**Atmospheric
Chemistry
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Discussions**

Interactive
Comment

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

Inspired by the very fruitful suggestion by the referee, 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

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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.

Both referees were doubtful about the accuracy of the formaldehyde measurements. We understand their concern since we did not have the chance to calibrate our PTR-MS for formaldehyde during the measurements at the SMEAR II station. As explained in the response to the referee no. 1, we anyway suppose that the precision of our formaldehyde measurements was reasonable. Since we think that information on the relative changes of the formaldehyde mixing ratio is very useful in many VOC studies, we want to include the results for formaldehyde in the manuscript.

Response to the specific comments

Page 9443, line 20: We added the manufacturer (MasCom GmbH, model MC-217) and the operating voltages of the SEM to the text.

Page 9444, line 2: The aim of the procedure was to produce a constant formaldehyde mixing ratio. Then we could assume that the short-term variations in the observed M31 signal were mainly due to the instrumental noise. The standard deviation of the signal was used to estimate the uncertainty of the measured ambient mixing ratio. However, we removed the paragraph since we wanted to improve our uncertainty estimates. In the revised manuscript, we present the detection limits for all measured compounds (Table 1).

Page 9446, line 18: We thank the referee for noticing this mistake. We checked both isotope ratios and calculated the results once again. The effect of the isotope ratios on the mixing ratios was marginal since the isotope ratios were taken into account twice in the mixing ratio calculation: first when determining the normalized sensitivities and the

relative transmission coefficients from the calibration data and again when calculating the normalized count rates from the measurement data.

Page 9447, line 20: As mentioned in the general response, we decided to use the relative transmission coefficient for the water cluster ions, α, in Eq. (4). We tried to determine the value of α using the method suggested by the referee, but unfortunately the results were not logical. The method yielded even negative values. We suppose that the changes in the parameter E/N affected the transmission and thus the relative changes in the primary and water cluster ion count rate could not be utilized to estimate α. Therefore, we determined the value of α using an iterative method explained in the revised manuscript.

Page 9455, line 16: We added examples of the actual sensitivities and the corresponding primary ion count rates to the text.

Page 9457, line 24: It is true that the accuracy of the formaldehyde measurements was questionable, which can explain the small difference between our results and those of the previous measurements at the same site. Please see the general response and the response to the referee no. 1 for a more detailed answer.

Page 9459, line 12: We either could not find an explanation for the difference in the sensitivities for α- and β-pinene reported by Warneke et al. (Environ. Sci. Technol., 2494–2501, 2003). The normalized sensitivity of our instrument for α-pinene was considerably lower than the value measured by Warneke et al. (page 9455, line 17). Since our definition of the normalized sensitivity differs slightly from that of Warneke et al., the values are not totally comparable. However, we think that the difference is substantial enough to show the importance of instrument specific calibrations.

Fig. 4: Right, the values of transmission coefficients range between zero and one (page 9446, line 8). There are values higher than one in Fig. 4 since it shows the relative transmission coefficients (Eq. (10)) instead of the absolute transmission coefficients. In the revised manuscript, the corresponding figure still shows the relative

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transmission coefficients but now the coefficients are proportional to the absolute transmission coefficient for the primary ions.

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

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