"A Disjunct Eddy Accumulation System for the Measurement of BVOC Fluxes: Instrument Characterizations and Field Deployment" by G.D. Edwards *et al*.

Response to Reviewer 3:

We thank the reviewer for carefully considering all the potential issues regarding making measurements of this kind. We feel that addressing these comments in an updated draft of the paper have further clarified these key areas.

Major comments

General comments:
1. The use of cartridges featuring Tenax adsorbents for measurements of certain range of BVOC requires lots of care as it could easily be responsible for much higher uncertainties than those specific to the DEA setup itself. On the other hand, with adequate quality control, cartridges can be excellent for a DEA setting as they offer a comfortable way of sample storage and are easy to use. A description of the limitations deriving from the use of the cartridges could be useful.

We agree with the reviewer that there are significant strengths and weaknesses when using sample cartridges. However, we feel that it is beyond the scope of this paper to consider all of these as there have been several reviews on this topic in the literature; these are described in section 3 of the paper with appropriate references. We have added additional sentences and references in this section to further highlight this fact.

2. *Although the breakthrough volume did not seem to be a problem, there are other common problems possibly arising either from: (a) losses due to leaks (small or large) at the fitting side; (b) inability to trap 100% of a compound (whether due to trapping temperature, humidity or specificity of a compound); or (c) from a wide array of artifacts whether due to the presence of MBO (which can dehydrate to isoprene), due to possible formation of iodides or the presence of oxidants not stripped by the KI scrubber. Consequently, even if the setup has minimized the DEA specific errors (deadband, high frequency losses, etc.), the error from the use of the cartridges might be substantial and in my opinion should be carefully estimated for the entire campaign and accounted for in the flux uncertainties. The term specific to cartridge use should be added to Eq. 8 and 9 to account for adsorbent-tube specific reproducibility. One way of determining such the error would be to sample the known amounts of BVOCs every Nth cartridge and look at the campaign variability in the targets. Although the authors mention they excluded the potential artifacts, it would be interesting to know how good the overall reproducibility was.*

The reviewer raises an excellent point regarding reproducibility and the precision of the measurement. This was carefully considered in the evaluation of the methodology in the lab tests that were preformed regarding this sampler system. In the interest of a general audience we did

not described all of the tests that were performed in this area. However, we have already accounted for the issues raised by the reviewer in the discussion section leading to the derivation of equation (8). As this equation is by its nature is a reflection of the ability of the sampler to reproducibly collect, preconcentrate and desorb samples to produce a chromatogram the peak in which yield all subsequent data we feel this equation has accounted for all routine cartridge 'issues' and further additions or terms is unnecessary.

3. It could be most useful to perform a validation of the presented DEA system by the comparison to a conventional eddy covariance technique utilizing a fast sensor such as PTR-MS or FIS, if not in the field perhaps in a short lab study. Numerous comparisons exist between disjunct eddy covariance (DEC) and virtual disjunct eddy covariance (vDEC) (e.g. Rinne et al., 2008; Langford et al. 2009) but the DEA setup presented by the authors featuring the adsorbent cartridges still remains to be validated.

We agree that this would be an absolute test of the sampler. Intercomparison exercises of the nature are valuable diagnostic tools in testing many aspects of new techniques and instrumentation. Data on BVOC concentrations and fluxes were available from and REA sampler (deployed by NCAR) and for concentrations only, from a PTR-MS (deployed by Washington State University). However, direct comparison between the DEA and these instruments was not included in this paper. The reason for this was mainly due to issues of data quality and overlap. During the campaign the PTR-MS was measuring a several different heights compared to the static DEA inlet. Unfortunately, the few days were the inlets were co-located the PTR-MS suffered from instrument problems and the operators do not have sufficient confidence in the data to make the comparison worth of publishing at this time. In addition The REA sampler could only offer coverage for 3, 30 minute averages of BVOC data for two days where the REA and DEA samplers was co-deployed. The agreement between the two instruments was excellent but given such limited coverage, it was decided not to include these data here. It is the hope of the authors that an additional companion paper can be drafted in the future to directly compare the relative performance of these platforms.

4. The authors emphasize several times in Sect. 3 that no artifacts were detected and the KI scrubber should have no influence on BVOC concentration. I am sure that the authors did a great job to look for these and applied rigorous quality control measures to avoid them, but as with all methodological papers, a description of encountered or expected challenges could be useful for researchers willing to pattern their instrument/analysis on the author's work. I am arriving at the following questions: (a) did the authors encounter any challenges with the use of the cartridges such as tube leaks, outliers in the data, variability in the blank/measured samples, any examples to show)? (b) could part of the isoprene peak be an artifact from MBO dehydration? c) could isoprene decompose to a compound that cannot be detected on the GC column/detector used in the analysis? d) how would be the peaks of small isoprene concentration different with and without the use of the KI scrubbers? Any tests to show?

Again, the reviewer raises excellent points that were considered for inclusion in the manuscript. We did all of the tests described but, in the interests of a concise paper decided not to include such a lengthy study. In reference to the specific concerns then, as described in the text, some data are missing due to issues such as tube leaks/signals below the limit of detection. Again, as described in the text no significant peaks in any of the blanks were observed in the lab tests or field deployment that could be due to artifacts. No significant decomposition of the isoprene peak was observed in lab tests where cartridges were stored for long period and as this forest site does not have any significant source of MBO (Carrol *et al*., 2000) this interference was assumed to be insignificant.

5. Were the adsorbent tubes obtained commercially or were they prepared manually? Based on our experience, it seems that the industrially packed tubes offer much less variable results. In my opinion, it may not even be possible to ensure exactly the same adsorbent density in manual preparation even ensuring the highest degree of care which might affect the variability of the results.

We agree with the reviewer that large uncertainties can be introduced through "in house" preparation of the cartridges described here and have shared in the frustration this can bring! Hence, these tubes were obtained commercially as described in the text with appropriate part number.

6. The authors advertise the system for BVOCs whereas in the analysis they constrain themselves to reporting only isoprenoid fluxes. What about methanol, MVK, MACR, acetaldehyde, acetone, hydroxyacetone, MBO, etc.? It would be appropriate to outline the range and limitations of the system somewhere in the text or amend the title.

During the samplers first field deployment we have focused on using this instrument to measure fluxes of the species described but, as described in this paper and others, DEA offers and excellent alternative to existing flux methodologies for a variety of atmospheric VOC's. Sentences alluding to this fact have been added to the introduction and conclusion paragraphs.

7. It might be helpful to know the overall dimensions of the whole system. Given the race for miniaturization, potentially more compact DEA, REA systems might follow up in the future.

The dimensions of the DEA sampler have now been included in the caption to Figure 1:

8. The concentration and flux results from CABINEX2009 are presented for individual days sometimes with gaps. I wonder if a diurnal figure combining the data from all panels could be used to derive the diurnal trend similarly as in Fig 6, but also with (a) the diurnal temperature using all data and (b) the diurnal temperature obtained only for those points for which the concentration/flux data are available. This would illustrate the degree to which the representativeness of the reported data could have been affected by the missing samples.

We do not feel the missing samples were likely to reveal any additional information about this well studied forest site. As shown by the results of this campaign the data obtained by the DEA system were fairly typical of those previously reported. We have decided to focus on the day-to-day variation in BVOCs as sometimes averaging all days together like the review suggests does not show the coupling between changes in the flux and concentration and changes in temperature and light levels. As terpene concentrations and fluxes are so closely correlated to temperature, this seems and obvious plot to make. However, as shown by the temperature data in Figures 7&8, temperatures during the measurement period varied little. This was combined with the average temperature of the whole campaign being over 4°C below the 30 year average as measured by researchers at the UMBS site. (http://umbs.lsa.umich.edu/research/data/monthly-temperature-records.htm) Plotting ΔT against measured flux and or/concentration produced plots with correlation coefficient that were on the order of 0.6. It was therefore decided not to include these data in the manuscript as no firm conclusion as to the nature of the data could be determined in this way. As the 1D model is a more compete test of our understanding of production/loss and chemical transformation of BVOCs it was decided to use the model to ascertain if the data measured here were at least in line with this current understanding.

9. Comparison with the sensible heat flux seems interesting. Similarly, the whole T dataset could be used to calculate H in comparison to the output from an isoprene emission algorithm (e.g Guenther et al., 2006). Yet another suggestion could be to compare simulated HDEA with the HEC.

The reviewer makes a valid point in that the sensible heat data do offer a window into the nature of the isoprene emission and plots to this effect have been made and used to form the basis of Figure 6. Our goal in this paper was to test the sampler against the model described as we feel that this is a better method of testing the *in situ* data since the model provides a more complete picture of all the production, loss and chemical transformation pathways likely to be encountered at this site, as shown in the model measurement comparison figures.

Specific comments:

p. 2706, l. 9 "However, PTR-MS cannot determine speciated monoterpene fluxes. . . " Although speciated monoterpene fluxes with PTR-MS are definitely difficult, I would not say entirely impossible. For example, in combination with a triple quad MS or linear ion trap (Müller et al., 2009) or in alternating E/N (Misztal et al., 2012) at least simple monoterpene mixtures can be separated and the flux could be indirectly determined (e.g. tracer ratio method). I suggest rewording or add "easily" after "cannot".

We agree with the reviewer in that there are some new papers in the literature regarding the possibility of speciated fluxes using the techniques described. The word 'easily' has been added to the text as suggested, together with the references described.

2. P. 2706 l. 12 "dominate" should be "dominant"

The typo was corrected

3. P. 2707 l. 3 insert "is that" after "accumulation"; "Is" should be "is"

The typo was corrected

4. P. 2707 l. 9 first "and" should be "both"

The typo was corrected

5. P. 2707 l. 12 delete "of"

The typo was corrected

6. P. 2710 l. 19 delete "form"

The typo was corrected

7. p. 2712 l. 9 "has" should be "have"

The typo was corrected

8. P. 2720 l. 25 replace "on" with "in"

The typo was corrected

9. Fig. 5: make multiplication sign different from the x sign

The typo was corrected

10. Fig. 6: It would be also helpful to add 1_ to Guenther et al 1993. Was the ambient or leaf surface temperature used in the algorithm? If the authors have prior 10 day and 1 day temperature and PAR data, they could consider using a more recent version of the algorithm such as Guenther et al. 2006? This could better pick up variabilities and potentially agree better. Were the data used to parameterize the algorithm or were the default parameters used?

We chose not to include the 1σ uncertainties for the data represented by the solution of the algorithm postulated by Guenther (*et al*., 1993) in order to maintain the clarity of the figure. We also recognize that there have been several revisions to this emission model since it appeared in the literature almost two decades ago. Our goal in this comparison was to show that using a

simplistic algorithm of isoprene emission, the DEA sampler provided data that were in the same general order of the likely BVOC concentration at this site. These data were also compared to a more complex emission model later in the paper.

11. Fig 7 and 8. How was the propagated uncertainty derived here? For example, in Fig 8H one can hardly see the error bars and there is no error bar at 15:30. Are the authors trying to say that their DEA flux uncertainty for this point was less than 5 _g m^-2 h^-1?

The uncertainty with these data was calculated from equation (9). We do not intend to imply that there are no uncertainties associated with the data the review references. In an attempt to create a scale that all flux data could be compared to each other, the relatively small fluxes observed in on the day in question do appear to be compressed on this scale, relative to other days. Consequently, the 1σ bar is difficult to see. However, as described in the text, even for this day, the uncertainly in the flux was still on the order of 12-40%.

12. Fig 8 caption: "Again, changes in flux mirror changes in ambient temperature over the course of the day" What about panel E or left hand side of panel F?

The confusing statement was re-worded.

13. Fig 9 the graphs are difficult to read. Can one of the error bars be replaced with shaded area?

Shading the figure as suggested does lose some of the clarity as the shading tends to overwhelm the already crowded figure; however, the figure was clarified with thicker error bars.