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***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 #1**

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This paper reports eddy covariance fluxes of biogenic VOCs above an orange plantation using the new PTR-TOF-MS technique. This is one of the first studies to use this technique to determine fluxes above a forest canopy. The results show that this is a powerful new method that overcomes many of the disadvantages of the relatively well established disjunct eddy covariance method used with unit-mass-resolution PTR-MS instruments. The major improvement is the ability of the PTR-TOF-MS to simultaneously obtain information for the entire mass spectrum at high frequency, resulting in

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continuous rather than disjunct data and the possibility to determine fluxes for many more (potentially all) species. The authors have effectively validated the technique by intercomparing the results with disjunct eddy covariance fluxes from PTR-MS data and vertical gradients measured with the same technique. They have also presented spectral analysis of the PTR-TOF-MS data. Though the majority of the flux of BVOCs is out of the canopy, the study also shows deposition of some species, consistent with observed vertical gradients and with reports from other sites. The paper is well written and the analysis is well supported. Overall, this study is highly valuable in demonstrating the validity of flux measurements using PTR-TOF-MS data. I recommend the manuscript be accepted for publication after revision of a few minor points, listed below.

## Specific Comments:

-The authors state that (p 20440 lines 24-26) “Winds were predominantly westerly during the day and easterly at night. During the daytime (...) footprints were mostly (>90%) within the orchard...” How does this compare to the nighttime footprint? The authors should address the possibility of sampling different sectors during the night vs. day.

-The authors describe their method for calculating the flux detection limit (p 20447 lines 25-30), but they do not state what the detection limit is. It would be useful to include this value, both to provide a reference for evaluating the small reported fluxes and as a point of interest to other investigators using the same technique. It is likely different for each species, but they could provide either a representative value or could include the detection limit for each mass peak in Table 2.

-I have a number of comments relating to Figure 7, which shows that at certain times the PTR-TOF-MS detected a substantial flux of acetone at high frequency that was not detected by the PTR-MS. The co-spectrum of 5 Hz PTR-TOF-MS data does not go to zero at high frequency, which seems to imply that there may be additional flux at higher frequencies that the PTR-TOF-MS is also missing. The authors should discuss

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this possibility. Also, can they provide a physical explanation for this high-frequency flux (which does not appear in the co-spectrum of sensible heat)?

In comparing the co-spectra for the continuous PTR-TOF-MS data (in panel a of Figure 7) to the disjunct data from the PTR-MS and PTR-TOF-MS (in panel b), the authors note that (p 20452 lines 19 - 21) “Figure 7b shows co-spectra of 1 Hz disjunct data from both instruments, and maximum peaks are located at higher frequency than that of continuous data shown in Fig. 7a, in spite of good agreement between the co-spectra, indicating non-continuous data may lose real flux information.” This sentence is confusing. I believe they’re referring to the shift in the (global) peak maxima to higher frequency in panel b relative to panel a, and not to the ‘high frequency flux’ in panel a, but this should be clarified. In addition, does the phrase “despite good agreement between the co-spectra” refer to good agreement between the co-spectra within each panel as opposed to between panels? Otherwise, it seems to contradict the earlier point.

Finally, it would be useful to know the magnitude of the discrepancy between the PTR-TOF-MS and PTR-MS fluxes. What is the difference between the fluxes calculated using the 5 Hz continuous and 1 Hz disjunct data in cases where a high frequency flux was observed (such as the interval in Fig. 7)? There seem to be two contributions to this difference: (1) any flux at frequencies greater than 1 Hz, which would be missed even when sampling continuously at 1 Hz (i.e., the difference between the two co-spectra in panel a) and (2) flux lost due to the change in the shape (or shift) of the co-spectrum when disjunct sampling is used (i.e., the difference between panel a and panel b). How significant are each of these contributions?

-The authors use the shape of the co-spectra and ogives in Fig. 5 to argue that there is loss of acetic acid flux, probably due to the sticky nature of this compound. However, Fig. 5 also shows that the co-spectra and ogives for masses 81.070 (monoterpenes) and 93.069 (toluene + para-cymene) are very similar to that for acetic acid, indicating that they too may experience losses. The authors state as much on p 20450 lines 18

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- 21, and also state that “...for the other compounds [81 and 93] the reason for the shift towards lower frequencies is currently not well understood. I agree that traditional physical arguments would not predict loss of flux of these species due to wall interactions, so it is an unexpected finding. However, the authors need to make clear at other points in the manuscript that this loss is observed. For example, on p 20449 lines 17 - 23, they discuss the co-spectra in Fig. 5d, and mention only that the mass 61 (acetic acid) co-spectrum exhibits indications of loss of flux. The other species shown in Fig. 5b show similar patterns and should also be discussed here and elsewhere when the flux losses are mentioned.

In terms of corroborating that such loss is in fact occurring, one approach would be to conduct a similar analysis on the other monoterpene ions (95 and 137) to determine whether their co-spectra and ogives indicate a similar pattern.

This does raise another question, however. The authors state that nominal masses 81, 95, and 137 are all associated with monoterpenes, and that GC data indicated that 89% of the total monoterpenes consisted of d-limonene. However, the diurnal average fluxes for these three masses (shown in Fig. 10) are markedly different. The authors suggest that this could be due to contributions from different monoterpenes at different times of day. This seems somewhat inconsistent with such a large majority of the monoterpene signal being due to a single compound. Some questions: first, are the differences in the diurnal average fluxes for these three masses statistically significant? The standard errors shown for mass 81 seem to indicate that they are, but the values for the other masses are not shown. Do the ratios of the 81, 95, and 137 ions observed during calibrations with d-limonene agree with the values cited in the text from other studies (Tani et al. 2003 and Misztal et al. 2012)? Are the GC measurements showing the vast majority to be d-limonene representative of all times of day, or is there a diurnal pattern (which might support the argument that the distribution of emitted species, and therefore the fragmentation pattern, changes over the course of the day)? (The first point raised above, about the difference between the day and

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night footprints, might have some bearing here. There is also some discussion of the speciation of monoterpene concentrations and fluxes in the Fares et al., 2012 study cited by the authors for the GC measurements that might be of relevance and could be referenced or summarized briefly here, but other than to say that such additional information would be helpful to the reader in understanding Fig. 10, the specifics of what to include and how to interpret it are left to the authors.) Of course, there may be differences between the contributions of individual monoterpene species to fluxes and concentrations, but the answers to these questions might give some insight into why the diurnal average fluxes of the three ions differ so markedly.

Technical corrections:

-p 20447 line 20 “it would not affect on...”

-p 20451 line 17: “Fragments pattern of monoterpenes...”

-p 20455 line 26: “The fractionation patterns...” should be fragmentation patterns.

-Figure 2 Caption: “Data for flux measurements of species with the PTR-MS...” reword for clarity.

-Figure 7 Caption: Description of panels (starting with “(a) Acetone data...” to end of caption) is difficult to follow and should be clarified. It could be revised so it's similar to the text, which contains a better description of the figures.

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

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