

Cloud Water Chemistry and Aerosol Processing: Assessing the Hydroxyl Radical Burst in Newly Formed Cloud Droplets Field Campaign Report

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May 2024



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Acronyms and Abbreviations

ACSM	aerosol chemical speciation monitor
ARM	Atmospheric Radiation Measurement
BB	biomass burning
BBOA	biomass burning organic aerosol
BC	black carbon
CF	cloud cover fraction
CLWC	cloud liquid water content
DtR	direct-to-reagent
ECMWF	European Centre for Medium-Range Weather Forecasts
ERA5	ECMWF Reanalysis v5
HYSPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectory model
LV-OOA	low-volatility oxygenated organic aerosol
OH	hydroxyl
OOA	oxygenated organic aerosol
PM	particulate matter
PMF	Positive Matrix Factorization
PSAP	particle soot absorption photometer
ROS	reactive oxygen species
RWC	rainwater content
SGP	Southern Great Plains
SOA	secondary organic aerosol
SVOOA	semi-volatile organic aerosol
VOC	volatile organic compounds

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1.0 Summary

1.1 Campaign Purpose

Aerosol particles are tiny liquid or solid particles in the atmosphere, ranging in size from a few nanometers to several micrometers in diameter. Aerosol-cloud interactions are the most uncertain aspect of the climate system, and models routinely underpredict aerosol particle formation. Clouds are well known to alter aerosol size, chemical composition, and radiative properties, but the processes are poorly characterized. Organics and sulfates are the most abundant materials in particles, and for each of these there are significant gaps in the understanding of the role of clouds in their formation and/or aging. Many of the cloud processes are driven by aqueous chemistry that depends on hydroxyl (OH) radicals, the subject of this project.

We recently found a new, substantial, and unrecognized source of hydroxyl radicals in cloud droplets. Following cloud droplet formation and in the presence of daylight, material in aerosols produces a burst of hydroxyl radicals within the first two minutes. The estimated contribution of the ‘OH radical burst’ to total OH radical concentrations in droplets based on limited data collected so far ranges from about the same to up to a factor of ~10 larger than other known sources, significantly enhancing the ability of cloud droplets to process organics present in the cloud condensation nuclei.

1.2 Campaign Scope

During the campaigns, which took place April-May and July-September 2022, we measured aerosol OH generation associated with particles collected at the U.S. Department of Energy Atmospheric Radiation Measurement (ARM) user facility’s Southern Great Plains (SGP) observatory. Further, we developed and deployed a new direct-to-reagent (DtR) sampler that captures hydroxyl radical formation within ~0.1 seconds of cloud droplet formation. We also collected particles on filters in parallel with the direct-to-reagent samples. We further analyzed the filter samples for black carbon (BC) and are still in the process of having the metals analyzed on the filters (the samples are finally scheduled to be run in the second week of May). We have also attempted to leverage several instruments available at the SGP observatory to characterize aerosols.

At the SGP, we were able to collect samples from a range of sources and cloud processing histories, including particles with continental, biomass burning (BB), and biogenic secondary organic origin. The resulting data set will greatly expand measurements of the phenomenon, which were previously limited to urban aerosol particles from transportation, industry, and residential wood burning.

1.3 Notable Events

The spring season at the SGP observatory offers a unique opportunity to capture and study a variety of BB aerosols. Our observations indicate that a significant portion of these aerosols are subject to long-range transport. In comparison, the local agriculture burning events are less frequent and the timing of these local events can be affected by annual fuel costs, etc., and thus may vary for a specific year. For example, during the year of our study, the timing of local agricultural burning events was notably postponed. Furthermore, predicting the time of day when the BB aerosols travel to the site is challenging.

However, our campaigns suggest a pattern in which these arrivals are more frequent in the late afternoon or around midnight.

2.0 Results

2.1 OH Burst and PM Composition

Figure 1 shows the OH burst for nascent cloud droplets measured with the DtR method during two field campaigns. We see a large variation among these measurements for both size fractions, ranging from 0.25 to 2.14 μM . The average OH burst measured for spring particulate matter (PM)_{2.5} and PM₁ samples was about 0.93 ± 0.54 and 0.90 ± 0.42 μM , respectively. There is a distinct seasonal variability; the average OH burst of all spring samples (0.91 ± 0.45 μM) was almost a factor of two larger than the summer average (0.52 ± 0.23 μM). The lower OH burst values among spring samples are comparable to the average level of summer samples, but large spikes are seen for some springtime samples.

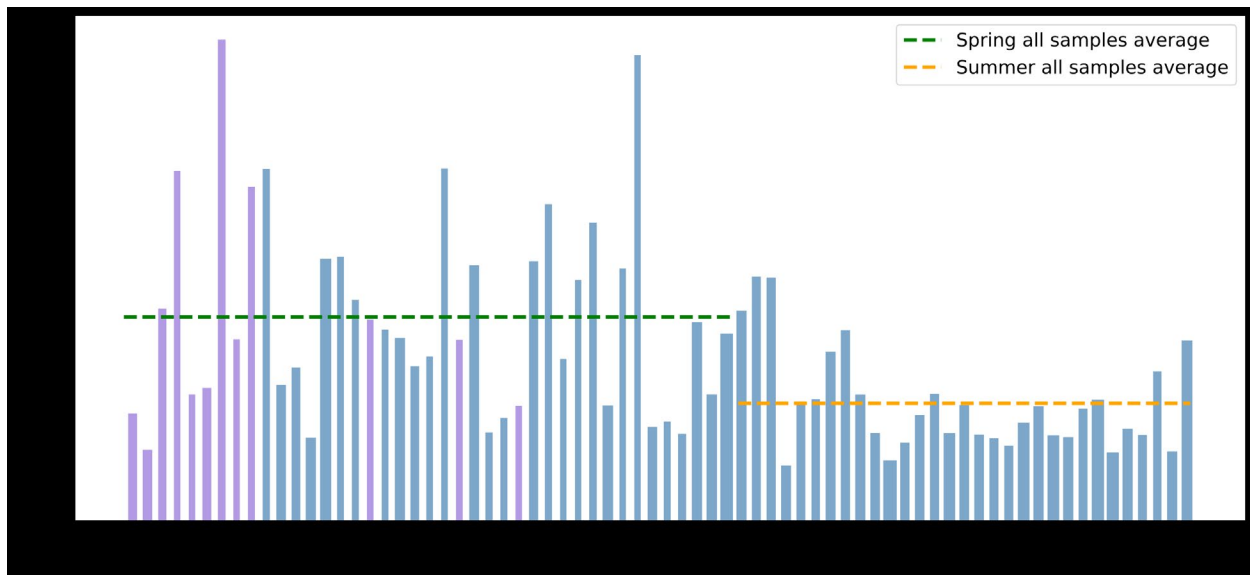


Figure 1. OH burst for DtR samples in two seasons. PM_{2.5} samples are colored in purple and PM₁ in blue. Different widths of bars indicate various sampling times. The green dashed line represents the average OH burst for all springtime samples and the orange dashed line represents the average of summer samples.

The large difference in the seasonal OH activities is largely attributed to the aerosol type or chemical composition. Air mass backward trajectory analysis indicates that spring is dominated by southerly and northerly winds. Aerosols and their precursors emitted during the active prairie burnings in the Kansas Flint Hills can be transported to the site by northerly or easterly winds within about a day. During the summertime, the deciduous and mixed forests east of SGP in northern Arkansas, Missouri, and southern Illinois can be a source of biogenic emissions, which may further contribute to secondary organic aerosol (SOA) formation at the site. Total organics comprise a major fraction of PM₁ for both seasons as shown in Figure 2.

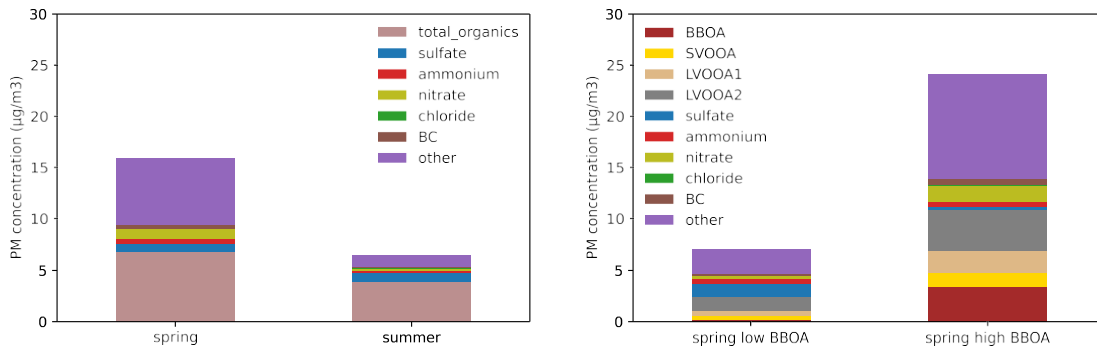


Figure 2. PM chemical composition for averaged spring and summer PM1 samples collected during the campaigns (left) and spring PM1 samples further characterized by different levels of biomass burning organic aerosol (BBOA) (right). Total PM concentration was determined by the measurement of particle mass on filters. BC was measured with an optical transmissometer. The aerosol chemical speciation monitor (ACSM) measured non-refractory PM1 species, including total organics, sulfate, nitrate, ammonium, and chlorides. “Other” indicates the difference between PM mass measured on the filters and the sum of BC and ACSM speciation data.

Further breakdown of the organics category was available for the spring months (only) based on Positive Matrix Factorization (PMF) analysis of the ARM ACSM instrument kindly provided by the ACSM mentor, Dr. Maria Zawadowicz.

Considering that a large fraction of our spring samples was affected by BB events, we further divided the spring samples into two groups depending on the mass fraction of BBOA and show the breakdown of the organics derived from PMF analysis. It is evident that biomass burning drastically changes PM mass concentration and chemical composition. The group with a larger influence from BB events has an average PM mass ~ 3.5 times that of the other group, and much of the mass is attributable to organics. BB events are associated with elevated BBOA concentration in the particles, with its mass fraction in total organic matter increased from 8.5% to 32%. Semi-volatile organic aerosol (SVOOA), low-volatility oxygenated organic aerosol (LV-OOA)I, and LV-OOAII are also highly enriched in the high-BB group, indicating BBOA was further oxidized to less volatile and more aged oxygenated organic aerosol (OOA) during its transportation to our sampling site.

2.2 Cloud Processing History

To understand the effects of cloud processing histories on aerosol particles’ ability to produce OH radicals, we develop a novel method using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model and European Centre for Medium-Range Weather Forecasts (ECMWF) Reanalysis v5 (ERA5) data to quantify the degree of cloud processing.

We calculated two-day backward trajectories for the duration of each sample with HYSPLIT. We use two cloud variables—fraction of cloud cover fraction (CF) and cloud liquid water content (CLWC) from the ERA5 data set to indicate the degree of cloud processing for our samples. Hourly resolution air mass trajectories obtained from HYSPLIT were linearly interpolated in space and time of the cloud variables. This provides information on the CF and CLWC along the trajectory. Additionally, a correction using rainwater content (RWC) in ERA5 was applied to the method to account for the effect of rain scavenging.

This methodology enables us not only to estimate the average extent of cloud processing over a specified time frame, but also to ascertain the timing of cloud occurrence prior to the transportation of the air mass to the site. To the best of our knowledge, this is the first time that particles cloud processing history has been linked to the formation of reactive oxygen species (ROS).

2.3 Dominant Factors in the OH Burst Chemistry

To investigate the dominant factors influencing the OH burst, we linked the OH formation metrics with aerosol chemical composition and cloud processing indicators (CF and CLWC). Multiple panels in Figure 3 represent the cloud processing indicators averaged across various time spans prior to the particles' arrival at the SGP site during the spring season.

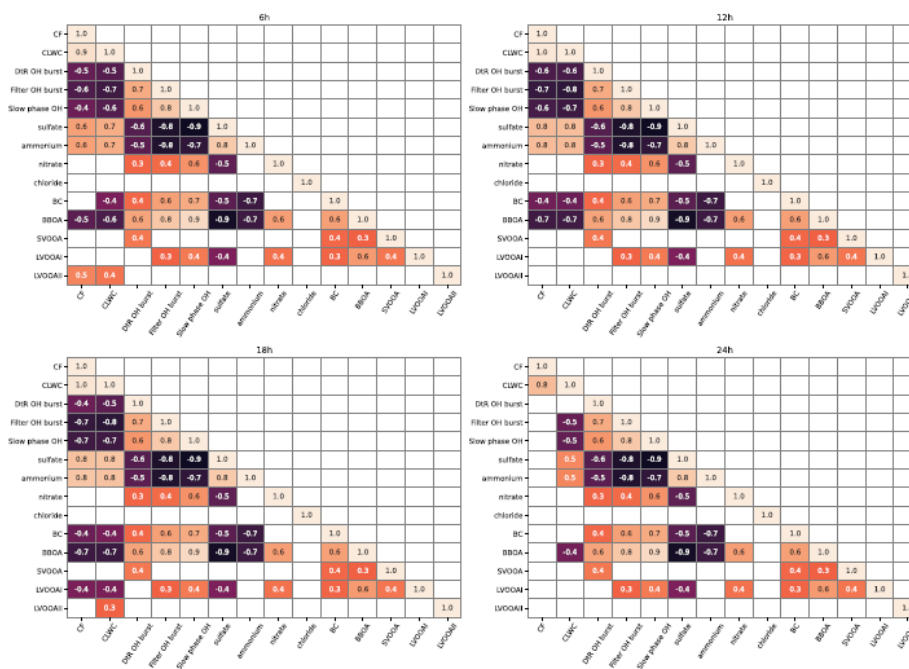


Figure 3. Correlation heatmaps for OH formation metrics (DtR and filter OH burst and slow-phase OH formation rate) and cloud processing indicators (CF and CLWC) for springtime samples. The cloud variables were averaged over different time scales (6-24 h) before aerosols arrived at the site. Only correlations with $p < 0.05$ are shown in the heatmaps. Summer samples were excluded from this analysis due to the infrequent cloud occurrences, which could introduce noise to the correlation assessment.

Chemically, a robust positive correlation was identified between the OH burst and BBOA. Given that BB is a significant source of volatile organic compounds (VOCs), free radicals, and reactive organic compounds, it likely promotes the OH burst through an increased presence of peracetic acid and organic organics hydroperoxides, elevated metals, and complex organic-metal interactions. BC demonstrates a moderate positive correlation with the OH burst, indicating a contribution from BB. Interestingly, the OH burst exhibits moderate negative correlations with sulfate and ammonium. A possible explanation is that the point sources of sulfate and the prairie burning emissions affect the site via different wind patterns, resulting in disparate timings for peaks of sulfate concentrations and the OH burst.

Our findings indicate a pronounced negative association between cloud variables and the OH burst, with the strongest correlations occurring at the 12-hour mark before subsequently diminishing. The negative correlation between cloud processing history and aerosols' ability to produce OH radicals supports our hypothesis on the aqueous OH chemistry. Aerosol particles in the atmosphere comprise organics, inorganic salts, trace metals, etc., with some components capable of generating OH radicals through chemical reactions. However, their contribution to OH formation is limited when they remain in the particle phase, likely partly due to the high viscosity that is believed to characterize many aerosol particles below their deliquescence point. When particles encounter clouds, they are diluted by cloud droplets. Simultaneously, the soluble parts of OH precursors dissolve, mix rapidly, and interact with each other to generate a burst of OH radicals. On the other hand, the weaker correlations after 12 hours may suggest that a one- or two-day timeframe might be too long to consider for cloud processing history, as the replenishment of OH precursors in particles by the ambient environment may reverse any cloud impacts.

Results from this campaign for the first time uncovered a negative association between cloud processing history with OH production, indicating cloud water is an important medium for aqueous OH chemistry. The recently discovered OH burst in nascent cloud droplets can produce OH radicals at a rate exceeding all conventional aqueous-phase processes. Given the short lifetime of cloud droplets (~15 mins) and the prevalence of organics in the particles as efficient sinks for OH, the OH burst could have a substantial influence on aerosol oxidation, aging processes, and subsequent climate effects.

3.0 Publications and References

Shen, J. 2023. Particulate matter-related reactive oxygen species chemistry in surrogate lung fluid and in cloud droplets. PhD Thesis, University of California, Los Angeles.

<https://escholarship.org/uc/item/1wh9k8t5>

Additional publications are forthcoming.

4.0 Lessons Learned

1. The Southern Great Plains site is an amazing resource. The Guest Instrument Facility is a wonderful space for researchers, incredibly well thought out. Even more, the staff at the site form an incredible support team, from the shipping and receiving folks and the security staff to the instrument people and up to the site engineers. We appreciated their can-do attitude, 24/7 flexibility, and helping my city-focused group adjust to life in the country, among other things. We very much appreciated the MillQ water. The site staff especially greatly exceeded what we thought possible.
2. It was not possible to get ultrapure ethanol delivered to the site.
3. During our campaign, the particle soot absorption photometer (PSAP) failed to provide reliable measurement on days significantly affected by biomass burning. Thankfully we had a backup plan for this critical component—we measured black carbon on our filters.

4. The site's weather conditions, such as the robust winds typical of the spring season and the elevated summer temperatures, may pose challenges to outdoor sampling equipment. Therefore, careful consideration of these factors is essential when planning instrument deployment to ensure the integrity and accuracy of data collection.
5. We have yet to get PMF results for the ACSM data for the summer and fall (late July-September of 2022). This data would be incredibly useful for our analysis, if it were possible for the instrument mentor, or someone else, to process the ACSM data for that period.



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