We thank the reviewer for the helpful comments. We have added more information as requested both in the manuscript and a supplemental information section. The revised manuscript places a greater focus on instrument performance and less on the ambient data, as suggested in the reviewer's general comments. The reviewer's specific comments are reproduced below, numbered and italicized. The conclusions of the manuscript have not changed.

(1) In particular, the paper should show the instrument response to a calibration and the different background methods, and discuss the time response and background levels that these diagnostic tests show. What is the time response? Showing a zero and cal will help quantify the claim of "immediate" in section 5.

Response: The time responses for calibrations and backgrounds are all very rapid. Fig. S3 shows the time series of an instrument calibration, where changes in signal due to varying the amount of analyte are sharp. Fig. S4 shows a short period of raw 1 second data during ambient sampling to demonstrate the response of the instrument to NO additions. The bottom panel is intended to show the time response between ambient and background levels of signal, which is only a few seconds.

(2) Additionally, a full mass spectrum would be useful, since Br- chemistry isn't familiar, and it will help support some of the claims (for example, that detection at lower masses is less subject to interference).

Response: A full mass spectrum denoting dominant peaks is shown in Fig. S1 as requested by the reviewer. Fig. 5 in the revised manuscript is better suited to demonstrate selectivity. The following has been added to Section 5.1 to discuss Fig. 5.

"The mass spectrum for a 24 hour period of ambient observations is shown in Fig. 5 and compared to a laboratory generated spectrum during HO_2 calibration. Few additional peaks are present in ambient spectrum, suggesting that Br^- ionization is selective at the mass-to-charge values shown in the figure. Further, the majority of the additional peaks have signal intensities much lower than the intensity of the HO_2 signal at *m/z* 112, which makes it unlikely that the species at the additional peaks and their respective isotopes will affect the signal at *m/z* 112."

(3) Mass spectra comparing zero and ambient would be especially useful for showing the selectivity.

Response: A comparison between mass spectra from HO_2 calibrations using pure air and ambient mass spectra is now shown in Fig. 5 in the revised manuscript. In general, very few additional peaks are observed, with many being of negligible magnitude in comparison to HO_2.

(4) In section 3, please add more experimental details to the reagent ion tests. How much HO2 was added?

Response: At the reviewer's suggestion, we have added more experimental details. The following was added to the revised manuscript.

"HO_2 were generated using the procedure in Section 3. HO_2 mixing ratios were typically in excess of 300 ppt for initial reagent ion evaluation, and varied by varying the gas humidity and velocity. NO was added in excess (2-4 ppm) to obtain the instrument background. NO was also added in small concentrations and in increasing increments to roughly test the kinetics suggested by the HO_2 signal response to additions of varying concentrations of NO as additional confirmation that the analyte being observed corresponded to HO_2. Tests were conducted at room temperature (293 K). The humidity of the gas stream was determined by the amount of water vapor added to produce HO_2. No additional sources of water vapor were present, nor was water directly added to the IMR."

(5) What was the reaction time and pressure in the IMR?

Response: IMR pressure is held at 100 mbar. The residence time is calculated to be 0.07 seconds based on IMR geometry. The pressure and residence time have been added to Section 2. IMR dimensions are given in Bertram et al. (2011) which was cited in the original manuscript. The following was added to the revised manuscript.

"The ion-molecule reaction region has a residence time of 0.07 seconds and is operated at a pressure of 100 mbar."

(6) *Was water added*?

Response: Water was not added independently of the water vapor required for HO_2 production.

(7) Were these tests performed with the quadrupole or TOF CIMS?

Response: All reagents with the exception of Cl^- were evaluated using both instruments. Cl^- was only evaluated using the quadrupole CIMS. This was mentioned in the original manuscript:

"The characterizations involving chloride reagent ions in the laboratory were conducted using the quadrupole CIMS. Unlike the other ions, which were evaluated using the HR-ToF-CIMS as well as the quadrupole CIMS, Cl^- was not revisited with the HR-ToF-CIMS instrument."

(8) For both instruments, add a discussion of water dependence to the detection. Does Br- cluster with water? And is the sensitivity dependent on water, as with I-?

Response: Br^- clusters with water, please refer to the mass spectrum (Fig. S1) in the supplement. A new figure was added to the manuscript to show the humidity dependence of instrument sensitivity (Fig. 3). The sensitivity does not show a humidity dependence when RH>10%. The corresponding discussion can be found in Section 4.1 in the revised manuscript.

(9) Fig. 1 states that collisional dissociation occurs in SSQ. Does this collisional dissociation region decrease sensitivity by breaking apart the cluster ions? Or does it remove water clusters?

Response: Collisional dissociation is intended to minimize excess clustering, primarily from water molecules. However, some fraction of the $Br^-(HO_2)$ may be de-clustered even under the weak electric fields in our instrument. We do not expect $Br^-(HO_2)$ to be a strong cluster based on the differences in electron affinities between the two species, as well as negative temperature dependence of sensitivity, which is discussed in Section 4.1 in the revised manuscript. Analysis similar to the one employed in recent work (Lopez-Hilfiker et al., 2016) may be performed in the future to estimate cluster stability.

(10) More details regarding the instrument performance with Br- would be valuable, since the Bertram et al reference uses a different ion chemistry.

Response: Discussion on parameters of operation and instrument performance is interspersed in other specific comments. Additions have been made to the manuscript where appropriate.

(11) The authors note an important point about zeroing and internal HO2 generation in section 5.1, but the discussion needs further detail. If 4 ppt HO2 are generated in the instrument, then the NO chemical titration zero used in ambient measurements will remove both ambient HO2 and instrument-generated HO2. Is this 4 ppt made in the instrument independent of ambient water and NOx?

Response: The NO addition does remove internal HO_2 generation together with sample HO_2. This was post-corrected. The same quantity of generated HO_2 seems to be present inside the instrument while sampling ambient as well as ultra-high purity N_2 gases (99.999%), suggesting that the generation is independent of sample composition, with the exception of water vapor, which changes the signal observed from generation due to water-vapor induced changes in sensitivity (if RH<10%). Section 5 reads as follows:

"The differences in HO_2 backgrounds observed between the different backgrounding methods and NO additions to N_2 gas were similar, representing ~4 ppt of HO_2 generated inside the instrument. The similarity suggests that HO_2 generation is independent of sample composition."

(12) Since NO also removes an instrument artifact, wouldn't it be better to use the scrubber, which presumably removes only the ambient HO2? Then the difference between the ambient signal and scrubbed signal would directly represent the ambient HO2 contribution, without having to subtract lab-determined artifacts. If the artifact does come from the N2 as suggested, please describe the N2 source and purity.

Response: Using the scrubber would provide a direct instrument background without need for post-correction, as the reviewer has noted. The contribution of the internally generated HO_2 was only investigated towards the end of the measurement period, therefore regular scrubber backgrounds were not performed, thus the need to use the NO background in this work. The choice of backgrounding method warrants further investigation. If internal HO_2 generation can be minimized or eliminated, we consider the NO titration to be preferable, as it may be more "selective". That is, a physical scrubber may also remove non-reactive species which may appear at the same nominal mass-to-charge, and act as potential sources of interference in low resolution instruments. While this was not a concern during our measurement period, it is not clear if this will hold true in all environments.

(13) Do filters on the N2 supply help?

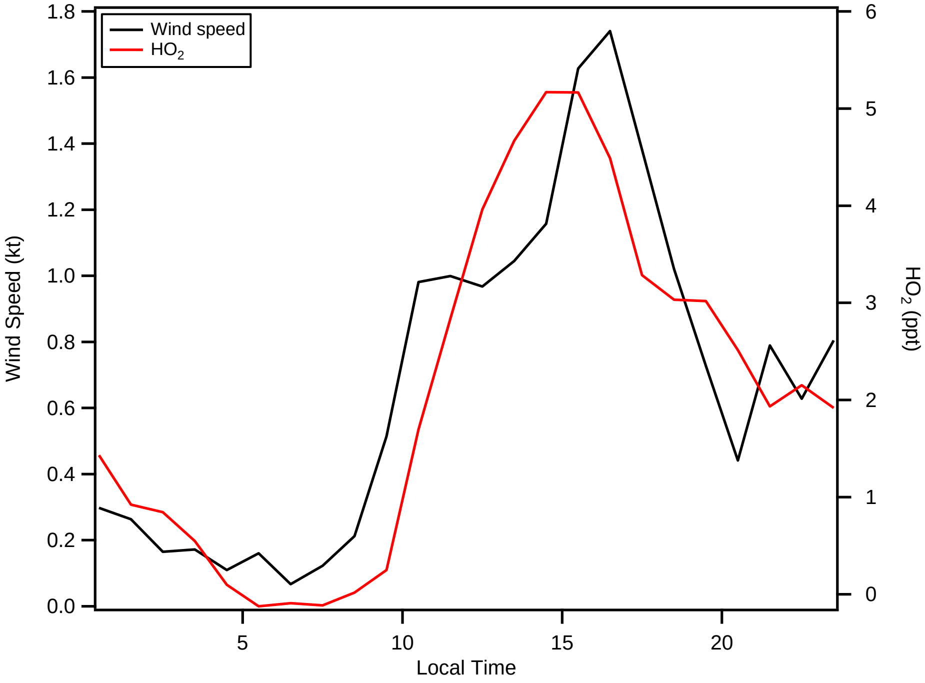
Response: No filters were placed in-line of the N_2 supply. A Carulite 300 catalyst (Carus–Air) was briefly placed in-line for the purpose of removing CO. No difference was observed.

(14) I'm confused by the discussion of the ambient measurements, and they were made for such a short period of time that diurnal averages may not be meaningful. Why aren't measurements averaged over the entire measurement period?

Response: The period used for Fig. 3 in the original manuscript was chosen to be consistent with the period chosen for Fig. 4 in the original manuscript. The authors have more confidence in the performance of the quadrupole CIMS over that period for the HNO_4 measurement. The diurnal profile for HO_2 in the revised manuscript has now been modified to encompass the entire sampling period, which is indicated in the figure caption.

(15) Did the wind speed change at night? I don't think the boundary layer height would explain the slow and steady decay of HO2 in the afternoon. The boundary layer height probably changes little from midday until sunset, whereupon it changes sharply.

Response: The wind speed diurnal profile shows a decrease at night for our sampling period. If wind speed is taken as an indicator of boundary layer height, then BLH may explain part of the decrease in the evening, as shown in the plot below.



(16) Furthermore, the explanation for a factor of 5 difference between the calculated and measured HO2 is murky, and it may be caused by uncertainties in other measurements. Rather than show this plot that potentially undermines the new technique, I think it would be more useful to show more instrument diagnostics as detailed above.

Response: We agree that the comparison between HO_2 calculated from the HNO_4 and NO_2 measurements is of limited value, given the multiple uncertainties present. Reviewer 2 has also commented that a similar comparison has been carried out before (not published) with large discrepancies. Therefore, Fig. 4 and the associated discussion have been moved to the supplemental information, as it may be a valuable reference for future studies.

(17) Pg1, line17 – missing a word. Diurnal pattern? Also, paper notes several possibilities for cause of the trend, so dictated should be changed to influenced.

Response: “Diurnal” has been modified to “diurnal profile”. “Dictated” has been changed to “influenced”.

(18) Pg1, line 18 replace ion counts with ion count rate. Replace baseline with instrument background.

Response: "…per 10^6 bromide ion counts (^{79}Br)" has been changed to "for a bromide ion ($^{79}Br^-$) count rate of 10^6…" in the revised manuscript.

(19) Pg2 line35. I think the authors have done much more than show a proof of concept. They have demonstrated that it can work in ambient air.

Response: The sentence has been modified from:

"In this work, we evaluated the potential of various chemical ionization schemes and provide proof of concept for the Br^- associative ionization of HO_2 to form a $Br^-(HO_2)$ adduct as a direct method for measuring HO_2 using chemical ionization mass spectrometry."

to:

"In this work, we evaluated the potential of various chemical ionization schemes and propose the Br^- ionization of HO_2 to form a $Br^-(HO_2)$ adduct as a direct method for measuring HO_2 using chemical ionization mass spectrometry."

(20) Pg2, line 18. Please reference or explain ROxMAS and PerCIMS – I don't think they will be familiar to most readers

Response: The methods have been more clearly referenced and the discussion of the general detection scheme has been expanded slightly.

(21) Pg3, line 3 remove repeating words.

Response: Repeating words have been removed.

(22) Pg3 line 4. Does atmospheric pressure interface mean that the ion molecule reactions occur at atmospheric pressure? Please give pressure and reaction time in IMR.

Response: The atmospheric pressure interface refers to the series of vacuum chambers/orifices between the inlet and the time-of-flight analyzer. The IMR is actually operated at 100 mbar. The residence time is ~0.07 seconds, though the effective reaction time is not accurately known due to mixing and flow dynamic considerations. The pressure and residence time have been added to the description of instrument description in the revised manuscript.

(23) Section 4. If this section were moved before section 3, it would be easier to understand

the HO2 calibrations used in the reagent ion tests.

Response: At the reviewer's suggestion, Section 4 has been moved before section 3.

(24) Section 5. Measurements in ambient air are useful to help support the selectivity. Mass spectra showing lab results and ambient results would be especially helpful.

Response: A figure has been added (Fig. 5 in the revised manuscript) comparing mass spectra between laboratory observations during an HO_2 calibration, and ambient data for a 24 hour period during ambient sampling. Attention should be paid to the number of additional peaks in the ambient spectrum, of which there are few, and to the intensity of the additional peaks relative to the HO_2 peak intensity at mass-to-charge 112, which demonstrates that the majority of peaks in the ambient spectrum are of insignificant signal intensity.

(25) Pg4, line 34. Please discuss the 5 Hz/ppt sensitivity and put it in context. The similar instrument (reported in Bertram et al) gets 300 Hz/ppt for a different reagent ion and molecule, and Lee et al shows I- sensitivity that varies considerably with compound.

Response: As the reviewer has noted, the sensitivity varies widely for different compounds and reagent ions, and depends on a number of parameters, including ionization rate and cluster stability, instrument transmission, etc. With this, putting the sensitivity into context of other sensitivities would not be particularly meaningful. Instead, we think that putting the sensitivity in terms of a detection limit, as done here, is more useful.

It is important to note that the configuration used by Bertram et al. (2011) utilizes a larger orifice (0.5 mm) before the SSQ, which means the transmission in that instrument is better and a higher maximum sensitivity is achievable. The diameter of the orifice used in our instrument for this sampling period is 0.3 mm. The orifice can be easily replaced with a larger orifice for future sampling.

(26) Does Br- react with other compounds? Or does it react w/HO2 much slower than the collision rate? Does 5 Hz/ppt represent a high or low sensitivity for this instrument?

Response: The sensitivity is representative of reaction rate and cluster stability, among other factors. The humidity and temperature dependence of the sensitivity to HO_2 observed and described in Section 4.1 support the idea that the observed product ion is a cluster. As such, the reaction may not proceed at the collision rate. It may also be the case that the reaction rate is fast but the cluster is weakly bound, or that the cluster product ion reaches a thermodynamic equilibrium with HO_2 and Br^-, whereby the sensitivity is not kinetically limited, but thermodynamically limited instead. The negative temperature dependence of the sensitivity, discussed in Section 4.1, suggests that the latter is true. A similar fundamental discussion of ion-molecule reactions is found in Huey and Lovejoy (1996).

(27) Pg5, line 10 change inches to SI

Response: "five inches" has been changed to "13 cm".

(28) Pg5, line 11 remove "data points"

Response: "data points" removed.

(29) Pg5, line13 how do longer baseline periods make data analysis easier?

Response: The software for processing instrument data "pre-averages" before processing to make data analysis less time-consuming. An averaging time of 1 minute was desired. If the background period is shorter than the averaging time, the background value will be higher than actual, because real signal has been averaged together with the background signal. The 1 minute background time was intended to be synchronized such that signal and background were not averaged together. This is not ultimately how the data was analyzed, and instead, the 1 second data was processed and post-averaged after the background periods were removed and subtracted. The following sentence has been removed to avoid confusion:

"The signal response to the NO addition is immediate and very short periods of time (<20 s) are required, though longer baseline periods were used here for ease of data analysis."

(30) Pg5 line 36. Please give more details about the HO2 calculation, or at least a reference. What constants are used for the thermal equilibrium?

Response: Details on the HO_2 calculation have been added to the SI. The constant used for thermal equilibrium is the recommended value, found in (Burkholder et al., 2015). The temperature dependence of the equilibrium constant is accounted for using temperature measurements.

(31) Pg6 line 29 add trend or pattern after diurnal

Response: Pg. 6 line 34 “diurnal” replaced by “diurnal pattern”.

(32) Pg6 line 33, replace is with was

Response: “is” replaced with “was”.

(33) Pg 6, line 32. I’m confused by the I- interferences. The additional peak is called 159.992, 159.9989, and 159.9889. Are these all the same peaks? Please clarify. The peak at 159.8345 appears to be a larger potential problem. Does that peak zero? If so, that would be the greater interference to I-HO2 with a unit mass resolution instrument, or it could represent a large background that would compromise the precision.

Response: The peak at 159.8345 pertains to $^{79}Br^{81}Br^-$. During the ambient measurement period, Br_2 was added as an additional calibrant. This is not a potential problem for I^- ionization. With respect to peaks 159.9920, 159.9989 and 159.9889, the inconsistency arises from significant uncertainty in peak assignment. With the reviewer’s comment, these data have been analyzed more carefully. The additional peak observed during laboratory NO_2 additions is observed at mass-to-charge 159.9896 while the additional peak observed during ambient sampling was observed at 159.990 Th. It is not clear whether 159.9896 (observed in the laboratory) is related to 159.990 (observed in the ambient), though the high resolution time series of peak 159.990 behaves as the diurnal profile for the NO_2. Furthermore, the peak intensity increases when NO is added to the sample during the background periods, therefore it may be related to NO_x. The values in the manuscript are now consistent with the revised values.

(34) Pg 7, line 4. Replace photochemical schemes with photochemistry

Response: “photochemical schemes” replaced with “photochemistry”.

(35) Pg7, line 10 Replace inherent with potential

Response: “inherent” replaced with “potential”.

(36) P7, line 12 – need to justify the decrease of interferences at lower mass with mass spectra. If collisional dissociation is large enough, the opposite may be true.

Response: Br^- ionization may proceed via clustering or proton transfer, therefore interferences at mass-to-charge 112 either must have a molecular weight of 33 g/mol or produce a product ion of the form X^- where the parent molecule (HX) has a molecular weight of 113 g/mol. It is also possible for product ions X^- to cluster with other neutrals and form a cluster $X^-(M)$ of nominal *m/z* 112. A lower mass-to-charge reduces the number of possible compounds which may undergo charge transfer to form product ions of the form X^- from charge exchange. The following has been added to the revised manuscript:

"Using Br^- also allows for the measurement of HO_2 at a lower *m/z* which may decrease the likelihood of measurement interferences and reduce ambiguity in peak identification, as a smaller number of possible chemical formulas for ion products are possible. Furthermore, Br has a high electron affinity, which makes the production of small charged ions from ionization and collisional dissociation unlikely."

(37) Pg 7, line 17 add cycle or pattern after diurnal, and remove associated

Response: The modification has been made.

(38) Pg 7 line 18 replace measurements with abundance

Response: The modification has been made.

(39) Figure 1 replace collision with collisional

Response: The modification has been made.

(40) Figure 3 - are these hourly averages? Why only 3 days?

Response: Figure 3 diurnal profiles represent median hourly values. The diurnal profiles in the revised manuscript now encompass the full sampling period, 6/9/2015 21:14:00 to 6/11/2015 13:28:00, and 6/15/2015 1:52:00 to 6/25/2015 1:32:00 local time.

(41) Figure 5. bin isn't defined, and what are the baselines? The baselines shown here seem to contradict the text, if the ion counts are count rates. It would be more helpful to put in terms of count rates as the rest of the manuscript.

Response: Ions/bin is not a count rate. It is also not possible to display the mass spectrum as ions/s unless the peaks are integrated. The spectra may be displayed as ions/s normalized by time of flight. However, the purpose of Figure 6 is to display the number of peaks present as well as the positions and relative intensities for each relevant nominal mass-to-charge. In the revised manuscript, each spectrum has been normalized to maximum peak height to serve that purpose and avoid misinterpretation.

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