Discovery of reactive chlorine, sulphur and nitrogen containing ambient volatile organic compounds in the megacity of Delhi during both clean and extremely polluted seasons

Sachin Mishra et al. 2024

We express our gratitude to Reviewer 1 for her/his careful and detailed reading of the manuscript and the insightful and helpful comments, which we were pleased to peruse. The helpful comments have contributed to improving the context, messaging and clarity of the original submission. Below, please find point-wise replies to the reviewer's comments and suggestions.

The point-wise replies (in blue) to the reviewer's comments (**in black**) are below. Changes made to the text are also provided after the replies (in red).

Response to Anonymous referee #1

Sachin Mishra et al. report VOC measurements in the megacity Delhi, where they applied a high resolution PTR-ToF-MS for the first time, which allowed them to observe species that had so far not been reported from there. Since VOC observations from India and South Asia in general are scarce, this work is a valuable and important addition to the literature. However, I have some concerns that should be addressed before publishing the paper in ACP.

We thank the reviewer for deeming the submitted work to be a valuable and important addition to the literature and below we make every effort to address the valid concerns raised by the esteemed reviewer.

General comments:

The paper is well structured and readable. However, in some places, e.g. in the abstract or at the end of the introduction, the paper reads a bit like an advert for the company selling the PTR-ToF-10k. I would ask the authors to cut down on the advertising. E.g., it is not necessary to include the brand name (“10k”) in the abstract. This is only necessary in the method description.

Thank you for deeming the paper well structured and easy to read! We regret the impression caused to the reviewer as our intention as fellow practitioners of the PTR-MS technique was simply to distinguish the instrument used in this work from previous PTR-MS deployments in Delhi, for which highlighting the model number-10K was useful to emphasize the significantly better mass resolution and sensitivity over previous instrument models, including by the same manufacturer, that were deployed in South Asia in previous studies. Appreciating the reviewer’s point, we have removed mention of -10K from the abstract and few other places where it was repetitive but retained it the methods section.

I have a general concern about the identification of compounds that the authors claim to be “unambiguous”. For example, they claim to have observed 42 pure hydrocarbons. But nowhere do they mention that the PTR method is subject to fragmentation and that these hydrocarbon masses could easily be, in part, fragmentation products of higher masses (Coggon et al., 2024; Pagonis et al., 2019).

We regret the confusion. Our use of "unambiguous" in no way implied that fragmentation isn't an important issue to consider, especially in a complex emission environment like Delhi. By "unambiguous" we simply implied that the attribution of the ion to its exact elemental composition as represented by its molecular formula, in terms of C, H , O , N and S atoms is umambiguous. This is in line with the usage of the term in the PTR-MS community previously as well where the term "unambiguous" was used to emphasize that in PTR-MS systems with lower mass resolution such as the PTR-TOF-MS 8000 (which in reality has mass resolution of 5000 for much of its dynamic range), even with similar mass accuracy, multiple peaks can be erroneously considered as a single one and remain unresolved as illustrated in the Figure shown below.

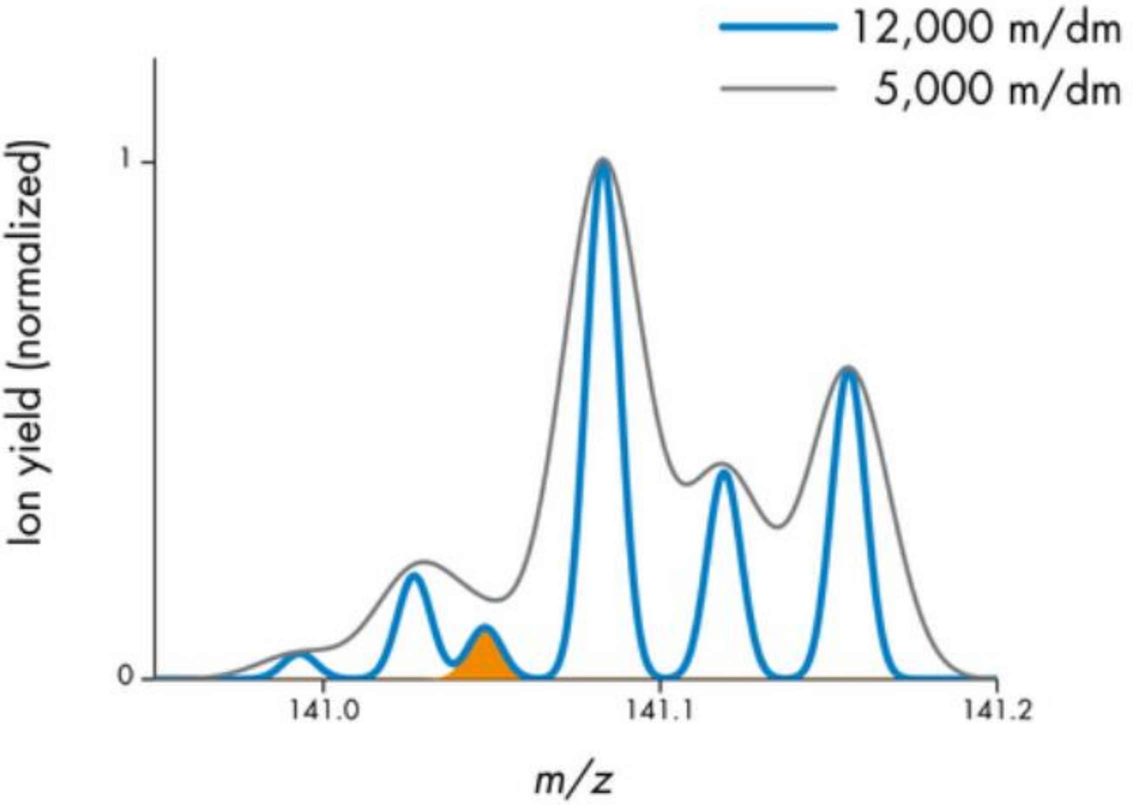


Image source: https://www.ionicon.com/blog/2023/the-advantages-of-high-mass-resolution-ptr-tofms-in-food-flavor-science

To quote from the description about the above Figure: "the superiority of the PTR-TOF 10k was found during the analysis of the complex headspace of chocolate for the presence of ethyl maltol ($C_7H_8O_3.H+$, m/z 141.055). With 5,000 m/Δm mass resolution at nominal m/z 141 the presence of five mass peaks is indicated (grey line). Interestingly, at about m/z 141.05 there appears to be rather a dip than a peak. By looking at the PTR-TOF 10k data (blue line) acquired from the same sample, the situation gets immediately ***unambiguous***."

Further due to the enhanced sensitivity of the PTR-TOF-10K used in our work (even reaching <1 ppt for some compounds), it was also possible to identify the corresponding major isotopic peaks.

Thus by additional manual checks that the height of the isotopic peak was not different from the expected peak height (e.g. for isoprene C_5H_8, the contribution to C-13 isotopes would be expected to be

~5.5%), we could further confirm that the parent peak's molecular assignment was correct and also not attribute the shoulder isotopic peaks to another compound with different elemental composition, as in that case, the height of the isotopic peak would differ from the value expected based on the natural abundance of isotopes of carbon, hydrogen, sulphur, nitrogen, chlorine and oxygen.

To illustrate this further, we call attention to data reported in a previously published paper from data acquired in India that used a PTR-TOF-8000 in the Table below. It can be noted that the C-13 isotopic contribution of a compound like furan with m/z 70.037 was likely mis-assigned to triazole, or at very least contribution of the isotope of furan which is more abundant was not subtracted as far as can be made out from the details provided in that work. Similarly, the C-13 isotope of isoprene detected at m/z 70.073 would be more plausible for the observed peak at m/z 70.073, which was attributed to butane nitrile by the authors. In our assignment due to the higher sensitivity and mass resolution of our PTR-TOF-MS-10K , we were able to detect the isotopic peaks and ensure those were not misassigned.

Data below sourced from Supplementary Table S1 (Jain et al., 2023, Atmos. Chem. Phys., 23, 3383–3408, 2023, https://doi.org/10.5194/acp-23-3383-2023-supplement)

Reported m/z	**Chemical formula assigned**	**Species name**	**Theoretical m/z**	**Mass accuracy (Da)**
70.038	$C_2H_3N_3$	Triazole	70.041	-0.003
More plausible candidate compound	**C_4H_4O**	**Isotope of furan**	**70.037**	**0.001**
70.073	C_4H_7N	Butane nitrile	70.066	0.007
More plausible candidate compound	**C_5H_9**	**Isotope of isoprene**	**70.074**	**-0.001**

The bold ones are the best fit at the reported m/z

It can be noted from the above that:

1. A species named triazole ($C_2H_3N_3$) was assigned at m/z 70.038 considering a mass accuracy error of -0.003 Da, but the isotope of furan would seem to be the correct one at this m/z as the mass accuracy error for the latter is only 0.001 Da. Note that isoptopic peaks for the two would be different too as the elemental composition is different with one containing nitrogen and the other not.

2. A species named butane nitrile (C_4H_7N) was assigned at m/z 70.073 considering a mass accuracy of 0.007 Da, but the isotope of isoprene would be more plausible at this m/z as the mass accuracy error for this is only - 0.001 Da. Again the isotopic peaks for the two would be different too as the elemental composition is different with one containing nitrogen and the other not.

We hope the above clarifies what the context in which the term "unambiguous" was used.

Appreciating that the meaning of this was not sufficiently clear in the original submission and also in response to a subsequent point mentioned concerning fragmentation at L199 later, we have now added the following text to make it more clear in the revised version after L199-200 (ACPD version of pdf):

"The term "unambiguous" is used in the context of the accurate elemental composition/molecular formula assignment of the ions by leveraging the high mass resolution (8000-13000 over entire dynamic mass range) and detection sensitivity (reaching even 1 ppt or better for many ions; see Table S2) of the instrument. This enabled ensuring peaks due to expected isotopic signals were not construed as new compounds if their height was exactly as expected for a shoulder isotopic peak based on the natural abundance of isotopes of carbon, hydrogen, nitrogen, sulphur, chlorine and oxygen that made up the more abundant molecular ion. Where an ion could occur significantly due to fragmentation of another compound, the same has also been noted in Table S2 during attribution of the compound's name."

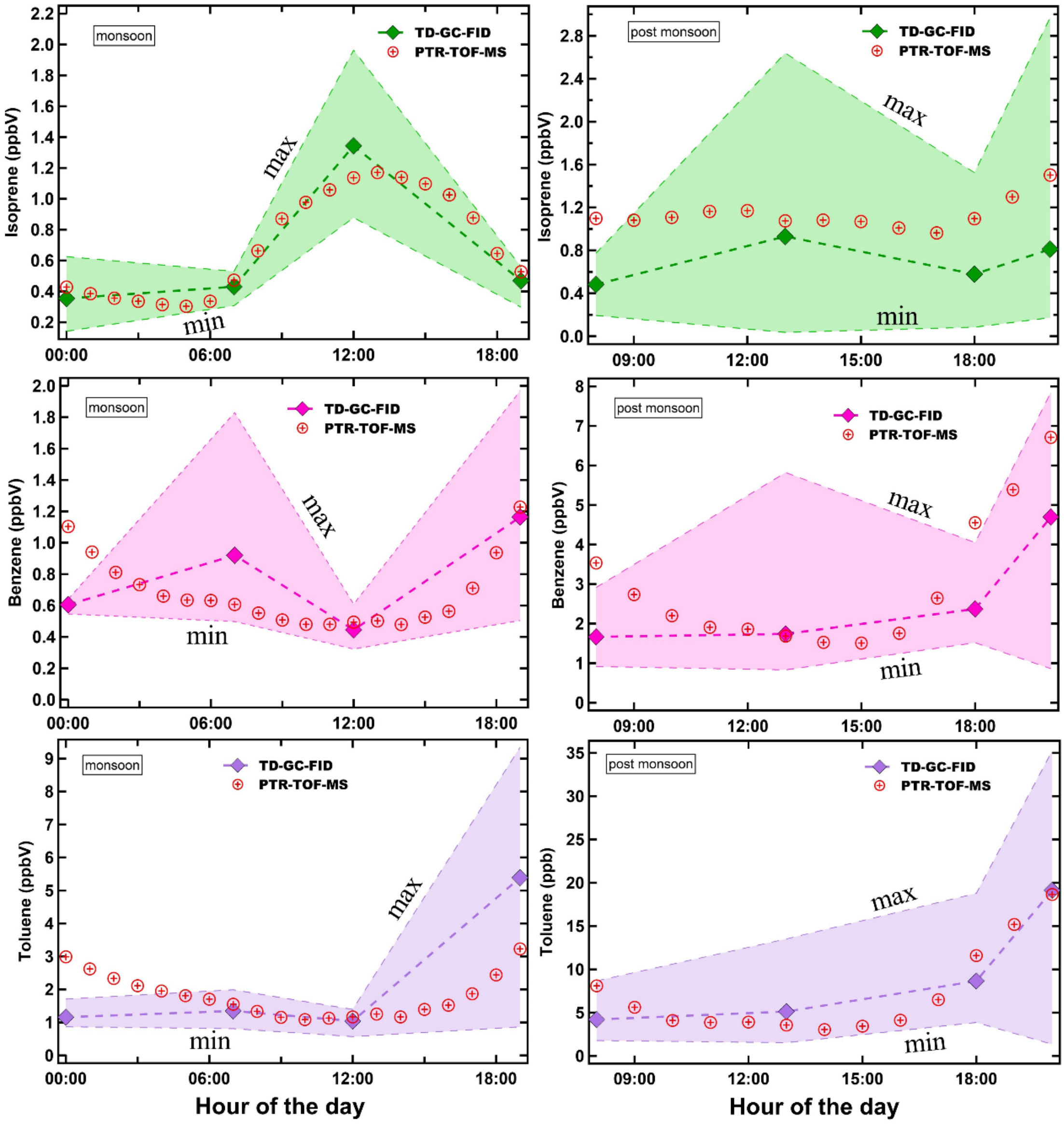
We agree wholeheartedly with the reviewer that fragmentation is an important issue that needs to be carefully considered while interpreting the mass assignments to specific compounds. We note that we considered known fragmentation issues and in Table S2 of the original submission, we also listed 8 of the 42 hydrocarbons that are likely to have significant contributions from fragment ions. This was based on the known fragmentations for the instrument operating conditions published previously in PTR-MS reviews, some of which (e.g. Yuan et al., 2017; Pagonis et al., 2019) we already cited in the original submission and is also mentioned in the reviewer's comment.

We thank the reviewer for drawing our attention to Coggon et al., 2024, which is a very valuable new study that sheds light on the impact of fragmentation on attribution of measured PTR-MS mass signals to important compounds like isoprene, toluene, benzene in atmospheric environments that are richly influenced by petrochemical industries and in specific urban environments. We also note that since our paper was submitted at the same time as Coggon et al. 2024 was finally published, we missed including it in our orginal submission and are grateful to the reviewer for pointing it out since including a discussion about its findings will help strengthen the new findings reported in the current study.

The suggestions and specific points are detailed below.

This includes isoprene, which can have substantial interference from higher aldehydes as well as substituted cyclohexanes (Coggon et al., 2024). Coggon et al. also described that the acetaldehyde mass is subject to interference from ethanol fragments, and benzene to fragments of other aromatics. I think the authors need to characterize their instrument's fragmentation at least for the most important compounds that they show diel plots for. The paper by Coggon et al. gives some pointers on how to correct for them, as well. Alternatively, if GC measurements were made at the same time, the authors could use those to identify compounds unambiguously.

We appreciate the reviewer's suggestions, especially since we also reported significant night time isoprene mixing ratios during the post-monsoon season, which may be surprising when compared to many ambient studies conducted in Europe and the USA, where isoprene is emitted primarily in the daytime from biogenic sources as a function of temperature and radiation. Besides considering the potential interferences due to fragmentation of higher molecular weight compounds as had already been flagged in previous PTR-MS reviews, we took additional measures to confirm the identity and diel profiles for the major compounds mentioned by the reviewer such as isoprene, benzene and toluene. Thus, during our campaign whole air samples were collected into 6 L passivated SilcoCan air sampling steel canisters (Restek) (Kumar et al., 2020; Vettikkat et al., 2020, Shabin et al., 2024) from the rooftop of the same building to measure isoprene, toluene and benzene using a thermal desorption gas chromatograph coupled to flame ionisation detectors (TD-GC-FID). Samples were collected during post monsoon season, four times a day [during start hourly intervals corresponding to 08:00, 13:00, 18:00, 20:00 local time; n=39] and during monsoon season also four times a day during the following hourly intervals [during start hourly intervals corresponding to: 00:00, 07:00, 12:00, 19:00 local time; n=15]. The results of the TD-GC-FID measurements in terms of season-wise hourly averaged values and corresponding minimum and maximum values observed for the same hourly interval are shown in the graph below alongwith PTR-TOF-MS data as reported in our original ACPD submission.



New Figure S7: Season-wise hourly averaged mixing ratios of isoprene, benzene and toluene measured using the TD-GC-FID are shown as diamonds and minimum and maximum values for that hourly sampling interval as shaded regions (in green for isoprene, pink for benzene and purple for toluene). The PTR-TOF-MS season-average mixing ratios values presented in Figure 4 are also shown for reference (red circles)

The above Figure has been added to the supplement with relevant details (new Figure S7) and the following accompanying text added to the main manuscript at Line 364 (ACPD version of pdf):

"The results of the TD-GC-FID measurements in terms of the season-wise hourly averaged values and corresponding minimum and maximum values observed for the same hourly interval alongwith the average PTR-TOF-MS values presented in Figure 4, are summarized in Figure S7. Even though the TD-GC-FID measurements present only a snapshot as the ambient sampling duration is shorter, the season-wise diel profiles are consistent with those obtained using the PTR-TOF-MS and the average mixing ratios obtained using the PTR-TOF-MS dataset also fall well within the range of mixing ratios observed using the TD-GC-FID. This provides further confidence in the high night-time isoprene observed during the post-monsoon season. The isoprene emissions at night during the post-monsoon season are likely due to combustion sources. Paddy residue burning and dung burning have the highest isoprene emission factors of ~0.2 g/kg (Andreae 2019) and more than 8 Gg of isoprene is released in the space of a few weeks during the post-monsoon season regionally from open paddy residue burning alone (Kumar et al., 2021). Previous studies from the region have also documented isoprene emissions from non-biogenic sources, which are active also at night (Kumar et al., 2020, Hakkim et al., 2021). In 2018 at another site in Delhi, using gas chromatography measurements made in pre-monsoon and post-monsoon, Bryant et al. 2023 reported average nocturnal mixing ratios of isoprene that were 5 times higher in the post-monsoon compared to the pre-monsoon and showed different diel profiles between the seasons. They found that the high night-time isoprene correlated well with carbon monoxide, a combustion tracer and suspected that in addition to the stagnant meteorological conditions, biomass burning sources could be a reason for the significant night time isoprene in Delhi in post-monsoon season and our findings using more comprehensive and high temporal resolution data further substantiate the surprising night-time isoprene.”

We also checked out the interferences mentioned in the valuable study by Coggon et al. 2024. As noted by Coggon et. al 2024 and in previous PTR-MS reviews, the interference at m/z 69.067 (at which isoprene is detected) due to fragment ions from other compounds depends on the instrument operating conditions (Townsend ratio), instrument design and the mixture of VOCs present in ambient air while co-sampling isoprene. Coggon et al. 2024 very nicely clarified both these aspects and found that when influenced by cooking emissions and oil and natural gas emissions and at higher Townsend ratios, these interferences can be quite significant and even account for upto 50% of the measured signal attributed to isoprene in extreme cases. As noted in Table S1 of the orginal submission, we operated the PTR-TOF-MS at 120 Td which minimizes fragmentation even when it occurs, compared to when operated at 135-140 Td. Secondly the type of restaurant cooking emissions present in Las vegas and emissions over Oil and Natural Gas petrochemical facilities in USA for which Coggon et al. 2024 reported the highest isoprene interferences, are absent/neglible in the atmospheric environment of Delhi. In the latter, open biomass burning sources such as paddy residue burning in post-monsoon season and garbage biomass fires that occur throughout the year are expected to play key roles. Even more specific GC based techniques have revealed that biomass combustion sources emit significant amounts of isoprene and furan. Our own supporting TD-GC-FID measurements alongwith those reported by Bryant et al. 2023 for post-monsoon season in Delhi, show that the night time isoprene in post-monsoon season is real. Concerning the interference on detection of acetaldehyde due to ethanol mentioned by the reviewer, we note that even in Coggon et al. 2024 this was reported to only be of significance in highly concentrated ethanol plumes such as those encountered on the Las-Vegas strip where ~1500 ppb of ethanol was present. On the contrary, in Delhi as noted in Table S2 of our orginal submission, ethanol values detected at m/z 47.076 were on average only 0.2 ppb (Interquartile range 0.16 ppb) during monsoon and 0.55 ppb (Interquartile range 0.5 ppb) in post-monsoon season, respectively whereas acetaldehyde detected at m/z 45.03 was 3.34 and 7.75 ppb during monsoon and post-monsoon season, respectively.

This gives us confidence that due to the different chemical environments, our attribution of isoprene, toluene and benzene in our PTR-TOF-MS data is accurate for Delhi.

Recognizing the importance of the potential interferences mentioned in Coggon et al., 2024 , which are important to clarify so as to provide confidence in the measurements reported in our work from Delhi, we now also add the following text which includes discussion of the potential interferences mentioned in Coggon et al., 2024 after line 250 (ACPD version of pdf):

“Fragmentation of certain compounds in specific atmospheric environments can cause significant interferences in the detection of major compounds like isoprene, acetaldehyde and benzene, as reported recently by Coggon et al., 2024. We checked these as well as an additional quality control measure. As noted by Coggon et al. 2024, isoprene can suffer significant interferences from higher aldehydes as well as substituted cyclohexanes, which can fragment and add to the signal at m/z 69.067 (at which protonated isoprene $C_5H_9^+$ is also detected). The magnitude depends on the instrument operating conditions (Townsend ratio), instrument design and the mixture of VOCs present in ambient air while co-sampling isoprene. Coggon et al. 2024 very nicely clarified both these aspects and found that when influenced by cooking emissions and oil and natural gas emissions and at higher Townsend ratios, these interferences can be quite significant and even account for upto 50% of the measured signal attributed to isoprene in extreme cases. We operated the PTR-TOF-MS at 120 Td which minimizes fragmentation even if it occurs, compared to when operated at 135-140 Td. Concerning the ambient VOC mixture and emission sources, we note that the type of restaurant cooking emissions present in Las Vegas and over Oil and Natural Gas petrochemical facilities in USA for which Coggon et al. 2024 reported the highest isoprene interferences, were absent/negligible at the study site in Delhi. In the latter, open biomass burning sources such as paddy residue burning in post-monsoon season and garbage biomass fires and traffic that occur throughout the year are more significant. Use of more specific though slower analytical techniques based on gas chromatography show that such biomass combustion sources emit significant amounts of isoprene (Andreae et al., 2019; Kumar et al., 2021). The above points and supporting TD-GC-FID measurements of isoprene, benzene and toluene (Fig S7) (data: Shabin et al., 2024), led us to conclude that such correction is unwarranted for our PTR-TOF-MS dataset. Concerning the interference on acetaldehyde detection due to ethanol, we note that even in Coggon et al. 2024 this was reported to only be of significance in highly concentrated ethanol plumes such as those encountered on the Las-Vegas strip where ~1500 ppb of ethanol was detected. On the contrary, in Delhi as listed in Table S2, ethanol values detected at m/z 47.076 were on average only 0.2 ppb (Interquartile range 0.16 ppb) during monsoon and 0.55 ppb (Interquartile range 0.5 ppb) in post-monsoon season, respectively, whereas acetaldehyde detected at m/z 45.03 was significantly higher at 3.34 and 7.75 ppb during monsoon and post-monsoon season, respectively."

References:

Coggon, M. M., Stockwell, C. E., Claflin, M. S., Pfannerstill, E. Y., Xu, L., Gilman, J. B., Marcantonio, J., Cao, C., Bates, K., Gkatzelis, G. I., Lamplugh, A., Katz, E. F., Arata, C., Apel, E. C., Hornbrook, R. S., Piel, F., Majluf, F., Blake, D. R., Wisthaler, A., Canagaratna, M., Lerner, B. M., Goldstein, A. H., Mak, J. E., and Warneke, C.: Identifying and correcting interferences to PTR-ToF-MS measurements of isoprene and other urban volatile organic compounds, Atmos. Meas. Tech., 17, 801–825, https://doi.org/10.5194/amt-17-801-2024 , 2024.

Andreae, M. O.: Emission of trace gases and aerosols from biomass burning – an updated assessment, Atmos. Chem. Phys., 19, 8523–8546, https://doi.org/10.5194/acp-19-8523-2019, 2019.

Shabin, M., Khatarkar, P., Hakkim, H, et al., Monsoon and post-monsoon measurements of 53 non-methane hydrocarbons (NMHCs) in megacity Delhi and Mohali reveal similar NMHC composition across seasons, Urban Climate, Volume 55, 101983, 2024.

Bryant, D. J., Nelson, B. S., Swift, S. J., Budisulistiorini, S. H., Drysdale, W. S., Vaughan, A. R., Newland, M. J., Hopkins, J. R., Cash, J. M., Langford, B., Nemitz, E., Acton, W. J. F., Hewitt, C. N., Mandal, T., Gurjar, B. R., Shivani, Gadi, R., Lee, J. D., Rickard, A. R., and Hamilton, J. F.: Biogenic and anthropogenic sources of isoprene and monoterpenes and their secondary organic aerosol in Delhi, India, Atmos. Chem. Phys., 23, 61–83, https://doi.org/10.5194/acp-23-61-2023, 2023.

Specific comments:

1. Title: I would recommend to change the title to "Observations of…" instead of "discovery of", since these compounds were not newly discovered but just observed in that location for the first time.

We appreciate the reviewer's comment. We had used the word discovery because although the compounds were reported previously, they have never been reported previously to occur collectively at the same site and that too under both clean (monsoon season) and extremely polluted conditions (post-monsoon season). The sources for each compound, namely methanethiol, dichlorobenzenes, C6-amides and C9-organic acids in the gas phase were also distinct pointing to industrial sources for the sulphur and chlorine containing compounds, photochemical source of the C6-amides and multiphase oxidation and chemical partitioning for the C9-organic acids. To our knowledge this is the first reported study world-wide to detect and observe only photo-chemically formed C6-amides in the gas phase.

Still heeding the reviewer1's and reviewer2's suggestion, we have now changed the title of the manuscript to :

"Reactive chlorine, sulphur and nitrogen containing volatile organic compounds impact atmospheric chemistry in the megacity of Delhi during both clean and extremely polluted seasons"

2. L 14 should be "COVID" capitalized

   Thank you for pointing this out. In the revised version the necessary change has been made.

3. L 22 why was this surprising? These compounds have been observed in other urban areas, so I do not find this surprising.

   We have removed the word "surprisingly", although to our knowledge, they have never been reported previously to occur collectively at the same site and that too under both clean (monsoon season) and extremely polluted conditions (post-monsoon season). The very limited prior reports are for individual compounds from different cities and mostly from source samples. It is also surprising that prior PTR-TOF-MS studies from Delhi (e.g. Jain et al. 2022; Wang et al., 2020) missed reporting these sulphur and chlorine compounds despite their unique isotope patterns that aid the identification.

4. L 33 should somewhere mention that Delhi is in India

   Thank you for the suggestion. We have added India to the relevant sentence.

5. L 72-73: FAME and NCR are unexplained abbreviations

   We appreciate the reviewer for pointing this out. These abbreviations have now been written in expanded form in the revised manuscript.

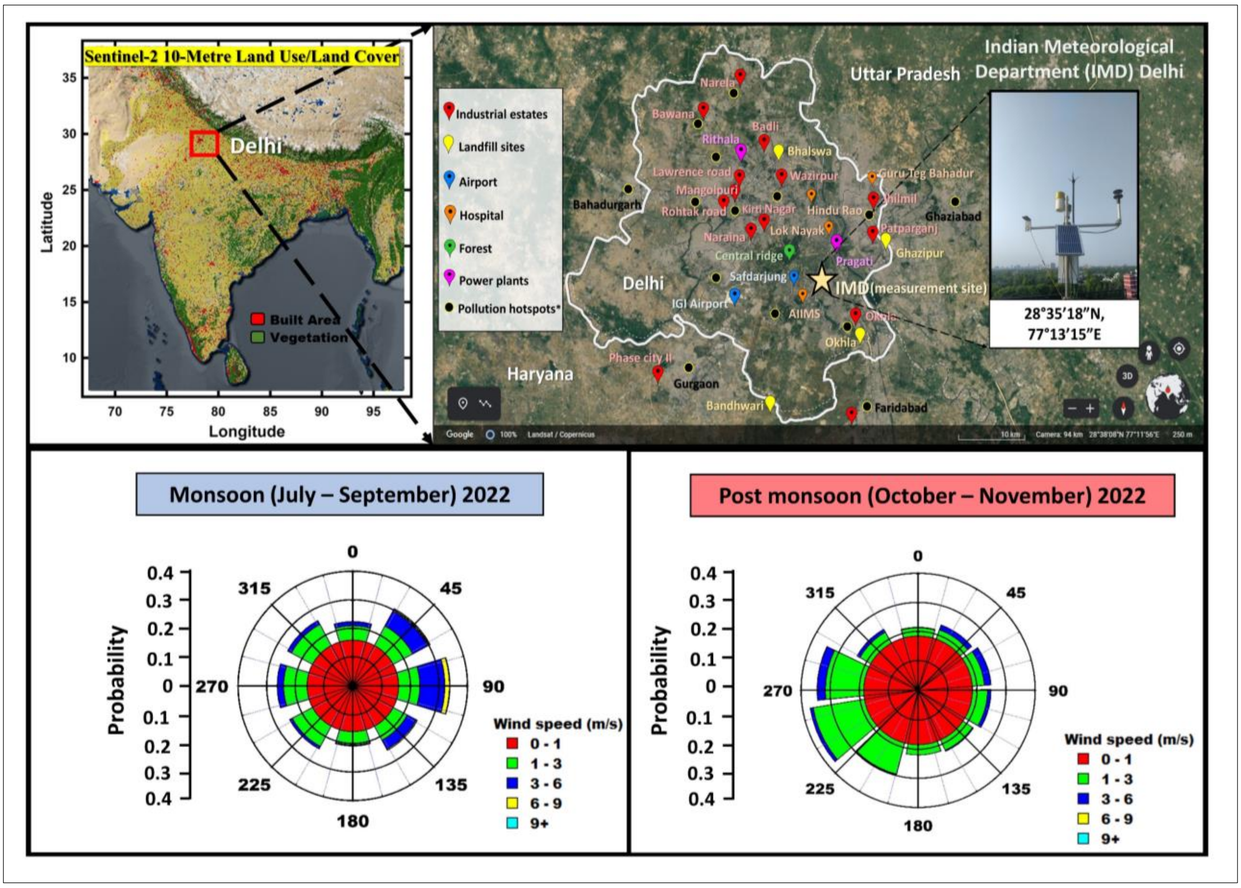
   Faster Adoption and Manufacturing of hybrid and Electric vehicles (FAME)

   National Capital Region (NCR)

6. Fig 1: a) the legend is illegible and b) the legend is too small

   We appreciate the reviewer's feedback. We revised Figure 1 and the legend font size has been changed to 18 to 14 in Fig 1.

Revised Figure 1 is shown below for easy perusal and been added to the revised submission.



7. Method section: Some more information of the inlet would be helpful. What was its length and diameter, was it heated for the whole length, what was the inlet residence time and flow rate?

   Thank you for the helpful suggestion. The length of the inlet line was 5m and it was made of Teflon (3 m 1/8inch O.D. and 2 m 1/4inch O.D). The total inlet residence time was ~2.7 seconds. The part of the inlet that was indoors (3 m of 1/8 inch O.D.) was heated to 80 degree Celsius throughout the study period. We think this short inlet residence time and heated inlet facilitated the detection of IVOCs, relative to previous studies. As mentioned in the manuscript, the outer inlet was protected by a Teflon membrane particle filter (0.2 µm pore size, 47 mm diameter) to ensure that dust and debris did not enter the sampling inlet.

   We have added the above additional information as new text after Line 170 (ACPD version of pdf):

   “The length of the inlet line was 5m and made of Teflon (3m 1/8 inch O.D. and 2m 1/4inch O.D). The total inlet residence time was ~2.7 seconds. The part of the inlet that was indoors (3 m of 1/8 inch O.D.) was well insulated and heated to 80 degree Celsius. We think this short inlet residence time and heated inlet facilitated the detection of IVOCs, relative to previous studies.”

   L 117: the verbal description of color symbols is not necessary, these should be legible in the legend. Why are hospitals shown? Are they VOC sources?

Thank you for the suggestion. We have removed the mention of colors from the main text now. The font size of the legends has also been increased from 14 to 18 to make it more legible.

The hospitals in the maps are retained based on previously published literature (Bessonneau et al., 2013; Riveron et al., 2023), which suggest that medical facilities can act as a source of VOCs (e.g., acetone).

References:

Bessonneau, V., Mosqueron, L., Berrubé, A., Mukensturm, G., Buffet-Bataillon, S., Gangneux, J.P., Thomas, O.:VOC contamination in hospital, from stationary sampling of a large panel of compounds, in view of healthcare workers and patients exposure assessment. PLoS One 8 (2), e55535, https://doi.org/10.1371/journal.pone.0055535, 2013.

Riveron, T.P., Wilde, M.J., Ibrahim, W., Carr, L., Monks, P.S., Greening, N.J., Gaillard, E. A., Brightling, C.E., Siddiqui, S., Hansell, A.L., Cordell, R.L.:Characterisation of volatile organic compounds in hospital indoor air and exposure health risk determination. Build. Environ. 242, 110513 https://doi.org/10.1016/j.buildenv.2023, 2023

8. L 179 this sentence is unnecessary and sounds again like an advert.

   In deference to the reviewer's suggestion, we have removed L179 from the revised version.

9. L 190 exchange "checked" with "compared"

   Thank you for your suggestion. We have replaced "checked" with "compared" in the relevant text.

10. L 199: What about fragments?

    We considered known fragmentation effects as well. The known fragments that were reported earlier at 120 Td, were considered and were mentioned in Table S2.

    In the revised version we make this more clear as also stated in the response to a related point made earlier by the reviewer by adding the following new text after L199 (ACPD version pdf):

    "The term "unambiguous" is used in the context of the accurate elemental composition/molecular formula assignment of the ions by leveraging the high mass resolution (8000-13000 over entire dynamic mass range) and detection sensitivity (reaching even 1 ppt or better for many ions; see Table S2) of the instrument. This enabled ensuring peaks due to expected isotopic signals were not construed as new compounds if their height was exactly as expected for a shoulder isotopic peak based on the natural abundance of isotopes of carbon, hydrogen, nitrogen, sulphur, chlorine and oxygen that made up the more abundant molecular ion. Where an ion could occur significantly due to fragmentation of another compound, the same has also been noted in Table S2 during attribution of the compound's name."

11. **L 208: Reproducible within how many %?**

    Thank you for the comment. We note that the drifts in sensitivity were accounted for by the regular calibrations but it was further re-assuring to observe that calibration results were reproducible and better than 15% for all compounds other than trimenthyl benzene (18.7%) and

dichlorobenzene (20.6%). So overall, the reproducibility across the 8 calibration experiments carried out during the measurement campaign was ~20%.
Reproducibility percentages were calculated using the standard deviation of the average of the eight calibration experiments and are shown for easy perusal in the Table below.

Protonated m/z	**Compound**	**Reproducibility %**
33.03	Methanol (CH_4O)	13.5
42.03	Acetonitrile ($C_2H_3N_1$)	2.7
59.046	Acetone (C_3H_6O)	7.3
69.067	Isoprene (C_5H_8)	10.2
79.052	Benzene (C_6H_6)	5.6
93.069	Toluene (C_7H_8)	9.7
107.085	Xylenes (C_8H_{10})	13.2
121.101	1,2,4-Trimethylbenzene (C_9H_{12})	18.7
146.977	Dichlorobenzene ($C_6H_4Cl_2$)	20.6

In the revised version we have added the following detail to Line 208 (ACPD pdf version) as follows:

"Results were reproducible (~21 % or better for all compounds) across all experiments ….."

12. **L 215: what is the overall uncertainty of the measured VOC concentrations? I assume it differs between compounds with a gas standard and compounds without one?**

Indeed. For compounds that were in the gas standard, the overall uncertainty calculated using the root mean square propagation of errors due to the accuracy of gas standard and flow controllers was ~13 % or better. For the rest of the compounds, it is estimated that the combined accuracy of the transmission function and the parameterized k-rates, put the overall uncertainty in the range of ±30% (Tobias et al., 2024). We have added this important information that was missing from the original submission and are grateful to the reviewer for drawing attention to it.

In the revised version we have added the following details after Line 215 (ACPD pdf version) as follows:

"The overall uncertainty calculated using the root mean square propagation of errors due to the accuracy of gas standard and flow controllers was ~13 % or better for compounds present in the VOC gas standard. For other compounds reported in this work, it is estimated that the combined accuracy of the transmission function and the parameterized k-rates, put the overall uncertainty in the range of ±30% (Reinecke et al., 2024)."

Reference:

Reinecke, T., Leiminger, M., Klinger, A., and Müller, M.: Direct detection of polycyclic aromatic hydrocarbons on a molecular composition level in summertime ambient aerosol via proton transfer reaction mass spectrometry, Aerosol Research, 2, 225–233, https://doi.org/10.5194/ar-2-225-2024, 2024.

13. fig 2: This is not a histogram, it is a bar chart?

    We regret the oversight. We have replaced “histogram” by “bar graph” in the Figure 2 caption.

14. L 249: Not just isomers, also fragments

    We agree and have added the following new sentence to reflect this in the revised version after L 249 (ACPD version of pdf):

    ”In addition, in some instances fragmentation of other compounds can complicate the compound attribution for a given ion.”

15. fig 3: I am not sure what information I am supposed to read from it, it is very small.

    We apologize for the inconvenience and have revised the Figure by increasing the font size from 12 to 14 as shown below:

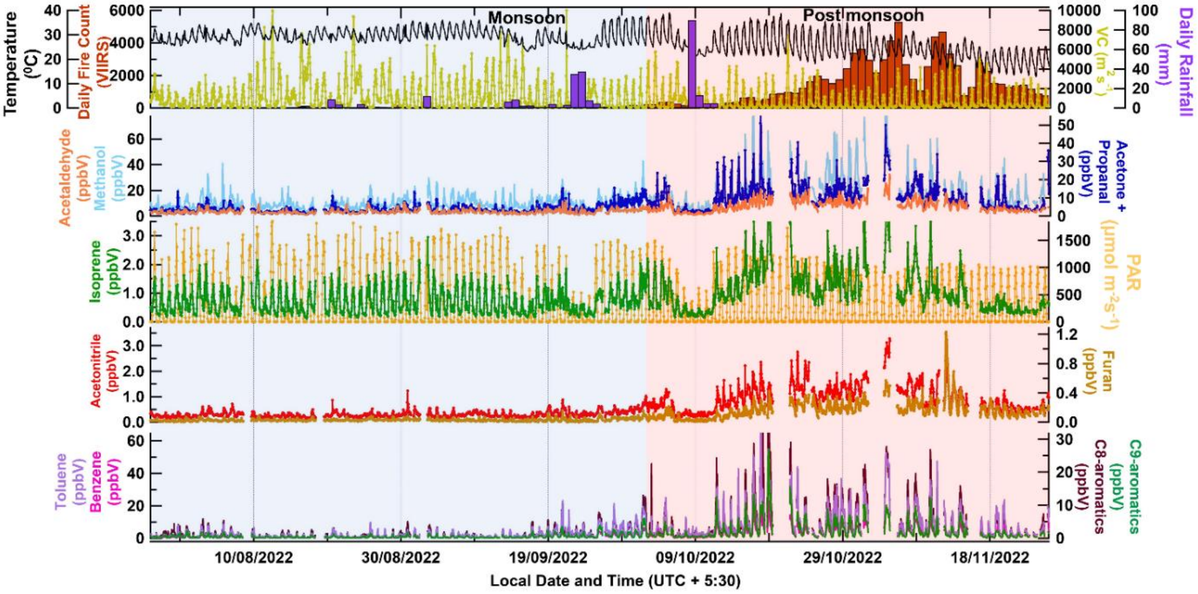


Fig 3 shows the time series of OVOCs (methanol, acetaldehyde, acetone+ propanal), Aromatics (toluene, benzene, sum of C-8 and C-9 aromatics), Isoprene (a biogenic chemical tracer), acetonitrile and furan (a biomass burning chemical tracer) along with meteorological parameters like Temperature, Photosynthetically active radiations (PAR), Daily rainfall; daily fire counts (VIIRS), and ventilation coefficient.

16. L 331: mention that these are diel averages.

    Ok. We have modified L 331 of the orginal version to reflect this as follows:

    "Figure 4 shows the *diel* box and whiskers plot *depicting the average, median, and variability (10th, 25th, 75th and 90th percentile)* of the same key VOCs like methanol, acetonitrile, acetaldehyde, acetone and propanal, furan, isoprene, benzene, toluene and C8 - aromatics for monsoon (derived from ~ 1704 data points, blue markers) and post-monsoon (derived from ~1368 data points, red markers) against the hour of the day (the horizontal axis represents the start time of the corresponding hourly bin)."

17. L 339 what does "CNG" stand for?

    CNG stands for Compressed Natural Gas.

    We now use the full form as well in the revised version to ensure clarity.

18. L 341: Why do traffic emissions "seem" to be a major contributor to acetaldehyde emissions? No reasoning is given.

    We regret that the reason was not mentioned clearly in the original submission. Actually in the preceding line where we cite Hakkim et al. 2021 for methanol from traffic emissions, the same work has shown that based on emission factor measurements of 74 VOCs from a range of Indian vehicle technology and fuel types, acetaldehyde was the fourth-highest emitted VOCs from traffic over India and petrol and diesel vehicles were major contributors. For convenience and easy perusal, we present the relevant figure below from Hakkim et al., 2021 which illustrates the same.

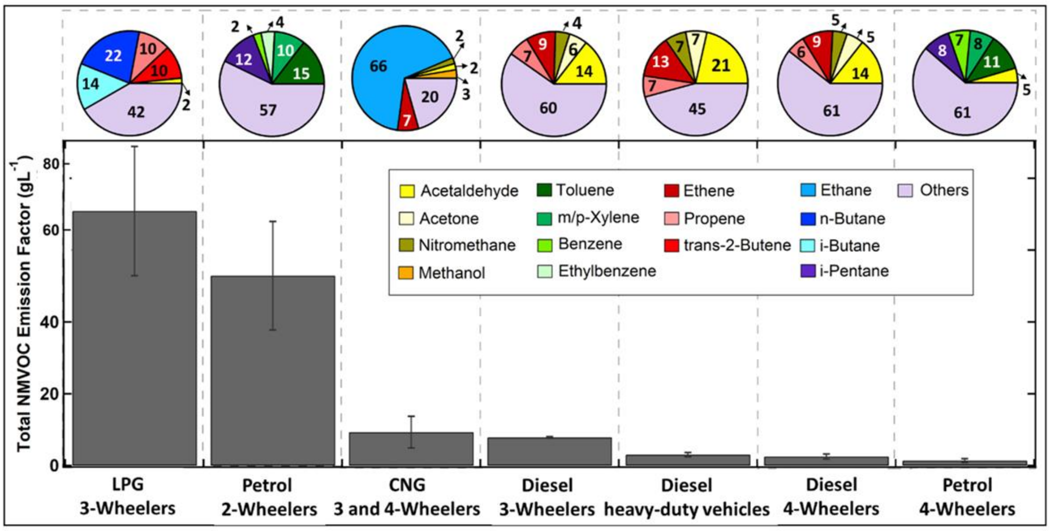


Fig. 1. Non-methane volatile organic compound emission factors (grams of NMVOC emitted per litre of fuel consumed) determined for different fuel and vehicle categories with contributions of the major 5 VOCs (selected based on their emission strength and reactivity) in percentage shown in the pie-charts. Error bars represent the standard error of averaged emission factor.

We have now revised the sentence as follows:

"Similarly, based on the correlation with toluene, traffic emissions seem to be a major contributor for acetaldehyde, acetone, sum of C8-aromatics and benzene in the morning and evening hours.

All these compounds are among the most abundant VOCs detected in tailpipe exhaust samples (Hakkim et al., 2021)."

References:

Hakkim, H., Kumar, A., Annadate, S., Sinha, B., and Sinha, V.: RTEII: A new high-resolution (0.1°× 0.1°) road transport emission inventory for India of 74 speciated NMVOCs, CO, NOx, NH3, CH4, CO2, PM2. 5 reveals massive overestimation of NOx and CO and missing nitromethane emissions by existing inventories, Atmos. Environ.: X, 11, 100118, https://doi.org/10.1016/j.aeaoa.2021.100118, 2021.

19. **L 346 and Fig. 4: The diel cycle of "isoprene" makes me strongly doubt that this is purely isoprene. Especially in the post-monsoon it is higher at night than during the day. This strongly indicates that there may be other compounds, e.g. cooking aldehydes, fragmenting on this mass (Coggon et al., 2024). As mentioned above, the authors should characterize their instrument's fragmentation especially onto C5H8H+. In FIg. 4: What does "VC" stand for?**

In Figure 4, VC stands for ventilation coefficient which is the product of the wind speed and boundary layer height. The lower the VC value, the more stagnant the conditions are, favouring accumulation of surface emissions within the boundary layer and leading to build-up of higher ambient concentrations.

We have now added the expanded form of VC beside the acronym in the Figure caption of Figure 4 in the revised version so that VC can be understood more clearly. Also in response to a suggestion by reviewer 2 the following text was added to the Methods section:

"Atmospheric ventilation or ventilation coefficient (VC) is a good proxy for the dilution and dispersion of air pollutants near the surface (Hakkim et al., 2019). It is defined as the product of boundary layer height (m) and wind speed (ms^{-1}). The VC represents the rate at which air within the mixed layer is transported away from a region of interest and provides information about how concentrations of pollutants are modulated through transport of air over that region."

Reference:

Hakkim, H., Sinha, V., Chandra, B. P., Kumar, A., Mishra, A. K., Sinha, B., Sharma, G., Pawar, H., Sohpaul, B., Ghude, S.D., Pithani, P., Kulkarni, R., Jenamani, R.K., and Rajeevan, M.: Volatile organic compound measurements point to fog-induced biomass burning feedback to air quality in the megacity of Delhi, Sci. Total Environ., 689, 295-304, https://doi.org/10.1016/j.scitotenv.2019.06.438, 2019.

The concerns pertaining to the night time isoprene have been addressed in detail while replying to the earlier general comments of the reviewer. The same are mentioned again for convenience.

We also checked out the interferences mentioned in the valuable study by Coggon et al. 2024. As noted by Coggon et. al 2024 and in previous PTR-MS reviews, the interference at m/z 69.067 (at which isoprene is detected) due to fragment ions from other compounds depends on the instrument operating conditions (Townsend ratio), instrument design and the mixture of VOCs present in ambient air while co-sampling isoprene. Coggon et al. 2024 very nicely clarified both these aspects and found that when influenced by cooking emissions and oil and natural gas emissions and at higher Townsend ratios, these interferences can be quite significant and even account for upto 50% of the measured signal attributed to isoprene in extreme cases. As noted in Table S1 of the orginal submission, we operated the PTR-TOF-MS at 120 Td which minimizes fragmentation even when it occurs, compared to when operated at 135-140 Td. Secondly the type of restaurant cooking emissions present in Las vegas and emissions over Oil and Natural Gas petrochemical facilities in USA for which Coggon et al. 2024 reported the highest isoprene interferences, are absent/neglible in the atmospheric environment of Delhi. In the latter, open biomass burning sources such as paddy residue burning in post-monsoon season and garbage biomass fires that occur throughout the year are expected to play key roles. Even more specific GC based techniques have revealed that biomass combustion sources emit significant amounts of isoprene and furan. Our own supporting TD-GC-FID measurements alongwith those reported by Bryant et al. 2023 for post-monsoon season in Delhi, show that the night time isoprene in post-monsoon season is real. Concerning the interference on detection of acetaldehyde due to ethanol mentioned by the reviewer, we note that even in Coggon et al. 2024 this was reported to only be of significance in highly concentrated ethanol plumes such as those encountered on the Las-Vegas strip where ~1500 ppb of ethanol was present. On the contrary, in Delhi as noted in Table S2 of our orginal submission, ethanol values detected at m/z 47.076 were on average only 0.2 ppb (Interquartile range 0.16 ppb) during monsoon and 0.55 ppb (Interquartile range 0.5 ppb) in post-monsoon season, respectively whereas acetaldehyde detected at m/z 45.03 was 3.34 and 7.75 ppb during monsoon and post-monsoon season, respectively.

This gives us confidence that due to the different chemical environments, our attribution of isoprene, toluene and benzene in our PTR-TOF-MS data is accurate for Delhi.

Recognizing the importance of the potential interferences mentioned in Coggon et al., 2024 , which are important to clarify so as to provide confidence in the measurements reported in our work from Delhi, we now also add the following text which includes discussion of the potential interferences mentioned in Coggon et al., 2024 after line 250 (ACPD version of pdf):

“Fragmentation of certain compounds in specific atmospheric environments can cause significant interferences in the detection of major compounds like isoprene, acetaldehyde and benzene, as reported recently by Coggon et al., 2024. We checked these as well as an additional quality control measure. As noted by Coggon et al. 2024, isoprene can suffer significant interferences from higher aldehydes as well as substituted cyclohexanes, which can fragment and add to the signal at m/z 69.067 (at which protonated isoprene $C_5H_9^+$ is also detected). The magnitude depends on the instrument operating conditions (Townsend ratio), instrument design and the mixture of VOCs present in ambient air while co-sampling isoprene. Coggon et al. 2024 very nicely clarified both these aspects and found that when influenced by cooking emissions and oil and natural gas emissions and at higher Townsend ratios, these interferences can be quite significant and even account for upto 50% of the measured signal attributed to isoprene in extreme cases. We operated the PTR-TOF-MS at 120 Td which minimizes fragmentation even if it occurs, compared to when operated at 135-140 Td. Concerning the ambient VOC mixture and emission sources, we note that the type of restaurant cooking emissions present in Las Vegas and over Oil and Natural Gas petrochemical facilities in USA for which Coggon et al. 2024 reported the highest isoprene interferences, were absent/negligible at the study site in Delhi. In the latter, open biomass burning sources such as paddy residue burning in post-monsoon season and garbage biomass fires and traffic that occur throughout the year are more significant. Use of more specific though slower analytical techniques based on gas chromatography show that such biomass combustion sources emit significant amounts of isoprene (Andreae et al., 2019; Kumar et al., 2021). The above points and supporting TD-GC-FID measurements of isoprene, benzene and toluene (Fig S7) (data: Shabin et al., 2024), led us to conclude that such correction is unwarranted for our PTR-TOF-MS dataset. Concerning the interference on acetaldehyde detection due to ethanol, we note that even in Coggon et al. 2024 this was reported to only be of significance in highly concentrated ethanol plumes such as those encountered on the Las-Vegas strip where ~1500 ppb of ethanol was detected. On the contrary, in Delhi as listed in Table S2, ethanol values detected at m/z 47.076 were on average only 0.2 ppb (Interquartile range 0.16 ppb) during monsoon and 0.55 ppb (Interquartile range 0.5 ppb) in post-monsoon season, respectively, whereas acetaldehyde detected at m/z 45.03 was significantly higher at 3.34 and 7.75 ppb during monsoon and post-monsoon season, respectively.”

References:

Coggon, M. M., Stockwell, C. E., Claflin, M. S., Pfannerstill, E. Y., Xu, L., Gilman, J. B., Marcantonio, J., Cao, C., Bates, K., Gkatzelis, G. I., Lamplugh, A., Katz, E. F., Arata, C., Apel, E. C., Hornbrook, R. S., Piel, F., Majluf, F., Blake, D. R., Wisthaler, A., Canagaratna, M., Lerner, B. M., Goldstein, A. H., Mak, J. E., and Warneke, C.: Identifying and correcting interferences to PTR-ToF-MS measurements of isoprene and other urban volatile organic compounds, Atmos. Meas. Tech., 17, 801–825, https://doi.org/10.5194/amt-17-801-2024 , 2024.

Andreae, M. O.: Emission of trace gases and aerosols from biomass burning – an updated assessment, Atmos. Chem. Phys., 19, 8523–8546, https://doi.org/10.5194/acp-19-8523-2019, 2019.

Shabin, M., Khatarkar, P., Hakkim, H, et al., Monsoon and post-monsoon measurements of 53 non-methane hydrocarbons (NMHCs) in megacity Delhi and Mohali reveal similar NMHC composition across seasons, Urban Climate, Volume 55, 101983, 2024.

Bryant, D. J., Nelson, B. S., Swift, S. J., Budisulistiorini, S. H., Drysdale, W. S., Vaughan, A. R., Newland, M. J., Hopkins, J. R., Cash, J. M., Langford, B., Nemitz, E., Acton, W. J. F., Hewitt, C. N., Mandal, T., Gurjar, B. R., Shivani, Gadi, R., Lee, J. D., Rickard, A. R., and Hamilton, J. F.: Biogenic and anthropogenic sources of isoprene and monoterpenes and their secondary organic aerosol in Delhi, India, Atmos. Chem. Phys., 23, 61–83, https://doi.org/10.5194/acp-23-61-2023, 2023.

L 377: Missing a “been” after “has”

Thank you for flagging the oversight.
We have added “been” after “has” in the main text.

20. L 388 the description of the instrument is a repetition that has already been given in the method section, also it again reads almost like advertising.

    In deference to the reviewer’s suggestion, we have removed L388 from the revised version as it is a repetition.

21. L 390: Why is this surprising? As the authors describe themselves, these compounds have been observed in many places before and can be expected in a megacity. I do not think the claim of the “surprise” is necessary for the paper.

    In our opinion, it is surprising because each of these compounds has a different primary source (industrial, photochemical , gas-aerosol partitioning), and although they have been observed individually in concentrated source samples at a few sites e.g. in Brazil, China and Russia and Korea, they have not been observed collectively at the same site in any other previous study and furthermore during both the clean (monsoon) and extremely polluted (post-monsoon) conditions. However we have removed the word surprising after heeding the reviewer’s comment.

22. L 411 a reference is missing for the deodorant and pesticide sources

    Thank you for pointing this out.

    We have now added relevant references to the main text in the revised version.

    References:

Chin, J.-Y., Godwin, C., Jia, C., Robins, T., Lewis, T., Parker, E., Max, P., and Batterman, S.: Concentrations and risks of p-dichlorobenzene in indoor and outdoor air, Indoor Air, 23, 40–49,https://doi.org/10.1111/j.1600-0668.2012.00796.x, 2013.

Bentley, R., Chasteen, T.G., Environmental VOSCs—formation and degradation of dimethyl sulfide, methanethiol and related materials, Chemosphere, https://doi.org/10.1016/j.chemosphere.2003.12.017 , 2004.

23. L 414-415 references missing

    We have now added the following relevant reference pertaining to use of methanethiol in methionine production to the main text in the revised version.

    Reference:

    François, J.M.:Progress advances in the production of bio-sourced methionine and its hydroxyl analogues, Biotechnology Advances, Volume 69, 108259, https://doi.org/10.1016/j.biotechadv.2023.108259, 2023

24. **L 419: Do the authors have any hypothesis of why dimethyl disulfide was not observed although it should be a major product?**

    Dimethyl disulfide has a very short atmospheric lifetime because of its high reaction rate constant ([1.98 ± 0.18] × 10^{-10} cm^3 $molecule^{-1}s^{-1}$) (Wine et al., 1981) with OH radicals. Although dimethydisulfide is the major product of the photo-oxidation of methanethiol, since methanethiol itself was on average only 48 ppt (monsoon) and 128 ppt (post-monsoon), we hypothesize that the ambient mixing ratios of DMDS were too low to be detected because based on the known yield of 50% (Wine et al., 1981) and its extremely short atmospheric lifetime, ambient levels would likely be below detection limit of the mass spectrometer at sites that are downwind of the source.

    We have added a sentence to clarify this in the revised version after L 419 as follows:

    "Dimethyl disulfide has a very short atmospheric lifetime spanning from 0.3 to 3 hours (Hearn et al., 1990), because of its high reaction rate constant ([1.98 ± 0.18] × 10^{-10} cm^3 $molecule^{-1}s^{-1}$) (Wine et al., 1981) with OH radicals. Although dimethydisulfide is a major product of the photo-oxidation of methanethiol (yield 50%; Wine et al., 1981), since methanethiol itself was on average only 48 ppt (monsoon) and 128 ppt (post-monsoon), and plumes occur only at night we hypothesize that the ambient concentrations of DMDS were too low to be detected by the mass spectrometer."

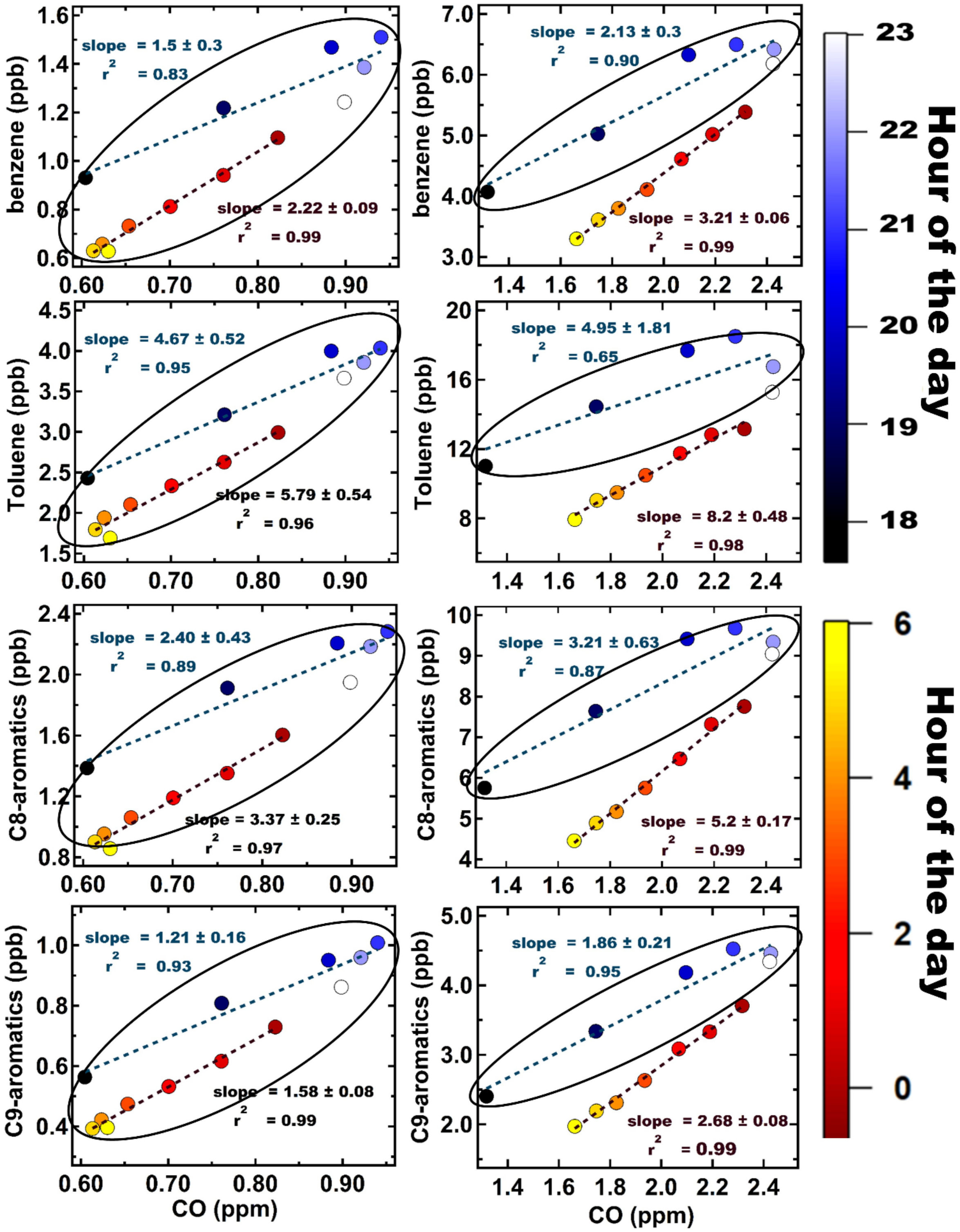
    Reference:

    Hearn, C. H., Turcu, E., and Joens, J. A.: The near U.V. absorption spectra of dimethyl sulfide, diethyl sulfide and dimethyl disulfide at T = 300 K, Atmos. Environ., 24A, 1939–1944, 1990.

    Wine, P. H., Kreutter, N. M., Gump, C. A., and Ravishankara, A. R.: Kinetics of hydroxyl radical reactions with the atmospheric sulfur compounds hydrogen sulfide, methanethiol, ethanethiol, and dimethyl disulfide, J. Phys. Chem., 85(18), 2660-2665, 1981.

25. fig 6: The plots make pretty clear that there are still two separate correlations in the monsoon time. I would suggest fitting these separately, and use the more similar slope between both as an argument for the discussion.

    Thank you for the helpful suggestion. We have now revised Fig 6 and use the more similar slope to make the argument about the influence of additional sources of these compounds during the post-monsoon season. We have also added new Figures to the supplement which present the wind rose for these compounds for the same nighttime data from which the emission ratios were derived, which show that stronger influence of plumes during the post-monsoon season relative to the monsoon season can atleast partially explain the reason for the statistically different emission ratio observed during the post-monsoon season in Fig 6.
    Revised Figure 6 is now shown below:



New wind rose plot added to the supplement is shown below:

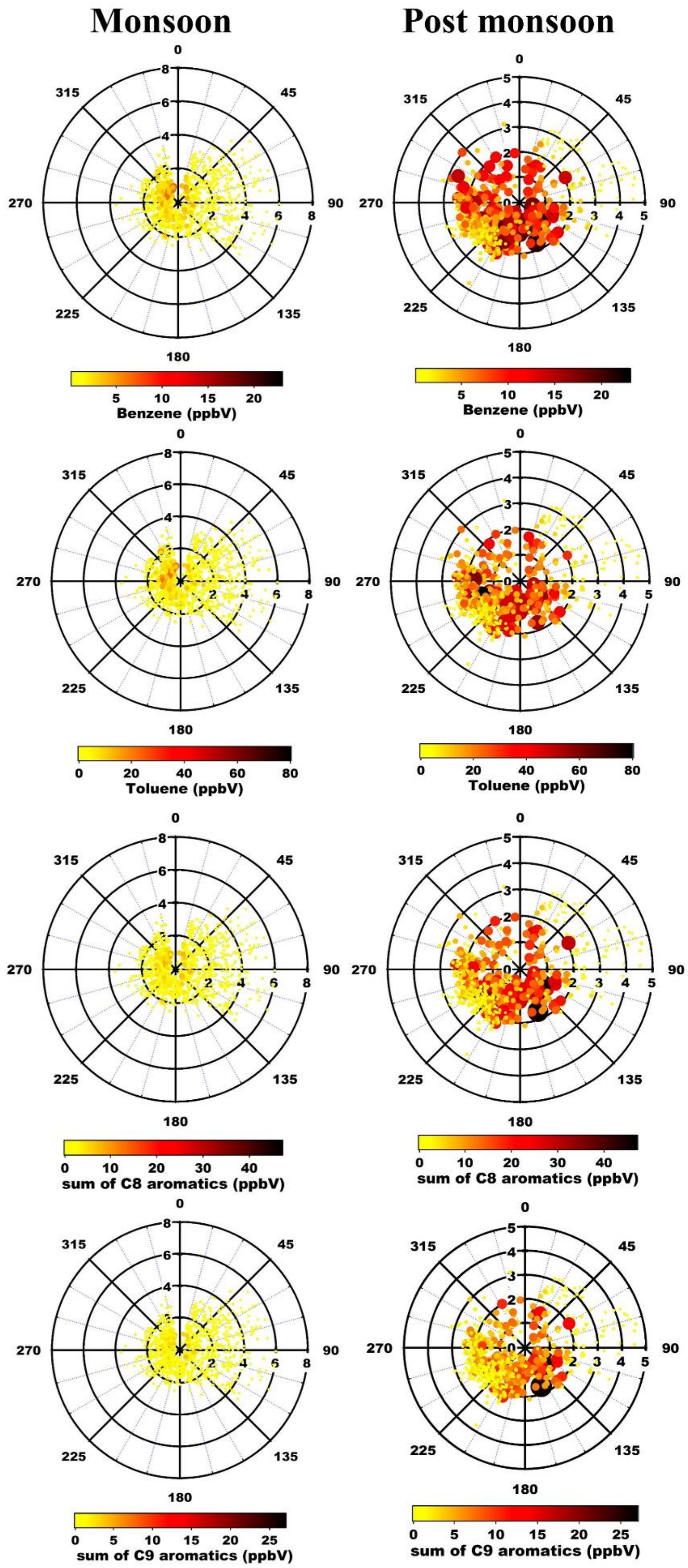


Figure S8 Wind rose of night-time benzene, toluene, C8 and C9 aromatic compounds at the receptor site during monsoon (left column) and post monsoon (right column) season

The discussion after L 582 (per original ACPD version) has also been completely rewritten and strengthened as follows:

"It can be noted from Fig. 6, that during the monsoon season (from 18:00 to 23:00 and 00:00 to 06:00 local time) and post-monsoon season (18:00 to 23:00), the observed emission ratios as inferred from the slopes and fits are not statistically different from each other (all highlighted by oval circles) with values for benzene/CO, toluene/CO, sum of C8-aromatics , sum of C9-aromatics/CO in the range of 1.2-2.43, 3.14-6.76, 1.97-3.84, and 1.05-2.07, respectively. All these emission ratios fall within the range of what has been reported for typical petrol 2 and 4 wheeler vehicles in India in tail pipe emissions (Hakkim et al., 2021). For the monsoon season, although two linear fits are observed from 18:00 to 23:00 and 00:00 to 06:00, the values of the emission ratios as inferred from the respective slopes for all compounds overlap or are very close to each other and within the uncertainties for all compounds. We hypothesize that the two fits are due to the change in relative numbers of 2 wheelers and 4 wheelers. In the post-monsoon season however, for the time period in the second half of the night (00:00-06:00), the emission ratios derived from the slopes are statistically different from the ones observed in monsoon season and the first half of night in post-monsoon season (18:00-23:00). When we examined the wind rose plots for the same night-time data of the aforementioned compounds for each season (Figure S8), we noted that during the post-monsoon season more pollution plumes from the south east sector which has industrial facilities and the north west sector (a major fetch region for biomass burning plumes from regional paddy residue burning in Punjab and Haryana) occurred. During the post-monsoon season due to dip in temperatures at night, the heating demand (Awasthi et al., 2024) and associated open biomass burning (Hakkim et al., 2019) also goes up, relative to the monsoon period nights. Hence overall we think that these additional sources in the post-monsoon season, do add to the burden of these mainly traffic emitted aromatic compounds and could help explain atleast partially the higher emission ratios observed during the post-monsoon season (00:00- 06:00), wherein values for benzene/CO, toluene/CO, sum of C8-aromatics , sum of C9-aromatics/CO values range from 3.15-3.27, 7.72-8.68, 5.03-5.37, 2.6-2.76, respectively, and are statistically different from the others (ones marked by oval circles)."

26. Table 1: **Are the reported values really emission ratios or enhancement ratios? The emission ratio would depend on the distance from the source and the photochemical processing that has happened in between emission and observation. How to calculate emission ratios from ambient observations is described in (Gouw et al., 2017). Real observed emission ratios from flux observations in urban areas are shown in the SI of (Karl et al., 2018)**

The ones shown within parantheses in Table 1 are emission ratios , not enhancement ratios.

We note that we had already perused the valuable work of de Gouw et al., 2017 and even cited the same in the same section. We took care to calculate the emission ratios using only night-time data when chemical loss of these compounds is negligible as their main oxidation occurs through OH radicals during daytime, as also noted by de Gouw et al., 2017. Further, the other studies referred to in Table 1 for comparison also reported emission ratios derived using nighttime data.

Although the caption of Table 1 in original submission mentioned the same as under :

"Table 1: Comparative summary of the average mixing ratio (ppb) and Emission Ratios of VOC/ CO (ppb/ppm) of Delhi (in parentheses) with other megacities of Asia, Europe and North America."

Based on the reveiwer's comment, we see merit in clarifying this further in the text in the revised version.

Hence the following new text has been added after L 515 (original ACPD version) to make the above more clear:

"It may be further noted that we took care to calculate the emission ratios using only night-time data when chemical loss of these compounds is negligible as their main oxidation is through OH radicals during daytime, as also noted by de Gouw et al., 2017. Further, the other studies referred to in Table 1 for comparison, have also reported emission ratios derived using only nighttime data."

Reference:

de Gouw, J. A., Gilman, J. B., Kim, S.-W., Lerner, B. M., IsaacmanVanWertz, G., McDonald, B. C., Warneke, C., Kuster, W. C., Lefer, B. L., Griffith, S. M., Dusanter, S., Stevens, P. S., and Stutz, J.: Chemistry of Volatile Organic Compounds in the Los Angeles basin: Nighttime Removal of Alkenes and Determination of Emission Ratios, J. Geophys. Res.-Atmos., 122, 11843– 11861, https://doi.org/10.1002/2017JD027459 , 2017.

27. L 530 ff: The discussion of enhancement ratios needs to take into account the different lifetimes of the aromatics. Therefore, a different enhancement ratio can be the result of different photochemical processing/oxidant levels.

We note that these are emission ratios and not enhancement ratios and that by using night time data only, the issue of complications due to daytime photochemical loss is inconsequential. Further, if we consider night time oxidation due to nitrate radicals, the reaction rate constant with NO_3 radicals is of the order of 10^{-15}-10^{-17} $cm^3 molecule^{-1} s^{-1}$(McGillen et al; 2020), rendering nighttime loss very slow to affect the source emission ratios within a few hours of transport time.

The reaction rate constant of OH and NO_3 radicals with benzene is 1.20×10^{-12} $cm^3 molecule^{-1} s^{-1}$ and 3.01×10^{-17} $cm^3 molecule^{-1} s^{-}$ (McGillen et al; 2020; Atkinson et al., 1991)

The reaction rate constant of OH and NO_3 radicals with toluene is 5.6×10^{-12} $cm^3 molecule^{-1} s^{-1}$and 6.6×10^{-17} $cm^3 molecule^{-1} s^{-1}$ (McGillen et al; 2020)

The reaction rate constant of OH and NO_3 radicals with ethylbenzene is 7×10^{-12} $cm^3 molecule^{-1} s^{-1}$ and 6.38×10^{-17} $cm^3 molecule^{-1} s^{-1}$ (McGillen et al; 2020; Sabljic et al., 1990)

The reaction rate constant of OH radicals with 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene are 3.27×10^{-11} $cm^3 molecule^{-1} s^{-1}$, 3.25×10^{-11} $cm^3 molecule^{-1} s^{-1}$ and 5.95×10^{-11} $cm^3 molecule^{-1} s^{-1}$ at 298K (McGillen et al., 2020)

The reaction rate constant of NO_3 radicals with 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene are 3.1×10^{-15} $cm^3 molecule^{-1} s^{-1}$, 2.7×10^{-15} $cm^3 molecule^{-1} s^{-1}$ and 1.6×10^{-15} $cm^3 molecule^{-1} s^{-1}$ at 298K (McGillen et al., 2020)

References

Atkinson, R.: Kinetics and mechanisms of the gas-phase reactions of the nitrate radical with organic compounds, J. Phys. Chem. Ref. Data, 20, 459, 1991.

McGillen, M. R., Carter, W. P. L., Mellouki, A., Orlando, J. J., Picquet-Varrault, B., and Wallington, T. J.: Database for the kinetics of the gas-phase atmospheric reactions of organic compounds, Earth Syst. Sci. Data, 12, 1203–1216, https://doi.org/10.5194/essd-12-1203-2020 , 2020.

Sabljic, A., & Güsten, H. (1990). Predicting the night-time NO3 radical reactivity in the troposphere. Atmospheric Environment. Part A. General Topics, 24(1), 73-78 https://doi.org/10.1016/0960-1686(90)90442-P 1990 .

28. L 534: Does "ER" stand for enhancement ratio here?

    ER stands for emission ratio here. We now clarify "When we peruse the emission ratios (ER)…"

29. L 552: again, the claim of "surprising" is not supported by previous literature and is also not necessary for the manuscript.

    Thank you for the feedback.
    In our opinion, it is surprising because each of these compounds has a different primary source (industrial for dichlorobenzene, photochemical for hexanamide , gas-aerosol partitioning for C9- organic acid), and although they have been observed near point sources individually at separate sites in Brazil, China and Russia and Korea, they have not been observed collectively at the same site in any other previous study and furthermore under both clean (monsoon) and extremely polluted (post-monsoon) air conditions. Also, earlier PTR-TOF MS studies in Delhi (Wang et al. 2020, Tripathi et al. 2021, Jain et al. 2022) missed these compounds.
    We have now clarified this as follows:
    "The detection of new compounds that have previously not been discovered in Delhi's air, under both the clean and polluted periods such as methanethiol, dichlorobenzenes, C6-amides and C9-organic acids in the gas phase was very surprising, considering there have been several PTR-TOF MS studies earlier (Wang et al., 2020; Tripathi et al., 2022; Jain et al., 2022). Our data points to both industrial sources of the sulphur and chlorine compounds, photochemical source of the C6-amides and multiphase oxidation and chemical partitioning for the C9-organic acids."

30. L 564: Why? Some more discussion would help.

    Thank you for the helpful suggestion.

    We have added the following additional discussion after L 564 (ACPD pdf version) as follows:

    "Overall, for many important aromatic VOCs, the levels measured in Delhi were even higher (> 5 times) than many other megacities of the world located in Europe and North America. Generally these aromatic compounds in megacities are primarily due to traffic and industrial emission sources, and this source is of course common to Delhi and megacities in Europe and North America. In Delhi, the highest ambient mixing ratios of these aromatic compounds occurred in the post-monsoon season. This is the period when enhanced open biomass burning occurs due to heating demand increase owing to dip in temperatures (Hakkim et al., 2019; Awasthi et al., 2024) and open fire emissions due to the seasonal post-harvest paddy stubble biomass burning in which more than 1 billion ton of biomass is burnt regionally (Kumar et al., 2021) within few weeks during mid October to end of November occur. This adds significantly to the atmospheric burden of these compounds, compared to megacities in developed countries where open biomass burning is better and more strictly regulated. Secondly, the meteorological conditions during post-monsoon season due to shallower boundary layer height and poor ventilation, and lack of wet scavenging due to absence of rain also slow down atmospheric removal of these compounds compared to megacities in Europe, wherein it rains more frequently throughout the year compared to Delhi."

Data availability: The data policy of ACP clearly states that data needs to be publicly available on a repository with a DOI. Availability upon request is no longer enough. (https://www.atmospheric-chemistry-and-physics.net/policies/data_policy.html)

Thank you for the suggestion. We agree and the data presented in manuscript will be publicly available as a Mendeley dataset as per the new data policy of ACP.

The data availability statement has been updated in the revised version.