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Atmospheric Measurement Techniques Discussions

Interactive comment on "First eddy covariance flux measurements by PTR-TOF" *by* M. Müller et al.

Anonymous Referee #2

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General Comments

This paper demonstrates the use of the new Ionicon PTR-TOF for eddy-covariance flux measurements. The standard PTR-MS has become the instrument of choice for micrometeorological flux measurements for selected VOCs such as isoprene, monoterpenes and some oxygenated VOCs, yet the unity mass resolution leads to many ambiguities in species identification. With its much higher mass resolution the PTR-TOF can address many of these ambiguities and is likely to quickly gain in popularity. The extension to flux measurements is a logical next step. The paper demonstrates the suitability of the instrument for this application and deals with the key challenge of the analysis, which is the treatment of the large data volume. The scope of the paper, focussing purely on the methane peak, is rather limited and I would have preferred to see a more comprehensive paper showing that the full mass spectra can be dealt with and

demonstrating the impact of the resolving power at m/z where it matters. This said, it is still a useful first paper on this approach.

Some quantitative information on accuracy and precision of the new flux measurement system should be included, to answer questions such as:

a) What is the flux detection limit, which can presumably be estimated from the noise around zero of Figure 5?

b) What is the expected performance against the PTR-MS, ignoring the higher resolving power? The two instruments differ not just in m/z resolution, but in terms of sensitivity (cps/ppb) and duty cycle per m/z. Presumably at some critical number of m/z monitored the performance of the PTR-TOF is theoretically better than that of the PTR-MS. This would be interesting to discuss. Similarly, straight eddy-covariance has the intrinsic advantage over vDEC that it averages over a larger number of eddy motions that contribute to the flux. Again, this should be mentioned.

I also miss a discussion as to how the background concentration is derived in the approach. Although the background does not carry a flux and therefore does not need to be taken into account for the calculation of fluxes, it greatly affects the concentration and therefore any deposition or exchange velocities that may be derived from the flux data.

Specific Comments

P3270, L2. The total response time of the PTR-MS is stated, but I miss the equivalent information for the newer PTR-TOF.

P3270, L16. In the PTR-MS, ions of all m/z are detected. However, for each m/z the instrument does not detect all ions and the duty cycle is not 100%. For example, some ions exit the pulser region between firing.

P3273, L6. There is no single approach for data treatment and data reduction of high resolution MS data and it is well worth describing different approaches, but in what way

does the PTR-TOF actually require a different treatment to the ToF-AMS?

P3274, L11. Does the application of different m/z calibrations in 6-minute steps not introduce step changes every 6 minutes? What is the impact for the analysis of a 30 minute flux segment?

P3277, L10. It is clear that the peak list was obtained for m/z at which, on average, a peak could be observed. However, an individual 6-minute spectrum may not have a signal at an individual peak that it significantly different from zero. Thus, the question arises whether the peak fitting function has a positive constraint. If so, is this really justifiable?

Technical Corrections

P3272, L4. Here it is stated that Figure 2 shows a 30 minute region, while in the caption to Fig. 2 a 4-hour period is stated. The time intervals are also inconsistent.

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 3265, 2009.