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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Modelling the impact of gas-phase pyruvic acid on acetaldehyde and peroxy radical formation in the boreal forest" *by* Philipp G. Eger et al.

Anonymous Referee #2

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The authors use a box model to analyze data from two field studies in Hyytiala (summer-autumn of different years), examining the potential impact of pyruvic acid (PYR) photolysis on acetaldehyde and HOx radical budgets in this boreal forest area. The topic is of interest and importance, and thus relevant to ACP readership. I have some significant concerns with the work, however, mostly related to assumptions made in the box model analyses; some of these are discussed by the authors, but I think there are others that need to be addressed (particularly in the context of how quantitative the conclusions are, given the uncertainties in PYR photolysis and depositional loss and the nature of some of the approximations made). More details follow.

One over-arching comment: Some of the ideas explored here have already been touched upon in the authors' previous publication on this topic (Eger et al., ACP 2020), and I found that some of the questions that came to mind were actually addressed in the previous paper. I would thus like to see a clear distinction made between the two works, via the addition of a paragraph or two to the end of the introductory material to summarize the findings of the previous study, and to set the stage for what is done in this paper.

More detailed comments:

Is it realistic to assume a mixed boundary layer (even in daytime) for fairly short-lived vegetative emissions? Can the authors be more quantitative or descriptive of what the implications of this assumption are?

Is the chemistry in the box model sufficiently detailed to capture HOx radical budgets accurately in this complex terpene-driven system, and thus assess changes driven by PYR photolysis? In particular, could there not be multiple sources of CH3C(O)O2 radicals from the terpene chemistry that is not included in the model? Do we really know enough about terpene oxidation to rule out PYR production?

Regarding OH in the IBAIRN modeling, I did not quite follow sentences near the bottom of page 5. Am I correct that OH is modeled (not constrained), but is lowered in the model via addition of extra reactivity to match the UV/OH correlation determined in other campaigns at the site? Please clarify.

Bottom of page 6 - Do the monoterpenes (MT's) have significantly different lifetimes and, if so, can the anything be said about how averaging their loss rates might impact the analysis?

Page 7 - I would like to get some sense of the variability in the average diel profiles shown, particularly for the emission rates of PYR and MT (Figure 2). This variability then carries forward to the data shown in Figures S3 and S4, correct?

Bottom of page 7 - The data showing the T-dependence of the PYR to MT emissions ratio look quite convincing. Isn't it likely, however, that this ratio is influenced also by light levels, thus complicating the analysis of the T-dependence?

Page 9 - Is PAN nominally in steady-state (or close to it)? If so, I am not sure it makes sense to consider its decomposition to be a source of CH3C(O)O2 radicals?

Page 10/11 - I have significant misgivings about doing anything quantitative with the HUMPPA campaign data, given the absence of PYR mixing ratio data. Surely, and as stated (to an extent) by the authors, the emissions ratios (E_PYR / E_MT) could be affected by changes in temperatures, light levels, vegetation, availability of plant litter, different soil moisture content, etc. etc. I would recommend nothing more than some qualitative estimates regarding the HUMPPA campaign data, rather than any sort of quantitative analysis. Also, I realize that inclusion/exclusion of the biomass burning impacted data made little difference to the findings, but is it not quite likely that there are biomass burning sources of acetaldehyde, MTs and possible PYR during these periods that are not factored into the analysis here?

Minor comments:

Page 4 - (R5) should have CO2 as the product, not CO.

Page 5, line 6 – IUPAC is missing the I.

Page 6, line 14 – Can some data be shown to demonstrate the statement made here stating that changes in the PYR mixing ratio could be reproduced by the model?

Pg. 7, line 9 - There is roughly a factor of two uncertainty in PYR deposition, and there is roughly a factor of four difference in the overall PYR quantum yield used in the different sensitivity studies. Thus, would not the uncertainty in the emission ratio be larger than a factor of two?

Page 8, line 25 – I am getting different numbers for the emissions ratios than are given here (on the basis of the branch emission rates given). Please check / confirm.

Page 9, line 29 – I think you are meaning to say that the fractional contribution of the alkanes drastically decreases?

Lastly, a bit of an aside: The authors might not yet be aware, but there was a presentation at the AGU a couple of months ago that appears to show the hydroxycarbene CH3COH + CO2 as the major channel at 351 nm (Osborne and co-workers). I don't think any quantum yields were reported.

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