

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

Anonymous Referee #1

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SPECIFIC COMMENTS - PART 2 (Detailed Discussion of the Paper)

3 VOC concentrations and fluxes

3a p4329, line 8+: "Due to lack of sufficient turbulence the expected nighttime emissions were less frequently observed. However, as shown in Figure 4, median turbulent nighttime fluxes were dominantly upward while a larger number of daytime fluxes were downward or insignificantly different from neutral (Fig. 3)." This is a misinterpretation of the data shown in Fig 3 and 4!

ad Figure 3: The depiction of the flux data does not allow to clearly conclude upward night time fluxes and downward or insignificant fluxes during the day. A larger graph and a vertical grid might improve the visualisation. There seem to be clear positive

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day time fluxes e.g. on DOY 162 and 166 and lot of scatter on the whole flux data set. On DOY 163 and 171 flux values are out of the depicted range - what magnitude are they and why are they not shown? The 95% confidence interval for the bag intercomparison may be one aspect of but is certainly not the overall detection limit for the flux measurement (see discussion above) - a proper analysis of the limit of detection would help interpreting the data!

ad Figure 4: This is in principle a good way to present the data but the data-set is too small.

I. The calculation of quartile values for very limited data-sets is questionable, for $N < 5$ it seems meaningless.

II. At 3a.m. median falls together with the upper quartile. How is that possible?

III. The downward flux at noon seems to be "almost significant" according to the depiction but that might be due to $N=3$ (two positive and one negative flux in this hour of the day within the 18 day period).

IV. At 11p.m. $N=2$: Is the median calculated as the arithmetic mean of the "middle" two data points? In this case there are only two data points at all. Presenting the mean value of two data points is certainly not an adequate way of data reduction.

V. There is not a single one-hour period where the whole inter-quartile range is negative but the authors state "a large number of day time fluxes were downward or ... neutral"!

VI. On the other hand fluxes at 1p.m., 2p.m. and 3p.m. are backed-up by $N=8, 10$ and 9 , respectively, and their inter-quartile range is positive. The authors ignore that and state downward daytime fluxes!

Overall it seems the data interpretation was dominantly driven by "the expected night-time emissions" rather than the data itself.

3b p4329, line 18+: "However, there is insignificant evidence from our data that night-

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time methanol emissions of beech may still be higher than daytime emissions at this stage of leaf development in the field." Why bother to discuss "insignificant evidences" - discuss the results that do allow a conclusion!

3c p4329, line 21+: "Similar to previous studies..." Which studies? Own ones or other work - no citations! In the 18 day measurement period (>800 half hours) only about 30 half-hour flux values are below the lower threshold (Fig 3). Which data points were selected to run a "robust regression" on to determine a Methanol deposition velocity of $1.1 \pm 0.5 \text{ cm s}^{-1}$? The authors may want to describe in more detail the criteria that led to the data sub-set from which deposition velocities were determined (e.g. significant flux, significant downward flux, significant downward flux during the day,... not just "when observed") . What data was used to determine the "ambient mixing ratio"?

3d p4329, line 29 to p4330, line 17:

"Other OVOC fluxes..."

"methanol was generally the highest of all OVOC fluxes"

"acetaldehyde and MEK largely insignificant..."

"...acetone fluxes were generally significant".

Even the discussion of the Methanol data seems to be very problematic (see above) therefore the authors may want to substantiate their conclusion about the "general significance of the acetone fluxes" by proper depiction and discussion of those data. A footprint analysis may help in general and particularly in those cases where the size of the forest and the adjacent ecosystems cause problems in the interpretation of the flux data.

3e p4330, line 27+: "Model runs that matched the measurements within a factor of two resulted in standard emission factors ranging from 0.10 to 0.37 $\text{mgC m}^{-2} \text{ h}^{-1}$ (0.2 to 0.8 $\text{nmol m}^{-2} \text{ s}^{-1}$), comparing well with typical values given by Holzke et al. (2006)." What does that mean? Did the authors have to tune "standard emission factors" throughout

the measurement period to match the measured data within a factor of two? What model approach was used? A standard emission factor is by definition a (constant) parameter of the emission model rather than a range of values (see Guenther et al, 1993** , citations therein and further algorithm development based on the "Guenther Algorithm"). The value is the (hypothetic) emission rate at defined standard conditions (30°C, 1000 PAR) and the model accounts for the variations of temperature and radiation. The emission model can only reflect factors for which it was developed. If other factors (e.g. seasonality, weather history, "limited fetch conditions",...) influence the measured fluxes the presentation of a range of standard emission factors for a model that is obviously not appropriate is not the way to go and certainly not a source of evidence for further conclusions (see next paragraph).

3f p4331, line 1+: "Hence, despite the limited fetch conditions for beech at this site (Dellwik and Jensen, 2005) our measurements are highly consistent with previous results from enclosure measurements on trees that grew in a similar climate." The authors conclude "high consistence" between their results and other work (whose? No citations) despite shortcomings (limited fetch conditions) of their own experiments. Consistence might be deducible because of shortcomings in the set-up, evaluation and interpretation rather than in spite of limited fetch conditions. The authors need to work on their arguments!

4 Canopy gradients

4a p4331, line 23+: "This was most prominent for methanol and the monoterpenes emitted in the canopy" How can the authors distinguish between VOC emitted in the canopy and advected VOCs? The gradient inlets were at 22, 14 and 5 meters, respectively but the canopy is some 25m high. Air samples drawn at 41m are segregated (up/down) and might be biased by the sampling procedure (Teflon pump, bag effect,...) and were therefore, correctly, not included in the gradient data. The authors might want to comment why they did not have one gradient inlet above/on top of the canopy.

4b p4332, line 5-6: "Hence, in both these cases, our gradient measurements support the conclusions from the previous section." This conclusion is far too general! Which conclusions from the section "VOC concentrations and fluxes" are supported by the gradient measurements? As discussed above some of the data on which the conclusions are based on are either not convincing or not (completely) shown.

4c p4332, line 7-8: "The gradient measurements cannot, unfortunately, support or reject the above estimated deposition velocity for methanol of approximately 1 cm s⁻¹." Are the gradient data inconsistent with the flux measurement results? State how the deposition velocity was estimated (see discussion above).

4d p4333, line 3+: The authors discuss "major changes in the gradients... after the wind direction shift on DOY 170..." and state "During the mornings of the last 4 days of the campaign..." (DOY 171, 172, 173, 174) "...the gradient inlet lines were used for the soil chamber flux measurements." For what periods are gradient data available? How can the authors exclude that the systematically missing data would not affect the discussion of gradient results? The gradient data shown (Fig 6 - methanol after DOY 164; Fig 7 - monoterpenes before DOY 165) do not allow to follow the author's arguments.

5 Soil chamber flux measurements

5a p4333. line 16+: soil chamber flux measurements Some questions about the chamber experiments are asked above regarding the set-up, adequacy of data-analysis and discussion of the results. The authors may want to make a point how the data shown in Tab 1 (1*sigma standard deviations of up to 150%) allow even a conclusion about the direction of the soil-chamber VOC exchange.

6 Conclusions

6a p4335, line 6-7: "Our result of 1 cm s⁻¹ was within the range of previously determined values." The values in the literature cited by the authors are 3-4 times smaller

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than ~1cm s-1. That cannot be declared "the same range"!

6b p4336, line 3-4: "Our results confirm that the biosphere-atmosphere exchange of oxygenated VOCs is highly complex." The complexity of the biosphere-atmosphere OVOC exchange is not reflected in the presented results. The paper rather confirms that the measurement of OVOC exchanged between biosphere and atmosphere is difficult.

6c p4334, line 24 - p4336, line 12: Conclusions General statement: The authors need to revise the whole Conclusions chapter for those conclusions that are fully or in part (see discussion above) not substantiated by the presented data. A thorough revision of the lines of arguments is necessary.

ADDITIONAL REFERENCES

** Guenther, A. B., Zimmerman, P. R., Harley, P. C., Monson, R. K. and Fall, R., 1993. Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analyses. *Journal of Geophysical Research* 98, 12609-12618.

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