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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Enhancement of biogenic emissions of VOCs in the semi-arid region of India during winter to summer transition period: Role of meteorological conditions" *by* Nidhi Tripathi and Lokesh Kumar Sahu

Anonymous Referee #3

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General comments:

The paper entitled "Enhancement of biogenic emissions of VOCs in the semi-arid region of India during winter to summer transition period: Role of meteorological conditions" by Tripathi and Sahu reports PTR-TOF-MS measurements of monoterpenes from a city in India during the period 1.02.2014 to 31.03.2014 and concluding that biogenic emissions increased in the transition from winter to summer. I was excited to see the title and new dataset but after going through the present manuscript and previous cited PTRTOFMS works by the same group, I realized a similar dataset (or

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same dataset except for the monoterpene data shown here with similar sounding title "Contribution of biogenic and photochemical sources to ambient VOCs during winter to summer transition at a semi-arid urban site in India" has already been published in the journal Environmental Pollution in 2017. The authors cite this work in the present submission where they state they used benzene and isoprene as supporting data (Lines 143) but I could not find any discussion of novelty upon the previous dataset expect for reporting signals measured by the authors at m/z 137. What was more disconcerting about the submission is that the main methods and analyses presented in the work are seriously flawed (please see specific comments below for results and discussion section).

The present manuscript lacks a cohesive structure, makes tall claims not backed by hard evidence and has loose statements. It is riddled with claims that are at times even illogical. For example by simply having a rise in ambient temperatures and presence of some vegetation, one cannot attribute increase in monoterpenes to rising biogenic emissions in an atmospheric environment which has perhaps even stronger anthropogenic sources of monoterpenes (from varied types of biomass burning such as garbage fires and leaf litter burning to name a few). The so called quantitative methodology applied by the authors which assumes terpenes to be biogenic emissions and relies on inter VOC ratios to benzene, a molecule that has much longer chemical lifetimes relative to the terpenes and hence higher accumulation tendency is deeply flawed for application in such a complex emission environment. The authors highlight that the PTR-TOF-MS system enabled them to acquire highly mass resolved measurements. However the information and analyses they have presented concerning monoterpenes in the work nowhere makes use of this instrumental advantage and infact the information they show is even less well analysed than that acquired using a lower mass resolution PTR-MS. They do not use the high mass resolving power to unravel monoterpenes fragmentation to even speculate on the indentity of the monoterpenes and do not even discuss the major fragment at m/z 81, which most monoterpenes like alpha pinene yield in a PTR-MS system. This is poor use of the instrumentation. Disturbingly

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the data quality control description also does not provide sufficient confidence that the measurements performed by the authors were done carefully and hence can be trusted, and are reliable.

The novelty of getting new data from a poorly sampled region on monoterpenes could have been the saving grace but even on this point concern about the quality of measurements and lack of novelty of the dataset in view of the previous published dataset puts a question mark on the utility of this work. The conclusion of increase in biogenic emissions and the title (highly misleading!) are not at all justified by the work presented in the manuscript. These points are elaborated using specific instances in the manuscript. Unfortunately considering the overall poor quality of the submission publication of the manuscript in ACP is not recommended.

Specific comments:

Introduction:

It is not well focused. Literature review of previous work is incomplete. For example in Line 89-90: The authors omit several important previous works (e.g. Sinha et al. 2014, Atmos Chem Phys) that have published isoprene data from India previously using PTR-MS including reporting the presence of strong biogenic and anthropogenic isoprene emitting sources, which highlighted that the city environments in South Asia are complex emission environments. These issues are therefore important to consider while using single molecular tracers in a quantitative manner as has been done by the authors.

Section 2: Measurement site Measurement site and PTR-TOF-MS instrumentation

Lines 100: It is clearly mentioned that car exhaust is a major source influencing the site, however subsequent analyses ignores this confounding influence on BVOC emissions as this source could explain most of the observed monoterpenes and isoprene.

Lines 110: Authors list some major tree species found in the area but do not describe

whether they are only monoterpene emitters or both isoprene and monoterpene emitters. If they are implicating such vegetation by using such leading remarks then why has isoprene only been reported superficially and just for MT/isoprene ratio calculations in this work?

Line 115: What about the role of agricultural emissions? Line 120: This information is useful but does not exclude the likelihood of anthropogenic sources in the city from combustion of varied biomass sources that are also upwind of the measurement site and closer to it mixing in additional terpene and VOC emissions.

Line 134: What good is high mass resolution of PTR-TOF-MS in this work when used to report only one ion, which is blindly ascribed to monoterpenes without any scrutiny? Also some monoterpenes can fragment and yield signals at m/z 79 (benzene? How have the authors accounted for such an effect if any? This is particularly critical as they use benzene signal as a purely anthropogenic tracer ! Line 137-139: Levels reported in the work are lower than 3 ppb so what good is knowing precision error at the such high values?

What about measurements to determine the instrumental background? How often were zeroes done? This is very important to know considering that lowest levels claimed to have been reported in the work were below 30 ppt. How were detection limits determined?

Line 141-143: Then why have the details and data for isoprene and benzene not been shown in same manner as the monoterpene data? Such fragmented approach to data usage and analysis is not desirable and encourages piecemeal approach to science.

Results and discussion:

Line 151: Weak winds were associated with higher mixing ratios. . .this could also be explained by more proximate anthropogenic sources like the road rather than transport of biogenic emission from the more distant forest. . ..

Line 160-161: Municipal waste burning (see Stockwell et al. Atmos Chem Phys 2015) can also co-emit the terpenes and benzene. . .hence these cannot be used as exclusive tracers as the authors have done so . . ..Also owing to different chemical lifetimes (hours to minutes for monoterpenes and isoprene and several days for benzene) the following assertion by the authors is not tenable: "However, to some extent, the ratio of monoterpenes to benzene (an 160 anthropogenic tracer) can take account of variations due to change in local meteorology and PBL"

Lines 161-163 and Table 1: "Hourly monoterpenes/benzene ratio exhibits large periodic variation which tends to follow the diurnal cycle of temperature. Monoterpenes/benzene ratio showed slightly increasing trend with average values of 0.19±0.03 and 0.26±0.07 ppbv ppbv-1 during first and second halves of February, respectively."

The explanation linking higher temperature in March and increased MT/benzene ratios to increased biogenic emissions is deeply flawed. The ratio does not have to increase just because of numerator's value increasing..in fact it can also increase if denominator decreases and numerator stays constant! Benzene mixing ratios could very well decrease because the open biomass burning that occurs in winter for domestic heating by people without access to clean energy sources may have reduced in intensity during the transition from winter to summer due to warmer conditions. . .in fact this seems more likely based on the site description and city population than the attribution to biogenic sources. . . Why have the authors not reported and shown the one minute (they have highly time resolved data) benzene, isoprene, monoterpene, acetonitrile and MT data and its average mixing ratios on same axis for the full period? These would have been helpful to gauge what was really going on. From Figure 2 also looking at the available data it is clear that this is the more likely reason for increase in MT/benzene ratios.

As the basic premises and assumptions on which the further calculations and analyses have been presented (e.g. Figure 9) are unsound, the authors' conclusion and findings are deeply flawed.

Note from Copernicus Publications: The last sentence of this comment has been removed on 13 December 2019 on request by the ACP executive editors.

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