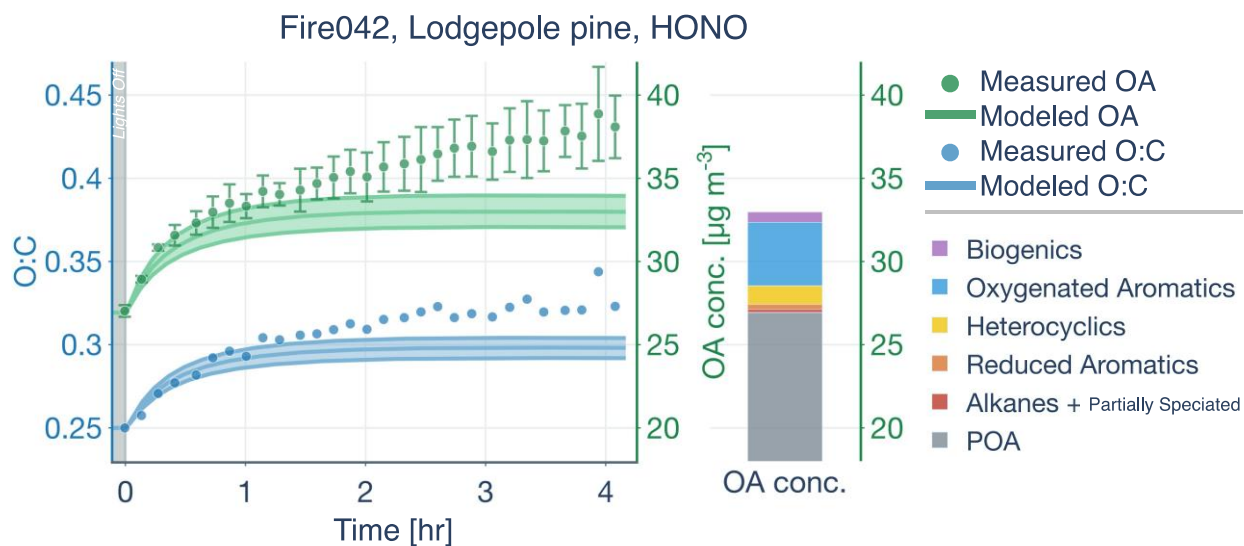


Figure S.14: Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a Lodgepole pine experiment performed at high  $\text{NO}_x$  conditions (Fire042). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.

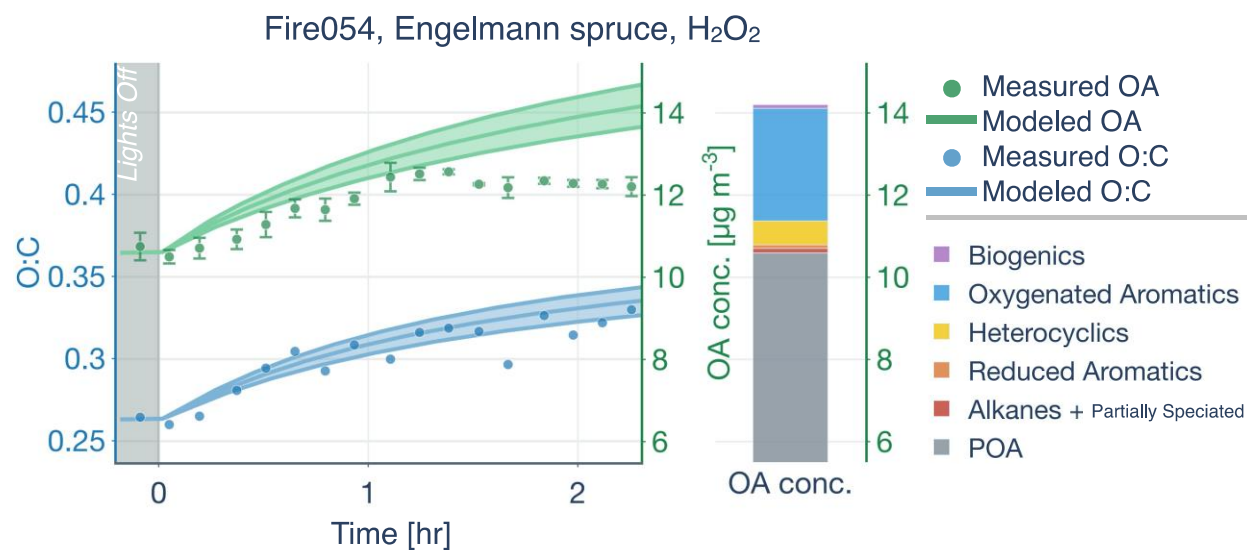


Figure S.15: Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for an Engelmann spruce experiment performed at high NO<sub>x</sub> conditions (Fire054). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.

### Fire063, Lodgepole pine, HONO

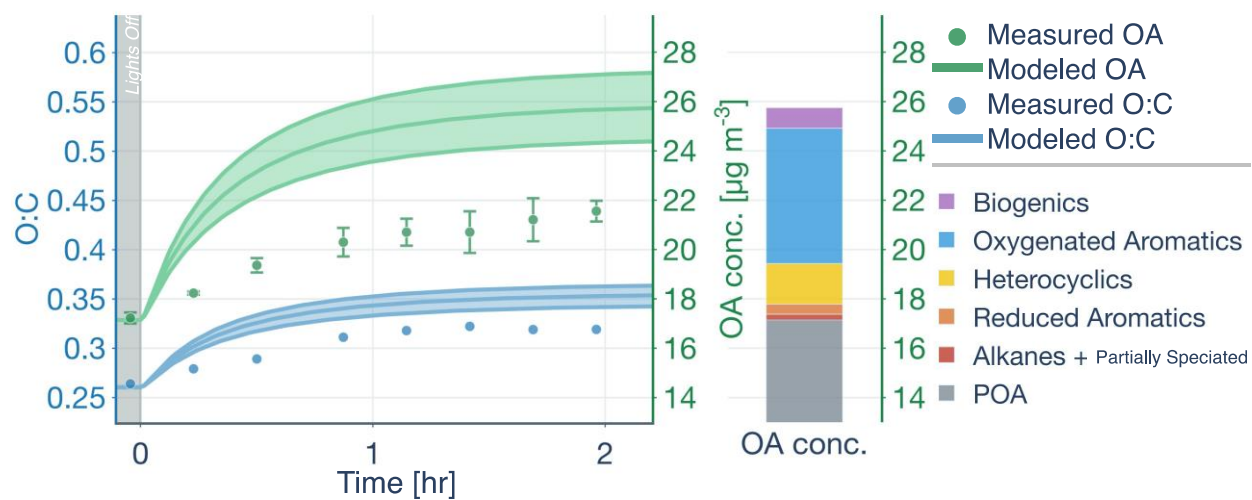


Figure S.16: Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a Lodgepole pine experiment performed at high  $\text{NO}_x$  conditions (Fire063). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.

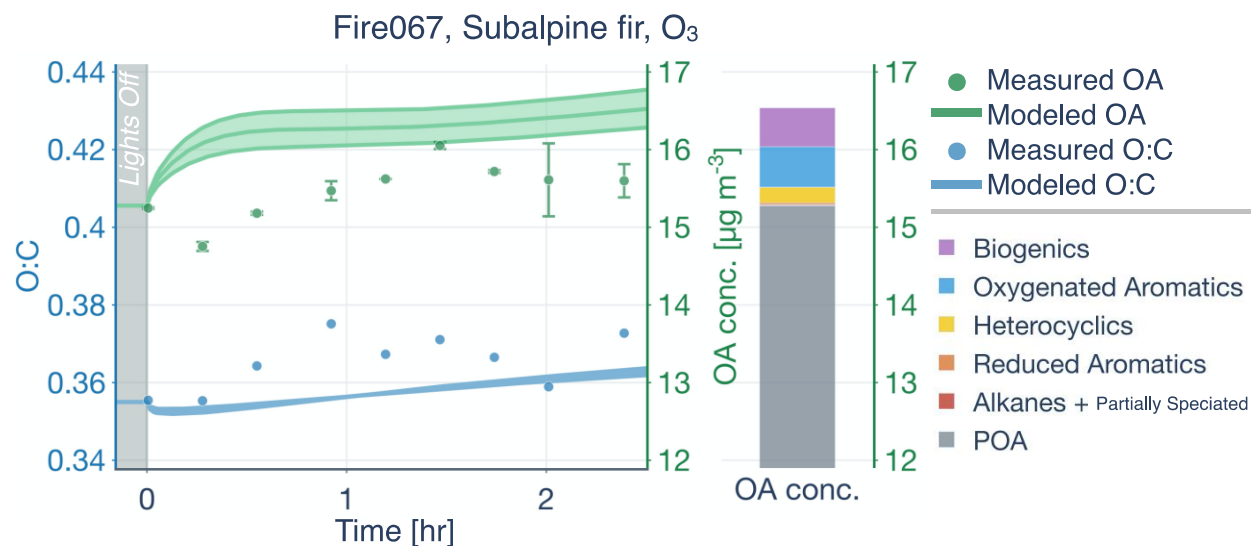


Figure S.17: Model predictions of OA mass concentrations (solid green line) and O:C ratio (solid blue line) compared with measurements (filled circles, same color scheme) for a subalpine fir experiment performed with additional ozone (Fire067). The bar to the right shows the modeled contributions of POA and precursor-resolved SOA to the end-of-experiment OA.



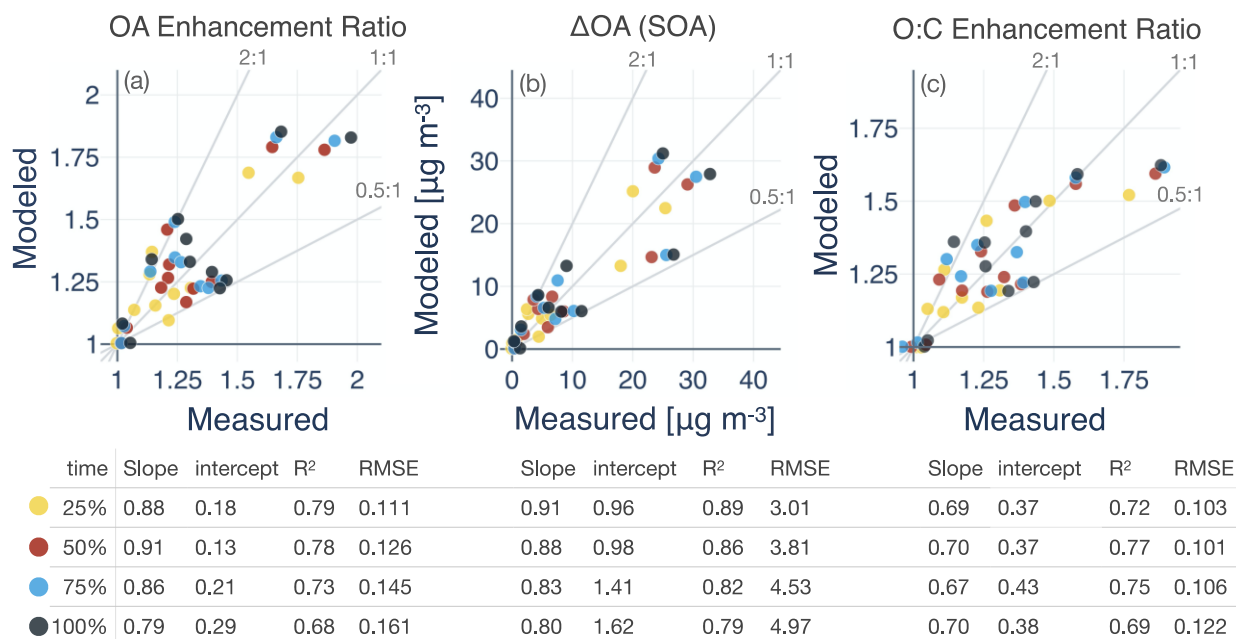


Figure S.18: Model-measurement comparison for (a) OA mass enhancement ratios (ratio of final to initial particle-wall-loss-corrected OA mass), (b) SOA production ( $\mu\text{g m}^{-3}$ ), and (c) OA O:C enhancement ratios (ratio of final to initial O:C ratios) for all eleven chamber experiments at four different time percentiles: 25%, 50%, 75%, and 100%.

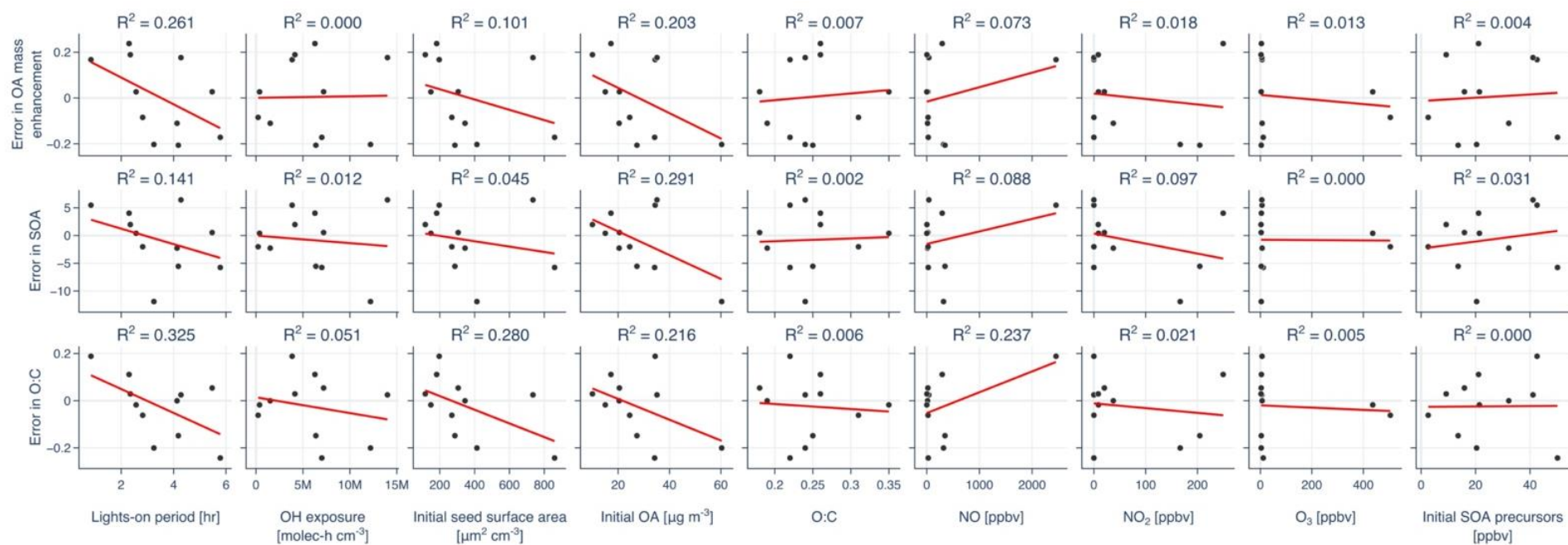


Figure S.19: Model error in OA mass enhancement ratio, SOA production, and OA O:C regressed against lights-on period, OH exposure, and initial concentrations of seed surface area, OA mass, O:C, NO, NO<sub>2</sub>, O<sub>3</sub>, and SOA precursors.

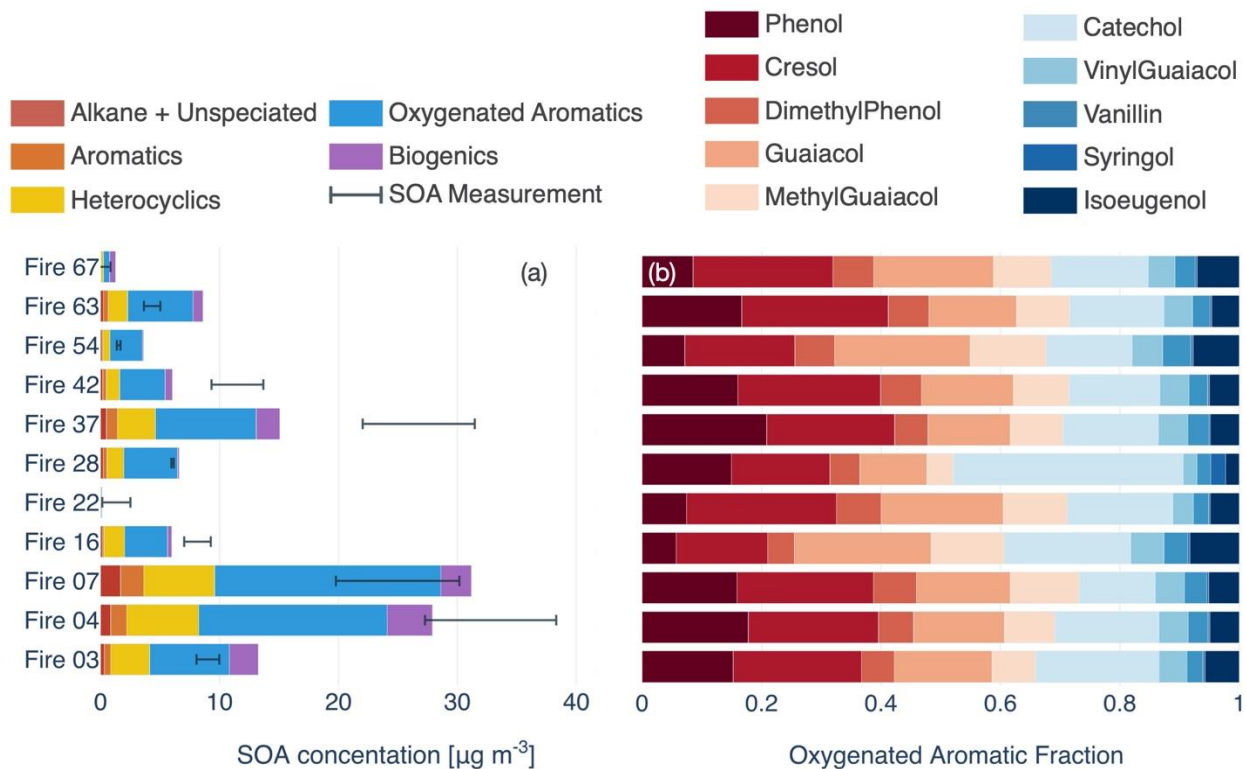


Figure S.20: (a) SOA mass concentrations apportioned by precursor class and (b) normalized precursor contributions to SOA arising from oxygenated aromatics. Data presented for all eleven chamber experiments.

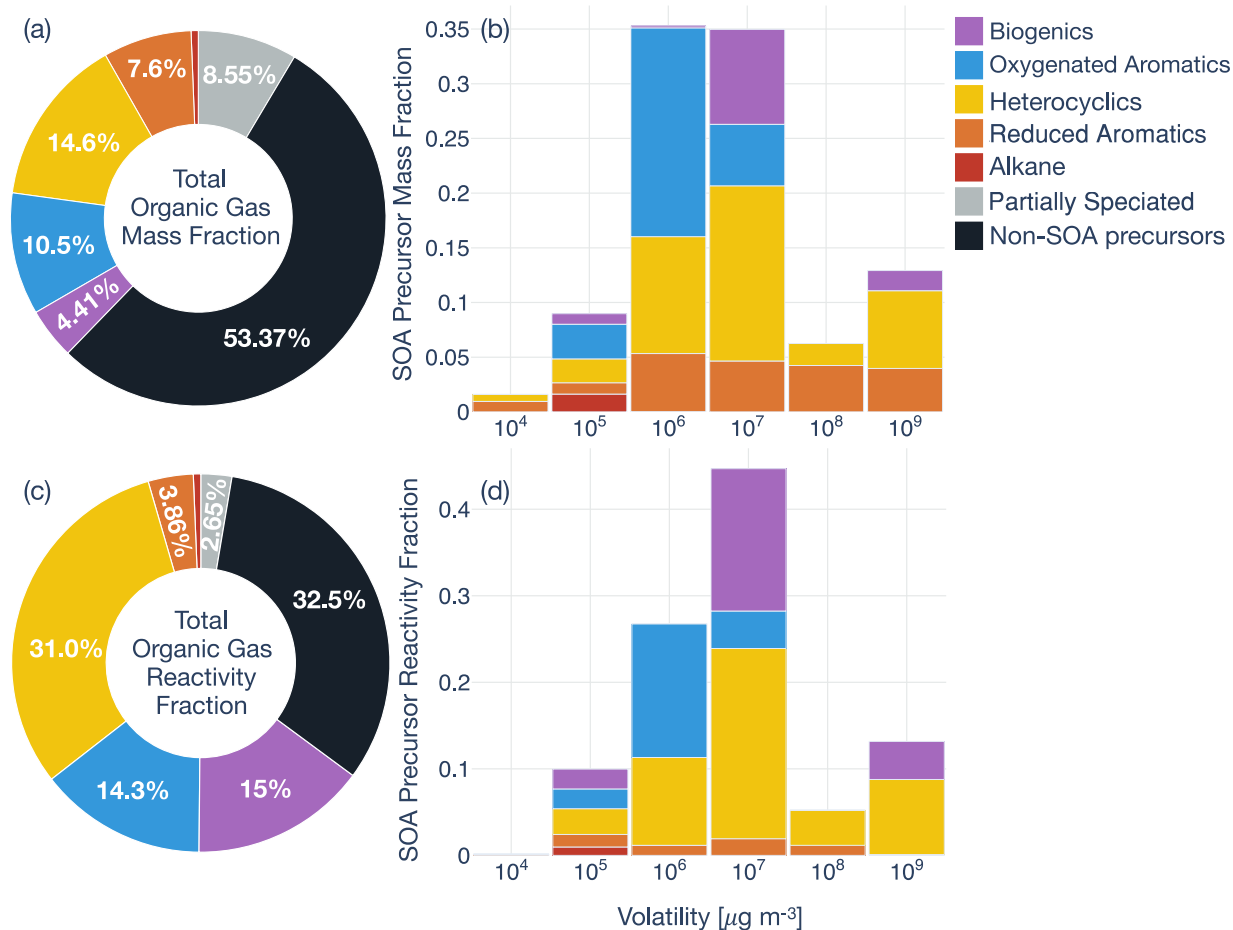


Figure S.21: (a) SOA precursor classes as a mass fraction of the total VOCs and (b) normalized distribution of SOA precursor emissions in volatility space. (c) SOA precursor classes as a fraction of the total VOC reactivity and (d) normalized distribution of SOA precursor reactivity in volatility space. Data are presented as an average of the emissions over the eleven chamber experiments.

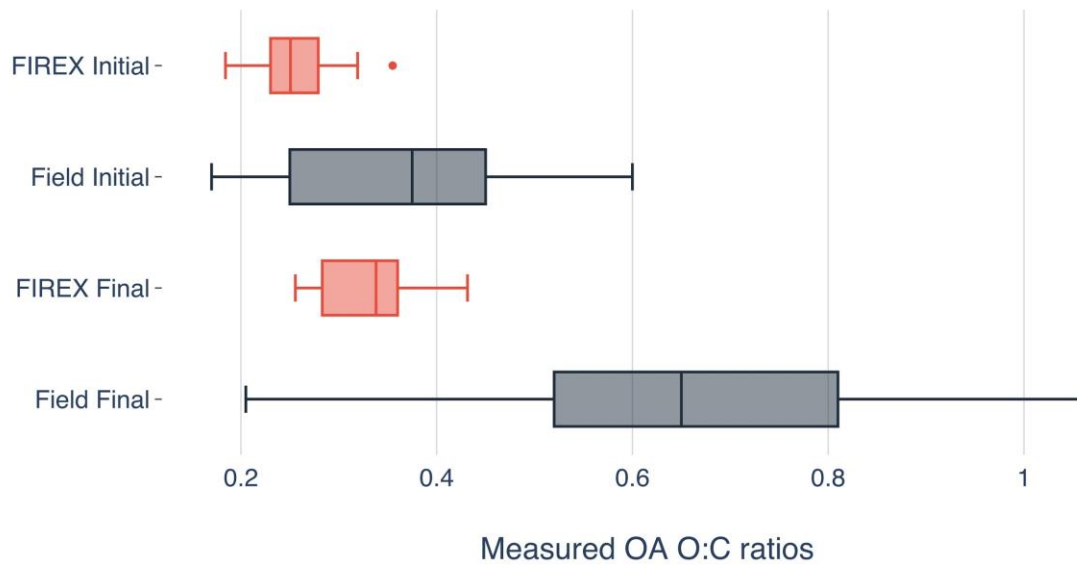


Figure S.22: Box plots for initial and final OA O:C ratios from the chamber experiments performed during FIREX and a host of field studies. The field studies are summarized in Hodshire et al.<sup>13</sup> The orange horizontal lines are medians and the dotted horizontal lines are means. Solid circles are outliers.

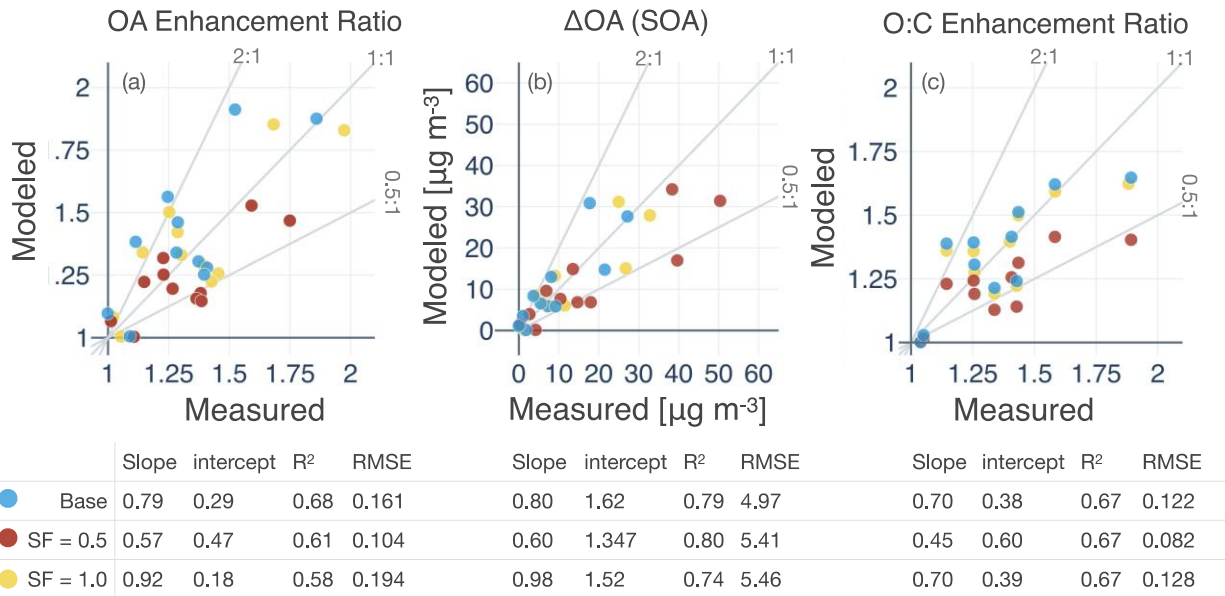


Figure S.23: End-of-experiment model-measurement comparison for (a) OA mass enhancement ratios (ratio of final to initial particle-wall-loss-corrected OA mass), (b) SOA production ( $\mu\text{g m}^{-3}$ ), and (c) OA O:C enhancement ratios (ratio of final to initial O:C ratios) for all eleven chamber experiments for three different assumptions about the scaling factor: constant scaling factor of 0.5 and 1 and a scaling factor as a function of the OA oxidation state.

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