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DOE/SC-ARM-22-007

Characterizing New Particle Formation and Growth Field Campaign Report

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December 2022

ARM

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How to cite this document:

Browne, EC, B Dobson, H Stark, M Canagaratna, and D Worsnop. 2022. Characterizing New Particle Formation and Growth Field Campaign Report. U.S. Department of Energy, Atmospheric Radiation Measurement user facility, Richland, Washington. DOE/SC-ARM-22-007.

Work supported by the U.S. Department of Energy,
Office of Science, Office of Biological and Environmental Research

Acronyms and Abbreviations

API-TOF	atmospheric pressure interface time-of-flight mass spectrometer
ARM	Atmospheric Radiation Measurement
CCN	cloud condensation nuclei
CIMS	chemical ionization mass spectrometer
CPC	condensation particle counter
NPF	new particle formation
SGP	Southern Great Plains
SMPS	scanning mobility particle sizer
TBS	tethered balloon system
VNATS	Vertically Resolved NPF and Transport Study

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1.0 Summary

New particle formation (NPF) and subsequent growth to sizes at which the aerosol particles can act as cloud condensation nuclei (CCN) is critical for understanding and modeling aerosol-climate interactions (Gordon et al. 2017, Dunne et al. 2016). While sulfuric acid is generally understood to play a central role in NPF and growth, measured sulfuric acid concentrations are insufficient to explain measured formation and growth rates in many locations even when stabilization by ammonia is considered (Kulmala et al. 2014, Riipinen et al. 2012). Extensive laboratory investigations have revealed that amines (Almeida et al. 2013), other reduced nitrogen compounds (Glasoe et al. 2015), and/or oxidized organic compounds (Kirkby et al. 2016) can enhance new particle formation rates and thus may explain, at least in part, the gap between our understanding of new particle formation and the measurements. Our knowledge, however, of the relative importance of these various pathways remains incomplete due to the limited number of ambient measurements, particularly in diverse ecosystems. Agricultural land use areas are particularly understudied despite accounting for ~41% of global land cover (Ellis et al. 2010). Improving our understanding of NPF requires measurements of NPF and the precursors to NPF and growth in a variety of ecosystems and ideally across seasons. The purpose of this campaign was to:

- Identify and quantify gas-phase bases (ammonia, amines, urea), oxygenated organics, and ambient ions at SGP in the fall and in the spring
- Investigate the connection between gaseous composition and rates of new particle formation and growth
- Investigate if novel nitrogen compounds (e.g., urea, diamines) contribute to particle formation, and
- Investigate the processes controlling the abundance of gas-phase bases.

To pursue these goals, we deployed a suite of analytical instruments at the U.S. Department of Energy Atmospheric Radiation Measurement (ARM) Guest User Facility at the Southern Great Plains (SGP) Central Facility in fall, 2021 (October 1-29) and spring, 2022 (April 6-May 6). The instruments included an ethanol chemical ionization mass spectrometer (CIMS) to quantify gas-phase bases important for NPF including ammonia and alkyl amines and an atmospheric pressure interface time-of-flight mass spectrometer (API-TOF) to characterize the chemical composition of ambient ions and provide insight into the composition of newly formed and growing clusters. We also deployed a trace-level, photolytic, true NO_2/NO/NO_x analyzer (Teledyne T200UP) during both campaigns.

During the two deployments, the instruments generally operated properly. The CIMS experienced two full days of downtime in October and two partial down days. In April, we experienced slightly more partial down days (six) due to a broken pressure sensor. Overall, the data coverage was excellent, and we obtained high-quality measurements of ammonia and alkyl amines. The API-TOF operated throughout both deployments. There were a few instances of reduced signal during both campaigns due to decreases in the inlet flow rate; however, the instrument kept operating and collecting data throughout. Since the primary use of the API-TOF is for qualitative rather than quantitative measurements, a reduction in signal has minor impacts on the data quality.

We were fortunate that both our measurement periods overlapped with the ARM spring Vertically Resolved NPF and Transport Study (VNATS, Principal Investigator: Chongai Kuang, Brookhaven National Laboratory), during which modified condensation particle counters (CPCs) were used to make

vertically resolved measurements of newly formed particles less than 3 nm in diameter via the ARM tethered balloon system (TBS). Future collaboration between the measurement teams will enable insights into the vertical distribution of new particle formation and provide constraints on how to connect ground-based measurements of aerosols and aerosol precursors to processes occurring aloft.

2.0 Results

Several of the objectives of the campaign were related to understanding gas-phases bases and their potential contribution to NPF at the site. While ammonia was abundant during both the spring and the fall, typically present at mixing ratios of a few parts per billion by volume (ppb_v) with morning spikes up to 10s of ppb_v (Figure 1 shows the ammonia concentrations in the fall), alkyl amines were below detection limit in the fall. Measurable amounts of the two carbon (dimethylamine or ethylamine; referred to as C2 amines) and the three carbon amines (C3 amines) were present during the spring. Diamines were not observed above the detection limit in either season. We observed urea during both seasons and analysis of that signal is ongoing. The strong seasonality in the amines and the relative lack of seasonality in ammonia was unexpected and contrasts with typical assumptions that ammonia and amine sources are similar. Analysis of the potential causes of the seasonality and the implications for our understanding of basic gases in the atmosphere is a continuing area of investigation.

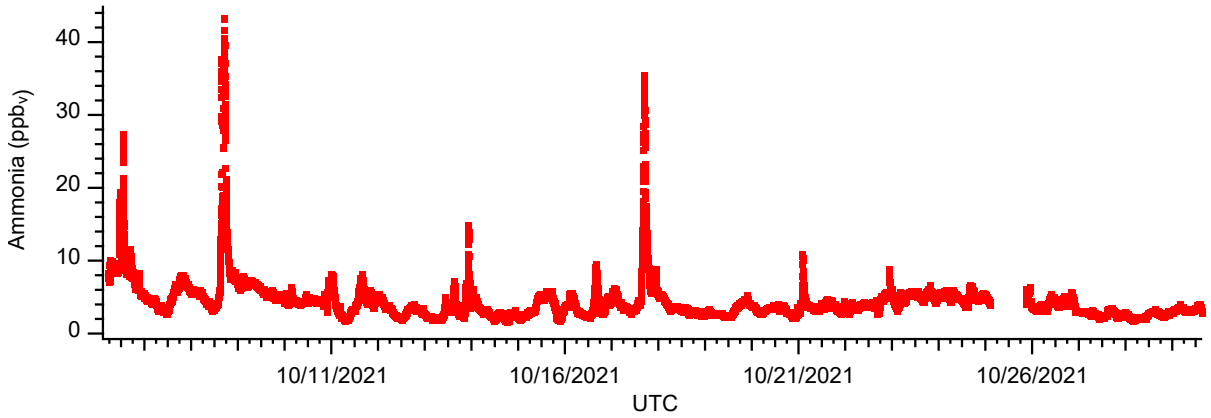

Figure 1. Ammonia mixing ratio during the fall measurement period.

We also observed a strong seasonality in surface NPF and the API-TOF measurements. Figure 2 provides an overview of the nano scanning mobility particle sizer (nano-SMPS) measurements during both deployments.

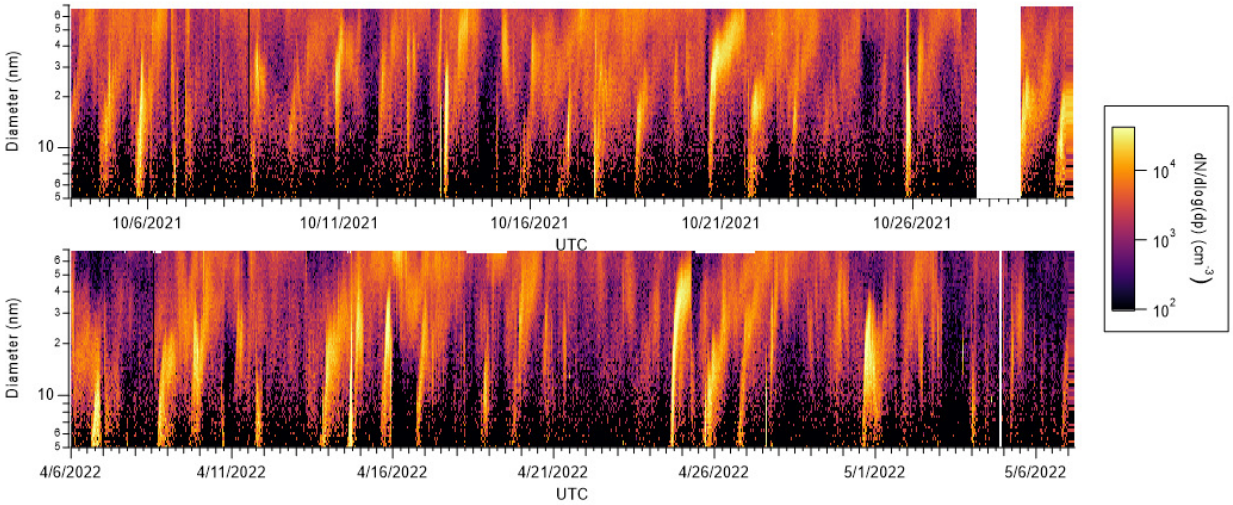

Figure 2. Aerosol size distributions as measured by the nano-SMPS during the (top) fall deployment and (bottom) spring deployment. In the fall, no-surface NPF events were observed whereas in the spring several events were observed.

The nano-SMPS is part of the Aerosol Observing System located at the SGP Central Facility (Kunag and Ermold 2022). During the fall deployment, no surface-based NPF events occurred, as can be seen by the lack of high particle concentrations at the lowest sizes of the nano-SMPS measurement. No higher-order sulfuric acid-base clusters were observed by the API-TOF either, further supporting a lack of NPF at the surface. The beginning of sulfuric acid clustering was observed in the API-TOF as shown in the lower panel of Figure 3; however, these clusters failed to grow into the characteristic sulfuric acid-base clusters characteristic of NPF. Shortly following the termination of sulfuric acid cluster growth measured by the API-TOF, the nano-SMPS measurements indicate the appearance of a particle mode centered at about 7 nm that continues to grow for a few hours (upper panel of Figure 3). Interpretation of these types of events are ongoing, but our initial hypothesis is that insufficient sulfuric acid exists at the surface to nucleate particles. Instead, nucleation occurs aloft, facilitated by the colder temperatures. Growth of the particles occurs at the surface where it is facilitated by higher concentrations of growth precursors. We will continue to investigate this idea in collaboration with Dr. Kuang and the TBS measurements of newly formed particles.

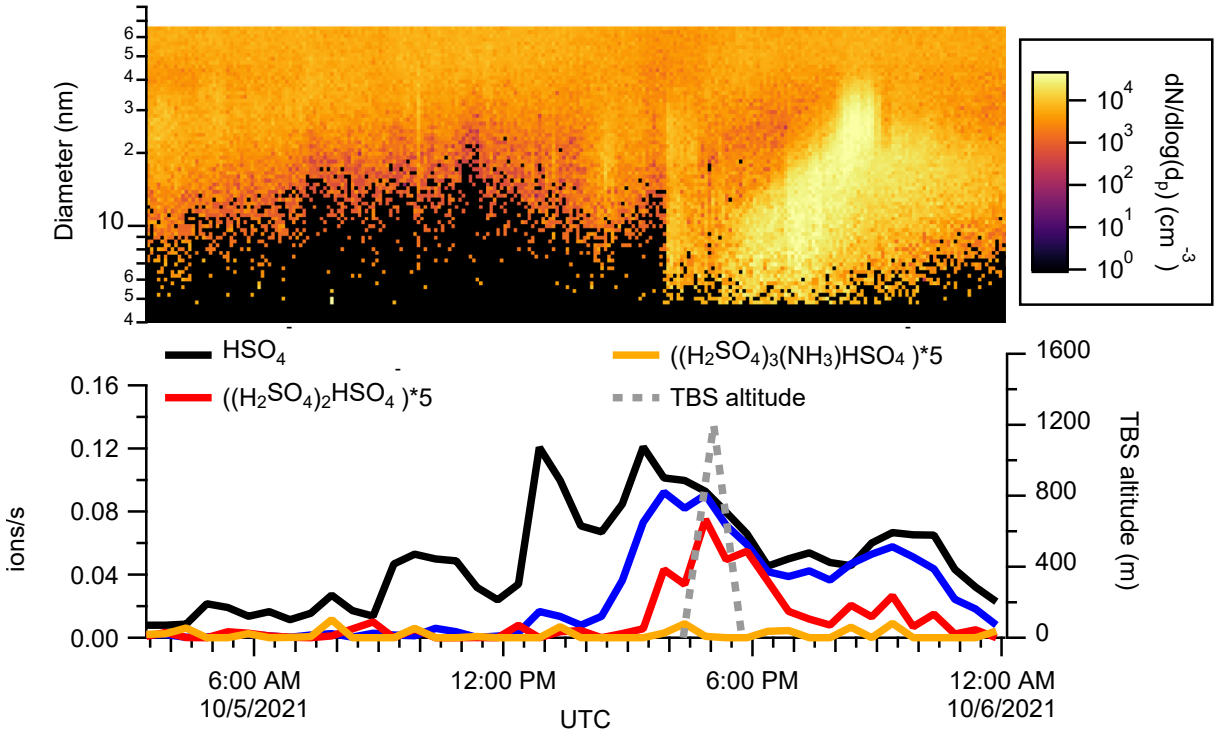

Figure 3. (Top) Surface based aerosol size distribution as measured by the nano-SMPS on 5 October 2021. (Bottom) API-TOF measurements of H_2SO_4 ion clusters indicating the "cluster event" observation occurring prior to the appearance of nano-SMPS mode centered at ~7-8 nm. The consecutively growing $(H_2SO_4)_nHSO_4$- clusters up to n=2 but lack of higher-order clusters suggests that insufficient H_2SO_4 was available to initiate NPF at the surface. The TBS flight is indicated in the bottom panel.

In contrast to the fall, surface-based nucleation was observed in the spring as seen in both the nano-SMPS and the API-TOF measurements. The API-TOF observed higher-order sulfuric acid clusters as well as sulfuric acid-ammonia and sulfuric acid-C2 amine clusters. As analysis progresses, we will investigate the factors influencing the seasonality of NPF at the site including the relative roles of amines and transport.

Overall, the two deployments were highly successful. Our measurements generated high-quality data, including some of the only high-time-resolution measurements of alkyl amines. The data will enable us to investigate all four of our initial objectives and by leveraging measurements taken as part of the VNATS study will allow us to investigate the vertical distribution of NPF.

3.0 Publications and References

3.1 Presentations

We are currently working on data analysis and manuscript preparation. To date the following presentations included measurements from the Characterizing New Particle Formation and Growth campaign.

Browne, EC, B Dobson, M Canagaratna, J Krechmer, H Stark, D Worsnop, and C Kuang. 2022. "New Particle Formation and Growth in the Southern Great Plains: Seasonal Differences and Vertical Gradients." Poster presentation at the U.S. Department of Energy ASR/ARM Principal Investigator meeting.

Browne, EC. 2022. "Atmospheric New Particle Formation and Growth: Importance of Gas-Phase Chemistry and Atmospheric State." Seminar presented at the Departments of Atmospheric Science and Chemistry, University of Wyoming, Laramie, Wyoming.

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4.0 Lessons Learned

We are extremely grateful to the SGP staff for their assistance throughout the campaign. Overall, the experience was extremely positive and productive. For the October deployment, we were the first users in the new Guest Instrument Facility. We were very pleased with the experience. The significant amount of power available through the uninterruptible power supply is a fantastic asset of the facility and helps ensure high-quality measurements with minimal instrument downtime.

A lesson learned from that fall deployment experience was that the wiring had been done with adjacent outlets on the same circuits. Given the electrical requirements of our analytical instruments, each of which required a dedicated circuit, this meant that instruments had to be physically spaced apart from each other to avoid circuit overload. Although minor, closer co-location is ideal. Floor space utilization can also be improved with alternating circuits on adjacent outlets. We voiced these concerns during the fall and as a result, the wiring was altered prior to the spring deployment allowing us to place the instruments closer together. We thank everyone for listening to our concerns and their prompt action. We believe others will benefit in the future from the improved power distribution.

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