

***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 #1

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This technical note describes the setup (inlet, calibrations, instrument background determination, and ambient air measurements) of a PTRMS instrument for accurate long-term VOC measurements at the forest site SMEAR II in southern Finland. Especially for the PTRMS community this note contains very valuable information, but might also be helpful for other researchers doing VOC measurements using other techniques. The note is well written and organized and a few specific comments should be taken into account.

My main concern with this technical note is the quantitative detection of formaldehyde.

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Due to the low proton affinity of formaldehyde the back reaction cannot be neglected. The authors cite the paper by Hansel et al, where the back reaction rate coefficient is measured, but do not take it into account. Many other papers also discuss the effect of reduced formaldehyde sensitivity in PTRMS, see e.g.: Wisthaler et al ACP 2008 and references therein. A low correlation coefficient between the water vapor mixing ratio and formaldehyde in ambient air does not mean that the detection of formaldehyde is not influenced by water in the drift tube. In ambient air formaldehyde mixing ratios are very likely independent of water vapor mixing ratios. The reduction in sensitivity needs to be determined, possibly in lab experiments, and taken into account. Even then formaldehyde measurements with PTRMS are still difficult as can be seen in Wisthaler et al 2008. I would therefore suggest to removed the discussion of formaldehyde and replace it with other very important compounds in atmospheric measurements by PTRMS such as acetone, acetaldehyde, isoprene, or acetonitrile.

All my other comments are fairly minor and could improve an otherwise very good paper.

The abstract could be more informative. It should present the main findings, but it rather advertises the methods that are used instead of the results.

Page 9441 line 25: The E/N used is rather low. What was the reason for using such a low drift voltage and what are the typical H_3O^+ to H_3OH_2^+ ratios observed during the campaign?

Page 9442 line 23: Did the zero air generator produce air with the same humidity as the ambient air? This is important for the primary ion distribution during the background measurements and for many background signals such as methanol M33. Also in Eq 5 a change in the primary ion count rate and drift tube pressure is taken into account, when measuring the background. How much is the change and how large is the influence on determining backgrounds? What is the reason for the changing drift tube pressure?

Page 9442 line 26: Were the stainless steel valves and the flow meter in line with

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the calibration gas? This could result in some memory effects and a slow response time. The time for equilibrating the calibration gas before each calibration seems rather short anyway. Were any tests done to determine, when the calibration signal was at equilibrium?

Page 9443, line 22: Can you provide the manufacturer of the SEM. How much was the actual change in SEM voltage between each calibration? Did the sensitivity of the SEM decrease significantly between calibrations? In some multipliers the sensitivity loss is mass dependent and will influence the relative transmission coefficient. In general an SEM that needs adjusting its voltage this frequently should be avoided in a long term measurement.

Page 9550, Eq 8: It should be noted here that the reaction time also changes slightly with the cluster distribution in the drift tube.

Page 9454 Figure 2: The actual background measurements should be shown in the Figure as well. This demonstrates the frequency and especially the variation in the background measurements more clearly.

Page 9554: Calibrations: Here it is important to give the primary ion signal count rate and also the actual sensitivities, not only normalized sensitivities. This will give the general audience a better sense of the PTRMS sensitivity. At this point the detection limits for each compound using the presented instrument setup should be given. This information should also be added to one of the Tables.

Page 9455, Figure 3: A time series of the calibration measurements in normalized and actual sensitivities could be added here. From Figure 3 the variability can be estimated, but should be discussed more clearly, including how the efficiency of the normalizing process.

Page 9455, Figure 4: To determine the relative transmission coefficient the measured sensitivities are used, but it is still important to discuss in more detail how the mea-

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sured sensitivities and the ones calculated from the transmission and rate coefficient compare.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 9435, 2008.

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