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Comment

## ***Interactive comment on “Plant physiological and environmental controls over the exchange of acetaldehyde between forest canopies and the atmosphere” by K. Jardine et al.***

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general comments:

The scientific question concerning the bi-directional exchange of acetaldehyde addressed in the paper is well within the scope of BG and merits publication, particularly due to the scarceness of available data in the field of oxygenated VOC. As pointed out by the authors, compensation point measurements of oxygenated VOC are extremely rare, even though the water solubility of these compounds lets inherently assume a deposition term (to the aqueous phase of the apoplast within the substomatal caves and/or humid leaf surfaces, respectively) competing with a potential physiological pro-

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duction/emission term. The paper presents interesting data on both leaf level and canopy flux measurements. In general the results are described concisely, but some details of the presentation and conclusions need improvement/clarification. According to the model by Niinemets and Reichstein (2003) the exchange is dependent on the source (production) term, the water solubility (Henry's constant), the stomatal conductance, and the (fast and slow) aqueous storage capacity. The idea that the production may also be compensated by (physiological) consumption within the plant, preventing further plant internal accumulation, is indeed a critical detail that extends the more physicochemical view of the aforementioned model. However, the impact of the stomata on the emission rate (and  $\Delta c$ , respectively) is also dependent on the size of the aqueous storage pool, the pH and the temperature; all influencing the Henry's law concept (see also Gabriel et al. 1999).

specific comments:

I actually like having put together canopy flux and the lab exchange data. However, from my point of view, I am not as positive on the general agreement between both data sets as the authors tend to declare. In the lab mainly emissions (and very high compensation points) were observed, and in the field mainly deposition. In Fig. 8 the calculated canopy fluxes mainly revealed deposition for Michigan (MI), and North Carolina (NC). In North Carolina the peak in LAI rather corresponds with the strongest deposition flux (substantiating the emission scenario stated on page 2660, line 8 ff). In the Michigan case the peak in LAI (0.7 at 20m) actually corresponds to a mix of the strongest emission (calculated for 22m) and the strongest deposition (calculated for 17m), both of similar magnitude. The observed deposition fluxes are similar to those reported in Karl et al. (2005). According to the high compensation point concentrations found by the enclosure measurements, a strong emission would have to be assumed at the field sites with ambient concentrations below those of the compensation points, even as measured under absolutely dark conditions in the lab. Highlighting and discussing the discrepancies of the different approaches (enclosures versus the

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Lagrangian approach) could be one focus of the paper. For example, Karl et al. (2005, ACP) reported that ambient temperature lead to higher compensation points. How did the temperatures applied in the lab compare to those in the field flux sites? The temperatures in the lab should have been higher than at the field sites to help to explain the discrepancies.

With compensation points under irradiation far exceeding any previous published values (page 2661, line 2), I wonder whether secondary production of acetaldehyde might have mimicked acetaldehyde emissions within the enclosure due to strong accumulation and degradation of primarily emitted reactive VOC precursor compounds (by O<sub>3</sub> at the enclosure inlet or OH produced by the 1000 Watt high intensity discharge lamp)? For highly reactive VOC emitted like e.g. b-Caryophyllene or a-Terpinene estimated atmospheric lifetimes are in the order of seconds to minutes, and gas phase oxidation could play a role. See Neeb et al. 1997 for details on the potential role of secondary production of carbonyls in enclosure studies. The secondary production of primarily emitted VOC is assumed to also play a major role in determining the profiles of oxygenated VOC within and above the canopy (Karl et al., 2005; Rottenberger et al. 2004; Holzinger et al. 2004), and we very recently learned that high isoprene mixing ratios do not necessarily deplete OH at least over forest canopies (Lelieveld et al. 2008, Nature).

With a residence time of 5min, could the plants have suffered from CO<sub>2</sub> depletion within the enclosure?

The discrimination rate of C<sub>13</sub> acetaldehyde by stomatal uptake (or respective enrichment in the enclosure air) was used as an additional indication of the preference by stomatal uptake of acetaldehyde versus the uptake by the leaf surface. Fractionation factors reflect both physiological (e.g. discrimination of the enzyme Rubisco in the case of CO<sub>2</sub>) and internal constraints of stomatal conductance and diffusion across cell walls. Indeed I found it an interesting approach to show the discrimination of acetaldehyde by observing the isotope ratios in the enclosure headspace air. If a dry dead leaf is put in the enclosure and no acetaldehyde uptake is observed (while the live leaf

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does take up), then deposition to this dry surface can be neglected. This is quite an important finding (and I would also be curious whether a humidified leaf surfaces would do the same). But I do not comprehend which additional information in this context the  $^{13}\text{C}$  discrimination does tell us (page 2661, line 19). As mentioned by the authors, the deposition to the surface of the live leaf surface would be prone to the  $^{13}\text{C}$  discrimination as well (via diffusion through the molecular-turbulent leaf layer, referring to Rb). The arguing is based on the assumption that the dead leaf surface can only be a temporary sink; but even then the diffusion through the molecular-turbulent layer at the leaf surface should not lead to a change in  $^{13}\text{C}$  discrimination, as the same rules of fractionation apply to diffusion to the surface (Rb) and through the stomata (Rs). May be I just missed the point, please clarify.

Moreover, a dry surface of dead leaves might not resemble the physicochemical properties of a live (humid) leaf. To inspire the discussion on the role of leaf surface, I might refer to measurements carried out in our lab (mentioned in Rottenberger et al. 2008): data provided experimental evidence that (passive) cuticular uptake can play a substantial role in the exchange process. Acetaldehyde uptake remained high when fumigating with mixing ratios of 15-25 ppb acetaldehyde even when stomatal closure of *Quercus ilex* leaves was artificially induced by treatment with abscisic acid. Also the exchange of organic acids of dead leaf litter was found to be strongly dependent on the water content of the dead leaves, with strong uptake on humid surfaces, which only ceased (and changed to emissions from a certain threshold level on) when leaves were dried. However, differentiation between the different impacts of pure physicochemical deposition onto the hydrophobic cuticle or onto humid leaf surface components and/or the involvement of active uptake by surface biological consumers could not be provided. I also have to acknowledge that live leaves with very low transpiration rate during dark conditions investigated in the manuscript discussed inhere did not act as a significant sink, though (page 2661, line 15).

The authors state (page 2654, line 14) that they used the mixing ratios at the enclosure

inlet to calculate the acetaldehyde exchange velocities (g gdw-1 ppbv-1 h-1), as was actually also the case in Rottenberger et al. (2008). However, in a very similar study of part of the same group (Karl et al. 2005), the mixing ratios at the enclosure outlet were used. Is there any reasoning for the change? This is a general problem in literature, as the slopes are of course different with the two approaches and the absolute numbers therefore not really comparable (as e.g., is also the case in Fig. 5). I have to admit, though, that I do not have a proper solution for this problem, but it might be a good start to bring this issue up in a discussion forum like BGD.

technical and minor corrections:

Page 2646, line 5: "Net ecosystem emission rates were inversely related to foliar density which influenced the extinction of light and the acetaldehyde compensation point in the canopy" might be misleading. I would propose: "Net ecosystem emission rates were inversely related to foliar density due to the extinction of light in the canopy and a respective decrease of the acetaldehyde compensation point."

Page 2646, line 22: "We conclude that the exchange of acetaldehyde between plant canopies and the atmosphere is fundamentally controlled by ambient acetaldehyde concentrations, stomatal conductance, and the acetaldehyde compensation point." I would propose to add the strong light/temperature dependence of production/emission in the abstract.

Page 2651, line 5: replace "though" by "through"

Page 2652, line 19: replace "though" by "through"

Page 2654, line 11: replace "Acetaldehyde exchange velocities (g gdw-1 ppbv-1 h-1) were estimated by determining the slope of the regression of acetaldehyde concentrations at the enclosure inlet in ppbv (x-axis) against the acetaldehyde exchange flux in g gdw-1 h-1 (y-axis)." by "Acetaldehyde exchange velocities (g gdw-1 ppbv-1 h-1) were estimated by determining the slope of the regression of acetaldehyde exchange flux in

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g gdw-1 h- (y-axis) against acetaldehyde concentrations at the enclosure inlet in ppbv (x-axis)", as it is expressed on page 2658, line 13.

Page 2654 line 14 (and also in the legend of Fig. 5): "The acetaldehyde exchange velocities are reported as the absolute value of the slopes (all slopes were negative)." I would propose to say the "... reported as negative values of the slopes (all slopes were negative)", which would actually say the same, but still leaves a change in sign open. In either way, and for the sake of consistency, the exchange velocities in Fig. 3 and 4 should then also be plotted in positive numbers, as in the comparison plot of Fig. 5. The units of Fig. 3+4 should additionally be given in m s<sup>-1</sup> (as in Fig.5). The assumptions and uncertainty of the dry weight to surface area conversion is already stated on page 2654, lines 17 ff.

Page 2656, line 27: replace "thee" with "three"

Page 2657, line 15: The procedure of flux calculations might need some more explanations (or at least cite Karl et al. (2004) also here for the calculation procedure, not only for the site details mentioned above).

Page 2660, line 6: replace "thee" with "tree"

Page 2665, line 10: replace "thee" by "three"

Page 2666, line 3: replace "though" by "through"

Page 2665, line 15: "... the driving force for acetaldehyde exchange with plants (EC) is relatively independent of stomatal resistance allowing stomatal behavior to strongly influence exchange rates." sounds contradictory to me.

Page 2666, line 3: "... degrade regional air pollution." may be misleading. I would propose "By increasing plant compensation points, future predicted increases in surface temperatures and landscape changes associated with a reduction in foliar density may potentially increase rather than mitigate regional air pollution."

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Fig. 6: as the long-term measurement was carried out throughout nighttime on 24. April 2007: it would be interesting to note whether the (none excised, unlike in Jardine 2008, I assume) branch was under light conditions or dark conditions, or whether a change in light conditions occurred without any change in the carbon isotope fractionation pattern.

cited literature:

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Neeb, P., Bode, K., Beck, J., Schäfer, L., Kesselmeier, J., and Moortgat, G. K.: Influence of gas-phase oxidation on estimated emission rates of biogenic hydrocarbons: In Proceedings of the 7th European Symposium on Physico-Chemical Behaviour of

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Atmospheric Pollutants: The Oxidizing Capacity of the Troposphere, Office for Official Publications of the European Communities, Luxembourg (EUR 17482) ISBN 92-828-0158-6, pp. 295-299, 1997b.

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