Biogeosciences Discuss., 5, S2577–S2584, 2009
www.biogeosciences-discuss.net/5/S2577/2009/

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.

Received and published: 9 January 2009

(reviewer's comments in italic)

In this manuscript the authors report their findings obtained from a field campaign in a Danish beech forest. Using relaxed eddy accumulation above canopy fluxes for methanol and for the sum of monoterpenes were determined. In canopy and sub canopy concentration gradients were used to find hints with respect to deposition of methanol and other OVOCs on soil and plant surfaces. These measurements were completed by checking deposition of OVOCs to litter or to bare soil using a quasi static chamber. The main results shown here are net emission fluxes important for assessing impacts of vegetation on atmospheric chemistry as well as the diurnal cycles of monoterpene and methanol emissions. The diurnal cycle of measured for monoterpene emissions is consistent to the light dependence of these emissions from Euro-

pean beech and the diurnal cycle of methanol emissions is attributed to the mechanisms of methanol emissions. Methanol emissions are coupled to leaf growth and the leaves of European beech predominantly grow during darkness. Fluxes for acetaldehyde and MEK were found to be insignificant and those of acetone and methanol were bidirectional showing also an impact of deposition. The authors also observed a strong increase in OVOC concentrations concurrent with hay mowing near to the measurement site. This finding confirms results from other studies that show agricultural activities may be a significant OVOC source in rural areas. The manuscript is quite good structured, in most cases easy to read, it contains important data and addresses relevant scientific questions within the scope of Biogeochemistry. Some of the basic results shown here have been reported before. However, the importance of the data as well as the difference between the observations made here and the observations reported in literature make this manuscript interesting and worth while to be published. Nevertheless, some points have to be mentioned or discussed in more detail.

We are grateful for the reviewer's encouraging comments. Please note that the manuscript was substantially rewritten according to comments by all reviewers. Some conclusions drawn earlier have been removed or altered.

Here are my points: 1) Concerning methanol emissions it is written (abstract and page 4332 first line) "Emission fluxes occurred dominantly late at night" From figures 3 and 4 I cannot see a clear and convincing hint for this statement. Furthermore, this statement is not supported from the sentence: "In addition, observed methanol fluxes did not follow a clear diurnal cycle on most days" (p. 4329 lines 4-6). Using the quite noisy data shown for the diurnal cycle of methanol emissions alone, this statement of dominant methanol emissions during night-time are indeed not convincing. In contrast, from the figures it seems that the diurnal cycle measured for the methanol emissions is due to an overlap of darkness emissions from growing leaves and emissions from mature leaves with a maximum during daytime. Both together might lead to a diurnal cycle as shown in the figures. This would also be understandable as the measurements were

BGD

5, S2577–S2584, 2009

made in June when the majority of beech leaves are mature. I believe that this part of the discussion should be deeper. This will improve the manuscript.

Indeed, this part of the manuscript was revised substantially. We now present a day versus night histogram of the methanol flux data and a more distinct discussion.

The revised manuscript now reads (4328-4329): "Measured methanol fluxes are shown 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 surface source. We can compare some aspects of our results to the controlled measurements on beech seedlings by Hüve and coworkers (Hüve 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

BGD

5, S2577–S2584, 2009

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 virtually all nights for which data is available."

Page 4328 lines 19 and 20 and p. 4334 last line (both sections consider the main emissions of methanol being during night-time) The phrases: "this is sharply contrasting the observations by Karl and coworkers" and "Methanol appears to be emitted dominantly at night" are written in a way implying that this behaviour is general. This is not the correct because diurnal cycles of methanol emissions might be different in another forest consisting of other trees. The parts discussing maximum methanol emissions during darkness should be written in a way that misunderstanding and generalization is clearly excluded.

We hope that the above new formulation is satisfactory in this regard. Also revised was the conclusions section, which now reads as follows: "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. Am-

BGD

5, S2577–S2584, 2009

bient 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 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 °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

BGD

5, S2577–S2584, 2009

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 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."

2) On page 4319 line 25 it is written: "groves of conifers comprising 20 percent of the total footprint" and on page 4331 lines 4 to 14 it is mentioned that the contribution of conifers to atmospheric monoterpene concentrations may largely exceed that of beech. Both statements imply a role of conifers for the monoterpene concentrations at the measurement site. In figure 2d it is shown that monoterpene concentrations during darkness were near to zero for the early warm phase of the field campaign. But monoterpene emissions from conifers are supposed to be independent of light intensity and quite strong during darkness. Therefore the statements regarding the role of conifers and the near to zero concentrations in darkness during the first warm phase seem to be inconsistent. If the contribution of the conifers was less than 20 percent during the first warm phase - may be because of the predominant wind directions - the

BGD

5, S2577–S2584, 2009

authors should add some words. This will avoid confusion for a reader.

We have addressed this issue in more detail in our reply to reviewer 2 and in the revised manuscript text. Footprint analysis shows that for SE wind directions up to 50 percent of the footprint may lie over the nearest conifer grove and this may have been observed on DOYs 166 and 171/172. Most of our data is from different wind directions with much smaller potential impacts from the conifer groves. Respective wording has been added to the revised manuscript.

By the way, the finding that monoterpene emissions from European beech are light dependent is not a recent finding; this was published already more than 10 years ago.

We have added the most relevant publication, Schuh et al., Journal of Atmospheric Chemistry 27, p. 291f., 1996, to the references list and into the first sentence of section 3, last paragraph (page 4330).

3) Two multiple ion detection programs were used, in both m/z = 81 and m/z = 137 were measured with dwell times of 2 s (page 4324). Please add some words why one of the programs had a much better detection limit (p. 4325, lines 9 and 10).

This was due to the longer dwell time, i.e. five versus two seconds.

4) On page 4326 lines 5 - 7 it is written: "Additional quality control included the removal of periods after a new bag had been installed, measured friction velocity was smaller than 0.2 ms, or rain had influenced the measurements." Nevertheless figure 2 shows data probably taken during rainfall and on page 4332 effects are mentioned that were observed during rainfall. Both statements together seem inconsistent. Please check and correct. If the authors decide to leave the data taken during rainfall there is an interesting point that should shortly be discussed. Figure 2b shows methanol concentrations and rainfall. No clear drop in methanol concentrations were observed, instead in one case an increase is shown (DOY 167). This behaviour should shortly be discussed as it might imply a negligible role of wet deposition for methanol.

BGD

5, S2577–S2584, 2009

Only concentration data acquired through the gradient inlets was plotted in Figure 2, and was retained because no water was aspirated through those inlets. All bag measurements used to calculate flux data were removed when rain was detected. That wet deposition removal for methanol is negligible has been shown theoretically by Crutzen and Lawrence (2000) and through measurements by Schade and Goldstein (2006).

Crutzen, P. J., and M. G. Lawrence (2000), The impact of precipitation scavenging on the transport of trace gases: A 3-dimensional model sensitivity study, J. Atmos. Chem., 37, 81-112.

Schade, G. W., and A. H. Goldstein (2006), Seasonal measurements of acetone and methanol: Abundances and implications for atmospheric budgets, Global Biogeochem. Cycles, 20, GB1011, doi:10.1029/2005GB002566.

5) In some cases gradients are given in ppb (e.g. Figure 8: y-axis). Please check units for gradients.

Figure 8 is a representation of mean concentration inside the beech forest in ppb, not just the difference in concentration. We have revised the manuscript to improve clarity on this.

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