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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Eddy covariance emission and deposition flux measurements using proton transfer reaction-time of flight-mass spectrometry (PTR-TOF-MS): comparison with PTR-MS measured vertical gradients and fluxes" *by* J.-H. Park et al.

Anonymous Referee #2

Received and published: 19 October 2012

General Comments:

The authors describe the validation of PTR-TOF-MS for determining emission and deposition fluxes via eddy covariance. The authors directly compare their measurements against both eddy correlation flux measurements and vertical gradients obtained using a traditional quadrupole .based PTR-MS. The reported advance is the simultaneous acquisition of the entire MS at high time resolution (5Hz) enabled by the use of a TOF

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mass analyzer as compared to a scanning quadrupole mass analyzer that obtains disjunct data when looking at an array of compounds.

The manuscript as written contains many comparison points (e.g., gradients vs fluxes, TOF vs QMS) and at times it was unclear what exact comparison question was being addressed. Since the primary (only) instrumental difference between the TOF and QMS based PTR instruments is the mass analyzer, I would have centered the manuscript on specific questions/deviations in flux calculations that could arise from the differing acquisition methods. For example: 1) how does the substantially improved TOF mass resolution impact the retrieved flux? 2) how does the reduced sensitivity of TOF compared to QMS impact flux measurements, 3) what is the effect of disjunct data on the retrieved flux. The authors briefly comment on the last point (Fig. 7b), however I would have greatly appreciated more discussion of this for a wide array of molecules at different S/N.

This being said, the paper represents a novel advance in the field and should be published in ACP, following the author's attention to the following specific comments.

Specific Comments:

1. Abstract line 3: Please replace "standard" with quadrupole.

2. Abstract line 23: What is meant by "mostly" acetone? If there are other molecules with the same exact mass, how can you know this? Or is the comment that most of the mass at UMR 59 is acetone by comparing QMS and TOF based approaches. If the is the case, please provide the number.

3. Page 20439 line 13: What is the metric for high sensitivity. Please provide numbers or a reference. As written this is arbitrary.

4. Page 20440 line 13: It would be very helpful for the authors to define here why we might expect the PTR and QMS based approaches to differ. Specifically with regard to mass resolution, sample frequency. The idea being that at the end of the manuscript

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a reader could assess if the science question they are pursuing necessitates TOF capabilities (e.g. if you want to look at 5 m/z values, is the data sufficient? What about 10, 20? At what point does a TOF win?)

5. Page 20442 line 2: What is the ion duty cycle for 60 micro-second pulse frequency? This number helps compare against the QMS approach for sensitivity.

6. Page 20442 line 28: What is the sensitivity of the QMS to these compounds in counts/ppt. How does this compare to the TOF? What is the precision of the two techniques as a function of the TOF extraction frequency or the number of m/z that the QMS is measuring within a given second.

7. Page 20443 line 4: How does the measured sensitivity compare to the calculated sensitivity? Is the given rate constant used for all molecules that were not directly calibrated for? How is fragmentation dealt with when not using a direct calibration?

8. Page 20446 line 7: Given that the attenuation factor is calculated for CH4, how can this possibly be applied to any polar molecule that will adsorb/desorb to/from inlet surfaces. It does not seem possible to "estimate a negligible" effect given that the parameters used to estimate this are for a molecule with wildly different molecular properties. There is absolutely no way acetic acid (or even methanol) will not be attenuated in an inlet line at ambient pressure/RH that is over 7m in length.

9. Page 20447 line 2: I am a bit confused by this statement. Do you mean to say that for the count rates measured here, (N likely greater than 100) that a Gaussian approximation can be made to the Poisson distribution, thus sigma n can be approximated as sqrt(N)? Is the instrument uncertainty limited by counting statistics or are there other sources of instrument uncertainty? In line 7, please be specific on the associated count rate, ambient concentration, and sampling rate here for the contribution of random error to the uncertainty in the concentration measurement.

10. Page 20451 line 6: Can the authors directly comment on the fraction of the UMR

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signal that is the specific ion they are looking for? For example, what fraction of m/z 33 is methanol vs other molecules based on the TOF spectra. This will highlight the use of a HR TOF.

11. Page 20451 line 20: Why is the comparison done at 30min averages? What does the 1s or even 10s correlation look like? What does the correlation look like for molecules at 1ppb or 100ppt?

12. Page 20453 line 14: The statement says MeOH concentrations often exceed 10 ppb. Here, the concentrations of MeOH never dip below 10ppb, reaching 40 ppb. A comment on the magnitude of the MeOH concentration should be given here.

13. Page 20476 Figure 7b: I think using the TOF data in a continuous fashion and it deresolved to disjunct form is very insightful. I would have liked to have seen more of this in the paper. Specifically, how disjunct does the data need to be before a significant flux error arises. This could easily have been an entire section, clearly addressing a key difference between TOF and QMS mass analyzers that to the best of my knowledge has not been demonstrated clearly for a wide range of compounds at various S/N.

14. Page 20479 Figure 10b: Why are the flux measurements of 81, 95, and 137 not correlated and at a fixed ratio with one another if they are fragmentation products of the same molecule? How well correlated are they in concentration, what about during calibrations? Does the ratio of 81:95:137 scale with concentration? Or should these ratios be held constant on the presence of only one monoterpene (as argued here)?

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 20435, 2012.