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 #3 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(Anonymous Referee #3, Aug 13, 2019):

Major questions:

1) Equation (1) seems to be a correction for the duty-cycle of ion extraction into the ToF region of a mass analyzer. For a ToF mass spectrometer a should be exactly equal to 0.5. Why not apply the known duty-cycle correction directly, before fitting equations (2) and (3)?

The reviewer is correct that equation (1) accounts mostly for the duty cycle of time-of-flight mass analyzers. However, there are other parameters that can influence the transmission in, e.g. diffusion in the reactor, or ion guide systems in the transfer region. The goal was to provide a general algorithm that can be used for a wide range of different designs – including quadrupole mass analyzers, where $a=0.5$ is not expected.

*2) The purpose of the paper is to evaluate the agreement between sensitivity calculated from reaction kinetics, and measured sensitivities. Any number of things could cause measured sensitivities to deviate from expected sensitivities, including mass-dependent transmission, differences in rate constant with H3O+ vs H2O*H3O+ or larger water cluster back-reaction, fragmentation, uncertainty in rate constant, and effect of contaminant reagent ions (e.g. O2+).*

The paper focuses almost exclusively on determination of mass-dependent transmission and states that quantitative detection is possible within 30%. Is the 30% uncertainty entirely attributable to difficulty in determining the transmission function? Is the largest source of error the transmission curve, reaction with water clusters, or some other effect?

The 30% uncertainty is not entirely attributable to the transmission function. We actually think that the major fraction is du to the other processes that are mentioned by the reviewer, namely differences in rate constant with H_3O^+ vs $H_2O*H_3O^+$ or larger water cluster back-reaction, fragmentation, and uncertainty in the rate constant. The individual contributions cannot be disentangled with the present set of measurements. However, the measurements using humidified carrier gas clearly shows the limitations of the simple kinetic model. Whether the accuracy of the transmission, water cluster effects, or uncertainty in the reaction rate constant are the largest source of error depends on the operating conditions and on the compounds that are considered. The effects of water clusters (i.e. lower rate constant and de-protonation) are extensively discussed in Section 3.3. The important result of this work is that we clearly define operating conditions that limit the total error to less than 30% for most compounds.

Specific/minor comments:

Page 9 line 11: "We find that typically 'flatter' transmissions (smaller parameter 'a' in Eq.1) were retrieved when the instruments were (deliberately) operated at lower E/N (thin lines in Figure 3)."

This seems a little strange because Eq.1 is a function of the mass analyzer, not the drift tube – why would the drift tube conditions affect the extraction duty-cycle? (or anything downstream)? Is it that the transmission as a function of mass is not actually changed, but is rather an artifact of lower reaction rate for certain compounds used to determine the transmission curve? If so, then this suggests that benzene etc. should be excluded from determination of the transmission curve, or that only dry air and/or high E/N should be used.

The transmission is also influenced by the conditions in the drift tube, e.g. by (mass dependent) diffusion, and the ion optics between the drift tube and the mass analyzer. The referee is right that the transmission of the mass analyzer does not change by changing E/N, however, the transmission of the whole system, which is relevant here, may change. Note that the performance of the algorithm is not compromised if one compound does not comply with the simple model, such as benzene with high abundance of water clusters.

Page 13 Line 22. Likely this is because m37 is consistently transmitted with higher efficiency than m19. Therefore if most reagent ions begin their journey into the downstream optics as m37, and then at some later point decluster to produce m19, the observed m19 will be higher during humidified measurements.

This is an interesting idea but we do not know if it is likely at all. Following the referee we would need to assume that most reagent ions pass the “high-masses-pass” filter as m37. After the filter there would have to be ion-molecule collisions that cause the de-clustering so that in the TOF region m19 is ‘only’ reduced by the duty-cycle. This could indeed explain the observed behavior. However, we have no exact information on the pressure and physical dimensions in this region, so we feel that it is too speculative to be added to the manuscript.

Page 14 line 13: A citation is needed for this sentence: “in traditional PTR-MS applications that focus on volatile organic compounds fragmentation of compounds is the exception rather than the rule”

We added the reference Lindinger et al. 1998.

Figure 3: It would be much easier to compare the transmissions of various instruments if the y-axis scale were the same in each subplot.

One important purpose of this Figure is to show the variability of transmission retrievals for the individual instruments. For many instruments this would be much harder to see if we used the same y-scale. Therefore we prefer to keep the current scales.