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Organic acids and cloud droplet acidity in recent years at Whiteface Mountain, NY, with a focus on wildfire smoke influence

Archana Tripathy et al.

Correspondence to: Sara Lance (smlance@albany.edu)

Measurement Methods:

For cloud water samples collected in 2018 and 2019, all chemical analyses were performed by the Adirondack Watershed Institute (AWI). LMWOA (formate, lactate, acetate, oxalate, malonate, pyruvate, succinate + malate) were measured using a Lachat QC 8500 ion chromatograph, along with SO_4^{2-} and Cl^-. Unfortunately, due to personnel issues during the COVID-19 pandemic and exhausted funding, a true detection limit could not be determined for the LMWOA measurements conducted at AWI. The lowest calibration standard (50 µg L^{-1}) was used as a conservative detection limit for this work. In 2019, malonate could not be measured as it co-eluted too strongly with an unidentified peak, preventing its quantification. Additionally, pyruvate and glyoxylate were not measured in 2019. Finally, succinate and malate co-eluted to the point of preventing their individual detection in 2018-19. Nitrate was measured by the cadmium reduction technique. Lawrence et al (2023) describes all chemical analyses in further detail for cloud water samples collected prior to 2022, except for the LMWOA measurements.

For cloud water samples collected from 2020 to 2022, all chemical analyses, except for LMWOA measurements, were conducted by the Adirondack Lake Survey Corporation (ALSC). LMWOA (formate, acetate, propionate, lactate, glyoxylate, and pyruvate) were measured at the Wadsworth Center using a Dionex IC-3000 ion chromatograph system with a Thermo Scientific AS11 high capacity (HC) column analytical column with a 3mmol L^{-1} NaOH eluent and suppressor module (Tripathy et al., 2024). Propionate was consistently below the detection limit in the samples. We attempted to measure malonate with this method but its co-elution with unidentified peaks in the samples prevented its reliable quantification. A similar co-elution issue has been observed previously in other studies using comparable anion exchange systems with KOH eluent (Chen et al., 2014). After discovering issues with the outgassing of formate and acetate as they sat in the autosampler, only 10 samples were run each day using an autosampler. Separately, a AS14 column with an 8mmol L^{-1} Na_2CO_3/ 1mmol L^{-1} $NaHCO_3$ eluent was used to measure chloride, nitrate, sulfate, and oxalate concentrations for cloud water samples collected in 2020 and 2021 (Khwaja et al., 1999), as it would take over 2 hours per sample for oxalate to elute using the AS11 HC column, and only about 30 minutes in the AS14 column. For cloud water samples collected in 2022, oxalate was measured at the ASRC lab using a Metrohm 761 Compact Ion Chromatograph with a Metrosep A Supp 5 250/4.0 column with a 3.2 mmol L^{-1} Na_2CO_3/ 1mmol L^{-1} $NaHCO_3$ eluent and a 20mmol L^{-1} H_2SO_4 suppressor solution.

In 2023 and 2024, all chemical analyses, including pH, conductivity, DOC, anions, cations, and the three LMWOAs (formate, acetate, and oxalate), were conducted at the ASRC lab by manual injection of each sample. The method mentioned in the above paragraph was used to measure anions, including three LMWOA. DOC was measured using a Sievers TOC analyzer. Cation measurements were conducted at the ASRC lab using a Metrohm 761 Compact Ion Chromatograph with a Metrosep C4 150/4 column with 2.5mmol L^{-1} HNO_3 and 25ug L^{-1} $RbNO_3$ eluent. pH, conductivity and anion measurements, including LMWOA were typically performed within a week of sample collection, and cation measurements were performed a couple of months later. Samples were stored frozen throughout the study and thawed overnight prior to analysis. 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.

Table S1. Summary of the sample collection years each organic acid was measured, the laboratories that conducted the measurements, and the corresponding method detection limits

Organic Acid	Collection Year	Labs measured	MDLs (mg L^{-1})
Formate	2018-19, 2020-21, 2022-24	AWI, Wadsworth Center, ASRC	0.05, 0.0041, 0.0212
Acetate	2018-19, 2020-21, 2022-24	AWI, Wadsworth Center, ASRC	0.05, 0.0119, 0.0285
Oxalate	2018-19, 2020-21, 2022-24	AWI, Wadsworth Center, ASRC	0.05, 0.0265, 0.0237
Pyruvate	2018, 2020-22	AWI, Wadsworth Center	0.05, 0.0167
Glyoxylate	2018, 2020-22	AWI, Wadsworth Center	0.05, 0.0073
Lactate	2018-19, 2020-22	AWI, Wadsworth Center	0.05, 0.0041
Malonate	2018	AWI	0.05
Succinate+Malate	2018-19	AWI	0.05

Reanalysis of old cloud water samples after long-term freezer storage:

Cloud water samples from 2018, 2019, 2021, 2022, 2023 and 2024 stored in freezers since collection and occasionally thawed/refrozen for analysis purposes were reanalyzed to determine the stability of LMWOAs after long term freezer storage. Previous analyses (DOC, acetate, formate, sulfate, oxalate, conductivity, and pH) were repeated to determine if the samples have degraded or chemically changed over time and hypothesize possible causes of such changes based on trends in the data (Figs. S1 and S2). It is expected that freeze-thaw cycles for analysis purposes have affected the samples in some capacity, primarily due to the activation of microbial activity during thawing, chemical interactions between organic components and possible volatilization of LMWOA in the samples. In the reanalyzed dataset, acetate often showed substantial increases as compared to the initial measurements although the magnitude of change did not have a clear trend. Several samples remained close to or below 1:1 line, showing that the effect of storage was not uniform on the concentration of acetate in the samples. Formate and Oxalate showed a similar variable response as acetate. A linear regression plot of formate concentrations showed a stronger correlation in the data ($r^2 = 0.745$) than acetate ($r^2 = 0.359$) and oxalate ($r^2 = 0.462$). DOC loss was also observed in reanalyzed dataset. 2023-24 samples changed little while 2019, 2021 and 2022 samples showed a stronger decrease in DOC. A linear regression gives $r^2 = 0.57$, but just 4 out of 17 samples seem to drive this weaker correlation. However, this change in LMWOA concentrations due to microbial degradation/fermentation or volatilization hypotheses cannot be verified from this dataset. Note that when the aged unfiltered sample from Day 3 was reanalyzed 10 months later, it exhibited unusually high levels (14.5x higher than original measurements) of acetate, while formate and oxalate were degraded up to 10-15% (noted as open X markers in Fig. S1). While freeze-thaw cycles are known to reduce viable microbial load by damaging the cells, they may also release the contents of cells when the cells lyse. Upon thawing, intact microbes may resume growth, potentially using the organic carbon from LMWOA or transforming it into acetate by redox reactions (Vaïtilingom et al., 2011, Liu et al., 2023). A clearer assessment of impacts from microbial degradation/formation for each analyte during long-term freezer storage and subsequent thawing would require further testing with a wide range of microbes. The LMWOA measurements reported in this paper were typically obtained within 1 week of collection. However, due to unforeseen delays during the pandemic, the 2020–2021 samples were analyzed for LMWOA in spring of 2022. Thus, organic acid measurements for 2020 and 2021 samples should be considered to have greater uncertainty due to potential degradation during long-term freezer storage.

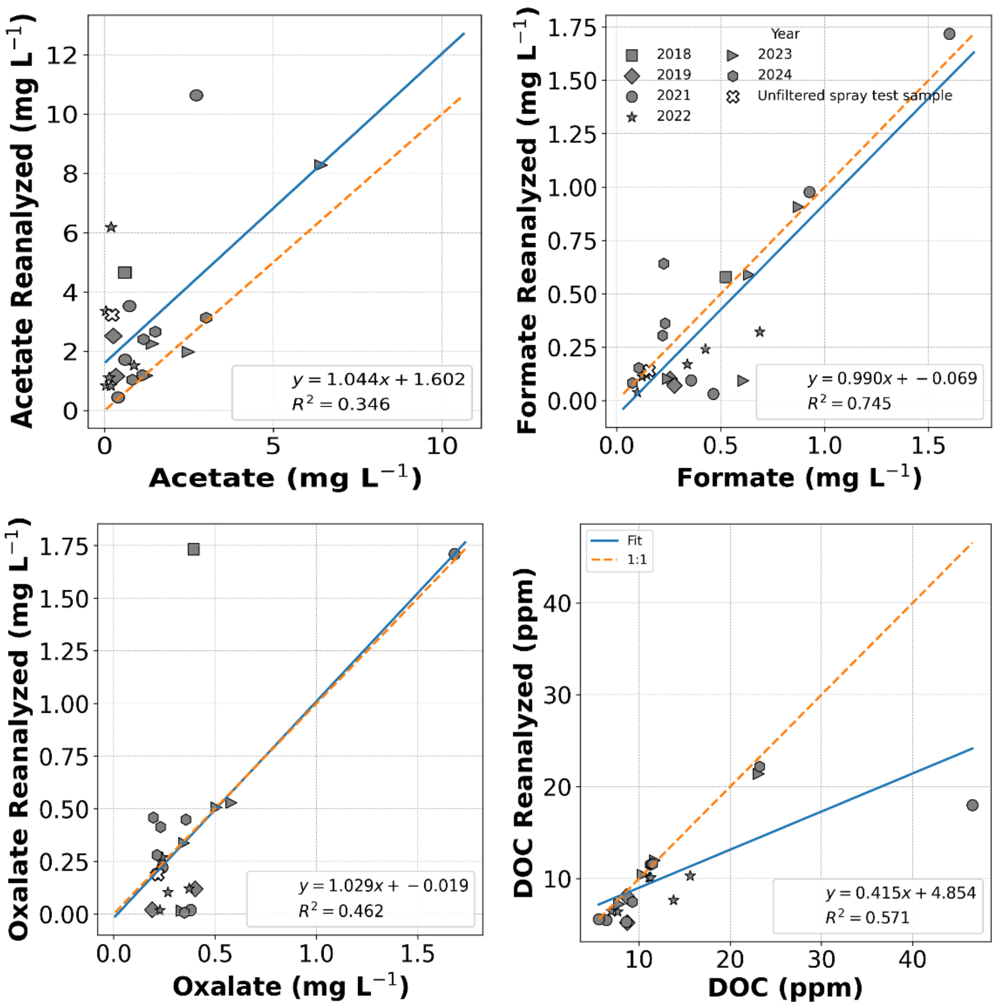

Figure S1. Linear regression plots of reanalyzed vs. original LMWOA (a) acetate, (b) formate, and (c) oxalate concentrations, and (d) DOC concentrations. Note that the linear fits on (a)-(c) do not include the unfiltered spray test sample, shown by the open “X” symbol.

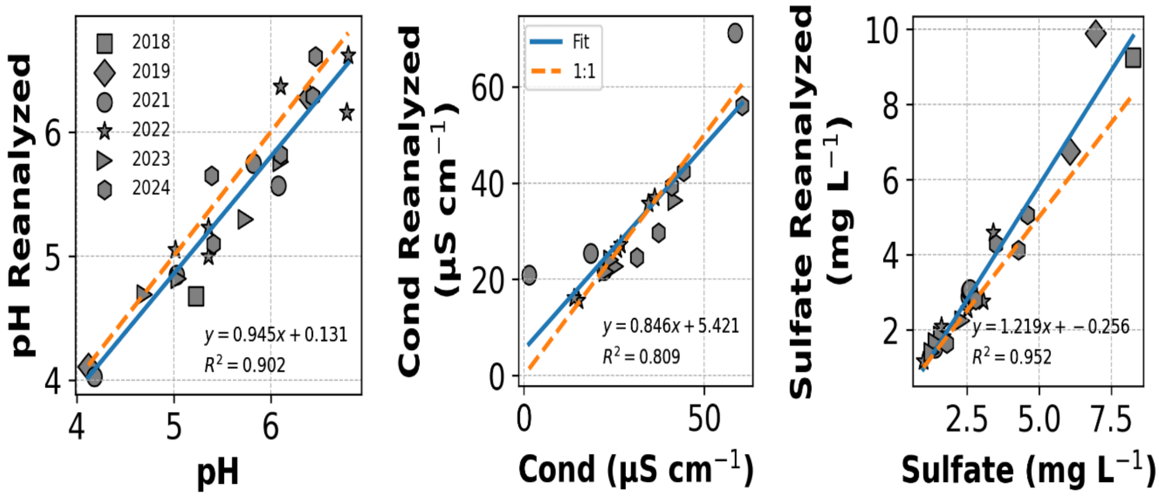

Figure S2. Linear regression plot of pH, conductivity and Sulfate (original vs reanalyzed concentrations)

The inorganic anion sulfate was also reanalyzed in the same samples and found to be stable over the years of long-term freezer storage with an r^2 of 0.952 and slope 1.2 as shown in Fig. S2. The bias is highly consistent, which can be explained by slight differences in analytical methods. Reanalyzed pH measurements were in good agreement with the old dataset whereas reanalyzed conductivity was observed to be more in 2021 samples.

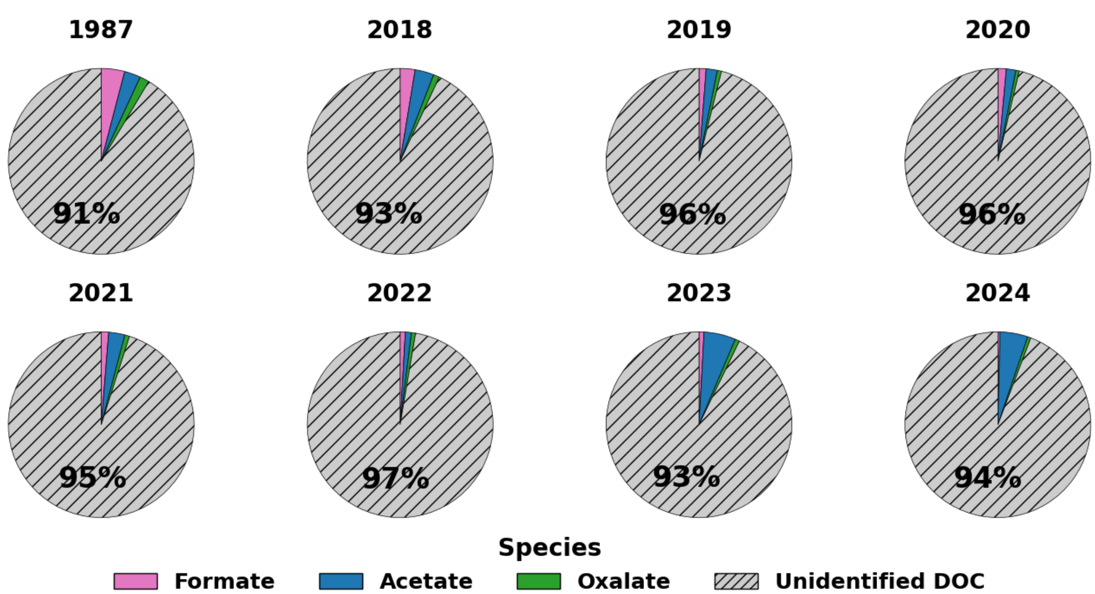

Figure S3. Annual mean contributions of measured low-molecular-weight organic acids to measured DOC concentrations in Whiteface Mountain cloud water (1987, 2018–2024)

Table S2. Summary statistics of undissociated fractions of LMWOAs along with cloud water pH_{TD}, the undissociated fractions were estimated based on pH_{TD} and acid dissociation constants (pKa) of each LMWOA

	undissociated acetate fraction					undissociated formate fraction					undissociated oxalate fraction					pH_{td}				
Year	mean	max	min	std	med	mean	max	min	std	med	mean	max	min	std	med	mean	max	min	std	med
2018	0.67	0.9	0.22	0.15	0.67	0.19	0.46	0.03	0.11	0.16	0.19	0.35	0.04	0.08	0.18	4.44	5.3	3.81	0.32	4.45
2019	0.64	0.92	0.3	0.13	0.63	0.17	0.54	0.04	0.1	0.14	0.18	0.39	0.05	0.07	0.16	4.48	5.12	3.67	0.28	4.53
2020	0.74	0.95	0.38	0.14	0.76	0.26	0.64	0.06	0.14	0.24	0.24	0.42	0.07	0.09	0.24	4.26	4.97	3.49	0.34	4.25
2021	0.68	0.94	0.38	0.14	0.7	0.2	0.61	0.06	0.11	0.18	0.2	0.41	0.07	0.08	0.19	4.4	4.96	3.55	0.31	4.4
2022	0.63	0.87	0.09	0.19	0.67	0.18	0.39	0.01	0.1	0.16	0.18	0.32	0.01	0.08	0.18	4.5	5.77	3.94	0.39	4.45
2023	0.58	0.95	0.09	0.18	0.61	0.15	0.62	0.01	0.11	0.13	0.16	0.41	0.01	0.08	0.15	4.6	5.77	3.52	0.39	4.56
2024	0.71	0.94	0.13	0.15	0.72	0.23	0.6	0.01	0.12	0.2	0.22	0.41	0.02	0.08	0.21	4.33	5.6	3.56	0.34	4.34

The seasonality of LMWOA is notably different compared to DOC, where median DOC concentrations peak in July, with no statistically significant differences between June and August. It should be noted that in September 2021, no samples were collected due to construction at the site, which decreases the total number of samples for September. The 2018 cloud water collection season experienced several pollution events due to warm temperatures and wildfire influence. Similarly, in 2021 and 2023, considerable smoke influence, particularly during July that may have contributed to the elevated organic acid concentrations observed during those years.

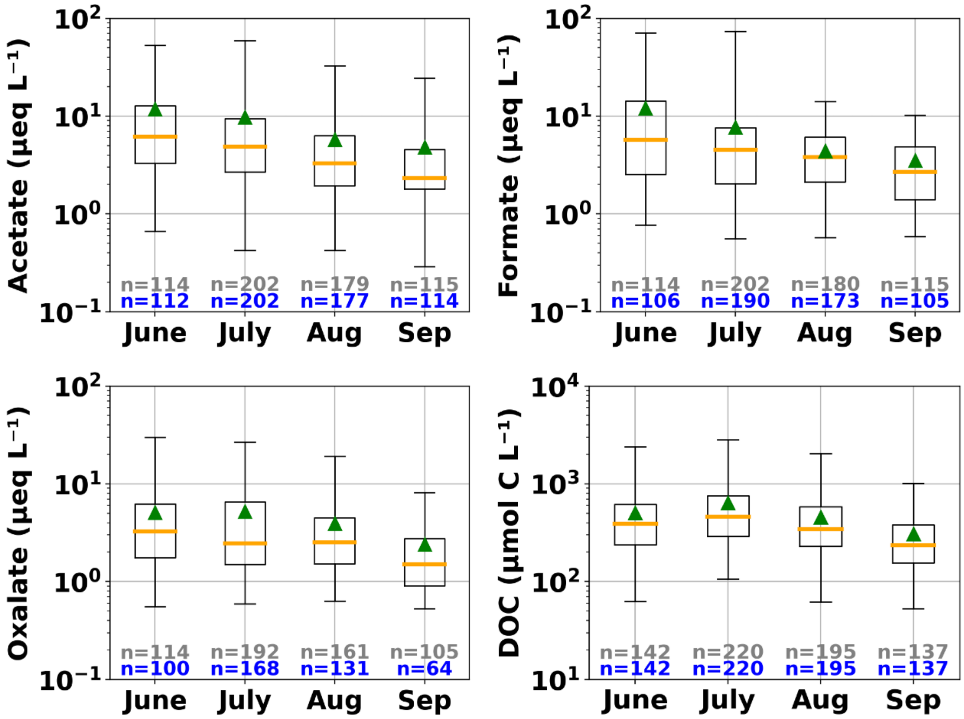

Figure S4. Box plots of monthly variation of 3 LMWOAs and DOC in cloud water at WFM during the collection season, **n** (in grey font) represents the number of total samples analyzed and **n** (in blue font) represents the number of samples reported in the plot above detection limit, orange line is the median and green triangle is the mean concentration, whisker extends from 1 to 99 percentile

Table S3. Summary statistics of LMWOA (μg L^{-1}) and DOC (ppb) in rinse and blank samples collected from WFM from 2018-2024

LMWOA	Min	Max	Median	Mean	Std Dev
Oxalate	0	4.41	0.02	0.42	0.84
Acetate	0	12.41	0.63	0.86	1.52
Formate	0	6.11	0.94	1.42	1.58
DOC	15.8	3360	476	339	483

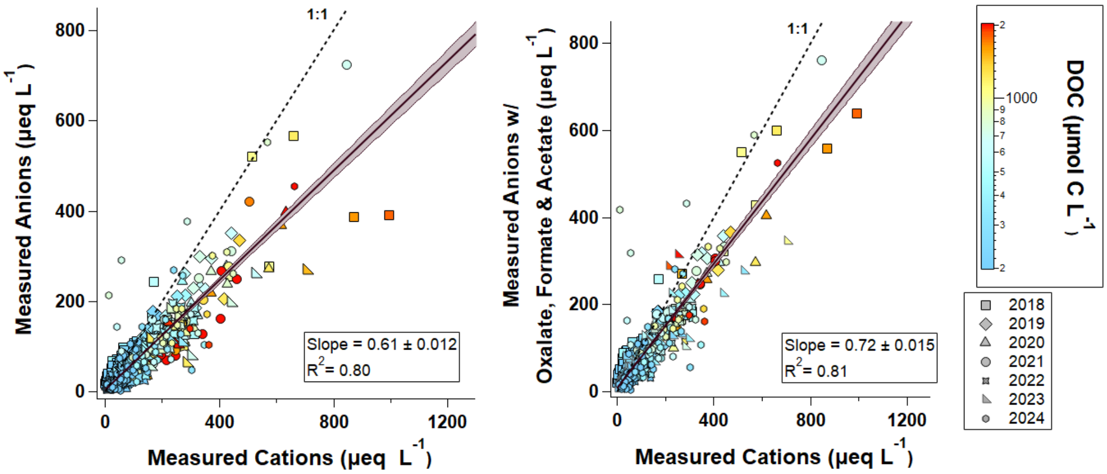

Figure S5. Measured anions versus cations in cloud water excluding and including the three major LMWOA in the left and right plots, respectively, colored by the measured DOC concentrations, with different marker shapes indicating different collection years. Slopes and linear correlation coefficients correspond to linear fits of all samples, with shaded area representing the 95% confidence band of the linear fit.

Table S4. Chemical analysis done by AWI to assess short-term stability of LMWOA for a cloud water sample in 2019

Sample	pH	Cond (uS cm^{-1})	[NO_3^-] (mg L^{-1})	[NH_4^+] (mg L^{-1})	TOC or DOC (mg L^{-1})	Acetate (mg L^{-1})	Formate (mg L^{-1})	Oxalate (mg L^{-1})
Unfiltered (Fresh)	4.88	10.9	1.55	0.86	2.94	0.101	0.111	0.057
Unfiltered (Aged 4 days)	4.93	11.3	1.52	0.78	2.98	0.111	0.131	0.054
Filtered (Fresh)	4.83	10.8	1.56	0.85	3.04	0.108	0.118	0.056
Filtered (Aged 4 days)	4.92	11.3	1.53	0.79	2.99	0.162	0.125	0.056

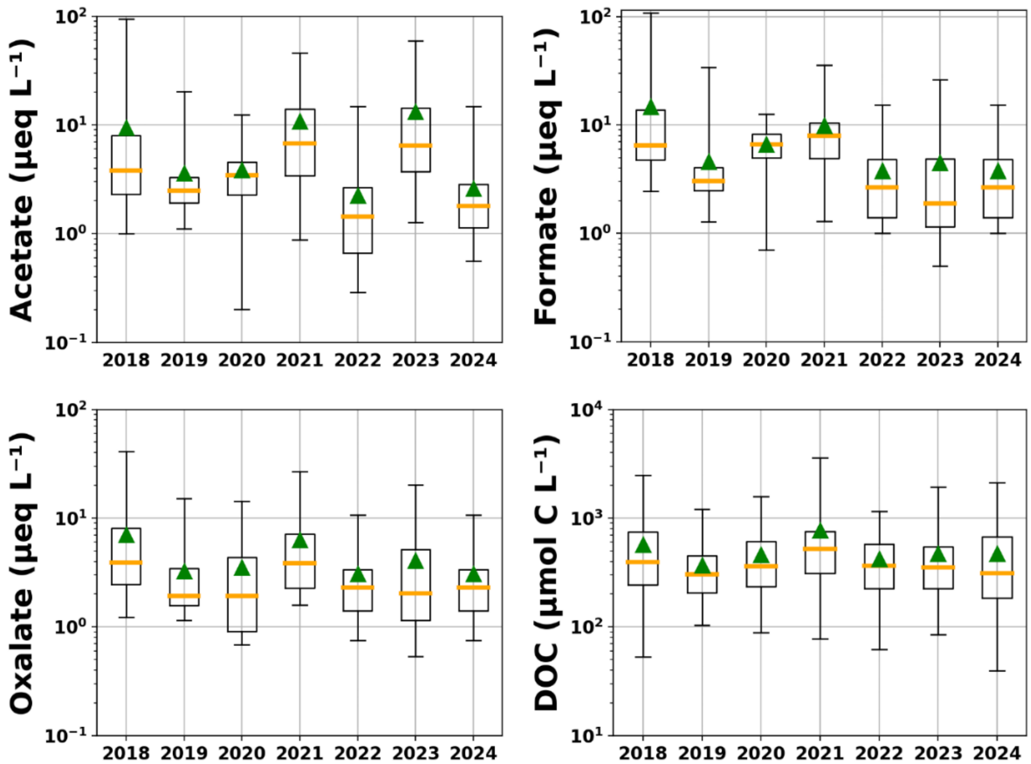

Figure S6. Box and whisker plots of yearly statistics for three LMWOA and DOC above detection limits in cloud water samples collected in summer. The orange line is the median concentration, and green triangle is the mean concentration. Whiskers extend from the 1^{st} to the 99^{th} percentiles.

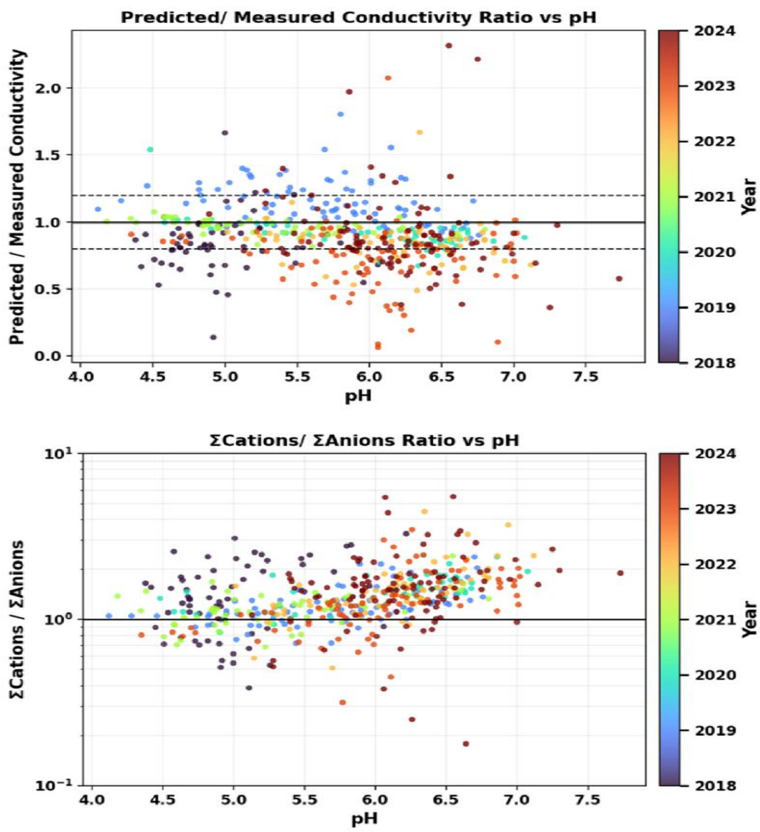

Figure S7: Predicted/ Measured conductivity ratio (top) and charge balance expressed as ΣCations/ ΣAnions ratio (bottom) as a function of the measured bulk cloud water pH for all cloud water samples from 2018-2024. The solid horizontal line indicates unity and dashed line in the top panel represents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

In the bottom panel of Fig. S7, 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.

Oxalate-to-Sulfate ratio-

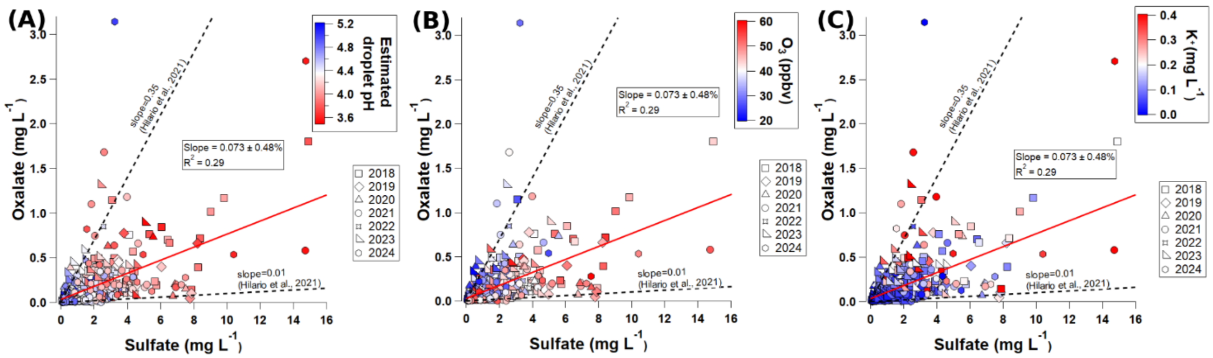

Figure S8: Measured Oxalate vs Sulfate concentrations (mg L^{-1}) in cloud water 2018-2024 colored by (A) estimated droplet pH, (B) O_3 mixing ratio (ppbv), and (C) K^+ concentrations (mg L^{-1}). The red line shows the linear regression for all years combined (slope = 0.073 ± 0.48%, R^2= 0.29) and the black dashed lines show the range of Oxalate: Sulfate mass slope reported by Hilario et al. (2021) in aerosol datasets from campaigns worldwide.

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