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Chemical Imaging of Atmospheric Organic Particles in the Eastern North Atlantic Field Campaign Report

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Chemical Imaging of Atmospheric Organic Particles in the Eastern North Atlantic Field Campaign Report

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Acronyms and Abbreviations

ACE-ENA	Aerosol and Cloud Experiments in Eastern North Atlantic
ACSM	aerosol chemical speciation monitor
ARM	Atmospheric Radiation Measurement
CCN	cloud condensation nuclei
CCSEM-EDX	computer-controlled scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy
ENA	Eastern North Atlantic
HYSPLIT	Hybrid Single-Particle Lagrangian Integrated Trajectory
IOP	intensive operational period
MOUDI	micro-orifice uniform deposit impactor
NOAA	National Oceanic and Atmospheric Administration
OVF	organic volume fraction
PSAP	particle soot absorption photometer
STXM-NEXAFS	scanning transmission X-ray microscopy coupled with near-edge X-ray absorption spectroscopy

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1.0 Summary

The ability to reliably predict future climate is hindered, in major part, by an insufficient understanding of atmospheric aerosol-radiation interactions and aerosol-cloud interactions. (IPCC 2013; Bony and Dufresne 2005) Factors affecting marine stratocumulus clouds are particularly important given that they are the dominant cloud type globally. Global climate models frequently misrepresent ubiquitous marine stratocumulus clouds for a variety of reasons, including a lack of understanding of how these cloud properties change with aerosol cloud condensation nuclei (CCN) concentration and composition.(Nam et al. 2012) Limited information is available regarding the sources of CCN in remote regions where marine stratocumulus clouds dominate. Measurements in these marine locations, which are periodically influenced by anthropogenic emissions, provide additional opportunity to study the impact of humans on cloud characteristics. The U.S. Department of Energy Atmospheric Radiation Measurement (ARM) user facility Eastern North Atlantic (ENA) observatory on Graciosa Island in the Azores is well suited to study these problems. The ENA site is exposed to a multitude of air masses as well as a variety of cloud regimes, as documented by passive and active satellite cloud retrieval. (Tselioudis et al. 2013) Thus, placing detailed aerosol and cloud measurements at the ARM ENA site may help gain a better understanding of the CCN budget and cloud interactions in remote environments.

To provide detailed information on aerosol morphology, composition, and microphysical properties, size- segregated sampling was carried out at the ENA observatory on Graciosa Island during two intensive operating periods (IOPs). IOP1 occurred from June 17 to July 18, 2017, and IOP2 occurred from January 9 to February 21, 2018. Daytime and nighttime sampling were carried out separately to investigate any diurnal differences of aerosol composition due to differing meteorology. For both IOPs, 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). (Laskin et al. 2006; Kilcoyne et al. 2003; Moffet et al. 2010) 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. (Pham et al. 2017; Ault et al. 2013; Hopkins et al. 2008) Ice nucleation characterization using optical microscopy with a cold stage has also provided critical information about water uptake. (Knopf and Lopez 2009) Sampling coincided with the Aerosol and Cloud Experiments in Eastern North Atlantic (ACE-ENA) field campaign so that detailed single-particle measurements could be obtained in the context of the larger field campaign. Sampling at the ENA 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 ENA observatory were used to select samples for detailed microscopic characterization.

For both IOPs, air masses from the Arctic, North America, and recirculating airflow around the eastern north Atlantic high prevailed during sampling. Sea spray aerosol was the dominant aerosol type observed

during all conditions. Sulfate-rich particles were also observed during a significant number of sampling events. These sulfate particles are thought to be due either to dimethyl sulfide oxidation or transport of pollution from North America. Evidence for primary biological particles was found based on the molecular nature of carbon and morphology. Primary biological particles were not frequently observed, however. Variations in the mixing of sea salt, 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 preliminary data analysis that has been carried out to date.

2.0 Results

Peripheral measurements located at the ENA observatory were used to guide selection of samples for detailed microscopic analysis. Figure 1 shows time series of aerosol absorption and chemical composition as well as time periods over which aerosol samples were selected for microscopic analysis. In general, aerosol absorption was low (<1 Mm^{-1}) during the measurement campaign, suggesting that these collections are representative of pristine conditions. The real-time aerosol chemical speciation monitor indicated that the main non-refractory chemical aerosol species was sulfate (sea salt and dust are refractory, and therefore not measured with this technique). Potential sources for sulfate include oxidation of dimethyl sulfide and long-range transport of fossil fuel combustion emissions from North America. Three time periods were selected for detailed STXM analysis. These periods contained aerosols that showed differences in chemical composition. The time period from June 26 to June 29 contained elevated sulfate with occasional influences from organics and absorbing aerosol. The time period from July 7 to July 11 contained relatively few absorbing aerosols, slightly elevated organics, and relatively low sulfate concentrations. The time period from July 14 to July 16 showed low levels of organics and absorbing aerosol.

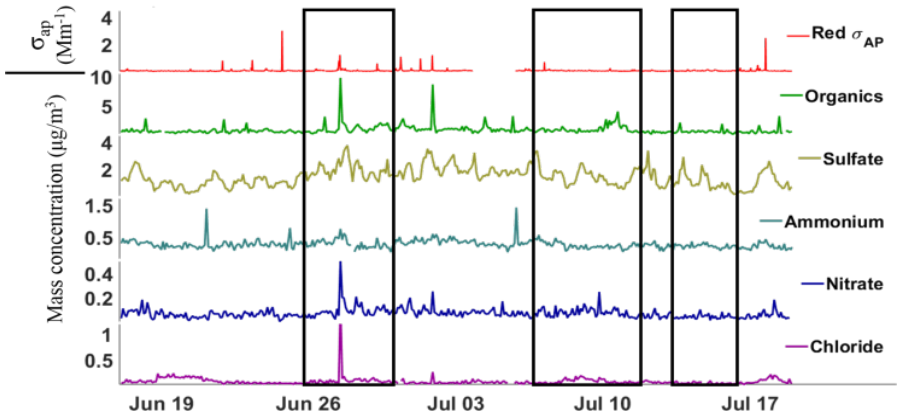

Figure 1. Time series showing absorption coefficient (σAP) from particle soot absorption photometer (PSAP) measurements and the mass concentration of aerosol phase organics, sulfate, ammonium, nitrate, and chloride from the aerosol chemical speciation monitor (ACSM) during IOP1.

Based on the time periods shown in Figure 1, selected IOP 1 samples were analyzed using STXM-NEXAFS. Figure 2 shows representative fields of view for three time periods having distinctly different air mass origins as indicted using the National Oceanic and Atmospheric Administration (NOAA) Hybrid

Single-Particle Lagrangian Integrated Trajectory (HYSPLIT). In general, when air masses originate from the North American continent, more soot particles are observed, suggesting an anthropogenic influence. (China et al. 2017) During the times when air masses were associated with recirculating flow over the ocean, much less soot was observed, suggesting that these particles were more representative of clean marine conditions. Particles sampled during clean marine conditions were observed to be primarily mixtures between inorganic and organic material. For these mixed organic/inorganic particles, two main particle types exist: sea spray aerosol, and aged sulfate particles (Zheng et al. 2018; Sanchez et al. 2018). Figure 2 shows that during the June 27 to June 29 time period, particles were internal mixtures of sea spray (indicated by cubic inorganic phases) and soot (indicated with red). The sources of soot in this environment may be due to long-range transport, ship emissions, or local sources on the island of Graciosa. The time period from July 7 to July 11 indicates the presence of more organic-rich phases mixed with inorganic phases (primarily sulfate). The time period associated with recirculating flow was associated with inorganic dominant particles composed of sea salt and sulfate (typically externally mixed).

Historically, single-particle analysis of the mixing state of carbonaceous aerosol has been carried out in a semi-quantitative fashion. Recent work has developed the quantitative capabilities of STXM-NEXAFS and scanning electron microscopy to quantitatively characterize the elemental composition of particles containing inorganic-organic mixtures. (Fraund et al. 2017, 2019) Following from this work, preliminary results showing the determination of individual particle organic volume fractions (OVFs) are shown in Figure 2. The OVF distribution for the particles sampled during the three events defined in Figure 1 all show that while the majority of the particles are dominated by inorganic material, a significant fraction of the particle volume is still composed of organic material. These results suggest that it is important to consider the organic fraction of particles when considering CCN efficiency, because organic material can make up a significant fraction of the particle composition.

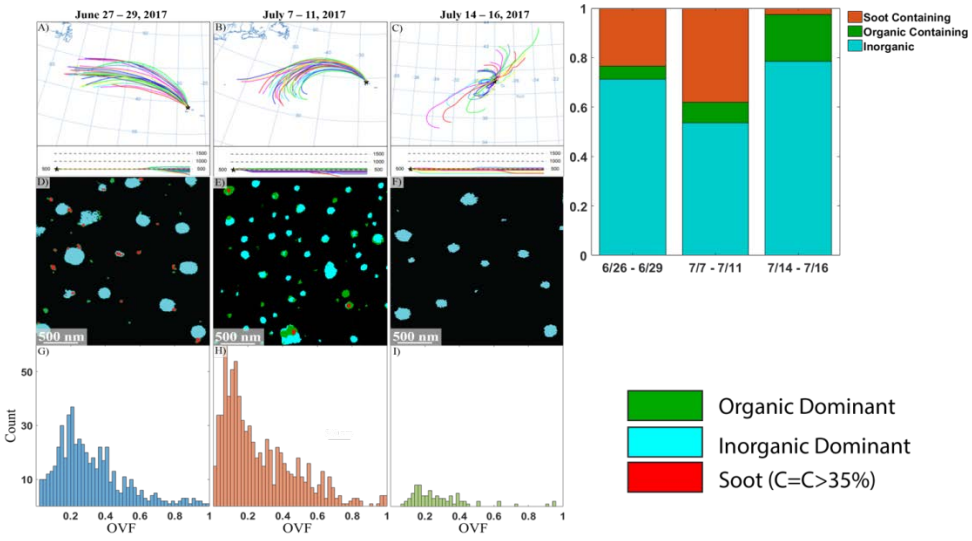

Figure 2. A-C) Back trajectories; D-F) spatially resolved composition maps derived from STXM, samples collected on MOUDI Stage 8 (0.18 – 0.32 µm); G-H) organic volume fraction (OVF) histograms derived from STXM data. (Right) Bar plot showing the relative fractions of different particle types identified with STXM.

Given the significance of the carbonaceous fraction for particles sampled in marine locations, it is important to determine the potential source of the organic material through detailed chemical characterization. Efforts to better characterize the elemental and molecular composition is demonstrated in Figure 3. Figures 3a and 3b show example C 1s NEXAFS spectra from individual particles demonstrating the range of carbon molecular composition. Sea-spray particles are typically characterized by resolved peaks for COOH and CO_3 functional groups, and little total carbon (determined as the difference between optical density at 320 and 278 eV). The spectrum shown in Figure 3a labeled "Stage 6" is from a suspected primary biological particle; this particle has as strong C-H feature in the NEXAFS spectrum as well as a large amount of total carbon. Similar features have been observed in controlled wave flume experiments. (Pham et al. 2017) Figure 3c is an example of a calcium map that shows the distribution of Ca among individual particles. Together with morphology and NEXAFS spectroscopy, calcium mapping is being used as a way to distinguish between particles that originate from seawater (and contain calcium) and those from other source.

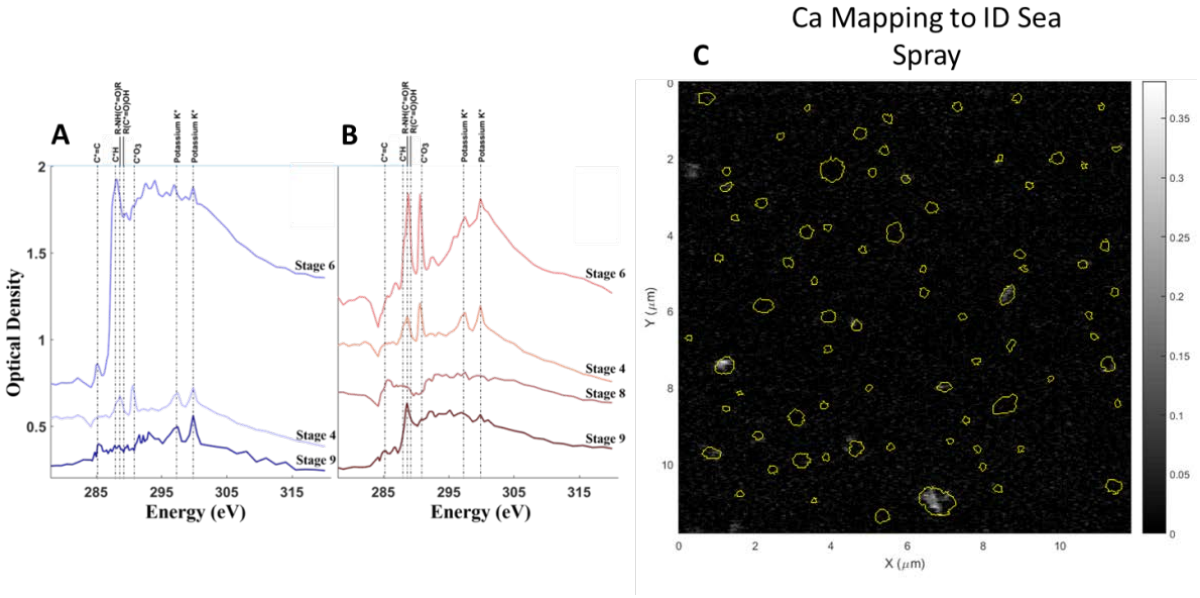

Figure 3. Spatially resolved composition maps for two different sampling periods during ACE-ENA IOP2.

Future work on samples from this field campaign is focused on analysis of IOP2 samples (recently started in Fall, 2018 using STXM-NEXAFS) and determination of ice nucleation efficiency (work by DA Knopf not shown here). Analysis of these samples will allow for a comparison between winter and early summer periods in the eastern north Atlantic. Higher wind speeds during the wintertime are expected to increase the relative fraction of sea spray aerosol relative to other sources. Also, differences in ocean productivity between winter and early summer may result in changes in the organic fraction of the particles.

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