Responses to Referee #1

1. The introduction section lacks of novelty. The references are old, except for the articles published by the group. No mention of studies in other part of the globe, despite the possibility to enrich the discussion, such as Shen et al. 2024 (https://doi.org/10.1016/j.scitotenv.2024.171775)

   Response- We thank the reviewer for this valuable feedback. We have revised the introduction section to provide a stronger global context and have cited more recent relevant studies from regions worldwide.

2. The collector used is a passive sampler, while most of the collectors used on other sites are active (Schmucke, puy de Dôme, ….). Do the authors have an idea of the comparability of the samplers in term of cut-off diameter of cloud droplets and concentrations of ions in the samples?

   Response- The Mohnen Passive cloud collector uses Teflon strings with diameters of 0.035-0.04 mm, giving a 50% cut-off diameter of 2-5 um of cloud droplets for typical summit wind speeds 2-10 m/s. In an intercomparison of 120 paired cloud water samples, the ion concentration ratios of H^+, NH_4^+, NO_3^-, and SO_4^{2-} between the Mohnen Passive and Daube-Caltech Active collectors fell between 0.9-1.1 for 90% of the samples, showing excellent agreement (Mohnen & Kadlecek, 1989).

3. How is pH measured? Could the author report the error on pH measurement in Fig. 7? I think everything is reported in Lawrence's paper, but it would be better to have access to the details directly in the text.

   Response- The details have been added to the supplement text. pH was measured using a Mettler Toledo InLab Routine Pro electrode in 2018-2019, an Orion 8102BNUWP probe in 2020-2022, and a Thermo Scientific Orion Star A215 pH/conductivity meter in 2023-2024, all with 5% precision and 98-102% accuracy, which is now briefly mentioned in the caption of Fig. 7.

4. The comparison of the sample treatment methodologies is very interesting but I wonder how oxalate is depleted in cloud synthetic solution filtered with 0.2 µm mesh. The authors explain that acetate and formate are prone to reach the equilibrium with the gas phase and explain their lower concentration, but oxalate is not volatile and I don't see any explanation in the text.

   Response- We thank the reviewer for raising this point. We agree that oxalate depletion cannot be explained by volatility. The loss is likely due to biological processing. The filtration process took longer than usual, increasing the sample temperature and exposure to the room , and also the microbial presence was later confirmed in the 0.2 micron filter used in the spray test by 16S DNA sequencing. The extended contact time may have led to potential microbial degradation of oxalate during filtration.

5. "However, the aged filtered sample exhibited 45% higher acetate concentration than the aged unfiltered sample. This difference was not due to loss of acetate in the unfiltered sample, since the aged unfiltered sample had 11% higher acetate concentrations than the fresh unfiltered sample." If I understand well, the fresh sample has concentration x, the aged unfiltered had concentration x+11% and the aged filtered sample (x+11%)+45%. This means that the concentration of acetate is increasing. I think that the explanation of a possible microbial contamination with Acetobacter

strains is insufficient: this puzzling result needs to be checked in light of the concentration of acetate. For concentration of the order of 1-2 micromolar and considering the potential coelution with lactic and glycolic acid, this difference could be not significant. I would suggest giving the actual concentration and not just the normalized value.

Response- Acetate increased from 0.101 mg/L to 0.162 mg/L upon aging in filtered sample (Table S4). We agree with the reviewer that this puzzling result could reflect analytical artifacts rather than true acetate concentration, given such low absolute concentration and potential coelution of acetate with other organic acids. We thank the reviewer for highlighting this possibility. Unfortunately, we are unable to verify the chromatograms of this particular test because the measurement was conducted 7 years ago at AWI and the data were lost from a database corruption issue after a sudden power outage. This is unfortunate, but this issue does not affect our cloud water dataset.

6. Line 268: growing season à late spring, early summer, canopy bloom…

   Response- Formate, acetate, and oxalate concentrations exhibited the highest concentrations in the growing season (June and July) compared to August and September, here growing season corresponds to early summer, when canopy growth and leaf expansion are most active.

7. Lines 279-280: reduced photochemical activity or reduced emission of precursors from vegetation?

   Response- We revised the sentence with the reviewer’s suggestion to specify “reduced emission of precursors from the surrounding vegetation”.

Responses to Referee #3

We thank the reviewer for their thorough and constructive evaluation of our manuscript and for recognizing the robustness of the dataset. We appreciate the reviewer's careful summary of our key findings. We also thank the reviewer for highlighting the relevance of this work in the context of increasing wildfire influence on cloud water chemistry.

1. Line 310-315 and Figure 6: The positive correlation between surplus NH4+ and LMWOA sum in samples with surplus NH4+ is a key finding. The authors note that for DOC-rich samples in 2023-2024, the relationship is less clear, possibly due to reactions forming unmeasured nitrogen-containing organics. This is a reasonable hypothesis. Could the authors provide a brief quantitative estimate or citation regarding the potential impact of such sink reactions? For instance, referencing approximate reaction rate constants or yields from previous studies would strengthen this discussion.

Response- We thank the reviewer for this suggestion. Unfortunately, this 7-year dataset does not include measurements of carbonyls (e.g., glyoxal, methylglyoxal) or nitrogen-containing organic compounds (CHON) (e.g., amides, imidazole, amines, nitro-aromatics). Even gas phase ammonia concentrations are not well constrained at WFM given the very low time resolution of those observations (2-weeks) and the location of the AMoN site at the base of the mountain rather than at the summit where the cloud water samples are collected. Given this is not a modeling study and lacks many observational constraints for even the major known reactive nitrogen and organic precursors, we don't believe it would be appropriate to include an estimate for such sink reactions here, as a quantitative estimate of secondary organo-nitrogen production would be unreliable under these circumstances.

However, to strengthen our argument, we have cited more published studies in the Introduction of the revised manuscript that discuss the abundance of nitrogen-containing organic compounds found in cloud water and the role of aqueous/multiphase reactions involving NH3/NH4+ in forming those compounds. We also add discussion in the revised manuscript about the findings of Ditto et al. (2021), in which nitrogen-containing functional groups such as imine, amine, amide, and azole were found abundantly in Boreal wildfire smoke plumes. They reported these functional groups were often present at comparable to greater relative abundance than carboxylic acid groups in organic aerosol. They also showed that CHO abundances decreased with plume age, whereas CHON abundances increased, suggesting nitrogen addition to organic compounds in the gas and/or particle phases.

Text added in the revised manuscript-

Growing evidence suggests that aqueous organic and reactive nitrogen chemistry are linked (Xu et al., 2020; Lv et al, 2022). Organic acids influence NH3/NH4+ partitioning and aerosol acidity (Hennigan et al., 2015; Tao and Murphy, 2019), as well as pH buffering in moderately acidic droplets (Zheng et al., 2023). Nitrogen-containing organic compounds comprise a major fraction of dissolved organic matter in cloud water (Cook et al., 2017; Bianco et al., 2019), with as much as half of detected organic molecules classified as CHON within cloud water samples at a mountain top site in southeastern China (Shu et al., 2025). Enrichment of CHN and CHON compounds has been directly linked to aqueous processing in several studies (Boone et al., 2015; Kim et al., 2019, Mattsson et al., 2025; Kuang et al., 2025; Jin et al., 2025). Lab studies have shown that dissolved NH3 may react with carbonyls to form nitrogen-containing organic compounds like imidazoles, with faster production observed in small, concentrated and/or evaporating droplets (De Haan et al., 2011; Lee et al., 2013; De Haan et al., 2020; Marracci et al., 2025}. However, Boreal wildfire smoke plumes have also shown increased contributions of CHON compounds with aging (Ditto et al., 2021), presumably in the absence of clouds (though relative humidity and aerosol liquid water content were not discussed in that paper). Likewise, organo-nitrogen production has been observed in chamber experiments held at 50% relative humidity (Liu et al., 2015), and NO3- BVOC oxidation can be an efficient nighttime source of organonitrates under cloud-free conditions (Slade et al., 2019; Ng et al., 2017), indicating that aqueous processes may not always be required for secondary formation of CHON compounds. Thus, the role of reactive nitrogen in aqueous SOA formation can be complex, potentially involving competing multiphase mechanisms, and different outcomes may be expected for clouds influenced by wildfire smoke, agricultural emissions and/or varying mixtures of biogenic and anthropogenic precursors.

2. Section 2.4.4 “contribution of LMWOAs to cloud droplet acidity”: The analysis of MAF and MAF* clearly demonstrates the growing importance of unmeasured anions. The authors state that including LMWOAs explains 5-40% of the missing acidity annually. To make this range more interpretable, could the authors add a brief discussion linking the yearly variability in this percentage to specific environmental conditions? For example, is the lower explanatory power (5%) associated with years of high wildfire smoke influence (like 2021, 2023), where higher molecular weight organics might dominate, as suggested later in the smoke section?

Response- We have rewritten this paragraph for clarity in section 3.4 of the revised manuscript.

Revised text -

Adding the new measurements of LMWOA to the "bottom up" calculation for estimated cloud droplet pH decreases pH_BU by 0.1–0.45 units and explains 5-36% of the cloud droplet acidity on an annual median basis. These findings are supported by previous studies where formic + acetic acids supplied up to 60% of droplet acidity in remote and mountain sites (Keene et al., 1983, Galloway et al., 1982; Keene et al., 1986; Andreae et al., 1988; Pye et al., 2020). The contribution of LMWOA to droplet acidity was greatest in 2018, 2021 and 2023, as exhibited by a greater difference between MAF and MAF in Fig. 8. The latter two of these years were heavily influenced by high primary LMWOA emissions from wildfire smoke events (Permar et al., 2023), with LMWOA contributing 30-33% to cloud droplet acidity on an annual median basis in 2021 and 2023. The meteorological and chemical properties associated with wildfire smoke events in these two years are contrasted in section 3.5 of this paper. However, the even stronger impact of LMWOA on cloud droplet acidity in 2018 likely resulted from different precursors and dominant reaction pathways than in 2021 and 2023, since the 2018 pollution events were associated with high temperatures, high O3 and high BVOC concentrations (Lawrence et al., 2024), with little influence from wildfire smoke.

3. Line 365-370 and Section 2.4.5 (Smoke Influence): The comparison between "Aged" and "Fresh" smoke events is insightful. The hypothesis that aging leads to oligomerization, increasing DOC while decreasing LMWOAs, is plausible. To further support this, could the authors comment on the potential changes in the average oxidation state (e.g., O:C ratio) or double bond equivalent implied by this transformation, even if not directly measured? Referencing previous work (e.g., Cook et al., 2017, cited in the manuscript) that observed such trends in smoke could strengthen the argument.

Response- We thank the reviewer for this suggestion. We would like to bring line 435-440 in the preprint manuscript to reviewer's attention where Cook et al (2017) had been cited again. Although we did not measure O:C ratio or double bond equivalent (DBE), our observations are consistent with chemical aging of smoke that increases DOC while decreasing the abundance of LMWOA, likely by aqueous phase accretion/condensation pathways that convert low molecular weight oxygenates into higher molecular weight multifunctional oligomer organic species. We have expanded this section to more clearly describe the findings of Cook et al. (2017) (starting on line 483 in the revised manuscript)

4. Line 455-460 and the Conclusion: The study rightly concludes that a substantial fraction of cloud droplet acidity and anions remains unaccounted for, pointing to unmeasured organic species. This has significant implications for atmospheric modeling and chemistry. To elevate the impact, the authors should more explicitly state the priority classes of compounds that future research should target based on their findings. For instance, should the focus be on di-/tricarboxylic acids beyond oxalate, organosulfates/nitrates, or humic-like substances (HULIS)? A specific recommendation would guide future analytical efforts.

Response- We thank the reviewer for this suggestion. We agree that future work should prioritize methods to measure total organic anions in the cloud water. FTIR spectroscopy would be a valuable addition since it can provide bulk total organic acid equivalents which would complement the ion budget the most (Coury and Dillner, 2008). We have added this suggestion to the conclusions section.

5. Line 85-110 (Site Description) and Generalizability: Whiteface Mountain is an excellent remote, forested site. The authors briefly note its relevance for studying long- range transport. In the conclusion or discussion, a short statement on the expected similarities or differences in LMWOA dynamics at other key site types (e.g., coastal, arid, or heavily polluted regions) would help readers assess the broader applicability of the trends observed here. This is particularly relevant given the global increase in wildfire smoke and changing emissions.

Response- We thank the reviewer for this suggestion. We have expanded the introduction section to add references to additional cloud water and aerosol measurement sites from diverse regions worldwide. We have also added a brief sentence in the discussion section to place our dataset from Whiteface Mountain in a broader context, noting how LMWOA behavior may vary across environments and using the oxalate-to-sulfate (OXL:SO_4) ratio to compare our findings with the global, multi-campaign datasets presented in Hilario et al. (2021) and added more details to the supplemental.

Text added in the revised manuscript-

“In our dataset, the oxalate-to-sulfate ratio (slope ≈ 0.075) is higher than the global aerosol median oxalate-to-sulfate (0.0217) reported by Hilario et al. (2021), while still falling within the broader variability observed across worldwide aerosol campaigns, where the highest values (~0.35) were associated with anthropogenically polluted air masses and sometimes influenced by coarse aerosol or smoke and lowest values (~0.01) corresponded to cleaner, less polluted or weakly processed air masses.”

6. Minor Comment: Line 150-155 (Equations 3-4): The assumption that other cations are negligible is standard but worth a quick justification. A reference to typical cation concentrations in remote cloud water (or a citation to the site's prior work like Lawrence et al., 2023) would suffice.

Response- We thank the reviewer for this comment. Below we provide additional analysis of the assumption that other cations are negligible in our dataset. We have added the figure and explanation to the supplement as well.

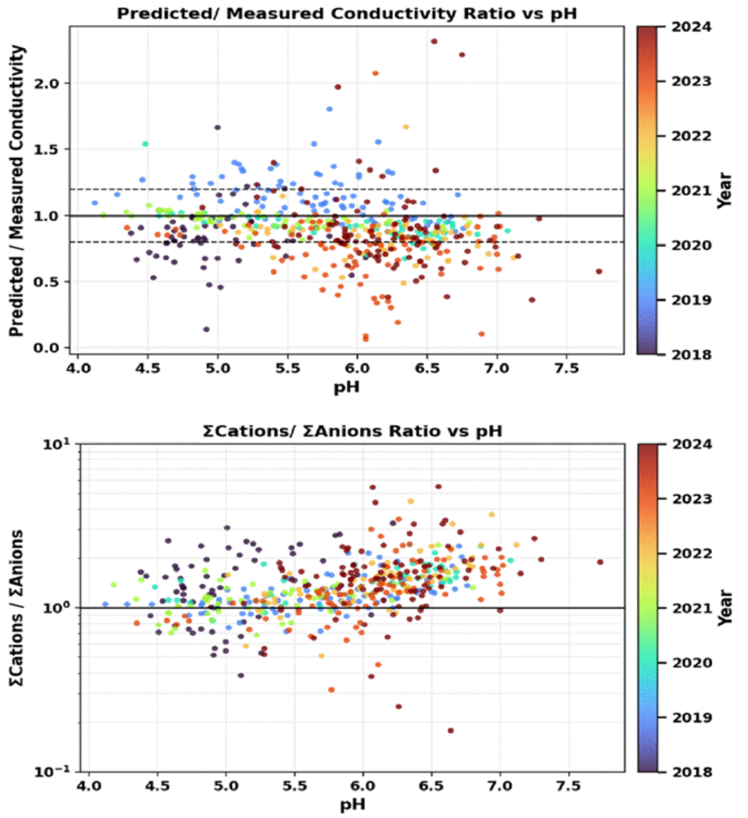

Fig S7: Predicted/ Measured conductivity ratio (top) and charge balance expressed as ΣCations/ ΣAnions ratio (bottom) as a function of the measured bulk cloud water pH for all cloud water samples from 2018-2024. The solid horizontal line indicates unity and dashed line in the top panel represents 20% uncertainty in Predicted/Measured conductivity

In the bottom panel, the total measured cations (H^+, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}) are consistently higher than the total measured anions (SO_4^{2-}, NO_3^-, Cl^-, and 3 LMWOA), with ΣCations/ ΣAnions ratio most frequently near unity and more often > 1, especially at higher bulk pH. This result suggests that the dominant charge imbalance is due to excess cations, implying that a larger fraction of the samples (~81.3% samples of the total) contain net missing anion equivalents. Additionally, as shown in the top panel, predicted/measured conductivity ratios are generally close to unity (within ±20%) for most samples at bulk pH < 5.5. At higher bulk cloud water pH, the measured conductivity more frequently exceeds predicted conductivity, further supporting the presence of additional unmeasured anions. The calculation for predicted conductivity is based on the sum of measured ion concentrations weighted by molar conductivity for each analyte, as in Lawrence et al. (2023) except for the addition of LMWOA in this study.