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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Non methane hydrocarbon (NMHC) fingerprints of major urban and agricultural emission sources active in South Asia for use in source apportionment studies" *by* Ashish Kumar et al.

Anonymous Referee #1

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This paper presents NMHC fingerprints of urban and agricultural emission sources in northern India based on whole air sampling. Similar to previous studies, i-pentane was found to be a tracer for petrol vehicular exhaust, propane for LPG emissions, acetylene for biomass burning, and alkenes for diesel exhaust. The authors report significant emissions of propane from paddy stubble fires, and suggest that isoprene can be used to distinguish paddy stubble burning from garbage burning.

This is an interesting research paper from an understudied part of the world with complex emission sources. However several issues need to be addressed before the paper

can be published, especially concerning uncertainty, data variability, and small sample size. The actual concentration data should be shown for both background and source samples, including average values with uncertainties. So far the data are shown as normalized source profiles, so the reader can't see the range of the data, how well the precision (which was determined for 5 ppb) applies to the measured concentrations, or how often the data were close to the detection limit. Many results in the paper need error bars. Another issue is the small sample size (as small as 1 sample for some sources) and how that limits the study and its application to other areas of India or South Asia. Also, since some of the source profile results are known from previous studies, the last sentence of the abstract perhaps overstates the novelty of this work. Additional comments are given below.

1. The title states "South Asia" but the paper is based on limited measurements near Mohali in northern India. What basis is there for extrapolating these results to all of South Asia? Emissions can vary from country to country (Page 5, Line 4) and even within countries. "Indo-Gangetic Plain" is probably a better choice for the title.

2. Page 5 Line 21: The sample size is quite small, with three flaming and three smoldering samples from paddy stubble fires, and five each from garbage burning. While any information is good from understudied sources and source regions, please discuss the limitations of the small sample size. Also show the reader the actual data (concentrations) by including a statistics table with uncertainties.

3. Page 7 Line 1: Does the text here mean that Panels e-g in Figure 1 and Figure S4 are based on just one sample each? This is a major source of uncertainty, since there is no way to quantify the variability in the evaporative source emissions or assign uncertainty. Please discuss this limitation.

4. Page 10 Line 11: Precision usually varies with concentration, but here the stated precisions are for 5 ppb. How does this change as the measurements go below 5 ppb or approach the detection limit? The precisions listed in Table 2 are very good (0.1-

0.4%), but for example 0.2% on an isoprene value of 200 ppt would be measuring to 0.4 ppt, which seems unrealistic. The overall uncertainty (Page 10, Line 23) will likewise be underestimated if the precision degrades at concentrations less than 5 ppb. Please show the reader the range of concentrations that was measured for each VOC, and discuss how well the precision applies across the range.

5. Page 10 Line 19: How often did the measurements go below detection? Please show a statistics table for the background measurements including their uncertainty, and also state the number of background samples that were collected for each source. On Page 11, Line 6 provide more detail about how the background data were used to correct the fire mixing ratios. How did uncertainty in the background measurements impact the normalized source profile concentrations?

6. Page 11 Line 5: From Table 1, benzene is the most abundant normalized compound in the garbage burning. What was its peak concentration? This is relevant for health considerations. Same question on Page 14 Line 5 for traffic.

7. Page 11 Line 9: The term "observed mass concentrations" is used here, but the text above describes an average excess concentration above background. Please clarify what is being discussed here and in the following text. By "acetylene was negligible in the smoldering fires", does this mean that the excess above background was <1%? What is the uncertainty in this result and how does it compare to previous work from smoldering fires?

8. Page 11 Line 11: How did the background isoprene concentration compare to the paddy fire concentration? Please show the data.

9. Page 13 Line 9: The evaporative LPG emissions were n-butane > propane > i-butane (Page 12 Line 10), but the LPG exhaust is n-butane > i-butane > propane. Why would the composition change from evaporative emissions to exhaust, to yield relatively less propane? How large are the error bars?

10. Page 14 Line 22: The three traffic samples were collected in March 2017 (Page 6 Line 9). This is very limited sampling at one time of year (and we don't know what time of day, or how long the sample duration was). While any information is good from undersampled regions, it seems a stretch to say that this represents the ambient traffic emissions mixture. Please discuss this limitation.

11. Page 15 Line 11: If diesel consumption is twice as much as petrol, please discuss in more detail why the traffic signal is dominated by the gasoline tracer i-pentane rather than the diesel tracer ethene. If diesel is more heavily used for freight transport across the country, how well can the three urban traffic samples represent other areas of the country, let alone South Asia? Please make sure to discuss the limitations of this study.

12. Page 15 Line 17: The normalized diesel exhaust graph (Figure 2d) shows very little C5-C8 alkane composition, with just some C6-C8 n-alkanes. Why is C5 included, especially if diesel emissions had <0.2% i-pentane? It would be better not to link the diesel exhaust and evaporative emissions together in this sentence, since their composition is quite different. In Figure 2, why is the diesel exhaust profile much simpler than the diesel evaporative signal? How does this compare to the literature, and what are the uncertainties?

13. Page 17 Line 6: Results are presented here to 2 significant figures without error bars. Please include uncertainty estimates and show the concentrations that were used to create the OFP results. Were average concentrations used? Discuss the limitations of sample variability and small sample size on the results.

14. Page 18: Similar comment as above. This paragraph has detailed OH reactivity and OFP results, without error bars, discussion of uncertainty, or comparison to the literature. For example, on Line 22 I was surprised to see styrene as the largest contributor to OH reactivity from traffic, and strong contributions from isoprene and 1-hexene. What were the measured styrene and isoprene concentrations in the three traffic samples? How do these results compare to the literature?

15. Page 19 Line 10: Same comment, all results need error bars. Here the first three results are probably not statistically different. In discussing BTEX, the fraction may be less important than the concentration of each VOC, especially benzene which is the most toxic. On Line 14, instead of "could severely impact", state how the concentrations compared to exposure limits. Same comment on P21 L22 of the conclusions.

16. Page 20 Line 4: Please use error bars and appropriate significant figures here and in Table 3. Show graphs of some ratios so we can see the variability, especially for small sample sizes. On Line 5, the T/B ratio of 3.41 is more like petrol evaporation rather than vehicular emissions, which has a lower ratio of about 2 in most of the studies cited on Line 6 (Barletta et al., 2005; Russo et al., 2010; Zhang et al. 2013).

17. Page 20 Line 17: Similar to earlier comments, please show the absolute amounts of i-pentane and n-pentane in the source samples, to see how large or small the concentrations were and how variable the ratios were. From Figure 2 there seems to be very little n-pentane in the LPG exhaust, which could lead to a high and uncertain pentane ratio. All ratios should have error bars.

18. Page 21 Line 3: Please clearly state which results were "very different" from the literature based on a statistical analysis. The uncertainties in your study are likely large but haven't been discussed or quantified. On Line 4 I disagree that these profiles can be used for accurate and reliable emissions estimates, since the sample size is so small. The study is a good beginning, but the results need realistic uncertainties.

19. Figure S4: Even though propene is more reactive than ethene, it's surprising to see so little ethene contribution to OH reactivity in smoldering paddy burning since its EF is typically higher than propene for crop residue fires. In Figure 1 I was surprised to see more propene than ethene in the normalized profiles for smoldering paddy burning, different from results for crop residue (rice straw) in Akagi et al. (ACP, 2011) and agricultural residue in Andreae (ACP, 2019). Please show the concentrations used in these calculations and expand the discussion.

20. Page 21 Lines 8-14: These sentences are very similar to the abstract. Page 22 Lines 9-12 and Line 13-15 also repeats from earlier text. The conclusions should provide fresh insights.

Please check the entire manuscript for grammar and typos. For example: Grammar (P4 L23, P6 L4-6, P7 L8-12, P8 L10-11, and so forth in the paper and supplement). Capitalization (P8, L1-8: synthetic, nitrogen, ozone; and so forth).

Page 5 Line 16: Define BTEX.

Page 5 Line 19: What was the sample duration for the whole air samples?

Page 6 Line 18: So 23 vehicles, with one sample per vehicle?

Page 9 Line 21: Please define the sensitivity factors and explain the results in Table S3. Avoid stating "with no drastic changes observed" and be specific about what the results mean.

Page 10 Line 1: What does respective refer to here?

Page 10 Line 7: pAs was first used on Page 9 Line 21; define there.

Page 11 Line 14: Reduced compared to what? Flaming?

Page 11 Line 20: Less styrene compared to what?

Page 12 Line 1: Why at night? I thought the daytime values subtracted off background?

Page 13 Line 18: Hong Kong also has an LPG fuel composition of n-butane > propane > i-butane, with about a 2:1 ratio of n-butane:i-butane, similar to your evaporative results (Tsai et al., ACP, 2006).

Page 14 Line 1: Guo et al. studied Hong Kong, not Taiwan.

Page 14 Line 19: i-Pentane is already known to be a gasoline tracer, but the wording here makes it seem like a novel result.

Page 15: This paragraph is more than 2 pages long.

Page 15 Line 9: Propane isn't listed on Line 6-7 as one of the major NMHC species. How much propane was measured from the traffic?

Page 16 Line 6: Define BSV and BSVI.

Page 17 Lines 6-12: These results are better presented as a Table. Similar comment on Page 18.

Figures 1, 2, S4, S5: State what the shading refers to (aromatic, alkene/alkyne, alkane). In Figure S4 the shading is shifted by one in the alkenes – please correct.

Figure S1: "Smouldering" here but "smoldering" in the main text.

Figure S2: The graphs are too small to clearly see.

Figure S3: There is no Figure S3, just S2 and S4 – please re-number.

Table 1: Please add the descriptions and sample sizes for the three evaporative fuel sources.

Table 2: Please put the compounds in a more logical order so they're easier to find.

Table 2: The abstract states that 49 NMHCs were measured, but Table 2 only lists 48. Was styrene double-counted as both aromatic and alkene? Same comment in the introduction and conclusions.

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