

Interactive comment on “Pyruvic acid in the boreal forest: first measurements and impact on radical chemistry” by Philipp G. Eger et al.

Anonymous Referee #2

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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. 1) I have some concerns about the measurement method. The largest is the use of an inlet that is heated to 200 oC. 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). However, it may also lead to unwanted chemistry in the heated inlet. Do the authors know that the signal for

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pyruvic is present in the CIMS if the sampled air is unheated? Is the measured pyruvic sample modified by heating of the inlet? 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. 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. 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? 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? If there are significant levels of 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. 4) The sensitivity is reported per MHz of I-. What was the typical sensitivity? In addition,

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if I(CN)₂⁻ is the true reagent ion why report sensitivity relative to I⁻? How were post mission calibrations related to the field data? 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. 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. 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 20 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. The use of the GC vs. PTR-MS 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? If it co-varies some days why not others? 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. 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? 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? 10) In summary,

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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. It would be very interesting if the boreal forest emits as much pyruvic acids as monoterpenes to the atmosphere.

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