

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.

A. Moravek et al.

a.moravek@mpic.de

Received and published: 15 June 2014

The authors thank anonymous referee #1 for the detailed review and positive evaluation of the manuscript. Also, we are grateful for the valuable comments and suggestions.

Comment: *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*
C1341

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.

Response: We thank the referee for the comment on the structure of the manuscript. We considered and discussed various different structures when drafting the manuscript and found that the content was best represented in the traditional structure. The main idea is that embedding the text in a clear well known structure would improve the clarity of the manuscript. In this way, the methods are clearly separated from the other parts, which is an advantage for reproduction of the setup and the experiments. Also, introducing a separate discussion section highlights the objectives and essential findings of the study.

Comment: *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.*

Response: To obtain an estimate on the general performance of the GC-ECD, the precision is compared to values from other GC-ECDs reported in literature. We agree with the referee that the absolute precision in the difference measurement is crucial for the flux measurements and not the relative precision at some arbitrary concentration. Unfortunately, other studies do not present the error of the concentration differences (e.g., determined by side-by-side measurements) and only present one precision value at one single concentration. Hence, the only way to put the performance of the GC-ECD into relation to other GC-ECDs was comparing the stated precision % values as an estimate (see Sect 4.1.1). The importance of the absolute precision in the difference measurement is highlighted also in Sect. 4.1.1, listing also the values of the presented flux measurement system.

Comment: *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.*

Response: We have investigated the thermal decomposition flux for our site (e.g. Eq. 15 in Doskey et al. [2004]) and found it to be small (e.g., highest median deposition during day was 0.007 nmol m⁻² s⁻¹ , which is less than 5% of the total PAN flux determined with the MBR measurements). Additionally, for the observed temperatures and range of NO/NO₂ ratios, the contribution of the flux loss for the reference height of 3 m agrees with the analysis from Doskey et al. [2004] (see their Fig. 3). Measurements of VOCs at the site showed very low concentrations (J. Kesselmeier, personal communication), which suggests that an additional O₃ flux component by the reactions with VOCs is unlikely. For completeness we added those two points to the manuscript in Sect. 4.3.

C1343

Comment: *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?*

Response: We agree with the referee that the shown period is based on a small data set. The setup, testing and adjustments of the system were very time intensive. Mainly the sampling procedure, flow and other operational settings had to be adjusted carefully to the conditions at the experimental site. Hence, the shown period represents the measurements when the HREA system was running with optimal settings. Unfortunately, measurements could not be extended for a much longer period. However, due to an increased surface resistance in the early autumn period and therefore even smaller deposition fluxes it is unlikely that prolonging the measurement period would have improved the precision of the mean HREA fluxes significantly. This note was added to the manuscript in Sect. 4.1.3.

Comment: *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.*

Response: We agree that the inter-comparison of both eddy covariance measurements with CIMS and HREA and MBR measurements with GC-ECD is very desirable. We included this as a suggestion for future work in Sect. 4.1.3 of the revised manuscript.

C1344

Comment: *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.*

Response: Font sizes for Figures 7 and 8 were enlarged. Metric measurements were used throughout the manuscript, besides for flow rate (L min^{-1}) and large time intervals (min, hrs).

References

Doskey, P. V., V. R. Kotamarthi, Y. Fukui, D. R. Cook, F. W. Breitbeil, and M. L. Wesely (2004), Air-surface exchange of peroxyacetyl nitrate at a grassland site, *J. Geophys. Res.-Atmos.*, 109(D10), 9, D10310.

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