
Response to Reviewer #2

Li et al. report interesting time-resolved VOC measurements on the Canton Tower in Guangzhou, China using a QiTOF PTRMS. The Guangzhou region is impacted by air pollution and underrepresented in atmospheric observations which is why data from this region are a valuable opportunity to learn about the processes and regional sources. The identification of these sources from the data must be challenging due to chemical complexity. PMF was utilized to help with this task and five factors were obtained from the PMF source apportionment conducted on the 225 VOC ions which were assigned different mostly anthropogenic categories. The observations focus on abundant VOCs and correlations with inorganic pollutants which might be helpful to understand variability of pollutants, oxidation and sources in the atmosphere. The text reads generally clear and there are rich figures to illustrate observations and thoughtful analyses. However, I'd have some comments and suggestions before the paper is published, and in particular there seem to be some issues or inconsistencies in a few compounds and PMF interpretations which hopefully can easily be addressed.

Reply: We appreciate the reviewer for the valuable comments and suggestions to improve the quality of our manuscript.

Major

Ethanol (e.g. Fig 1) is rather high as for the outdoor atmosphere and what I am most surprised with is that it is attributed to human emissions from tower visitors. If ethanol was emitted by human visitors on the tower why were siloxanes, not co-emitted? It is difficult to get convinced that such a large concentration of ethanol comes from human breath as is suggested in the SI Page 19. Was maybe a sanitizer dispenser in the vicinity to the sampling inlet? A picture or at least a schematic of the inlet location would be useful (as well as the info if the particle filter was used or not).

Reply: We appreciate the reviewer for the valuable suggestions. As shown in Figure S1, the observation room is located on the 450-m Look Out platform below the ramp, on which visitors can walk around. Therefore, measured concentrations of VOCs were impacted by visitor-related emissions, such as human breath, cooking, and the volatilization of personal care products. In addition, the campaign was conducted in August-November of 2020, during which stringent control measures were implemented to prevent the spread of the COVID-19 pandemic. For example, visitors must wear masks and ethanol-containing products (e.g., medicinal alcohol spray and 75%-ethanol bacteriostatic gel) were extensively used to wipe public utilities. The total usage of ethanol-containing products had a strong dependence on 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. Therefore, we concluded that the enhanced ethanol concentrations were mainly attributed to visitor-related emissions, predominantly from the volatilization of ethanol-containing products and personal care products. The human breath, cooking, and volatilization of personal care products also contribute to measured ethanol concentrations but may not account for comparable fractions to that the visitor-related source. 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 the revised manuscript, we have provided more pictures (Figure S1) and descriptions to introduce the sampling site and the field campaign. [see P: 6: L:126-135]

"*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.*”

The concentration data at least for ethanol are inconsistent. Ethanol concentration is shown in multiple figures with overlapping times in Fig 1 and 11. Ethanol concentration is different in those figures (e.g. 9/30, 9/29).

Reply: We appreciate the reviewer for the valuable suggestions. Reasons for causing the differences in ethanol concentrations in Figures 1 and 11 in the original manuscript are the differences in time resolutions of ethanol concentrations. In the original manuscript, Figure 1 shows time series of ethanol concentrations at time resolutions of 10 min and Figure 11 shows hourly mean concentrations of ethanol. In the revised manuscript, hourly mean concentrations of ethanol, as well as other VOC species, were used in Figure 1 to keep consistent with those in Figure 11.

The lack of dependence on wind direction (L397) is surprising and makes me wonder if the instrument may have been sampling from indoors, indoor plumes, or if there may have been a leak in the line or other factor which would explain high ethanol, and acetic acid concentrations. Wind roses or polar plots for VOCs would also be useful to help in clarifying these issues and help in source interpretations.

Reply: We appreciate the reviewer for the valuable suggestions. Indeed, it would be very useful to show the dependence of VOCs concentrations on wind direction. However, wind speed and wind direction were not measured at 450 m during the campaign because the measurements of winds can be easily changed by the structure of the CTT. This is the reason why we performed a cluster analysis of backward trajectories of air masses in this study to roughly investigate the dependence of VOCs concentrations and factor contributions on wind direction. [see P: 26 in SI]

In addition to instrument maintenance (usually several hours), there were no people in the observation room. Therefore, concentrations of various VOC species will exhibit insignificant diurnal variations if there is a leak in the sampling tubing.

The PMF analysis results seem surprising to me. It almost seems like the same compounds and factor profiles appear in every factor (Figure S5). Methanol and acetone appear in multiple factors as most abundant. Visitor factor is lacking siloxanes. Given it is the QiTOF with very high sensitivity, I'd expect the clearer factors including biogenic, oxygenated biogenic, and cooking could be obtained without merging. I wonder if optimizing uncertainties or dividing the dataset into shorter periods could further help in those source interpretations.

Reply: We appreciate the reviewer for the valuable suggestions. As known, many OVOC species have very complex sources (e.g., various primary emission sources and secondary formation) in urban environments. Therefore, many OVOC species were abundant in different PMF factors and this is consistent with the results in previous studies (Gkatzelis et al., 2021; Pallavi et al., 2019) that used measurements of PTR-ToF-MS for PMF analysis. Therefore, likely sources of the PMF factors based on PTR-ToF-MS measurements were usually determined using the combination of factor profile and diurnal variation patterns of factor contributions. As for contributions of the visitor-related source, the human breath and volatilization of personal care products may only account for a small fraction. As a typical tracer of VCPs, D5 siloxane was mainly attributed to the VCP-dominated source, as shown in Figure 8.

As also suggested by the reviewer, we have tried performing the PMF calculation many times by changing the uncertainties of different VOCs species and the analyzing time scales and we believe that the present results were optimal according to our analysis.

Gkatzelis, Georgios I., Coggon, Matthew M., McDonald, Brian C., Peischl, Jeff, Gilman, Jessica B., Aikin, Kenneth C., Robinson, Michael A., Canonaco, Francesco, Prevot, Andre S. H., Trainer, Michael, and Warneke, Carsten: Observations Confirm that Volatile Chemical Products Are a Major Source of Petrochemical Emissions in U.S. Cities, Environmental Science & Technology, https://doi.org/10.1021/acs.est.0c05471, 2021.

Pallavi, Sinha, B., and Sinha, V.: Source apportionment of volatile organic compounds in the northwest Indo-Gangetic Plain using a positive matrix factorization model, Atmospheric Chemistry and Physics, 19, 15467-15482, https://doi.org/10.5194/acp-19-15467-2019, 2019.

Minor

I really like Table S1 with nicely tabulated masses and formulas identifications and sensitivities with clear note which ion was explicitly calibrated. I think it is exemplary for all PTRMS papers. I only have minor suggestions here: 69.03 should be furan (not fural), 51.99 monochloramine, 71.03 add MACR. Did you not see D5 fragment at 355.06? This is extremely surprising as is the unexpected D5 fragment at 299. I am again curious what the E/N ratio was.

Reply: We appreciate the reviewer for pointing out the mistakes and providing valuable suggestions. We have revised or added compounds for corresponding signals in Table S1. Ion signals at m/z 299.06 and 355.06 are all D5 fragments in PTR-ToF measurements, but measurements of m/z 355.06 were excluded from the PMF analysis due to its relatively low signals during the campaign.

As suggested by the reviewer, we have provided more information to introduce the PTR-ToF-MS used in our study. In H_3O^+ mode, the PTR-ToF-MS was operated with a drift tube pressure of 3.8 mbar, a drift tube temperature of 120 °C, and a drift tube voltage of 760 V, resulting in an E/N value of ~120 Td. [see P: 7: L:143-146]

It is mentioned that ethyl acetate was one of the most abundant VOCs, but how did the authors exclude butyric acid or subtracted it from the signal?

Reply: We appreciate the reviewer for the valuable comments. In addition to ethyl acetate, ion signals measured at m/z 89.06 were also likely contributed by butyric acid because PTR-ToF-MS cannot resolve signals of isomers. In this study, we attributed ion signals of m/z 89.06 to ethyl acetate for two important reasons. First, in addition to formic acid, molecules of other organic acids can easily fragment when measured by PTR-ToF-MS (Haase et al., 2012; Praplan et al., 2014). Second, ambient concentrations of butyric acid were significantly lower than those of ethyl acetate in urban environments, as ethyl acetate is frequently used as solvents for various applications (Zheng et al., 2013). For example, the mean concentration of butyric acid measured by a I ToF-CIMS (I ToF-CIMS could accurately measure concentrations of butyric acid) in the GIG campaign was only 0.24±0.17 ppb (Ye et al., 2021), which was much lower than that of ethyl acetate (2.27±2.36 ppb) measured by the PTR-ToF-MS.

Haase, K. B., Keene, W. C., Pszenny, A. A. P., Mayne, H. R., Talbot, R. W., and Sive, B. C.: Calibration and intercomparison of acetic acid measurements using proton-transfer-reaction mass spectrometry (PTR-MS), Atmos. Meas. Tech., 5, 2739-2750, 10.5194/amt-5-2739-2012, 2012.

Praplan, A. P., Hegyi-Gaeggeler, K., Barmet, P., Pfaffenberger, L., Dommen, J., and Baltensperger, U.: Online measurements of water-soluble organic acids in the gas and aerosol phase from the photooxidation of 1,3,5-trimethylbenzene, Atmos. Chem. Phys., 14, 8665-8677, 10.5194/acp-14-8665-2014, 2014.

Ye, C., Yuan, B., Lin, Y., Wang, Z., Hu, W., Li, T., Chen, W., Wu, C., Wang, C., Huang, S., Qi, J., Wang, B., Wang, C., Song, W., Wang, X., Zheng, E., Krechmer, J. E., Ye, P., Zhang, Z., Wang, X., Worsnop, D. R., and Shao, M.: Chemical characterization of oxygenated organic compounds in the gas phase and particle phase using iodide CIMS with FIGAERO in urban air, Atmos. Chem. Phys., 21, 8455-8478, https://doi.org/10.5194/acp-21-8455-2021, 2021.

Zheng, J., Yu, Y., Mo, Z., Zhang, Z., Wang, X., Yin, S., Peng, K., Yang, Y., Feng, X., and Cai, H.: Industrial sector-based volatile organic compound (VOC) source profiles measured in manufacturing facilities in the Pearl River Delta, China, Sci Total Environ, 456-457, 127-136, https://doi.org/10.1016/j.scitotenv.2013.03.055, 2013.

Nowhere in the text or SI PTRMS parameters are shown. It would be great to provide at least E/N, which is a common practice in a PTRMS papers, because it helps interpret the VOC data and estimate expected fragmentations.

Reply: We appreciate the reviewer for the valuable suggestions. The E/N of PTR-ToF-MS was ~120 Td during the campaign. In the original manuscript, these information were not provided because they have been introduced in our previous papers (Wang et al., 2020a; Wu et al., 2020a; He et al., 2022). We have provided related information in the revised manuscript. [see P: 7: L:143-150]

"*In H_3O^+ mode, the PTR-QiToF-MS was operated with a drift tube pressure of 3.8 mbar, a drift tube temperature of 120 ℃, and a drift tube voltage of 760 V, resulting in an E/N (E refers to electric field and N refers to number density of buffer gas in the drift tube) value of ~120 Td (Townsend). Raw data of PTR-ToF-MS were processed and analyzed using Tofware software (Tofwerk AG, v3.0.3) and please refer to our previous works (Wang et al., 2020a; Wu et al., 2020a) for details*"

Fig. 3: I wonder why the traffic rush hours are not clearly seen on the plots presenting aromatics. The period was probably not during the lockdown if the visitors are allowed in the tower. Ethanol and monoterpenes coincide with lunch and dinner so might be cooking emissions(?).

Reply: We appreciate the reviewer for the valuable suggestions. As shown in Figure 3, diurnal profiles of aromatics (e.g., benzene and toluene) usually exhibited bimodal patterns in morning and evening rush hours at ground level due to the combined effects of enhanced traffic emissions and strong atmospheric stability. However, the measurements of VOCs at 450 m were less affected by traffic emissions from the ground in morning and evening rush hours due to enhanced atmospheric stability (largely limiting the vertical mixing of surface emissions).

The CTT campaign was conducted in August-November of 2020, during which ethanol-containing products (e.g., medicinal alcohol spray and 75%-ethanol bacteriostatic gel) were still extensively used to prevent the spread of the COVID-19 pandemic. For example, medicinal alcohol (75%) spray was widely used to wipe public utilities and 75%-ethanol bacteriostatic gel was extensively used as sanitizer for hands. [see P: 14: L:346-352] The total consumption of ethanol-containing products was dependent on the number of visitors on the CTT. 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., ethanol and 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]

Fig. 5: Super interesting effect of Typhoon on VOC concentration reduction. I wonder about the dependence of the observed concentrations on the wind speed.

Reply: We appreciate the reviewer for the valuable suggestions. A cluster analysis of backward trajectories of air masses [see P: 26 in SI] was performed in this study to roughly investigate the dependence of VOCs concentrations and factor contributions on wind direction due to the lack of wind measurements during the campaign.

In Figure 5, what we want to discuss was not the dilution or transport effect of the Typhoon on the measurements of VOCs but impacts of the closure of the 450-m platform on changes in measured concentrations of various VOC species. The 450-m platform was closed on October 13-15 due to the influence of Typhoon Kompasu. On these days, mixing ratios of ethanol, CO_2, and monoterpenes exhibited similar variation patterns to benzene (a typical tracer of traffic emissions). However, mixing ratios of ethanol, CO_2, and monoterpenes exhibited quite different variation patterns from benzene when the 450-m platform was re-open (October 16–21). These results further confirm the fact that visitor-related emissions contributed to the VOCs measurements when the 450-m platform was open.

I could not find in the main text or SI how exactly the PTRTOF data were processed, what software was used for mass scale alignment, peak fitting, as well as quality control, formula assignment, compound inference, total number of ions detected and steps taken for ion reduction or any abundance filters. This info would be greatly appreciated in the methods or SI.

Reply: We appreciate the reviewer for the valuable suggestions. Raw data of PTR-ToF-MS were processed (e.g., mass scale alignment and peak fitting) and analyzed (e.g., formula assignment, mass calibration, and compound inference) using Tofware software (Tofwerk AG, v3.0.3). Signals of 3035 ions with m/z up to 510 were obtained at time resolutions of 10 s. Original ion signals measured by PTR-ToF-MS may be affected by the change in ambient humidity. Therefore, effects of changes in humidity on measured signals of various VOCs were excluded using humidity-dependence curves determined in the laboratory. We have provided these descriptions in the revised manuscript. [see P: 7: L:146-150] More detailed information on the processing of PTR-ToF-MS data has been provided in our previous papers (Wu et al., 2020; Wang et al., 2020) and was thus not repeated in the present work.

"*Raw data of PTR-ToF-MS were processed and analyzed using Tofware software (Tofwerk AG) and please refer to our previous works (Wu et al., 2020a; Wang et al., 2020a) for details. Signals of 3035 ions with m/z up to 510 were obtained at a time resolution of 10 s.*"

Wu, C., Wang, C., Wang, S., Wang, W., Yuan, B., Qi, J., Wang, B., Wang, H., Wang, C., Song, W., Wang, X., Hu, W., Lou, S., Ye, C., Peng, Y., Wang, Z., Huangfu, Y., Xie, Y., Zhu, M., Zheng, J., Wang, X., Jiang, B., Zhang, Z., and Shao, M.: Measurement report: Important contributions of oxygenated compounds to emissions and chemistry of volatile organic compounds in urban air, Atmos. Chem. Phys., 20, 14769-14785, https://doi.org/10.5194/acp-20-14769-2020, 2020.

Wang, C., Yuan, B., Wu, C., Wang, S., Qi, J., Wang, B., Wang, Z., Hu, W., Chen, W., Ye, C., Wang, W., Sun, Y., Wang, C., Huang, S., Song, W., Wang, X., Yang, S., Zhang, S., Xu, W., Ma, N., Zhang, Z., Jiang, B., Su, H., Cheng, Y., Wang, X., and Shao, M.: Measurements of higher alkanes using NO+ chemical ionization in PTR-ToF-MS:

important contributions of higher alkanes to secondary organic aerosols in China, Atmos. Chem. Phys., 20, 14123-14138, https://doi.org/10.5194/acp-20-14123-2020, 2020.

I am quite intrigued by the chromium ion reported in the SI Table. Did its signal show some ambient structure or was it coming from the ion source? There are many cool molecules in this table that could be useful to explore as source markers and complement PMF.

Reply: We appreciate the reviewer for the valuable suggestions. Figure R1 shows the time series of mixing ratios of m/z 84.9 (CrO_2) from October 24 to November 3, 2020, during the CTT campaign. Mixing ratios of m/z 84.9 exhibited similar, to some extent, variations to those of ambient humidity. Therefore, we agree with the reviewer's opinion that measurements of ion signals at m/z 84.9 were possible impurities contributed by the ion source. However, the mean concentration of the signal at m/z 84.9 was only 7 ppt during the campaign, which had negligible impacts on the results of this study and thus was kept in the analysis.

In this work, online measurements of more than 200 VOC species made at the 450 m site were predominantly attributed to five sources using the PMF analysis method. We admit that the PMF method has shortcomings in identifying sources of VOCs and each of the five PMF factors may contain contributions from various emission sources. For example, the daytime-mixed source may contain contributions from biogenic emissions, secondary formation, evaporation of solvents, and other sources that have strong dependences on solar radiation, temperature, and humidity. To clearly identify contribution sources of VOCs measurements at species levels in urban upper air, VOCs measurements with more species (e.g., NMHCs, organic acids, and higher alkanes) are required. This is also one of the primary works in our upcoming studies.

Technical

L 75 “were” should be “are””

Reply: We appreciate the reviewer for pointing out this mistake and it has been corrected. [see P: 4: L:76]

L109 “by far” should be “so far”

Reply: We appreciate the reviewer for pointing out this mistake and it has been corrected. [see P: 5: L:110]