Atmospheric
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Discussions

Interactive comment on "Application of a GC-ECD for measurements of biosphere–atmosphere exchange fluxes of peroxyacetyl nitrate using the relaxed eddy accumulation and gradient method" *by* A. Moravek et al.

Anonymous Referee #1

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Review of Moravek et al AMTD 2014

This paper describes the application of a GC-ECD instrument to the measurement of PAN fluxes by both the Relaxed Eddy Accumulation (REA) and Modified Bowen Ratio (MBR) methods. PAN is a major component of atmospheric reactive nitrogen, and dry deposition is considered a significant sink of PAN and a possible source of fixed nitrogen to ecosystems. However, much uncertainty remains in the efficiency of dry deposition and which processes are most important. Thus, there remains a need for

instrumentation capable of measuring the dry deposition flux.

This paper and methodology is therefore of interest to readers of AMT. It is well written, and very detailed. While the field test of the instrument was less successful than would be ideal for a demonstration paper, the authors have provided a substantial theoretical assessment of the methodology and guidance for how to improve the acquisition of PAN fluxes with the technique in the future. In fact, the demonstrate how very challenging it will be to measure PAN fluxes. I therefore recommend publication once a few minor comments and suggestions are addressed.

Overall, I commend the authors on the comprehensive assessment of the use of a GC-ECD instrument to measure PAN fluxes.

1. Structure. I suggest the authors attempt a different organization to the paper that might stream line the description of methodology and results. I suggest as much as possible to describe the methodology or setup together with the corresponding results in the same section. This will likely reduce some redundancy and improve the flow. This paper essentially describes two different applications with the GC-ECD and at times the separate descriptions, e.g. sections 2.3, 2.4, and 2.5 become redundant or hard to follow. I think also the description of the simulations could be combined with the results of those simulations, similarly for the calibration too. So in summary, perhaps not use the traditional "Introduction, Methods, Results, Discussion" but instead divide the paper by the important topics such as "Calibration, Precision and Accuracy, Theoretical Expectations, Field Test". This is just a suggestion – and not required for publication.

2. Instrument precision. The authors conclude that precision in the GC-ECD measurement is a limiting factor in making flux measurements. I think it is important to better highlight that it is the absolute precision in the difference measurement that is crucial, not the relative precision at some arbitrary concentration. While this is done mostly in the conclusions section, the authors more than once refer to other previously published

reports of 1% precision for GC-ECD, but this reference is not useful and in fact somewhat misleading for the purpose herein. I suggest recasting references to previous literature reports to be consistent with the precision needed for the flux measurement and needed for comparison to the GC-ECD used in the study.

3. Similarity to O3. Based on both Doskey and Wolfe papers, there is a suggestion that thermal decomposition of PAN may in fact contribute significantly to the net flux. This would seem to be in conflict with the assumption of similarity to O3. Moreover, O3 fluxes may be driven by reactions with reactive BVOC (see papers by Goldstein group). It is always difficult to make the similarity case (since each molecule is different), but the authors could discuss the validity of this assumption further.

4. Deployment. The authors have about 6 days of data to evaluate the HREA method. This seems like a rather small data set to use for assessment. Was the instrument deployed for longer but this period was the only time it was functioning optimally? How would two or three times more data improve the accuracy of the mean flux estimated from the HREA data?

5. Possible future work – the authors should suggest a direct comparison between the CIMS approach and the GC-ECD HREA or MBR approaches given the potential for interferences in the CIMS measurement by peroxy acetic acid. The authors mention this issue for the CIMS, but cast it as a background signal problem. It is in fact a potential interference that could be missed depending upon how the background was measured.

6. Minor points- Metric measurements should be used throughout, font size on axes labels for Figures 7 and 8 needs to be larger. These would be very hard to read on a printout, and require significant zooming on a computer.

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Interactive comment on Atmos. Meas. Tech. Discuss., 7, 1917, 2014.

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