

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

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We thank the referee for the critical 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#3: I reiterate Anonymous Referee 2’s main concerns, especially that the results of the study are less generalisable than claimed by the authors. I also encourage changing the focus of the paper from all possible forest canopies to specific chemical processes within coniferous forest canopy types.

A: We agree with the referee that the title of the manuscript may be too general. However, as mentioned also in the answers to the comments by referee #2, our view is

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that the results are applicable not only to coniferous forest but also other forests with similar canopy shape. Also the approach in which chemistry is described as chemical lifetime is applicable also for compounds other than BVOC, although not to all reactive compounds. As one of the main aspects of the manuscript is to explore the applicability of stochastic Lagrangian transport model for the problem at hand, we will change the title to “Effect of chemical degradation on fluxes of reactive compounds – a study with a stochastic Lagrangian transport model”. We will also emphasize more the limitations of our approach in the revised manuscript.

R#3: If the flux degradation is really dependant on u^* (barely mentioned until the conclusion), then why does the paper focus Da ? I'm not sure how widely used a table of Da will be, given the parameters used in the calculation are specific to a coniferous forest.

A: We agree that we didn't express this issue in an explicit and clear manner in the original manuscript. As mentioned also in the response to the referee #2, The dependence on u^* is implicit to the definition of Da (or Da_h) which is inversely proportional to the u^* . Thus the F/E ratio, dependent on Da , is also dependent on u^* . This will be clarified in the revised manuscript

Additional comments not dealt with by other reviewers:

R#3: Knowing the position and sampling height of the species considered here is key to determining the chemical degradation vs flux. A schematic of the sampling setup for each of the instruments would be helpful and answer many of the next few questions that I have included to help clarify the setup.

A: A schematic of the sampling locations and list of sampling heights etc., have been presented by Williams et al. (2011). We will refer to this paper but not add a schematic to the revised manuscript as we feel it being somewhat out of scope with the study.

R#3: Section 3.1: Was a height profile of OH observed through the canopy? Or was

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sampling at a fixed height? Was this above or in the canopy? Was the LIF OH data corrected for potential interferences? If not, will this change the LIF-CIMS relationship? What was the maximum and minimum OH observed? Figure 7 shows OH observed at night. Was OH observed at night throughout the measurement period?

A: OH was only measured at two heights, above the canopy at 24 meters and in a small clearing at the height of 1.5 meters. Thus there is very little information on the OH profile within the canopy. The referee undoubtedly points toward Mao et al. (2012) indicating a potential inconsistency of OH measurements with the LiF technique, in particular in high VOC environments such as the boreal forest. The CIMS and the LiF agreed well after the background was subtracted from the LiF OH, so the interference is taken into account. This was the primary cause that we used the CIMS determined OH for the analysis in this paper. However, as a consequence, we increased the uncertainty also of the OH concentrations by the CIMS.

R#3: Section 3.2: Can you please clarify the NO₃ sampling position? The text suggests that NO₃ is sampled at canopy height but 10m from the canopy. Is the sampling tower in a clearing? Could sampling in a clearing negate the sampling 'in canopy' comment if the canopy is that sparse/broken?

A: The sampling height was at the canopy height but 10 m away from the nearest tree horizontally. This is now clarified in the revised manuscript. The sampling tower was indeed in a small clearing due to logistic reasons (for instrumentation during the campaign, see Williams et al., 2011).

R#3: What is the chemical impact of 1ppt upper estimate of NO₃ vs the observed night-time OH? If NO₃ is below LOD, should it be included at all?

A: In the manuscript we state that the LOD is 1 ppt, but also that, based on steady state calculations using known production rates and losses, about 1 ppt might be expected. Thus it is appropriate to use this level. The relative loss rates of VOC due to OH and NO₃ will depend on the respective rate coefficients and concentrations. Nighttime OH

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was about 2×10^5 molec /cm³ which is a factor of up to 100 less than the 1 ppt NO₃ (2×10^7 molec /cm³), NO₃ will likely be more important for loss of those substances like pinene or limonene etc to which it is highly reactive. We will add data on the relative importance of the oxidants to the chemical loss of our three target compounds during day and night to the revised manuscript and discussion based on this.

R#3: Section 3.3: Does the 3m height difference between NO₃ sampling and O₃ sampling have an effect on the study? Could the ozone profile between the 16.8m sampling point and a height above be used to interpolate an ozone mixing ratio at the NO₃ sampling height? How does the O₃ sampling height relate to the OH sampling height?

A: As we use very simple approach to canopy profiles, chemical lifetime being constant with height or just a step change at displacement height, this small height difference should not make a big difference. The ozone concentration does not change dramatically with height above the canopy. Thus we feel that interpolation complicates our simple approach without bringing any advantage. OH was measured at a lower height but on a small clearing.

R#3: Section 4.2: Would the canopy structure affect the height profile of the oxidant concentrations? Could the authors used variable O₃ and OH height profiles and show them? Specifically, the use of a discontinuous c doesn't seem very realistic when the oxidative profile will gradually change through the canopy.

A: As detailed in the responses to the referee #2, we chose to use a very simple oxidant profile, as we do not have closer information on the shape of the profile. The canopy density would of course affect the oxidant profile but for two reasons we decided not to include this feedback. First, in using the same oxidant profile with all canopy densities we can isolate the effect of canopy density on transport time. Second, in our model we do not have a feedback from canopy density to oxidant profile. Thus we would need to do further assumptions and modeling to have this dependence.

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R#3: Section 4.3: Is this section applicable to all forest canopies (eg. dense rainforest) or just to specific canopies (e.g. sparse coniferous)?

A: This section is mostly applicable to the sparse canopies, as this was the canopy structure used in these model runs. The density of the rainforest may induce reverse stability below the canopy and to de-couple the below canopy flow from that above the canopy. We will mention this in the revised manuscript.

R#3: Section 4.4: What is the emission profile of the isoprene, α -pinene and β -caryophyllene used in the study? Is the emission concentrated in the canopy or at the ground? The light and heat profile of the alkene emission and the heat profile of the terpenes emission should be discussed. It would make Figure 8 easier to understand. What concentrations of isoprene, etc. were observed during HUMPPA-COPEC? These concentrations will go some way to determine the reactive pathways active in the canopy.

A: In this study no measurements of actual VOC fluxes were used and the Figure 8 shows just modeled flux-to-emission ratios. Based on the earlier studies at the site we know that most of the monoterpenes originate from the canopy. The forest is only a low isoprene source. Our knowledge on sesquiterpene source distribution is even sparser but we know that both canopy and ground are sources. We will add discussion on the effect of the diurnal cycle of F/E ratio to the apparent temperature and light dependencies of the compounds discussed in the manuscript.

R#3: That NO₃ is below LOD suggests a low NO_x environment. Can this be confirmed?

A: The NO_x concentrations were 75 % of the time below 0.5 ppb thus confirming the low NO_x environment.

R#3: Figure 8: Figure 7 uses mixing ratios of the oxidants. Could the absolute mixing ratio loss of isoprene, α -pinene and β -caryophyllene be added as additional panels to

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Figure 8?

A: As the model does not give mixing ratio losses but losses of flux, this cannot be done. Also the absolute flux losses depend on absolute magnitude of emission or flux, which are not in the scope of this paper. However, we have added a Table on the relative effects of the oxidants on the oxidation of the three example VOCs.

Minor comments:

R#3: P31821 L25: What do you mean by K-theory? Reference or explanation needed.

A: K-theory refers to 1st order closure of the turbulent flow. A suitable reference will be added.

R#3: P31825 L2: Full stop missing?

A: Indeed. This will be added.

R#3: P31825 Eqn 7: Need to explain all the parameters. This goes for ALL equations.

A: This will be done.

R#3: P31826 L22: "Out of consideration"? What does this mean?

A: This sentence was not well formed and not very clear. We will rephrase it in the revised manuscript.

R#3: P31831 Eqn 13: What is g?

A: g is the acceleration by gravity. This will be added to the revised manuscript.

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