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EPCAPE – Ultrafine Particle Properties Field Campaign Report

J Smith

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J Smith, University of California, Irvine

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Acronyms and Abbreviations

ARM	Atmospheric Radiation Measurement
EPCAPE	Eastern Pacific Cloud Aerosol Precipitation Experiment
EPCAPE-UPP	EPCAPE Ultrafine Particle Properties
HRMS	high-resolution mass spectrometry
HTDMA	hygroscopicity tandem differential mobility analyzer
MOUDI	micro-orifice uniform deposit impactor
nano-SMPS	nanometer scanning mobility particle sizer
PDF	probability density function
RH	relative humidity
TDCIMS	thermal desorption chemical ionization mass spectrometry
UHPLC	ultra-high-performance liquid chromatography
VTDMA	volatility tandem differential mobility analyzer

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1.0 Summary

The U.S. Department of Energy Atmospheric Radiation Measurement (ARM) user facility's Eastern Pacific Cloud Aerosol Precipitation Experiment – Ultrafine Particle Properties (EPCAPE-UPP) campaign combined a unique suite of instruments to probe the chemical and physical properties of ultrafine (sub-100-nm) atmospheric particles from 15 April to 15 June 2023 at the Mt. Soledad campaign site near San Diego, California. This project seeks to answer the questions:

- What is the composition of ultrafine marine aerosol particles?
- How does their composition relate to climatically important properties?

Our approach combined direct measurements of size-fractionated ultrafine particles together with measurements of size-resolved ultrafine particle hygroscopicity and volatility. While the focus of this project is on the formation and evolution of ultrafine particles in a marine setting, the measurements and insights gained will be directly applicable to the formation and evolution of larger particles, with implications for air quality and climate in this important coastal region.

During the campaign, we operated five instruments that measured:

- Size-resolved particle hygroscopicity. A hygroscopicity tandem differential mobility analyzer (HTDMA) measured the hygroscopic growth factor of particles with mobility diameters of 30, 60, and 90 nm. Size-selected particles were treated to 85% relative humidity (RH). The main data product was the probability density function (PDF) of the diameter growth factor at 85% RH.
- Size-resolved particle volatility: A volatility tandem differential mobility analyzer (VTDMA) measured the volatility of particles with mobility diameter of 30, 60, and 90 nm. Size-selected particles were treated to temperatures of 40, 80, and 160 °C. The main data product was the PDF of the diameter growth factor (<1) at each temperature.
- Size-resolved particle composition: We measured the molecular composition of ultrafine particles using thermal desorption chemical ionization mass spectrometry (TDCIMS). We analyzed two populations: size-selected particles with mobility diameter of 30 nm and "bulk ultrafine" particles, meaning a collection efficiency-weighted average of all particles smaller than 100 nm. The main data products for this measurement are time series of the ion abundance of each detected compound. This can be related to actual atmospheric particulate matter concentrations (e.g., ng/m^3) for specific compounds for which we have calibration data.
- Nanoparticle size distribution: We measured the nanoparticle size distribution using a nanometer scanning mobility particle sizer (nano-SMPS). This instrument measured the number-size distribution over the mobility diameter range of 3-105 nm every five minutes. This can be combined with other size-distribution measurements to obtain a "complete size distribution" over the entire size range that is relevant to atmospheric processes.
- Filter collection for offline chemical analysis: We collected daily filters of particles with diameters < 80 nm by sampling after the last impactor stage of a micro-orifice uniform deposit impactor (MOUDI). Samples were immediately stored in a freezer located onsite. Once these are transported to the laboratory, we cut filters in half and perform two extractions and analyses: extracting with water and performing ion chromatography and extracting with acetonitrile and performing ultra-high-performance liquid chromatography (UHPLC) + high-resolution mass spectrometry

(HRMS) to detect oxidized organics. For the latter analysis, we combined extracts over one week since sample sizes were so small.

Figure 1 shows the sampling strategy for TDCIMS, HTDMA, and VTDMA measurements. The TDCIMS repeated its cycle every two hours, whereas the HTDMA and VTDMA cycled once every three hours.

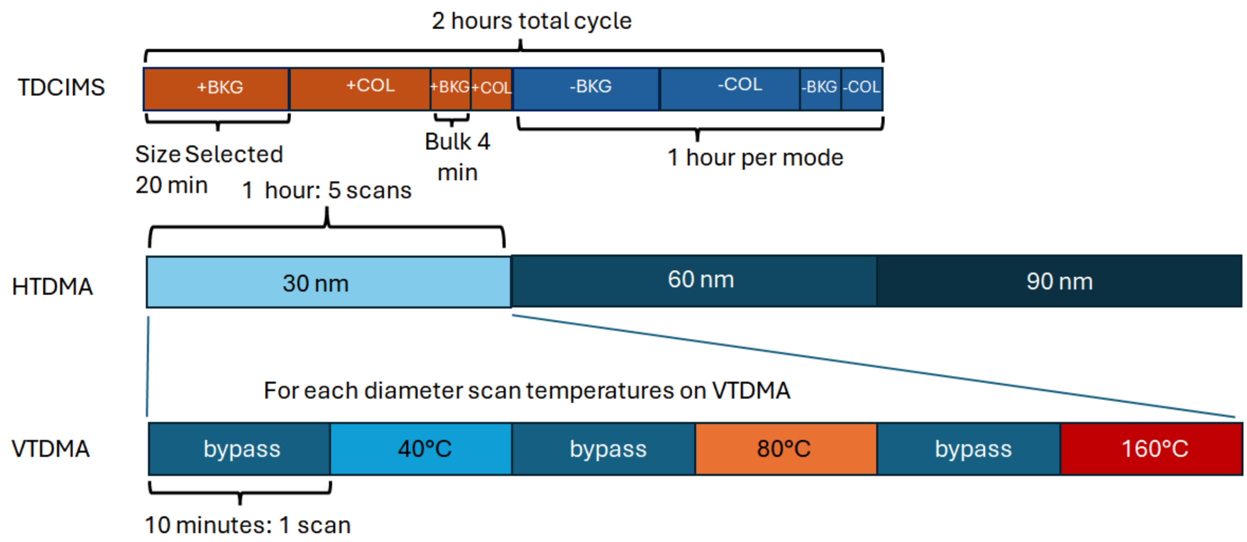

Figure 1. Sampling cycle for TDCIMS, HTDMA, and VTDMA. The TDCIMS cycled between positive and negative background/collection modes (+BKG/+COL and -BKG/-COL, respectively). A 20-min collection was performed for size-selected particles and a 4-min collection was performed for “bulk ultrafine” sampling, resulting in a 2-hr cycle time. The VTDMA cycle shown above was repeated for each particle diameter selected by the HTDMA, and both took 3 hours to complete a full cycle.

2.0 Results

We have completed the processing of the data from the HTDMA, VTDMA, and nano-SMPS. The nano-SMPS data were inverted using software developed by Washington State University and written in the Igor Pro programming language. Figure 2 shows the time series from those measurements (lower plot) and compares these to the overlap region of the regular SMPS-derived size distribution (top plot), the latter of which only extends down to 10 nm in diameter. Overall, these two measurements show excellent agreement. The process of creating a merged size distribution, which will incorporate measurements from the nano-SMPS and regular SMPS, is currently underway.

For the two TDMA data sets, this has involved performing a data inversion procedure using the TDMAInv program written by Martin Gysel and colleagues (Gysel et al. 2009). Figure 3 shows the resulting 85% RH growth factor PDFs for 30-, 60-, and 90-nm-diameter particles and Figure 4 shows the resulting growth factor PDFs for 90-nm-diameter particles.

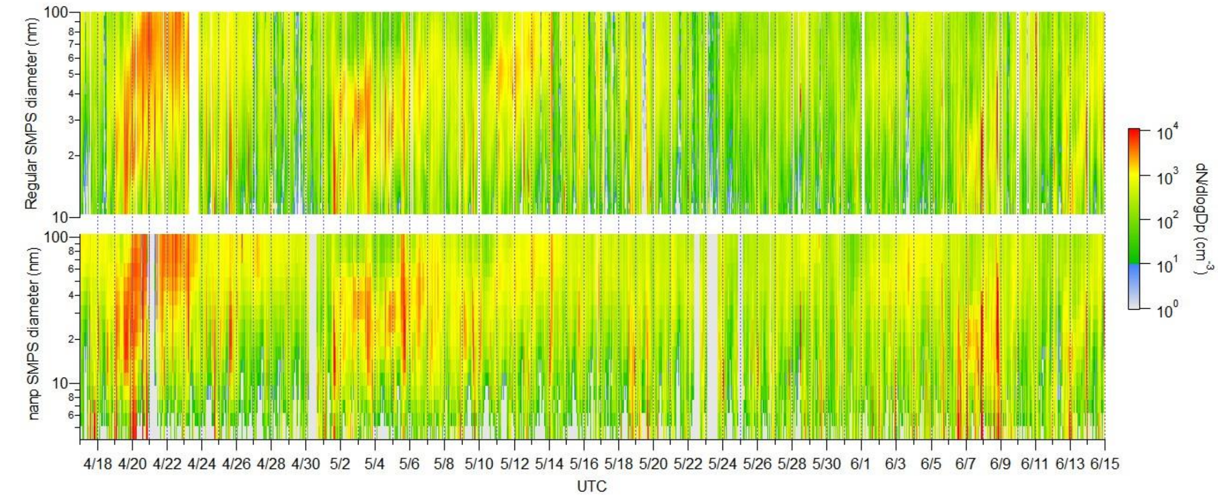

Figure 2. Time series of the number-size distributions of sub-100-nm-diameter particles from the (top) regular SMPS compared to (bottom) the nano-SMPS size distributions.

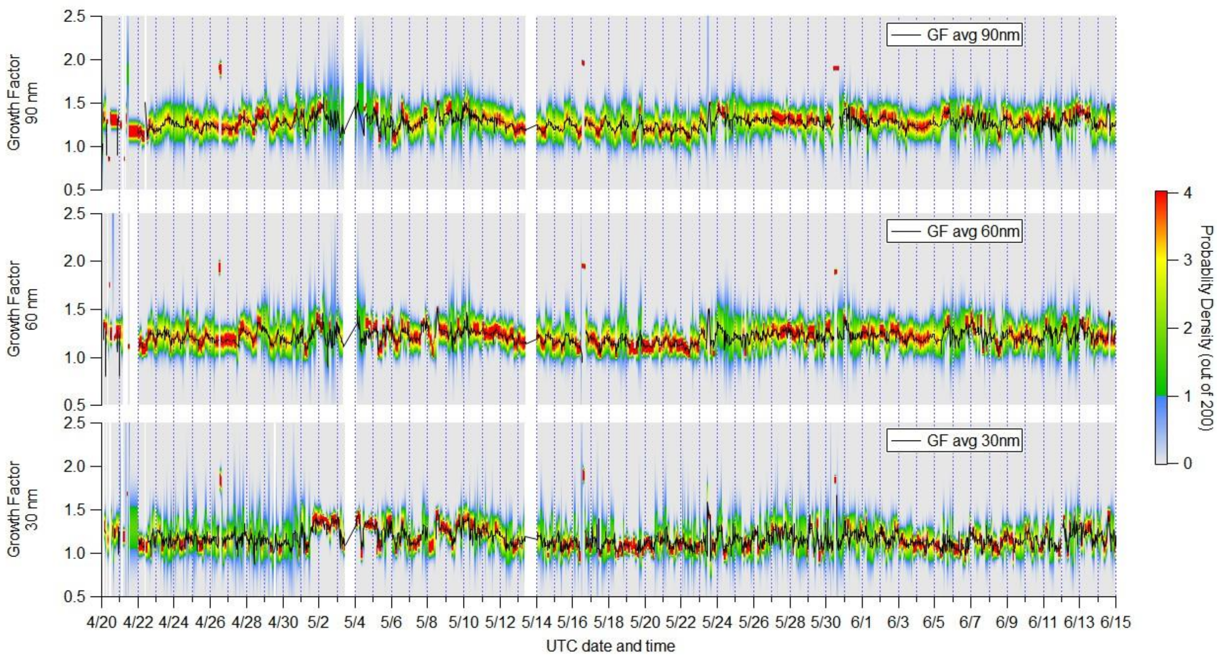

Figure 3. Time series of growth factor PDFs for 30-, 60-, and 90-nm-diameter particles during EPCAPE-UPP. Calibrations were performed with NaCl particles on 4/26, 5/16, and 5/30 and appear as brief events with PDFs of ~1.7.

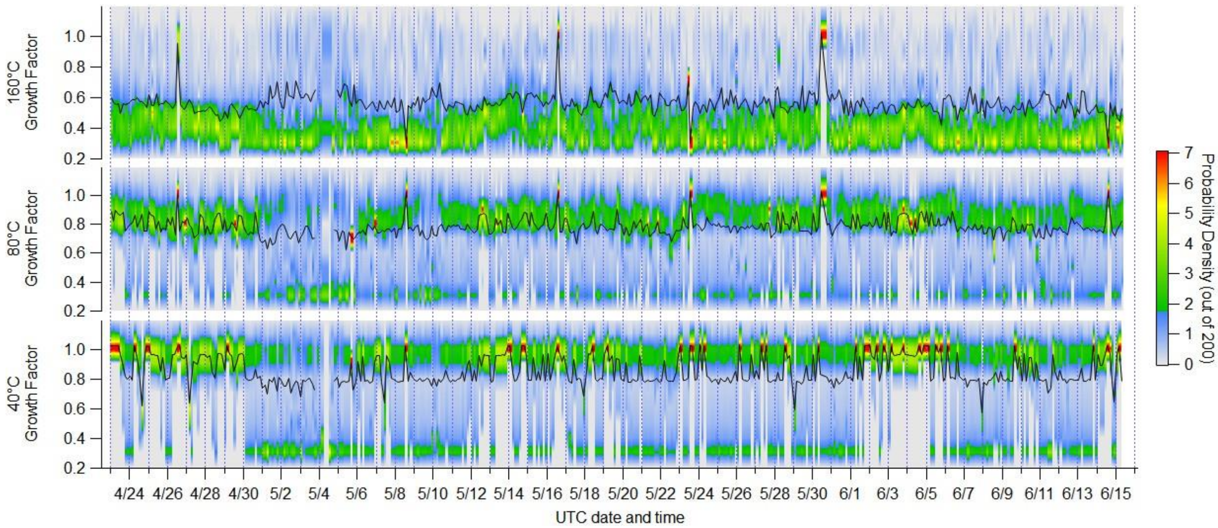

Figure 4. Time series of growth factor PDFs for 90-nm particles when treated at 40, 80, and 180 °C temperatures. Also plotted is volume-averaged growth factor (black traces). Calibrations were performed with NaCl particles on 4/26, 5/16, and 5/30 and appear as brief events with PDFs of 1.

Filter samples of sub-80-nm-diameter particles have been analyzed for ammonium and aminium ions. Analysis of filter samples by UHPLC-Orbitrap MS is currently underway and should be completed before June 2024.

TDCIMS analysis is currently underway and should be completed before the end of summer 2024.

3.0 Publications and References

3.1 Presentations

Kapp, A, and J Smith. 2023. "EPCAPE-UPP (Ultrafine Particle Properties)." Presented at EPCAPE Science Meeting, held remotely, July 6.

Kapp, A, N Nguyen, K Kramer, and J Smith. 2024. "Update on EPCAPE-Ultrafine Particle Properties." Presented at EPCAPE Science Meeting, held remotely, April 4.

3.2 References Cited

Gysel, M, GB McFiggans, and H Coe. 2009. "Inversion of tandem differential mobility analyser (TDMA) measurements." *Journal of Aerosol Science* 40(2): 134–151, https://doi.org/10.1016/j.jaerosci.2008.07.013

4.0 Lessons Learned

We want to acknowledge the hard work of the ARM site support staff for a smooth campaign. We especially express our appreciation to Daniel for going above and beyond to help us out.

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