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Atmospheric Measurement Techniques 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.

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The authors feel very honoured by the positive evaluation of our manuscript and thank anonymous referee #2 for reviewing the manuscript. Also, we are grateful for the valuable comments and suggestions.

Comment: *While the authors' analytical system is unique, I feel credit should be given to others who have developed similar systems addressing the issues*

described in this manuscript. Thus, I suggest consulting Arnts et al, JGR 2013, http://onlinelibrary.wiley.com/doi/10.1002/jgrd.50215/abstract, and previously cited Park et al., Atmos. Environm. 44, 2010 and JGR 116, 2011, and/or Schade and Goldstein, JGR-D 106, 2001. This particularly with respect to instrument comparative precision as the main factor of flux determination. For instance, the authors could have used an internal standard such as these other researchers did, or explain in section 4.2 why that maybe impractical in their circumstances.

Response: We agree with referee #2 that the use of an internal standard can be an effective method to adjust for instrumental variations and thereby reducing the uncertainties of the GC analysis. Especially for REA systems with dual channel GCs, as the ones described by Schade and Goldstein [2001] and Park et al. [2010], the use of an internal standard is important to compensate for changes in the absolute sensitivity of the detectors. As in our case only one detector was used and the precise addition of an internal standard would have been difficult due to small mass flow variations in the main inlet line (which was an effect of maintaining a constant lag time during the HREA application), an internal standard was not added. Attempts to use CCl_4 (which is fairly constant in the atmosphere and is also detected by the GC-ECD) as an internal standard failed as variations were too large to explain the uncertainties in the PAN measurements. Instead of using an internal standard we made extensive side-by-side measurements before, during and after the experiments to adjust for systematic differences between the two pre-concentration units. As suggested by the referee, we discuss in Sect. 4.2 of the revised version of the manuscript briefly the use of an internal standard, citing also the references mentioned above.

Besides the issue of the precision, the influence of the inlet line on REA fluxes is of major importance, which was addressed to some extent also by the REA systems described in Schade and Goldstein [2001] and Park et al. [2010]. This is considered in detail in our previous publication about tube effects on REA fluxes (to which is referred at several points in the manuscript).

Comment: *The statement on page 16, line 16f. refers to the authors previous paper, but I cannot easily find why the artificial time delay of 30 s "should" results in a zero offset between channels, unless it was determined that the covariance power at that time scale is essentially negligible. Maybe an additional sentence or two could clarify this; maybe the fast response ozone data can be used? In our group, we simply open both reservoirs at the same time, which avoids any spurious fluxes arising from "unexpected" covariances, and should also address valve effects.*

Response: During the side-by-side measurements in the HREA mode, a similar switching pattern as during the HREA operation was essential to ensure that the actual sampling time and the pressure conditions were identical with the HREA sampling. This was an important requirement for the employment of the pre-concentration units as reservoirs. Moravek et al. [2013] investigated the effect of an erroneous lag time on REA fluxes in detail. The derived parameterisations for different scalars indicate that for an artificial lag time of 30 s the obtained HREA flux is negligible for most environmental conditions. However, we agree that a larger artificial time lag can be chosen for future experiments to avoid any potential contribution from lower frequencies. We added this remark to the manuscript in Sect. 2.6.2.

References

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Park, C., G. W. Schade, and I. Boedeker (2010), Flux measurements of volatile organic compounds by the relaxed eddy accumulation method combined with a GC-FID system in urban Houston, Texas, Atmos. Environ., 44(21-22), 2605-2614.

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