Biogeosciences Discuss., 5, S2567–S2576, 2009
www.biogeosciences-discuss.net/5/S2567/2009/

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 comments in italic)

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 interpretation of results.

We are grateful for the reviewer's comments. We have added an extended discussion on the acetone data, but refrained from further expansion based on the fact that very small changes were observed, and that both the bag data and the gradient data did not point to any significant fluxes at this site. A short discussion on the inadequacy of our technique to measure minor fluxes was added to the revised manuscript text. The relevant parts are included in the reply to reviewer 1.

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.

We have addressed most of the issues with the technique in our detailed reply to reviewer 1. Concerning the REA part of our flux measurement technique, we believe that it deserves more credit than given here. It has a solid theoretical foundation (e.g. Katul et al., J. Appl. Meteorol. 35(10), 1996), as it is an EC-derived technique making no assumptions about the fluxes such as the flux-gradient technique. REA has been tested against EC in several studies, and so has using sonic temperature to calculate the b-factor in setups that use a deadband (e.g. Schade and Custer, Atmos. Environ. 38, 2004). The reviewer is correct in that the use of moving parts, sample storage, and particularly the need to estimate a tubing lag time in certain setups adds to the uncertainty of the flux calculation. That cannot be avoided, and we have added a

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respective statement regarding the lag time estimate into the setup section (see also reply to reviewer 1).

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 percent 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 percent 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 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.

We are similarly puzzled than the reviewer. We have, prior to submission, contacted Dr. Gallagher, as well as sources in Denmark with access to metadata from 1996, to discuss these results and come to a plausible explanation. In several exchanges with the British colleague, we were unable to satisfactorily determine why the concentration would have been higher in 1996, or lower in 2007. In 1996, the samples were collected and stored on the cartridges for several days during shipment to the UK for analyses.

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While it is to be expected that sabinene converted largely to other monoterpenes during transit or analyses (e.g. Dindorf et al., JGR 111, D16305, 2006), higher total monoterpene abundances cannot be explained that way. The finding of large monoterpene emissions (largely the same typical pine-monoterpenes found for the Soroe site) from a winter barley and wheat field in that same publication may suggest that their samples were contaminated somehow during transit, despite strict protocols. While this could explain higher abundances it cannot explain higher fluxes because the contamination would have to be selectively on the 'up'-cartridges. While Dr. Gallagher acknowledged possible issues with the GC method, such as column overloads, this unlikely caused the systematically higher abundances and fluxes. We found that their highest abundances and fluxes occurred during the days after a rain storm on 8 June 1996, corresponding to results from a pine forest ecosystem (Schade et al., GRL 26(14), 1999), which supports the speculation about the conifer grove influence. However, lack of nighttime data prevents further analysis. We also ran the Kljun et al. parameterized flux footprint model (http://footprint.kljun.net) to assess the conifer groves' potential impact on the measurements and found that both in 2007 and in 1996, up to, respective up from 50 percent of the footprint was likely over the nearest grove. While logging or similarly disturbing activities in the conifer groves during 1996 would explain the monoterpene difference, no such activities were recorded for Lille Boegeskov in 1996. With respect to our data, we now point in the manuscript to two periods with SE winds, for which the monoterpene flux seemed anomalously high (see reply to reviewer 1). Based on the above, we can only speculate on the abundance and flux differences.

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 m2/m2, but in the modeling exercise, the canopy consists of three layers, each with LAI of 1 m2/m2. 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

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change, is there a discernible pattern? Higher following warm days, for example?

We have now explained our procedure more clearly (see reply to reviewer 1). LAI above 19 m agl in the forest was about 3. We now use 1 to 1.5 as input (for LAI above 14 m agl) to account for emissions in the lower part of the canopy. The range stemmed from accepting a discrepancy of a factor of two between measurements and model, using the standard emission factor as a variable. Hence, no assumptions were made about what the correct factor should be or whether it changed over time.

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 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

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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 gC/m2/h but don't provide a nighttime estimate, which based on Fig. 4, appears to be less.

This section was largely rewritten due to comments from all reviewers. The new text and replaced Figure can be found in the reply to reviewer 1.

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.

The reply to reviewer 1, and the text in the revised manuscript outline the flux calculation procedure (and possible caveats) in more detail. We also report the acetone flux data now in a new graph, which is included in the reply to reviewer 1.

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.

We have reevaluated our data and now also report on a relationship between above-canopy fluxes towards the canopy and a sub-canopy gradient toward the canopy, which would be expected if methanol is deposited within the canopy. Details can be found in our reply to reviewer 1. The revised manuscript contains a short discussion, but we again refrain from a more detailed discussion due to the limited size and noisiness of the data set. It appears clear however, that no comparable deposition to the findings by Karl and coworkers (2004, 2005) occurred in the sub-canopy at this beech forest site.

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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 production 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.

We have now added a data sample of chamber results to the manuscript. It is displayed in our reply to reviewer 1. The chamber effect was measured by placing the chamber onto a Plexiglas bottom, wherefore a potential additional effect 'from that bottom' (max. +13The reviewer is correct in that the assumption of the chamber effect being the sole production source means that there is 'no room' for a production in the soil when equilibrium is reached. While this assumption was not directly used with our data, it appears reasonable with respect to the commonly large production rates in the chamber. For equation 3, it is irrelevant because that equation is only based on a (net) production being present, not where it happens. The fact that the chamber is 'leaking' is common for closed chambers. In the CO exchange studies by Ralf Conrad for instance, a piece of low ID tubing open to the atmosphere was used to make sure that chamber pressure was maintained. A leak-free chamber would change pressure,

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and thereby affect soil trace gas flux, when retrieving or injecting an air sample. Not using a soil collar avoids disturbing the subsoil (with effects that can last for days) and maintains a very small leak for pressure equilibration (as long as the location is flat). It does not, however, provide for a reproducible measurement at the same soil location with a defined amount and area of soil below it (hence the method is intrinsically 'noisier'. Again, the leak is not affecting analysis with respect to equation 3, because (i) it is very small, and (ii) as long as the soil acts as a sink, the leak is simply part of the (net chamber) production.

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 be make progress in understanding the complex behavior of these bidirectional fluxes, or assess the relative importance of stomatal vs. non-stomatal deposition.

We wholeheartedly agree with the reviewer. Some language in that respect was in the manuscript conclusions section, and has been largely retained.

Minor specific suggestions. p. 4316, l. 13 "contrasted with earlier results"

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The abstract was largely rewritten.

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

Approximately 24-25 m. This was given on page 4320, line 14.

p. 4320, l. 6 what is the manufacturer/model of the plant canopy analyzer?

A plant canopy analyzer was not used. Rather, the permanent, onsite sub-canopy PAR measurement gradient was used together with a leaf orientation model (see e.g. Jones: Plants and Microclimate, Cambridge University Press, 2nd Ed., 1992)

p. 4321, l. 4 the sonic extended west; was this the dominant wind direction?

As seen in Figure 2, wind direction changed frequently. West orientation was chosen for practical (installation) reasons, but westerlies (SW to NW) are also the most common wind directions in Europe.

p. 4321, l. 19 please give manufacturer for PTR-MS

Done.

p. 4322, l. 16 "(same model as on tower gradient)"

Inserted.

p. 4322, l. 19 control channels or control ports?

Changed to 'control ports'.

p. 4325, l. 2 monoterpene emissions by no means restricted to conifers

Changed to 'numerous tree species'.

p. 4334, l. 3 "comes as no surprise"

This section was rewritten.

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

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We reanalyzed the data and corrected an error. No fluxes appear as emissions any more in the Table. However, the table header was changed to read 'exchange velocity'.

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

Letters were added to the graph.

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