Organic Acids In Cloud Water, Aerosols And Cloud Droplet Residuals at the Summit Of Whiteface Mountain (WFM)

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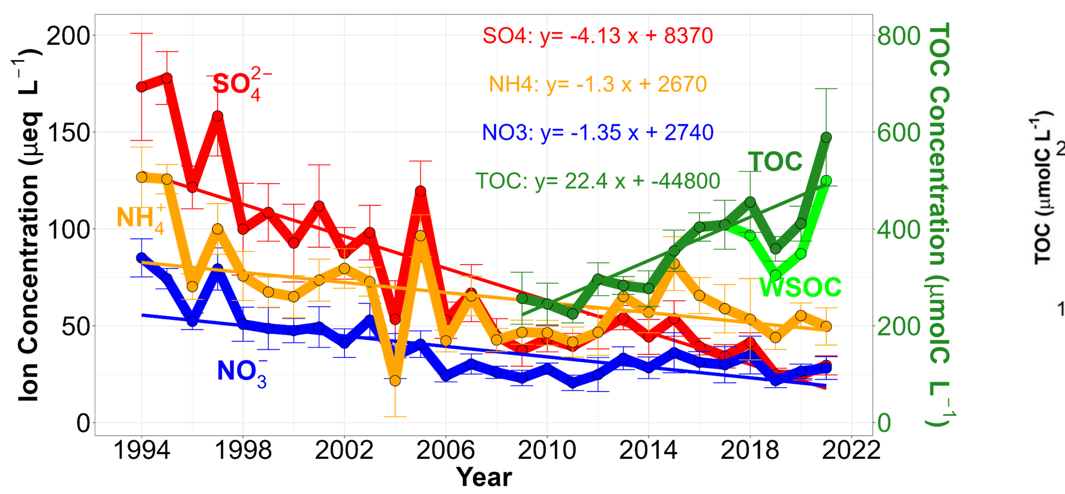
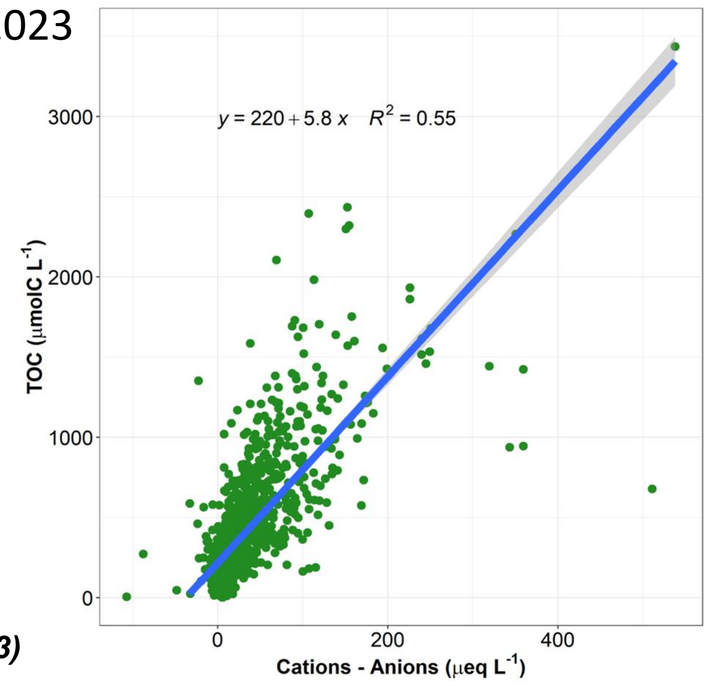
Multi-phase Atmospheric Chemistry at WFM

1. Cloud water (dilute aqueous droplets suspended in the air at >= 100% RH) - samples from 2018-2023
2. Aerosols or Cloud Droplet Residuals (suspended in the air at < ~100% RH) - 2023 summer samples
3. Gas phase (volatile organic compounds) - 2022-2023 canister samples

Organic acids are expected to be an important subset of Missing Anions



Lawrence et al., ACP (2023)



Long term Trends-

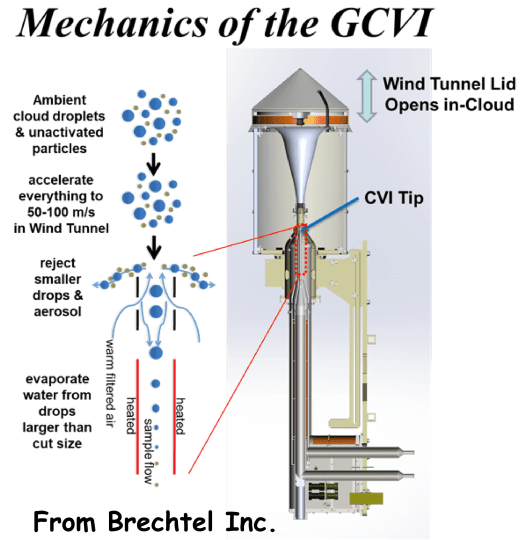
- Sulfate ion decreasing
- Little decrease in reactive nitrogen (NO_3, NH_4) after 2009
- TOC increasing trend (measurement began in 2009)
- Ion imbalance (cations–anions) correlates with TOC.
- Increasing pH in cloud water can enhance gas-aqueous phase partition of organic acids.
- Growing fraction of samples with excess NH_4^+ may be a driving factor for the above processes.

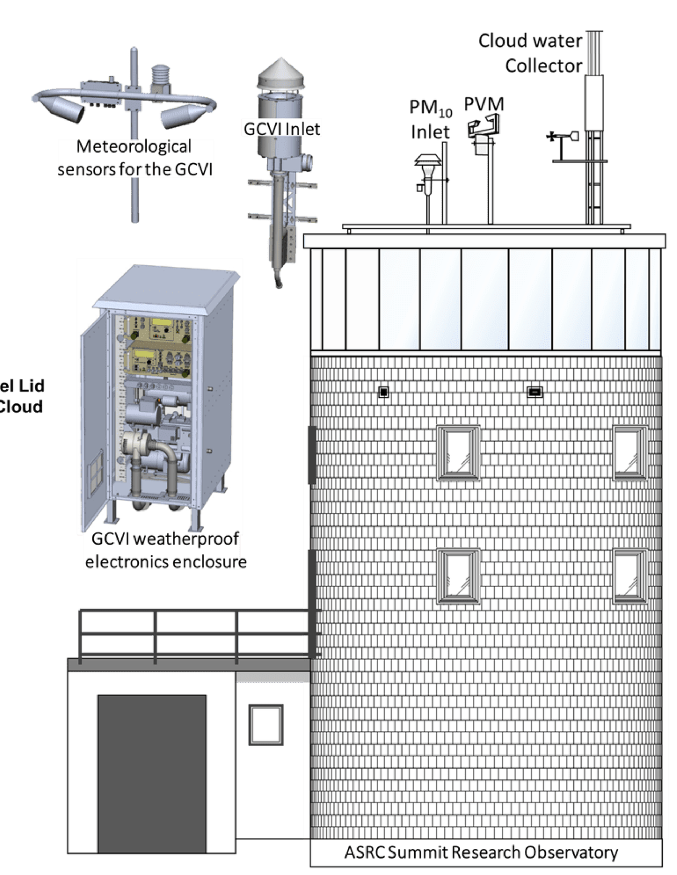
Sampling and Measurement Techniques

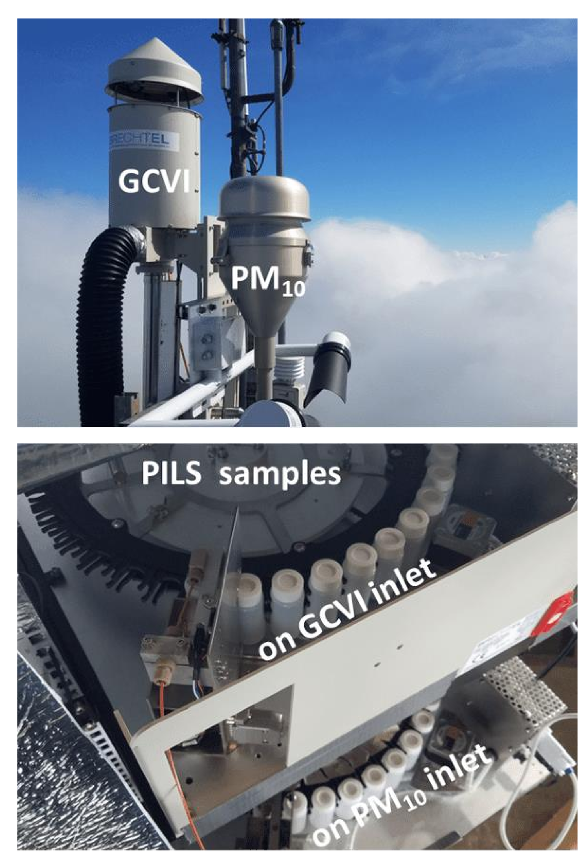
New Instrumentation to measure cloud droplet residuals and aerosols

Installation of a new Ground-based Counterflow Virtual Impactor (GCVI) inlet allow droplets to be sampled continually into an airstream by instruments within the ASRC Summit Research Observatory.

Mechanics of the GCVI







Particle-Into-Liquid Samples (PILS) are collected at 6hrly intervals on 1 of 2 carousels:

1. when the summit is in cloud - cloud droplet residual via GCVI inlet
2. when the summit is in clear air - aerosol via PM10 inlet

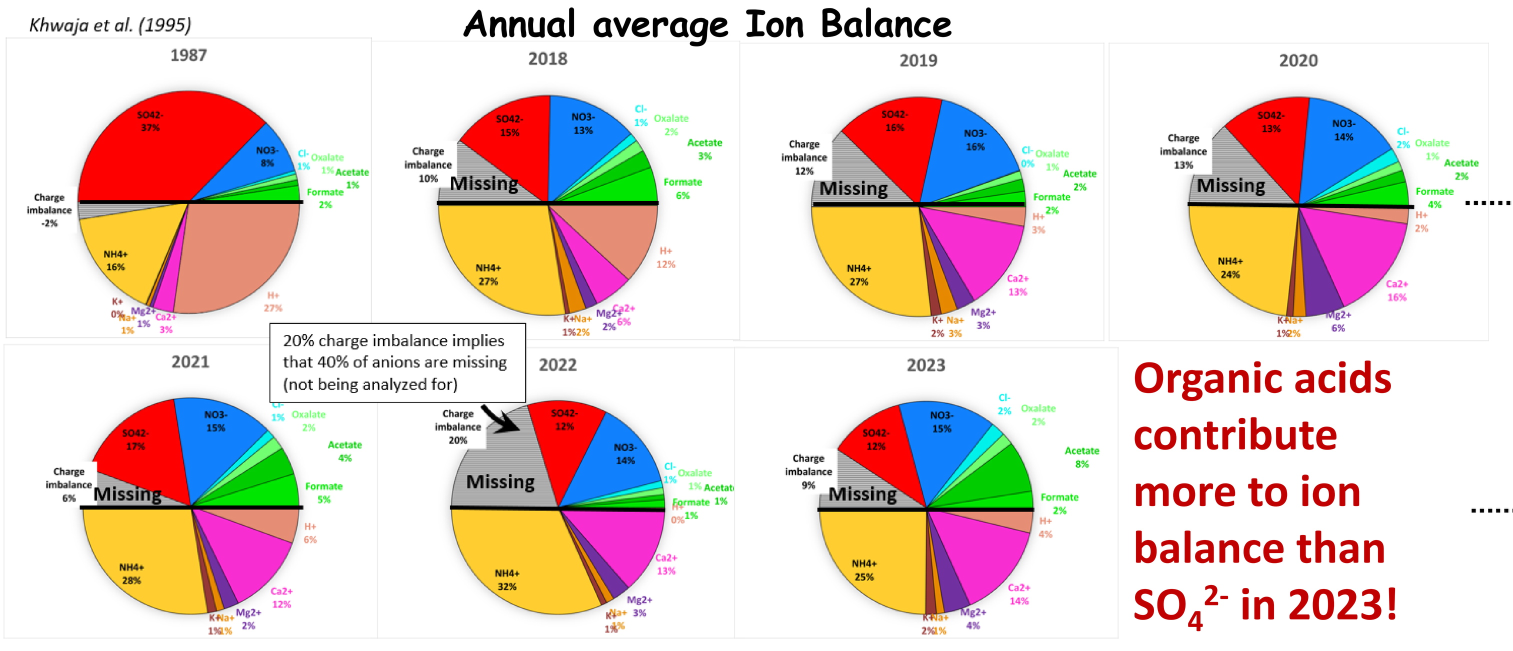
This allows us to compare the chemical composition of cloud droplet residual and cloud water from the same cloud event, and also compare to the aerosol chemical composition before and after cloud events.

Lab Measurements for PILS samples and 2023 cloud water samples

- Metrohm IC for anions and cations: Sulfate (SO_4^{2-}), Nitrate (NO^{3-}), Chloride (Cl^-), Formate, Acetate, Oxalate, Ca^{2+}, Na^+, Mg^{2+}, K^+, and Ammonium (NH_4^+)
- Sievers 900 TOC analyzer – WSOC (Water Soluble Organic Carbon)

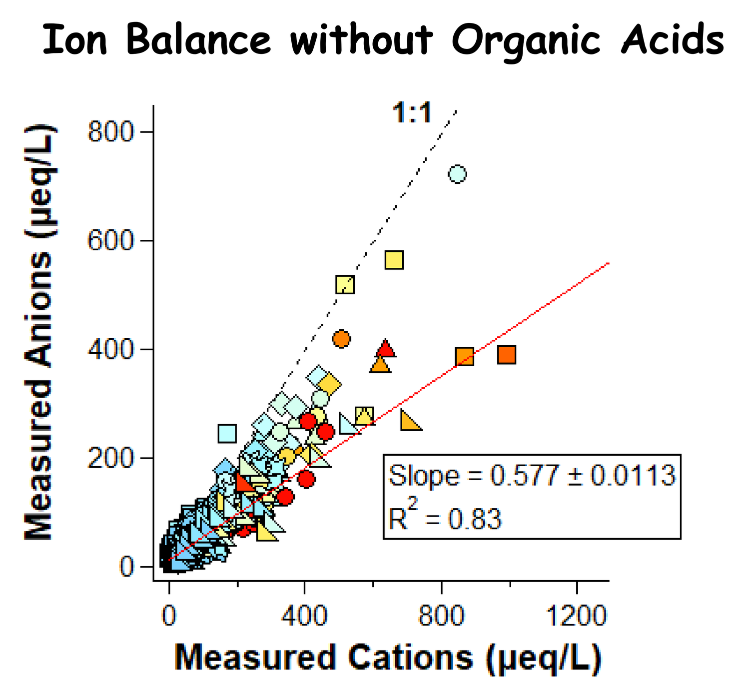
Cloud Water Organic Acids Improve Ion Balance

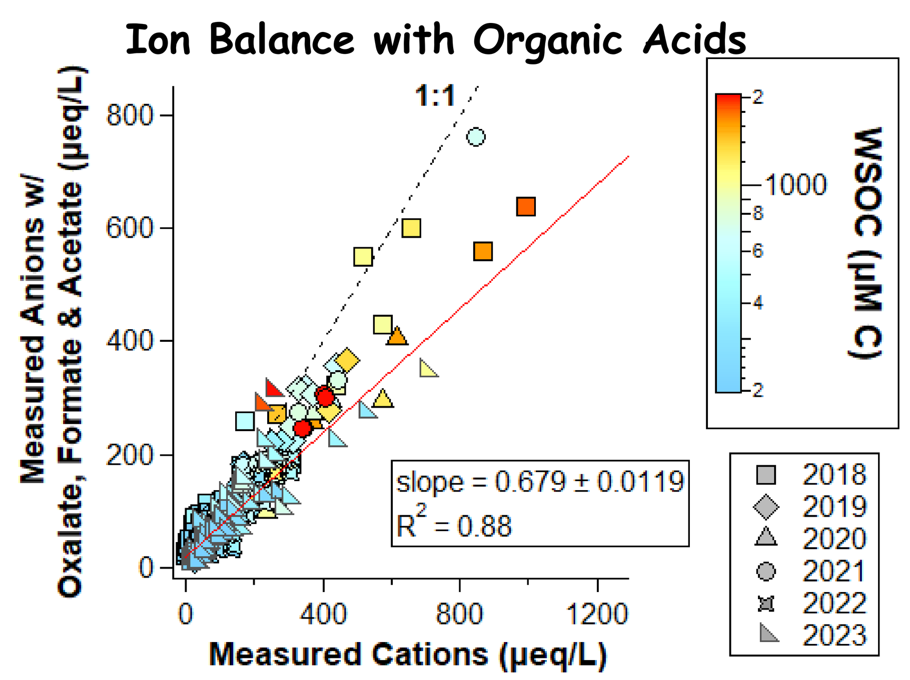
The three most abundant organic acids (Formate, Acetate and Oxalate) account for 6-22% of anions on an annual basis. On average, 14-40% of anions still unaccounted for. ↖ and account for 5-10% of TOC



Organic acids contribute more to ion balance than SO_4^{2-} in 2023!

Evaluating on a sample-by-sample basis, organic acids (OA) increase the slope for measured anion versus cation concentrations from 0.58 to 0.68 and increase the linear correlation coefficient from 0.83 to 0.88 over the 6 years period 2018-2023.





Organic Acids and "Surplus Ammonium" (ie NH_4^+-SO_4^{2-}-NO_3^-)

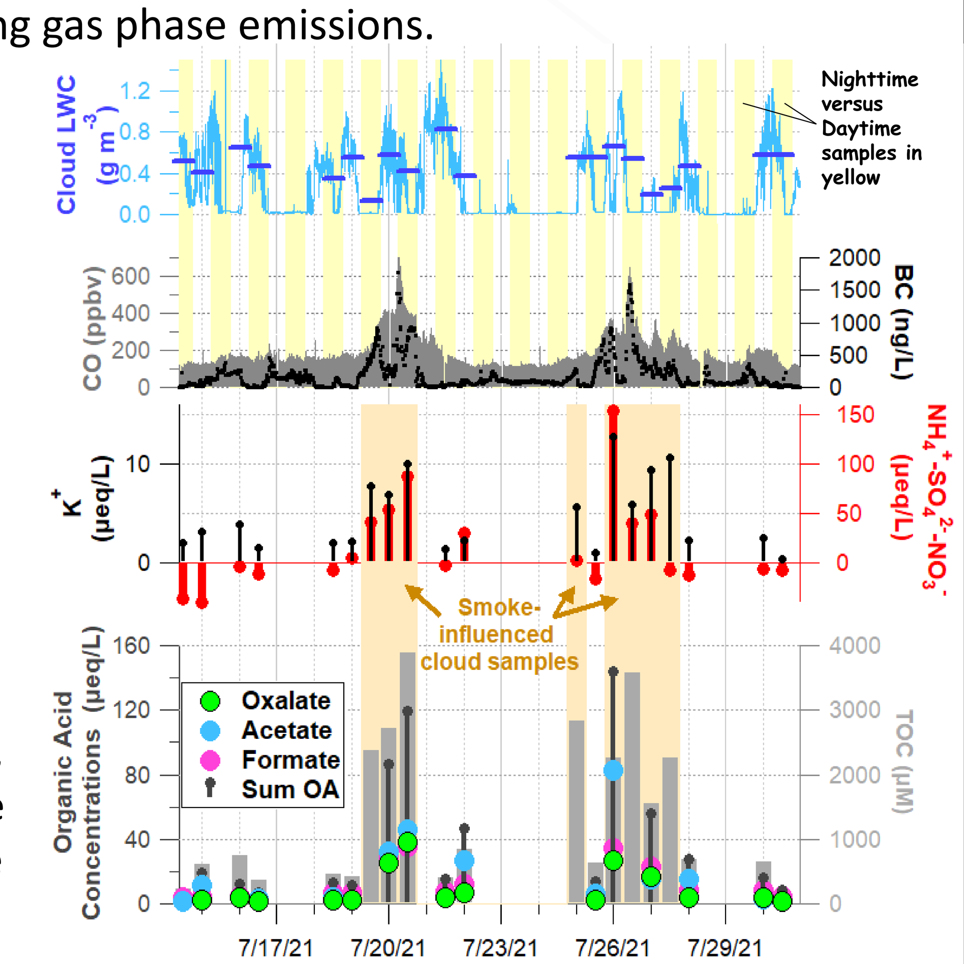
For a growing number of cloud water samples in this "New Chemical Regime", NH_4^+ exceeds SO_4^{2-} + NO_3^-, and this "Surplus NH_4" often correlates with organic acids, suggesting that the prevalence of NH_4^+ and organic acids are chemically linked, likely through chemical processes involving gas phase emissions.

Influence of Smoke

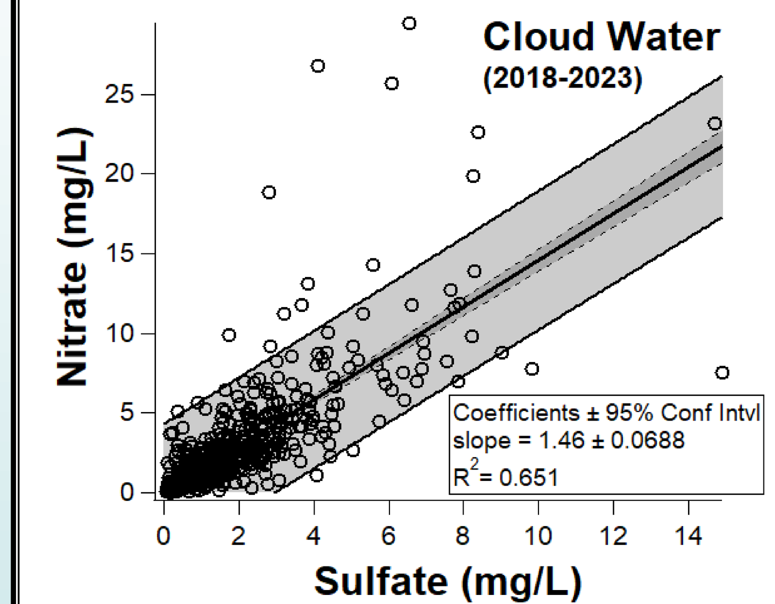
Smoke plumes are known to be highly enriched in organic matter (Liu and Peng, 2019).

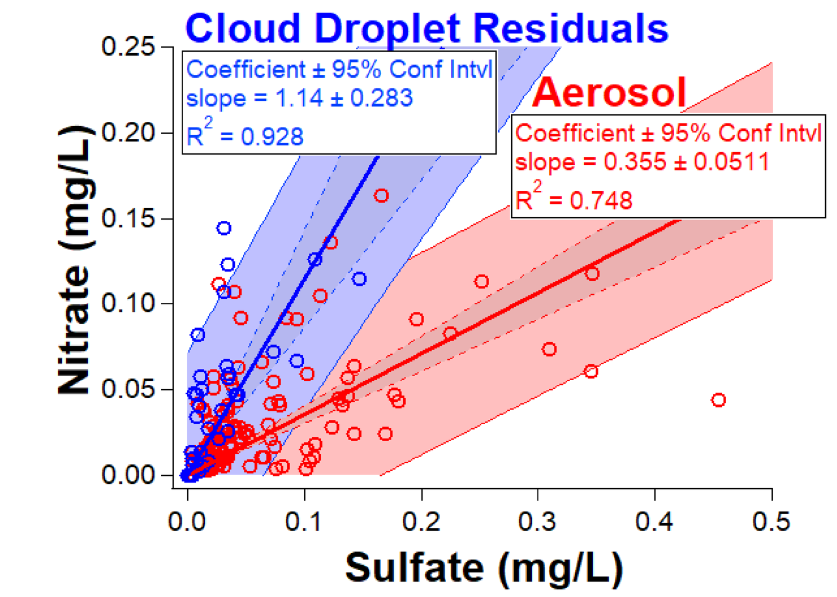
While ammonia is often thought to be associated with agriculture (fertilizers and animal waste), smoke plumes can be enriched in ammonia as well (Bray et al., 2018).

Smoke-influenced cloud water samples exhibit high concentrations of both organic acids & surplus NH_4^+, as exemplified by two wildfire smoke episodes intercepted across NY State in July 2021 (Shrestha et al, 2022).



Comparing Bulk Cloud Water, Droplet Residual and Aerosol: Nitrate versus Sulfate Concentrations

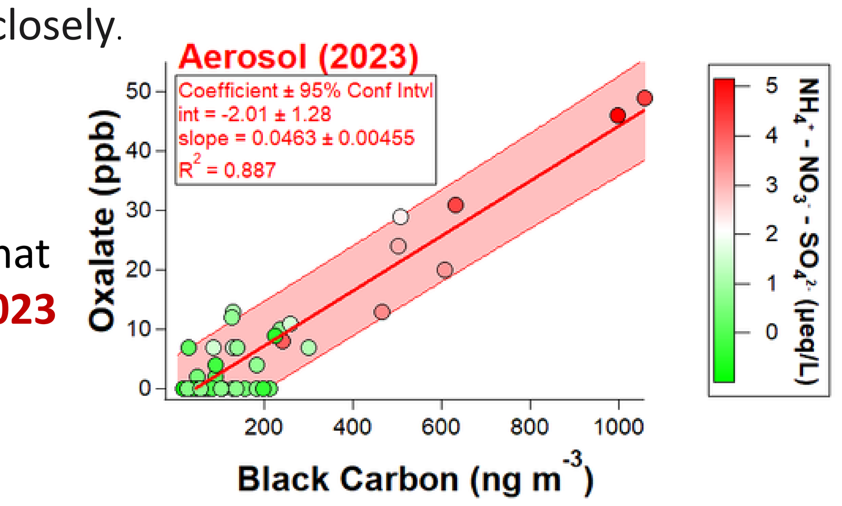


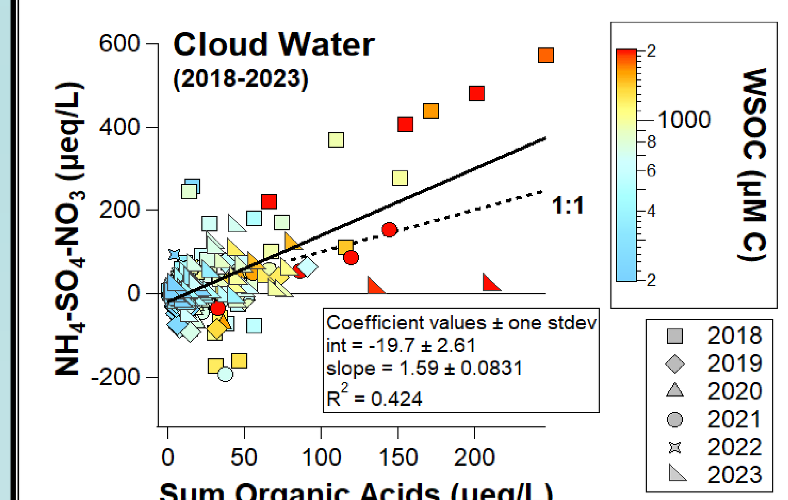


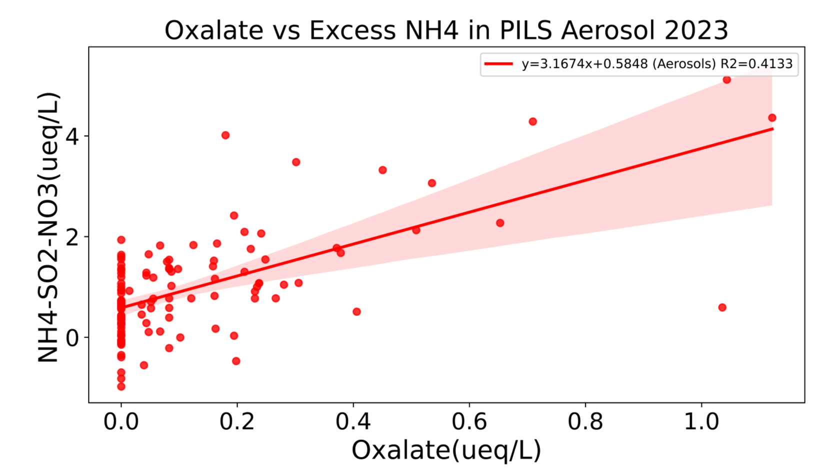
Cloud water and droplet residuals both have higher NO_3^-/SO_4^{2-} than aerosols (HNO_3 gas partitions to condensed phase when water is present). Some aerosol samples are likely already cloud processed, explaining the overlap between aerosol and droplet residual data, which we will be evaluating closely.

Oxalate and Surplus NH_4^+

Aerosol oxalate concentrations are well correlated with black carbon, suggesting that **wildfire smoke encountered at WFM in 2023 was an important driver for the observed oxalate concentrations.**



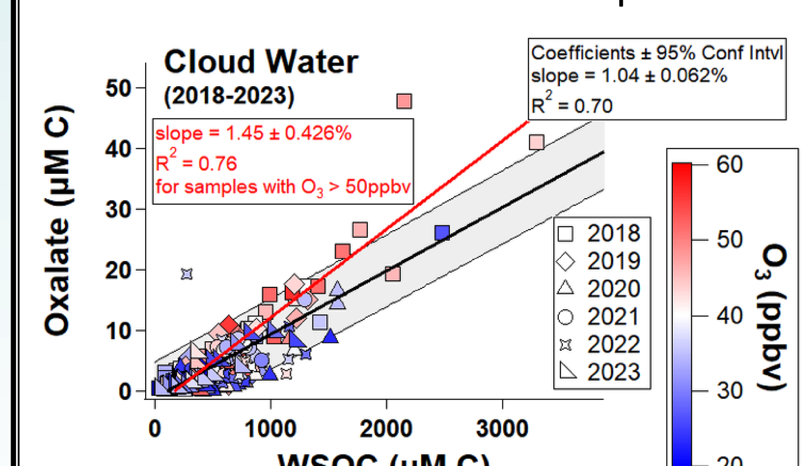


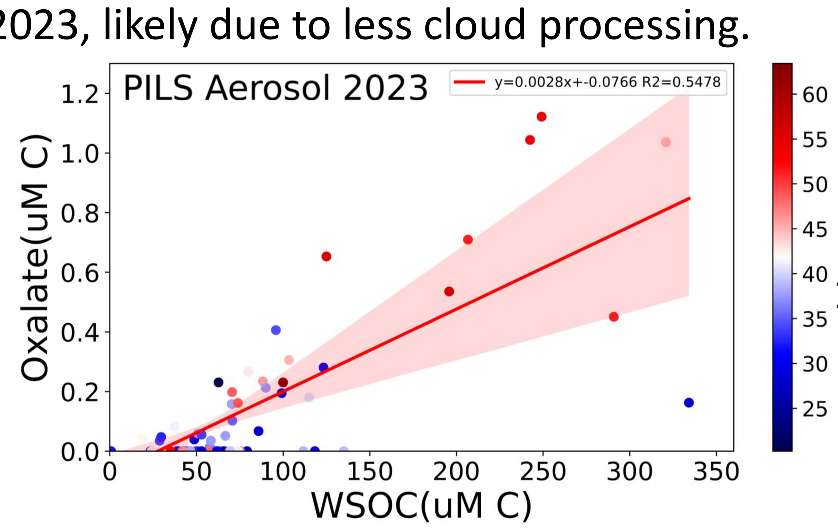


Surplus NH_4^+ is well correlated with formate + acetate + oxalate in cloud water samples. However, for PILS aerosol samples, surplus NH_4^+ is much better correlated with oxalate alone. We hypothesize that this difference is due to formate and acetate being largely in their protonated state within aerosol particles, due to their lower water content. Measuring pH in the PILS samples could provide further insights.

Oxalate and Ozone

Oxalate consistently accounts for ~1% of cloud water WSOC, and this ratio exhibits an increase with ozone (O_3) , as seen previously by Mochizuki et al. (2017), increasing to ~1.4% for samples with > 50 ppbv O_3. By contrast, oxalate accounts for only ~0.3% of WSOC in the PILS aerosol samples from 2023, likely due to less cloud processing.





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