

## HI-SCALE Nanoparticle Composition and Precursors Field Campaign Report

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June 2017

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# **HI-SCALE Nanoparticle Composition and Precursors Field Campaign Report**

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June 2017

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

## Acronyms and Abbreviations

AMPMS	ambient pressure proton transfer mass spectrometry
APi-TOF	ambient pressure inlet time of flight
ARM	Atmospheric Radiation Measurement
CIMS	chemical ionization mass spectrometry
DOE	U.S. Department of Energy
ELVOC	extremely low volatility organic compound
Et-CIMS	ethanol chemical ionization mass spectrometry
G-1	Gulfstream-1
GIF	Guest Instrument Facility
HI-SCALE	Holistic Interactions of Shallow Clouds, Aerosols, and Land-Ecosystems
IOP	intensive operational period
NCP	Nanoparticle Composition and Precursors
nm	nanometer
NPF	new particle formation
SBIR	Small Business Innovation Research
SGP	Southern Great Plains
SMPS	scanning mobility particle sizer
TDCIMS	thermal desorption chemical ionization mass spectrometry

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## 1.0 Summary

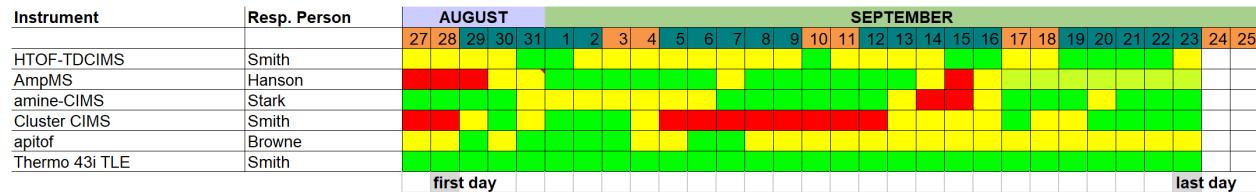
From 21 August to 27 September, 2016, during the second Intensive Operational Period (IOP) of the Holistic Interactions of Shallow Clouds, Aerosols, and Land-Ecosystems (HI-SCALE) field campaign, a suite of instruments were placed in the Guest Instrument Facility (GIF) at the Central Facility of the U.S. Department of Energy (DOE) Atmospheric Radiation Measurement (ARM) Climate Research Facility's Southern Great Plains (SGP) site in Lamont, Oklahoma. The goal of these measurements was to fully characterize the formation and evolution of atmospheric aerosol particles through measurements of gas-phase precursor and ambient nanoparticle composition. Specifically, we sought to:

1. investigate the role of acid-base chemistry in new-particle growth through measurements of ammonia and amines as well as organic and inorganic acids in both atmospheric nanoparticles and the gas phase;
2. investigate the contribution of other surface-area or volume-controlled processes to nanoparticle formation and growth, such as the uptake of extremely low volatility organic compounds (ELVOCs);
3. evaluate the performance of a new instrument being developed with funding from the DOE Small Business Innovation Research (SBIR) program for measuring gas-phase amines and related compounds; and
4. together with colleagues measuring on the ground and onboard the ARM Gulfstream-1 (G-1) aircraft during HI-SCALE, create a comprehensive data set related to new particle formation and growth that can be used in modeling efforts by the research team as well as DOE collaborators.

The project, called HI-SCALE: Nanoparticle Composition and Precursors (HI-SCALE:NCP), featured the following investigators and instruments:

- James Smith (University of California–Irvine)
  - Nanoparticle composition by thermal desorption chemical ionization mass spectrometry (TDCIMS)
  - Gas-phase, low-volatility aerosol precursors by chemical ionization mass spectrometry (CIMS)
  - Sulfur dioxide gas measurements by a commercial pulsed fluorescence gas analyzer (ThermoFisher Scientific model 43i-TLE). This instrument was provided by ARM and the research team was responsible for the deployment, data post-processing, and archiving.
- Harald Stark (Aerodyne Research, Inc.)
  - Gas-phase amines by CIMS using ethanol as reagent ion (Et-CIMS). This was a new instrument developed with funding by DOE's Atmospheric Systems Research Small Business Innovation Research (SBIR) program.
- Eleanor Browne (University of Colorado–Boulder)
  - Ambient ions by ambient pressure inlet time-of-flight (APi-ToF) mass spectrometry.
- David Hanson (Augsburg College)
  - Gas-phase amines and related compounds by ambient pressure proton transfer mass spectrometry (AMPMS).

During the 4-week campaign, we observed several intense nucleation events. Data analysis and modeling efforts are currently underway; already it appears that we have obtained our richest and most complete set of observations to date on the particles and gases associated with new-particle-formation events. Figure 1 summarizes the status of various measurements during the campaign. Most of the instruments operated properly. As typically occurs, difficulties were encountered for several prototype instruments, but valuable insights were gained as to how the design of those instruments might be revised to improve performance.



**Figure 1.** Summary of measurement status during the campaign. Color codes are: Red: instrument offline; Yellow: instrument working part of the day or operating at slight impairment; Green: instrument operating at full capacity.

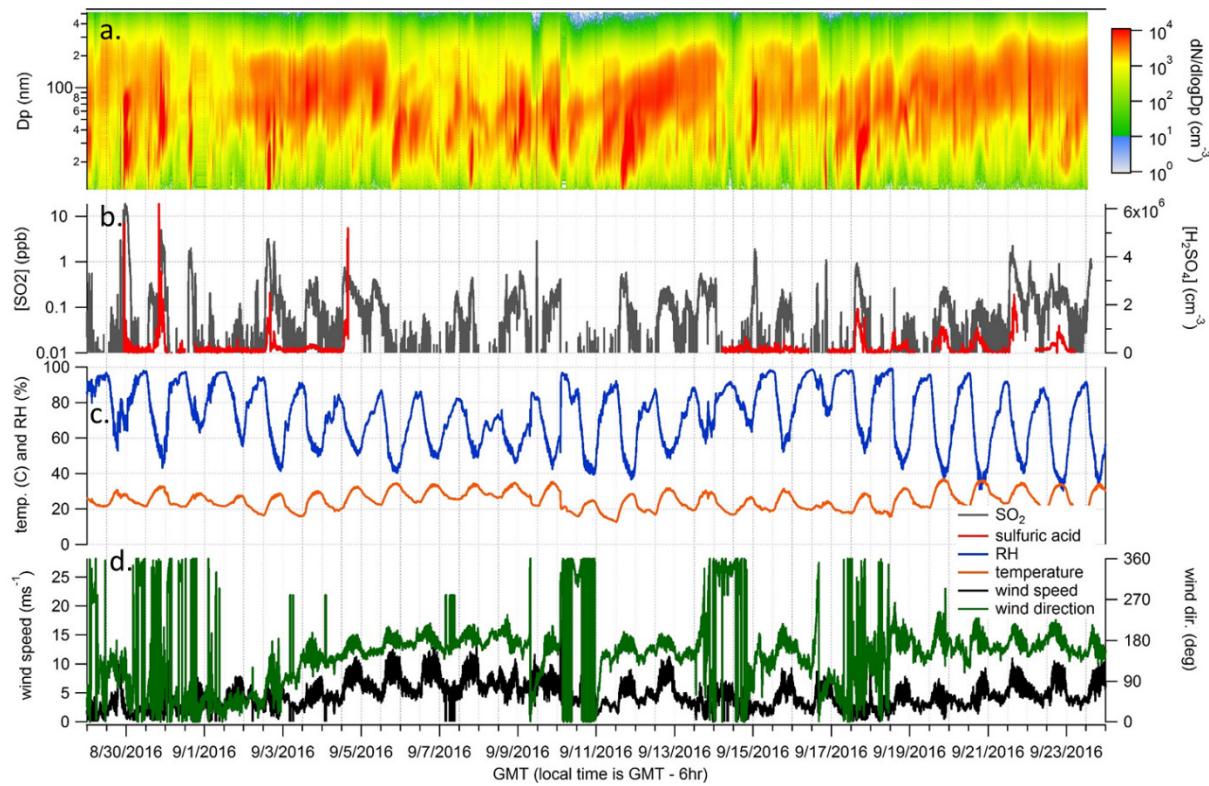
## 2.0 Results

During the 28 days of the campaign, we observed eight regional new-particle-formation events and several interrupted or partial events. Figure 2 provides an overview of the aerosol climatology during the campaign. Plot (a) shows particle size distributions from the ARM scanning mobility particle sizer (SMPS). New particle formation events are characterized by the sudden appearance of particles at the minimum detected diameter of the SMPS (10 nm) followed by subsequent growth of the size distribution over several hours. This occurred most notably on 11 and 17 September. On both of these days the G-1 aircraft made measurements over the SGP site, which sets up these days as extremely important “golden days” for closer study. Plot (b) shows SO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> as measured by pulsed fluorescence and CIMS, respectively. SO<sub>2</sub> is a precursor for H<sub>2</sub>SO<sub>4</sub>, the latter of which is often associated with new-particle formation. Plots (c) and (d) show meteorological data that may be useful in interpreting the data and attributing the sources of gas-phase precursors. For the first week of the campaign, the air masses originated primarily from the north, later shifting to the south for the final three weeks. Our prior measurements from the 2013 New Particle Formation Study (Hodshire et al. 2016) have shown that winds from the south often brought in air from more polluted areas such as the Houston metropolitan area with sulfate often dominating in nanoparticles during these periods, whereas northerly winds were often associated with rural emissions and higher levels of organic compounds.

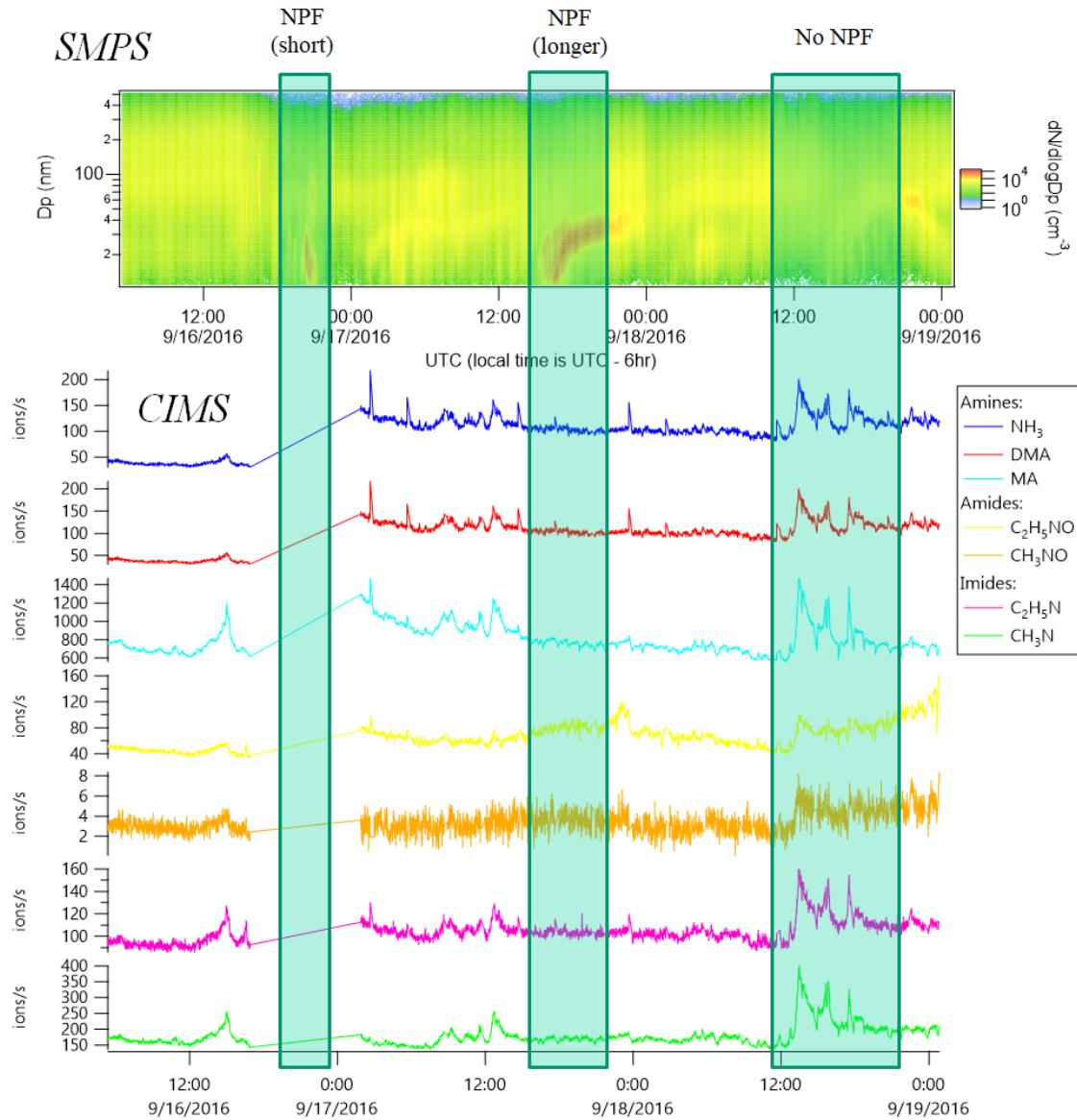
One major objective of this campaign was to test prototype instruments. One of these was the Et-CIMS, which was developed by members of the research team with funding from DOE’s SBIR program. The Et-CIMS was designed to measure gas-phase amines and related compounds, which are believed to play an important role in atmospheric new particle formation and growth. (Smith et al. 2010) Preliminary evaluation of the performance of that instrument shows that it was indeed able to detect a large variety of amines as well as amides and imides. Figure 3 shows some representative preliminary data spanning the period of the 17 September new-particle-formation “golden day.” Interestingly, the intense particle formation event did not coincide with elevated concentrations of any of the measured species. In fact the strongest peaks in these compounds occurred during periods of no new-particle formation.

TDCIMS measured nanoparticulate sulfate during the campaign. Representative data collected by the instrument, along with data from the API-TOF, are shown in Figure 4 for the 17 September “golden day.” Both instruments showed increases in gas-phase sulfuric acid clusters and particulate sulfate during new particle formation. These data will allow quantification of the role of sulfuric acid in new-particle formation, which has been done previously but never for a rural site like this.

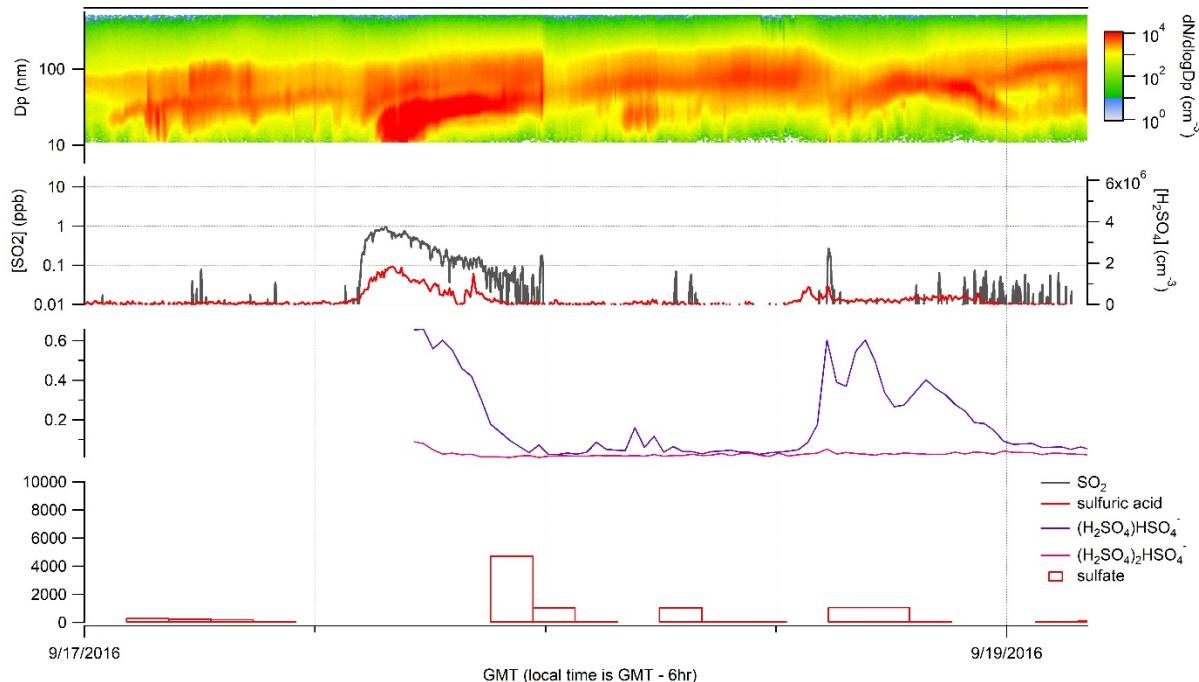
The analysis of these measurements is still underway, especially comparison of these measurements with those performed aloft onboard the G-1 aircraft. Nevertheless, it is apparent that these ground-based observations obtained during the second phase of HI-SCALE show some very significant new-particle-formation events with excellent coverage by measurements by our instrument suite.



**Figure 2.** Overview of observations relevant to new particle formation during the second phase of HI-SCALE. (a) Particle size distribution. (b) Sulfur dioxide gas and sulfuric acid. (c) Relative humidity and temperature. (d) Wind speed and direction.



**Figure 3.** (top) Particle size distributions during the campaign along with (bottom) measurements from the Et-CIMS of amines, amides, and imides. Periods with and without new-particle formation (NPF) are indicated by the blue boxes.



**Figure 4.** Measurements of sulfuric acid dimer and trimer, along with TDCIMS-derived measurements of particulate sulfate, for the 17 September new-particle-formation event.

## 3.0 Publications and References

### 3.1 Presentations

Data analysis and the preparation of manuscripts are currently underway. The following presentations featured measurements from HI-SCALE: NCP.

Smith, JN, et al., Overview of phase 2 surface measurements during HI-SCALE, 2017 Joint User Facility and PI Meeting, Tysons, Virginia, March 16, 2017 (breakout presentation).

Stark, H, et al., Ambient measurements of amines and related nitrogen-containing compounds in a rural environment using protonated ethanol chemical ionization high-resolution mass spectrometry, 2017 Joint User Facility and PI Meeting, Tysons, Virginia, March 16, 2017 (poster presentation).

### 3.2 References

Hodshire, AL, MJ Lawler, J Zhao, J Ortega, C Jen, T Yli-Junti, JF Brewer, JK Kodros, KC Barsanti, DR Hanson, PH McMurry, JN Smith and JR Pierce. 2016. "Multiple new-particle growth pathways observed at the US DOE Southern Great Plains field site." *Atmospheric Chemistry and Physics* 16(14): 9321-9348, [doi:10.5194/acp-16-9321-2016](https://doi.org/10.5194/acp-16-9321-2016).

Smith, JN, KC Barsanti, HR Friedli, M Ehn, M Kulmala, DR Collins, JH Scheckman, BJ Williams, and PH McMurry. 2010. "Observations of aminium salts in atmospheric nanoparticles and possible climatic

implications." *Proceedings of the National Academy of Sciences of the United States of America* 107(15): 6634-6639, [doi:10.1073/pnas.0912127107](https://doi.org/10.1073/pnas.0912127107).

## 4.0 Lessons Learned

We are very grateful for the assistance provided by the SGP staff during the campaign.

