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Interactive Comment

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.

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general comments:

The scientific question concerning the bi-directional exchange of oxygenated VOCs addressed in the paper is well within the scope of ACP and certainly merits publication. The high uncertainties still remaining in current emission estimates of oxygenated VOCs can be understood (i) due to the complexity of the matter, but also (ii) due to scarceness of available data. The paper presents very interesting data on both leaf level and canopy flux measurements. The scientific methods and assumptions of the



manuscript are valid, and the overall presentation well constrained. In general the results are described concisely, but I agree with the other referees that some of the units/tables/figures need improvement. In contrast to referee #2, I actually like having put together canopy flux and lab exchange data, even though the different approaches revealed some contrasting results. I would not suggest to completely remove these data (as suggested by referee #2), but in contrast I felt that highlighting discrepancies of the different approaches (enclosures versus micromet) should be one focus of the paper. Moreover, as the authors describe observations of primary physiological data (photosynthesis, transpiration, stomatal conductance) in the Experimental section, I would propose to include those in the result section and the discussion.

specific comments:

Abstract: I would suggest adding a note about the decrease in emission of oxygenated compounds in the post-ozone-fumigation phase, as I think it is an important finding (indicative of physiological stress symptoms).

Introduction: I would propose to add the most recent paper on methanol and MVK/MACR flux measurements deploying EC measurements by Spirig et al. (Spirig et al., Atmos. Chem. Phys., 5, 465-481, 2005), also as a reference in the discussion section: actually the daytime mean emission rate reported by Spirig et al. 2005 (0.31 mg m-2 h-1) fits perfectly to the daytime ILT (0.52) and EC (0.32) measurements of this manuscript, even though it was a mid-latitude forest canopy comprised mainly of Quercus robur.

Experimental: The basics of flux calculations and theory of the deployed methods are referred to elsewhere, which results in a well constrained M&M section. However, I would encourage the authors to give some more details in the methods used, as this manuscript attracts different communities, from leaf level (enclosures) to canopy level (micromet). For example comprehension of the difference between the meaning of "mean exchange velocity" and "net exchange velocity" (integral over the canopy height)

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Results/ Discussion: The authors state that rates of photosynthesis, transpiration and stomatal conductance were calculated for the enclosure measurements, but no results are mentioned in the following sections. Nothing interesting? For example, the authors state that the decrease of emission in the days following ozone fumigation may have been due to enzyme depression, but changes in primary physiology were not significant. There would be a good chance to show these data in table 2 (mean day-time photosynthesis, or max. photosynthesis, best: gross photosynthetic capacity, if available).

Like referee #2, I also am also keen on the compensation point increasing exponentially with temperature, as it is already mentioned in the abstract as one important finding.

technical and minor corrections:

Page 5877, line 23: replace "Rottenberger et al. (2004) reported the compensation point of acetaldehyde for a tropical tree species ..." by "... for 3 tropical tree species ..." or, more general: "... for tropical tree species ..."

Page 5879, line 9: add full stop after "Phytron"

Page 588, line 17: close parenthesis after "dispersion matrix"

Page 5883, line 19: 4 leaf enclosure experiments means 4 individuals? Please specify.

Page 5884, line 29: does "wound VOC emissions" mean "acetaldehyde emissions", or other compounds related to wounding (e.g. hexenals, like given above)? I find this phrase misleading.

Page 5889, line 10: The deposition of acetaldehyde during daytime is in accordance with gradient measurements by Rottenberger et al. (2004) above a tropical forest site, indicative of a strong uptake of acetaldehyde (and formaldehyde) on the canopy scale all day long (Rottenberger et al. 2004, Ecological Applications, 14(4), 2004, pp. S247-

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S262).

Page 5891, line 2: to prevent misunderstanding, I would propose to not use the term "flux" in conjunction with enclosure measurements, but rather "exchange rate" or "emission rate". To be more specific, the authors might start the sentence with "Enclosure measurements conducted on sweetgum ...".

Page 5891, line 22: Couldn't find any case where Kuhn et al. (2002) reported 0.6 nmol m-2 s-1 with a respective ambient mixing ratio of 2.5 ppb for acetic acid, as stated in the text. Rather Kuhn et al. (2002) gave calculated mean deposition velocities of 0.17 cm s-1 for the tree species Apeiba tibourbou and 0.22 cm s-1 for Hymenaea courbaril. With a given LAI of 5.5 (Kuhn et al. 2005) at that site these would translate to similar values as given for tropical vegetation by Karl et al. (2004). Even though Kuhn et al. (2002) indicated that those calculated deposition velocities rather represent a lower bound estimate, I would propose to give the quoted numbers.

Page 5892, line 6: "For all oxygenated VOCs investigated during this study ..."? This is not the case for acetic acid and acetaldehyde (Table 4).

Page 5894, line 13: the low acetaldehyde compensation point concentration found for the canopy is in good agreement with values below 0.6 ppb under clean air conditions of the wet season and of 1.1 - 2.1 ppb under polluted conditions of the dry season for different tropical tree species reported by Rottenberger et al. 2004 (Ecological Applications, 14(4), 2004, pp. S247-S262).

Table 3: The finding that the emission of acetaldehyde is dependent on the different phenological stage of the plant, i.e. old needles (especially in senescence) tend to emit more acetaldehyde than younger needles is confirmed by Rottenberger et al. (2005, Atmospheric Environment 39 (12), 2275-2279). I assume that the negative Eo of -0.33 ś0.08 ng g-1 h-1 (uptake applying zero-air) and the CP<0 for young leaves arose from measurement errors, or from invalid extrapolation of the linear correlation measured in a higher concentration range, respectively.

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Figure 3: I find diel cycles of mixing ratio profiles quite informative (e.g. as contour plot like in Karl et al. 2004, JGR 109, D18306, doi:10.1029/2004JD004738) and I would propose to show these in conjunction with the source/sink profiles.

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