

***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.**

R. Taipale et al.

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We thank the referee for the careful review and the valuable comments.

The page and line numbers (etc.) below refer to the paper published in Atmospheric Chemistry and Physics Discussions unless otherwise noted.

General response

The referee's main comment concerns the quantitative measurement of formaldehyde. We certainly agree with the referee that it would be important to determine the sensitivity of our PTR-MS for formaldehyde as a function of humidity. Unfortunately, we did

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not have the chance to calibrate the instrument for formaldehyde during the measurements at the SMEAR II station. On the other hand, we did not want to use the humidity dependent sensitivity equations presented by Inomata et al. (Atmos. Chem. Phys., 8, 273–284, 2008) since we think that the sensitivity has to be determined specifically for each instrument.

Instead, we developed a consistent method for determining a relative transmission curve to calculate mixing ratios for VOCs not present in our calibration gas standard. We also took the abundance of the water cluster ions into account in the normalized count rate. This reduces the effect of humidity on the sensitivity since the water cluster ion signal correlates strongly with the ambient water vapour mixing ratio (page 9458, line 3; Ammann et al., Atmos. Chem. Phys., 6, 4643–4651, 2006). As mentioned in the text (page 9453, line 3), the accuracy of the data calculated using the relative transmission curves is significantly lower than the accuracy of the data based on the measured normalized sensitivities. However, we suppose that the precision of the formaldehyde data is reasonable since we determined the relative transmission curves systematically and took account of the water cluster ions. Although we appreciate the sound suggestion by the referee to remove the results for formaldehyde, we still want to present our results because we think that information on the relative changes of the formaldehyde mixing ratio is very useful in many VOC studies.

Inspired by the comment of the referee no. 2, we replaced the combined transmission coefficient in Eq. (4) with the relative transmission coefficient for the water cluster ions (the variable α in the revised manuscript) to make the equation physically more justified and intuitive. Still, Eq. (4) in the revised manuscript is mathematically identical to Eq. (4) in the discussion paper. Due to this replacement, we calculated our results once again and modified the text, equations, tables, and figures accordingly. The changes were mainly marginal but certainly improved the quality and consistency of the paper. We also inserted a paragraph describing the determination of detection limits.

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Response to the specific comments

Abstract: We revised the abstract to make it more informative.

Page 9441, line 25: We chose to use a rather low value for the parameter E/N to suppress the effect of fragmentation. The count rate of $\text{H}_3\text{O}^+\text{H}_2\text{O}$ ions was 6–34% of the count rate of H_3O^+ ions. We added this ratio to the manuscript.

Page 9442, line 23: The zero air generator produced zero air from ambient air. It is well possible that the water vapour mixing ratio of zero air differed from that of ambient air. To reduce the effect of changing humidity, we took the water cluster ion count rate into account when subtracting the VOC background signals (Eq. (5)). The primary ion count rate and the drift tube pressure did not change remarkably between the actual and zero air measurements during the presented measurement period. However, we want to take these variables into account also in the last term of Eq. (5) since the changes can be significant if there is a long time period between the actual and zero air measurements. The small fluctuations in the drift tube pressure (about 3 Pa at maximum) were due to a minor trouble in the pressure controller of the PTR-MS inlet.

Page 9442, line 26: Exactly, valves and flow meters can cause memory effects and hence a slow response time. We tried to minimize these effects by regulating the standard gas flow with a stainless steel needle valve instead of a mass flow controller, which has more surface and can therefore enhance the memory effects. In addition, the flow meter was installed in the calibration system only during the flow measurement (page 9443, line 1). In the tests we made with the calibration system, the VOC signals reached an equilibrium in 30–45 min when a mixture of zero air and standard gas was fed into the PTR-MS. Since this measurement stage lasted about 90 min in the presented calibrations, we believe that the memory effects did not disturb the calibration measurements.

Page 9443, line 22: Right, the sensitivity of the SEM is an important factor especially in long-term PTR-MS measurements. As discussed in the text (page 9443, line 22), we

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optimized the operating voltage of the SEM before each calibration, which reduced the effect of the changing sensitivity. We increased the SEM voltage by 100 V in March–April and also in July–August. According to our experience, such ageing of the SEM is normal, considering that the PTR-MS was operating continuously during the measurement period. We added the manufacturer (MasCom GmbH, model MC-217) and the operating voltages to the manuscript.

Page 9450, Eq. (8): We added this note to the text.

Page 9454, Fig. 2: We think that Fig. 2 illustrates the effect and importance of the subtraction of the VOC background signals explicitly. It gives an idea of the ratio of the actual measurement signal to the background signal for different compounds. Since the figure does not demonstrate the temporal variation of the background signals very clearly, we reported that information in the text (page 9454, line 4). The insertion of the actual background signals would make the figure too ambiguous.

Page 9454, Calibrations: We inserted examples of the actual sensitivities and the corresponding primary ion count rates in the text. We also determined the detection limits for all compounds measured in the ambient mixing ratio measurements (Table 1 in the revised manuscript).

Page 9455, Fig. 3: Yes, the stability of calibration gives a lot of crucial information on the long-term performance of the PTR-MS. However, we present a long time series of the normalized sensitivities and discuss the efficiency of the normalizing process in our accompanying paper (Ruuskanen et al., submitted to Atmos. Chem. Phys. Discuss., 2008), where we also show long time series of VOC mixing ratios measured at the SMEAR II station.

Page 9455, Fig. 4: We added a figure which shows the compatibility of the measured normalized sensitivities with the values calculated from Eq. (9) using the relative transmission coefficients derived from the relative transmission curves.

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