Atmos. Chem. Phys. Discuss., 11, C15566–C15568, 2012
www.atmos-chem-phys-discuss.net/11/C15566/2012/

Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #3

Received and published: 21 February 2012

General comment – This paper presents an interesting approach to quantify the chemical loss of a range of biogenic volatile organic compounds (bVOCs) between their emission within and below the canopy and the flux measurements above the canopy. I encourage publication of the manuscript after addressing the major concerns of the other referees and the major comments here. 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. 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.

Additional comments not dealt with by other reviewers:
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.
Section 3.1: Was a height profile of OH observed through the canopy? Or was 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?
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? 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?
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?

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 τ_c doesn't seem very realistic when the oxidative profile will gradually change through the canopy.

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

Section 4.4: What is the emission profile of the isoprene, a-pinene and B-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. That NO3 is below LOD suggests a low NOx environment. Can this be confirmed? **Figure 8:** Figure 7 uses mixing ratios of the oxidants. Could the absolute mixing ratio loss of isoprene, a-pinene and B-caryophyllene be added as additional panels to Figure 8?

Minor comments:
P31821 L25: What do you mean by K-theory? Reference or explanation needed.
P31825 L2: Full stop missing?
P31825 Eqn 7: Need to explain all the parameters. This goes for ALL equations.
P31826 L22: "Out of consideration"? What does this mean?
P31831 Eqn 13: What is g?

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