

## Responses to Reviewer 2

We wish to express our sincere appreciation to the reviewer for their thorough review, which has substantially improved the paper. Our responses are as follows:

**I share the first reviewers concerns about the use of cations in the analysis and whether they were in ionic forms or not. Cations are not only from dust but are present in trace amounts from many sources as shown in the work of Reff et al. (2009) et al.**

This is a legitimate concern and we thank the reviewers for bringing this to our attention. Note that for all cloud water samples that were filtered during collection (as we have been routinely doing since taking over the cloud water monitoring program in 2018), we can be more confident that the reported measurements for calcium and magnesium are cationic, since any insoluble particles  $>0.4\mu\text{m}$  would have been removed through filtration prior to analysis. Also note that the most recent years are the most impacted by calcium (with the greatest measured cation to anion ratio and the greatest difference between the measured bulk cloud water pH and estimated cloud droplet pH), in spite of filtration.

However, for the majority of the long-term monitoring program, samples were not filtered. The assumption has long been that all measured calcium and magnesium were fully dissolved within cloud water due to the dilute aqueous solutions that comprise cloud droplets. This assumption has been “baked in” to every previous analysis conducted with this dataset to our knowledge (including Aleksic et al., 2009; Schwab et al., 2016; Pye et al., 2020; Lee et al., 2022), given that only the “ion balanced” samples (including Ca and Mg, assumed to be in their ionic form) have been labeled as “Valid”. Since this is an important assumption behind our analysis as well, we tested this assumption by conducting additional analysis of 10 unfiltered cloud water samples that were archived from 2018-2020. Only a small number of samples could be re-analyzed in this way, because we do not have archived cloud water samples prior to 2018 when routine filtering began. To our knowledge, this sort of test was never conducted on samples from the historical dataset. For our reanalysis of these samples, we used a Metrohm 761 Compact Ion Chromatography (IC) system to measure cationic  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . We re-analyzed these samples twice; once without filtering and once filtering the samples through a  $0.4\ \mu\text{m}$  polycarbonate filter. We found that there were virtually no differences between the filtered and unfiltered IC measurements. When compared to the original unfiltered elemental measurements, we also found very little difference (over a wide range of pH values, 4.5-6.4), consistent with the measured Ca and Mg being completely dissolved for these samples.

In the supplemental material, we also show that, if  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are associated with  $\text{CaCO}_3$  and  $\text{MgCO}_3$ , we expect them to be completely dissolved for the full range of pH and dilution that have been observed for cloud water samples collected at WFM. Note that other forms of calcium and magnesium, e.g.  $\text{CaCl}_2$ ,  $\text{Ca}(\text{NO}_3)_2$  or  $\text{Ca}(\text{OH})_2$ , are even more soluble and even more likely to be completely dissolved at the pH and liquid water contents encountered at WFM.

Detailed information about the IC analysis and the  $\text{CaCO}_3$  and  $\text{MgCO}_3$  solubility calculations as a function of pH described above can be found in section 4 of the supplemental material.

Reff et al. (2009) identify calcium originating primarily from Unpaved Road Dust, Agricultural Soil, Bituminous Combustion (i.e. fly ash) and Construction Dust. These potential sources for calcium aerosol do not detract from our argument that the calcium found in cloud droplets resides almost exclusively in supermicron aerosol and not in submicron aerosol (the latter of which comprise the vast majority of particles acting as CCN). While several additional combustion sources for calcium are identified in Reff et al. (2009), atmospheric sources of calcium from e.g. Wildfires or Prescribed Burning are also likely to be supermicron aerosol associated with mineral dust lofted by updrafts rather than secondary mechanisms like condensation of calcium onto submicron aerosol, on account of the extremely high temperatures required to melt or vaporize calcium (e.g.  $\text{CaCO}_3$  has a melting point of 1500-2400 Fahrenheit). However, we attempt to clarify in the manuscript that we are making an assumption about the calcium mixing state, which is supported by only a handful of measurements in the region, and that additional measurements would be needed to better constrain the cloud droplet pH estimate.

Aleksic, N., Roy, K., Sistla, G., Dukett, J., Houck, N., & Casson, P. (2009). Analysis of cloud and precipitation chemistry at Whiteface Mountain, NY. *Atmospheric Environment*, 43(17), 2709-2716. <https://doi.org/10.1016/j.atmosenv.2009.02.053>

Lee, J. Y., Peterson, P. K., Vear, L. R., Cook, R. D., Sullivan, A. P., Smith, E., et al. (2022). Wildfire smoke influence on cloud water chemical composition at Whiteface Mountain, New York. *Journal of Geophysical Research: Atmospheres*, 127, e2022JD037177. <https://doi.org/10.1029/2022JD037177>

Pye, H. O., Nenes, A., Alexander, B., Ault, A. P., Barth, M. C., Clegg, S. L., ... & Zuend, A. (2020). The acidity of atmospheric particles and clouds. *Atmospheric chemistry and physics*, 20(8), 4809-4888. <https://doi.org/10.5194/acp-20-4809-2020>

Schwab, J. J., Casson, P., Brandt, R., Husain, L., Dutkewicz, V., Wolfe, D., ... & Dukett, J. E. (2016). Atmospheric chemistry measurements at Whiteface Mountain, NY: Cloud water chemistry, precipitation chemistry, and particulate matter. *Aerosol and Air Quality Research*, 16(3), 841-854. <https://doi.org/10.4209/aaqr.2015.05.0344>

**Can more information be provided on the trends in cloud water itself? Based on the criteria on Page 5 for cloud collection, has the fraction of the year when samples are collected changed over time? This could help link changes in cloud water composition to changes in general atmospheric state. How often are cloud samples being dumped due to bottles being**

**too full? Given the role of valid/invalid samples in the analysis, some commentary on the actual sample coverage would be useful.**

The cloud water collection season is approximately from June 1<sup>st</sup>- September 30<sup>th</sup> with slight variability year to year due to construction projects on the observatory or weather conditions (for example, some years start several days late or end several days early to prevent riming of the outdoor components of the cloud water collection system when inclement spring or fall weather is expected). We report the number of samples collected each year in Figure 4 of the manuscript, which is dictated mostly by sample collection rate (hourly, 3-hourly or 12-hourly).

In further consideration of this question, we now evaluate the fraction of time that the measured meteorological conditions at the summit of WFM allowed for cloud water collection within each summer month over the period 2009-2021 (as shown in Figure R1 below). The September data ends in 2020 because deployment ended early in 2021 for renovations of the silo roof. In our analysis shown below, there is some evidence that June cloud events at WFM have grown less frequent in recent years, but June also experienced the greatest year to year variability. The other months may also show very slight declines (not statistically significant). The same meteorological data for this analysis is not available prior to 2009. However, fractions of time with LWC > 0.05g m<sup>-3</sup> from 2001-2010 were reported by Schwab et al. (2016) (copied below in Figure R2), which show substantial variability but no obvious seasonal or long-term trends. Note that we had already shown in the supplement the median LWC over the long-term monitoring program for both valid and invalid datasets, which did not exhibit significant trends.

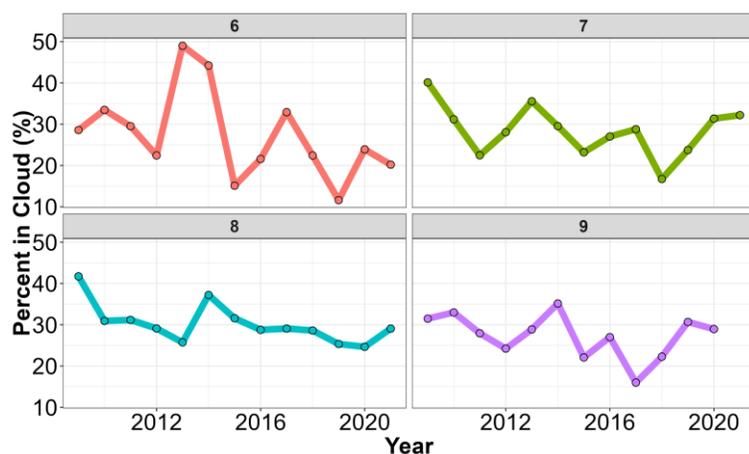


Figure R1. Percent of time that the measured meteorological conditions at the summit of WFM allowed for cloud water collection (temperature > 2C, wind speed > 2m/s, LWC > 0.05g m<sup>-3</sup> and no rain detected), separated by month (6 = June, 7 = July, 8 = August, 9 = September). Time periods when these measurements were not available, due to weather or instrumentation issues, are not included.

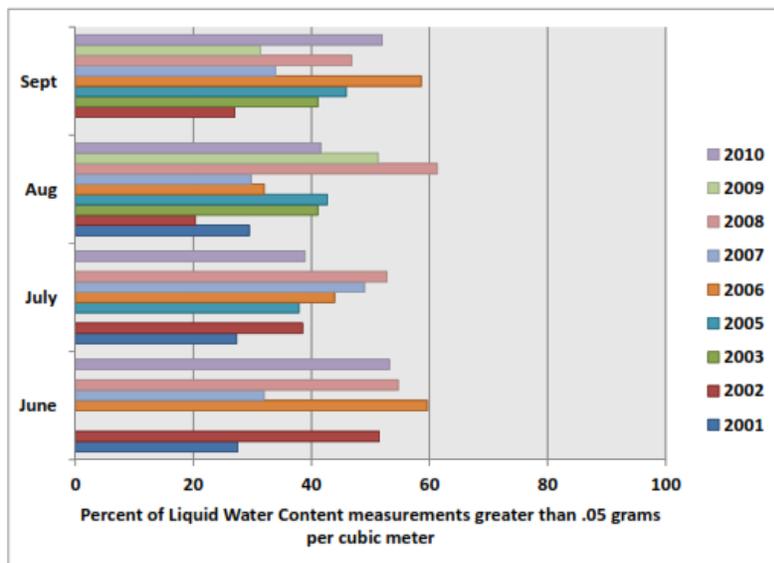


Figure R2. From Schwab et al. (2016)

Unfortunately, we do not have all the necessary information to report on how frequently the 1L accumulator was filled before the one-hour sampling period was over (after which the cloud collector would withdraw back into its housing, according to Baumgardner et al., 1997). This information would be relevant to all samples prior to 2015, since the 3-hourly sampling implemented 2007-2013 was accomplished by combining up to 3 one-hour samples, and the 12-hourly sampling implemented in 2014 was accomplished by combining up to 12 one-hour samples. In 2015, the 12L accumulator was installed so that cloud water never filled the accumulator after shifting to a 12-hourly collection cycle. With this current system, while extra cloud water is sent to waste once the 1-liter ISCO bottle is full, the 1L sample retained is an aliquot of the greater volume contained within the accumulator, and no sampling time is lost due to insufficient accumulator capacity. We might expect that, given cloud water tends to be more enriched in pollutants at the leading edge of the sampling period and become more dilute after several hours of collection (e.g. Khwaja et al., 1995), that samples with limited collection volume (i.e. which potentially occurred on occasion prior to 2015) would have higher concentrations than if they had had unlimited collection volume capacity. That type of bias we would expect could make the observed increasing TOC trend appear to be lower than it actually was. The potential impact on ion imbalance is unclear.

In consideration of this question, we also added another figure to the supplement (Figure S3) to show the percentage of invalid samples each year separated by month, which shows that “valid” and “invalid” samples are found in (and are growing more frequent in) all summer months. Much of the month-to-month variability in the “Percent Invalid” is due to the different thresholds used for low concentration and high concentration samples that have traditionally been applied for validity criteria based on ion balance. The cation/anion ratio, as reported in Fig. 5 of the manuscript, has shown steadier growth and is a better measure because it does not contain these arbitrary shifting thresholds.

As mentioned in the manuscript, precipitation (rain and snow) chemistry data from the base of WFM also shows a steady increase in cation/anion ratio (shown below by season in Figure R3, with the summer cloud water collection season corresponding to the green trace), which likewise correspond to a growing fraction of “invalid” samples. Given that rain water and cloud water collection typically do not take place at the same time (since rain events are intentionally excluded from the cloud water sampling periods), and the rain water samples are handled completely independent of the cloud water samples, the good agreement between cloud water and rain water observations provide evidence that neither sampling artifacts nor shifting meteorological conditions are likely to be major driving factors behind the growing trend in cation/anion ratios observed in both datasets.

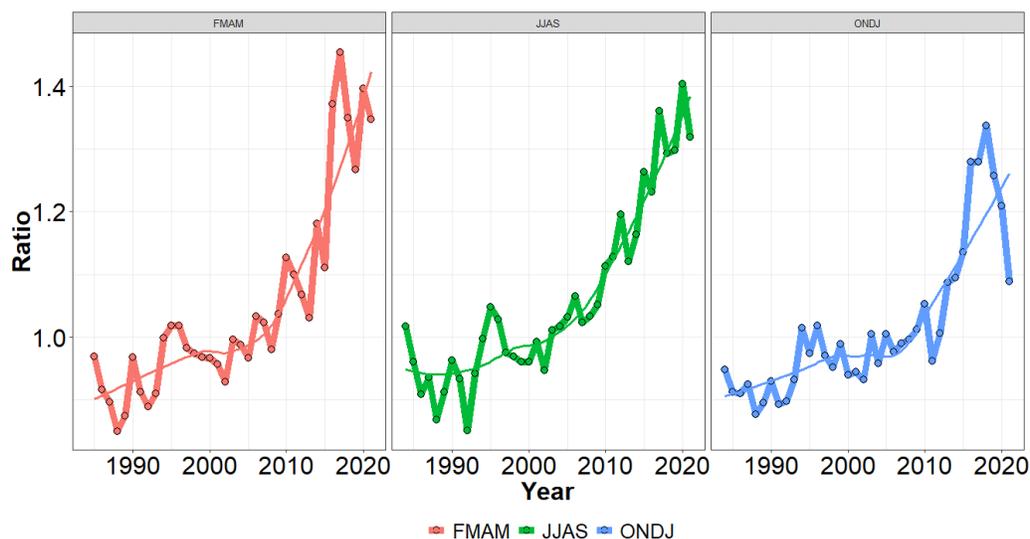


Figure R3. Annual median cation/anion ratios for rain water samples collected at the base of WFM, reported by the National Acid Deposition Program (NADP), separated by season (FMAM = February, March, April, May; JJAS = June, July, August, September; ONDJ = October, November, December, January).

Baumgardner, R. et al. (1997), Development of an automated cloud water collection system for use in atmospheric monitoring networks. *Atmospheric Environment*, 31(13), 2003-2010. [https://doi.org/10.1016/S1352-2310\(96\)00325-1](https://doi.org/10.1016/S1352-2310(96)00325-1)

Khwaja, H. A., Brudnoy, S., & Husain, L. (1995). Chemical characterization of three summer cloud episodes at Whiteface Mountain. *Chemosphere*, 31(5), 3357-3381. [https://doi.org/10.1016/0045-6535\(95\)00187-D](https://doi.org/10.1016/0045-6535(95)00187-D)

Minor comments:

- 1. The code availability is excellent. Consider creating a persistent identifier (doi) for the github code as well. Several free services are available.**

We thank the reviewer for pointing this out. A DOI was created for the github code to help ensure reproducibility of our results, which can be found here:

<https://doi.org/10.5281/zenodo.7379622>

**2. Is there any information on the seasonality and likely WSOC parent hydrocarbons important for the unmeasured anions? Are they likely biogenic or anthropogenic?**

The seasonality of TOC is something we neglected to include within the manuscript. A new figure (Figure S9) was added to the supplement to remedy this oversight. June and July typically exhibit the highest concentrations of TOC while September exhibits the lowest concentrations. Theil-Sen regression analysis shows that June, July and September all have statistically significant increasing trends, with June and September driving the yearly trend. No other measured analytes in WFM cloud water exhibit consistent seasonality. Text discussing this figure was added to the manuscript.

Unfortunately, we have no measurements relevant to parent hydrocarbons that coincide with the TOC measurements at WFM. The increased concentrations of TOC in June and July suggests that perhaps there is an important biogenic component to TOC during the growing season, but that is not something we can substantiate at present given the lack of chemical speciation data. We also looked at seasonality of the TOC versus ion imbalance (Figure R4 below), which indicated higher slopes (more ion balance for a given TOC concentration) in June and September and more variability in July. Potassium concentrations in excess of 5mg/L (frequently found by Cook et al., 2017 and Lee et al., 2022 to distinguish biomass burning influenced cloud water) were frequently shown to coincide with the highest TOC concentrations and highest ion imbalance across all months, also shown in Figure R4, which could indicate that much of the ion imbalance is associated with biomass burning smoke influence.

Seasonality of potential smoke impact on WFM cloud water samples was discussed in the recently published paper Lee et al. (2022). In that study, the high smoke probability samples were more frequent in June and July than in August and September. However, unfortunately, those authors chose to only include the so-called “valid” data in their analysis, which excludes a large number of samples in recent years (and we know from our study that those samples also tend to have much higher TOC concentrations).

Cook, R.D. et al., 2017, Biogenic, urban, and wildfire influences on the molecular composition of dissolved organic compounds in cloud water, *Atmospheric Chemistry and Physics*, 17, 15167-15180. <https://doi.org/10.5194/acp-17-15167-2017>

Lee, J. Y., Peterson, P. K., Vear, L. R., Cook, R. D., Sullivan, A. P., Smith, E., et al. (2022). Wildfire smoke influence on cloud water chemical composition at Whiteface Mountain, New York. *Journal of Geophysical Research: Atmospheres*, 127, e2022JD037177. <https://doi.org/10.1029/2022JD037177>

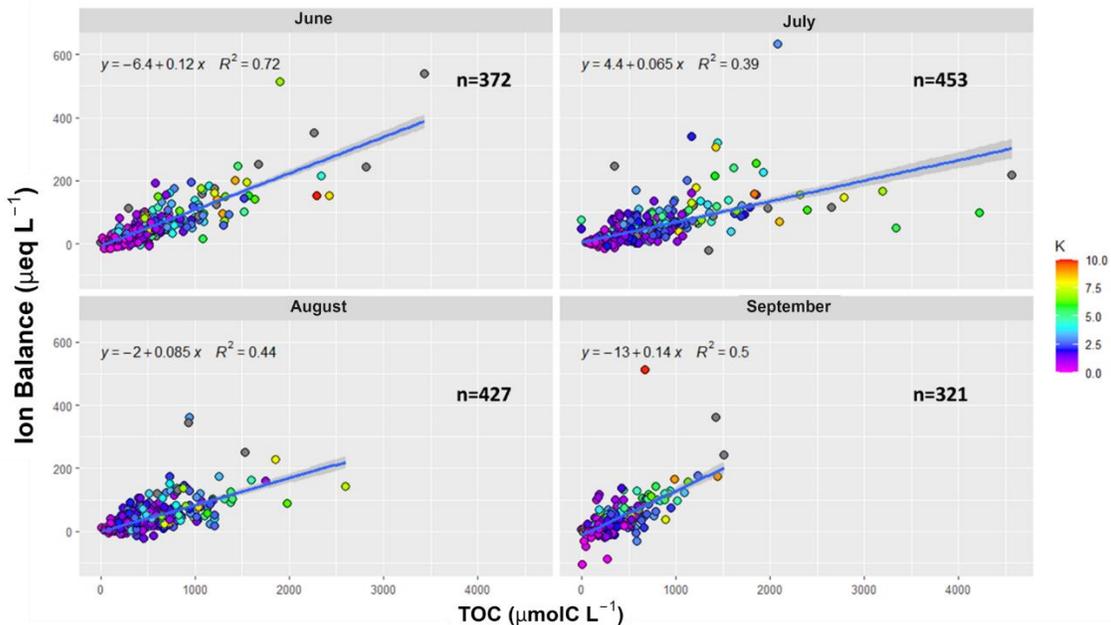


Figure R4. Measured ion imbalance (Cations –Anions) versus TOC concentrations (measured in 2009-2017 and inferred from WSOC measurements in 2018-2021) for cloud water samples collected at WFM from 2009 to 2021, separated by month. Note that markers colored grey have K<sup>+</sup> concentrations exceeding the maximum 10mg/L of the colorscale.

**3. Figure 5: Could measurement uncertainty be propagated to the cation/anion ratio?**

Median standard error bars are added to the cation/anion ratio plot in Figure 5 to better capture the sample to sample variability.

**4. Is cloud water S always in the form of inorganic sulfate (SO<sub>4</sub><sup>2-</sup>)? Are hydroxymethanesulfonate or isoprene organosulfates ever included in the cloud water sulfate concentrations?**

Hydroxymethanesulfonate and isoprene organosulfates have never been included in the WFM cloud water monitoring measurements, so we cannot say to what degree they might have been present in cloud water.

**5. What is the likely source of WSOC and insoluble OC in this data set? Are they likely changing over time. Figure 3 plots with both WSOC and TOC trends are very helpful.**

We currently do not have the capability of determining the sources of insoluble OC nor the potential changes in insoluble OC over time in this dataset, as these observations were not made during the long-term monitoring program. The paper mentioned previously (Lee et al, 2022) discussed insoluble residual particles, but only for 5 samples in 2014 and 2015 (not enough to evaluate trends). Lance et al. (2020) showed evidence

that at least some black carbon aerosols were effectively wet scavenged and incorporated into cloud droplets during a 2017 pilot study at WFM. It's possible that the concentration of insoluble particles has decreased, as the ratio of elemental to organic carbon concentrations in PM<sub>2.5</sub> have decreased, based on measurements across NY state from 2001-2015 (Blanchard et al., 2019). However, PM<sub>2.5</sub> and cloud water may not be experiencing the same trends in WSOC/TOC, as cloud water can be influenced by particles larger than 2.5 $\mu$ m (as we believe to be the case with calcium and magnesium containing particles) and cloud water can also be influenced by dissolved organic gases.

Blanchard, C.L., S.L. Shaw, E.S. Edgerton, J.J. Schwab (2019). Emission influences on air pollutant concentrations in New York state: II. PM<sub>2.5</sub> organic and elemental carbon constituents, *Atmospheric Environment*, 3, 100039, <https://doi.org/10.1016/j.aeaoa.2019.100039>

Lance, S., et al. (2020). Overview of the CPOC Pilot Study at Whiteface Mountain, NY: Cloud Processing of Organics within Clouds (CPOC). *Bulletin of the American Meteorological Society*, 101.10, E1820-E1841, <https://doi.org/10.1175/BAMS-D-19-0022.1>

**6. Could some bounding analysis be performed on the amount of organic acids needed to reconcile the data and how that fits with the measured WSOC and likely abundance of organic acids?**

We thank the reviewer for this comment as it led us to think in more detail about estimating the contribution of organic acids to TOC. By assuming the missing anions are organic acids, we can estimate the fraction of TOC that is ionic. We introduce the carbon to charge ratio ( $C/z$ ), which is the ratio of carbon atoms to carboxylic acid functional groups in a given compound. We then multiply this ratio by the ion imbalance to estimate the contribution of organic acids to TOC. Four different  $C/z$  ratios are selected to give a range of potential contributions;  $C/z = 1$  representing compounds like formic and oxalic acid,  $C/z = 2$  representing compounds like acetic and succinic acid,  $C/z = 3$  representing compounds such as lactic and propionic acid, and  $C/z = 5$ , potentially representing large organic molecules often classified as humic-like substances. This analysis shows that organic acids could contribute as much as 12% of TOC in WFM cloud water if  $C/z = 1$  and 58% of TOC in WFM cloud water if  $C/z = 5$ , and Theil-Sen regression indicates significant increasing trends since 2009 ( $p = 0.0327$ ). A section discussing this finding was added to the manuscript and a new figure was added to the supplementary material (Figure S15).