

Responses to the comments from Anonymous Referee #2

Interactive comment on “Measuring OVOCs and VOCs by PTR-MS in an urban roadside microenvironment of Hong Kong: relative humidity and temperature dependence, and field inter-comparisons” by Long Cui et al.

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Cui et al. show VOC measurements from PTR-MS in Hong Kong. They also discuss humidity dependence of formaldehyde in PTR-MS and inter-comparison with several other techniques, including DNPH, canister samples, online GC-FID. However, this manuscript generally does not provide much new information and new technique. Many

10 valuable experiences from over 20 years of work in the PTR-MS community are not fully reflected in the data processing procedures in this manuscript. The inter-comparison results are not as good as those previously reported in the literature, but the authors do not provide good reasons about it. Thus, I do not think this manuscript is suitable to publish in AMT, unless this manuscript is totally re-written and provide more
15 information that can support new idea/technique.

Response: we thank the reviewer very much for the critical comments which would help us to improve our work. The major concerns of the reviewer are on (1) the significance of this study and (2) the weakness of the discussion part about inter-comparisons between PTR-MS and other techniques or even other previous studies.

20 Below we first address these major concerns and then reply individually the specific comments. For clarity, the reviewer’s comments are listed below in black italics, while our responses and changes in manuscript are shown in blue and red, respectively.

(1) On the significance of this study

We agree with the reviewer that the present study is based on the PTR-MS technique,
25 which has been studied worldwide through the past 20 years. Here we just would like to state the significance of our study.

Indeed, PTR-MS is not a brand new technique for measuring OVOC and VOC, and the other techniques used in this study also have a relative long history. But very few studies used PTR-MS at roadside microenvironment for OVOC and VOC
30 measurements, even less studies has been conducted at a sampling site with

extremely huge traffic volume as in our study, because the traffic density of Hong Kong is one of the largest worldwide, and the Mong Kok site which was selected as the sampling location has the largest traffic volume in Hong Kong. Besides, **it was the first time that PTR-MS was used in Hong Kong to measure ambient OVOC and VOC.**

5 So it is very necessary and important to do the inter-comparison between PTR-MS and other techniques in an urban roadside microenvironment of Hong Kong.

Moreover, few studies have conducted inter-comparisons between PTR-MS and alternative methods for OVOCs. **Even fewer studies have investigated inter-comparison between PTR-MS and DNPH-HPLC in urban roadside areas** as stated

10 in “Section 3.5” of our manuscript. Because only DNPH-HPLC method has been used for measuring ambient OVOCs in Hong Kong, and there is no on-line techniques (e.g. DOAS instrument and Hantzsch monitor) have been used in Hong Kong before and recently. It is more necessary to conduct the inter-comparison between PTR-MS and DNPH-HPLC for OVOCs in Hong Kong. Our study firstly investigated the influence 15 of relative humidity and temperature of inlet air for OVOC and VOC measurements separately. And better agreement was found between PTR-MS and DNPH-HPLC for formaldehyde than previous other studies by using the simulation model of this study.

Overall, although there is no brand new technique for OVOC and VOC measurement in this study, this study provide some new insights into the relative humidity and temperature dependence for PTR-MS measurement, and some useful information of the inter-comparison between PTR-MS and other techniques in an urban roadside microenvironment in Hong Kong. These results should be useful for OVOC and VOC measurement by PTR-MS in other urban roadside areas with high traffic volume of the world.

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(2) On the weakness of the discussion part

Actually, not all of the inter-comparison results are not as good as those previously reported in the literature, especially for HCHO measurement by using the simulation model firstly raised by this study. Moreover, if only inter-comparisons for OVOC and 30 VOC in urban areas are conducted, we can easily find that the inter-comparison results

are almost all close to other studies when the same techniques were used. We agree with the reviewer that more discussions should be provided to illustrate the difference or similarity with other studies. Although we have discussed the comparisons with other studies in “Section 3.5” of the original manuscript, we accept the comments and suggestions of the reviewer to expand more in our revised manuscript in “Section 3”.

Specific comments

1. Hong Kong is just one city in Pearl River Delta region. Thus, the authors might want to introduce more previous work in PRD region, rather than just Hong Kong. Several researchers have reported PTR-MS results in PRD region [Wang et al., 2016], and more in other parts of China, but the authors do not acknowledge these references in the introduction.

Response: thanks for the good comments and suggestions. The reference was added in the revised manuscript. And related information was added in the revised manuscript as follows.

“PTR-MS has been used in China for environmental studies throughout these years (Wang et al., 2014; Wang et al., 2016). But PTR-MS was firstly used in an urban roadside microenvironment of Hong Kong to measure ambient OVOCs and VOCs in this study.”

2. Formaldehyde humidity dependence in PTR-MS. Several papers have discussed this issue previously [Inomata et al., 2008; Vlasenko et al., 2010; Warneke et al., 2011]. Especially, Valsenko et al. derived explicit equations to fit the sensitivity vs. absolute humidity, based on the equilibrium between forward and backward reactions. In this manuscript, the authors tried to fit the observed rate coefficient (k) and sensitivity with relative humidity, temperature and absolute humidity. All of these tests are just using one dataset with different parameters/equations to derive curves for the correction, but without knowing the physical meaning of parameters/equations. The best way to do it should use the equations shown in Valsenko et al. Thus, Figure 2-8 should be replaced with one Figure similar to Fig. 5 in Valsenko et al.

Response: thanks for the comments. Several previous studies have discussed the humidity dependence of formaldehyde either discussed the sensitivity variance against relative humidity only or against absolute humidity. But temperature also lead to the sensitivity variance in our study. No matter RH&T or absolute humidity is chosen to do the simulation, the sensitivity variance of formaldehyde depends on the amount of water vapor concentration in ambient air, because the proton affinity (PA) of formaldehyde is just slightly higher than that of water, so the backward reaction of protonated formaldehyde with H₂O is not negligible. Moreover, the simulation model raised in this study could offer a better agreement for formaldehyde than using the fitting results by absolute humidity. It is easier to measure RH and T of ambient air for further correction of formaldehyde results by PTR-MS in practice.

3. PTR-MS operations: how often the instrument is calibrated, how is background determined, how often do you do background, how often the humidity dependence curve for formaldehyde is conducted (just one in 2 years?).

Response: the instrument was calibrated every six days, and the background level was determined by using the zero air generated by a Gas Calibration Unit (GCU) (IONICON Analytik GmbH, Innsbruck, Austria) for half-hour each day, and the humidity dependence curve for formaldehyde was conducted every month. Details can be found in the revised manuscript as follows.

“Zero air was generated by a Gas Calibration Unit (GCU) (IONICON Analytik GmbH, Innsbruck, Austria) with a VOC-scrubber installed inside the GCU. Background level was determined by using the zero air for half-hour each day. The relative humidity and temperature of inlet gas were set by adjusting the humidification chamber and a dew point mirror inside the GCU. Ionimed mix-VOCs gas standard was diluted with four different ratios (0.08, 0.06, 0.04 and 0.001) to calibrate the PTR-MS. The accuracy and the measurement precision of the PTR-MS was 20% and 10%, respectively. The accuracy of PTR-MS measurement was dependent on the accuracy of the reaction rate coefficient, fragmentation, gas standard and flow rate (Salisbury et al., 2003; Kim et al., 2009). The precision was determined based on the standard deviation of the background

signal at each mass during 5-min average measurement for each specie. Calibrations were done every six days for ensuring the accuracy of PTR-MS.”

4. PTR-MS data processing: how signal is normalized, do you see sensitivity drift with
5 time, how background is interpolated (especially formaldehyde). The authors should
apply the widely accepted data reduction methods shown in many previous papers
(most important ones [de Gouw and Warneke, 2007; de Gouw et al., 2003]).

Response: the sensitivity was defined as the signal of RH^+ ions obtained at a VMR of
1 ppbv and normalized to a standard H_3O^+ signal ($I_{\text{H}_3\text{O}^+}$) of 10^6 counts s^{-1} as presented
10 in many previous studies (de Gouw et al., 2003; de Gouw and Warneke, 2007). The
sensitivity only drifted a little during the whole sampling period. The background was
determined by introducing the zero air generated by GCU, and the background level
varied within the difference less than 5% for all species, the monthly averaged
background level was used during each sampling month.

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5. Inter-comparison: In addition to PTR-MS, the QA/QC procedures should be provided
to evaluation the data quality. Previous studies also found many
limitations/interferences for DNPH method, such as formaldehyde [Wisthaler et al.,
2008], aldehydes [Herrington and Hays, 2012] and ketones [Ho et al., 2014]. Without
20 acknowledging these interferences, the inter-comparison is meaningless. From Figure
9 in the manuscript, the bad agreement for acetone might be a DNPH issue.

Response: thanks for the kind comments and suggestions. The mentioned references
were added and the related part was expand in the revised manuscript as follow.

“Wisthaler et al. (2008) reported the inter-comparison between PTR-MS and DNPH-
25 HPLC in an atmosphere simulation chamber, good agreement was found between PTR-
MS and DNPH-HPLC while ambient air was introduced into the chamber, but the
concentration of HCHO measured by DNPH-HPLC was less than by PTR-MS, which
could be caused by some interferences for DNPH-HPLC method or the varying
performance of the KI ozone scrubber. Overestimation of DNPH-HPLC for HCHO in
30 the presence of NO_2 was also reported by Herrington and Hays (2012), because NO

can be oxidized to NO₂ in the upstream ozone scrubber, and NO₂ will react with DNPH to form 2,4-dinitrophenylazide (DNPA), which has the similar chromatographic properties with the formaldehyde-DNP-hydrazone. Hence, the intercept of -0.03 for HCHO inter-comparison between PTR-MS and DNPH-HPLC in this study may be 5 explained by the interference of NO₂ because of the high NO_x levels at the roadside sampling site.”

“Low acetaldehyde collection efficiencies (CEs), ranging from 1 to 62% was found by Herrington et al. (2007) for the typical 24-hour sampling period which can lead to the underestimation of acetaldehyde by DNPH-HPLC method. And this artifact is 10 consistent with the result for acetaldehyde inter-comparisons in this study. It was found that ketone concentrations determined by DNPH-HPLC method could be underestimated by 35 ~ 80% under high RH (>50%) condition when the temperature is about 22 °C (Ho et al., 2014). This DNPH issue could explain the 12% difference between PTR-MS and DNPH-HPLC for MEK and the relative bad agreement for 15 acetone in our study.”

6. Eq. 7: If you use m107 to calibrate C2 benzenes, then C2 benzenes should not be corrected. Where is 0.2235 from? Note that only ethylbenzene fragments significantly. Thus, Eq. 6 should be [Benzene]=[m79]-0.2235*[m107]*f. f is the fraction of 20 ethylbenzene in ethylbenzene+xylenes, which can be from GC-FID measurements. Then, PTR-MS measurements would somewhat rely on GC-FID measurements. How would this reliance affect inter-comparison?

Response: thanks for the comments. Since higher aromatics (ethylbenzene and propylbenzene) can start to fragment into ions at 79 amu (de Gouw and Warneke, 2007), 25 this fragmentation could lead to the overestimation of benzene at 79 amu and underestimation of C2-benzenes at 107 amu (Rogers et al., 2006).

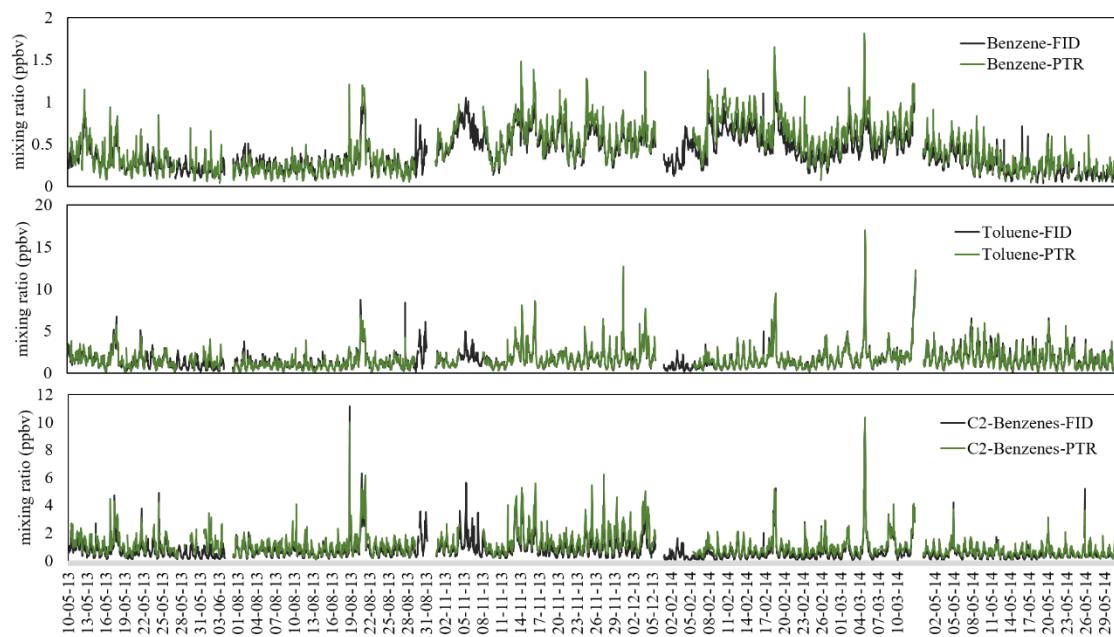
(S_{Ethylbenzene} / S_{Benzene}) BF_{Ethylbenzene} [Ethylbenzene] is the fragment from ethylbenzene to 79 amu. In this study, (S_{Ethylbenzene} / S_{Benzene}) = 1.58, BF_{Ethylbenzene} = 32%, [Ethylbenzene] = 0.3615 [C₂-Benzenes], where 0.3615 was the fraction of 30 ethylbenzene in C₂-Benzenes.

Thus, 0.1827 [C₂-Bzenes] was the fragment from ethylbenzene to 79 amu. Then, [C₂-Bzenes] = [M107] + 0.1827 [C₂-Bzenes], so [C₂-Bzenes] = 1.2235 [M107]. [Benzene] = [M79] - 0.1827 [C₂-Bzenes] = [M79] - 0.1827 · 1.2235 [M107] = [M79] - 0.2235 [M107]. In this case, PTR-MS would somewhat rely on GC-FID measurements or canister results, **because the PTR-QMS used in this study cannot differentiate isomers. And this is really the limitation of PTR-QMS. But this is a better way to get a more reliable results if the fraction of ethylbenzene in C₂-Bzenes can be obtained from other techniques (e.g. GC-FID).**

7. Figure 1 should only contain the periods with only PTR-MS measurements. The time series of VOCs should be also shown.

Response: thanks for the comments. Figure 1 was used to explain why we set the air condition at RH = 80% and T = 25°C for calibration. In order to present the time series of VOCs measured by PTR-MS, Figure. 10 was added in the revised manuscript as follows.

“Time series of benzene, toluene and C2-benzenes results obtained by on-line GC-FID and PTR-MS during the sampling period were plotted in Fig. 10.”



“Figure 10. Measurement results for benzene, toluene and C2-benzenes obtained during

the field study at MK in Hong Kong. The black lines show the on-line GC-FID data, and the green lines show the PTR-MS results.”

References

5 de Gouw, J., and Warneke, C.: Measurements of volatile organic compounds in the earth's atmosphere using proton-transfer-reaction mass spectrometry, Mass spectrometry reviews, 26, 223-257, 10.1002/mas.20119, 2007.

de Gouw, J. A., Goldan, P. D., Warneke, C., Kuster, W. C., Roberts, J. M., Marchewka, M., Bertman, S. B., Pszenny, A. A. P., and Keene, W. C.: Validation of proton transfer 10 reaction-mass spectrometry (PTR-MS) measurements of gas-phase organic compounds in the atmosphere during the New England Air Quality Study (NEAQS) in 2002, Journal of Geophysical Research: Atmospheres, 108, 10.1029/2003jd003863, 2003.

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