

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

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The authors thank the reviewers for their good comments and suggestions that helped to improve the quality of the manuscript. In the following we respond to the individual comments and describe their realization.

Comments on the review by Anonymous Referee 1:

Thanks a lot for the great comment. Indeed, except of the high time resolution of 0.1 s, the interfering mass peaks on m/z 33 for methanol flux measurements only show slow changes in time. Therefore they don't interfere with the methanol flux measurements. Nevertheless, methanol was chosen as an example to demonstrate the capability of the PTR-TOF as a flux detector and to point out the need for a
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precise data evaluation. Currently we are preparing a manuscript that deals with the compounds measured during a cutting period that will demonstrate the supremacy of the PTR-TOF compared to a PTR-MS.

Comments on the review by Anonymous Referee 2:

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

Reply: The definition of a flux detection limit is difficult, as it is dependent on several variables like background concentration and the degree of turbulence. Therefore the noise around zero in Figure 5 cannot be taken to determine a detection limit for the total methanol measurement (as the turbulence during night time was significantly lower compared to daytime). Currently we try to define the flux detection limit by comparing the signals of isotopes. It is planned to publish the result in one of the upcoming publications.

Comment: What is the expected performance against the PTR-MS?

Reply: The PTR-MS has, mass range dependent, about 10 times more sensitivity compared to the PTR-TOF when monitoring only one compound. Therefore, by monitoring 10 different m/z ratios (primary ions included!), the PTR-TOF, that always measures the full mass spectrum, starts to be superior to the PTR-MS. A detailed performance characterization of the PTR-TOF is now published (Graus et al., 2010, doi:10.1016/j.jasms.2010.02.006) and cited in the manuscript.

Comment: I also miss a discussion as to how the background concentration is derived in the approach.

Reply: P3270, L23 states: “Background measurements (zero calibration) were automatically performed every 7 hours each lasting 25 min using VOC-free air at ambient humidity levels. This air was provided by a continuously flushed, home-built catalytic

converter at 350 °C. Sensitivity calibrations were performed twice a week by dynamic dilution of VOCs from a multi-component gas cylinder (Apel Riemer Environmental Inc.) into purified air.”

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

Reply: Both instruments utilized the same inlet line and both instruments have the same drift tube. Therefore, both instruments have similar response times.

Comment: 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 before firing.

Reply: Indeed at TOF-MS with orthogonal extraction never has 100% duty cycle. In our case, we have a geometric duty cycle of about 30% and an additional mass dependent duty cycle. Therefore our duty cycle is between 8% for low m/z and 30% for high m/z . Therefore “all ions” is changed to “all pulsed ions”.

Comment: In what way does the PTR-TOF actually require a different treatment to the TOF-AMS

Reply: The HR-TOF-AMS is based on the H-TOF platform, that is, indeed, very similar to TOFWERKS G-TOF platform. Nevertheless, recorded mass spectra are quite different. The TOF-AMS uses an analog to digital converter (ADC) for data recording whereas the PTR-TOF utilizes a time to digital converter (TDC) with a much higher time resolution (but a lower dynamic range). Therefore, the AMS acquisition bin width is 1 ns compared to up to 0.025 ns of the PTR-TOF's TDC. In addition, by applying the V-mode, the PTR-TOF ($R = 5000$) has about twice the mass resolving power than the HR-TOF-AMS ($R = 2100$, DeCarlo et al., Anal. Chem. 2006, 78, 8281-8289). The biggest differences are the expected mass peaks caused by the different ionization

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methods, electron impact ionization with a high amount of fragmentation (AMS) and the soft proton transfer reaction ionization of the PTR-TOF. According to DeCarlo et al., 2006, AMS mass peaks are fully characterized by a list of ions applicable to atmospheric aerosols. As a result of the high mass peak capacity caused by the soft ionization and the various application areas of PTR-TOF, this list has to be regenerated for every experiment.

Comment: 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?

Reply: It is true, that m/z calibrations cause a shift of the summation intervals for “stick-spec” calculation. But as the average signal of the high time resolved data (0.1 s spectra) for every 6 min dataset is compared to the fitted signal for the corresponding 6 min dataset, no step changes are introduced. Therefore no impact for the analysis of a 30 minute flux segment is expected.

Comment: The question arises whether the peak fitting function has a positive constraint. If so, is this really justifiable?

Reply: Every measurement has a positive constraint, background noise. Fitting background gives you a count rate appropriate to the background noise level. Therefore a background correction cancels this positive constraint to a slight statistical deviation around zero (compare to detection limit).

Technical corrections:

P3272, L4: Figure 2 depicts a cutout of a 4 h (July 26, 2009; 10:00 - 14:00) integrated PTR-TOF spectrum at m/z 33.

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

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