

## Comment on acp-2022-313

Anonymous Referee #1

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Referee comment on "Long-term monitoring of cloud water chemistry at Whiteface Mountain: the emergence of a new chemical regime" by Christopher E. Lawrence et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-313-RC1>, 2022

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Lawrence et al take a new and novel look at long-term records of cloud chemistry from Whiteface Mountain, NY. Their chief finding is the shift in cloud composition from a sulfate-dominated, acidic regime to a higher pH environment with decreased sulfate, increased organics, and increased mineral components. They make a case for increased importance of organic acids, but unfortunately present no recent direct speciated measurements to support this hypothesis. They also discuss increasing concentrations of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , but did not actually measure these species. Elemental Ca and Mg were measured using atomic emission and atomic absorption techniques, but incorrectly reported here as cation species. Attention to these and other matters could make a stronger manuscript.

- Abstract, lines 5-7: This sentence seems largely irrelevant to the abstract.
- Abstract, line 12: I suggest referring to an "inorganic" ion balance.
- In the abstract and throughout the manuscript the authors refer to measurements of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ; however, the measurement techniques they report measure elemental Ca and Mg, not the cationic form. The cation concentrations will be equal to or lesser than the elemental concentrations. This reporting issue can be easily corrected in the manuscript, but that does not solve the problem of using these species in calculating the ion balance or the inferred  $\text{pH}_{\text{TD}}$  (eqn. 6).
- The authors correctly point out the important variations that often exist among the pH of individual cloud droplets. In calculating the inferred pH, they attempt to remove one factor that changes the pH of drops that form on coarse mode dust aerosol. They neglect, however, that other factors will still contribute to variations in pH among other, remaining cloud drops.
- Line 34: Sulfate is not necessarily formed photochemically in the aqueous phase as many of the key reactions can occur in the dark. The oxidants (e.g.,  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ ) may have previously formed photochemically. It would be simpler to just say  $\text{SO}_2$  is oxidized to form sulfate.
- Line 34: I do not think there is compelling evidence that significant nitrate is formed via aqueous phase chemistry in many environments. This sentence should just focus on sulfate.
- Lines 36-38: more references are needed here.
- Lines 71-73: Please state clearly that this result is specific to New York.

- Line 93: The cited reference (Anastasio et al., 1994) is missing from the reference list
- Lines 97-99: Please state the materials used for the tubes and sample bottles.
- Line 101: Please state how long the LWC had to exceed the threshold to activate the collector. How quickly was the collector turned off when LWC dropped?
- Line 114: How was sample dilution from residual rinse water accounted for? I doubt the collector dried quickly in a humid environment.
- Line 121: Is there evidence that the refrigeration "prevented" microbial degradation? This is a strong claim and contradicts your statement in line 135 that degradation occurs down to 0 C. Perhaps the refrigeration "reduced" microbial degradation.
- Lines 130-131: What evidence do you have that filtration prevented microbial degradation?
- Section 2.2: Please add descriptions of pH and conductivity measurements. These are key to your analysis.
- Lines 161-162: Do you have any evidence to support the claim that nitrite is negligible compared to nitrate? Is this true now even at higher pH values where HONO solubility would increase?
- Line 156: Please define "AWI"
- Section 2.2. As mentioned earlier, the atomic emission and absorption techniques utilized measure elements, not ions. This applies to Ca, Mg, Na, and K.
- Section 2.2. Please add description of how NH<sub>4</sub><sup>+</sup> and metals were measured in the most recent years' samples collected by the Lance group.
- Section 2.2. This section briefly described many different measurement techniques used by different investigators/labs during different time periods. As mentioned above, it is incomplete. It is also confusing and difficult to follow. I suggest adding a composition measurements table that would outline measurement methods, associated time periods, and relevant QC info (detection limits, accuracy, precision).
- Figure 3:
  - The colors for TOC and WSOC are difficult to distinguish in panels a and c.
  - It is probably worth mentioning that Pye et al (2020) report pH in cloudwater from WFM back to the mid-70s and that the values between the mid-70s and mid-90s are relatively flat (and acidic).
  - Please more clearly explain what the error bars represent. Mean standard error of what? And does it make sense to center such error bars on plots of median values?
- Line 261: NH<sub>4</sub><sup>+</sup> concentrations increase then decrease in recent years. Why is just the increase mentioned?
- Line 313: Bicarbonate increases with increasing pH to a point, then decreases as carbonate ion becomes more prevalent.
- Lines 342-343: Increasing pH does increase the abundance of the deprotonated acid anion. It also increases the effective solubility of the gas phase acids, which also raises concentrations in solution. The authors need to pay more attention to the importance of the gas phase source of organic acids here and throughout the manuscript, especially for low molecular weight and highly volatile formic and acetic acids.
- Given the primary claim of this manuscript that organic acid anions are increasingly present in WFM cloud water, I am really puzzled that these compounds were not measured in samples collected by the authors. These are not especially difficult measurements. Having measured values would greatly strengthen the manuscript and enable a more complete assessment of ion charge balance and effect of the weak organic acids on droplet pH. Even in standard IC analyses, there may be evidence of these compounds in the anion chromatograms. Have the authors reviewed these?
- Table 1. The number of significant digits presented here seems hard to justify.
- Section 6: I found myself struggling to determine how useful the analysis and discussion were in this section.
  - The claim that this is a "new chemical regime" seems a bit overdramatic. Yes, WFM was dominated for decades by acidic sulfate conditions, but other parts of the world have long known cloud compositions that look more like the "new chemical regime" at WFM. The idea that species other than sulfate and H<sup>+</sup> might be important

contributors to cloud composition is not new.

- A stronger case for the change in regime would be made by having more complete speciation information. Organic acids are likely key, as hypothesized, but not measured. Ca, Mg, Na, and K should really be measured as cations to do the analyses included here. And why do the authors largely ignore K and Na in this analysis?
- The authors' constructs of pHTD, pHBU, and MAF in equations 6-8, are perhaps as confusing as helpful. MAF, in particular, is simply an ion balance equation, although  $K^+$ ,  $Na^+$ , and  $Cl^-$  are neglected.
- Section 6 goes on for many pages. At a minimum, I suggest the authors streamline the portions presented in the main text and move some of the material to supplementary information.