

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 (HO_2 and $\text{CH}_3\text{C}(\text{O})\text{O}_2$), 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 CH₃C(O)O₂ in detail and find that the contribution of pyruvic acid to CH₃C(O)O₂ 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 CH₃C(O)O₂) 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 α-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 vinyloxy 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 CH₃C(O)O₂ 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 detailed 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 CH₃CHO 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 + 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 CH₃CO₃ have been converted to CH₃C(O)O₂

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 be 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