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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Technical note: Water vapour concentration and flux measurements with PTR-MS" *by* C. Ammann et al.

Anonymous Referee #1

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The authors present a novel technique to use water vapour fluxes derived from the cluster ion (m/z 37) as a quality control tool for VOC flux measurements by PTR-MS. The authors convincingly show that the relationship between the ion count at m/z 37 and absolute relative humidity is sufficiently robust for reliable water vapour fluxes to be derived. The technique is particularly useful as the measurement of m/z 37 is almost always a by-product when making VOC flux measurements with the PTR-MS. The paper makes for a very interesting read and is in the scope of ACP. I have only a few minor comments which should be addressed.

Scientific comments:

1. Page 5331, line 10-12. The authors are correct that there is no eddy-covariance

instrumentation available to measure fluxes of all BVOCs detected by the PTR-MS with a higher time resolution. However, there are instruments that target individual compounds, such as the Fast Isoprene Sensor (FIS), and comparisons have been performed (e.g. Jardine and Baker, 2003).

2. Could the authors please specify how their data were treated prior to calculations of the ogives. For example, the small contribution of low frequencies would suggest that McMillen filtering was applied. If this is the case, the filtering would be partially responsible for the good congruence of the ogives at low frequencies. If filtering were not applied, low frequencies may affect different tracers differently, e.g. under certain conditions deposited species may have a different low frequency contribution to compounds that are ejected from deep in the canopy. How would this affect the empirical spectral correction technique?

3. It would be interesting to consider whether a mechanistic understanding of the relationship between humidity and m/z 37 counts could be developed. Does the observed relationship follow the theoretical expectation? Is there any chance of predicting the relationship as a function of drift tube pressure and field strength?

4. Page 5341. I am doubtful that a sensible recommendation can be made as to the value of f_limit. Surely this value depends of the frequency response of the measurement system and the magnitude of the damping. In extreme cases, frequencies may be damped down to much lower frequencies. How does the recommendation compare to the frequency at which the co-spectrum is expected to have its maximum (or the ogive a deflection point).

5. Could the authors comment on the relative merits of empirical spectral correction methods based on the analysis of ogives compared with those based on co-spectra. It seems to me that the former is biased towards fitting of low frequencies, while the latter is biased towards fitting of the peak. Hence the former would be more suitable in conditions of strong damping (where the peak frequency is also affected), while

the latter would be more suitable in conditions where low-frequency contributions are important (and may differ between compounds).

6. Page 5341. The authors correctly point out that damping affects water more than other gases that do not interact with walls, and that this effect is not included in Moore's correction approach. However, there are alternative explanations why the empirical method derives larger damping than Moore's approach, depending on exactly how Moore's approach was implemented by the authors. On this aspect, more information should be provided in the manuscript. Firstly, although spectra are calculated on 20 Hz data, they actually represent 1.4 Hz data (due to measurement cycle of 0.7s). Secondly, the tube Reynolds number of 1620 is marginal for the flow to be fully turbulent. Does the implementation of the Moore correction take this relatively low Reynolds number into account?

Technical comments:

7. Page 5330, line 22. An 'e.g.' could be added to the references in parentheses, as there are many other papers on BVOC flux measurements by PTR-MS.

8. Page 5332, line 12. 'Sensitivity' would be a more appropriate term for the cps/ppb than the 'count rate'.

9. Page 5332, line 23. 'filed' should read 'field'.

10. Page 5332, last line. 'And' at the start of the sentence does not sound quite right.

11. Page 5333, line 15. Add manufacturer details to instrumentation.

12. Eq. (1). If time relates to the detection time, then I think one needs to form the product w(t) x c(t + tdel) or, alternatively, w(t - tdel) x c(t).

13. Page 5338, line 8. Maybe the authors should clarify that they here talk about the sensible rather than the latent heat flux.

14. Page 5338, line 20 (two occurrences). 'with' should read 'width'

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15. Page 5339, line 6. The use of the word ‘known’ suggests that the theoretical transfer function is fully determined. Maybe the use of a phrase like ‘assumed a priori’ may be more appropriate.

16. Fig. 5. X-axis labels are missing on my print out.

References:

Jardine, K.J. and Baker, B. (2003) Virtual disjunct eddy covariance flux measurements of biogenic volatile organic compounds from Ponderosa and Loblolly pine forests using proton transfer reaction mass spectroscopy. Eos. Trans. AGU 84(46), Fall Meet. Suppl., Abstract A32A-0115

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