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Biogeosciences Discussions

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

G. W. Schade et al.

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reviewer's comments in italic:

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 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 95ad 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 nighttime emissions" rather than the data itself.

We have reanalyzed the data regarding bag effects, including bag changes (see reply to Part 1), and background. A few more data points were deemed unreliable. The previously depicted range in Fig. 3 had been chosen for visibility. We agree with the reviewer that the previous Figure 4 is an unfortunate depiction, more confusing than helpful. We have removed the graph and now a histogram instead (available at http://geotest.tamu.edu/userfiles/226/BGDreplygraphs.htm). This shows that – while many measurements fall on the central, non-significant-flux-bar – more daytime than nighttime measurements showed deposition fluxes. However, daytime fluxes were also significantly higher on the emission side of the histogram. These fluxes occurred on the warmest days. We do not speculate any longer what this may or may not mean with respect to the previous, controlled chamber experiments by Hueve et al.

The revised manuscript now reads (4328-4329): "Measured methanol fluxes are shown

BGD

5, S2626–S2639, 2009

in Fig. 3. Significant emission fluxes above the canopy were observed during the whole campaign. Unfortunately, campaign start was delayed by several weeks, missing the leaf-out period in May. An analysis of the onsite PAR measurements above the canopy and at three levels below the canopy top (19, 14, and 5 m) showed that two thirds of onsite LAI are above 19 m but any LAI increases during June 2007 at the tower itself were negligible (<0.3 m2 m-2). Hence, the potentially most intensive methanol emission period was likely missed. In addition, observed methanol fluxes did not follow a clear diurnal cycle on many days, with the exception of the period of and following the warmest day (DOY 162, 11 June 2007), on which the highest fluxes occurred in the early afternoon. Also during this period, elevated morning emissions (08:00 h standard time) were more common. Figure 4 shows the distribution of daytime and nighttime methanol fluxes. Daytime fluxes displayed a maximum near zero flux, and a leptokurtic distribution with tails at both the emission and deposition ends. Nighttime fluxes were fewer due to the turbulence criterion, but displayed a mean emission flux and a near-normal distribution (median = mean). Median 10:00 to 16:00 h methanol fluxes before DOY 167 were 0.06 mg C m-2 h-1, but dropped to <0.01 mg C m-2 h-1 after DOY 167. Median midnight to 06:00 h methanol fluxes for the whole period were 0.02 mg C m-2 h-1 and remained unchanged. In addition, only 4 out of 33 measurements during these nighttime hours were towards the canopy suggesting a small but consistent late night source. We can compare some aspects of our results to the controlled measurements on beech seedlings by Hueve and coworkers (Hueve et al., 2007). At the end of their experiment when leaf expansion had not yet ceased, these authors recorded a daytime methanol emission rate of approximately 0.22 nmol m-2 s-1, and a several times higher rate at night. Our median, LAI-adjusted 10:00 to 16:00 h flux of approximately 0.3 nmol m-2 s-1 for the first period is surprisingly similar to the seedling value. However, our median nighttime fluxes as well as the second period daytime fluxes were much lower. Possible explanations may lie in the age of the beech trees, particularly the lack of stomatal control in the beech seedlings versus the strong stomatal control of the mature trees at the Soroe site as evident from near zero water vapor fluxes during

BGD

5, S2626–S2639, 2009

virtually all nights for which data is available."

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

Agreed. See above.

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 +/- 0.5cm 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"?

This section has been rewritten for clarification to read:

"Measured negative methanol fluxes (deposition) were not strongly correlated with any other measured parameter. We merely found a tendency of deposition fluxes to increase with ambient methanol mixing ratio. A resistant regression (minimizing the sorted squared residuals) to all negative flux values versus the in-canopy mixing ratios suggested an exchange velocity of -1.1+-0.9 cm s-1. This is comparable to the upper limits reported by Karl and coworkers (Karl et al., 2004, 2005a) for the maximum LAI region of a tropical and a pine forest, respectively. However, the uncertainty of this value is high and therefore its significance low."

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

BGD

5, S2626–S2639, 2009

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.

We have added a plot for the acetone flux data (available at http://geotest.tamu.edu/userfiles/226/BGDreplygraphs.htm). The respective paragraph (page 4330) now reads:

"Other OVOC fluxes were generally lower than those of methanol, with exceptions after the wind shift on DOY 170, which we attribute to the nearby hay field mowing (Sect. 4). Similar to methanol, acetone fluxes were found to be bidirectional: Emissions were observed on the two warmest days (DOY 161, 162), while deposition was observed for most of the remaining period until the DOY 170 wind shift. Aggregated acetone fluxes, shown in Figure 5, were significantly correlated (r2=0.53, p<0.01) with ambient temperature, similar to previous studies (e.g. Schade and Goldstein, 2001). The temperature dependence factor evaluated from Fig. 5 (using both regressions) was 0.04+-0.02 K-1, the standard emission 0.05+-0.02 mg C m-2 h-1 (22 ng m-2 s-1) at 30 deg C. This is significantly less than previously found for pine forests (Karl et al., 2005; Schade and Goldstein, 2001; Janson et al., 1999), but comparable to Norway spruce needle measurements (Grabmer et al., 2006; Janson and de Serves, 2001). A compensation-point equivalent temperature of approximately 20 deg C resulted from the temperature-dependence (Fig. 5), but a correlation of deposition fluxes with ambient mixing ratios of acetone was not found. Acetone abundance was generally below 1 ppb under these conditions, which suggests that its deposition depends on more factors than just abundance. We also analyzed the flux data for m/z 45 (acetaldehyde) and m/z 73 (MEK), but the results showed mostly insignificant fluxes when compared to the error estimate from the bag intercomparison samples. Still, when considering the largest bag differences found in each case, exchange velocities of several centimeters

BGD

5, S2626–S2639, 2009

per second can be calculated. Hence, our flux measurement method is not appropriate to determine small VOC fluxes."

*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 mgC m-2 h-1 (0.2 to 0.8 nmol m-2 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).*

The reviewer's point is well taken. For the model, we assumed uniform top-of-canopy-distribution (above 19 m agl) of three 1 m2 m-2 LAI layers. As described in the text, the model listed by Holzke et al. (2006) was used with a variable standard emission, but the same for all layers. Due to the potential errors in our measurements, and the spread of emission rates found by Holzke et al. (2006) we considered a factor of two difference between measurements and model as an acceptable range. The only pertinent variable for that range in the model is the standard emission rate, for which reason we gave it in the manuscript. Again, we have reevaluated the data, and now also include a range for LAI in the top layers (>14 m agl) as another variable. To clarify the procedure, the manuscript now reads:

"Monoterpene fluxes from European beech have been measured by Schuh et al.

BGD

5, S2626–S2639, 2009

(1997), and were recently reevaluated by Holzke et al. (2006) and Dindorf et al. (2006) on trees in northern Germany. All these authors found substantial, light-driven emissions and a high variability of standard emission factors (at 1000 micromol m-2 s-1 PAR and 30 deg C). Our own measurements, shown in Fig. 6, confirm the diurnal cycle of emissions with maximum fluxes on the warmest, cloud-free days of the campaign. To compare to the previously published leaf and branch chamber emission data, we carried out a series of model runs using the light- and temperature dependence model given by Holzke et al. (2006). We assumed a three-layer canopy top (>14 m agl) with LAI values of 1 to 1.5 m-2 m-2 each as estimated from the sub-canopy PAR gradients, uniform canopy temperatures equal to the sonic virtual temperature, and an ellipsoidal leaf angle distribution with a twice as high portion of horizontally oriented leaves. LAI and standard emission factor were treated as variables, but remained the same for all layers. Accepting a deviance of a factor of two between model and measurements resulted in possible standard emission factors between 0.10 and 0.38 mg C m-2 h-1 (0.2 to 0.8 nmol m-2 s-1). The best match was achieved for an emission of 0.19 mg C m-2 h-1, and the resulting emissions curve is included in Figure 6. The results compare well with typical values given by Holzke et al. (2006), and are strongly driven by the high flux data on days with good fetch conditions, such as early in the campaign. Somewhat more limited fetch conditions for beech at this site occur under SE winds (Dellwik and Jensen, 2005). Under these conditions up to half the flux footprint (calculated using the parameterized model of Kljun et al., 2004) may contain the nearest conifer grove, and we note that higher than expected monoterpene mixing ratios and fluxes occurred on DOY 166 and the night of DOY 171/172. Although in good agreement with expectation from enclosure measurements, our results contrast with those of Gallagher and coworkers (Gallagher et al., 2000). These authors found five to ten times larger monoterpene mixing ratios and fluxes at the Soroe site in 1996. In addition, their fluxes were dominated by delta-3-carene, alpha-pinene, beta-pinene, and limonene, which are typical pine forest monoterpenes, while beech emissions were dominated by sabinene in past studies (Schuh et al., 1997; Dindorf et al., 2006; Holzke et al.,

BGD

5, S2626–S2639, 2009

2006). Although part of the monoterpene composition difference may be explained by sabinene decomposition on the trap during storage (Dindorf et al., 2006), this cannot account for the large abundance differences. As we found no record of forest activities during 1996, such as logging, that would result in large monoterpene emissions we can only speculate that their setup at 31 m height was strongly influenced by nearby emissions from the large conifer patch to the SE, which was one dominant wind direction during their study days. Footprint analysis shows that approximately 50 percent of the 6 and 7 June 1996 footprints encompassed the conifer area, which, together with higher temperatures during these measurements, may have contributed to the higher monoterpene abundances and fluxes."

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!

We have worked on improving these, see above.

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.

BGD

5, S2626–S2639, 2009

In the case of the monoterpenes, it is hard to imagine how the observed daytime canopy maximum can be created by advection, given the fact that monoterpenes are highly reactive during the daytime, and are generally higher in abundance at night in environments where their emission is not or only weakly controlled by light.

Another inlet was not installed for practical reasons: (i) it would have required installations alongside the mast, because only that extends beyond the canopy, and climbing the mast was limited for security reasons; (ii) the setup required a substantial sampling time per level (for the methanalyser), which essentially limited the cycle to three inlets if a total cycling time of one hour was to be achieved; and (iii) we did not anticipate problems with the sampling bags. The canopy inlet at 22 m was in the middle of the beech canopy, reaching from 17-19 to maximum 25 m.

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.

Agreed, as it is possible that the methanol nighttime maximum is due to advection. We have changed this section. It now reads as follows:

"The measured within (22 m) to sub canopy (5 m) gradients generally showed decreasing VOC mixing ratios towards the ground. This was most prominent for methanol and the monoterpenes emitted in the canopy. Figure 7 shows interpolated mean methanol mixing ratios as a function of height and time of day during the cooler part of the campaign: Mixing ratios were higher at night with a maximum in the early morning hours, and displayed nighttime vertical gradients of up to 0.04 ppb m-1, while daytime mixing ratios were flat. While in principle consistent with the nighttime canopy emissions under reduced turbulence as discussed above, regional advection over the forest from other sources could also produce such a pattern (see below). In fact, the morning drop

BGD

5, S2626–S2639, 2009

of ambient methanol mixing ratios of up to 20 percent per hour seen in Fig. 7 was observed for nearly all VOCs measured. As it was observed less frequently during the early June warm period, we interpret the drop as down-mixing of clean marine background air from the residual layer, particularly under northerly wind directions. This is supported by the fact that both sensible heat flux and friction velocity maximized around noon, the same time mixing ratios started to increase again. The gradient graph for monoterpenes, Figure 8, shows the opposite diurnal development compared to methanol: maximum mixing ratios and vertical gradients in the early afternoon as expected from light and temperature-driven emissions in the canopy. In this case, the gradient measurements are consistent with the findings in the previous section."

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).

Again, we are thankful for the reviewer's comment, which made us re-evaluate the data. The first sentence in that paragraph was obviously confusing. We have now changed the discussion in that paragraph to read as follows:

"The observed methanol gradients cannot support the estimated exchange velocity of -1.1 cm s-1, because we lack an additional unbiased above-canopy mixing ratio measurement. However, we found a weak correlation between the u*-normalized 14-22 m methanol gradient and the above-canopy net methanol deposition flux, which would be expected for a deposition into the canopy assuming that this process also creates a mixing ratio minimum at the 22 m level with respect to the sub-canopy measurements at 14 m. Hence, the methanol gradient measurements generally support an uptake in the canopy when above-canopy fluxes were negative."

For the reviewer's convenience, the observed relationship (Figure x3) has been posted at http://geotest.tamu.edu/userfiles/226/BGDreplygraphs.htm.

BGD

5, S2626–S2639, 2009

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 author8217;s arguments.

Several more days than the last four of the campaign were available for the calculation. Also, this affected only the methanol-graph, former Figure 6, but more so because of the additional zero catalyst measurements rather than the chamber measurements. To avoid a large "jump" in the extrapolation graph caused by too few data being averaged for the 09:00 hour, we used linear extrapolation of the surrounding data. This only affected how the graph appeared surrounding that hour, not the rest of the day. The text refers to Figure 8 (now Figure 9), not Figure 6; in reference to methanol, "(data not shown)" was in the manuscript text.

*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 percent percent) allow even a conclusion about the direction of the soil-chamber VOC exchange.*

See the reply to the reviewer's previous comments.

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

We respectfully ask the reviewer to consult the cited contributions by Karl and cowork-

BGD

5, S2626–S2639, 2009

ers from 2004 and 2005. The abstract of these publications does not reflect the full range of deposition velocities calculated/measured by those authors.

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.

We have revised the entire conclusions section. It now reads

"Our canopy flux and gradient measurements complement recent laboratory and field enclosure measurements on methanol and monoterpene emissions, respectively, from European beech. Methanol appeared to be emitted during both day- and nighttime, while monoterpenes were emitted only at daytime as their production in Fagus sylvatica leaves is light dependent. In-canopy monoterpene mixing ratios were highest during daytime as well, in line with expectations. Our monoterpene findings therefore confirmed previous laboratory and field enclosure studies. This was less clear for methanol as our data did not confirm the large nighttime emissions found in a seedling study. A small but consistent nighttime emission after midnight correlated with higher in-canopy mixing ratios only during the cooler part of the campaign. We speculate that the strong stomatal control of leaf trace gas exchange and the timing of our study probably contributed to this behavior. Ambient mixing ratios for methanol were variable with generally small gradients towards the ground. When methanol deposition to the canopy was observed, it was weakly correlated with higher ambient mixing ratios and a lower mixing ratio within the canopy as compared to below canopy. However, our data set is too small and too noisy to retrieve net deposition velocities from these relationships with an adequate uncertainty level. If methanol dry deposition to canopies were occurring

BGD

5, S2626–S2639, 2009

at a velocity of 1 cm s-1 ubiquitously, and at all times, this process would be a more important sink than previously thought. On the other hand, our reported fluxes and previously published canopy and enclosure based methanol fluxes likely already incorporate a deposition term, realizing that reported fluxes are usually net fluxes. Field studies are essentially incapable of determining gross fluxes, and budget models based on them thus cannot constrain the individual flux terms but rather only the net fluxes (e.g. Jacob et al., 2005). Possibly, controlled fumigation experiments instead may be able to determine the different roles of gross emission and deposition, as well as possible compensation points. Other VOC species analyzed included acetone, acetaldehyde, and MEK. Like methanol fluxes, acetone fluxes were found to be bidirectional. However, despite a relationship with ambient temperatures, its biosphere-atmosphere exchange pattern remained elusive. In this beech ecosystem, it was dominantly emitted above 20 deg C, and deposited below that temperature. In other ecosystems acetone was still emitted at much lower temperature (Janson and de Serves, 2001; Schade and Goldstein, 2001), wherefore temperature alone should not be used to extrapolate biospheric acetone emissions. A similar argument holds for acetaldehyde and MEK, neither of which showed a clear-cut diurnal emission or deposition pattern. Considering that our flux determination method was inadequate to resolve small exchange fluxes in the field, we infer instead from the measured sub-canopy vertical distributions that exchange fluxes must have been small because of the absence of strong gradients for these OVOCs. This was further supported by the soil exchange flux tests. In general, soil exchange fluxes were towards the soil, only occasionally showing emissions. Slow deposition to the soil surface was observed for most OVOCs measured, consistent with the general absence of strong gradients below the canopy. We also found no single ambient mixing ratio compensation point with the soil for any of the OVOCs, but tendencies suggesting differences between plant litter and mineral soil OVOC exchange and possible effects of soil microbial activity, such as increased sub-canopy gradients towards the ground after rainfall. Future measurements should include soil fumigation tests and soil respiration measurements to evaluate the soil VOC exchange further. Our results may show

BGD

5, S2626–S2639, 2009

again that firm conclusions about the biosphere-atmosphere exchange of oxygenated VOCs cannot be drawn from campaign-style field investigations because these are too short to evaluate existing complexity. In addition, it is difficult if not impossible in the field to determine gross fluxes or small exchange fluxes of minor VOCs. In addition, canopy-level flux measurements result only in net fluxes to the atmosphere, but the exchange process seems much more complex: Though the production mechanism for methanol (and other OVOCs) in leaves may be the same throughout the plant kingdom, its diurnal and seasonal patterns alongside differing plant physiologies can strongly affect emissions to the atmosphere. At the same time oxygenated VOC deposition may occur, possibly down both stomatal and non-stomatal pathways. Thus, more controlled enclosure studies alongside carefully devised field measurements appear necessary to shed more light on these complex carbon exchanges."

Interactive comment on Biogeosciences Discuss., 5, 4315, 2008.