Response to Referee #1

We sincerely appreciate the Referee #1's effort in reviewing our manuscript, and thank them for all the constructive comments which will certainly help increase the scientific quality of the manuscript. Below are our answers to the specific comments.

In the following, the original comments are in ***italic bold font*** and our responses are in regular font.

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.

>> As the referee suggested, we specified footprints at nighttime in the manuscript and added text to "The nighttime footprints (22:00 - 02:00 PST) were more varied with contributions from a combination of different citrus tree species in the surrounding orchard blocks (i.e. Valencia orange + Parent Navel orange (41 %), Valencia orange + Murcott mandarin (38%), and Valencia orange + Parent Navel orange + Murcott mandarin (21%)."

-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.

>> We think that defining a flux detection limit for bi-directional species is not appropriate. For bi-directional species the sum of emission and deposition fluxes could coincidently result in net flux around zero when averaging a 30-min period even if both wind and concentration are well measured. We think the flux data measured are real and meaningful, even when the value is very close to zero. As stated in the manuscript, we define a detectable flux by taking the absolute value of the cross correlation by time shift of 0.2 second step for each 30-min data (the same manner as lag time evaluation), and then we averaged those 30-min absolute cross correlation data for whole measurement periods. If there is a significant peak (S/N=3) at time shift 0 sec, we assert that the compound has meaningful flux throughout the measurement period.

-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 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)?

>> These unexpected additional high frequency features may be of interest, and the reason is still unknown. To further investigate this issue, higher time resolution (more than 5Hz) and more data will be required since PTR-TOF-MS was not able to capture all eddies at higher frequencies as Referee #1 pointed out and it is hard to discuss with such few data points. In addition, this occurred indeed very few times throughout the campaign as mentioned in the manuscript. Through figure 7, what we intended to demonstrate is that 1) PTR-TOF-MS EC flux measurement is reliable compared to PTR-MS measurement though it seems still not perfect to capture higher frequency features of acetone flux, and 2) disjunct sample could have some loss of real flux information in some circumstances due to lower time resolution and discontinuous sample.

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 cospectra, 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.

>> Yes, that is correct. To clarify this we added each frequency range of max peaks for figure 7a and b, and changed the sentence to "in spite of good agreement between the co-spectra within each panel".

Finally, it would be useful to know the magnitude of the discrepancy between the PTRTOF- 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 cospectra 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?

>> As Referee suggested, we added the information with a sentence "From this example, 1 Hz continuous and disjunct data lost respectively 24% (1.34 nmol m^{-2} s^{-1}) and 39 % (1.07 nmol m^{-2} s^{-1}) of flux estimated by 5 Hz continuous data (1.76 nmol m^{-2} s^{-1})"

-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 - 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.

>> We thank Reviewer #1 for this excellent suggestion. We added the text "Co-spectra of w' (m/z 81.070)′, and w' (m/z 93.069)′ also demonstrate some loss of signal, but with different features (fall-off at different frequencies) than acetic acid, indicating loss processes may differ by chemical species.".
In addition, we have tried to check co-spectra and ogives of m/z 95 and 137 as Reviewer #1 suggested. The results showed that m/z 137 was very similar with m/z 81 shown in figure 5 (d) and (f), but m/z 95 was more similar to m/z 59 (acetone) shown in figure 5(c) and (e), implying the loss process of specific monoterpene species may be different by molecular properties due to their fragmentation patterns.

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 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.

>> We thank the Referee #1 for this full discussion. To show differences among 3 masses we now indicate error bars for the other species. Based on our calibration with d-limonene

standard, the ratio of *m/z* 81:95:137 was 4: 0.8 : 1, and this is in the range of Tani et al.(2003) and Mistzal et al (2012), but from the real ambient measurement, the ratios varied by time of the day, indicating flux contribution to each mass can be changed from different fragmentation patterns of MT species. GC measurements were conducted during 1 month from this campaign, but not simultaneously with the PTRTOFMS measurements, so there also could be seasonality differences for monoterpene emissions. As the Referee #1 pointed out, the fraction of MTs species should also be different when the footprint changed during nighttime due to contributions from different Citrus species as we noted in the new text added to Section 2.1.

Technical corrections:

>> We would like to thank the reviewer for all technical corrections.

-p 20447 line 20 "it would not affect on..."

>> We omitted "on".

-p 20451 line 17: "Fragments pattern of monoterpenes..."

>> We changed "Fragmentation patterns of monoterpenes"

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

>> Yes, "The fragmentation patterns…" is right. Thanks.

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

>> We rewrote the sentence for clarity, so now the statement is "PTR-MS flux data (m/z 33, 59, 69, 81 and 113) were sampled with dwell times of 0.2 seconds (overall 5Hz disjunct) after collecting the primary ion signal (m/z 21 and 37) for the first 0.1 seconds."

-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.

>> As the reviewer suggested, the sentence is rewritten as "Each line presents the normalized co-spectra of sensible heat flux (broken black line) and acetone flux; (a) original 5 Hz data from PTR-TOF-MS (red line with open circle), 1 Hz reduced data from PTR-TOF-MS (solid cyan line), (b) 1 Hz disjunct sub-sampled (similarly to PTR-MS data acquisition) from PTR-TOF-MS (dotted green line), and ~ 1 Hz disjunct data from PTR-MS (solid blue line with plus)."

Response to Referee #2

We would like to thank Referee #2 for the constructive comments and corrections which will certainly help increase the scientific quality of the manuscript. Below are our answers to the specific comments.

In the following, the original comments are in ***italic bold font*** and our responses are in regular font.

Specific comments:

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

>> We have replaced as suggested.

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.

>> Propanal and acetone have the same empirical formula, thus these compounds can contribute to the same m/z signal in both PTR instruments. Ambient concentrations of propanal at the site are minor as determined by a few periods of GCMS measurements, so we think adding 'mostly' is appropriate.

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

>> As suggested, we now included a reference 'Businger and Delany (1990)'

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 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?)

>> We think that figure 2 and the Section 2.2 well describe the difference between PTR-TOF-MS and PTR-MS with regard to mass resolution and sampling frequency. Moreover, in Section 3.3 we have shown that some occasional discrepancies between two instruments in flux measurement may happen by different time resolution of data. So, our analysis shows that TOF 'wins' already when 5 m/z ratios are measured, which is the upper limit of compounds that can be measured with a quadrupole PTR-MS.

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.

>> The duty cycle depends on the measured m/z ratio and is taken care of through the applied mass transmission correction. Details are given in Holzinger et al. (2010b).

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.

>> At the end of Section 2.2, we added the text "During the measurement period, the averaged sensitivities for PTR-TOF-MS ranged between 8 and 36 ncps/ppbv, similar to that reported by Ruuskanen et al (2011). For PTR-MS, the sensitivity to each measured compound has been reported by Fares et al., (2012a). Calculation of VOC volume mixing ratios using transmission factors and reaction rate constants was done according to the method described in Holzinger et al. (2010b)."

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?

>> For a few compounds we used calibration standards and the measured sensitivity agreed well with the calculated sensitivity using basic reaction kinetics as outlined in Holzinger et al. (2010a and 2010b). Thus, for calibrated compounds the accuracy is better than 20%. For all other compounds the concentration has been calculated using default values for the reaction rate constant and the accuracy should be within ± 30%.

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.

>> We agree with the reviewer #2's point on this issue. However, the current knowledge on VOC molecular characteristics is poorly understood. We rewrote sentences as below to clearly address it.
"We estimate an error (< 0.15%) due to this effect assuming similar VOC characteristics with CH_4. However, this error estimate is probably not representative for most VOCs. Especially some condensable and/or sticky compounds such as acetic acid may suffer from much larger dampening errors. For better estimates we would need to characterize the attenuation parameters for all individual compounds. We discuss further about the inlet dampening of fluctuations for condensable or sticky species causes a systematic underestimate of the flux in Sect. 3.2 for acetic acid (m/z 61.027)."

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.

>> This uncertainty calculation is not for concentration, but for flux estimation, when noise by vertical wind measurement and noise by concentration measurement were multiplied, thus there will be a random error in flux calculation. The data in each 0.2 sec (5 Hz) include a noise based on the Poisson distribution which is defined as sqrt(N), thus σ_n is the variance of the noise (sqrt(N)).

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

>> It depends on ambient concentration and the intensity of the $^{17}O^{16}O^{+}$ signal, which is a minor impurity from the ion source. For example, m/z 33 is very well described in Muller et al., (2010) as we referenced in the Introduction. This advantage of PTR-TOF-MS is not the focus of this manuscript as this has been already shown elsewhere (Jordan et al., 2009, Muller et al 2010).

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?

>> Eddy flux measurements must cover a longer period (typically 30 minutes) that must include all relevant eddy frequencies that cover the transport. As we inter-compare mixing ratios and fluxes 30 min are the shortest period typically used.

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.

>> The statement 'often exceed 10 ppb' is the usual case in the boundary layer in vegetated area region during summer and this is consistent with our result. We also mention the range (7.3 – 43.6 ppbv) in the manuscript (Page 20453 line 20).

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.

>> As shown in figure 6d, general acetone flux discrepancy between PTR-TOF-MS and PTR-MS is not significant (linear regression slope is close to 1) since the flux is calculated as an averaged value of w'c' over long enough time period. However, in a few cases, where PTR-TOF-MS measured higher fluxes than PTR-MS (highly deviating data points from the regression curve, i.e. >3 sigma error), the flux carrying eddy feature may affect significantly by disjunct sample as shown in figure 7. In addition, there is not negligible contribution to the acetone flux at higher frequency (>0.5 Hz) as shown in figure 7 (a) under some circumstances (here, for 14:00 PST on 22 July 2010). Under this specific condition with the data acquisition sequence we set, PTR-TOF-MS showed better

performance in capturing all eddy features. However, these occurred very few times and we would need more data to fully dissect this issue.

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)?

>> Even though we mentioned 89% of monoterpene was limonene, diurnal profiles of MT species are associated with different footprints (different source), particularly nighttime when MT concentration is generally higher and the footprint was dominated by more limonene source orange trees (Valencia orange and Parent Navel orange). Based on our calibration with d-limonene standard, the ratio of m/z 81:95:137 was 4: 0.8 : 1, and this is in the range of Tani et al.(2003) and Mistzal et al (2012), but from the real ambient measurement, the ratio varied by time, indicating flux contribution to each mass can be differ from different fragmentation patterns of MT species. For example, the signal of many MTs is dominated at m/z 137 rather than 81 showed, so m137 flux is contributed by other MTs rather than limonene. GC-MS measurement was not performed at the same time, so the fraction of different MTs could not be confirmed by coincident speciated measurements.