TRACER Filter Correction Field Campaign Report

RK Chakrabarty

March 2023
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March 2023

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### Acronyms and Abbreviations

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>AAE</td>
<td>Ångström absorption exponent</td>
</tr>
<tr>
<td>ACSM</td>
<td>aerosol chemical speciation monitor</td>
</tr>
<tr>
<td>AMF</td>
<td>ARM Mobile Facility</td>
</tr>
<tr>
<td>ANC</td>
<td>Ancillary</td>
</tr>
<tr>
<td>AOS</td>
<td>Aerosol Observing System</td>
</tr>
<tr>
<td>ARM</td>
<td>Atmospheric Radiation Measurement</td>
</tr>
<tr>
<td>ASR</td>
<td>Atmospheric System Research</td>
</tr>
<tr>
<td>BC</td>
<td>black carbon</td>
</tr>
<tr>
<td>BrC</td>
<td>brown carbon</td>
</tr>
<tr>
<td>CCSEM/EDX</td>
<td>computer-controlled scanning electron microscopy/energy dispersive x-ray spectroscopy</td>
</tr>
<tr>
<td>CI</td>
<td>chemical imaging</td>
</tr>
<tr>
<td>nano-DESI-HRMS</td>
<td>nanospray desorption electrospray ionization coupled to high-resolution mass spectrometry</td>
</tr>
<tr>
<td>ELVOC</td>
<td>extremely low volatile organic compound</td>
</tr>
<tr>
<td>EMSL</td>
<td>Environmental Molecular Sciences Laboratory</td>
</tr>
<tr>
<td>IOP</td>
<td>intensive operational period</td>
</tr>
<tr>
<td>IPN</td>
<td>integrated photoacoustic nephelometer</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>LVOCS</td>
<td>low volatile organic compound</td>
</tr>
<tr>
<td>MAC</td>
<td>mass absorption cross-section</td>
</tr>
<tr>
<td>NIR</td>
<td>near-infrared</td>
</tr>
<tr>
<td>PSAP</td>
<td>particle soot absorption photometer</td>
</tr>
<tr>
<td>QA</td>
<td>quality assurance</td>
</tr>
<tr>
<td>QC</td>
<td>quality control</td>
</tr>
<tr>
<td>rBC</td>
<td>refractory black carbon</td>
</tr>
<tr>
<td>SP2</td>
<td>single-particle soot photometer</td>
</tr>
<tr>
<td>SSA</td>
<td>single scattering albedo</td>
</tr>
<tr>
<td>SVOC</td>
<td>semi-volatile organic compound</td>
</tr>
<tr>
<td>TAP</td>
<td>tricolor absorption photometer</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscope</td>
</tr>
<tr>
<td>TRAC</td>
<td>time-resolved aerosol collector</td>
</tr>
<tr>
<td>TRACER</td>
<td>Tracking Aerosol Convection Interactions Experiment</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>Vis</td>
<td>visible spectrum</td>
</tr>
<tr>
<td>VOC</td>
<td>volatile organic compound</td>
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1  Major episodes based on dominant aerosol species and associated mean particle-phase optical properties during the TRACER IOP (July-August, 2022). ................................................................. 3
1.0 Summary

The principal investigator (PI; R Chakrabarty) and his group participated from July 1st to August 30th, 2022 for a total of 60 days at the main site (La Porte, Texas) of the U.S. Department of Energy (DOE) Atmospheric Radiation Measurement (ARM) user facility’s Tracking Aerosol Convection interactions ExpeRiment (TRACER) field campaign to characterize aerosol emissions at the site (Figure 1). As part of this Intensive Observation Period (IOP), co-located measurements of in situ and filter-based aerosol properties were conducted alongside the ARM First Mobile Facility (AMF1) to address the following research questions of importance to both ARM and DOE’s Atmospheric System Research (ASR) program:

- What are the error bounds and biases for ARM filter-based measurements of spectral (UV-Vis-IR) optical properties for aerosols during TRACER?
- What are the (if any) identifiable dependencies for the errors/biases on aerosol size, morphology, and composition?

The participation was in part also designed to complement the larger TRACER science goals to understand convective cloud life cycles and aerosol-convection interactions. This research focused on understanding the relationship between particle composition and optical properties, specifically, how aerosol mixing state and optical properties change within the humid urban industrial environment of LaPorte, Texas. The La Porte site is characterized as a coastal, industrial site because of its close proximity to the Gulf of Mexico and oil industries. Thus, the site was ideal for studying these interactions, given the highly photochemically active summer environment and the vast diversity of aerosol sources that could mix and be convectively processed.

The PI’s group deployed several instruments including custom-built, multi-wavelength, integrated photoacoustic-nephelometer (IPN) spectrometers[1,2] (real-time, contact-free, first-principle measurement of UV-Vis-IR aerosol absorption and scattering coefficients, single scattering albedo [SSA], and Ångström absorption exponent [AAE]), two filter-based tricolor absorption photometers (TAP; Brechtel Model 2901)[3], and filter-based samplers for conducting electron microscopy analysis and UV-Vis-IR spectrophotometry of solvent-extracted organic aerosols[4,5]. The IPNs and TAPs were operated at 1-sec time resolution throughout the 60-day sampling period. Single-particle aerosol sampling for chemical imaging (CI) was performed in collaboration with Professor Alexander Laskin’s group at Purdue University using their time-resolved aerosol collector (TRAC). The ARM Mobile Facility (AMF1) Aerosol Observing System (AOS) trailer conducted parallel measurements of filter-based aerosol absorption using the particle soot absorption photometer (PSAP; Radiance Research), chemical composition using the aerosol chemical speciation monitor (ACSM), and refractory black carbon (rBC) concentrations using the single-particle soot photometer (SP2).
Figure 1. (a) Schematic of instrument setup in field during the TRACER campaign at La Porte, Texas. The PM2.5 cyclone inlet was set at a height of 15 feet (4.6 meters) above the ground under a rain shield and covered with metal mesh to prevent blockage in the tube by water droplets and obstacles. The diffusion dryer removed excess water content from the sampled aerosol. (b) the PI’s instruments inside the ARM AMF1 Guest Trailer was strategically located adjacent to the ARM AMF1 AOS trailer during TRACER, and (c) pictures of the suite of PI’s optical characterization instruments inside the Guest Trailer.

Time-tagged sampling allowed us to compare and contrast optical particle properties and their sources against atmospheric transport patterns, diurnal cycles, and other factors. Our preliminary data analysis
suggests that the months of July and August 2022 at the La Porte site could be divided into periods comprised dominantly of dust, sodium, dust mixed with carbonaceous, sulfates, and carbonaceous, respectively (see Table 1).

### Table 1

<table>
<thead>
<tr>
<th>Episode</th>
<th>Dominant Aerosol Species</th>
<th>Mean SSA 405–1047 nm</th>
<th>Mean MAC [m²/g] 405 nm</th>
<th>Mean AAE 405/1047 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jul 22-27</td>
<td>Saharan Dust</td>
<td>0.92 ± 0.10</td>
<td>1.12</td>
<td>1.2</td>
</tr>
<tr>
<td>Aug 1-3</td>
<td>Sodium (Marine)</td>
<td>0.95 ± 0.10</td>
<td>1.05</td>
<td>1.4</td>
</tr>
<tr>
<td>Aug 9-11</td>
<td>Dust &amp; carbonaceous</td>
<td>0.85 ± 0.21</td>
<td>2.82</td>
<td>1.9</td>
</tr>
<tr>
<td>Aug 12-18</td>
<td>Sulfate mixed with Organics</td>
<td>0.79 ± 0.09</td>
<td>4.78</td>
<td>2.7</td>
</tr>
<tr>
<td>Jul 12-18: Aug 20-28</td>
<td>Carbonaceous</td>
<td>0.80 ± 0.08</td>
<td>3.98</td>
<td>2.5</td>
</tr>
</tbody>
</table>

All data products, after QA/QC, are being finalized for submission to the ARM Data Center as a PI Data Product and algorithm codes to the ARM repository on GitHub.

## 2.0 Results

Funded by a DOE Environmental Molecular Sciences Laboratory (EMSL) large-scale user grant, chemical imaging analysis of the particle elemental composition mixing state and morphology were performed using EMSL’s computer-controlled scanning electron microscopy/energy dispersed analysis of X-rays (CCSEM/EDX)[6]. We obtained detailed knowledge about the composition of non-volatile aerosol constituents at the particle scale using CCSEM/EDX analysis at a statistical level of approximately \( N = 2000 \) analyzed particles per sample (for example, see Figure 2). Samples were classified and selected for prioritized analysis based on episodes identified in Table 1. This was complemented by high-resolution transmission electron microscopy analysis to provide internal heterogeneity of particles at the nanometer scale. To probe the volatility of the particles, we used a transmission electron microscope (TEM) with a heating stage that goes up to 300 °C under vacuum conditions. Aerosol sampling was performed using the TRAC onboard ARM’s tethered balloon system (TBS; Figure 2). Offline analyses of ground and airborne particle samples are ongoing, and producing characterizations of particle composition, mixing state, size, and morphology from ground level to 1.5-km altitude for both the LaPorte and Ancillary (ANC) sites.
Figure 2. Representative size-resolved aerosol composition measured using EMSL’s CCSEM/EDX for samples corresponding to the (a) Organosulfate-dominated “ship emissions” period (August 12-18) and (b) Carbonaceous-dominated (July 12-18) “biomass burning” periods of the ground-based IOP during TRACER. (c) Size-resolved multi-modal microanalysis of samples collected by ARM’s TBS (Courtesy: Dr. Swarup China [collaborator]) during a flight day of TRACER. Particles are dominated by carbonaceous (smaller size) or sulfate (larger size) particles. High-altitude particles are dominated with organic carbon (500-950m Ascending).

2.1 Molecular Chemical Composition and Volatility Distribution

EMSL’s nanospray desorption electrospray ionization coupled to high-resolution mass spectrometry (nano-DESI-HRMS) was used to characterize the aerosol molecular composition of PM2.5 collected on Teflon filters collected during the IOP. The nano-DESI-HRMS[7] is an in situ technique and analysis was done directly from the aerosol filter, bypassing sample preparation steps and preserving sample integrity.
2.2 Unexpected Findings

Figure 3 summarizes findings of 10 days in August (9-19) during which the sampled air was dominated by chemical flares from surrounding industries. During this episode, we observed a previously unreported phenomenon: near-infrared (NIR) light absorption dominated by brown carbon (BrC) aerosols. This class of BrC are ‘optically dark’ and absorb strongly across the visible and NIR wavelengths. They are insoluble in water and common organic solvent, and their optical properties approach those of BC[8-10]. Observational evidence of this class of BrC in ambient environments and its significance with respect to atmospheric shortwave absorption remain elusive.

Figure 3. Aerosol light absorption and composition during chemical flaring episode (August 9-19 of the TRACER campaign). (A) Optically dark brown carbon (BrC) contributed to 40% of total absorption at 1047 nm (NIR wavelength). (B) High-resolution mass spectrometry of aerosol filter samples collected during this time frame suggest organosulfates (CHOS), a class of low-volatility organic compound, dominated the aerosol composition. (C) Electron microscopy image of a typical organosulfate aerosol abundant on filter samples corresponding to this period.

3.0 Publications and References

3.1 Presentations/Meetings

3.2 References


