Response to Comments from Reviewer #2

In this file, the comments from the reviewers are shown in black. The responses to the comments are shown in blue and the changes to the manuscript are shown in bold blue.

General Comments:

This paper describes the development and application of H3O+ traditionally used with quadrupoles to now commercially available time of flight mass spectrometers. The advantages of TOF compared to quadrupole mass analyzers has been described be- fore in detail for many different ion chemistries and even the same ion chemistry as described in this manuscript.

This instrument of the instrument was deployed on the NOAA WP-3D aircraft as part of SONGNEX and its performance during the campaign was compared with other traditional flight instruments. The manuscript is generally well organized and while it is not novel, is a thorough characterization of an instrument which will certainly participate in many flight and other measurement campaigns.

Reply: We would like to thank the reviewer for these valuable comments.

Ln 52 here and beyond the text could be shortened. The advantages of PTR with TOF technology are not new – and while it is useful to have the context of performance of other configurations, this may be better suited for the results and discussion section.

Reply: We shortened and re-organized the two paragraphs starting Line 52 significantly (from 493 words to 341 words) in the revised manuscript. The two paragraphs in the revised manuscript are shown below:

Proton transfer reaction mass spectrometry (PTR-MS) has been an important scientific tool for VOC measurements, associated with high sensitivity and fast time response (Lindinger et al., 1998;de Gouw and Warneke, 2007;Blake et al., 2009). Early PTR-MS instruments used quadrupole mass spectrometers (QMS) for ion detection. PTR-QMS instruments usually step through several pre-selected masses consecutively each with a dwell time of 0.1-1 s (Warneke et al., 2015). The time resolution of PTR-QMS is generally sufficient for ground-based measurements targeting VOC mixing ratios, but not ideal for aircraft measurements or eddy covariance flux measurements of more than a few species. Other mass analyzers, e.g. ion traps (Warneke et al., 2005;Steeghs et al., 2007;Mielke et al., 2008) and time of flight (ToF) mass spectrometers (Blake et al., 2004;Ennis et al., 2005;Tanimoto et al., 2007), have been used to overcome some of these inherent drawbacks in PTR-QMS.

The PTR-TOF instruments introduced by Ionicon Analytik in 2009, had both much higher sensitivities (10-50 cps/ppbv) and better mass resolution (m/ Δ m=~6000) than earlier PTR-TOF instruments (<5 cps/ppbv and m/ Δ m=100-1200) (Jordan et al., 2009). The high mass resolution of the ToF analyzer facilitates separation of isobaric isomers (Graus et al., 2010;Sulzer et al., 2014), which enables quantification of more species and reduces possible chemical interferences (Warneke et al., 2015). PTR-TOF instruments have been used successfully in several field campaigns at ground sites to measure concentrations and fluxes

of a large suite of VOCs (Müller et al., 2010;Holzinger et al., 2013;Kaser et al., 2013;Park et al., 2013). A PTR-TOF with mass resolution up to ~1000 was deployed on the NASA P-3B research aircraft during the DISCOVER-AQ campaign, demonstrating much higher time resolution and hence better spatial resolution of airborne VOC measurements (Müller et al., 2014). Recently, a newer version of PTR-TOF equipped with a quadrupole ion guide (PTR-QiTOF) was developed and is more sensitive (by a factor of ~25) than previous version of PTR-TOF using electrostatic ion lens systems (Sulzer et al., 2014). However, detailed characterization (e.g. humidity dependence) and applications to ambient measurements for PTR-QiTOF instruments are not currently available in the literature.

Ln 107 This is the same drift tube from the PTR-MS? If so this could just be stated, otherwise the differences to the commercial version could be highlighted.

Reply: H₃O⁺ ToF-CIMS uses the same drift tube as PTR-MS. We changed the sentence to:

In the new H_3O^+ ToF-CIMS, the IMR chamber was replaced by a drift tube that is the same as used in PTR-QMS (Figure 1). The drift tube is comprised of stainless steel rings separated by Teflon rings for both vacuum sealing and electronic insulation (de Gouw and Warneke, 2007).

Ln 137 If the instrument response is on the order of seconds what is the purpose of zeros for 90s? Is the response best described by a single or double exponential? Does the instrument (inlet, and instrument surfaces) not ever change on a timescale faster than the 40 minute zero frequency?

Reply: Based on our field tests, the instrument response was better than 1 s in SONGNEX. However, switching from ambient measurement to background can cause some pressure and flow instability for 2-3 seconds. All quantified VOC species were stable in 10 s after switching. To reduce the uncertainty of background measurements, we decided to average over a longer period. Thus, we measured the background for 90 s for each cycle.

VOC backgrounds in PTR-MS and H_3O^+ ToF-CIMS can change over time. The changes are mainly related to ambient humidity and instrument running time (see discussions in section 3.4 in the revised manuscript). The background variations can be very quick for aircraft sampling, as the aircraft ascends and descends often. To overcome this, we rely on the relationship of measured backgrounds with humidity and instrument running time to interpolate background measurements.

Ln 180 Given that the quadrupoles are now switchable on the TOF-CIMS with significant changes in the transmitted mass range it would be good to state what settings were used (frequency, amplitude, high-med-low coil)

Reply: We added amplitudes, frequencies and coil settings of SSQ and BSQ used for our instrument in section 3.1 in the revised manuscript.

Ln 217 It is not clear if the goal here was to optimize the sensitivity (i.e. to VOC alone) or also the reagent ions. As the regent ions are likely heavily influenced by the mass transmission window of the quadrupoles it would seem like the absolute magnitude of the reagent ion signal should be of significantly less importance. Perhaps only optimizing VOC sensitivity is indeed what was done – if so then simple rewording would make this more clear. **Reply:** The main goal for the experiments on RF amplitudes of SSQ and BSQ was to optimize the sensitivities of VOCs. However, other effects are also need to be considered to avoid the complexity of mass spectra, such as O_2^+ signals. We added this information in the revised manuscript by modify the last sentence of this paragraph:

To optimize VOC sensitivities and reduce the complexity of mass spectra, the RF amplitudes of the SSQ and BSQ were set to 50 V and 350 V, respectively.

Ln 225 (4) Discharge could easily be ruled out by turning off the ion source and measuring any residual ions of O2+ or VOC – It seems unlikely that at this pressure 80-100 V would lead to discharge.

Reply: We did the experiments as the reviewer suggested. No residual ions of O_2^+ was observed. However, we suspect that ions going through the SSQ might make it easier to start a discharge in SSQ when RF amplitudes were set high. This issue is stated explicitly in the instrument manual that discharge would happen with RF amplitudes at 200 V at 2 mbar. We modified the sentence somewhat in the revised manuscript.

The high O_2^+ signals are possibly due to discharge in the SSQ (TOF-CIMS manual indicates that discharge happens with >200 V RF amplitudes), but it warrants further investigation.

Ln 243 The last sentence of this section (Ln 254 onwards) is more clear to me than the beginning of the section which seems unnecessarily long. **Reply:** We have re-written this paragraph to make it more clear and concise in the revised

manuscript.

The larger H_3O^+ signals at higher humidity in the H_3O^+ ToF-CIMS are the result of the low transmission efficiency of H_3O^+ ions compared to other heavier masses, as demonstrated from the dependence of the reagent ions with SSQ pressures above. The low transmission of H_3O^+ ions is related to low-mass cut-off of RF-only quadrupoles (Chernushevich et al., 2001). A reagent ion detected either as H_3O^+ or $H_3O^+(H_2O)$ may undergo many collisions and travel as both H_3O^+ and $H_3O^+(H_2O)$ in the quadrupole ion guides, similarly as shown by previous ion mobility measurement (Warneke et al., 2001). As a result, the transmission efficiency of an reagent ion in the quadrupoles reflects the averaged transmission efficiencies of ions with m/z 19 and m/z 37 weighed by the time the ion spends as H_3O^+ vs. $H_3O^+(H_2O)$. The strong increase in H_3O^+ signal intensity with humidity reflects the fact that while ions may be detected as H_3O^+ , they spent a larger fraction of time as $H_3O^+(H_2O)$ in the SSQ at higher humidity and are therefore transferred with a higher average transmission efficiency.

Ln 427 This section seems to be just a demonstration of the resolving power which has been shown many times before – also for this same ion chemistry. What is new here?

Ln 448 Clearly the Quad version suffered from interferences that the TOF can separate, but this is not new, nor the fact that many ions are measured – I suggest either re- organizing this or removing this section as this has already been shown in pervious publications.

Reply: Per the suggestion from the reviewer and reviewer #1, section 3.4 "Mass resolving power and separation of isobaric masses" along with Figure 8 in the original manuscript have been moved from main text to SI in the revised manuscript. It should be noted that mass

resolution of ToF-MS can be affected by various voltage settings of the quadrupole ion guides and ion lenses from user-tuning processes. Thus, mass resolution might be different among the instruments using the same TOF-MS. Considering this, we added three sentences in section 2 to mention mass resolution (m/ Δ m) of the instrument:

The typical mass resolution (m/ Δ m) for the H₃O⁺ ToF-CIMS during the SONGNEX campaign is shown in Figure S2. The m/ Δ m in the range of m/z 30 - 200 (where most VOCs were detected), are 3900-5900 with higher resolution for heavier masses. These mass resolutions are sufficient to separate many isobaric ions (see details in SI and Figure S3).

Ln 485 Given the changing background signals – would shorter more frequent checks be more representative of the instrument background?

Reply: Aircraft flight time for a field campaign is limited and hence valuable. Thus, balancing ambient measurements and background are important. Background was measured every 20-40 min during SONGNEX (it was stated as 30-40 min in the original manuscript and now it is corrected in the revised manuscript), which would result in 12-24 background measurements for an 8-hour flight. As shown in Figure S9 in the revised manuscript, these background measurements are enough to characterize the background variations with both instruments running time and humidity. With a better characterization of the inlet flow dynamics, we should be able to make shorter background checks. With the same amount time devoted to background measurements, the number of background checks can be larger, as proposed by the reviewer.

Ln 511 Can the fitting routine not also reduce the pure counting statistics by effectively fitting out the noise for well defined peaks? That is, for each point in the mass spectrum its signal is governed by counting statistics, but for each high resolution peak, many of these individual data points (in mass space) are fit. Therefore in the high resolution fitting procedure the individual counting statistics limitations can be "averaged out" by fitting, resulting in fit intensities which (at least for well defined peaks) are actually better than pure counting statistics would dictate.

Reply: That is an interesting thought. Each ion signal in the TOF mass spectra is obviously not a delta function, rather a distribution of m/z, which can be related to its time of flight. This distribution is caused by the variations of electronics and variability in ion trajectories. The distribution is commonly referred as peak shape. Fitting to the ion peaks using a peak shape is basically integrating ion counts along m/z axis (peak area) for a certain period (e.g. 1 s). There are usually 8-16 data points go into the peak fitting for a well-defined peak in the mass range of m/z 12-180. Precision for the integral is better than the precision of the individual data points that go into the peak fitting. However, the basic principle of the fitted peak area (i.e. the integral) is counting. Thus, the fitted ion counts for a well-defined peak still follow the Poisson distribution, as shown in previous studies (Müller et al., 2011;Cubison and Jimenez, 2015).

Ln 537 While this is a nice plot, it is unclear why not just show the best quad sensitivity and the best TOF? Or what the point of the different measurements of quad sensitivities over time is meant to suggest?

Reply: The results of PTR-QMS from previous campaigns indicate that instrument performance can be improved significantly by many small/moderate modifications to the instrument, which are as a result of better understanding of the instrument. Although PTR-TOF performance has been enhanced notably in the recent years, but the good practice of thorough instrument characterizations of PTR-QMS should be transplanted to PTR-TOF instruments. We added one sentence here in the revised manuscript.

The results of PTR-QMS also suggest the variability in sensitivity of a single instrument due to small changes in electronics tuning and hardware configurations.

Ln 555 This is repetitive, and is general knowledge that a quad has lower duty cycle for many compounds than a TOF. Once above in the introduction is reasonable but does not need later repetition.

Reply: The two sentences are deleted in the revised manuscript and the remaining one sentence in this paragraph is modified and combined with the previous paragraph:

The total counts measured in each 15-second period (the typical cycle time for PTR-QMS) are calculated and shown in the middle panel in Figure 10. In terms of total counts in 15-second period, the overall signal to noise of the ToF instruments will compares very favorably to the PTR-QMS.

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