

Response to Reviewers' comments

Reviewer 1

PTR-ToF-MS provides a powerful tool to measure VOCs in the atmosphere, and analysis of the full mass spectrum dataset is rare, particularly for cities in China. This paper presents a detailed analysis of VOC observations made by PTR-ToF-MS and GC-MS/FID. It confirms the importance of oxygenated VOCs in the urban atmosphere: nearly 80% of PTR ions, or 60% of total VOCs, 20% of the total OH reactivity. It also suggested that about only 12% of the OH reactivity and below the instrument uncertainty, is not accounted for in the deployed instrument payload ('Missing' reactivity). The paper is in general carefully written and is of interest to the ACP community. Thus I'd recommend a publication. A few specific comments are :

Reply: We would like to thank the reviewer for the insightful comments, which helped us tremendously in improving the quality of our work. Please find the response to individual comments below.

- Page 4, line 95: *It is an overstatement and vague. At least one study has reported the importance of OVOCs in the urban air, and another in review (see below). Nevertheless, it is still quite new work.*

Reply: Thank you for the insight comments. This sentence is modified in the revised manuscript:

However, there is only a limited number of studies to conduct such analysis in urban air to better evaluate the roles of these oxygenated species (Karl et al., 2018; Sanchez et al., 2020).

-*The mass resolving power of the PTR-ToF-MS: what is the resolving power to separate isoprene and furan for this instrument?*

Reply: The mass resolving power of the PTR-ToF-MS is $>3500\text{ m}/\Delta m$ for m/z 50 and larger ions. The figure below shows the relationship between mass resolution and m/Q , and the fitting result of isoprene and furan in the average mass spectrum of PTR-ToF-MS on a typical day (Sep. 20, 2018). The ion peaks of isoprene and furan can be well separated by the ToF analyzer. We include this information in the revised manuscript.

Here, the mass resolving power of PTR-ToF-MS is $>3500\text{ m}/\Delta m$ for m/z 50

and larger ions, which can separate well for the ion peaks of isoprene and furan (Figure S7). An average concentration of 0.05 ± 0.03 ppb for furan was observed during the campaign.

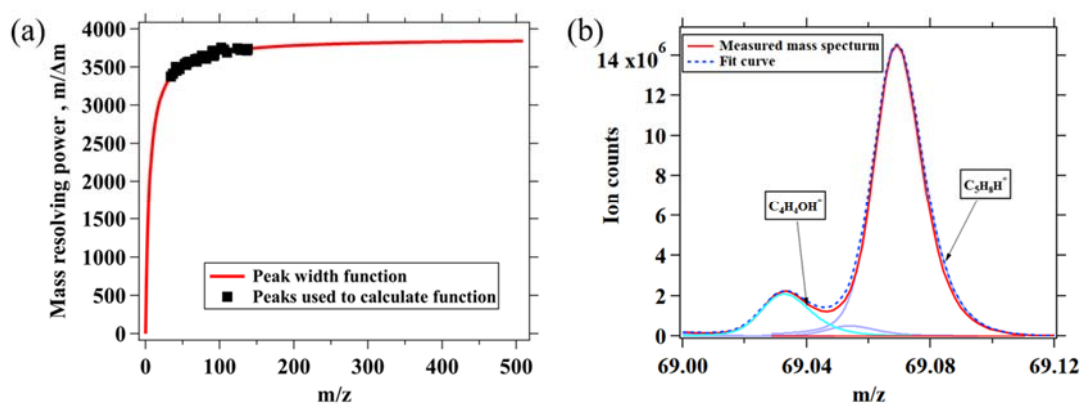


Figure S7. (a) The relationship between mass resolving power and m/Q . (b) High resolution peak fitting for m/z 69 to separate ion peaks of isoprene and furan for the average mass spectrum of PTR-ToF-MS on a typical day (Sep. 20, 2018).

- Section 3.1. The overview of selected VOCs is a weak section of this paper. The interpretation of VOC sources here is oversimplified. For example, OVOCs only came from photochemical/secondary sources, while the biogenic source can actually play a significant role (See its own Section 3.3). Secondary formation of furan to explain the nighttime decrease. It could be due to the nighttime transport pattern or nighttime source variation. I would suggest a revision of this section and focusing on the large pattern rather than going into too specific details and simplifying the explanation, which in many cases could be wrong. Just leave the source attribution to Section 3.3, or discuss the consistency of results between the two sections/analyses.

Reply: Thanks for the comment. In this section, we mainly show diurnal variations of the selected typical VOCs, which provides a basis for subsequent analysis for sources and VOCs compositions. As the result, the description of the sources for the VOCs discussed is more descriptive in section 3.1, rather than in a more quantitative way as section 3.2 and section 3.3.

Regarding of the specific conclusions for different VOCs, we would like to deal with one by one below:

(1) For example, OVOCs only came from photochemical/secondary sources: We did not claim OVOCs only come from secondary sources. Based on different diurnal variations between hydrocarbons and formaldehyde/acetone, we conclude secondary

formation contributed significantly to concentrations of the two OVOCs.

(2) *The biogenic source can actually play a significant role:* In the original manuscript, we wrote “biogenic emissions are also an important source of VOCs” in the beginning of the paragraph to describe that biogenic emissions are important for VOCs in the atmosphere, not specifically for the campaign. For clarification, we changed the two sentences in the revised manuscript:

Biogenic emissions are also an important source of VOCs in the atmosphere, with isoprene as one of the largest components (Guenther et al., 2012). According to Figure 1, a regular diurnal profile is observed for isoprene during the campaign, with the highest concentration around noon.

(3) *Secondary formation of furan:* We are not using secondary formation to explain nighttime decrease of furan. Actually, secondary formation explains the small variation of furan concentration during the daytime. Considering its high reactivity ($4.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), the lifetime of furan during the day should be around 2 hours, using OH concentration determined in the main text. If there is no secondary formation, furan concentrations should decrease significantly in the afternoon, as many hydrocarbons did. Thus, there should be secondary sources to maintain the concentrations of furan during the daytime.

The variations of furan concentrations during the daytime are small. Considering that furan is highly reactive ($4.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, lifetime 2.0 h using OH concentration determined above), it implies that furan is secondary produced during the daytime.

- Section 3.2. *Can the authors comment on why Sekimoto et al (2017) method didn't work here for the instrument here? Is there anything about the affected ion chemistry in the PTR-QiToF-MS. This could be important for the PTR-MS community for quantifying many VOCs without calibrations.*

Reply: We re-checked the relationship between the sensitivity and rate constants for proton-transfer reactions of H_3O^+ with VOCs. We found that the reason for the lack of linearity in the original manuscript: we used the thermal rate constant in the original manuscript, while the kinetic rate constants should be used. The kinetic rate constants consider the much higher energetic collisions that is controlled by both temperature in the drift tube and also the E/N ratio (120 Td) (Cappellin et al., 2012; Sekimoto et al., 2017). After using the kinetic rate constant of each VOC, we obtained the linear

relationship between the sensitivity and kinetic rate constant for proton-transfer reactions of H_3O^+ , and used this linearity to re-calculate the concentration of uncalibrated species.

As discussed in section 2.2, a total of 31 VOCs species were calibrated using either gas cylinders or liquid standards. For other VOCs, we used the method proposed in Sekimoto et al. (2017) to determine the relationship between VOCs sensitivity and kinetic rate constants for proton-transfer reactions of H_3O^+ with VOCs (detailed discussions in the SI). As shown in Figure 3, a clear linear relationship was obtained. The fitted line in Figure 3 is used to determine sensitivities of the uncalibrated species. Following the discussions in Sekimoto et al. (2017), uncertainties of the concentrations for uncalibrated species are around 50%.

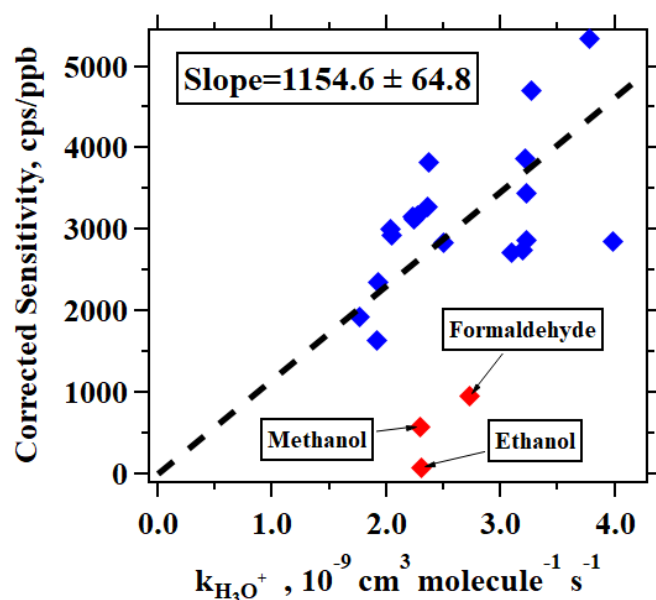


Figure 3. Corrected sensitivities as a function of kinetic rate constants for proton-transfer reactions of H_3O^+ with VOCs. The dashed line indicates the fitted line for blue points. The red points are not used, as these compounds (formaldehyde, methanol, ethanol) are known to have lower sensitivities.

- Can propagated errors of uncalibrated species be estimated here? How would those errors affect the conclusions?

Reply: As discussed above, we use the linear relationship between sensitivities and rate constants for proton-transfer reactions of H_3O^+ with VOCs to determine sensitivity of uncalibrated species. Following the discussions in Sekimoto et al. (2017),

uncertainties of the concentrations for uncalibrated species are around 50%. Regarding of the effect of uncertainties for uncalibrated species on the conclusions, we added the following sentences in the Section 3.4 in the revised manuscript:

Adding up these contributions, it significantly narrows the gap between the measured and calculated OH reactivity, leaving only 11% of OH reactivity as “missing” during the campaign. Considering the large uncertainties for both concentrations (~50%) and rate constants of the uncalibrated species (on the order of 100%), the missing reactivity can ranged in 0%-19%. Nevertheless, the determined missing reactivity would be well below the estimated uncertainty (20%) for the OH reactivity measurements by the CRM method, indicating that gap between measured and calculated reactivity can be significantly narrowed after taking into account all of the species by PTR-ToF-MS.

- Page 15, lines 401-402: For OH reactivity, LOH may be a better symbol as KOH would suggest it is a rate constant, but it is actually a loss rate.

Reply: Thanks for your advice.

The formula has been changed in the revised manuscript:

$$L_{OH} = k_{CO}[CO] + k_{NO}[NO] + k_{NO_2}[NO_2] + k_{SO_2}[SO_2] + k_{O_3}[O_3] + k_{CH_4}[CH_4] + \sum_i^n k_{VOC_i}[VOC_i]$$

Reference: Karl, T., M. Striednig, M. Graus, A. Hammerle, and G. Wohlfahrt (2018), Urban flux measurements reveal a large pool of oxygenated volatile organic compound emissions, Proceedings of the National Academy of Sciences, doi:10.1073/pnas.1714715115.

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