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DOE/SC-ARM-25-002

Metal Particles at EPCAPE Field Campaign Report

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July 2025

ARM

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How to cite this document:

Li, H. 2025. Metal Particles at EPCAPE Field Campaign Report. U.S. Department of Energy, Atmospheric Radiation Measurement user facility, Richland, Washington. DOE/SC-ARM-25-002.

Work supported by the U.S. Department of Energy,
Office of Science, Office of Biological and Environmental Research

Acronyms and Abbreviations

ARM	Atmospheric Radiation Measurement
ASR	Atmospheric System Research
CCN	cloud condensation nuclei
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
EPCAPE	Eastern Pacific Cloud Aerosol Precipitation Experiment
ICP-MS	inductively coupled plasma mass spectrometry
IN	ice nuclei
LASSO	least absolute shrinkage and selection operator
LOD	limit of detection
RfCs	inhalation reference concentrations
TARTA	Toxic-metal Aerosol Real-Time Analyzer
TBS	tethered balloon systems
XRF	X-ray fluorescence

Contents

Figures

Tables

1.0 Summary

This project aimed to evaluate the performance of Toxic-metal Aerosol Real-Time Analyzer (TARTA) in quantifying toxic metal particle concentrations in real time during the U.S.. Department of Energy (DOE) Eastern Pacific Cloud Aerosol Precipitation Experiment (EPCAPE). This field campaign was conducted from October 20 to November 30, 2023, at Mount Soledad in San Diego, California. The campaign was part of the DOE Atmospheric Radiation Measurement (ARM) user facility, specifically designed to improve understanding of marine stratocumulus clouds and their interactions with atmospheric aerosols.

Aerosols, including metal-containing particles, influence cloud formation, microphysical properties, and precipitation processes. Understanding the behavior and characteristics of metals in the atmosphere is essential for studying aerosol chemistry and assessing their potential effects on the climate. Some trace metals dissolved from dust particles into cloud droplets (such as Fe and Mg) have the ability to catalyze the formation of sulfates in the aqueous phase (Bianco et al. 2017). Cloud condensation nuclei (CCN) that activate gain sulfate mass on their traverse through clouds and become easier to activate on subsequent passes (Alexander et al. 2009). In addition, metals can also influence the formation of secondary aerosols by affecting aerosol acidity (Deguillaume et al. 2004, Hallquist et al. 2009). The acidity of aerosols is a key determinant of their thermodynamics and chemical kinetics in atmospheric chemistry, so understanding the role of metals in this process is crucial.

The metal constituent of particles is rarely measured at DOE ARM user sites. Traditional atmospheric metal measurement techniques (i.e., X-ray fluorescence [XRF] and inductively coupled plasma mass spectrometry [ICP-MS]) are not feasible for routine practice due to their time-consuming nature. Real-time metal detection technologies are relatively new and expensive (e.g., Cooper Environmental's Xact-625 and Horiba's PX-375 analyzers), making them difficult to deploy on a large scale. However, the advantages of inexpensive, high temporal resolution, compactness, low maintenance requirement, and power efficiency of TARTA (Toxic-metal Aerosol Real-Time Analyzer, developed by Dr. Tony Wexler and Dr. Li, funded by California Air Resources Board) make it a promising tool to deploy on a large scale across DOE ARM facilities. TARTA provides simultaneous monitoring of more than 15 metal compounds in ambient air (e.g., Cr, Mn, Zn, Ni, Co, Pb, Cd, Hg, V, and Cu). TARTA measurements can also be useful for source identification and linking the metal fingerprints to CCN and ice nuclei (IN) characteristics in collaboration with other ARM/Atmospheric System Research (ASR) instrumentation.

This study aligns with the ARM Decadal Vision T1, which prioritizes comprehensive field measurements for advancing atmospheric science, by deploying a guest instrument at an ARM observatory. The integration of TARTA's data set with cloud microphysical measurements provides insights into how metal aerosols influence cloud droplet formation and cloud longevity. Additionally, the ability of TARTA to detect toxic metals in real time is particularly valuable in assessing local air quality impacts, including pollution episodes from marine shipping emissions, urban sources, and potential wildfire plumes transported into the study region.

During the campaign, several notable events were recorded and lessons were learned:

- Many metals were below detection limits with a sampling time of 25 minutes and a flow rate of 16.7 L/min, with only Fe, Zn, and Mg consistently detected. A larger pump and longer sampling duration could improve sensitivity for trace metals.

- The study measured mean concentrations of 196 ± 168 ng/m³ (Mg), 8.6 ± 2.2 ng/m³ (Zn), and 52 ± 12 ng/m³ (Fe).
- Routine site visits were essential for cleaning and replacing corroded electrodes, ensuring consistent data collection.

2.0 Results

2.1 Analysis of TARTA Measurements

During this study, a TARTA was deployed at the sampling platform established by the research team from Los Alamos National Laboratory as part of the "EPCAPE-PT-LANL campaign." TARTA sampled air through the primary inlet, which was connected to a URG cyclone to remove particles larger than 2.5 µm (Figure 1). During the experiments, air samples were drawn through tubing at a flow rate of 16.7 L/min and impacted onto the ground electrode. The sampling duration was 25 minutes, followed by 10 high-voltage sparks to detect and remove deposited particles (Li et al. 2021, 2024). An ASEQ LR1 spectrometer was used to collect atomic emission spectra. Prior to field deployment, the instrument was calibrated following the quantification methods described in Li et al. (2022), using aqueous solutions of standard metal particles in a controlled laboratory environment.

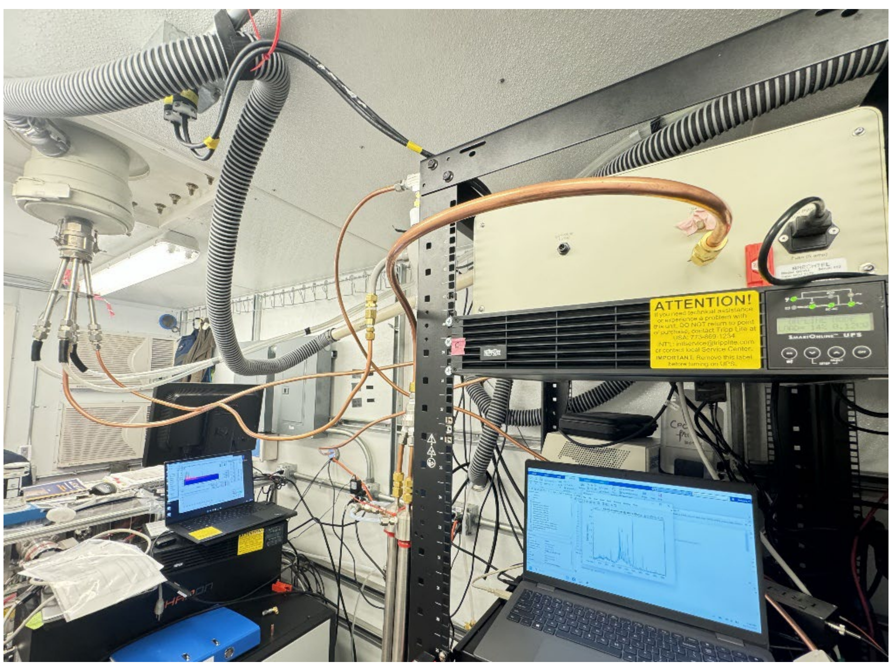

Figure 1. The inlet of TARTA is connected to the main inlet of the Los Alamos National Laboratory's sampling platform. TARTA is positioned behind the laptop on the right side of the screen. The spectra displayed on the laptop represent TARTA's measurements.

Unattended sampling was conducted from October 20 to November 30, 2023. During this period, site visits were made on November 3 and November 28 for routine maintenance and data collection. These visits included replacing corroded TARTA electrodes and cleaning the sampling tubing to ensure measurement accuracy. Additionally, an unplanned visit on November 8, 2023, was necessary due to a malfunction detected through remote monitoring. Despite attempts at both remote and onsite repairs, the issue persisted. It was determined that the failure was likely caused by the humid environment, which led to electrode corrosion and condensation-induced damage to the high-voltage electrical components. After necessary repairs, the device was redeployed on November 16, 2023.

Figure 2 shows the average of all spectra obtained by TARTA from the study. At the beginning of each sampling day, we performed "background" experiments to verify that no contamination was present on the electrodes. Spectra from the "background" experiments contain emission lines of W (the major material of electrodes), as well as Na, Mg, and Ca (alkali and alkaline earth metals). The detection of Na, Mg, and Ca is not surprising, given their abundance in the air and low ionization energies. During normal operations, we detected the emission lines of other metals in the ambient air (such as Fe, Zn, Cu, and Cr), likely originating from anthropogenic sources. The deposition of particles from the ambient air onto the ground electrode resulted in greater spectral intensities of Na, Mg, and Ca than the "background" experiments.

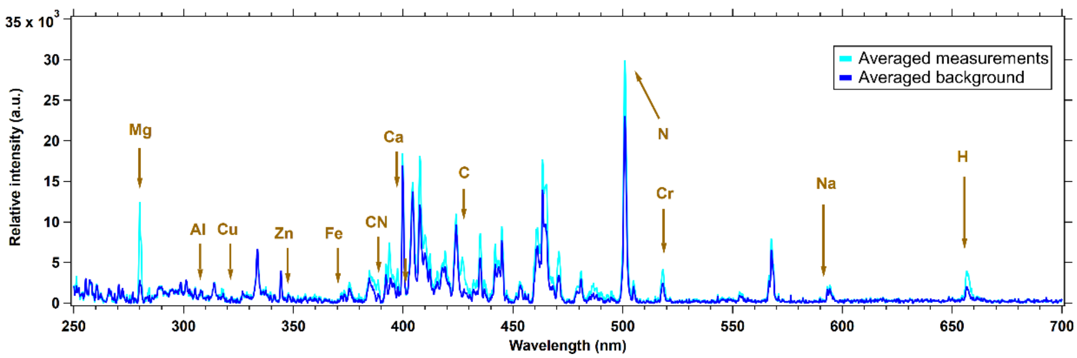

Figure 2. TARTA spectra showing the detection of multiple elements at the sampling site. Each spectrum represents the average of all spectra collected under the same environmental conditions.

We then conducted a quantitative analysis of the acquired spectra to determine the concentrations of particulate metals in the field samples. Concentrations were derived using a multivariate calibration model based on least absolute shrinkage and selection operator (LASSO) regression (Li et al. 2022). This machine learning-based approach used spectral intensities across multiple wavelengths to improve elemental concentration estimates while automatically correcting plasma-induced continuous radiation and reducing prediction uncertainties through spectral feature selection. Although TARTA is capable of detecting over 15 elements, many metals were found to have concentrations below the 60-minute-based limit of detection (LOD = 1σ/S, Table 1). To ensure data reliability, only elements detected above the LOD threshold more than 60% of the time were retained for analysis, resulting in a time series of Fe, Zn, and Mg concentrations (Figure 3). During the sampling period, the average concentrations for these elements were 196 ± 168 ng m^{-3} (Mg), 8.6 ± 2.2 ng m^{-3} (Zn), and 52 ± 12 ng m^{-3} (Fe).

Table 1. Detection limits of TARTA at a sampling duration of 25 minutes and flow rate of 16.7 L min^{-1}.

Element	TARTA 1.0 (3.3σ)	TARTA 1.0 (2σ)	TARTA 1.0 (1σ)	Commercial instruments		inhalation reference concentrations (RfCs) - EPA
				Xact 625 (1σ)	PX-375 (2σ)	
Al	57	35	17	170	-	-
Be	46	28	14	-	-	50
Cd	59	36	18	4.4	10.8	-
Co	27	17	8	0.2	-	6
Cr	27	17	8	0.2	4.2	100 for Cr(VI)
Cu	28	17	9	0.1	1.8	-
Fe	48	29	14	0.3	-	-
Hg	67	40	20	0.2	2.4	300
Mg	57	35	17	-	-	-
Mn	44	27	13	0.3	1.8	50
Ni	30	18	9	0.2	-	20
Pb	55	33	17	0.2	1.5	150
V	17	10	5	0.2	-	100
Zn	30	18	7	0.1	0.9	-

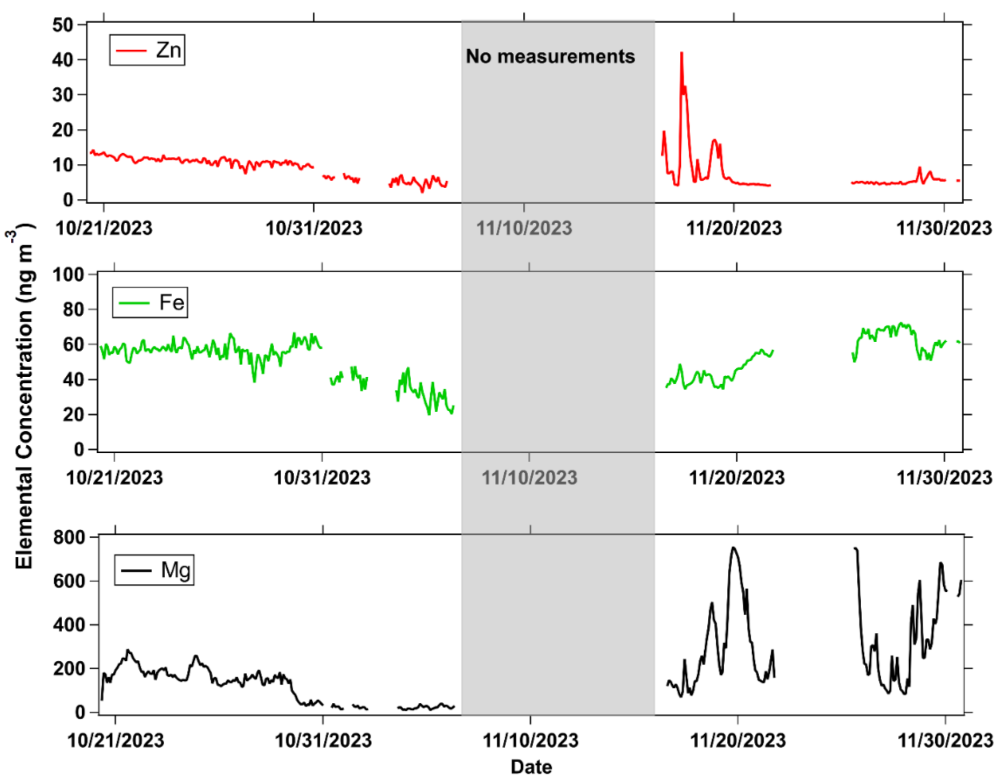

Figure 3. Time series of elemental concentrations detected by TARTA, with data shown only for elements that exceeded detection limits more than 60% of the time. The shaded areas indicate periods when TARTA was undergoing troubleshooting, during which no measurements were recorded.

2.2 Further Research Opportunities

The successful deployment of TARTA in this small-scale field campaign underscores its potential as a long-term toxic metal screening tool at DOE ARM user sites and in tethered balloon systems (TBS) for vertical profiling of aerosol properties. The findings will contribute to refining climate models, informing regulatory policies, and supporting environmental health research.

Despite these successes, several challenges were identified that require further investigation. The high humidity at the sampling site contributed to electrode corrosion and condensation-related malfunctions, highlighting the need for a pre-sampling air dryer to prevent moisture-related damage. Additionally, the presence of salt in the environment poses a risk of accelerated electrode degradation, which may necessitate the frequent change of electrodes. Another critical limitation is the detection of metals at low concentrations—while TARTA's sensitivity is sufficient for many elements, detecting trace levels of metals in clean air environments may require a larger pump to increase the sampled air volume or longer sampling duration (e.g., two hours) to enhance detection capabilities. Addressing these challenges will improve the robustness and reliability of TARTA for future field deployments, particularly in coastal or high-humidity regions.

2.3 Collaborations

Kyle Joseph Gorkowski, Allison C Aiken, Manvendra Dubey – Los Alamos National Laboratory

3.0 Publications and References

Alexander, B, RJ Park, DJ Jacob, and S Gong. 2009. "Transition metal‐catalyzed oxidation of atmospheric sulfur: Global implications for the sulfur budget." *Journal of Geophysical Research – Atmospheres* 114(D2), https://doi.org/10.1029/2008JD010486

Bianco, A, M Vaïtilingom, M Bridoux, N Chaumerliac, J-M Pichon, J-L Piro, and L Deguillaume. 2017. "Trace Metals in Cloud Water Sampled at the Puy De Dôme Station." *Atmosphere* 8(11): 225, https://doi.org/10.3390/atmos8110225

Deguillaume, L, M Leriche, A Monod, and N Chaumerliac. 2004. "The role of transition metal ions on HOx radicals in clouds: a numerical evaluation of its impact on multiphase chemistry." *Atmospheric Chemistry and Physics* 4(1): 95–110, https://doi.org/10.5194/acp-4-95-2004

Hallquist, M, JC Wenger,U Baltensperger, Y Rudich, D Simpson, M Claeys, J Dommen, NM Donahue, C George, AH Goldstein, JF Hamilton, H Herrmann, T Hoffmann, Y Iinuma, M Jang, ME Jenkin, JL Jimenez, A Kiendler-Scharr, W Maenhaut, and J Wildt. 2009. "The formation, properties and impact of secondary organic aerosol: current and emerging issues." *Atmospheric Chemistry and Physics* 9(14): 5155–5236, https://doi.org/10.5194/acp-9-5155-2009

Li, H, L Mazzei, CD Wallis, SA Davari, and AS Wexler. 2021. "The performance of an inexpensive spark-induced breakdown spectroscopy instrument for near real-time analysis of toxic metal particles." *Atmospheric Environment* 118666, https://doi.org/10.1016/j.atmosenv.2021.118666

Li, H, L Mazzei, CD Wallis, and AS Wexler. 2022. "Improving quantitative analysis of spark-induced breakdown spectroscopy: Multivariate calibration of metal particles using machine learning." *Journal of Aerosol Science* 159: 105874, https://doi.org/10.1016/j.jaerosci.2021.105874

Li, H, L Mazzei, CD Wallis, and AS Wexler. 2024. "Detection of Atmospheric Particulate Metals in Near Real-Time: Tunnel, Urban, and Rural Environments." *Aerosol and Air Quality Research* 24(10): 240117, https://doi.org/10.4209/aaqr.240117

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