We thank the reviewer for the excellent comments. Generally speaking, the revised manuscript and associated supplemental information section include a significant amount of detail not included in the original manuscript in order to address the reviewer’s concerns. The reviewer’s specific comments are italicized and numbered. The conclusions of the manuscript remain unchanged.

Specific comments

(1) A more detailed description of the most widely used methods is suggested.
Response: The discussion on the most widely used methods has been expanded. Methods are cited more clearly.

(2) Also, while not all papers published with these various methods need be included in the references, this reviewer suggests including the most recent papers as well as those related to the initial development of these methods.
Response: Recent publications using PERCA, CIMS, and LIF techniques for peroxy radical measurements have been added in the introduction.

(3) Equation 1 is a correct description of the amount of HO2 produced in the photolysis of water vapor by 184.9 nm radiation. There is inconsistency with standard photochemical symbol usage. The symbol σ (sigma) is typically used for absorption cross sections (as used in this paper). Quantum yields, though, are usually represented by φ (phi). The photolysis time is usually represented by t (tee), while τ is usually reserved for lifetime, chemical or otherwise. The radiation flux is usually represented by I (eye) or F (eff) rather than q (cue). Also, the equation should have delta values for [HO2] and the photolysis time, since it describes the increase in HO2 from the photolysis. If the HO2 is below the detection limit in the absence of photolyzing radiation then the equation is correct without the deltas.
Response: Equation 1 symbols have been modified as per the reviewer’s suggestion. The symbol ϕ is reserved for the quantum yield. The photon flux is now represented by I. τ was changed to t. “[HO₂]” on the left hand side and “t” on the right hand side have been changed to “Δ[HO₂]” and “Δt”.

(4) Title, abstract, and method description. Direct versus indirect measurements. This reviewer takes issue with the assertion that this method is direct. Indeed it can be argued that all
chemical ionization mass spectroscopic methods are indirect. Direct ionization of analyte (though photoionization, electron impact or other) could perhaps be considered a direct method. The most direct methods do not rely on calibrations, but instead depend on fundamental spectroscopic and/or physical parameters. The statement in the abstract that (1) “The indirect nature of current HO2 measurements introduces challenges in accurately measuring HO2...” is confounding and not justified. A method could be very indirect, but very accurate. It is recommended that the emphasis on the directness of this method be removed from the title, abstract, and body of the revised paper.

Response: The reviewer is correct that CIMS measurements may be considered inherently indirect. However, we believe it to be important to emphasize that our method does not require additional chemical titration, therefore the terminology is kept as is.

(5) Body of paper, various locations. The term “diurnal” and “diurnals” are used as nouns. Diurnal is most definitely an adjective and should describe a noun such as “profile” or “behavior”. Suggest changing throughout the paper.

Response: All instances of diurnal are now accompanied by appropriate nouns.

(6) Abstract and body. The discussion of the diurnal behavior of HO2 being dictated (affected or determined?) by morning vehicle NOx emissions is not consistent with the information shown in Figure 3. This may be due to the fact that the data is presented as a 4-day diurnal average, or a plotting error. At any rate, HO2 increases with the UV flux, and the small delay in the increase (between about 8 and 10 AM) could be due to elevated NO levels, but there are likely contributions from low O3 levels and perhaps other causes (clouds, winds, temperature profiles). Suggest rewording the discussion of this impact.

Response: “Dictated” has been reworded to “influenced”. The following:

“Fig. 3 shows the diurnal profile of HO2, as well as the diurnals of the UV radiation intensity, NO and O3 concentrations. The difference in the time between peak actinic flux and peak HO2 concentration is due to the suppression of HO2 by the presence of NO from morning-time traffic emissions.”

has been modified to read:
“Fig. 4 shows the diurnal profiles of HO₂, UV radiation index, NO and O₃ concentrations. The difference in the time between peak actinic flux and peak HO₂ concentration is at least partially due to the suppression of HO₂ by the presence of NO from morning-time traffic emissions.”

(7) The slow decay in the afternoon and evening is expected, but not to the degree shown by the observations. Indeed at sundown (2000 hours), the observed HO₂ is about half that at the midday peak. The slow decay is also not expected given the non-zero values of NO after sundown. This could imply non-photolytic sources of HO₂ rather than slow chemistry. The discussion should examine all possible causes.

Response: We agree that there must be non-photolytic HO₂ production. A discussion of all possible causes in the absence of additional auxiliary measurements would be speculative, however, and distract from the main points of the paper. We believe that a full investigation of HO₂ sources/sinks in relation to measurements taken using this technique should be conducted as future work.

The sentence

“The slow decay of HO₂ may partially be explained by HO₂ production from oxidation of biogenic volatile organic compounds (BVOCs), which are abundant in the Southeast United States (Geron et al., 2000; Guenther et al., 2006), as well as a decrease in boundary layer height. However, additional measurements would be required to constrain sources and sinks.”

is modified to

“The slow decay of HO₂ may partially be explained by non-photolytic HO₂ production, e.g., from oxidation of biogenic volatile organic compounds (BVOCs), which are abundant in the Southeast United States (Geron et al., 2000; Guenther et al., 2006), as well as a decrease in boundary layer height. However, additional measurements would be required to constrain sources and sinks.”
(8) The timing of the peaks in UV flux compared to HO2 is discussed on page 5 (line26). It states that there is a difference in the time of the peaks, but Figure 3 seems to show that the peaks coincide.

Response: UV flux and HO2 peaks coincide in Figure 3 for the 4-day period displayed. The comment in the text was intended to address the diurnal profile for the entire measurement period, which is now used for Figure 3 in the revised manuscript. It appears that for the remainder of the sampling period, the HO2 peaks slightly later (30 minutes to 1 hour) than earlier in the sampling period.

(9) Page 1, line 28. suggest “…production of ozone via its reaction with NO.”

Response: The modification has been made.

(10) Page 1, lines 29-30. This statement is worded in a confusing way. Suggest reworking to make the point clear.

Response: It is not clear to the authors what the reviewer finds confusing so we leave the sentence as it is. The fate of RO2 radicals and SOA formation are strongly dependent on the ratio of HO2/NOx as discussed in the review papers cited.

(11) Page 1, line 33. The lifetime of HO2 depends on a number of factors including the NO level. While it is true that the lifetime is less than one minute in urban atmospheres, it can be longer in remote environments.

Response: “(τ ≤ 1 min)” removed. The statement that transport is unimportant remains valid.

(12) Page 2, lines 11-12. It is stated that converting HO2 to OH with NO introduces additional complexity. While this could be true, it is not necessarily so. Suggest rewording this sentence.

Response: Pg. 2 lines 11-12, the sentence has been reworded from:
“However, these techniques do not measure HO2 directly, requiring HO2 to be titrated with NO, which introduces additional complexity.”
to:
“However, these techniques do not measure HO₂ directly, requiring HO₂ to be titrated with NO, which may introduce additional complexity.”

(13) Page 2, lines 15-16. While most researchers use PERCA to measure HO₂+RO₂, there is no reason why techniques such as oxygen dilution could not be employed. This reviewer does not believe that the technique fundamentally precludes speciation. Someone has just not yet been successful in doing so. Suggest rewording.

Response:
Lines 15-16 modified to:
“However, addition of NO to a sample stream containing organic peroxy radicals results in additional HO₂ production. So far, speciation of HO₂ from other peroxy radicals using chemical amplification has not been successful, though previous attempts have been made (Miyazaki et al., 2010).”

(14) Page 2, line 35. After description of previous techniques and their pitfalls, the Br-CIMS (and other ionization schemes) is briefly introduced. While not mentioned here or elsewhere, it is known that cluster-based ion techniques can suffer from issues such as variable cluster stability, which can depend on ambient conditions and water vapor concentrations. While this reviewer understands that the authors want to put their technique in the best light, it is also appropriate to recognize and discuss potential problems. Suggest adding such a discussion somewhere, probably on pages 3-4. Page 3, line 13.
Response: We have added discussion regarding the effect of water vapor in Section 4.1, as well as Fig. 3 to show that effect. The discussion on temperature has been moved to Section 4.1. The dependence of instrument sensitivity on both humidity and temperature are fully expected and do not detract from the merit of the technique.

(15) It is stated that “…only the integrated peak data is used in this paper…” This needs a bit of explanation, but this reviewer assumes you mean the integrated area of the peak. Also, the word data is plural, so it should be “…data are used…”. 
Response: The data used are actually the sum of the integrated area of all peaks at the nominal mass-to-charge, summed to a unit mass intensity. The following sentence in the original manuscript has been revised for clarity from:

“In order to demonstrate the generalizability of the technique to instruments with unit mass resolution, only the integrated peak data is used in this paper, though the high resolution capabilities were exploited to diagnose and address possible artifacts during the method development.”

To:

“In order to demonstrate the generalizability of the technique to instruments with unit mass resolution, only the unit mass resolution data are used in this paper, though the high resolution capabilities were exploited to diagnose and address possible artifacts during the method development.”

(16)   Page 3, lines 26-29. In the discussion of chloride and iodide ionization schemes, it is stated that the Cl⁺(HO₂) cluster was not observed. What is not stated is whether any ions were observed. In other words, were full mass scans conducted with the quadrupole CIMS?

Response: Full mass scans were conducted using the quadrupole CIMS. The primary ions corresponded to Cl⁻(HCl) and associated isotopes with intensities higher than saturation for our detector. Ions corresponding to Cl⁻(HNO₃) and Cl⁻(CF₃COOH, a PFA-Teflon impurity) were also observed. Cl⁻(HO₂) was not observed as originally stated.

The following has been added in pg. 4, lines 28-30 for clarity:

“Full mass spectra obtained using the quadrupole CIMS identified Cl⁻(HCl), Cl⁻(HNO₃), and Cl⁻(CF₃COOH) as prominent ions. However, the Cl⁻(HO₂) cluster was not observed.”

(17)   Page 3, line 33. Suggest “...we observed that addition of NO₂...”. Also, one needs to be careful that the mixture contains no NO. With a mixture in N₂, it is very likely that it does contain NO. It is better to employ mixtures of NO₂ in air or oxygen to minimize the amount of NO. Also, there are techniques for removing NO from a mixture of NO and NO₂. Page 3, line 35. Suggest “... addition of NO₂ showed an increase...”.

Response: The NO₂ may contain NO, but the direct addition of NO does not have the same effect. The signal increase at m/z 160 is not attributed to HO₂, therefore, this would not be related
to HO$_2$ production from the addition of small amounts of NO in the NO$_2$ mixture. Suggested modifications to text have been made.

(18) Page 3. The method of determining the instrument background is discussed on page 6, line 15, but it is probably better to include in this section (pages 3-4).
Response: The NO additions are now mentioned in Section 4 in the revised manuscript: “NO was added in excess (2-4 ppm) to obtain the instrument background.”
The discussion regarding the differences in background methods stems from ambient observations and is best left in that section.

(19) Regarding the production of HO$_x$ radicals in radioactive ion sources, this phenomenon is well known. Other CIMS researchers add reagents to the flow over the ion source to minimize this issue. It is suggested that experiments with reagents added to the ion source be conducted to determine whether the internal HO$_2$ can be eliminated, thus reducing the background and the impact of its variability. It may be that NO is not the best reagent in this case, but that is the obvious first choice.
Response: We thank the reviewer for this suggestion. Indeed, HO$_x$ generation in radioactive sources has been a known issue. In the case of OH, there are a number of available scavengers (e.g. propane, C$_3$F$_6$) added to remove the internally generated OH. This procedure is possible partially because the CIMS instrument configuration for OH measurements is such that mixing is minimized between the ion source flow and the sample flow. With regards to HO$_2$, the authors are not aware of anything other than NO that may be used as a scavenger.

Furthermore, using our configuration, where both flows mix significantly, this may not be successful. Any reagent added directly to the ion source flow will react significantly with sample analyte. The residence time in the IMR is ~0.07 seconds. The residence time in the Po-210 source using a flow rate of 2 sLPM and the dimensions provided by the manufacturer provides an upper limit of 0.03 seconds, assuming that the volume inside the Po-210 source is at atmospheric pressure (which is not the case). Taking 0.03 seconds to be the reaction time inside the ion source and assuming an NO concentration of 1x10$^{13}$ molec/cm$^3$ in the ion source gas, 90% of internally generated HO$_2$ is reacted, while 25% of sample HO$_2$ is reacted using $k = 8.00x10^{-12}$ cm$^3$ molec$^{-1}$ s$^{-1}$. This may be acceptable, and the effect of having a continuous NO
flow into the instrument can be accounted for during calibration, but will negatively impact sensitivity.

A more successful approach may be to modulate the NO concentration and contact time in the sample line such that HO₂ titration is efficient at atmospheric pressure, but inefficient inside the IMR, where the pressure is a factor of 10 lower (and can be further decreased).

Regardless, background characterization and optimization warrant further effort and will be the subject of future work.

(20) **Page 3, line 8.** I was surprised that the ion source flow is the same as the sample flow, resulting in a 1:1 dilution of the sample. Also, N₂ was used as the main component of the ion source flow. Is this optimum, or does it not matter what is used. Perhaps a different configuration of the ion source could be optimum for this measurement.

Response: Similar dilutions have been employed in Lee et al. (2014) and Bertram et al. (2011) using the HR-ToF-CIMS. N₂ is typically the main component of the ion source flow. It would be undesirable in most cases to produce ions from additional components (such as O₂), therefore air is not used. It is possible to use other gases, such as Argon, but this is usually unnecessary. We have yet to explore different dilutions. However, future work will include varying the ratio of sample to reagent flow in the context of minimizing the importance of internally generated HO₂.

(21) **Page 4, line 4.** It is stated that there were no observed artifacts with the Br-CIMS approach. This disguises what was tested.

Response: This has been clarified.

“Unlike the other reagent ions, the Br⁻ ionization scheme was found to be sensitive to HO₂, the measurements were reproducible, and there were no observed positive artifacts, making this an ideal scheme for measurements of HO₂.”

Modified to:

“Unlike the other reagent ions, the Br⁻ ionization scheme was found to be sensitive to HO₂, the measurements were reproducible, and there were no observed positive artifacts from NO₂ or O₃, making this an ideal scheme for measurements of HO₂.”
(22) Suggest testing every possible gas in the troposphere of reasonable concentration, and listing the gases tested here. Other factors should also be tested such as aerosol loading, and inlet temperature and pressure.

Response: For tropospheric constituents to be potential artifacts in the Br\(^-\)(HO\(_2\)) measurement they must meet one of the following criteria:

1) Possess a molecular weight of 33 g/mol and cluster with Br\(^-\)
2) Produce a product ion of the form X\(^-\) from an acid (MW=113 g/mol) stronger than HBr by proton transfer
3) Produce HO\(_2\) by proton transfer
4) Generate HO\(_2\) by other means

The first possibility can readily be discarded. The second possibility is unlikely, as organic acids, diacids, peroxyacids, etc. all possess even molecular weights. A molecular weight of 113 g/mol is required. Further, the species must be in sufficiently high concentrations and possess stronger gas-phase acidity than HBr. The third possibility requires a proton transfer reaction with H\(_2\)O\(_2\) or reaction with other small abundant molecules such as formaldehyde. A response at m/z 112 was observed from sampling H\(_2\)O\(_2\) and HCHO in an environmental chamber. However, the response was ~0.25 cps/ppb for H\(_2\)O\(_2\) and 0.002 cps/ppb for HCHO, which is insignificant. Further, it is unclear whether the signal increase is a result of Br\(^-\) ionization of these components, or whether HO\(_2\) was formed prior to the instrument by an unknown surface process. Regardless, the amount of signal produced is negligible for atmospheric application. It is also important to mention that SO\(_2\), which is a common atmospheric constituent, elicits no instrument response at m/z 112 or 114 even at concentrations >10 ppm. The fourth possibility is more difficult to rule out. However, it would likely be a neutral process which is independent of detection scheme. Furthermore, the diurnal profile presented here does not suggest any obvious artifacts.

The effect of temperature is discussed in Section 4.1. The effect of pressure was not tested and is subject of future work in the context of sensitivity/selectivity. It is unclear what effect the reviewer expects aerosol loading to have, but this was not explored.

The following was added in the revised manuscript:

“The Br\(^-\)(HO\(_2\)) measurement selectivity was explored further in the laboratory. In addition to high concentration additions of NO\(_2\) and O\(_3\), other common atmospheric constituents were
sampled with the instrument to assess the possibility of other potential artifacts. Large concentrations (>10 ppm) of SO$_2$ were added, which did not elicit a response. Hydrogen peroxide and formaldehyde were sampled from the Georgia Tech Environmental Chamber facility (Boyd et al., 2015) at concentrations in excess of several ppm, eliciting responses of 0.25 cps/ppb and 0.002 cps/ppb, respectively. It is not clear whether the observed signal response is due to ion-molecule reaction with Br$^-$ or unidentified wall reactions within the experimental chamber. Regardless, contribution to the HO$_2$ signal from these species is insignificant at atmospheric levels and under most experimental conditions in the laboratory.”

(23) Temperature is discussed later in the paper, but this reviewer suggest that this discussion be moved to this section. Page 4, line 6. Suggest “…signals were observed.”
Response: The temperature discussion has been moved to Section 4.1 under reagent ion characterizations. “…signals was observed.” refers to “no increase” in the sentence so the modification was not made.

(24) Page 4, lines 16-20. In the introduction to the calibration procedure, it is stated that humidified and dry air were mixed together. How was the air humidified? If a bubbler was used, this could be problem. It is known that bubblers can produce small droplets that evaporate downstream and produce additional water vapor that is not accounted for.
Response: The air was humidified using bubblers. This detail has been added to Section 3. The dew point is measured at the inlet of the CIMS, after irradiation of the sample. Even if droplets were formed as a result of using bubblers, the additional water vapor will have been accounted for.

(25) Also, it is stated that an AADCO air generator was used. Does this approach produce clean enough air for this important part of the instrument characterization?
Response: AADCO 737-14 manufacturer specifications state that concentrations of hydrocarbon, methane, and CO levels in the output gas are below 5 ppb which is significantly better than zero air (1 ppm THC), which is typically used for HO$_2$ calibrations.
(26) Since the photolysis of water produces OH, any hydrocarbons (in addition to CO discussed on line 30), particularly fast reacting ones, could influence the HO2 amounts produced.

Response: C\textsubscript{3}F\textsubscript{6} was added in large abundance (40 ppm in the gas) to compete for OH and prevent hydrocarbon oxidation as a diagnostic test. No change was observed in the signals during the calibration. The addition of C\textsubscript{3}F\textsubscript{6} to the gas flow during calibration has been noted in that discussion in the revised manuscript.

(27) Also, any NOx present could cause additional problems. To overcome potential problems, suggest doing at least some experiments with very high purity air in cylinders with low hydrocarbon content.

Response: Presumably, the reviewer is referring to possible contribution from RO\textsubscript{2}+NO reaction where the RO\textsubscript{2} is derived from oxidation of trace hydrocarbons in the carrier gas. As a test, methane (up to 1% in the gas) was added to react with OH and produce CH\textsubscript{3}O\textsubscript{2}. If NO is present in sufficient quantities such that the RO\textsubscript{2}+NO reaction contributes to the HO\textsubscript{2} signal, the addition of methane should result in a signal increase. However, this was not the case and no signal response was observed. One could argue that a RO\textsubscript{2} that reacts more rapidly with NO could be formed from another hydrocarbon which would contribute to the HO\textsubscript{2} response in the presence of similar amounts of NO, but this seems unlikely, especially given the test described in comment (26). Nevertheless, experiments using very high purity air in “clean” cylinders will be conducted in the future.

(28) Various parameters of the calibration system should be given (e.g. total flow, range of dew points, impacts of using different slits, humidities, and flows on instrument performance).

Response: Flow conditions and velocities were given in Section 3. Please also refer to response to comment (31). Different slits were not tested. Water vapor mixing ratios are also given: “The water vapor mixing ratios varied between 0.66 and 8.20 parts-per-thousand.”

(29) Page 4, line25. It is stated that the Creasey et al. (2000) (reference not in the reference list) water vapor cross section was used, but it is not stated why.
Response: The absorption cross-section value used here, determined by Creasey et al. (2000), is a result of recent determinations of absorption cross-sections for water vapor. The value determined in that work is in agreement with results reported from other recent determinations performed by Cantrell et al. (1997). The authors are aware that more recent determinations have been made by other authors, and that a summary of cross-sections is provided by Burkholder et al. (2015). The recommended values given in Burkholder et al. (2015) are provided in 1 nm wavelength increments. Interpolating between the value at 184 nm and 185 nm gives an absorption cross-section of of $7.31 \times 10^{-20}$ cm$^2$ for a wavelength of 184.9 nm, which is no different than the value reported by Creasey et al. (2000) of $(7.22 \pm 0.22) \times 10^{-20}$ cm$^2$. In any case, using the recommended value would not change the HO$_2$ values calculated. We do not believe justification needs to be added to the manuscript for the use of this value. The reference has been added to the revised manuscript.

(30) Also, why was the approach of photon flux measurement using a phototube employed rather than an actinometric method? Actually, it would be better to use multiple approaches.

Response: There is no particular reason for choosing this calibration method. The procedure employed here which requires direct measurement of the lamp photon flux has been used previously (Faloona et al., 2004; Sjostedt et al., 2007). We agree using multiple approaches would be best. Future work will compare multiple approaches.

(31) Page 4, line 28. The discussion of measurement of flow velocity needs some more detail.

Does the velocity profile match laminar or plug flow? Is the Reynolds number such that the flow in the photolysis section is turbulent or laminar? Is the entrance length sufficient that fully developed flow can be expected?

Response: The following has been added to Section 3.

“Flow velocities varied between 400-800 cm/s (Re > 4000) to promote plug flow conditions. The slit allowing light into the tube was located such that the distance before irradiation after entry into the tube was 10 times the hydraulic diameter, allowing the flow profile to fully develop. Plug flow conditions were confirmed by measuring the flow velocity both at the center line and near the wall of the tube, showing no observable differences.”
Page 4, line 31. Suggest saying specifically the range of HO2 values employed in the calibrations (i.e. xx to yy pptv). Suggest rewording to “...were kept low so as to calibrate at atmospherically relevant levels...”. It should be recognized that there are conditions where HO2 can get above the 45 pptv shown in Figure 2.

Response: The sentence has been reworded to the following:
“The HO2 concentrations were kept low (2-45 ppt) to calibrate for the HO2 levels observed during ambient sampling and to avoid non-linearity in the calibration curve due to depletion of HO2 through HO2 radical-radical recombination.”

Page 4, line 35. The issue of the intercept may be related to contaminants in the air (discussed above). For example, a carbonyl compound could be present that photolyzes at the mercury lamp wavelength. Suggest working (and describing that work) to minimize this “extra” HO2 produced.

Response: Given that the source appears to be independent of OH (see comment (26)), trace NOx (see comment (27)) and water vapor mixing ratio, photolysis of a carbonyl containing compound may be the cause of the extra HO2, as the reviewer suggests. Because the constant extra HO2 does not affect the sensitivity, varying gas purity to ascertain the source of the extra HO2 will be investigated in future work.

Page 5, Calibration section. One needs to include uncertainties in the signals (random fluctuations) used to derive the calibration to get an overall calibration uncertainty. Also, it is convention to give the uncertainty at the 95% confidence interval, although whatever confidence level or sigma value is used should be stated. It should also be stated how stable the calibration is with time.

Response: Table S1 was made to describe the 1σ uncertainties of the parameters used for the HO2 uncertainty calculation, and is referenced in the revised manuscript. The combined uncertainty, accounting for signal fluctuations is 18% (1σ). A conservative estimate of 20% was given in the original manuscript, which we will continue to use. This value is very typical. The signal fluctuation uncertainty does not contribute significantly to the overall uncertainty. The uncertainty is primarily due to the measurement of the lamp photon flux.
(35) Page 5, line 9. Suggest “...and can therefore be affected...”, since it depends on wind direction.


(36) Page 5, line 10. The length of the inlet is given, but the reaction time (derived from length, diameter and flow) should also be given. Also suggest using “minimize” rather than “avoid”.

Response: The sentence:
“The instrument was located outside in an enclosure, allowing a short inlet of approximately 13 cm to avoid HO_2 losses on the walls of the sample tubing.”

was changed to:
“The instrument was located outside in an enclosure, allowing for a short 1 cm inner diameter Teflon inlet of approximately 13 cm in length. The residence time of ambient sample in the tube was short (0.3 seconds) which helps to minimize HO_2 surface losses on the sample tubing.”

(37) Page 5, line 11. It is stated that 4 ppm NO is added to determine the background. What is the concentration in the inlet resulting from such additions? Has the amount been optimized through systematic studies and/or calculations? Such experiments should be performed and described. Also, it would be helpful to be given information on the size of the background compared to ambient signals.

Response: It was calculated that 40 ppb were required to remove greater than 99% of the sample HO_2 given the expected contact time (~0.06 s) in the inlet, before introduction of the sample into the IMR. The 4 ppm stated in the manuscript is the NO concentration in the sample gas, resulting from the addition of 10 sccm of an 810 ppm mixture of NO/N_2. 4 ppm (which is much higher than 40 ppb) was chosen to account for reaction with other constituents in the sample (primarily O_3) and imperfect mixing. The following has been added to clarify the concentration of NO in the inlet: “A solenoid valve was used to perform periodic additions of 10 sccm from an NO/N_2 mixture (Scott-Marrin, 810 ppm) into the sample stream every 10 minutes on a 10% duty cycle to obtain the measurement background.”
Page 5, lines 14-15. It is stated that the m/z 112 signal is normalized for reagent ion signal at m/z 79. Is it clear that the detector and associated electronics are fast enough to measure count rates in the $10^6$ range? Experiments conducted to verify this should be described.

Response: The HR-ToF-CIMS does not count events, but rather measures a voltage which is converted to a count rate under the assumption that the voltage is linear with the number of counts. As such, the relevant parameter is not “speed” but rather MCP detector saturation. The manufacturer has conducted such tests, observing saturation only at counts greater than $2 \times 10^7$ cps, which is an order of magnitude higher than the reagent ion counts observed here.

Page 5, line 26. It says that there is a difference in time between the peak UV flux and peak HO$_2$ concentrations in Figure 3, but this reviewer does not see this. Perhaps it is a problem with the time scales in the figure. Please investigate this.

Response: See response to comment (4).

Page 5, lines 31-34. Suggest indicating that the sources of HO$_2$ from biogenic VOCs after sundown is due to non-photolytic processes. This is obvious, but suggest being explicit.

Response: The sentence was modified to say the following.
“The slow decay of HO₂ may partially be explained by non-photolytic HO₂ production, e.g., from oxidation of biogenic volatile organic compounds (BVOCs), which are abundant in the Southeast United States (Geron et al., 2000; Guenther et al., 2006)…”

(42) It is also not clear how a change in the boundary layer height would affect the decay of HO₂ after dark.
Response: Refer to response to comment (15), Reviewer 1.

(43) Page 5, lines 35-36. Suggest stating that the calculation of HO₂ from observations of HNO₄ and NO₂ depends on the temperature dependent equilibrium coefficient. Give the value used. Show the equation for calculating HO₂ using this approach. Do some calculations to indicate the time scale for approach to equilibrium at the conditions of the study (range of temperatures and concentrations).
Response: As suggested by Reviewer 1, the figure comparing measured HO₂ and calculated HO₂ has been moved to the SI. A more detailed discussion of the equilibrium assumption as well as how the calculation is performed has been added to accompany that figure under the title “HNO₄ measurement calculation to infer HO₂ abundance and comparison with Br⁻(HO₂) measurements” in the supplemental information section. The time scales associated with the forward and back reactions are very fast, and only relevant in the context of the time scale of NO fluctuations, which perturb the equilibrium. Therefore, the validity of the equilibrium assumption depends on the time scale associated with NO changes in our sampling site. A more thorough treatment of this assumption will be presented in Chen et al. (2016, in preparation).

(44) Page 6, line 3. A positive bias in the HNO₄ measurement is mentioned. This should be discussed a bit more, giving indications of how large the bias appears to be (based on measurement-model comparisons in previous studies, for example), and its possible causes.
Response: Without a constrained model to accompany our observations, it is difficult to ascertain the magnitude of the potential bias. We suspect that NO₂ may play a role, as we have observed HNO₄ production from NO₂ during laboratory characterizations, and a possible contribution in the presence of ozone even at ozone concentrations below 100 ppb, which is relevant to our sampling site. To our knowledge, HNO₄ measurements with iodide have only been published by
Veres et al. (2015). The modeled-measured comparison in that work does not observe a higher maximum, but rather a several hour difference when the HNO$_4$ concentration reaches a maximum, which is not what is observed here. Therefore, we cannot comment on this with certainty.

(45) Page 6, line 7. Here the laboratory studies on temperature effects on sensitivity are described. Suggest moving this back to the laboratory studies section.
Response: The discussion on temperature effects on sensitivity has been moved to Section 4.1.

(46) Page 6, line 13. It is stated that the measured diurnal profile of HO$_2$ agrees with expectations. This is vague enough to be not of much use. Especially since the diurnal profiles shown in Figure 4 differ significantly. The scaled profiles are within about 20% at the peak, but differ by a factor of 2-3 at midnight.
Response: While we do not have an independent method for validation of the Br-CIMS technique in this work, we disagree with the reviewer. A certain HO$_2$ diurnal behavior is expected for HO$_2$, despite the number of factors that affect its behavior. The diurnal profile presented here may not be conclusive, but demonstrates that the technique is promising and warrants further characterization.

(47) Page 6, line 17. A “metal wood scrubber” was used to remove HO$_2$ to compare with the NO addition method of background determination. Did you verify that there was enough contact time to remove all the HO$_2$? For example, double or triple the amount of contact to see if it makes a difference.
Response: A setup similar to the calibration setup discussed in Section 3 was placed before the scrubber during these tests to confirm that the scrubber was effective at removing HO$_2$. HO$_2$ was generated but not observed when the scrubber was in line. HO$_2$ generation by the mercury lamp in ambient air was confirmed by measurement without the scrubber in line.

(48) Page 6, line 25. The discussion of the iodide-CIMS seems a bit out of place here. Perhaps this should be moved to the discussion of the investigation of various ionization schemes.
Suggest hypothesizing why this approach doesn’t work. Is it purely a resolution issue or some other problem?

Response: The discussion of the iodide-CIMS here is specific to atmospheric measurements and not laboratory characterization therefore it is best it remains in this section. The resolving power of the instrument during this time period was ~3000, which should be sufficient to separate the peaks in Fig. 6. The high resolution time series of the different peaks at nominal m/z 160 appear to be mostly independent of each other. It is not clear why the I(HO₂) measurements were not successful. The following was added to section 5.2.

“The resolving power of the instrument during the sampling period was ~3000 and the high resolution time series of the major peaks at nominal m/z 160 appear to be mostly independent of each other, which suggests that resolution is not a limiting factor.”

(49) Page 7, line 6. Suggest “… charge exchange ionization is not feasible…”.

Response: Page 7 line 3-4 “…charge exchange ionization will not be feasible in the real atmosphere…” modified to “…charge exchange ionization is not feasible in the real atmosphere…”

(50) Page 7, line 12. It is stated that observations at lower m/z decreases the likelihood of interferences. This statement needs explanation because it is not obvious that is true.

Response: See response to reviewer 1, comment (37).

(51) Page 7, line 16. Work on reagent addition to the source, may eliminate the issue of source-produced HO₂, making increased performance using higher activity sources possible.

One can encounter space charge issues as the activity is increased, with the result of no improved sensitivity.

Response: See response to comment (15) regarding reagent addition. We do not believe we are near encountering space charge issues as we have used more active sources with improvements in sensitivity in the quadrupole-CIMS instrument.

(52) Page 7, references. In the future, suggest listing the reference as hanging paragraphs, so the first author’s last name can easily be found.
Response: Modification made.

(53) Page 11. Suggest “Figure 1. Schematic diagram of the...”. Suggest giving information on the roles of the various ion guiding components (quadrupoles, ion optics) and how they are configured. Indicate whether or not the inlet region is dark, or transparent to solar radiation.
Response: Recommended modification has been made. The caption now reads:
“Figure 1: Schematic diagram of the High Resolution Time-of-Flight Chemical Ionization Mass Spectrometer. Sample air enters the flow tube through a 0.5 mm orifice where it is ionized at 100 mbar. The contents of the ion-molecule reaction region are sub-sampled through a 0.3 mm orifice into the small segmented quadrupole (SSQ) chamber held at 2.5 mbar. Collisional dissociation occurs in the SSQ. Ion products are then collimated by the big segmented quadrupole (BSQ) where they also dissipate energy by collisions with background gas at reduced pressure. The subsequent ion lenses then focus and accelerate the ion beam towards the time-of-flight analyzer.”

(54) Page 12. Suggest adding the word “laboratory” to indicate the calibration studies are not done in the field. Suggest indicating the variability of the calibration results (error bars and/or multiple calibration curves).
Response: The modification has been made. A second calibration curve has been added. The slopes differ by ~7%.

(55) Page 13. Suggest indicated that these are “average” diurnal profiles for the time period indicated. Suggest changing the tic marks on the x-axis to every 4 or 6 hours, so that noon and midnight re clearly indicated. In the text and/or the caption, indicate the wavelength range and instrument for the UV flux measurement.
Response: The diurnal profiles are hourly median values. This has been indicated in the caption. Tic marks are now every 4 hours. The spectral response range for the UV sensor is between 280 and 360 nm. The following has been added to Section 5:
“An additional UV sensor was employed with the Vantage Pro2 weather station to obtain an UV index measurement between 280 and 360 nm.”
Page 15. The signal levels for the bromide ion CIMS are much higher than shown in the calibrations in Figure 2. This significantly changes the relative levels of background, signal and the interference at m/z 112.0127 at ambient HO2 levels. Suggest either showing a spectrum at realistic ambient levels or discussing the relative amounts of background, signal, and interference at ambient levels.

Response: The y-axis in Fig. 5 (original manuscript) on page 15 does not give a count rate. To avoid confusion, the y-axis has been normalized to maximum peak height for each spectrum. The purpose of the figure is to show the location and number of peaks present at the nominal mass-to-charge values of interest. It is also important to note that if one wishes to compare the relative intensities of the peaks in each normalized spectrum, the relevant metric is the peak area, and not the peak height. The relative amounts of ambient signal and background can be observed in Fig. S4 in the supplement.

References


Chen, D., Huey, L. G., Tanner, D. J., Li, J., Ng, N. L., and Wang, Y. H.: Inferring hydroperoxyl radical (HO2) in an urban site via the measurement of pernitric acid (HO2NO2) using
chemical ionization mass spectrometry (CIMS), in prepration, to be submitted to Atmos. Meas. Tech., 2016.


