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Interactive comment on “The bi-directional exchange of oxygenated VOCs between a loblolly pine (*Pinus taeda*) plantation and the atmosphere” *by* T. Karl et al.

T. Karl et al.

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General Response:

The reviewer expresses concern about showing both laboratory/enclosure and field data in one paper. It is probably true that in most papers this is not done (in many cases because field measurements are not available). However we feel that a comparison of these two datasets is very important to be of any relevance for atmospheric science aiming at up scaling VOC emissions. We disagree that field data should be omitted (=ignored) and only things that can be explained should be presented. It is the essence of science to learn from unexpected observations. Our results show that the up-scaling for some oxygenated VOC emissions is more challenging (e.g. acetaldehyde) than for others (e.g. methanol).

RC: Putting together flux and lab data highlights several contrasting issues, and at the end I felt confused rather than armed with new knowledge.

AC: Yes, we agree that the comparison between field and laboratory data contrast each other for some compounds (e.g. acetaldehyde), while there is generally good agreement for others (e.g. methanol, acetone). However, we don't think that this necessarily confuses the reader rather than pointing towards insufficiencies in our current understanding of canopy scale exchange mechanisms. There is also concern that field data will presented in a separate paper. This is actually not the case! The paper by Baker et al. will focus on an intercomparison of VOC fluxes measured by eddy covariance, disjunct eddy accumulation and relaxed eddy accumulation techniques. This paper will also incorporate and focus on results on isoprene and monoterpene emissions, none of which is presented in the present manuscript. In the present manuscript we merely report eddy covariance flux data for validation purposes of the gradient measurements.

RC: The way the material is presented further amplifies the heavy style of the MS. All tables have units that need to be multiplied with something and are also far from SI. SI for time is s not h. Unit 1/đC does just not have a place in a scientific journal. ”

AC: Ok, changed units to seconds and temperature to Kelvin in tables, but did not change Celsius to Kelvin in the text, since most readers are more familiar with the Celsius scale.

RC: If we are interested in the amount of carbon that is emitted/deposited g is just fine, if we are interested in chemistry, we should present the data in mol. The world of units is rich in things like nano, piko and femto confirming to IUPAC standards. I recommend getting rid of the multipliers in units in the text, tables and figures.

AC: We changed/revised units where necessary. Tables 1-3 were completely revised and simplified as suggested by both reviewers. We recognize that fitting to (E0 x exp (b x T)) [which in mathematical terms is no different to (E303 x exp (b x (T-303))], caused some confusion as to how to refer to a standard emission rates. This is now changed and the standard emission rate is defined as E303.

RC: Why on the earth, we move further to flux units cm s-1 as the presentation of data goes on?

AC: This is not a flux unit but an exchange velocity. It normalizes the flux by the ambient concentration. This is a more useful unit for atmospheric modeling because deposition is usually expressed and quantified as a deposition velocity (F=vd x C). For those who are not familiar with the concept of deposition velocities we report fluxes (in g/m2/s) in table 4.

RC: We learn much further in acetaldehyde part that E0 is the intercept.

AC: Ok, changed to E0c (emission at 0 ppbv ambient air concentration) and E0c303 (standard emission at 0 ppbv ambient air concentration) this should be clearly distinct from the standard emission rate which we now define as E303.

AC: Results/Discussion/Conclusion: As suggested by both reviewers we merged and clarified these sections. We deleted portions of the discussion section and merged the rest with the results section now called Results and Discussion.

RC: The determinations of the compensation point in Fig. 1 are not always convincing, especially for younger needles. e.g., in lower left panel, flux rate first increases with increasing outside concentration then decreases and then increases again. How does this constitute a fit? There are recent detailed models on oxygenated VOC emission/uptake available, partly explaining such effects by stomata. These fluctuations need discussion.

AC: We selected periods where the stomatal conductance did not change significantly. The variation observed for younger needles where caused during transitional periods caused by temperature changes most likely affecting the production rate. The leaf exchange model (the reviewer refers to) is not capable of modeling the biochemical production of VOCs and would not provide any more insights. We present a revised figure that shows typical daytime data where the temperature fluctuations were less than 1 žC. The resulting fits listed in Table 3 changed by less than 30%.

RC: Nowhere is demonstrated how the temperature dependences of the compensation points look like, but the quality of data is crucial. As for this specific figure, the panels should be better labeled to get rid of upper/lower left/right terminology, and also extensive statistics for every point are likely not needed. Simple error bars would be ok.

AC: We added a figure showing the temperature increase of the compensation point The quality of the fit of the temperature dependent compensation point experiment is reflected by the error bars (1sigma). We also included R. We now label each panel and avoid referencing to each individual figure panel. However, especially in the light of the reviewers concerns on the quality of data and variability, we believe that the statistic plots are appropriate, since they contain all the information necessary to assess uncertainties.

RC: Several aspects of diurnal variation in fluxes contrast to lab measurements as authors also admit. Can we have at least a rough idea of the breath of error bars in flux measurements, e.g. are really the leaves of Liquidambar a sink during the day?”

AC: Error bars are added to former Figure 3 and are based on an earlier study (Karl et al.,2004) comparing different counter-gradient schemes. The leaves of Liquidambar do not necessarily have to be a sink, if dry deposition to other surfaces dominate over the emission from Liquidambar. The field observations could be rationalized due to a combination of (low) methanol emission fluxes from Liquidambar and dry deposition.

RC: Can the contrasting effects be understood if we look at diurnal courses of humidity and temperature? Right now there are too many things open and the paper may be stronger if the flux data are completely removed (especially given that they will be also published separately)

AC: No, diurnal humidity fluxes at the canopy scale are dominated by loblolly pine trees and with these we get a good agreement between laboratory and field data for methanol and acetone. For acetaldehyde we believe that biochemical differences between field and laboratory might be a major reason for different exchange rates. Also, these data will not be published in a separate paper as explained earlier!

RC: Ěand temperature curves of compensation points provided or the open issues should be furnished with a understandable context.

AC: Again, we disagree that field data should be omitted (=ignored) and only things that can be explained should be presented. We clarified the corresponding text. Briefly, acetaldehyde: there is no clear evidence that plant physiological differences (between field and laboratory data) reflected by temperature and humidity are the main reason for the observed discrepancies. It appears that biochemical differences (e.g. substrate, amount of enzyme or enzyme activity) mostly likely affected the production rate as stated in the text. Methanol and Acetone: (see also response to comments by reviewer 1) Methanol and acetone emissions agree between field and laboratory expermiments for loblolly pine. We do not see a big discrepancy here. Understory species typically 'see' less light and therefore transpiration rates and stomatal conductance were likely lower in the field resulting in lower emissions. Overall the canopy acted as sink which could be explained by a combination of small emission and dry deposition to the ground and other surfaces. We note that only the exchange rate of the more soluble/polar species (methanol) is significantly below 0. Leaf age differences could also have contributed to the fact that sweetgum showed higher methanol emissions in the laboratory.

RC: The difficulties associated with the dichotomy of the data become particularly clear in the Abstract, where lab and field are completely mixed. For instance, Abstract tells of ozone experiment, but it is not clear whether it was condicted in the field or in the lab. From where the evidence for specific statements comes is also not clear. Different sets of data should be better separated.

AC: Whenever applicable we now state laboratory or field data.

RC: - p5876,l3. MVK+MAC is nowhere defined. Not that it does not make sense to me, but this paper likely tries to address a broad audience, I guess, not only specialists.

AC: Ok, we mention methyl vinyl ketone and methacrolein in abstract and text.

RC: p5876,l13-14. This exponential increase is nowhere shown.

AC: Yes, the temperature dependence is shown in Table 2.

RC: -p5878,l19 tells that a mechanistic model has been developed. Why not to use this here or what we need to know beyond this model?

AC: For field data the model is not applicable because of too many unknowns. For laboratory measurements it could help to include more detailed biochemical production mechanisms for acetaldehyde in the future. For long term datasets the model could be used to normalize data according to plant physiological parameters and together with better parameterization of biochemical production mechanisms provide more insights in acetaldehyde metabolism. In the present study changes of acetaldehyde exchange during steady state conditions were mostly related to changes in the production rate. We acknowledge that during transitional periods (e.g. light off) the dynamics of VOC x-change can be influenced by plant physiological changes. However this is not the focus in the present study.

RC: -p5879 add USA to equipment manufactures.

AC: Ok. Added USA where necessary.

RC: -p5879,l13. What is zero air? Air without CO2? or without CO2, O2 and water vapor?

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AC: By definition air contains 20% oxygen! We mainly refer to zero air as air without VOCs, CO2 and any other impurities (also includes water vapor).

RC: -p5880, middle This effect seems that important that a figure is warranted. How small is small in line 17?" and "-p5884,l25-30. This is not visible in Table 2.

AC: Our previous statement might have been somewhat misleading. It is true that the background for compounds shown in Figure 2 during the addition of ozone in the empty glass cuvette was typically much less impacted than the background in Teflon lines. It is also true that the overall increase in the empty cuvette for these species was typically much less compared to when a plant was placed inside the cuvette ($<$20%). However the background for some compounds, in particular for acetaldehyde increased significantly. E.g. for experiments with a plant kept inside the cuvette, the concentration change of acetaldehyde was on the order of 4-8 ppb. For comparison, the acetaldehyde background for the blank could increase by as much as 2 ppb. We added these concentration data in the paragraph on acetaldehyde in the revised manuscript; thus a real quantitative analysis of the compensation point change during ozone fumigation is not possible due to varying conditions of the acetaldehyde background. This was also the reason why we did not include the data in former table 2. (now table 3). We also added a reference: Northway et al. (2004) reported similar artifact formation of acetaldehyde due to high levels of ozone in Teflon tubing.

RC: -p5880 last line. This is too specific for those not familiar with Duke FACE. Fingerprint modelling (p5883,l6-7) suggests that at night some of the flux originates from elevated CO2 site. Could this have an effect on the data?"

AC: Footprint modeling? It is noted that the CO2 fumigation was turned off at night - the main wind direction pointed towards 300 degrees and only one ring was in that direction. The overall contribution to the total upwind area was only $<$10%). We do not think that this had a big impact.

RC: -p5881 Baker et al . 2005 paper. I would not leave the crucial details for this paper. However, it seems that only the gradient analysis is used in the current MS, why to describe then everything?

AC: We added a reference on eddy covariance flux techniques for details and think any other information on eddy covariance and relaxed eddy accumulation methods will be more appropriate in the intercomparison paper. We only use the disjunct eddy covariance data to validate the gradient measurements presented in this manuscript. We also extended the discussion on concentration measurements using PTR-MS as suggested by both reviewers.

RC: -p5882,l1. The problem with Pt catalyser in PTR MS is that it leaves a certain part unburnt and this is strictly concentration dependent. Check it out, accounting for this residual VOC term is important for calibration.

AC: We note that the internal instrument background noise has nothing to do with calibration! From calibration plots one can actually determine the instrument's internal background, which gives a separate means for assessing it. Concerning questions raised about the catalyst: It does not make sense that the efficiency of the catalyst should only be a problem with the PTR-MS instrument as implied by the reviewer's statement. The efficiency depends of course on the design (=amount of Pt, what Pt material (wool or pellets) and the temperature distribution inside). We operate the catalyst at 430C using a composite of Pt wool and Pt pellets and did not encounter any problems. In fact a study by Apel et al. (A Platinum-Based Cataltyic Converter for Generating Ultra-Pure Air for use in Atmospheric Chemistry Measurements." E. Apel, A. Hills, D.D. Riemer) assessed the efficiency of Pt catalytic converters for various VOCs and observed that it was not concentration dependent and greater than 98% even at much lower temperatures of 250C.

RC: - p5883,l21. Specific leaf weight is a meaningless term. Isn't that Jarvis published in 1985 a paper entitled Specific leaf weight equals 1.0. Always!

AC: Ok, changed to leaf mass per area (LMA)

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RC: p5906. Figure legend should tell that these are the compounds formed due to oxygenation rather than oxygenated compounds to agree with the main text reference to Holzinger."

AC: We changed the text to: "compounds produced from secondary gas phase oxidation."

RC: -p5888. MeOH. Why not CH3OH then.

AC: Ok, changed to methanol.

RC: -Appendix is not needed.

AC: Ok, moved appendix to experimental section.

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