Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC2
https://doi.org/10.5194/acp-2021-403-RC2, 2021

Comment on acp-2021-403

Anonymous Referee #2

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-RC2, 2021

General Comments

This paper presents the chemical compositions of an impressive 159 cloud water samples, which were collected around the Philippines using a rare airborne technique during the CAMP2EX campaign. The concentrations of total organic carbon (TOC), organic acids, inorganic ions, and an alkyl amine were quantified, representing a large amount of effort in chemical analysis. While the collection and chemical analysis of these samples will be a substantial contribution to this field, the data analysis and interpretation require some additional work to reflect the strength of such a large and rare set of samples. I suggest that the authors: (1) further analyze and interpret the dataset to form a cohesive story; (2) re-evaluate and clarify the study objectives; then (3) reorganize to reflect the objectives.

The observations about the dataset presented in each subsection of the Results are generally clear, but it is difficult for the reader to deduce conclusions or a story. The majority of the Results section feels like a list of observations, rather than findings with interpretation and discussion. The section discussing Clark is more complete than the others; it would be ideal if the interpretation of other subsections of the Results were discussed in this way. More examples below.

The overall purpose and objectives of the paper seem to vary between sections, making the cohesive story of the paper unclear. In particular, the study hypotheses outlined in the Introduction section aim to contrast with recent work from Metro Manila; while this Stahl et al., 2020 aerosol study is clearly impactful, these hypotheses only frame a small part of your story (in addition, the contrast with this work is concerning because of a lack of control of variables; please see Specific Comments). While the contrast is interesting, either control over the variables should be established, or these hypotheses should be secondary within the paper. Of course there are many possibilities, but some suggestions of objectives based on the current Results section include: the presentation of a new set of samples collected using the AC3 cloud water collector or more generally at high altitude from this region; the contrast of the dataset with other atmospheric waters from the

region and globally; the evidence for interactions between organic acids and dust/sea salt particles; the study of the cloud water vertical profiles of organic carbon and species.

Finally, to more clearly align with the paper results, the sections should be reorganized and revised to frame the same set of objectives. For example, the material in the first half of the Introduction is generally not explored in the Results. Also, the types of clouds from which samples were collected seems to be prominent in the abstract, but no further analysis by cloud type is discussed. Yet another example is that the Conclusion now includes insights that are not within the Results section (see Specific Comments).

Specific Comments

- Some insights currently in the Conclusion would normally be placed in a Results and Discussion or Discussion section. The "Cumulative Results" section is somewhat confusing; I'm not certain where the discussion and interpretation was intended to go.
- There are some issues with comparing the results of the present cloud samples with the Stahl et al., 2020 aerosol samples from Metro Manila: (1) chemical components in the cloud droplets could also contain different transported material from other regions, and not specifically Metro Manila; (2) the samples were not collected concurrently, leading to possible different chemical sources and processes; and (3) some aerosol will remain interstitial in the cloud and not be observed in cloud chemistry.
- Figure 1: This figure is very similar to Figure 2 in Herckes, Valsaraj & Collett, 2013 with a few updates. At the least, an obvious mention that the figure is based on their Figure 2 is warranted, but please consider just referencing their figure instead of including it here. If you keep the figure, is there a particular order to the studies included? For example, in their Figure 2, the studies are organized by TOC concentration.
- Section 2.3.1: How soon after were samples analyzed? Was this time fairly consistent between flights? Degradation of organic acids in atmospheric water samples without preservation from microbes and peroxides can affect the organic acid concentrations rapidly (e.g., for microbes: 10.1016/0960-1686(91)90198-G).
- The presented standard deviation values are confusing. In line 608, for example, the values appear to indicate that the contribution of these species to TOC mass in ~a third of the samples (based on a normal distribution) was below -5 %. Similar observations can be made about Table 3. Please clarify or check values. Is this simply a result of the data being non-normally distributed? Perhaps medians and percentiles should be used. Please state that the uncertainty values expressed throughout the paper are standard deviations.
- Be careful about using specific organic acids as "markers" for sources. Organic acids are known to originate from many sources; using a particular species to demonstrate without uncertainty that an air mass containing it was from one of those sources is not often supported by the literature.
- The Four cases identified accounted for only 60 of the samples. The other 99 samples are not discussed in particular. Can anything be said about these "non-case" samples?
- The implications of the DCA versus MCA comparisons, and the percent contributions to the subcategories, aren't clear since the acids analyzed differ from other studies. Why not discuss percent contributions to TOC or to total speciated organics (perhaps Table 3 could be percent of TOC)? Also, since glycolate is typically much less abundant than acetate and formate, I think it's more relevant to say that those two species were the most abundant, rather than saying that MCA concentrations were higher.

- Section 3.2 (Vertical Profiles): The analysis in this section in particular feels unfinished. There are many more questions you could answer with this dataset. What are the implications of your findings? Are there any trends between specific species' vertical profiles? How do these profiles compare with past profiles of cloud water or even in-cloud aerosol (for example, 10.1002/2017JD027900, 10.1029/2012JD018089, or 10.5194/acp-20-3931-2020; the concentrations might need to be converted to air equivalent concentrations to compare)? Did you look at any other AMS ions or fractions of organics (e.g., f43, f44, or f60)?
- Please check significant digits throughout the paper; for example, some reported carboxylic acid concentrations have five significant digits, which is quite high, and in line 248 the TOC concentrations have many reported digits.
- Can black carbon mass be removed from the Metro Manila aerosol to make the comparison of quantified organic/total mass reasonable between Metro Manila aerosol (Stahl et al., 2020) and the present work (for example, line 338, line 605)?
- DMA is the 4th most abundant speciated organic compound, but it was only observed above its LOD in one of the four cases. Please check that this makes sense.
- Why was malonate not quantified?
- Hilario et al., 2021 (10.5194/acp-21-3777-2021) appears to be quite related; that paper should be included in the discussion and interpretation of the present results.

Technical Corrections

Please note: this is extensive; please do not respond to each of these.

- Figure 3: Why are the species (organic acids, etc.,) presented in pie charts instead of vertical profiles? Is there information gained by presenting the more zoomed-in plots with zoomed-out overlays, or could (a), (c), and (d) be just the zoomed-out and give the same essential information? In (b), please label/describe which of the pies corresponds to which elevation.
- Figure 2: How was your map generated? Please clarify what is meant by the "midpoint of the cloud water samples" in the caption.
- Please ensure that context is given for each new paragraph. For example, in line 531, "...absolute concentrations of most organics were greatly enhanced..." does not have a qualifier to specify which samples the statement refers to.
- Parallel construction of plural nouns: for example, in line 534, "...glutarate ... and succinate ... accounted for a higher mass fraction than other cases...", there are two mass fractions discussed.
- Specify the quantity/parameter being discussed (statements should be literally correct): for example, in line 621, "...vertical profiles of AMS organic and m/z 44…", the quantity would be the mass or concentration of these fragments.
- Avoid the generic word "level" throughout your paper in favor of using a more precise word such as "concentration" or "mass".
- Line 84-85: if all types of fogs and clouds are being considered, 15 % is perhaps low. For example, see Figure 6 in https://doi.org/10.1016/j.atmosres.2013.06.005.
- Line 106: Were the samples collected for this paper not part of the CAMP2EX

campaign?

- Line 109: While these airborne observations are clearly still important, it might be worth mentioning that there are some high elevation studies of organic acids in fog/cloud water that have been carried out in SE Asia. For example, Mount Tai in China (https://doi.org/10.5194/acp-17-9885-2017) and others you cite, Japan (https://doi.org/10.2343/geochemj.2.0601), and Jeju Island in Korea (https://doi.org/10.1016/j.atmosenv.2004.09.049; Decesari et al., 2005, which you cite).
- Line 141: Based on the work of Crosbie et al., 2018, it seems that, "...efficiently collects cloud droplets with effective diameters > 20 μm" is a vast oversimplification. It would strengthen this paper if limitations of the sampling technique were directly addressed. This should include possible sampling concerns, especially droplet size-dependent collection efficiency (because chemical composition of droplets can depend on droplet size), evaporation of organic species, or concentration due to water evaporation. Please also add information about the setup of the AC3 during the campaign (and/or a relevant citation), such as pipe position. Correspondingly, in line 267 (Section 3.1), it would be beneficial to mention how the AC3 collection efficiency with respect to droplet size might be anticipated to affect differences in composition from other collectors.
- Line 152: How was pH measured?
- Line 152: please elaborate on the background removal. If it is accurate that the 10th percentile of all sample concentrations was subtracted as a background, please justify that procedure.
- Line 175: How were limits of detection calculated?
- Section 3.1, second paragraph: It would be more useful for the reader to focus this paragraph. Several of these species could be categorized as oxidation products mainly coming from aqueous reactions, and some could be particularly categorized as marine-sourced. Perhaps more importantly, some of the listed sources I find misleading. For example, I could not find any evidence of direct emission of oxalic acid/oxalate from biogenic sources in the Boone et al., 2015 paper cited, and oxalic acid has been discussed as being mainly from oxidation in the aqueous phase (10.1016/S1352-2310(03)00136-5, Warneck et al., 2003, is a clear example). In contrast, pyruvic acid has been found to be an oxidation product and to be directly emitted to the atmosphere (10.5194/acp-20-3697-2020). These should match interpretations in the Results.
- Line 309: Please use a more specific word than "good" and cite why. Please also list your source for expecting the deviation from 1.00 would be accounted for by H+ and metals (for example, the Straub 2017 paper). In addition, pH was measured; could the H+ be included in your calculations?
- Line 335: "...the measured ions in cloud water should contribute relatively more...." Please provide literature sources to support this. Please also consider that particle size is important in cloud nucleation and partitioning from the gas phase.
- Cases:
  - I would suggest putting North last so that the reader has more context. Please reorganize/revise the "North" section. In particular, the relationship to the Stahl, et al. organic acids concentrations and the split of the marine discussion are confusing.
  - What other studied air masses can be compared to these cases? What makes these samples unique or similar?
  - Please include more about the interpretation of the acetate/formate ratio as a marker for degree of oxidation. Most papers relate the ratio to biogenic versus anthropogenic sources, including in Talbot et al., 1988, Coggon et al., 2014 and elsewhere (10.1029/JD093iD02p01638). The Wang et al., 2007 paper is just one exception.
- In Section 4.3 (Biomass Burning), peat fires should be discussed because this is referenced in other papers throughout the paper.
- Line 502: Oxalate appears to be more abundant than succinate in biomass burning

samples.

- Line 528: “This motivates more attention…”: several studies, including those that you are citing, have done more in-depth chemical analysis of organic species in BB impacted cloud water.
- Line 562: What implications does the observation of DMA have?
- Line 582: Why was adipate the only organic acid correlated with calcium ion if there is evidence of organic acids partitioning to dust particles?
- Line 614: Please state that the monocarboxylic acids measured were higher volatility than the dicarboxylic acids; monocarboxylic acids include less volatile species such as longer chain acids. Why would the precursors be gaseous?
- Line 619: Is this usage of “significantly” accurate - does this indicate statistical significance?
- Line 652: Succinate was not discussed previously as being from biomass burning.