# Speciated and total emission factors of particulate organics from burning western U.S. wildland fuels and their dependence on combustion efficiency

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## **Supporting Information:**

- 1. Sampling position and diagram of DEFCON, Direct Emission Fire CONcentrator
- 2. I/SVOCs from the FIREX FSL experiments-- University of California, Berkeley-Goldstein Library of Biogenic and Environmental Spectra (UCB-GLOBES)
- 3. Conversion of instrument response to mass loadings and emission factors
- 4. Internal/external standards and mass loading calibration curves
- 5. Classifying unidentified compounds into chemical families
- 6. Classified I/SVOC mass fractions averaged over fuel type
- 7. EFs for families of compounds as a function of MCE

## 1. Sampling position and diagram of DEFCON, Direct Emission Fire CONcentrator:

Smoke was collected directly from the stack at a position ~17 m above the burn (Figure S1). A flow of 10.3 LPM was pulled through DEFCON. 300 sccm of the flow was diverted to two parallel absorbent tube sampling channels (150 sccm each channel). The reminder of the smoke flow (10 LPM) was then passed through a 1.0  $\mu$ m cyclone prior to collection on a 10 cm quartz fiber filter. Flow rates were continuously monitored to ensure correct flows. All metal surfaces except for the cyclone and filter holders were passivated with Inertium® to minimize loss of oxygenated organics (Williams et al., 2006). A diagram of DEFCON is given in Figure S2.



Figure S1 Diagram of the smoke stack in the burn room and the placement of DEFCON

## 2. I/SVOCs from the FIREX FSL experiments-- University of California, Berkeley-Goldstein Library of Organic Biogenic and Environmental Spectra (UCB-GLOBES):

The mass spectrum and retention index of each compound separated by the TD-GC×GC-EI/VUV-HRToFMS was compared to the NIST mass spectral database (2014 version) and/or to previous literature. Table S1 provides a list of all 149 identified compounds and its identification method. In addition, all separated and unique compounds from the 29 analyzed burns were compiled into UCB-GLOBES (FIREX), https://nature.berkeley.edu/ahg/data/MSLibrary/. Information includes compound chemical classification, deuterated and non-deuterated *n*-alkane retention indices, mass spectrum, instrument/method details, derivatization agent, list of fuel, and, if found in 10 or more burns, the slope, intercept, standard errors, and  $R^2$  for the model log(EF)=slope(MCE)+int. UCB-GLOBES (FIREX) is NIST MS Search compatible and can be used in the future to better identify biomass-burning derived organic compounds found in the atmosphere. Table S1 List of identified compounds and their sources, characteristic EI ions and retention index (RI). Compounds were identified using a combination of RI, mass spectrum, VUV parent ion mass, or standard matching.

Compound name	Underiv. Formula	Derivatized Formula	Exact Mass (no deriv)	Exact Mass (Deriv)	Top 5 masses (deriv)	RI	ID Method	Comments
Glycerol 3TMS	C3H8O3	C12H32O3Si3	92.047	308.166	69, 73, 147, 131, 205	1266	RI, MS, VUV	All forms of pine, dung,
Glyceric acid 3TMS	C3H6O4	C12H30O4Si3	106.027	322.145	73, 147, 189, 133, 117	1319	RT, MS, VUV	Rotten log
Catechol 2TMS	C6H6O2	C12H22O2Si2	110.037	254.116	73, 254, 239, 45, 74	1307	RT, MS, VUV, STD	All
Hydroquinone 2 TMS	C6H6O2	C12H22O2Si2	110.037	254.116	239, 254, 73, 240, 255	1393	RT, MS, VUV, STD	All
Resorcinol 2TMS	C6H6O2	C12H22O2Si2	110.037	254.116	239, 254, 73, 69, 91	1372	RT, MS, VUV, STD	All forms of pine, ground, manzanita, juniper
1,2-cyclohexanediol	C6H12O2	C12H28O2Si2	116.084	260.162	'147, 73, 142, 81, 245'	1253	RT, MS, VUV	Duff
Butanedioic acid 2TMS	C4H6O4	C10H22O4Si2	118.027	262.106	147, 73, 75, 148, 45	1306	RI, MS, VUV	All
3-methylcatechol 2TMS	C7H8O2	C13H24O2Si2	124.052	268.131	73, 268, 74, 45, 253	1379	RI, MS, VUV	All
4-methylcatechol 2TMS	C7H8O2	C13H24O2Si2	124.052	268.131	73, 69, 268, 253, 45	1390	RT, MS, VUV, STD	All
Benzoic acid TMS steroisomer 1	C7H8O2	C10H16O2Si	124.052	196.092	105, 179, 135, 77, 194	1242	RI, MS, VUV	All
Benzoic Acid TMS steroisomer 2	C7H8O2	C10H16O2Si	124.052	196.092	105, 179, 135, 77, 194	1234	RI, MS, VUV	All
Methylhydroquinone 2TMS	C7H8O2	C13H24O2Si2	124.052	268.131	268, 253, 73, 237, 254	1454	RI, MS, VUV	All
5-(hydroxymethyl) furfural TMS	C6H6O3	C9H14O3Si	126.032	198.071	183, 109, 111, 73, 81	1304	RI, MS, VUV	All
Maltol TMS	C6H6O3	C9H14O3Si	126.032	198.071	183, 184, 153, 75, 111	1277	RT, MS, VUV, STD	All
Pyrogallol 3TMS	C6H6O3	C15H30O3Si3	126.032	342.150	239, 73, 342, 240, 211	1531	RT, MS, VUV	All
Pyroglutamic acid TMS	C5H7NO3	C11H23NO3S i2	129.043	273.122	84, 75, 73, 41, 45	1492	RT, MS, VUV, STD	All
Methylsuccinic acid 2TMS	C5H8O4	C11H24O4Si2	132.042	276.121	73, 147, 217	1317	RT, MS, VUV	All forms of pine, bear grass, dung, manzanita

3-hydroxyacetophenone TMS	C8H8O2	C11H16O2Si	136.052	208.092	193, 73, 208, 43, 75	1466	RI, MS, VUV	All
3-Hydroxybenzoic acid 2 TMS	C7H6O3	C13H22O3Si2	138.032	282.111	267, 223, 193, 73, 282	1558	RI, MS, VUV	All
4-Hydroxybenzoic acid 2TMS	C7H6O3	C13H22O3Si2	138.032	282.111	267, 223, 73, 193, 268	1622	RI, MS, VUV	All
1-4:3-6-Dianhydro- alpha-d-glucopyranose TMS	C6H8O4	C9H16O4Si	144.042	216.081	73, 129, 75, 155, 170	1338	RI, MS, VUV	All
Arabinonic acid, 1,4- lactone 3TMS	C5H8O5	C14H32O5Si3	148.037	364.156	73, 147, 117, 75, 217	1627	RI, MS, VUV	All pine forms, bear grass, manzanita
P-Coumaric alcohol 2TMS	C9H10O2	C15H26O2Si2	150.068	294.147	73, 205, 294	1625	RI, MS, VUV	All forms of pine and juniper
2, 4- dihydroxyacetophenone 2TMS	C8H8O3	C14H24O3Si2	152.047	296.126	217, 73, 281, 218, 75	1688	RI, MS, VUV	All forms of pine
Vanillin TMS	C8H8O3	C11H16O3Si	152.047	224.087	194, 193, 209, 73, 195	1529	RT, MS, VUV, STD	All forms of pine, peat, juniper
Arabinitol 5TMS	C5H12O5	C20H52O5Si5	152.068	512.266	73, 217, 147, 103, 205	1713	RI, MS	All pine forms except rotten log
Protocatechoic acid 3TMS	C7H6O4	C16H30O4Si3	154.027	370.145	193, 73, 370, 355, 311	1812	RT, MS, VUV	All forms of pine, peat, sage, juniper
Syringol TMS	C8H10O3	C11H18O3Si	154.063	226.103	196, 211, 181, 69, 197	1391	RT, MS, VUV, STD	All
4-nitrocatechol 2TMS	C6H5NO4	C12H21NO4S i2	155.022	299.101	73, 284, 299, 45, 74	1738	RI, MS, VUV, STD	All
Nonanoic acid TMS	C9H18O2	C12H26O2Si	158.131	230.170	69, 75, 131, 73, 117	1353	RT, MS, VUV, STD	All
1-8- dihydroxynaphthalene 2TMS	C10H8O2	C16H24O2Si2	160.052	304.131	73, 304, 217, 45, 74	1815	RI, MS, VUV	All
Umbelliferone TMS	C9H6O3	C12H14O3Si	162.032	234.071	219, 234, 73, 220, 191	1818	RT, MS, VUV	All forms of pine, dung, manzanita, grasses, sage, juniper
Deoxy-ribo-hexonic acid 1-4-lactone 3 TMS	C6H10O5	C15H34O5Si3	162.053	378.171	73, 147, 129, 155, 103	1764	RI, MS	All
Galactosan 3TMS	C6H10O5	C15H34O5Si3	162.053	378.171	217, 73, 204, 218, 147	1654	RT, MS, VUV, STD	All

Levoglucosan 3 TMS	C6H10O5	C15H34O5Si3	162.053	378.171	73, 204, 217, 147, 189	1698	RT, MS, VUV, STD	All
Mannosan 3TMS	C6H10O5	C15H34O5Si3	162.053	378.171	73, 217, 204, 191, 147	1676	RI, MS	All forms of pine
4-Coumaric acid 2TMS	С9Н8О3	C15H24O3Si2	164.047	308.126	293, 219, 73, 249, 308	1934	RI, MS, VUV	All
Eugenol TMS	C10H12O2	C13H20O2Si	164.084	236.123	206, 221, 236, 179, 73	1464	RT, MS, VUV	Engelmann spruce duff
4-vinylveratrole	C10H12O2		164.084		164, 149, 91, 77, 121	1358	RT, MS, VUV	Duff
Isoeugenol TMS	C10H12O2	C13H20O2Si	164.084	236.123	206, 205, 236, 207, 69	1562	RI, MS, VUV	All forms of pine, dung, grasses, juniper
Acetovanillone TMS	C9H10O3	C12H18O3Si	166.063	238.103	193, 223, 208, 73, 238	1612	RI, MS, VUV	All
Phloretic acid 2TMS	C9H10O3	C15H26O3Si2	166.063	310.142	179, 73, 180, 75, 45	1806	RT, MS, VUV	Bear grass, pine, manzanita
3-(Methylthio)benzoic acid TMS	C8H8O2S	C11H16O2SSi	168.025	240.064	225, 181, 151, 240, 75	1640	RI, MS, VUV	Rotten log
Methyl 3,4- dihydroxybenzoate 2TMS	C8H8O4	C14H24O4Si2	168.042	312.121	193, 73, 312, 194, 45	1714	RI, MS, VUV	All forms of pine
Vanillic acid 2TMS	C8H8O4	C14H24O4Si2	168.042	312.121	297, 267, 223, 253, 282	1755	RT, MS, VUV, STD	All
1-acenaphthenone	C12H8O		168.058		140, 168, 139, 73, 89	1665	RI, MS, VUV	Pine, sage, juniper
Homovanillyl alcohol 2TMS	C9H12O3	C15H28O3Si2	168.079	312.158	209, 73, 312, 210, 179	1702	RT, MS, VUV	All
Methylsyringol TMS	C9H12O3	C12H20O3Si	168.079	240.118	210, 69, 211, 225, 240	1476	RT, MS, VUV	All
Methyl nitrocatechol 2 TMS isomer 1	C7H7NO4	C10H15NO4S i	169.038	241.077	73, 296, 45, 313, 180	1771	RI, MS, VUV	All
Methyl nitrocatechol 2 TMS isomer 2	C7H7NO4	C10H15NO4S i	169.038	241.077	73, 298, 75, 45, 74	1828	RI, MS, VUV	All
Gallic acid 4TMS	C7H6O5	C19H38O5Si4	170.022	458.180	281, 73, 443, 458, 179	1947	RI, MS, VUV	Manzanita

1,4-Dihydroxy-2,6- dimethoxybenzene 2TMS	C8H10O4	C14H26O4Si2	170.058	314.137	284, 314, 73, 299, 269	1669	RI, MS, VUV	All
4-phenylphenol TMS	C12H10O	C15H18OSi	170.073	242.113	211, 227, 73, 242, 310	1771	RI, MS, VUV	All
Shikimic acid 4TMS	C7H10O5	C19H42O5Si4	174.053	462.211	204, 73, 147, 205, 206	1803	RT, MS, VUV	Pine and pine litter
Esculetin 2 TMS	C9H6O4	C15H22O4Si2	178.027	322.106	73, 322, 307, 45	2093	RT, MS, VUV	Sage
Coniferyl aldehyde TMS	C10H10O3	C13H18O3Si	178.063	250.103	220, 219, 250, 192, 73	1839	RT, MS, VUV	All
Phenanthrene	C14H10		178.078		178, 73, 176, 152, 177	1791	RT, MS, VUV, STD	All
9-fluorenone	C13H8O		180.058		180, 152, 151, 181, 150	1745	RI, MS, VUV	All
Benzocinnoline	C12H8N2		180.069		152, 180, 151, 76, 150	1913	RI, MS, VUV	All
Coniferyl alcohol 2TMS	C10H12O3	C16H28O3Si2	180.079	324.158	219, 193, 73, 309, 220	1946	RI, MS, VUV	Pine and juniper
Homovanillic acid 2TMS	C9H10O4	C15H26O4Si2	182.058	326.137	73, 209, 179, 267, 326	1761	RI, MS, VUV	All
Syringaldehyde TMS	C9H10O4	C12H18O4Si	182.058	254.097	73, 204, 217, 224, 147	1695	RT, MS, VUV, STD	Pine and manzanita
Dihydroconiferyl alcohol 2TMS	C10H14O3	C16H30O3Si2	182.094	326.173	206, 205, 236, 73, 326	1811	RI, MS, VUV	All
6H- Cyclobuta[jk]phenanthr ene	C15H10		190.078		190, 189, 95, 191, 187	1928	RI, MS, VUV	Pine, shrubs, bear grass
Scopoletin TMS	C10H8O4	C13H16O4Si	192.042	264.082	234, 206, 264, 73, 249	2031	RT, MS, VUV	Sage, rotten log, duff
Quinic acid 5TMS	C7H12O6	C22H52O6Si5	192.063	552.261	73, 345, 255, 147, 69	1851	RT, MS, VUV	Pine, manzanita, sage
9-methylanthracene	C15H12		192.094		192, 191, 189, 190, 165	1936	RI, MS, VUV	All
Methylanthracene isomer	C15H12		192.094		192, 191, 189, 190, 193	1906	RI, MS, VUV	All forms of pine, dung, bear grass, sage
1-methylanthracene	C15H12		192.094		192, 191, 189, 190, 193	1912	RI, MS, VUV	All

Methyl caffeate 2TMS	C10H10O4	C16H26O4Si2	194.058	338.137	73, 323, 249, 308, 338	2087	RI, MS, VUV	All forms of pine, ground, grasses, juniper
Pinitol 5TMS	C7H14O6	C22H54O6Si5	194.079	554.277	73, 217, 247, 147, 159	1788	RT, MS, VUV, STD	Pine and pine litter
Naphthalic anhydride	C12H6O3		198.032		154, 126, 198, 63, 50	2038	RI, MS, VUV	Pine and juniper
D-Arabino Hexonic acid 3-deoxy-2,5,6-tris-O- (TMS)-lactone	C9H10O5	C18H34O5Si3	198.053	414.171	73, 147, 129, 103, 75	1783	RI, MS	All
Syringic acid 2TMS	C9H10O5	C15H26O5Si2	198.053	342.132	73, 75, 312, 159, 297	1890	RT, MS, VUV, STD	All forms of pine, ground, manzanita, juniper
β-Carboline, 7-hydroxy- 1-methyl TMS	C12H10ON 2	C15H18N2OS i	198.079	270.119	255, 270, 73, 240, 75	1922	RT, MS, VUV	All forms of pine, juniper
Vanillyl glycol 3TMS	C10H14O4	C19H38O4Si3	198.089	414.208	73, 147, 117, 205, 209	1955	RT, MS, VUV	All forms of pine and juniper
Fluoranthene	C16H10		202.078		202, 203, 200, 201, 101	2077	RT, MS, VUV, STD	All
Pyrene	C16H10		202.078		202, 200, 203, 201, 101	2132	RT, MS, VUV, STD	All
Acephenanthrene	C16H12		204.094		202, 200, 203, 201, 101	2101	RT, MS, VUV	All
Pimanthrene	C16H14		206.110		206, 191, 204, 205, 189	2058	RT, MS, VUV	All
Anthraquinone	C14H8O2		208.052		208, 152, 180, 76, 151	1980	RT, MS, VUV, STD	Sage, lodgepole pine forms
Ethyl homovanillate TMS	C11H19O4	C14H27O4Si	215.128	287.168	252, 179, 209, 73, 282	1771	RT, MS, VUV	Pine litter, duff, rotten log, dung, and grasses
Benzofluorene	C17H12		216.094		216	2109	RT, MS, VUV	All forms of pine and shrubs
Octanoic acid TMS	C8H16O2	C11H24O2Si	216.155	144.115	73, 75, 117, 201, 131	1255	RT, MS, VUV, STD	All
2, 3-5, 6-dibenzoxalene	C16H10O		218.073		218, 73, 189, 91, 219	2191	RI, MS, VUV	Lodgepole
Benzo[b]naphtho[1,2- d]furan	C16H10O		218.073		218, 189, 219, 204	2135	RT, MS, VUV	Pine, manzanita, sage, bear grass
Benzo[kl]xanthene	C16H10O		218.073		218, 202, 217, 203, 219	2203	RT, MS, VUV	All pine forms
Hydroxypyrene	C16H10O	C19H18OSi	218.073	290.113	218, 189, 73, 219, 95	2152	RT, MS, VUV	Lodgepole pine

Vanillic acid isobutyl ester TMS	C12H16O4	C15H24O4Si	224.105	296.144	241, 256, 225, 73, 242	1861	RT, MS, VUV	All forms of pine, peat, manzanita
Cyclopenta[cd]pyrene	C18H10		226.078		226, 224, 227, 113, 225	2468	RT, MS, VUV	Pine, shrubs, bear grass
9-Tetradecenoic acid TMS	C14H26O2	C17H34O2Si	226.193	298.233	73, 75, 117, 283, 129	1836	RT, MS, VUV	Bear grass, duff, pine
Chrysene	C18H12		228.094		228, 226, 229, 114, 227	2482	RT, MS, VUV, STD	Pine, shrubs, bear grass
Benzanthrone	C17H10O		230.073		230, 202, 101, 200	2516	RT, MS, VUV	Lodgepole, pine, and manzanita
B-Cyclocostunolide	C15H20O2		232.146		217, 232, 91	1928	RT, VUV	sage, juniper
1-(10-Methylanthracen- 9-yl)ethanone	C17H14O		234.104		219, 191, 189, 234, 190	2405	RT, MS, VUV	All forms of pine
Retene	C18H18		234.141		219, 234, 204, 203, 220	2225	RT, MS, VUV, STD	All
Ethylhexyl benzoate	C15H22O2		234.162		105, 70, 77, 112, 83	1707	RT, MS, VUV, STD	All forms of pine and shrubs
Heptadecane (C17)	C17H36		240.282		57, 71, 43, 131	1698	RT, MS, VUV, STD	Dung, peat, rice straw, and pine bark
Confertin	C15H20O3		248.141		248, 81, 119	2043	RT, MS, VUV	Sage
Benzo[a]pyrene	C20H12		252.094		252, 250, 253, 126, 113	2886	RT, MS, VUV, STD	Pine, sage, juniper
Benzofluoranthene isomer 1	C20H12		252.094		252, 253, 250, 125, 126	2792	RT, MS, VUV, STD	Pine, sage, juniper, manzanita
Benzofluoranthene isomer 2	C20H12		252.094		252, 250, 253, 73, 126	2873	RT, MS, VUV, STD	Pine, juniper
11-Hexadecenoic acid TMS	C16H30O2	C19H38O2Si	254.225	326.264	55, 69, 83, 41, 96	1938	RT, MS, VUV	All
Palmitic acid TMS	C16H32O2	C19H40O2Si	256.240	328.280	117, 73, 313, 75, 129	2042	RT, MS, VUV, STD	All
Nonadecane (C19)	C19H40		268.313		57, 71, 43, 131	1897	RT, MS, VUV, STD	All
Heptadecanoic acid TMS	C17H34O2	C20H42O2Si	270.256	342.295	73, 117, 75, 129, 327	2112	RT, MS, VUV, STD	All forms of pine, dung, peat, and bear grass
Methyl 13- methylpentadecanoate	C17H34O2		270.256		74, 87, 270	1922	RT, VUV	Pine, ground, and grass
Arbutin 4TMS	C12H16O7	C24H48O7Si4	272.090	560.248	73, 182, 254, 129, 103	2563	RT, MS	Manzanita

<b>Divanillyl 2TMS</b>	C16H18O4	C22H34O4Si2	274.12050 9	418.200	209, 73, 210, 179, 211	2468	RT, MS, VUV	All forms of pine, dung, juniper
Dibutyl phthalate	C16H22O4		278.152		149, 57	1857	MS, VUV	All
Linoelaidic acid TMS	C18H32O2	C21H40O2Si	280.240	352.280	75, 73, 67, 81, 95	2206	RT, MS, VUV	All
Oleic acid TMS	C18H34O2	C21H42O2Si	282.256	354.295	73, 75, 117, 129, 55	2220	RT, MS, VUV	All
Icosane (C20)	C20H42		282.329		57, 131, 71, 85	1998	RT, MS, VUV, STD	All
Dehydroabietal	C20H28O		284.214		159, 269, 173, 209, 241	2278	RT, MS, VUV	All forms of pine
Stearic acid TMS	C18H36O2	C21H44O2Si	284.272	356.311	117, 73, 75, 341, 129	2238	RT, MS, VUV, STD	All
Isopimaral	C20H30O		286.230		187, 131, 105, 91, 145	2241	RT, MS, VUV	Pine and pine litter
Henicosane (C21)	C21H44		296.344		57, 131, 71, 43	2100	RT, MS, VUV, STD	All
18-Methyl-nonadecanol TMS	C20H42O	C23H50OSi	298.324	370.363	75, 355, 97, 73, 69	2348	RI, MS, VUV	All forms of pine, grass, sage
Dehydroabietic acid TMS	C20H28O2	C23H36O2Si	300.209	372.248	239, 240, 73, 173, 357	2386	RT, MS, VUV	All
Abietic acid TMS	C20H30O2	C23H38O2Si	302.225	374.264	256, 241, 185, 213, 73	2424	RT, MS, VUV, STD	Pine and bear grass
Isopimaric Acid TMS	C20H30O2	C23H38O2Si	302.225	374.264	241, 73, 242, 359, 105	2354	RT, MS, VUV, STD	All forms of pine
Isopimaric acid TMS isomer	C20H30O2	C23H38O2Si	302.225	374.264	241, 256, 73, 257, 242	2342	RT, MS, VUV, STD	All forms of pine and bear grass
Pimaric acid TMS	C20H30O2	C23H38O2Si	302.225	374.264	121, 73, 120, 257, 91	2307	RT, MS, VUV	All forms of pine and bear grass
Sandaracopimaric acid TMS	C20H30O2	C23H38O2Si	302.225	374.264	73, 121, 120, 119, 81	2323	RT, MS, VUV	All forms of pine and juniper
Docosane (C22)	C22H46		310.360		57, 71, 43, 131	2199	RT, MS, VUV, STD	Pine and grass
Hexadecanoic acid, 3,7,11,15-tetramethyl TMS	C20H40O2	C23H48O2Si	312.303	384.342	117, 73, 75, 369, 129	2438	RT, MS, VUV	All
7-Oxo-dehydroabietic acid TMS	C20H26O3	C23H34O3Si	314.188	386.228	253, 268, 73, 187, 386	2598	RI, MS, VUV	Pine and bear grass

Tricosane (C23)	C23H48		324.376		57, 71, 43, 85	2299	RT, MS, VUV, STD	All
7-Oxodehydroabietic acid methyl ester	C21H28O3		328.204		253, 254, 187, 211, 328	2585	RI, MS, VUV	All forms of pine
Tetracosane (C24)	C24H50		338.391		57, 97, 83, 55	2393	RT, MS, VUV, STD	All
3,4- divanillyltetrahydrofura n 2TMS	C20H24O5	C26H40O5Si2	344.162	488.241	209, 210, 73, 179, 488	2981	RT, MS, VUV	All
Pentacosene	C25H50		350.391		83, 57, 97, 43	2494	RT, VUV	Ground, manzanita, bear grass
Pentacosane (C25)	C25H52		352.407		57, 71, 131, 85	2501	RT, MS, VUV, STD	All
1-tetracosanol (C24 Alcohol)	C24H50O	C27H58OSi	354.386	426.426	75, 411, 97, 57, 412	2743	RT, MS, VUV, STD	All
Matairesinol 2TMS	C20H22O6	C26H38O6Si2	358.142	502.221	209, 73, 179, 210, 502	3160	RT, MS, VUV	Pine, pine litter, and juniper
Hexacosene	C26H52		364.407		57, 69, 97, 111, 83	2595	RT, MS, VUV, STD	Ground, manzanita, bear grass
Hexacosane (C26)	C26H54		366.423		131, 57, 83, 55	2595	RT, MS, VUV, STD	Pine, ground, and grass
Heptacosane (C27)	C27H56		380.438		57, 71, 85, 69, 43	2701	RT, MS, VUV, STD	All
Stigmasta-3,5 diene	C29H48		396.376		147, 81, 145, 105, 91	3106	RT, MS, VUV	All
Nonacosane (C29)	C29H60		408.470		57, 71, 85, 43, 69	2901	RT, MS, VUV, STD	All
β-sitosterol TMS	C29H50O	C32H58OSi	414.386	486.426	129, 73, 75, 95, 121	3347	RT, MS, VUV, STD	All
10-nonacosanol TMS	C29H60O	C32H68OSi	424.464	496.504	229, 73, 75, 369, 83	3062	RT, MS, VUV, STD	All forms of pine, juniper
<b>Tocopherol TMS</b>	C29H50O2	C32H58O2Si	430.381	502.421	237, 73, 236, 502, 238	3138	RT, MS, VUV	All
Triacontane (C30)	C30H62		436.501		57, 71, 85, 43	3001	RT, MS, VUV, STD	All
Hentriacontane (C31)	C31H64		464.532		57, 71, 85, 69, 43	3102	RT, MS, VUV, STD	All
Dotriacontane (C32)	C32H66		492.563		57, 71, 85, 131	3202	RT, MS, VUV, STD	All

Tritriacontane (C33)	C33H68	520.595	57, 71, 69, 43,	3302	RT, MS, VUV,	All
			85		STD	
Tetratriacontane (C34)	C34H70	548.626	57, 71, 85,	3399	RT, MS, VUV,	All
			131		STD	
Pentatriacontane (C35)	C35H72	576.657	71, 57, 85,	3500	RT, MS, VUV,	All
			131		STD	

#### 3. Conversion of instrument response to mass loadings and emission factors:

Internal standard was injected onto each sample filter prior to analysis on the TD-GC×GC-EI/VUV-HRToFMS. This was done to correct for matrix effects and slight changes in instrument performance. The internal standard mixture consisted of relevant biomass burning deuterated compounds (see next section). The total volume of each chromatographic peak was integrated and normalized to the nearest internal standard peak volume. The normalized peak volume was then converted to mass loading by finding the nearest standard compound of the same compound class in first and second dimension and using its accompanying mass loadings calibration curve (see next section for more details). In other words, compounds classified as sugars (see SI for more details) were converted to mass loadings based upon the calibration of the nearest sugar standard. Unknown compounds were matched to the nearest standard compound regardless of chemical classification.

Mass loading calibration curves were determined by measuring the instrument's response to varying amounts of 99 standard compounds typically found in biomass burning organic aerosol particles. We estimate the systematic uncertainty in the mass loadings for the unknown compounds at a factor of 2 and unidentified but classified compounds at roughly  $\pm 30\%$ . This is based upon calculating mass loadings of other standard compounds not included in the 99-compound standard mixture. Sampled compounds that exactly matched a standard compound have a lower uncertainty ~ $\pm 10\%$  primarily due to instrument variation. Since the same data inversion factor was applied to the same observed compound across all samples, these systematic uncertainties do not affect the trends observed in this study but may affect the mass fractions each compound contributes to the total observed mass from a burn.

The background-subtracted compound mass loading was then converted to emission factors by first normalizing to the background-corrected CO<sub>2</sub> mass sampled. CO<sub>2</sub> concentration (by volume) was measured in real-time by the open-path Fourier transform infrared spectroscopy (OP-FTIR). Details of this measurement can be found in Selimovic et al. (2017). The mass of CO<sub>2</sub> that pass through a filter was calculated by first converting the CO<sub>2</sub> volume concentration into mass concentration. CO<sub>2</sub> mass concentration was then numerically integrated over the filter sampling time then multiplied by the total volumetric flow through the filter. The normalized organic compound mass loadings were converted to emission factors,  $EF_{compound}$ , via the fire-integrated  $EF_{CO2}$  following the formula below (units are given in parentheses).

$$EF_{compound} = \frac{\Delta mass \ of \ compound \ (ng)}{\Delta mass \ of \ CO_2 \ (g)} \times EF_{CO2} \ (g/kg \ dry \ fuel \ burned)$$

The  $\Delta$  indicate change over background. EFs<sub>CO2</sub> for each burn during FIREX Fire Lab campaign are also presented Selimovic et al. (2018) and were determined by the carbon mass balance method (Ward and Radke, 1993; Yokelson et al., 1996). The carbon mass was summed over the gaseous species detected by the OP-FTIR, with CO<sub>2</sub>, CO, and CH<sub>4</sub> accounting for 97-99% of the total emitted carbon. Including the carbon mass of the I/SVOCs would only slightly decrease the EFs reported here and thus their contributions to the carbon mass balance were assumed to be negligible.

#### 4. Internal/external standards and mass loading calibration curves:

A mixture of deuterated internal standards was injected onto every filter prior to analysis. The mixture consisted of 34 compounds that are either found in biomass burning organic aerosols (BBOA) or have functional groups that closely resemble compounds in BBOA. A full list of internal standard compounds is given in Table S2.

Internal Standard Compounds							
d3-vanillin	d4-4-methoxy-benzaldehyde						
d6-syringic Acid	d8-anthraquinone						
d8- methylcatechol	d4-phthalic acid						
d3- vanillic Acid	d5-benzoic acid						
d4-3-nitrobenzoic Acid	d5-C10 acid						
d5-4-hydroxybenzaldehyde	d12-C14 acid						
d9-1-nitropyrene	d31-C16 acid						
d26-C12 alkane	d35-C18 acid						
d28-C13 alkane	d43-C22 acid						
d30-C14 alkane	d7-cholesterol						
d34-C16 alkane	d5-Cholestane						
d38-C18 alkane	d5-3-hydroxy-1,5-pentanedioic acid						
d42-C20 alkane	C6 diacid						
d46-C22 alkane	d31-pentadecanol						
d50-C24 alkane	6 <sup>13</sup> C -glucose						
d54-C26 alkane	2 <sup>13</sup> C-pentaerythritol						
d58-C28 alkane	d10-pyrene						
d62-C30 alkane	d10-phenanthrene						
d66-C32 alkane	d12-perylene						
d70-C34 alkane	d12-chrysene						
d74-C36 alkane	d14-dibenzanthracene						

Table S2 list of internal standards used on each sample

A more extensive mixture of standards was used to calibrate the mass loading sensitivity of the TD-GC×GC EI-HRToFMS directly after all the Fire Lab samples were run. This mixture of external standards contained 99 compounds that have been previously observed in biomass burning emissions. These compounds represent all the compound families as described in the main paper and are given in Table S3. Various mass loadings were injected onto separate blank quartz fiber filters and analyzed with the TD-GC×GC EI-HRToFMS. The volume ratio between the total external standard peak and the nearest total internal standard peak were then correlated to the respective mass loading ratio. Example mass loading calibration curves are shown in Figure S3. In general, the linearity between mass loading and instrument response was good ( $R^2$ >0.9) over a wide range of normalized mass loadings; this may not be true at extremely low and high mass loadings for some compounds. Measured levoglucosan mass loadings did exceed the upper limits of the calibration curve for some of the conifer burns; in these cases, the calibration curve was extrapolated and may lead to higher uncertainty in levoglucosan EFs. Furthermore, several PAH external standard compounds showed poor linearity because their peaks in the chromatogram co-eluted with the nearest internal standard peak at high mass loadings. These high mass loading points were not taken into account for the calibration curve. This assumption is valid as the volumes of the PAH peaks were not observed during the FSL experiments to be within this high mass loading range.

External Standard Compounds						
Cholesterol	Retene	C7 carboxylic acid	C12 alkane			
Stigmasterol	Naphthalene	C8 carboxylic acid	C13 alkane			
β-sitosterol	Phenanthrene	C9 carboxylic acid	C14 alkane			
Ergosterol	Pyrene	C10 carboxylic acid	C15 alkane			
α-Amyrin	Acenaphthene	C11 carboxylic acid	C16 alkane			
Levoglucosan	Acenaphthylene	C12 carboxylic acid	C17 alkane			
Levoglucosenone	Anthracene	C13 carboxylic acid	Pentadecane, 2,6,10,14- tetramethyl-			
Mannosan	1,2-Benzanthracene	C14 carboxylic acid	C18 alkane			
Galactosan	Benzo(a)pyrene	C15 carboxylic acid	Hexadecane, 2,6,10,14- tetramethyl-			
Guaiacol	Benzo(b)fluoranthene	C16 carboxylic acid	C19 alkane			
Syringol (2,6- Dimethoxyphenol)	Benzo(g,h,i)perylene	C17 carboxylic acid	C20 alkane			
Syringic Acid	Benzo(k)fluoranthene	C18 carboxylic acid	C21 alkane			
Syringaldehyde	Chrysene	C20 carboxylic acid	C22 alkane			
Sinapinalehyde	Dibenz(a,h)anthracene	C22 carboxylic acid	C23 alkane			
Vanillin	Fluoranthene	C23 carboxylic acid	C24 alkane			
Vanillic acid	Fluorene	C24 carboxylic acid	C25 alkane			
4-hydroxybenzoic acid	Indeno(1,2,3-cd)pyrene	C26 carboxylic acid	C26 alkane			
p-Anisic acid (4- methoxybenzoic acid)	Maltol	C28 carboxylic acid	C27 alkane			
3,5-dimethoxyphenol	5-(Hydroxymethyl) furfural	D-(+)-glucose	C28 alkane			
Phthalic acid	4-Nitrocatechol	D-(+)-mannose	C29 alkane			
Abietic acid	5-Nitrovanillin	L-(-)-mannose	C30 alkane			
Isopimaric acid	2,4-Dinitrophenol	D-(+)-galactose	C31 alkane			
Resorcinol		D-Pinitol	C32 alkane			
Hydroquinone		Pyrocatechol	C33 alkane			
4-Methylcatechol			C34 alkane			

Table S3 List of external standards used to determine the mass loading calibration curve of the TD-GC×GC-EI-HRToFMS



Figure S3 Example mass loading calibration curves for cholesterol, levoglucosan, retene, and sinapinaldehyde. Each external standard compound is normalized to the nearest internal standard (IS) compound. Colors are coded based upon the broad compound family: cholesterol=sterol, levoglucosan=sugar, retene=PAH, and sinapinaldehyde=methoxyphenol

#### 5. Classifying unidentified compounds into chemical families:

The 1D RI and the 2D retention time of an unidentified compound were first examined to ballpark potential family choices. Larger molecules like sterols have lower vapor pressures, and thus higher RI, than sugars. Derivatized methoxyphenols are more polar than derivatized sugars but have similar vapor pressures; therefore, methoxyphenols elute later in the second dimension than sugars. After the possible families were narrowed down, the electron ionization (EI) mass spectrum of the unidentified compound was then analyzed for specific ions and patterns that signify particular functional groups. For example, derivatized sugars exhibit 204 and 217 m/z and PAHs show little fragmentation. Derivatized sugars also show significant fragmentation with vacuum ultra violet light (VUV) ionization, making them easier to distinguish from compounds with benzene rings in the VUV mass spectrum. Each of the ~3000 compounds, including identified compounds, were analyzed using this method and placed into a family. Example compounds for each category are given in Table S3. The bulk of the unidentified compounds could not be placed into a category and remain unknown. More work needs to be done to synthesize standards of a wider variety of compounds in order to better identify/classify the unknown compounds.

Family Name	Example compound (underivatized)
Non-cyclic	
aliphatic/oxygenated	3.7.11.15 tetramethyl beyadecanoic acid
Sugars	
Juguis	OHO
	Levoglucosan
PAHs/methyl/oxygenated	ÇH <sub>3</sub>
	1-Methylanthracene
Resin acids/diterpenoids	
	H H
Storols/tritornonoids	
Sterois/triter periorus	
	L L L L L L L L L L L L L L L L L L L
	но
	β-Sitosterol
Organic nitrogen	OH
	Pyroglutamic acid
Aromatic oxygen	
heterocycles	
	ОТОТОН
	Scopoletin
Oxygenated cyclic	
aikanes	но
	ОН
	Arabino-1,4-lactone
Methoxyphenols	
	Syringol
	Synngor

Table S4 List of chemical families and examples for each family (without derivatization)



## 6. Classified I/SVOC mass fractions averaged over fuel type

The average mass fractions of total observed I/SVOCs for the chemical families across each fuel types (see Figure 3) are given in Table S5.

	Shrubs	Grass	Wood	Coniferous Litter	Conifers	Peat	Dung	Coniferous Duff	Woody Debris
Unknown	50%, 5%	59%, 6%	52%, 14%	48%, 9%	57%, 13%	50%	50%	59%, 15%	88%, 1%
Non-cyclic aliphatics/oxy	12%, 9%	8%, 2%	8%, 2%	7%, 2%	6%, 2%	26%	9%	9%, 2%	1%, 0%
Sugars	12%, 3%	12%, 2%	21%, 8%	15%, 6%	18%, 10%	3%	14%	9%, 6%	5%, 1%
PAH/methyl+oxy	1%, 1%	0%, 0%	1%, 1%	2%, 0%	1%, 0%	1%	0%,	2%, 0%	1%, 0%
Resin acids /diterpenoids	0%, 0%	0%, 0%	0%, 0%	8%, 1%	3%, 2%	0%	0%	3%, 2%	0%, 0%
Sterols, triterpenoids	1%, 0%	0%, 0%	0%, 0%	1%, 0%	0%, 0%	0%	1%	0%, 0%	0%, 0%
Organic nitrogen	13%, 8%	12%, 1%	8%, 4%	14%, 1%	10%, 5%	15%	22%	11%, 6%	1%, 1%
Oxy aromatic heterocycles	1%, 2%	1%, 0%	1%, 0%	0%, 0%	1%, 0%	0%	0%	0%, 1%	0%, 0%
Oxy cyclics	0%, 0%	3%, 2%	0%, 0%	1%, 0%	1%, 1%	0%	1%	1%, 1%	0%, 0%
Methoxyphenols	3%, 1%	3%, 2%	7%, 3%	3%, 0%	2%, 1%	4%	3%	4%, 1%	3%, 1%
Substituted phenols	7%, %	1%, 0%	0%, 0%	1%, 0%	1%, 1%	1%	1%	1%, 0%	0%, 0%
Substituted benzoic acids	1%, 1%	0%, 0%	0%, 0%	0%, 0%	0%, 0%	0%	0%	0%, 0%	0%, 0%
Average MCE.	0.958	0.898	0.958	0.955	0.931	0.840	0.902	0.871	0.878

Table S5 Mass fraction (in %) and standard deviation of each of the chemical families for the various fuel types.

# 7. EFs for families of compounds as a function of MCE:

Emission factors for each of the 12 families (including unknowns) were summed together in each fire-integrated sample. Figure S4 displays all of the family EFs as a function of modified combustion efficiency (MCE). This figure is an expansion of Figure 4 in the main paper. EFs for all chemical families exhibit a clear dependence on MCE, with smoldering burns producing 2-4 orders of magnitude more I/SVOC emissions. Logarithmic fits of the form log(EF)=slope(MCE)+int were also applied to these observations with the fit parameters displayed on each of the panels.



Figure S4 Emission factors (EFs) of each of the 12 chemical families as a function of modified combustion efficiency (MCE). Each panel/color represents a different chemical family and the different symbols show the different fuel types. Dashed lines are of the log(EF)=slope(MCE)+int fits with the parameters provided in the panel. Note, peat (open pentagon) was not included in the fits except for non-cyclics aliphatic/oxy (red).

Chemical Family	Slope ± error	Intercept ± error
Total	$-11.44858 \pm 1.87$	$11.58506 \pm 1.74$
Unknown	$-12.05974 \pm 2.05$	$11.8919 \pm 1.90$
Non-cyclic Aliphatic/Oxy	$-9.21952 \pm 1.54$	$8.29706 \pm 1.42$
Sugars	$-8.85359 \pm 2.29$	$8.30773 \pm 2.12$
PAH/methyl+oxy	$-14.63717 \pm 2.07$	$12.40498 \pm 1.91$
<b>Resin Acids/diterpenoids</b>	$-14.84408 \pm 4.22$	$12.63297 \pm 3.90$
Sterols/triterpenoids	$-9.42488 \pm 1.93$	$7.23105 \pm 1.79$
Organic Nitrogen	$-6.97334 \pm 2.07$	$6.41579 \pm 1.91$
<b>Oxy Aromatic Heterocycles</b>	$-8.46896 \pm 2.33$	$6.50727 \pm 2.15$
Oxygenated Cyclic	$-11.1686 \pm 2.84$	$9.04829 \pm 2.63$
Methoxyphenol	$-11.45675 \pm 1.72$	$10.03962 \pm 1.59$
Substituted Phenol	$-9.45183 \pm 3.22$	$7.63392\pm2.98$
Substituted Benzoic Acid	$-8.58551 \pm 2.49$	$5.9437 \pm 2.30$

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