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DOE/SC-ARM-23-032

TRACER Carbonaceous Aerosols Thrust – University of California, Davis Field Campaign Report

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August 2023

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How to cite this document:

Cappa, C, Q Zhang, R Dal Porto, Z Zheng, R Farley, M Dubey, A Aiken, K Gorkowski, K Benedict, J Lee, K Carrico, M Jensen, C Kuong, and J Flynn. 2023. TRACER Carbonaceous Aerosols Thrust – University of California, Davis Field Campaign Report. U.S. Department of Energy, Atmospheric Radiation Measurement user facility, Richland, Washington. DOE/SC-ARM-23-032.

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
APS	aerodynamic particle sizer
ARM	Atmospheric Radiation Measurement
BC	black carbon
BNL	Brookhaven National Laboratory
CAPS-SSA	cavity-attenuated phase shift spectroscopy single-scatter albedo
CAT	Carbonaceous Aerosols Thrust
CRD-PAS	cavity ringdown-photoacoustic spectrometer
ETSP	event trigger single particle
LANL	Los Alamos National Laboratory
MAC	mass absorption coefficient
OOA	oxygenated organic aerosol
PM	particulate matter
PMF	positive matrix factorization
rBC	refractory black carbon
RH	relative humidity
SEMS	scanning electrical mobility sizer
SP-AMS	soot particle aerosol mass spectrometer
TRACER	Tracking Aerosol Convection Interactions Experiment
UCD	University of California, Davis

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1.0 Summary

The broader U.S. Department of Energy Atmospheric Radiation Measurement (ARM) user facility's TRacking Aerosol Convection interactions ExpeRiment (TRACER) campaign aims to increase our understanding of convective cloud life cycles and aerosol-convection interactions. Our TRACER Carbonaceous Aerosols Thrust-University of California, Davis (TRACER-CAT-UCDavis) study complemented these broader aims by characterizing and quantifying the optical properties and composition of carbonaceous aerosols during part of the TRACER intensive sampling period (July 1-July 31, 2022) at the first ARM Mobile Facility (AMF1) main site (M1) in La Porte, Texas.

Our measurements complemented the suite of instrumentation already provided by the AMF1, expanding the capabilities through deployment of unique, state-of-the-science instrumentation. The instrumentation included: (i) two cavity-attenuated phase shift spectroscopy single-scatter albedo (CAPS-SSA) instruments operating at 530 nm and 630 nm, and that were modified to characterize particle light absorption, extinction, and scattering at elevated humidities; (ii) the UC Davis dual-wavelength cavity ringdown-photoacoustic spectrometer (CRD-PAS), which characterizes dry particle extinction and absorption at 405 nm and 532 nm; (iii) a soot particle aerosol mass spectrometer (SP-AMS) that operated in "laser only" mode that characterized the size-dependent compositions of black carbon (BC)-containing particles; (v) a thermal denuder, to remove coatings on particles; and (vi) a scanning electrical mobility sizer (SEMS), to characterize particle mobility diameters from 10-1300 nm. Our measurements occurred alongside complementary observations made by Los Alamos National Laboratory (LANL) during the TRACER-CAT-LANL study, including a humidified CAPS-SSA instrument operating at 450 nm.

Our primary scientific interest is in understanding the relationship between particle composition and light absorption, with a particular focus on the influence of water uptake. While it is known that coatings on BC can enhance absorption, the extent to which this occurs in the atmosphere and the specific role that water plays as a coating remain unclear.

The TRACER-CAT-UCDavis measurements were made with near-complete coverage for the CRD-PAS, SP-AMS, and SEMS throughout the intensive period. The UC Davis humidified CAPS-SSA instruments had significant challenges with operation owing to the demanding conditions (large temperature fluctuations, high humidity), exacerbated by supply chain issues that delayed resolution of these challenges. However, the humidified CAPS-SSA instrument operated by LANL operated throughout the intensive period with near-complete coverage. The dry light extinction measurements from the CRD-PAS measurements and the LANL CAPS-SSA exhibited a good correlation, although the CAPS-SSA systematically measured greater extinction values than expected. While all instruments, with the exception of an aerodynamic particle sizer (APS), measured behind a common particulate matter (PM)2.5 µm cyclone, the greater extinction measured by the LANL CAPS-SSA compared to the CRD-PAS may have resulted from different losses of larger particles in the sampling lines from the cyclone to the instruments; the tubing length was shorter from the cyclone to the LANL CAPS-SSA, consistent with this idea. A summary of the TRACER-CAT-UCDavis measurements, along with some of the TRACER-CAT-LANL measurements, are shown in the figure below. Notably, there were periods when the contributions of presumed dust were substantial and even dominated the observed light extinction and absorption. Also, there was a clear shift in the behavior of submicron particles from before July 16, 2022 to after, with the prior period exhibiting regular episodes of new particle formation and the latter period exhibiting rapid variations in the concentrations of small particles.

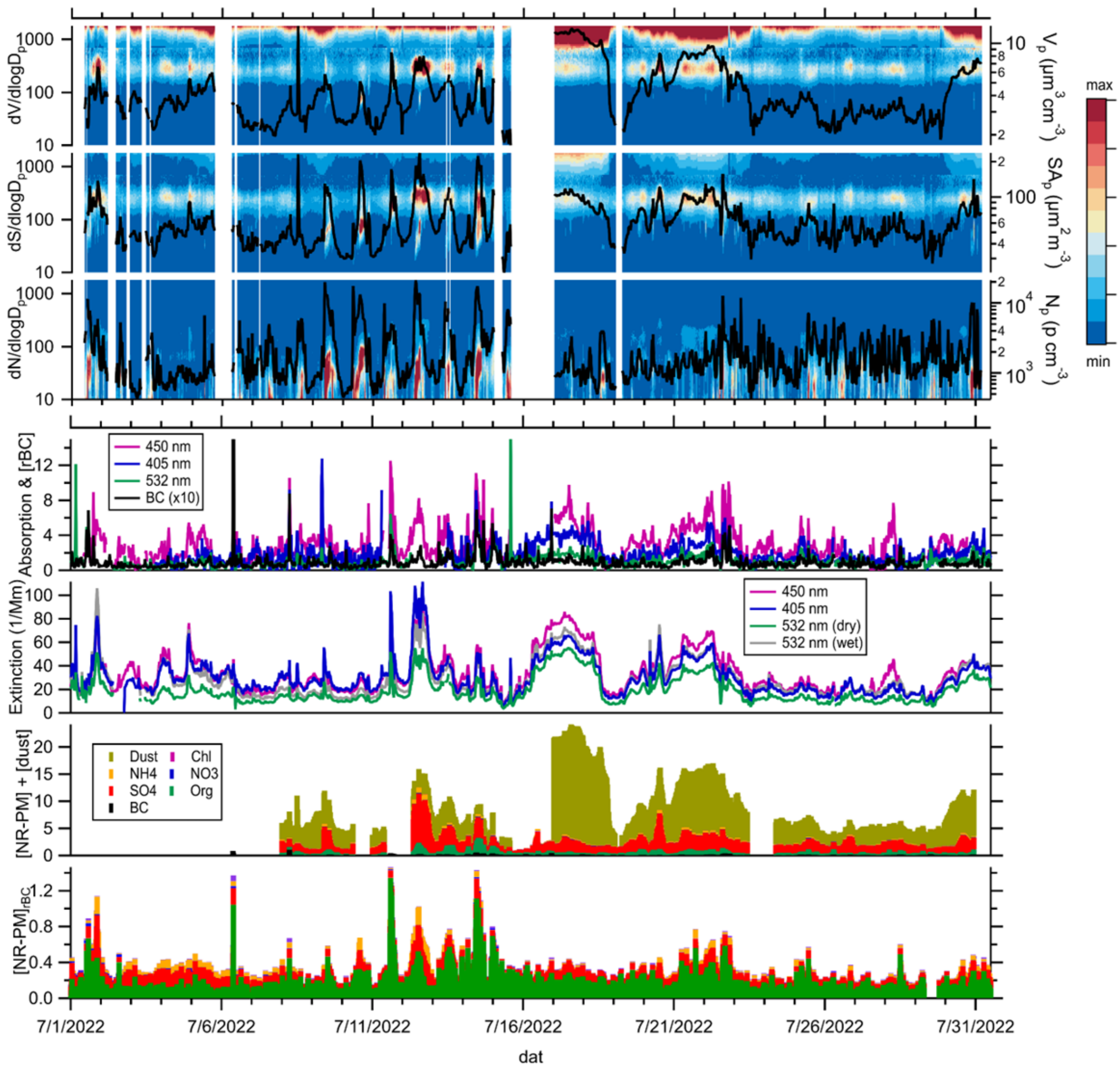

Figure 1. Summary of measurements from the TRACER-CAT-UCDavis campaign.

2.0 Results

Here we highlight some preliminary results developing from the TRACER-CAT-UCDavis measurements shown above. A commonly derived intensive parameter from measurements of particulate light absorption is the mass absorption coefficient (MAC), which is typically defined as absorption divided by the concentration of black carbon particles. Thus, the MAC is referenced to absorption by pure BC; observation of MAC values greater than the reference value indicate absorption owing to other species, such as brown carbon or dust, or enhanced absorption by BC owing to the presence of coatings on the BC. Previous analyses have often considered the relationship between the MAC and the ratio between the concentration of coating material and the BC concentration (the coating-to-core ratio).

In TRACER-CAT-UCDavis we found no clear relationship between the observed MAC and the coating-to-core ratio. Instead, we observe a clear relationship between the MAC and the ratio between the BC concentration and the estimated dust concentration (Figure 2). This illustrates that dust is an important contributor to the total absorption during the TRACER-CAT-UCDavis campaign. We will use these measurements to estimate the absorption properties of dust in future work.

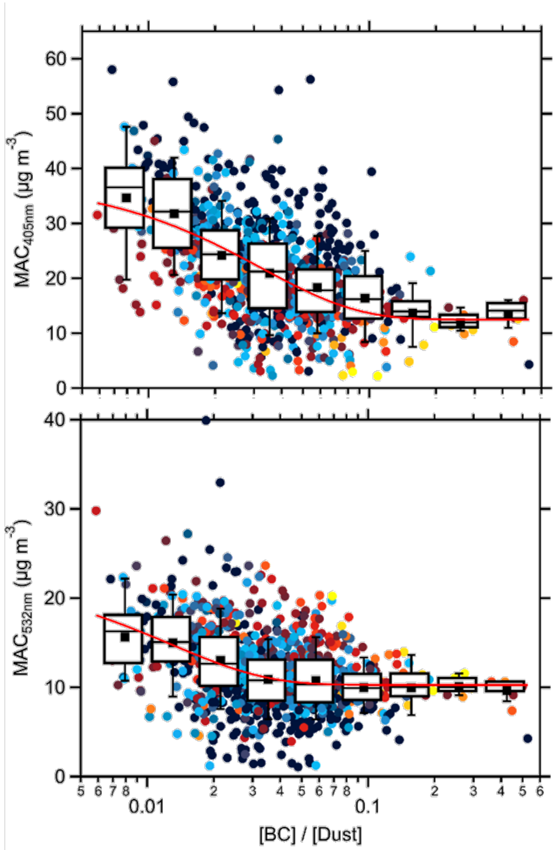

Figure 2. Relationship between the observed MAC at 405 nm (top) and 532 nm (bottom) versus the BC-to-dust ratio.

Considering the influence of water uptake on the optical properties (not shown), we find that the observed water-uptake effect for extinction (the ratio between extinction at elevated relative humidity [RH] to that of dried particles) varies with the ratio between non/less-hygroscopic components (i.e., dust, BC, and organic aerosol) and the more hygroscopic components (i.e., inorganic salts). However, the magnitude of the increase in extinction upon humidification depends on the extent of drying; particles dried to <40% RH exhibited a greater increase than those dried to only 50%, likely reflecting the importance of efflorescence to the measurements.

Looking at the influence of humidification on light absorption, we find, using the CAPS-SSA measurements from LANL, a relationship between the absorption change upon humidification and the inorganic salt-to-BC concentration ratio (Figure 3). We continue to explore relationships between the absorption humidification effect and aerosol properties.

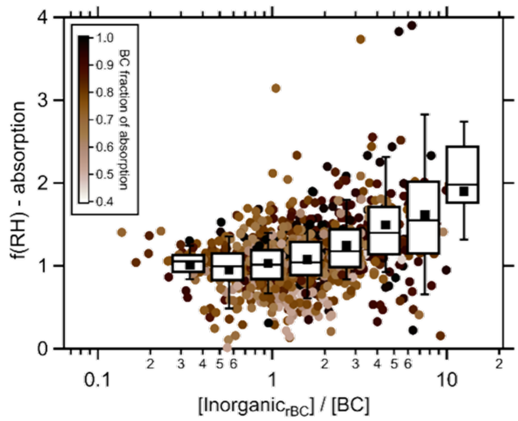

Figure 3. Relationship between the increase in absorption upon humidification and the ratio between inorganic salt concentrations and the concentration of BC.

A high-resolution soot particle aerosol mass spectrometer (SP-AMS) was used to selectively measure refractory black carbon (rBC) and its associated coating material both in the ensemble size-resolved mass spectral mode and the event trigger single-particle (ETSP) mode in Houston, Texas, during the TRACER field campaign in summer 2022. The average (± 1s) rBC concentration was 62 ± 116 ng m^{-3} and the BC coatings were primarily composed of organics (63%) and sulfate (26%). Positive matrix factorization (PMF) analysis of the ensemble mass spectra of BC-containing particles resolved four distinct types of soot aerosol, including an oxidized organic aerosol ($OOA_{BC,PMF}$) factor associated with processed primary organic aerosol, an inorganic sulfate factor ($SO_{4,BC,PMF}$), an oxidized rBC factor ($O\text{-}rBC_{PMF}$), and a mixed mineral dust/biomass burning aerosol factor with significant contribution from potassium ($K\text{-}BB_{BC,PMF}$). Additionally, the K-Means clustering analysis of the single-particle mass spectra identified eight different classes, including soot particles enriched of hydrocarbon-like organic aerosol ($HOA_{BC,ETSP}$), sulfate ($SO_{4,BC,ETSP}$), two types of rBC, oxygenated organic aerosol (OOA) ($OOA_{BC,ETSP}$), chloride ($Cl_{BC,ETSP}$), and nitrate ($NO_{3,BC,ETSP}$), respectively.

The single-particle measurements highlight substantial variations in BC coating thickness with coating to rBC mass ratios ranging from 0.1 to 100. The mixing state index (χ), which denotes the degree of homogeneity of the soot aerosol, varied from 4 to 94%, indicating intermediate states between internal and external mixture (Figure 4). These findings highlight the intricate nature of soot aerosol and underscore the necessity for additional research to fully comprehend the diverse range of soot particles present in different environments, which is crucial for accurate climate change assessment. We continue to work in our assessment of BC-containing particle properties and linking these to the observed optical properties.

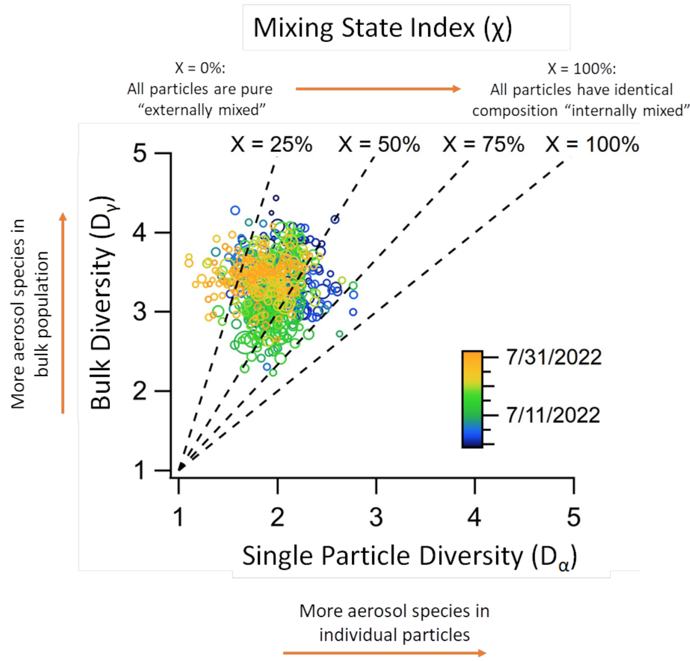

Figure 4. A look at the mixing state of BC-containing particles with respect to the bulk diversity and the single-particle diversity.

3.0 Publications and References

Results from TRACER-CAT-UCDavis have thus far been presented at the American Geophysical Union Fall Meeting in December 2022 and the July 2023 International Conference on Carbonaceous Particles in the Atmosphere, as follows.

Farley, R, JE Lee, L-H Rivellini, AKY Lee, R Dal Porto, K Gorkowski, ASM Shawon, K Benedict, AC Aiken, MK Dubey, C Cappa, and Q Zhang. 2023. "Diverse sources and atmospheric processing of soot aerosol in Houston: Insights from measurements of black carbon composition and mixing state." ICCPA. https://iccpa.lbl.gov/wp-content/uploads/sites/10/2023/07/13th-ICCPA-Program.pdf

Dal Porto, R, CD Cappa, RN Farley, JE Lee, K Gorkowski, K Benedict, Q Zhang, AC Aiken, and MK Dubey. 2022. "Impact of humidification on ambient aerosol optical properties; Field observations from TRACER-CAT in Houston, TX." AGU. https://agu.confex.com/agu/fm22/meetingapp.cgi/Paper/1079179

Farley, RN, S Collier, CD Cappa, TB Onasch, LR Williams, and Q Zhang. 2022. "Aqueous Phase Processing of Black Carbon Containing Aerosols in an Urban Environment." AGU. https://agu.confex.com/agu/fm22/meetingapp.cgi/Paper/1157154

Gorkowski, K, R Dal Porto, CD Cappa, RN Farley, Q Zhang, S Jordan, ASM Shawon, A Meyer, AC Aiken, JE Lee, K Benedict, and MK Dubey. 2022. "Laboratory and Ambient Comparison of Hygroscopicity and Optical Properties of Aerosols." AGU. https://agu.confex.com/agu/fm22/meetingapp.cgi/Paper/1155502

Lee, JE, K Gorkowski, K Benedict, A Meyer, AC Aiken, Q Zhang, RN Farley, R Dal Porto, CD Cappa, and MK Dubey. 2022. "Mixed Carbon Aerosol Properties in Houston, TX (TRACER-CAT): Role of chemistry in absorption, scattering, and humidification." AGU. https://agu.confex.com/agu/fm22/meetingapp.cgi/Paper/1195961

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