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Atmospheric Chemistry and Physics Discussions

Interactive comment 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" *by* G. J. Phillips et al.

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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

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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.

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.

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. 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?

Beyond its contribution to discovering a potential artifact on PAN measurement by

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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.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 20181, 2012.