Electronic Supplementary Material (ESI) for Environmental Science: Atmospheres.

Supporting Information

Photolytic aging of organic aerosol from pyrolyzed urban materials

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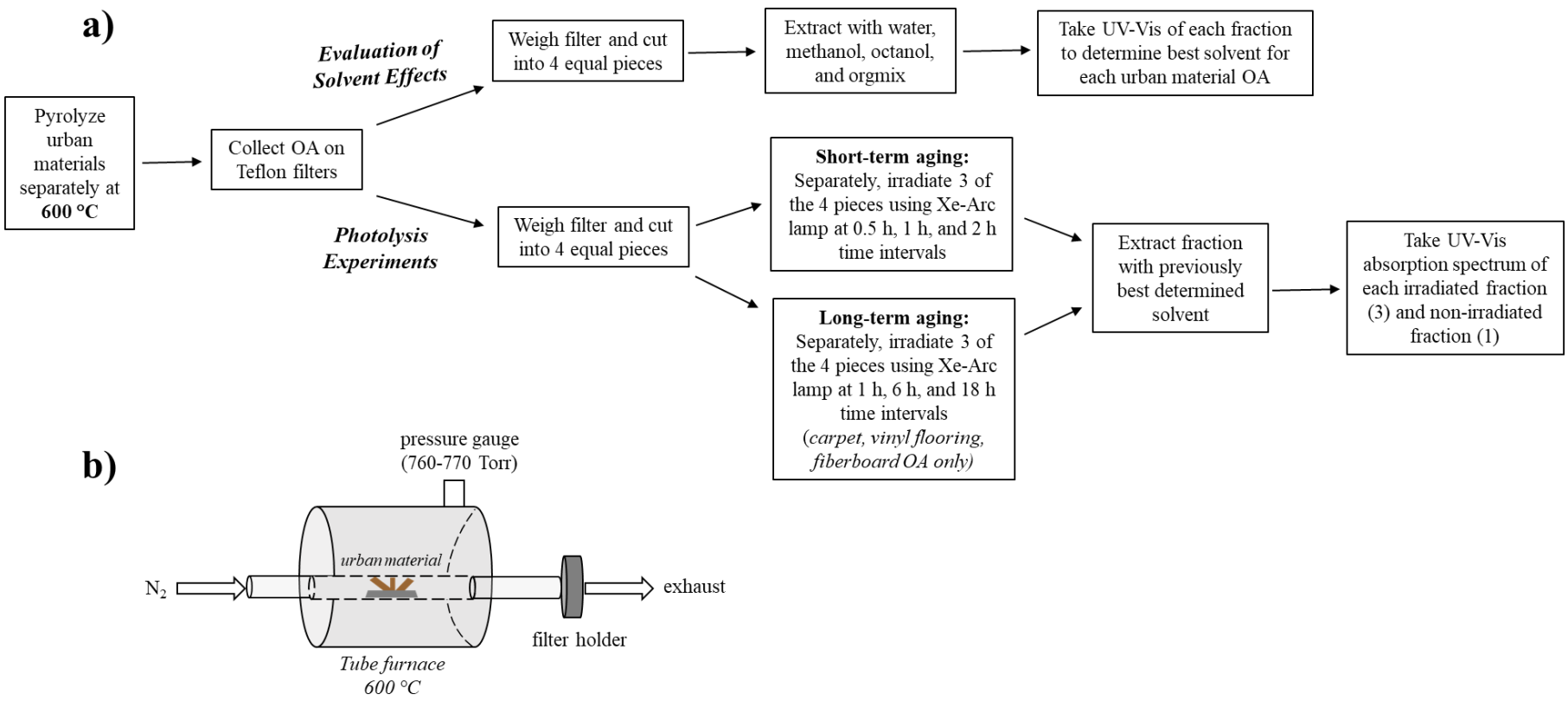
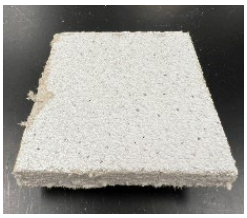
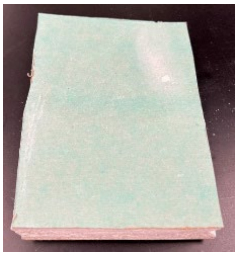
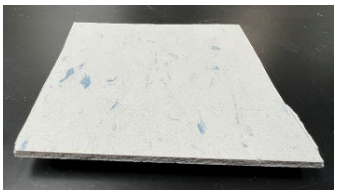


Scheme S1. Experimental flowchart (a) for pyrolysis experiments conducted with all ten urban materials (separately). Organic aerosol generated through pyrolysis is labeled as "OA". All OA samples were generated in a tube furnace at 600 °C under N_2 (b). First, experiments were conducted by collecting on Teflon filters (top arrow). An evaluation of solvent effects was performed to determine the best solvent for extraction, as each material yielded OA with unknown composition. Each filter was cut into four equal pieces, and each was extracted in a different solvent: water, methanol, octanol, and orgmix (acetonitrile/dichloromethane/hexane 2:2:1 by volume). UV-vis absorption spectra were utilized to determine which solvent was best suited per material. Photolysis experiments (downward arrow) were conducted on separately collected OA. Similar to the solvent investigations, each filter was cut into quarters and irradiated with various times (short-term aging and long-term aging). Subsequent extraction and UV-Vis absorption measurements were utilized to determine how irradiated fractions differed from the non-irradiated fraction. A schematic of the laboratory pyrolysis setup is shown in panel b.

Table S1. Summary of urban materials pyrolyzed in this study. All pyrolysis runs were conducted at 600 °C unless noted otherwise. All values are reported as the average amongst three replicates with uncertainty values reported to one standard deviation. Emission factors (from Teflon filter collection experiments) are reported in the units of grams of collected OA per kilogram of urban material utilized in pyrolysis. Approximately 200 mg of urban material was pyrolyzed in each experiment. Carpet pyrolyzed at 800 and 1000 ° C were only tested once (no uncertainty values reported). Best extraction solvent was determined based on greatest overall absorbance and expression of spectral features (**Figure S3)**.

Urban Material	**Picture of Urban Material & Description of material**	**Average mass collected (mg)**	**Average emission factor ($g\ kg^{-1}$)**	**Best extraction solvent**
Electrical 12 AWG wire (white PVC coating)	 Flexible PVC coated 12 AWG copper wires. The PVC acts as electrical cable insulation. It is stable under 70 °C.	2.0 ± 0.5	1.3 ± 0.4	Orgmix
Ceiling Tile	 Used in commercial suspended ceilings. Composed of a combination of mineral wool, fiberglass, gypsum, perlite, clay, cellulose, and starch. Many of these components (except mineral wool, perlite, and clay) have melting points or thermally degrade at temperatures less than 600 °C.	5.1 ± 1.8	9.0 ± 3.6	Orgmix
Fabric		3.1 ± 1.4	16 ± 2	Orgmix

	Commonly present in furniture, clothing, and linens. Combustible at temperatures greater than 300 °C.			
Electrical 23 AWG wire (purple PVC coating)	 Flexible PVC coated 23 AWG copper wires. The PVC acts as electrical cable insulation. It is stable under 70 °C. Purple dye pigment composition is unknown.	3.1 ± 1.1	13 ± 6	Orgmix
Lumber	 Commonly used for construction framing and finishings (in floors, wall panels, and window frames). Combustible and thermally degrades at temperatures greater than 370 °C.	11 ± 6	47 ± 15	Octanol *(used orgmix for photolysis experiments)*
Drywall	 Commonly used to create walls and ceilings in construction. Combustible and thermally degrades at temperatures greater than 250 °C.	1.5 ± 0.8	1.0 ± 0.3	Orgmix

Fiberboard	 Commonly used as a wood alternative in walls, door boards, floor, and furniture. Combustible at temperatures greater than 220 °C.	3.1 ± 0.6	6.0 ± 0.9	Methanol
Vinyl Flooring	 Commonly used as flooring in kitchens, bathrooms, and industrial settings, as it is water resistant. Made of PVC plastic pieces and resin that re heated/pressed into thin layers on top of a fibrous backing. Breaks down at temperatures greater than 70 °C.	3.0 ± 0.5	13 ± 4	Octanol *(used orgmix for photolysis experiments)*
Plywood	 Commonly used as a pure wood alternative in flooring, cabinets, shelving, and furniture. It is made of 3 or more layers of wood veneer. Thermal degradation begins at 110 °C.	8.8 ± 0.6	37 ± 9	Orgmix

Carpet		6.9 ± 1.2	30 ± 4	Methanol
Carpet pyrolyzed at 800 °C (1 trial)		9.8	41	Methanol **poor solubility*
Carpet pyrolyzed at 1000 °C (1 trial)	Carpet is composed of nylon and polyester fibers secured to a rubber latex backing. Melting occurs at temperatures greater than 270 °C.	20.1	67	Methanol **poor solubility*

Figure S1. Sample photographs of filters containing organic aerosol (OA) generated through the pyrolysis of ten urban materials at 600 °C under N_2. The OA differed in appearance amongst urban materials.

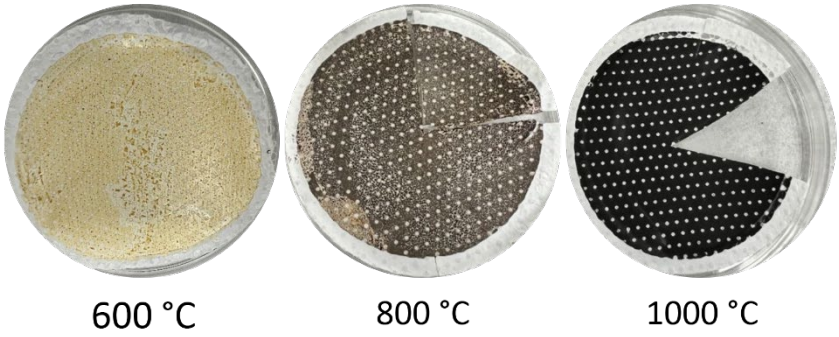


Figure S2. Sample photographs of filters containing OA generated through the pyrolysis of carpet at 600, 800, and 1000 °C under N_2. Pyrolysis temperatures greater than 600 °C yielded OA that was poorly soluble due to presence of black carbon (BC).

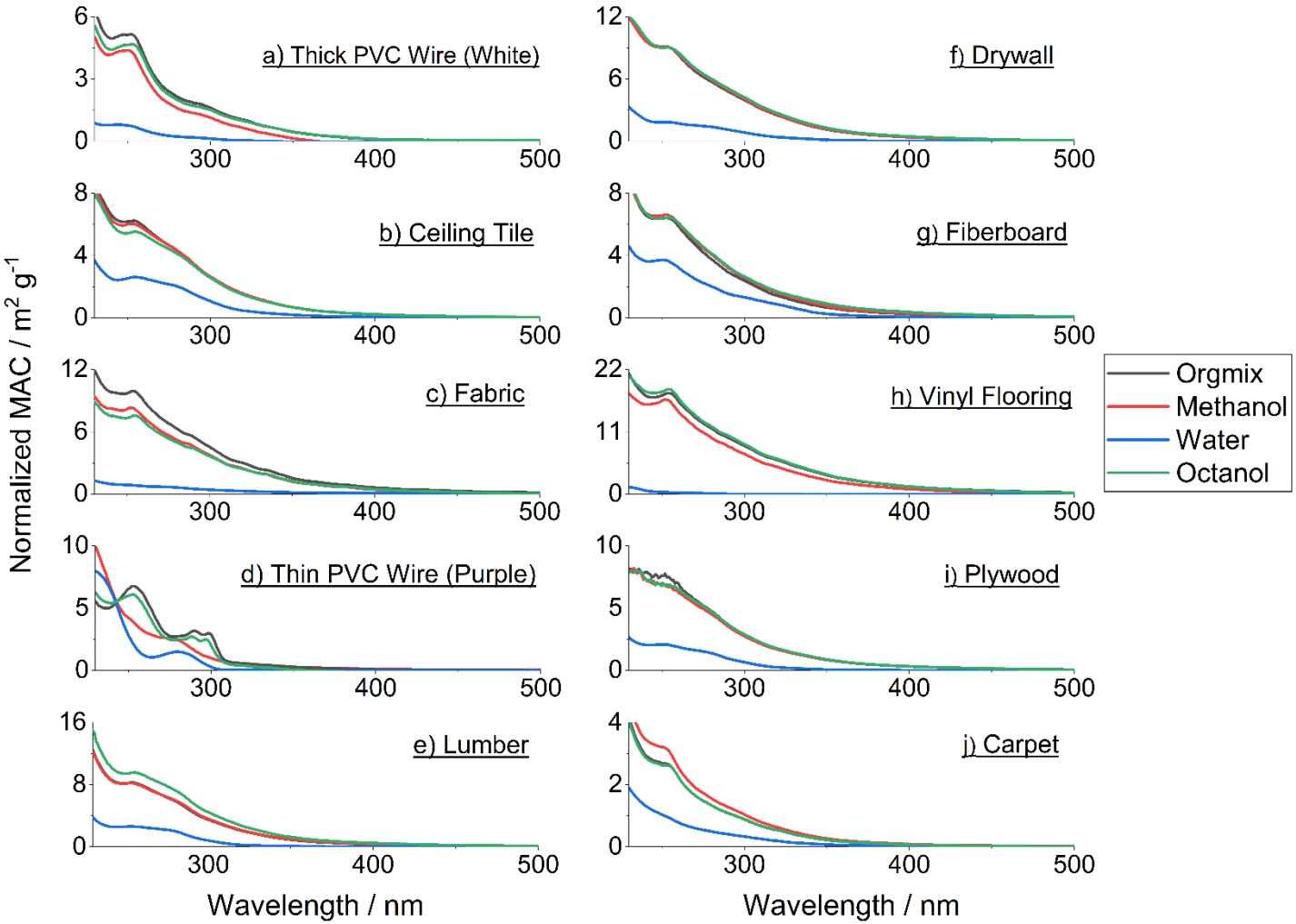


Figure S3. UV-Vis absorption spectra recorded after the pyrolysis of urban materials (a-j) and extraction in orgmix (grey), methanol (red), water (blue), and n-octanol (green). The *MAC* values assume complete extraction of OA from the filter. The lowest *MAC* observed for water indicates that it does not extract the OA fully and is the least effective solvent tested for all materials. Plywood extracts were diluted by a factor of ten for absorbance measurements.

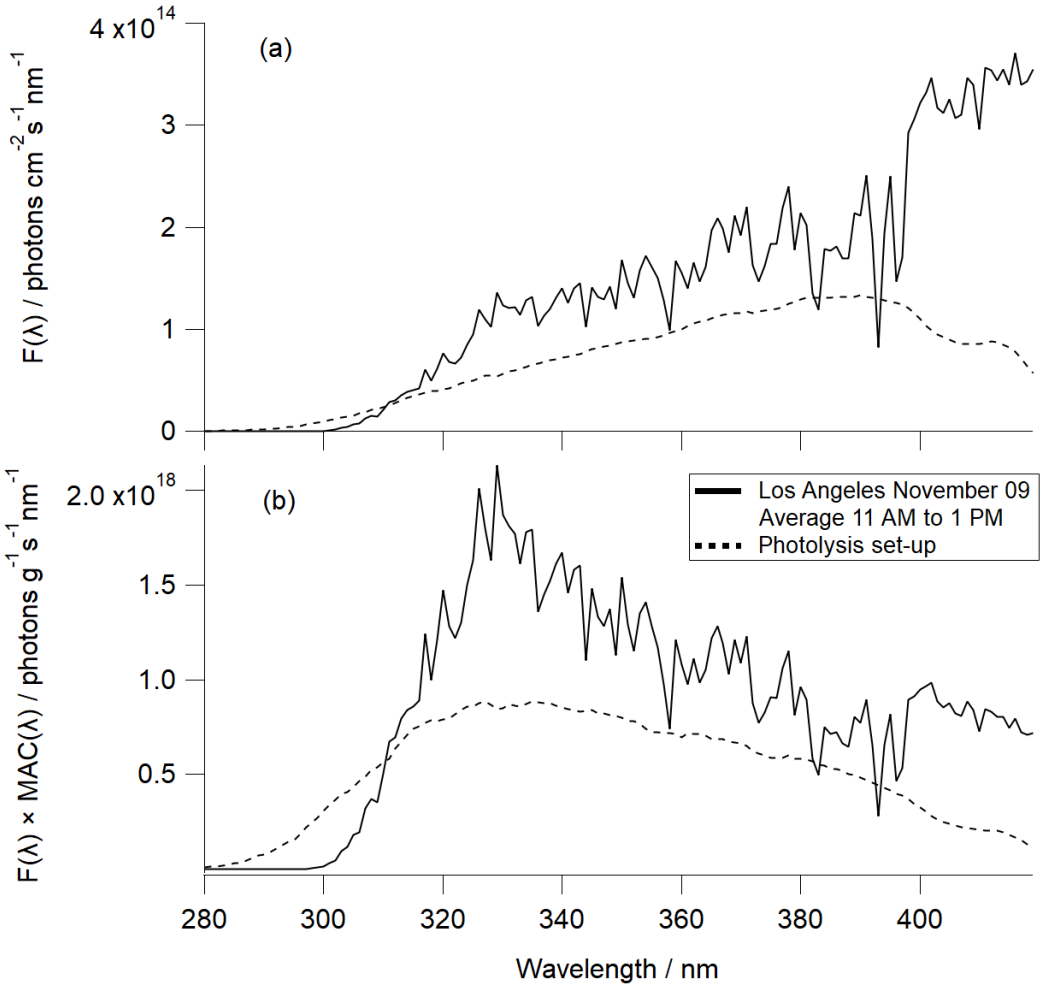


Figure S4. The spectral photon flux density (*F(λ)*) over the actinic range of the Xenon arc lamp used in laboratory photolysis experiments (dashed line) compared to the averaged solar spectrum in Los Angeles, California (Latitude/Longitude: 34°/118°) for November 9th between the hours of 11 AM to 1 PM (solid line). Panel (a) shows *F(λ)* as a function of wavelength. Panel (b) shows a product of spectral photon flux density and the mass absorption coefficient average across all 10 unaged urban OA ($F(\lambda) \times MAC_{average}$), which better illustrates the wavelength at which photolysis is taking place. The "Quick TUV" calculator [Madronich, S. ACOM: Quick TUV https://www.acom.ucar.edu/Models/TUV/Interactive_TUV/ (accessed November 03, 2022)] was used to estimate the spectral flux densities. The parameters used in the Quick TUV calculator were:

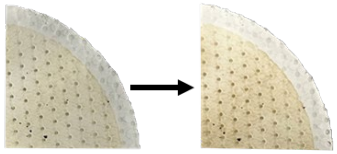
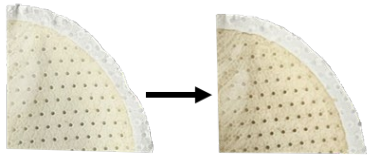
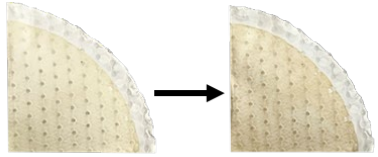
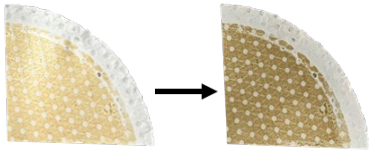
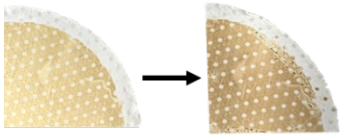
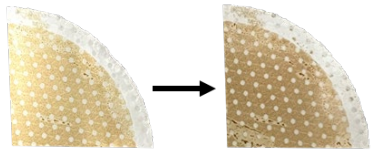
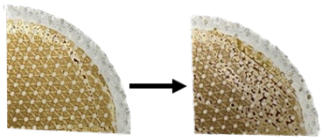
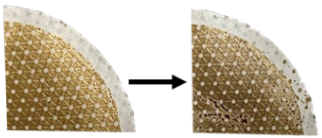
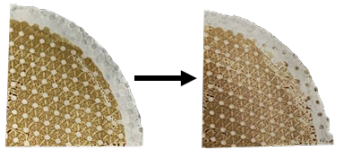
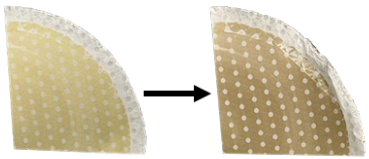
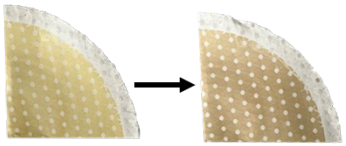
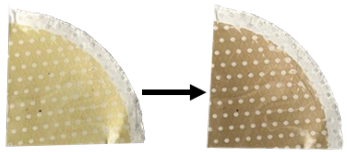
-Latitude/Longitude: 34°N 118°W
-Date and Time: November 9, 2022
-Overhead Ozone: 300 du
-Surface Albedo: 0.1
-Ground Altitude: 0 km
-Measured Altitude: 0 km
-Clouds Optical Depth/Base/Top: 0:00/4.00/5.00
-Aerosols Optical Depth/S-S Albedo/Alpha: 0.235/0.990/1.000

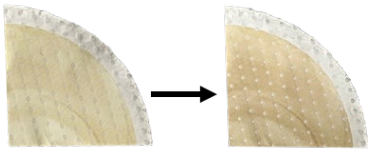
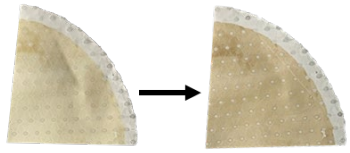
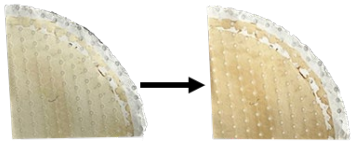
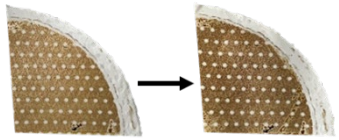
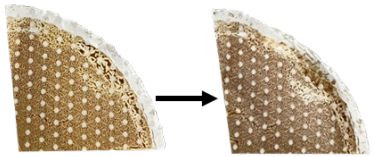
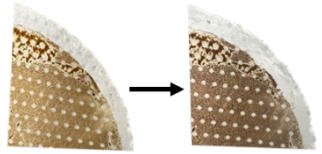
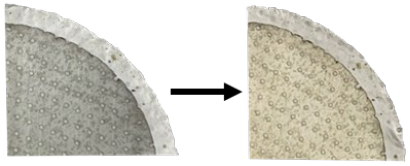
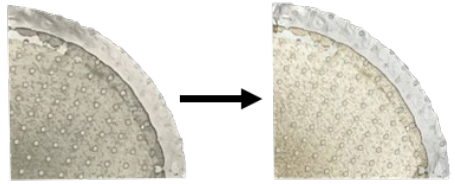
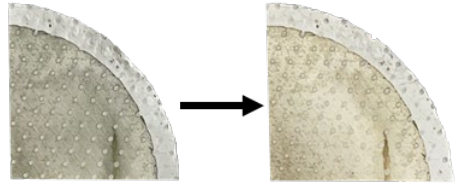
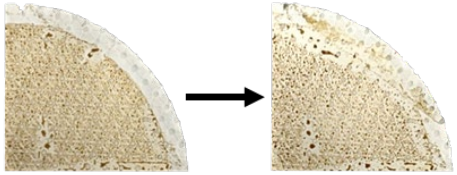
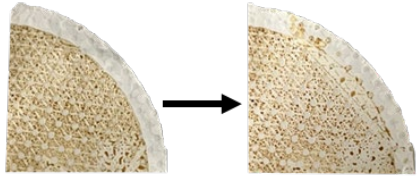
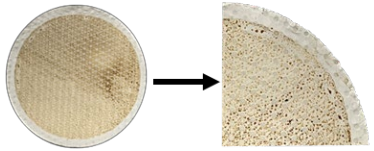
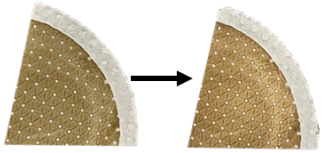
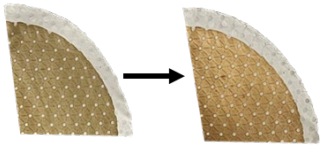
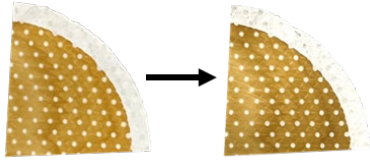
-Sunlight Direct Beam/Diffuse Down/Diffuse Up: 1.0/1.0/0.0
-4 Streams Transfer Model

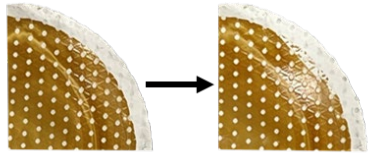
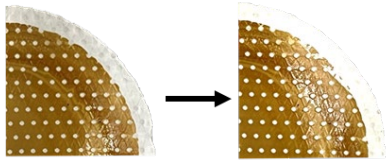
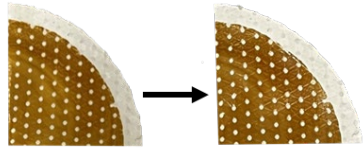
Table S2. The integrated photon flux and the number of hours equivalent to one hour under the laboratory photolysis set-up for the 2 h average solar flux in Los Angeles (11 AM to 1 PM) on November 9, 2022. The value in the last column represents the ratio of the solar integrated flux to the UV lamp's integrated flux.

Wavelength range of comparison	**Integrated *F(λ)* x *MAC(λ)* from the UV lamp (photons g^{-1} s^{-1})**	**Integrated *F(λ)* x *MAC(λ)* from the 2 h average sunlight in Los Angeles (photons cm^{-2} s^{-1})**	**One hour under lamp is equivalent to _ h under sunlight in Los Angeles at time specified:**
Full UV (280-400 nm)	6.91×10^{19}	1.05×10^{20}	0.7

Table S3. Pictures of OA collected on Teflon filters and irradiated with UV light for 0.5 h, 1 h, and 2 h. Each column has a picture of the quarter of the filter prior to photolysis then, after the arrow, a picture of the same quarter after the specified irradiation time. Visually, three classifications can be made: 1) OA darkened after irradiation, 2) OA bleached after irradiation, and 3) OA remained unchanged. These results are correlated with trends observed in the UV-Vis absorption spectra. The factor of change in the normalized, integrated *MAC* values (400-700 nm) are reported after the urban material name. Note that fabric unaged to 2 h pictures are from a separate filter trial than the two previous time increments but, nevertheless, show the same trend.

Urban Material	**Unaged (0 h)**	**Unaged (0 h) → 0.5 h**	**Unaged (0 h) → 1 h**	**Unaged (0 h) → 2 h**
1) Photoenhancement: OA darkened with 2 h irradiation				
Thick PVC Wire (white) 1.8x increase				
Ceiling Tile 1.6x increase				
Lumber 5.5x increase				
Drywall 2.8x increase				

Fiberboard 3.0x increase				
Plywood 1.5x increase				
2) Photobleaching: OA bleached with 2 h irradiation				
Thin PVC Wire (purple) 1.2x decrease				
Carpet 1.5x decrease				
3) OA remained unchanged after 2 h irradiation				
Fabric 1.0x decrease				

Vinyl Flooring 1.0x decrease				

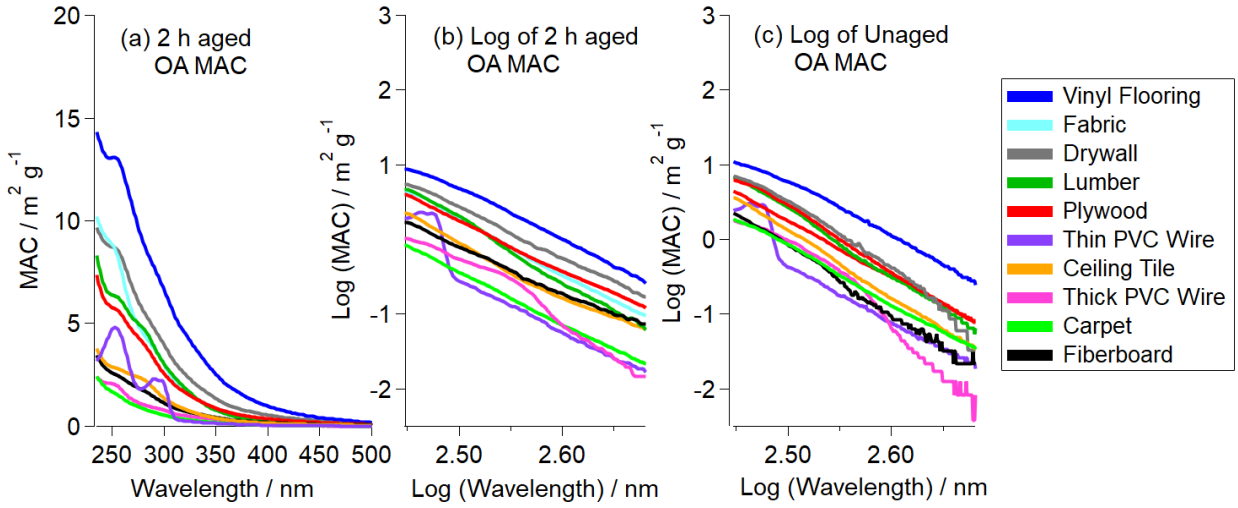


Figure S5. Panel (a) shows the wavelength-dependent *MAC* values recorded after pyrolysis of urban materials, photolytic aging for 2h, and extraction in the best-suited organic solvent (**Table S1 and Figure S3**). *MAC* values were calculated assuming 100% extraction efficiency from the Teflon filter. Panels (b) and (c) show log-log plots of the 2h aged OA *MAC* and unaged OA *MAC*, respectively, as a function of wavelength. The effective *AAE*, shown in **Figure 1b** of the manuscript, were obtained from the linear fits of these spectra in the 280-480 nm range. The linear trendlines are not shown in panels (b) and (c) for simplicity. Boxcar averaging of the *MAC* data (over 5 nm range) was utilized to improve signal-to-noise ratio.

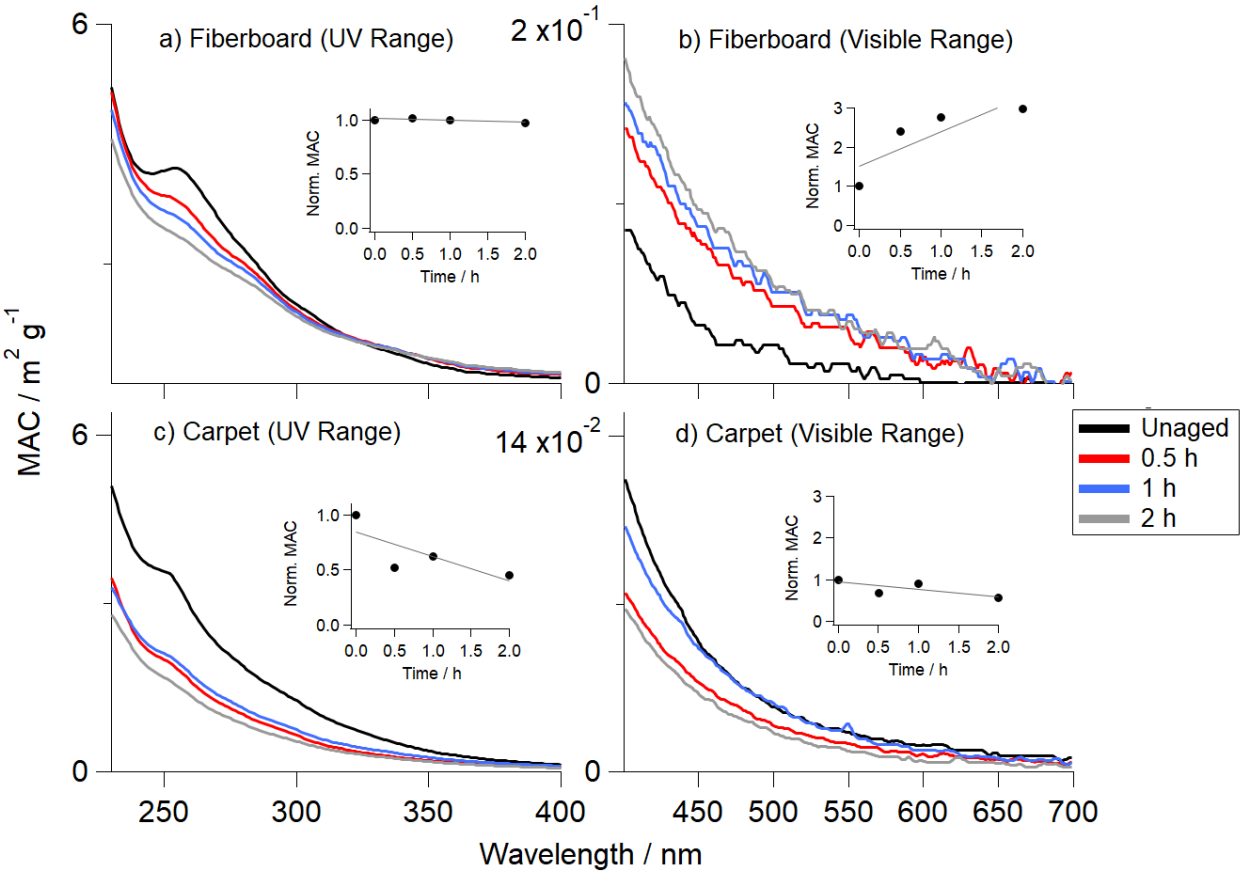


Figure S6. Wavelength-dependent mass absorption coefficient (*MAC*) values recorded after photolysis on Teflon filters and the subsequent extractions of fiberboard OA (a and b) and carpet OA (c and d). Each quarter of the filter was aged separately for 0.5 h (red), 1 h (blue), or 2 h (grey) and is compared with the unaged fraction (black). The integrated *MAC* values (normalized to the unaged value) are shown as a subplot in each panel, with the UV integrated over 280-400 nm and the visible integrated over 400-700 nm. Boxcar averaging of the *MAC* data (over 5 nm range) was utilized to improve signal-to-noise ratio.

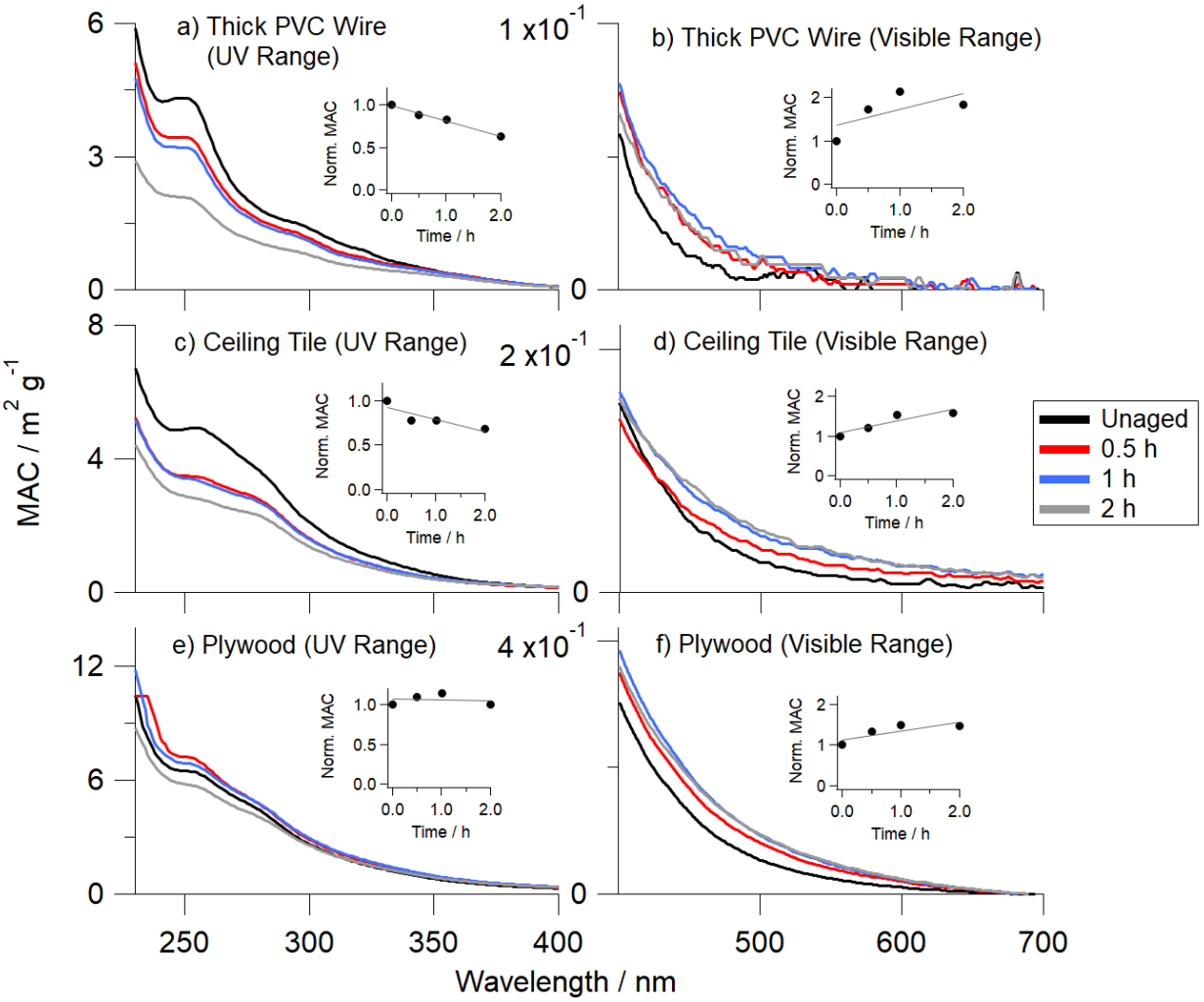


Figure S7. Wavelength-dependent mass absorption coefficient (*MAC*) values recorded after photolysis on Teflon filters and the subsequent extractions of thick PVC wire OA (a and b), ceiling tile OA (c and d), and plywood OA (e and f). Each quarter of the filter was aged separately for 0.5 h (red), 1 h (blue), or 2 h (grey) and is compared with the unaged fraction (black). The integrated *MAC* values (normalized to the unaged value) are shown as a subplot in each panel, with the UV integrated over 280-400 nm and the visible integrated over 400-700 nm. Boxcar averaging of the *MAC* data (over 5 nm range) was utilized to improve signal-to-noise ratio.

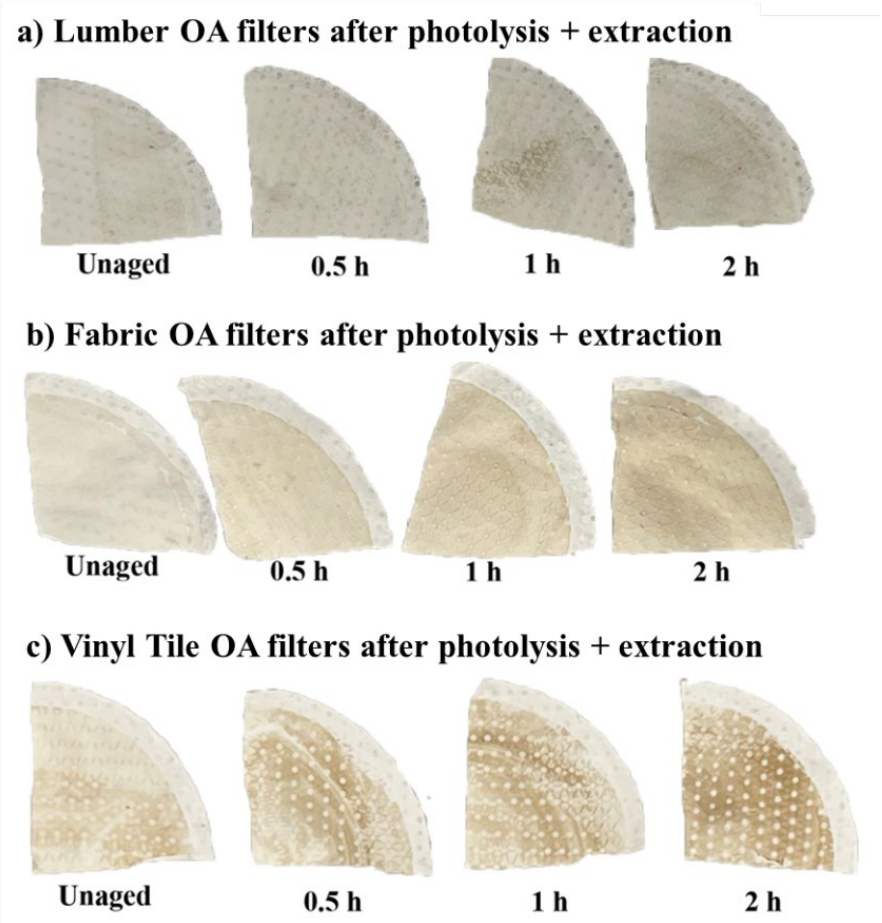
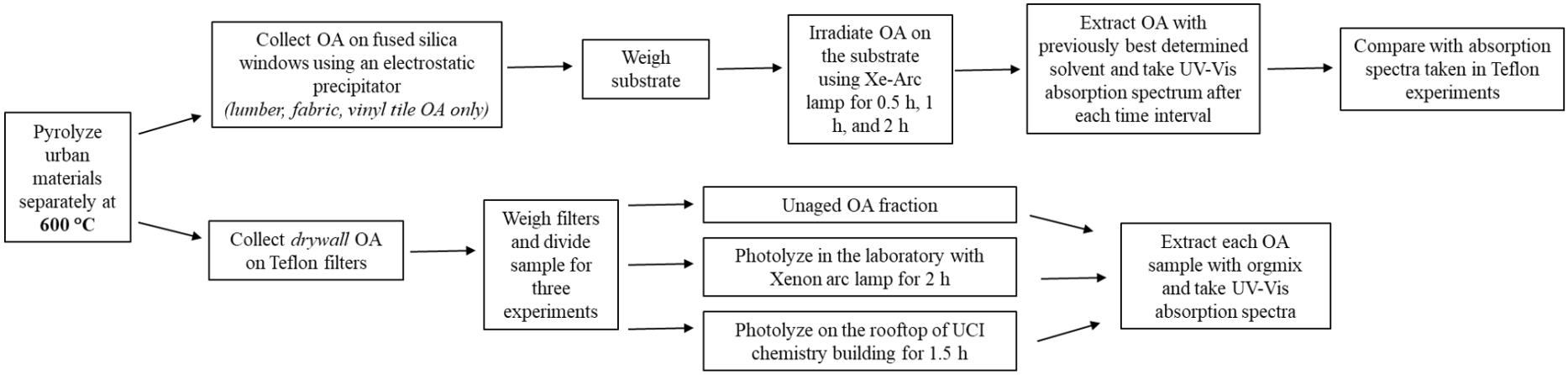


Figure S8. Pictures of Teflon filters after photolysis and subsequent extraction of lumber OA (a), fabric OA (b), and vinyl tile OA (c). Orgmix was used in the extraction of all OA. Only these 3 urban materials left behind residual OA on Teflon filters after extraction.



Scheme S2. For lumber, fabric, and vinyl tile OA, residual material remained embedded in the fibers on the Teflon filters after photolysis and extraction. To reconcile this, experiments were conducted on fused silica windows (top arrow). This method allowed for photolysis to be conducted directly on the window surfaces, and after that subsequent extraction and absorption measurements were taken. Each time point came from a different pyrolysis collection, as each extraction removed all OA from the window. The second set of control experiments (downward arrow) compared photolytic exposure in the lab versus that outside on the rooftop of the UCI chemistry building on November 9, 2022. Spectral flux density calculations concluded that two hours of exposure with the Xenon arc lamp equated to 1.5 hours in the sunlight between hours greatest solar flux in Irvine, CA (11 AM to 1 PM). Drywall OA was generated and exposed to irradiation by sunlight and the Xenon arc lamp. Subsequent extraction and absorption measurements were taken and compared with an unaged drywall OA sample

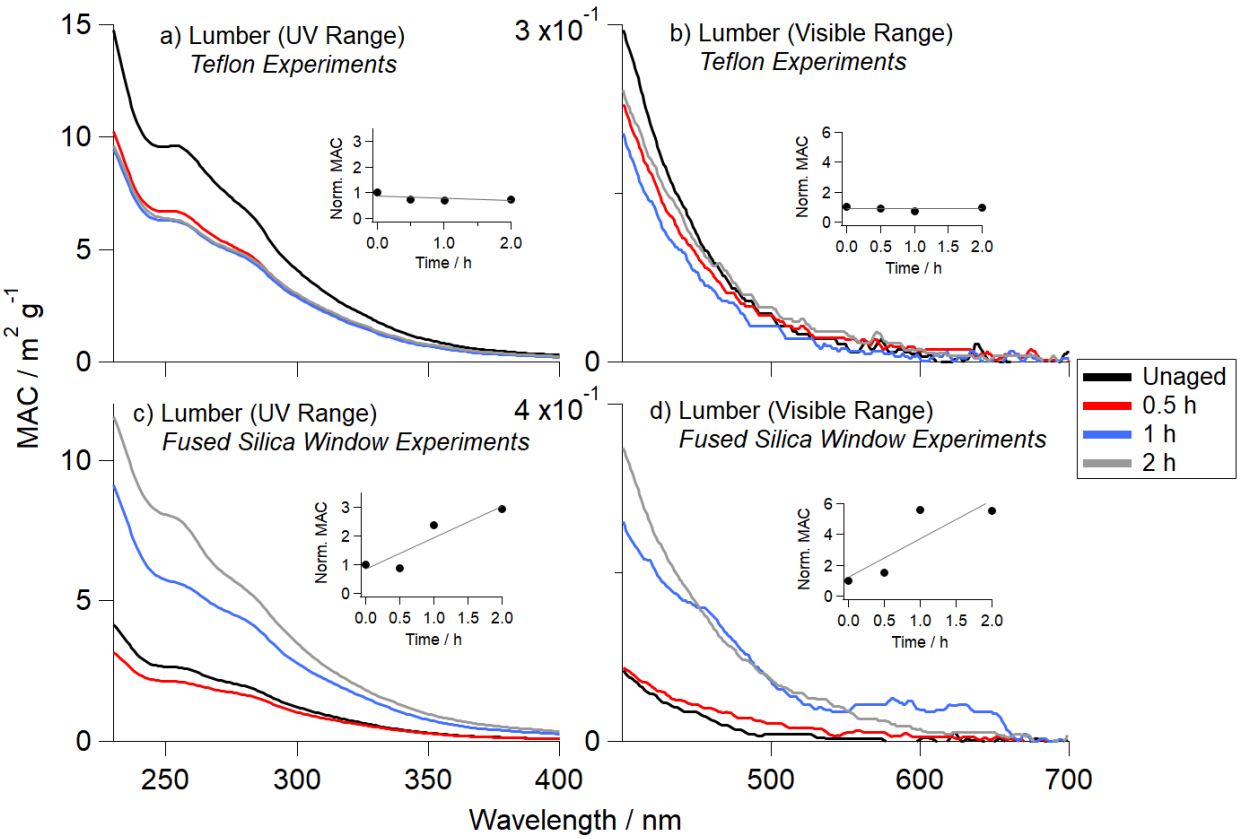


Figure S9. Wavelength-dependent mass absorption coefficient (*MAC*) values recorded after photolysis and subsequent extraction of lumber OA in orgmix. Teflon experimental results are shown in panels a and b. Fused silica window experimental results are shown in panels c and d. Each quarter of the filter was aged separately for 0.5 h (red), 1 h (blue), or 2 h (grey) and is compared with the unaged fraction (black). The integrated *MAC* values (normalized to the unaged value) are shown as a subplot in each panel, with the UV integrated over 280-400 nm and the visible integrated over 400-700 nm. Boxcar averaging of the *MAC* data (over 5 nm range) was utilized to improve signal-to-noise ratio.

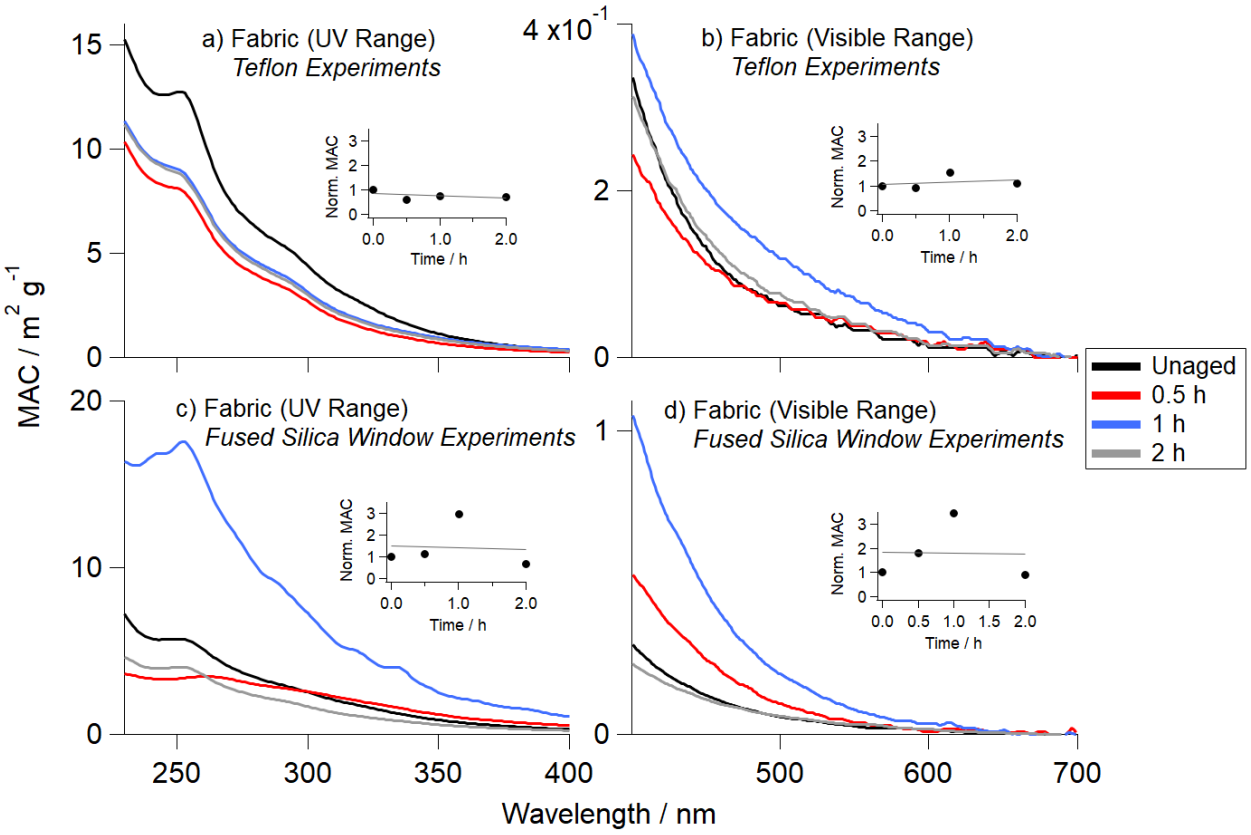


Figure S10. Wavelength-dependent mass absorption coefficient (*MAC*) values recorded after photolysis and subsequent extraction of fabric OA in orgmix. Teflon experimental results are shown in panels a and b. Fused silica window experimental results are shown in panels c and d. Each quarter of the filter was aged separately for 0.5 h (red), 1 h (blue), or 2 h (grey) and is compared with the unaged fraction (black). The integrated *MAC* values (normalized to the unaged value) are shown as a subplot in each panel, with the UV integrated over 280-400 nm and the visible integrated over 400-700 nm. Boxcar averaging of the *MAC* data (over 5 nm range) was utilized to improve signal-to-noise ratio.

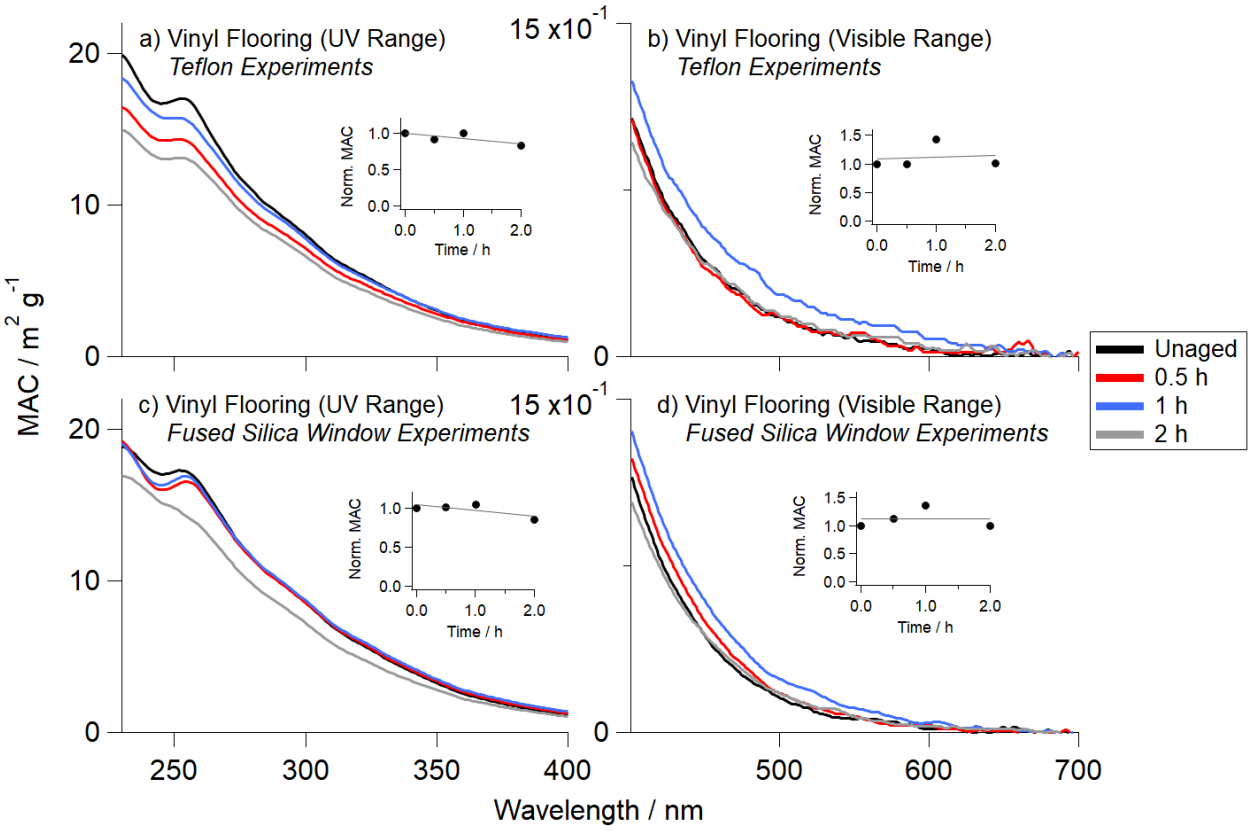


Figure S11. Wavelength-dependent mass absorption coefficient (*MAC*) values recorded after photolysis and subsequent extraction of vinyl tile OA in orgmix. Teflon experimental results are shown in panels a and b. Fused silica window experimental results are shown in panels c and d. Each quarter of the filter was aged separately for 0.5 h (red), 1 h (blue), or 2 h (grey) and is compared with the unaged fraction (black). The integrated *MAC* values (normalized to the unaged value) are shown as a subplot in each panel, with the UV integrated over 280-400 nm and the visible integrated over 400-700 nm. Boxcar averaging of the *MAC* data (over 5 nm range) was utilized to improve signal-to-noise ratio.

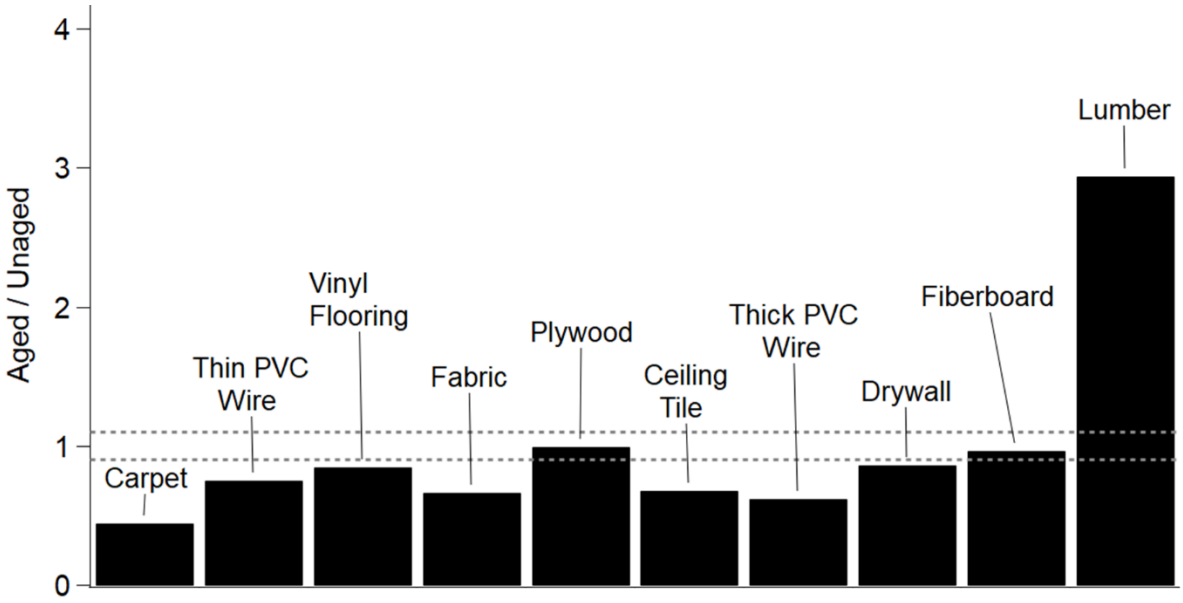


Figure S12. Ratios of the 2 h aged to unaged integrated, UV range *MAC* values. The reported ratios were calculated by integrating the *MAC* values in the UV range (280-400 nm) then referencing the 2 h aged integrated *MAC* value to that of the unaged, integrated *MAC* value. The dashed line (0.9 to 1.1) indicates the threshold for the change.

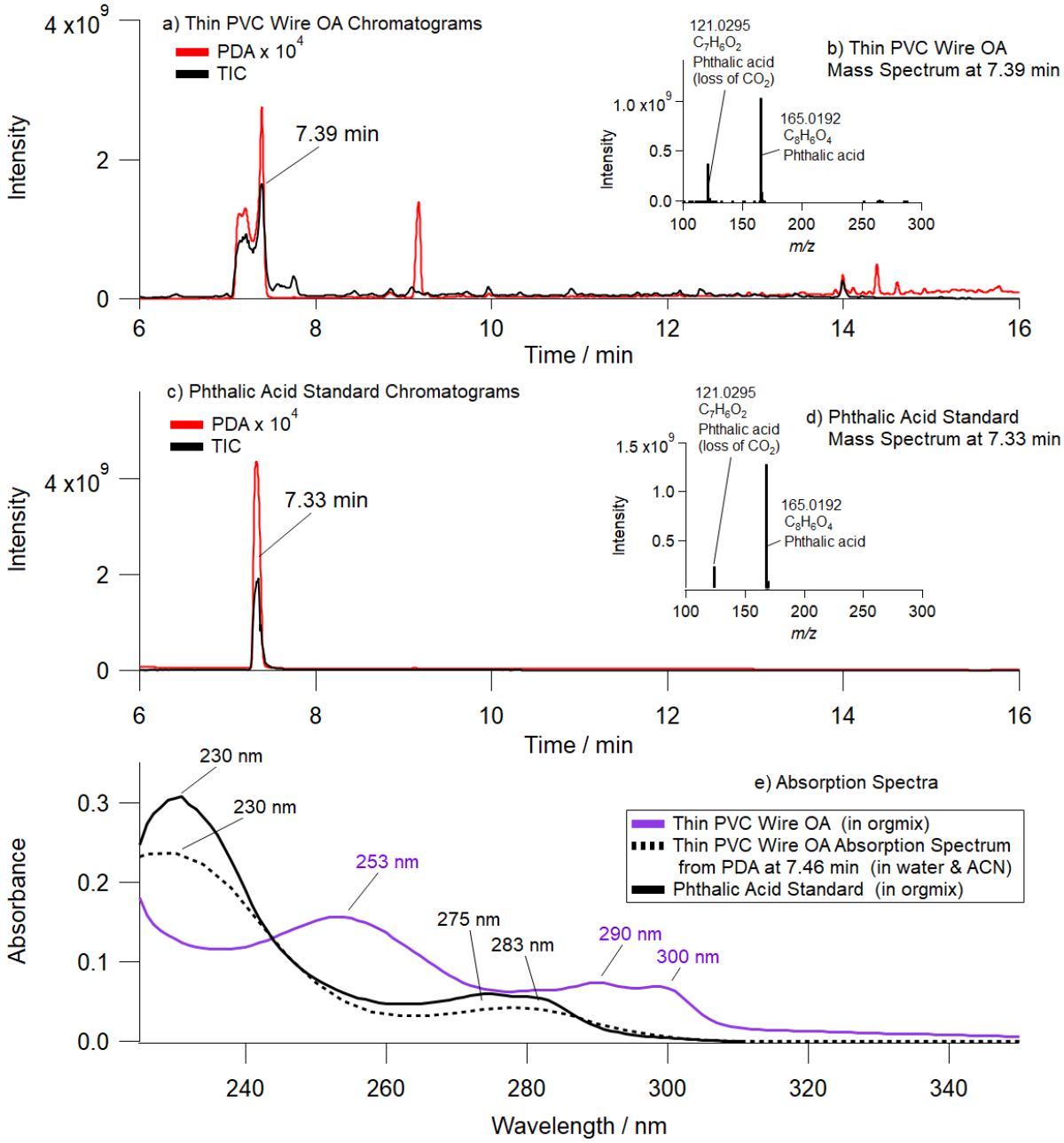


Figure S13. UHPLC-PDA-HRMS data for thin PVC wire OA and phthalic acid standard: a) Thin PVC Wire OA PDA chromatogram (red) and TIC chromatogram (black); b) mass spectrum of thin PVC wire OA at TIC retention time 7.39 min; c) phthalic acid standard PDA chromatogram (red) and TIC chromatogram (black); d) mass spectrum of phthalic acid standard at TIC retention time 7.33 min; e) absorption spectra of thin PVC wire OA (purple, from **Figure 1**), thin PVC wire OA detected by PDA (dashed), and phthalic acid (black). A 0.07 min correction was made to TIC chromatograms to account for the delay time between PDA and Orbitrap detectors. All PDA traces were offset by x10^4 to account for differences in intensity between PDA and Orbitrap detection. Note in panel (c): retention time is slightly earlier than panel (a) due to phthalic acid standard dissolved in water only and not acetonitrile.

Appendix A. Preliminary high-resolution mass spectrometry information.

The chromatograms and mass spectra presented in **Figure S13a-d** were recorded with a Thermo Scientific Vanquish Horizon ultrahigh pressure liquid chromatograph coupled to a Vanquish Horizon photodiode array spectrophotometer and to a Q Exactive Plus high-resolution mass spectrometer (UHPLC-PDA-HRMS) with a resolving power up to 1.4 x 10^5 at *m/z* 200.

The separation was performed on a reverse-phase column (Waters, ACQUITY Premier HSS T3 Column, 2.1 x 150 mm, 1.8 µm particles, and 100 Å pores) with temperature kept at 30 °C and injected volume of 10 µL. The eluent flow was 0.3 mL min^{-1} and consisted of Optima grade water acidified with 0.1 % *v/v* formic acid (eluent A) and Optima grade acetonitrile acidified with 0.1 % *v/v* formic acid (eluent B). The gradient was: 0–3 min 95 % A; 3-14 min linear ramp to 95 % B; 14–16 min hold at 95 % B; 16 min return to 95 % A and hold until 22 min in preparation for the next run. PDA data was collected at 5 Hz over 190-680 nm range with 4 nm effective bandwidth.

Mass spectra were obtained with *m/z* range of 100-1500 in the negative ion mode. The parameters of the heated electrospray ionization (HESI) ion source settings of the Orbitrap were: -2.5 kV spray voltage, 320 °C capillary temperature, 300 °C probe heater temperature, S-Lens ion funnel RF level 30, 50 units of sheath gas (nitrogen) flow, 10 units of auxiliary gas (nitrogen) flow, 1 unit of spare gas (nitrogen) flow.

Thin PVC wire OA (350 µg mL^{-1}) and phthalic acid standard (> 99 %, TCI America, 235 µg mL^{-1}) were run on UHPLC-PDA-HRMS. A 0.07 min delay time (between PDA and Orbitrap detectors) correction was applied to all presented TIC chromatogram traces in **Figure S13**. Thin PVC wire OA's largest PDA/TIC peak at 7.39 min (**Figure S13a**) and the mass spectrum (**Figure S13b**) confirmed that a compound with molecular formula $C_8H_6O_4$ was responsible for light absorption in this sample. $C_8H_6O_4$ was presumed to be phthalic acid and a standard solution was run on HRMS for confirmation. Phthalic acid standard was dissolved in Optima water (with 0.1 % *v/v* formic acid) without any acetonitrile (ACN), as phthalic acid solubility is poor in ACN. This caused a slight shift in the retention time (**Figure S13c**) compared to that of thin PVC OA in **Figure S13a**, which was dissolved in water and ACN for HRMS preparation. The mass spectrum (**Figure S13d**) exhibited the main ion of phthalic acid (*m/z* 165.0192) and fragment of phthalic acid (loss of CO_2, *m/z* 121.0295) was a minor ion at this retention time.

Figure S13e shows the absorption spectrum for thin PVC wire OA (purple trace, **Figure S13e**) as originally presented in **Figure 1** of the manuscript. This spectrum exhibits distinct absorption bands at 253 nm, 290 nm, and 300 nm. Phthalic acid standard was dissolved in orgmix and an absorption measurement was taken using a UV Vis spectrometer (black trace, **Figure S13e)**. Thin PVC wire OA absorption spectrum from the PDA detector of the HRMS (dashed line, **Figure S13e**) and phthalic acid standard solution exhibited the same spectral features at 230 nm, 275 nm, and 283 nm. As these peak wavelengths do not match that of the thin PVC wire OA (purple trace), we conclude that phthalic acid is not the compound responsible for the distinctive absorption in thin PVC wire OA, however, it is responsible for most of the overall sample's absorption in the PDA. Follow up studies on urban OA chemical composition will look further into identifying the compound responsible for absorption bands at 253 nm, 290 nm, and 300 nm.

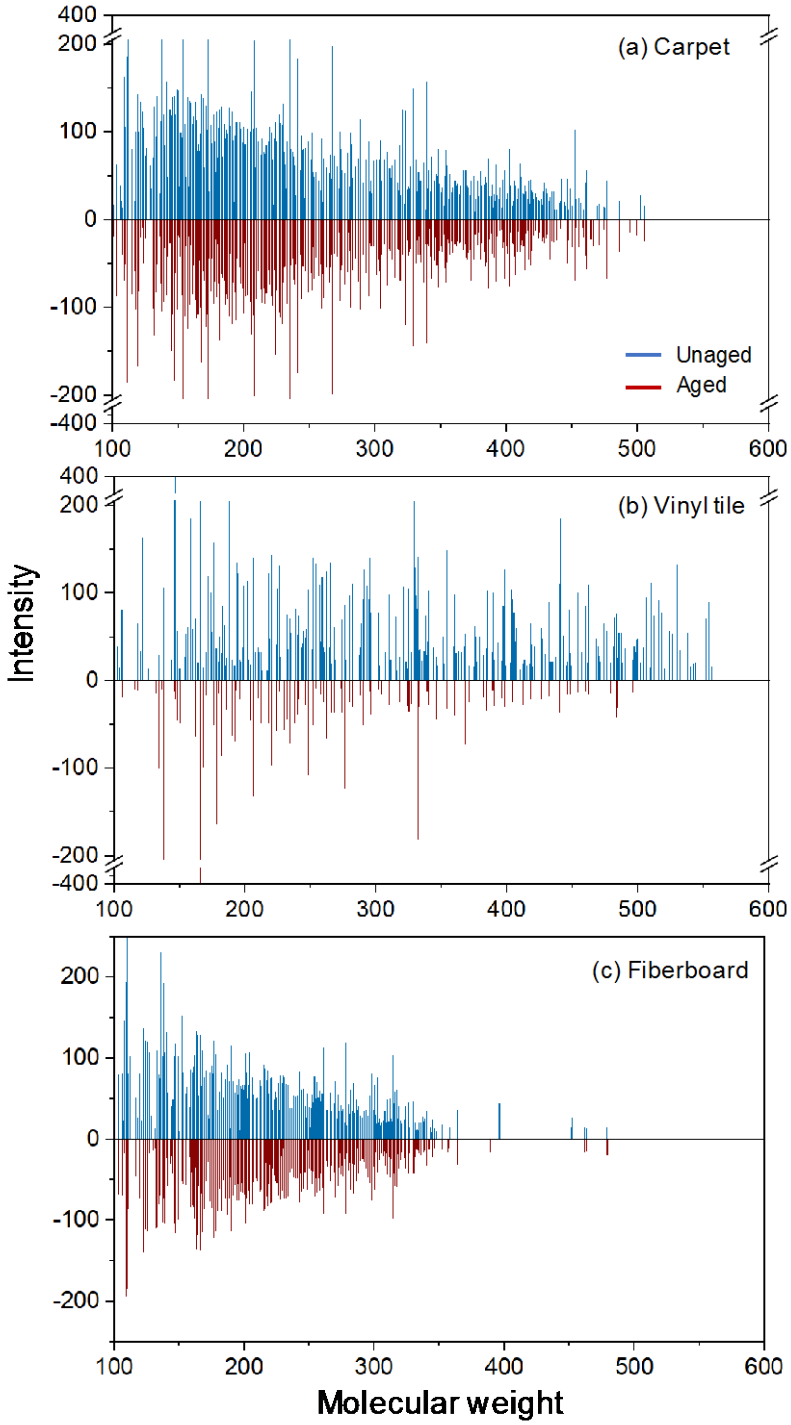


Figure S14. Reconstructed mass spectra of individual organic components identified in the time-integrated TPD-DART-HRMS experiments with the OA collected from pyrolysis of carpet (a), vinyl tile (b) and fiberboard (c) materials. Unaged OA is presented in blue, whereas OA aged 2 h under UV radiation are presented in red. To facilitate visual comparison, MS peaks detected in aged OA samples are plotted as negative signal, and intensities of all peaks are scaled to the cubic root of the originally recorded values.

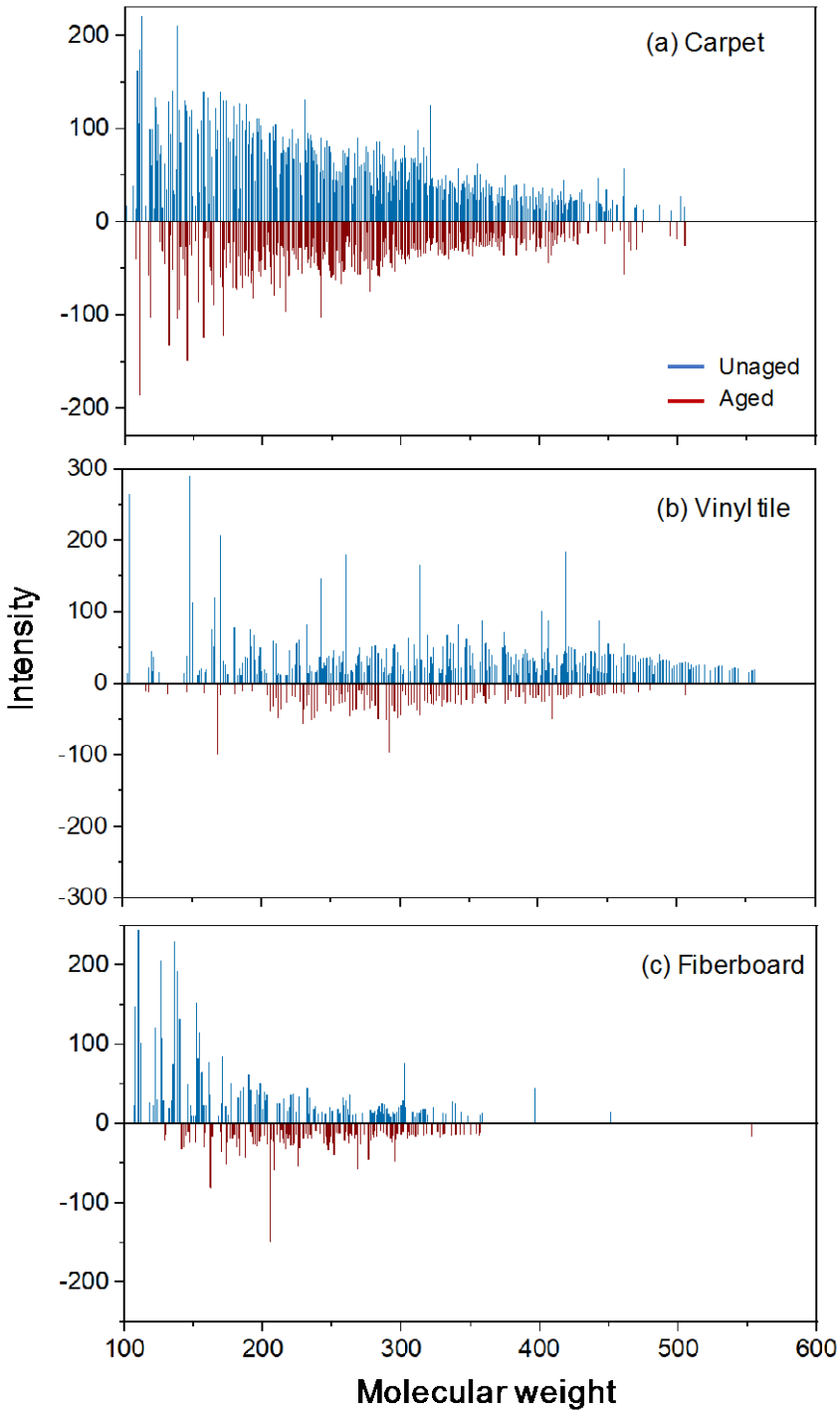


Figure S15. Reconstructed mass spectra of *the unique OA components.* Peaks unique to unaged OA + peaks that decreased by 10 % after aging are presented in blue, whereas peaks unique to aged OA + peaks that increased by 10% after aging are presented in red. These components were identified in the time-integrated TPD-DART-HRMS experiments with the OA collected from pyrolysis of carpet (a), vinyl tile (b) and fiberboard (c) materials. To facilitate visual comparison, MS peaks detected in aged OA samples (red) are plotted as negative signal, and intensities of all peaks are scaled to the cubic root of the originally recorded values.

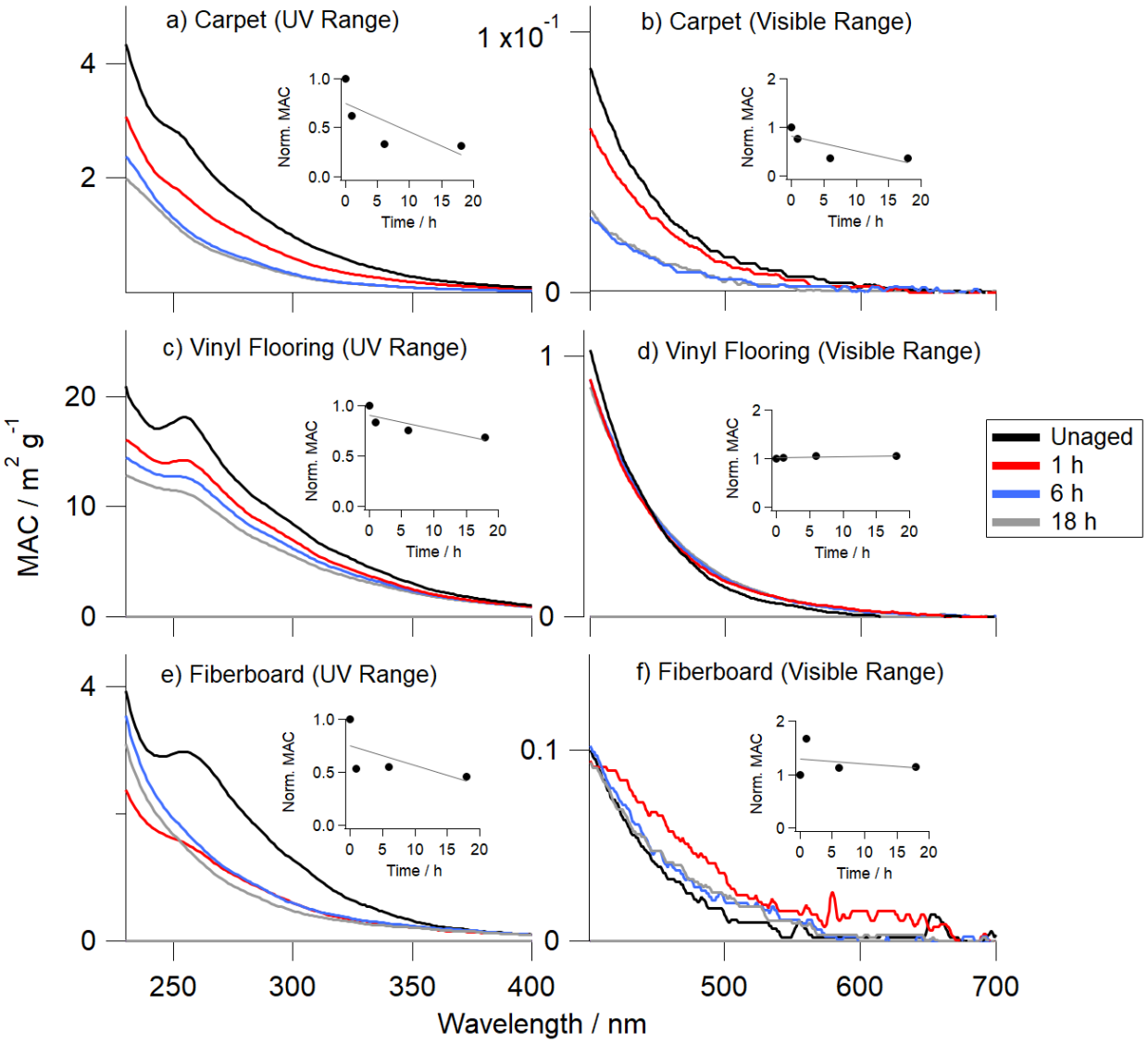


Figure S16. Long-term photolysis experiments. Wavelength-dependent mass absorption coefficient (*MAC*) values recorded after photolysis on Teflon filters and the subsequent extractions of carpet OA (a and b), vinyl flooring OA (c and d), and fiberboard OA (e and f). Each quarter of the filter was aged separately for 1 h (red), 6 h (blue), or 18 h (grey) and is compared with the unaged fraction (black). The integrated *MAC* values (normalized to the unaged value) are shown as a subplot in each panel, with the UV integrated over 280-400 nm and the visible integrated over 400-700 nm. Boxcar averaging (over 5 nm range) was utilized.

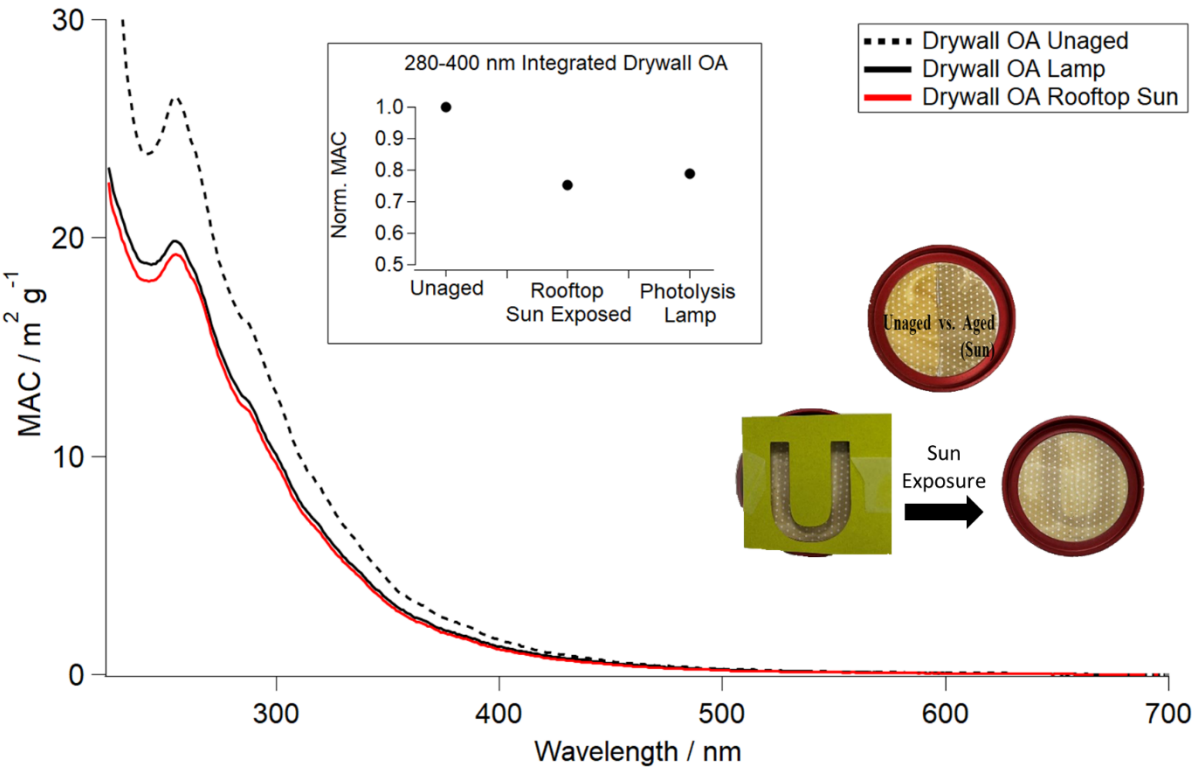


Figure S17. Wavelength-dependent mass absorption coefficient (*MAC*) values recorded for unaged drywall OA sample (black, dotted), drywall OA sample after photolysis using the Xenon arc lamp (black), and drywall OA sample after photolysis on the rooftop in direct sunlight (red). The integrated *MAC* values (normalized to the unaged value) for the UV integrated over 280-400 nm are shown in the subplot, with the UV integrated over 280-400 nm. The drywall OA aged samples bleached similar amount, within 5% of each other. Consistent with previous laboratory drywall OA experiments, photolytic exposure darkens this urban material's pyrolysis products. This is represented in the pictures of the unaged OA vs. aged OA filter and the "U" cutout which darkened during the sunlight exposure.