Reply to RC2

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:

This paper presents the first measurements of pyruvic acid in a boreal forest. There are pyruvic acid measurements in other locations but not many. In addition, pyruvic acid (unlike many other organic acids) has an active photochemistry and photolyzes rapidly. This allows it serve as a source of acetaldehyde which is probably the most important point in the paper. I think the results are interesting and probably should be published but I think the authors need to address some issues first.

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) I have some concerns about the measurement method. The largest is the use of an inlet that is heated to 200 °C. This is done so the instrument can measure PANs (it would be nice to see these concentrations in the SI at least as well and may help rule out contributions to PiBN which could have a very large sensitivity).

On page 5 we already rule out a contribution from PiBN (or PnBN) at *m/z* 87 as the signal was not affected by addition of NO (which would prevent detection of both). We also note that the sensitivity to pyruvic acid, which we mention on page 4 (4.8 Hz pptv^{-1} per 10^{6} Hz of I^{-}), is ≈ a factor 5 greater than for PAN (1.04 Hz pptv^{-1} per 10^{6} Hz of I). The PAN dataset can be found in Eger et al, 2019.

However, it may also lead to unwanted chemistry in the heated inlet. Do the authors know that the signal for pyruvic is present in the CIMS if the sampled air is unheated? Is the measured pyruvic sample modified by heating of the inlet?

During the IBAIRN campaign the inlet as continuously heated. We found no significant change in the pyruvic acid signal when operating the inlet "hot" or at room temperature during laboratory calibrations.

I assume the aerosol filter before the CIMS takes out all the organic aerosol that might evaporate. However, I would think it might significantly impact the transmission and time response to pyruvic. Was this tested? Could this filter significantly smear out the pyruvic observations? I would be especially concerned at high RH.

We agree that any inlet line and filter will serve to smear out the pyruvic acid signal over time scales of several minutes, thus precluding detection of very sharp concentration changes. As we see rapid concentration changes over time scales of 10 mins, we do not think that the stickiness of pyruvic acid will be large enough to change the diel profile of pyruvic acid and have added some text to mention this.

Owing to its large affinity for surfaces, we expect that sharp changes in pyruvic acid mixing ratios (timescales of minutes) will be smeared out over timescales of 10s of minutes because of adsorption and desorption on the inlet line and the filter and filter-holder. We do not expect that this will significantly impact the pyruvic acid time-series over the course of the diel cycle.

2) My second concern about the method is the measurement of the pyruvic background. In addition, I don't understand how the LOD for the instrument is defined. I assume it depends on the variability of the background? So this should be clearly defined. I also don't understand how the background is measured. It seems like the steel wool scrubber doesn't react fast and so the authors chose not to use this as a background measurement? It is also stated that the background varies with the overall signal. OK if this is true then at least show this in the SI. There is also a mention that backgrounds are derived when the measurement is near LOD or when the instrument is overflowed with synthetic air. So I really don't understand how the

background signal is measured and interpolated as function of time. I think this needs to be clearly explained in detail with graphical examples at least given in the SI. I also don't understand how overflowing with zero air is considered preferable to scrubbing ambient air – I am sure it is easier to deal with but I am not sure it is valid. Especially if the zero air is a different RH or temperature than ambient. My guess is that pyruvic acid is similar to nitric acid and the whole key to the measurement may be accurately measuring the instrument background.

As the pyruvic signal did not go to zero (but tracked the ambient concentration) when scrubbing ambient air to obtain a background signal we could not use variability in the background signal to estimate the LOD. We have modified the text that describes how the background signal on *m/z* 87 was obtained: The zero air was passed through the heated inlet and thus at the same temperature as ambient air when entering the IMR.

Owing to pyruvic acid's high affinity for surfaces, it typically took 5–10 minutes to remove > 90 % of the signal, which resulted in a background signal that co-varied with the ambient signal at *m/z* 87. This is illustrated in Fig. S2 of the supplementary information in which we show the raw signal at *m/z* 87 and the signal at the same mass when sampling via the scrubber. The background signal for *m/z* 87 (red dashed line in Fig. S2) was therefore determined from measurements in which pyruvic acid mixing ratios were close to the detection limit during the early part of the campaign. This choice could be confirmed by examining the background signal when the inlet was overflowed with zero-air (red points in Fig S2.). 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.

3) Did you measure formic or acetic acid during the campaign? Formic should be readily apparent at its cluster with I-. Is there evidence for acetic acid at 59?

Our instrument has very low sensitivity to organic acids as clusters with I^-. This is related to collisional dissociation effects and was mentioned in our recent publication (Eger et al., 2019) describing this instrument. As described in Eger et al. (2019), we measure the sum of acetic acid and peracetic acid at *m/z* 59.

The presence of butanoic acid is ruled out in part by assuming a similar sensitivity as acetic acid (i.e. lower than for pyruvic). Why not just measure the butanoic sensitivity?

We did not calibrate the QI-CIMS for detection of butanoic acid. Unfortunately, this cannot be done retrospectively as the instrument is no longer operated with the same ion-source. As stated in the text, enhanced levels of butanoic acid at this remote site are highly unlikely.

If there are significant levels or formic and acetic then you might expect other carboxylic acids as well. I also don't think you can argue that the lack of butanoic in the Matilla et al work argues that it is not present in this region. The pyruvic acid is certainly very different in many respects between the two locations if this is true.

We argue that butanoic acid (which is found in anthropogenically impacted air masses) is unlikely to be present at levels of > 2ppb (necessary to explain the *m/z* 87 signal). We cannot rule out that butanoic acid will contribute to some extent to the *m/z* 87 signal. We write:

Similar arguments help us to rule out a large contribution on *m/z* 87 from butanoic acid, which accompanies anthropogenic activity (e.g. traffic emissions, see Mattila et al. (2018)) and would not acquire continuously high concentrations at this site. Assuming similar sensitivities for butanoic and acetic acid, i.e. 0.62 Hz $pptv^{-1}$ (Eger et al., 2019) butanoic acid mixing ratios sometimes exceeding 2.5 ppbv would be required to account for the entire signal at *m/z* 87. In the absence of independent measurements of butanoic acid during IBAIRN, we can only conclude that it is unlikely to represent a significant fraction of the CI-QMS signal at *m/z* 87.

4) The sensitivity is reported per MHz of I-. What was the typical sensitivity?

The sensitivitiy (i.e. ion count at *m/z* 87 per ppt of pyruvic acid) depends on the concentration of primary ions (e.g. I-) in the ion-moleule reactor and must therefore be cited as a "normalised sensitivity" as we have done.

In addition, if I(CN)2- is the true reagent ion why report sensitivity relative to I-?

We suggest on page 4 that, analogous to acetic acid, $I(CN)_2^-$ may play a role in pyruvic acid detection with our electrical discharge ion source. We cannot prove this. However, as the C- and I-atoms both stem from CH_3I, we expect the concentration of $I(CN)_2^-$ to be proportional to that of I^-, which (unlike $I(CN)_2^-$) was continuously monitored during the campaign and thus serves as the best primary ion to which we can normalise signal. We now write:

The $I(CN)_2^-$ ion was not monitored continuously during the IBAIRN campaign and the signal at *m/z* 87 was converted to a mixing ratio after normalisation to the ion count of the major primary ion, I^-. As the I and C atoms in $I(CN)_2^-$ stem from CH_3I, we expect the concentration of $I(CN)_2^-$ to be proportional to that of I^- (which was monitored continuously).

How were post mission calibrations related to the field data?

We determined the sensitivity per ppt of pyruvic acid normalised to I^-, and determined that there was no significant humidity dependence. The text on page 4 has been modified:

As detection of pyruvic acid during IBAIRN was not expected, the instrument was calibrated post-campaign by simultaneously monitoring the output of a diffusion source (98 % pyruvic acid, Sigma-Aldrich) with the CI-QMS and 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 paladium catalyst at 350 °C (Veres et al., 2010). A calibration curve is given in Fig S1 of the supplementary information. The CI-QMS sensitivity to pyruvic acid was found to be independent of relative humidity (RH) for RH > 20 %. In dry air the sensitivity drops to about 60 % of that observed with humidified air reflecting the importance of water clusters in the reaction with the primary ion.

5) The Jardine et al., 2010 observations were done in a biosphere and are not truly ambient and in my opinion are closer to a chamber experiment. So I would not classify them as ambient measurements.

The salient point is that the high mixing ratios of pyruvic acid reported by Jardine et al. were the result of emissions from the biosphere. Perhaps “enclosure” would be the better term (rather than chamber). We now write:

Mixing ratios of pyruvic acid (up to 15 ppbv) were reported in an experimental tropical rain forest enclosure (Jardine et al., 2010) and were accompanied by isoprene levels exceeding 100 ppbv with other terpenoids up to ~ 10 ppbv.

6) I don’t understand including the contaminated “sawmill” days in the data. I think it only confuses things. I would remove from the dataset and concentrate on the clean boreal forest conditions.

We have removed the figure (2) that focussed on the saw-mill events and now only mention this in passing.

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.

7) I am not sure I agree with the following statement “On several days the pyruvic acid mixing ratios co-vary with those of isoprene and monoterpenes, with night-time maxima resulting from emissions into the very shallow boundary layer, which is especially apparent in the period 9–15 September 2016”.

I certainly can’t make it out from the way the data is presented. If this statement is to be maintained it needs to be backed up with a figure that shows it more clearly. If it co-varies some days why not others?

The use of the GC vs. PTRMS data for isoprene and monoterpenes also needs to be clarified as they look pretty different. Is there a measurement of boundary layer height to back up this statement?

We observe coincident maxima and minima in the mixing ratios of pyruvic acid, isoprene and monoterpenes. We have replaced the previous Figure 2 (saw-mill) with one that focusses on this period to illustrate this. Co-variance will be weakened if the sinks of pyruvic acid do not vary in the same way as those of isoprene and monoterpenes. As pyruvic acid lifetime will be influenced by dry deposition and uptake to aerosol (whereas the lifetimes of isoprene and monoterpenes are not), we expect loss of correlation if these processes are important. The day- night variation of the boundary layer height is already mentioned in Section 3. We have added a Figure (new Fig. 2) to make the co-variation of pyruvic acid with isoprene and mono-terpenes more apparent. The new text is:

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 highlighted (grey shading) in Fig. 2 which focuses on a section of the campaign in which the pyruvic acid mixing ratios were rather variable and we compare them with those of isoprene and monoterpenes. There is apparent co-variation of pyruvic acid with isoprene and monoterpenes, the night-time maxima resulting from emissions into the very shallow boundary layer. As we discuss later, the mixing ratios of highly soluble pyruvic acid will be more strongly influenced by deposition of scavenging by aqueous particles than isoprene or monoterpenes so that there is no reason to expect continuously high correlation between these trace-gases as meteorological conditions change.

Also I think Figure 3 is misleading. I am not convinced that you have a regular diurnal variation in pyruvic. There needs to be error bars in this figure that represents the deviation from average.
The point of this figure is not to show that there is a regular diel variation in pyruvic acid. The time series indicates that this is not the case. We use this median profile to make some calculations that are representative for a longer period and to indicate that pyruvic acid, isoprene and mono-terpenes have a common maximum at ~ 17:00 UTC.
We agree that the variability needs to be addressed and now show a plot in the SI with the 25 and 75% percentiles for each trace gas.
We have made a new Figure 3 with 25th and 75th percentiles as well as the median. We have separated this from (new) Fig. 4 which shows the medial diel profiles of OH, O_3 and J_{pyr}.

8) WRT the pyruvic observations I am most bothered/intrigued that it doesn’t seem to go to zero at night for the latter part of the campaign. This is very different than the Matilla et al. work which shows that the pyruvic goes to zero at night and also is greatly diminished during the day at lower altitudes. This implies efficient dry deposition in Colorado that I think should be active in Finland as well. Given that the RH goes to 100% on several nights as well I would expect dew formation and even greater enhancements in the loss of pyruvic at night. This needs to be addressed by the authors. Do they think the loss of pyruvic to the forest at night is minimized? Do emissions need to go up at night to explain observations?
The boundary layer was very shallow at night (35 m) compared to day (> 500m). For constant emission, even if the loss rate at night was a factor of 5 greater (i.e. due to uptake to surfaces), we would still have seen a nocturnal increase in the mixing ratio of pyruvic acid. Potentially great differences in boundary layer dynamics make comparison with Matilla et al difficult.

9) I am also struck by the lack of correlation of pyruvic with temperature, J, etc. If pyruvic is truly emitted by vegetation then I think at the least it should be related fairly strongly to temperature. Is there an example of plant metabolite emissions that are unrelated to temperature? or PAR?
The same statement could be made about monoterpenes at this site. The emission of monoterpenes is stronger during the (warm) day, but the mixing ratios are higher at night. This is caused by boundary layer height variations (see above).

10) In summary, I think the authors have demonstrated that the observed pyruvic levels are not due to isoprene or terpene photochemistry. However, I am not totally convinced they are observing only pyruvic acid. I am also skeptical that vegetation would emit pyruvic in a manner needed to explain the observations. So I do think that the authors need to restate their conclusions (i.e. in abstract) especially since they have not demonstrated a flux of pyruvic to the atmosphere. I agree that further measurements including flux and altitude profiles would be very useful to sort this out.
We are not the first to suggest that pyruvic acid is directly emitted by vegetation. The enclosure experiments of Jardine et al strongly indicate that this is the case. As we mention in the text, we cannot exclude contributions from other trace gases, but suggest that pyruvic acid is the dominant source of signal at *m/z* 87. As we indicate in the conclusions, further measurements e.g. using high resolution mass-spectrometry and chromatographic separation methods would be useful in confirming the results of this study.

It would be very interesting if the boreal forest emits as much pyruvic acids as monoterpenes to the atmosphere.
Indeed. As we conclude, the dependence of pyruvic acid emissions on temperature, season etc. require more studies using specific analytical methods.