

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.

Anonymous Referee #1

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Report on AMT-2016-130 The paper reports on a field inter-comparison between PTR-MS 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. 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

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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 down-played, yet are certainly a key feature of the system that make it particularly suited to long-term VOC monitoring. The discussion on the observed discrepancies could also be expanded upon. At present most of the emphasis is on the humidity-dependent performance of the PTR-MS detection, yet not much is said about potential under- or over-estimation of the data by the other techniques with which PTR-MS is compared. 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. Page 3, line 10: which model PTR-MS was used? Page 3, line 13: H₃O⁺ was used as the “reagent ion”, not the “ion source”. Please correct. Page 3, line 20: replace “flow tube” with “inlet line” to avoid confusion with the flow drift tube of the instrument (reaction chamber) 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 O VOCs presented in the inter-comparison, perhaps most suitably in the form of a table. 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 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. 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? 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

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

Throughout: Please be consistent in the use of VOC and VOCs for singular and plural, respectively (similarly for OVOC). Abstract, line 24 and p2, line 12: place parentheses around ECD and not electron capture detection. Page 2, line 29: change to “HCHO can be protonated by the following reaction”. Page 2, line 32: change “is just slight higher” to “is just slightly higher”. Page 7, line 22: “C2-benzenes” not “C2-benzens”. Page 9, line 24: “field” not “filed” sampling study. Figure 1 caption: should be “dashed lines” not “das lines”.

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