

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

Sachin Mishra et al. 2024

We thank the editor and reviewers for their kind comments on the revised version. Below, please find point-wise replies to the minor remaining reviewers' comments. We hope these revisions are now adequate for the manuscript to be accepted in ACP.

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

I thank the authors for their thorough review of the manuscript, and I think the current version is greatly improved. There are just two very minor points that I would like to see revised.

We thank the reviewer for deeming the revised submission to be greatly improved!

There are just two very minor points that I would like to see revised.

1) In their response to my comment no. 29 (L.552/ L. 759 in the new manuscript version with tracked changes), the authors revised their text 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."

a) The authors should refrain from "discovered" and instead use the more neutral word "observed". (Similarly, the heading of section 3.4 should be revised. I would be happy with the wording "first observation in Delhi" but the connotation of "discovery" is for me the first time in the world.)

b) "there have been several PTR-TOF-MS studies earlier" should be clarified as meaning studies in Delhi.

c) I am missing a hypothesis as to why previous studies have not seen these compounds. Could it be that they were measured but not reported (after all, not everyone reports or identifies all peaks detected) - maybe due to improvements in analysis software? Or could it be that the location or year caused differences in the nearby emission sources? I assume the previous studies were done in different places in Delhi. Are any of the reported potential sources nearby the measurement location in this study?

Reply: Out of regard for the reviewer's minor comments in 1a and 1b above, we have revised the relevant text which now reads as follows:

“The detection of new compounds that have previously not been observed 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 in Delhi 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.”

Concerning the hypothesis on why previous PTR-TOF-MS studies did not report these compounds, as highlighted in our detailed replies to reviewer 2. We are mentioning the main ones below for convenience.

We think the previous PTR-TOF-MS studies had significant limitations in terms of quality control of the dataset as well as some technical limitations of the instruments used (all were PTR-TOF-MS 8000).

For example in Jain et al., 2022, the background measurements to correct for instrument background were performed using a dry zero-air cylinder only every 2 weeks. Given how dirty the ambient air in Delhi can get, such a frequency may not always account for changes in instrumental background. In our work we collected the instrument background every 30 min for 5 min as stated in the original submission (L 171-173). Further no information was provided by Jain et al. (2022) concerning the overall uncertainty and detection limits of the measured compounds that could not be calibrated. They used a generic proton transfer reaction rate of  $2 \times 10^9 \text{ cm}^3 \text{ s}^{-1}$  for compounds that were not in the calibration standard. All the previous works used a PTR-TOF-MS 8000, the mass resolution of which was at best ~5000 and detection limits even for the calibrated compounds were in the range of 40 ppt to 250 ppt, based on information about the instrument as reported by the authors (Sahu and Saxena, 2015; Sahu et al., 2017). Finally their mass spectral assignment had issues e.g. extensive assignments of  $^{13}\text{C}$  isotopic peaks of hydrocarbons to reduced nitrogen compounds were made, which can be perused from the works and also as pointed out in our replies to the queries raised by reviewers during the interactive discussion.

In terms of technical limitations of the PTR-TOF-MS instruments deployed in those previous works the following pertinent to note:

The PTR-TOF-MS 10000 deployed in our work had significantly better detection limits (reaching even 0.3 ppt for some compounds) and significantly higher mass resolution (8000-13000) which enabled us to detect and resolve the isotopic peaks for many compounds, thus providing an additional parameter for identification and quantification of methanethiol, C6-amide, dichlorobenzene and C-9 organic acids. It is unlikely that they did not detect the compounds because of site differences, because one of them was actually deployed in the same campus and same building of IMD as our deployment. We can also rule out local emission source because we did not observe high values of methanethiol and dichlorobenzene only at low wind speeds but rather from a specific fetch region which is known to have multiple industries and is located east and south of the measurement site.

2) In L. 645 the revised paper mentions the "insightful study by Salvador et al.". I think that, although Salvador et al. would surely be delighted by this assessment, judgments like "insightful" should be refrained from in a scientific paper.

Thank you for the comment. We agree and have now removed the adjective “insightful” from the relevant sentence in the newly revised version.

## Response to Anonymous referee #2

Comment: The authors still failed to respond properly to reviewer 2, specific comment#7 regarding the "increasing" baseline of some of the VOCs indicated in figure 3. The authors should consider applying a baseline correction procedure that will reduce the baseline into zero to low signal, thus providing accurate concentration of the VOCs.

Thank you for the comment. The relevant comment#7 of reviewer 2 is being reproduced below for convenience again:

Comment #7. Figure 3: “The baseline concentrations of some VOCs were evidently different for both monsoon and post-monsoon seasons. An obvious example is the isoprene, particularly during mid-October when baseline concentration is increasing even at nighttime while a clear flat baseline is observed during clean monsoon. The same insights can be applied to acetonitrile and acetaldehyde. Any possible explanation? Does this impact the measured concentration between the two periods?”

We regret that our previous reply was not clear to the reviewer. Here we would like to reiterate that these are not chamber measurements, where while measuring the same matrix, instrumental backgrounds can result in shifting of baseline values but measurements made in ambient air. Further:

- 1) We can rule out completely that a shifting “instrumental” baseline has any effect on the ambient profile time series shown in Figure 3, which have been carefully corrected for any changes in the “instrumental background” through stringent quality control. As stated previously in the manuscript (original submission (L 171-173), in our work we collected the instrument background every 30 min for 5 min and the reported VOC mixing ratios have been “background” subtracted. Furthermore, in response to the reviewer’s concern we also showed how low the instrument backgrounds typically were in Fig S3 of the revised supplement using the 2 min averaged data.
- 2) The reason for higher “baseline” values in the time series of Fig 3 during the polluted post-monsoon season is the increased ambient pollution due to enhanced biomass burning emissions and reduced ventilation coefficient in the polluted post-monsoon season. This leads to an increase in the regional nighttime background values of compounds co-emitted by biomass burning such as isoprene, acetaldehyde and acetonitrile. These have already been justified by comparison with complementary TD-GC-FID measurements of isoprene and toluene and benzene in addition to the PTR-TOF-MS in the revised manuscript.

We hope the above conclusively clarifies the concern of reviewer 2.

### References:

Jain, V., Tripathi, S.N., Tripathi, N., Sahu, L.K., Gaddamidi, S., Shukla, A.K., Bhattu, D., and Ganguly, D.: Seasonal variability and source apportionment of non-methane VOCs using PTR-TOF-MS measurements in Delhi, India, *Atmos. Environ.* 283, 119163, 2022. <https://doi.org/10.1016/j.atmosenv.2022.119163>, 2022.

Sahu, L.K., Saxena, P., 2015. High time and mass resolved PTR-TOF-MS measurements of VOCs at an urban site of India during winter: role of anthropogenic, biomass burning, biogenic and photochemical sources. *Atmos. Res.* 164–165, 84–94. <https://doi.org/10.1016/j.atmosres.2015.04.021>.

Sahu, L.K., Tripathi, N., Yadav, R., 2017. Contribution of biogenic and photochemical sources to ambient VOCs during winter to summer transition at a semi-arid urban site in India. *Environ. Pollut.* 229, 595–606. <https://doi.org/10.1016/j.envpol.2017.06.091>.