Reply to RC1

In the following, the referee's comments are reproduced (black) along with our replies (blue) and changes made to the text (red) in the revised manuscript.

General statement:

The manuscript presents gas-phase measurements of pyruvic acid in the boreal forest during the IBAIRN campaign. The average mixing ratio of pyruvic acid was 96 pptv with a maximum of 327 pptv. The contribution of isoprene oxidation and direct emission of gaseous pyruvic acid to the source strength is assessed in this work. The photolytic fate of gaseous pyruvic acid results in the production of acetaldehyde and peroxy radicals in the boreal forest. This is an interesting manuscript for the readers of Atmospheric Chemistry and Physics and should be published after a revision. Specific comments are provided below to improve the manuscript before publication.

We thank the referee for the positive evaluation of our manuscript and the useful comments and suggestions. We have modified the manuscript according to the comments listed below.

Specific comments:

1) The revised version of the manuscript should change its title by deleting the word "First". Such attribution is unnecessary and conflicts with other previous field measurements of pyruvic acid.

We changed the title by replacing the word "first" with "gas-phase"

"Pyruvic acid in the boreal forest: gas-phase mixing ratios and impact on radical chemistry"

In addition, while measuring pyruvic acid as described, the manuscript should indicate what other species were monitored. It is unlikely that the work was specific for pyruvic acid but that a mass range was analyzed. This range should be provided in the text and considerations for correlated species should be made in the revision to avoid fractionation of the data by reporting it together.

We added a paragraph to the method section describing that we also measured PAN, SO_2, HCl and a combined signal of PAA and acetic acid. Further we clarify that this data set has already been published in Eger et al. (2019) which describes the instrument in detail.

As well as pyruvic acid, the CI-QMS also measured mixing ratios of PAN, SO_2, HCl and a combined signal due to acetic and per-acetic acid. These measurements are described in Eger et al. (2019).

2) References to original papers introducing a concept or finding as well as the most recent literature should be both carefully highlighted in the manuscript. For example, in p. 1 l. 28, by reading Magel et al. (2006) it is clear the concept for the wide availability of pyruvic acid in the central metabolism of plants is not introduced by them but actually by Eisenreich et al., Trends in Plant Sciences 2001, 7, 78-84, DOI: 10.1016/S1360-1385(00)01812-4. Similarly, the source for Jardine et al. (2010) could be checked.

We have added the Eisenreich et al. reference.

Pyruvic acid ($CH_3C(O)C(O)OH$), the simplest α-keto-acid, is omnipresent in plants where it is central to the metabolism of isoprene, monoterpenes and sesquiterpenes (Eisenreich et al., 2001; Magel et al., 2006; Jardine et al., 2010).

In addition, in p. 2 l. 13 and l. 15, there have been four recent reports for the heterogeneous photooxidation of aromatics emitted during biomass burning that produced oxocarboxylic acids, including pyruvic acid by Pillar et al., which should be briefly described here: i) Pillar et al., Environmental Science & Technology 2017, 51, 951-4959, DOI: 10.1021/acs.est.7b00232; ii) Pillar et al., Environmental Science & Technology 2014, 48, 14352-14360. DOI: 10.1021/es504094x; iii) Pillar-Little et al., Environments 2018, 5, 104. DOI: 10.3390/environments5090104; and iv) Pillar et al., Journal of Physical Chemistry A 2015, 41,10349-10359. DOI: 10.1021/acs.jpca.5b07914.

We have modified the text. We now separate gas-phae and condensed-phase processes and include the formation of pyruvic acid (and 3-oxo-propionic acid) in the oxidation of aromatics formed during biomass burning.

There are several known routes to the photochemical formation of gas-phase pyruvic acid in the troposphere. In clean air, pyruvic acid is generated during the photo-oxidation of isoprene via the ozonolysis of methylvinylketone (MVK) and subsequent hydrolysis of the Criegee intermediates formed (Jacob and Wofsy, 1988; Grosjean et al., 1993; Paulot et al., 2009). Pyruvic acid is found in the photolysis (in air) of methylglyoxal (Raber and Moortgat, 1995), itself formed from the OH-initiated oxidation of several biogenic VOCs (Arey et al., 2009; Obermeyer et al., 2009) including monoterpenes (Yu et al., 1998; Fick et al., 2003). Pyruvic acid is also formed in the reactions of peroxy radicals generated in the oxidation of propane, acetone and hydroxyacetone (Jenkin et al., 1993; Warneck, 2005) and in the gas-phase photo-oxidation of aromatics in the presence of NOX (Grosjean, 1984; Praplan et al., 2014).

In the condensed phase, the aqueous-phase oxidation of methylglyoxal leads to the formation of pyruvic acid (Stefan and Bolton, 1999). Biomass burning also results in the formation of pyruvic acid (Andreae et al., 1987; Helas et al., 1992) where the heterogeneous photooxidation of particle-phase aromatics plays a role (Pillar et al., 2014; Pillar et al., 2015; Pillar and Guzman, 2017; Pillar-Little and Guzman, 2018). The latter also results in formation of a further oxo-carboxylic acid with the same mass (3-oxo-propionic acid). Finally, pyruvic acid is believed to be directly emitted by vegetation as indicated by measurements of very high mixing ratios under oxidation-free conditions in a tropical rain-forest biome (Jardine et al., 2010).

3) P. 2 l. 21-23 and p. 8 l. 25: There are some differences with more current literature than the cited, which need to be considered here and estimated during a comparison of phase processes and drivers for pyruvic acid loss in the conclusions sections of the manuscript. Particularly, the photochemical loss of pyruvic acid in water was evaluated by Eugene and Guzman, J. Phys. Chem. A 2017, 121, 15, 2924-2935, DOI: 10.1021/acs.jpca.6b11916, to occur with a lifetime of only ~22 min, and was indicated to vary by ~2-times in the gas phase.

This section (title: Atmospheric sinks of gas-phase pyruvic acid) focuses on the gas-phase losses of pyruvic acid. As the reviewer states, the rate of irreversible loss of pyruvic acid to the condensed-phase will change the overall loss rate constant for gas-phase pyruvic acid.

In the revised version we consider (section 3.1) the heterogeneous loss of gas-phase pyruvic acid to available aerosol in more detail when deriving a gas-phase lifetime (and source strength).

We also consider the loss of pyruvic acid via heterogeneous uptake to particles, which can be assessed via Eq. (1).

$$k_{\text{het}} = \frac{\gamma\,\bar{c}\,A}{4} \qquad (1)$$

where γ is the uptake coefficient, A the aerosol surface area density (in $\text{cm}^2\ \text{cm}^{-3}$), $\bar{c}$ the average thermal velocity (in cm s^{-1}).

Using, the mean aerosol surface area observed during IBAIRN of $2 \times 10^{-7}\ \text{cm}^2\ \text{cm}^{-3}$ (Liebmann et al., 2019), with $\bar{c} = 2.65 \times 10^4\ \text{cm s}^{-1}$ at 290 K and an uptake coefficient of 0.06 reported for the uptake to aqueous surfaces (Eugene et al., 2018) we derive $k_{\text{het}} = 8 \times 10^{-5}\ \text{s}^{-1}$.

The overall loss rate (photolysis + deposition heterogeneous loss) of pyruvic acid is then $L_{\text{pyr}} = 2.8 \times 10^{-4}\ \text{s}^{-1}$, corresponding to a lifetime of ≈ 1h. We emphasise that the calculated lifetime (and thus the source strength we derive below) are very sensitive to the estimated deposition rate and are thus subject to major uncertainties. In addition, the appropriate uptake coefficient may be less than its value on pure water if the aerosol contains a large mass fraction of organic material which will reduce the rate of accommodation of pyruvic acid at the surface as has been seen for other trace gases e.g. N_2O_5 (Folkers et al., 2003; Abbatt et al., 2012).

Similarly, the lifetime for the loss of pyruvic acid reacting with OH radical in water was evaluated to be 1-10 days and in the gas phase to be 2-months.

While the rate constant for loss of aqueous phase pyruvic acid via reaction with OH is of interest in understanding the overall fate and role of pyruvic acid, it does not impact on the photochemical fate of (and production of gas-phase radicals from) gas-phase pyruvic acid, which are the foci of this manuscript.

4) P. 2 l. 28-30: It would be important to indicate here that one of the factors that enhances the solubility of pyruvic acid, as indicated to be “highly soluble” was explained in a paper by Guzman et al., J. Am. Chem. Soc. 2006, 128, 10621-10624, DOI: 10.1021/ja062039v; in terms of a cooperative reversible equilibrium of hydration that converts the carbonyl group into a geminal diol.

We now cite the Guzman et al paper on the underlying reason for the high solubility of pyruvic acid:

With a Henry’s law solubility of ≈ 3×10^5 M atm^{-1} (Staudinger and Roberts, 1996), pyruvic acid is highly soluble (due to formation of a germinal diol, (Guzman et al., 2006)) and wet and dry deposition and partitioning.

Similarly, for the mention of pyruvic acid “partitioning into the aerosol-phase” there should be a description here of recent work discussing the crystal structure of pyruvic acid by Heger et al., Acta Crystalographica E 2019, 75 (6), 858-862, DOI: 10.1107/S2056989019007072, and the novel study of the partitioning of gas phase pyruvic acid into water by Eugene et al., Langmuir 2018, 34, 9307-9313, DOI: 10.1021/acs.langmuir.8b01606. The last Langmuir paper should also be connected to the text about water clusters of pyruvic acid and pyruvate in p. 4 l. 26, and to the text in p. 8 l. 19-21 by including the reactive uptake coefficient of gaseous pyruvic acid by water reported to be 0.06.

We have modified the text on the loss of pyruvic acid to include heterogeneous uptake.

We also consider the loss of pyruvic acid via heterogeneous uptake to particles, which can be assessed via:

eq. 1

$$k_{\text{het}} = \frac{\gamma\, \bar{c}\, A}{4} \qquad (1)$$

Where γ is the uptake coefficient, A the aerosol surface area density (in $\text{cm}^2\ \text{cm}^{-3}$), $\bar{c}$ the average thermal velocity (in cm s^{-1}). Using, the mean aerosol surface area observed during IBAIRN of 2×10^{-7} $\text{cm}^2\ \text{cm}^{-3}$ (Liebmann et al., 2019), with $\bar{c} = 2.65 \times 10^4$ cm s^{-1} at 290 K and an uptake coefficient of 0.06 reported for the uptake to aqueous surfaces (Eugene et al., 2018) we derive $k_{\text{het}} = 8 \times 10^{-5}\ \text{s}^{-1}$.

The overall loss rate (photolysis + deposition heterogeneous loss) of pyruvic acid is then $L_{\text{pyr}} = 2.8 \times 10^{-4}\ \text{s}^{-1}$, corresponding to a lifetime of ≈ 1h. We emphasise that the calculated lifetime (and thus the source strength we derive below) are very sensitive to the estimated deposition rate and are thus subject to major uncertainties. In addition, the appropriate uptake coefficient may be less than its value on pure water if the aerosol contains a large mass fraction of organic material which will reduce the rate of accommodation of pyruvic acid at the surface as has been seen for other trace gases e.g. N_2O_5 (Folkers et al., 2003; Abbatt et al., 2012).

Finally, connected to the contribution of pyruvic acid to “SOA formation”, it would be appropriate to include original related literature and the most updated papers:

i) Guzman et al., J. Phys. Chem. A 2006, 110, 3619-3626, DOI: 10.1021/jp056097z;
ii) Guzman et al., J. Phys. Chem. A 2006, 110, 931-935, DOI: 10.1021/jp053449t;
iii) Xia et al., J. Phys. Chem. A 2018, 122, 6457- 6466, DOI: 10.1021/acs.jpca.8b05724,
iv) Eugene and Guzman, Molecules 2019, 24, 1124; DOI: 10.3390/molecules24061124 et al.,
v) Eugene and Guzman, Environ. Sci. Technol. 2019, DOI: 10.1021/acs.est.9b03742;
vi) Mekic at al., Environ. Sci. Technol. 2018, 52, 12306- 12315, DOI: 10.1021/acs.est.8b03196; and
vii) Mekic et al., Atmos. Environ. 2019, 219, 117046, DOI: 10.1016/j.atmosenv.2019.117046.

We already provide six references (between 2006 and 2017) that indicate that pyruvic acid is implicated in SOA formation. We would like to emphasise that the role of pyruvic acid in forming SOA is not the central theme of this manuscript and is only mentioned to give breadth to the role of pyruvic acid in the atmosphere. We see little gain in extending our list by a further 7 references, 5 of which are from the same research group. To update our reference list we now cite (additionally) the 2019 publication of Mekic et al., and Eugene et al.

…..thus contributing to SOA formation (Carlton et al., 2006; Tan et al., 2012; Griffith et al., 2013; Reed Harris et al., 2014; Eugene and Guzman, 2017; Eugene and Guzman, 2019; Mekic et al., 2019)

5) P. 4 l. 15: In standard analytical chemistry work the limit of detection (LOD) is established with a 99% chance of being greater than a blank for three times the standard deviation. It is confusing here that a value of 15 pptv is provided with 2 sigma for 10 s. This issue requires clarification.

Detection limits for trace-gases are often quoted at either 2σ or 3σ. We prefer to stick to 2σ as in our previous publication describing this instrument (Eger, P. G., Helleis, F., Schuster, G., Phillips, G. J., Lelieveld, J., and Crowley, J. N.: Chemical ionization quadrupole mass spectrometer with an electrical discharge ion source for atmospheric trace gas measurement, Atmos. Meas. Tech., 12, 1935-1954, doi:10.5194/amt-12-1935-2019, 2019.)

6) P. 4 l. 23-24: More details about how the oxidation was accomplished in this work (and not in the reference cited) should be provided here. An associated calibration curve should be added to the supplementary information.

We now give the most important details.

…an infrared absorption spectrometer measuring CO_2 (LI-COR) following the complete oxidation of pyruvic acid to 3 CO_2 molecules in air, using a palladium catalyst at 350 °C (Veres et al., 2010)….

and provide a plot of the calibration curve in the supplementary information

This is now provided in Fig. S1 of the supplementary information.

7) P. 5 l. 4-5: This statement is unclear. What is the meaning of a 30 % ± 10 pptv mixing ratio? Clarify the units.

The uncertainty consists of a relative term (30 %) and a constant term (10 pptv). We now write:

We have increased the total uncertainty on the pyruvic acid mixing ratios to 30% of the mixing ratio ± 20 pptv to take account of this.

8) From p. 5 l. 22 to p. 6 l. 14, and Figure S1: The general idea and the analysis are acceptable but do not explain that the anion at m/z 87 could also be assigned to 3-oxopropanoic acid.

We are unaware of measurements of gas-phase 3-oxopropanoic acid which has been associated with SOA and biomass burning. During the IBAIRN campaign we were not impacted by biomass burning. However, we now mention that 3-oxopropanoic acid has the same chemical formula as pyruvic acid and could (in principal) contribute to the signal at *m/z* 87.

……the signals at *m/z* 214.921 ($C_3H_4O_3 \cdot I^-$) and *m/z* 87.008 ($C_3H_3O_3^-$) confirmed the assignment of *m/z* 87 to a molecule with three of each C- and O-atoms, and thus to pyruvic acid (2-oxo-propionic acid) or an isomer thereof such as 3-oxo-propionic acid, $HC(O)CH_2C(O)OH$ (also known as formyl acetic acid or malonaldehydic acid).

…… We cannot rule out that 3-oxo propionic acid contributed to our CI-QMS signal at *m/z* 87 (or the HR-L-ToF-CIMS signal at *m/z* 87.008). However, as 3-oxo propionic acid has only been observed in the particle-phase and is associated with air masses impacted by biomass burning (Pillar and Guzman, 2017) our assumption that pyruvic acid is the dominant contributor to the signal at *m/z* 87 during IBAIRN appears justified.

9) P. 7 l. 21-30: This observation for the activity associated to the saw mill appears anecdotic in the context of evaluating pristine emissions from the natural boreal forest environment. The revisions should consider if the text is contradicting the objective of the manuscript.

We agree and have reduced the discussion related to the "saw-mill event" to a few lines.

During two periods of a few hours duration (9th-10th Sept), operations from a nearby saw-mill were apparent as elevated monoterpene mixing ratios (Eerdekens et al., 2009; Williams et al., 2011; Hakola et al., 2012). The influence of the saw-mill could be confirmed by examining 48 h back trajectories (HYSPLIT, Draxler and Rolph (2011). These periods are indicated in Fig. 1.

10) After the text is revised, and the calculations are rechecked based on the comments above and the inclusion of the reactive uptake coefficient of gaseous pyruvic acid by water in the model, some editions of section *3.2* will be needed in the revised manuscript.

The lifetime of pyruvic acid has been re-calculated and now includes heterogeneous uptake (see comment and reply above). The inclusion of heterogeneous loss of pyruvic acid reduces its lifetime from 1.4 to 1 hour. This impacts on its source strength (this has been recalculated, see above) but not on its mixing ratio in the gas-phase. Section 3.2 deals with the impact (gas-phase only) of the measured mixing ratios of (gas-phase) pyruvic acid. We have changed the heading of this section to emphasise this:

3.2 Role of gas-phase pyruvic acid in the troposphere.

Technical Corrections:

P. 3. l. 20: Delete “but unexplored atmospheric component”.

We deleted the words as suggested.

P. 4 l. 18-20: The statement “Laboratory … lower” is unnecessary and can be deleted.

We deleted this statement as suggested.

P. 9 l. 26: Add a mention to “Gas Phase”.

We now write:

3.2 Role of gas-phase pyruvic acid in the troposphere.

P. 10 l. 3: Insert “gaseous” before pyruvic.

We now write:

Photolysis of gas-phase pyruvic acid.

P. 12 l. 9: add “in the gas phase” at the end.

We now write:

during pyruvic acid photolysis in the gas-phase.