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Acronyms and Abbreviations

AGL	above ground level
ALS	Advanced Light Source
ARM	Atmospheric Radiation Measurement
ASR	Atmospheric System Research
BAC	bulk aerosol collector
CCSEM/EDX	computer-controlled scanning electron microscopy/energy-dispersive X-ray spectroscopy
DESI	desorption electrospray ionization
DOE	U.S. Department of Energy
EC	elemental carbon
EMSL	Environmental Molecular Sciences Laboratory
FICUS	Facilities Integrating Collaborations for User Science
FTICR	Fourier-transform ion cyclotron resonance mass spectrometry
HESI	heated electrospray ionization
HRMS	high-resolution mass spectrometer
HYSPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectory
IN	inorganic carbon
LBNL	Lawrence Berkeley National Laboratory
LCMS	liquid chromatography mass spectrometry
OC	organic carbon
PNNL	Pacific Northwest National Laboratory
POPS	printed optical particle spectrometer
SEM	scanning electron microscopy
SOA	secondary organic aerosol
STAC	size-and-time-resolved aerosol collector
STMX/NEXAFS	scanning transmission X-ray microscopy/near-edge X-ray absorption fine structure spectroscopy
TBAC	time-resolved bulk aerosol collector
TBS	tethered balloon system
TEM	transmission electron microscopy
TRACER	Tracking Aerosol Convection Interactions Experiment

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1.0 Summary

We investigated physicochemical properties of aerosol at different altitudes during the U.S. Department of Energy (DOE)'s Atmospheric Radiation Measurement (ARM) user facility Tracking Aerosol Convection Interactions Experiment (TRACER). We used ARM's tethered balloon system (TBS) and multi-modal offline analysis techniques available at DOE's Environmental Molecular Sciences Laboratory (EMSL) at Pacific Northwest National Laboratory (PNNL) and at the Advanced Light Source (ALS) at the Lawrence Berkley National Laboratory (LBNL). The main scientific aim of this project was to understand the influence of the vertical profile of aerosol composition on the properties of deep convective clouds. The effect of aerosol properties on convective activity is still poorly understood and debated. For example, previous studies suggested that higher concentration of hygroscopic aerosol may lead to lower collection efficiency and eventually delay in onset of precipitation and total amount of precipitation. However, some observations suggested that increased aerosol concentration may result in vigorous convection and a higher amount of precipitation. In addition, the radiative forcing of the ambient aerosol is strongly influenced by the vertical distribution of aerosols and their chemical composition, and not well constrained in climate models. The estimation of the indirect effect of aerosol also has a significant uncertainty due to the spatial variation of the aerosol, especially at the cloud base. Detailed size-resolved chemical composition studies of aerosol and their microphysical properties, along with in situ measurements from ARM's mobile facilities, help to improve our understanding of the role of aerosol in deep convective cloud formation over a broad range of environmental thermodynamic and aerosol conditions.

Figure 1. TBS deployment at the ancillary site under overcast conditions on September 4, 2022. Photo courtesy of D. Dexheimer.

Aerosol samples were collected by deploying an automated size-and-time-resolved aerosol collector (STAC) and via ARM's TBS. The TBS system was deployed at the ancillary site. Determining the size-resolved chemical composition of particles is crucial for understanding several atmospheric processes, including warm and cold cloud formation, but challenging to accomplish using currently

available sampling devices. We performed preliminary analysis of aerosol samples using EMSL's microscopy, spectroscopy, and mass spectrometry platforms. In addition, we deployed a time-resolved bulk aerosol collector (TBAC) to collect enough bulk aerosol material for extraction-based high-resolution mass spectrometry (HRMS) analysis (e.g., liquid chromatography mass spectrometry [LCMS], Fourier-transform ion cyclotron resonance mass spectrometry [FTICR]). HRMS analysis will provide detailed molecular aerosol composition up to five different altitudes. In addition, we collected samples during day and night at ground level for both single-particle and bulk analysis using a bulk aerosol collector (BAC), TBAC, and a cascade impactor. Sampling was performed for the first two weeks of June, July, August, and September. The TBAC system was not available during June, but the system was deployed during July, August, and September of 2022. We collected over 200 samples under different atmospheric conditions during the campaign. We characterized filter samples collected at ground level and aloft via TBS to discern potential molecular-level signatures for distinct weather patterns. To understand the variations in vertically resolved SOA composition, comparative analysis has been performed on ground- and TBS-collected filter samples.

To achieve our goals, we performed filter analysis via solid-phase extraction with flow-injection heated electrospray ionization (HESI) as well as nanospray desorption ESI (nano-DESI) coupled to HRMS. Additionally, multi-modal chemical imaging techniques have been used such as computer-controlled scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (CCSEM/EDX) to characterize the single-particle chemical compositions and their morphologies. Carbon features in the particles are probed with scanning transmission X-ray microscopy with near-edge X-ray absorption fine structure spectroscopy (STXM/NEXAFS) at ALS/LBNL to determine particle mixing state. We performed Hybrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT) simulation to determine the sources of the airmass. Our analysis suggests that, during our sample collection, on several occasions air masses came from the southeast U.S. and across the Gulf of Mexico. These analyses, along with in situ measurements, guided us to select interesting events.

We present some preliminary single-particle analysis as well as molecular composition of organic aerosol in this report. We have been investigating the samples that were collected during pre- and post-convection. A significant fraction of these samples was influenced by salt particles from sea breeze. We screened most of the samples that were collected during June, July, and August. All the samples have good loading for single-particle analysis. We performed CCSESM/EDX and STXM/NEXAFS analysis of selected samples (interesting events) to determine the size-resolved chemical composition and mixing state of particles. The BAC and TBAC samples at ground level also have good loading but samples that are dominated by salts are challenging to analyze to determine their molecular composition. However, we have been optimizing our methods to analyze these samples. The aloft samples have relatively lower mass loading and we have been testing the feasibility of samples that can be analyzed using HRMS. Our preliminary analysis focused on variation of particle molecular composition during day and night at the ground site. We have been sharing some of our collected samples with our Atmospheric System Research (ASR)/ARM colleagues for their analysis as well. More comprehensive analysis is in progress in collaboration with other ASR/ARM scientists under the ARM-EMSL Facilities Integrating Collaborations for User Science (FICUS) program.

Physicochemical properties of aerosol at different altitudes will help to better constrain models and improve representation of aerosol in deep convection cloud models. These observations will also help in understanding the microphysics of deep convective clouds.

2.0 Results

Figure 2 shows representative SEM images of particles collected from June 3 and June 4 flights. We observed the presence of biological particles (marked by green arrow) in these samples. However, a major fraction of submicron size particles is dominated by sulfate and carbonaceous particles.

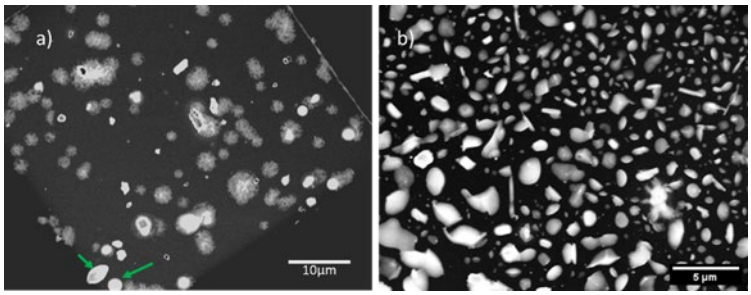

Figure 2. Representative SEM images of particles from samples collected on June 3, 2022 stage D and June 4, 2022 stage C STAC impactor samples. Green arrow indicates the presence of biological particles.

Figure 3a shows a representative flight pattern during the TRACER campaign on June 3, 2022. During the TBS flight, a printed optical particle spectrometer (POPS, Handix Scientific) was used to measure the particle concentration and size distribution, while one iMet radiosonde and one wind speed and direction sensor were used to monitor meteorological conditions. Aerosol particles were collected using the STAC platform deployed on the ARM TBS system. The STAC has an array of 20 four-stage cascade impactors (50% cut-offs for stages A, B, C, and D are 2.3, 0.62, 0.42, and 0.12 µm, respectively) to collect particles on the transmission electron microscopy (TEM) grids (carbon Type-B TEM grids and silicon nitride substrates) for offline individual particle analysis. In this example, we collected three STAC impactors: IM1 (ascending from 0 to 500 m above ground level [AGL]), IM 2 (ascending from 500 to 950 m AGL), and IM3 (descending from 450 to 0 m AGL). During this flight, particle concentration decreases with increasing altitudes based on the POPS measurements.

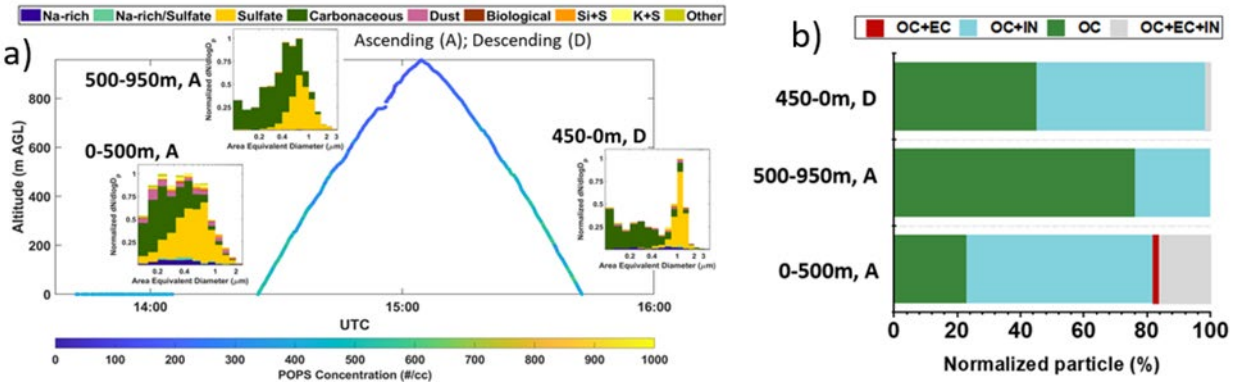

Figure 3. a) TBS flight profile during June 3, 2022. Color bar represents POPS concentration and insets show size-resolved composition of particles from CCSEM/EDX. b) Normalized particles fraction of different particle types derived from STXM analysis.

Aerosol particles collected on stage D were analyzed with CCSEM-EDX at EMSL to probe morphology (size and shape) and relative element percentage of 15 elements (C, N, O, Na, Mg, Al, Si, P, S, Cl, K, Ca,

Mn, Fe, and Zn) of individual particles. Based on this information, we classified each particle as carbonaceous, sulfate, sodium-rich (Na-rich), sodium-rich with sulfate (Na-rich/sulfate), dust, biological, silicon with sulfate (Si + S), potassium with sulfate (K + S), and others. Figure 3a shows that the major fraction of particles are carbonaceous and sulfate particles at all altitudes. The fraction of carbonaceous particle increases and that of sulfate particles decreases with a decrease in particle size. It has been shown that the sulfate with an area-equivalent diameter greater than 0.6 μm might be the product of aqueous phase processing. Moreover, the sulfate fraction is higher at lower altitudes (IM1 and IM3). These stage D samples were also analyzed with STXM/NEXAFS at beamline 5.3.2.2 to probe the carbon functional groups and mixing state of organic (OC), inorganic (IN), and elemental carbon (EC). Figure 3b shows the fraction of different particle types classified by STXM-NEXAFS. It shows that at higher altitudes (IM2) there is a higher fraction of OC than at lower altitudes (IM1 and IM3), which is consistent with CCSEM-EDX results. These OC+IN particles might be sulfate particles based on the CCSEM analysis. Some OC+EC and OC+EC+IN particles are in the IM1 sample, which might be due to local anthropogenic emission.

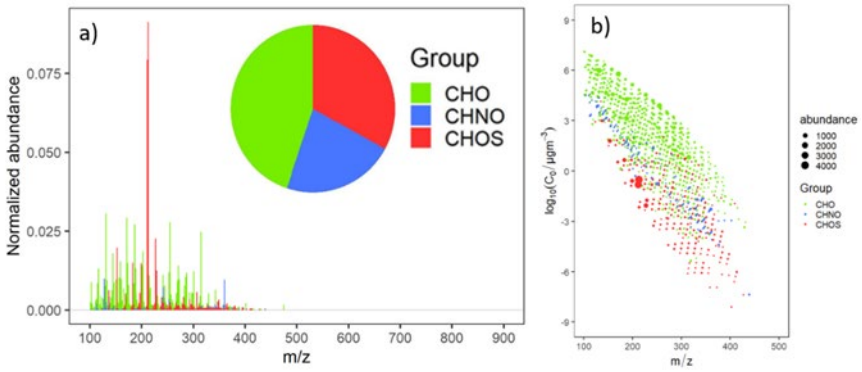

Figure 4. a) High-resolution mass spectra for aerosols sampled during August 4, 2022 under cloudy conditions. Inset pie chart shows fraction of molecular formula detected in the sample for different groups. b) Estimated saturation mass concentration versus m/z and color-coded by different groups.

Figure 4 shows an example of mass spectra acquired by nano-DESI HRMS for aerosol samples that were collected during August 4, 2022, under cloudy conditions. Resolved peaks were processed to determine the molecular formula. We calculated double bond equivalents, average carbon oxidation states (OS_c), volatilities ($\log_{10}C_0$; C_0: saturation mass concentration [$\mu g/m^3$]), modified aromaticity indexes (AI_{mod}), and glass transition temperatures (Tg_{RH}; temperature- and relative humidity-dependent) according to empirical models. Figure 4b shows the estimated saturation mass concentration for different groups. As expected, organosulfate compounds are relatively less volatile. In general, organosulfate compounds are abundant in most of the TRACER samples that we have investigated so far. Significant number of samples are influenced by sea breeze and contain salt particles, which makes HRMS analysis challenging. Currently we have been exploring several extraction methods to remove salts from the samples. Our plan is to work with ASR scientists to analyze a substantial number of these samples through ARM-EMSL FICUS projects and data will be shared with the ASR/ARM community.

3.0 Publications and References

We have presented or plan to present our preliminary results in scientific meetings and conferences. We have plans to publish several manuscripts as part of this ARM field campaign.

Gautam, T, GW Vandergrift, LN Nurun, Z Cheng, D Dexheimer, and S China. 2023. “Deep Convective Cloud Formation: Characterization of Secondary Organic Aerosols during TRACER-ARM Campaign.” Presented at the American Association for Aerosol Research Annual Conference. Portland, Oregon.

Cheng, Z, NN Lata, D Dexheimer, MA Marcus, GW Vandergrift, T Gautam, C Kuang, LA Steiner, and S China. 2023. “Investigate the vertical profile of size-resolved aerosol chemical composition and aerosol mixing state during TRacking Aerosol Convection interactions ExpeRiment (TRACER).” Poster presented at the American Association for Aerosol Research Annual Conference, Portland, Oregon.

Gautam, T, GW Vandergrift, LN Nurun, Z Cheng, M Zawadowicz, C Kuang, A Steiner, L Yee, A Goldstein, R Chakrabarty, D Dexheimer, and S China. 2023. “Investigating secondary organic aerosols under convective clouds during TRACER-ARM campaign in SW Houston, Texas.” Virtual poster presented at the Joint Atmospheric Radiation Measurement (ARM) User Facility/Atmospheric System Research (ASR) Principal Investigators (PI) Meeting.

Cheng, Z, NN Lata, D Dexheimer, MA Marcus, GW Vandergrift, T Gautam, C Kuang, LA Steiner, and S China. 2023. “Investigate the vertical profile of size-resolved aerosol chemical composition and aerosol mixing state during TRacking Aerosol Convection interactions ExpeRiment (TRACER).” Poster presented at the Joint Atmospheric Radiation Measurement (ARM) User Facility/Atmospheric System Research (ASR) Principal Investigators (PI) Meeting.

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