Authors response to the reviewers. (Response in blue)

We would like to thank the reviewers our paper on “Peroxyacetyl nitrate (PAN) and peroxyacetic acid (PAA) measurements by iodide chemical ionisation mass spectrometry: first analysis of results in the boreal forest and implications for the measurement of PAN fluxes”. We appreciate the care and time taken by the reviewers and their co-workers.

The manuscript describes the detection (either intentionally or otherwise) of PAA using iodide ionization with CIMS. We show that when operated with a priori knowledge of the sensitivity of the system to PAA it is possible to learn about the oxidising environment of the atmosphere. Whilst highlighting potential artefacts when deriving PAN deposition velocities we pointed out that sensitivities in individual instruments are likely to different and the particular zeroing method chosen can mitigate any issues if measuring concentrations.

We feel we are justified in making the point that, although it is likely concentration measurements of PAN are instantaneously correct using addition of NO for analytical zeroes, eddy covariance flux measurements may be prone to systematic errors if the instrument is sensitive to two species, i.e. PAN and PAA and entitling the manuscript accordingly. New groups of researchers who attempt to measure EC fluxes of PAN using I-CIMS should be aware of this.

J. Roberts

This paper describes observations of peroxyacetic acid with the same iodide ion CIMS that is used for acyl peroxynitrates. This paper could be a very important addition to the literature and presents some results that the atmospheric measurements community will do well to pay attention to and address in future research. The research as presented brings up a number of questions, and the paper contains some errors and omissions that need to be dealt with. As you will see below, I think a healthy sense of skepticism is in order here, since there are contravening studies that did not observe a PAA effect, but should have, based on this paper’s assessment of how and when there is significant PAA. Assuming the comments and questions are taken care of, this paper should be acceptable for publication. A list of general and specific question and comments follow.

We thank J. Roberts for his review and comments. His main general point is that detection of PAA is somehow peculiar to our ICIMS. However, whilst it is true that the ICIMS system used in Zheng et al. 2012 did not detect PAA, in a dataset measured in the BEARPEX (J. Thornton, review for this paper) campaign (Min et al. figure 9 in http://www.atmos-chem-phys.net/12/9763/2012/acp-12-9763-2012.pdf) there is strong evidence for PAA in the background signal. Whether or not on those occasions it made any difference to data interpretation is matter for a long and complex discussion which would include in canopy chemistry, fluxes of absolute humidity causing errors and the actual sensitivity of the BEARPEX ICIMS to ambient PAA.

General comments;

The naming convention for PANs used in this paper is not consistent, and is something of a hybrid between the method that seems to be favored by Europeans: acyl peroxynitrates (e.g. acetyl peroxynitrate) and the method that names them as anhydrides of two acids: e.g. peroxyacetic nitric anhydride. Either is fine as they both lead to the correct structure, but the term used in the introduction “Acyl peroxy nitric anhydrides” is clearly not correct, and really peroxyacetyl nitrate isn’t correct either. I would urge the authors to pick from one of the correct ones. This shouldn’t be too big a problem since the acronym PAN can be used for the bulk of the paper.

We will do as urged and remain faithful to a consistent system of nomenclature.

There are a number of studies that compare PANs measurements that were not addressed in this paper, and those studies show no evidence of a significant PAA signal. The first paper in that regard is the original Slusher et al., 2004[Slusher et al., 2004] who showed intercomparisons with the NCAR GC/ECD instrument, and found no evidence of spurious signals that could be due to PAA. It should be noted that these measurements were not a part of a comprehensive study, so we don't know the corresponding NOx levels etc., and were made at the NCAR Mesa Lab, hence had some urban impact.

As we have pointed out in the manuscript, the zero generated via the addition of NO would include any contribution from PAA. Therefore, the PAN data generated would not include the full signal from PAA, only the signal left from the difference between consecutive zeroes. Any errors may therefore be within the variation of the CIMS-GC comparison. Slusher et al. state that "In a cursory check, no difference was observed between PAN measurements obtained this (heated metal tubing) way versus NO addition." It is therefore not unlikely that during ambient measurements made at NCAR in November that PAA made no obvious contribution. Clear evidence may be apparent in a time series of the background signal measured via NO addition (not reported in Slusher et al. 2004) as in the review of this manuscript by Joel Thornton with the comparison of the unpublished PAA data from Crounse and Wennberg. This was also demonstrated PAA is also in the final version of Min et al. 2012 referred to in the discussion part of our paper. The authors added a plot of the background measured during the campaign (see reference above)

The second is a more comprehensive summary of PANs measurements by Wooldridge et al., that covers a number of field studies in which the PAN TD-CIMS has been used, compared with several different methods, although the paper focuses on the TD-LIF method for total PANs. Again, there is no evidence of a significant PAA effect.

Again, it is difficult for us to assess these comparisons from the information presented in this paper as differences between measures is usually put down to NOx artefacts in the TD-LIF system. We have included the Wooldridge paper in a short discussion of the CIMS technique comparisons in the introduction.

A third set of PANs measurements were conducted for the very purpose of comparing the various techniques in use by the community at that time: the PAN Intercomparison Experiment, PIE, conducted in Boulder CO., in 2005. Some of the data from that appear in Wooldridge et al.,[Wooldridge et al., 2010] and the data have been presented in a poster at AGU [Tyndall et al., 2005], but unfortunately they have never been written-up in publication form. That experiment was in summer, on a mesa at the edge of the city, and so had a range of conditions in which one would think PAA would be formed. Again, there was no evidence of a PAA signal in the CIMS data.

For reasons we give above, we would not necessarily expect any unambiguously obvious effect from PAA in the PAN concentration time series as it would be a function of the zeroing frequency and method in addition to the particular instrument sensitivity to PAA. Again the effect of PAA was not observed when the BEARPEX datasets were originally measured. It was only by going back to the original raw background data that an effect was noticed.

Since I know the authors to be careful and accomplished experimentalists and I believe their observations, this brings up an interesting conundrum; why is this PAA signal present in their instrument at their site, when it has not been apparent in other studies? Could the answer be in the ion chemistry and the particular instrumental conditions used? The ion chemistry that is proposed as the reason PAA is detected as acetate; $CH_3C(O)OOH + I^- \Rightarrow CH_3C(O)O^- + HOI$ (R1) does appear to be exothermic (although I got a slightly different answer than the authors), however the mechanism is a bit more complicated than for $CH_3C(O)OO + I^- \Rightarrow CH_3C(O)O^- + IO$ (R2). Could there be an activation energy to R1 that would make the relative detection of PAA and PA radical dependent on instrumental conditions? Here I'm thinking of the kinetic energy of collisions in the collisional dissociation chamber and their role in providing that activation energy. In that regard, it seems crucial that details about that part of the instrument be provided (see below) in order to assess that effect. Another possible reason for the apparent interference of PPA is if the instrument in this study was operated in a way that caused much larger losses of PA radical between the TD zone and ion flow tube. Again, more details on the operating conditions, but more importantly the resulting signals, e.g. reagent ion counts, net PAN sensitivities, will help in addressing those questions.

We have added a number of extra details to the description of the measurement. We have added details with regard to the inlet characteristics and distances from the TD region to the IMR orifice and the orifice material. See replies to reviewers comment s below. As is apparent in J. Thornton's review ours is not the only ICIMs with the ability to detect PAA although it would seem the sensitivity to PAA in our instrument is nearer to the sensitivity of PAN and therefore more problematic.

Specific Comments;

Abstract – Page 20182, Line 8: CH3C(O)O2- should be CH3C(O)O- Lines 10 and line 15: there should be some numbers attached to the statements "high temperature and low NOx" and "the range of mixing ratios of NOx". Line 17: It is not clear if the HO2 being talked about here is measured or modeled (assumed).

We have corrected the error, clarified the NOx and temperature conditions and clarified the point re. HO_2.

Introduction – Page 20182, Line 21: The PAN naming system needs to be fixed at this point, and made consistent throughout the paper.

We have fixed the naming convention.

Page 20183, Line 22: CH3C(O)O is not an alkoxy radical, that would be RO, it is more properly termed a carboxyl radical.

This has been corrected.

Page 20184, Line 4: It should read k4 not k3.

This has been corrected.

Page 20184, Line 24-28: It would be nice to have a summary of the levels of PAA that have been observed in other places.

We have added text to this section summarizing levels of PAA measured in previous studies.

Page 20185 Line 10 or so: This is a good place to mention the intercomparisons of the TD-CIMS with other methods.

We have added a short discussion in the introduction of previous reports of CIMS PAN comparisons.

Instrumentation – Pages 20186-20189, This is where it would help to have a lot more details on the experiment. What is the diameter of the TD tube, and what is the flow rate into the instrument? What material is the inlet orifice made of? What are the typical reagent ion (I-) counts produced by the ion source. What are the dimensions of the IMR and is the IMR voltage biased relative to ground? What are the conditions in the CDC, voltages, pressure?

These details will be added to the text: The TD tube was a 3/8" teflon tube with and approximate inner diameter of ¼" which is connected to the inlet orifice by means of a brad fitting and compressed by an O-ring leaving a gap of approximately 10 mm between the orifice and the TD region. The flowrate into the instrument was 1 LPM and the total inlet subsample flow from the bypass flow was 2 LPM. The inlet orifice is made of FEP coated stainless steel and the size of the orifice is controlled by a stepper motor which uses a feedback loop maintaining the IMR pressure at 21 Torr. The ionizer was a Po-210 sealed source produced by NRD and the total flow into the IMR was 2LPM with 1LPM from the inlet and 1 LPM of N2/CH3I mixture. The ion source produces typically on the order of 1 million counts of I-. The IMR is approximately 10 cm long, maintained at 21 Torr and is separated from the CDC by an orifice of 0.8 mm diameter. The pressure in the CDC is maintained at approximately 400 mTorr and biased relative to the IMR to decluster any H3C(O)O−(H2O)n and increase the sensitivity toward H3C(O)O.

Does the zeroing method also destroy PAA?

Yes it does. This has been made clearer in the text.

The PAN photosource discussion needs more details. This system undoubtedly produces PAA, probably a lot of it since these systems are set up to have an over abundance of radicals, so that NO is converted to NO2 and the PAN formation reaction is the major fate of NO2. Also, this source has been widely used by a number of groups measuring PANs and so could serve as the first means to check for PAA interferences.

It would be very informative to know what the level of signal from the photosource was through the cold inlet, and if there was any data for the photosource running without NO.

The signal from the photosource with a cold TD region was on the order of 10% of the total signal measured whilst the TD region was hot. We have expanded the description of the photosource to include details of the normalised signal levels obtained.

Page 20187. Line 25-29. It is interesting the instrument gives a signal for acetic acid since the reaction; CH3C(O)OH + I- => CH3C(O)O- + HI is endothermic by about 34 kcal/mole. So only a tiny fraction of the cluster CH3C(O)OHI- should break part to make acetate if everything is at room temperature. Could this be a clue as to why this system seems more sensitive to PAA than others? What is the sensitivity to acetate?

We do not know the absolute sensitivity to acetic acid as the correction was applied in a relative sense, although is it likely very low. The sample of PAA in acetic used for the tests was mostly acetic acid and therefore the small intereference from the acetic acid had to be removed.

Page 20188. Line 1. Should be ‘the raw data were..’

This has been corrected.

Page 20188. Line 27. Do the authors mean CH3C(O)OO- or CH3C(O)O- here? Is CH3C(O)OO- ever observed in the system. The reaction of PAA with I- will be even more endothermic than for acetic acid, based on aqueous-phase pKas.

We mean acetate and the mistake has been corrected.

Page 20188-20189. Here we need to know what the reagent ion counts were in order to put the PAA sensitivity into perspective. If PA radical is lost through the inlet doesn’t this mean the k6/k7 is larger than 2.5? Isn’t this loss one area that may explain why other studies have not seen an effect that could be due to PAA?

We give details of the reagent counts to put the PAA sensitivity into context.

Page 20189, Line 6. One thing to keep in mind when dealing with m/z 85 (MPAN) is that CF3O- appears at the same mass and probably comes from CF3OH, which seems to be present in many samples of PFA tubing. It shouldn't proton-transfer with I-, but will with acetate.

We will add a statement to effect that the CF3OH ion is a potential interference at m/z 85.

Page 20189, Lines 15-25. The effect of acetate is due to proton transfer reactions with the corresponding carboxylic acid as discussed by Veres et al., [Veres et al., 2008], and will depend on the levels of acetate, relative to those of iodide. It would be good to have a sense of what those levels were, so we could compare to observations in other CIMS systems.

The "usual" levels of the I- ion are of the order of 8-900 000 Hz compared to an acetate ion count rate in the 10^2 to 10^3.

Page 20190, Line 5. Should be 'hydroxyphenyl'.

This has been corrected.

Page 20190, Line 18. It would be good to put these PAA measurements in context. Are they higher than other sites?

We will add a discussion of the relative levels of PAA detected in other studies.

Page 20192-20193. Steady state model. This is a useful way to look at the chemistry, and the authors note the limitations of assuming, for example one number for HO2 (30 pptv – which seems high to me). It would be good to note that the time to reach steady state for this system can be fairly long, and will be temperature dependent due to reaction 2.

There is a paper in preparation describing the HOx radical measurements in detail. We will add a reference to this in the hope it will be available in the near future. However the 30 pptv HO2 level was not unusual for this campaign.

Page 20192, Line 3. Don't you mean the production terms in reactions 1 and 4?

This has been corrected.

Page 20192, Line 15. The IUPAC page has a fairly certain number for this branching ratio (0.41±0.2) so I'm not sure why this statement is here, perhaps they are referring to the temperature dependence? Also, the authors should tell us what number they used for their calculation – it seems like it was 0.4 for the case I checked. Also, we need to know the OH that was used in the calculation.

The IUPAC errors encompass a PAA yield of 0.2 or 0.6, which, in broad terms range from minor (0.2) to dominant (0.6). We felt justified in calling this uncertain. The value used in the calculation was indeed 0.4 and the OH concentration was 2×10^6 molecule cm^{-3}.

Page 20193, Line 12. Wasn't HO2 measured at the site?

Yes. However the data is still being finalised and was only available at the same measurement location during the latter half of the campaign.

Page 20193, Line 24. What is EC? It needs to be defined at first use.

We have defined EC in the title of the discussion.

Page 20195, Line 15. The discussion of the results presented by Min et al., of the PANs and total peroxynitrates fluxes should note that the above-canopy comparison of the two methods was excellent, implying little or no sensitivity to peroxyacids in the CIMS. These data were not included in the Wooldridge paper. Also, it is not clear from the text which method showed larger fluxes, from context (and reading Min et al.,) it was the CIMS measurement, but this should be phrased more clearly here.

Min et al added a figure to the acp manuscript, in the light of our acpd paper, to show that the CIMS background indeed shows a sensitivity to something which is qualitatively similar to the diurnal cycle we observed in Finland. We have made the description clearer.

References

Slusher, D. L., L. G. Huey, D. J. Tanner, F. M. Flocke, and J. M. Roberts (2004), A thermal dissociation-chemical ionization mass spectrometry (TD-CIMS) technique for the simultaneous measurement of peroxyacyl nitrates and dinitrogen pentoxide, J. Geophys. Res., 109(D19), D19315, doi:19310.11029/12004JD004670.

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Wooldridge, P. J., et al. (2010), Total peroxy nitrates (PN) in the atmosphere: The thermal dissociation-laser induced fluorescence (TD-LIF) technique and comparisons to speciated PAN measurements, Atmos. Meas. Tech., 3, 593-607.

Joel A. Thornton

This paper presents important new observations of acetyl peroxy nitrate (PAN) and peroxy acetic acid (PAA) during the HUMPPA-COPEC campaign at Hyytiala forest during summer 2010. The measurements were made using Iodide-ion chemical ionization mass spectrometry (I-CIMS). The measurements of PAA were serendipitous in that the ability of the I-CIMS to detect PAA was not recognized until after measurements commenced. Post-campaign analysis and calibration produced a relatively rare dataset of collocated PAA and PAN measurements that the authors briefly analyze in terms of a photochemical steady state model to demonstrate the potential utility of such measurements. The paper is clearly written and contains important insights about instrumentation and atmospheric chemistry in a boreal forest. I therefore recommend publication after a few questions and discussion points are addressed.

We thank Joel Thornton for his extensive comments and suggestions, and especially for providing the reanalysis of the raw data from the BEARPEX campaign. We assume this is the same data that has been presented in the ACP version of the Min et et al. paper in the BEARPEX special issue. We will include a reference to this review and the estimation of the effect of the artefact in the discussion section of our paper. We will make it clearer that the NO addition method for the zero mitigates the effect of the artefact and thus makes the flux determination far more problematic than the concentration determination.

Main Comments

It is clearly an important finding that Iodide ionization can lead to signals that correspond to peroxy acids, compounds which are predicted by most photochemical models to be important chainterminating products of acyl peroxy radical reactions with HO2. Such a capability will certainly be utilized in future measurement campaigns. In that regard, it would be useful to have more details on instrument operation and calibration.

As raised by another referee of this manuscript (James Roberts, NOAA) and in the discussion of a previous manuscript about TD-CIMS measurements of APNs (Zheng et al 2011), such detection capabilities are often highly dependent on the instrument configuration and operating parameters. Instrument response functions for desired analyte compounds must ultimately be determined for the operating conditions of each instrument or if instrument parameters for a specific instrument are changed. Phillips et al rightly mention that the detection efficiency for PAA will be different for different I-CIMS instruments, but more information on their parameters will be helpful (see more below for detailed questions in this regard).

Phillips et al discuss PAN observations made during BEARPEX, with a different I-CIMS and reported by Wolfe et al 2009 and Min et al 2012, in regards to the potential importance of a PAA interference in that data set. Inspired by the Phillips et al manuscript, we went back to our datasets to examine this possibility. For the purposes of facilitating discussion and hopefully shedding more light on this topic, I am providing below some unpublished data from the BEARPEX campaign to both support the Phillips et al assertion in this paper and to also illustrate the previous point that instrument parameters and operation, and potentially measurement location, are all likely to be important in determining the PAA detection efficiency. During BEARPEX, in addition to the UW-CIMS measuring APNs by TD-I-CIMS, the Caltech group deployed a CF3O- CIMS capable of measuring PAA which has been describe previously (Crounse et al – see references in the present manuscript).

1. Removing the PAA Interference from PAN Concentration Measurements

The first point to make, which was also mentioned briefly by Phillips et al, but perhaps not emphasized enough, is that a fast determination of the PAA contribution to signal at m/z 59 (acetate ion) can be made by the addition of nitric oxide (NO) to the thermal dissociation inlet. NO titrates the acetyl (or acyl) peroxy radicals but not PAA. Thus, the signal resulting from NO additions can be subtracted away from the total signal to produce a more robust PAN measurement. This is how the background signal at m/z 59 was determined during BEARPEX with the UW-CIMS.

As discussed in Wolfe et al 2009, subtracting a signal obtained with the inlet heater off (cold) from that obtained with the heater on (thermally dissociating APNs), is likely not sufficient for background determination, nor is the use of a hot metal tube. Both are problematic because the scrubbing is not selective to APNs and/or because detection efficiencies are likely temperature dependent. While acyl peroxy radical concentrations entering the ionization region are very low with the inlet heater off, there may be an enhanced/decreased sensitivity either to PAA or acyl peroxy radicals leading to positive or negative biases. Similarly, a hot metal inlet likely scrubs PAA as well as PAN, therefore biasing the background measurement low and the PAN concentration high. Note, NO addition does not rule out the possibility that acetate ion chemistry (Veres et al) might lead to positive artifacts at m/z corresponding to other APN.

Figure 1. PAN (top), PAN background measured by NO addition (middle), and PAA measured by Caltech during BEARPEX 2007.

2. Contribution of PAA to m/z 59 During BEARPEX

In Figure 1 (of this report), the time series of PAN mixing ratios from the UW-CIMS during BEARPEX are presented (top) along with the PAN-equivalent background measured at m/z 59 by NO addition (middle), and the PAA mixing ratios measured by the Caltech CIMS (bottom). All units are parts per trillion by volume (pptv). The PAN-equivalent background was obtained by taking the measured count rate during an NO titration and applying the PAN sensitivity of 4.5 Hz/pptv. The NO-determined background is usually of order 10% of the corresponding PAN mixing ratio (after the background was subtracted). Using the Caltech PAA measurements as the true PAA value during BEARPEX, the UW-CIMS detection efficiency for PAA relative to PAN appears to be substantially smaller than that for the Mainz CIMS reported by Phillips et al.

In spite of this apparently low detection efficiency for PAA exhibited by the UW-CIMS, the measured background signal does in fact correlate very strongly (R2 = 0.7) with the Caltech PAA measurements, as shown in Figure 2, providing support for the attribution of signal at m/z 59 to PAA by Phillips et al. In contrast, the UW-CIMS PAN mixing ratios, which have had the background signal removed, do not correlate with the Caltech PAA measurements (R2 ~ 0.02 over all data). There may be specific periods within the dataset where stronger correlations between PAN and PAA exist, as might be expected given similar precursors, but we have yet to perform a full analysis.

The slope of the relationship in Figure 2 implies a UW-CIMS sensitivity to PAA of 0.4 Hz/pptv with a heated inlet, while that for PAN was determined independently to be ~ 4.5 Hz/pptv. There are certainly situations when PAA could be 10x PAN, though not during BEARPEX, at which point the signal-to-background would be poor. Future campaigns in remote (low NOx) regions that utilize a TD-CIMS for PAN might thus provide more insights into specific instrument conditions which amplify the detection efficiency to PAA.

3. On the Contribution of PAA to the PAN EC Flux During BEARPEX

Figure 2. PAN background measured by NO addition versus Caltech PAA mixing ratios.

Given the nearly 10x less efficient detection of PAA by the UW-CIMS compared to PAN, the influence of PAA on the eddy covariance flux measurements of PAN using the same instrument is likely to be within the reported error. A very rough estimate of its contribution follows. If we assume PAA dry deposits at the limit of turbulent transfer, corresponding to a deposition velocity of ~3 cm/s at Blodgett Forest, we might expect a PAN-equivalent flux of approximately 0.1 ppt m/s on average during the day, reaching up to ~ 0.3 ppt m/s at a maximum. For that estimate, I assumed an average PAN-equivalent PAA concentration of 40 pptv based on Figure 2. The average daytime PAN flux reported by Wolfe et al 2009 during BEARPEX was 1.5 ppt m/s (downward) with a reported uncertainty of +/-40% encompassing the potential effect of PAA. Moreover, it seems rather unlikely that PAA dry deposition occurs at the transport limit especially for the warm and dry conditions during which the largest PAN fluxes were measured during BEARPEX. Thus the above estimates of PAA contributions to PAN fluxes during BEARPEX likely represent upper-limits.

That said, with a higher detection efficiency to PAA than the UW-CIMS measuring over a wetter forest canopy, Phillips et al are indeed correct that the impact of PAA on PAN fluxes could be substantial. One possible solution for obtaining PAN fluxes in such conditions that was not suggested by Phillips et al might be to perform disjunct eddy covariance measurements using a heated TD-CIMS alternatively operated with and without NO addition. For example, the signal at m/z 59 could be recorded under NO titration conditions for some period of time (e.g. 15 minutes) followed by a similar period measuring the total m/z 59 signal. The signal obtained with the NO addition would represent the PAA contribution to the total flux measured without NO addition. A careful uncertainty analysis would be warranted as, to my knowledge, this approach has not been attempted, and the flux difference between the two modes would ultimately be nonlinearly related to the PAA detection efficiency relative to PAN.

Minor Suggestions for Revisions

The authors have done a decent job at communicating their instrument parameters, but more could be provided. For example, what is the average electric field strength in the IMR, CDC, and Octopole regions? Are these known/calibrated? This latter question refers to the often very small spatial distances between electrodes/optics in these instruments which can produce relatively large fields but the effects of which are not easily verified.

I suggest the I(H2O)-/I- ratio at a specific humidity and IMR temperature be reported by investigators using this approach, as a way to start making comparisons among instruments in terms of "effective collision energy". The metric is by no means perfect, but it would provide at least one means of comparison.

As detailed in the reply to J. Roberts we will add more detail to the description of the instrument and provide more details of the normalised signal levels.

On Pg 20188, lines 1 – 25; calibrations to PAA and the effect of RH are described. The sensitivity to PAA is reported at 290K. Presumably, PAA sensitivity depends on inlet T. Did the authors test this affect? It might be instructive for gauging the impact of PAA as an interference in other TD-CIMS PAN measurements.

We know the sensitivity at the two normal inlet temperatures, i.e ambient and 150 C. We will add the details to the manuscript. We need this to properly correct the PAN data. The instrument was approximately 30% less sensitive to PAA with the TD operating at 150 C.

Pg 20187, lines 28; The sensitivity to PAN should be stated more clearly, perhaps summarize instrument parameters in a table.

We will add these details.

How are changes in total ion current addressed in the analysis? Is there a normalization to total ion current (I + I-H2O)? Does this change systematically with inlet T?

We normalised the data to the PAN calibrations, which in turn are a function of the total ion current and the PAN concentration.

The analysis of PAA/PAN ratios is interesting, and obviously would benefit from a more complete treatment (constant HO2 is obviously incorrect). However, I feel it is adequate for the purposes of this paper.

We hoped to demonstrate the utility of such a dataset whilst remaining within the constraints of the quality of the data and obvious disadvantages of hourly background corrections with a changing signal.

The comment on Pg 20195, line 7 is debatable, and too vague. How exactly is SMEAR-II Hyytiala "similar" to Blodget Forest (BFRS)? I would say they are quite different in many important ways. BFRS routinely experiences drought conditions and a strong diel cycle during summer, it is a managed ponderosa pine plantation with very little species variety, it has very reproducible meteorology day to day and year to year, and it is at 1.5 km asl.

We agree that this is a wishy-washy statement and the comment has been amended to make it clearer and useful.

ACKNOWLEDGEMENTS

G. M. Wolfe (NASA Langley), J. D. Crounse (Caltech), and P. O. Wennberg (Caltech) contributed unpublished data from the BEARPEX campaign for this report, and only G. M. Wolfe read the report for accuracy prior to submission.

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Anonymous Referee #3

This is an interesting paper, but more provocative than careful. The other two referees have covered the instrumental issues in this paper quite thoroughly; instead I will focus on the analysis and the presentation. The only thing I will add to the instrument part of the discussion is to note that the paper reports that Wolfe et al didn't publish some parameters of their instrument operation (pg 20195). An e-mail to ask them would have been a good way to address that.

We thank the reviewer for the comments. J. Thornton, in his review has treated the potential effect of PAA within the Wolff et al. paper and we have included this in our discussion. We do not agree that we are being "more provocative than careful" as we have deployed an instrument and found it sensitive to another species and attempted to recover our dataset. As is demonstrated by the finding that the BEARPEX ICIMS was likely sensitive to PAA we felt it was important to report these findings and at least attempt to make a critical discussion of previous work.

Analysis: The analysis would benefit from a more thorough reading of the series of Roberts papers on the ratios of MPAN/PAN and the more recent papers from the Cohen group papers on APNs. Those papers come to the conclusion that the concentration of APNs depends on the chemistry over a much longer timescale than the thermal time scale for PAN decomposition. It is possible that the equations presented in those papers reduce to the one presented in this paper, but it is not obvious. Either way, the paper should explain its analysis in the context of those other equations which build on different assumptions.

We feel we have explained that the analysis is simple but appropriate for our dataset. Our main finding is that we are sensitive to PAA and we report the time series of PAA in terpene dominated forested environment. It is clear that there are limitations to our approach but we feel that a deeper analysis of the NOy/VOC/PAN/radical budgets is beyond the scope of this paper and will be addressed for fully in another publication.

The paper should address the potential for interferences in measurements of other APN molecules more explicitly. I am unclear on whether it is suggesting that an analog peracid will be detected at the same mass as every APN. This is important because on of the puzzles raised in Turnipseed et al, and Wolfe et al is that the fluxes of different APNs are different from each other.

We agree with the reviewer that it is important; however we do not feel we have much to add. We are reporting that we observed a similar "background" signal at mass-to-charge ratios used for monitoring PPN, PBN, and MPAN. However, we did not calibrate these PANs and we didn't calibrate for potential peracids at these masses. We can only say that it is possible that we were sensitive to these other peracids. We have made this clearer in the manuscript.

Presentation: Given the complete absence of work on fluxes in this paper, the prominence given to unsubstantiated claims about other flux measurements is inappropriate. The flux comments do not belong in the abstract or the conclusions. The authors should focus on what they have accomplished.

We disagree with the reviewer. We do not need to attempt to measure fluxes in order to point out that by attempting to measure PAN fluxes by eddy covariance whilst detecting both PAN and (highly soluble) PAA we would have been measuring the variability of a convolution of the two chemical species. This is a major finding of this paper and we feel we are justified in giving it due prominence.

It is for the community to judge the epistemic warrant of this paper and the possible consequences for previous measurements.

J.W. Munger

This paper presents an interesting finding that an iodide chemical ionization mass spectrometric method (ICIMS) for detecting PAN is also sensitive to peroxyacetic acid (PAA). This is fortuitous, as PAA is a competing product in PAN formation and the PAA/PAN ratio is an indicator of photochemical activity. The finding stems from a somewhat accidental discovery that the ICIMS had a signal when it was operated in a mode that precluded PAN detection. Lab calibrations subsequent to the field study confirmed that the unknown signal was PAA and quantified its response so that simultaneous PAN and PAA concentrations during the measurement campaign could be reported.

The co-sensitivity to PAA has important implications for PAN measurements by the ICIMS method and is discussed in the paper. As other reviewers point out the sensitivity to PAA is apparently not constant for all versions of ICIMS and more details about the design and operating parameters for this instrument need to be presented. It is reasonable to point out the potential for similar artifacts in other PAN measurements, but without having details of each instrument it has hard to support definitive statements about magnitude of PAA artifact. The results in this paper should prompt other investigators to examine their ICIMS for PAA sensitivity.

As detailed in the reply to for the review of J. Roberts we have provided much more instrumental information. We agree with J. W. Munger that we cannot make definitive statements as to effect of a potential PAA co-sensitivity in other authors work as it is near-impossible to account of all the variables in the instrument and its setup during field and lab measurements. It is for users of the ICIMS technique to verify in their own systems, as per the review of J. Thornton, any sensitivity to PAA.

Based on the results presented in this paper subsequent modification of the ICIMS method should seek either to enhance and stabilize the sensitivity to PAA so it can be accurately quantified or reduce sensitivity in order to measure PAN unambiguously.

We agree. We have run the instrument subsequently with a much more frequent and efficient temperature switching of the inlet system and will look to publish the results in the near future.

This paper makes the suggestion that PAN could be measured unambiguously by making a zero measurement using NO addition or an unheated inlet to subtract off a background that included the PAA. As the authors note the accuracy of this approach depends on the frequency of zeroing and the extent of PAA variability. The data shown for the full measurement campaign suggest that PAA and PAN vary together, which makes this approach for zeroing somewhat suspect. I'd like to see an example of data from a shorter interval, perhaps a single representative day, to evaluate the temporal variability in PAA and show an assessment of how well a strategy that subtracted off the PAA contribution by zeroing would work.

We have added a plot of PAA, total organic peroxides and PAN on the 26th July to illustrate the short term variability in the data and the accuracy with respect to this technique for zeroing.

This should include a discussion on page 20189 assessing the accuracy of using a linear interpolation between hourly zeros with a cold inlet. Perhaps the organic peroxide data are a good indicator for variations in PAA. How large would the deviations from a linear trend be?

We agree that hourly zeroes were not an ideal solution to the problem, however the TD region of the inlet took a reasonable amount of time to cool and any more frequent zeroing regime would have resulted in less data. The plot of the organic peroxides alongside the derived PAA shows that the linear interpolation was “not too bad” in most cases although there were regions of the time-series where non-linear behaviour was observed in the organic peroxide data. We have included a short discussion of the possible errors as suggested.

Beyond its contribution to discovering a potential artifact on PAN measurement by ICIMS and using that artifact to quantify a second species of interest this paper points out the importance of carefully characterizing the underlying chemistry for any analytical method that involves forming a derivative from the analyte of interest. Secondly, when deploying novel instrumentation the measurement protocol should include modes of operation that will test the underlying assumptions about what species contribute to the measured signal. This work serves as a cautionary tale for a variety of measurement approaches.

We agree with the reviewer and thank him for his comments and suggestions.