

Response to Comments from Reviewer # 1

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 introduces a H₃O⁺ ToF-CIMS, an instrument based on PTR-MS technology using a time-of-flight mass spectrometer instead of a quadrupole employed in classical PTR-QMS.

The abstract of the manuscript creates the impression that the use of a time-of-flight mass spectrometer represents the major novelty of this instrument, which is clearly not the case. As the authors mention in the text, PTR-TOF-MS are available since more than 10 years and were commercialized several years ago. The first PTR-TOF-MS used an electrostatic lens system to transfer ions from the chemical ionization region to the TOF-MS. A recent paper by Sulzer et al. (2014) describes an PTR-Qi-TOF using a quadrupole to transfer the ions to the time-of-flight mass spectrometer, similar to the H₃O⁺ ToF-CIMS presented in this manuscript. Therefore I have difficulties to recognize the novelty of this instrument. The authors repeatedly point to the advantages of the H₃O⁺ ToF CIMS compared with a PTR-QMS. However, the PTR-TOF-MS or even better, the PTR-Qi-TOF, would be much more appropriate for comparison. Given the described high humidity dependence of the H₃O⁺ CIMS, its applicability in field experiments might be questioned, since it strongly complicates data post-processing and interpretation.

A pretty long part of the manuscript is dedicated to the inability of the small segmented quadrupole (SSQ) to map the primary ion distribution present in the drift tube onto the detector. However, for proper data analysis it is crucial that the signals at the detector represent the actual conditions in the chemical ionization region, since normalization of protonated VOC signals to a not well defined number of primary ions could introduce large errors. I'd assume the simplest way to test this is to use two VOCs of similar mass, one of which is reacting with H₃O⁺ only, while the other reacts with H₃O⁺ and H₃O⁺(H₂O). That way it should be possible to infer if the measured ratio of H₃O⁺ to H₃O⁺(H₂O) ions corresponds to the ratio present in the drift tube of the instrument.

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

The above contains several significant comments, which we will address in detail below. In summary, we will argue that:

1. There are two motivations to describe our instrument in the literature. First, we used the instrument to produce several important data sets, including for airborne measurements over several oil and gas production regions in the U.S., and therefore believe that a detailed instrument description in the literature is warranted (as reviewer #2 noted). Second, the manuscript describes a relatively simple modification of an existing Aerodyne ToF-CIMS instrument that many groups own and will be interested in.

2. The humidity dependence of product ion signals in the H₃O⁺ ToF-CIMS is not different from a quadrupole PTR-MS. The need to account for the primary ion distribution arises from the normalization procedure that most researchers use to correct for ion source drifts. If done

properly, our manuscript showed that the calibration of the system is very reproducible (Figure 9) and that the measurements compare well with those from simultaneous hydrocarbon measurements by GC-MS (Figure 12).

More details on these two main comments follow below:

First, we want to address the reviewer's comment that "given the described high humidity dependence of the H_3O^+ CIMS, its applicability in field experiments might be questioned". We show below that the humidity dependence of raw VOC signals in the H_3O^+ ToF-CIMS is quite similar to that observed in PTR-QMS. Figure R1 compares the humidity dependence of raw signals of acetone and toluene in H_3O^+ ToF-CIMS and in a PTR-QMS shown in de Gouw and Warneke (2007). The results of both acetone and toluene are similar between H_3O^+ CIMS and PTR-QMS. A difference between the two instrument arises during the normalization process. In H_3O^+ CIMS, the raw signals were normalized to H_3O^+ signals, which increase moderately with humidity due to the low mass cut-off issue in the RF-only quadrupole ion guides [Chernushevich *et al.*, 2001]. As a result, the humidity dependent curves for normalized signals in Figure 5 look steeper than the curve of raw signals.

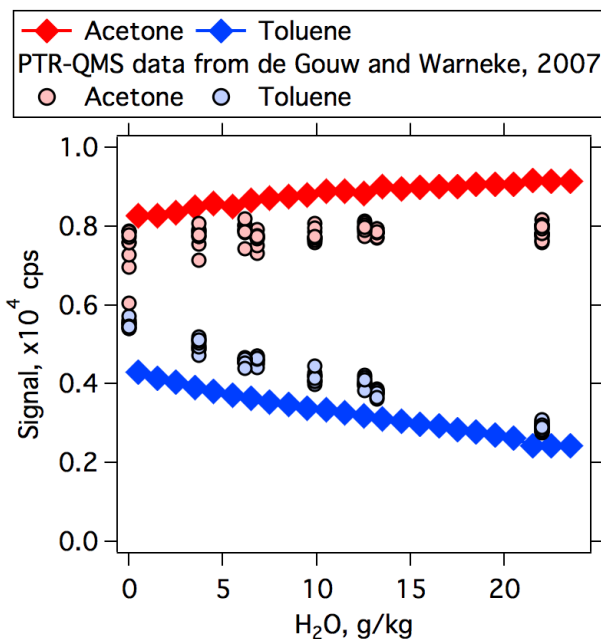


Figure R1. The humidity dependence of raw signals of acetone and toluene from H_3O^+ ToF-CIMS compared with the reported humidity dependence of raw signals of the two compounds in a PTR-QMS from Figure 6B in *de Gouw and Warneke* [2007]. Note that similar signal levels between the two instruments shown in (B) are coincident. The relative changes at different humidity levels should be compared.

We would like to note that low mass cut-off issue may not only happen in the ToF-CIMS instrument from Aerodyne, but also in the PTR-QiTOF instrument by Ionicon (both instruments use the same Q-ToFMS provided by ToFwerk AG). Thus, PTR-QiTOF may have a similar problem of proper normalization. As noted by the reviewer in a later comment, humidity dependence of reagent ions and VOC signals in PTR-QiTOF has not been reported yet. It will take the effort of

the community to address the low mass cut-off and the non-linear relationship between H_3O^+ and $\text{H}_3\text{O}(\text{H}_2\text{O})^+$.

Figure 8 in the revised manuscript (Figure 9 in the original manuscript) shows the in-flight calibration results of benzene, isoprene, acetone and acetaldehyde during SONGNEX. After accounting for humidity, no clear dependence of the corrected signals on $R_{37/19}$ (i.e. m_{37}/m_{19}) was observed. It indicates that the humidity dependence has been taken into account properly. The good agreements between the H_3O^+ ToF-CIMS measurements and the post-flight GC-MS analyses of canister samples (Figure 11 in the revised manuscript) also show that the effects of humidity are properly accounted for. In conclusion, these data and analyses show that the field deployment of this system did result in high-quality atmospheric data with documented uncertainties.

Aerodyne ToF-CIMS instruments have been delivered to many research groups around the world in the recent years (<https://sites.google.com/site/citofms/groups>). Several groups have tried to use radioactive source to generate water clusters $(\text{H}_2\text{O})_n\text{H}^+$ for measuring various species in the atmosphere [Kim *et al.*, 2015; Yatavelli *et al.*, 2012; Zheng *et al.*, 2015]. Our study provides the expected performance of the instrument if other ToF-CIMS users would like to conduct similar modifications (adding a drift tube and a hollow cathode ion source) to generate hydronium ions (H_3O^+) under better controlled conditions.

The reviewer #2 pointed out that the instrument has been used in the NOAA SONGNEX campaigns (and some other some campaigns) and will be used in the future. Thus, it is important to document the instrument in detail. This manuscript would be helpful as background information to future publications that use data from H_3O^+ ToF-CIMS. Several publications are currently submitted, under preparation and being considered.

In the end of the comment, the reviewer proposed a way to infer the reagent ion distribution and to compare the measured ratio of H_3O^+ to $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ ions corresponds to the ratio present in the drift tube of the instrument. This approach had been looked at and much of the idea has been demonstrated in Figure 5C. In Figure 5C, we looked at the signal at high humidity ($R_{37/19}=1.4$) relative to signal at dry condition for different compounds. We separate the species based on their dipole moments (D), which determine whether the ligand reactions between VOC species and $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ happen. Thus, the difference between the species with dipole moment <1 and with dipole moment >1 reflects the fraction of $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ in the system. A rough estimate from the graph would be $\sim 30\%$ when $R_{37/19}=1.4$. This is generally consistent with the estimate in Figure 3 and section 3.2. Figure 3 provides a more direct way to infer and quantify this effect. We first determine the transmission ratio of H_3O^+ to $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ ($T_{\text{H}_3\text{O}^+}/T_{\text{H}_3\text{O}^+(\text{H}_2\text{O})}$) by introducing large amounts of methanol and acetonitrile into the system at different humidity. Then the signals of H_3O^+ in the drift tube can be estimated from the measured signals and determined $T_{\text{H}_3\text{O}^+}/T_{\text{H}_3\text{O}^+(\text{H}_2\text{O})}$. Based on Figure 3, we demonstrate that the low mass cut-off of the quadrupoles leads to the non-linear relationship between H_3O^+ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})$.

Based on the comments from the reviewer, the main changes in the revised manuscript include:

- (1) In the abstract section, we added a sentence to underline the low mass cut-off issue of quadrupole ion guides. We also modified the sentence on mass resolution.

The ToF analyzer with mass resolution ($m/\Delta m$) of up to 6000 allows the separation of isobaric masses, as shown in previous studies using similar ToF-MS.

While RF-only quadrupole ion guides provide better overall ion transmission than ion lens system, low mass cut-off of RF-only quadrupole causes H_3O^+ ions to be transmitted less efficiently than heavier masses, which leads to unusual humidity dependence of reagent ions and difficulty obtaining a humidity independent parameter for normalization.

- (2) In the introduction section, we added a sentence to note that a fully characterization of PTR-QiToF is not available in the literature.

However, a detailed characterization (e.g. humidity dependence) and applications to ambient measurements for PTR-QiToF instruments are not currently available in the literature.

- (3) In section 3.2, the description on how low-mass cut-off of RF-only quadrupoles leads to the unusual humidity dependence of reagent ion was modified.

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 $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ may undergo many collisions and travel as both H_3O^+ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ 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. $\text{H}_3\text{O}^+(\text{H}_2\text{O})$. 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 $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ in the SSQ at higher humidity and are therefore transferred with a higher average transmission efficiency.

- (4) Figure R1 was incorporated into Figure 4 in the revised manuscript. It shows that humidity dependence of VOC raw signals in H_3O^+ ToF-CIMS is similar to that of PTR-QMS. The signals of acetone and benzene were shown in the original manuscript. For better comparison with those in *de Gouw and Warneke* [2007] as shown in Figure R1, the signals of benzene were replaced by toluene in Figure 4 in the revised manuscript.

- (5) In the conclusion section, we added/modified a few sentences:

We showed that the low transmission of H_3O^+ ions as the result of low mass cut-off of RF-only quadrupoles and secondary ion chemistry inside the quadrupole ion guides lead to the unusual humidity dependence of reagent ions. This issue complicates signal normalization and interpretation of the humidity dependence of VOC sensitivities.

We also note that transmission efficiency of H_3O^+ ions may be compromised when tuning for best VOC sensitivities. Thus, the low transmission of H_3O^+ ions may be heavily influenced by various settings of the quadrupole ion guides.

It is unknown whether the next generation of PTR-MS (i.e. PTR-QiTOF) that uses quadrupole ion guides for ion transmission is affected by the similar low mass cut-off problem and secondary ion chemistry in the quadrupole ion guide.

Specific comments:

Line 79: Although isobaric compounds cannot be separated by a PTR-QMS, they are still measurable.

Reply: We changed this sentence to: “..., which enables quantification of more species and reduces possible chemical interferences”.

Line 136ff: I guess you mean catalytically cleaned air was passed to the instrument for 90 s every 30-40 min and the catalytic converter was continuously flushed with ambient air. Nevertheless, I doubt that you were able to measure a proper background of semi-volatile, sticky compound masses in such short time periods.

Reply: Yes, the reviewer is correct. There was a small flow (~8 sccm) continuously flushing the catalytic converter (see Figure S1 in the SI). It allowed us to obtain proper backgrounds in the short time. For all quantified species, background signals approached a stable value within 10 seconds, so backgrounds could be reliably determined.

We added a sentence here: “The catalytic converter was flushed using ambient air continuously for quick switch between ambient and background measurements.”

Line 140: same here for sticky compounds probably contained in the calibration gas standard.

Reply: The flow of gas standard was maintained all the time in the flights during SONGNEX. Some sticky compounds (e.g. methanol) need some time to be transported quantitatively through the metal surface in regulator and mass flow controller. Two 2-way valves controlled the gas standard flow to either the inlet or the exhaust (see Figure S1) to switch between calibration and background/ambient.

Line 141: Why did you add calibration gas to ambient air? This way varying concentrations of compounds contained in ambient air and measured at the same mass-to-charge ratios as the calibration gas compounds could affect your calibration results.

Reply: We mainly added gas standard to clean air from the catalytic converter for calibration. We also added gas standard to ambient air occasionally, when the aircraft was in the free troposphere and ambient concentrations of VOCs were relatively stable. Adding gas standard to ambient air can be used to compare with the results from adding gas standard to air from the catalytic converter. This can help us to partially exclude fluid dynamic problems (e.g. laminar flow and poor mixing) in the inlet system and matrix effects in analyzing. During SONGNEX, no difference between the two types of calibrations was observed (Figure 9 contains both types). We changed the sentence to:

Calibrations were conducted by adding the gas standard flow to clean air from the catalytic converter. Gas standard was also added to ambient air at times when ambient VOC concentrations were stable (e.g. in free troposphere).

Line 143ff: since you measured up to m/z 500, trichlorobenzene is not really suitable to calibrate the mass scale at the high end of the m/z range.

Reply: In this study, we have been mainly working on the masses below m/z 181, in which mass calibration should be relatively accurate. All of the VOCs reported in this study are in this mass range. We also tried other species for the purpose of mass calibration, including iodobenzene and 1,4-diiodobenzene. But, they fragment more than trichlorobenzene in the instrument.

We also would like to point out that the reason we chose to measure up to m/z 500 is not our interest to these high masses. It actually avoids time-of-flight wrap-around in the mass spectrum as there is no significant signals above m/z 500.

Line 163ff: I can imagine that in H_3O^+ TOF-CIMS the signals at m/z 19 and m/z 37 are in saturation and therefore not suitable to calibrate the mass axis.

Reply: We did not observe any evidence showing that m/z 19 and m/z 37 in the instrument are not suitable for mass calibration due to saturation. There are several diagnostic panels in Tofware to explore whether any ions included in mass calibration distorting the results (e.g. “time-series mass calibration plots”) [Stark *et al.*, 2015].

Line 294: Why do you normalize to the H_3O^+ ion signal only, although you write that H_3O^+ is likely to cluster with other water molecules in the SSQ? Normalization to the sum of H_3O^+ and $H_3O^+(H_2O)$ ions seems to be more suitable in this case.

Reply: That is indeed how we have always analyzed data from our PTR-QMS instrument. In that instrument, H_3O^+ went down with humidity and $H_3O^+(H_2O)$ went up, with the sum approximately a constant after accounting for their different transmission efficiencies. In the present instrument, on the other hand, both H_3O^+ and $H_3O^+(H_2O)$ increase with humidity for reasons outlined in the manuscript. Therefore, the sum signal will not be inherently better for normalization purposes than just H_3O^+ .

The main goal of normalization process is take into account the variations of reagent ions while humidity is constant (e.g. ion source performance). The best normalization practice is normalizing to a parameter, which is related to reagent ions and is humidity independent. This would not introduce extra humidity dependence in the normalization process.

In section 3.2, we show that the transmission of H_3O^+ is much lower than $H_3O^+(H_2O)$ and the transmission ratio $T_{H_3O^+}/T_{H_3O^+(H_2O)}$ are humidity dependence. This means the relationship between H_3O^+ and $H_3O^+(H_2O)$ is non-linear. Thus, adding them up directly as proposed by the reviewer or utilizing X factors as widely used for PTR-QMS [de Gouw *et al.*, 2003] is not proper. Therefore, rather than deriving a complicated equation from H_3O^+ and $H_3O^+(H_2O)$ signals to obtain a parameter that is humidity independent, we choose to normalize to H_3O^+ directly.

The fifth paragraph in section 3.2 explained most of the idea presented here. A sentence is added to this paragraph to make the description clear.

The main goal of normalization process is to take into account the variations of reagent ions associated with constant humidity (e.g. ion source performance) and the best practice is normalizing to a parameter, which is related to reagent ions and is humidity independent.

Section 426: this part is completely redundant. Why should the mass resolution of the H₃O⁺ TOF-CIMS be different from that of other instruments using the very same TOF-MS? Also the advantages of a TOF-MS compared with a QMS have been extensively discussed previously.

Reply: Per the suggestion from the reviewer and reviewer #2, 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 ($m/\Delta m$) of the instrument:

The typical mass resolution ($m/\Delta m$) for the H₃O⁺ ToF-CIMS during the SONGNEX campaign is shown in Figure S2. The $m/\Delta m$ 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).

Line 433: isobaric ions have per definition the same nominal mass.

Reply: We changed the sentences to “**These mass resolutions are sufficient to separate many isobaric ions.**” Note that this sentence is moved to section 2 in the revised manuscript.

Line 490ff: it is common knowledge that (VOC) instrument backgrounds change with instrument running time and humidity!

Reply: We agree with the reviewer that many people in this community know this issue. But, very few studies have reported explicitly how this issue is addressed in data reduction processes. As far as we know, only one paper from our group explicitly dealt with this issue by relating formaldehyde backgrounds in PTR-QMS with m_{37}/m_{19} ratios [Warneke *et al.*, 2011].

For PTR-QMS, it is quite easy to visual check 10-15 masses for their potential variations of backgrounds. However, there are orders of magnitude more masses from the mass spectra of ToF-CIMS (and PTR-TOF). The only way to properly deal with the issue is checking them individually by a programmed routine. From our perspective, it is an important aspect of data processing procedure and one that has not been described in the literature. Thus, it is necessary to highlight this issue and provide a framework to take it into account in data processing.

Line 649: Given the high humidity dependence of the H₃O⁺ TOF-CIMS caused by the SSQ, its removal might ameliorate this issue. This would result in an instrument similar to the mentioned PTR-QiTOF-MS, for which systematic investigations of the humidity dependence introduced by the quadrupole interface are obviously missing so far.

Reply: We are also looking forward to seeing humidity dependence of reagent ions and VOC signals from the PTR-QiTOF instruments.

Fig. S3: how comes you have double data points for some BSQ voltages? C3

Reply: We repeated the experiments for some BSQ amplitude voltages (260 V and 350 V).

Fig. S6: any explanation for the outlier around m/z 110

Reply: The outlier is m/z 111 from the experiment of catechol. The reason of higher results obtained from catechol than other compounds is unknown. We checked again with our data and we did not find any problem in our experiment for catechol.

Fig S8: pretty brave to specify the masses with four decimal places...

Reply: We changed all of the masses to be with three decimal digits. Other places in the revised manuscript have been also changed.

References:

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