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Comment on acp-2022-116

Anonymous Referee #1

Referee comment on "Variations and sources of volatile organic compounds (VOCs) in urban region: insights from measurements on a tall tower" by Xiao-Bing Li et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-116-RC1, 2022

Li. et al. presents observations of volatile organic compounds (VOCs) collected from ~450 m above ground level in Guangzhou, China, from mid-August to early-November. The authoers were able to identify ~225 species using the Vocus PTR-MS. There were other measurements on the tower, including meteorology, CO2, O3, NO, NO2, NOx, and PM2.5; as well as, measurements of VOCs at a ground site ~5.7 km away from the tower and ceilometer for boundary layer height ~13.5 km from the tower. The authors look at both diurnal pattersn and positive matrix factorization to identify sources of the VOCs, which include daytime-mixed, visitor-related, vehicular+industry, regional transport, and VCP-dominated. Also, the authors used autocorrelation to further identify the sources (which I found to be very informative). The authors use the PMF results to show the source contributions of the VOCs observed at the tower. Finally, they look at the profiled measuremend of NOx, O3, and PM2.5 to look at the boundary layer dynamics throughout the measurement period and potential for residual layer vs nocturnal boundary layer chemistry.

As the authors noted, there are minimal measurements of VOCs at an elevated location (important for boundary layer dynamics and to look at regional background vs near-term sources), especially in China. That fact makes this paper of interest and importance for ACP. There are some aspects the authors could do to improve the paper, which I provide below, prior to publishing the paper in ACP.

1) Further clarification in methods, specifically in the sampling.
1a) The authors noted that their was ~5 m long and was "extended to the outside wall of the observation room." However, it is not clear if this line is sampling inside the tower or outside the tower. This aspect is important for clarification in other points presented below.
1b) Was the sampling line heated or tested for potential losses of lower volatility / oxygenated species? There are some high molecular weight and/or oxygenated species that may have experienced lost.
1c) Further description of the observation level would be beneficial to understand the

results presented. E.g., are the windows open or is the observation level "leaky"? If the line is sticking outside the tower (1a, unclear), it is surprising to see the "visitor-contribution" (more on that below). Thus, description about the observation level would be beneficial.
1d) How was the data smoothed or extrapolated for the 3-D vertical profiles in Fig. 9? A description of that in Sect. 2.3 would be beneficial.

2) Something either in Sect. 3.1 or later that would be beneifical would be the OH-reactivity (and maybe even NO3-reactivity as some of this is later discussed in the context of residual layer chemistry) contribution of the compounds observed. As the authors note in line 606 - 609, though VCPs contributed a smaller amount of mixing ratio, some high reactivity compounds were in that class. As the combination of mixing ratio and reaction rate dictates the importance of the compound to urban chemistry, seeing how the classes weight out in reactitivity space would be of great benefit.

3) Currently, Fig. 2 is too busy to interpret well and follow along with the authors' argument. What would be more informative would be to highlight the compounds that show XX difference between ground and elevated platform measurements (e.g., 50%, factor 2, or somethin else). Though seeing "family" (which is different than PMF) is informative, know which compounds are different can be equally important.

4) Fig. 3 and potentially other diurnal plots. Sometimes it's difficult to discern the differences the authors mention in the diurnal profiles eithere between ground-level and tower or working vs non-working. I would strongly recommend either as a figure in the main paper or a supplemental figure showing the ratios of these compounds and if they are statistically different or not.

5) Source analysis of the VOCs. It is surprising that authors are seeing such a large source of ethanol and CO2 from visitors (comment 1c). It would be of use to better understand why this source is so large (is it due to experimental set up); whereas, e.g., they do not observe much VOCs from cooking when there are restaurants in the lower levels of the tower. Further, though the visitor profile is different from the VCP-dominated source, I would still recommend the authors be a little more cautious in this discussion. E.g., what the authors call the visitor-related compounds are also compounds that can generally be "VCP" in nature. Though it is a local source, it contributes/impacts the VCPs mixing ratio and chemistry.

6) I'm very suprised by the fractional contribution pie chart in Fig. 7 vs the time series fractional contribution. E.g., it appears that visitor-related is typically on order 5-10% with maybe the observations in October being greater than 20% while daytime-mixed is the largest contributor during most of the study. Not sure if it is howing the data is being weighed/average.

Minor

1) The authors use the word "significantly" or "significant" throughout the text. I would strongly recommend the authors use a different word when there is a difference unless they have conducted statistical analysis (e.g., Student's T-Test) to determine if there is significan difference.

2) Another statistics aspect to be careful in includes when the authors look at the r values and state that it is well correlated. E.g., an r value of 0.62 (line 336) indicates that CO2 can explain ~38% of the observed ethanol mixing ratios.

3) Fig. 6, the PMF factors having similar colors to the ground and tower observations makes it difficult to interpret. I would recommend different colors for the PMF results.