

***Interactive comment on* “Technical Note:  
Quantitative long-term measurements of VOC  
concentrations by PTR-MS – measurement,  
calibration, and volume mixing ratio calculation  
methods” by R. Taipale et al.**

**Anonymous Referee #2**

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Taipale et al. present a detail description on calibration procedures for a PTRMS instrument used for long-term measurements at the SMEAR-II station. As such the manuscript can provide a valuable source for the PTRMS community to assess their ability to use the instrument for quantitative VOC measurements. The following specific comments should be considered:

P9443, line 20: It should be noted what SEM (manufacturer) was used for this study.

P9444, line 2: Formaldehyde. It is not clear why this procedure would help to deduce

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the background noise for formaldehyde. What was the internal background on this PTRMS mass channel?

P9446, line18: Shouldn't the exact isotope ratio (incl. H isotopes) be more like 489? Similarly the isotope ratios for H<sub>2</sub>O.H<sub>3</sub>O<sup>+</sup> should be checked.

P9447, line 20: It is not clear why the transmission can not be determined for H<sub>3</sub>O<sup>+</sup> and H<sub>2</sub>O.H<sub>3</sub>O<sup>+</sup>. At lower E/N some of the H<sub>3</sub>O<sup>+</sup> should cluster and result in more H<sub>2</sub>O.H<sub>3</sub>O<sup>+</sup>. The difference between the relative decrease of H<sub>3</sub>O<sup>+</sup> and the relative increase of H<sub>2</sub>O.H<sub>3</sub>O<sup>+</sup> should contain information about the transmission efficiency. From figure 4 it looks like the transmission between mass channel 19 and 37 are definitely quite different; it is not clear why the same transmission coefficient (e.g. eq 4) should be used.

P9455, line 16: For the general readership typical total sensitivities of the instrument would also be worth noting. The concept of normalized sensitivities can be misleading. For example if the total primary ion count rate of the system was on the order of 1e4 - 1e5 Hz, the actual sensitivities would be one to two orders of magnitude lower than the reported normalized sensitivities.

P9457, line 24: The way formaldehyde concentrations are calculated is not convincing, because the backward reaction is not taken into account. Hansel et al. show that this can result in 5-10 times lower sensitivities due to k(backward). Equation (R1) therefore does not hold true for formaldehyde because, (RH<sup>+</sup>) +H<sub>2</sub>O -> (H<sub>3</sub>O<sup>+</sup>) +R. Could this explain the difference when comparing with results from previous formaldehyde measurements at the site?

P9459, line12: A-, b- pinene. The authors refer to a paper by Warneke et al. (2003) who saw quite different sensitivities between these two monoterpenes based on a GC-MS intercomparison. It is not clear why this should be the case. Warneke et al. (2003) do not provide an explanation for this; it is noted that monoterpenes stored in gas cylinders (particularly some of the pinenes) can interconvert over time.

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Figure 4: The authors plot a transmission curve in figure 4. By definition the transmission in a mass spectrometer can only be 100% (e.g. 1) . It is counterintuitive and makes no sense to scale a qms transmission curve such that it gives values greater than one.

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