**Atmospheric
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Interactive
Comment

Interactive comment on "Biogenic volatile organic compound emissions during BEARPEX 2009 measured by eddy covariance and flux-gradient similarity methods" *by* J.-H. Park et al.

Anonymous Referee #1

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This manuscript presents ecosystem level fluxes of biogenic VOCs from a pine forest that has been the subject of many past studies within this group. The eddy covariance (EC) fluxes of the major BVOCs at this site appear reasonable and the methodology is sound. The authors attempt to extend the use of the PTR_MS instrument to compounds that are at difficult to measure by EC due to their very low concentraions by using a flux-gradient method relative to their EC methods (this is often referred to as the modified Bowen ratio technique). This allows for a slower analysis time that is needed for the trace species. However, there are some serious concerns on how the authors have applied the flux-gradient methodology that need to be addressed before this manuscript should be published.

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Interactive Discussion

Discussion Paper

(1) The authors state that, " Disadvantage of this approach (the relative flux gradient method) is that the vertical source and sink profiles of H_2O, CO_2, or sensible heat may differ significantly from those of BVOCs resulting in errors in the similarity assumption for K among these different tracers." However, this is exactly the assumption that they are making when they use specific BVOCs as the reference compound. The vertical source/sink profiles for different BVOCs also vary. According to their own data, methanol has a significantly large soil source whereas MBO is primarily emitted from the canopy – so these compounds have significantly different source/sink profiles. In this way, I do not see any difference between using a specific BVOC as your reference compound as opposed to some other scalar such as CO_2 or H_2O. It is only an advantage here because it can all be done with one instrument.

(2) Along these same lines – BVOCs that are reactive can be considered to have very different source/sink vertical profiles (i.e. there is a constant reactive source/sink with height). Patton et al. (Bound-Lay. Met, 2001, 100, 91-129) have clearly shown that the eddy diffusivity of a compound depends directly on its reactivity (or atmospheric lifetime). So you cannot apply an eddy diffusivity derived from a conserved scalar (for example, methanol) to a reactive scalar one that has a lifetime similar to the turbulent transport (example – a reactive sesquiterpene) without incorporating substantial errors. This will apply both to reactive compounds emitted that then decay with vertical transport (e.g., sesquiterpenes) as well as those produced by photochemistry (e.g., oxidation products). The fluxes that are derived via the gradients for these compounds may reflect some relative trends (such as diurnal patterns), but will likely be incorrect as a quantitative measure of how much mass is moving between the ecosystem and atmosphere. This is an especially difficult problem for SQTs since the PTR_MS measures a mixture of compounds that could range over several orders of magnitude in their atmospheric chemical reactivity. In this case, it is nearly impossible to determine a proper eddy diffusivity.

(3) I am also concerned about the sampling scheme employed for the flux-gradient

method. From Fig. 1 it appears that measurements are made on the lower (9.5 m) gradient level for only 6 min. out of the entire hour. The basic concept of the flux-gradient method is to measure an average concentration over the entire flux period, or, at least, a close representation of that average. I have my doubts that measurements from 12% of the flux averaging period can adequately represent the average concentration over the entire hour due to changing airflows and environmental conditions. Although concentrations from levels within the canopy can be informative, if the major purpose of the study was to report above-canopy fluxes, I would have recommended cycling only between the above-canopy inlets to obtain a better representative average concentration. This is especially true for this particular experimental setup, since the lowest inlet level is well within the roughness sublayer where it is well known that sweep-ejection flows within the canopy can create counter-gradient fluxes which invalidate K-theory (see Cellier and Brunet, Ag. For. Met., 1992, 58, 93-117 for one example – there are many others).

Other specific comments:

(1) page 25086 – description of the profiling system. What is the residence time in each of the inlets and were any inlet tests conducted to see if losses of the heavier or oxygenated compounds were occurring. Bouvier-Brown et al., (2009a) reported losses of $\sim 40\%$ for linalool from an 18-m long inlet line as well as some losses for several other compounds. Here, you have 30 m lines – although the residence time may be less.

(2) page 25088, lines 13-15. Were the mixing ratios of the 5 monoterpenes used in the calibration tank reflective of the typical ambient concentrations? This is probably not too critical as the ion-molecule rate coefficients are all typically within 10-20% of each other.

(3) Page 25093, lines 15-19. The authors report higher SQT mixing ratios than the previous study of ambient concentrations (Bouvier-Brown, 2009a) and suggest some were

missed in that study. Yet, Fig. 11 shows that the canopy-scale fluxes presented here underestimate the flux compared to scaling up of branch-level data (Bouvier-Brown, 2009c). This seems contradictory since the 2009a study measured the same SQTs as the leaf level study and quantified losses in their sampling procedure for those specific SQTs. The scaled-up emission calculated from the branch level should be for the same set of SQTs that were measured in the 2009a study.

(4) page 25094, line 10. You are limited by how many ions you can measure fast, but also by sensitivity. It would be quite difficult to measure SQTs (204) by EC even if you only did this ion! The main reason to do gradients is that it gives you the ability to signal average and increase your detection ability.

(5) page 25094, eqn.4. Eddy diffusivity is typically parameterized as a function of height. Please state the height at which you are calculating the eddy diffusivity.

(6) page 25095, lines 19-22. You do not show the comparisons between the K's determined by the 3 different species (only the diurnal averages). But this is an important part to the story – this shows that, regardless of individual source/sink profiles, you can use a single Kuniv to describe the eddy diffusivity – i.e., that your similarity assumption works in this situation! If you use EC flux and gradients to compute Kuniv over a given hour – it seems a bit circular to then go back and say that the gradient fluxes agree with the EC fluxes. Then the fluxes should only show variability only due to the timing mismatch (i.e, the hourly gradient flux does not completely overlap the 30 min . EC flux). One further question here – did the authors compute eddy diffusivity and/or gradient fluxes between the two upper gradient levels (13.6 and 17.8 m). This would be a good internal check.

(7) page 25096, lines 17-21. The authors report observing both emission and deposition for several ions (masses 71, 113, 151, etc.) that were monitored. The reported fluxes were very small and variable. Not only would this be sensitive to not measuring a representative concentration at the lowest inlet height, but could also be sensitive to

wind flow patterns and turbulence changes. Small changes in horizontal and vertical advection could easily be reflected in the observed small gradients and imply a vertical turbulent flux.

(8) Page 25100, line 25-30. It is a bit presumptive to assume that the majority of SQTs emitted at this site are highly reactive and would be the cause of the measured lower emission rates. The major identified SQT from prior leaf level and ambient measurements was a-bergamotene. Its reaction with ozone has not been studied to my knowledge. Only estimates of its rate constant have been reported (Bouvier-Brown et al., 2009a) with a fairly moderate reaction rate (giving similar atmospheric lifetimes for reactions with both ozone and OH). If the SQTs at this site are reactive and you are using a passive-scalar eddy diffusivity (see General Comment #2), then your discrepancy reported here is even larger, since chemistry is causing you to measure too large of a concentration gradient and overestimate the emission flux.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 25081, 2012.