

### Responses to the comments from Anonymous Referee #3

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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The authors have applied a suite of techniques to measure VOC and OVOC at a roadside site in Hong Kong and have compared the data to those generated by a PTR-MS. Measurements of formaldehyde are examined in detail and a method has been developed to address the RH and T dependence of the calibration for future studies.

10 This approach seems reasonable. OVOCs measured by PTR-MS are compared with a DNPH method and aromatics measured by PTR-MS are compared to in-situ GC-FID and canister samples. Besides my question regarding the fitting method below, the comparison has been done well enough, very much along the line of previous groups.

*Response: we appreciate the reviewer for the positive comments and helpful suggestions. The manuscript has been revised and improved based on these suggestions. 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.*

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However, I cannot help feeling though that there is an opportunity missed here. Surely the GC-FID also measured the OVOC (i.e. not just the aromatics)? Can their peaks not be calibrated by carbon number and compared with the PTR-MS/DNPH/can methods as well? The result would be an assessment/validation of the in-situ GC-FID measurement of OVOC which could be of use to the group in future measurement campaigns where the PTR-MS is not available. Moreover, do the canister data not deliver values of acetone, propanal and acetaldehyde for comparison? This again would be an interesting comparison extension to this study. There has been much discussion of potential canister artifacts previously but they may compare well under the conditions where ozone is low.

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*Response: many thanks for the comments. We understand that it will be better if other techniques (on-line GC-FID and canister samples) can measure OVOC. Unfortunately,*

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both on-line GC-FID and canister samples cannot measure OVOC in this study. Only less than 30 C<sub>2</sub>-C<sub>9</sub> NMHC species without any OVOC species were measured by the on-line GC-FID as previous studies in Hong Kong (Xue et al., 2014;Ou et al., 2015). The canister data covered a wide range of NMHC species (C<sub>2</sub>-C<sub>10</sub>; >50 species), but these species only contained alkanes, alkynes, aromatics, halocarbons and sulphur compounds as stated by Colman et al. (2001). Hence, **OVOC can only be measured by PTR-MS and DNPH-HPLC methods in this study.** But it is a good suggestion that we will try to measure more OVOC species by different techniques in our future field campaigns.

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One of the greatest problems in sampling and measuring OVOC will be ozone as it can make OVOC (and remove reactive alkenes) when trapped in canisters or concentrators. If ozone was measured at this site it would be very interesting to compare the degree of fit with ozone levels. Most city roadside sites show low ozone, due to the titration of NO, but in the afternoon it is likely that ozone levels will increase as photochemical production and down-mixing kick in. This would mean correlation could be expected to deteriorate later in the afternoon if ozone reactions become important. Examining this influence of local ozone on the quality of fit would be a very interesting addition to this paper. It is likely to impact the GC and DNPH methods more than the PTR-MS.

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Response: thanks for the suggestions. A temperature controlled copper tube coated with KI is used as the ozone scrubber in the ATEC Model 2200 automated sampler (Model 2200, Malibu, CA) to remove ozone during carbonyl sampling with DNPH cartridges in this study. Additionally, an ozone scrubber (Sep-Pak; Waters Corporation, Milford, MA) was also connected to the DNPH cartridge for each sample. It has been reported widely that the artifacts can be eliminated by installing the ozone scrubber upstream, and the oxidants at ambient level can be removed efficiently (Rodier et al., 1993;Sirju and Shepson, 1995;Helmig, 1997).

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Moreover, the ozone level at the sampling site during the sampling period was quite low (less than 10 ppbv), and the maximum ozone level was less than 40 ppbv even in the afternoon because of the high traffic volume at the sampling site. According to Sirju

and Shepson (1995)'s study, ozone concentration below 40 ppbv is a typical value of clean ambient air, and using KI trap is effective to remove ozone for both urban and rural areas. Besides, ozone removal efficiency >99% was measured for the scrubber with ozone levels of 100 ppb in earlier studies. Our study also showed good correlations for formaldehyde and acetaldehyde between the PTR-MS and DNPH-HPLC method. Hence, ozone is not the major interference for OVOC measurement by DNPH-HPLC method. The relative bad agreement for acetone might be a DNPH issue but not ozone interference (Ho et al., 2014). In the revised manuscript, more information of ozone scrubber usage and the inter-comparison part was expanded as follows.

“An ozone scrubber (Sep-Pak; Waters Corporation, Milford, MA) was used to remove ozone during carbonyl sampling with 2,4-dinitrophenylhydrazine (DNPH) cartridges (Waters Sep-Pak DNPH-silica, Milford, MA).”

“Wisthaler et al. (2008) reported the inter-comparison between PTR-MS and DNPH-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 the presence of NO<sub>2</sub> was also reported by Herrington and Hays (2012), because NO can be oxidized to NO<sub>2</sub> in the upstream ozone scrubber, and NO<sub>2</sub> 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 explained by the interference of NO<sub>2</sub> because of the high NO<sub>x</sub> levels at the roadside sampling site.”

For the correlation plots a simple  $y=mx+c$  form is used. This assumes that the x-axis parameter is correct and without error. More appropriate in this case would be to use orthogonal distance regression to account for error in both axes, since the DNPH method will also contain errors to some degree.

Response: thanks for the excellent comments. Firstly, the linear regression is used by many previous studies for comparison analysis (Warneke et al., 2001;de Gouw and Warneke, 2007;Warneke et al., 2011;Jobson et al., 2010;Wang et al., 2014;Kuster et al., 2004;Kato et al., 2004). Because “Section 3.5 - comparison with other studies” is one of the key parts in this manuscript, it is better to choose the same analytical method to conduct the comparison for those parameters (namely slope, intercept and correlation coefficient). Secondly, the error bar of the y-axis parameter stands for the standard deviation of 24-hour averaged PTR-MS data as stated in Figure 9 and Figure 12. But both DNPH cartridge samples and canister samples were collected once during 24 hours. So the standard deviation was not existed for DNPH cartridge and canister sample. Therefore, only error bar of the y-axis parameter was plotted.

The PTR-MS accuracy is given as 20% and the precision as “about 10%”. Since this paper is an instrumental comparison I think it is necessary to expand on this and explain where the 20% comes from and the measurement precision of each species. Likewise the GC-FID accuracy and precision is given as the same as for the PTR-MS, but without explanation. How these figures arrived at should be given in more detail.

Response: thanks for the useful comments and suggestions. We agree the point of the reviewer, and we expand on the methodology part and give more explanation in the revised manuscript. Several parameters (reaction rate coefficient, fragmentation, flow rate, gas standard...) lead to accuracy, most important is the reaction rate coefficient (Salisbury et al., 2003). One important part of our study was to study the experimental reaction rate coefficient, and it also point out the significance of our study. The related information were added in the manuscript as follows.

“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.”

“The accuracy was based on weekly span checks and monthly calibration. The precision was based on the 95% probability limits for the integrated precision check results (Ling et al., 2013;Lyu et al., 2016).”

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The potential interference of ozone may be an explanation of the relatively poor fit of PTR-MS vs DNPH for acetaldehyde (and also acetone) in figure 9 (D and E). It might be illuminating to color the points as a function of daily average ozone (if available).

Response: thanks for the kind comments. Actually, ozone is not the key issue for the relative poor fit of PTR-MS vs DNPH for acetaldehyde (and also acetone) as stated in the third response. The relatively poor fit is mainly caused by the DNPH issue for ketones and low collection efficiencies for acetaldehyde because of the long time sampling period for DNPH cartridge samples. More detailed explanation for the inter-comparison between PTR-MS and DNPH-HPLC was expanded in the revised manuscript as follows.

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“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 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 acetone in our study.”

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Minor points. Introduction, line 4. Perhaps a more relevant reference concerning the human health impacts would be Lelieveld et al. (doi:10.1038/nature15371).

Response: thanks for the comments. The reference was added in the revised manuscript.

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“Special attention has been paid on the characteristics” should be “paid to”.

Response: thanks for the comments. It has been revised in the manuscript.

5 Section 2.2, give details of the particulate filter (i.e. material, pore size, how often changed).

Response: thanks for the comments. Details of the particulate filter is added in the revised manuscript as follows.

“An in-line particulate filter (4.7 mm Teflon-membrance filter assembly, Whatman Inc., Clifton, NJ, USA) was used to prevent particles from entering the instrument.”

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Section 2.4 line 20. What were these strict QA/QC procedures? If necessary give the reference where they are detailed directly afterwards.

Response: thanks for the comments. References were added afterwards and the manuscript was revised as follows.

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“The accuracy was based on weekly span checks and monthly calibration. The precision was based on the 95% probability limits for the integrated precision check results (Ling et al., 2013; Lyu et al., 2016).”

Section 3.3. line 2, was glyoxal measured, perhaps it can contribute to mass 59?

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Response: thanks for the comments. Glyoxal was not measured in this study, and acetone occupies the most (90 ~ 100%) at mass 59 (de Gouw and Warneke, 2007). So glyoxal did not affect the acetone measurement significantly by PTR-MS. But it is good suggestions that we will explore the influence of glyoxal on acetone measurement by PTR-MS in the future.

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Section 3.3 line 3 “benzens” should be benzenes.

Response: thanks for the comments. It has been revised in the manuscript.

Figure 8 Xaxis label is misspelt “Measuremeasured”.

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Response: thanks for the comments. It has been revised in the manuscript.

Conclusions, line 24, filed should be field.

Response: thanks for the comments. It has been revised in the manuscript.

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