

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

Anonymous Referee #1

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SPECIFIC COMMENTS - PART 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.

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.

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

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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.

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.

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 accuracy, precision and detection limit of the REA fluxes.

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

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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 were 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 its 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? 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?

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 12min 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 30min. The authors may want to clarify how these numbers fit into their estimation for

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the chosen width of the dead-band.

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?

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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?

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?

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) were 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 $2.6 \cdot 10^6$ cps primary ions - please, discuss that.

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!

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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).

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?

III. King (1999) states that "With some a priori knowledge of approximate values for C_{eq} 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, $1 \times \sigma$ standard deviation are 50 to 150% (!) 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?

ADDITIONAL REFERENCES

* Apel, E. C., A. J. Hills, R. Leub, S. Zindel, S. Eisele, and D. D. Riemer, A fast-GC/MS system to measure C₂ to C₄ carbonyls and methanol aboard aircraft, J. Geophys. Res., 108(D20), 8794, doi:10.1029/2002JD003199, 2003.

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