

Atmos. Chem. Phys. Discuss., referee comment RC1
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Comment on acp-2021-150

Anonymous Referee #1

Referee comment on "Varying chiral ratio of pinic acid enantiomers above the Amazon rainforest" by Denis Leppla et al., Atmos. Chem. Phys. Discuss.,
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The manuscript by Leppa et al. reports chirally specified measurements of secondary organic aerosol (SOA) at the Amazon Tall Tower Observatory (ATTO) at different altitudes during three measurement campaigns at different seasons. The authors support their observation from the field work with that of the lab experiments. The experiments appeared to be well designed, the manuscript is well written, well structured, and the discussed topic is well suited to the ACP journal.

I have several minor comments, which I think can improve this manuscript.

Introduction section: Generally ambient pinic acid is linked to VOC such as alpha-pinene, which is mainly emitted by conifer forest. It is not surprising to see such compounds in the boreal forest e.g. somewhere in northern Europe. Can authors write a couple of sentences on the vegetation type at the sampling site that could explain their observation of pinic acid (and their enantiomers)? I realise that the authors indicated additional contribution sources of alpha-pinene from the local fauna, such as termites, but what about the main contribution source? I also realise the authors are citing other publication that describes the sampling site, however; I feel the vegetation type at the sampling point needs to be described in this manuscript as well as it could possibly explain the abundance and prevalence of the certain enantiomers.

Lines 49-51: "It has been shown that physical and chemical properties, such as melting point and water solubility, can then be determined by stereochemistry (Katsumoto et al., 2010; Baker et al., 2015; Cash et al., 2016)." I completely support this statement. My question is along this line (but likely needs to be addressed in either experimental or results and discussion sections), has the author considered the effect of the sample preparation on the recovery and observation of one or the other enantiomer in their study (please see my comment on the extraction below)?

Experimental section: Line 85: "This also ensured sufficient aerosol mass on the filter".

Question: Sufficient for what? For LC/MS analysis? Please clarify.

"One half of each filter was extracted three times with 1.5 mL in a 9:1 mixture of methanol and water (Fisher Scientific, Optima™ grade) on a laboratory shaker for 30 min. The resulting extracts were combined and filtered through 0.2 µm PTFE 105 syringe filters (Carl Roth, Rotilabo® KC94.1) to remove undissolved material. The solvent was then completely evaporated under a gentle N₂ stream and 700 µL of a 9:1 mixture of water and acetonitrile (Fisher Scientific, Optima™ grade) was added to the remaining residue."

Question: What is the point for using methanol/water for extraction and then resuspending the extracts in water/acetonitrile. I understand that likely the authors wanted to match their sample solvent with that of mobile phase, but I am not sure if this is clear to the reader. Also, do you expect any methylation of the carboxylic and hydroxylic groups when extracting in methanol? I assume not within the 30 min of the extraction process, but could the authors state whether their samples were evaporated to dryness immediately or stored (e.g. in the fridge) prior to evaporation step and for how long? Also, does the selected extraction solvent affect solubility of one or the other enantiomer? Was this checked? Does this have any effect on your results and conclusion? Does the evaporation step have any affect on this as well?

Question: Besides MS calibration, have you run any system suitability mixtures to assess the target sensitivity and chromatographic performance?

Results and discussion: Figure 4, it would be useful to add the reasons for the observed gaps e.g. on the 25th, 27th of October (plot 'a') to the legend or adding the break lines to the date axis. This also applies to the Figure 4b, c, and d.