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

Anonymous Referee #2

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General Impression

The paper by Rinne et al. attempts to provide a more generalised approach to estimating the chemical loss of some key biogenic volatile organic compounds between emission and flux measurement above the canopy. It does this by coupling a Lagrangian stochastic particle model to a model that predicts in-canopy turbulence on the basis of canopy characteristics. The paper partially achieves the goal by providing normalised plots of the effect and some lookup tables. 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 emphasis. The paper should be published after these and some additional concerns expressed below have been addressed. Major comments.

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.

The limitations of the Damkoehler 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 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. 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 m)) and u* should already depend on the canopy. Taking it another step further, even tau_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. 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 $Da$. What is the rationale for stopping the investigations at $Da=0.45$?

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 Hyytiala, but also discuss uncertainties, e.g. due to the turbulence parameterisation in the so-called unresolved basal layer, the 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 $\sigma_w/u^*$ profiles predicted by the model for the different canopies. 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.

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.

Minor scientific comments.

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

P31825, l19: 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.

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. Fig. 2. Is it really realistic to use a discontinuous $\tau_c$ 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.

Technical corrections and English: P 31821, l16: Better: “Thus, the larger the Damkohler number is, the more likely is it for the chemical degradation to cause significant”

P31825, l6: “In the parameterisation the parameter alpha of the beta-distribution “

P31825, l7: What is ‘the other’ parameter? Explain!

P31825: l14 states that alpha was adjustable, while line 7 states that it was constant. Please clarify.

P31826, l7 reads better without the word ‘such’.

P31827, l4. Write ‘canopy-top’ as in the following line.

Section 3 should be called ‘Measurements of oxidants during HUMPPA-COPEC’

P31827, l12: Better: ‘Our measurement of ‘; also, a full stop is missing at the end of this sentence.

P31827, l14: the bracket is incorrect

Section 3.2. Please clarify if the instrument measures NO3 and N2O5 individually or only their sum. Is the description of the approach really required? In my opinion, it would suffice that the direct measurement of NO3 was insufficiently sensitive to resolve the concentrations at Hyytiala and that they were therefore estimated.

P31829, l22. Starting the sentence with ‘Because’ would make it lot more readable. Replace ‘traverse’ with ‘cross’ or ‘move’ (2 occurrences).
P31830, l1. “by the chemical sink.”
P31834, l10: “We have used a stochastic”
P31834, l18: “flux-to-emission ratio”

Caption to Fig. 2: “below the displacement height”

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 31819, 2011.