

## **Supplementary text**

### **ST-1. Chamber cleaning**

Between experiments, the smog chamber was flushed with zero air (from generator) for a minimum of 24 hours before starting the next experiment. The flow rate was varied somewhat but was at least  $10 \text{ L min}^{-1}$  up to usually no more than  $20 \text{ L min}^{-1}$ . The furnace was also cleaned during this time and was reconnected to the chamber while it is still flushing. Even when precautions were taken, this can introduce additional contaminants, which were also flushed out before a new burn. This additional flushing can take anywhere from 6 – 24 hours. When the chamber was not needed immediately, flushing continued at a constant  $10 \text{ L min}^{-1}$  to prevent room air from leaking into the chamber. Number concentrations were below  $25 - 40 \text{ particles cm}^{-3}$  as measured by the CPC before a new experiment began.

### **ST-2. Parameters affecting the combustion of biomass fuels**

Details on the parameters affecting combustion such as air-to fuel ration, combustion rate, fuel moisture content, fuel particle size and residence time of flu gases and adiabatic combustion temperature are described here.

#### **a) Combustion time**

The combustion time for our fuels was between 5 and 10 minutes. The exact time is unknown since we could not see into the furnace during combustion. The ash left on boat was less than 3% of the fuel mass.

#### **b) Fuel moisture content**

The moisture content of the biomass fuel samples was 10%. As measured in subsequent experiments

#### **c) Fuel particle size**

Heat transfer to wood particles is directly proportional to the exposed surface area of the sample. Smaller particles have a larger surface area to mass ratio than larger particles. This in turn means a faster rate of heat transfer to the particles and, consequently, a faster combustion rate.(Simmons, 1983). In this work, small twigs were used for combustion, fuel particle size can be approximated as a cylinder of mass 0.5 g, with an average radius of 0.25 cm and an average length of less than 5 cm, giving an upper limit of  $0.0012 \text{ m}^3$  for the volume, an upper limit of  $0.000825 \text{ m}^2$  for the exposed surface area of the fuel, and a lower limit of  $0.405 \text{ kg/m}^3$  for the density of the fuel used. Typically, whole twigs with a thin layer of bark were used, although occasionally two or more smaller pieces may have been used to achieve the same mass. Occasionally, these twigs were also split open. These factors could increase the surface area of the fuel by approximately  $0.000325 \text{ m}^2$  for the same fuel mass.

#### **d) Adiabatic fuel combustion temperature**

The adiabatic fuel combustion temperatures were 3706 C and 3679 C for acacia and eucalyptus, respectively.

#### **e) Residence time**

We calculated that the residence time of combustion gases within the tube furnace to be ~9.2 seconds.

## Supplementary Figures

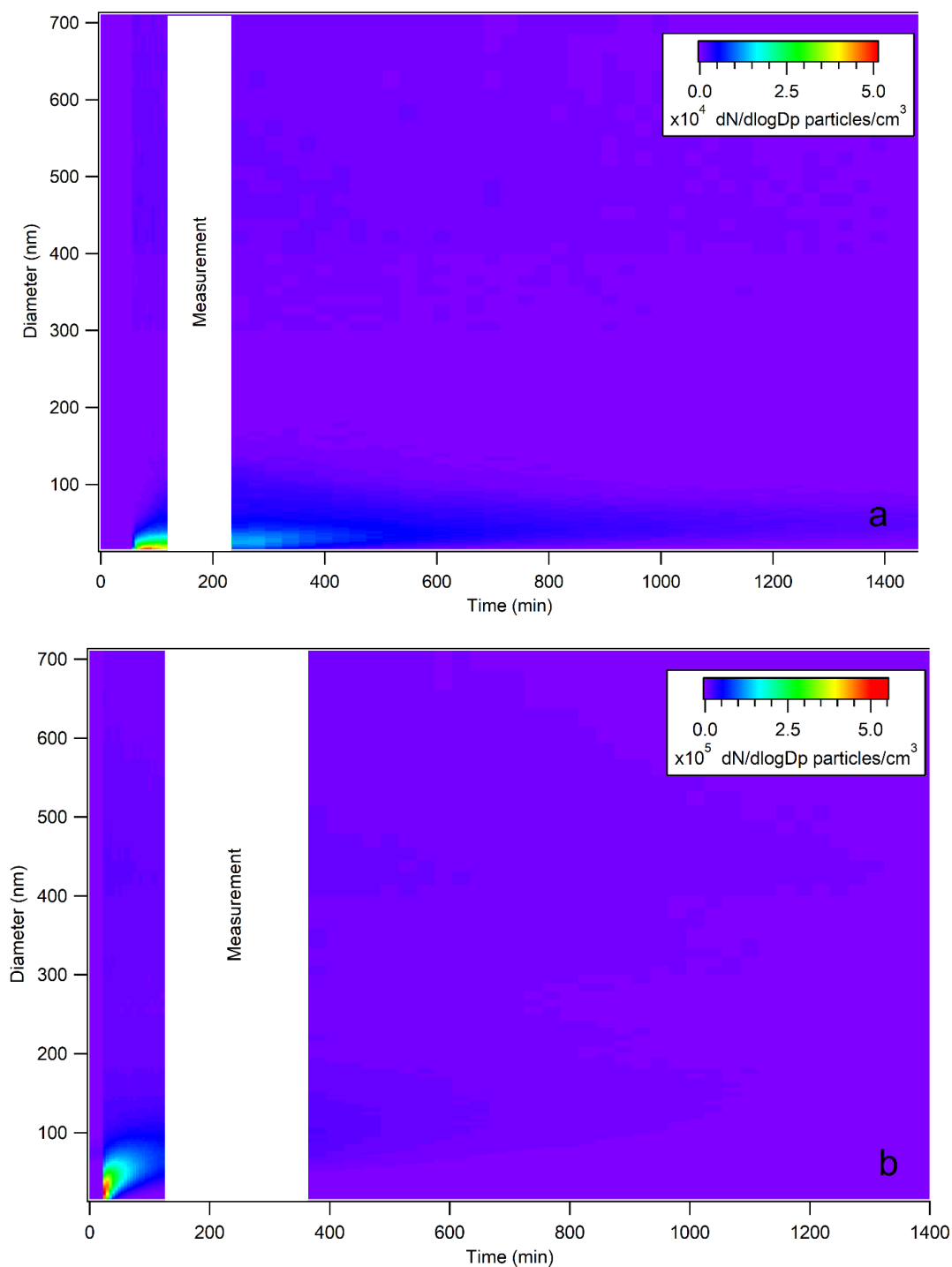


Figure S1: Examples of particle size distributions (number density in  $\text{dN}/\text{dlogDp}$ ) as a function of time (min) for Eucalyptus under (a) smoldering-dominated and (b) flaming-dominated conditions as they aged in the dark.

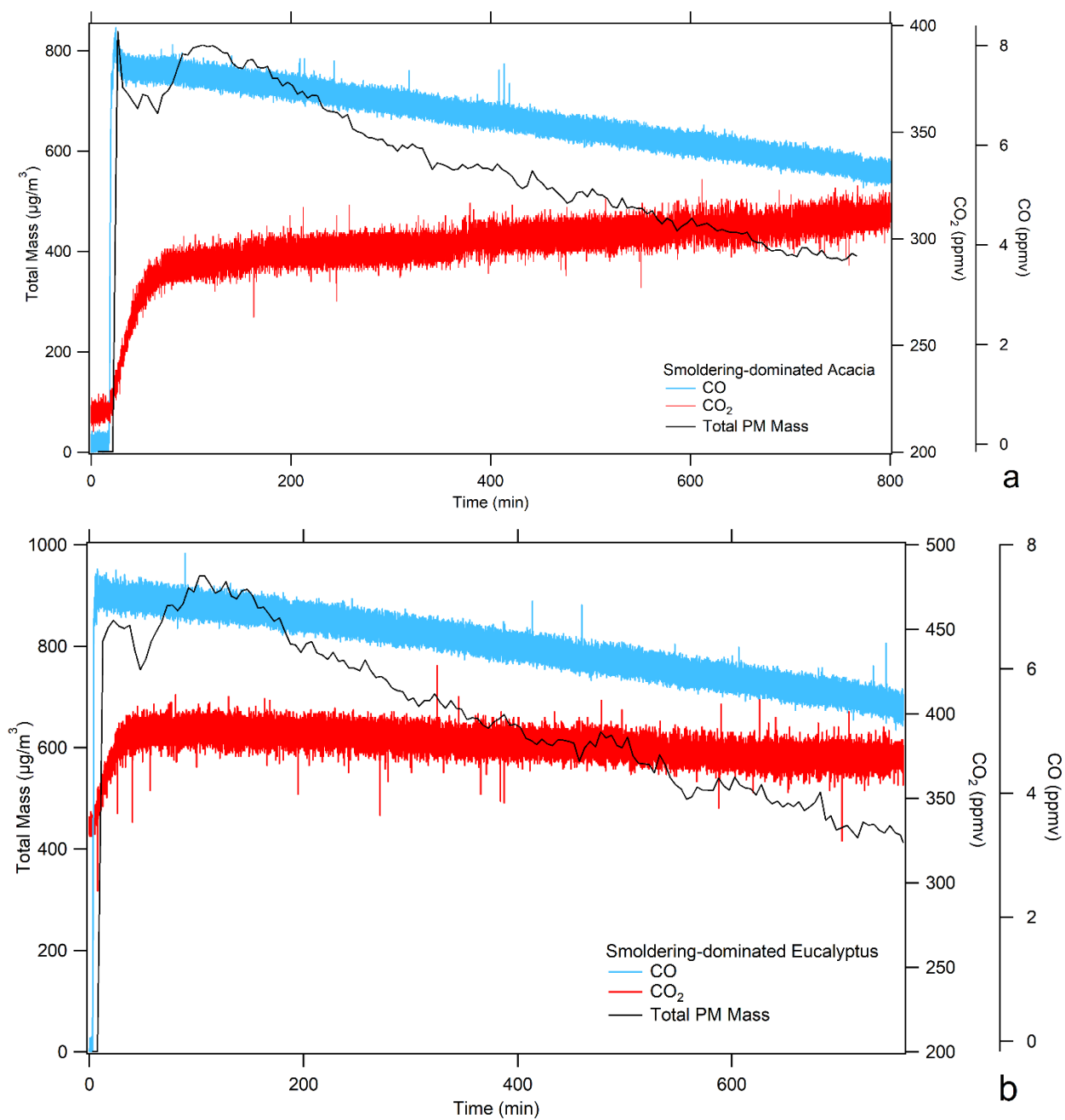


Figure S2: The temporal evolution of total particle mass in  $\mu\text{g}/\text{m}^3$ , CO, and CO<sub>2</sub> concentration (both in ppmv) for smoldering-dominated (a) Acacia and (b) Eucalyptus. Note the different scale for each. None of these are background corrected.

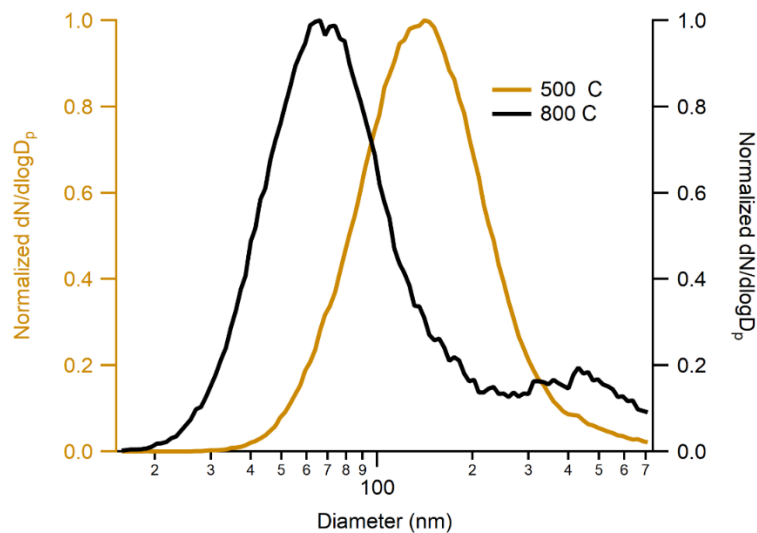


Figure S3: Normalized particle size distribution for smoldering-dominated (at 500 °C) and flaming-dominated (at 800 °C) burning cases. The relative particle concentrations at 200 nm are lower compared to equivalent mobility particles with charges of +2 (314 nm) and +3 (418 nm). On the other hand, for lower temperature burn, concentration at 200 nm size is about 3.5 time larger than that of +2 (314 nm) and about 9 times larger than +3 (418 nm) size.

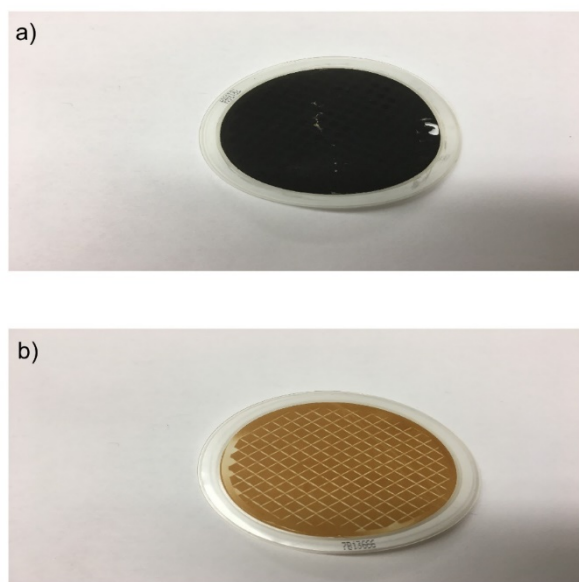


Figure S4: Visual appearance of aerosol collected on the filter during a) 800°C and b) 500°C burning.

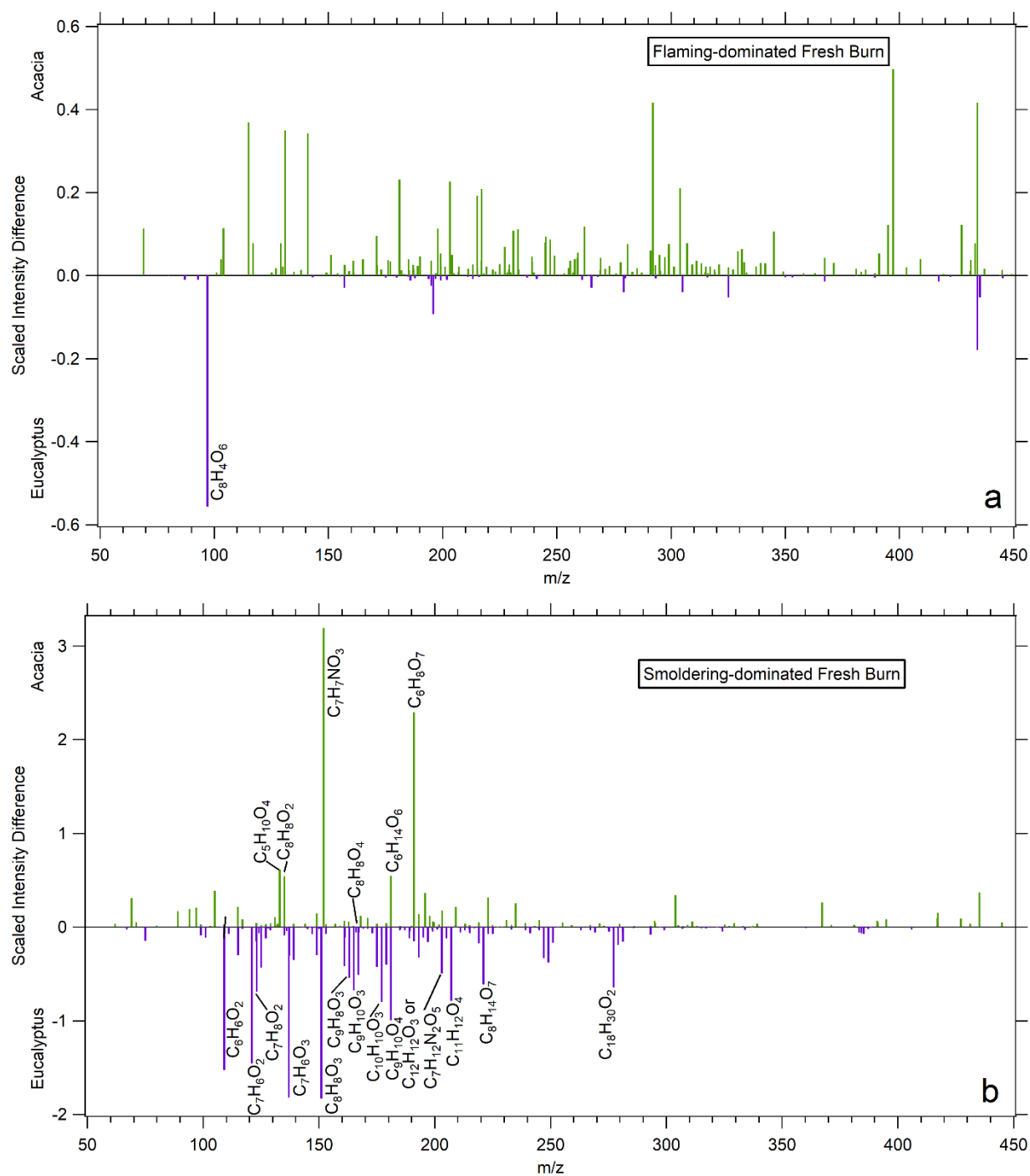


Figure S5: A comparison of fresh Acacia and Eucalyptus fuels combusted at under (a) flaming-dominated and (b) smoldering-dominated conditions in terms of the scaled intensity difference (see Section 2.5 of Part 2 for an explanation of these calculations). Briefly, the peak intensity for each compound identified in the XCMS analysis was divided by the total peak intensity and that difference was taken between the samples. Species more present in Acacia-derived BB aerosols have positive values (green lines), while those more present in Eucalyptus-derived BB aerosols have negative values (purple lines). Peaks that were present in the XCMS analysis but were found to be present in significant amounts in the blank sample have been excluded. Compounds having an absolute difference greater than

0.5% have been labeled and are listed in Table S2. Far more differences are revealed in the smoldering-dominated burn and different classes of compounds are expressed in different relative amounts for Acacia and Eucalyptus combustion.

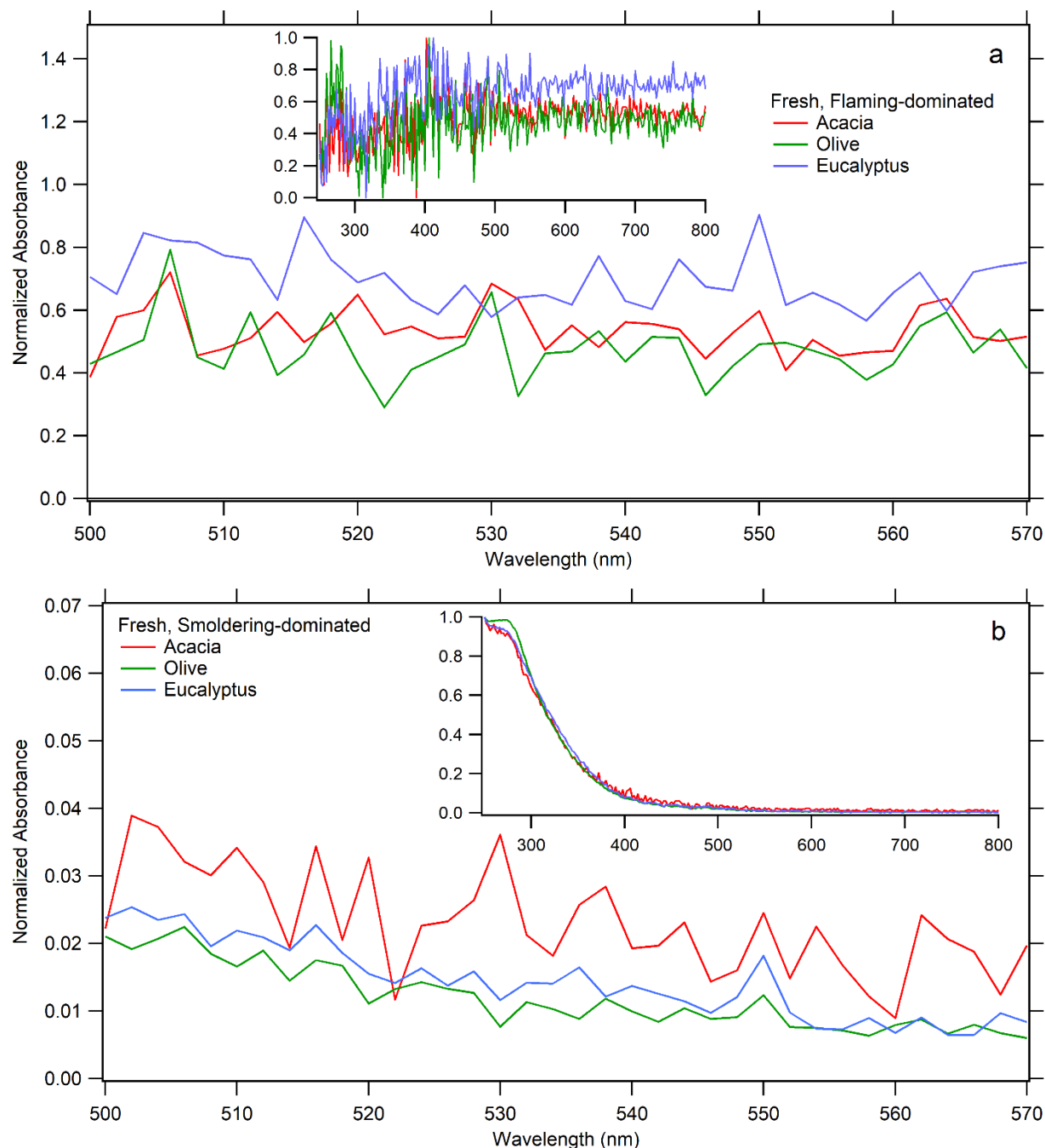


Figure S6: The normalized integrated UV/Visible spectra for fresh Acacia-, Olive-, and Eucalyptus-derived BB aerosol under (a) flaming-dominated and (b) smoldering-dominated conditions. These plots focus on the same spectral region as SSA measurements, with the entire spectrum in the inset. These spectra have been averaged over the entire chromatogram, background subtracted, and normalized, as described in Section 2.6 of Part 2 of this work.

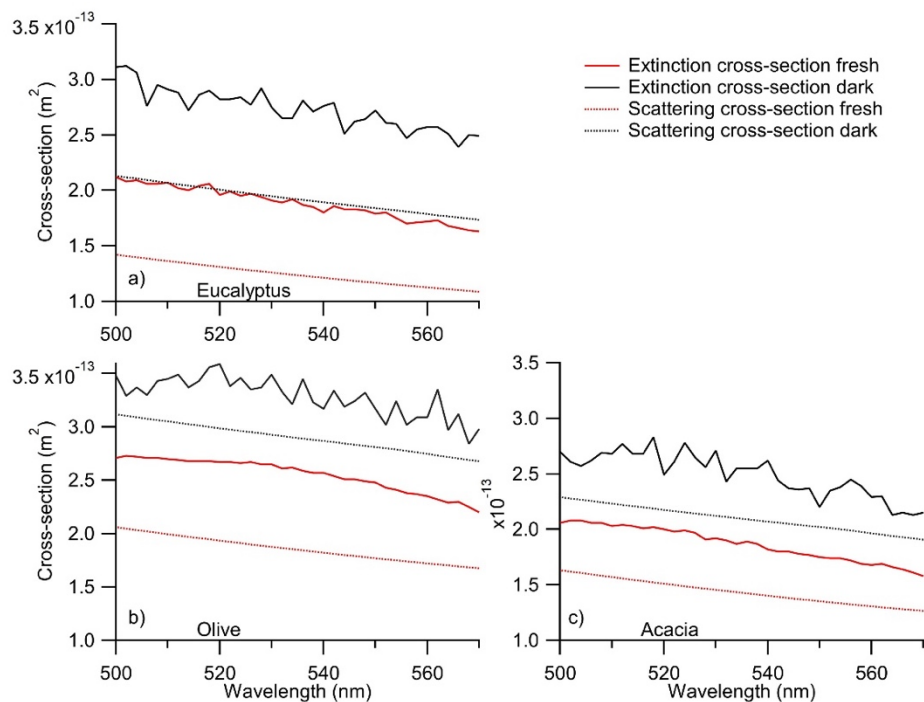


Figure S7: Impact of dark aging on extinction and scattering cross-section of 300 nm aerosol emitted during smoldering-dominated combustion cases for (a) Eucalyptus, (b) Olive, and (c) Acacia.

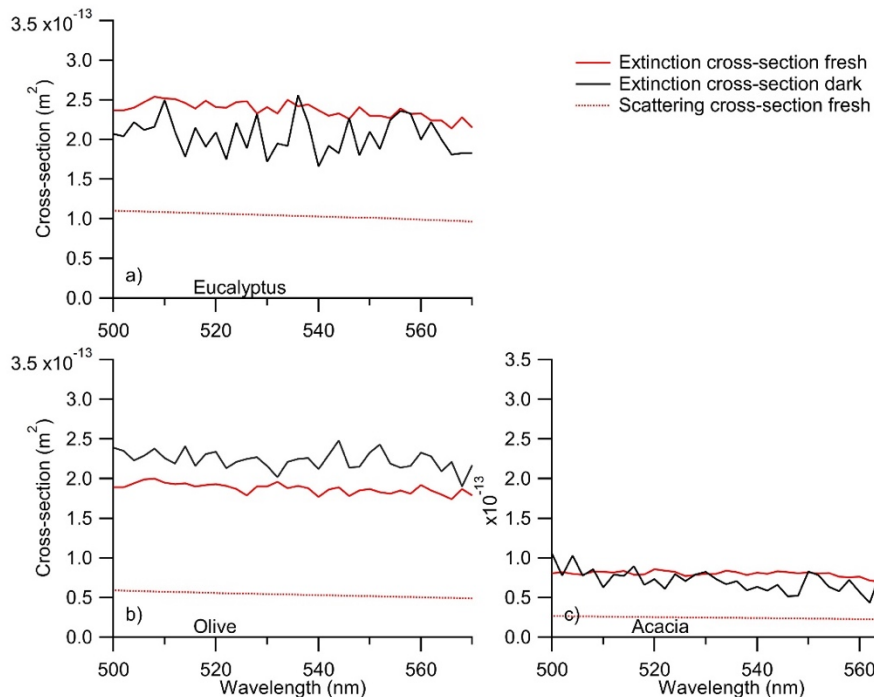


Figure S8: Impact of dark aging on extinction cross-section of 300 nm aerosol emitted during flaming-dominated combustion cases for (a) Eucalyptus, (b) Olive, and (c) Acacia.

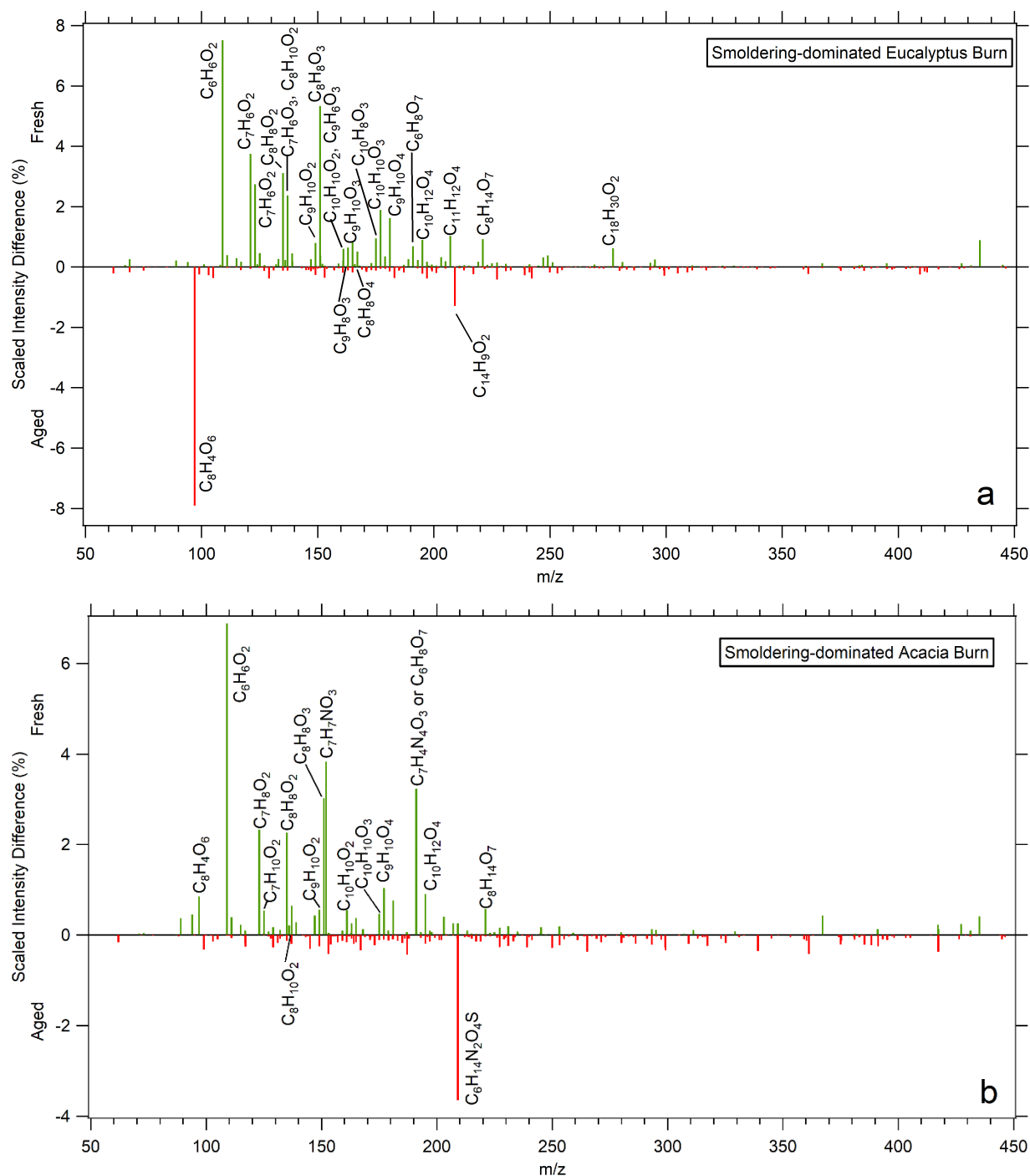


Figure S9: A comparison of smoldering-dominated BB aerosol combustion of (a) Eucalyptus and (b) Acacia under fresh and photochemically aged conditions with VOCs, in terms of the scaled intensity difference (see Section 2.5 of Part 2). Species more present in the fresh sample have positive values (green lines), while those more present in the aged sample have negative values (red lines) (i.e. species with positive values have been removed because of the aging



process, while those with negative values are either produced or represent a greater relative contribution to the aged sample). Peaks that were present in the XCMS analysis but were found to be present in significant amounts in the blank sample have been excluded. Compounds having an absolute difference greater than 0.5% have been labeled and are listed in Tables S3 and S4. In both cases, there is a net removal of many compounds.

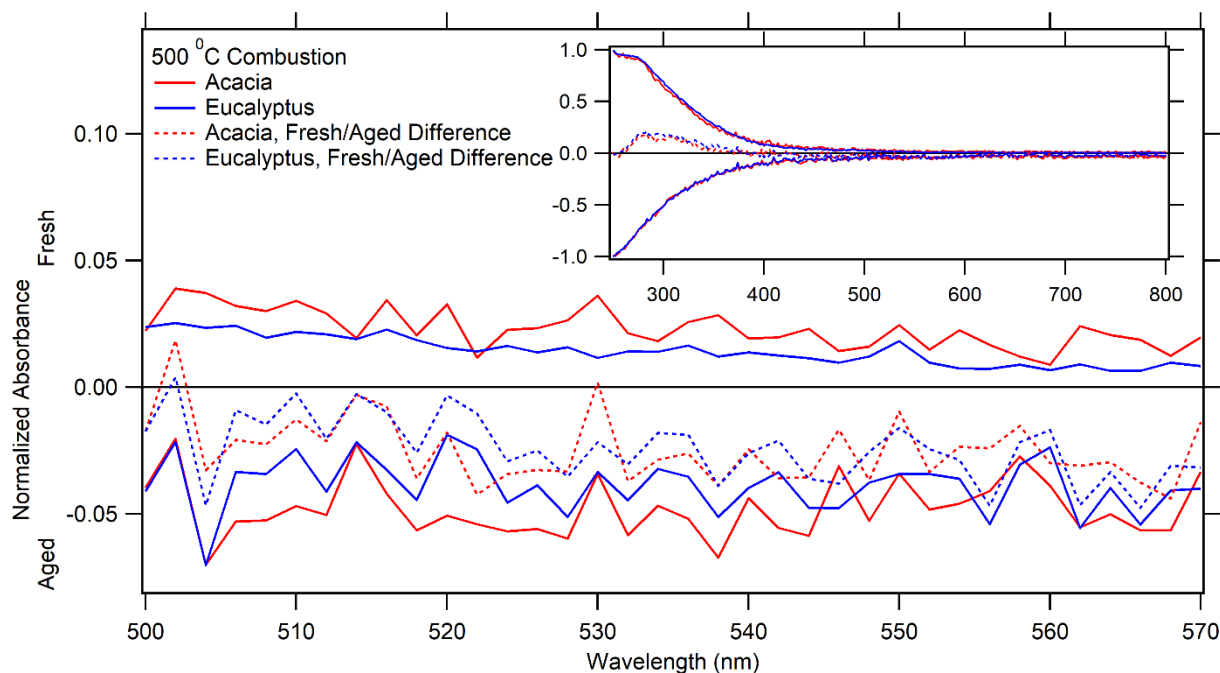


Figure S10: The UV/Visible spectrum Acacia- and Eucalyptus-derived BB aerosol combusted at 500 °C, showing the result from fresh combustion with positive values and photochemically aged with negative values. These spectra have been averaged over the entire chromatogram, background subtracted, and normalized, as described in in Section 2.6 of Part 2 of this work. The differences between them are highlighted with the dashed line, which is the difference between the two spectra. These plots focus on the same spectral region as SSA measurements, with the entire spectrum in the inset.

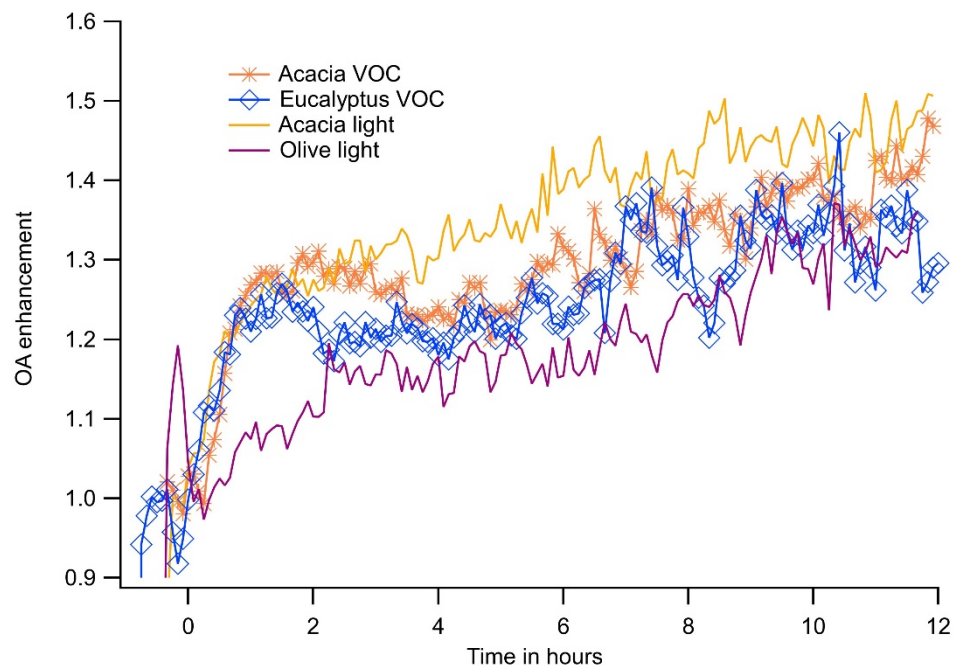


Figure S11: Variation of the organic aerosol enhancement with photochemical aging time under light and light plus VOC aging for different fuels listed in the legend.

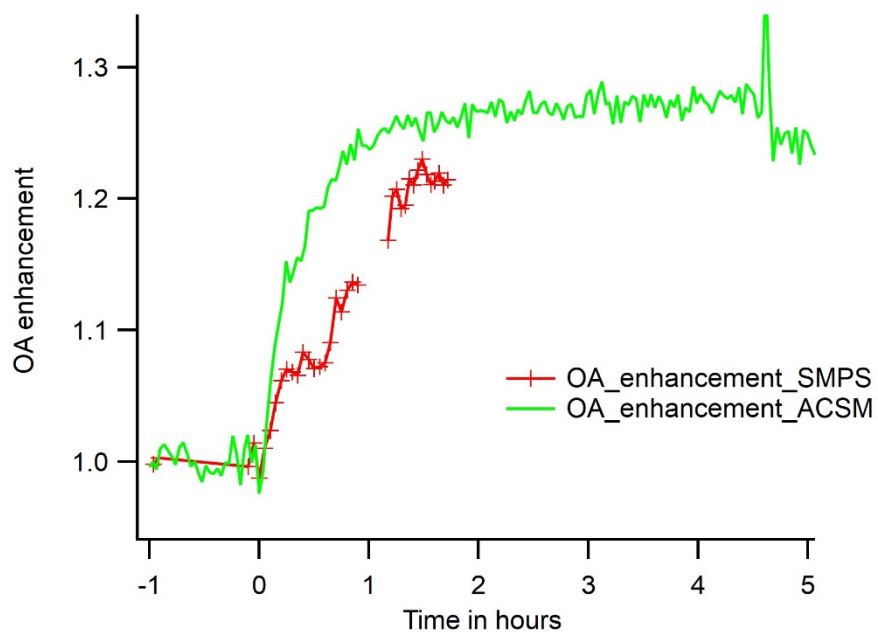


Figure S12: A comparison of OA enhancement, calculated based on SMPS and ACSM measurements.

Table S1: Size selected SSA of different fuels measured at 500°C and 800°C burn conditions with different aging conditions.

Fuel type	Size nm	Measurement conditions	Average SSA 500°C burn case	Average SSA 800°C burn case
Eucalyptus	200	Fresh	$0.645 \pm 0.017$	$0.468 \pm 0.012$
		Aged (dark)	$0.716 \pm 0.025$	-
		Aged (light)	$0.876 \pm 0.021$	-
		Aged (VOC)	$0.953 \pm 0.024$	-
	300	Fresh	$0.660 \pm 0.018$	$0.439 \pm 0.010$
		Aged (dark)	$0.707 \pm 0.020$	-
		Aged (light)	$0.931 \pm 0.027$	-
		Aged (VOC)	$0.978 \pm 0.023$	-
	400	Fresh	$0.668 \pm 0.018$	$0.427 \pm 0.009$
		Aged (dark)	$0.715 \pm 0.020$	-
		Aged (light)	$0.959 \pm 0.029$	-
		Aged (VOC)	$0.995 \pm 0.024$	-
Acacia	200	Fresh	$0.727 \pm 0.024$	$0.325 \pm 0.028$
		Aged (dark)	$0.817 \pm 0.025$	-
		Aged (light)	$0.902 \pm 0.019$	-
		Aged (VOC)	$0.844 \pm 0.025$	-
	300	Fresh	$0.769 \pm 0.027$	$0.309 \pm 0.012$
		Aged (dark)	$0.847 \pm 0.026$	-
		Aged (light)	$0.935 \pm 0.020$	-
		Aged (VOC)	$0.913 \pm 0.025$	-
	400	Fresh	$0.857 \pm 0.030$	$0.308 \pm 0.026$
		Aged (dark)	$0.908 \pm 0.025$	-
		Aged (light)	$0.967 \pm 0.021$	-
		Aged (VOC)	$0.912 \pm 0.026$	-
Olive	200	Fresh	$0.675 \pm 0.038$	$0.283 \pm 0.007$
		Aged (dark)	$0.826 \pm 0.031$	-
		Aged (light)	$0.961 \pm 0.020$	-
		Aged (VOC)	-	-
	300	Fresh	$0.728 \pm 0.052$	$0.287 \pm 0.006$
		Aged (dark)	$0.886 \pm 0.029$	-
		Aged (light)	$0.991 \pm 0.021$	-
		Aged (VOC)	-	-
	400	Fresh	$0.816 \pm 0.054$	$0.290 \pm 0.006$
		Aged (dark)	$1.002 \pm 0.037$	-
		Aged (light)	$1.015 \pm 0.021$	-
		Aged (VOC)	-	-

Table S2. Molecular differences between fresh Acacia- and Eucalyptus-derived BB aerosols emitted by smoldering-dominated combustion (upper section) and flaming-dominated combustion (lower section), measured by negative ion mode UPLC/ESI-HR-QTOFMS analysis. Species are ordered in terms of increasing scaled intensity difference, with positive values associated with Acacia-derived BB aerosols and negative values associated with Eucalyptus-derived aerosols. The mass difference is calculated as the difference between the observed median mass and the monoisotopic peak (typically singly deprotonated) of the formula determined using MassHunter. Suggested species marked with an asterisk can, and likely do, have multiple isomers present. Those marked with a 't' are particularly tentative assignments. Based on the present literature, the suggested identities are listed along with their compound type. The acronyms used here are for compounds attributed to lignin pyrolysis products (LPP), distillation products (DP), sugar/cellulose products (SCP), nitro-aromatic compounds (NAC), oxidized polyaromatic hydrocarbons (OPAH), and oxidized anthropogenic volatile organic compounds (OAVOC).

	Scaled Intensity Difference	<i>m/z</i>	Mass Difference (ppm)	Formula	DBE	Suggested Identity	Compound Type
Smoldering	-1.831%	151.04030	-0.95	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	5	vanillin,* methoxybenzoic acid,* or hydroxy anisaldehyde*	LPP
	-1.822%	137.02442	0.72	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	5	salicylic acid* or dihydroxybenzaldehyde*	LPP
	-1.526%	109.02969	-3.37	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	4	dihydroxybenzene	
	-1.459%	121.02951	-0.59	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	5	benzoic acid or hydroxybenzaldehyde*	DP or LPP
	-0.998%	181.05101	0.3	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	5	homovanillic acid*, dimethoxybenzoic acid*, or syringaldehyde*	LPP
	-0.801%	177.05542	1.16	C <sub>10</sub> H <sub>10</sub> O <sub>3</sub>	6	coniferaldehyde	LPP
	-0.790%	207.06602	1.5	C <sub>11</sub> H <sub>12</sub> O <sub>4</sub>	6	sinapaldehyde	LPP
	-0.691%	123.04541	-0.81	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	4	guaiacol*	LPP
	-0.677%	165.05548	5	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>	5	hydroxy-methoxyacetophenone* (apocynin, paeonol, etc), caffeyl alcohol*, veratraldehyde,* or phloretic acid*	DP
	-0.647%	277.21747	-1.11	C <sub>18</sub> H <sub>30</sub> O <sub>2</sub>	4	octadecatrienoic acid (likely linolenic acid)	Lipid
	-0.616%	221.06665	0.61	C <sub>8</sub> H <sub>14</sub> O <sub>7</sub>	2	dihydroxydimethoxyoxane-2-carboxylic acid* <sup>t</sup>	SCP
	-0.545%	163.0399	nc	C <sub>9</sub> H <sub>8</sub> O <sub>3</sub>	6	caffeic aldehyde,* coumaric acids*	DP
	-0.510%	167.03508	-0.03	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub>	5	vanillic acid*	LPP
	-0.499%	203.07032	-10 - 10	C <sub>12</sub> H <sub>12</sub> O <sub>3</sub> or C <sub>7</sub> H <sub>12</sub> N <sub>2</sub> O <sub>5</sub>	7 or 2	dimethylmethoxycoumarin* or glycyl-glutamic acid <sup>t</sup>	DP
	0.543%	135.04513	-2.25	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	5	anisaldehyde*, acetophenone, methylsalicylaldehyde*, or methylbenzoic acid*	LPP
	0.545%	181.07191	-1.1	C <sub>6</sub> H <sub>14</sub> O <sub>6</sub>	0	mannitol, sorbitol, or galactitol	SCP
	0.612%	133.05005	3.92	C <sub>5</sub> H <sub>10</sub> O <sub>4</sub>	1	deoxyribose or monoacetalglycerol <sup>t</sup>	SCP
Flaming	0.994%	666.05964	-	-	-	too many options	-
	2.293%	191.0198	-2.5	C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>	3	citric acid	SCP
	3.190%	152.03565	-4.2	C <sub>7</sub> H <sub>7</sub> NO <sub>3</sub>	5	nitroanisole*, nitroresol, or nitrobenzyl alcohol*	NAC
	-0.556%	96.960662	9	C <sub>8</sub> H <sub>4</sub> O <sub>6</sub>	7	dihydroxyphthalic acid	OAVOC
	0.497%	397.27546	-	-	-	too many options	-
	0.560%	666.05967	-	-	-	too many options	-
	0.789%	982.993	-	-	-	no formula found	-

Table S3. Molecular difference between fresh and aged Eucalyptus revealed by negative mode MS analysis. See the caption of Table S2 for more details.

	Scaled Intensity Difference	<i>m/z</i>	Mass Difference (ppm)	Formula	DBE	Suggested Identity	Compound Type
	-8.301%	666.05954	-	-	-	too many options	-
	-7.909%	96.960595	9	C <sub>8</sub> H <sub>4</sub> O <sub>6</sub>	7	dihydroxyphthalic acid	OAVOC
	-1.292%	209.06166	-6.5	C <sub>14</sub> H <sub>10</sub> O <sub>2</sub>	10	dihydroxyanthracene	OPAH
	-0.546%	649.55411	0.06	C <sub>39</sub> H <sub>74</sub> N <sub>2</sub> O <sub>5</sub>	4	unknown, potential dinitro species	-
Smoldering	0.501%	161.02415	-0.12	C <sub>9</sub> H <sub>6</sub> O <sub>3</sub>	7	umbelliferone or other hydroxycoumarin*	DP
	0.504%	167.03476	-0.03	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub>	5	vanillic acid	LPP
	0.597%	161.06082	-0.94	C <sub>10</sub> H <sub>10</sub> O <sub>2</sub>	6	methoxycannamaldehyde, methylcinnamic acid, methylhydrocoumarin	DP
	0.618%	277.21747	-1.11	C <sub>18</sub> H <sub>30</sub> O <sub>2</sub>	4	octadecatrienoic acid (likely linolenic acid)	Lipid
	0.641%	163.04002	-0.14	C <sub>9</sub> H <sub>8</sub> O <sub>3</sub>	6	caffeic aldehyde,* coumaric acids*	DP
	0.686%	191.01981	-1.54 or -8.07	C <sub>7</sub> H <sub>4</sub> N <sub>4</sub> O <sub>3</sub> or C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>	8 or 3	unknown; citric acid	SCP
	0.796%	149.06075	-0.03	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	5	acetylanisole,* hydrocinnamic acid,* tolylacetic acid	DP
	0.814%	165.05560	-0.14	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>	5	hydroxy-methoxyacetophenone* (apocynin, paeonol, etc), caffeyl alcohol,* veratraldehyde,* phloretic acid*	DP
	0.865%	137.06088	0.98	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub>	4	anisyl alcohol, creosol, dimethoxybenzene*	DP
	0.891%	195.06638	-0.15	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub>	5	acetosyringone*, homoveratic acid*	LPP
	0.919%	221.06627	0.61	C <sub>8</sub> H <sub>14</sub> O <sub>7</sub>	2	dihydroxydimethoxyoxane-2-carboxylic acid* <sup>†</sup>	SCP
	0.942%	175.0402	0.03	C <sub>10</sub> H <sub>8</sub> O <sub>3</sub>	7	methoxycoumarin,* methylhydroxycoumarin*	DP
	1.030%	207.06603	1.5	C <sub>11</sub> H <sub>12</sub> O <sub>4</sub>	6	sinapaldehyde	LPP
	1.621%	181.05061	0.3	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	5	homovanillic acid*, dimethoxybenzoic acid,* or syringaldehyde*	LPP
	1.888%	177.05541	1.16	C <sub>10</sub> H <sub>10</sub> O <sub>3</sub>	6	coniferaldehyde	LPP
	2.371%	137.02443	0.72	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub>	5	salicylic acid* or dihydroxybenzaldehyde*	LPP
	2.737%	123.04531	-0.81	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	4	guaiacol	LPP
	3.107%	135.04510	-2.25 - 0.05	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	5	anisaldehyde,* methylbenzoic acid*, acetophenone, or methylsalicylaldehyde*	LPP
	3.746%	121.02951	-0.59	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	5	benzoic acid, salicylaldehyde	DP or LPP
	5.335%	151.04027	-0.95	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	5	vanillin,* methoxybenzoic acid,* or hydroxy anisaldehyde*	LPP
	7.514%	109.02957	-3.37	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	4	dihydroxybenzene	LPP
Flaming	-5.654%	96.961	9	C <sub>8</sub> H <sub>4</sub> O <sub>6</sub>	7	dihydroxyphthalic acid	OAVOC
	-1.247%	649.55378	-2.61	C <sub>39</sub> H <sub>74</sub> N <sub>2</sub> O <sub>5</sub>	4	unknown, potential dinitro species	-
	-0.844%	163.040	-0.14	C <sub>9</sub> H <sub>8</sub> O <sub>3</sub>	6	caffeic aldehyde,* coumaric acids*	DP
	0.856%	666.060	-	-	-	too many options	-
	1.237%	982.99221	-	-	-	no formula found	-

Table S4. Molecular difference between fresh and aged Acacia revealed by negative mode MS analysis. See the caption of Table S2 for more details.

	Scaled Intensity Difference	<i>m/z</i>	Mass Difference (ppm)	Formula	DBE	Suggested Identity	Compound Type
Smoldering	-3.652%	209.06134	-7.41	C <sub>6</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub> S	1	unknown	-
	0.521%	736.13744	-0.53	C <sub>44</sub> H <sub>23</sub> N <sub>3</sub> O <sub>9</sub>	35	unknown	-
	0.539%	125.06093	-3.35	C <sub>7</sub> H <sub>10</sub> O <sub>2</sub>	3	cyclohexene carboxylic or heptadienoic acid	Lipid
	0.549%	161.0607	-0.94	C <sub>10</sub> H <sub>10</sub> O <sub>2</sub>	6	methoxycannamaldehyde, methylcinnamic acid, or methylhydrocoumarin	DP
	0.557%	149.06125	-0.03	C <sub>9</sub> H <sub>10</sub> O <sub>2</sub>	5	acetylanisole,* hydrocinnamic acid,* tolylacetic acid	DP
	0.575%	221.06668	0.61	C <sub>8</sub> H <sub>14</sub> O <sub>7</sub>	2	dihydroxydimethoxyoxane-2-carboxylic acid* <sup>t</sup>	SCP
	0.641%	137.06111	-4.02	C <sub>8</sub> H <sub>10</sub> O <sub>2</sub>	4	anisyl alcohol, creosol, dimethoxybenzene*	DP
	0.763%	181.05141	0.3	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	5	homovanillic acid*, dimethoxybenzoic acid*, or syringaldehyde*	LPP
	0.852%	96.960701	9	C <sub>8</sub> H <sub>4</sub> O <sub>6</sub>	7	dihydroxyphthalic acid*	OAVOC
	0.901%	195.06627	-0.15	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub>	5	acetosyringone* or homoveratic acid*	LPP
	1.038%	177.05542	1.16	C <sub>10</sub> H <sub>10</sub> O <sub>3</sub>	6	coniferaldehyde	LPP
	1.306%	666.05965	-	-	-	too many options	-
	2.259%	135.04538	-2.25	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	5	anisaldehyde*, acetophenone, methylsalicylaldehyde*, or methylbenzoic acid*	LPP
	2.327%	123.04542	-0.81	C <sub>7</sub> H <sub>8</sub> O <sub>2</sub>	4	guaiacol	LPP
	3.016%	151.04032	-0.95	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	5	vanillin*, methoxybenzoic acid*, or hydroxy anisaldehyde*	LPP
	3.233%	191.01941	-1.54 or -8.07	C <sub>7</sub> H <sub>4</sub> N <sub>4</sub> O <sub>3</sub> or C <sub>6</sub> H <sub>8</sub> O <sub>7</sub>	8 or 3	unknown; citric acid	SCP
	3.821%	152.03561	4.2	C <sub>7</sub> H <sub>7</sub> NO <sub>3</sub>	5	nitroanisole*, nitroresol*, or nitrobenzyl alcohol*	NAC
	6.886%	109.02984	-3.37	C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>	4	dihydroxybenzene	LPP
Flaming	-1.423%	103.02421	-4.1	C <sub>4</sub> H <sub>8</sub> O <sub>3</sub>	1	hydroxybutanoic acid, methoxypropanoic acid	Lipid
	-0.604%	147.04672	-8.72	C <sub>9</sub> H <sub>8</sub> O <sub>2</sub>	6	cinnamic acid	DP
	0.783%	397.26686	-0.08	C <sub>26</sub> H <sub>38</sub> O <sub>3</sub>	8	uncertain	-
	0.819%	96.960676	nc	C <sub>8</sub> H <sub>4</sub> O <sub>6</sub>	7	dihydroxyphthalic acid*	OAVOC
	3.467%	666.05938	-	-	-	too many options	-

**References:**

Simmons, W. W.: Analysis of Single Particle Wood Combustion in Convective Flow, PhD, University of Wisconsin, Madison, WI, 1983.