*Comments by reviewer #1 (Dr. Yokelson) are reproduced in the sans-serif font below. All comments have been numbered by us for convenience. Our responses follow each comment in a blue, italicized, serif font. Text additions to the manuscript, for example, significantly modified sentences, appear in the manuscript in red color. Deletions from the manuscript are not explicitly shown but are described in the responses below. Minor editorial edits to the text are not explicitly shown to prevent a cluttered view.*

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Review of Molecular Composition of Particulate Matter Emissions from Dung and Brushwood Burning Household Cookstoves in Haryana, India, by Fleming et al.

By Bob Yokelson

The authors have successfully identified numerous individual chemical species that absorb UV light in an important, but under-studied type of biomass burning aerosol (wood and dung cooking fires). The authentic cooking fire samples are difficult to obtain and the author's samples were subsequently analyzed off-line with a unique, extremely powerful array of coupled optical and mass-spectral techniques. The team has a great deal of relevant expertise in all aspects of the study and it includes leading practitioners of these advanced analysis techniques. The large body of data represents a significant investment of effort and the work should definitely be published. With some straightforward improvements the paper could be very good. I provide an overview followed by specific suggestions referenced to page and line number in order of appearance.

Overview:

More information is needed about the sampling, calculations, and error budget in the paper. A few additional sampling details and equations are given in the SI, but more are needed and should be in the main paper. Currently, the emission factors are said to be "orders of magnitude" upper limits, but it's proposed via limited comparisons that the MAC are "OK" – though they are given without an error estimate. The final MAC seem potentially "high" to me and their application should be clarified. Along with more detail on the sampling, the associated uncertainty in each step should be discussed near the beginning of the paper so the context and limitations are clear as the discussion is read, rather than reader wondering and only potentially finding out later in the paper. I suggest a clear and commonly-used format would be to clarify how each step is done and discuss/estimate individually the different sources of error of each of these steps in order. For instance:

1. What were the inlet positions w.r.t. to the fires? Flaming produces a greater vertical velocity and flux of products than smoldering. Gas-particle partitioning is proportional to particle concentration and is also temperature dependent. Further from the source the smoke has diluted and cooled to some degree and vertical velocity doesn't need to be measured. A detailed diagram with distances, temperatures, concentrations (description of any dilution?), etc should be given in the paper.

*Figures S2.1 and S3.1 have been added to the supplementary information section, showing the dilution system and the positions of inlets with respect to the stoves, respectively. The probe position was fixed directly above the stove to allow for normal cooking activities, but still compare emissions. There are always tradeoffs in sampling emissions from solid fuel use in households. Emissions tests in laboratories using controlled hoods and dilution systems etc. have the benefit of more controlled sampling, but use water boiling tests that have systematically been shown not to reflect those during actual cooking, the subject of this paper. The discrepancies between field testing during actual cooking and water boiling tests are large (Johnson et al., 2008) and thus we elected to sample during actual cooking.*

*Cooking occurred in a real village kitchen (what we would consider to be the porch of the home), which made it challenging to sample well-mixed smoke. Although, the smoke diluted into the surrounding air before entering the dilution system, and subsequently filters were collected at ambient temperature. We acknowledge there are common artifacts with the filter sampling, for example, some of the smaller molecules we are observing in the mass spectra would be in the gas-phase in a diluted plume but they get trapped on the filter if there is a lot of organic material collected.*

2. What were the relative positions of the canister and filter inlets? Were they close or in wellmixed smoke?

*The gases and particles were sampled from the same inlet stream. We added Figures S2.1 and S3.1 as well as a description of Figure S2.1, P4, L4-11 of supplementary information section to clarify our sampling approach. Gases were collected in a Kynar bag over the course of the whole cooking event from which the canisters were filled.*

3. What was the relative timing of the canister and filter sampling? Canisters tend to fill quickly at a non-constant rate while the filters were acquired over the whole fire.

*Thank you for pointing this out. We agree that the description of the gas sampling was not very clear. Canisters sampled the average (not instantaneous) gas-phase emissions over the cooking event, similar to the filter (particle) samples. Figures S2.1 and S3.1, P4 L4-11 of supplementary information were added to clarify this.*

4. When the results from two filters are coupled, what was the spatial and temporal overlap of the filter collection?

*Results from different filters were combined for samples done under as similar conditions as possible in terms of fuel type, stove, approximate moisture content, and meal cooked. Cookstove BBOA samples were collected over the course of a month. This is explained in P8, L29-31 of the manuscript. The filters used for chemical analysis always occupied the same space in the sampling train, shown in Figure S2.1. In terms of particle mass measurements, the gravimetric and chemical analysis filters were collected at the same time (same cooking event), however at different locations in the sampling train. This is now better described on P5, L5 in the main paper as well as in the supplementary information, P4, L15-19.*

5. The authors evidently measured extraction efficiency once at 50%, but did not specify 50% of what (PM2.5, OA, etc)? Nor is it stated if the extraction efficiency is the same for all chromophores. Later in

paper it's stated that the extraction efficiency was "lower sometimes." How much lower? Maybe give a range and consult some studies where extraction efficiency has been estimated by comparison to some familiar term e.g. OA measured by AMS or conventional OC analyses.

*We will address this question in comment #9. We have now constrained the MAC values by incorporating sources of error.*

6. Ionization efficiency is maybe stated near the end of the paper to be higher for polar compounds, but some polar compounds that are ubiquitous in BBOA like levoglucosan were not seen in some samples. Can this be explained?

*In electrospray ionization mass spectrometry (ESI-MS) different analytes have to compete for charge with each other leading to different ionization efficiencies for the same compound depending on what else is present in the mixture. This is known as the "matrix effect". Such matrix effects are likely responsible for inconsistent observation of some of the less ionizable compounds such as levoglucosan. This explanation was added to the manuscript, P8, L22-26.*

7. Given the realistic limitations of any technique, in the introduction or after the fleshed-out experimental/error section then maybe a brief summary of the strengths and weaknesses of various approaches to understanding aerosol optical properties is in order to provide context for readers. For instance, my understanding is that laser-based techniques would be well-suited for measuring the overall absorption of real aerosol (after drying) that contains BC, BrC, and other species at specific wavelengths, but non-power law features are an issue in fitting the crosssection at unmeasured wavelengths, they certainly cannot identify individual compounds, and they have some uncertainty in differentiating between BrC and coating effects (e.g. Pokhrel et al., 2017). Extractions (I think) eliminate BC and coating effects so that only BrC is probed. Following with off-line analysis by broadband UV absorption, retention times, and exact mass is very powerful for measuring the true BrC spectral shape and compound identification. But quantification and how the MAC relate to real-world aerosol is not clear from the paper now.

*We believe that adding a detailed description of the advantages and disadvantages of different techniques would make the paper too long. A recent comprehensive review by Laskin et al. (2015) has a long section explaining the instruments used to measure optical properties, as well as their limitations and advantages. Nevertheless, we added several sentences to explain the difference between the absorption coefficients reported by different methods. For example, we stated in the introduction section that "methods that do direct measurements on aerosol particles without dissolving them report* $MAC_{aerosol}$*, whereas measurements on extracted material report* $MAC_{bulk}$*." Here and in the experimental section we refer readers to Laskin et al., (2015) for more information about other methods.*

8. In light of above, provide some at least brief, rough guidance on how the overall optical properties of real BC-containing aerosol (coating effects and all) could be estimated from the extraction results that are presented. It seems possible using independently measured BC emissions, but I did not find that in the paper.

*We have added text on P12, L16-24 to the manuscript, estimating MAC for the real aerosol based off the approach of Stockwell et al. (2016). Uncertainties were also added in the text on P12, L25-33. For AAE, we clarified that this is an AAE for extracted OC only, and clarified that the cited Chen and Bond (2010) AAE value was also for the extracted OC. We also added a statement suggesting that whole aerosol (extractable and non-extractable components) will have lower AAE by comparing to Stockwell et al. (2016) in P13, L4-6.*

9. Make sure to specify what is being measured throughout (e.g. the MACs are absorption of what per mass of what?) and provide uncertainties.

*We now more explicitly state how we calculate MAC on P12, L8, and throughout the paper (please see #7). MAC values are still calculated based off the assumption that 50% of the total PM mass was extracted, however, they are better constrained. Uncertainties were added to Figure 8 and in the text that incorporate a 40% relative error for extraction efficiency, as well as flow rates (10% relative error).*

10. BBOA almost certainly contains 1000's of species. The mass spectra obtained depend on variable detection limits and loading and natural variability makes the number of samples important. Thus, throughout the paper, I would refer to "observed" complexity, with actual complexity beyond the capabilities of current instruments.

*We agree that the actual complexity is beyond the capabilities of our instrument. We are only probing the extractable, ionized constituents observed across multiple trials of the same cookfire type. Furthermore, the instrument is not capable of distinguishing structural isomers. We added word "observed" before complexity throughout the manuscript.*

11. Some new species are observed, but many species commonly observed by other techniques are missing some or all of the time. It would be helpful to clarify which off-line compound identification techniques access which types of chemical space well and, if possible, the relative mass contributions to total OA measured by various techniques. This could be a sentence or two in the paragraph recommended in point 7 above.

*The following paper shows that nano-DESI is particularly sensitive to nitrogen-containing compounds, compared to similar-sized compounds that do not contain nitrogen. This is conveyed on P10, L4-5, but we added this additional reference that backs up this point specifically for nano-DESI. We believe that it is beyond the scope of this paper to explain complimentary off-line techniques; this is something that should probably be done in a future review.*

*Laskin, J., Laskin, A., Roach, P. J., Slysz, G. W., Anderson, G. A., Nizkorodov, S. A., Bones, D. L. and Nguyen, L. Q.: High-Resolution Desorption Electrospray Ionization Mass Spectrometry for Chemical Characterization of Organic Aerosols, Anal. Chem., 82(5), 2048–2058, doi:10.1021/ac902801f, 2010.*

12. Tracers and markers are not the same thing and these terms are frequently misused. Tracers are emitted in a narrow, well-characterized ratio to the observable of interest and can be used to quantify impacts at receptor sites. Markers are useful but typically emitted in highly variable amounts by unique sources and useful qualitatively.

*Thank you for defining these terms. We replaced "tracers" with "markers" in the subheading for section 3.2. Additionally, the paragraph discussing LG (P8 L22-26) was edited with these definitions in mind. We also use levoglucosan to show this technique will preferentially ionize other constituents, and therefore, sugars, and broadly lignin-derived compounds, are underrepresented/absent from the reported inventory of the observed species.*

Comments on text in order of appearance:

P1, L13: "organic particles" should be "organic matter in particles" or "organic aerosol" to allow for the possibility of internally mixed particles.

*"organic particles" was changed to "organic aerosols," and similarly on P1 L22-23.*

P1, L20: "selected "extractable"" or similar seems appropriate before "compounds" or "numerous" instead of "selected"

*"numerous" was added before "compounds."*

P1, L21: The fact that many of these species are newly observed will make the reader curious if they are newly observed because they are relatively rare or because most of the organic matter in BBOA was previously un-speciated. If that question can be answered it would be great to do so in the paper somewhere. A related fine point is that if most of the observed compounds are newly seen despite the fact that numerous other compounds have already been seen in BBOA, then it is unlikely that this study probes the true molecular complexity. This is an empirical, observed molecular complexity impacted by detection limits and loading.

*It is possible that the newly identified species represent a small fraction of the BBOA particle mass, but they show up prominently in the mass spectra because they are readily ionized by nano-DESI. However, there have not been many studies of chemical composition of smoke produced by burning of dung, so it is also conceivable that these species have not been reported before because of the paucity of observations. Future studies should attempt to quantify relative contributions of different classes of compounds to the particle mass. We agree that we are not able to probe true molecular complexity with this technique. In the paper, we clarify in all instances that this is observed molecular complexity.*

P1, L22: "stove-specific combustion conditions" might be better than "stove" if the stoves impact emissions by impacting the mix combustion processes?

*We agree that both stove and fuel types affect the combustion conditions, but here we are just listing the variables we had to work with changing for each cookfire.*

P1, L23: "emission factor" and "observed molecular complexity"

*"Emissions factor" was changed to "emission factor," and "observed" added to "molecular complexity."*

P1, L25-7: These MACs seem ~2x too high compared to other studies if they are referenced to g of PM2.5, especially as a lower limit? And it should be clear what they are for; real aerosol with BC included or just the BrC? If BC is added back to represent real aerosols, how is that done?

*We partly addressed this question when answering comments #7 and #8. When editing the text, we made it clear in the text that the MAC reported is just for the extractable potion of the organic matter, and does not include contribution from BC. Furthermore, we made it clear that it is MAC of the bulk material from which particles are made, and not MAC of the aerosol.*

P2, L12: "depends to some extent" since amount of PM and individual susceptibility to various toxins matter a lot.

*The addition was made.*

P2, L20: lifetime of BrC also important.

*We agree. However, since the focus of this paper is primary emissions of BrC; we opted to leave the discussion of BrC aging processes out.*

P2, L24: probably don't need same reference twice?

*The second reference was deleted.*

P2, L25: "a photoacoustic spectrometer" should be "photoacoustic extinctiometers (PAX)" (throughout) and "895" should be "870", L26: "cook" > "cooking"

*These changes were made.*

P2, L26-29: The EFs for BrC quoted from Stockwell et al are actually their EF Babs at 405 nm (not the same thing as explained next). These include absorption by BC and BrC. Different EFabs, tentatively for just the BrC are also provided though.

Some relevant background on Stockwell et al 2016 from the corresponding author:

Lack and Langridge (2013, Table 1) recommended an MAC for "BrC," but actually meant an MAC referenced to the mass of "BrC-containing OA." They clarified that their MAC was an average value for BBOA but that the MAC can range a lot. The OA MAC was later found to depend on BC/OA by Saleh et al 2014. We used the concept of an EF for "BrC" based on the Lack and Langridge MAC in Stockwell et al, but have since abandoned that terminology as we think it is too easy to misinterpret. Meanwhile, in the Stockwell paper cited here we tried to present qualifying text as follows: "The BrC mass calculated this way is considered roughly equivalent to the total organic aerosol (OA) mass, which as a whole weakly absorbs UV light, and not the mass of the actual chromophores. The MAC of bulk OA varies substantially and the BrC mass we calculate with the single average MAC that we used is only qualitatively similar to bulk OA mass for "average" aerosol and even less similar to bulk OA for non-average aerosol (Saleh et al., 2014). The BrC mass estimated by PAX in this way was independently sampled and worth reporting, but the filters and mAMS provide additional samples of the mass of organic aerosol emissions that have lower per-sample uncertainty for mass. Most importantly, the optical properties from the PAX (SSA, AAE, and absorption EFs calculated as detailed below) are not impacted by MAC variability or filter artifacts."

Thus, our EF BC and the values listed just above are the best to compare to in Stockwell et al. Thanks to the authors, we rechecked our cooking fire table, found one error that only impacts the SSAs, and have posted a corrigendum. (We discovered that the SSA labels in Table 4, but not Table S8 had been reversed: it should be SSA 870 and then SSA 405 below that in Tab 4.)

Then finally, the more robust estimates of speciated PM2.5 mass from the same study that we alluded to in Stockwell et al., 2016 can now be found in Jayarathne et al. (2017) and are useful for comparisons with this work as will be pointed out.

Jayarathne, T., Stockwell, C. E., Bhave, P. V., Praveen, P. S., Rathnayake, C. M., Islam, Md. R., Panday, A. K., Adhikari, S., Maharjan, R., Goetz, J. D., DeCarlo, P. F., Saikawa, E., Yokelson, R. J., and Stone, E. A.: Nepal Ambient Monitoring and Source Testing Experiment (NAMaSTE): Emissions of particulate matter from wood and dung cooking fires, garbage and crop residue burning, brick kilns, and other sources, Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-510, in review, 2017.

*Thank you very much for these detailed explanations. Your discussion brings up an excellent point that we did not make clear enough in the original version of the manuscript. All molecules absorb radiation to a different extent. Classifying some of them as chromophoric and other as not chromophoric is arbitrary. Therefore, MAC should always be calculated by normalizing the measured absorption coefficient by the mass concentration of all molecules present in the material, not just the ones that are arbitrarily designated as chromophores. This is a common approach followed in papers that report MAC measurements for extractable organic material, and also the approach followed in this paper.*

*For unfortunate reasons, MAC is used in the literature to denote two different quantities. One is mass-normalized absorption cross section of aerosols ($MAC_{aerosol}$), which is absorption coefficient of air containing dispersed aerosol particles divided by their mass concentration. $MAC_{aerosol}$ is particle size dependent. The other one is mass-normalized absorption coefficient of the material from which aerosol particles are made ($MAC_{bulk}$), which does not depend on particle size. To help minimize confusion between the two, we renamed our MAC into $MAC_{bulk}$ throughout the paper.*

*We elected to compare our results to measurements by Stockwell et al. (2016) by approximately converting our emission factors for $MAC_{bulk}$ to emission factors for $MAC_{aerosol}$. The new paragraph on pages 12-13 is dedicated to such a comparison.*

*The cited EFs are now correct in paper. P3,L11-17 was amended to clarify these are absorption EFs of total OC. We will compare with Jayaranthne in our next paper that deals specifically with EFs for $PM_{2.5}$ and EFs of individual VOCs.*

P2, L31-32: Just an observation that the dung is expected to have lower MAC than wood consistent with lower BC/OA per Saleh et al 2014.

*Thank you for the suggestion. A reference to Saleh et al. (2014) was incorporated into explaining Pandey's result.*

P3, L13: Should "The" which could imply "all" be "Many"?

*This change was made.*

L17-19: This second half of the sentence starting with "while" is unclear in and also ceanothus is from US NW.

*The sentence was clarified to the following.*

*"Fuels utilized in the FLAME studies were selected to represent North American wild fires, and the publications focus on non-woody biomass fuels such as detritus and litter as well as ceanothus from the US Pacific Northwest."*

P3, L21: N accounts for a small mass fraction of BB PM2.5 so N-containing organics are likely a small fraction of the total BBOA?

*We added "detected" in front of species.*

P3, L25: eliminate "The most" since that will quickly be dated?

*The suggestion was implemented.*

P3, L32: "more" or "additional"?

*"more" was changed to "additional."*

P4, L4-5: I'm sure this is worthwhile data regardless if it is the first or last data, but it seems unlikely this would be the first detailed study of brushwood or dung smoke since these sources have been studied intensively for > twenty years. A recent example that contains examples of historical references is Jayarathne et al. (2017). Simoneit et al have been characterizing smoke for > 20 years.

*"For the first time" was removed, and the sentence was reworded to the following.*

*In this study, the chemical composition of cookstove smoke produced from actual cooking events is probed in detail. Here we compare particle-phase constituents in cookfire smoke produced from different stoves and fuels.*

P4, L23-30: The pictures are useful, but Fig 1A currently shows a concoction of unidentified tubing and a diagram is also needed. Questions arise with some also in the overview. How did the authors ensure representative sampling of well-mixed emissions for all devices? For instance, was the data corrected for the different vertical velocity in the smoke column above the fire? This is important because during flaming, the flux of emissions can be much greater than during smoldering. What were the flow rates and residence times in inlets, was any dilution used, were the downstream filters side by side or in series, were the pumps downstream of the filters, how were filters stored during the 25-30 hours not at -80 C (in a cooler with dry or blue ice or at ambient T, what was ambient T if relevant?), were backgrounds or field blanks taken, error in gravimetric analysis, etc? #1-3

*See answers to #1-3. Filters were stored at ambient temperature in the field and on the airplane, which is now described on P5, L10-11.*

P4, L24: "BBOA" > "PM2.5"

*This change was made.*

P5, L1-9: The next step after filter collection and before mass spec is filter extraction, i.e. how was extraction done, what is extraction efficiency compared to total BBOA and is it the same for all the species detected, etc? As written it sounds as if the filter is inside a capillary. It may not be possible to estimate extraction efficiency if done by a droplet flowing over the filter surface? But the bottom line should be clear.

*Nano-DESI extracts the material before it flows into the HRMS. It was shown in Roach et al., 2010a, 2010b that Nano-DESI dissolves all material extractable in the electrospray solvents (ACN/$H_2O$). We agree that the description of nano-DESI was not very clear. We have expanded the explanation of Nano-DESI.*

P5, L6-7: Why positive mode and are there species only seen in negative ion mode?

*Samples were only run in the positive ion mode. Smith et al. (2009) using same technique for BBOA found 1.5-4 times fewer peaks in the negative ion mode, suggesting the BBOA constituents more readily ionize in positive ion mode. They found largely the same species in the negative ion mode as the positive ion mode, but additional were found in the positive ion mode.*

P5, L7 What are MRFA and Ultramark, what is the relevance of the calibration species, how were the cal results applied?

*MRFA is a Met-Arg-Phe-Ala acetate salt (523.65 amu), and Ultramark 1612 (700<amu<1900) is a mixture of fluorinated phosphazines. Along with caffeine (194.19 amu), these standards are used to calibrate the mass accuracy of the HRMS over a wide m/z range. These compounds are usually used without explanations in the mass spectrometry literature, but we translated some of this detail into the sentence.*

P5, L8-10: Filter deposits may not be uniform. What percent of peaks were seen in only one sample or had S:N < 3. This is useful context that helps relate reported complexity to observed complexity, which is itself a subset of actual complexity.

*This is a common, unresolved problem for direct infusion ESI-MS. The recorded ESI-MS spectra routinely contain spurious peaks appearing in the ionization process at random m/z values. One way to identify the actual chemical species in the sample is to run mass spectra for the same sample multiple times. The probability of having spurious peaks appearing at the same m/z value is very low, so the peaks appearing in all three mass spectra must be genuine. Further, low signal-to-noise and/or unusually high peak FWHM are useful indicators of spurious peaks, and help to filter these peaks out. In summary, we only keep the peaks in the final table when we are confident they are not coming from mass spectrometer noise.*

P5, L12: Does Kendrick analysis with CH2 and “H2” base units help with O-containing species?

*As long as the species have the same parent molecule (this can include oxygen and other atoms), and only differ in CH2 units, one can use Kendrick analysis to link species in the families.*

P5, L13: “mass-calibrated”

*The change was made.*

P5, L16: About what percent of signal or number of peaks was above m/z 350?

*Peaks above 350 m/z were minority species both in number and signal. This was highly variable, but on average, 9% of the number of peaks was above 350 m/z, while 6% of the total signal was above 350 m/z. These averages are now included in the manuscript.*

P5, L20: K is normally the most abundant alkali metal in BB-PM (not Na). S and Cl can be highin dung (Hosseini et al and numerous other papers). Brief explanation of why not included?

*While K is abundant, potassium-organic adducts were not observed in the mass spectra. This is due to the relative affinity of organic molecules for $Na^+$ and $K^+$, where the binding energies of organic molecules to $Na^+$ are much larger compared to $K^+$. We do observe inorganic adducts containing potassium.*

*The majority of the organic molecules contained carbon, hydrogen, oxygen, and nitrogen. Adding the possibility of S and Cl did not change the assignments. The small percentage of unassigned peaks could probably be assigned with S or other elements, but adding sulfur alone did not allow us to assign more peaks or change the assignments. This information was added to the manuscript on P5, L4-6.*

P5, L22: No “O” in the formula, but it is in the explanation?

*Oxygen was deleted from the explanation.*

P5, L27: Why is the extraction solvent mixture different here, i.e. not containing water? What fraction of mass is extracted and of what types of compounds (in summary form)?

*For measuring MAC values, our goal was to extract as much organic material as possible. Therefore, we chose three solvents covering a range of polarities; ACN, DCM, and hexanes. On the other hand, an ACN/water mixture was always used for electrospray (including nano-DESI) because less polar solvents* *do not work well in ESI. The fraction of mass extracted is unknown, and it is the largest source of uncertainty in MAC calculations. We tried to estimate extraction efficiency in a separate experiment with a small number of filters from the same campaign (different filters than the ones analyzed), and got varying results of 30-60%. Therefore, we calculated MAC assuming 50±20% extraction efficiency. We expect to extract a range of compounds with this solvent mixture, from very polar organic molecules, such as nitrophenols, to polycyclic aromatic hydrocarbons.*

P6, L16: It should be specified that this is an MAC for the extracted BrC only. Are the units (cm) consistent with the reported MAC (m)? "Cmass" is the "solution mass concentration" of what and how measured?

*This change was made.* $C_{mass}$ *refers to the mass concentration of all the extractable organics in the solution.*

P6, L17-18: Another filter collected where and when? Here is an example why the spatial and temporal overlap of the filter collection is important to describe in experimental section. How are PM2.5 on the other filter and "Cmass" connected?

*See answer to #4. After accounting for flows, the PM mass on the gravimetric filter is assumed to be the same as the chemical analysis filter. We multiplied this by the extraction efficiency (0.5) to get* $C_{mass}$*. Two sentences were added to the manuscript to make this more clear (P7, L4-7).*

P6, L20: So is the target mass reference for the MAC PM2.5 mass then?

*Yes, it is. See previous comments for the changes we made to make this clear.*

P6, L20-21: How do they do know the mass extraction efficiency was < 50% sometimes and why would a lower mass extraction mean the MACs are a lower limit? What if the extraction got all the chromophores, but only half the total mass, then would the raw MAC be a factor of two high? It seems the impact on the MAC would depend on the relative extraction efficiency of the chromophores and other constituents.

*Please see responses to #5 and #9 above. We no longer say that the MAC values are lower limits, because we have been able to constrain them with uncertainties. We agree that the MAC values are highly dependent on the extraction solvents and the particle constituents.*

P6, L21: Again it seems the AAE are for the BrC component only? Can the authors add a sentence on how their AAE and MAC can be adjusted to represent real aerosol that also contains BC?

*Please see response to comment #8.*

P6, L27: Abundance is usually used to indicate how many there are of an item. Peak area or height is usually used to estimate the signal strength or amount of compound. Should "abundance" be replaced by "area" or something else?

*In mass spectrometry, the current convention is to say "peak abundance". Use of "peak area" and "peak intensity" is discouraged. Therefore, we retained "abundance" throughout.*

P6, L27-29: So if I understand this and the SI right, the EFPM(total) was estimated separately (in a sparsely described experiment) and then EFPM(total) was partitioned among the peaks observed on the MS according their relative intensity. If so this should be stated as a sentence in the main text. It's a concern that the real EF could be ten times or even several "orders" of magnitude lower. Should the authors reconsider even reporting EF directly as such? Maybe it's safer to label them as "upper limit EF in the tables and figures to spare potential future misinterpretation? Also, can the error be reduced or the error budget be tightened up? For instance, the authors may detect some species that have been better quantified from these sources in other studies? Can they use their ratios to any overlap compound with the extensive quantitative analyses reported in Jayarathne et al 2017 and many others? Ratios to levoglucosan or PAHs for instance may be helpful to constrain the "EFs" to a realistic range?

*We agree that the calculations done in our initial submission were too approximate. We made the suggested additions, including P4, L15-19 and Figure S2.1 in the supplementary information, and P5, L4-5 in the main paper to clarify the $EF_{PM}$ total calculations. We no longer report the upper limit for the emission factors; it was changed to relative abundance.*

P6, L28-30 and Figure 2 comments: It's true that authors show non-identical spectra from the sources even though the two dung spectra look pretty similar. But proof of distinct signatures requires enough samples to quantify the variability in each source. Right now it's not clear if the method uncertainty is larger or smaller than natural variability or what the observed variability is. The authors should try to characterize observed source to source variation with some metric (# or % of unique peaks) and this is done to some extent later in the paper, which is good. As noted above, the y-axis label should be "Upper limit EF" or "approx. relative abundance" Relevant to earlier comments, the spectra are too simple to represent all the components of BBOA although more details might be revealed with a log scale.

*The results and discussion section starts broadly with Figure 2 showing that brushwood/chulha has the most observed $C_xH_yO_z$ (blue), and dung/angithi has almost nitrogen-containing peaks (purple and red). Dung/chulha is somewhere in the middle with many nitrogen-containing peaks as well as $C_xH_yO_z$ peaks. We think it is overwhelming to show all mass spectra in the main paper. Instead, Table S1.1 contains the same info for all samples to show that these truly are representative spectra, and you can see these differences apart from natural variability. This is explained on P7, L18-23. The y-axis was changed to relative abundance on Figure 2.*

P7, L8: Dung has much higher N-content than wood and that makes excellent sense based on known plant and animal physiology. The Gautam reference has much higher N than normal for wood. See Stockwell et al 2016 for dung and Coggon et al Fig 3 for wood or many other sources referenced in these papers.

*The Gautam reference was retained, since the wood used in this study is different (shrub wood rather than tree wood). Nevertheless, nitrogen content for wood and dung fuels from Stockwell et al. (2016) and*

*Hatch et al. (2015) references were also added to the text. This would indeed help explain increased N content in the dung smoke.*

P7, L8-11: This sentence doesn’t quite make sense. Typo? Punctuation?

*The punctuation was changed.*

P7, L12: Could provide a few key citations on lignin pyrolysis – there are many. It would be interesting if the authors could show that the cellulose preferentially ends up in the gas phase? But maybe the method has low sensitivity for sugars (from cellulose), which are usually abundant in BBOA (Christian et al., 2010; Jayarathne et al., 2017)?

*We agree that references should be added here; we cited Collard and Blin (2014) and Simoneit (1993). Unfortunately, we cannot show that cellulose decomposition products preferentially end up in gas phase due to the limitations of our technique.*

P7, L 14: Dung and embedded grasses are both high in Cl content (Stockwell et al., 2016 and references there-in, especially Lobert et al., 1999) so expect high Cl from cooking with dung and ag residues as in Stockwell et al. 2014-2015 ACP papers.

*A sentence and the references were added to P8, L4-5.*

P7, L15-16: Clarify if these large peaks were included when the EF was partitioned?

*We no longer are reporting emission factors for particle-phase chemical species because they were too approximate.*

P7, L21-26: K is well-known to be enhanced in biomass (Table 1 in Hosseini et al., 2013) and K has a very long history as a biomass burning “tracer” (e.g. Sullivan et al., 2014 and references there-in). It is well-known that K is primarily emitted by flaming while levoglucosan is primarily emitted by smoldering. If the stoves had different flaming/smoldering ratios that could explain variability in K production.

*This is a good point that dung/chulha had a higher combustion efficiency on average compared to dung/angithi. We added this in the discussion as well as the references below, specifically, P8, L3-4, 15-17.*

Hosseini, S., Urbanski, S., Dixit, P., Li, Q., Burling, I., Yokelson, R., Johnson, T., Shrivastava, M. K., Jung, H., Weise, D., Miller, W., and Cocker III, D.: Laboratory characterization of PM emissions from combustion of wildland biomass fuels, J. Geophys. Res., 118, 9914–9929, doi:10.1002/jgrd.50481, 2013.

Sullivan, A. P., May, A. A., Lee, T., McMeeking, G. R., Kreidenweis, S. M., Akagi, S. K., Yokelson, R. J., Urbanski, S. P., and Collett Jr., J. L.: Airborne characterization of smoke marker ratios from prescribed burning, Atmos. Chem. Phys., 14, 10535-10545, doi:10.5194/acp-14- 10535-2014, 2014.

P7, L27-30: There is a difference between a tracer and a marker and levoglucosan (LG, a cellulose pyrolysis product) is the latter. If LG was a good tracer then it would be in all the samples and at reproducible amounts. LG is in fact normally found to be a major, but variable component of BBOA (Sullivan et al 2014; Jayarathne et al 2017; Christian et al 2010). If LG is missing from many of the samples that suggests detection issues that could cause some of the BBOA species to escape the analysis procedures used.

*Thank you for defining these. See our response to #12 for explanation.*

P7, L31 - P8, L2: There were more than three spectra of each stove/fuel combo, but three were chosen how? Then peaks not appearing in all three spectra of a combo were discarded why? Then the remaining peaks were scaled and the spectra for each stove/fuel combo were averaged together. I think that is the right order, which may be jumbled in the text?

*Sample selection was explained in more detail (P8-9, L29-32, 1), and sentences were reordered correctly. Peaks not appearing in all three sample runs were discarded to ensure they are real peaks (see earlier explanation). We added "ensuring reproducibility" to the end of the statement to convey this.*

P8, L6-12: First compounds found from all three cooking types are listed. Then compounds only found from brushwood are discussed. That I can follow. Then the compounds that are found in all dung cooking. But not unique to dung cooking? It's not clear here what the difference between sections 3.5.1 and 3.5.2 is. I.e. what is the difference between "common to" and "detected in all"?

*We agree it was confusing as written. It was changed to the following. We next show compounds common to dung cookfire emissions (Section 3.5.1, Table 2). Lastly, we discuss BBOA compounds detected in either dung/chulha and dung/angithi cookfires (Section 3.5.2).*

P8, L11-12: If the stove material caused the emissions it potentially might not matter what the fuel is since all fires heat the stove.

*This is an excellent point. This is why we were always careful to specify both the fuel and the stove in the text because both contribute to the compounds emitted in the smoke.*

P8, L14-17: The true number of constituents for all the PM types is much greater than observed so maybe just say ~we saw more peaks from A than B.

*This was clarified.*

P8, L15-30: Can this overview of the results section be re-phrased or re-organized to make it easier to follow?

*We tried different approaches to organizing data and their discussion but elected to retain the current one because it appeared to be the most logical to the authors.*

P9, L4-5: “detected elemental” and the relative insensitivity for sugars, or anything else needs to be discussed earlier – maybe in the introduction or at latest the experimental section.

*We kept our wording “Biases the elemental make up” instead of “detected elemental composition,” because we feel both are correct. We now discuss this disclaimer on P8, L22-26 when we discuss levoglucosan.*

P9, L6-8: I don’t believe the %N in Gautam et al, it goes against all the other studies I’ve seen dating back to Susott et al., 1996, unless Gautam et al included the foliage with their wood.

*We also find the measurements of %N in Gautam et al. hard to explain. This sentence was deleted from the manuscript. Please see above comment on Gautam et al. regarding the difference of fuels in the studies you are referring to.*

P9, L17: All biomass is ~25% lignin, 25% hemicellulose, and ~50% cellulose polymers though the monomer units differ.

*A sentence was added to emphasize this point (P10, L17-18).*

P9, L18: delete “at”

*This was corrected.*

P9, L18-19: by “commonly detected” do they mean by their group or are there references to other groups? There are numerous studies that characterized BBOA.

*The sentence was modified to the following.*

*This suggests that perhaps 20% of the compounds listed in Table 1 might be reproducibly detected in BBOA samples using ESI-MS, regardless of biomass type.*

P9, L20-21: “found” to “observed” better?

*This was corrected.*

P9, L25: “coniferyl” alcohol and that comes only from conifers whereas the others are unique to hardwoods or grasses, which are probably more relevant in India.

*We appreciate you pointing out this typo. It is now fixed.*

P9, L30: In the experimental overview, the range of ionization efficiencies could be provided? #6

*Unfortunately, information on relative ionization efficiencies of different species is limited, and the efficiencies depend too strongly on the matrix effects. We are not in a position to provide this information.*

P9, L31: Jayarathne et al also discuss species unique to dung

*Absolutely, we no longer say in the manuscript that we are the first to speciate $PM_{2.5}$ from dung cookfires.*

P10, L1: important to qualify "the observed chemical …was far more complex" etc

*This change was made.*

P10, L2: By "reproducibly" it means "seen" in all "n" samples, but not in the same ratio to total PM2.5? That should be clear if so.

*We are not reporting the ratio to total $PM_{2.5}$. We explain the average abundance of the peak as Low, Medium, or High described on P9, L2-4.*

P10, L5-6: This is a little hard to follow as the authors use "found in all dung …" in the section header, then next mention "detected exclusively" in one type or another, and then "combine all…" Maybe change "Hereafter" to "However" would help with the transition?

*"Hereafter" was changed to "however."*

P10, L10 - P11, L6; Figures 5 -7: Jayarathne et al 2017 and references there-in quantified numerous PAHs for similar fuels, which may be helpful to compare to.

*This is great complimentary work, however, with electrospray we can only detect heterocyclic polycyclic aromatic compounds or substituted PAHs, so we cannot easily compare to the data. In response to this comment, we are currently measuring PAHs by a more conventional method and we plan to attempt a comparison for PAH emission factors in a follow up publication.*

P11, L8: At the outset useful to state what these MACs represent: absorption due to extractables only per PM2.5 mass? I think the mass reference is not extract mass or mass of chromophores. It's important in the larger context if they are MAC that don't include the BC component or any un-extracted chromophores.

*See explanation in #8-9.*

P11, L8-11: "browner" OA from wood cooking makes sense empirically given the higher EC or BC to OA ratio for these fires per Saleh et al., 2014, Jayarathne et al., 2017. The latter reference also reports higher PM emissions from dung cooking than wood cooking in agreement with cited previous work. Their measured and cited EFPM2.5 from South Asia for wood and dung cooking may be useful to compare to.

*A sentence was added to interpret the results using these references (P12, L12-14). In the next paper we will discuss our $EF_{PM2.5}$ in more detail, and will compare our results to Jayarathne et al. (2017) then. $EF_{PM2.5}$ is only brought up here to put our MAC values in context.*

P11, L12: The MAC is the absorption coefficient per mass of PM. In order to convey the absorption per unit fuel consumption, "coefficient by" should probably be replaced by "emission factor of"

*We now include both absorption of coefficient per mass of PM as well as the approximate absorption coefficient per unit fuel consumption for the whole aerosol using the approach described in Stockwell et al. (2016). See explanation for #8.*

P11, L 11-13: On the overall absorption per unit fuel consumption. This was evaluated by Stockwell et al., (2016) for particles containing BC and BrC and, with higher uncertainty, for just the BrC component, with the following results (in m2 /kg) (variability also shown in reference).

Wood Dung

EF Babs 405 10.6 5.85

EF Babs-405-BrC 8.40 5.43

EF Babs 870 1.04 .197

Wood-burning aerosol absorbed about 5 x more per kg burned at 870 because of the higher BC emissions, but just 2 x more at 405 for the overall particles. More BrC absorption per unit fuel consumption was observed on average for wood, but within variability the amounts overlapped. Can the authors use BC/EC EFs for these fire types to get their own estimates for absorption EFs for real fires?

*Thank you, we incorporated this. Please see our response for explanation #8.*

P11, L14-21: Throughout this section, for this work and other work, the mass reference (PM2.5, OA, etc?) should be rechecked and specified and uncertainties for the MACs should be provided. It makes sense that the brushwood MAC is larger than the dung MAC given the BC/OA dependence of MAC described by Saleh et al. (2014) as noted above.

*Please see our response to #9. A sentence was added showing our results are consistent with Saleh et al., 2014 (P12, L12-14).*

At a cursory glance, it seems like the MAC values at ~400 nm that the authors selected for comparisons are on average higher than values in Lack and Langridge, the extensive tables in Olson et al 2015, or Bluvshtein et al., (2017). It could be helpful if the authors could include these studies in their discussion and comment on any implications there may be.

Olson, M. R., Garcia, M. V., Robinson, M. A., Van Rooy, P., Dietenberger, M. A., Bergin, M., and Schauer, J. J.: Investigation of black and brown carbon multiple-wavelength-dependent light absorption from biomass and fossil fuel combustion source emissions, J. Geophys. Res.: Atmos., 120, 6682-6697, doi:10.1002/2014JD022970, 2015.

*In order to compare apples to apples we elected to only compare our measurements to studies that reported* $MAC_{bulk}$*. We cannot easily compare our results to studies reporting* $MAC_{aerosol}$ *(such as the paper by Olson mentioned here) because we would need to know the size distribution of particles, as well as their real refractive index for such a comparison.*

P11, L22-26: If my understanding is correct, one advantage of extraction techniques is that the BC is eliminated along with uncertainties in BrC attribution due to BC coatings or AAE. If that is right, the authors should clarify this is an AAE for the BrC only. Also, the AAEs can depend on the choice of wavelengths fit with a power law and this study has much better wavelength coverage than just the 2-3 wavelengths commonly used in optical in-situ approaches. The overall AAE with BC included is also important to describe real in-situ aerosol. The AAE with BC included may be lower since the AAE of BC is near 1. Stockwell et al obtained AAEs of 3 and 4.6 for wood and dung, respectively using an optical in-situ approach on aerosol containing BC. Can the authors estimate overall absorption values for real intact BC-containing aerosol from their extract values? It seems doable using EFBC and BC optical properties.

*We specified that this AAE is for OC/BrC only. We added P13, L4-6 to state that in situ AAE for cooking aerosol will be lower.*

P11, L25: Why is BC mentioned? Per above, isn't it eliminated in the extraction process? It's not clear why the authors say the following: "However, the observed absorption can be definitively attributed to BrC since AAE values of 2 or greater indicate that light absorption comes from BrC as opposed to BC (Kirchstetter et al., 2004; Laskin et al., 2015)." Pure uncoated BC has an AAE near 1, but any aerosol AAE can have some contribution from BC if BC is present. I think the definitive attribution comes from the fact that BC and BC coating effects are eliminated in the extraction.

*This sentence was deleted; we agree BC should not be mentioned.*

P11, L27: Move first sentence to P12, L17?

*We decided to keep it as is, because these paragraphs still focus on chromophore identification, even if we are not yet discussing the chromophores themselves.*

P12, L4: "lignin-derived"?

*This change was made.*

P12: L3-16: This is great stuff. I wonder if retention times were measured for standards to support identifications.

*At this time, standards were not used to support identifications (because we did not know what to expect when running the mass spectra). The reference absorption spectra had to be consulted during the data analysis stage.*

P12: L22-28: On line 24, why were the early eluters ignored? Combining line 22 and line 26, is the conclusion that polar compounds tend to be detected more efficiently, but elute earlier and may be ignored? Minor tweaks to text could likely clarify this section.

*We changed the wording of this sentence, and cited Lin et al., 2016, which explains this in more detail.*

P12, L29 – P13, L2: It’s neat that absorption features can be used with mass and retention times to support compound identification. In the example given, the results were inconclusive. When two components contribute to the observed absorption one could theoretically resolve that if the absolute cross-sections are known. Figure 10 legend and trace colors should be consistent. I don’t see a red trace.

*It is theoretically possible to calculate the relative contributions of each chromophore, in this case, ethyl-3-methoxybenzoate and veratraldehyde. If the focus of the study was to compare to standards, and get quantitative information about the contributions of different structures, we would definitely do this analysis. First, we do not have a full reference spectrum of veratraldehyde. Additionally, the solvents for the reference spectra are usually different from the mobile phase (mostly* $H_2O$*). As for the red trace, we believe this is an error that occurred in the proofs (it was red in the initial submission but changed color in the ACPD document). We will need to ask the editor about this, and we appreciate you pointing this out.*

P12, L33 “that peaks”

*The change was made.*

P13, L15: “observed chemical complexity” – in general measuring true complexity is likely beyond scope of any one study? The main benefit of this study is a wealth of new chemical information and tying that to absorption. For the former point, if not already done, it might be worth flagging which peaks are new. Since many commonly observed species were not seen, but some new ones were, perhaps a good topic for the conclusions is if this approach occupies a unique niche in “chemical space”?

*We agree that true chemical complexity cannot probed by this technique alone or this study alone. We changed wording to “observed chemical complexity”.*

P13, L31-32: This could be taken as: this study is the first to see non-lignin-derived entities in BBOA? Seems unlikely, clarify?

*We agree and clarified the sentence.*

On SI:

Position/timing of cans is not clarified, etc.

*Please see the responses to questions #1-3.*

*Comments by reviewer #2 are reproduced in the sans-serif font below. Our responses follow each comment in a blue, italicized, serif font. Text additions to the manuscript, for example, significantly modified sentences, appear in the manuscript in red color. Deletions from the manuscript are not explicitly shown but are described in the responses below. Minor editorial edits to the text are not explicitly shown to prevent a cluttered view.*

-----------------------------------------------------------------------

The Fleming et al. manuscript reports on chemical speciation of fine particulate matter (PM2.5) emitted from cookstoves. Two types of stoves were evaluated, as well as two types of fuel (dung and brushwood). The stoves were operated under realistic conditions (e.g., traditional meals, local cook). Samples were collected onto PTFE filters and were analyzed off-line using advanced high-resolution mass spectrometry techniques. In addition to expanding the list of reported compounds in biomass burning PM2.5 samples, brown carbon (BrC) chromophores were identified and mass absorption coefficients (MAC) were estimated. There are many strengths of this manuscript, including the effort to represent real world conditions, the application of advanced instrumentation, and the novelty of the reported results. This study likely represents the most comprehensive analysis of the chemical composition of brushwood- and dung- generated primary PM2.5. The manuscript is well written and should be of interest to biomass burning, air quality and climate communities. It is thus appropriate for publication in ACP. Minor technical and editorial comments are provided below.

Technical:

Sample collection: have particle losses through the aluminum tubing been characterized? Would any size dependent losses bias the results?

*We have not characterized particle losses in aluminum tubing, but we expect it to be similar to copper or stainless steel tubing. The length of tubing was minimized in the set up to reduce particle losses. However, since small particles tend to diffuse to the walls, this could be an issue for $PM_{2.5}$.*

*There are practical limitations in sampling emissions from solid fuel use in households. Emissions tests in laboratories using controlled hoods and dilution systems etc. have the benefit of more controlled sampling, but the use of water boiling tests have systematically been shown to not reflect those during actual cooking, the subject of this paper. We anticipate that the discrepancies between field sampling during actual cooking and water boiling tests are much larger than one would expect from losses of small particles to the walls of the tubing. Thus, we chose to sample during actual cooking events with the associated constraints.*

MAC estimation: Can some uncertainty bounds be given for, 1. use of a separate filter for total mass and 2. range of estimated extraction efficiencies? Fig. 8 should include some uncertainty bounds/shading.

*Thank you for this suggestion. Uncertainties were added to Figure 8 and in the text that incorporate a 40% relative error for extraction efficiency, as well as flow rates (10% relative error).*

EF approximation: Is it reasonable to assume the peak abundances are proportional to mass concentrations? It would be useful to provide support for this assumption in either the manuscript or the supporting information. Given the uncertainties and required caveats, is there adequate justification for reporting emissions factors? Relative peak abundance may be more appropriate.

*We agree that the emission factors provided could be biased given different ionization and extraction efficiencies for different constituents. Therefore, we have changed the y-axis on Figure 2 to relative ion peak abundance (which is measured explicitly in the experiment).*

Nano-desi results (p. 7): The fractions of CxHyOzNw are relatively similar within and across fuel and stove types, with the exception of the brushwood sample RE007. That sample also appears to have a higher moisture content. Can any linkages between moisture content and PM2.5 chemical composition be made? Does this also influence the presence of BrC chromophores and can the differences between the values reported in this paper and in prior work be attributed in part to difference in fuel moisture (e.g., p. 11, line 17-20)?

*We were hoping to see this connection as well. However, in the samples we collected, binned into wet and dry fuels, there was not a clear trend with moisture content and* $PM_{2.5}$ *composition.*

Levoglucosan: The suggestion that levoglucosan may be a “good” tracer for the two fuel types may be misleading in the context given (i.e., present in less than half of the dung and brushwood/chulha samples). It is suggested to revise this statement.

*We agree this was confusing. Levoglucosan should have been seen in all samples, however, the chemical constituents compete for charge in direct infusion ESI, and therefore we do not see it in all samples. We have added this explanation on P8, L22-26. We have amended the concluding statement on P8, L26-27, where we say levoglucosan serves as a marker rather than a tracer.*

Editorial:

The motivation for this work, as articulated in the introduction, is a bit unclear. There is quite a bit of discussion on the health implications of solid fuel use in cookstoves, and it is noted that the work was done as part of a larger study documenting the contribution of household combustion to ambient pollution (p. 4, line 4); however, the focus on MAC and BrC chromophores implies a greater relevance to climate. There is little to no discussion on the health implications of the identified compounds and no discussion of the local to regional implications of the findings (e.g., whether or not the MAC values and emissions factors are significant to suggest regional climatic influence).

*The health effects of particulate matter as they relate to chemical constituents from combustion are largely unknown. For example, cigarette smoke is now known to have 1000s of compounds that have various levels of toxicity. We always look for the usual suspects, for example PAHs, but the particle-phase is much more complex. It is essential to characterize this complexity before we can even start correlating the chemical composition to health effects. We are not in a position to evaluate the health effects of the smoke, but we recommend to future researchers to correlate newly observed organics with health effects (P15, L16). On the contrary, we do have access to methods that allow us to characterize the optical* *properties of cookstove particles, and so we do this in the manuscript. Since local to regional implications of the findings involve many other factors, including the effects of cloud formation, secondary organic aerosol formation, as well as chemical aging of particles. These effects are the subject of more detailed atmospheric modeling which is not covered in this paper, but is forthcoming.*

p. 2, line 9-10: The clause "of pregnant women" after infants is a bit strange as written. Does this mean that exposure is through the mother? If so, one possible revision could be: "infants of women exposed while pregnant".

*We took your suggestion on wording.*

p. 2, lines 25-28: The discussion of estimated EFs from the Stockwell et al. manuscript is awkward as written. Revision is recommended.

*The text was reworded for clarification purposes.*

p. 3, line 33: "prescribed" instead of "prescribing" ?

*The change was made.*

p. 5, line 50: "O"/oxygen does not need to be defined for DBE equation

*The change was made.*

p. 6, line 20: Remove "the" after "Since"

*The change was made.*

p. 13, line 3: SIC is undefined

*It is defined on P13, L24.*

Fig. 3: is confusing and provides little to no additional information beyond other figures and tables. Authors should consider removing it.

*Respectfully, we have elected to keep Figure 3. It may seem unnecessary to careful readers, however, it serves as a visual for the construction of the paper that readers can refer back to as they are reading the results and discussion.*

Fig. 5: "terpenes" is misspelled in figure legend
*Thank you for catching this. The change was made.*

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

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**Abstract.** Emissions of airborne particles from biomass-burning are a significant source of black carbon (BC) and brown carbon (BrC) in rural areas of developing countries where biomass is the predominant energy source for cooking and heating. This study explores the molecular composition of organic aerosols from household cooking emissions, with a focus on identifying fuel-specific compounds and BrC chromophores. Traditional meals were prepared by a local cook with dung and brushwood-fueled cookstoves in a village of Palwal district, Haryana, India. The cooking was done in a village kitchen while controlling for variables including stove type, fuel moisture content, and meal. The particulate matter ($PM_{2.5}$) emissions were collected on filters, and then analyzed via nanospray desorption electrospray ionization/high resolution mass spectrometry (nano-DESI-HRMS) and high performance liquid chromatography/photodiode array/high resolution mass spectrometry (HPLC-PDA-HRMS) techniques. The nano-DESI-HRMS analysis provided an inventory of numerous compounds present in the particle phase. Although several compounds observed in this study have been previously characterized using gas chromatography methods, a majority of species in nano-DESI spectra were newly observed biomass-burning compounds. Both the stove (*chulha* or *angithi*) and the fuel (brushwood or dung) affected the composition of organic aerosols. The geometric mean of the $PM_{2.5}$ emission factor and the observed molecular complexity increased in the following order: brushwood/*chulha* (7.3±1.8 g $kg^{-1}$ dry fuel, 93 compounds), dung/*chulha* (21.1±4.2 g $kg^{-1}$ dry fuel, 212 compounds), and dung/*angithi* (29.8±11.5 g $kg^{-1}$ dry fuel, 262 compounds). The mass-normalized absorption coefficient ($MAC_{bulk}$) for the organic-solvent extractable material for brushwood $PM_{2.5}$ was 3.7±1.5 $m^2$ $g^{-1}$ and 1.9±0.8 $m^2$ $g^{-1}$ at 360 nm and 405 nm, respectively, which was approximately a factor of two higher than that for dung $PM_{2.5}$. The HPLC-PDA-HRMS analysis showed that, regardless of fuel type, the main chromophores were $C_xH_yO_z$ lignin fragments. The main chromophores accounting for the higher $MAC_{bulk}$ values of brushwood $PM_{2.5}$ were $C_8H_{10}O_3$ (tentatively assigned to syringol), nitrophenols $C_8H_9NO_4$, and $C_{10}H_{10}O_3$ (tentatively assigned to methoxycinnamic acid).

## 1 Introduction

Approximately 3 billion people live in residences where solid fuels (coal, wood, charcoal, dung, and crop residues) are combusted for cooking (Smith et al., 2014). Approximately 57% of Indian households report use of wood (49%) or crop residues (9%) as their primary cookfuels, while 8% report dung as a primary cookfuel (Census of India, 2011). However, many households will routinely use two or more of these fuels for their cooking needs, often in combination, in simple, home-made traditional stoves, or *chulhas*. These biomass-burning cookstoves have low combustion efficiencies and produce significant emissions of pollutants, including fine particulate matter ($PM_{2.5}$).

The epidemiological literature statistically links household air pollution from solid biomass to acute lower respiratory infections in children; heart disease, stroke, cataracts, and cancers in adults, as well as low birth weight for infants of women exposed during pregnancy (Smith et al., 2014). $PM_{2.5}$ are small enough to infiltrate deep into the lungs and penetrate the body's defenses, and therefore $PM_{2.5}$ exposure has been commonly used for estimating risks from both ambient air pollution and cigarette smoke (Finlayson-Pitts and Pitts, 2000). The degree of adverse health effects of cookstove smoke likely depends on the chemical composition of the $PM_{2.5}$, however, the exact relationship between the chemical composition and health effects is largely unknown (Araujo et al., 2008).

Household cooking is estimated to be responsible for 26-50% of ambient $PM_{2.5}$ in India (Chafe et al., 2014; Guttikunda et al., 2016; Lelieveld et al., 2015). Of this emissions mixture, carbonaceous particles affect climate directly by scattering and absorbing incoming solar radiation and indirectly by acting as cloud condensation nuclei (Crutzen and Andreae, 1990). In addition to black carbon (BC), which absorbs solar radiation across the entire visible spectrum, some molecules in biomass burning organic aerosols (BBOA) efficiently absorb blue and near-UV solar radiation resulting in classification of BBOA as brown carbon (BrC) (Laskin et al., 2015). Modeling studies have shown that in certain geographic areas climate warming by BrC has the potential to outweigh cooling by scattering organic aerosols (Feng et al., 2013). South Asia has been identified as one of these unique regions where emissions from cookstoves are a significant source of regional BrC (Feng et al., 2013).

Cookstove emissions have been studied in both the laboratory and field settings. Field studies typically involve observations and measurements during daily cooking activities in rural village homes. For example, Xiao et al., (2015) measured BC and $PM_{2.5}$ throughout the day for 6 different houses to monitor indoor concentrations in the household. In the laboratory, water boiling test (WBT) protocols are utilized to evaluate stove performance (Global Alliance for Clean Cookstoves, 2014). The WBT standard protocols are made up of three phases to represent the stove's combustion efficiency while cooking: (1) high power, cold start (2) high power, hot start (3) low power, simmer (Global Alliance for Clean Cookstoves, 2014). While the WBTs can be carried out under more controlled conditions, recent studies have found that the WBTs fail to capture periods of low combustion efficiency in cooking events (Chen et al., 2012; Johnson et al., 2008, 2009). This is due to daily cooking activities involving more than just boiling water (Johnson et al., 2009). Some cooking techniques require a smoldering fire, for example, the cooking of *chapatti*, a traditional Indian bread (Johnson et al., 2009). Alternately, these low combustion efficiency periods may be a consequence of multitasking around the home (Johnson et al., 2009). The literature estimates that emissions of $PM_{2.5}$ (Roden et al., 2009) and $CO/CO_2$ ratios (Johnson et al., 2008; Kituyi et al., 2001; Ludwig et al., 2003) are underrepresented by the WBTs relative to field measurements by a factor of 3. There are also concerns that WBTs cannot be scaled to real cooking events and that climate models may underrepresent global emissions from biomass-burning cookstoves (Chen et al., 2012; Johnson et al., 2008, 2009).

A number of studies have characterized optical properties of cookstove BBOA. Depending on the measurement approach, different metrics of aerosol absorption have been reported. In general, methods that do direct measurements on aerosol particles without extraction report mass-normalized absorption cross section of aerosols ($MAC_{aerosol}$). Absorption measurements with the extracted material report mass-normalized absorption cross section of bulk material ($MAC_{bulk}$). In this paper, we use subscript "bulk" to help minimize confusion between $MAC_{bulk}$ and $MAC_{aerosol}$. The two can be related if the particle size distribution is known (Laskin et al., 2015). An advantage of $MAC_{bulk}$ is that it can be used to calculate the imaginary refractive index of the organic material (Laskin et al., 2015). For particles that are made of material with real refractive index of 1.5 and that are small in diameter relative to the wavelength, $MAC_{aerosol} \sim 0.7\times MAC_{bulk}$ (Laskin et al., 2015).

Stockwell et al., 2016 utilized photoacoustic extinctiometers (PAX) to conduct in situ absorption measurements at 405 and 870 nm, resulting in particle absorption coefficients for the whole aerosol and just organic compounds from cook fire emissions in Nepal. With a literature-recommended $MAC_{aerosol}$ of $0.98 \pm 0.45$ $m^2 g^{-1}$ at 404 nm for only organic compounds (Lack and Langridge, 2013) and measured particle absorption coefficient by the PAX, they approximated particle absorption emission factors (EFs) due to just organic compounds in particles. OC absorption EFs were 1.5 times higher for the hardwood smoke (EF=8.40 g $kg^{-1}$ fuel) compared to the dung smoke (EF=5.43 g $kg^{-1}$ fuel). Pandey et al. (2016) collected $PM_{2.5}$ on filters from cookfires in India, fueled by wood, agricultural residues, dung, and a mixture thereof and reported $MAC_{aerosol}$ values. They found that the $MAC_{aerosol}$ at 550 nm was a factor of 2.6 higher for fuel wood (1.3 $m^2$ $g^{-1}$) compared to dung (0.5 $m^2$ $g^{-1}$) (Pandey et al., 2016). This is consistent with Saleh et al., 2014, who found that for BBOA, effective absorptivity of OA increases with BC to OA ratio. In that particular study, they measured OC/EC was 15.4 for dung, and 12.1 compared to fuel wood.

Many organic components of BBOA have been successfully characterized in previous studies by electrospray ionization high resolution mass spectrometry (ESI-HRMS) (Budisulistiorini et al., 2017; Laskin et al., 2009; Lin et al., 2012, 2016, 2017; Smith et al., 2009; Wang et al., 2017; Willoughby et al., 2016). For example, ESI-HRMS was used to analyze the particle-phase organic constituents of smoke samples collected during the Fire Lab at Missoula Experiment (FLAME) campaign (Laskin et al., 2009; Smith et al., 2009). Fuels utilized in the FLAME studies were selected to represent North American wild fires, and the publications focused on non-woody biomass fuels such as detritus and litter as well as *ceanothus* from the US Pacific Northwest. Smith et al. (2009) reported an inventory of species in particle-phase BBOA, with 70 percent of compounds being reported for the first time. Laskin et al. (2009) examined the nitrogen-containing species, and observed that a large fraction of the detected species were N-heterocyclic compounds. Lin et al. (2016) identifies fuel-specific BrC chromophores in particles collected from the FLAME-4 experiments via high performance liquid chromatography/photodiode array/high resolution mass spectrometry (HPLC-PDA-HRMS). Two of the four fuels were woody biomass specific to North America. They found that nitroaromatics, PAHs, and polyphenols were responsible for the light absorption by BBOA (Lin et al., 2016). Recent papers investigated the chromophores in BBOA from Lag Ba'Omer, a nationwide bonfire festival in Israel (Bluvshtein et al., 2017; Lin et al., 2017). They found nitroaromatics to be the most prominent chromophores in these samples. Budisulistiorini et al. (2017) similarly identified 41 chromophores from Indonesian peat, charcoal, and fern/leaf burning with a method relying on chromatographic separation and simultaneous detection by spectrophotometry and ESI-MS. They identified three types of chromophores: oxygenated, nitroaromatics, or sulfur-containing (Budisulistiorini et al., 2017).

The goal of the current study is to understand the composition of cookstove BBOA in additional detail than afforded by previous measurements. We do this by 1) generating and collecting BBOA from prescribed cooking events carried out by a local cook, and 2) using high-resolution mass spectrometry techniques to characterize their particle-phase composition. It is part of a larger study attempting to document the contribution of household combustion to ambient air pollution in India. In this paper we provide an inventory of particle-phase compounds produced from actual cooking events detected by nano-DESI-HRMS, and an assessment of BrC chromophores specific to the biomass type used based on HPLC-PDA-HRMS analysis. In addition, we compare particle-phase constituents in cookfire smoke produced from different stoves and fuels.

## 2 Experimental Methods

### 2.1 Field Site

This study was conducted at the SOMAARTH Demographic, Development, and Environmental Surveillance Site (Balakrishnan et al., 2015; Mukhopadhyay et al., 2012; Pillarisetti et al., 2014) run by the International Clinical Epidemiological Network (INCLEN) in Palwal District, located approximately 80 km south of New Delhi. SOMAARTH covers 51 villages across three administrative blocks, with an approximate population of 200,000. Palwal District has a population of approximately 1 million over ~1400 km$^2$; 39% of residents in the district use wood as their primary cookfuel, followed by dung (25%) and crop residues (7%) (Census of India, 2011).

### 2.2 Sample Collection

Over 34 days in August-September 2015, PM$_{2.5}$ samples were collected from a kitchen in the village of Khatela, Palwal, Haryana, India. Figure 1 shows (A) the kitchen setup and (B) the stoves (*angithi* and *chulha*) and fuels (dung and brushwood) used. The stoves and fuels were obtained locally and traditional meals were prepared by a local cook. The cook was instructed by the experimenters to prepare a particular, standard meal using the selected fuel and stove. All *angithi* cookstoves burned dung and were used to prepare buffalo fodder. *Chulha* cookstoves burned either brushwood or dung fuels and were used to prepare a traditional meal of *chapati* and vegetables for 4 people. Vegetables were cooked in a pressure cooker that rests on top of the *chulha* (Figure 1B). *Chapatti* were cooked in the air space next to the fuel, as is typical for this area. Brushwood/*angithi* cookfires were never tested because this combination is not frequently used in the local households. Figure S2.1 shows a diagram of sample collection. $PM_{2.5}$ emissions were sampled via three-pronged probes that hung above the cookstove. Air sampling pumps (PCXR-8, SKC Inc.) created a flow of BBOA emissions through aluminum tubing during cooking events. BBOA was captured through cyclone fractionators (2.5 µm cut point, URG Corporation) and the resultant flow was taken through a stainless steel filter holder containing a PTFE filter (Teflon B, SKC Inc., 47 mm). One filter was collected for chemical analysis (Teflon B), and another filter for gravimetric analysis (Teflon A). Flows were measured via a mass flowmeter (TSI 4140) before and after each cooking event to ensure it had not varied more than 10%. The pumps were turned on before cooking began so that emissions from the entire cooking event were captured and turned off when the fire was out. Stove dimensions and their distance from the probe inlets are detailed in Figure S3.1. Prior to analysis, filters were stored in petri dish slides at -80°C other than during transportation and use. This includes time at the field site (1-6 hours) and transportation back to the United States (24 hours). During these times, samples were stored at ambient temperature.

### 2.3 Nano-DESI-HRMS analysis

$PM_{2.5}$ collected on PTFE filters were analyzed with an LTQ-Orbitrap$^{TM}$ high resolution mass spectrometer (ThermoFisher Scientific) equipped with a custom built nano-DESI source (Roach et al., 2010a, 2010b). Nano-DESI consists of two electrified capillaries, with a small (< 1 mm) droplet (solvent bridge) forming at the point of their contact. The nano-DESI solvent mixture (70% $CH_3CN$/30% $H_2O$, optimized for the stability of the nano-DESI source) flows through an electrified capillary at a flow rate of 0.3-1 µL/min. The droplet is lowered to the substrate's surface, where the analyzed material is extracted by the solvent and immediately sprayed in the ESI inlet. It has been shown that the nano-DESI dissolves all extractable material on the filter surface (Roach et al., 2010a, 2010b). To ensure the material on the filter is not depleted the droplet is moved across the filter's surface at roughly 0.2 cm/min. The spray voltage was 3.5 kV; the instrument was operated in positive ion mode. The mass accuracy of the HRMS was calibrated over a wide *m/z* range with a ThermoFisher Scientific standard calibration mixture. Two separate mass spectra were obtained from different portions of the filter to ensure reproducibility. Only peaks that showed up in both spectra were retained for further analysis.

Peaks with signal-to-noise ratios of greater than 3 were extracted from the time-integrated nano-DESI chromatograms using Decon2LS software. Peaks containing $^{13}C$ isotopes were excluded from analysis. Sample and solvent blank mass spectra peaks were clustered with a tolerance of 0.001 *m/z* using a second-order Kendrick analysis with $CH_2$ and $H_2$ base units (Roach et al., 2011). The spectra were internally mass-calibrated by assigning prominent peaks of common BBOA compounds first, and fitting the observed-exact *m/z* deviation to a linear regression curve. The *m/z* correction introduced by the internal calibration was <0.001 *m/z* units, but even at these small levels, the correction helped reduce the ambiguity in the assignments of unknown peaks. We focused on analyzing peaks with *m/z*< 350, as peaks above this *m/z* value were small in abundance (on average 6% of total abundance) and number of peaks (9% of the total number of peaks) and in many cases could not be assigned unambiguously. Exact masses were assigned using the freeware program Formula Calculator v1.1 (http://magnet.fsu.edu/~midas/download.html). The permitted elements and their maximal numbers of atoms were as follows: C (40), H (80), O (35), N (5), and Na (1). Peaks that could not be assigned within the described parameters had small abundances and were not pursued further. There were a few notable exceptions, namely, the potassium salt peaks discussed below. Conversely, potassium-organic adducts were not observed presumably due to the higher affinity of organic molecules to $Na^+$ compared to $K^+$. Permitting sulfur, chloride, and phosphorus did not increase the fractions of assignable peaks, nor did it change the assignments for the peaks we report. The double-bond equivalent (DBE) values of the neutral formulas were calculated using the equation: $DBE = C - H/2 + N/2 + 1$, where C, H, and N correspond to the number of carbon, hydrogen, and nitrogen atoms, respectively.

## 2.4 HPLC-PDA-HRMS

The samples were further analyzed with an HPLC-PDA-HRMS platform (Lin et al., 2016). To prepare the samples for analysis, half of the PTFE filter was extracted overnight in mixture of acetonitrile, dichloromethane, and hexane solvents (2:2:1 by volume, 5 mL total), which was empirically found to work well for extracting a broad range of BBOA compounds (Lin et al., 2017). The solutions were then filtered with PVDF filter syringes to remove insoluble particles (Millipore, Duropore, 13mm, 0.22 µm). The solutions were concentrated under $N_2$ flow, and then diluted with water and dimethyl sulfoxide (DMSO) to a final volume around 150 µL. The separation was performed on a reverse-phase column (Luna C18, 2 x 150 mm, 5 µm particles, 100 Å pores, Phenomenex, Inc.). The mobile phase comprised of 0.05% formic acid in LC/MS grade acetonitrile (B) and 0.05% formic acid in LC/MS grade water (A). Gradient elution was performed by the A/B mixture at a flow rate of 200 µL/min: from 0-3 min hold at 90% A, 3-62 min linear gradient to10% A, 63-75 min hold at 10% A, 76-89 min linear gradient to 0% A, 90-100 min hold at 0% A, then 101-120 min hold at 90% A. The ESI settings were as follows: 5 µL injection volume, 4.0 kV spray potential, 35 units of sheath gas flow, 10 units of auxiliary gas flow, and 8 units of sweep gas flow. The solutions were analyzed in both positive and negative ion ESI/HRMS modes.

The HPLC-PDA-HRMS data were acquired and first analyzed using Xcalibur 2.4 software (Thermo Scientific). Possible exact masses were identified by LC retention time using the open source software toolbox MZmine version 2.23 (http://mzmine.github.io/) (Pluskal et al., 2010). Formula assignments were obtained from their exact *m/z* values using the Formula Calculator v1.1

## 2.5 $MAC_{bulk}$ and AAE

Selected filter halves of the samples were extracted as described in section 2.4. Absorption spectra of the extracts were collected with a dual-beam UV-Vis spectrophotometer (Shimadzu UV-2450). $MAC_{bulk}$ values were calculated from the following equation:

$$MAC_{bulk}(\lambda) = \frac{A_{10}(\lambda)\cdot\ln(10)}{b\cdot C_{mass}} \tag{1}$$

where $A_{10}$ is the base-10 absorbance, b is the path length of the cuvette (m), and $C_{mass}$ is the mass concentration of the extracted organic material in (g $m^{-3}$). The largest uncertainty in $MAC_{bulk}$ came from uncertainty in $C_{mass}$ of the extract. First, the overall mass of $PM_{2.5}$ on the filter had to be estimated from another filter collected specifically for gravimetric analysis. The $PM_{2.5}$ mass on the chemical analysis filter was calculated from the mass on the gravimetric analysis filter after accounting for different flows through the two filters (See Figure S2.1). This calculation assumed the same $PM_{2.5}$ collection efficiency for both filters. The particle mass distribution on the filter was assumed to be uniform, and the extraction efficiency of $PM_{2.5}$ mass was estimated to be 50% by comparing the weights of filters before and after the extraction. Uncertainties incorporate flow rate measurements (10% relative error) and extraction efficiency of $PM_{2.5}$ mass (40% relative error). Absorption angstrom exponents (AAE) were calculated for both samples by fitting the log($MAC_{bulk}$) vs. log($\lambda$) to a linear function over the wavelength range of 300 to 700 nm. It should be noted that there are many methods for measuring optical properties of $PM_{2.5}$ particles, and the method used here provides $MAC_{bulk}$ and AAE of extractable organic bulk material. The advantages and limitations of other methods are explained in Laskin et al. (2015).

## 3 Results and Discussion

### 3.1 Nano-DESI-HRMS analysis of cookstove particles

Representative nano-DESI mass spectra from the three major types of cookfires sampled are shown in Figure 2. It is clear from the mass spectra in Figure 2 that the three combinations of fuel/stove types lead to distinct particle compositions. We compare the particle composition of the three major cookfire types by averaging the percentage of $C_xH_yN_w$, $C_xH_yO_z$, and $C_xH_yO_zN_w$ peaks in the nano-DESI spectra from multiple samples. Samples used and a summary of the following discussion is detailed in Table S1.1. The overwhelming majority of detected species by nano-DESI in dung cookfire smoke $PM_{2.5}$ was attributed to $C_xH_yN_w$, compounds that contain only carbon, hydrogen, and nitrogen atoms. The average count-based fractions from $C_xH_yN_w$ species were 79.9%±4.4% and 82.1%±1.0% for dung/*chulha* and dung/*angithi* experiments, respectively, but only 23.8%±7.8% for brushwood/*chulha* experiments. All nitrogen-containing compounds in the smoke $PM_{2.5}$ come from the nitrogen content in the fuels (Coggon et al., 2016) which is likely higher for dung. For example, Stockwell et al. (2016) reported the nitrogen content of yak dung as 1.9% by weight, while it is found to be lower for woods such as black spruce (0.66% by wt) and ponderosa pine (1.09% by wt) (Hatch et al., 2015). It should be noted that another study of fuels in India found the nitrogen content was roughly the same brushwood (1.4±0.3% by wt) and dung (1.4±0.1% by wt) (Gautam et al., 2016), so additional characterization of fuel composition in the future is desirable. In contrast to dung fuel, $PM_{2.5}$ from brushwood cookfire smoke contained higher fractions of $C_xH_yO_z$ species. Specifically, 43.1%±14.6% in brushwood/*chulha* cookfires were assigned as $C_xH_yO_z$ species compared to only 4.1%±0.9% and 3.2%±3.3% for dung/*chulha* and dung/*angithi* experiments, respectively**.** Many of the $C_xH_yO_z$ formulas were consistent with species reported previously as lignin pyrolysis products (Collard and Blin, 2014; Simoneit et al., 1993). Fractions of $C_xH_yO_zN_w$ did not correlate well with fuel/stove variables and ranged from 4.1% to 34.4% in the analyzed samples.

Potassium (Hosseini et al., 2013; Sullivan et al., 2014) and levoglucosan (Jayarathne et al., 2017; Simoneit et al., 1999) are well-established flaming and smoldering BB tracers, respectively. Gas-phase chlorine species have been observed in BBOA previously (Lobert et al., 1999; Stockwell et al., 2016). Therefore it is not surprising that inorganic salt peaks containing potassium and chlorine were observed in more than half of dung cookfires (8 out of 14) and all brushwood cookfires. These peaks were pursued apart from the original analysis because the peak abundance was very large in many mass spectra, and they served as convenient internal *m/z* calibration points. These mass spectra all contained $K_2Cl^+$ as the most prominent salt peak, and $K_3Cl_2^+$ was also present in a few mass spectra. Isotopic variants of these salts, namely with either $^{37}Cl$ or $^{41}K$ (24% or 6.7% natural abundance) instead of $^{35}Cl$ or $^{39}K$ (76% or 93.3% natural abundance), were also found. The resolving power of the HRMS instrument is insufficient to distinguish the isotopic shifts from Cl and K ($\Delta\ mass_{37Cl\text{-}35Cl}$= 1.997 Da, $\Delta\ mass_{41K\text{-}39K}$= 1.998 Da) but one or both of the isotopes were consistently present in all mass spectra containing potassium ions. Adducts corresponding to a replacement of K by Na were also detected. The observed potassium signals may have depended not only on the potassium content of the fuel but also on the amount of flaming combustion (combustion efficiency), the specific food items cooked, or the stove material itself. Inorganic salts were observed in all *chulha* cookfire $PM_{2.5}$ samples regardless of fuel type and were absent in all *angithi* cookfire $PM_{2.5}$ samples. On average, chulha stoves have a higher combustion efficiency (dung/*chulha* 90.7% ± 0.6%, dung/*angithi* 87.5% ± 1.8%) consistent with more flaming combustion, and therefore more potassium emissions. The *Chulha* stove produced meals for people or animal fodder, respectively. Also, the *chulha* was made mainly from brick with a local covering of local clay, whereas the *angithi* only from clay. With the presently available data it is impossible to determine whether the potassium salts originated from flaming combustion, the *chulha* material or is the result of different food items cooked.

Levoglucosan was present in 3 out of 8 dung/*chulha* cookfires, 4 out of 6 dung/*angithi* cookfires, and 4 out of 11 brushwood/*chulha* cookfires. We expect levoglucosan to be found in BBOA from all fires based on other studies (Jayarathne et al., 2017), and we therefore conclude that levoglucosan peak must have been suppressed in the nano-DESI source by the more ionizable components of the mixture. By extension of the same logic, ions corresponding to other carbohydrates, and more broadly to lignin-derived CHO species, were likely suppressed by this technique, and therefore a significant fraction of BBOA constituents may be absent in this inventory. Due to the variability in observing levoglucosan, we conclude for ESI-MS studies, levoglucosan serves as a marker rather than a tracer for digested biomass burning and woody biomass burning.

### 3.2 Particle-phase biomass burning markers

An inventory of compounds that were reproducibly observed in samples from three different cooking events using the same fuel/stove combination was compiled. Samples were chosen for the inventory considering the measured fuel moisture content and meal cooked, with the goal of comparing samples from similar cookfires (see SI Table S1.1 for sample details). Peaks that did not appear in mass spectra of all three samples were discarded to ensure reproducibility and help filter out noise peaks from the nano-DESI source. The remaining peak abundances were first normalized to the largest peak abundance then the three mass spectra were averaged. Since the absolute peak abundances varied in individual spectra, only approximate relative abundances are reported here grouped into three logarithmic bins, denoted as LOW (<1%), MEDIUM (1-9.99%), HIGH (10-100%). This analysis was completed for the emissions from each of the three types of cookstove-fuel combinations studied in this work.

Figure 3 summarizes how reproducibly-detected $PM_{2.5}$ compounds are organized in the inventory. First, we will provide a list of compounds common to the emissions from all 3 types of cookfires including: dung/*chulha*, dung/*angithi*, and brushwood/*chulha* (Section 3.3, Table 1). Then, we will discuss compounds exclusively found in the brushwood/*chulha* cookfire emissions (Section 3.4, Table S4.1). We next show compounds common to dung cookfire emissions (Section 3.5.1, Table 2). Lastly, we discuss BBOA compounds detected in either dung/*chulha* and dung/*angithi* cookfires (Section 3.5.2). Within section 3.5.2 we discuss compounds unique to the dung/*chulha* (Table S4.2) and the dung/*angithi* (Table S4.3) cookfire experiments, as well as the compounds they had in common (Section 3.5.1, Table 2).

The numbers of reproducibly-detected formulas are shown in Figure 3 in blue. $PM_{2.5}$ from dung cookfires had a higher observed chemical complexity (i.e., had more observed peaks) than $PM_{2.5}$ from brushwood cookfires. Further, there were more observed peaks in $PM_{2.5}$ from dung/*angithi* cookfires compared to dung/*chulha* cookfires. There were 93 compounds reproducibly detected in the brushwood/*chulha* cookfire $PM_{2.5}$ samples compared to 212 and 262 for dung/*chulha* and dung/*angithi* cookfires, respectively. There were five compounds the *chulha* cookfires had in common, with two of them being the potassium salt peaks described earlier. There was one compound ($C_{14}H_{16}O_3$) shared by only dung/*angithi* and brushwood/*chulha*. Because of the small number of these peaks, they will not be discussed in this paper. In the following sections, we will discuss compounds that are common in all cookfires, as well as unique compounds.

Figure 4 summarizes the BBOA inventory described in more detail in sections 3.3-3.5, i.e., compounds common to dung/*chulha*, dung/*angithi*, brushwood/*chulha* cookfires; compounds found exclusively in the emissions from brushwood/*chulha* cookfires; and species that are unique to dung cookfires. Figure 4A pie charts compare the fraction of count-based, normalized abundance in each elemental category. $PM_{2.5}$ compounds shared among all samples of this study are diverse. In terms of count-based abundance, compounds emitted from all dung-burning cookfires are largely nitrogen-containing. From Figure 4B, the common compounds make up the vast majority (97%) of detected compounds from the brushwood/*chulha* cookfires. Similarly for the dung cookfires, the common cookfire compounds (grey) and dung cookfire compounds (brown) make up 95% or more of the mass spectra abundance as shown in Figure 4B. Therefore, the common compounds (Table 1) and dung compounds inventories (Table 2) contain the bulk of the $PM_{2.5}$ species in terms of count-based abundance.

### 3.3 Compounds common to dung/*chulha*, dung/*angithi*, brushwood/*chulha* cookfires

Table 1 provides a complete list of eighty reproducibly-detected compounds that were common to emissions from all cookfires. These common compounds make a large contribution to the mass spectra for every cookfire type (Figure 4), with MEDIUM being the most common relative abundance given in Table 1. More than half of the abundance (59%) was due to the nitrogen-containing compounds ($C_xH_yN_w$ or $C_xH_yO_zN_w$), as shown in Figure 4a. ESI detection likely biases the elemental make up of smoke $PM_{2.5}$, as nitrogen-containing species are more easily ionized compared to sugars and lignin-derived compounds (Laskin et al., 2010; Wan and Yu, 2006). Nevertheless, a large overlap in the $C_xH_yN_w$ and $C_xH_yO_zN_w$ species was observed.

The common compounds make up a large fraction for all cookfire types. This is especially true for the sample from brushwood/*chulha* cookfires, where their fraction is ~86% in number. Many of these $C_xH_yO_z$ species have elemental formulas consistent with typical lignin- and cellulose-derived products such as anisaldehyde, veratraldehyde, vinylguaiacol, syringylethanone, trimethoxyphenylethanone, etc. reported previously in the literature (Laskin et al., 2009; Simoneit et al., 1993; Smith et al., 2009). These tentative molecular assignments are listed in Table 1 alongside their elemental formulas. Approximately 20% of the common compounds (17 out of 80 formulas) have been also identified in earlier studies reporting molecular characterization of $PM_{2.5}$ samples collected from burning of one or more of the following fuels: Alaskan duff, ponderosa pine duff, southern United States pine needles, or ceanothus fuels (Laskin et al., 2009; Smith et al., 2009). Many of these fuels are non-woody and all are undigested biomass, very different kinds of biomass from those used as cookstove fuels in this study and in this region of India. This suggests that perhaps 20% of the compounds listed in Table 1 might be reproducibly detected in BBOA samples using ESI-MS, regardless of biomass type. The overlap is not surprising, as all biomass is composed of three polymers: lignin, hemicellulose, and cellulose (Collard and Blin, 2014).

### 3.4 Compounds found exclusively in the emissions from brushwood/*chulha* cookfires

Table S4.1 lists the compounds observed exclusively in the samples from brushwood/*chulha* cookfires. Many of them correspond to lignin-derived products that have been previously identified in BBOA by gas chromatography methods, as indicated in Table S4.1 (Lee et al., 2005; Simoneit, 2002; Simoneit et al., 1993; Smith et al., 2009). Lignin is an essential component of wood, comprising roughly a third of its dry mass (Collard and Blin, 2014; Simoneit, 2002). Lignin is generally composed of *p*-coumaryl, coniferyl, and syringyl alcohol units. During pyrolysis, the coumaryl, vanillyl, and syringyl moieties, respectively, are preserved and are found in smoke. More generally, the lignin pyrolysis products found in smoke contain a benzene ring, often with hydroxy and/or methoxy substituents. Based on these previous observations and the assumption that these are lignin pyrolysis products, tentative molecular structures were assigned to $C_xH_yO_z$ compounds. It is likely that some $C_xH_yO_z$ molecular species specific to the emissions from the brushwood burning were not detected in this study due to their low ionization efficiency.

### 3.5 Species Unique to Dung Smoke $PM_{2.5}$

#### 3.5.1 Compounds emitted from both dung/*angithi* and dung/*chulha* cookfires

Overall, the chemical composition of $PM_{2.5}$ samples of dung-burning emissions was observed to be far more complex than the samples from the brushwood-burning cookfires. Table 2 lists the 115 compounds found exclusively and reproducibly in the dung-fueled samples. These compounds are largely $C_xH_yN_w$, as shown in Figure 4b. Only a few of the elemental formulas, $C_8H_{16}N_2$, $C_{11}H_8N_2$, and $C_{13}H_{11}ON$, have been reported previously (Laskin et al., 2009; Smith et al., 2009).

#### 3.5.2 Analysis of compounds found in all dung-burning cookfires

In addition to the common dung compounds listed in Table 2, there were compounds detected exclusively in the emissions from either dung/*chulha* cookfires (Table S4.2) or dung/*angithi* cookfires (Table S4.3). All of these compounds are nitrogen-containing, and none have been reported previously, to the best of our knowledge. However, in this section, we combine all compounds found in dung-burning cookfire $PM_{2.5}$, presented in Tables 2, S3.2, and S3.3, and discuss their possible molecular character.

Figure 5 shows the double bond equivalent (DBE) as a function of the carbon number of compounds detected in all investigated samples. The DBE versus C dependence for classes of compounds with different degrees of unsaturation, including: terpenes (red), polyenes (orange), polycyclic aromatic hydrocarbons (yellow shaded, PAHs) are also shown to aid the classification of the compounds observed in the $PM_{2.5}$ samples. Thirty of the 193 formulas fall in the PAH region of the plot suggesting that they have aromatic structures (Figure 5a). Figure 5b compares the DBE values of the molecular components detected in the emissions exclusive to brushwood/*chulha* cookfires (Table S4.1) and the common compounds from all studied samples (Table 1). In general, the DBE increases with carbon number for the compounds common to all cookfires. Only eight of the 87 compounds fall directly in the PAH region. There are more aromatic structures specific to the dung smoke compared to the compounds detected in all cookfires.

Detected nitrogen compounds with high DBE values are likely N-heterocyclic PAH compounds. Figure 6 displays possible structures for the select detected nitrogen-containing compounds with a high DBE. Purcell et al. (2007) found that pyridinic PAH compounds were readily ionized from standard mixtures of N-heterocyclics in positive-ion ESI. This gives us more confidence in our observation of $C_{13}H_9N$, tentatively acridine, and $C_{11}H_8N_2$, tentatively β-carboline, which have pyridinic nitrogen atoms and likely have high ionization efficiencies. The peak abundances of these compounds are significant, with medium and high designations, respectively. $C_{12}H_9ON$ cannot have a pyridinic nitrogen and is tentatively assigned as phenoxazine.

Kendrick analysis identifies homologous series of structurally related compounds that share a core formula and differ in the number (n) of additional $CH_2$ units (Hughey et al., 2001). 172 of the 193 detected compounds from the dung-burning cook fire emissions can be grouped into 43 homologous series based on the Kendrick mass defect plot, as shown in Figure 7. There are 15 homologous series and 5 independent formulas that make up the 61 total $C_xH_yN_w$ (red) compounds. This suggests that there are at least 20 distinct types of structures that made up the observed $C_xH_yN_w$ species. Similarly, there are 30 homologous series for $C_xH_yO_zN_w$ (purple) formulas and 12 $C_xH_yO_zN_w$ formulas yielding at least 42 distinct types of structures for this formula category. There are no homologous series from $C_xH_yO_z$ species, presumably because only a few members of this group can be detected by ESI-based methods in the $PM_{2.5}$ from the dung cookfires. From this analysis, we find that on the whole, there are at least 66 unique types of structures from the 193 compounds detected from dung-burning cookfire emissions. This Kendrick analysis suggests that some of the observed N-heterocyclic PAHs have alkyl substituents. For example, phenoxazine and β-carboline (Figure 6) serve as the core molecules in the homologous series $C_nH_{2n-15}ON$ and $C_nH_{2n-14}N_2$, respectively (Figure 7).

### 3.6 Light-absorbing properties and chromophores from cookstove emissions

Figure 8 show $MAC_{bulk}$ values, which represent bulk absorption coefficient normalized by mass concentration of organic solvent extractable components. The $MAC_{bulk}$ values were determined assuming that 50 percent of the particle mass could be extracted from the filter. Error bars account for the uncertainties in the extraction efficiency (relative error 40%), and flows during sample collection (relative error 10%). $MAC_{bulk}$ values for the samples from the brushwood burning are roughly twice that of dung between 300-580 nm. Assuming higher EC/OC for wood compared to dung as reported in Jayarathne et al. (2017), the results are consistent with Saleh et al. (2014), who predict higher effective OA absorbance for higher BC to OA ratios.

$MAC_{bulk}$ values at 400 nm were 1.9±0.8 $m^2\ g^{-1}$ and 0.9±0.4 $m^2\ g^{-1}$ for the samples from brushwood/*chulha* and dung/*chulha* cookfires, respectively. For comparison, Kirchstetter and colleagues reported $MAC_{bulk}$ of 2.9 $m^2\ g^{-1}$ at 400 nm for the BrC in biomass smoke samples (Kirchstetter et al., 2004). Chen and Bond measured $MAC_{bulk}$ values at 360 nm of nearly 2.0 $m^2\ g^{-1}$ for methanol extracts of particles resulting from oak pyrolysis, and nearly 2.5 $m^2\ g^{-1}$ for pine wood pyrolysis (Chen and Bond, 2010). Our $MAC_{bulk}$ value at 360 nm for brushwood was larger at 3.7±1.5 $m^2\ g^{-1}$, possibly due to a more efficient extraction of a broader range of chromophores by the solvents utilized. The pyrolysis temperature and wood composition could also contribute to the difference. Our $MAC_{bulk}$ value at 360 nm for dung was lower compared to our brushwood sample at 1.8±0.8 $m^2\ g^{-1}$. This could be a combined result of the likely lower pyrolysis temperature and difference in the biomass composition (Chen and Bond, 2010).

While the $MAC_{bulk}$ values are smaller for the dung/*chulha* cookfires, the $PM_{2.5}$ emission factors (a detailed analysis of the emission factors will be reported in a follow up paper) are more than a factor of 2.5 higher for dung/*chulha* fires (21.1±4.2 g $kg^{-1}$ fuel) compared to brushwood/*chulha* fires (7.3±1.8 g $kg^{-1}$ fuel). The product $MAC_{bulk} \times EF$ can be used to estimate the contribution of smoke to the absorption coefficient for the per unit mass of the fuel burned. At 400 nm, $MAC_{bulk} \times EF$ = 19.0±9.2 $m^2\ kg^{-1}$ fuel and 13.9±6.8 $m^2\ kg^{-1}$ fuel for dung/*chulha* fires and brushwood/*chulha* fires, respectively. For particles that are small in diameter relative to the wavelength, $MAC_{aerosol} \sim 0.7\times MAC_{bulk}$ (Laskin et al., 2015). Based on this we can estimate $MAC_{aerosol} \times EF$ = 13.3±6.5 $m^2\ kg^{-1}$ fuel and 9.7±4.8 $m^2\ kg^{-1}$ fuel for dung/*chulha* fires and brushwood/*chulha* fires, respectively. The values are somewhat higher than the “EF $B_{abs}$ 405 just BrC” values reported by Stockwell et al. (2016) at 405 nm, which were 8.40 $m^2$ $kg^{-1}$ fuel and 5.43 $m^2$ $kg^{-1}$ fuel for hardwood cooking smoke and dung cooking smoke, respectively. However, both the present results and the data from Stockwell et al. (2016) show that the dung-based and wood-based fuels make comparable contributions to the absorption coefficient of the smoke for same amount of fuel consumed.

The AAE values for the extractable organics in brushwood and dung samples are 7.51 and 6.8, respectively. Our brushwood AAE fits into the lower end of the AAE range for extracted organics presented in Chen and Bond, 6.9 to 11.4 (Chen and Bond, 2010). Typical AAE values cited in the literature for BrC in BBOA are in a range of 2-11 (Kirchstetter et al., 2004; Laskin et al., 2015). The AAE of the entire cooking aerosol (with the contribution of the insoluble BC included) should be lower. For example, Stockwell et al. (2016) reported in situ measurements of AAE of 3.01 and 4.63 for brushwood and dung cooking particles, respectively.

We now focus on identifying selected chromophores that contribute to the high $MAC_{bulk}$ we observe for cookstove $PM_{2.5}$. Two cookfires using dung and brushwood fuels were selected for a more detailed analysis of the light-absorbing molecules (BrC chromophores). The dung cookfire utilized an *angithi* cookstove to prepare buffalo food. The brushwood cookfire was used to prepare a traditional meal of rice and lentils with a *chulha*. More detailed sample information is provided in Table S1.3. The samples were analyzed using HPLC-PDA-ESI/HRMS platform following the methods described elsehwere (Lin et al., 2015, 2016, 2017). The identified chromophores and their PDA chromatograms are illustrated in Figure 9, and the retention times and peaks in the absorption spectra are listed in Tables 3 and 4 for the emissions from brushwood and dung cookfires, respectively.

The BrC chromophores for both brushwood and dung samples are largely $C_xH_yO_z$ compounds (Tables 4 and 5). We conclude that lignin-derived BrC chromophores account for the majority of the extracted light-absorbing compounds in both samples. We also found a few nitrogen-containing BrC chromophores (e.g., $C_9H_7NO_2$ and $C_8H_9NO_3$) in both the brushwood and dung samples. The woody and digested biomasses shared 3 strongly-absorbing chromophores, $C_8H_8O_4$ (tentatively vanillic acid), $C_{10}H_{12}O_3$ (tentatively ethyl methoxybenzoate), and $C_{13}H_{10}O_2$, as well as comparably weaker absorbing chromophores. $C_{10}H_{10}O_3$ is another strong absorber of near UV radiation that was found in both samples. In the brushwood-derived $PM_{2.5}$, $C_{10}H_{10}O_3$ elutes at 18.3 min ($\lambda_{max}$= 337 nm), while in the dung smoke sample, it is not oberved until 24.5 min ($\lambda_{max}$= 299, 308 nm). These are clearly different chromophores with the same chemical formula, possibly coniferaldehyde and methoxycinnamic acid. $C_9H_8O_3$ is a similar case, in which the same chemical formula appears at different retention times in the selected ion chromatograms (SICs) for brushwood- and dung-derived $PM_{2.5}$. In the brushwood-derived $PM_{2.5}$ sample, $C_9H_8O_3$ coelutes with $C_9H_7NO_2$ at 17.3 min (Table 3). In the dung $PM_{2.5}$ sample $C_9H_8O_3$ coelutes with $C_8H_8O_4$ and $C_9H_{10}O_4$ at 14.4 min (Table 4). The $C_9H_8O_3$ formula could correspond to coumaric acid for either retention time. Because the compound coelutes with other potential chromophores, we refrained from assigning a proposed structure to the chemical formula.

There were light-absorbing molecules specific to brushwood-derived $PM_{2.5}$ (Table 3) that could account for higher $MAC_{bulk}$ values compared to the dung-derived $PM_{2.5}$. $C_8H_9NO_4$ is a possible nitroaromatic compound with its absorbance peaking around 335 nm. $C_8H_{10}O_3$, tentatively syringol, is closely related to syringic acid, a lignin monomer. The formula was also detected in the dung-derived $PM_{2.5}$ sample, but the absorption was lower by approximately a factor of 20, and therefore is not considered a main chromophore.

There were strongly-absorbing BrC chromophores in the $PM_{2.5}$ generated by burning dung fuel that eluted in the first couple of minutes of the sample run (See Figure 9b). These early-eluting chromophores were likley polar compounds that were not retained well by the column and thus could not be assigned. The challenges with assigning co-eluting chromophores in BBOA were previously noted by Lin et al. (2016). For both $PM_{2.5}$ samples, most of the chromophores eluted in the first 30 minutes of the run shown in Figure 9. Compounds eluting in the range of 30 to 60 min were also satisfactorily separated, but these were weakly absorbing. The non-polar PAH compounds absorbing in UV-Vis range are not ionized by the ESI source and subsequently not detected by HRMS (Lin et al., 2016). It is possible that additional light-absorbing molecules essential to dung smoke were strongly retained by the column and eluted after 60 min.

Absorption spectra recorded in tandem with the mass spectra provide additional constraints on the assignments. For example, at 15.6 minutes, $C_{10}H_{12}O_3$ and $C_9H_{10}O_3$ coeluted in both BBOA samples. These compounds were given the tentative assignments of ethyl-3-methoxybenzoate and veratraldehyde, respectively. The UV-Vis absorbance of ethyl-3-methoxybenzoate shown in Figure 10 provides a reasonable match for the recorded PDA spectra for both samples at a retention time of 15.6 min. Veratraldehyde, which is derived broadly from lignin, has an absoprtion spectrum that peaks at 308 nm in aqueous solution (Anastasio et al., 1997). Therefore, both ethyl-3-methoxybenzoate and veratraldehyde contribute to the spectrum observed by the PDA detector, and cannot be completely separated with this HPLC protocol.

For many formulas, multiple structural isomers were observed in SICs, with peaks appearing at more than one retention time. This behavior has been observed for other types of BBOA samples, described in Lin et al. (2016), and is inherent to lignin's nature, such that a single $C_xH_yO_z$ chemical formula can correspond to multiple possible structural isomers. There are several cases in which chemical formulas show up multiple times in Tables 4-5. An example from the brushwood $PM_{2.5}$ (Table 3) is $C_9H_{10}O_4$ which elutes at 10.6 and 14.4 minutes. $C_9H_{10}O_4$ has been previously found in lignin pyrolysis BBOA in the forms of homovanillic acid and syringealdehyde (Simoneit et al., 1993). $C_8H_8O_4$ and $C_9H_{10}O_3$ are additional examples of the similar occurance in the sample of dung-derived $PM_{2.5}$, as they both appear twice in the SICs as shown in Table 4. One peak corresponding to $C_8H_8O_4$ is very likely vanillic acid (Simoneit, 2002; Simoneit et al., 1993). $C_9H_{10}O_3$ could be either veratraledehyde or homoanisic acid, both have been observed from lignin pyrolysis (Simoneit et al., 1993). Collectively, these results indicate that many of the lignin-like chromophores have multiple structural isomers, some of which have likely been observed before (Simoneit, 2002; Simoneit et al., 1993).

## 4 Summary

Molecular analysis of $PM_{2.5}$ emissions from three types of cookstove-fuel combinations showed that the observed chemical complexity of particle composition increased in the following order: brushwood/*chulha*, dung/*chulha*, dung/*angithi*. The compounds accounting for the additional complexity in dung-derived emissions were mostly $C_xH_yO_zN_w$ and $C_xH_yN_w$ species, which have not been identified before in cookstove BBOA. A substantial portion of the compounds specific to dung cookfires appeared to be aromatic based on their degree of unsaturation. The $CH_2$-Kendrick analysis of the nitrogen-containing species from dung cookfires indicated that many may be structurally related by substitution with alkyl chains of variable length.

The estimated $MAC_{bulk}$ values for the $PM_{2.5}$ emissions samples from brushwood/*chulha* and dung/*chulha* cookfires were comparable in magnitude and wavelength dependence to the values previously observed for BBOA samples. While the $MAC_{bulk}$ values for the brushwood-derived BBOA were higher than those for the dung-derived BBOA, the particle emission factors had the opposite relationship. Therefore, per unit mass of burned fuel, the dung and brushwood fueled cookstoves may have comparable contribution to the overall light absorption. A set of $PM_{2.5}$ samples from brushwood/*chulha* and dung/*chulha* cookfires was analyzed using HPLC-PDA-HRMS to identify BrC chromophores. The vast majority of chromophores observed for both fuel types were lignin-like $C_xH_yO_z$ compounds. There were three retention times at which strongly-absorbing chromophores eluted for both samples: $C_8H_8O_4$ (vanillic acid), $C_{10}H_{12}O_3$ (methoxybenzoate), and $C_{13}H_{10}O_2$. There were also fuel-specific chromophores such as $C_{10}H_{10}O_3$ (distinct isomers for each fuel type), $C_8H_{10}O_3$ (syringol, brushwood), and $C_{12}H_{10}O_4$ (dung).

In this study we have characterized a wide range of particle-phase compounds produced by cookstoves, including the lignin-derived $C_xH_yO_z$ compounds that have commonly been identified in wood burning studies, and less common nitrogen compounds. Specifically, from dung cookfires, we detected what we presume to be aromatic nitrogen-containing compounds with few or no oxygen atoms in them. Our inventory of chemical formula is just the starting point for comprehensively characterizing particle-phase cookstove emissions. Future efforts should focus on the identification of compounds, more precise emission factor quantification for specific compounds, evaluation of toxicity, and modeling the effect of these compounds on secondary air pollution formation in aging smoke plumes.

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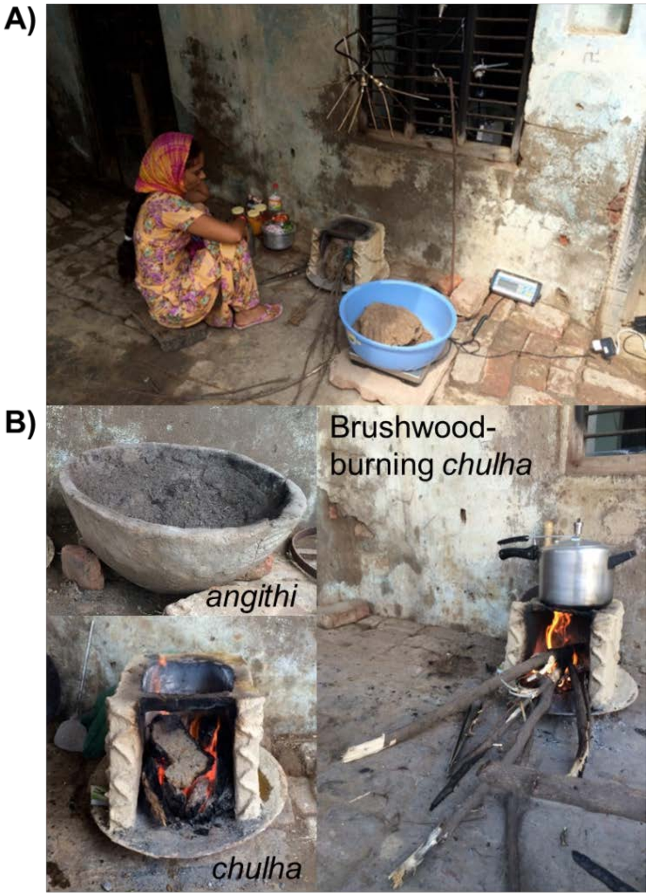

**Figure 1: The field site and set-up for cooking events. A) The kitchen set-up at the field site. B) The stoves and fuels used in this study: *angithi*, dung-burning *chulha*, and brushwood-burning *chulha*.**

5

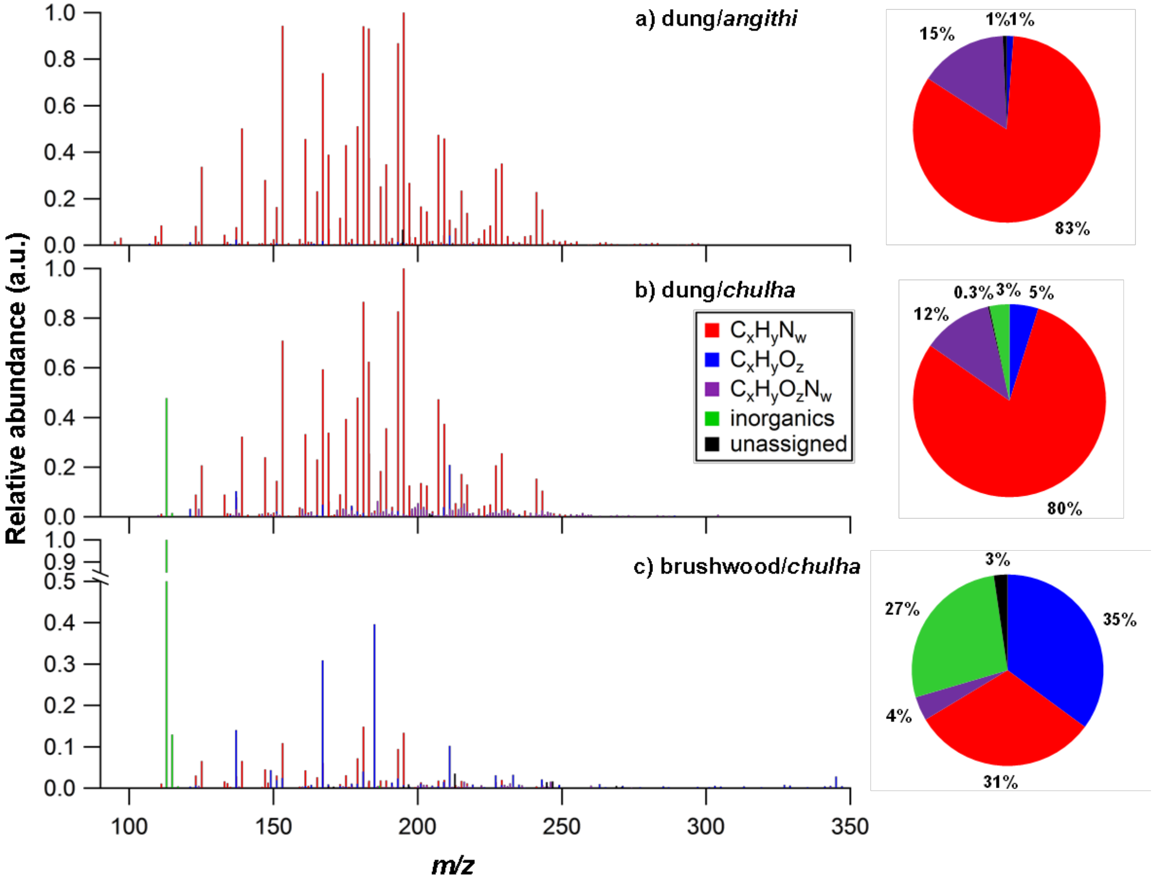

**Figure 2: Representative nano-DESI mass spectra collected for a) dung/*angithi* b) dung/*chulha* and c) brushwood/*chulha* cookfires. Relative abundance is plotted against *m/z.* Peaks are colored by their elemental makeup, $C_xH_yN_w$ (red), $C_xH_yO_zN_w$ (purple), $C_xH_yO_z$ (blue), potassium salts (green), and unassigned (black). The pie charts**
5 **illustrate the fraction of count-based, normalized peak abundance that is attributed to each elemental category.**

*Note to reviewers: The y-axis was changed to relative abundance.*

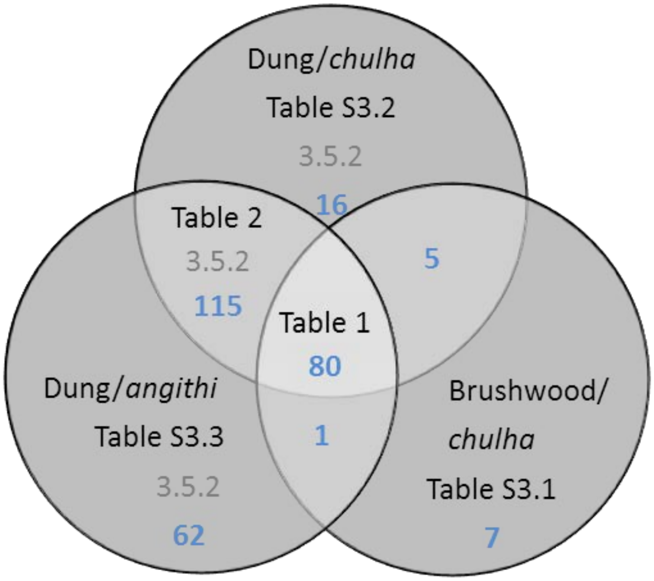

**Figure 3: An overview of the particle-phase compounds inventory based on the results of molecular characterization using nano-DESI-HRMS. Each area of the Venn diagram contains the bolded number of reproducibly-detected formulas in blue as well as the Table that lists peaks for each category. Merging all the Tables listed here provides a complete inventory of compounds detected in this study. Section 3.5.2 does not contain any tables and instead is a discussion of compounds in Tables 3, S3.2, and S3.3.**

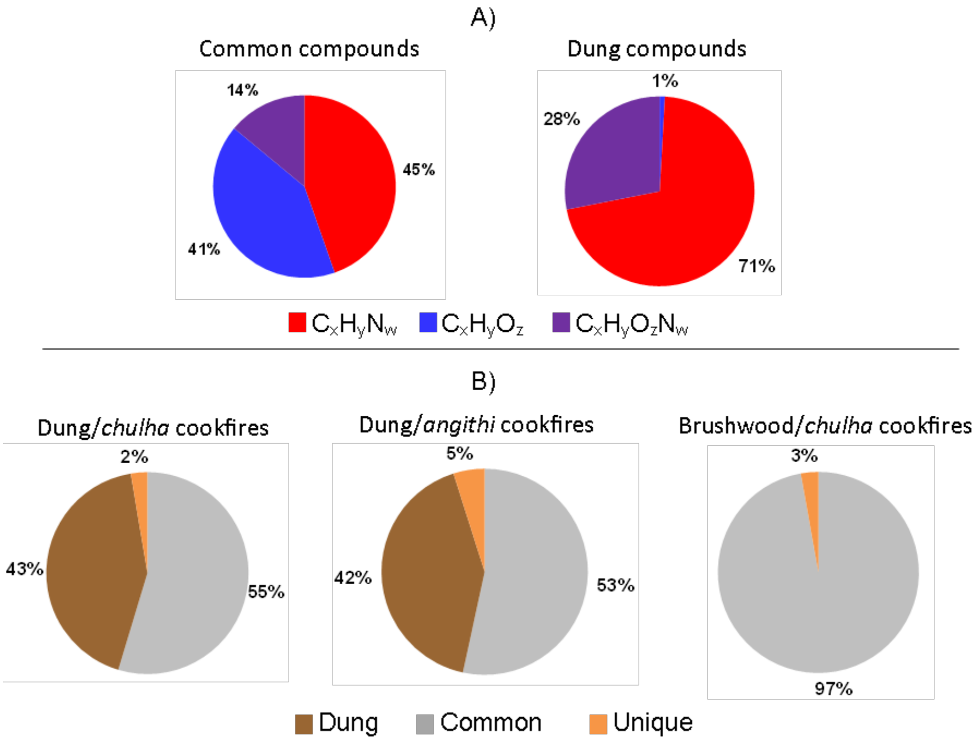

**Figure 4: A summary of the inventory in terms of the count-based, normalized peak abundances. A) Contribution of $PM_{2.5}$ compounds to each elemental formula category for those found in all cookfires and those found in all dung-burning cookfires. B) The compounds by cookstove type classified as compounds common to all cookfires in grey, compounds common to all dung cookfires in brown, and unique compounds in orange.**

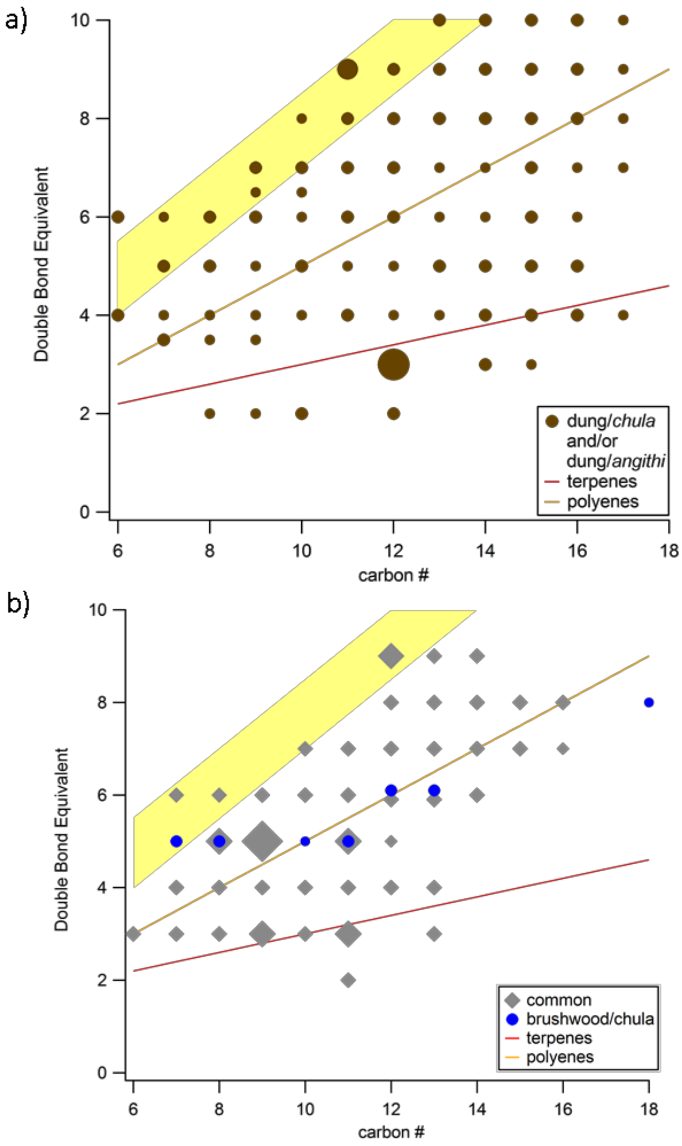

**Figure 5: Double bond equivalent (DBE) as a function of the carbon number for a) a combined set of compounds detected from all dung cookfires (brown circle) and b) compounds all cookfires have in common (grey diamond) as well as compounds exclusively found in brushwood (blue circle). Markers representing one or multiple species are sized by their LOW, MEDIUM, and HIGH designations. The curves illustrate theoretically where terpenes (red) and polyenes (orange) would fall. Similarly, the yellow-shaded region shows were PAHs would appear, including: cata-condensed PAHs with 0, 1, and 2 heterocyclic nitrogen atoms and circular PAHs.**

***Note to reviewers: We fixed a typo in the legend.***

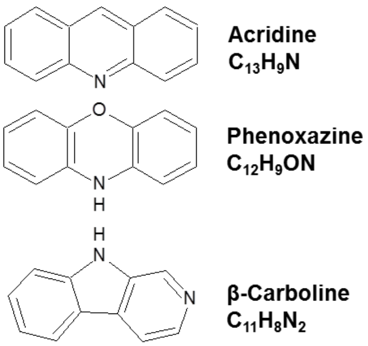

**Figure 6: Possible structures of N-heterocyclic PAHs found in dung cookfire emissions. $C_{13}H_9N$ was detected reproducibly in dung/*chulha* emissions only, while $C_{12}H_9ON$ and $C_{11}H_8N_2$ were reproducibly detected in all dung cookfires.**

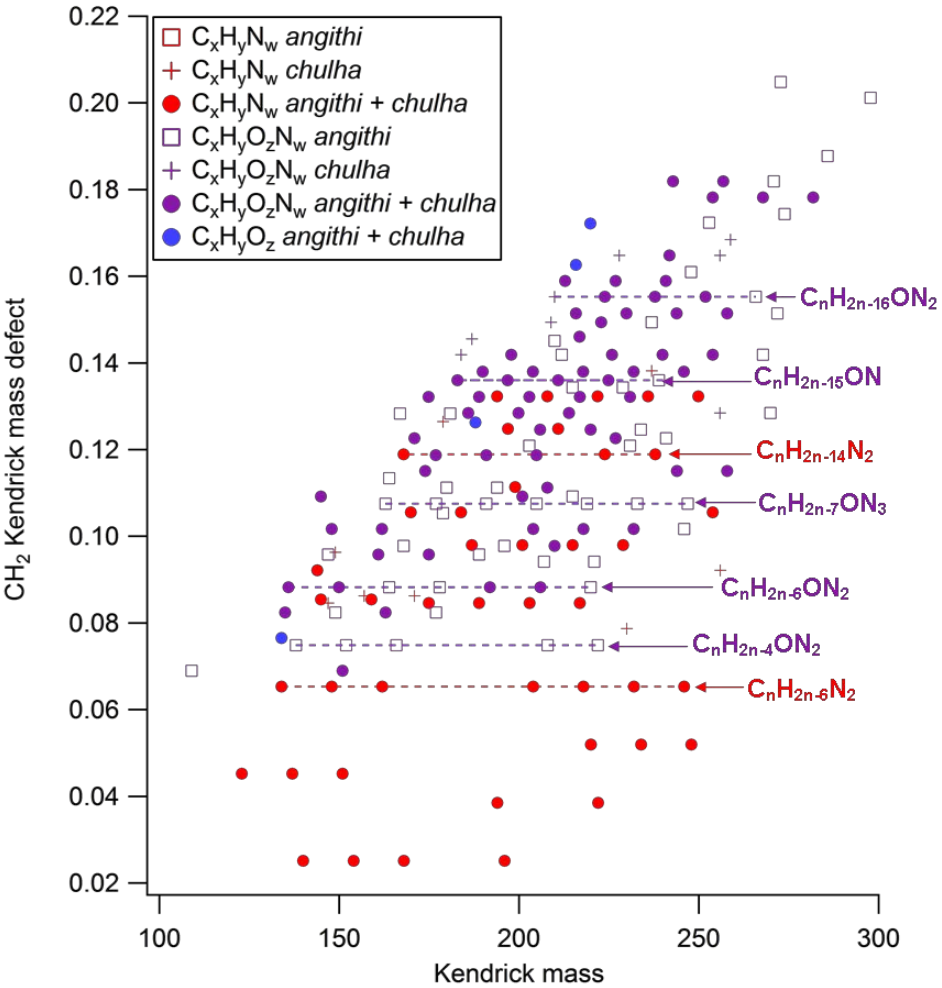

**Figure 7: The $CH_2$ Kendrick mass defect plot for compounds emitted only from dung stoves. The marker color determines the compound category for $C_xH_yN_w$ compounds (red), $C_xH_yO_z$ (blue), or $C_xH_yO_zN_w$ (purple). Marker shape indicates the stove(s) that reproducibly produced the compound: *chulha* and *angithi* (●), *angithi* (□), or *chulha* (+). Homologous series are identified with dotted horizontal lines, and suggest they have similar structures.**

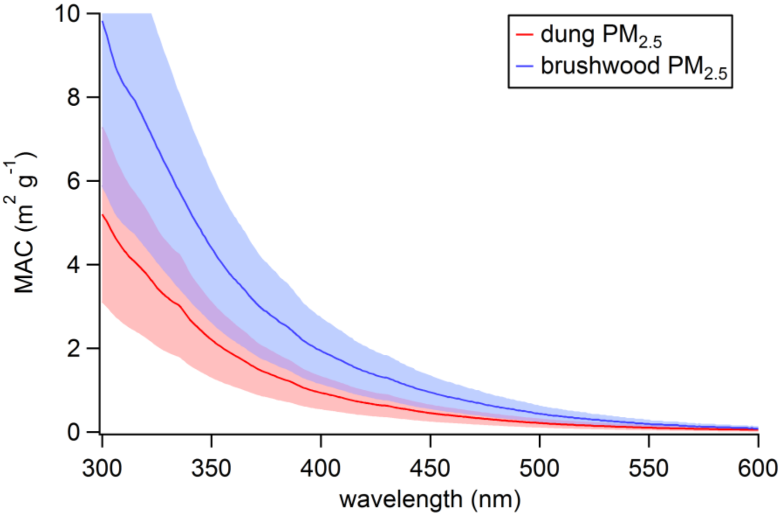

**Figure 8: Comparing $MAC_{bulk}$ ($m^2\ g^{-1}$) for organic solvent extractable material from brushwood /*chulha* (blue) and dung/*chulha* (red) samples. Shaded regions represent errors due to extraction efficiency and sampling flow rates.**

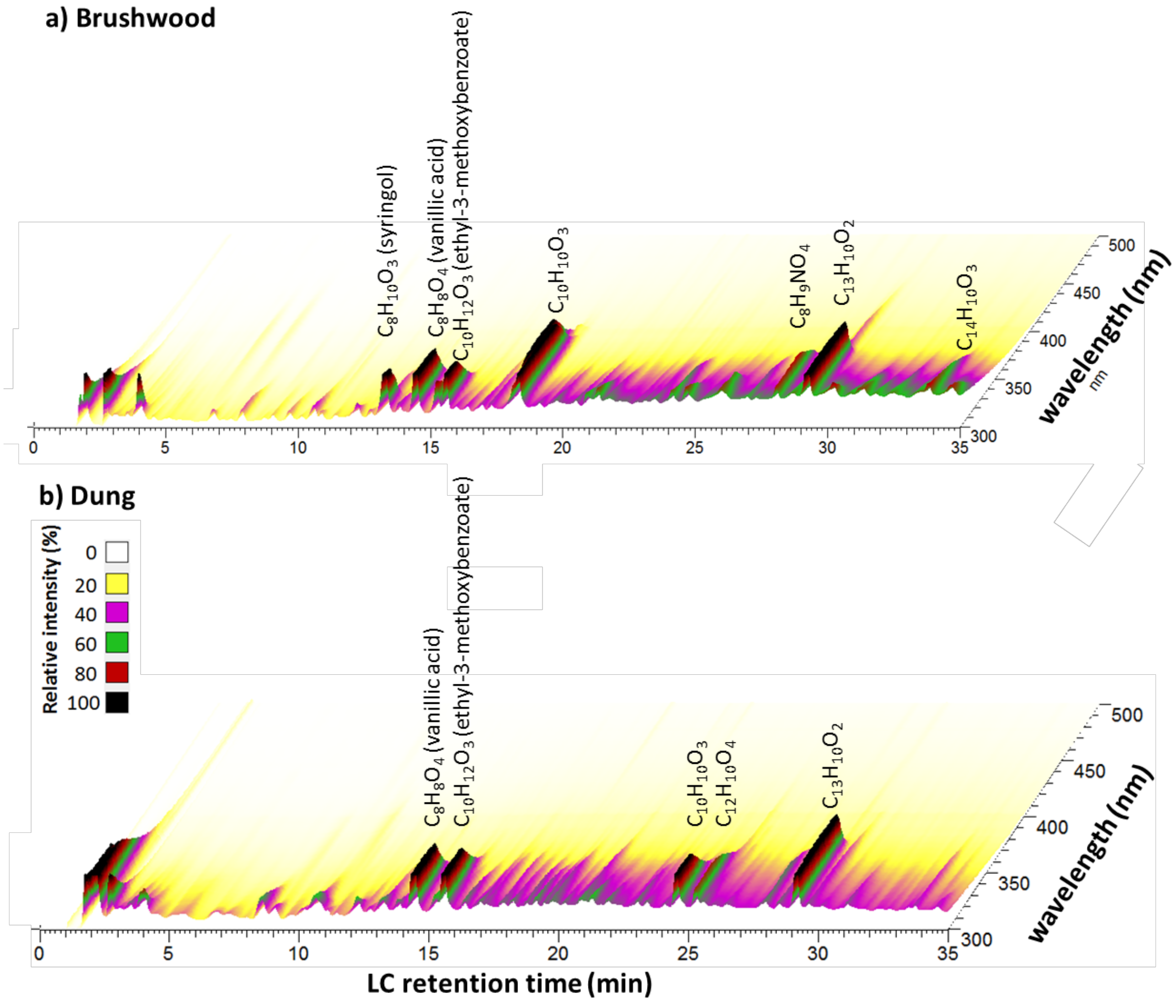

**Figure 9: HPLC-PDA chromatogram showing BrC chromophores detected in the emmision samples from a) brushwood and b) dung cookfires. The strongest-absorbing molecules and their corresponding PDA retention times are given above the peak.**

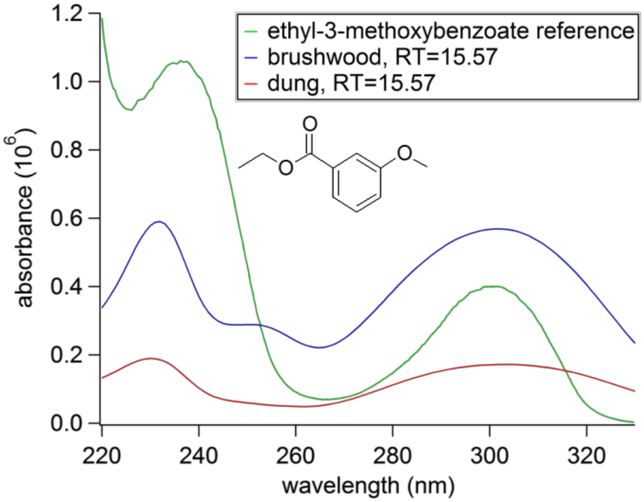

**Figure 10: UV-Vis absorption spectra from the PDA analysis of cookstove BBOA samples. The blue and red curves represent the background-subtracted absorbance at retention time of 15.57 min for brushwood-derived $PM_{2.5}$ and dung-derived $PM_{2.5}$, respectively. The reference absorption spectrum of ethyl-3-methoxybenzoate was reproduced from the NIST Chemistry WebBook database (Talrose et al., 2017). The structure of ethyl-3-methoxybenzoate is pictured.**

**Table 1: List of common compounds found in all $PM_{2.5}$ samples regardless of fuel or stove type. Tentative molecular structure assignments are listed when the compound has previously been identified in the chemical biomass-burning literature, supported by the references in the last column. Count-based, normalized peak abundances are designated LOW (<1%), MEDIUM (1-9.99%), HIGH (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 |
|---|---|---|---|---|---|---|
| 111.091 | 111.092 | $C_6H_{10}N_2$ | 3 | MEDIUM | | (Smith et al., 2009) |
| 121.064 | 121.065 | $C_8H_8O$ | 5 | MEDIUM | | |
| 123.091 | 123.092 | $C_7H_{10}N_2$ | 4 | MEDIUM | | |
| 124.075 | 124.076 | $C_7H_9ON$ | 4 | MEDIUM | | |
| 125.107 | 125.107 | $C_7H_{12}N_2$ | 3 | MEDIUM | | (Smith et al., 2009) |
| 133.075 | 133.076 | $C_8H_8N_2$ | 6 | MEDIUM | | (Laskin et al., 2009) |
| 134.071 | 134.071 | $C_7H_7N_3$ | 6 | MEDIUM | | (Laskin et al., 2009) |
| 137.059 | 137.060 | $C_8H_8O_2$ | 5 | HIGH | Anisaldehyde | (Simoneit et al., 1993; Smith et al., 2009) |
| 137.106 | 137.107 | $C_8H_{12}N_2$ | 4 | MEDIUM | | (Smith et al., 2009) |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| 138.090 | 138.091 | $C_8H_{11}ON$ | 4 | LOW |  |  |
| 139.122 | 139.123 | $C_8H_{14}N_2$ | 3 | MEDIUM |  | (Smith et al., 2009) |
| 147.091 | 147.092 | $C_9H_{10}N_2$ | 6 | MEDIUM |  |  |
| 151.074 | 151.075 | $C_9H_{10}O_2$ | 5 | MEDIUM | Vinylguaiacol |  |
| 151.122 | 151.123 | $C_9H_{14}N_2$ | 4 | MEDIUM |  |  |
| 153.138 | 153.139 | $C_9H_{16}N_2$ | 3 | HIGH |  |  |
| 159.091 | 159.092 | $C_{10}H_{10}N_2$ | 7 | MEDIUM |  | (Laskin et al., 2009) |
| 160.075 | 160.076 | $C_{10}H_9ON$ | 7 | MEDIUM |  | (Laskin et al., 2009) |
| 161.059 | 161.060 | $C_{10}H_8O_2$ | 7 | MEDIUM |  |  |
| 161.106 | 161.107 | $C_{10}H_{12}N_2$ | 6 | MEDIUM |  |  |
| 162.102 | 162.103 | $C_9H_{11}N_3$ | 6 | LOW |  |  |
| 163.074 | 163.075 | $C_{10}H_{10}O_2$ | 6 | MEDIUM |  |  |
| 165.138 | 165.139 | $C_{10}H_{16}N_2$ | 4 | MEDIUM |  |  |
| 167.069 | 167.070 | $C_9H_{10}O_3$ | 5 | HIGH | Veratraldehyde | (Simoneit et al., 1993) |
| 167.153 | 167.154 | $C_{10}H_{18}N_2$ | 3 | MEDIUM |  |  |
| 173.106 | 173.107 | $C_{11}H_{12}N_2$ | 7 | MEDIUM |  |  |
| 174.090 | 174.091 | $C_{11}H_{11}ON$ | 7 | MEDIUM |  |  |
| 175.074 | 175.075 | $C_{11}H_{10}O_2$ | 7 | MEDIUM |  |  |
| 175.122 | 175.123 | $C_{11}H_{14}N_2$ | 6 | MEDIUM |  |  |
| 177.053 | 177.055 | $C_{10}H_8O_3$ | 7 | MEDIUM |  |  |
| 177.090 | 177.091 | $C_{11}H_{12}O_2$ | 6 | MEDIUM |  |  |
| 177.101 | 177.102 | $C_{10}H_{12}ON_2$ | 6 | LOW |  |  |
| 177.137 | 177.139 | $C_{11}H_{16}N_2$ | 5 | LOW |  | (Laskin et al., 2009) |
| 179.069 | 179.070 | $C_{10}H_{10}O_3$ | 6 | MEDIUM | Coniferaldehyde |  |
| 179.153 | 179.154 | $C_{11}H_{18}N_2$ | 4 | MEDIUM |  |  |
| 181.169 | 181.170 | $C_{11}H_{20}N_2$ | 3 | HIGH |  |  |
| 183.090 | 183.092 | $C_{12}H_{10}N_2$ | 9 | HIGH |  |  |
| 183.184 | 183.186 | $C_{11}H_{22}N_2$ | 2 | MEDIUM |  |  |
| 186.090 | 186.091 | $C_{12}H_{11}ON$ | 8 | MEDIUM |  | (Laskin et al., 2009) |
| 187.122 | 187.123 | $C_{12}H_{14}N_2$ | 7 | MEDIUM |  |  |
| 188.106 | 188.107 | $C_{12}H_{13}ON$ | 7 | MEDIUM |  |  |
| 189.101 | 189.102 | $C_{11}H_{12}ON_2$ | 7 | MEDIUM |  | (Laskin et al., 2009) |
| 189.137 | 189.139 | $C_{12}H_{16}N_2$ | 6 | MEDIUM |  |  |
| 191.069 | 191.070 | $C_{11}H_{10}O_3$ | 7 | MEDIUM |  |  |
| 191.117 | 191.118 | $C_{11}H_{14}ON_2$ | 6 | LOW |  |  |
| 191.153 | 191.154 | $C_{12}H_{18}N_2$ | 5 | LOW |  |  |
| 193.085 | 193.086 | $C_{11}H_{12}O_3$ | 6 | MEDIUM |  |  |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| 193.169 | 193.170 | $C_{12}H_{20}N_2$ | 4 | MEDIUM |  |  |
| 197.106 | 197.107 | $C_{13}H_{12}N_2$ | 9 | MEDIUM |  |  |
| 199.122 | 199.123 | $C_{13}H_{14}N_2$ | 8 | LOW |  |  |
| 200.106 | 200.107 | $C_{13}H_{13}ON$ | 8 | MEDIUM |  |  |
| 201.137 | 201.139 | $C_{13}H_{16}N_2$ | 7 | MEDIUM |  |  |
| 202.085 | 202.086 | $C_{12}H_{11}O_2N$ | 8 | MEDIUM |  | (Laskin et al., 2009) |
| 203.117 | 203.118 | $C_{12}H_{14}ON_2$ | 7 | MEDIUM |  |  |
| 203.153 | 203.154 | $C_{13}H_{18}N_2$ | 6 | MEDIUM |  |  |
| 205.085 | 205.086 | $C_{12}H_{12}O_3$ | 7 | MEDIUM |  |  |
| 207.184 | 207.186 | $C_{13}H_{22}N_2$ | 4 | MEDIUM |  |  |
| 209.079 | 209.081 | $C_{11}H_{12}O_4$ | 6 | MEDIUM |  |  |
| 209.200 | 209.201 | $C_{13}H_{24}N_2$ | 3 | MEDIUM |  |  |
| 211.095 | 211.096 | $C_{11}H_{14}O_4$ | 5 | HIGH | Syringylethanone/ trimethoxyphenylethanone | (Simoneit et al., 1993) |
| 211.121 | 211.123 | $C_{14}H_{14}N_2$ | 9 | MEDIUM |  |  |
| 213.137 | 213.139 | $C_{14}H_{16}N_2$ | 8 | MEDIUM |  | (Laskin et al., 2009) |
| 214.121 | 214.123 | $C_{14}H_{15}ON$ | 8 | MEDIUM |  |  |
| 215.153 | 215.154 | $C_{14}H_{18}N_2$ | 7 | MEDIUM |  |  |
| 216.100 | 216.102 | $C_{13}H_{13}O_2N$ | 8 | MEDIUM |  |  |
| 217.132 | 217.134 | $C_{13}H_{16}ON_2$ | 7 | MEDIUM |  |  |
| 217.168 | 217.170 | $C_{14}H_{20}N_2$ | 6 | MEDIUM |  |  |
| 219.100 | 219.102 | $C_{13}H_{14}O_3$ | 7 | MEDIUM |  |  |
| 227.153 | 227.154 | $C_{15}H_{18}N_2$ | 8 | MEDIUM |  |  |
| 229.132 | 229.134 | $C_{14}H_{16}ON_2$ | 8 | MEDIUM |  |  |
| 229.168 | 229.170 | $C_{15}H_{20}N_2$ | 7 | MEDIUM |  |  |
| 230.116 | 230.118 | $C_{14}H_{15}O_2N$ | 8 | MEDIUM |  |  |
| 231.147 | 231.149 | $C_{14}H_{18}ON_2$ | 7 | LOW |  |  |
| 232.095 | 232.097 | $C_{13}H_{13}O_3N$ | 8 | MEDIUM |  |  |
| 235.095 | 235.096 | $C_{13}H_{14}O_4$ | 7 | MEDIUM |  |  |
| 241.168 | 241.170 | $C_{16}H_{20}N_2$ | 8 | MEDIUM |  |  |
| 243.147 | 243.149 | $C_{15}H_{18}ON_2$ | 8 | MEDIUM |  |  |
| 243.184 | 243.186 | $C_{16}H_{22}N_2$ | 7 | LOW |  |  |
| 244.131 | 244.133 | $C_{15}H_{17}O_2N$ | 8 | MEDIUM |  |  |
| 246.111 | 246.112 | $C_{14}H_{15}O_3N$ | 8 | MEDIUM |  |  |
| 249.110 | 249.112 | $C_{14}H_{16}O_4$ | 7 | MEDIUM |  |  |

**Table 2: List of compounds found exclusively in the emissions from dung cookfires, regardless of stove type. The labels for the peak abundances are the same as in Table 1. All species unless otherwise noted were detected as protonated ions.**

| Observed *m/z* | Calculated *m/z* | Chemical formula of neutral species | DBE | Relative average abundance |
|---|---|---|---|---|
| 124.099 | 124.099 | $C_7H_{12}N_2^*$ | 3 | MEDIUM |
| 135.080 | 135.080 | $C_9H_{10}O$ | 5 | LOW |
| 135.092 | 135.092 | $C_8H_{10}N_2$ | 5 | MEDIUM |
| 136.076 | 136.076 | $C_8H_9ON$ | 5 | LOW |
| 137.071 | 137.071 | $C_7H_8ON_2$ | 5 | MEDIUM |
| 138.115 | 138.115 | $C_8H_{14}N_2^*$ | 3 | LOW |
| 141.138 | 141.139 | $C_8H_{16}N_2$ | 2 | LOW |
| 145.076 | 145.076 | $C_9H_8N_2$ | 7 | MEDIUM |
| 146.060 | 146.060 | $C_9H_7ON$ | 7 | MEDIUM |
| 146.084 | 146.084 | $C_9H_{10}N_2^*$ | 6 | LOW |
| 149.071 | 149.071 | $C_8H_8ON_2$ | 6 | LOW |
| 149.107 | 149.107 | $C_9H_{12}N_2$ | 5 | LOW |
| 151.086 | 151.087 | $C_8H_{10}ON_2$ | 5 | LOW |
| 152.107 | 152.107 | $C_9H_{13}ON$ | 4 | LOW |
| 152.130 | 152.131 | $C_9H_{16}N_2^*$ | 3 | LOW |
| 155.154 | 155.154 | $C_9H_{18}N_2$ | 2 | LOW |
| 160.099 | 160.099 | $C_{10}H_{12}N_2^*$ | 6 | LOW |
| 162.091 | 162.091 | $C_{10}H_{11}ON$ | 6 | LOW |
| 163.086 | 163.087 | $C_9H_{10}ON_2$ | 6 | MEDIUM |
| 163.123 | 163.123 | $C_{10}H_{14}N_2$ | 5 | MEDIUM |
| 164.107 | 164.107 | $C_{10}H_{13}ON$ | 5 | LOW |
| 169.076 | 169.076 | $C_{11}H_8N_2$ | 9 | HIGH |
| 169.170 | 169.170 | $C_{10}H_{20}N_2$ | 2 | MEDIUM |
| 171.091 | 171.092 | $C_{11}H_{10}N_2$ | 8 | MEDIUM |
| 172.075 | 172.076 | $C_{11}H_9ON$ | 8 | MEDIUM |
| 175.086 | 175.087 | $C_{10}H_{10}ON_2$ | 7 | MEDIUM |
| 176.070 | 176.071 | $C_{10}H_9O_2N$ | 7 | LOW |
| 176.107 | 176.107 | $C_{11}H_{13}ON$ | 6 | LOW |
| 176.118 | 176.118 | $C_{10}H_{13}N_3$ | 6 | LOW |
| 178.086 | 178.086 | $C_{10}H_{11}O_2N$ | 6 | LOW |
| 184.075 | 184.076 | $C_{12}H_9ON$ | 9 | MEDIUM |

| | | | | |
|---|---|---|---|---|
| 185.107 | 185.107 | $C_{12}H_{12}N_2$ | 8 | MEDIUM |
| 187.086 | 187.087 | $C_{11}H_{10}ON_2$ | 8 | MEDIUM |
| 188.118 | 188.118 | $C_{11}H_{13}N_3$ | 7 | LOW |
| 189.091 | 189.091 | $C_{12}H_{12}O_2$ | 7 | LOW |
| 190.086 | 190.086 | $C_{11}H_{11}O_2N$ | 7 | MEDIUM |
| 190.133 | 190.134 | $C_{11}H_{15}N_3$ | 6 | MEDIUM |
| 191.081 | 191.082 | $C_{10}H_{10}O_2N_2$ | 7 | LOW |
| 192.102 | 192.102 | $C_{11}H_{13}O_2N$ | 6 | LOW |
| 193.133 | 193.134 | $C_{11}H_{16}ON_2$ | 5 | LOW |
| 195.091 | 195.092 | $C_{13}H_{10}N_2$ | 10 | MEDIUM |
| 195.185 | 195.186 | $C_{12}H_{22}N_2$ | 3 | HIGH |
| 197.201 | 197.201 | $C_{12}H_{24}N_2$ | 2 | MEDIUM |
| 198.091 | 198.091 | $C_{13}H_{11}ON$ | 9 | MEDIUM |
| 198.102 | 198.103 | $C_{12}H_{11}N_3$ | 9 | LOW |
| 199.086 | 199.087 | $C_{12}H_{10}ON_2$ | 9 | MEDIUM |
| 200.118 | 200.118 | $C_{12}H_{13}N_3$ | 8 | LOW |
| 201.102 | 201.102 | $C_{12}H_{12}ON_2$ | 8 | MEDIUM |
| 202.122 | 202.123 | $C_{13}H_{15}ON$ | 7 | LOW |
| 202.133 | 202.134 | $C_{12}H_{15}N_3$ | 7 | LOW |
| 204.101 | 204.102 | $C_{12}H_{13}O_2N$ | 7 | LOW |
| 204.149 | 204.150 | $C_{12}H_{17}N_3$ | 6 | MEDIUM |
| 205.097 | 205.097 | $C_{11}H_{12}O_2N_2$ | 7 | LOW |
| 205.133 | 205.134 | $C_{12}H_{16}ON_2$ | 6 | MEDIUM |
| 205.169 | 205.170 | $C_{13}H_{20}N_2$ | 5 | MEDIUM |
| 206.117 | 206.118 | $C_{12}H_{15}O_2N$ | 6 | LOW |
| 207.112 | 207.113 | $C_{11}H_{14}O_2N_2$ | 6 | LOW |
| 207.149 | 207.149 | $C_{12}H_{18}ON_2$ | 5 | LOW |
| 209.107 | 209.107 | $C_{14}H_{12}N_2$ | 10 | MEDIUM |
| 209.128 | 209.128 | $C_{11}H_{16}O_2N_2$ | 5 | LOW |
| 211.144 | 211.144 | $C_{11}H_{18}O_2N_2$ | 4 | MEDIUM |
| 212.106 | 212.107 | $C_{14}H_{13}ON$ | 9 | MEDIUM |
| 212.118 | 212.118 | $C_{13}H_{13}N_3$ | 9 | LOW |
| 214.086 | 214.086 | $C_{13}H_{11}O_2N$ | 9 | MEDIUM |
| 215.117 | 215.118 | $C_{13}H_{14}ON_2$ | 8 | MEDIUM |
| 216.149 | 216.150 | $C_{13}H_{17}N_3$ | 7 | LOW |
| 217.085 | 217.086 | $C_{13}H_{12}O_3$ | 8 | LOW |
| 217.097 | 217.097 | $C_{12}H_{12}O_2N_2$ | 8 | MEDIUM |

| | | | | |
|---|---|---|---|---|
| 218.103 | 218.104 | $C_{10}H_{11}ON_5$ | 8 | LOW |
| 218.117 | 218.118 | $C_{13}H_{15}O_2N$ | 7 | LOW |
| 218.165 | 218.165 | $C_{13}H_{19}N_3$ | 6 | LOW |
| 219.112 | 219.113 | $C_{12}H_{14}O_2N_2$ | 7 | MEDIUM |
| 219.149 | 219.149 | $C_{13}H_{18}ON_2$ | 6 | LOW |
| 219.185 | 219.186 | $C_{14}H_{22}N_2$ | 5 | MEDIUM |
| 221.080 | 221.081 | $C_{12}H_{12}O_4$ | 7 | LOW |
| 221.128 | 221.128 | $C_{12}H_{16}O_2N_2$ | 6 | MEDIUM |
| 221.201 | 221.201 | $C_{14}H_{24}N_2$ | 4 | MEDIUM |
| 223.122 | 223.123 | $C_{15}H_{14}N_2$ | 10 | MEDIUM |
| 223.216 | 223.217 | $C_{14}H_{26}N_2$ | 3 | MEDIUM |
| 224.107 | 224.107 | $C_{15}H_{13}ON$ | 10 | LOW |
| 225.102 | 225.102 | $C_{14}H_{12}ON_2$ | 10 | MEDIUM |
| 225.138 | 225.139 | $C_{15}H_{16}N_2$ | 9 | MEDIUM |
| 226.122 | 226.123 | $C_{15}H_{15}ON$ | 9 | MEDIUM |
| 227.117 | 227.118 | $C_{14}H_{14}ON_2$ | 9 | MEDIUM |
| 228.101 | 228.102 | $C_{14}H_{13}O_2N$ | 9 | MEDIUM |
| 228.138 | 228.138 | $C_{15}H_{17}ON$ | 8 | MEDIUM |
| 230.164 | 230.165 | $C_{14}H_{19}N_3$ | 7 | LOW |
| 231.112 | 231.113 | $C_{13}H_{14}O_2N_2$ | 8 | MEDIUM |
| 232.133 | 232.133 | $C_{14}H_{17}O_2N$ | 7 | LOW |
| 233.128 | 233.128 | $C_{13}H_{16}O_2N_2$ | 7 | LOW |
| 233.164 | 233.165 | $C_{14}H_{20}ON_2$ | 6 | LOW |
| 233.201 | 233.201 | $C_{15}H_{24}N_2$ | 5 | MEDIUM |
| 235.216 | 235.217 | $C_{15}H_{26}N_2$ | 4 | MEDIUM |
| 237.138 | 237.139 | $C_{16}H_{16}N_2$ | 10 | MEDIUM |
| 239.117 | 239.118 | $C_{15}H_{14}ON_2$ | 10 | MEDIUM |
| 239.153 | 239.154 | $C_{16}H_{18}N_2$ | 9 | MEDIUM |
| 241.133 | 241.134 | $C_{15}H_{16}ON_2$ | 9 | MEDIUM |
| 242.117 | 242.118 | $C_{15}H_{15}O_2N$ | 9 | LOW |
| 243.112 | 243.113 | $C_{14}H_{14}O_2N_2$ | 9 | LOW |
| 244.096 | 244.097 | $C_{14}H_{13}O_3N$ | 9 | LOW |
| 245.128 | 245.128 | $C_{14}H_{16}O_2N_2$ | 8 | MEDIUM |
| 245.164 | 245.165 | $C_{15}H_{20}ON_2$ | 7 | MEDIUM |
| 247.143 | 247.144 | $C_{14}H_{18}O_2N_2$ | 7 | LOW |
| 247.216 | 247.217 | $C_{16}H_{26}N_2$ | 5 | MEDIUM |
| 249.232 | 249.233 | $C_{16}H_{28}N_2$ | 4 | MEDIUM |

| | | | | |
|---|---|---|---|---|
| 251.153 | 251.154 | $C_{17}H_{18}N_2$ | 10 | LOW |
| 253.133 | 253.134 | $C_{16}H_{16}ON_2$ | 10 | LOW |
| 255.112 | 255.113 | $C_{15}H_{14}O_2N_2$ | 10 | LOW |
| 255.148 | 255.149 | $C_{16}H_{18}ON_2$ | 9 | LOW |
| 255.185 | 255.186 | $C_{17}H_{22}N_2$ | 8 | LOW |
| 258.112 | 258.112 | $C_{15}H_{15}O_3N$ | 9 | LOW |
| 259.143 | 259.144 | $C_{15}H_{18}O_2N_2$ | 8 | LOW |
| 259.180 | 259.180 | $C_{16}H_{22}ON_2$ | 7 | LOW |
| 269.127 | 269.128 | $C_{16}H_{16}O_2N_2$ | 10 | LOW |
| 283.143 | 283.144 | $C_{17}H_{18}O_2N_2$ | 10 | LOW |

*species detected as an ion-radical

**Table 3: The list of rentetion times, absorption peak maxima, and chemical formulas of the BrC chromophores detected in the brushwood smoke sample. Tentative assignments are given based on compounds previously identified in the lignin pyrolysis literature.**

| LC retention time (min) | $\lambda_{max}$ (nm) | Nominal molecular weight (amu) | Chemical formula(s) | Tentative assignment |
|---|---|---|---|---|
| 6.26 | 383 | 192 | $C_9H_8N_2O_3$ | |
| 7.15 | 392 | 141 | $C_7H_8O_3$ | |
| 10.55 | 305 | 183 | $C_9H_{10}O_4$ | Homovanillic acid/syringealdehyde |
| 13.29 | 265 | 155 | $C_8H_{10}O_3$ | Syringol |
| 14.44 | 305 | 169<br>183 | $C_8H_8O_4$<br>$C_9H_{10}O_4$ | Vanillic acid<br>Homovanillic acid/syringealdehyde |
| 15.57 | 299 | 181<br>167 | $C_{10}H_{12}O_3$<br>$C_9H_{10}O_3$ | Ethyl-3-methoxybenzoate<br>Veratraldehyde |
| 16.95 | 313, 334 | 186 | $C_{11}H_7NO_2$ | |
| 17.25 | 331 | 165<br>162 | $C_9H_8O_3$<br>$C_9H_7NO_2$ | |
| 18.13 | 341 | 209 | $C_{11}H_{12}O_4$ | |
| 18.32 | 229, 337 | 179 | $C_{10}H_{10}O_3$ | |
| 19.78 | 305, 330 | 194 | $C_{10}H_{10}O_4$ | Ferulic acid |
| 24.11 | 290, 330 | 259 | $C_{15}H_{14}O_4$ | |
| 28.07 | 334 | 184 | $C_8H_9NO_4$ | |
| 29.24 | 330 | 198<br>230 | $C_{13}H_{10}O_2$<br>$C_{13}H_{10}O_4$ | |
| 33.81 | 340 | 227 | $C_{14}H_{10}O_3$ | |

**Table 4: The list of retention times, absorption peak maxima, and chemical formulas of the BrC chromophores detected in the the dung smoke sample. Tentative assignments are given based on compounds previously identified in the lignin pyrolysis literature.**

| LC retention time (min) | $\lambda_{max}$ (nm) | Nominal molecular weight (amu) | Chemical formula(s) | Tentative assignment |
|---|---|---|---|---|
| 8.50 | 295 | 167 | $C_8H_9NO_3$ | |
| 9.09 | 282,300 | 166<br>168 | $C_9H_{10}O_3$<br>$C_8H_8O_4$ | |
| 10.59 | 252, 289, 393 | 182 | $C_9H_{10}O_4$ | Homovanillic acid/syringealdehyde |
| 12.22 | 282 | 122 | $C_7H_6O_2$ | Benzoic acid |
| 14.44 | 306 | 168<br>182<br>164 | $C_8H_8O_4$<br>$C_9H_{10}O_4$<br>$C_9H_8O_3$ | Vanillic acid<br>Homovanillic acid/syringealdehyde |
| 15.57 | 300 | 174<br>166 | $C_{10}H_{12}O_3$<br>$C_9H_{10}O_3$ | Ethyl-3-methoxybenzoate<br>Veratraldehyde |
| 16.35 | 286 | 174 | $C_{11}H_{10}O_2$ | |
| 18.28 | 290, 330[a] | 162 | $C_{10}H_{10}O_2$ | |
| 19.5 | 323[a] | 220 | $C_{12}H_{12}O_4$ | |
| 19.72 | 331[a] | 194 | $C_{10}H_{10}O_4$ | Ferulic acid |
| 20.85 | 352[a] | 188 | $C_{12}H_{12}O_2$ | |
| 24.54 | 299, 308 | 178 | $C_{10}H_{10}O_3$ | |
| 25.28 | 290, 320 | 218 | $C_{12}H_{10}O_4$ | |
| 29.17 | 332 | 198<br>230 | $C_{13}H_{10}O_2$<br>$C_{13}H_{10}O_4$ | |
| 29.60 | 358[a] | 213 | $C_{13}H_9O_3$ | |

[a] signifies a shoulder, rather than a clear peak

# 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.

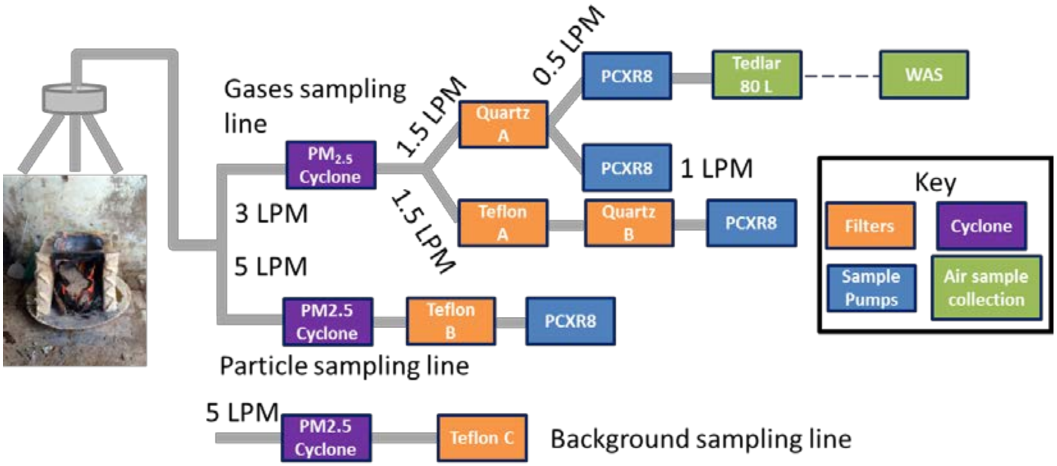
| Sample | Date | Fuel | Stove | Moisture (% wet basis) | Meal |
|---|---|---|---|---|---|
| RE015 | 8/28/15 | brushwood | chulha | 29.5 | rice |
| T2 | 8/18/15 | dung | angithi | 10.8[a] | buffalo fodder |

[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. PM2.5 emission factor calculation

$PM_{2.5}$ emission factors are briefly mentioned when comparing absorbance by particles from different cookfire types (Section 3.6). Here we explain how they were calculated. Figure S3.1 shows the sampling lines used to collect emissions in this study. Emissions flowed through a $PM_{2.5}$ cyclone and subsequent quartz filter to remove particles, so that gases were collected over the entire cooking event in an 80 L Kynar bag (Gases sampling line, Figure S2.1). After pumps were turned off, a whole air sample (WAS) of average gas-phase emissions over the cooking event was collected from the Kynar bag. Stainless steel canisters, (2 L) evacuated and prepped prior to the trip, were used to collect WAS. The background WAS sample was collected as a grab sample in the kitchen before cooking began for the day. One background sample was collected per day, and that measurement was used for all experiments that day. Ideally, background samples should be an integrated sample collected at the same time as the sample. However, we were limited in the number of cans, and the equipment brought to India.

**Figure S2.1. Diagram of sampling lines used in the study.**



A separate filter reserved for gravimetric analysis was used for fine particle emissions measurements (Teflon A). 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 (Teflon B). 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 WAS samples. The WAS samples were taken back to UCI where ther were 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).

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

In equation (2), $C_i$ 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 (Zhang 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.

## S3. Gas and $PM_{2.5}$ collection details

**Figure S3.1. Stoves used in the study, the *angithi* and *chulha*, are pictured. Stove measurements and distances from the stoves to the inlet probes are found in the tables below.**

| *Chulha* measurements | Distance (cm) |
|---|---|
| Inner height | 25 |
| Inner width | 21 |
| Inner depth | 23 |
| Width of walls | 4.6 |
| Top of *chulha* to probe inlets | 58 |

| *Angithi* measurements | Distance (cm) |
|---|---|
| Inner diameter | 44 |
| Outer diameter | 50 |
| Outer height | 20 |
| Height from inside bottom of stove to probe inlets | 83 |
| Top of *angithi* to probe inlets | 64 |

## S4. Species exclusively detected in dung/*chulha* and dung/*angithi* cookfires

**Table S4.1. 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 S4.2: List of reproducible compounds detected exclusively in the emissions from dung/*chulha* cookfires. The labels for peak abundances are the same for Table S4.1. 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 S4.3: List of reproducible compounds detected exclusively in the emissions from dung/*angithi* cookfires. The labels for peak abundances are the same for Table S4.1. 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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