

Responses to the comments from Anonymous Referee #1

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 paper reports on a field inter-comparison between PTRMS and several other techniques in the detection of VOCs and OVOCs at an urban site. The paper is well-structured and provides a thorough overview of the current state of knowledge, as well as sufficient details of the analytical approach of the study. The data treatment and discussion on the whole are comprehensive and sound. The presented figures and tables are clear and offer an excellent overview of the data obtained.

Response: we thank the reviewer very much for the valuable comments and suggestions, which can help to improve the manuscript substantially. In the revised manuscript, we have addressed these comments, and adopted the suggestion to synthesize our results and compare against existing findings of previous studies. 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.

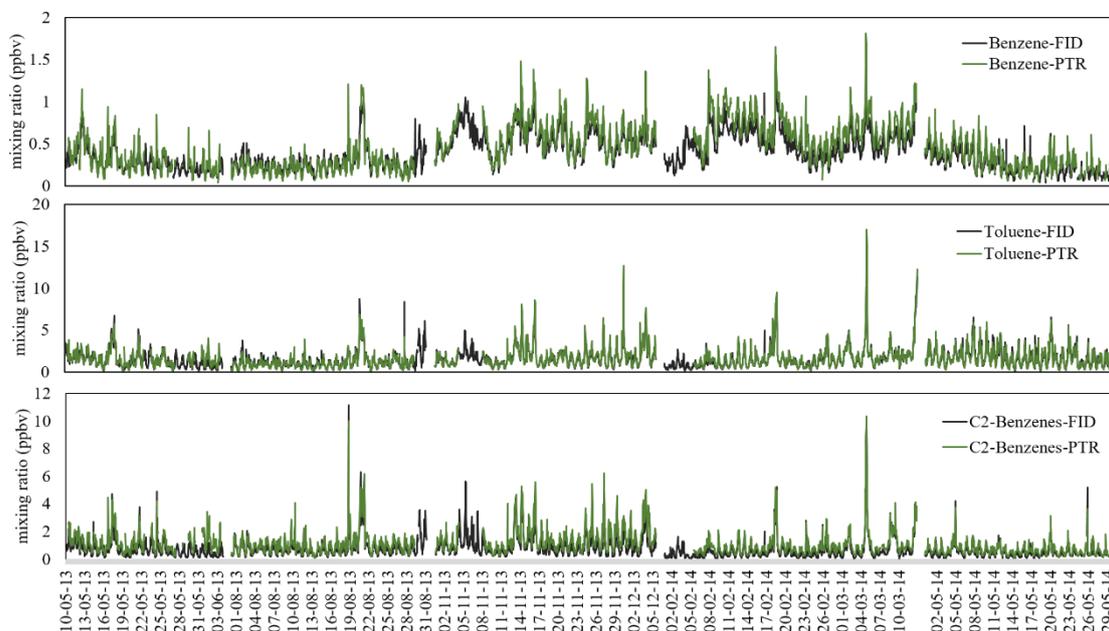
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20 In discussing and comparing the data between PTR-MS and the other techniques, however, one aspect that is missing is the recognition of the high time resolution of measurements by PTR-MS compared to the other techniques; it all very well to compare absolute concentrations of different species detected by each technique in comparison to PTR-MS, but the rapid and continuous analysis by PTR-MS are somewhat downplayed, yet are certainly a key feature of the system that make it particularly suited to long-term VOC monitoring.

Response: thanks for the helpful comments and suggestions. Because each cartridge and canister sample was collected during 24 hours. It is not appropriate to plot the time series of PTR-MS v.s. DNPH-HPLC (or off-line canister). But the time series of benzene, toluene, C2-benzenes obtained by PTR-MS and on-line GC-FID were plotted

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in Fig. 10 as in the revised manuscript.

“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.”



5 “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.”

The discussion on the observed discrepancies could also be expanded upon. At present
10 most of the emphasis is on the humidity-dependent performance of the PTR-MS
detection, yet not much is said about potential under- or overestimation of the data by
the other techniques with which PTR-MS is compared.

Response: thanks for the excellent comments and suggestions. We have expand the
mentions part in the revised manuscript as follows.

15 “Beauchamp et al. (2013) used a similar mixed gas standard for PTR-MS calibration,
low sensitivity of HCHO was also found below 2 ncps ppbv⁻¹ when the RH ranged
from 20% to 100%. Moreover, strong nonlinear dependence on RH for HCHO was
found by Beauchamp et al. (2013), and the sensitivity of HCHO significantly decreased
by about 50% when the RH of inlet air increased from 20% to 100%, which is

comparable to our study.”

“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 NO₂ 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 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 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.”

Further specific comments are as follows: Page 2, lines 32-34: Please acknowledge the first reports of these reactions in the detection of HCHO by PTR-MS, namely: Hansel et al. *Int. J. Mass Spectrom.*, 167/168, 697–703, 1997.

[Response: thanks for the comments. The reference was added in the revised manuscript.](#)

Page 3, line 10: which model PTR-MS was used?

Response: thanks for the comments. Model PTR-QMS 500 was used in this study. It was added in the revised manuscript as follows.

5 “A commercially available PTR-MS instrument (PTR-QMS 500, IONICON Analytik GmbH, Innsbruck, Austria) was used in this study. PTR-MS instrument has been described in detail elsewhere (Lindinger et al., 1998;de Gouw et al., 2003;de Gouw and Warneke, 2007).”

Page 3, line 13: H₃O⁺ was used as the “reagent ion”, not the “ion source”. Please correct.

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

Page 3, line 20: replace “flow tube” with “inlet line” to avoid confusion with the flow drift tube of the instrument (reaction chamber).

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

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Page 3, line 30: how were the accuracy and precision values stated for the PTR-MS instrument determined? The same applies to these values presented for the other instruments in the study. It would also be desirable if the authors presented the limits of detection of the VOCs and OVOCs presented in the inter-comparison, perhaps most suitably in the form of a table.

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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.

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“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.,

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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
5 was based on the 95% probability limits for the integrated precision check results (Ling et al., 2013;Lyu et al., 2016).”

Page 5, Eq. 1: this is an unusual presentation of how to calculate the VMR from the analyte and reagent ion signal intensities in PTR-MS. If the authors choose to present
10 it like this, I think that further details are needed of how they arrived at this arrangement, either by explanation or by a suitable reference. Please also indicate how the value of the constant was reached.

Response: thanks for the good comments and suggestions. We have changed the equation to a more used equation, which can be found in the reference (de Gouw and
15 Warneke, 2007). The manuscript was revised as follow.

“Experimental *k* values of selected VOC and OVOC species were obtained under different ambient conditions, and RH ranged from 25% to 100% and T ranged from 5°C to 25°C through this method.

$$\text{VMR} = \frac{\mu_0 N_0}{kL} \times \frac{E}{N^2} \times \frac{I_{\text{RH}^+} \times \text{TR}_{\text{H}_3\text{O}^+}}{I_{\text{H}_3\text{O}^+} \times \text{TR}_{\text{RH}^+}} \quad (1)$$

20 where,

VMR - the volume mixing ratio, ppbv;

μ_0 - the reduced mobility, $\text{cm V}^{-1} \text{s}^{-1}$;

N_0 - the gas number density at standard pressure (1 atm) and temperature (273.15 K);

k - the reaction rate coefficient, $10^{-9} \text{ cm}^3 \text{ s}^{-1}$;

25 L - the length of the drift tube, 9.3 cm in this study;

E - the electric field strength, V m^{-1} ;

N - the air density in the drift tube, m^{-3} ;

I - the numbers of detected ions, cps;

TR - the transmission factor of respective ions.”

Page 5, lines 28-30, discussion relating to sensitivity dependence of HCHO to relative humidity: the authors should acknowledge and discuss similar work performed on the same VOC standard using the same equipment, in which similar observations were made, namely: Beauchamp et al. Meas. Sci. Technol., 24, 125003, 2013. How do the present measurements compare to those reported in the aforementioned article?

Response: thanks for the excellent comments. The reference was added in the revised manuscript. And this part was expanded as follows.

“Beauchamp et al. (2013) used a similar mixed gas standard for PTR-MS calibration, low sensitivity of HCHO was also found below 2 ncps ppbv-1 when the RH ranged from 20% to 100%. Moreover, strong nonlinear dependence on RH for HCHO was found by Beauchamp et al. (2013), and the sensitivity of HCHO significantly decreased by about 50% when the RH of inlet air increased from 20% to 100%, which is comparable to our study.”

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Page 9, lines 3-4: the authors start this section by referring to a comparison between PTR-MS and DNPH-HPLC data for acetone and propionaldehyde, but in the next sentence discuss other compounds and an unrelated figure. The discussion on the former reappear at the end of this paragraph but with no presentation of the data: are the data for acetone not shown? Consider repositioning the discussion on those data to the start of the paragraph and indicate that the data are not presented.

Response: thanks for the good suggestions. This part was revised in our manuscript as follows.

“As shown in Fig. 9, good linear correlations were found for formaldehyde, acetaldehyde and MEK with correlation coefficients of 0.79, 0.75, 0.93, respectively, and with slopes of 1.00 ± 0.10 , 1.10 ± 0.33 , and 0.88 ± 0.058 , respectively. For acetone, the slope is 0.76 ± 0.23 (PTR-MS to HPLC) with a correlation coefficient of 0.60.”

“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

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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 NO₂ 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 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 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.”

Figures 9 and 11: where are the error bars for the DNPH-HPLC and off-line GC-MSD/FID/ECD analyses, or is there no measurement error associated with these systems?

Response: thanks for the excellent comments. 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 (in the revised manuscript). 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.

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Figure 11 and 12 captions: the authors should elaborate in the caption on what the “corrected“ data are. Errors.

Response: thanks for the suggestions. It has been revised in our manuscript as follows.

5 “Figure 11. Inter-comparison between ambient aromatic hydrocarbon measurements by PTR-MS and by on-line GC-FID during the field study at MK in Hong Kong: (A) benzene, (B) toluene, and (C) C2-benzenes. Original data are plotted in black dots, grey dots represent **the corrected data based on Eq. (6) and Eq. (7)**. Linear regression fits for original and corrected data are indicated by the solid black line and the solid grey line respectively. Dashed line is the 1:1 line for reference.”

10 “Figure 12. Inter-comparison between ambient aromatic hydrocarbon measurements by PTR-MS (**corrected based on Eq. (6) and Eq. (7)**) and by off-line canister measurements using GC-MSD/FID/ECD during the field study at MK in Hong Kong: (A) benzene, (B) toluene, and (C) C2-benzenes. Linear regression fits are indicated by the solid black line. Error bar stands for the standard deviation of 24-hour averaged
15 PTR-MS data. Dashed line is the 1:1 line for reference.”

Throughout: Please be consistent in the use of VOC and VOCs for singular and plural, respectively (similarly for OVOC).

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

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Abstract, line 24 and p2, line 12: place parentheses around ECD and not electron capture detection.

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

25 Page 2, line 29: change to “HCHO can be protonated by the following reaction”.

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

Page 2, line 32: change “is just slight higher” to “is just slightly higher”.

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

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Page 7, line 22: “C2-benzenes” not “C2-benzens”. Page 9, line 24: “field” not “filed” sampling study.

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

- 5 Figure 1 caption: should be “dashed lines” not “das lines”.

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

References

10 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.

Salisbury, G., Williams, J., Holzinger, R., Gros, V., Mihalopoulos, N., Vrekoussis, M., Sarda-Estève, R., Berresheim, H., von Kuhlmann, R., Lawrence, M., and Lelieveld, J.: Ground-based PTR-MS measurements of reactive organic compounds during the 15 MINOS campaign in Crete, July–August 2001, *Atmos. Chem. Phys.*, 3, 925-940, 10.5194/acp-3-925-2003, 2003.