Atmospheric Measurement Techniques Discussions

Interactive comment on "A disjunct eddy accumulation system for the measurement of BVOC fluxes: instrument characterizations and field deployment" *by* G. D. Edwards et al.

Anonymous Referee #3

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The nicely written paper by Edwards et al. is refreshing the usefulness of the disjunct accumulation eddy covariance technique and describes an adsorbent-cartridge based measurement system accompanied by field results. This can be of interest to a potentially large user community who do not have access to a fast-response sensor (e.g. PTR-MS or PTR-ToF-MS) but who would still like to measure ecosystem fluxes of the biogenic organics. Unfortunately, the measurements are not validated against conventional eddy covariance measurements utilizing a fast sensor and the study bases on the correlations with isoprene emission models and atmospheric chemistry models.

I would find the paper appropriate for the publication in AMT, in particular, given that BVOC flux measurements only cover relatively small portion of the globe and the device is likely to support more routine BVOC fluxes at a relatively low cost. However, as with any new instrument, one needs to make absolutely certain that a thorough testing/validation has been done. I will refrain myself from adding more comments to the DEA methodology itself which has already been covered extensively by the two other reviewers and should be further polished. I will mainly focus on the instrument characterization and on the outputted results some of which are indeed novel but whose uncertainties need to account for all sources of errors. The following comments should be addressed before the publication.

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.

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.

3. It could be most useful to perform a validation of the presented DEA system by the comparison to a conventional eddy covariance techinique 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.

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?

5. Were the adsorbent tubes obtained commercially or were they prepared manu-

ally? 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.

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.

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.

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.

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 H_{DEA} with the H_{EC}.

Specific comments:

1. 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".

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

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

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

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

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

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

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

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

10. Fig. 6: It would be also helpful to add 1σ 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?

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.

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Are the authors trying to say that their DEA flux uncertainty for this point was less than 5 μg m^{-2} h^{-1}?

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?

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

References:

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