

## ***Interactive comment on “Methanol and other VOC fluxes from a Danish beech forest during springtime” by G. W. Schade et al.***

**Anonymous Referee #2**

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Given the dearth of studies (virtually all of which are cited here) examining above-canopy fluxes of light-weight oxygenated VOC, I welcomed the appearance of one more. In this submission, the authors estimate above-canopy fluxes using the relaxed eddy accumulation technique, within canopy concentration gradients, and soil uptake using static enclosures. In all cases, VOC mixing ratios were measured using PTR-MS. Although numerous m/z values were included in the measurement protocol (including those associated with methanol, acetone, acetaldehyde, isoprene, total monoterpenes, methyl ethyl ketone and the reaction products methacrolein and MVK), only data concerning methanol and monoterpenes is presented in any detail. The manuscript is well-written and clear for the most part, and relevant to potential readers of BGSD. Unfortunately, I don't have great confidence in either the reliability of the data or the

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interpretation of results.

The Relaxed Eddy Accumulation technique is difficult and prone to error, relying as it does on rapid switching valves, pumps, bags or adsorbent cartridges, etc. This is particularly true when measuring relatively low concentrations of light-weight oxygenated compounds which are sticky and have their own analytical problems. I commend the authors for being honest and forthcoming about some of the difficulties encountered, in particular problems with the Tedlar reservoirs, but I confess I'm not left with a great deal of confidence in the extremely noisy data sets which result. In general, for those compounds that can be measured at several Hz using PTR-MS or other analytical instruments, I have much greater confidence in eddy covariance methods than in relaxed eddy accumulation.

Relatively few concrete conclusions are drawn from the data. One is that monoterpene emissions from *Fagus sylvatica* are light-dependent, evidenced by a clear diurnal pattern, with fluxes and within canopy concentrations peaking around mid-day to early afternoon. This result is a useful confirmation of several previous studies at both canopy and leaf scales, which clearly demonstrated a light-dependency of such emissions, but contributes nothing new to our understanding. The observed monoterpene concentrations at 21 m were on average only about 10% of those observed at the same site (but at 31 m) during the same time period several years previously. The authors make a plausible argument, based on the mixture of observed monoterpenes and wind direction, that the high mixing ratios and fluxes seen in the previous study represented emissions from a small grove of pine trees a few hundred meters to the SE, although if pines occupy only about 20% of the site, it's somewhat implausible that they should totally dominate the observations. Although winds also came from the SE for a substantial portion of the measurement period in the current study, at no time did total monoterpene mixing ratios exceed about 100-150 ppt. Perhaps samples collected within the canopy at 21 m are shielded somewhat from any upwind pine emissions, but they should have been observed in fluxes and mixing ratios at 41 m. And since no

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attempt was made to speciate the observed monoterpenes in this study or compare them with leaf-level emissions, it is difficult to assess their proposed explanation for the discrepancy between their and previous results.

I'm a bit confused about how the monoterpene fluxes were modeled (p. 4330, l. 25). LAI at the site is reported to be 5 m<sup>2</sup>/m<sup>2</sup>, but in the modeling exercise, the canopy consists of three layers, each with LAI of 1 m<sup>2</sup>/m<sup>2</sup>. Was data from each measured day fit independently to the model, resulting in a range of best-fit standard emission factors? If so, wouldn't it be preferable to obtain a value for standard emission factor that best fit all the data, since the (questionable) assumption is that standard emission factor shouldn't change over the two week study? If standard emission factor does appear to change, is there a discernible pattern? Higher following warm days, for example?

The second major conclusion of the manuscript is that MeOH emissions occur "dominantly late at night"? This observation is broadly consistent with the elegant results of Hüve et al. who demonstrated very strong correlations between leaf expansion rates in beech (which were highest during the night) and rates of MeOH emission. However, I have difficulty reconciling the authors' conclusion with the data presented in Fig. 4, in which the highest rates of emission apparently occur during the day. It almost appears as if they were expecting high nighttime emissions and interpreted their results in the light of that expectation (see, for example, p. 4329, l. 7, "the expected nighttime emissions were less frequently observed"). The seemingly unlikely/anomalous MeOH deposition observed around noon is apparently the result of only 3 days of observation. On what basis were the remaining days excluded? The authors also cite the fact that observed mixing ratios were highest late at night as evidence for significant nighttime emissions, but acknowledge that they may also have resulted from the concentrating effect of a shallow nighttime boundary layer. I think the mixing ratio maximum suggests the occurrence of nighttime emissions, but without any other information, it's very difficult to quantify those emissions or compare them with emissions during the day. Furthermore, if MeOH emissions are largely the result of the demethylation of

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pectin during leaf expansion, there's little reason to expect enhanced nighttime emissions during this campaign, since leaf expansion had apparently largely ceased several weeks earlier. Finally, statements such as (p. 4329, l. 5) "MeOH fluxes did not follow a clear diurnal cycle on most days" or (p. 4329, l. 18) "there is insignificant evidence that nighttime MeOH emissions of beech may still be higher than daytime emissions" seem to contradict the major conclusion of the paper. The authors provide a median daytime flux of 0.08 mgC/m<sup>2</sup>/h but don't provide a nighttime estimate, which based on Fig. 4, appears to be less.

Given the difficulties in measuring MeOH and interpreting the data, I have little confidence in statements concerning the flux of acetone or other BVOC, for which no data is presented.

Results reported here contrast with a number of previous reports which have demonstrated deposition of MeOH and other BVOC at night and in lower canopy levels. Although MeOH deposition was observed, it doesn't seem to have followed any discernible pattern, except that is tended to be observed (as one would expect) when ambient mixing ratios were high. Lack of any nighttime deposition may be due to significant nighttime production of MeOH, as the authors suggest, but by the authors' admission, the data set is too small (and noisy?) to draw any conclusions about the relative importance of emission/deposition.

I have no experience measuring fluxes using static chambers, but I found the description of the method (Sect. 2.5) very confusing. If the chamber is ventilated, how do you correct for leaks into the chamber without using some sort of tracer compound? Similarly, if the chamber is placed directly on the ground (i.e., without some sort of collar extending into the soil) how can you preclude leaks at the soil-chamber interface? By 'chamber effect' do you mean the release/uptake of various VOC by the walls of the chamber? And when you determine the 'chamber effect', is the chamber placed onto a plexiglass bottom section? You indicate that the assumption of zero production is not valid for VOCs, but I don't understand "all OVOCs. . . showed a zero order produc-

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tion rate as the chamber effect." Does the concentration inside the chamber equilibrate within 10-15 minutes? If so, then I agree that sources equal sinks, but how can the source term be equated with the 'chamber effect'? Doesn't this imply no production from the soil itself? I'm sorry, I just don't understand the procedure. Perhaps a plot illustrating the time course of concentration changes over the course of an experiment would clarify things for me. Little soil chamber data is presented, but based on standard deviation values reported, deposition rates were extremely variable, perhaps to be expected.

The authors make the valid point that "controlled enclosure studies alongside carefully devised field measurements appear necessary to shed more light on these complex carbon exchanges" particularly if we wish to partition net fluxes into emission/deposition and distinguish stomatal and non-stomatal definition. I will take this opportunity to encourage the flux community to begin developing a more unified theory of bi-directional OVOC fluxes, based on the assumption that all such fluxes follow compensation point behavior. In the absence of non-stomatal deposition, fluxes should obey Fick's law, being proportional to the difference in partial pressure between the internal air space of the leaf (in equilibrium with the aqueous phase concentration) and that in ambient air outside the leaf boundary layer. The partial pressure inside the leaf presumably represents a balance between rates of production and consumption while that outside the leaf is independent of leaf processes. Only by making extensive measurements of compensation point behavior (at the leaf/branch scale) as a function of temperature, light (?) and any other potentially controlling variables can we make progress in understanding the complex behavior of these bidirectional fluxes, or assess the relative importance of stomatal vs. non-stomatal deposition.

Minor specific suggestions.

p. 4316, l. 13 "contrasted with earlier results"

p. 4319, l. 24 what is the average canopy height?

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- p. 4320, l. 6 what is the manufacturer/model of the plant canopy analyzer?
- p. 4321, l. 4 the sonic extended west; was this the dominant wind direction?
- p. 4321, l. 19 please give manufacturer for PTR-MS
- p. 4322, l. 16 "(same model as on tower gradient)"
- p. 4322, l. 19 control channels or control ports?
- p. 4325, l. 2 monoterpene emissions by no means restricted to conifers
- p. 4334, l. 3 "comes as no surprise"

Table 1. Why not report soil emissions, rather than classify them as Not Applicable?

Fig. 2 You refer in the text to Fig. 2a-d, but letters don't appear on the figure

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