Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2020-11-RC1, 2020

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Source characterization of volatile organic compounds measured by PTR-ToF-MS in Delhi, India" *by* Liwei Wang et al.

Anonymous Referee #1

Received and published: 26 March 2020

The authors present measurements of volatile organic compounds (VOCs) using two proton transfer reaction time of flight mass spectrometers (PTR-ToF-MS) at an urban and suburban location in New Delhi in the wintertime. The positive matrix factorization (PMF) model is used to apportion various VOCs to different sources for each site. The authors find that six VOC factors could explain the observations for both sites, two factors related to traffic emissions, two to solid fuel combustion, and two secondary factors. The authors do a good job justifying the naming conventions for each factor at each site. However, it would be beneficial if these discussions were extended to back trajectory comparisons for the two sites, and comparisons to previous publications. Also, further discussion regarding VOCs excluded from the analysis (all masses above m/z 60) or not measured (alkanes, alkenes) that could dominate the VOCs mass, and

reactivity should be performed. This manuscript is suited for publication in ACP after the above revisions.

Specific comments

The authors could run a PMF combining the two datasets in one Matrix to generate common solutions. This way a possibly better statistical separation of the factors between the two sites could be achieved. Also, when comparing the two sites it would be great if a back-trajectory analysis could be performed in order to support that emissions from the city center travel from IITD to MRIU and therefore represent more aged air.

Line 143: How much of the total mass, and reactivity do these masses represent? Also, there are more m/z's not included in the mass list chosen for PMF like formic acid, ethanol, formaldehyde, and other masses related to fragments below m/z 60. These masses may represent the majority of the reactivity and should be further discussed, especially in the context of quantifying the effect of each emission source. I consider that results from the PMF when including the lower molecular weight compounds should at least be presented in detail in the SI and further discussed in the main text.

Line 164: The time that the temperature is higher from 21-25 Feb the VOCs are not measured at MRIU. Could the authors provide a box and whiskers of the temperature for the two periods? Also, for both periods, could they provide the temperature changes only when VOC measurements exist? This goes for Fig. S1 too. Could they provide the 25th and 75th percentile for Fig S1?

Line 180: What about comparing the absolute concentrations. Do these masses show the same diurnal patterns at the two sites? Please elaborate more.

Line 182-190: It will be more informative to include all the diurnal profiles for (i) the different VOC families, (ii) NOx, and (iii) CO for both sites in a supplementary figure.

Line 230: Here and throughout the text, it will be nice if the authors add for each chemical formula the actual m/z of detection in order for the readers to connect it better to the Figures.

Line 234: Please perform a more detail comparison to NOx. What is the R2 of (i) traffic1 vs NOx, (ii) traffic2 vs NOX, and (iii) traffic1+traffic2 vs NOx?

Line 237: this trend could also be driven by meteorology. A higher boundary layer leads to more dilution therefore a decrease of pollutants midday.

Line 238-243: The differences discussed between traffic1 and traffic2 are not supported by the figures. Traffic1 is in general higher than traffic2 even during nighttime when traffic2 is supposed to dominate the traffic emissions due to the heavy-duty vehicles. Also, the diurnal profiles of the two factors are very similar. The only difference is an increase of traffic1 midday that could also be due to the influence of other sources to traffic1, e.g. cooking. Please discuss more in the main text and provide more proof for the naming of these factors. Comparing to other studies of traffic emissions using PTR-ToF-MS could be of value, e.g. Gentner, et al. (1).

Line 243-245: This would be the dominant VOC source based on the VOCs included in the PMF analysis. It would be beneficial to include a discussion of the VOCs not included in the PMF analysis, especially smaller alkanes and alkenes that could substantially contribute to the total VOCs.

Line 246-270: The SFC factors can be further compared to previous studies in more detail. Sekimoto, et al. (2) found a high- and low-temperature factor related to biomass burning emissions. The factors found in this study are available to the public and could, therefore, be used to directly compare to this study.

Line 292-293: Define “similar”, e.g. within XX% for XX% of the masses. Masses that are higher should be discussed.

Line 308-327: The discussion of the oxygenated factors and the comparison of the two sites in this paragraph is hard to follow.

Line 264: Anthropogenic monoterpenes can also originate from fragranced volatile chemical product usage. Emissions from fragrances and personal care products have been found to coincide with traffic emissions (3, 4) which would explain why the monoterpenes are loaded in the traffic factor. Further discussion on this topic may be of interest.

Line 374-375: This sentence doesn’t make sense.

Line 376-377: More detailed comparison of the results of this study to previous studies is required. For example, what is the ratio of the oxygenated compounds relative to aromatics for previous studies and this study?

Line 406-407: Give numbers. It is a 50-50 split between traffic and SFC emissions for the majority of the time.

Line 409: At MRIU it is again a 50-50 split. Precise discussion of the differences with numbers will be great in this paragraph.

Line 412-414: No discussion on toluene that is different than benzene is provided. Toluene is attributed predominantly to traffic at both sites. Wouldn’t the authors expect toluene emissions from biomass burning based on existing literature cited in this manuscript? A detailed comparison of the ratios of aromatics to different studies may be of value here.

Line 463-466: A discussion on the missing VOCs should be performed if the comparison of the different emissions is made. What is the contribution in mass, and reactivity of the missing VOCs? How is it expected to distribute among the different emission sources based on inventories?

Comments on Figures Figure 5-6: Add error bars to the diurnal profiles. If it gets too busy split into two figures. A way to better focus on the differences in the factors from the two sites could be to plot the following: Traffic1(IITD) – Traffic1(MRIU) / Traffic1(MRIU) VS m/z This will better show the relative difference between the two. Now differences between many masses that are low in concentration but could still be important markers are not shown at all. Why is it that for Figure 6 the two oxygenated factors from both sites are not included? Why not extend figure 5 and add the two oxygenated factors there?

Figure 6: Label is missing the triangle markers explanation. It will also be better to add the SecVOC factors for both sites in this comparison.

Figure 8: Add suggested compounds in parenthesis.

Technical comments

Line 19: Explain abbreviation “IITD”. Line 21: Explain abbreviation “MRIU”. Line 36: Change to “gas-to-particle partitioning”. Line 69: Change to “of the VOC pollution levels” Line 77: Maybe add the number of VOCs used for PMF since you already discussed what has been used in the literature before. Line 145: Define “extremely”. Line 169: How would they have an impact on the emission profiles? Please elaborate. Line 205: Maybe rephrase. Sentence too long and hard to follow. Line 211: delete “was resolved”. Also, define reasonable. What is the contribution of hydrocarbons in the secondary factors? Line 216: A graph providing the comparison of the different spectra in the SI will be more informative. Fig S4 is not informative regarding the comparison of the different a-value results. Line 291: delete “that”. Also, why would the change in concentrations result in a better factor separation? Please, elaborate. This sentence is in general not easy to follow. Based on which figure are the authors concluding this? Line 247-248: What is the meaning of the chemical formulas written here? Line 293: Delete “very”. Line 311: Delete “very” and define how different. Line 351: Provide m/z and chemical formula for the broader audience. Line 354: Change to “alcohols”. Line 357: Delete “very”. These values are low only compared to the primary anthropogenic emissions but a considerable value for biogenic emissions. Line 369: Delete “in”. Line 385: Replace “by” with “but can”. Line 399: Replace to “of the low”.

Line 418: Please give a number for “majority”. Line 419: replace “mainly” with “by XX% and XX% during the night and morning, respectively,”. Line 446: Please support with back trajectory. Line 468-469: Please support with back trajectory.

References

1. Gentner DR, et al. (2013) Chemical Composition of Gas-Phase Organic Carbon Emissions from Motor Vehicles and Implications for Ozone Production. Environmental Science & Technology 47(20):11837-11848. 2. Sekimoto K, et al. (2018) High- and low-temperature pyrolysis profiles describe volatile organic compound emissions from western US wildfire fuels. Atmos. Chem. Phys. 18(13):9263-9281. 3. Coggon MM, et al. (2018) Diurnal Variability and Emission Pattern of Decamethylcyclopentasiloxane (D5) from the Application of Personal Care Products in Two North American Cities. Environmental Science & Technology 52(10):5610-5618. 4. McDonald BC, et al. (2018) Volatile chemical products emerging as the largest petrochemical source of urban organic emissions. Science 359(6377):760-764.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2020-11, 2020.