Supporting Information

Molecular Composition of Particulate Matter Emissions from Dung and Brushwood Burning Household Cookstoves in Haryana, India

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S1. Samples utilized in this study

Table S1.1: Samples utilized in sections 3.1-3.5. Representative mass spectra shown in Figure 2, section 3.1 correspond to samples M10, L7, and M1. The % abundance for $C_xH_yO_z$, $C_xH_yN_w$, and $C_xH_yO_zN_w$ peaks from the nano-DESI mass spectra are given as well as arithmetic means and standard deviations for each cookfire category: brushwood/*chulha*, dung/*chulha*, and dung/*angithi*.

Sample	Date	Fuel	Stove	Moisture (% wet basis)	Meal	$C_xH_yO_z$ (% abundance)	$C_xH_yN_w$ (% abundance)	$C_xH_yO_zN_w$ (% abundance)
M10	8/26/15	brushwood	chulha	18.0	chapati	35.1	31.3	4.1
RE007	8/30/15	brushwood	chulha	29.5	chapati	34.3	15.8	34.4
RE032	8/28/15	brushwood	chulha	17.7	chapati	60.0	24.3	11.0
						43.1±14.6	23.8±7.8	16.5±15.9
H5	8/14/15	dung	chulha	6.9[a]	chapati	4.4	75.6	14.1
L7	8/21/15	dung	chulha	10.5[a]	chapati	4.8	79.8	11.7
P2	8/20/15	dung	chulha	10.8[a]	chapati	3.2	84.4	11.9
						4.1±0.9	79.9±4.4	12.6±1.3
C7	8/11/15	dung	angithi	8.3[a]	buffalo fodder	1.4	82.3	14.1
M1	8/17/15	dung	angithi	10.9[a]	buffalo fodder	1.2	83.0	15.2
P1	8/19/15	dung	angithi	10.4[a]	buffalo fodder	7.0	81.0	11.7
						3.2±3.3	82.1±1.0	13.6±1.8

[a] Dung moisture content was measured using a commercial moisture probe, and converted to a real value, moisture on a % wet basis, using Gautam et al., 2016.

Table S1.2: Samples utilized in section 3.6 for MAC and AAE analyses.

Sample	Date	Fuel	Stove	Moisture (% wet basis)	Meal
D2	8/8/2015	dung	chulha	8.3[a]	chapati
N6	8/26/16	brushwood	chulha	13.9	rice

[a] Dung moisture content was measured using a commercial moisture probe, and converted to a real value, moisture on a % wet basis, using Gautam et al., 2016.

Table S1.3: Samples analyzed in section 3.6 via HPLC-PDA-HRMS.

Sample	Date	Fuel	Stove	Moisture (% wet basis)	Meal
RE015	8/28/15	brushwood	chulha	29.5	rice
T2	8/18/15	dung	angithi	10.8[a]	buffalo fodder

[a] Dung moisture content was measured using a commercial moisture probe, and converted to a real value, moisture on a % wet basis, using Gautam et al., 2016.

S2. Scaling of abundances in mass spectra to approximate emission factors

A separate filter reserved for gravimetric analysis was used for fine particle emissions measurements. These filters were pre-weighed on a Cahn-28 electrobalance after equilibrating for a minimum of 24 hours in a humidity and temperature-controlled environment (average temperature 18.9 degrees Celsius, standard deviation 0.4 degrees Celsius, average relative humidity 64%, standard deviation 7%). This PTFE filter collected cookstove emissions on a separate line than the filter analyzed by nano-DESI-HRMS and HPLC-PDA-HRMS techniques. Another gravimetric filter was collected in the background during the cooking event, and was equilibrated and weighed in the same way. The masses for the background and sample filters were utilized after accounting for the difference in flow rates. Then, the background mass was subtracted from the sample mass to obtain the mass of PM (m_{PM}) in the following equation.

$$\frac{EF_{PM}}{EF_{CO}} = \frac{m_{PM}/V_{air}}{m_{CO}/V_{air}} \tag{1}$$

The concentration of CO was measured using Whole Air Samples (WAS). The air sample was taken back to UCI where it was injected into a GC-FID with a Ni catalyst that converts CO into detectable CH_4. Other gases were also detected using a GC system comprised of 3 gas chromatographs equipped with 5 columns (DB-1, Restek 1701, DB-5ms) and detectors (FID, ECD, MS). A complete list of gaseous emission factors will be reported in a separate manuscript.

EF_{CO} was produced using the carbon-balance method. This method traces carbon in the form of emitted CO_2, CO, CH_4, other hydrocarbons, and PM and utilizes the relative concentrations of these compounds to evaluate emission factors. The total gas-phase carbon emissions were approximated with the concentrations of 86 gases, measured using WAS. The ratio of the mass concentration of carbon in CO (C_{CO}) to the total mass concentration of detected gas-phase carbon was calculated using equation (2).

$$C_{CO}\ emitted\ (g) = \frac{C_{CO}(g\ m^{-3})}{\sum_1^{86} C_1+C_2+C_3+\cdots+C_{86}} \cdot C_T\ (kg) \cdot \frac{1000\ g}{1\ kg} \tag{2}$$

Where C_i represents the mass of carbon in compound i per m^3 of air. C_T specifically refers to the net mass of carbon in the fuel, and is adjusted for ash and char carbon. The carbon content of the fuel was taken to be 33% for buffalo dung and 45% for brushwood fuels based on standard values from Smith et al. (2000). Carbon in ash was calculated by assuming standard values of 1.23% and 14.4% of the dry brushwood and dung mass, respectively (Smith, et al., 2000). Then, we calculated EF_{CO} using equation (3).

$$EF_{CO}\left({}^{g\ CO}/_{kg\ fuel}\right) = \frac{C_{CO}\ emitted(g) \cdot \frac{28.01\ g}{12.00\ g}}{mass_{fuel}(kg)} \tag{3}$$

Where $mass_{fuel}$ is the net dry fuel in kg burned for the cooking event.

To scale peak intensities (A_i) of the ESI mass spectra, we assumed that peak abundances are proportional to the relative mass concentrations, and hence emission factors (EFs), of the corresponding compounds. In other words,

$$A_i \propto EF_i \tag{4}$$

where A is the peak abundance for compound i. We also assumed that the detected species are the only species that contribute to EF_{PM}.

$$\sum EF_a + EF_i + \cdots + EF_z = EF_{PM} \tag{5}$$

Where Σ is the sum over EFs of all compounds present in the mass spectrum.

Therefore, we used the following to calculate the EF for compound i.

$$EF_i = \frac{A_i}{\sum A_a + A_i + \cdots + A_z} \cdot EF_{PM} \tag{6}$$

Note that the emission factors calculated this way are approximate and likely too high due to the exclusion of the compounds ESI is not sensitive to detect. Therefore, the EFs shown in Figure 2 of the main text should be interpreted as a relative approach to compare different samples of this study rather than absolute measurement.

S3. Species exclusively detected in dung/*chulha* and dung/*angithi* cookfires

Table S3.1. List of reproducible compounds found exclusively in the brushwood samples. Tentative molecular structure assignments are listed when the compound has previously been identified in the chemical biomass-burning literature. Normalized, relative peak abundances are designated LOW (<1%), MEDIUM (1-9%), High (10-100%). All species were detected as protonated ions.

Observed *m/z*	Calculated *m/z*	Chemical formula of neutral species	DBE	Relative average abundance	Tentative assignment(s)	References
123.043	123.044	$C_7H_6O_2$	5	MEDIUM	Benzoic acid/hydroxybenzaldehyde	(Smith et al., 2009)
153.054	153.055	$C_8H_8O_3$	5	MEDIUM	Vanillin/anisic acid	(Simoneit, 2002; Simoneit et al., 1993)
195.100	195.102	$C_{11}H_{14}O_3$	5	MEDIUM	Dimethoxyphenylacetone	(Simoneit et al., 1993)
197.080	197.081	$C_{10}H_{12}O_4$	5	LOW	Acetosyringone	(Simoneit et al., 1993)
207.100	207.102	$C_{12}H_{14}O_3$	6	MEDIUM		
236.126	236.128	$C_{13}H_{17}O_3N$	6	MEDIUM		
335.147	335.149	$C_{18}H_{22}O_6$	8	LOW	Disyringyl	(Simoneit, 2002)

Table S3.2: List of reproducible compounds detected exclusively in the emissions from dung/*chulha* cookfires. The labels for peak abundances are the same for Table S3.1. All species were detected as protonated ions.

Observed *m/z*	Calculated *m/z*	Chemical formula of the neutral species	DBE	Relative average abundance
260.127	260.128	$C_8H_9N_3$	8	MEDIUM
257.200	257.201	$C_6H_7N_5$	7	MEDIUM
257.164	257.165	$C_{11}H_{11}N$	8	LOW
257.128	257.128	$C_{12}H_{13}N$	9	LOW
238.133	238.134	$C_{13}H_9N$	10	MEDIUM
231.185	231.186	$C_{11}H_8ON_2$	6	MEDIUM
229.097	229.097	$C_{11}H_9O_2N$	9	LOW
211.086	211.087	$C_{14}H_{11}ON$	10	LOW
210.091	210.091	$C_{13}H_{10}ON_2$	10	LOW
188.070	188.071	$C_{13}H_{12}O_2N_2$	8	LOW

185.071	185.071	$C_{15}H_{22}N_2$	9	MEDIUM
180.081	180.081	$C_{15}H_{15}N_3$	10	LOW
172.112	172.112	$C_{15}H_{16}O_2N_2$	7	LOW
158.096	158.096	$C_{16}H_{20}ON_2$	7	MEDIUM
150.077	150.077	$C_{17}H_{24}N_2$	6	LOW
148.087	148.087	$C_{15}H_{17}O_3N$	6	LOW

Table S3.3: List of reproducible compounds detected exclusively in the emissions from dung/*angithi* cookfires. The labels for peak abundances are the same for Table S3.1. All species were detected as protonated ions, except for $C_{12}H_{13}ON$, which was detected as a $[M+Na]^+$ ion.

Observed *m/z*	Calculated *m/z*	Chemical formula of the neutral species	DBE	Relative average abundance
110.060	110.060	C_6H_7ON	4	MEDIUM
139.086	139.087	$C_7H_{10}ON_2$	4	LOW
148.075	148.076	C_9H_9ON	6	LOW
150.091	150.091	$C_9H_{11}ON$	5	LOW
153.102	153.102	$C_8H_{12}ON_2$	4	LOW
164.082	164.082	$C_8H_9ON_3$	6	LOW
165.077	165.077	$C_7H_8ON_4$	6	LOW
165.102	165.102	$C_9H_{12}ON_2$	5	LOW
167.118	167.118	$C_9H_{14}ON_2$	4	LOW
168.065	168.066	$C_8H_9O_3N$	5	LOW
169.097	169.097	$C_8H_{12}O_2N_2$	4	LOW
174.102	174.103	$C_{10}H_{11}N_3$	7	LOW
178.097	178.097	$C_9H_{11}ON_3$	6	LOW
178.122	178.123	$C_{11}H_{15}ON$	5	LOW
179.118	179.118	$C_{10}H_{14}ON_2$	5	LOW
180.101	180.102	$C_{10}H_{13}O_2N$	5	LOW
181.097	181.097	$C_9H_{12}O_2N_2$	5	LOW
182.081	182.081	$C_9H_{11}O_3N$	5	LOW
190.122	190.123	$C_{12}H_{15}ON$	6	LOW
192.113	192.113	$C_{10}H_{13}ON_3$	6	LOW
195.112	195.113	$C_{10}H_{14}O_2N_2$	5	LOW

197.128	197.128	$C_{10}H_{16}O_2N_2$	4	LOW
198.127	198.128	$C_{14}H_{15}N$	8	LOW
204.113	204.113	$C_{11}H_{13}ON_3$	7	LOW
206.128	206.129	$C_{11}H_{15}ON_3$	6	LOW
208.144	208.144	$C_{11}H_{17}ON_3$	5	LOW
209.164	209.165	$C_{12}H_{20}ON_2$	4	LOW
210.088	210.089	$C_{12}H_{13}ON$[a]	7	LOW
213.102	213.102	$C_{13}H_{12}ON_2$	9	MEDIUM
216.113	216.113	$C_{12}H_{13}ON_3$	8	LOW
216.138	216.138	$C_{14}H_{17}ON$	7	LOW
220.144	220.144	$C_{12}H_{17}ON_3$	6	LOW
221.164	221.165	$C_{13}H_{20}ON_2$	5	LOW
222.160	222.160	$C_{12}H_{19}ON_3$	5	LOW
223.180	223.180	$C_{13}H_{22}ON_2$	4	LOW
230.128	230.129	$C_{13}H_{15}ON_3$	8	LOW
231.185	231.186	$C_{15}H_{22}N_2$	6	MEDIUM
232.144	232.144	$C_{13}H_{17}ON_3$	7	LOW
232.180	232.181	$C_{14}H_{21}N_3$	6	LOW
234.159	234.160	$C_{13}H_{19}ON_3$	6	LOW
235.143	235.144	$C_{13}H_{18}O_2N_2$	6	LOW
237.232	237.233	$C_{15}H_{28}N_2$	3	LOW
238.122	238.123	$C_{16}H_{15}ON$	10	MEDIUM
240.138	240.138	$C_{16}H_{17}ON$	9	MEDIUM
242.153	242.154	$C_{16}H_{19}ON$	8	LOW
244.180	244.181	$C_{15}H_{21}N_3$	7	LOW
245.200	245.201	$C_{16}H_{24}N_2$	6	LOW
247.179	247.180	$C_{15}H_{22}ON_2$	6	LOW
248.175	248.176	$C_{14}H_{21}ON_3$	6	LOW
249.123	249.123	$C_{13}H_{16}O_3N_2$	7	LOW
254.117	254.118	$C_{16}H_{15}O_2N$	10	LOW
263.247	263.248	$C_{17}H_{30}N_2$	4	LOW
267.148	267.149	$C_{17}H_{18}ON_2$	10	LOW
269.164	269.165	$C_{17}H_{20}ON_2$	9	LOW

271.180	271.180	$C_{17}H_{22}ON_2$	8	LOW
272.127	272.128	$C_{16}H_{17}O_3N$	9	LOW
273.159	273.160	$C_{16}H_{20}O_2N_2$	8	LOW
274.106	274.107	$C_{15}H_{15}O_4N$	9	LOW
275.138	275.139	$C_{15}H_{18}O_3N_2$	8	LOW
283.216	283.217	$C_{19}H_{26}N_2$	8	LOW
287.138	287.139	$C_{16}H_{18}O_3N_2$	9	LOW
299.138	299.139	$C_{17}H_{18}O_3N_2$	10	LOW

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