Referee 1

We thank the referee for detailed and helpful comments, which are repeated below in black text. Our replies are in blue. We note that both reviewers suggested that making quantitative statements regarding the impact of pyruvic acid photolysis on e.g. CH_3CHO or radical production was not possible given the very concise reaction scheme used. In the light of these comments we have re-done the box-modelling using a comprehensive reaction mechanism drawn from the MCM.
We have also performed quantum chemical calculations to evaluate the fate of methylhydroxy carbene, now believed to be the major product of pyruvic acid photolysis at actinic wavelengths. The manuscript has thus been substantially rewritten.

General comments

Building upon the results reported in a previous study (Eger et al., doi.org/10.5194/acp20-3697-2020), this paper presents a modeling analysis of the potential impact of pyruvic acid photolysis on the chemistry and composition of the boreal forest boundary layer, for the conditions of summer and autumn campaigns at the SMEAR II field station in Hyytiälä, Finland. An observationally-constrained box model is used to investigate the contributions of pyruvic acid photolysis to the formation of acetaldehyde and peroxy radicals (HO2 and CH3C(O)O2), and these contributions are reported to be significant and potentially dominant. The analysis takes account of reported large disagreements in the overall quantum yield and product channel contributions for pyruvic acid photolysis, and therefore highlights an urgent need for further experimental studies on the photochemistry of this species. As with Eger et al. (2020), this paper highlights a potentially important role for pyruvic acid in the boreal forest environment. A difficulty I have is whether the reported observationally-constrained modeling study is genuinely robust enough to allow the reported quantitative conclusions to be drawn, and therefore if this paper builds substantially upon the information already reported by Eger et al. (2020). I have some serious concerns about the simplicity of the chemical mechanism used and the organic chemistry it represents. As presented (Table S2), the mechanism is a substantially simplified representation of the likely set of processes that were actually occurring in the vicinity of the campaign site. While the use of simplified chemistry can be fully adequate and justifiable, there is only limited discussion of and justification for the processes that are included and (more importantly) those that are omitted in the present work. As a result, I find it quite difficult to judge how reliable some of the reported conclusions are, particularly those that relate to radical sources and contributions (see further below).
We have now performed a more detailed box-modelling study (described in section 2.3) using the CAABA/MECCA atmospheric chemistry box model with >600 gas-phase species and ~2000 gas-phase reactions and photolysis steps.

In addition, the complete set of observations that are ideally required to allow the model to be constrained are not available for either of the autumn (IBAIRN) or summer (HUMPPA) campaigns. In particular, the abundance of pyruvic acid itself was not measured during HUMPPA, but was derived from the inferred emission rate of monoterpenes using a parameterization based on the autumn IBAIRN campaign. Eger et al. (2020) report that (unlike monoterpenes) pyruvic acid emission depends on both T and PAR, and the present paper indicates that the IBAIRN parameterization may not be transferable to other times of the year (page 8, line 3). Despite this, this is exactly what is done for the HUMPPA

simulation without any further discussion, justification or caveats. It is noted that the most impressive result (i.e. 94 % of acetaldehyde formation) is derived from that analysis and appears in the Abstract. Conversely, acetaldehyde was not measured during IBAIRN, and the reported contributions of pyruvic acid photolysis for that campaign only take account of the acetaldehyde sources that are represented in the model, which are probably incomplete.
We agree that the extrapolation to the HUMPPA-campaign was associated with great uncertainty and have removed this from the paper.

Although the presented work, and the previous study of Eger et al. (2020), provide interesting evidence for an important role for pyruvic acid in the boreal forest environment, the model used in the present modeling study is too simplistic to allow the reported quantitative conclusions to be drawn. The authors should consider addressing the shortcomings and omissions in the chemical mechanism and represented precursor species, possibly by using a customized version of an existing tool such as the MCM. I agree with the recommendations for further experimental studies on the photochemistry of pyruvic acid and on its emission rate, but these recommendations already appear in Eger et al. (2020).
We have now performed a more detailed box-modelling study using the CAABA/MECCA atmospheric chemistry box model with >600 gas-phase species and ~2000 gas-phase reactions and photolysis steps. CAABA/MECCA uses a reduced mechanism based on the MCM.

Specific comments

The chemical mechanism used for the reported simulations (Table S2) contains only selected reactions. Some of these have incomplete product sets and some are parameterized, and I can find no clear discussion or justification of what these are based on or why they are considered adequate. With the exception of pyruvic acid photolysis itself, very little is represented explicitly or fully. As a result, there is a potentially enormous amount of missing organic chemistry which could otherwise contribute to the formation of the species of interest (i.e. acetaldehyde and peroxy radicals, including HO2 and CH3C(O)O2), suggesting that the simulated contributions arising from pyruvic acid photolysis are consistently overestimated. One very clear indication of missing organic chemistry is the CH3C(O)O2 budget reported in sections 3.2 and 3.3. Decomposition of the (observed) PAN is calculated to be the major or dominant CH3C(O)O2 source. However, because PAN is a reservoir (rather than a primary source) this is approximately balanced by CH3C(O)O2 loss by reaction with NO2, indicating that an equivalent primary source is required from elsewhere. This is clearly not fully represented in the simulations.
We now consider the formation of $CH_3C(O)O_2$ in detail and find that the contribution of pyruvic acid to $CH_3C(O)O_2$ production rates are reduced as the referee correctly points out, but are still significant.

As discussed in the literature (e.g. Fischer et al., doi.org/10.5194/acp-14-2679-2014), the sources (of $CH_3C(O)O_2$) can include oxidation or photolysis of co-called “immediate” precursor carbonyls (e.g. acetaldehyde, methylglyoxal, acetone, MEK) and a suite of terpene and isoprene oxidation products. In practice, CH3C(O)O2 can be formed from the reactions of O3 with a-pinene, limonene, 2-carene and 3-carene (i.e. the measured terpenes and also many other BVOCs), from the further chemistry of peroxy radicals containing the C(OO)C(=O)CH3 substructure. These are formed as co-products with OH, following decomposition of relevant Criegee intermediates and reaction of the resultant vinoxy fragment with O2. The relevant chemistry in the applied chemical mechanism, O3 + terpenes —-> OH therefore omits the C10 organic radical co-product and all its associated organic chemistry. The missing chemistry for this pathway (and for other pathways) not only includes sources of CH3C(O)O2 and other peroxy radicals, but the set of ozonolysis pathways also potentially produces "immediate" CH3C(O)O2 precursors such as methylglyoxal (and larger C(O)C(O)CH3 species) and acetone. In general terms, the OH- O3- and NO3-initiated chemistry represented for monoterpene oxidation is severely limited, inadequately parameterized or completely absent, and the chemistry of other BVOCs (e.g. sesquiterpenes) is also not considered, even though reported to be significant at SMEAR II (Hellén et al., doi.org/10.5194/acp-18-13839-2018).

We now consider the formation of $CH_3C(O)O_2$ in detail, including those pathways associated with terpene degradation insofar as they are implemented in the MCM and CAABA/MECCA.

It is noted that the authors confirm that there must be missing sources of CH3C(O)O2 in their model (final sentence of section 3.3), to account for the observed formation of CH3C(O)OOH during HUMPPA reported by Crowley et al. (doi:10.5194/acp-18-13457- 2018). In view of this, it is not clear why the reported contributions of pyruvic acid photolysis to CH3C(O)O2 formation (e.g. in the Abstract) are not adjusted downwards, or at least qualified, to reflect this. Other than pyruvic acid photolysis, the only sources of acetaldehyde represented in the model appear to be the reactions of OH with ethane, propane and n-butane. These are highly parameterized, only making fractional yields of acetaldehyde and no other products, and incorrectly acting as a radical sink. Other than a brief footnote to Table S2, no justification for this representation is given. There are potentially other precursors to acetaldehyde that may be individually or collectively important, including ethanol, larger oxygenates (e.g. propanal and MEK: Hellén et al., doi.org/10.5194/acp-4-1771- 2004), any species with a C=CHCH3 substructure (e.g. propene, 2-butenes, 2-butenal, 2-hexenal: Hellén et al., doi.org/10.5194/bg-3-167-2006, doi.org/10.5194/acp-4-1771- 2004) and additional alkanes to those already represented.

The degradation chemistry for the alkanes is now treated properly (no longer heavily parameterised) and a much more detailaed reaction scheme (involving oxidised organics such as MEK) has been used.

Other comments

Page 2, line 13: Should probably also include CO2 for completeness. The description in section 2.2.1 also identifies formation of CH3C(O)OH + CO as an "important" channel. If this is the case, should these products also be listed here?

This section has been re-written and the description (based on existing literature) of the possible photolysis products has been moved to a new extended section (1.1)

Page 2, line 21: CH3C(O)O2 and HO2 (i.e. the other pyruvic acid photolysis products of interest) are also more immediate precursors to PAA.

This is correct, but this paragraph deals with the possibility of constraining CH_3CHO mixing ratios by measuring PAA. We now write "This finding was supported by the simultaneous measurement of PAA (which is formed e.g. via the degradation of acetaldehyde in remote environments)"

Page 3, line 2: Is "large" emphasizing that the biogenics are large (i.e. monoterpenes rather than isoprene) or indicating that the emissions are large? It is not clear.

We have amended the text and write "an area that is characterised by large emission rates of biogenics (mainly monoterpenes) and low NO_x concentrations"

Page 3, line 15: Presumably, photolysis rates of other species were also required and were/could be calculated in the same way. The reaction listing in Table S2 also includes photolysis of glyoxal and H2O2 (although the former photolysis rate is based on that of NO2), but somewhat surprisingly not CH3CHO. There are probably other omissions too, such that the species for which photolysis is represented seem rather arbitrary.
Yes, this selection of J-values was exemplary rather than comprehensive and we have removed it. We now write “Photolysis rate coefficients were derived using actinic flux measurements from a spectral radiometer (METCON GmbH).......” The new model considers the photolysis of 325 gas-phase species.

Page 4, lines 17-32: Some of the presented information would seem to require associated citations. Currently, there are none.
This text has been moved to section 1.1 and is more extensive with properly citations to the literature studies.

Page 4, reaction (R5): The products of this reaction should be HO2 + CO2.
Correction made

Page 4, line 31: For clarity and consistency, "CH3CO3 + HO2" should be written "CH3C(O)O2 and HO2".
Correction made

Page 5, line 6: "UPAC".
Correction made (IUPAC)

Page 5, line 9, and Table 1: "CH3CO3" should be "CH3C(O)O2" for consistency. Please also check whole paper for consistency.
Throughout the manuscript all occurrences of CH_3CO_3 have been converted to $CH_3C(O)O_2$

Page 5 and Table 1: The considered products of pyruvic acid photolysis are given as either "CH3CHO" or "CH3C(O)O2 + HO2". Although these are the products of interest, they do not describe either the primary photolysis products, or the full set of products following secondary chemistry (which I think are "CH3CHO + CO2" and "CH3C(O)O2 + HO2 + CO2").
We now deal with the products of pyruvic acid in detail in section 1.1 (including the formation of methylhydroxy carbene) and in the supplement (Table S1).

Page 5, lines 1-10. From what is written, it is not clear why the IUPAC recommendation differs so much from the recent study of Reed Harris et al. (2017). Perhaps the studies on which the IUPAC recommendation is based should also be cited and described, as IUPAC presumably judged those to be more reliable and convincing.
The literature on pyruvic acid photolysis is now treated in greater detail in section 1.1 with an additional table in the supplement (S1).

Pages 5 and 6, sections 2.2.2 and 2.2.3. It should probably be stated again clearly what measurements were used to constrain the model for each of the campaign simulations, so that the additions and omissions can be placed in context.
We describe the new box-model in section 2.3 and also list all parameters and trace gases that were used to constrain the model. The mechanism will be made available for download.

Page 5, line 24: "OH" should be "The concentration of OH".
Correction made.

Page 5, lines 28 and 29: The basis for the assigned additional OH reactivity for unmeasured OVOCs sounds rather arbitrary. In practice, there could an abundance of both missing sources and missing sinks of OH that are unaccounted for in the simple model used.
We now calculate OH using the detailed model and state that this compares well with the concentrations calculated from the parameterisation developed for this site using UVB radiation levels. We no longer nudge the losses of OH.

Page 6, line 27: delta-limonene should probably be d-limonene. Is delta-carene 2- carene or 3-carene?
Corrected. We now write (49 % α-pinene, 13 % β-pinene, 27 % carene (sum of 2-carene and 3-carene) , 3 % d-limonene and 8 % camphene)

Page 10, line 2: Should "preceding" be "proceeding"?
Correction made

Page 11, lines 14, 16 and 22. Insert "photolysis" after "pyruvic acid".
Correction made

Referee 2

We thank the referee for detailed and helpful comments which are repeated below in black text. Our replies are in blue. We note that both reviewers suggested that making quantitative statements regarding the impact of pyruvic acid photolysis on e.g. CH_3CHO or radical production was not possible given the very concise reaction scheme used. In the light of these comments we have re-done the box-modelling using a comprehensive reaction mechanism drawn from the MCM.
We have also performed quantum chemical calculations to evaluate the fate of methylhydroxy carbene, now believed to be the major product of pyruvic acid photolysis at actinic wavelengths. The manuscript has thus been substantially rewritten.

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.
We have now performed a more detailed box-modelling study using the CAABA/MECCA atmospheric chemistry box model with >600 gas-phase species and ~2000 gas-phase reactions and photolysis steps. CAABA/MECCA uses a reduced mechanism based on the MCM.

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.
The paper has been substantially revised. Along with the detailed box-modelling we have now done, we have also performed a theoretical analysis of the fate of methylhydroxy carbene formed initially in pyruvic acid photolysis. Overlap between the papers is substantially reduced.

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?
As we describe in detail, we have attempted to use realistic boundary-layer heights as this in central to the calculation of deposition velocities and emission rates for pyruvic acid and monoterpenes. If the boundary layer is not well mixed, the emission rates we derived (based on measurements close to ground level) will be biased high and the deposition losses biased

low. We now write "Further, our calculations are based on the assumption that the sources for pyruvic acid and MT emissions are evenly distributed and measurements made at ~ 8.5 m above the ground are representative of the entire boundary layer (i.e. that the boundary layer is well-mixed, including the very shallow boundary layer at night). A gradient in pyruvic acid mixing ratios at night cannot be ruled out, which would impact on our results. If the boundary layer is not well mixed, the emission rates we derived will be biased high and the deposition losses biased low. We estimate that the emission ratio ($E_{\mathrm{pyr}} / E_{\mathrm{MT}}$) in Eq. (2) is associated with an overall uncertainty of a factor ~2.

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?
We have now performed a more detailed box-modelling study using the CAABA/MECCA atmospheric chemistry box model with >600 gas-phase species and ~2000 gas-phase reactions and photolysis steps. We now consider the formation of $CH_3C(O)O_2$ in detail, including those pathways associated with terpene degradation insofar as they are implemented in the MCM and CAABA/MECCA.

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.
It is correct that OH was not measured during IBAIRN. However, many years of OH measurements at this site have been used to derive a simple expression that reproduces OH levels reasonably well from measurements of UVB. Our new box-model runs generate OH levels that are in agreement with those based on the UVB calculation and this is now stated in the text.

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?
We no longer quote the average lifetime as this information is superfluous. We recognise that treating the MT non-explicitly introduces significant uncertainty into the calculation and now mention this in the text.

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?
This is correct. We now refer to our previous paper (Eger et al, 2020) in which we plot the diel profiles of monoterpenes and pyruvic acid along with the 25 % and 75 % percentiles as an indicator of variability. To maintain clarity of presentation, we have chosen not to include this variability in the present Figure 2.

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?
The temperature dependence is highly uncertain as it is strongly influenced by the deposition term for pyruvic acid, which is dependent on the boundary-layer (and its insolation / temperature dependent variability). In order to emphasise this we now write: "We note that

(like the values of E_{pyr}) the temperature dependence derived is strongly influenced by the insolation-dependent diel variation of the MXL height and thus carries significant uncertainty."

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?
This is correct. In evaluating our new model results, we do not consider PAN as a net source of $CH_3C(O)O_2$

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?
We agree that the use of pyruvic emissions derived in the autumn to the same site in the summer carries great uncertainty, and we have removed the HUMPA analysis from the paper.

Minor comments:

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

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

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?
In our new box-model runs pyruvic acid was always constrained by observations. We no longer make this statement.

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?
The uncertainty in the relative emission ratio depends on the contribution to losses by photolysis and by deposition. Note that uncertainty in the BL-height cancel with this approach. We have not considered the different quantum yields. We have adopted the text to clarify this.

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.
The emission-ratios quoted are based on the emission rates (in µg C gdw^{-1} h^{-1}) listed in Table 2 and take into account the number of carbon atoms in pyruvic acid (3), isoprene (5) and monoterpenes (10).

Page 9, line 29 – I think you are meaning to say that the fractional contribution of the alkanes drastically decreases?
Based on the new box-model results, this text has been re-written.

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 CH_3COH + CO_2 as the major channel at 351 nm (Osborne and co-workers). I don’t think any quantum yields were reported.
We thank the reviewer for this information. The work was recently published (Samanta et al, 2021, Phys. Chem. Chem. Phys.). As this result changes the picture substantially, we have performed quantum chemical calculations on the fate of the carbene and changed box-model scenario “C” to consider carbene chemistry. This is a totally new section in the paper.