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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 1 (Detailed Discussion of the Paper) 1 Introduction 1a There are two Karl et al. 2005 citations - use Karl et al. 2005a and Karl et al. 2005b to make the citations unambiguous.

Done

1b p4318: line13-16: "...the same authors..." Karl et al. 2004 and Karl et al. 2005a, b are not the same authors, only the first author is the same person.

Changed to give correct citation: "In another, detailed laboratory and field study on loblolly pine (Pinus taeda), Karl et al. (2005a) confirmed that the flux of ..."

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1c p4319: line 6-8: "Although their PTR-MS measured abundance were seemingly misinterpreted, the flux results of Asensio (Asensio et al., 2007) for a Mediterranean soil are in accordance with these data." The mass-to-compound assignment by Asensio et al. (2007) is questionable and the deduction of volume mixing ratios for most compounds given is in deed not comprehensible. The authors may want to specify of which data they conclude "accordance" to the flux results of Asensio and co-workers: Schade and Custer (2008), Schade and Custer (2005) or this paper? The authors need to discuss how misinterpreted PTR-MS measured abundances can possibly lead to correct flux results. In case the deductions by Asensio et al. (2007) are not convincing the authors should not use the results for their arguments.

We have removed the reference to Asensio et al.

2 Measurement setup 2a p4321: line 13-14: "....normally closed isolation valves..." The authors may want to add "(not shown in Fig 1)" or depict them along with all the other valves.

Added "not shown in Fig 1" as suggested by the reviewer.

2b Teflon membrane pumps (KNF Neuberger, UN-035STI) were tested by Apel and co-workers and are shown to be an artificial source of Acetaldehyde, Propanal, Butanal and Acetone (Apel et al., 2003) . Those authors fixed that problem replacing the Teflon pumps by metal-bellow pumps. In their paper they conclude "Before definitive arguments can be made on budgets of carbonyl species and on the agreement between measurements and models, demonstration of artefact free operation is necessary" (Apel et al., 2003). Here Schade et al. used a Teflon membrane pump (KNF model N86 KTDC B) to fill the REA reservoirs. The authors need to state if and how they tested their in-line used Teflon membrane pump against OVOC artefacts and what the results are. They may want to state why they decided to use Teflon pumps. If no artefact tests have been carried out or OVOC artefacts are in deed an issue the authors may want to elucidate how a concentration offset in both up and down reservoir affects*

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accuracy, precision and detection limit of the REA fluxes.

We are well aware of the Apel paper. The potential interference coming from their pump was small but not negligible due to the low ambient mixing ratios measured in their study. We found that the bag to canopy top mixing ratio correlation often included an offset (higher bag mixing ratio), which may be explained by a pump effect. Making the reasonable assumption that the artifact in question is due to outgassing, then the area of the pump head exposed to the gas transported, the pump-to-ambient pressure, and the pump head temperature are important parameters. In all cases, these are known to be (pump head area, pressure difference) or were likely higher for the AC pump used by Apel et al. In our case, any artifact may therefore be smaller. We had tested for obvious artifacts in the laboratory by sampling ambient air, then ambient air at the outlet of the pump pushing into a Tedlar bag, and then that same air from out of the Tedlar bag. We found no statistically significant differences between the count rates of these setups at the beginning of the field campaign and so concluded that the setup was appropriate. As described in the manuscript, we later found (stirred by the temperature effect, and having the benefit of a longer data set) that the described REA sampling setup was not completely neutral for several of the m/z ratios monitored. As the discrepancy between the two channels was assessed through sampling the same air into both bags through the same pump, any artifact contribution from the pump was included in the procedure to determine the up- versus down-draft differences. As described in the manuscript (particularly Figure 3), this increased the noise and the detection limit for fluxes in the setup. The revised manuscript will include a slightly expanded discussion of this issue.

2c p4321, line 4+: "An 8mm ID PTFE sampling line for above-canopy sampling ran from the sonic down into the instrument shed, where it was converted to a 6.35mm ID PFA line connected to two membrane pumps in series (Rietschle Thomas model LM22) drawing air at 11.5-12 L min-1. Another 3.5 L min-1 of this main line flow was routed through a Teflon-coated membrane pump..." p4321, line 24+: "Line volume and *flow considerations suggested that lag times between entering the tubes and arriving at the REA valves or instruments were 11 s and <10 s for the above-canopy and gradient lines, respectively." The flow regime in the inlet line is crucial for the dispersion of air packages in the line. Stability of the line flow rate (total 15-15.5 L min-1; was that estimated from data sheets, measured, continuously monitored or/and controlled) and longitudinal dispersion puts a limit to the precise determination of lag times. This is of particular importance for the correct segregation of upwind and downwind samples. Line effects may add to the uncertainty of the lag time depending on compound properties and humidity. The authors should answer/discuss following questions/comments concerning the lag-time in order to substantiate the correctness and significance of their REA flux data. I. On page 4321, line 26+ the authors mention the determination of the REA lag-time. Please, present that data (e.g. in a discussion note). What shape does the Acetone "peak" have upon arrival at the PTR-MS? How many repetitions where done, how significant is the resulting lag-time value (precision, accuracy) and how broad is the Acetone peak arriving at the lower end of the above-canopy line in comparison to it's width at the inlet? How do sensor separation, speed and direction of the approaching air flow affect the lag-time? Does the test result for Acetone also hold for Methanol?*

While we agree with the general notion of the reviewer's concerns, we believe that a detailed discussion of these issues does not belong in this manuscript as it cannot be done with our data. Rather, some of the raised issues were previously discussed in the excellent work of Karl and coworkers (ACP 2, 279-291, 2002), who used high frequency PTR-MS measurements through a similar sampling tube. As we have no high frequency data available, we have to rely on previous investigations such as theirs to evaluate potential 'line losses' (attenuation of high frequency concentration fluctuations as a result of longitudinal dispersion and wall-interactions in the sample line). In our case, the achieved flow rate in an approx. 50 m long line corresponds to a typical half power frequency of 5-6 Hz as calculated by Karl et al. (ACP 2, 279-291, 2002). Our typical Reynolds numbers were 5000 or higher. The flow rate used for this calculation was measured at least once a day with an electronic mass flowmeter and was never found to be outside the given interval, varying by at most 0.2 L min-1 between measurements. Therefore we assume it to be constant within 5 percent.

On the shape of the acetone peak upon arrival at the PTR-MS: The amount of acetone entering the sample line after a balloon pop is not reproducible, and is probably not an ideal, instantaneous release of a tracer next to the inlet either, as would be needed for a precise analysis. However, the peak shape as a function of acetone amount detected (presumably the measure the reviewer suggests) can reveal some information on line effects. The balloons received 1-2 drops of commercial grade acetone before blowing them up. They were then lifted to the Danish colleague on the tower in a bag. He popped a total of 14 balloons near the inlet. Figure x1 (available at http://geotest.tamu.edu/userfiles/226/BGDreplygraphs.htm) shows all successfully measured acetone peaks, normalized to their maxima (13 out of 14). Although the peak maxima varied by a factor of ten, peak width at half maximum was consistently five or six measurements (at 4 Hz). We fitted skew normal distributions to all peaks, and found a standard deviation of 2.76+-0.17 (1 sd) and a negligible skewness (0.05+-0.17), the latter not showing a consistent peak tailing as would be expected for a wall interaction. Assuming acetone were released instantaneously (peak width: 0.25 s), the observed peak broadening could be used as an indicator of low pass filtering in the line. Degrading the sonic temperature data (10 Hz) by a Gaussian filter of the average shape of the acetone peaks revealed that less than 10 percent of flux was lost that way, consistent with the argumentation using the Karl et al. (ACP, 2002) data above. Because our REA method discriminates against the majority of high frequency fluctuations, the potential systematic flux underestimation from a loss due to line effects was likely much smaller than these 10 percent.

Methanol was not tested in a similar fashion. However, our previous measurements and comparisons of w-Ts with w-methanol cospectra at the Braunschweig agricultural site (Custer and Schade, Tellus B, 2007) showed no significant differences that would have lead to a similar line loss investigation. We cannot answer the last question on sensor separation etc. because we did not carry out a systematic study on these parameters. Again, popping commercial party balloons with large but unknown VOC concentrations inside next to a sonic anemometer is a qualitative and not reproducible method for this type of study.

II. On page 4322, line 4+ the authors state that lag times between 10.5 and 12s seconds were used to "properly lag" anemometer data and switching of the segregation valves. Please, explain the procedure of choosing on-line the proper lag-time and/or give references to the respective literature. Which parameters did that procedure use?

The lagtime was preset for every 30 min sample, not chosen online. The calculation from the balloon pops revealed a lag variation of 0.6 s (note that resolution is +-0.25 s at best). Due to additional uncertainties (e.g. difference between valve and PTR-MS detector locations, which led to a 1-s correction), the correct lag time was probably unknown to +-1 s. As previously shown by Baker et al. (JGRD 104(D21), 26107f., 1999) and Schade and Goldstein (JGRD 106(D3), 3111f., 2001), such an offset (<10 percent) could lead to a flux underestimation of up to 20 percent. Due note of this possibility will be made in the revised manuscript.

*2d p4322, line 8+: "The discrimination factor b was chosen according to the desired total volume that was needed to supply the methanalyzer with a sufficiently large sample. In our case, this volume was approximately 21 L for a 12 min sampling time at 1.75 L min-1, which led to a chosen b ranging from 0.8 to 0.9 under the local turbulence conditions." 1.75 L min-1 * 12 min results in 20 L. According to the description of the sampling setup the REA sampling flow is 3.5 L min-1 and the sampling period is 30 min. The authors may want to clarify how these numbers fit into their estimation for the chosen width of the dead-band.*

The REA sampling flow INTO the bags was 3.5 L min-1. The sampling OUT OF the bags was 1.75 L min-1. The revised manuscript now reads: "In our case, this volume

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was approximately 21 L for a 12 min sampling time at 1.75 L min-1 out of a filled bag, which led to a chosen b ranging from 0.8 to 0.9 for filling the bags at 3.5 L min-1 under the local turbulence conditions."

2e p4322, line 23 - p4323, line 25: The authors report various artefacts due to the use of Tedlar bags (with polypropylene fittings) as REA storage reservoirs and they mention a method to rule out some systematic differences. Upon their "estimation" that the artefacts are "not significant" they decide to report the REA flux data. That paragraph, however, leaves open a couple of questions. I. As is known Polypropylene has poor chemical stability against oxidation agents. How do the authors rule out VOC artefacts due to the exposure of the fittings (and other materials used in-line) to ozone in the sample air. II. What does "...leaky bags...were replaced as soon as possible." mean and how were the leaky bag data treated? As a quality control measure the authors state that data for periods after (how long?) bag exchange were discarded (p4326, line 5+) - what about the data before? III. What does "...significant differences..." mean in the context of bag effects? The authors may want to explain their reservoir comparison procedure more detailed, present the result and discuss which artefacts can be ruled out by that procedure (and which not) and what difference between up- and down sample is numerically significant, thus being able to give a detection limit for the flux determination for each analysed compounds. IV. The storage time for updraft samples is systematically longer than that of downdraft samples and the PTR-MS sampling and analysis from the reservoirs is 12 min shifted. Do the reservoir comparison data indicate a trend that even "short storage" times cause significant biases? V. Could systematic differences in up and downdraft samples (e.g. different ozone concentrations, humidity, etc) result in an over or underestimation of REA fluxes that cannot be ruled out by the reservoir comparison procedure? VI. A signal drop due to a temperature change of -5K may be explained by adsorption of VOC to the bag wall rather than "desorption from or diffusion through the bag wall". What happens to the adsorbed VOC - does it desorb and thereby bias the measured concentrations in dependence of concentration and temperature history of the setup? How do the authors rule out that *there is no "carry over effect" from each REA sample to subsequent ones? VII. The authors state "While such rapid temperature changes did not occur at other time(s) of the day, they suggest possible biases of certain VOC mixing ratios even for the short storage times used in this study." How significant (numerically) are the possible biases and which are the VOC affected?*

The reviewer's concerns surround the same issue, wherefore we will address them together.

- In our point of view, it is fundamentally interesting, and important to report possible biases with a bag material so routinely and widely used for air sampling. Unfortunately, time constraints did not allow us to test the artifact in detail. However, another recent publication (Beauchamp et al., J. Breath Res., 2, 1-19, 2008) describes recent and past work on Tedlar bag artifacts, indicating that short-term storage (< 1h) could be regarded as artifact-free, but that large temperature-changes can cause large bag effects, similar to our findings.

- We did not, as the reviewer seems to assert, classify the artifact as "not significant". Choosing such wording was, however, confusing, and we will reword the respective sentence in the revised manuscript. What we found was that the artifact is not limited to a certain bag. It was discovered by chance (temperature drop) and analyzed using the sample system's intercomparison samples (see below).

- Insofar it is not helpful to speculate about which part of a bag or air sample leads to the problem, or which effect can be ruled out or not, etc. (see also Beauchamp et al. paper), but rather whether the artifact can be corrected for. As the intercomparison samples integrate over all parts of the setup being discussed, we think the answer to this question is yes. Whether the procedure systematically affects determined REA fluxes cannot be answered.

- Because the intercomparison samples were taken at near equal time intervals, and we were unable to correlate the bag differences to any other parameter measured, we have treated the artifact problem as being stochastic. To correct the VOC bag difference time line, the bag difference in the intercomparison samples was extrapolated in time using a smooth spline function (R-software). As bags were exchanged sometimes before a bag had been measured on an intercomparison at least three times, the single sample was extrapolated forward in time to the bag change assuming a constant value, and two (or three) available samples per bag were averaged over the time period they covered. This is shown in Figure x2 (available at http://geotest.tamu.edu/userfiles/226/BGDreplygraphs.htm)

- To determine the horizontal lines in the manuscript's Figure 3, we used the 95 percent conf. interval of all individual samples multiplied with median values of beta and sigma(w). The revised manuscript will instead report the actual beta and sigma(w) values (plus an assumed 10 percent error, minor compared to the bag effect), such that the error limits vary over time (similar to Spirig et al, 2005).

- Our choice of smooth spline interpolation of the intercomparison samples to create a correction vector is reasonable but not based on any known artifact behavior. Hence, we estimated the additional potential bias on the flux calculation from using a simple linear extrapolation throughout the time series (Figure x2 available at http://geotest.tamu.edu/userfiles/226/BGDreplygraphs.htm) and compared the two calculated fluxes. The difference was random and not larger than 7 percent on average.

- Possible carry-over: If present, such an effect would depend on concentration-difference between samples and bag temperature changes. In our case both these changes occurred generally very gradually except as indicated in the manuscript. The effect would likely act as a low pass filter, but would be very small based on volume considerations.

2f p4324, line 13+: "Background counts were evaluated once a day..." de Gouw and Warneke (2007) show that background values vary with (absolute) humidity; amongst others there is a particularly strong humidity dependence of the background signal at *mass 33. Humidity certainly varies strongly above a forest during the course of the day. How were the background counts "evaluated"? How can the authors rule out that diurnal variations of VOC mixing ratios (as shown in Fig 2) are masked by background value variations?*

We appreciate the reviewer's comment regarding the possibility of non-stable background conditions. Background values were measured with the same program than the ambient (gradient) air (now clarified in the text). The manuscript contained an error as the measurements were carried out in the morning and evening, aka TWICE a day, on several days during the campaign. We found no significant differences for m/z 33 between morning and evening nor from day to day. Taking our measured m/z 37 to m/z 21 ratio as a measure of the humidity effect as pointed to by the reviewer, all our data would be at the left side of Figure 4 in de Gouw and Warneke (2007), because m/z 37 counts were never larger than 7 percent (most commonly <3 percent) of those of m/z 21, except for the chamber measurements (discussed below). Therefore we have corrected for background using uniform values determined from the measurements. It appears that our instrumental setup did not show the functionality described by de Gouw and Warneke (2007) in their Figures 46, at least not to the same extent. Only mass m/z 45 showed a different variation, dropping near exponentially throughout the first half hour of the background measurement to a stable final value. We cannot explain that behavior at this point in time.

*2g p4325, line 6-10: The authors deduct "detection limits better than 0.05ppbv for all species in the second program...". Based on what signal to noise ratio (S/N) was these detection limits estimated? The given value might not hold for S/N=2 (typical for limit of detection, 3 or higher for limit of quantification), 85 cps at mass 33 and 1.7 to 2.6*1E6 cps primary ions - please, discuss that.*

These limits were calculated based on the discussion by de Gouw and Warneke (2007) and this reference will be given at the respective position in the revised manuscript. A value of 50 ppt arises from an S/N=3, I(H_3O^+)=2, S=20, and a dwell time of 5 s.

2h p4325, line 15-16: "...a reaction time t of 11ms (for the proton transfer reaction)..." An E/N of 125Td as stated (p4324, line 5) and a supposed length of the drift cell of some 10cm results in a reaction time in the order of 10-4 s. If the authors used in deed the formulae in equation 1 and 2 for there VMR and flux calculations those numbers will be off by two orders of magnitude (or the drift tube is 10m long). Please clarify!

We apologize for the typo: It should have been 0.11 ms.

2i p4326, line 8 to p4327, line 14: Soil-Atmosphere VOC exchange experiment I. Was the soil temperature measured in the area covered by the chamber or somewhere else? What was the air, soil and chamber temperature during those experiments and how did those temperatures evolve during the course of the experiments? Static chambers tend to be critical for water condensation on the inner surface particularly on moist soil. A water film (even if there is no visual steaming-up apparent) is a sink for water soluble VOCs. That would mask the measurement results. How did the authors make sure that no condensation happened and what data do they have to substantiate the data quality (e.g. time series of air, soil and chamber temperatures and humidities).

As explained in the manuscript text on page 4333, line 23f., soil temperatures were monitored by the tower's main system several meters away from the chamber setup, and were between 13 and 14 deg C during all tests. We have no chamber air temperature and humidity measurements. However, unless reaching extremes due to solar heating (of the soil actually), chamber air temperature should not affect trace gas exchange significantly. As it was cloudy or overcast during all tests, and the canopy at the Soroe site is closed with very few sunflecks reaching the ground at any point in time, chamber heating affecting the results can be excluded. Water condensing on the walls of the chamber could theoretically affect mixing ratios. Assuming that up to 1 mL of water (a high estimate) builds up on the chamber walls and Henry's law is obeyed, approximately one third of chamber methanol (the investigated VOC with the highest solubility; chamber volume: 11 L) could be found in the liquid phase. Our experience is that already smaller water amounts make for an easily visible layer of condensate, which we did only experience in a few cases on the lower parts of the chamber towards the end of the enclosure periods. Note also that this calculation assumes that Henry equilibrium is not obeyed for the topsoil water evaporating to provide the condensate, and that the production by the chamber itself is negligible during condensation. Especially the latter assumption seems unreasonable. Chamber production was typically between 0.1 and 0.3 ppb methanol per minute, and would have lead to a rapid saturation of any condensate with methanol. Hence, water condensation at the chamber walls, even when not visible, is unlikely to have governed chamber air concentrations.

II. "While such behavior has been documented extensively for CO (King, 1999), this is not the case for VOCs." Does that mean VOC behave differently (i.e. VOC emission by materials - "chamber effect") or does it mean that the authors did not find literature that documents the behaviour of VOCs in incubation chambers?

The sentence’s meaning may have been confusing from the previous sentence. What was meant is that simultaneous production and consumption in the soil, such as documented for CO, has not been extensively documented for VOCs (this is independent of the type of evaluation of flux). The revised manuscript now reads: "Using equation 3 assumes simultaneous sources (E) and sinks (vdepŒVMRt) in the soil, with production of zero and consumption of first order in concentration. While such behavior has been documented extensively for CO (King, 1999), there is no such documentation for VOCs."

*III. King (1999) states that "With some a priori knowledge of approximate values for Ceq and consumption rate constants, non-linear regression analysis can also reliably estimate the parameters for Eq. 1 (Eq 3 in this discussion paper). However, the adequacy of such analyses depends sensitively on the size of a dataset, variance in the data and the accuracy of initial parameter estimates." Here the authors say "Results were pooled due to the small amount of samples..." (p4333, line 27). The data set shown in table 1 indicates 7 to 13 repetitions, 1*sigma standard deviation are 50 to 150 percent (!) of the reported deposition velocities. How do the authors come to the* *conclusion that their way of analysis is adequate? How can the conclusions about the deposition of OVOCs based on those data be of any significance?*

We have reevaluated our soil enclosure measurements. A calculation error was found and corrected. As a result, value and variability for methanol dropped, and most other calculated VOC fluxes were found to insignificant with the error margins. Table 1 was corrected accordingly. In reply to the reviewer's comment on variability: The mere fact that the calculated deposition velocities showed a high variability does not invalidate the results. Our analyses did not have to estimate any of the parameters in equation 3. Particularly, equilibrium mixing ratio was always achieved. No non-linear statistics were needed. Due to relatively small mixing ratio differences between start and end of each experiment, the unequivocal counting noise of the PTR-MS lead to relatively large determination limits. However, soil uptake of methanol was always evident, and often evident for acetaldehyde (hence the difference in number of samples reported). A data sample is (now given in the manuscriupt) at http://geotest.tamu.edu/userfiles/226/BGDreplygraphs.htm as new Figure 10) As possibly not clear to the reviewer, the limited number of enclosure tests was not intended as a systematic study of this forest's soil trace gas exchange behavior, but rather a semi-quantitative evaluation, revealing direction and magnitude of flux. In summary, it seems justified to pool the results and present them as obtained.

On the possible humidity effect on background counts during higher chamber humidities: Unlike for ambient measurements, the chamber tests showed m/z 37 to m/z 21 ratios ranging from 5 up to 20 percent. According to the work of de Gouw and Warneke (2007) this could correspond to a changing background corresponding to up to 1.5 ppb for methanol (Figure 4 in that publication). Assuming this functionality were also true for our measurements (see also discussion above) calculated mixing ratios and their changes during the chamber measurements could be biased. However, we found that the measured 37/21 ratio did not change by more than 2 percent (absolute, such as in 37/21 = 0.11 to 0.13) during any test between when the chamber was on the ground and when ambient air was measured by laying the chamber on its side, and no changes in the 37/21 ratio were observed during the last, wettest day, measurements. We also tested whether changes in the m/z 32 counts (oxygen) during the chamber enclosures could be interpreted as having caused the observed m/z 33 behavior. We found that this could have contributed at most about 10 percent (about 5 cps, similar to the counting noise at m/z 33) to the observed drop in chamber m/z 33. Therefore, any observed changes in methanol (or other VOC) mixing ratio inside the chamber have unlikely resulted from changes in humidity only. However, the obtained ambient mixing ratios between the enclosure tests (at 10 cm above ground) were approximately 1 ppb lower compared to the previous 5 m gradient inlet data on the last two, wet measurement days. It is possible that this discrepancy was caused by lowered background levels, and we have therefore changed the respective text passages in the manuscript.

In the revised manuscript, we will include a data example. The altered text reads: "During the last four mornings of the campaign, the gradient sampling line to the PTRMS was moved to the flux chamber for a series of soil trace gas exchange tests within an approximate 5 m distance from the instrument trailer. The same data acquisition program than for the gradient measurements was applied. A time series data example for methanol is shown in Figure x. We investigated count rates at both m/z 32 (16O2+) and m/z 37 (first water cluster), both used as a measure of possibly varying m/z 33 background, to determine whether the observed drops in m/z 33 were indeed caused by soil consumption. Higher humidity in the chamber could suppress the drift tube O2+ abundance, but the affect, when present, was found to explain at most 10 percent of the m/z 33 decrease. No such change in humidity or O2+ count rates was generally observed between ambient ground level and chamber enclosure readings, while drops in m/z 33 count rates were always observed. Nevertheless, changes in m/z 33 background, not evaluated during the chamber tests, may have contributed to the observed variability. Also, because only a limited number of enclosure tests were performed, and because the soil in the tested area may have been disturbed by foot traffic, the results should be viewed with some caution. We found that methanol uptake dominated for

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this location, and was generally consistent with the equilibrium assumption with chamber production, as well as from one day to the next. As variability was relatively high, we pooled similar tests and summarized the calculated exchange velocities in Table 1. Soil temperatures during all these tests, measured by the main system several meters away, were between 13 and 14 deg C. Although soil moisture was not measured at this time, it can be inferred from previous relations between soil moisture and rain (Pilegaard et al., 2001) to have increased from 25 percent (DOY 171) to 31 percent (DOY 174). With few exceptions the calculated exchange velocities for the remaining VOC were insignificant, but allowed upper estimates of +-0.1 cm s-1. Due to the consistency between this relatively slow soil exchange and the observed weak gradients toward the ground it appears unlikely that exchange velocities were significantly higher at other soil locations in this forest. Although more measurements are needed to confirm exchange fluxes of this soil, some general tendencies were observed: the beech litter heap showed emissions of m/z 69 and 71. The mineral soil from which the litter had been removed and the tree stump with moss showed slightly higher deposition velocities for methanol. Mass 69 was nearly always emitted, at particularly large rates from the litter heap, similar to observations by Warneke and coworkers (1999). Mass 33 (methanol) was always found to be produced by the chamber and taken up in subsequent soil enclosure tests (Figure x). We also found a tendency towards lower equilibrium methanol count rates in the chamber as soil humidity increased. However, this effect may have been at least in part due very high ambient humidity levels rather than microbial activity. Large ambient humidity levels can lower methanol background counts (de Gouw and Warneke, 2007), and this effect may be inferred from the calculated methanol ground-level mixing ratios, which were significantly lower than the respective 5 m gradient level data on the last two, wet days. Hence, the ground-level methanol abundances may have been underestimated on those days."

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