

Aerosol Growth in the Eastern North Atlantic (AGENA) Field Campaign Report

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April 2023



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Acronyms and Abbreviations

ACE-ENA	Aerosol and Clouds Experiments in the Eastern North Atlantic
AGENA	Aerosol Growth in the Eastern North Atlantic
ARM	Atmospheric Radiation Measurement
ASR	Atmospheric System Research
BVOC	biogenic volatile organic compounds
CCN	cloud condensation nuclei
CN	total particle number concentration
CPC	condensation particle counter
DMS	dimethyl sulfide
DOE	U.S. Department of Energy
ENA	Eastern North Atlantic
FCPC	fine condensation particle counter
NPF	new particle formation
oVOC	oxygenated volatile organic compound
ppb	parts per billion
ppt	parts per trillion
SMPS	scanning mobility particle sizer
TVOC	total volatile organic compound concentration
UHSAS	ultra-high-sensitivity aerosol spectrometer
VOC	volatile organic compound

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1.0 Project Summary

The overarching scientific objective of the U.S. Department of Energy (DOE) Atmospheric Radiation Measurement (ARM) user facility's Aerosol Growth in the Eastern North Atlantic (AGENA) field campaign is to determine the source of condensable material that contributes to the growth of Aitken-mode aerosol particles to cloud condensation nuclei (CCN) in the remote marine boundary layer at the ARM Eastern North Atlantic (ENA) atmospheric observatory on Graciosa Island, Azores.



Figure 1. Logo for the AGENA field campaign.

This project has three specific objectives:

1. Determine the atmospheric abundance and distribution of key marine reactive gases and their oxidation intermediates at the ENA ARM site. These measurements will be used to examine how the distribution of dimethyl sulfide (DMS) and volatile organic compound (VOC) oxidation products, in a composition and volatility framework, vary as air is sourced from different sectors.
2. Characterize particle number-size distributions and the chemical composition of particles growing to CCN sizes and determine particle growth rates in the context of measurements of condensable material. These observations will be used to explore how particle composition responds to the abundance and speciation of marine reactive gases and the volatility distribution of oxidized organics.
3. Connect measurements of CCN chemical composition and precursor gas concentrations with determinations of the composition of condensable mass inferred from hygroscopicity measurements made at the ENA site.

To address these specific objectives, we successfully carried out the AGENA project during summer, 2022 (1 June-15 July). This included the deployment of a pair of high-resolution time-of-flight mass spectrometers for measurement of VOC, oxygenated volatile organic compounds (oVOC), and particle composition to the ENA ARM observatory on Graciosa Island. The measurement period is commensurate with the largest number of aerosol growth events, and peak ocean biological activity. In addition, we supplemented existing measurements of particle number distributions (made using the onsite ultra-high-sensitivity aerosol spectrometer [UHSAS]) with a principal investigator-owned scanning mobility particle sizer (SMPS). The instrumentation was operated from the ground with varying levels of temporal

information (e.g., high-time-resolution mass spectrometers will operate as fast as 1Hz, while integrated filter measurements may require as much as one-hour averaging times).

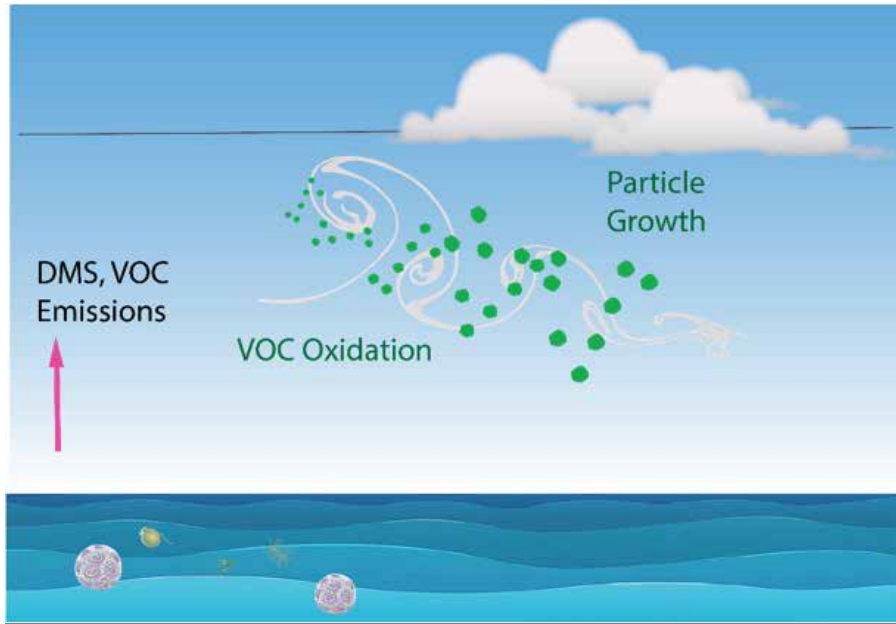


Figure 2. The emission and oxidation of reactive gases of marine origin contribute to the formation and growth of CCN in marine environments.

The successful completion of the proposed work will provide needed insight on the chemical drivers for particle growth over marine environments that can be directly compared with existing laboratory and model representations of marine boundary-layer chemistry. The work directly addresses the DOE Atmospheric System Research (ASR) program’s commitment to using in situ instrumentation at ARM field sites to advance process-level understanding of aerosol-cloud interactions in remote regions. Specifically, our project addresses aerosol processes including the formation and growth of aerosol particles in marine environments. The work also builds on prior DOE commitments to studying marine aerosol in this region (e.g., Aerosol and Clouds Experiments in the Eastern North Atlantic [ACE-ENA]) and ongoing laboratory and modeling initiatives of DMS-sulfate chemistry.

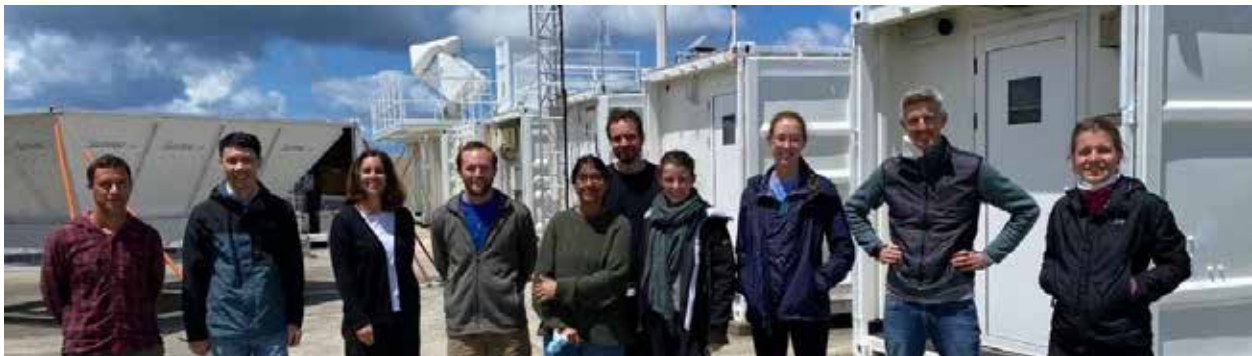


Figure 3. AGENA scientists at the ARM ENA observatory during Summer, 2022.

2.0 Preliminary Results

2.1 Scientific Objective 1

Six weeks of continuous, high-time-resolution measurements of VOCs were made by the real-time Vocus (RT-Vocus) instrument at ENA during AGENA. Our results broadly show that both the VOC concentration and molecular composition at the site are strongly dependent on local meteorology, such as onshore versus offshore winds, local pollution, and back trajectories of sampled air masses. This suggests that the VOC profile carries unique and specific information on the sources of different molecules at ENA.

A four-day VOC time series for a representative period of clean marine air, characterized by onshore winds, minimal local pollution, and back trajectories not passing over land in the previous five days is shown in Figure 4. The total VOC concentration (TVOC) during this period of clean marine air is low, roughly two parts per billion (ppb), and exhibits some diurnal dependence with higher VOC concentrations during the days and lower concentrations during the nights. Additionally, we find that the majority of the TVOC (>85%) during clean marine air periods at the site is carried by roughly 10 molecules. These molecules can be grouped by their class, with well-known marine biogenic VOC like DMS, methanethiol, and monoterpenes carrying a small fraction of this TVOC, shown in green in Figure 4. The largest fraction of TVOC is carried by oxygenated molecules commonly measured in marine air, such as methanol (MeOH), ethanol, and acetone, shown in blue in Figure 4. These molecules can have a direct biogenic or photochemical marine source and can also be oxidation products of other marine VOC. Lastly, a small fraction of TVOC represents other calibrated molecules, such as aromatics, nitrogen-containing molecules, and larger aldehydes or ketones. Given that the majority of common VOC and expected marine biogenic volatile organic compounds (BVOC) have been calibrated and quantified, this analysis suggests that the remaining fraction of TVOC that has been quantified with an average calibration factor may represent more novel molecules in very low concentration.

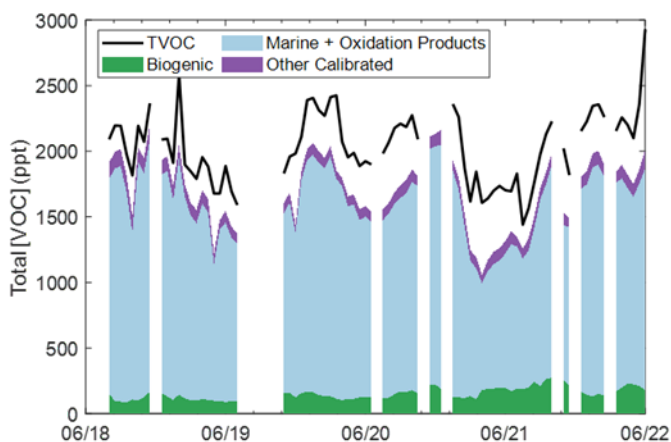


Figure 4. Time series showing total VOC measured by the RT-Vocus at AGENA during a representative period of clean marine air.

The full time series for a selection of molecules in each of the categories in Figure 4 is shown in Figure 5. DMS was on average 75 parts per trillion (ppt; Figure 5a) and showed considerable temporal variability

during the study, with minimums close to 0 and maximums exceeding 300 ppt during some periods. This variability reflects changes in variables related to oceanic biological productivity, such as chlorophyll-a and sea surface temperature, and the trajectory of the air mass during the few days prior to arrival at the site. MeOH measurements (Figure 5b) also varied widely, with the 20th and 80th percentiles being 390 and 870 ppt, respectively, but showed no correlation with DMS, highlighting the different sources of these two molecules. Other calibrated molecules like that of C₉H₁₈O (Figure 5c), likely representing nonanal or an isomer, were much lower than both DMS and MeOH throughout the study, with maximums near 10 ppt. Despite low concentrations, measurements of molecules like nonanal provide unique opportunities to determine the extent to which non-biogenic pathways, such as seawater ozonolysis, can be a source of volatile organic compounds at remote ocean sites. Finally, an important grouping of the other calibrated molecules in Figure 2 are aromatics, such as the C8 aromatics shown in Figure 4d. While not of a marine source, these measurements are equally valuable to the study, as they provide extremely sensitive, molecular-specific information on local pollution sources that are needed to ensure data quality when using this data set to analyze marine atmospheric chemistry.

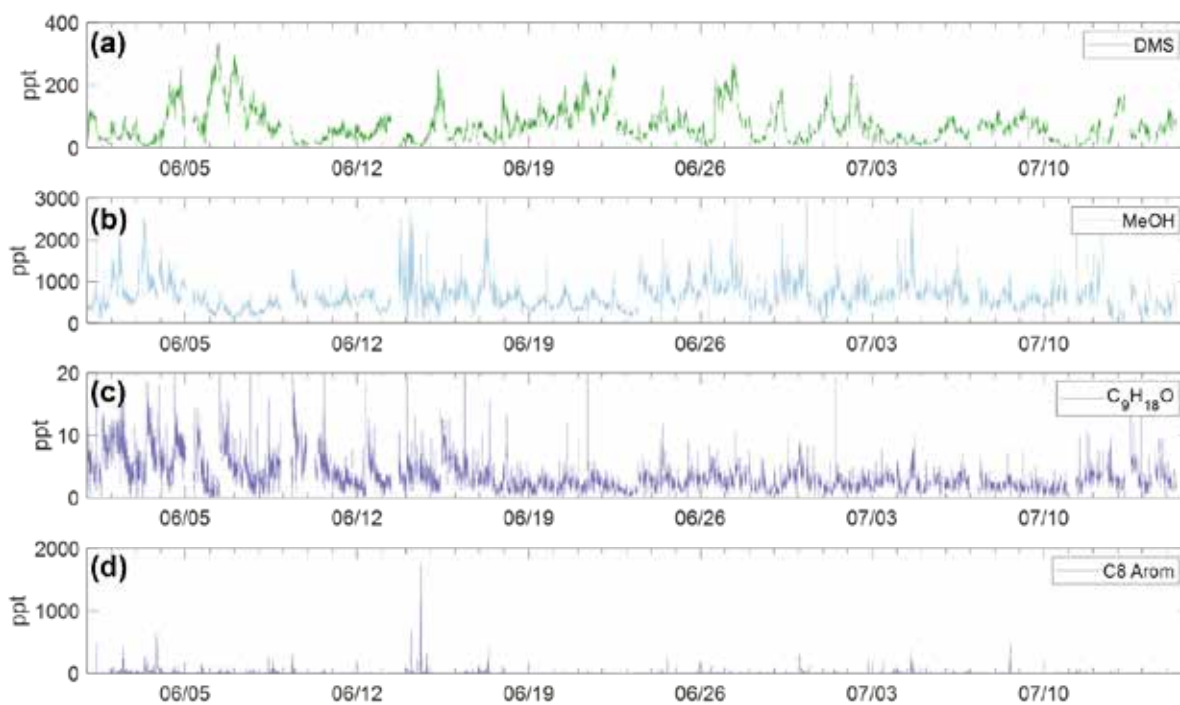


Figure 5. Full campaign time series for (a) dimethyl sulfide (DMS), (b) Methanethiol (MeOH), (c), Nonanal (C₉H₁₈O), and (d) C8 aromatics.

Stemming from the time series data in Figure 5, this data set also demonstrates that the breakdown of molecules contributing to clean marine TVOC in distinct parts of the study is different. An example of this is shown in the two pie figures in Figure 6, contrasting two air masses with different trajectories sampled six weeks apart. Despite roughly the same concentration of TVOC, the compositions are unique. The air mass in Figure 4a has a large contribution of oxygenated VOC, with acetone and methanol in a 2:1 ratio, and a large contribution of monoterpenes. While oxygenated VOC still make up a majority of the TVOC in Figure 4b, the ratio of acetone, MeOH, ethanol, propanol, and aldehydes are different, and monoterpenes result in <1% of TVOC. These types of findings are expected to be a result of different oceanic and meteorological properties along the air mass back trajectory, and provide opportunities to test

which, if any, oceanic variables can explain these differences. Understanding how the TVOC composition varies by time and trajectory based on oceanic conditions also has important atmospheric chemistry implications as the different molecules in Figure 6 have bimolecular reaction rate constants with O_3 and OH that span orders of magnitude.

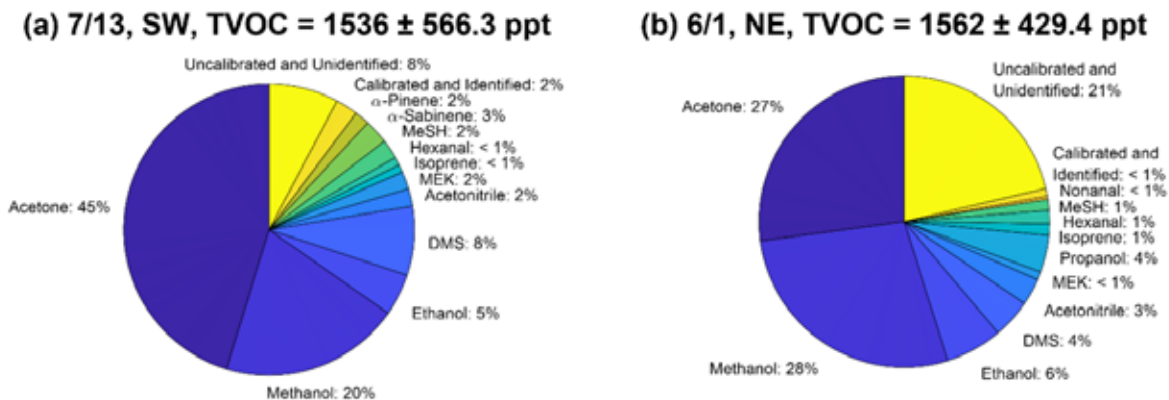


Figure 6. VOC composition for an air mass arriving at ENA (a) on July 13th from the southwest and (b) on June 1st from the northeast.

2.2 Scientific Objectives 2 and 3

An SMPS (TSI Inc.) consisting of a long differential mobility analyzer (DMA, model 3081) and a condensation particle counter (CPC, model 3750) was deployed at the ENA site throughout the AGENA campaign. This instrument measured the size-resolved concentrations of dry aerosols in the mobility size range of 10.6–461 nm with a time resolution of four minutes. Particle loss during transport in the inlet system was corrected. Therefore, the evolution of dry particle size distribution was obtained, which provided basic information for exploring aerosol growth over the ENA.

Overall, the total particle number concentration (CN) measured by SMPS showed good agreement with that measured by a fine condensation particle counter (FCPC, > 10 nm, model 3772, TSI Inc.), indicating good instrumental performance during the campaign. The aerosol observations were frequently influenced by local anthropogenic pollution from the sources such as the airport and the town of Santa Cruz. The polluted plumes will lead to extremely high concentrations of small particles, which can obscure the natural variations. To minimize the interference of local pollution on subsequent data analysis, a machine learning model was developed to identify and remove the polluted periods based on the different temporal variation patterns of CN and CO concentrations between polluted and clean regimes. The size distributions after the data clean are shown in Figure 7a.

During the AGENA campaign, the aerosol particles mostly showed a bimodal number size distribution containing an Aitken mode and an accumulation mode (Figure 7b), which is typically observed in the remote marine boundary layer. The mode diameters of median size distribution were 51 nm (Aitken) and 168 nm (accumulation), respectively. As shown in Figure 7c, the number concentrations of these two modes were at a similar level, with median concentrations of 153 and 152 cm^{-3} and mean concentrations of 177 and 153 cm^{-3} for Aitken and accumulation modes, respectively. However, high-concentration (> 300 cm^{-3}) occurrences were more frequent for the Aitken mode than for the accumulation mode.

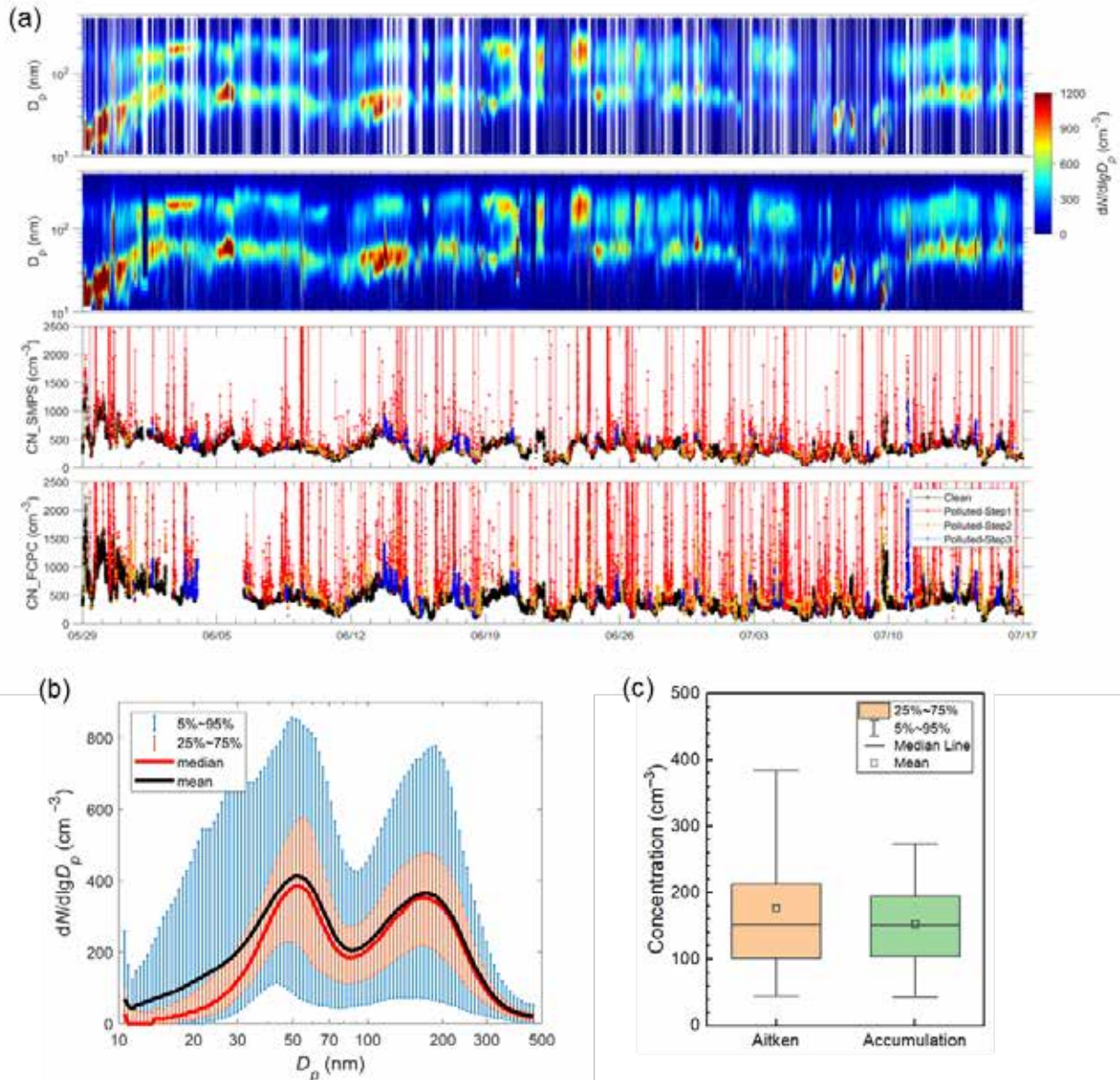


Figure 7. (a) The SMPS-derived aerosol size distributions after and before the data clean and the time series of total particle number concentrations measured by SMPS (CN_SMPS) and FCPC (CN_FCPC) with different colors representing the clean and polluted data identified by different data screening steps. (b) The overall particle size distribution. (c) Box plots for the number concentrations of Aitken- and accumulation-mode aerosol particles.

A total of 11 Aitken-mode growth events were identified based on the evolution of aerosol size distribution. The event-averaged growth rates were between 0.6 and 2.1 nm hr^{-1} . Different condensed species, such as sulfate and organics, may have contributed to these growth events, and they can be identified by combining the gaseous and particulate chemical composition measurements and the changes in aerosol hygroscopicity. Additionally, two new particle formation (NPF) events were observed on 29 May and 9 July. The first NPF was followed by a strong condensational growth, which allowed the newly formed particles to grow to $\sim 67 \text{ nm}$, thus significantly increasing the concentration of CCN.

3.0 Publications and References

Bertram, T, DB Kilgour, C Jernigan, O Garmash, S Aggarwal, J Zinke, X Gong, S Zhou, J Zhang, B Cunha, T Silva, C Mohr, JA Thornton, ME Salter, P Zieger, and J Wang. 2022. “Aerosol Growth in the Eastern North Atlantic”. Presented at American Geophysical Union Fall Meeting. Chicago, Illinois.

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