Review of Phillips et al PAN and PAA measurements using I-CIMS

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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.

**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 chain-terminating 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,



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

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
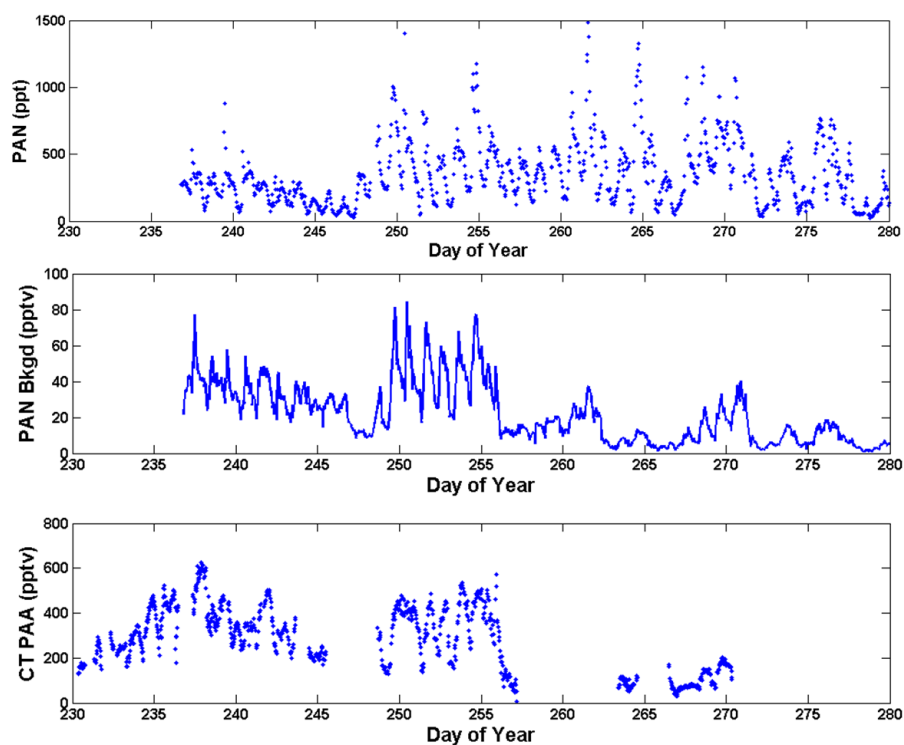
addition does not rule out the possibility that acetate ion chemistry (Veres et al) might lead to positive artifacts at m/z corresponding to other APN.

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



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

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.
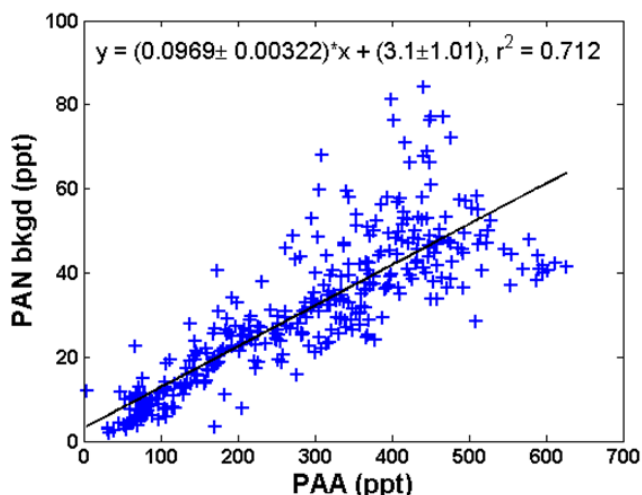
In spite of this apparently low detection efficiency for PAA exhibited by the UW-CIMS, the measured background signal does in fact correlate very strongly ($R^2 = 0.7$) with the Caltech PAA measurements, as shown in Figure 2, providing support for the attribution of signal at m/z 59 to PAA by Phillips 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 ($R^2 \sim 0.02$ 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

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.

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.

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

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?

The analysis of PAA/PAN ratios is interesting, and obviously would benefit from a more complete treatment (constant $HO_2$ is obviously incorrect). However, I feel it is adequate for the purposes of this paper.

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.

ACKNOWLEDGEMENTS

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