

The paper “*Biomass burning sources control ambient particulate matter but traffic and industrial sources control VOCs and secondary pollutant formation during extreme pollution events in Delhi*” discusses the sources responsible for air pollution problems in Delhi. For this, they made stationary ambient gas-phase measurements at a prominent location in urban New Delhi and performed source apportionment analysis on the collected data. The chemical profiles of the factors were compared with previous measurements and tracers to identify sources. The work is quite timely since New Delhi is one of the most polluted cities in the world, and regulatory policies are currently being restricted by our limited understanding of the sources in the region.

We thank the referee for recognizing and highlighting the importance of this research work.

Yet I have significant concerns, which I think should be resolved prior to proceeding with publication. Some of my biggest concerns are with the conclusions drawn and stated quite imposingly in the conclusion section. Hence, I'll discuss those first before moving to the next major ones.

Line 606-607: fresh paddy burning is shown to be a negligible source of VOCs but the largest sources of PM<sub>2.5</sub> and PM<sub>10</sub>. This is highly confusing to me. PM<sub>2.5</sub> would be formed from the secondary oxidation of a lot of gas-phase organic molecules emitted from paddy burning. As such it should be emitting precursors of SOA. Or are the authors suggesting that paddy-burning directly emits particulate matter into the atmosphere but no VOCs?

Thank you for seeking this important clarification. Yes, we are suggesting that paddy straw burning is a source of primary aerosol. It is important to note that paddy straw contains a rigid, microscopic structures made of silica known as phytolite. Upon burning, this structure is converted into a glassy ash. The mass of this type of aerosol emitted during the combustion process appears to be quite high when compared to the mass of VOCs emitted in the same combustion process. The high ash formation is a well known fact in engineering circles. Co-combustion of more than 10% of paddy straw alongside with other fuels in power generation units causes severe equipment fouling, due to the potassium (K) rich glassy ash formed (Lui et al. 2022 <https://doi.org/10.1016/j.energy.2022.123950>, Madhiyanon et al. 2020 <https://doi.org/10.1016/j.joei.2020.04.001>). We have inserted a scanning electron microscopy image of ash collected from the electrostatic precipitator of an industrial boiler fired with rice husk and straw to our supplement to illustrating the coarse mode nature of the ash generated during the combustion of phytolite containing biomass.

The reality appears to be that much of the aerosol emitted during paddy residue burning is 1) primary and 2) relatively coarse. The root cause of the discrepancy between the contribution to the VOC mass and the contribution to the PM mass appears to be that the glassy ash particles are bigger and have a higher density than organic aerosol and contribute more to the total aerosol mass, that secondary aerosol particles with smaller size and lower density. Just like dust, this ash cannot be detected by AMS and since the chemical composition is >96% SiO<sub>2</sub> with minor amounts of K, any routine CMB analysis would likely attribute this type of aerosol to the natural dust fraction. This explains why earlier studies may have failed to recognize the importance of ash aerosol. We have added a figure (Figure S10) and revised the text to reflect this more clearly as follows:

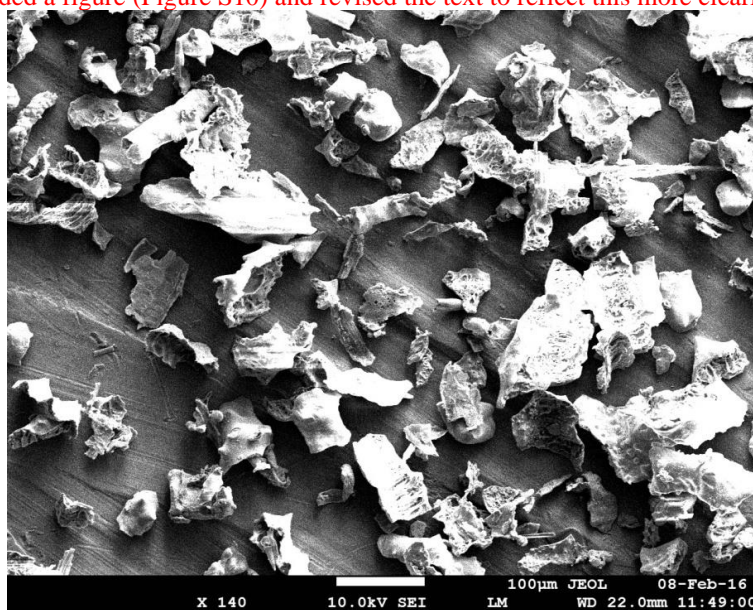


Figure S10 SEM image of rice ash from the electrostatic precipitator of an industrial boiler fired with rice husk and straw, illustrating the coarse mode nature of the ash generated during the combustion of phytolith containing

biomass.

“While fresh paddy burning was a negligible source of VOCs (6 %), it was the largest source of PM<sub>2.5</sub> & PM<sub>10</sub> (23 % & 25 %) in the Delhi NCR regions during our study period, likely because combustion of phytolite containing rice straw triggers the formation of coarse mode ash (Figure S10) that contributes significantly to the PM burden. PM<sub>2.5</sub> & PM<sub>10</sub> are the two main criteria air pollutants regulated under the national ambient air quality standard that are thought to be the leading cause of the air pollution emergency in November in Delhi annually (Khan et. al., 2023).”

It is, however, important to note that we do not claim that paddy burning is not a VOC source. In Section 3.2., we clearly state that it is the largest source of a relatively long list of VOCs.

The main point that we are making is that in terms of its relative contribution to the overall pollution levels of certain pollutants when compared to other sectors such as e.g. road transport, this activity is far more important as a PM<sub>2.5</sub> and PM<sub>10</sub> source than it is as a VOC source/SOA precursor source. We have shifted the supplementary figure to the main text and revised the text to make this clearer. The revised text to clarify this aspect reads as follows:

“Figure 6 shows that this factor explained the largest percentage share of O-heteroarene compounds such as furfural ( $C_5H_4O_2$ ), methyl furfural ( $C_6H_6O_2$ ), hydroxy methyl furfural ( $C_6H_6O_3$ ), furanone ( $C_4H_4O_2$ ), hydroxymethyl furanone ( $C_5H_6O_3$ ), furfuryl alcohol ( $C_5H_6O_2$ ), furan ( $C_4H_4O$ ), methyl furans ( $C_5H_6O$ ), C2-substituted furans ( $C_6H_8O$ ), and C3-substituted furans ( $C_7H_{10}O$ ), which are produced by the pyrolysis of cellulose and hemicellulose, and have previously been detected in biomass burning samples (Coggon et al., 2019; Hatch et al., 2015; 2017; Koss et al., 2018; Stockwell et al., 2015). Figure 6 also shows that this factor explains the largest share of the most abundant oxidation products that result from the nitrate radical-initiated oxidation of toluene as well as from OH-initiated oxidation of aromatic compounds under high  $NO_x$  conditions, namely nitrotoluene ( $C_7H_7NO_2$ ) and nitrocresols ( $C_7H_7NO_3$ ) (Ramasamy et al., 2019), which indicates a certain degree of aging of the plumes. These nitroaromatic compounds are significant contributors to SOA and BrC, (Palm et al., 2020, Harrison et al., 2005). It also explains several other nitrogen containing VOCs such as nitroethane ( $C_2H_5NO_2$ ), the biomass burning tracer acetonitrile ( $CH_3CN$ ) and pentanenitrile ( $C_5H_9N$ ). The presence of pentanenitrile isomers in biomass burning smoke has previously been confirmed using gas chromatography-based studies (Hatch et al., 2015, Hatch et al., 2017). In addition the factor explains the largest percentage share of acrolein ( $C_3H_4O$ ), hydroxyacetone ( $C_3H_6O_2$ ), cyclopentadienone ( $C_5H_4O$ ), cyclopentanone ( $C_5H_8O$ ), diketone ( $C_4H_6O_2$ ), pentanedione ( $C_5H_8O_2$ ), hydroxybenzaldehyde ( $C_7H_6O_2$ ), guaiacol ( $C_7H_8O_2$ ), and the levoglucosan fragment ( $C_6H_8O_4$ ), many of these compounds are known to form during lignin pyrolysis (Hatch et al., 2015, Koss et al., 2018; Nowakowska et al., 2018), while dimethylbutenedial ( $C_6H_8O_2$ ), trimethylbutenedial ( $C_7H_{10}O_2$ ) are ring opening oxidation products of aromatic compounds (Zaytsev et al., 2019).”

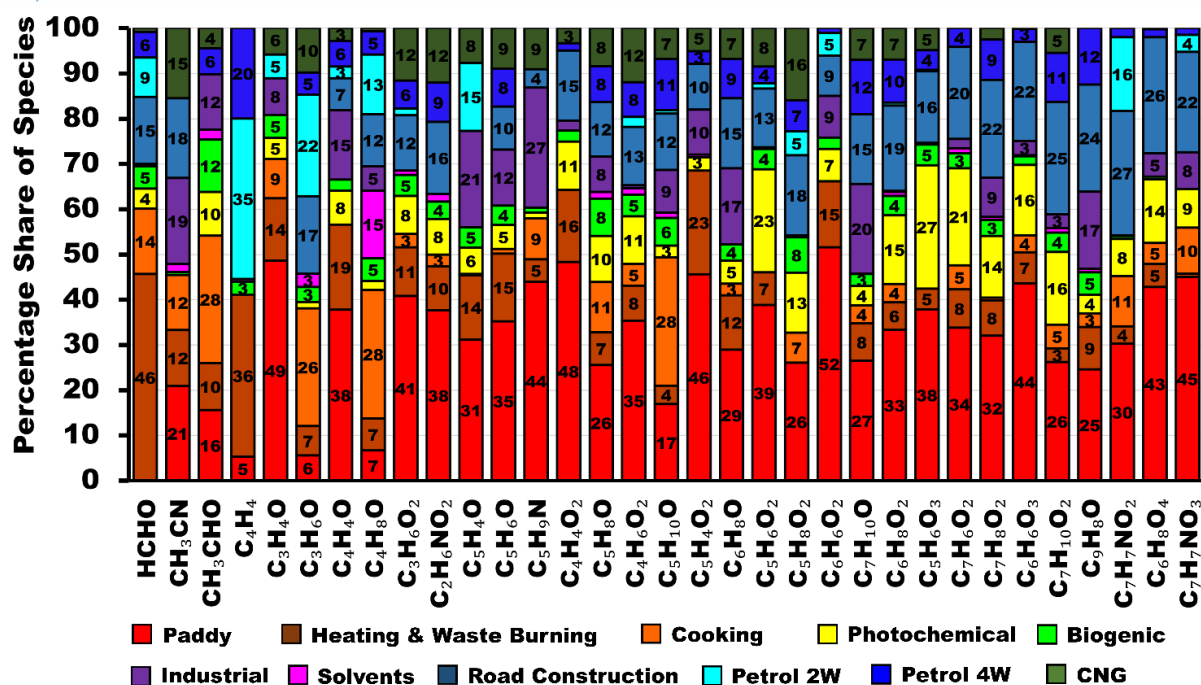


Figure 6: VOC species to which different forms of biomass burning contribute the highest percentage share of the atmospheric burden in Delhi

Is it possible that the PTR-TOF did not measure or fragment a lot of precursor species emitted from paddy burning?

The proton transfer reaction technology is a soft ionization technique and the operating conditions of 120 Td during the deployment further facilitate negligible fragmentation. In addition, the instrument deployed in this work was equipped with extended volatility range technology which has been missing from previous PTR-TOF studies conducted in Delhi. This has been explained in detail in the companion paper (Mishra et al., 2024) and such a system enabled us to detect and measure an unprecedented long list of IVOCs emitted from other sources (industries and asphalt paving), hitherto undetected in ambient gas phase observations without fragmentation. The PMF VOC source signature further matched observational data obtained via source samples collected directly on burning paddy fields. Hence, there is no evidence of loss of VOCs. It is also important to note that we could measure a lot of SOA precursor species and some of their first-generation oxidation products e.g. nitrotoluene ( $C_7H_7NO_2$ ), nitrocresols and ring opening oxidation products of aromatic compounds such as dimethylbutenedial ( $C_6H_8O_2$ ), trimethylbutenedial ( $C_7H_{10}O_2$ ) and could successfully attribute them to paddy

burning factor. However, the total VOC mass attributed to this factor  $11.6 \mu\text{g m}^{-3}$  is less than the  $\text{PM}_{2.5}$  ( $20.7 \mu\text{g m}^{-3}$ ) and  $\text{PM}_{10}$  ( $36.5 \mu\text{g m}^{-3}$ ) mass attributed to this factor. Since the factor has a photochemical age of less than 24 hours, and the SOA yields (in terms for % of mass converted to aerosol) for many compounds on such timescale are  $<20\%$ , the overall SOA contribution to the  $\text{PM}_{2.5}$  mass is smaller than the mass contribution of primary ash particles. Thus, it is highly unlikely that the PTR-TOF-MS missed measuring many precursors due to inlet losses or that the compounds fragmented massively in the system used in this work. We have added the following text and supplementary figure S9 and S10 to the end of this section to make this clearer:

“Figure S9 shows the volatility oxidation state plot for all 111 VOCs in which the marker size represents the percentage share of each compound explained by the paddy residue burning factor and markers are colour coded by the number of carbon atoms. The plot shows evidence of the first- and second-generation oxidation products of C5 and C6 hydrocarbon transitioning from the VOC to the IVOC range along trajectories expected for the addition of =O functionality to the molecule (Jimenez, et al. 2009), while C7 hydrocarbons progress along trajectories expected for both the addition of -OH and =O functionality. This indicates that paddy residue burning contributes significantly to the SOA burden. However, the fact that the  $\text{PM}_{10}$  mass associated with this factor ( $36.5 \mu\text{g m}^{-3}$ ) is 1.8 times larger than the  $\text{PM}_{2.5}$  mass ( $20.7 \mu\text{g m}^{-3}$ ) and 3 times larger than the VOC mass ( $11.6 \mu\text{g m}^{-3}$ ) released during the same combustion process, points towards the relatively coarse ash formed from the phytolith skeleton of rice straw (Figure S10) as the dominant aerosol source.”

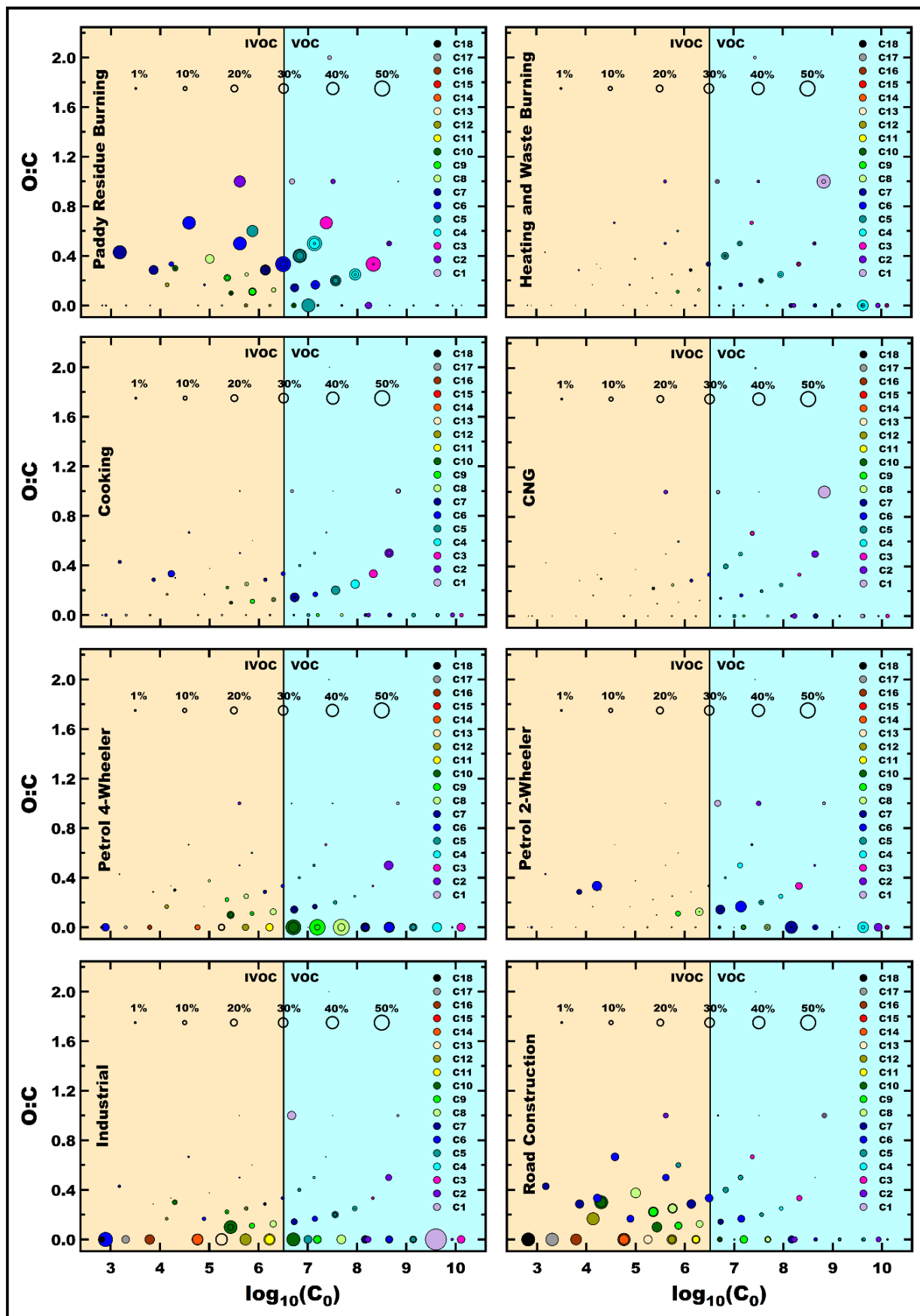


Figure S9: Volatility oxidation state plots for all factors that individually contribute more than 3% to the total SOA formation potential.

Line 620 (also 566-568): “The transport sector’s PM emissions are dominated by the non-exhaust emissions of the CNG-fuelled commercial vehicle fleet.” This sounds somewhat unlikely. Which non-exhaust emissions are the authors referring to emitting from CNG vehicles? I can think of break/tyre-wear as a possible source but that contributes primarily to coarse PM, not so much to fine. Are there evaporative emissions of some kind? I imagine CNG itself would have negligible potential to form ambient PM given its small molecular size.

Yes, tire wear, break wear and dust re-suspension are precisely the sources we are implicating and those sources are well supported by the PMF output, because the  $PM_{10}$  emissions attributed to this source in the PMF ( $22.5 \mu\text{gm}^{-3}$ ) are indeed are twice as large as the  $PM_{2.5}$  emissions attributed to this source ( $10.4 \mu\text{gm}^{-3}$ ). According to a recent emission inventory for Delhi (Nagpure et al., 2016 <https://doi.org/10.1016/j.atmosenv.2015.12.026>) their contribution to transport sector PM is one order of magnitude larger than that of the tailpipe emissions and two orders of magnitude larger than the VOC mass. The SOA formation potential of the dominant VOC in the tailpipe exhaust of this vehicle class, methanol, and ethanol is very small hence SOA is not a significant contributor to the PM mass associated with the CNG factor. We have now expressed this more clearly.

“Also, sources that are generally targeted by most clean air action plans such as tailpipe exhaust emissions of private vehicles and industries are responsible for less than one-quarter of the particulate matter mass loading that can be traced with the help of gas-phase organic molecular tracers. Instead, the transport sector’s PM emissions are dominated by the non-exhaust emissions such as road dust suspension, break wear and tire wear of the CNG-fueled commercial vehicle fleet, which according to a recent emission inventory for Delhi are one order of magnitude larger than the transport sector tailpipe exhaust emissions (Nagpure et al., 2016). “

On the other hand, the transport sector in Delhi would have diesel trucks which are known to be large emitters of SOA precursors.

The majority of heavy-duty vehicles in Delhi, have transitioned to CNG fuel. So have internal delivery vehicles and most taxis. There are strict restrictions on the entry of diesel trucks. This shift aligns with Delhi's strict adoption of Euro-6 norms in 2018, and restrictions that completely ban the use of more than 10-year-old diesel vehicles within city limits, which forces owners to sell these into the second hand market of less restrictive states or convert them to CNG with a conversion kit (Krelling et al., 2022 <https://doi.org/10.1016/j.tranpol.2021.10.019>), the administration heavily subsidizes the price of CNG which was 1.5 times lower per km than that of diesel during the study period. Commercial transport is price sensitive, hence, the number of diesel vehicles on the roads is very low. Diesel-fuelled trucks typically circumvent city borders when they pass by Delhi. This practice is influenced by heavy fines on entry of old vehicles and also stringent time regulations imposed on the entry of diesel trucks. The recent changes in both regulations and their enforcement have resulted in halving the diesel sales in the Delhi NCR over the past 5 years. A random selection of pictures clicked in the timespan of less than 10 minutes while driving around Delhi pasted below supports the fact that diesel trucks are hardly plying across the city and hence not important enough to get their own PMF factor. The CNG cylinders mounted in the place where the diesel tank used to be are easily visible on most trucks. We have now inserted the following supplementary figures and text into Section 3.2.4. to clarify:

“This study attributes a large share of these non-tailpipe emissions to trucks, buses and other commercial vehicles that are typically fuelled by CNG, because commercial diesel vehicles of <10 years age face severe entry restrictions, that limit their use within the Delhi NCR while older diesel vehicles have been completely banned from plying within City limits. Policy interventions in favour of CNG use (Krelling & Badami, 2022) have resulted in a halving of diesel sales, a rapid conversion of Delhi’s HDV fleet to CNG (Figure S12), and a significant reduction in tailpipe exhaust emissions.”



**Figure S12: Random selection of photographs clicked while driving around Delhi. One can clearly see the white CNG cylinders mounted in the place where the fuel tank used to be during vehicle conversion. Photo credits: Kriti Annika Sinha**

Dust resuspension has been attributed to non-exhaust emissions, but I am not sure if I agree with that classification. Dust is not a vehicular source. Hence, I would like the authors to extensively elaborate on what forms PM from non-exhaust emissions from CNG vehicles.

Dust can be natural and windblown but it can also be anthropogenic. When dust is suspended from the road or more importantly by off-road usage of heavy vehicles e.g. during construction activity it is classified as an anthropogenic transport sector emission (see e.g. the recent review by Harrison et al. 2021, <https://doi.org/10.1016/j.atmosenv.2021.118592>). Particularly when it comes to avoidable road transport, these emissions would not be present if the same transport demand had been satisfied via freight train/passenger train/metro rail/tram. The road transport share of these anthropogenic emission can be reduced by 1) modal shifts of the transport demand towards rail and 2) wet road cleaning to reduce the silt burden on the road in case of road dust suspension and 3) regenerative braking in case of EVs. However, certain types of activity by HDVs that suspend a very large amount of dust e.g. during transport of construction material to construction sites or during the movement of waste are hard to eliminate. A picture of a waste disposal truck (marked with a red arrow) moving on one of the Delhi's "garbage mountains" with a dust plume (encircled with a red square) trailing behind the vehicle is pasted below. We hope that the reviewer agrees such a "dust plume" should not be labelled as a "natural" dust plume, even though in the case of trucks moving on construction sites the suspended dust aerosol will be chemically indistinguishable from natural soil minerals suspended by wind alone. Since the anthropogenic dust is transported in the air alongside with the tailpipe emission plume, our PMF is capable of tracking this type of "dust plumes" to their primary source, namely, HDV movement.



We also modified the text in Section 2.4 to make things clearer:

“CNG-fuelled vehicles are identified as the third largest source of  $PM_{10}$  (15 %) and  $PM_{2.5}$  (11 %) and contribute 9 % to the total VOC burden (Fig. 4). The much higher contribution of this source to the coarse mode particulate matter burden ( $22.5 \mu\text{g m}^{-3} PM_{10}$ ) when compared to the fine mode particulate matter burden ( $10.4 \mu\text{g m}^{-3} PM_{2.5}$ ), confirms earlier emission-inventory-based estimates which flagged that non-tailpipe emissions such as brake and tire wear and road dust resuspension have become the dominant transport sector related particulate matter sources in the Delhi-NCR region (Nagpure et al., 2016). Non-tailpipe emissions such as brake and tire wear and road dust resuspension contribute most to the  $PM_{10}$  burden, although they have also become the largest source of transport sector fine mode aerosol and VOC emissions in some countries that have transitioned to Euro-6 norms (Harrison et al., 2021).”

This also reads somewhat contrary to lines 260-264 where petrol vehicles are shown to be major contributors to SOA.

We did not state that petrol vehicles contribute most to the SOA at the receptor sited. Petrol 4W and 2W vehicles contribute significantly to the SOA formation potential because they are the largest source of several aromatic compounds in the NCR. However their contribution to the  $PM_{10}$  ( $10.8 \mu\text{g m}^{-3}$ ) and  $PM_{2.5}$  ( $4 \mu\text{g m}^{-3}$ ) mass in the PMF is much smaller than that of CNG vehicles, primarily because non-tailpipe emissions such as break-wear and dust suspension scale with vehicle weight and these vehicles tend to be lightweight. It is very important to keep in mind that 1) SOA particles are smaller and 2) SOA particles are less dense ( $\sim 1.4 \text{ g/cm}^3$ ) than break wear (up to  $5 \text{ g/cm}^3$ ) and road dust ( $\sim 2.6 \text{ g/cm}^3$ ) and 3) only a small percentage share of the VOC burden is converted to SOA. This is why the non-tailpipe PM emissions of vehicles that are following emissions norms of EURO 4 or better tend to be larger than the tailpipe aerosol emissions and the mass of the SOA formed. However, a large contribution to the SOA formation potential at the receptor site does not necessarily equate a large contribution to the SOA mass at the receptor site, because the 4-wheeler emissions impacting the site mostly have a photochemical age on the timescale of minutes. While the factor contributes the largest percentage share of many C6 to C10 hydrocarbons, it hardly contributes towards the measured mass of the first- and second-generation oxidation products of those very same compounds at the receptor site. We have added the following text to make this clear:

“Figure S9 shows that this factor contributes significantly to the burden of C6- to C10 hydrocarbons, and hence SOA formation potential. However, due to freshly emitted plumes, it hardly contributes to the burden of the first- and second-generation oxidation products of these hydrocarbons at the receptor site. Instead, this factor is likely to contribute to secondary pollution formation downwind of the Delhi NCR.”

while a distinction has been made between 2-wheeler and 4-wheeler petrol vehicles, no significant discussion exists on the contribution of diesel vehicles. This needs to be explained in more detail.

Diesel vehicles do have a distinctive source fingerprint and would have been identified by the PMF if they had major impact on the air quality in the Delhi NCR. They do not have major impact, because policies have restricted their usage in recent years including 2022. The only noticeable diesel emissions impacting the receptor site are mixed into the road construction factor and reach the receptor simultaneously with the evaporative emissions of freshly laid asphalt. This is now clarified in section 3.1 as follows:

The OVOC source fingerprint of the road construction factor matched the source fingerprint of asphalt mixture plants and asphalt paving ( $R=0.9$ , Li et al., 2020), while the hydrocarbon source fingerprint matched diesel-fuelled road construction vehicles ( $R=0.6$ , Che et al., 2023).

Line 650-651: Authors state that “all” previous studies from the region have attributed PM to BB or fossil-fuel burning, and that we need to look beyond these sources. While I agree that a larger set of sources need to be identified, I think there is already some work done on this front. Kumar et al. 2022 ACP <https://acp.copernicus.org/articles/22/7739/2022/acp-22-7739-2022.pdf>

Kumar et al. 2022 identified “cooking-related OA using EESI-TOF PMF analysis, but sadly did not include this source in the final pie charts of their paper, because their AMS-PMF analysis could not find this particular source, while ESI data was only reported in counts per second and not quantitatively. Instead, the paper reported three primary factor HOA, BBOA-1 and BBOA-2 and one aged biomass burning factor in addition to three SOA factors without naming the activities responsible for the formation of BBOA-1 and BBOA-2. The paper that reported results that most closely relate to the results of our study would be Cash et al. 2021. We have added a discussion of the Cash et al results to these lines

“This new approach of combining VOC tracers with PM measurements provides great potential for improved source apportionment in complex emission environments, at a level of detail that is more meaningful than just attributing emissions to biomass burning or fossil-fuel burning, which has been the case in all previous studies from the region to date. Previously in Delhi-MCR region, Kumar et al. 2022 identified “cooking-related OA using EESI-TOF analysis but due to analytical limitations, the paper only reported quantitative pie charts for three primary factors, namely HOA, BBOA-1 and BBOA-2, without naming the activities responsible for the formation of BBOA-1 and BBOA-2. One of the more comprehensive AMS based studies (Cash et al., 2021) spanning pre-monsoon, monsoon and post monsoon season of the year 2018 identified three different primary biomass burning factors, namely cooking organic aerosol (6% of  $PM_{10}$ ), solid fuel organic aerosol ( $\leq 11\%$  of  $PM_{10}$ ), and semi-volatility biomass burning organic aerosol ( $\leq 13\%$  of  $PM_{10}$ ), that broadly appear to correspond to our solid fuel-based cooking (4% of  $PM_{10}$ ), residential heating and waste burning (23% of  $PM_{10}$ ), and paddy residue burning (25% of  $PM_{10}$ ) factors. However, the study failed to name and attribute two of these three factors in policy relevant ways, could not identify the significant contribution of coarse mode fly ash to the total aerosol burden, and also was unable to distinguish between different fossil-fuel related sources.”

Figure 5: I notice that road construction and solvent factors show opposing temporal trends. Road construction peaks in the afternoon while solvents are higher during early morning or night hours. The authors state in lines 425-426 that the solvents contribute the most to the VOC burden at night. Given that both these sources are evaporative in nature, how could they show opposing temporal trends? Are there any specific sources of solvents in Delhi that are prominent during nighttime?

The road construction factor primarily involves evaporative emissions released during degassing from the road surface, emissions are greatest when the asphalt has just been paved and hence peak during the hours when construction activity is more prevalent. Conversely, compounds associated with the solvent factor predominantly originate from an industrial point sources that appears to operate 24/7. They reach the receptor in episodic but intense plumes that are not accompanied by combustion tracers. Hence, we attribute this factor to the venting of chemicals from some industrial stacks. This type of activity results in the highest concentrations at night when emissions mix into a shallower nocturnal boundary layer. However, the factor also displays episodes with high concentrations during daytime. This indicates that daytime fluxes can actually be quite high and just mix into a larger volume. We looked for some specific types of industrial units located 1) SW of the receptor with the highest source strength after midnight and 2) NE of the receptor with the highest source strength in the evening before midnight. The best source match we found for this type of source was collected from a plot situated opposite a polymer manufacturing unit and next to a pet food manufacturer in an industrial area at Jahangir Puri ( $R=0.7$ ) NE of the receptor. We have updated the text in Section 3.1 and lines 425ff to make the difference clearer:

“The OVOC source fingerprint of the road construction factor matched the source fingerprint of asphalt mixture plants and asphalt paving ( $R=0.9$ , Li et al., 2020), while the hydrocarbon source fingerprint matched diesel-fuelled road construction vehicles ( $R=0.6$ , Che et al., 2023). The factors identified as solvent usage and



evaporative emissions matched ambient air grab samples collected from an industrial area at Jahangir Puri (R=0.7), and Dhobighat at Akshar Dham (R=0.5) in this study.”

“These compounds point towards stack venting of VOCs from chemical-, food-, or pharmaceutical industries or polymer manufacturing as likely sources of these emissions (Hodgson et al., 2000, Villberg et al., 2001, Jankowski et al., 2017, Gao et al., 2019). This assessment is broadly confirmed by the fact that the best match (R=0.7) for this source was collected from a plot situated opposite a polymer manufacturing unit and next to a pet food manufacturer in an industrial area at Jahangir Puri NE of the receptor site.”

One can also check the temporal trends in PCBTF, Texanol and p-dichlorobenzene, D4- and D5-siloxane that are known tracers of VCP sources. Some of these can be measured with PTR-ToF.

Thank you for this comment. We appreciate that Volatile Chemical Products (VCP) have emerged as an important source in recent studies conducted in western countries, in which emissions from industrial and other sources have been regulated to a greater extent and VCP emissions from cosmetic and perfume usage and that of sanitation products have transitioned to becoming major sources of some VOCs in the urban environment. In India, however, these products are expensive and can only be afforded by a limited subset of the urban population. The vast majority of the population, even in a city like Delhi, struggle to meet their daily food needs and expenses on education and healthcare, which likely has kept VCPS from being a major source so far. Hence it is not surprising that this factor did not appear in the 11-factor PMF solution. Except for dichlorobenzene none of the compounds passed our quality control filter, which means either the signal at the m/z was not above the detection limit or the compound presence could not be confirmed via isotopic peaks of the correct height for the isotopes of the compound. At our site, the dominant dichlorobenzene sources appear to be industrial in nature.

The authors should more clearly discuss how they calculated the total VOC mass in the paper. This is important because the fractions of other measured species are drawn from the total, and this can introduce significant bias in the conclusions regarding source contributions if the total VOC mass is not comprehensive enough.

We have added a few sentences to clarify this point:

“The total VOC mass was included as a weak species and was calculated as the sum of the mass of the individual 111 VOC species included in the PMF. Overall, the 111 VOC species included in our analysis and their isotopic peaks explained 86% of the VOC mass detected during our study period. The remaining 119 m/z that accounted for 14% of the detected VOC mass could not be included in our PMF analysis mostly because signals were below the detection limit for close to 50% of the observation period, or because compound identity could not be confirmed via isotopic peaks.”

The chemical profiles shown in Figure 3 run up to C<sub>10</sub>H<sub>16</sub> and there is some additional discussion in the paper about IVOCs. However, sources such as road construction emit minimally in the VOC space, and more in the IVOC and SVOC space. The authors should discuss how they prevented biases from creeping into their conclusions.

The main rationale behind choosing these compounds shown in Figure 3 is, that the normalized height of the bar displaying that compound should be at least 0.1x the height of the tallest peak in at least one of the factor profiles. Most of the IVOCs did not meet the inclusion criteria for Figure 3. The figure serves to depict the chemical fingerprints of all the factors and very low bar heights are invisible on the y-axis, while the compound formula will clutter the x-axis of the figure and will make it hard to read. We have now clarified this as follows:

“Figure 3 shows the source profile of the eleven factors that our PMF analyses resolved. Out of the 111 VOCs only those whose normalized source contribution exceeded 0.1 when divided by the most abundant compound in the same source profile in at least one of the sources, were included in the figure.”

Fresh asphalt does have a very characteristic VOC signature in the OVOCs space in the form of a very distinct double peak at C<sub>3</sub>H<sub>6</sub>O and C<sub>4</sub>H<sub>8</sub>O that is not accompanied by methanol peaks as is usually the case in a solvent factor, and neither accompanied by the furanes, aldehydes and organic acids that are usually seen in biomass burning source fingerprints. This makes the identification so easy and clear. The factor identity has been confirmed via cross correlation analysis as follows:

“The OVOC source fingerprint of the road construction factor matched the source fingerprint of asphalt mixture plants and asphalt paving (R=0.9, Li et al., 2020), while the hydrocarbon source fingerprint matched diesel-fuelled road construction vehicles (R=0.6, Che et al., 2023).”

Also, there should be at least some discussion in the paper about the inlet system used upstream of the PTR-ToF as this can prove crucial in the detection of many species (lines 132-133).

A detailed discussion about this as well as the inlet system is given in the companion paper (Mishra et al., 2024 10.5194/egusphere-2024-500) and now also mentioned and included in the revised MS as follows:

“It is worth mentioning again that as a significant improvement over other previous PTR-TOF-MS deployments in Delhi, the inlet system of the instrument used in this work was designed for sampling and detection of low-volatility compounds with the extended volatility range technology (Piel et al., 2021). The inlet system of the instrument as well as the ionization chamber is fully built into a heated chamber and the inlet capillary is further fed through a heated hose to ensure there are no “cold” spots for condensation. The entire inlet system is made of inert material (e.g. PEEK or siliconert treated steel capillaries to keep surface effects minimal. Further the overall inlet residence time was less than 3 seconds, throughout the campaign.”

Piel, F., Müller, M., Winkler, K., Skytte af Sättra, J., and Wisthaler, A.: Introducing the extended volatility range proton-transfer-reaction mass spectrometer (EVR PTR-MS), *Atmos. Meas. Tech.*, 14, 1355–1363, <https://doi.org/10.5194/amt-14-1355-2021>, 2021.

Furthermore:

Lines 182-184: The “pulling up” and “pulling down” should be briefly explained. It sounds vague in its current form.

We regret the confusion, as "pulling up" and "pulling down" are normally common terms used in PMF discussions. We have added the following text to clarify:

“The rotational ambiguity can be reduced using this option with the aid of prior knowledge by encouraging the model to minimize (pull down) or maximize (pull up) the total mass assigned to specific hourly observations or compounds in source profiles as much as possible within a pre-defined permissible penalty on Q.”

Lines 187-188: It is quite amazing that the bootstrap found all 100% of the runs stable and well-mapped to the base solution. In principle, this may suggest that your dataset yields only one solution which is super robust. Is this what you are saying?

The reviewer has interpreted this correctly. 100% stable bootstrap solutions for the constraint run indeed indicate that with the help of the constraints a robust solution has been achieved for this particular dataset.

I acknowledge citations, but in lines 180-187, I recommend briefly describing the rationale behind application of different constraints to help the reader assess.

Thank you for highlighting this important aspect. As can be seen from our list of constraints this has been primarily accomplished by pulling down some night-time plumes from combustion sources that the model’s base model run had left behind in the BVOC and photochemistry factors. Stopping the model from mixing some of the combustion emissions into non-combustion sources turns out to be an extremely efficient way to force the model to resolve the combustion sources properly, and prevent factor swapping. The solution can be further refined by identifying one major characteristic plume per source and pulling it up. The selected plumes should originate from one dominant source only, should have plume enhancement ratios that matches source samples as closely as possible, and should be among the strongest plumes attributed to the source in the base run. Pulling up as little as one such plume for each of the anthropogenic sources, minimizes the factor swapping between similar sources

We have added the following details:

“The rotational ambiguity can be reduced using this option with the aid of prior knowledge by encouraging the model to minimize (pull down) or maximize (pull up) the total mass assigned to specific hourly observations or compounds in source profiles as much as possible within a pre-defined permissible penalty on Q. The primary problem of the base run solutions is that night-time biomass burning plumes contaminate both the biogenic and the photochemical factor. To minimize this in our constrained run, we have pulled down primary emissions (acetonitrile, toluene, C8 aromatics, and C9 aromatics) in the biogenic and photochemical factors. We also pulled down the top-7 strongest nighttime plumes contaminating the biogenic and photochemical factors. In addition, we pulled up the highest plume event for all the anthropogenic emission-related factors as detailed in Table S2. The overall penalty to Q (the object function) was 4.9 %, which is within the recommended limit of 5 % (Norris et al., 2014; Rizzo & Scheff, 2007).”

Lines 229-234: The comparisons stated here are very on point, which is great. But it is not clear how contributions from heavy vehicles, e.g. road construction vehicles, were separated from other diesel-based sources, such as transport trucks.

We appreciate the referee’s comment. As also mentioned in the above replies, the majority of heavy-duty vehicles in Delhi have been switched to CNG. This includes all commercial diesel vehicles such as trucks, buses and taxis. Even private diesel vehicles that are older than 10 years are not permitted to ply in the city. This is why the only diesel emissions we see in the PMF are emissions that reach the receptor site during daytime simultaneously with compounds that are diagnostic of fresh asphalt paving. It appears that construction

machinery is the dominant HDV class that has not yet completely been converted. The revised text now reads as follows:

“The factors identified as CNG (R=1.0), petrol 4-wheelers (R=0.9), and petrol 2-wheelers (R=0.6) matched tailpipe emissions of the respective vehicle types and fuels (Hakkim et al., 2021). The petrol 4-wheelers (R=0.9), and petrol 2-wheelers (R=0.7) also matched traffic junction grab samples from Delhi (Chandra et al., 2018). The OVOC source fingerprint of the road construction factor matched the source fingerprint of asphalt mixture plants and asphalt paving (R=0.9, Li et al., 2020), while the hydrocarbon source fingerprint matched diesel-fuelled road construction vehicles (R=0.6, Che et al., 2023).”

I recommend to put some correlation plots in the SI that compare the chemical profiles of the source factors obtained in this study with the sources from literature that are discussed here.

We thank the referee for the suggestion. We have now modified the text (see below) and added the R values to the main text. but don't think correlation plots are necessary since the source profiles as presented in the revised version can already be visually compared with the help of Figure 3.,

“The PMF factor profile matched best against source samples collected from burning paddy fields (R=0.6, Kumar et al., 2020) for the paddy residue burning factor. The cooking factor matched emissions from a cow-dung-fired traditional stove called angithi (R=0.7, Fleming et al., 2018). The residential heating & waste burning factor had a source fingerprint matching emission from leaf litter burning, (R=0.7, Chaudhary et al., 2022), waste burning (R=0.7, Sharma et al., 2022), and cooking on a chulha fired with a mixture of firewood and cow dung (R=0.9, Fleming et al., 2018). The factors identified as CNG (R=1.0), petrol 4-wheelers (R=0.9), and petrol 2-wheelers (R=0.6) matched tailpipe emissions of the respective vehicle types and fuels (Hakkim et al., 2021). The petrol 4-wheelers (R=0.9), and petrol 2-wheelers (R=0.7) also matched traffic junction grab samples from Delhi (Chandra et al., 2018). The OVOC source fingerprint of the road construction factor matched the source fingerprint of asphalt mixture plants and asphalt paving (R=0.9, Li et al., 2020), while the hydrocarbon source fingerprint matched diesel-fuelled road construction vehicles (R=0.6, Che et al., 2023). The factors identified as solvent usage and evaporative emissions matched ambient air grab samples collected from an industrial area at Jahangir Puri (R=0.7), and Dhobighat at Akshar Dham (R=0.5) in this study. The factor identified as industrial emissions showed the greatest similarity to ambient air grab samples from the vicinity of the Okhla waste-to-energy plant (R=0.8), Gurugram (R=0.7) and Faridabad (R=0.8) industrial area. The biogenic factor showed the greatest similarity to leaf wounding compounds released from *Populus tremula* (R=0.8, Portillo-Estrada et al., 2015) as well as BVOC fluxes from *Mangifera indica* (R=0.4, Datta et al., 2021).”

Lines 252-253: As a reader, I was surprised to see a comparison with NW-IGP and Mohali. It was quite sudden and not consistent throughout the paper. This should be rephrased in a way that gives a reader some context on which regions are being compared and why.

We have rephrased this as follows:

“Figure 4 shows the relative contribution of different sources to the total pollution burden of VOCs, PM<sub>2.5</sub> and PM<sub>10</sub> at the receptor site. In the megacity of Delhi, transport sector sources contributed most (42±4 %) to the total VOC burden, while it contributed much less (only 24 %) to the total VOC burden in Mohali a suburban site 250 km North of Delhi during the same season (Singh et al., 2023). On the other hand, the contribution of paddy residue burning (6±2 %) and the summed residential sector emissions (17±3 % in Delhi and 18 % in Mohali) to the total VOC burden during post-monsoon season were similar at both sites.”

Lines 262-270: Add error values to the average percentages to account for the variability in these fractions during the study period.

This text has been substantially simplified. Uncertainties have been added to the segments that were retained. However, uncertainties reflect the uncertainty of the PMF model imposed by the stability of the bootstrap runs, not the ambient variability. No uncertainty was added to the SOA formation potential because the uncertainty of the widely used SOAP factors has not been quantified so far. This prevents meaningful error propagation from VOC mass to SOAP.

“Figure 4 shows the relative contribution of different sources to the total pollution burden of VOCs, PM<sub>2.5</sub> and PM<sub>10</sub> at the receptor site. In the megacity of Delhi, transport sector sources contributed most (42±4 %) to the total VOC burden, while it contributed much less (only 24 %) to the total VOC burden in Mohali a suburban site 250 km north of Delhi during the same season (Singh et al., 2023). On the other hand, the contribution of paddy residue burning (6±2 %) and the summed residential sector emissions (17±3 % in Delhi and 18 % in Mohali) to the total VOC burden during post-monsoon season were similar at both sites. The contribution of the different factors to the SOA formation potential (Fig. 4e), stands in stark contrast to their contribution to primary particulate matter emissions. SOA formation potential was dominated by the transport sector (54 %) while direct

PM<sub>10</sub> (52±8%) and PM<sub>2.5</sub> (48±12%) emissions were dominated by different biomass burning sources (Fig. 4 b & c). CNG-fuelled vehicles also contribute significantly to the PM<sub>10</sub> (15±3 %) and PM<sub>2.5</sub> (11±3 %) burden.”

Line 284: I am not sure whether a correlation R of 0.5 could be considered significant.

We have deleted this.

Line 288: 0.027 and 0.047 are quite small values. What is your error bound on these numbers?

We have added the uncertainties of the slope. Numbers appear to be small because fire counts are very high (several thousands) but the slopes and resulting PM enhancements are very significant:

“Figure S6 shows that the PM<sub>2.5</sub> and PM<sub>10</sub> mass loadings at the receptor site increased by 0.027±0.006 and 0.047±0.01 μg m<sup>-3</sup> respectively for each additional fire count within the 24-hour fetch region whenever the trajectories are arriving through north-west and south-west region. It is very interesting to note that the incremental increase in PM<sub>2.5</sub> and PM<sub>10</sub> mass loadings for each additional fire count were almost four times higher than the former regions when the trajectory fetch region was south-east with 0.11±0.01 and 0.19±0.02 μg m<sup>-3</sup>, respectively, likely because the complete burns of entire fields (Figure S7) that are prominent in Punjab can be more easily identified as a fire activity with satellite-based detection (Liu et al., 2019, 2020), while the partial burns (Figure S8) that are more prevalent in the eastern IGP and in Haryana have larger omission errors (Liu et al., 2019, 2020).”

Figure 5: The increase in NO<sub>x</sub> in petrol 2W panel during morning commute hours is not reflected in 2W or 4W factors. Does this make sense? Also why are the 2-wheeler petrol vehicle factor contributions high throughout the night and drop near the morning commute hours? I would imagine the 2W vehicles on the road to decrease substantially during the night.

Our PMF has a 4W dominated petrol vehicle factor, containing emissions from the immediate vicinity of the receptor (i.e. within Central Delhi), that have a plume age on the timescale of minutes based on the highest correlation of the factor being with NO emissions. The 2W dominated petrol vehicle factor is aged shows a much higher correlation with NO<sub>2</sub> than with NO and emissions appear to occur in the rural hinterland and outskirts. Their transport time appears to be on the scale of hours. The 2-wheeler factor has been identified as such primarily based on the benzene to toluene ratio which differs between 2-wheelers and 4-wheelers and is better preserved longer during photochemical aging when compared to the emission ratios of C8 and C9 aromatics. However, it is clear from the presence of OVOCs in the source profile and the low correlation of the factor time series with NO that most plumes in the 2W factor are aged, and hence are expected to reach the receptor several hours after the peak evening traffic. The morning peak in NO<sub>x</sub> coincides primarily with the peak in cooking emissions and is not triggered by either of these factors. We have revised the text of both sections to make this distinction clearer:

“Figure 4 shows petrol 4-wheeler contributed 20 %, 25 %, and 30 % to the VOC mass loading, OFP, and SOAP, respectively. The source fingerprint of this source matched tailpipe emissions of petrol-fuelled 4-wheelers (Hakkim et al., 2021) and is characterized, in descending rank of contribution, by C8-aromatics, toluene, C9-aromatics (C<sub>9</sub>H<sub>12</sub>), benzene, butene + methyl tert-butyl ether (MTBE) fragment, propyne, propene, methanol and C2-substituted xylenes + C4-substituted benzenes (C<sub>10</sub>H<sub>14</sub>). Figure 5 shows that emissions peak in the evening between 7 pm and midnight with average VOC mass loadings >70 μg m<sup>-3</sup> and reach the receptor site from most wind directions. Emissions are strongly correlated with NO (R=0.8), CO (R=0.7), and CO<sub>2</sub> (R=0.7) indicating the receptor site is impacted by fresh combustion emissions from this source and the atmospheric age of most plumes is on the timescale of minutes.”

“Figure 4 shows petrol 2-wheeler contributed 14 %, 12 %, and 20 % to the VOC mass loading, OFP, and SOAP respectively. The source fingerprint of this source matched tailpipe emissions of petrol-based 2-wheelers (Hakkim et al., 2021) and are characterized, in descending rank of contribution, by toluene, acetone + propanal, C-8 aromatic compounds, acetic acid (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>), propyne (C<sub>3</sub>H<sub>4</sub>), methanol (CH<sub>3</sub>OH), benzene (C<sub>6</sub>H<sub>6</sub>), the MTBE fragment and C-9 aromatics (C<sub>9</sub>H<sub>12</sub>). A key difference of the petrol 2-wheeler source profile in comparison to the petrol 4-wheeler source profile is the lower benzene to toluene ratio, which is supported by the GC-FID analysis of tailpipe exhaust (Kumar et al., 2020). Figure 5 shows that emissions peak in the evening between 8 pm and 10 pm with average VOC mass loadings >50 μg m<sup>-3</sup> and reach the receptor site from most wind directions. Emissions are strongly correlated with NO<sub>x</sub> (R=0.6), CO (R=0.6) and CO<sub>2</sub> (R=0.7), but have a lower correlation with NO (R=0.5) (Table S5), and a larger contribution of oxygenated compounds to the source profile, indicating that the emissions have been photochemically aged. This suggests that contrary to 4-wheeler plumes which originate from the immediate vicinity of the site in central Delhi (Figure S1), 2-wheeler plumes reach the receptor after prolonged transport from more distant rural and suburban areas on the outskirts of the city. In such areas, people often favour two-wheelers over four-wheelers.”

Line 326: 3.2.2 Title: By waste disposal, do the authors mean waste burning? These can be very different things with different mechanisms of emissions if combustion is not involved in one versus the other.

We appreciate the referee's helpful comments and have changed the names to heating and waste-burning

Line 354: BB emissions are attributed to solid fuel-based cooking and a cow dung-fired traditional stove is discussed. These measurements were made at IMD Lodhi Road, which appears to be a highly urbanized area. How do the authors justify BB-based cooking activities near such location? Is regional transport important for fresh emissions?

In a mega city like Delhi, there is a socio-economic spectrum of society. Among its residents are many who continue to rely on traditional solid fuels for their cooking and heating needs due to financial constraints. It is also important to remember that the air shed is much larger than just Central Delhi and this is not a PMF factor containing fresh emissions as can be seen by the low  $R=0.1$  with NO. Solid fuel usage is very much prevalent in the villages of Haryana and Uttar Pradesh which are located within a radius of less than 60 km from the receptor. We have modified the text as follows:

The activity peaks from 8 am to noon time, with a secondary peak in the early evening hours and persists throughout monsoon and post-monsoon season. Emissions reaching the receptor site show no correlation with NO ( $R=0.1$ ) indicating plumes are not fresh.

Furthermore, cooking's contribution to PM10 is discussed, which is understandably low. However, what about PM2.5 that can be formed from the oxidation of gas-phase cooking emissions?

Yes cooking appears to be more of a VOC than a PM source. However, for this factor the percentage contribution to the SOA formation potential is lower than its percentage contribution to the VOC burden because most VOCs emitted are small OVOCs with limited SOA formation potential. The volatility oxidation space plot also shows very little evidence of first- and second- generation oxidation products progressing from the VOC into the IVOC region. The text has been modified to include this information:

The cooking factor is a daytime factor and explains 10 % of the total VOC mass loading, 10% and 8 % to the ozone and SOA formation potential (Fig. 4) but only a negligible share of the total PM<sub>10</sub> ( $\leq 4$  %) burden. The volatility oxidation space plot (Figure S9) also shows very little evidence of IVOC oxidation products that could partition into the aerosol phase.

Minor points:

Line 86: "at" Lodhi Road. **done**

Line 190: extra "T" at the start. **done**

Line 264: "Direct", do you mean "Primary" ? **yes, however these details were deleted in response to a comment of reviewer 1**

Line 642: "at this time of the year..." Which time of the year? This is written casually. **Revised to:**

While several recent efforts in some sectors (e.g. residential biofuel and cooking) appear to have yielded emission reduction benefits, the narrative to blame the post-monsoon pollution exclusively on the more visible sources (e.g. paddy residue burning), needs to be corrected so other sources are also mitigated.

Figure 3: Remove the word "PMF" from all figure legends. **We prefer to retain the legend in all panels. The figure is easier to comprehend when legends of all individual panels are complete.**

Figure 5: Add y-axis labels to the wind rose plots. **These are conditional probability roses showing a probability between 0 and 1. We now explain this more clearly in the figure legend**

**The polar plots (right column) depict the conditional probability of a factor having a mass contribution above the 75th percentile of the dataset during a certain hour of the day between midnight (centre of rose) and 23:00 local time (outside of rose) from a certain wind direction. This probability is determined by dividing the number of observations above the 75<sup>th</sup> percentile by the total number of measurements in each bin.**