We sincerely thank the editor and reviewers for the valuable comments and suggestions, which are very helpful in improving our manuscript. We herein provide the point-by-point response and the changes made to the original manuscript according to the comments and suggestions. The response is in the indent and blue, and the revised text is in the indent and green. The line numbers mentioned in the response correspond to the revised manuscript unless otherwise specified.

Reviewer:

This manuscript describes a series of tests performed on the newly developed Vocus PTR-MS to characterize the instrument response to humidity and various internal settings (voltages and pressures) for 21 commonly measured volatile organic compounds. The authors show that sensitivities and ion distributions for most species showed little variation with humidity, and provide recommendations for instrument settings to maximize sensitivities. The manuscript is well written, straightforward, easy to follow, and provides useful benchmarks that instrument users and developers will certainly find helpful. I would recommend publication following clarification of a few minor points:

Response: We appreciate the positive comments from the reviewer and the response to specific comments are provided below.

1. It should be mentioned somewhere which species are in which standard tank, and some evidence needs to be provided that the various fragments of each compound in an individual tank do not overlap with each other in any way that could obfuscate the results. Were these compounds ever tested outside the tanks to check that?

Response: Thanks for the suggestion. We have now included a new entry (Cylinder No.) in Table 1 (P17) to show the species in each cylinder.

L159 and L160: Table 1.

L405: The cylinder numbers for the VOCs studied are also shown here

As for the potential interference, we carefully compared the anticipated protonated ions, fragmented ions, and adduct ions as expected from reactions R1-R5 (also referring to literature for dealkylation for R5, e.g., for α-pinene). There is one such case. The protonated signals (MH^+) of acrolein and methacrolein (m/Q = 57 and 71, respectively) overlap with the fragmented ions ($[MH - C_xH_y]^+$) of n-butanal and pentanal, respectively (with x = 1, i.e., losing a methyl group). From the structurally analogous hexaldehyde, long-chain aldehydes should have a fragmented ion $[MH - C_xH_y]^+$ as that of hexaldehyde, but the signal percentages should be very small (see Figure 2, ~2% for hexaldehyde). Therefore, fragmented ions ($[MH - C_xH_y]^+$) of n-butanal and pentanal have little effect on the signal of MH^+ of acrolein and methacrolein, and the signals at m/Q = 57 and 71 are considered directly to belong to $[MH]^+$ of acrolein and methacrolein, respectively. In that case, the fragmented ions $[MH - C_xH_y]^+$ for n-butanal and pentanal cannot be obtained here, and it is assumed to be of a low signal percentage as that of hexaldehyde (~2%). We have included a few sentences in L215 to clarify that.

L215-L220: Some dealkylated fragments ($[MH - C_xH_y]^+$) of long-chain aldehydes (e.g., n-butanal and pentanal) might overlap with the protonated ions ($[MH]^+$) of unsaturated aldehydes (i.e., acrolein and methacrolein). Yet since the intensities of the former are expected to be low by analogy with that of hexaldehyde (~2%, Figure 2), the ions at those m/Q values are only considered as the protonated ions of unsaturated aldehydes (the latter).

In addition, n-butanal and methyl ethyl ketone are isomers. But they are in different cylinders and will not interfere with each other (as stated in L166 in the manuscript).

As shown in the response to the 2nd comment of Reviewer 1, we used a few measures to find the fragmented and adduct ions of a specific VOC, and reconstruct the mass spectrum (shown in Figures S2-S4). We did not do all the 21 compounds individually, but we did used a permeation/diffusion tube device to generate toluene. The mass

spectra of toluene from the mixed-VOC cylinder (reconstructed) and from the individual VOC are shown below in Figure R2.1.

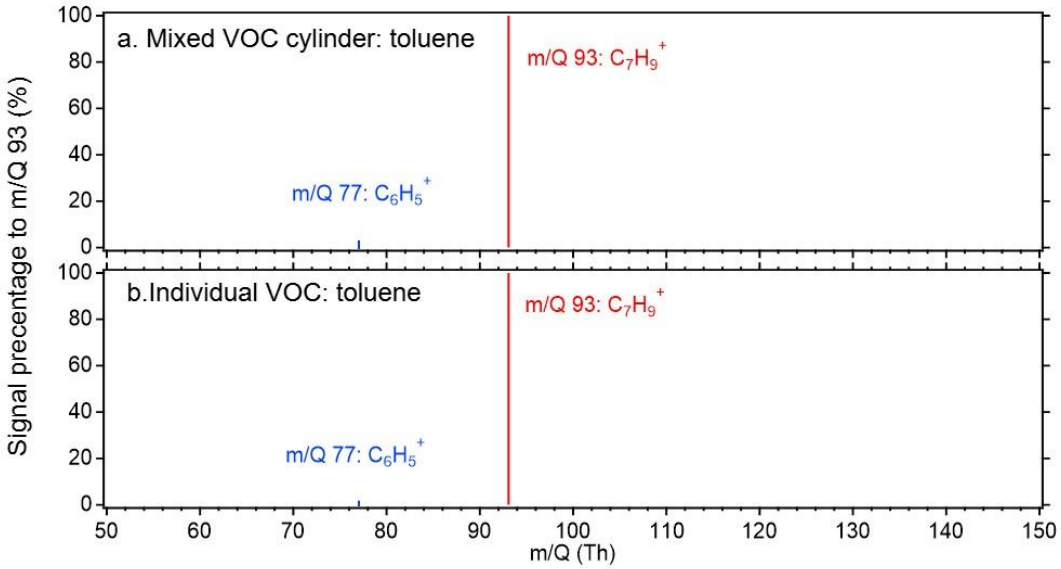

Figure R2.1. Mass spectra of toluene from (a) mixed VOC cylinder and (b) from individual VOC.

2. How long were the tanks allowed to equilibrate on the instrument before ramping concentrations, humidity, and other variables? And was it ever demonstrated that the wait times of 30 minutes for one tank and 120 minutes for the other (L 171-173) were sufficient for stabilisation? From Figure S5 it appears that some species' signals are still creeping up by the end of the step. How much error could this introduce in the calibrations and the determinations of their sensitivities to instrument parameters?

Response: For most VOCs, especially hydrocarbons, the signal can attain stability within 10 minutes. For oxygenated VOCs (OVOCs), such as benzaldehyde and m-tolualdehyde, it does take longer (Figure S5). That is the reason why we prolonged the equilibration time for cylinder II, which contains mainly OVOCs and nitriles (Table 1). Even for a shorter equilibration time of 30 min for cylinder I, the overlapping species acetone and acetaldehyde showed deviations of only less than ±1.5% in sensitivity.

Therefore, we believe that for OVOCs in cylinder II, the equilibration time of 120 min is sufficient to reach a relatively stable signal for quantification.

We have included in the revised manuscript the following descriptions on this.

L172: The 2-hour stabilization time for cylinder II, which contained mainly OVOCs and nitriles, should be sufficient because even with half-an-hour stabilization time for cylinder I, the overlapping species acetone and acetaldehyde showed deviations of less than ±1.5% in sensitivity.

L410: with a deviation of less than ±1.5%.

3. Similarly, was it ever demonstrated that 15 minute steps of humidity (L 181-182) were sufficient to allow for signal stabilisation at each step?

Response: In doing the RH-controlled experiments, the concentrations of the VOCs were fixed at certain desired levels first. Then the RH of the experimental setup was ramped up and down, as shown in Figure S6. The RH within the experimental setup can fluctuate, but the standard deviations of RH change are normally less than 5%. This difference is in general smaller than the RH intervals we set for stepping (e.g., panels a-h in Figure 5), and therefore allows us to draw conclusions from the general trend of RH increasing and decreasing.

4. L 484: "the rest one" should be "the other one"

Revised.

L493: other.