
Response to Reviewer #1

Li. et al. presents observations of volatile organic compounds (VOCs) collected from ~450m above ground level in Guangzhou, China, from mid-August to early-November. The authors 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 patterns 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 measurements 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.

Reply: We appreciate the reviewer for the valuable comments and suggestions, which are important for the improvement of our manuscript.

1) Further clarification in methods, specifically in the sampling.

1a) The authors noted that there 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.

Reply: We appreciate the reviewer for the valuable suggestions. The ~5 m long tubing was connected to a reserved sampling port on the wall of the observation room to draw air sample from outside the tower. We have provided a picture (Figure S1(f)) to show the sampling port on the outside wall of the room and rephrased related sentences to make this point clearer. [see P: 7; L: 150-156]

"To measure VOCs concentrations outside the tower, a ~5 m long Perfluoroalkoxy (PFA) Teflon tubing (OD: 1/4") was used to connect the inlet of the instrument and the sampling port (Figure S1). The PFA Teflon tubing has been proven to be effective in measuring ambient concentrations of VOCs (Deming et al., 2019; Liu et al., 2019) and has been widely used in field studies (de Gouw et al., 2003a; Hu et al., 2011; Wu et al., 2020a). Air sample in the tubing was drawn by a pump at a flow rate of ~5 L min^{-1}."

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.

Reply: We appreciate the reviewer for the valuable suggestions. The sampling line was not heated during the campaign. PFA Teflon tubing has been tested for potential losses of various VOC species in the literature (Deming et al., 2019; Liu et al., 2019) and has been proven to be the most suitable material so far to sample ambient air for VOCs analysis. In addition, the sampling flow rate was ~5 L min^{-1}, leading to a relatively small residence time (<3 s) of air sample in the tubing. PFA Teflon tubing has been widely used in the literature for VOCs analysis and thus was not tested in this study.

Deming, B. L., Pagonis, D., Liu, X., Day, D. A., Talukdar, R., Krechmer, J. E., de Gouw, J. A., Jimenez, J. L., and Ziemann, P. J.: Measurements of delays of gas-phase

compounds in a wide variety of tubing materials due to gas–wall interactions, Atmos. Meas. Tech., 12, 3453-3461, 10.5194/amt-12-3453-2019, 2019.

Liu, X., Deming, B., Pagonis, D., Day, D. A., Palm, B. B., Talukdar, R., Roberts, J. M., Veres, P. R., Krechmer, J. E., Thornton, J. A., de Gouw, J. A., Ziemann, P. J., and Jimenez, J. L.: Effects of gas–wall interactions on measurements of semivolatile compounds and small polar molecules, Atmos. Meas. Tech., 12, 3137-3149, 10.5194/amt-12-3137-2019, 2019.

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.

Reply: We appreciate the reviewer for the valuable suggestions. We have provided more descriptions and pictures (Figure S1) to introduce the observation level of the campaign on the CTT. The observation room is located below a ramp with stairs, namely the 450-m Look Out platform, on which visitors can walk around outside for a panorama of downtown Guangzhou but were not allowed to enter the observation room. The observation room has a reserved sampling port, as shown in Figure S1(f), so that the instruments can measure concentrations of chemical species outside the tower. As shown in Figure S1(g), a louver is located ~3 m below the sampling port. [see P: 6; L: 126-135] Detailed revisions are listed as follows:

"*The observation was conducted in a room (Figure S1) at the 450-m Look Out platform (Jin et al., 2022), which is a ramp with stairs and is located on the top of the main body of the CTT. The observation room is located below the ramp and a sampling port is reserved on the wall outside the tower. A louver is located ~3 m below the sampling port. The 450-m Look Out platform is a famous tourist attraction with an opening time of local time (LT, UTC+8) 10:00–22:30, and visitors could walk around for a panorama of downtown Guangzhou. On each day, there are two busiest tourist hours, roughly at LT 11:00–14:00 and 18:00–21:00, on the 450-m platform. In*

addition, there are three restaurants between 376 and 423 m. The VOCs measurements were interrupted during October 8–12 due to instrument malfunction."

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.

Reply: We appreciate the reviewer for the valuable suggestions. The observations made by different tower platforms were extrapolated for the 3-D vertical profiles using the bilinear method. That is, linear interpolations for concentrations of these pollutants were performed on both spatial (altitude) and temporal scales. Related descriptions have been provided in the manuscript. [see P: 8; L: 177-180]

"*Contour plots of vertical profiles of NOx, ozone, Ox (O_3+NO_2), and $PM_{2.5}$ concentrations were made using the bilinear method in Igor software (v8.04). Linear interpolations for concentrations of these pollutants were performed on both spatial (altitude) and temporal scales.*"

2) Something either in Sect. 3.1 or later that would be beneficial would be the OH reactivity (and maybe even NO_3-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 reactivity space would be of great benefit.

Reply: We appreciate the reviewer for the valuable suggestions. We have calculated contributions of VOC categories (Figure 2) and PMF factors (Figure 7) to the total OH reactivity and provided related results and discussions in the revised manuscript. Contributions of different VOC categories and PMF factors to NO_3 reactivity are not discussed in this study because only a small fraction of VOC species can be effectively oxidized by NO_3 radicals.

In section 3.1, we calculated the average contributions of each VOC category to both total concentrations and OH reactivity. [see P: 10-11; L: 237-257] At 450 m, $C_xH_yO_1$ had the largest contribution (67%) to TVOC concentrations but only contributed to 40% of the total OH reactivity. C_xH_y only accounted for 9% of TVOC concentrations but contributed to 37% of the total OH reactivity. At ground level, each VOCs category accounted for comparable fractions in total VOCs concentrations and OH reactivity to those measured at 450 m.

In section 3.4, we also discussed contributions of different PMF factors to the total OH reactivity. [see P: 16; L: 411-413] We find that the VCP-dominated (22%) and vehicular+industrial (23%) sources had comparable contributions to the total OH reactivity, even though large differences existed in their contributions to the TVOC concentrations (28% vs. 11%). These results further confirm that VCPs emissions should be given more attentions when making control strategies for VOCs in urban region.

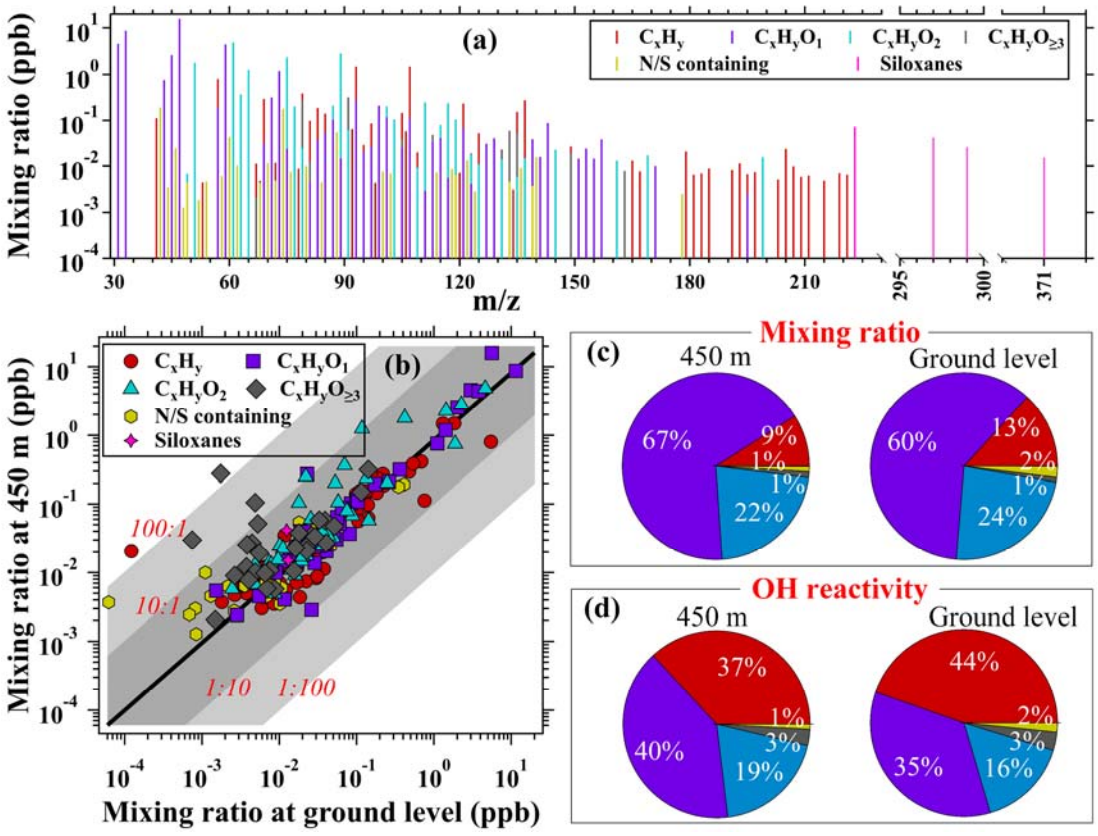

Figure 2 in the revised manuscript

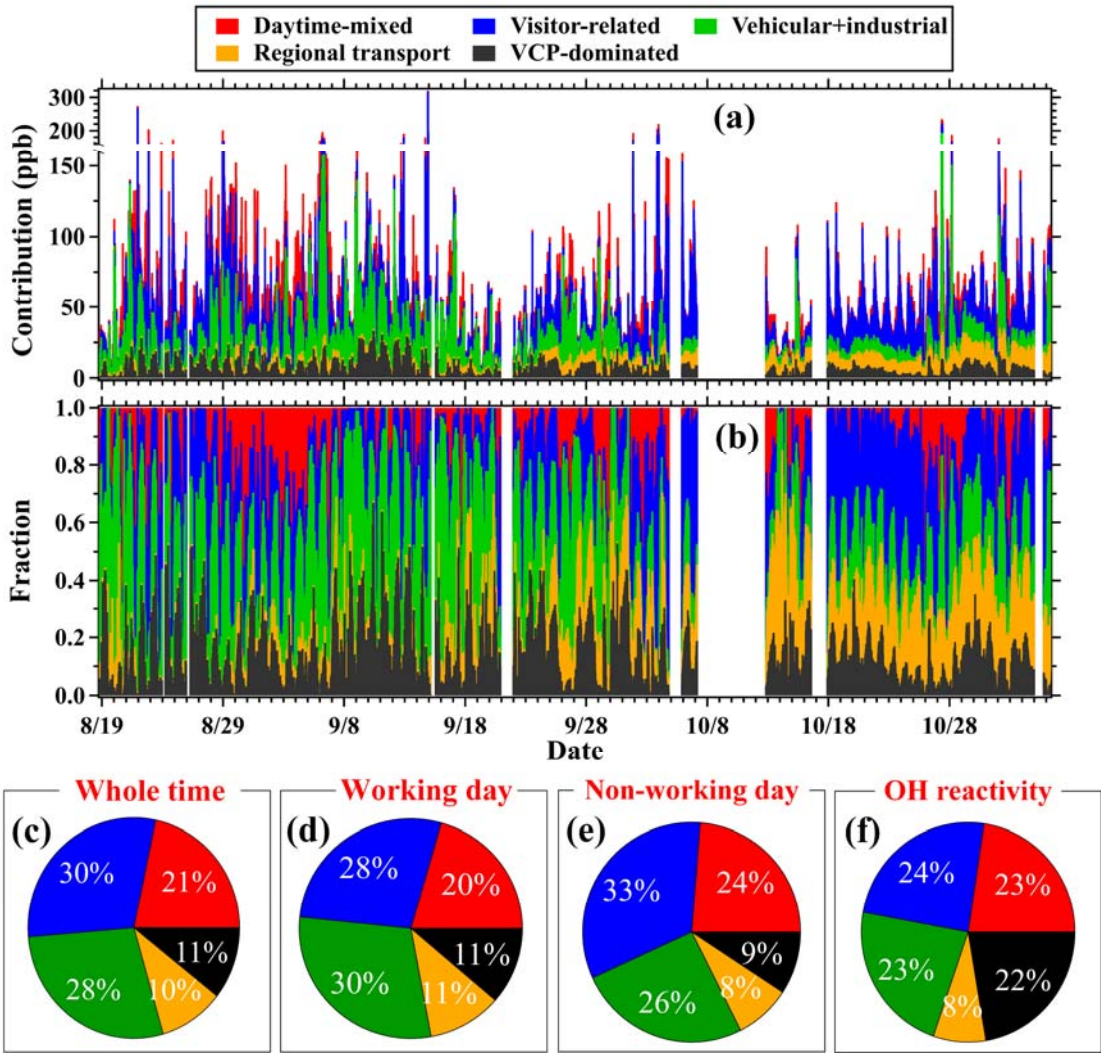

Figure 7 in the revised manuscript

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 something else). Though seeing "family" (which is different than PMF) is informative, know which compounds are different can be equally important.

Reply: We appreciate the reviewer for the valuable suggestions. In this study, the VOCs measurements contain more than 200 species and thus it is quite difficult to discuss the differences in VOCs measurements between 450 m and the ground level at species levels. In section 3.2, we have presented and discussed the differences in concentrations and diurnal patterns of some typical VOC species. In addition, ratios of concentrations of 225 species measured at 450 m to those at ground level are provided

as a function of m/z in Figure S2. In the revised manuscript, the VOCs measurements made at the GIG site were mainly used to identify differences in contributions of different VOCs categories to the total concentrations and OH reactivity between 450 m and the ground level. These results can primarily reveal the differences in contribution sources of VOCs measurements between urban upper air and the ground level. However, the differences in concentrations of various VOCs between 450 m and the ground level were not highlighted because the two field campaigns were conducted at different times and sites.

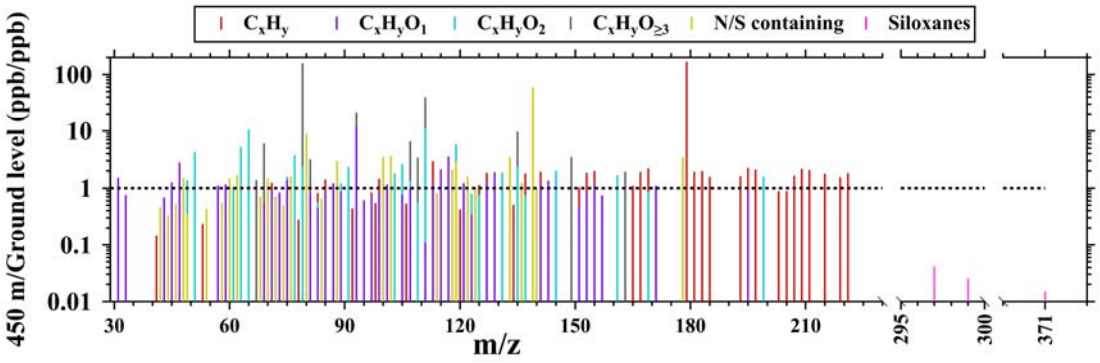

Figure S2(a) in the revised manuscript

4) Fig. 3 and potentially other diurnal plots. Sometimes it's difficult to discern the differences the authors mention in the diurnal profiles either 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.

Reply: We appreciate the reviewer for the valuable suggestions. In the revised manuscript, we have provided figures in SI showing diurnal variations in ratios of concentrations of the selected VOC species (Figure S3) and contributions of the five factors (Figure S8) between non-working and working days. The diurnal variations in ratios of concentrations of the selected VOC species between 450 m and the ground level were not highlighted because the two VOCs datasets were obtained at different times and sites.

As also suggested by the reviewer, the statistical significance levels (*p* values) of differences were determined using the Student's t-test. [see P: 8: L:188-189]

5) Source analysis of the VOCs. It is surprising that authors are seeing such a large source of ethanol and CO_2 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.

Reply: We appreciate the reviewer for the valuable comments and suggestions. During the CTT campaign, the observation room was located on the 450-m Look Out platform, which is a ramp with stairs and is located on the top of the main body of the CTT. The observation room is located below the ramp, namely the 450-m Look Out platform, on which visitors can walk around outside for a panorama of downtown Guangzhou. Therefore, measured concentrations of VOCs were impacted by visitor-related emissions. We have provided more pictures (Figure S1) and descriptions to introduce the sampling site and the field campaign. The revisions about site description are listed as follows: [see P: 6: L:126-134]

"*The observation was conducted in a room (Figure S1) at the 450-m Look Out platform (Jin et al., 2022), which is a ramp with stairs and is located on the top of the main body of the CTT. The observation room is located below the ramp and a sampling port is reserved on the wall outside the tower. A louver is located ~3 m below the sampling port. The 450-m Look Out platform is a famous tourist attraction with an opening time of local time (LT, UTC+8) 10:00–22:30, and visitors could walk around for a panorama of downtown Guangzhou. On each day, there are two busiest tourist hours, roughly at LT 11:00–14:00 and 18:00–21:00, on the 450-m platform. In addition, there are three restaurants between 376 and 423 m.*"

In addition, the CTT campaign was conducted in August-November of 2020, during which visitors must wear masks when visiting the CTT and ethanol-containing products (e.g., medicinal alcohol spray and 75%-ethanol bacteriostatic gel) were extensively used to prevent the spread of the COVID-19 pandemic. The total usage of ethanol-containing products was closely associated with the number of visitors, which can be manifested by the similar diurnal patterns of ethanol concentrations and the number of visitors at the 450-m platform. A detailed discussion on impacts of visitor-related emissions on VOCs measurements has been provided in Section 3.3. [see P: 14-15: L:345-379]

In addition, we also agree with the reviewer's opinion that the VOCs measurements may be affected by cooking emissions because the restaurants are located ~30 m below the observation site. Emission intensities of VOCs (e.g., monoterpenes) from cooking-related sources were also closely associated with the number of visitors. We have provided related discussions in the revised manuscript. [see P: 14-15: L:354-359]

"*In addition, the restaurants are located ~30 m below the observation site and emission intensities of VOCs (e.g., monoterpenes) from cooking-related sources were also closely associated with the number of visitors. Therefore, the VOCs measurements made at the 450-m platform were inevitably affected by visitor-related emissions, such as human breath, cooking, and volatilization of ethanol-containing and personal care products (Veres et al., 2013).*"

We also agree with the reviewer's opinion that the visitor-related compounds are also compounds that can generally be "VCP" in nature, which has been discussed in SI as follows. [see P: 22: L:119-125 in SI] In this study, we aim to investigate sources of VOCs in urban upper air as the VOCs measurements at high altitudes can be used to better characterize urban emissions at large spatial scales. It is very important to exclude VOCs emissions from local sources. Therefore, we believe that it is more suitable to separate visitor-related emissions from VCPs.

"*It should be noted that large fractions of ethanol emitted from personal care products were generally attributed to the VCP source in previous studies (McDonald et al., 2018; Gkatzelis et al., 2021). This is correct when the observation site was not affected by intensive emissions from a known source such as visitors at the 450-m platform. The visitor-related source was resolved in PMF to separate contributions of VCPs from those emitted by visitors.*"

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.

Reply: We appreciate the reviewer for the valuable suggestions. We have rechecked the calculations for the PMF analysis and confirmed that the results in Figure 7 are correct. Figure 7(a-b) shows stacked time series of fractions and contributions of the five PMF factors at high time resolutions of 10 min, producing an illusion that the daytime-mixed source had larger contributions than other factors. We have rearranged the stack order of the five factors in Figure 7(a-b) in the revised manuscript.

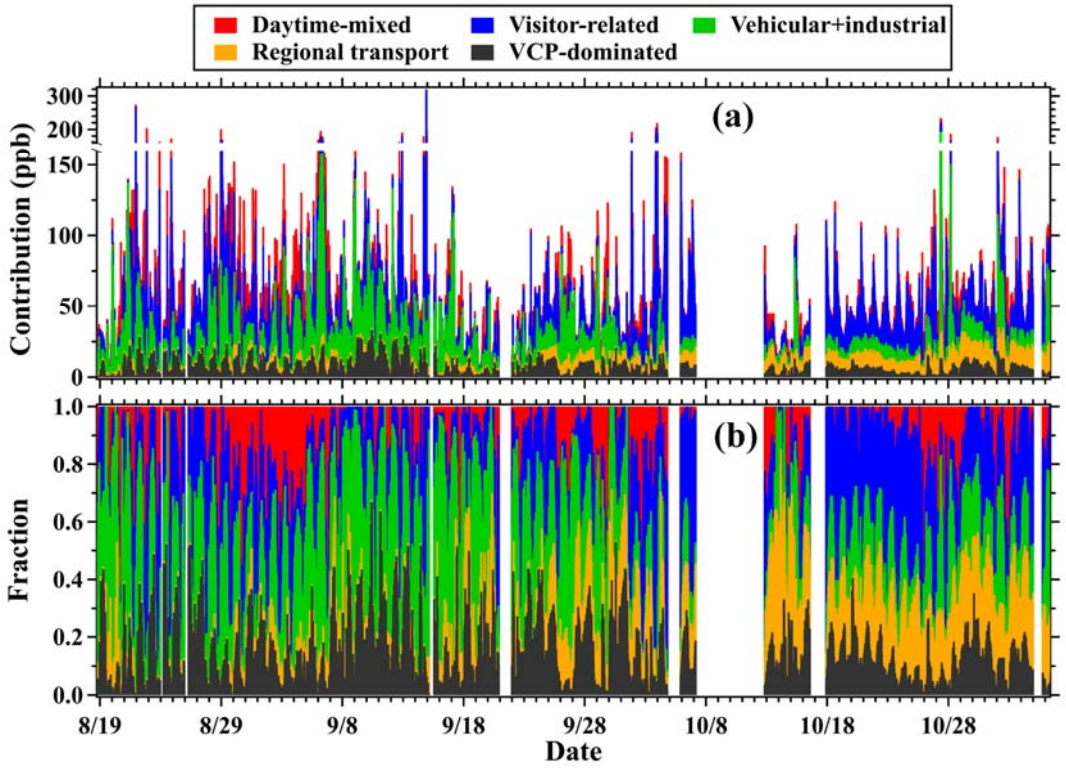

Figure 7(a-b) in the revised manuscript

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 significant difference.

Reply: We appreciate the reviewer for the valuable suggestions. In the revised manuscript, the Student's t-test was used to determine the statistical significance levels of differences when performing comparisons. Otherwise, the words "significantly" and "significant" have been replaced with other words (e.g., “notably” and “markedly”).

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 CO_2 can explain ~38% of the observed ethanol mixing ratios.

Reply: We appreciate the reviewer for the valuable comments. As suggested by the reviewer, we have provided significance levels (*p* values) when performing comparison (t-test) or fitting (F-test) analysis in the revised manuscript. As for the correlation between CO_2 and ethanol, the *p* value of the linear fitting was lower than 0.01 ($p<0.01$). In addition, the correlation coefficient (*r*) generally decreases with increased sample size. In this study, the correlation coefficient between mixing ratios of CO_2 and ethanol was calculated at 10-min time resolutions (Figure 5(b)) and the sample size was more than 10,000. Therefore, we think that the mixing ratios of CO_2 and ethanol was well correlated with the *r* value of 0.62. [see P: 15: L:363-366]

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.

Reply: We appreciate the reviewer for the valuable suggestions. We have changed colors of the VOCs categories for the ground and tower observations in Figure 2. The present colors for PMF analysis have a good contrasting effect and remain unchanged. [see P: 40]