

## ***Interactive comment on “Comparison of VOC measurements made by PTR-MS, Adsorbent Tube/GC-FID-MS and DNPH-derivatization/HPLC during the Sydney Particle Study, 2012: a contribution to the assessment of uncertainty in current atmospheric VOC measurements” by Erin Dunne et al.***

**Anonymous Referee #2**

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General comment: This manuscript presents data from a comparison of VOC measurements made by PTR-Q-MS, Adsorbent tube GC-FID/MS and DNPH-HPLC in an urban area. The VOC selected for comparison were C6- to C8-aromatics, isoprene and C1- to C3-carbonyl compounds. Compared to the two other methods the PTR-MS measurements were found to overestimate the VOC mixing ratios by a factor of 1.18 to 2.01. Most of the discussion is based on the assumption of positively biased

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PTR-MS measurements due to possible isobaric compounds or fragments on the respective  $m/z$  signals. Therefore the authors mainly apply data corrections considering these interferences to reduce the observed overestimation by PTR-MS. Literature data on observed interferences in PTR-MS measurements combined with potentially interfering compounds measured by AT-GC-FID/MS were taken into account to correct the PTR-MS mixing ratios. This procedure improved the comparison. A critical review of the AT-GC\_FID/MS measurement is not taken into account. The comparison of the PTR-MS data to the DNPH-HPLC data discusses two possible reasons for the observed regression slope of  $> 1$ . An overestimation of PTR-MS measurements due to possible isobaric compounds or fragments, or an underestimation of the DNPH-HPLC measurements. It is stated but not proven that the respective  $m/z$  signals of the PTR-MS measurements were dominated by the carbonyl compound of interest and on the other hand the underestimation by the DNPH-method cannot be ruled out. In the case of DNPH-acetone measurements, there are indications but no proof for a negative bias due to high humidities.

Specific comments: Chapter 3.1 Inter-comparison of PTR-MS and AT-VOC samples analysed by GC-FID-MS: The discussion is solely based on the assumption that PTR-MS is biased by positive interferences to explain the results. Can underestimation by the AT-VOC technique be ruled out? If so please discuss. Page 7 Line 24: The authors use the fragmentation patterns for alkylbenzenes to correct their data adapted from Gueneron et al. (2015) which provides those fragmentation patterns for E/N 80 Td and E/N 120 Td. While the PTR used has an E/N of  $\sim 100$  Td ( $V(\text{Drift}) = 445$  V,  $T(\text{Drift}) = 60^\circ\text{C}$ ,  $p(\text{Drift}) = 2.16$  mbar) the literature values for E/N 120 Td were used which imply a high fragmentation and therefore overestimates the contribution of  $m/z$  79 from alkylbenzenes. Therefore the slope of 1.27 is only a lower estimate. Figure 3: The extraction mass of the DNPH cartridge sample is estimated to be increased by condensed water. Please plot the dew point / rRH with the data. As the DNPH cartridges were sampled at  $7^\circ\text{C}$  the extraction mass should correlate with the dew point. All datasets exceeding a dew point of  $7^\circ\text{C}$  should be omitted or lab tests of the

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influence of condensing water on the sampling/derivatization should be included in the discussion. Page 12 Line 12: Please proof the statement 'Overall, the PTR-MS signal at m/z 59 was dominated by acetone'

Technical comments: Page 1 Line 17 and Page 12 Line 23: Non consistent values: median of 0.13 vs. median of 0.11 Page 1 Line 20: A slope with a value of 1.08 stated as the lower range of slopes is not stated in the following text/tables. Page 4 Line 10: 'Cheng et al. (2008a)' is missing in the reference list. Page 4 Line 15: Remove 'and' from the sentence 'a PAMS gas standard (Spectra Gases, Linde NJ USA) and were used' Page 4 Line 25: 'Ellis and Mayhew 2014' is missing in the reference list. Table 2: The uncertainty of the calibration factors is 6% or higher. This is not reflected in the number of significant digits of the given values Page 6 Line 10: Add 'of' to the sentence 'The results this inter-comparison' Page 6 Line 11: Add 'are' to the sentence 'conclusions about the uncertainty in current VOC measurements presented' Page 7 Line 3: 'benzene data yielded a slope of  $1.47 \pm 0.04$ '; Figure 1a and table 5 provides a slope off 1.27. Which number is correct? If Figure 1a and table 5 provides an already corrected dataset please state so in the captions. Page 7 Line 7: 'Slope of  $\sim 1.5$ ' → see previous comment Page 7 Line 13: Rephrase sentence Page 9 Line 29: Remove 'Ne' at the end of the line Page 9 Line 38: Change 'din' to 'in' Page 12 Line 15: Please complete the sentence: 'guarded against as stated' Page 12 Line 20: The statement 'Inter-comparisons have been made between three independent techniques' is not correct. Although 3 different techniques were used the inter-comparison took only place between two techniques for each of the evaluated compounds. Please clarify.

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