

## Supporting Information

### **Molecular characterization and photoreactivity of organic aerosols formed from pyrolysis of urban materials during fires at the wildland-urban interface**

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**Summary:** seven figures and two tables with supporting information; description of additional experimental details for sample preparation and analysis.

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## Appendix A. Generation of Pyrolyzed Urban Material OA, UHPLC–PDA–HRMS Sample Preparation, and HRMS Analysis

### Generation of Urban Material OA

As described in Hopstock *et al.*,<sup>1</sup> ten urban materials were pyrolyzed, separately, in a Thermolyne F21135 tube furnace under a constant flow of N<sub>2</sub> at 600 °C. Details on the main chemical components of each urban material can be found in the Supporting Information (Table S1) of our previous work.<sup>1</sup> Generated smoke was passively pushed through the quartz combustion tube and Teflon tubing onto PTFE filters (Millipore Sigma, Fluoropore Membrane Filter, FGLP04700, 47 mm, 0.22 μm pore size). Each Teflon filter was weighed using a Sartorius ME5–F microbalance (± 1 ug precision) and OA mass loading ranged from 1.5 to 11 mg. These mass loadings were used to adjust the amount of solvent used for the extraction in order to keep the mass concentrations of the extracts approximately equal for high-resolution mass spectrometry (HRMS) analysis (about 1 mg mL<sup>-1</sup> of dissolved OA in the final DMSO extract). To minimize the amount of cross-contamination between pyrolysis experiments, the internal quartz tube was rigorously cleaned with “orgmix” (acetonitrile, dichloromethane, hexane 2:2:1 by volume), water, and isopropanol, and then dried using clean air. A flow of N<sub>2</sub> was used to purge all clean air from the quartz tube prior to beginning each pyrolysis run. In addition, Teflon tubing connecting the furnace quartz tube outlet to the filter holder was replaced with new tubing prior to switching in between urban materials to minimize the amount of carry-over.

Each filter was cut into quarters. Filter quarters were irradiated using a Xenon arc lamp (Newport Model 66902) with most of the radiation between 280–400 nm. As described at length in Hopstock *et al.*,<sup>1</sup> one hour in our photolysis setup is approximately equivalent to 0.7 h under a typical Los Angeles solar flux (an average taken for 11 AM to 1 PM on November 9th) as

calculated using the “Quick TUV” calculator (Madronich, S. ACOM: Quick TUV, 2019).<sup>2</sup> Unaged and aged OA samples were used in the HRMS analysis in this paper. OA solutions were then rotary evaporated to near dryness and frozen until HRMS studies in this work could be conducted. This HRMS study only utilized data collected for the unaged and 2 h aged samples.

### **UHPLC–PDA–HRMS Sample Preparation and Analysis**

Prior to HRMS analysis, the frozen urban material OA (previously irradiated and dried) were brought to room temperature, and then dissolved in dimethyl sulfoxide (DMSO; Millipore, > 99.9 % purity) in order to achieve a good level of solubility across all urban materials.<sup>3</sup> DMSO was chosen as an alternative to orgmix, as this solvent system is incompatible with LC columns. The final OA concentration for each OA extract was about 1 mg mL<sup>-1</sup>. This mass loading was chosen to yield sufficiently high PDA and mass spectrometry signal for all materials tested. Insoluble residues within the extracts were removed by filtering through nylon membrane syringe filter discs (0.2 µm, Merck Millipore) that were prewetted with fresh DMSO. To recover remaining analytes, fresh DMSO was then used to rinse the extraction vial, and this extract was also filtered through a nylon membrane syringe filter.

OA extracts were analyzed with a Thermo Scientific Vanquish Horizon ultrahigh pressure liquid chromatograph coupled to a Vanquish Horizon photodiode array spectrophotometer and a Q Exactive Plus high–resolution mass spectrometer (UHPLC–PDA–HRMS). This platform allows for BrC chromophores to be separated while taking a full UV–Vis absorption spectrum at each retention time.<sup>4</sup> The separation was performed on a reverse–phase column (Luna Omega Polar C18, 150 x 2.1 mm, 1.6 µm particles, 100 Å pores, Phenomenex Inc.) which has higher retention of nonpolar compounds and, subsequently, elutes more polar compounds earlier in the run. The

column compartment temperature was held at 30 °C. An injection volume of 10 µL was used for all samples. The autosampler box was kept at 23 °C to avoid DMSO freezing below 19 °C.

The eluent flow was 0.3 µL min<sup>-1</sup> and consisted of water (Optima LC/MS grade, Fisher Chemical) acidified with 0.1 % v/v formic acid (solution A) and acetonitrile (Optima LC/MS grade, Fisher Chemical) acidified with 0.1 % v/v formic acid (solution B). Formic acid was added to the mobile phase systems to enhance the retention of organic acids on the C18 column and assist in the protonation/detection of sample analytes in the positive ionization mode. A 45 min LC gradient adapted from Siemens *et al.* (2022) was employed in this study.<sup>5</sup> The LC gradient was: 0–3 min (5 % B); 3–25 min linear ramp to 100 % B; 25–35 min held at 100 % B (the length of 5 column passes of acetonitrile to remove any nonpolar components still retained by the column); 35 min return to 5 % B and held until 45 min in preparation for the next run. Total ion chromatograms are presented in **Figures S1** and **S2**. UV–vis absorption spectra were collected continuously by the PDA in a wavelength range of 190–680 nm at an acquisition frequency of 5 Hz and a 4 nm effective bandwidth.

Eluting analytes were ionized using heated electrospray ionization (HESI) operating in both positive (+) and negative (–) modes. Mass spectra were recorded for the *m/z* range of 100–1500 Da at a mass resolving power of 140,000 at *m/z* 200. Mass calibration was performed using commercial calibration solutions containing caffeine, MRFA, and Ultramark 1621 (Thermo Scientific, PI-88323 and PI-88324). The parameters of the HESI ionization source were as follows: –2.5 kV (in (–) mode) and 4 kV (in (+) mode) spray voltages, 250 °C capillary temperature, 250 °C probe heater temperature, S–Lens ion funnel RF level 30, 80 units of sheath gas (nitrogen) flow, 10 units of auxiliary gas (nitrogen) flow, and 8 unit of sweep gas flow.

It should be noted that while DMSO worked well to extract the samples, it created complications within the LC system. We found that over time, repeated injection of DMSO samples caused the swelling of Peek tubing and subsequent pressure increases within the LC column. In addition, a subset of OA components that were soluble in DMSO but not soluble in water/acetonitrile precipitated in the guard column, further increasing pressure in the column. Besides pressure increases, residual DMSO was present in the ionization source even after rigorous flushing and cleaning with methanol. Despite these issues, we elected to continue using DMSO to detect as many OA compounds as possible. We recommend exercising maximum caution when using DMSO in future studies.

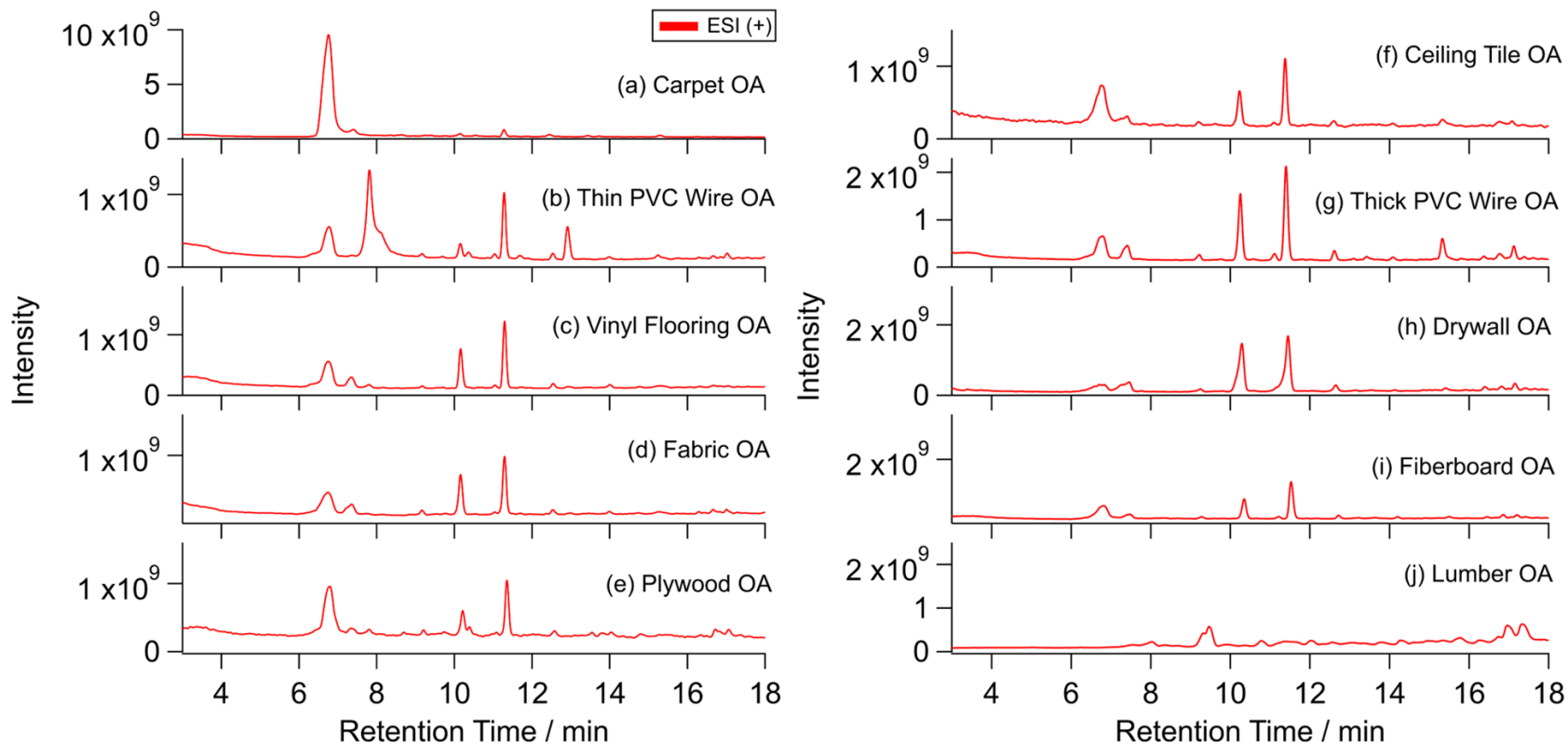
### **HRMS Data Analysis**

Raw UHPLC–PDA–HRMS data were initially viewed using Thermo Scientific Inc. Xcalibur software. Subsequently, an open–source MZmine 3.9 code (<http://mxmine.github.io/>) was used to perform peak picking, peak deconvolution, extracted ion chromatogram construction, peak smoothing, and  $^{13}\text{C}$  isotope filtering.<sup>6</sup> Raw Xcalibur data were imported into MZmine and low intensity peaks were filtered out using a minimum ion intensity of  $10^4$ . The mass detection was performed for separation occurring within 3–25 min using centroided data. The “ADAP chromatogram builder” function was used to build extracted ion chromatograms with threshold parameters of  $5 \times 10^5$  (minimum peak height) and tolerance of 0.001  $m/z$ . For reference, the maximum signal intensity was  $10^9$  for both ionization modes. Full width half maximum thresholds and noise levels of chromatograms varied amongst OA samples and BrC standards.

Molecular formulas were assigned similarly to previous work.<sup>7,8</sup> Extracted ions were assumed to be  $[\text{M} + \text{H}]^+$ ,  $[\text{M} + \text{Na}]^+$ , and  $[\text{M} - \text{H}]^-$  ions. For the purposes of this work, the formula

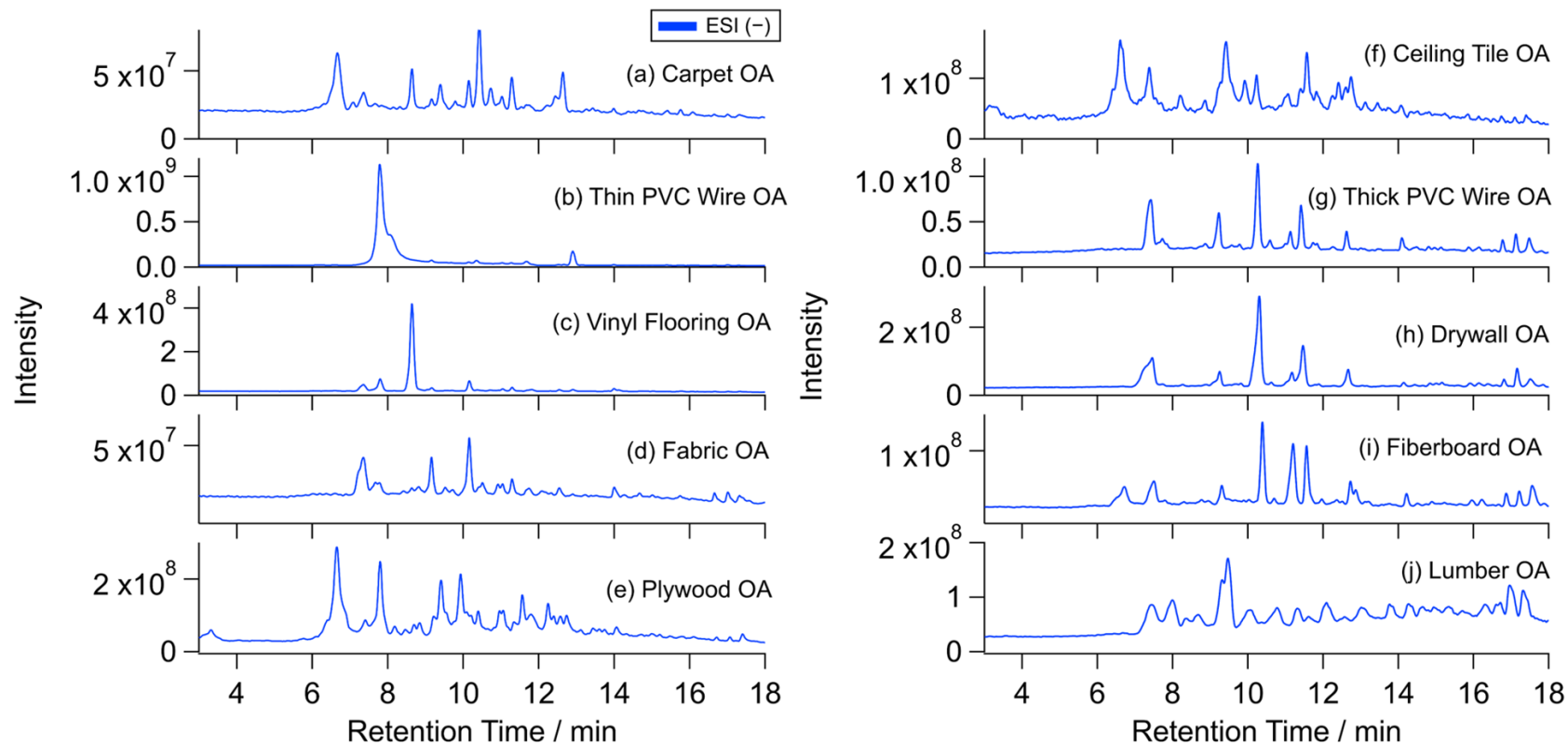
assignments were restricted to compounds containing  $C_cH_hO_{0-40}N_{0-6}$  (c and h were unrestricted) with an accuracy of  $\pm 1$  ppm. Additionally, a single Na atom was allowed for assignments of MS features detected in ESI(+). The assigned ion formulas were corrected for the ionization mechanism and all HRMS results below are reported as formulas of neutral OA compounds. The double bond equivalent (*DBE*) was calculated according to **Equation S1**.

$$DBE = n_C - \left(\frac{n_H}{2}\right) + \left(\frac{n_N}{2}\right) + 1 \quad \text{Equation S1}$$

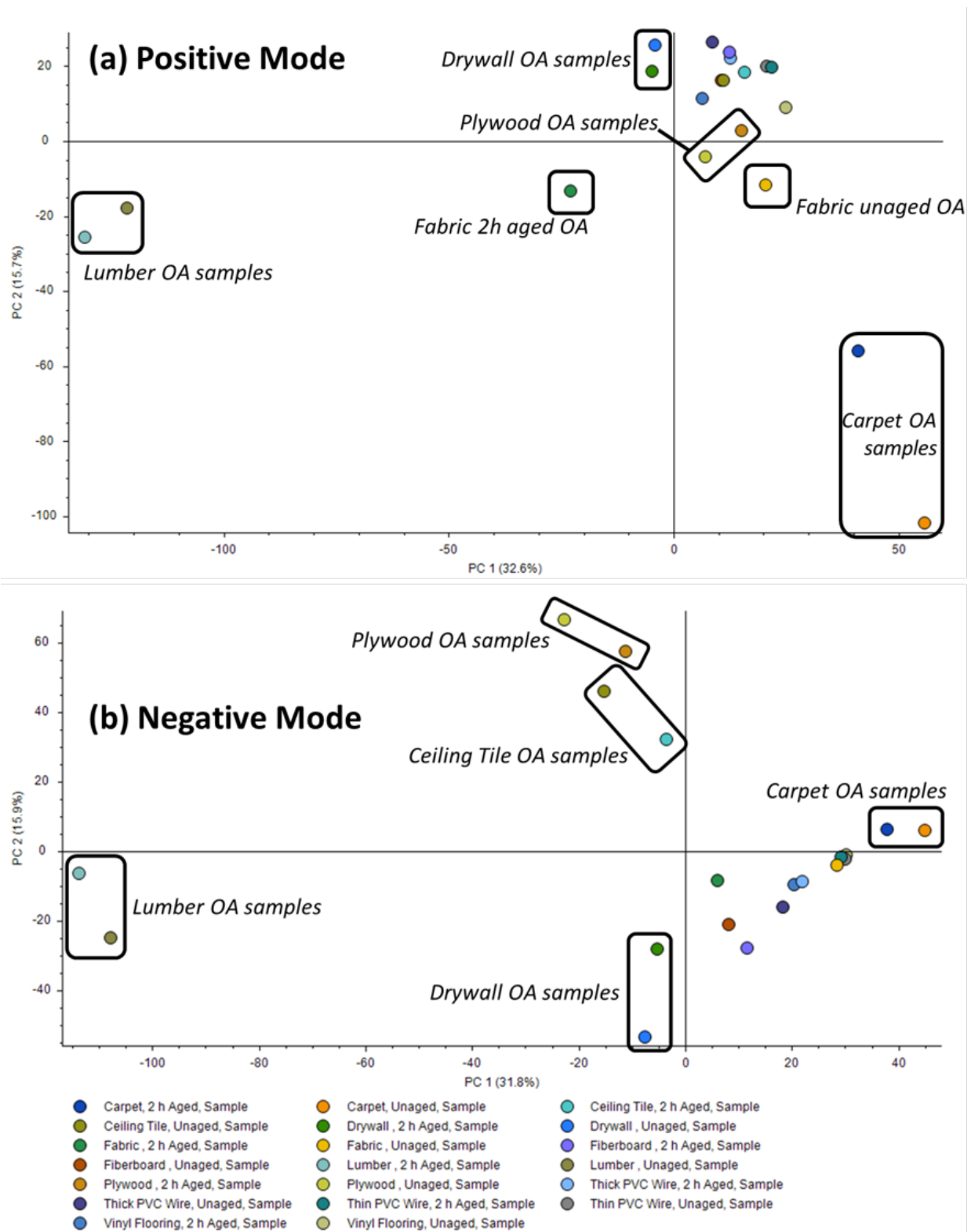


**Figure S1.** UHPLC–ESI total ion chromatograms collected in the *positive* ionization mode for the ten unaged OA samples (panels a–j). Notable peaks include:  $C_6H_{11}ON$  peak (6.76 min) for all urban material OA (except lumber); the  $C_8H_6O_4$  peak (7.80 min) largely present in thin PVC wire OA (b); the  $C_{24}H_{44}O_4N_4$  peak (10.16 min) for all OA except carpet and lumber; and the  $C_{18}H_{33}O_3N_3$  peak (11.29 min) in all OA except carpet, fiberboard, and lumber.

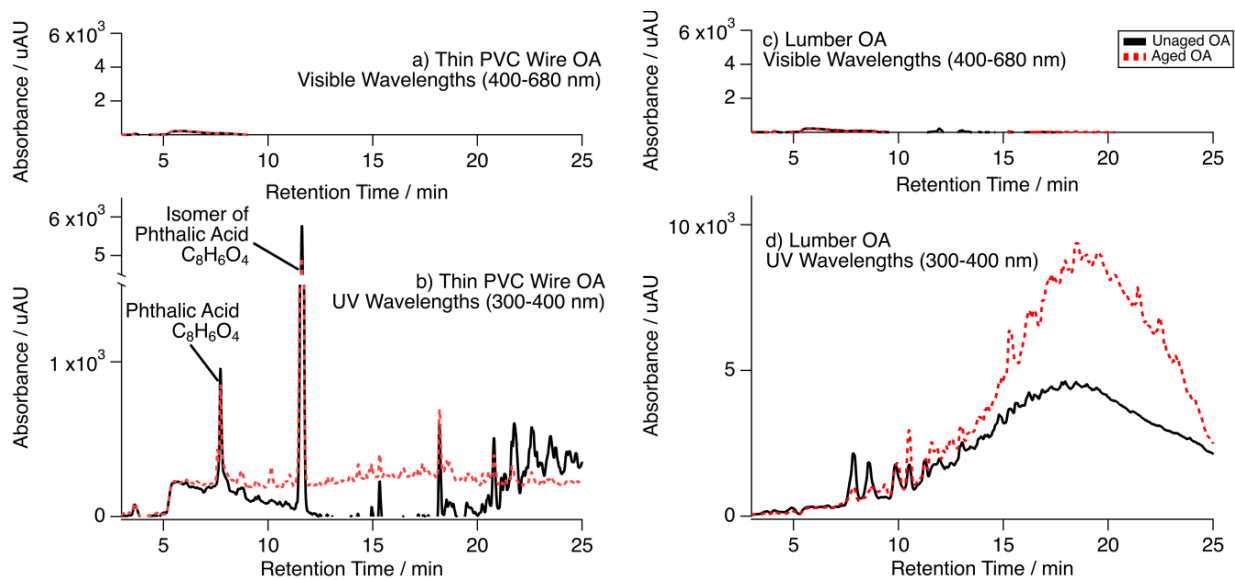




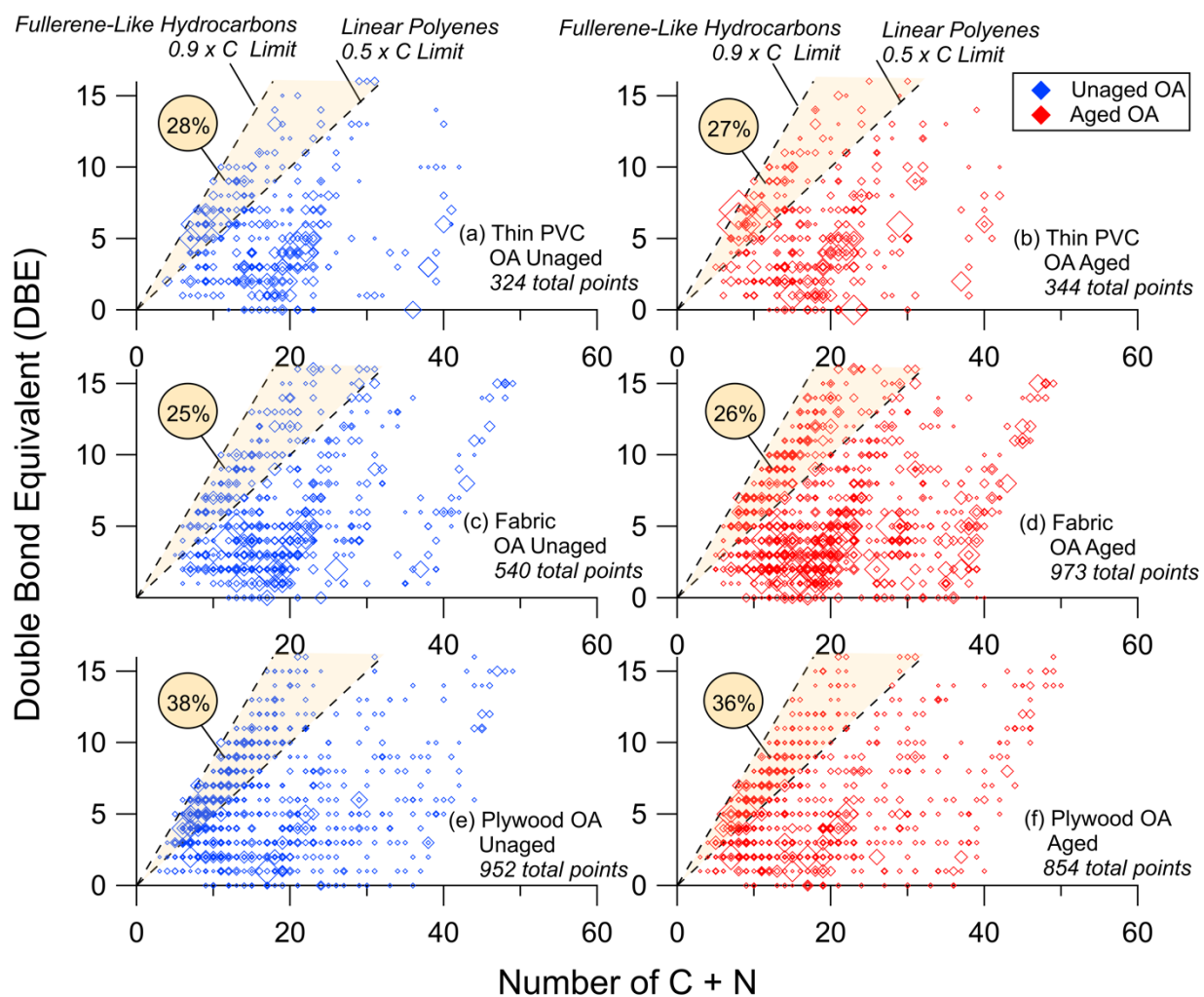
**Figure S2.** UHPLC-ESI total ion chromatograms collected in the *negative* ionization mode for the ten unaged OA samples (panels a–j). Notable peaks include: the  $C_8H_6O_4$  peak (7.80 min) largely present in thin PVC wire OA (b); and the  $C_8H_6O_4$  peak (8.64 min) in vinyl flooring OA (c), identified as terephthalic acid.



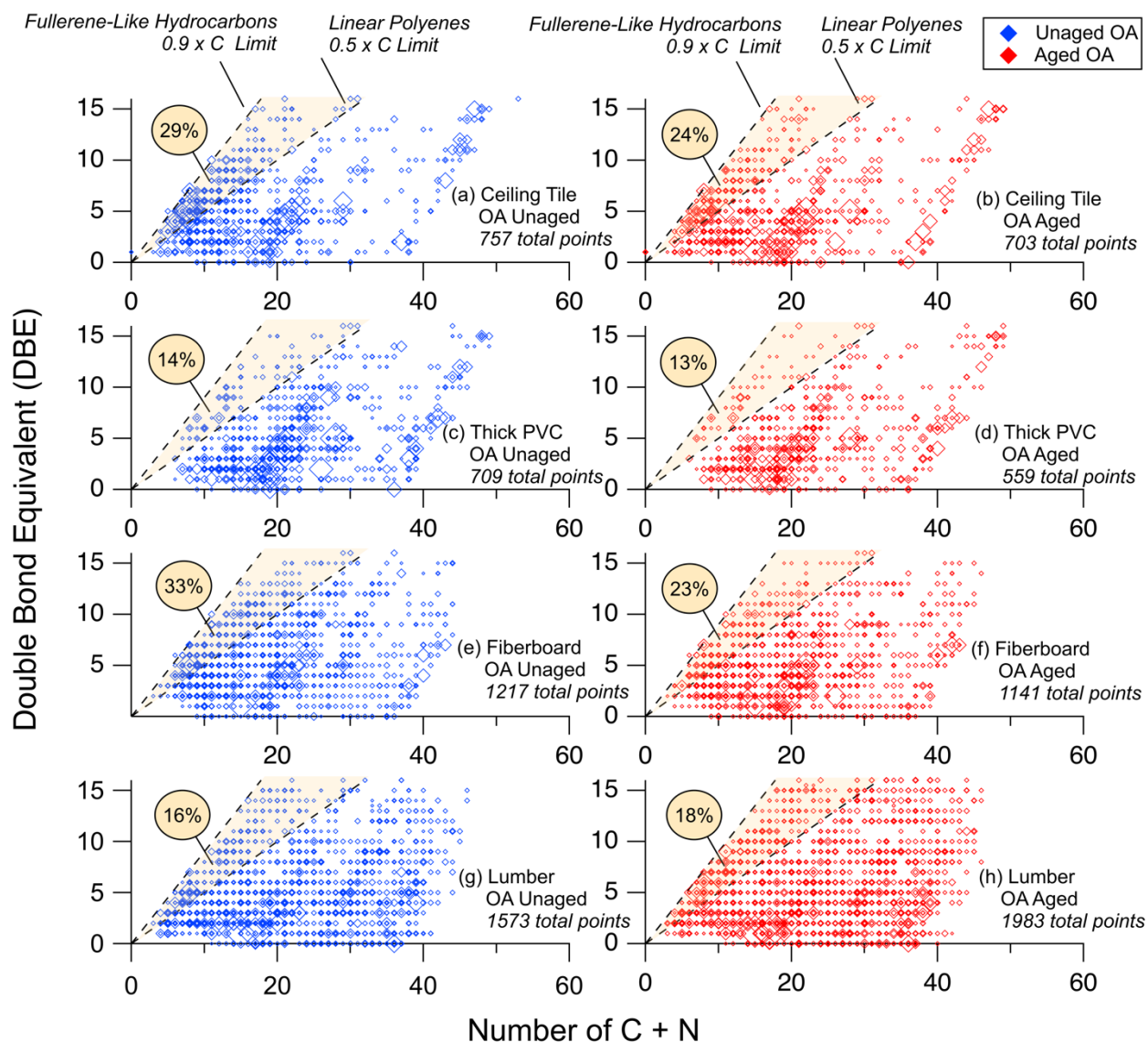
**Figure S3.** Principal component analysis of all 20 urban samples (unaged and 2 h aged) run in the positive mode (panel a) and negative mode (panel b). Statistical comparison was performed by the Compound Discover program. Outlier samples are boxed for ease of comparison.



**Figure S4.** Photodiode array detector (PDA) chromatograms of thin PVC wire and lumber OA. Unaged spectra are presented in black and aged spectra are presented in red. The PDA signal integrated over UV wavelengths (300–400 nm) is plotted separately from visible wavelengths (400–680 nm). Thin PVC wire OA (a and b) and lumber OA (c and d) were selected to showcase PDA response to cases of photobleaching and photoenhancement, respectively.

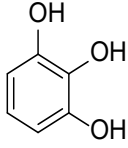
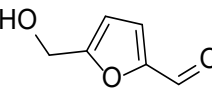
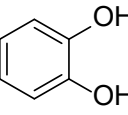
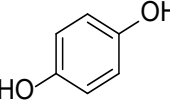


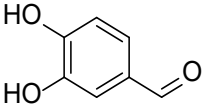
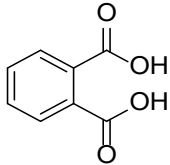
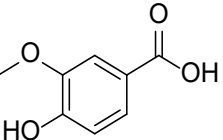
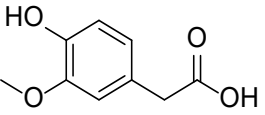
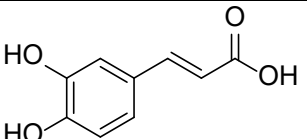
**Figure S5.** Plot of double bond equivalent (DBE) versus number of carbon and nitrogen (C+N) atoms from assigned OA unaged and aged species in thin PVC wire (a and b), fabric (c and d), and plywood (e and f) OA. The size of each symbol is arbitrarily scaled to the cubic root of the corresponding MS peak intensity. Reference lines show DBE/(C+N) values corresponding to fullerene-like hydrocarbons ( $0.9 \times C$  limit) and linear polyenes ( $0.5 \times C$  limit).<sup>3,5</sup> Yellow circles display the percentage of data points (by number) that fell within the dashed lines and orange shaded region and, thus, are predicted to be potential BrC chromophores. The total number of points is provided in each panel. The presented data comes from both the positive and negative ionization modes.

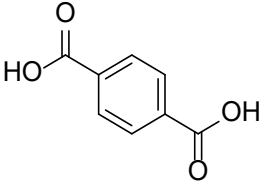
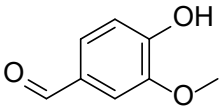
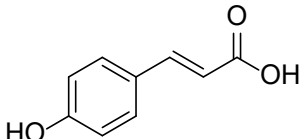
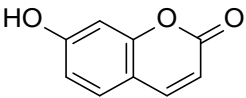
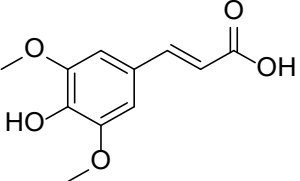


**Figure S6.** Plot of double bond equivalent (DBE) versus number of carbon and nitrogen (C+N) atoms from assigned OA unaged and aged species in ceiling tile (a and b), thick PVC wire (c and d), fiberboard (e and f), and lumber (g and h) OA. The size of each symbol is arbitrarily scaled to the cubic root of the corresponding MS peak intensity. Reference lines show DBE/(C+N) values corresponding to fullerene-like hydrocarbons ( $0.9 \times C$  limit) and linear polyenes ( $0.5 \times C$  limit).<sup>3,5</sup> Yellow circles display the percentage of data points (by number) that fell within the dashed lines and orange shaded region and, thus, are predicted to be potential BrC chromophores. The total number of points is provided in each panel. The presented data comes from both the positive and negative ionization modes.

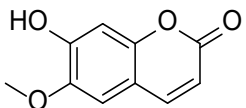
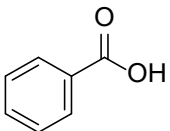
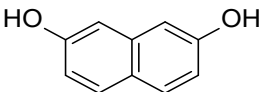
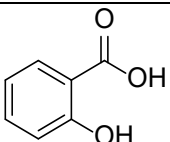
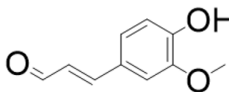
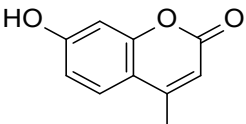
**Table S1.** Identified BrC species in OA samples. Authentic BrC standards from Moschos *et al.* were run on a UHPLC–PDA–HRMS system at the University of California, Irvine (UCI). Standard components that were found in the OA samples are listed below in order of increasing retention time.<sup>9</sup> The peak # corresponds to the extracted ion chromatogram label in **Figure S7**. The *m/z* are provided for each ionization mode (when present). Catechol (compound #3) was not part of the Moschos *et al.* standards, this was identified by an additional standard prepared at UCI. Grey shading in the last 10 columns indicates the OA sample(s) that each BrC standard component was identified in. Note that this table does not make a distinction between unaged and aged OA. For simplicity, if a standard compound was found in one of the four data files for each OA class (ESI (+/-) files for both the unaged and aged samples), then it was included in the table below.

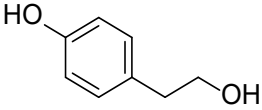
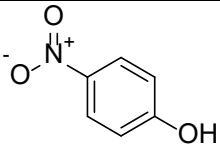
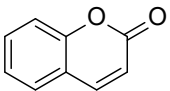
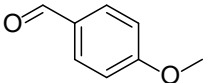
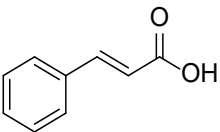
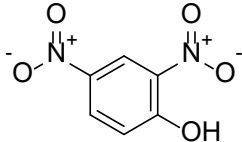
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1	Pyrogallol		C <sub>6</sub> H <sub>6</sub> O <sub>3</sub>	125.0240 (-)	3.83 (-)										
2	5-hydroxymethylfurfural		C <sub>6</sub> H <sub>6</sub> O <sub>3</sub>	127.0389 (+)	5.04 (+)										
3	Catechol		C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	109.0290 (-)	6.63 (-)										
4	Hydroquinone		C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	109.0293 (-)	7.46 (-)										

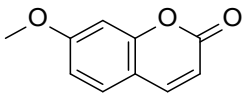
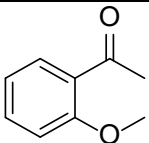
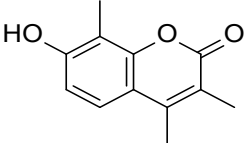
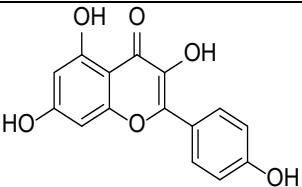
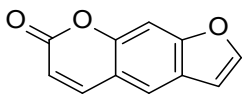
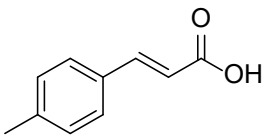
# peak	Component Name	Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
5	3,4-Dihydroxybenzaldehyde		C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	139.0390 (+)	7.99 (+)										
6	Phthalic acid		C <sub>8</sub> H <sub>6</sub> O <sub>4</sub>	167.0335 (+) 165.0189 (-)	8.36 (+) 8.35 (-)										
7	Vanillic Acid		C <sub>8</sub> H <sub>8</sub> O <sub>4</sub>	167.0347 (-)	8.96 (-)										
8	Homovanillic acid		C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	181.0504 (-)	9.01 (-)										
9	Caffeic acid		C <sub>9</sub> H <sub>8</sub> O <sub>4</sub>	181.0493 (+)	9.01 (+)										

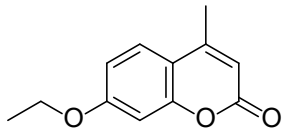
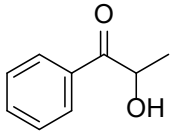
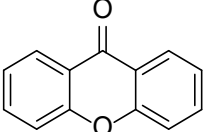
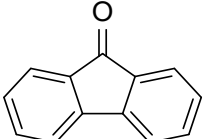
# peak	Component Name	Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
10	Terephthalic acid		C <sub>8</sub> H <sub>6</sub> O <sub>4</sub>	165.0189 (-)	9.08 (-)										
11	Vanillin		C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	153.0543 (+) 151.0397 (-)	10.19 (+) 10.19 (-)										
12	p-Coumaric acid		C <sub>9</sub> H <sub>8</sub> O <sub>3</sub>	165.0543 (+) 163.0397 (-)	10.29 (+) 10.27 (-)										
13	Umbelliferone		C <sub>9</sub> H <sub>6</sub> O <sub>3</sub>	161.0240 (-)	10.67 (-)										
14	Sinapinic acid		C <sub>11</sub> H <sub>12</sub> O <sub>5</sub>	223.0606 (-)	10.68 (-)										

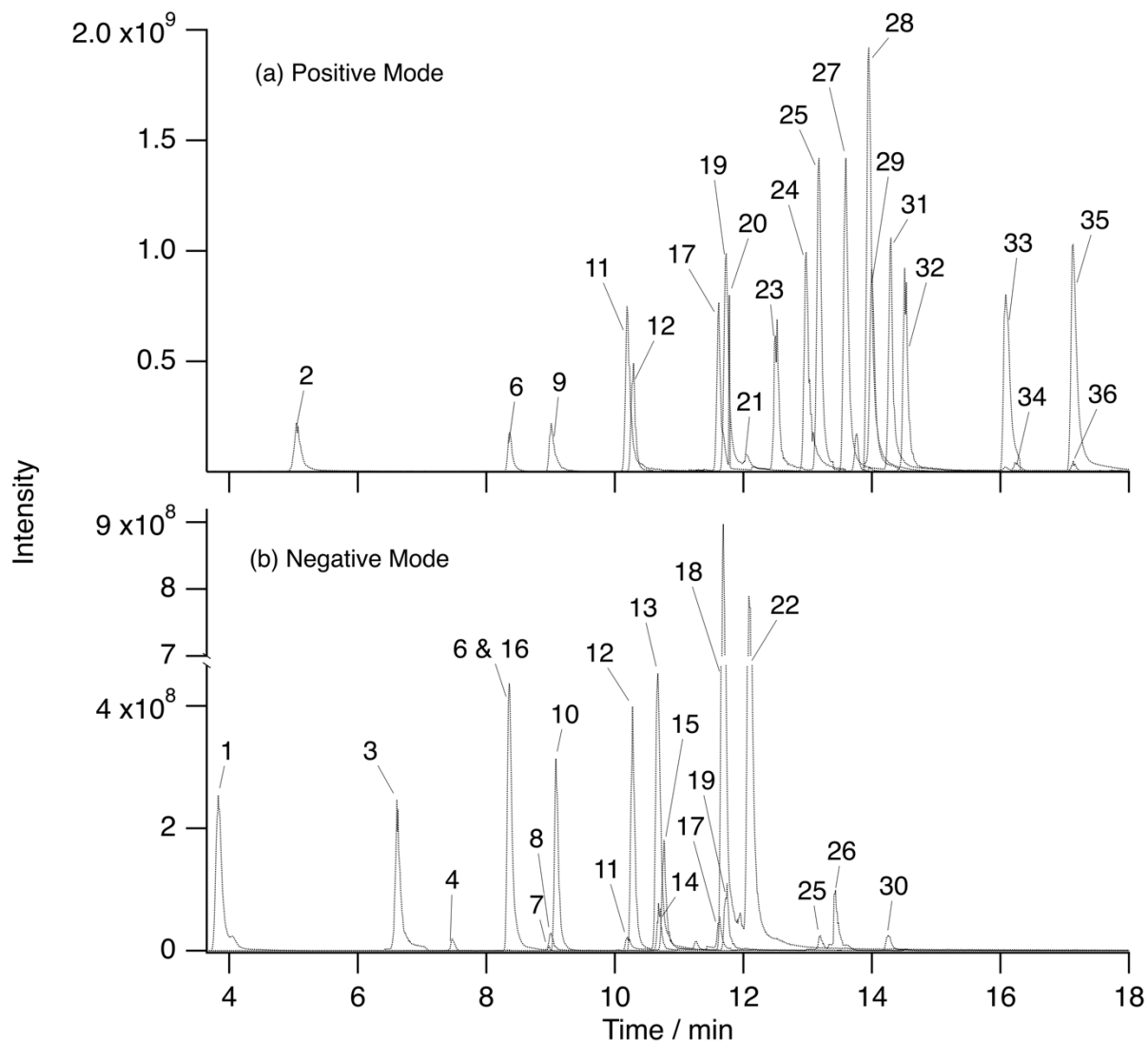


# peak	Component Name	Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
15	Scopoletin		C <sub>10</sub> H <sub>8</sub> O <sub>4</sub>	193.0496 (+) 191.0345 (-)	10.76 (+) 10.76 (-)										
16	Benzoic acid		C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	123.0440 (+) 121.0293 (-)	11.29 (+) 8.35 (-)										
17	2,7-Dihydroxynaphthalene		C <sub>10</sub> H <sub>8</sub> O <sub>2</sub>	161.0592 (+) 159.0449 (-)	11.62 (+) 11.62 (-)										
18	Salicylic acid		C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	137.0240 (-)	11.69 (-)										
19	Coniferaldehyde		C <sub>10</sub> H <sub>10</sub> O <sub>3</sub>	179.0700 (+) 177.0553 (-)	11.73 (+) 11.75 (-)										
20	4-Methylumbelliferone		C <sub>10</sub> H <sub>8</sub> O <sub>3</sub>	177.0543 (+)	11.78 (+)										

# peak	Component Name	Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
21	Tyrosol		C <sub>8</sub> H <sub>10</sub> O <sub>2</sub>	139.0754 (+)	12.03 (+)										
22	4-Nitrophenol		C <sub>6</sub> H <sub>5</sub> NO <sub>3</sub>	138.0193 (-)	12.08 (-)										
23	Coumarin		C <sub>9</sub> H <sub>6</sub> O <sub>2</sub>	147.0439 (+)	12.52 (+)										
24	4-Methoxybenzaldehyde		C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	137.0597 (+)	12.98 (+)										
25	trans-Cinnamic acid		C <sub>9</sub> H <sub>8</sub> O <sub>2</sub>	149.0594 (+) 147.0449 (-)	13.19 (+) 13.20 (-)										
26	2,4-Dinitrophenol		C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> O <sub>5</sub>	183.0043 (-)	13.42 (-)										

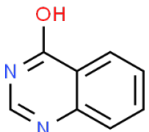
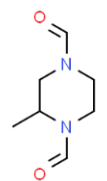
# peak	Component Name	Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA	
27	7-Methoxycoumarin		C <sub>10</sub> H <sub>8</sub> O <sub>3</sub>	177.0544 (+)	13.59 (+)											
28	2'-Methoxyacetophenone		C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	151.0751 (+)	13.95 (+)											
29	7-Hydroxy-3,4,8-trimethylcoumarin		C <sub>12</sub> H <sub>12</sub> O <sub>3</sub>	205.0857 (+)	14.00 (+)											
30	Kaempferol		C <sub>15</sub> H <sub>10</sub> O <sub>6</sub>	285.0401 (-)	14.00 (-)											
31	Psoralen		C <sub>11</sub> H <sub>6</sub> O <sub>3</sub>	187.0389 (+)	14.30 (+)											
32	4-Methylcinnamic Acid		C <sub>10</sub> H <sub>10</sub> O <sub>2</sub>	163.0748 (+)	14.51 (+)											

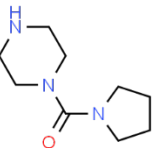
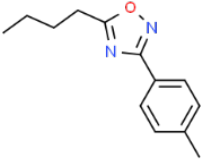
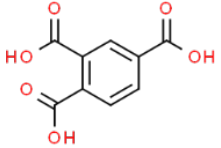
# peak	Component Name	Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
33	7-Ethoxy-4-methylcoumarin		C <sub>12</sub> H <sub>12</sub> O <sub>3</sub>	205.0859 (+)	16.08 (+)										
34	2'-Hydroxypropiophenone		C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	151.0752 (+)	16.22 (+)										
35	Xanthone		C <sub>13</sub> H <sub>8</sub> O <sub>2</sub>	197.0598 (+)	17.13 (+)										
36	9-Fluorenone		C <sub>13</sub> H <sub>8</sub> O	181.0646 (+)	17.62 (+)										

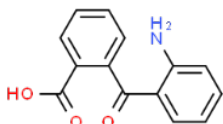
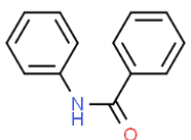
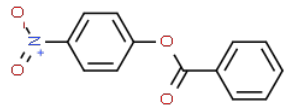


**Figure S7.** Extracted ion chromatograms (EICs) corresponding to the BrC species identified in OA samples, utilizing the BrC standard solutions from Moschos *et al.* (2024).<sup>9</sup> UHPLC–PDA–HRMS system at the University of California, Irvine was operated in both the positive (panel a) and negative (panel b) ionization modes. Peaks are labeled with the number corresponding to that of each compound in **Table S1**. Peaks 5 and 16 (corresponding to 3,4–dihydroxybenzaldehyde (+) and benzoic acid (+), respectively) are not labeled due to peak intensities being too small to showcase on this plot.

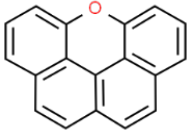
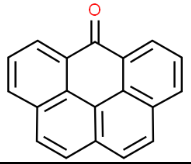
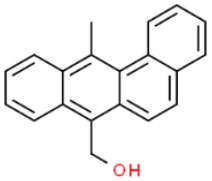
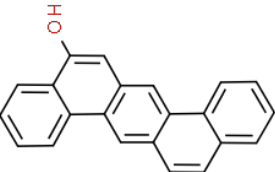
**Table S2.** Compounds that appear to be unique to each urban material OA. Tentative structural assignments were proposed by the Compound Discover program (Thermo Scientific) by utilizing various online databases to determine the best match. Note that these structures were **not verified** using internal standards. Grey shading in the last 10 columns indicates the OA sample that each component was identified in. There is no distinction between unaged and aged OA.

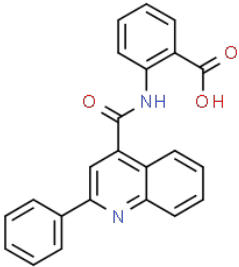
Component Name & Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Description	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
4-hydroxyquinazoline 	C <sub>8</sub> H <sub>6</sub> N <sub>2</sub> O	145.0408 (-)	7.86	—										
2-Methyl-1,4-piperazine dicarbaldehyde 	C <sub>7</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub>	157.0970 (+)	8.65	—										

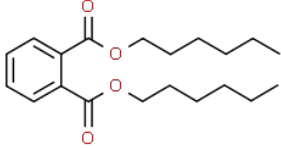
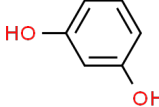
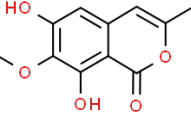
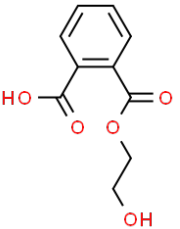
Component Name & Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Description	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
1-Piperazinyl(1-pyrrolidinyl) methanone 	C <sub>9</sub> H <sub>17</sub> N <sub>3</sub> O	184.1449 (+)	11.68	—										
—	C <sub>13</sub> H <sub>17</sub> NO <sub>3</sub>	236.1281 (+)	13.58	—										
—	C <sub>14</sub> H <sub>18</sub> N <sub>2</sub> O	231.1492 (+)	13.75	—										
5-Butyl-3-(p-tolyl)-1,2,4-oxadiazole 	C <sub>13</sub> H <sub>16</sub> N <sub>2</sub> O	217.1336 (+)	15.42	—										
1,2,4-Benzenetricarboxylic acid 	C <sub>9</sub> H <sub>6</sub> O <sub>6</sub>	209.0091 (-)	6.18	Intermediate for resins, plasticizers, dyes, inks, and adhesives										

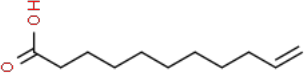
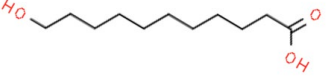
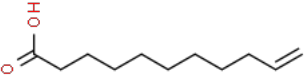
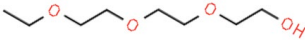
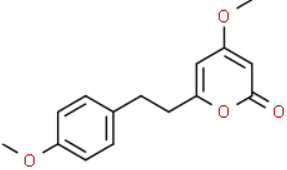
Component Name & Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Description	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
—	C <sub>8</sub> H <sub>9</sub> NO <sub>4</sub>	184.0607 (+)	7.79	—										
—	C <sub>17</sub> H <sub>8</sub> N <sub>4</sub> O <sub>4</sub>	355.0422 (+)	7.81	—										
2-(2-Aminobenzoyl) benzoic acid 	C <sub>14</sub> H <sub>11</sub> NO <sub>3</sub>	242.0812 (+)	11.84	Dye intermediate										
Benzanilide 	C <sub>13</sub> H <sub>11</sub> NO	196.0768 (-)	11.87	Used in dye making										
4-Nitrophenyl benzoate 	C <sub>13</sub> H <sub>9</sub> NO <sub>4</sub>	244.0604 (+)	11.77	—										

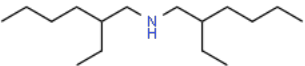
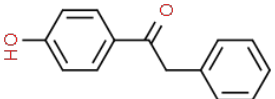

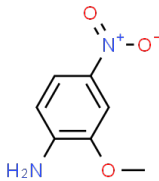


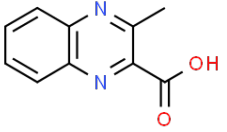
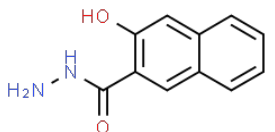
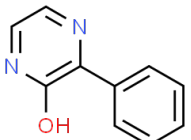
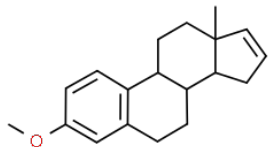
Component Name & Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Description	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
5,6a-Dihydronaphtho[2,1,8,7-klmn]xanthene 	C <sub>18</sub> H <sub>10</sub> O	243.0803 (+)	19.18	—										
Naphthanthrone 	C <sub>19</sub> H <sub>10</sub> O	255.0803 (+)	20.14	—										
7-Hydroxymethyl-12-methylbenz[a]anthracene 	C <sub>20</sub> H <sub>16</sub> O	273.1272 (+)	20.61	—										
Benzo[k]tetraphen-5-ol 	C <sub>22</sub> H <sub>14</sub> O	295.1114 (+)	22.59	—										

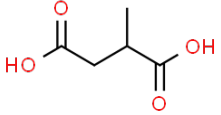
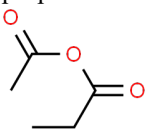
Component Name & Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Description	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
—	C <sub>15</sub> H <sub>10</sub> N <sub>4</sub> O <sub>5</sub>	325.0651 (-)	17.84	—										
—	C <sub>20</sub> H <sub>13</sub> N <sub>3</sub> O <sub>3</sub>	344.1030 (+)	19.33	—										
—	C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> O <sub>9</sub>	405.0917 (+)	19.33	—										
—	C <sub>33</sub> H <sub>24</sub> N <sub>4</sub> O <sub>11</sub>	653.1485 (+)	19.34	—										
2-(2-Phenylquinoline-4-carboxamido) benzoic acid 	C <sub>23</sub> H <sub>16</sub> N <sub>2</sub> O <sub>3</sub>	367.1103 (-)	21.49	—										

Component Name & Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Description	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
Dihexyl phthalate 	C <sub>20</sub> H <sub>30</sub> O <sub>4</sub>	335.2215 (+)	22.82	Used in textiles (vinyl upholstery); primarily used to soften PVC										
Resorcinol 	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	111.0441 (+)	5.37	Used in plastic production										
Reticulol 	C <sub>11</sub> H <sub>10</sub> O <sub>5</sub>	223.0599 (+)	8.10	—										
2-(2-hydroxyethoxycarbonyl) benzoic acid 	C <sub>10</sub> H <sub>10</sub> O <sub>5</sub>	211.0603 (+)	8.66	Patented for resins (aqueous resin composition, coating film), used in methods for forming multilayer coating films and adhesives										

Component Name & Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Description	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
10–Undecenoic acid 	C <sub>11</sub> H <sub>20</sub> O <sub>2</sub>	189.1854 (+)	13.40	Used as a precursor in the manufacture of polymers										
11–Hydroxyundecanoic acid 	C <sub>11</sub> H <sub>22</sub> O <sub>3</sub>	201.1497 (-)	13.39	Used in the production of resins										
10–Undecenoic acid 	C <sub>11</sub> H <sub>20</sub> O <sub>2</sub>	189.1854 (+)	13.40	Used as a precursor in the manufacture of polymers										
2–[2–(2–Ethoxyethoxy)ethoxy]ethanol 	C <sub>8</sub> H <sub>18</sub> O <sub>4</sub>	179.1279 (+)	7.46	Used in the production of paints, plastics, and films										
7,8–Dihydroyangonin 	C <sub>15</sub> H <sub>16</sub> O <sub>4</sub>	259.0977 (-)	14.55	Patented as a preservative										

Component Name & Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Description	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
Bis(2-ethylhexyl) amine 	C <sub>16</sub> H <sub>35</sub> N	242.2840 (+)	18.09	Patented as a modified epoxy resin										
1-(4-hydroxyphenyl)-2-phenylethan-1-one 	C <sub>14</sub> H <sub>12</sub> O <sub>2</sub>	213.0913 (+)	14.41	Patented as a plasticizer										
Laurixamine 	C <sub>15</sub> H <sub>33</sub> NO	244.2635 (+)	15.64	Used in the production of polymers and metallic pigments										
—	C <sub>19</sub> H <sub>35</sub> NO <sub>5</sub>	356.2456 (-)	16.57	—										
—	C <sub>19</sub> H <sub>38</sub> N <sub>2</sub> O	311.3070 (+)	24.75	—										
4-Nitro-o-anisidine 	C <sub>7</sub> H <sub>8</sub> N <sub>2</sub> O <sub>3</sub>	167.0463 (-)	5.75	—										

Component Name & Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Description	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
3-Methyl-2-Quinoxalinecarboxylic Acid 	C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> O <sub>2</sub>	187.0515 (-)	8.83	Acute toxicity; eye irritant										
3-Hydroxy-2-naphthohydrazide 	C <sub>11</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub>	201.0671 (-)	9.22	Epoxy resin for fiber-reinforced composite materials										
3-Phenyl-2-pyrazinol 	C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> O	173.0713 (+)	10.37	—										
3-Methoxyestra-1,3,5(10),16-tetraene 	C <sub>19</sub> H <sub>24</sub> O	269.1901 (+)	22.46	—										

Component Name & Structure	Neutral Molecular Formula	Observed <i>m/z</i> and ESI mode detected	LC Retention Time (min)	Description	Carpet OA	Thin PVC Wire OA	Vinyl Flooring OA	Fabric OA	Plywood OA	Ceiling Tile OA	Thick PVC Wire OA	Drywall OA	Fiberboard OA	Lumber OA
Methylsuccinic acid 	C <sub>5</sub> H <sub>8</sub> O <sub>4</sub>	131.0352 (-)	3.21	—										
—	C <sub>8</sub> H <sub>16</sub> N <sub>2</sub> O <sub>2</sub>	173.1288 (+)	5.55	—										
—	C <sub>7</sub> H <sub>11</sub> NO <sub>2</sub>	142.0867 (+)	5.86	—										
Acetic propanoic anhydride 	C <sub>5</sub> H <sub>8</sub> O <sub>3</sub>	117.0549 (+)	10.61	—										
—	C <sub>12</sub> H <sub>18</sub> O <sub>6</sub>	259.1177 (+)	13.41	—										

## References

- (1) Hopstock, K. S.; Klodt, A. L.; Xie, Q.; Alvarado, M. A.; Laskin, A.; Nizkorodov, S. A. Photolytic Aging of Organic Aerosol from Pyrolyzed Urban Materials. *Environ. Sci.: Atmos.* **2023**, *3* (9), 1272–1285. <https://doi.org/10.1039/D3EA00078H>.
- (2) Madronich, S. *ACOM: Quick TUV calculator, National Center for Atmospheric Research Atmospheric Chemistry Observations and Modeling [code]*. [https://www.acom.ucar.edu/Models/TUV/Interactive\\_TUV/](https://www.acom.ucar.edu/Models/TUV/Interactive_TUV/) (accessed 2022-11-03).
- (3) Lin, P.; Fleming, L. T.; Nizkorodov, S. A.; Laskin, J.; Laskin, A. Comprehensive Molecular Characterization of Atmospheric Brown Carbon by High Resolution Mass Spectrometry with Electrospray and Atmospheric Pressure Photoionization. *Anal. Chem.* **2018**, *90* (21), 12493–12502. <https://doi.org/10.1021/acs.analchem.8b02177>.
- (4) Hettiyadura, A. P. S.; Garcia, V.; Li, C.; West, C. P.; Tomlin, J.; He, Q.; Rudich, Y.; Laskin, A. Chemical Composition and Molecular-Specific Optical Properties of Atmospheric Brown Carbon Associated with Biomass Burning. *Environ. Sci. Technol.* **2021**, *55* (4), 2511–2521. <https://doi.org/10.1021/acs.est.0c05883>.
- (5) Siemens, K.; Morales, A.; He, Q.; Li, C.; Hettiyadura, A. P. S.; Rudich, Y.; Laskin, A. Molecular Analysis of Secondary Brown Carbon Produced from the Photooxidation of Naphthalene. *Environ. Sci. Technol.* **2022**, *56* (6), 3340–3353. <https://doi.org/10.1021/acs.est.1c03135>.
- (6) Schmid, R.; Heuckeroth, S.; Korf, A.; Smirnov, A.; Myers, O.; Dyrland, T. S.; Bushuiev, R.; Murray, K. J.; Hoffmann, N.; Lu, M.; Sarvepalli, A.; Zhang, Z.; Fleischauer, M.; Dührkop, K.; Wesner, M.; Hoogstra, S. J.; Rudt, E.; Mokshyna, O.; Brungs, C.; Ponomarov, K.; Mutabdzija, L.; Damiani, T.; Pudney, C. J.; Earll, M.; Helmer, P. O.; Fallon, T. R.; Schulze, T.; Rivas-Ubach, A.; Bilbao, A.; Richter, H.; Nothias, L.-F.; Wang, M.; Orešič, M.; Weng, J.-K.; Böcker, S.; Jeibmann, A.; Hayen, H.; Karst, U.; Dorrestein, P. C.; Petras, D.; Du, X.; Pluskal, T. Integrative Analysis of Multimodal Mass Spectrometry Data in MZmine 3. *Nat Biotechnol* **2023**, *41* (4), 447–449. <https://doi.org/10.1038/s41587-023-01690-2>.
- (7) Fleming, L. T.; Lin, P.; Laskin, A.; Laskin, J.; Weltman, R.; Edwards, R. D.; Arora, N. K.; Yadav, A.; Meinardi, S.; Blake, D. R.; Pillarisetti, A.; Smith, K. R.; Nizkorodov, S. A. Molecular Composition of Particulate Matter Emissions from Dung and Brushwood Burning Household Cookstoves in Haryana, India. *Atmos. Chem. Phys.* **2018**, *18* (4), 2461–2480. <https://doi.org/10.5194/acp-18-2461-2018>.
- (8) Nizkorodov, S. A.; Laskin, J.; Laskin, A. Molecular Chemistry of Organic Aerosols through the Application of High Resolution Mass Spectrometry. *Phys. Chem. Chem. Phys.* **2011**, *13* (9), 3612. <https://doi.org/10.1039/c0cp02032j>.
- (9) Moschos, V.; Christensen, C.; Mouton, M.; Fiddler, M. N.; Isolabella, T.; Mazzei, F.; Massabò, D.; Turpin, B. J.; Bililign, S.; Surratt, J. D. Quantifying the Light-Absorption Properties and Molecular Composition of Brown Carbon Aerosol from Sub-Saharan African Biomass Combustion. *Environ. Sci. Technol.* **2024**, *58* (9), 4268–4280. <https://doi.org/10.1021/acs.est.3c09378>.