

***Interactive comment on* “Effect of chemical degradation on fluxes of reactive compounds” by J. Rinne et al.**

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Received and published: 27 March 2012

Answers to the comments by the anonymous referee #2

We thank the referee for the critical and informed comments and for suggestions to improve the paper. Below we answer these comments, and give indication how these will be taken into account in the revised manuscript.

R#2: However, due the variability between canopies and chemical interactions encountered by different compounds, the findings are less generalisable than the authors suggest and remain relevant mainly to bVOCs and coniferous forest. This should be clarified throughout the manuscript and I suggest to rename the title to “Effect of chemical degradation on fluxes of reactive bVOCs over coniferous forest” to reflect this

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emphasis.

A: We do agree that the paper is not able to give a general results for all possible vegetation types and chemical compounds. This will be made clearer in the revised manuscript. However, we do think that our results are more general than the referee beliefs. First, the use of chemical lifetime as a metric allows generalization for many other compounds than VOCs. The Equation (4) to calculate the chemical lifetime of BVOCs is given only as an example and chosen, as it will be utilized in the case study. Furthermore, the turbulence model used to create the turbulence fields used in transport model does not differentiate between coniferous and deciduous forests. Thus its results should be applicable also for deciduous forest if it has similar canopy structure. To emphasize the conceptual nature of the paper we will modify its title to “Effect of chemical degradation on fluxes of reactive compounds – a study with a stochastic Lagrangian transport model”.

R#2: As pointed out above, the paper title claims to deal with reactive compounds in general. However, a first order decay approach is not applicable to many compounds and as a result the vertical profile (in and above-canopy) of the chemical time-scale can be complex. For, example the degradation of soil NO during emission, the degradation of O₃ during deposition (through interaction with this NO, but in certain conditions also bVOCs) or the dynamic partitioning of the heterogeneous NH₄NO₃-NH₃-HNO₃ system is poorly described by this approach.

A: We will clarify the revised manuscript by adding statement that this approach is only applicable for compounds to which the first order decay can be applied.

R#2: The limitations of the Damkohler number as a predictor of the importance of chemical interactions needs to be discussed further. Da represents the local ratio of the local turbulent to local chemical time-scale and only predicts how important chemistry is at a particular height. The importance of chemistry on modifying the flux between emission and measured flux is the integrated effect over all Da numbers encountered

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during the transport process. In fact, in the Lagrangian transport model the first order decay acts as a ‘chemical clock’, which would allow the authors the mean overall transport time between emission and detection to be extracted. This transport time is a better descriptor of the effect of turbulence than the diffusive time-scale used in the paper. The former accounts for the canopy structure and the point of emission, the latter does not. It would be interesting to show a vertical profile of $Da(z)$ to illustrate this.

A: We agree that the Damköhler number as defined in equations (5) and (6) is not the best metric for estimating the effect of chemistry on fluxes, especially in the case of forest canopies. This is briefly mentioned in the manuscript (page 31821, lines 17-22). However, it is a parameter, which can be calculated with the data usually available for most flux measurement experiments, unlike the transport time, which requires modeling. Thus the use of Da is justifiable in order to make the results more useful for field experiments. It is a very good idea to present the calculated transport times and we will do so in the revised manuscript. We will also add discussion on these as compared to the Damköhler numbers at different heights.

R#2: Related to this, I am unsure that $Da(h)$ is the best parameter against which to present the results. For example, for a given meteorological situation (i.e. u^*), the value of $Da(h)$ presumably differs between the different canopies explored in Fig. 3. In fact, the driving parameter should be the wind speed well above the canopy (e.g. $u(50\text{ m})$) and u^* should already depend on the canopy.

A: We choose to present the results against Da_h because this is a parameter, which can be easily derived from the data available for many flux measurement experiments. High-level wind, contrary to the u^* , is usually not available for many flux measurement experiments. The model used in this study is constructed in a way that all velocities are normalized by u^* . Thus this parameter has in the model a non-dimensional value of 1. Similarly the length scales are normalized by canopy height. The wind speed to friction velocity dependence indeed depends on the canopy structure.

R#2: Taking it another step further, even τ_c depends on the canopy structure, because the concentration gradients and emission profiles will respond to it. By showing results for the same $Da(h)$ for different canopies, the authors are not showing the full effect the canopy structure and LAI have on the importance of chemical degradation.

A: We choose to show the results for the same Da_h for different canopies in order to show only the effect the changes the difference in canopy density have via changes in transport time. This in our opinion isolates the effect better, but of course does not give the full picture of the effect due to canopy density. Also, there is no feedback in our modeling approach between canopy structure and τ_c profile, so additional model would be needed to address this issue. We will add discussion on this to the revised manuscript.

R#2: Related to this, the Conclusion Section states that flux degradation was mostly dependent on u^* , but this is actually not shown in the main body of the manuscript, which focuses on the relationship with Da .

A: The Da as defined in the manuscript (Eqs. (5), (6) and (11)) depends linearly on the inverse of the u^* , and as the F/E ratios were mostly dependent on Da this implies dependence on u^* (and τ_c). We acknowledge that this was presented in a confusing manner and will be more explicit about it in the revised manuscript.

R#2: What is the rationale for stopping the investigations at $Da=0.45$?

A: This highest Da was originally chosen to represent the β -carephyllene lifetime in the conditions of our measurement site. One could of course choose even higher Da , but the applicability of the model would become questionable at very high Da values.

R#2: The Massman and Weil canopy turbulence model is not without uncertainties, which should be discussed. The authors should mention how well it performed against the canopy turbulence measurements at Hyytiälä, but also discuss uncertainties, e.g. due to the turbulence parameterisation in the so-called unresolved basal layer, the

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layer closest to the ground, where measurements are difficult to perform. Here parameterisations of different models diverge greatly. It would also be interesting to see the σ_w/u^* profiles predicted by the model for the different canopies.

A: The below canopy measurement at Hyytiälä site have been compared to Massman and Weill model earlier by Rannik et al. (2003). Typically the measurements do not show a constant σ_w/u^* profile predicted by the MW99 model, but decrease with decreasing height. Thus it may be that the fluxes of reactive compounds originating from the ground vegetation would be affected even more if observed profile were used. We will include discussion on this subject on the revised manuscript. We will also include a discussion on the possible effect of basal layer.

R#2: It would be nice to see an exploration of the results in terms of the fraction of the flux degradation that occurs within the canopy compared with that above the canopy, for different conditions.

A: We will add a section discussing this issue to the revised manuscript. In principle this can be analyzed from Figures (2)-(4).

R#2: Like Referee 1 I was left wondering whether in-canopy stability might have a larger effect on F/E than the above-canopy stability. I also noticed that the stability range is incorrectly stated on page 31831. It should read $|L| > 150$ m. This actually not a very extreme range, and the authors could consider exploring a wider range, e.g. $|L| > 20$ m.

A: It is true that the opposite below canopy stability could have an important effect on the transport times and thus on the F/E ratios. However our model is currently unable to deal with different stabilities below and above canopy. We will add discussion on this issue and point out that this could open a possibility for future investigations. It is true that the statement for $|L| = 150$ being very extreme is wrong. We will conduct some new simulations with more extreme stabilities and add discussion on these. However, it could be that the model is not well applicable in these extreme stabilities.

Minor scientific comments.

R#2: Equation (6): should this use z or $z-d$?

A: We used z as the mixing volume is given by the height from the ground not from the displacement height.

R#2: P31825, I19: often the height of the release is unknown. How do the authors propose the effect should be estimated in those conditions? Related to this, even in the spruce forest a bVOC emission may come from the zero plane displacement height, depending on where temperature and light peak.

A: In the case of unknown source height we are not able to estimate the F/E ratio but only the possible range of it. This is a good point as it shows that for the very reactive compounds the flux measurement conducted above the canopy does not constrain the actual emission well, even if we were able to estimate the chemical lifetime of the compound.

R#2: P31826: It seems counter-intuitive that the flux footprint is less than unity for a decaying tracer. Shouldn't it be greater than unity? After all, the flux footprint accounts for all the measured flux and more. A cumulative footprint of 80% means that 80% of the flux originates from within the footprint. In the case of a decaying tracer all the measured flux originates to the footprint (if integrated to infinity), and even more.

A: Taking the definition of footprint function (e.g. Eq. 8.1 in Rannik et al., 2012) we see that the cumulative footprint is defined as the ratio of the flux to the surface exchange occurring between the measurement point and distance x . Thus for emission of inert compound this approaches unity with x approaching infinity while for emission of reactive compound this stays at a value below unity as x approaches infinity.

R#2: Fig. 2. Is it really realistic to use a discontinuous τ_c that changes abruptly at the canopy height? Table 1 states that for spruce $d/h=0.5$, but in Fig. 4B a different value is used.

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A: The discontinuous τ_c is of course not very realistic. However, as we do not have more information on the oxidant profiles we choose to have this kind of very simple profile. The d/h given in Table 1 refers to the displacement height obtained from turbulence model. The line in Figure 4B refers to the source height, which was at the height of d/h of pine canopy.

Technical corrections and English:

A: All these will be taken into account when revising the manuscript. Below are answers to some selected questions.

R#2: P31825, I7: What is ‘the other’ parameter? Explain!

A: We will add the equation describing the LAI distribution to the revised manuscript to clarify this.

R#2: P31825: I14 states that α was adjustable, while line 7 states that it was constant. Please clarify.

A: We agree that this section was confusingly written. In fact the α was varied to modify the canopy shape between pine and spruce simulations. We will rewrite this section.

R#2: Section 3.2. Please clarify if the instrument measures NO_3 and N_2O_5 individually or only their sum. Is the description of the approach really required? In my opinion, it would suffice that the direct measurement of NO_3 was insufficiently sensitive to resolve the concentrations at Hyytiälä and that they were therefore estimated.

A: The NO_3 and N_2O_5 were measured individually. We have clarified this and shortened the description of the measurement but we feel that it is required for the sake of completeness.

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ACPD

11, C16230–C16237,
2012

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