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Acronyms and Abbreviations

AAE	absorption Ångström exponent
ASOP	airborne soil organic particles
BrC	brown carbon
CCSEM-EDX	computer-controlled scanning electron microscopy-energy-dispersive X-ray spectroscopy
HI-SCALE	Holistic Interactions of Shallow Clouds, Aerosols, and Ecosystems
HYSPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectory model
IOP	intensive operational period
MOUDI	micro-orifice uniform deposit impactor
PSAP	particle soot absorption photometer
SEM	scanning electron microscopy
SGP	Southern Great Plains
SP	soot particle
STXM-NEXAFS	synchrotron-based scanning transmission X-ray microscopy-near-edge X-ray absorption spectroscopy
TB	tar ball

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1.0 Summary

The main goal of this field project was to characterize the chemical and physical properties of atmospheric particles representative of the Southern Great Plains (SGP) environment to establish a relationship between the composition of aerosol particles and their atmospheric impacts. The specific research efforts were focused on in-depth microscopy studies of chemical and physical properties of atmospheric organic particles collected at the U.S. Department of Energy's Atmospheric Radiation Measurement (ARM) SGP observatory. An array of novel molecular-level characterization and chemical imaging approaches were used to characterize chemical composition of particles and elucidate fundamental processes governing their atmospheric aging, evolution of chemical composition, optical properties, cloud formation ability, and implications for particle-cloud interactions – the most challenging problems relevant to predictive understanding of aerosol effects on climate.(1, 2)

Atmospheric particles consist of a complex mixture of organic compounds with a wide range of molecular structures, morphologies, physical properties, and chemical reactivity. The chemical composition, morphology, and phase state of atmospheric particles are of crucial importance for understanding the formation and reaction mechanisms of particles, their atmospheric evolution, and their impact on climate. It is of great interest to understand how the chemical and morphological particle microstructure affects their physicochemical properties such as chemical reactivity, thermodynamics of gas-particle partitioning, phase separations inside individual particles, hygroscopicity, optical properties, and ability to form liquid droplets (cloud condensation nuclei) and ice crystals (ice nuclei) in clouds. The phase state of organic particles, which yet remains poorly understood, plays a key role in their physicochemical properties and has important implications in various atmospheric processes. Fundamental understanding of these physicochemical properties and their possible evolution in time requires advanced analytical approaches for chemical imaging of particles with a resolution on the scale of 10-100 nm.(3) Comprehensive characterization of the size-dependent chemical composition of individual particles collected at the site was carried out using advanced molecular-level characterization and imaging approaches to identify their possible sources and to correlate to their climatic properties.

To provide detailed information on aerosol morphology, composition, and microphysical properties, size-segregated sampling was carried out at the SGP site during selected days over a broad time period spanning 2016-2018, including two intensive operational periods (IOPs) of the Holistic Interactions of Shallow Clouds, Aerosols, and Ecosystems (HI-SCALE) field campaign.(4) Winter and summer sampling was carried out to investigate any seasonal differences of aerosol composition due to differing meteorology and emission sources. A micro-orifice uniform deposit impactor (MOUDI) was used to collect particles for microscopic and microphysical analysis. A variety of microscopic substrates (formvar-coated copper grids, silicon chips, silicon nitride windows, or molybdenum substrates) were used. Microscopic chemical characterization was carried out using computer-controlled scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (CCSEM-EDX) and the synchrotron-based scanning transmission X-ray microscopy coupled with near-edge X-ray absorption spectroscopy (STXM-NEXAFS).(5-7) Two light sources were used for this analysis: 1) the Advanced Light Source at Lawrence Berkeley National Laboratory, and 2) The Canadian Light Source. Both the CCSEM-EDX and STXM-NEXAFS techniques have proven to be valuable tools to provide a detailed characterization of individual marine particles – particularly with respect to particles containing organic material.(8-10) Ice nucleation characterization using optical microscopy with a cold stage has also provided critical

information about water uptake.(11) Sampling coincided with the HI-SCALE field campaign so that detailed single-particle measurements could be obtained in the context of the larger field campaign. Sampling at the SGP field site also has the advantage of being co-located with long-term measurements of aerosols, trace gases, meteorology, and radiation. The collocated measurements at the SGP site were used to select samples for detailed microscopic characterization.

Amorphous solid organic particles have been observed in many of the samples collected at SGP, and they have been classified as airborne soil organic particles (ASOP) or tar balls (TB) based on smoke and precipitation data. Events of ASOP and TB particles were strongly correlated with high values measured for the absorption Ångström exponent (AAE ~ 2.6), indicating their optical properties characteristic of brown carbon (BrC). Spectro-microscopy analysis of these particles showed characteristic differences in NEXAFS spectral fingerprints of ASOP and TB based on the –COOH/C=C and –COOH/COH peak ratios, with ASOPs having lower peak ratios.(12) These results highlight the similarities between ASOP and TB and show how they may be differentiated. Common sulfate-rich particles were also observed during a significant number of sampling events. Variations in the mixing of ASOP, TB, organics, soot, and sulfate were observed depending on sampling time and air mass characteristic. Analysis of samples using microscopy and spectroscopy is still under way. The results presented here represent the initial data analysis that has been carried out to date.

2.0 Results

Peripheral measurements located at the SGP ground site and meteorological records were used to guide selection of samples for detailed microscopic analysis. Figure 1 shows time series of aerosol absorption and particle number concentration as well as time periods over which aerosol samples were collected for microscopic analysis. Because ASOP and TB have optical properties of BrC, their substantial presence in the air can be inferred from bulk optical properties measured at the site. Particle soot absorption photometer (PSAP) data were used to calculate the AAE and are shown in Figure 1 alongside the corrected absorption coefficients. CO and particle number concentrations are also shown in Figure 1 to provide further information on the air mass origin and particle loading. Figure 1 shows how both red and blue absorption coefficients and AAE changes over the course of this IOP. Note that during many of the rain events (denoted by vertical red stripes) the absorption coefficients decrease rapidly due to a decrease in aerosol concentration. The vertical gray bars show sampling dates from which substrates were selected for chemical imaging.

Elevated AAE values suggested the presence of spherical BrC particles; therefore, these measurements were used to select samples for a detailed analysis of particle morphology using microscopy. To this end, SEM images of tilted samples were taken and a wide range of soot particle (SP)% values characteristic of particle light-absorption were observed, from less than 5% to near 70%. Figure 2 shows three different representative electron microscopy and spectro-microscopy images for three days where the SP% values of individual particles were high. The top row shows the tilted SEM images used to identify solid amorphous particles. Pink arrows point to a few identified SPs to highlight how much they stick out above the substrate compared to the others. Also of note in the SEM images is the presence of what looks like fractal soot in the April 28 and May 5 samples.

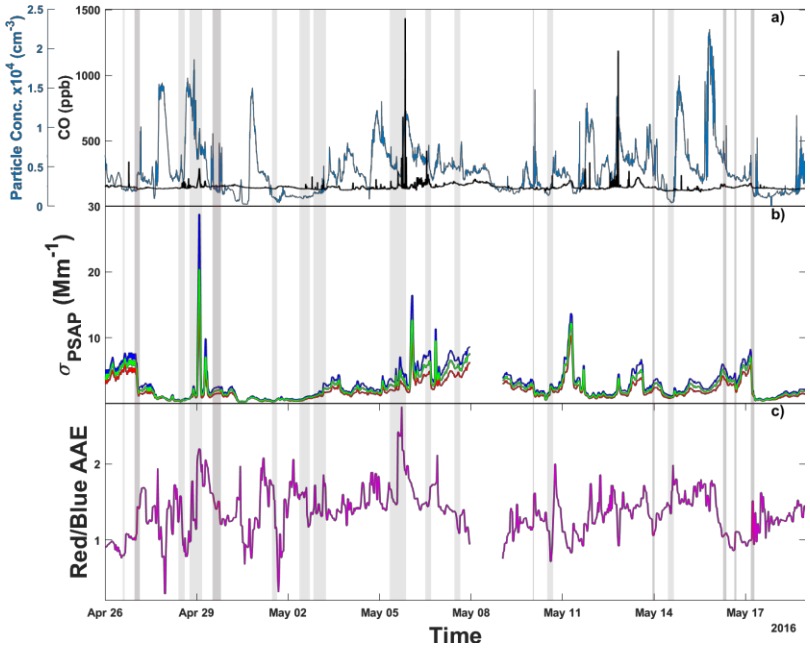

Figure 1. Time series for a) CO and ambient particle concentration, b) red (660 nm), green (522 nm), and blue (470 nm) absorption coefficients, and c) absorption Ångström exponent (AAE) calculated from red and blue absorption coefficients. Gray vertical bars represent aerosol sampling periods; red vertical bars represent periods of rainfall.

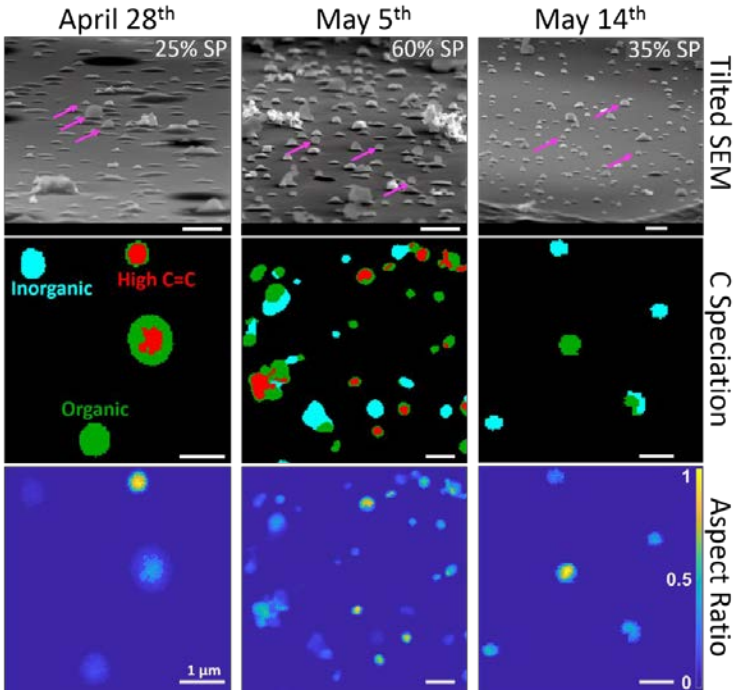

Figure 2. (top) SEM tilted (75°) images show differences in amorphous solid organic particles concentration between three samples. Pink arrows point to a few the solid organic particles. (middle) Carbon speciation maps with red representing regions with enhanced C=C bonding, green representing organics, and teal representing inorganics. (bottom) Aspect ratio images calculated from dividing thickness by the area equivalent diameter of each particle.

The middle and bottom row of images shown in Figure 2 are STXM images and they are both of the same field of view. The middle row shows carbon speciation maps where each pixel is assigned as either inorganic dominant, organic dominant, or as a region with high C=C bonding in accordance with Moffet et al. 2010.(13) The bottom row shows the thickness of each of the particles as calculated using previously published thickness equations (14) normalized by the individual area equivalent diameter. Values close to 0 represent flat particles while values closer to 1 represent taller, possibly spherical particles. As was suggested in the SEM images, soot is present in both the April 28 and May 5 samples, while the May 14 sample has only organic and inorganic particles. In the April 28 and May 5 samples, it is these soot particles which are the tallest and look the most spherical. In contrast, the May 14 sample has a possibly spherical particle that is only comprised of organic dominant pixels.

To investigate the nature and source of the solid organic particles and determine which can be confidently classified as ASOP or TB, smoke, fire, and precipitation data were used and hybrid single-particle Lagrangian integrated trajectory model (HYSPLIT) back trajectories were calculated. These data for the events when the three samples had elevated SP% are shown in Figure 3 for April 28, May 5, and May 14.

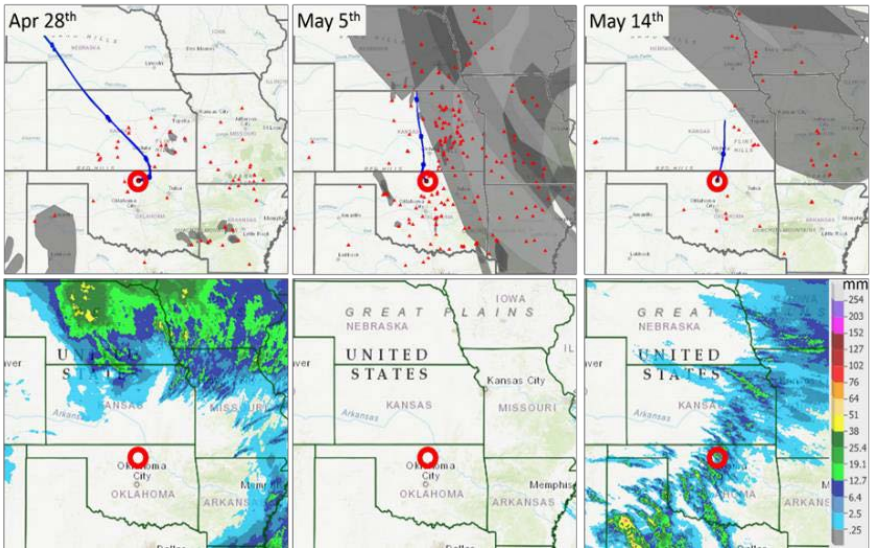

Figure 3. Smoke, fire, and precipitation data along with HYSPLIT back trajectories for three sample dates. The red circle represents the sampling site while the small red triangles represent fires. The gray overlay seen in the top row represents detected smoke particles. The bottom row shows the 24-hour average precipitation amount over the sampling date. The top row maps were obtained using the AirNow-Tech navigator. HYSPLIT trajectories for April 28 and May 5 are for 24 hours. The May 14 back trajectory was truncated at 10 hours due to a rain event with significant precipitation scavenging.

BrC particles like TB or ASOP and their place in the global aerosol budget are not yet well understood. In our results shown here, BrC has been shown to measurably affect bulk optical properties such as the AAE and on multiple days ASOP and TB were observed to comprise a significant fraction of the fine-mode aerosols.

Chemical imaging using SEM was used to identify solid organic particles in a number of samples taken at SGP. High fractions of solid organic particles showed a strong correlation with the average AAE over the sampling periods. These samples were further classified into samples with tar balls and samples with

ASOP by comparing smoke and precipitation data during their collection periods. Further analysis into the differences between supposed ASOP- and tar ball-laden samples was performed with STXM/NEXAFS. Samples unaffected by recent rain, but that were collected while smoke plumes were present, showed a higher –COOH/C=C peak ratio and showed an elevated –COH peak. The elevated –COH peak may be due to the presence of sugars such as levoglucosan or other less oxidized molecules. The sample from May 14 was collected a short 10 hours after a recent rain event and had less influence from smoke plumes. This sample showed a much more subdued –COH peak and a smaller –COOH/C=C peak ratio. Comparing the ambient spectra collected here with previously collected spectra supported the presence of tar balls in the smoke-affected samples and also supported the presence of ASOPs in the sample taken after a recent rain event. Peak ratios between –COOH and C=C and between –COOH and COH were calculated, emphasizing the difference between tar balls and ASOPs and between the smoke-affected samples and the samples with recent rainfall.

Future work on samples from this field campaign will focused on analysis of particle samples from fall and winter-early spring seasons. Analysis of these samples will allow for a comparison between winter and early summer periods in the SPG.

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3.1 Publications

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