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Comment on acp-2021-403

Anonymous Referee #1

Referee comment on "Total organic carbon and the contribution from speciated organics in cloud water: airborne data analysis from the CAMP^{2}Ex field campaign" by Connor Stahl et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-403-RC1, 2021

Stahl et al. report a unique and interesting set of cloud composition measurements in SE Asia. A large number of cloud water samples was collected from a research aircraft using a well-characterized axial-flow cloud sampler during the CAMP2Ex campaign, with analysis for inorganic ions and TOC as well as carboxylic and dicarboxylic acids, MSA, and dimethylamine. Observations of cloud water organic speciation are rare, especially from higher altitude clouds typically accessible only by aircraft, as are measurements more generally of cloud composition from this part of the world. The authors do a good job presenting this rich dataset and look at interesting phenomena such as variations in TOC with altitude and differences in TOC and organic speciation between clouds impacted or not impacted by biomass burning. They also do a good job placing their findings into the larger context available from other published studies. I do have several suggestions to improve the manuscript:

- The authors need to think more about the effects of cloud water pH on their findings. Especially when studying uptake of gas phase weak acids, such as formic and acetic acids, cloud pH is a critical determinant of the effective Henry's Law solubility. Differences in the contributions of formate and acetate to measured TOC, a major focus of the manuscript, are quite possibly due to differences in pH between samples/regions. Because cloud water pH values in the region are likely roughly comparable to the pKa values for formic and acetic acids, even small changes in pH can lead to large changes in protonation/deprotonation state and significant resulting changes in partitioning from the gas phase. The manuscript mentions that cloud pH was measured. These measurements definitely need to be added to the paper. They are important in their own right but also critical to understanding gas-aqueous partitioning for key organic acids.
- Line 141: the statement here that the cloud sampler "efficiently collects cloud droplets with effective diameters > 20 um" is misleading and not especially helpful. The Crosbie et al. (2018) paper cited does talk about collecting a large fraction of cloud water when the cloud drop effective diameter is > 20 um, but this is not the most helpful comparison for the reader. As pointed out by Crosbie et al., the collector also efficiently collects smaller drops. The reference to "effective diameter" is not helpful here. The "effective diameter" is a property of the cloud drop size distribution. What is really relevant here, and what the authors should provide, is the collection efficiency of the cloud water collector as a function of physical cloud drop diameter. It is typical in

such summary statements, for example, to report the 50% cut-size diameter of the collector.

- Lines 145-146: The authors here point to a lack of leaching of organics from their plastic sample vials into the collected cloud water. More likely is the loss of cloud organics sticking to the surfaces of the plastic vials. Was this examined?
- Line 159: How "immediate" was the analysis of collected cloud water? How much time elapsed between flying through a cloud and completing lab analysis? Loss of organic acids can be significant even at 24 hr after collection, due to rapid microbial degradation.
- Line 200: acetic and formic acids "absorb" in cloud droplets; they do not so much "adsorb" to the droplet surface.
- The authors need to carefully evaluate their use of significant digits in the manuscript. The numbers of significant digits presented are often too large (normally one would present one digit more than the last digit reliably quantified) and inconsistent (e.g., 0.018 – 13.660 ppm C).
- Line 251: the Straub et al. samples were not collected in San Diego but over the Pacific ocean west of San Diego.
- Lines 267-268: differences between cloud water collectors in droplet sizes collected are relevant because cloud drop composition often varies across the cloud drop size spectrum. This point should be made more clearly for the reader and relevant references cited.
- Line 270: Here and elsewhere, please state precisely what is meant by the +/- values given. Are these +/- one standard deviation?
- Lines 308-311: Why didn't the authors include H+ (from their pH measurements) in the calculated charge balances? For the weak organic acids, were the ionized fractions calculated, using sample pH, to properly estimate the charge balance? For example, part of the measured "acetate" concentration is present as acetate and part as acetic acid in the cloud sample.
- Line 314: Na should be shown as Na+
- The analysis of the BB-impacted periods is interesting, however, I am puzzled why the authors don't use the AMS *m/z* 60 smoke marker to support their analyses. At a minimum, the abundance of *m/z* 60 should be examined between periods identified as BB-impacted and those that are assumed to not be BB-impacted.
- The authors are generally cautious to not over-interpret correlations between species concentrations. To educate the reader, however, I suggest that they point out that correlations between cloud water species concentrations are sometimes high simply due to the common effect of LWC-related dilution across species.
- Lines 483-488: The importance of cloud drop uptake of water-soluble organic gases should also be mentioned here.
- The use of acetate:formate ratios as a proxy for aged emissions is interesting, but the authors should demonstrate that these changes are not at least partly due to differences between the effective Henry's Law solubility of formic vs. acetic acids which will vary with cloud pH.
- Lines 604-606: uptake of water-soluble organic gases can also be a factor contributing to greater organic mass contributions in cloud water, although this effect is also present for ammonia and nitric acid.
- Lines 641-644: While organic acid adsorption onto coarse alkaline aerosols could well enhance uptake of these species in cloud water vs. their measurement in submicron aerosol sampled by the AMS, the alkaline nature of these coarse aerosols could also raise cloud pH and increase solubility of weak organic acids like formic and acetic acids. With the information available in this study, differentiating between these two effects is likely quite challenging.