Final Author's response to reviewer comments on "Validity and limitations of simple reaction kinetics to calculate concentrations of organic compounds from ion counts in PTR-MS" by Rupert Holzinger et al.

We thank referee #2 for their insightful and high-quality comments on our manuscript. In the following we address their comments point by point. The referee comments are copied to this document in *blue* font.

Report #1(referee #2):

Major concerns:
1. Page 7, line 20: The authors have used equation 11 to calculate the residence time for all the instruments except for "PTR3 HAR". I have a question here: Can this equation be applied to the case of the instruments with quadrupole-type drift tubes (e.g., TOFqi and Vocus)? Eq. 11 is originally for static lens ion optics in which ions move linearly, and therefore, the drift tube length can be used directly for the calculation of the time. In contrast, ions move spirally in the quadrupole-type drift tube. This means ion trajectories are quite long compared to the drift tube length. The authors should clarify how they consider this matter.

Answer: Note that the TOFqi instruments apply an static electric field along the reaction chamber, so eq. 11 applies. The quadrupole in these instruments is used in the ion-transfer region between the reaction chamber and the mass analyzer – a region where no ionization should occur. This situation is indeed different for the Vocus instrument, where a RF field is applied across the entire length of the reaction chamber. However, the residence time is determined by the static electrical field in the direction of the ion drift. The RF-components are perpendicular to this direction and suppress the diffusive broadening of the ion beam. The RF components have insignificant influence on the residence time and in eq. 11 we used only the static electric field in the drift direction.

We added following footnote to clarify this in the manuscript: *"Note that we used only the static electric field in the drift direction in Eq. 11 to calculate the residence time for the Vocus. The RF-components are perpendicular to the drift direction and have little influence on the residence time in the reactor."*

2. Page 9, line 12 etc.: The authors state that primary ions undergo approximately 1000 times more collisions with the analyte gas in the PTR3 instrument. Taking into account this matter and Figure A1, I think that the following proton transfer reaction between analyte gas (R) and ion (RH⁺) should be considered, as well as de-protonation (RH⁺ + H₂O→H₃O⁺ + R). R1H⁺ + R2→R2H⁺ + R1 (if PA(R2) > PA(R1), PA: proton affinity) The authors should discuss how the analyte sensitivities are affected by this reaction in case of the PTR3 instrument. Additionally, the density of water molecules in the drift tube should be discussed if de-protonation is considered.

De-protonation through collision with a high PA compounds can become relevant if their concentration is in the proximity of 100 nmol/mol or higher. Practically this is not an issue that needs to be considered, because such high concentrations are outside the operation range of the PTR3 instrument (the primary ions would be titrated almost completely). The concentration of water vapor certainly needs to be accounted for in an advanced reaction kinetic model for PTR3. However, this is beyond the scope of this work, which is evaluating the inter-comparability of standard PTR-MS systems.

3. Figure A1 in page 27: The measured sensitivities for isoprene and alpha-pinene are quite low compared to the expected ones. Do these results mean that excess fragmentation occurs in the PTR3 instrument? In the case of the PTR3 instrument, is there a possibility that CID (collision-induced dissociation)-like fragmentation occurs? It would be good if the authors could suggest any reasons for quite low sensitivities for isoprene and alpha-pinene in the PTR3.

E/N in the PTR3 is low, so fragmentation is not expected. Figure A1 also shows "adjusted expected" sensitivities for these compounds, which are in better agreement with the measured

sensitivities. As we explained in appendix A (just above Fig A1), these adjustments are based on Smith et al. (2001), who found that isoprene is not ionized by higher water clusters.

Minor concerns: 4. Page 27, line 19: "t_react" should be defined here or in the main text.

Done. We expanded the sentence starting at line 20 as follows:

"Where $10^{-9} \frac{p_{react}}{k_B T_{react}}$ corresponds to a volume mixing ratio of 1 ppbv (with p_{react} and T_{react} corresponding to the pressure and temperature in the reactor, respectively, and k_B to the Boltzmann constant); $I(H_3O^+ \cdot (H_2O)_n)$ is the ion current of the n-th hydronium water cluster in counts per second; k_r, t_{react}, and c_{H2O} correspond to the forward reaction rate constant, the residence time in the reactor, and the water vapor number density, respectively."