

**Direct Measurement of Small Particle Growth
and Aging at the Atmospheric Radiation
Measurement Southern Great Plains Observatory
Field Campaign Report**

D Collins
X Du

Z Zhe

August 2023



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D Collins
Z Zhu
X Du
All at University of California, Riverside

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Acronyms and Abbreviations

ARM	Atmospheric Radiation Measurement
AS	ammonium sulfate
CAGE	Captive Aerosol Growth and Evolution
CDT	Central Daylight Time
DRH	deliquescence relative humidity
ERH	efflorescence relative humidity
KS	potassium sulfate
NPF	new particle formation
RH	relative humidity
SGP	Southern Great Plains
SOA	secondary organic aerosol
UV	ultraviolet

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1.0 Summary

Two identical Captive Aerosol Growth and Evolution (CAGE) chambers were operated at the U.S. Department of Energy Atmospheric Radiation Measurement (ARM) user facility's Southern Great Plains (SGP) observatory in the late summer and fall of 2021. The field study was scheduled to begin in spring, 2020, but was delayed because of the pandemic. CAGE chambers are designed to expose particles to an environment that mirrors that of the surroundings with or without a controlled perturbation designed to assess a sensitivity. The analysis here focuses on roughly the last two months of the overall study period during which measurements were almost continuous and when several perturbation experiments were conducted.

Though the utility of a dual-chamber system is the ability to measure the influence of a single change on top of ambient conditions, both chambers were initially operated in the same way, with ambient air pulled through the gas exchange channel in both and ammonium sulfate particles injected into both. The similar time-dependent particle growth observed in the chambers for those periods provides confidence in differences observed during the subsequent perturbation experiments. The growth rate of particles in the reference chamber into which only ammonium sulfate particles were injected and for which only ambient air was pulled through were used to describe time-of-day averages. The average growth rate was highest in the evening and in the morning after sunrise and lowest in the late afternoon.

The sensitivity of particle growth to secondary aerosol precursor gases was studied by adding them at a controlled rate to the ambient air flow pulled through one of the two chambers. Addition of 5 ppb of α -pinene resulted in an average particle growth rate of 4.4 nm hr^{-1} , compared with that of just 0.8 nm hr^{-1} in the reference chamber. The added α -pinene also triggered one new particle formation (NPF) event in the early evening just before sunset and another in the morning just after sunrise. Similarly, addition of 5 ppb of SO_2 to one chamber led to a pair of NPF events and to increased particle growth rate, though unlike the impact of added α -pinene, growth was enhanced only during the daytime when OH concentration is highest.

The influence of aerosol liquid water on secondary aerosol formation and particle growth was investigated by injecting ammonium sulfate seed particles into one chamber and potassium sulfate particles into the other. Particles were injected into the two chambers four times over a 1.5-day period. The chamber relative humidity (RH) history during and following each injection was used to determine whether each particle type was crystalline or aqueous. For the case when both particle types remained crystalline throughout the period, they were tracked and for the case when they remained aqueous, the magnitude and time-dependence of the growth of both were almost exactly the same. For the other two cases the ammonium sulfate particles deliquesced upon injection and remained aqueous, while the potassium sulfate particles remained crystalline. For those two cases, the aqueous particles grew substantially faster than did the crystalline particles, providing evidence of the role of aerosol liquid water on secondary aerosol formation and particle growth.

2.0 Results

The CAGE chambers were operated at SGP from August 9 to November 20, 2021, though the analysis here focuses mostly on the second half of that period. A photo of the chambers outside of the former Aerosol Observing System trailer is shown in Figure 1. For much of the time, one of the chambers was used as a reference or control, with only dried ammonium sulfate seed particles injected and only ambient

air pulled into the inlet and through the gas exchange channel. The sensitivity of particle growth to changes in the composition of the gas or seed particles was evaluated through perturbation of the other chamber.



Figure 1. The two chambers positioned outside of the trailer that housed the supporting instrumentation.

Using measurements from the reference chamber made throughout the study, the time-of-day-dependent particle growth rate was calculated and is shown in Figure 2. The average growth rate remains positive throughout the day, with a minimum in the late afternoon before sunset and maxima in the evening and in the morning after sunrise. The general pattern is somewhat similar to that observed using a previous version of the CAGE chamber at a forested site north of Houston, Texas in the late summer and early fall of 2016 (Sirmollo et al. 2021), though the growth rates at SGP in the fall were significantly lower. Particle growth at night was comparable to that during the day.

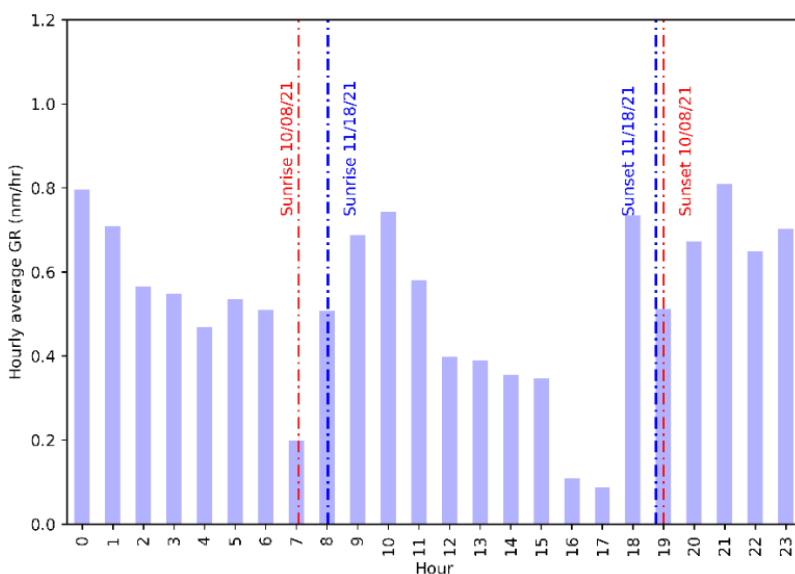


Figure 2. Time-of-day average particle growth rate. A total of 1212 values were used to calculate the averages. The time of sunrise and sunset for the first (October 8) and last (November 18) day of measurements used for this are also indicated.

2.1 Effect of α -Pinene on Particle Growth Rate

Oxidation of α -pinene results in the formation of secondary organic aerosol (SOA) through equilibrium partitioning and acid-base reactions. Though the amount and properties of SOA from α -pinene oxidation have been studied extensively, those studies are typically done under tightly controlled conditions, with the gas composition and ultraviolet (UV) and visible spectra quite different from those in the environment. Contrasting the growth in reference (ambient air only) and perturbed (ambient air + α -pinene) CAGE chambers provides a measure of the sensitivity to the addition for the measurement location. The α -pinene was continuously injected from a compressed gas cylinder at a rate controlled with a mass flow controller to increase the mixing ratio in the air flushed through the gas exchange channel by 5 ppb.

Time series of the measured size distributions and resulting mode diameters and growth rates during the 2.5-day perturbation experiment are shown in Figure 3. Averaged over the experiment, the growth rate in the perturbed chamber was 4.4 nm hr^{-1} , which was significantly higher than the 0.8 nm hr^{-1} observed in the reference chamber. Variability in concentrations of oxidants and of other precursor gases and in environmental conditions resulted in a large range in the amplitude of the enhancement. Additionally, the added α -pinene triggered NPF events in the early evening of November 1 and early morning of November 2.

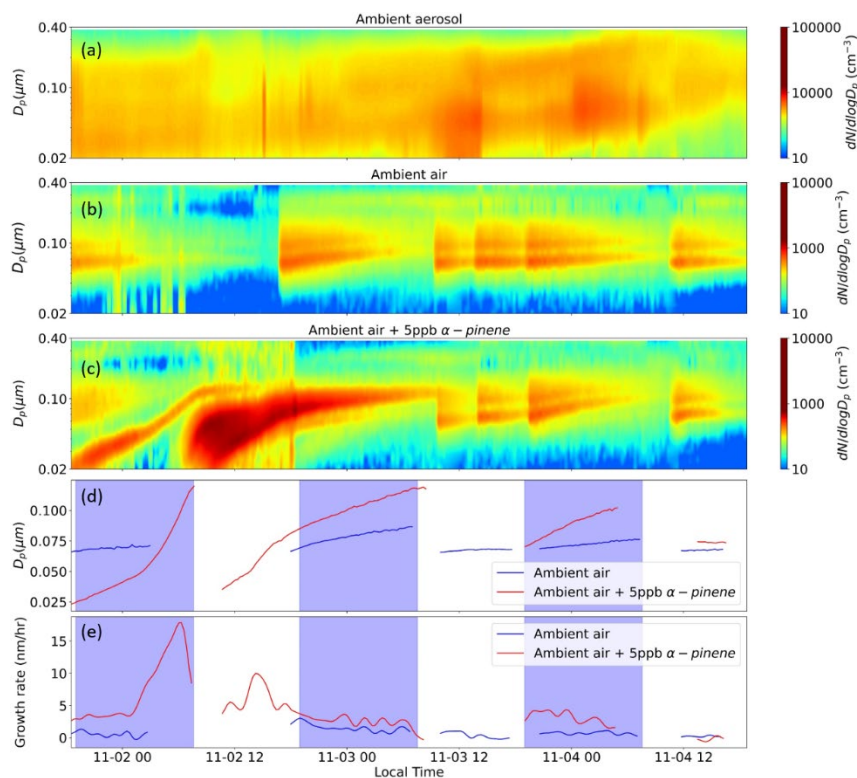


Figure 3. Time series of measurements and calculated parameters over 2.5 days during which 5 ppb of α -pinene was added to the ambient air pulled through one of the two chambers. (a) Ambient aerosol size distribution time series, (b) size distribution time series for the reference chamber, (c) size distribution time series for the perturbed chamber, (d) time series of the lognormal fit diameters of tracked modes in the two chambers, (e) particle growth rates calculated from the time series of lognormal fit diameters.

2.2 Effect of SO₂ on Particle Growth Rate

Hodshire et al. (2016) reported that particle growth from condensation of H₂SO₄ that forms from gas-phase oxidation of SO₂ was significant at SGP during a study in spring 2013. During the study described here, the ambient SO₂ mixing ratio was low and often at or close to the detection limit, which is at least partly a reflection of the significant downward trend in SO₂ emissions throughout the U.S. Just as was done for the α -pinene perturbation experiment, SO₂ was continuously added at a controlled rate to increase the mixing ratio of the ambient air pulled through the gas exchange channel in one of the two chambers by 5 ppb, while only ambient air was pulled through the other. Figure 4 shows the same set of time series as for the α -pinene perturbation experiment for the 4-day SO₂ perturbation.

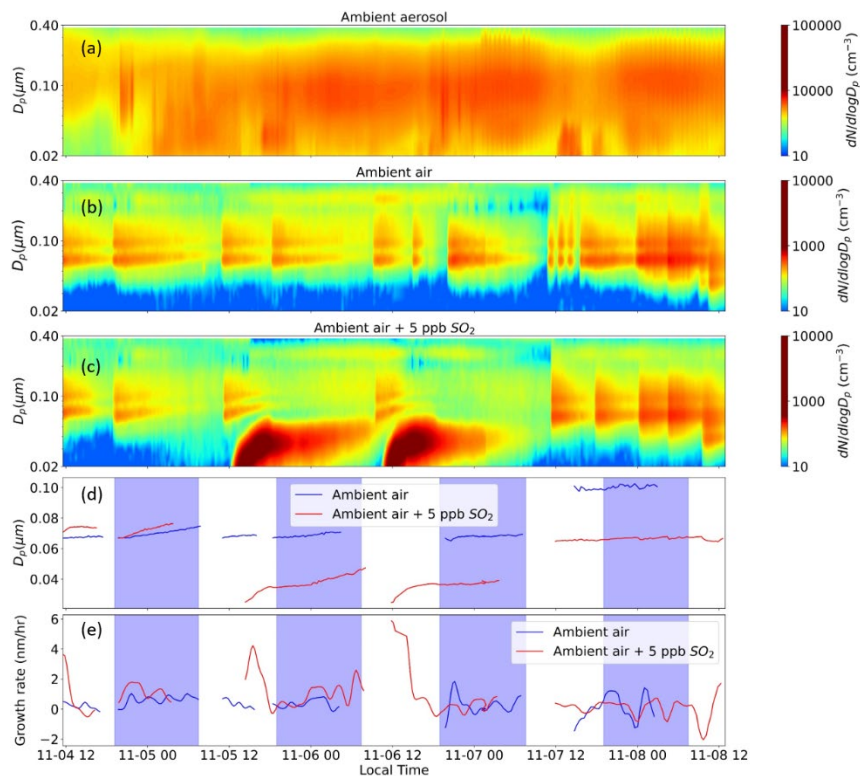


Figure 4. Time series of measurements and calculated parameters over 4 days during which 5 ppb of SO₂ was added to the ambient air pulled through one of the two chambers. (a) Ambient aerosol size distribution time series, (b) size distribution time series for the reference chamber, (c) size distribution time series for the perturbed chamber, (d) time series of the lognormal fit diameters of tracked modes in the two chambers, (e) particle growth rates calculated from the time series of lognormal fit diameters.

NPF events occurred in the perturbed chamber starting at approximately 08:00 CDT on November 5 and 6. Unlike with the addition of α -pinene, which is highly reactive with both O₃ and OH, the introduction of SO₂ led to increased growth only during the daytime. The growth rate in the reference chamber varied little throughout the period, with an average value of approximately 0.5 nm hr⁻¹. In contrast, the average daytime growth rate in the perturbed chamber was approximately 2.5 nm hr⁻¹, with the highest values observed during the two NPF events.

2.3 Effect of Aerosol Liquid Water on Particle Growth Rate

To examine the impact of seed particle composition and, especially, seed particle water content on secondary aerosol formation and resulting particle growth, a monodisperse mode of dry ammonium sulfate (AS) particles was injected into one chamber and one of dry potassium sulfate (KS) particles into the other. An important difference between the two seed particle types is their deliquescence RH (DRH) and efflorescence RH (ERH), with AS having a DRH of 80% and ERH of 35% and KS having a DRH of 96% and an ERH of 60%. Initially crystalline particles will deliquesce if the chamber RH exceeds the DRH and will remain aqueous until the chamber RH falls below the ERH. Particles were injected into both chambers four times during the 1.5-day period analyzed, as identified by the numbers above each of pair of curves in Figure 5b. At the times of the first and second injections, the chamber RH was above the DRH of AS, but below that of KS. For as long as those particle modes could be tracked, the RH did not increase above the DRH of KS or decrease below the ERH of AS. Thus, in both cases the AS particles remained aqueous and the KS particles remained crystalline. At the time of the third injection and for as long as those particle modes could be tracked, the chamber RH was below the DRH of either particle type and so both the AS and KS particles remained crystalline. At the time of the fourth injection the chamber RH was close to 100% following a period of precipitation and never fell below the ERH of either particle type for as long as the modes were tracked. Therefore, both the AS and KS particles remained aqueous. The periods during which particles of each type were aqueous are indicated by markers added to the curve segments in Figure 5b.

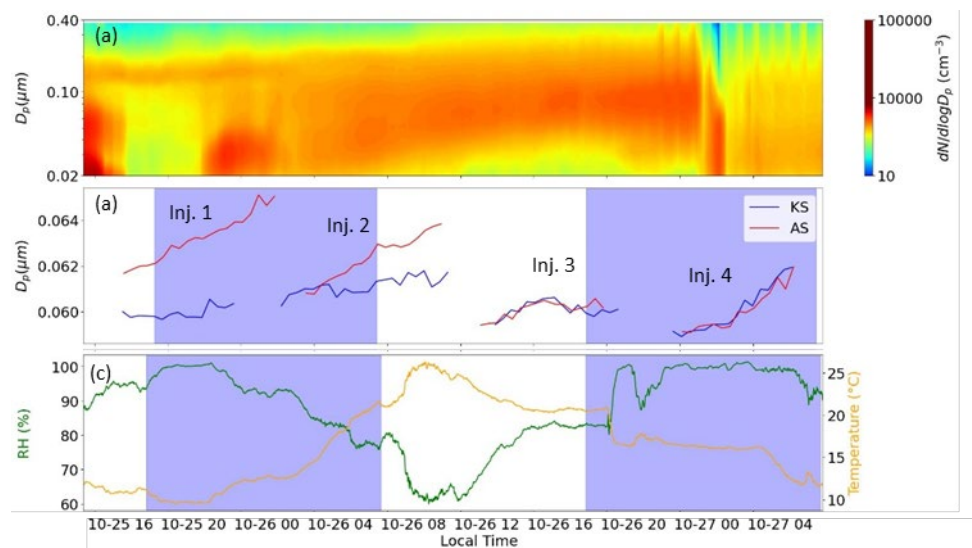


Figure 5. Time series of measurements and calculated parameters over 1.5 days during which ammonium sulfate seed particles were intermittently injected into one chamber and potassium sulfate particles into the other. (a) Ambient aerosol size distribution time series, (b) time series of the lognormal fit diameters of particle modes in both chambers. The numbers above each pair of curves represent the injection number as described in the text. Markers on the curves indicate times when the particles were expected to be aqueous based on the injection time and chamber RH history. (c) Ambient RH and temperature.

Following the third and fourth injections when the AS and KS particles had the same phase state, the magnitude and time-dependence of their growth were almost identical. The growth of both particle types was significantly higher when they were aqueous than when they were crystalline, though it is not

possible to attribute that difference only to water content because the measurements are separated in time. The similarity in growth during those two periods suggests the seed particle composition alone (AS or KS) was relatively unimportant. In contrast, the aqueous AS particles grew substantially faster than did the crystalline KS particles following the first two injections, both during the day and at night. Collectively, these results provide direct evidence that aerosol liquid water can substantially influence secondary aerosol formation and particle growth.

3.0 Publications and References

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