

## **TRACER-Ultrafine Aerosol Formation and Impacts (TRACER-UFI) Field Campaign Report**

J Smith  
J Pierce

D Collins

March 2023



## **DISCLAIMER**

This report was prepared as an account of work sponsored by the U.S. Government. Neither the United States nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the U.S. Government or any agency thereof.

# **TRACER-Ultrafine Aerosol Formation and Impacts (TRACER-UF) Field Campaign Report**

J Smith, University of California, Irvine  
D Collins, University of California, Riverside  
J Pierce, Colorado State University

March 2023

How to cite this document:

Smith, J, D Collins, and J Pierce. 2023. TRACER-Ultrafine Aerosol Formation and Impacts (TRACER-UF) Field Campaign Report. U.S. Department of Energy, Atmospheric Radiation Measurement user facility, Richland, Washington. DOE/SC-ARM-23-009.

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

## **Acronyms and Abbreviations**

AMF1	first ARM Mobile Facility
ARM	Atmospheric Radiation Measurement
CAGE	Captive Aerosol Growth and Evolution
CIMS	chemical ionization mass spectrometer
HOM	highly oxidized molecule
HRTofMS	high-resolution time-of-flight mass spectrometer
HTOF	high-resolution time-of-flight
IOP	intensive operational period
LTOF	long time-of-flight
M1	AMF1 main site
PTFE	polytetrafluoroethylene
TDCIMS	thermal desorption chemical ionization mass spectrometer
TI-CIMS	transverse ionization inlet chemical ionization mass spectrometer
TRACER	Tracking Aerosol Convection Interactions Experiment
TRACER-UF1	TRACER-Ultrafine Aerosol Formation and Impacts
UV	ultraviolet

## Contents

Acronyms and Abbreviations .....	iii
1.0 Summary.....	1
2.0 Results .....	2
3.0 Publications and References .....	4
3.1 References Cited .....	4
3.2 Presentations .....	4
4.0 Lessons Learned .....	4

## Figures

1 Schematic showing measurement configuration during TRACER-UFI. ....	2
2 Size distributions taken from (a) CAGE chamber and (b) ambient air. ....	3
3 (top) Size distribution of new particle formation event formed within CAGE on 2 August 2022. (center) TI-CIMS-measured gas-phase sulfuric acid concentration measured within CAGE. Concentrations are estimated pending application of instrument calibration. (bottom) TDCIMS- measured sulfate in particles generated within CAGE. ....	3

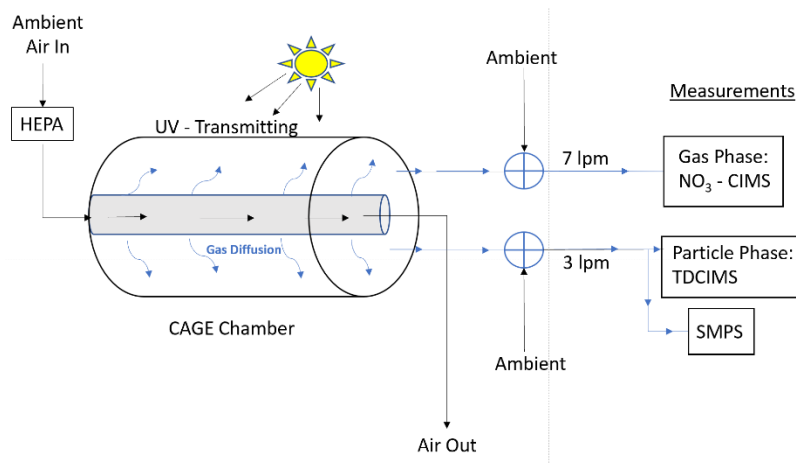
## 1.0 Summary

As a sub-campaign of the U.S. Department of Energy Atmospheric Radiation Measurement (ARM) user facility's Tracking Aerosol Convection Interactions Experiment in Houston, Texas, TRACER-Ultrafine Aerosol Formation and Impacts (TRACER-UFI) employed a unique suite of instruments and facilities for understanding the chemical species and mechanisms responsible for the formation of ultrafine particles in the Houston atmosphere during the TRACER intensive operational period (IOP). Our approach combined direct measurements of low-volatility precursors and size-resolved ultrafine (sub-100-nm diameter) particles together with measurements of gas-particle partitioning of ambient vapors onto freshly nucleated nanoparticles, the latter using the University of California, Riverside Captive Aerosol Growth and Evolution (CAGE) chamber.

TRACER-UFI took place between July 1 and August 31, 2022, at the First ARM Mobile Facility (AMF1) main site (M1) in La Porte, Texas. The Smith group operated a chemical ionization mass spectrometer with a transverse ionization inlet (TI-CIMS; Li et al. 2019) for online measurements of the low-volatility, highly oxidized molecules (HOMs) and sulfuric acid and a thermal desorption chemical ionization mass spectrometer (TDCIMS; Voisin et al. 2003) for online measurements of size-resolved nanoparticle chemical composition. The Collins group deployed and operated the CAGE chamber. CAGE is a  $\sim 2$  m<sup>3</sup> all-Teflon cylindrical chamber that is placed outside and adjacent to the trailer housing the previously mentioned instrumentation. The chamber is suspended in a powder-coated, stainless steel, rectangular enclosure that is covered in UV-transmitting Plexiglas G-UVT acrylic panels. The use of UV-transmitting materials for the chamber and enclosure, together with a UV-reflective gasket sheet below the chamber, results in a solar spectral intensity inside that is similar to that just outside. Ambient air is drawn through an all-Teflon filter mounted above the enclosure and through the center of the chamber in a channel that is wrapped with a permeable polytetrafluoroethylene (PTFE) membrane. Efficient gas exchange across the membrane results in trace gas concentrations inside that track those outside.

The use of CAGE provides a unique opportunity for studying new particle formation from the oxidation of the vapors measured at the M1 site. Essentially, it answers the question: What is the potential for the gas molecules that we measured at M1 to oxidize and form new particles? Ambient observations of new particle formation are often difficult to interpret because inevitably two phenomena contribute to atmospheric composition: (1) the oxidation of vapors in the air directly above the site followed by their partitioning into particles and (2) the transport of newly formed particles to the site, the latter of which may have been formed by a process that is different from that observed at the site (e.g., nanoparticles formed in marine environments from wave breaking and bubble bursting). CAGE allows us to study process (1) and, through comparison with ambient measurements, allows us to infer the contribution of process (2) to the composition of ultrafine particles in the Houston atmosphere.

From the discussion in the previous paragraph, it can be seen that much can be learned by combining measurements of the composition of gases and particles produced inside CAGE with gases and particles in ambient air. Our measurements therefore alternated between CAGE air and ambient air continuously throughout the campaign. Figure 1 shows the measurement configuration. Switching occurred every 35 minutes. Ambient particle sampling was size-selected for 30 nm, while CAGE particles were not size-selected but were typically smaller than 100 nm.

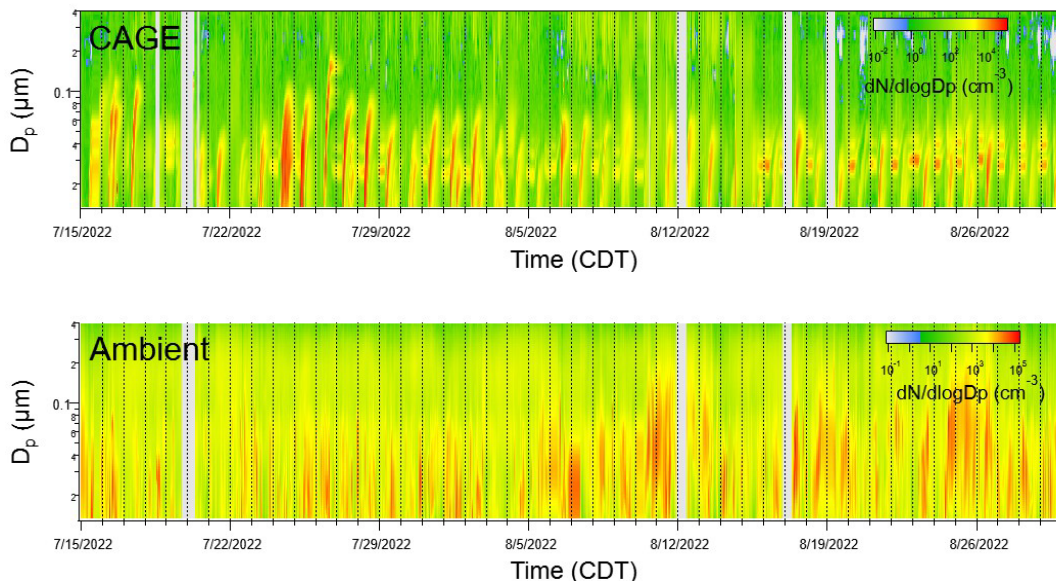


**Figure 1.** Schematic showing measurement configuration during TRACER-UFI.

TI-CIMS was employed using nitrate reagent ion and a high-resolution time-of-flight mass spectrometer (HRToFMS) employing a long time-of-flight (LTOF) mass analyzer (Tofwerk AG). The transverse ionization inlet is based on the cluster CIMS design developed by Dr. Fred Eisele at the National Center for Atmospheric Research for the study of low-volatility sulfuric acid clusters and is effective at minimizing water clustering that can occur as the ions pass through the supersonic jet expansion into vacuum. The composition of nanometer-sized particles as small as 8 nm was determined using TDCIMS. The TDCIMS uses electrostatic classification to select nanometer-sized charged particles, electrostatic precipitation to collect this fraction on a metal filament, resistive heating (room temperature to  $\sim 600^{\circ}\text{C}$ ) to desorb the chemical constituents of this fraction to the gas phase, and a chemical ionization source coupled to a HRToFMS employing a high-resolution time-of-flight (HTOF) mass analyzer (Tofwerk, AG) to identify and quantify those constituents.

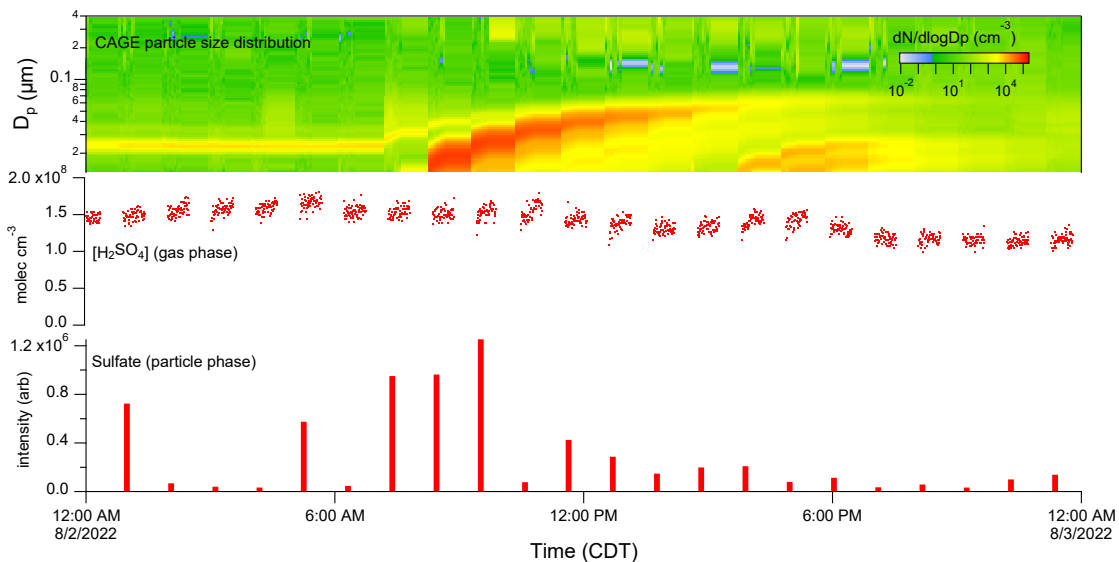
## 2.0 Results

While data processing and analysis are ongoing, it is already apparent that we have collected a unique data set that will address important questions relating to ultrafine particle formation in this region. Figure 1 shows size distributions taken from within CAGE (panel a) and in ambient air (panel b). One of the most striking results is that new particle formation was observed most days in CAGE during the TRACER-IOP while rarely observed in ambient air. The intensity of events within CAGE appears to be highest in late-July and early-August. The causes of these high-intensity events will be further explored using data from our TI-CIMS and TDCIMS measurements of the composition of gaseous precursors and nanoparticles, respectively.



**Figure 2.** Size distributions taken from (a) CAGE chamber and (b) ambient air.

With regard to our measurements of gases and particles in both ambient air and in CAGE, some initial findings warrant mentioning. Inorganic sulfates, including those derived from sulfuric acid, were found to be the dominant species in nanoparticles measured both in ambient air and in CAGE. Figure 2 shows one example of measurements from CAGE of the event from 2 August 2022. This observation suggests an important role for sulfuric and/or methanesulfonic acid in new particle formation and growth in this setting.



**Figure 3.** (top) Size distribution of new particle formation event formed within CAGE on 2 August 2022. (center) TI-CIMS-measured gas-phase sulfuric acid concentration measured within CAGE. Concentrations are estimated pending application of instrument calibration. (bottom) TDCIMS-measured sulfate in particles generated within CAGE.



Modeling by Professor Pierce’s group at Colorado State University is currently underway to attempt to reconcile observed growth rates, nanoparticle composition, and gas phase. Professor Smith’s group continues to process TDCIMS and TI-CIMS data to identify and quantify the gas- and particle-phase constituents. Professor Collins’ group is working to further characterize important aspects of CAGE such as wall loss rates.

## 3.0 Publications and References

### 3.1 References Cited

Li, X, S Chee, J Hao, JPDD Abbatt, J Jiang, and JN Smith. 2019. “Relative humidity effect on the formation of highly oxidized molecules and new particles during monoterpene oxidation.” *Atmospheric Chemistry and Physics* 19(3): 1555–1570, <https://doi.org/10.5194/acp-19-1555-2019>

Voisin, D, JN Smith, H Sakurai, PH McMurry, and FL Eisele. 2003. “Thermal desorption chemical ionization mass spectrometer for ultrafine particle chemical composition.” *Aerosol Science and Technology* 37(6): 471–475, <https://doi.org/10.1080/02786820300959>

### 3.2 Presentations

The following presentation was given at a conference. Manuscripts are currently in-preparation.

Wakeen, J, X Du, S O’Donnell, JR Pierce, DR Collins, and JN Smith. 2022. “Ultrafine Aerosol Particle Formation and Impacts in Houston during TRACER.” Presented at the Annual Conference of the American Association for Aerosol Research. Raleigh, North Carolina.

## 4.0 Lessons Learned

The TRACER-UFI team is extremely grateful to the ARM support staff for their tireless work in making this campaign run smoothly. We encountered no insurmountable challenges during the campaign but will briefly mention a few main lessons learned. Firstly, the use of the 8’ x 20’ ground-level office trailer by Mobile Mini as a lab space during the campaign was largely a success. Our main modifications are summarized below, but Professor Smith is happy to supply additional details if needed:

- Weather-tight feedthroughs through the windows were straightforward, as the window could be removed and replaced by a piece of plywood that was weather-sealed around the edges.
- Power was supplemented by a “construction spider box” that was separately connected to the circuit breaker.
- The air conditioner struggled with our vacuum pumps in the trailer. Once these were moved outside in a “deck box” that was modified to include a roof fan for ventilation, the trailer was fine.
- Liquid nitrogen dewar delivery was somewhat unpredictable but that is not an uncommon challenge. We did not lose a single moment of measurement from lack of this, so we have no complaints!



U.S. DEPARTMENT OF  
**ENERGY**

---

Office of Science