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Influence of Organic-Containing Aerosols on Marine Boundary Layer Processes

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LONG-TERM GOALS

The long-term goal is to develop sufficient understanding of the properties and behavior of marine aerosols to reliably predict their dynamics in atmospheric models.

OBJECTIVES

This research aims to improve understanding of the composition (inorganic, organic, biological), and properties, including water vapor uptake and CCN behavior, of marine aerosols.

APPROACH

Through the integration of laboratory experiments, Twin Otter aircraft missions, and physiochemical modeling, this research is addressing the following questions:

1. How do the magnitudes and timescales of aerosol growth in the presence of sub-saturated water vapor vary with particle phase morphology? What physiochemical properties of the particle phase most influence this variability?
2. What role does particle phase morphology play in the activation and growth of cloud condensation nuclei?
3. Is there evidence of complex particle-phase behavior in the marine atmosphere? How do particle phases and growth factors vary with aerosol composition and ambient conditions such as relative humidity and temperature?
4. How well do current state-of-the-art thermodynamic and kinetic models capture the complex relationship between particle phase and water vapor uptake?
5. What is the abundance of and the role played by biological material in the marine aerosol?

WORK COMPLETED

1. Comprehensive laboratory study of the hygroscopicity and CCN behavior of inorganic-organic aerosols.

2. Navy Twin Otter field experiment, Biological Ocean Atmospheric Study (BOAS), July 2015, eastern Pacific Ocean off Monterey, CA.

RESULTS

1. Hygroscopic and CCN Behavior of Model Inorganic-Organic Aerosols

The hygroscopic and CCN behavior of inorganic aerosols is well established. Marine aerosols contain both inorganic and organic material. The hygroscopic and CCN behavior of mixed inorganic-organic aerosols is not well established. Moreover, particles that comprise both inorganic and organic substances have been shown to behave like highly viscous material, for which water uptake and CCN behavior are not well established. We began this investigation with well-defined aerosol chemical systems.

The water-uptake behavior of ideal aerosol systems comprised of polyethylene glycol (PEG) and mixtures of PEG and ammonium sulfate (AS) was measured under subsaturated (RH = 30 – 90%) and supersaturated (supersturation = 0.6%) RH conditions. PEG was chosen as a model compound for these experiments because previous studies of PEG-AS particles (using optical and Raman microscopy) have shown that such particles undergo phase separations in which a PEG shell fully engulfs an AS core at RH < 90%. Suppression of the reactive uptake of N_2O_5 and isoprene-derived epoxydiols by PEG-ammonium bisulfate particles observed at low to moderate RH values was attributed to the presence of a viscous PEG shell. Further, the availability of PEG with a range of polymer chain lengths/molecular weights allows for the comparison of water-uptake behavior across aerosol systems with differing viscosities, but nearly identical chemical properties. Herein, experiments were conducted with systems containing PEG with average molecular weights of from 200, 1,000, and 10,000 g/mol, corresponding to a range in viscosity of 0.004 – 4.5 Pa s under dry conditions.

While evidence suggests that viscous aerosol components can suppress water uptake at RH < 90%, under supersaturated conditions, an increase in CCN activity with increasing PEG molecular weight was observed. This can be attributed to an increase in the efficiency of PEG as a surfactant with increasing molecular weight. This effect is most pronounced for PEG-AS mixtures and, in fact, a modest increase in CCN activity is observed for the PEG10,000-AS mixture as compared to pure AS, as evidenced by a 4% reduction in critical activation diameter (Figure 1). Experimental results are being compared with calculations of hygroscopic growth at thermodynamic equilibrium using the state-of-the-art Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients model. The extent to which kinetic limitations may have contributed to experimentally observed water uptake is being further explored with the Kinetic Multi-Layer Model of Gas-Particle Interactions. Experimental results suggest that the competing effects of organic-component viscosity and surface-tension depression may lead to RH-dependent differences in hygroscopicity for oligomers and other surface-active compounds present in marine atmospheric aerosols for which PEG serves as a surrogate. *Thus, despite high viscosities under dry conditions, the presence of these compounds in marine atmospheres may contribute to enhancements in CCN activity and may alter cloud properties.*

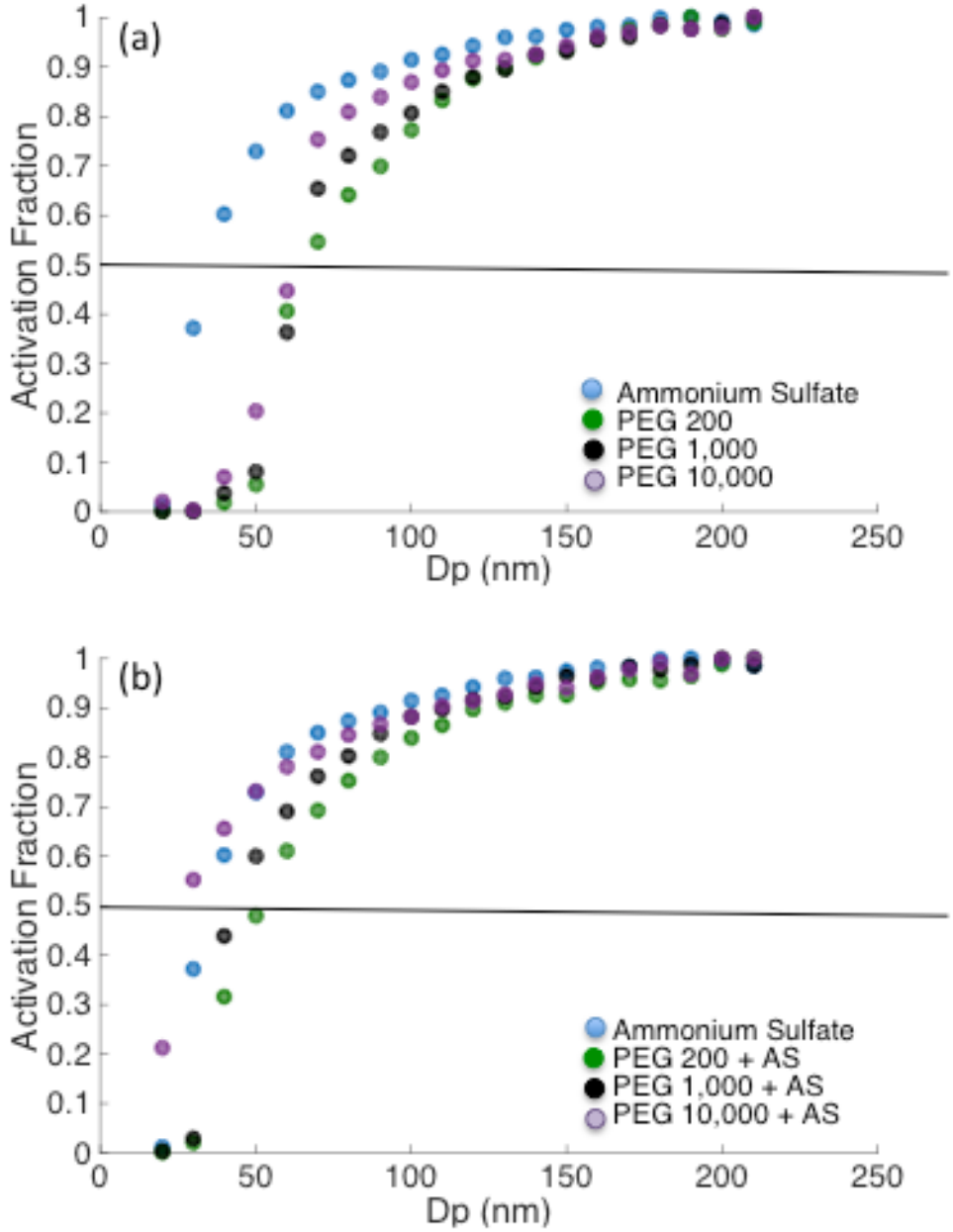

Figure 1. CCN activation fraction as a function of particle diameter (D_p) for (a) aerosol systems comprised of polyethylene glycol (PEG) and (b) aerosol systems comprising a mixture of PEG and ammonium sulfate (AS). CCN measurements were carried out for PEG with average molecular weights of 200, 1,000, and 10,000 g/mol (corresponding to a range in viscosity of 0.004 – 4.5 Pa s under dry conditions). Critical activation diameter is defined as the particle diameter at which 50% of the particles are activated to form CCN (50% activation fraction indicated by solid black line). CCN activity, as measured by critical activation diameter, increased with increasing molecular weight of the PEG for both pure PEG and mixed PEG-AS aerosol systems. CCN activity of the PEG 10,000-AS system exceeded that of pure AS, suggesting that the presence of surface-active oligomers in marine aerosols may contribute to enhancements in CCN activity and may alter cloud properties.

2. Biological Ocean Atmospheric Study (BOAS), July 2015

We conducted a Twin Otter field study in July 2015. A major goal of the aircraft campaign was to determine, for the first time, the biological content of marine aerosols. Because of this emphasis, the mission was called the Biological Ocean Atmospheric Study (BOAS). See Figure 2.

Table 1 gives a summary of the 15 flights during BOAS. A total of 29 cloud water samples were collected onboard the Twin Otter using a Mohnen slotted-rod collector. Samples were tested for pH (Oakton Model 110 pH meter calibrated with pH 4.01 and pH 7.00 buffer solutions). Detailed analysis of chemical composition was conducted with ion chromatography (IC; Thermo Scientific Dionex ICS – 2100 system) and inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7700 Series). See Figures 3 and 4.

Table 1. BOAS flight summary, July 2015.

RF	Flight Date	Objective	Meteorological conditions
1	7/2/15	Chase a ship to calibrate instrument sensitivity	Cloudy
2	7/6/15	Bioparticle characterization and search for bio-markers	Clear
3	7/7/15	Characterization of longitudinal gradients in bioparticle concentrations under clear conditions	Clear
4	7/8/15	Characterization of longitudinal gradients in bioparticle concentrations under clear conditions	Clear
5	7/9/15	Characterization of the vertical concentrations of bioparticles under clear conditions	Clear
6	7/10/15	Land/ocean contrast in bioparticles concentrations	Clear
7	7/13/15	Characterization of the vertical composition of particles over land and ocean	Clear
8	7/14/15	Chase a ship to characterize instrument interferences	Cloudy
9	7/15/15	Characterization of longitudinal gradients in bioparticle concentrations under cloudy conditions	Cloudy
10	7/16/15	Characterization of the diurnal patterns of typical urban plumes advected over the ocean	Cloudy
11	7/17/15	Characterization of bioparticles in oceanic regions impacted by continental, biogenic emissions	Cloudy
12	7/21/15	Characterize the bioparticle contribution to clouds	Cloudy
13	7/22/15	Characterize the bioparticle contribution to clouds	Cloudy
14	7/23/15	Characterize the diurnal parttern of typical urban plumes advected over ocean	Cloudy
15	7/24/15	Characterize the bioparticles emitted from a typical agricultural source	Clear

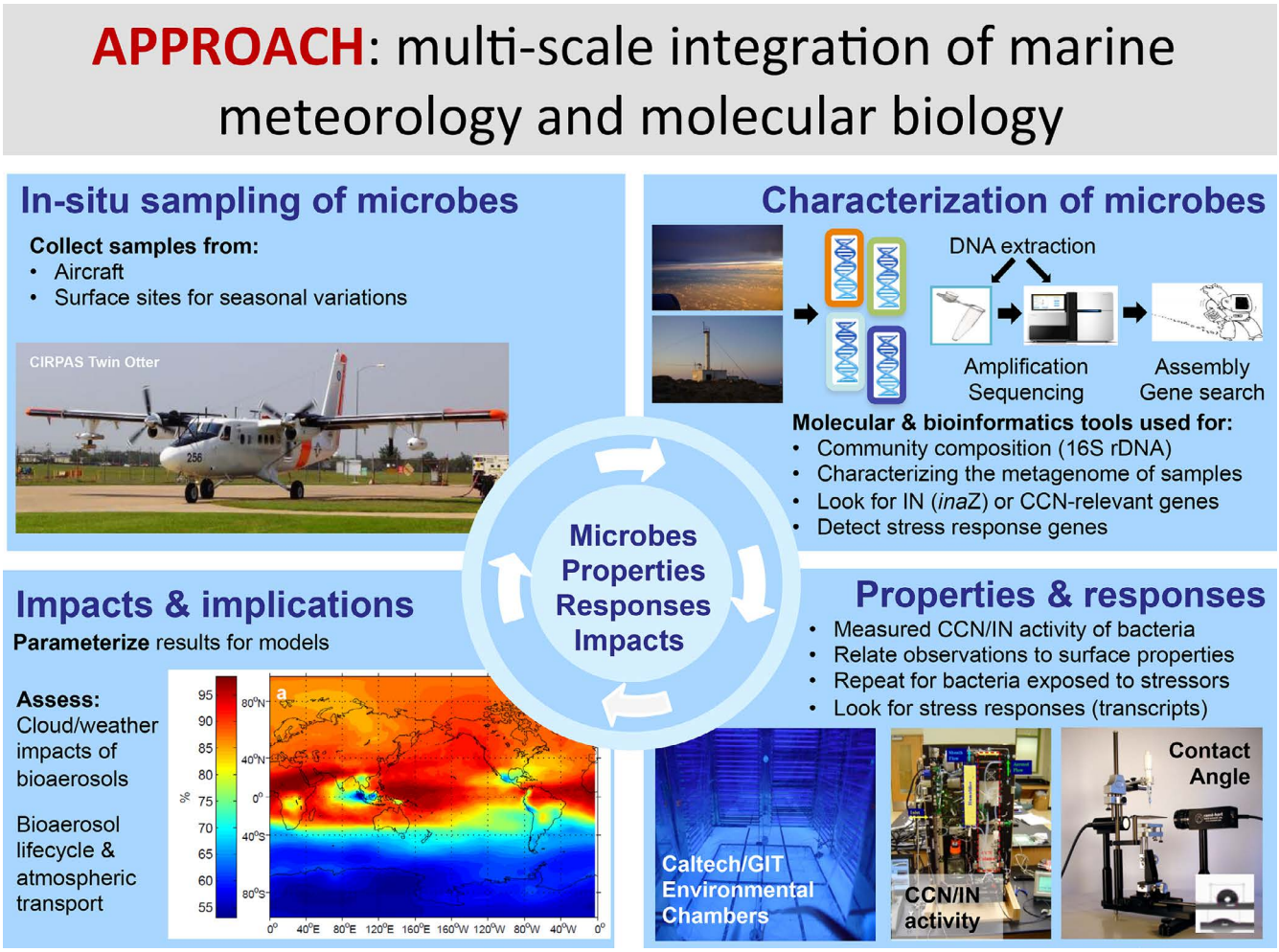

Figure 2. Biological Ocean Atmospheric Study (BOAS).

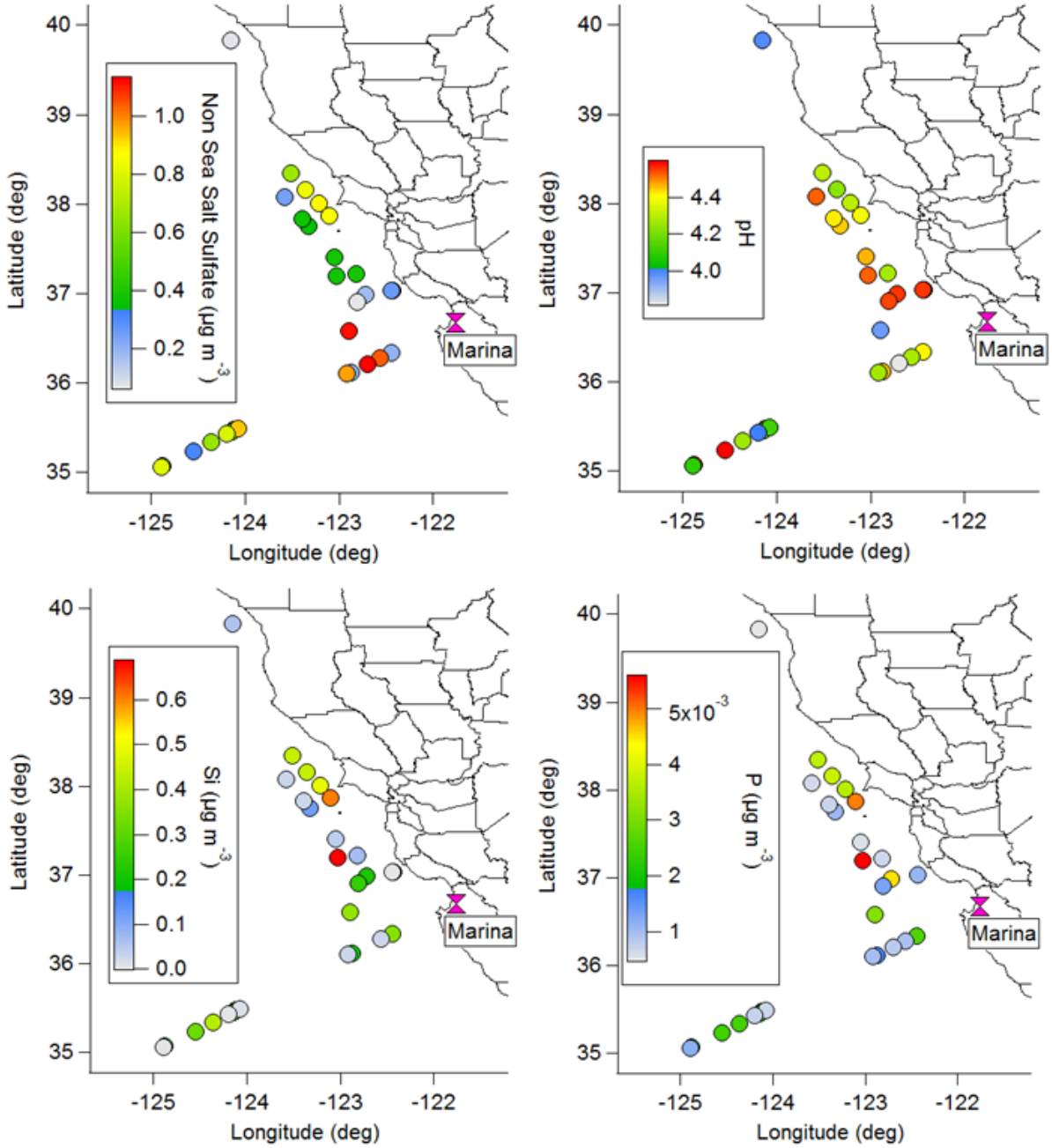

Figure 3. Spatial map of cloud water pH and air-equivalent concentrations of a few representative constituents studied during BOAS out of more than 60. Shown are non sea salt sulfate, phosphorus, and silicon.

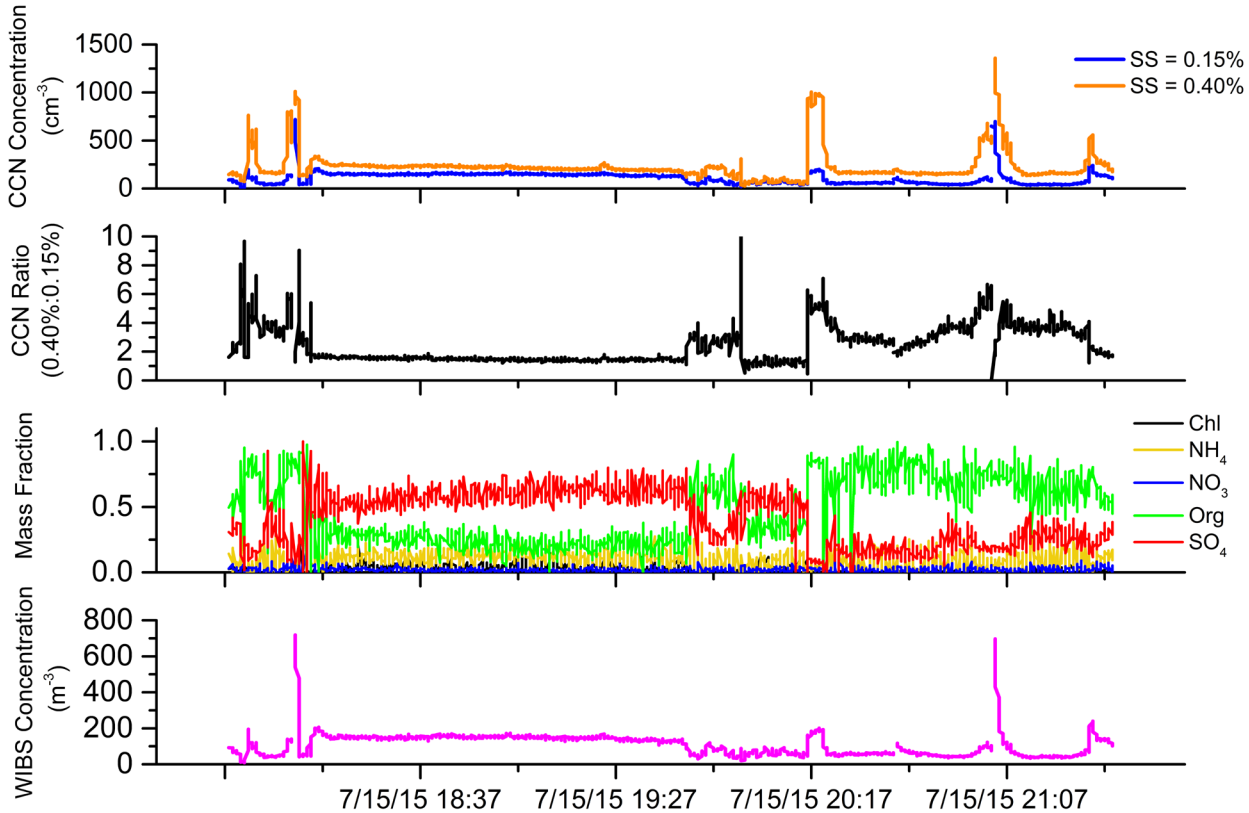

Figure 4. Example of exploratory analyses investigating the factors influencing critical supersaturation for cloud condensation nuclei (CCN) activation in marine atmospheres. Shown here are (a) CCN concentrations measured at two supersaturations (SS = 0.15% and SS = 0.40%), (b) the ratio of CCN concentrations measured at SS = 0.40% to those measured at SS = 0.15% (CCN Ratio), (c) mass fractions of particle-phase chloride (Chl), ammonium (NH_4), nitrate (NO_3), organics (Org), and sulfate (SO_4), and (d) concentrations of fluorescent particles measured with the WIBS. All data are from Research Flight 9, which was conducted over the phytoplankton bloom under windy and cloudy conditions. Preliminarily, CCN ratios appear to approach 1.0 when sulfate mass fractions are higher and increase with the mass fraction of organics. Sulfate concentrations are moderately correlated with WIBS-measured concentrations of fluorescent particles (R^2 = 0.63), while concentrations of fluorescent particles and organics are poorly correlated (R^2= 0.07).

IMPACT/APPLICATIONS

This project is anticipated to have two major impacts: (1) A more thorough understanding of the hygroscopic and CCN behavior of mixed inorganic/organic aerosols, typical of those present in the marine atmosphere; and (2) A set of baseline data on the biological content of marine aerosols.

RELATED PROJECTS

None

PUBLICATIONS

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