"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 2"

We thank the reviewer for the excellent discussion on the effect of using the dead-band approach in DEA with the pros and cons of the technique eloquently described. These useful comments have, in our opinion, enhanced the manuscript considerably.

General Comments:

The major point of contention with this manuscript is the use of a sampling threshold or dead-band with the DEA technique which excludes sampling of the small eddies (small w'). This is contrary to the basic theory of both eddy accumulation and disjunct sampling and should lead to a systematic overestimation of the flux by artificially increasing the concentration difference, or ΔC, between the up and down reservoirs. The authors do note this and show that by assuming scalar similarity and simulating the DEA sampling with temperature, this overestimation is small (8- 9% on average) and can be corrected for.

Since corrections based on similarity are necessary, this is technically not a "direct flux" measurement per se anymore. Although the methods used for correction seem appropriate, at some point, one must step back and ask: What is the advantage of using a sampling threshold (or dead-band) with the DEA technique? In the analogous Relaxed Eddy Accumulation (REA), the use of the 0.6_w dead-band typically increases the concentration differences by ~1/3 which is compensated for by re-computing the empirically-derived b-coefficient (see description in manuscript, pg 2718, lines 14-20).

This b-coefficient usually decreases from about 0.6 (no threshold) to 0.4 (with 0.6_w threshold). The authors show that the use of a DEA threshold only leads to an 8-9% overestimate in the heat flux. This is tantamount to saying that one has increased ΔC by 8-9%.

This is an expected result since the small eddies are sampled proportionately (as opposed to REA where the flow is constant and all eddies are sampled equally) and should only constitute a small amount of the total sample volume within the different reservoirs. So, the question becomes: Does an increase of 8-9% in ΔC result in marked improvement in the precision of the concentration analysis to offset the uncertainty that is added by the need to make similarity corrections?

Other points discussed by the authors as reasons for using a sampling threshold are (1) incorrect volume measurement for very small samples (small w') and (2) errors in measuring small w' values by the anemometer. I would suggest that both of these are very minor issues since the w'-values where these are important are very small and will likely only contribute less than 5% to the total sample volume in either reservoir. For example, erroneous sample volumes that are 30% too low (maximum underestimate at sample time of _1 sec, see Figure 2) will likely

only result in a 1 or 2 % error(possibly less?) in the total reservoir sample volume since they occur infrequently and contribute such small amounts of volume. In summary, although a sampling threshold can be used with DEA and corrected for accordingly as done in this manuscript; the fact that you are collecting sample volume proportional to the vertical wind velocity makes the use of this threshold relatively unnecessary.

We thank the reviewer for succinctly framing the advantages and disadvantages in using the dead-band system as describe here. We agree and have made a conscientious effort to show that this is this method of flux measurement is not 'true' DEA but represents something new. As with all new instruments one must as one's self "is it a better instrument than those already described in the literature"? Our attempt in using this dead-band approach was indeed to trade off one issue associated with accumulation techniques, insuring large enough differences between C_{up} and C_{down} to be statistically significant, verses the need to make corrections to the data based on similarity theory. As described in the text, the reasons for using the dead-band were based on the uncertainties that we felt were likely to be introduced through issues associated with mass flow control. As knowledge of the total volume accumulated is critical in the assessment of concentration samplers of this type (as described in Martins (2008)) we decided to use the dead-band method as a way of eliminating this potential flow control issue while eliminating eddies that contribute almost nothing to the overall flux. As this was the first field deployment of the instrument a very conservative bandwidth was chosen an as described in the text, it is clear from the data that this was indeed too conservative. One of the conclusions of this paper we hope to make known to the community is that the dead-band approach can be used in DEA with proper care, and maybe useful for some other species but the but pros and cons verses the more established techniques need to be carefully balanced.

Specific Points:

Equations (7) and (9). Reviewer #2 is correct – the first term on the right hand side should have the average of the absolute values – not the absolute value of the average. It is written correctly in Eqn (2).

This typo has been corrected

Page 2706, lines 17-20. I would also include the flux-gradient methods as an "accumulation" method. Although not included in the name, air samples are often collected over some time period and analyzed later offsite.

The gradient method can be considered an accumulation methodology and the text has been changed to reflect this, with additional references.

Page 2707, line 9. ": : :and with mechanically undisturbed wind measurements: : :" Is this not true of any flux methodology?

We agree that this is indeed true, but this is especially true of DEA based approach as described by Turnipseed *et al*. (2009)

Page 2709, Eqn. 9. Since the authors are using the planar fit method to rotate the coordinate system, this should minimize the second term of the rhs of Eqn (9). How different are the flux values upon using Eqn (9) relative to the simplified Eqn (2)?

Use of the coordinate rotation is especially significant at this particular field site (as indicated in the text), but this issue has been further emphasized with additional sentences in this paragraph. As the site sits on a shallow slope, the effect of not rotating the anemometer *via* this methodology can lead to significant errors in the determination of vertical winds. A reference to previous work in this area has been included in the revision.

Page 2711, lines 14-24. I am a bit concerned on how well isoprene is trapped on Tenax-TA. Our experience has always been that we need to cool the tubes below about 15oC to get quantitative adsorption of isoprene with Tenax-TA. Please briefly describe the lab tests that were done to look at isoprene breakthrough. One further point – I assume that the 28^{o}C field temperature in line 23 is the ambient temperature. However, what is more important is the temperature within the DEA sampler which could be several degrees warmer than ambient when sitting out on the tower, depending upon the ventilation, pumps and heating devices within the sampler. The authors should comment on if they believe this could be a potential problem.

We agree with the reviewer that species like isoprene are quite difficult to trap using Tenax-TA. Lengthy lab experiments were performed in order to ascertain breakthrough volume. However, this discussion was truncated for the paper in order to maintain a concise manuscript. The test was conducted with a gas phase standard containing 8ppb of isoprene. Repeated samples were then taken from this standard at ambient temperatures by flowing onto a two blank cartridges joined in tandem *via* a Swagelok union. If the first cartridge was subject to breakthrough, an isoprene peak would be expected in the second cartridge. When 5 liters of isoprene rich air had been sampled by the combined system, the end cartridge was thermally desorbed as normal. Results showed that there was no discernable isoprene peak in the second cartridge showing that in 5 liter sample, all isoprene was trapped quantativly in the first cartridge over a range of temperatures. In addition, the reviewer is correct in that that 28^{o}C was ambient temperature but, in fact the sampler was cooler than ambient. The instrument sits in an all weather Pelican case and the sampler is cooled with two internal fans. We therefore do not believe this issue to be a problem. The description of Figure 1 has been changed to include the fact that the system was internally cooled this way.

Page 2714, line 6-7. In terms of improving the overall technique, what factors could be improved in order to have smaller uncertainty (in other words – where is the largest source of uncertainty in Eqn. (9)).

As described in the text, the largest sources of uncertainty are the determination of the sample volume at low flow rates and, more importantly, the uncertainty in the concentrations of the individual species, based upon the factors described in equation (8)

Page 2714, line 9-13. Was the sonic anemometer and DEA inlet also located at the sampler height (26.6 m). If so, this seems very close to the average canopy height of 24 m (only 2.6 m above canopy). For a reasonably rough canopy typical of a deciduous forest, care must be taken since similarity relationships are not as robust and turbulence is not as homogeneous this close to the canopy. Typically flux measurements are often made _10 m above the canopy.

We agree with the reviewers concerns and hence, felt the need to undertake the rigorous evaluation of the stationarity of this location as described in section 4 of the paper along with carefully evaluation of the data from equation (10). As described, the DEA sampler was placed on a platform 26m above the canopy, with the sonic anemometer and inlet co-located 2m above. The text has been changed to clarify the location of the inlet and sonic.

Page 2715, first paragraph. I assume that the planar fit rotation angles were applied on-line to the wind velocities during the DEA sampling.

The reviewer is correct; the text has been changed to reflect this fact.

Page 2718, line 18-20. I believe this is incorrect. For DEA with no sampling threshold, no correction factor is necessary. But, since this work uses a sampling threshold, this causes a systematic overestimate of _C (and, thus the flux). Even though fairly small, it is true that an empirical correction is necessary for these measurements.

The effect of this very small correction factor, a psdueo 'β' coefficient similar to that used in REA measurements, has been derived for this re-written section.

Page 2719, line 2 – should read "Bowling et al., (1999)"

This date for this citation has been corrected.

Page 2719, line 16-17. However, the 8.6% difference is a systematic overestimate as opposed to random uncertainty. There is a difference here.

We agree and have changed the wording to avoid confusion as to this important issue.

Page 2723, line 14. The authors state that "no calibration standards" were available. However, the FID used responds on a per carbon basis – therefore, calibration with any hydrocarbon can be used to quantitate all other hydrocarbons. It is true that one needs to know what the retention time of the other monoterpenes – this does require some type of sample of the known compound.

The text has been changed to "primary monoterpene standards" to clarify this area.

Page 2724, first paragraph. In discussing monoterpene concentrations and comparing them with previous studies it is important to relate the average temperatures during those measurement periods. The measurements here showed slightly lower concentrations, but that could just be due to lower temperatures during this sampling period.

We agree with the reviewer and believe this is very likely the case as the ambient temperatures in CABINEX were several degrees cooler than normally observed at this field site. However, without additional supporting data as to monoterpene concentrations during this campaign, we feel it is difficult to comment further on this comparison to literature values with any real confidence.

Page 2725, section 9. It is not surprising that fluxes compare better than concentration measurements. The flux comparison only relies on scaling up of the leaf-level measurements whereas determining concentration in the 1-d model also relies on how well the loss processes (chemical losses) are simulated (in addition to the scaling up issues). Overall, it seems that this modeling exercise is a bit overly complicated and uneccessary – why not just plot your flux measurements as a function of temperature and then plot equation (14) with an appropriate _-factor (page 2726, lines 7-9) for this canopy. This should show if the measured fluxes are reasonable or not.

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^{o}C below the 30 year average measured 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.

Page 2727, lines 20-22. Given the large modeling uncertainties shown in Figures 9 and 10, it would seem that just about any measurement would lie "within the uncertainty". This is why I would contend that a simpler comparison such as described in my last comment is a more robust metric than the 1-D model.

We recognize that owing to the complex nature of the model, significant uncertainly exists when the errors are propagated. However, we feel that, as describe above this was a more robust test of the data than simple temperature correlations. Having said this, the measured data and model agree very well and all data points irrespective of the model 'error bars' leading us to again conclude that the DEA data are in line with prediction.

Page 2729, line 4. The authors suggest that smaller thresholds could be used – as

mentioned in my general comments – I would contend that thresholds are not necessary at all in the DEA technique.

We agree with this conclusion and the summary paragraph in the manuscript has been changed to reflect this.

Figures 7 and 8. Even though the DEA flux measurements are discontinuous throughout the day, I would assume that the ambient temperature measurements are not. I would recommend plotting the entire day of temperature measurements so readers can see these changes over the entire course of the day.

These data are seen on the secondary Y axis in Figures 7&8, emphasizing the small diurnal variation in diurnal temperature observed in the campaign as previously described.