Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2020-1108-RC1, 2021

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Long-term measurements (2009–2015) of non-methane hydrocarbons (NMHCs) in a megacity of China: implication for emission validation and source control" *by* Yarong Peng et al.

Anonymous Referee #2

Received and published: 8 January 2021

The authors present an analysis of long-term VOC measurements in Shanghai. The main results are that ambient mixing ratios of alkanes showed an increasing trend, while aromatics and acetylene decreased. Alkenes did not reveal a trend. According to a PMF analysis emissions from vehicles, petrochemical industry and solvent use decreased, while emissions of natural gas and evaporation increased. Those results appear to be non-consistent with the emission inventory. In terms of O3 formation the authors state that decreasing VOC concentration would yield lower O3 forming potential, even more important for Shanghai as O3 formation would be in a VOC limited

regime in that area.

When I first saw the paper I found it interesting, but when I read the supporting text materials my concerns grew and I had the impression that the conclusions the authors were drawing were not always well justified. I provide my detailed comments below. Apart from that I have been frustrated at times to see citations in the text without listing appropriate references, which is just bad. The use of English language in this paper is often poor and sometimes difficult to decode. It needs polishing.

Page 2, L28: "... of which composition varied significantly". I only saw that ethane and alkenes changed significantly (see Fig. 1 and associated discussion).

Page 2, L28-30: This statement cannot be done as long as biogenic VOCs, foremost isoprene are not considered.

Page 3 L72-77: At some point the authors say the measurement site was 15 m above the ground, then at some point they say the site was at a five-story building. I somehow assume the site was on the rooftop of that building. However, I am not so much interested in how many stories a building would have, but I would rather be interested in what height the building would have and - assuming the site was on the rooftop - what the height of the sampling inlet above the rooftop was, and whether the rooftop had any outlet ducts. I neither saw the citation of Wang et al., 2016 nor Liu et al., 2019 in the list of references. What Wang et al., 2020 paper are the authors referring to, as in the list of references there is Wang et al., 2020a and Wang et al., 2020b....? The last sentence of this paragraph is very generic and vague: what do the authors consider "at a large enough temporal scale"?

Page 3 L79: There have been many auto-GCs in use in the world for decades. Why is this GC in particular a "high-performance" instrument?

Page 4, L81-82: Still, I want to know briefly some standard information about the specifications of the traps, their temperature during preconcentration, the duration of preconcentration, the GC columns and the carrier gas used. Also, what sampling line (material, diameter, length) was used? Chromatograms for each channel should be shown.

Page 4 L83-84: Here the authors refer to Text S1. So I add my comments about Text S1 here as well. What specific VOCs were in the calibration gas? At what concentration were the single-point calibrations done? Apart from that it is not correct that using single-point calibration ensures the stability of the instrument. I do not understand the last sentence in the first paragraph ("Then...later years"). The authors state "...concentrations of most species measured agreed well with standard gas". How do the authors know this when actually the standard gas is used for calibration? The uncertainty should be calculated for each VOC individually and not for a group of VOCs.

Page 4, L86-87: I cannot see in Table 2 that the responses of most species agree well with the standard. In fact many VOCs show slopes well below 1, in particular alkenes, foremost 1,3 butadiene, which is well-known for potential losses in GC preconcentration.

Page 4, L88: Data cannot be "efficient".

Page 4, L91-93: How can a trap be "out of work" for acetylene, while it is still properly working for all the remaining VOCs for an entire year? While it is true that acetylene shows challenges in GC analyses, I find it very astonishing/inconsistent that according to table S2 acetylene shows pretty good values for precision and accuracy. At this point I cannot follow at all the authors' statement in L91-93.

Page 4, L95-105: Here the authors refer to Text S2 and Text S3. So I add my comments about Text S2 and Text S3 here as well. Text S2: I understand that the VOC data in the analysis of this paper has been corrected for meteorology. So why then can the authors make statements about evaporation processes (which depends on temperature) and regional transport (which would depend on wind) later on in the text, e.g. as shown in Figure S6 and other places in the paper?

Text S3: Equation 3-2 was derived for a rural area and in their paper Ehhalt and Rohrer (2000) point out that the coefficients should only be used for that specific rural airmass composition. Why do the authors think that equation 3-2 would be applicable the same way for the highly polluted area of the megacity Shanghai? I do not agree with the authors that Figure S5 shows insignificant trends of chemical loss for NMHCs over seven years. Just looking into L-Alkanes I would assume an overall increase by an order of 30% or so, while L-Alkenes show an overall decrease by about 25%. Also, L-Aromatics and L-Acetylene show high interannual variability, albeit no visible longterm trend. Apart from that I find it quite surprising to see an overall positive trend in OH concentrations (I would guess on the order of 30-50%), which the authors do not comment on at all.

The sentence "While the oxidation of NO3...neglected in this study" is irrelevant as this study did not include biogenic VOCs, anyway.

The comparison analysis in the last paragraph does not mean anything as the "whole-day" data would obviously include nighttime data as well.

Page 4, L108-112: I do not understand a couple of things here: In the first place, I do not see an appropriate definition of uncertainty for individual VOCs here. Anyway, assuming accuracy as shown in Table S2 as a proxy for uncertainty I do not understand why the authors kept VOCs with appreciable uncertainty for the PMF analyses (e.g. ethane, i-butane, n-butane, n-pentane, m/p-xylene) while they stated they wanted to remove VOCs with high uncertainty. Also, they state they wanted to remove VOCs with high reactivity, while they kept highly reactive ethylene, propylene, and m/p-xylene. Also, the authors state that they wanted to keep source tracers. If they knew what the source tracers were why would they need to perform a PMF analysis in the end? Would this a priori assumption not already induce some bias per se? Also, why did the authors not include acetylene, a well-known combustion/vehicle exhaust marker (e.g. Leuchner and Rappenglueck, 2010). The authors state that those selected 16 VOCs contributed > 75% of the total NMHCs together. What basis did they use for this percentage, i.e. concentration, mixing ratio, ppbC or something else?

Page 5, L154-157: I do not agree on this (see my comments above on Text S3).

Page 5, L168: "The contribution of species...". Contribution to what?

Page 7, L211-216: This is not conclusive as long as biogenic VOCs, foremost isoprene are not considered.

Page 7, L226-229: I am not completely convinced about those statements on the T/B ratio. This ratio could also have changed due increased traffic emissions and/or changes in the traffic fleet (gasoline vs diesel, for instance). From Table S4 I see that in fact toluene decreased more than benzene over those years. However, I also see that xylenes - also typical tracers for solvents as toluene, - decreased way less than toluene or benzene.

Page 8, L236-257: This entire section is entirely based on the assumption that acetylene can be used as "...a marker for urban emissions". I doubt this. As mentioned earlier acetylene is a great tracer for combustion processes. It would not necessarily show up in appreciable amounts in other "urban emissions" like LPG or evaporation (again see for instance Leuchner and Rappenglueck, 2010).

Page 8, L264: I do not completely agree about the statement of little month-to-month variations; November and December data significantly stick out.

Page 8, L267-268: I do not agree. Propane has about the same kOH and ethane actually has a kOH which is about four times less than for benzene.

Page 8, L269-272: I thought the VOC data was corrected for meteorology. Why is there a dependence on temperature and wind? Also, if there is "heavy pollution" why would this only show up in three VOCs? In this case absolute values should be shown along with a definition what the authors would consider "heavy pollution".

Page 9, L273-274: What would be those "more indicative species"?

Page 9, L280-283: Again, with regard to petrochemical industry I suggest that the authors refer to Leuchner and Rappenglueck (2010).

Page 9, L286-287: Again, I thought the VOC data was corrected for meteorology.

Page 11, L349-352: This is not supported by the data shown in the paper, as Figure S5 does show changes and important VOCs like isoprene were not considered.

Figures S3: Datasets cannot be efficient. Also, what does the percentage exactly refer to?

Table S4: Are those VOC mixing ratios arithmetic means or medians? It would be helpful to include percentiles as well.

Table S6, last column: Contributions to what?

Reference:

Leuchner M. and Rappenglueck B. (2010): VOC Source-Receptor Relationships in Houston during TexAQS-II, Atmos. Environ., 44, 4056-4067, doi:10.1016/j.atmosenv.2009.02.029

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