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Influence of Organic-Containing Aerosols on Marine Boundary Layer Processes

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Award Number: N00014-14-1-0097

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

The proposed research aims to improve understanding of both water vapor and organic uptake by marine aerosols, as well as the ways in which the particle phase influences and is influenced by these processes.

APPROACH

Through the integration of laboratory experiments, a Twin Otter aircraft mission, and modeling, this research will address the following questions:

1. How do the magnitudes and timescales of aerosol growth in the presence of sub-saturated organic vapors and water vapor vary with particle phase morphology? What physiochemical properties of the particle phase and the condensing gas-phase species 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?

WORK COMPLETED

The following tasks have been completed:

1. Completion of a major satellite data analysis of marine aerosols and clouds (see Publications section).
2. Initial laboratory studies of the hygroscopic behavior of well-defined inorganic/organic aerosols.

These two areas are described below.

RESULTS

1. Changes in aerosol concentrations affect cloud albedo and Earth's radiative balance. Of all cloud forms, low-level marine clouds exert the largest impact on the planet's albedo. Marine warm cloud properties are thought to depend on aerosol levels and large-scale dynamic or thermodynamic states. We have carried out a comprehensive analysis of multiple measurements from the A-Train constellation of Earth-observing satellites, to quantify the radiative forcing exerted by aerosols interacting with marine clouds. Specifically, we analyzed observations of co-located aerosols and clouds over the world's oceans for the period August 2006–April 2011, comprising over 7.3 million CloudSat single-layer marine warm cloud pixels. We find that thermodynamic conditions—that is, tropospheric stability and humidity in the free troposphere—and the state of precipitation act together to govern the cloud liquid water responses to the presence of aerosols and the strength of aerosol–cloud radiative forcing. See Figure 1.

2. While current models generally treat organic and mixed organic-inorganic aerosol particles as well-mixed liquids, recent work has demonstrated that these particles can exist in multiple phase states depending on their chemical composition and on ambient conditions such as relative humidity (RH) (Cappa et al., 2008; Ciobanu et al., 2009; Virtanen et al., 2010; Bertram et al., 2011; Koop et al., 2011; Krieger et al., 2012). For example, non-ideal interactions between aerosol components can result in phase separations in which an inorganic-electrolyte-rich phase and an organic-rich phase co-exist within one particle (Ciobanu et al., 2009; Bertram et al., 2011; Zuend et al., 2010; Song et al., 2012; You et al., 2012; Zuend et al., 2012, 2013). Organic aerosols have been shown to exist in an amorphous, highly viscous semi-solid state under atmospherically relevant conditions (Virtanen et al., 2010; Koop et al., 2011; Saukko et al., 2012). This complex phase behavior has major implications for aerosol hygroscopicity (which describes the efficiency of water uptake) and not accounting for it in modeling studies can lead to large errors in predictions of aerosol water content and cloud droplet activation and growth (Koop et al., 2011; Zuend et al., 2010; Bertram et al., 2011).

   Hygroscopic growth factors (HGFs) were measured for nine laboratory-generated aerosol systems representative of mixed organic-inorganic marine aerosols at relative humidities ranging from 40 to 90% with the Differential Aerosol Sizing and Hygroscopicity Spectrometer Probe (DASH-SP). With the aim of exploring the extent to which water uptake varies with particle phase, experiments were performed for chemical systems for which particle phase behavior as a function of RH has been characterized in previous work. Table 1 summarizes the composition and expected phase behavior of the aerosol systems studied here, as observed in previous studies. In addition to variability in phase behavior, the aerosol systems were varied in their complexity (in terms of their dry composition) and ranged from single-component organic systems, to two-component systems consisting of one organic and ammonium sulfate, to more

complex systems consisting of dicarboxylic acid mixtures and ammonium sulfate (Table 1). Measured HGFs were accompanied by modeling data from the rigorous thermodynamic model AIOMFAC (Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients; Zuend et al., 2008, 2010, 2011; Zuend and Seinfeld, 2012, 2013). AIOMFAC is an equilibrium thermodynamic model that explicitly accounts for molecular interactions between all components in an aqueous solution and predicts the presence of phase separations, as well as the composition of all phases present within a particle (Zuend et al., 2008, 2010). Measured HGFs were also compared to those modeled assuming the simplified case of ideal mixing among all aerosol components.

We observed variability in measured water-uptake behavior and model-measurement agreement across aerosol systems with differing phase behaviors. AIOMFAC-predicted and ideal HGFs were in good agreement with experimental HGFs for aerosol systems that exist as well-mixed liquids across the range of RHs tested; however, substantial disagreement between experimental and ideal HGFs was observed for phase-separated particles. This disagreement was greatest at low to moderate RHs, whereas experimental HGFs approached the ideal curve at high RH as phase-separated particles merged to a single phase with increased water content. An example of our results for an aerosol system that undergoes phase separations at low-to-moderate RH (2-methyglutaric acid + ammonium sulfate) is shown in Figure 2. For the viscous sucrose-containing aerosol systems, we observed evidence for glass transitions and inhibition of water transfer between the particle and gas phases. The extent to which water uptake by marine aerosols is driven by ideal, equilibrium partitioning has implications for predicted aerosol scattering efficiencies, aerosol radiative properties, and cloud droplet activation and growth.

Table 1. Aerosol systems for which hygroscopic growth factors were measured at relative humidities ranging from 40 to 90% with the DASH-SP. With the aim of exploring the extent to which water uptake varies with particle phase, hygroscopic growth curves were measured for chemical systems for which particle phase behavior as a function of RH has been characterized in previous studies. Systems were chosen based on their atmospheric relevance and to explore a range of RH-dependent phase behaviors.

Aerosol System	Organic:Inorganic Mass Ratio	Phase Behavior	References(s)
Citric Acid + Ammonium Sulfate	2:1	No phase separation observed	You et al. (2012)
Diethylmalonic Acid + Ammonium Sulfate	2:1	Phase separation at RH ≤ 89%	You et al. (2012)
2-Methylglutaric Acid + Ammonium Sulfate	2:1	Phase separation at RH ≤ 75%	You et al. (2012)
C5 dicarboxylic acids mixture (glutaric, methylsuccinic, dimethlymalonic) + Ammonium Sulfate	1:1	No phase separation observed	Song et al. (2012)
C6 dicarboxylic acid mixture mixture (2-methylglutaric, 3 - methylglutaric, 2,2-dimethylsuccinic) + Ammonium Sulfate	1:1	Transition from phase-separated particle with partially-engulfed morphology to single liquid phase at RH = 74%	Song et al. (2012)
C7 dicarboxylic acid mixture (3-methyladipic, 3,3-dimethylglutaric, diethylmalonic) + Ammonium Sulfate	1:1	Transition from phase-separated particle with core-shell morphology to single liquid phase at RH = 89 – 90%	Song et al. (2012)
Sucrose	N/A	Glass transition at RH = 24 – 53%, depending on timescale of RH change	Tong et al. (2011), Zobrist et al. (2011)
Sucrose + Ammonium Sulfate	1:1	Unknown	This study
Sucrose + Ammonium Sulfate	2:1	Unknown	This study

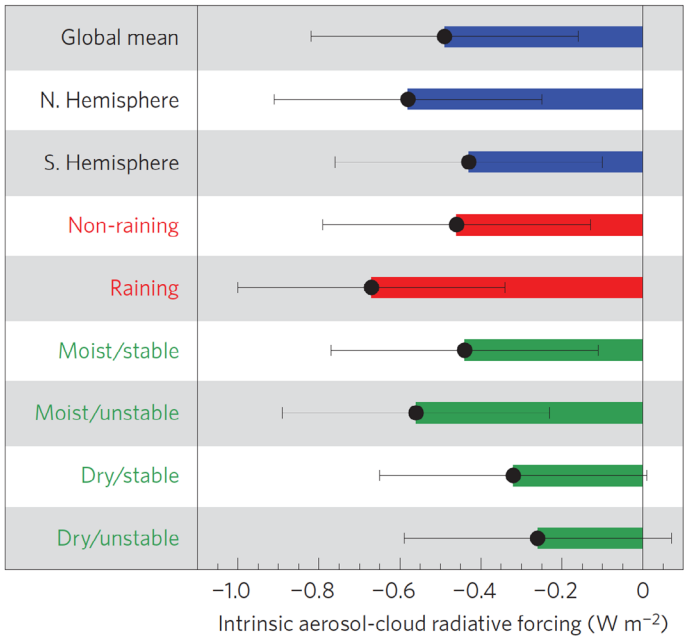

Figure 1. Estimated intrinsic aerosol-cloud radiative forcing by global marine warm clouds. The estimates (short-wave component at the top of the atmosphere) are separated into global, Northern, and Southern Hemisphere; non-raining and raining clouds; and different environmental conditions for non-raining clouds. For the environmental conditions, 'dry' and 'moist' refer to free tropospheric humidity <40% and >40%, respectively; 'stable' and 'unstable' refer to lower tropospheric stability ($\theta_{700\ hPa}$—$\theta_{surface}$) <17 K and >17 K, respectively. The error bars are calculated on the basis of the standard error of the regression slope.

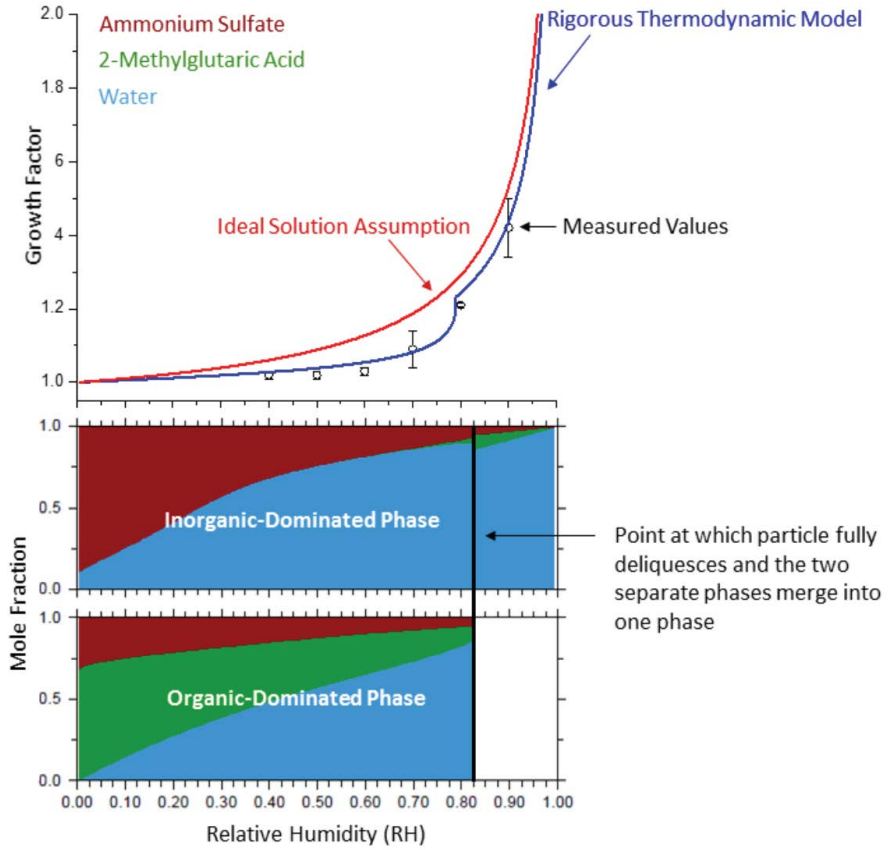

Figure 2. Example of measured and modeled hygroscopic behavior of laboratory-generated, idealized mixed organic-inorganic marine aerosols. The top panel shows a comparison between measured hygroscopic growth factors (black circles), those modeled accounting fully for non-ideal behavior and phase separations when present with the rigorous thermodynamic model AIOMFAC (blue), and those modeled assuming the particles can be represented as thermodynamically-ideal, well-mixed liquids (red). Hygroscopic growth factor describes the ratio of particle diameter at a given relative humidity (RH) to particle diameter under dry conditions, with the change in particle size attributable to water uptake. The bottom panels illustrate the chemical composition of all phases present in the particles as a function of RH. For this aerosol system, an organic-dominated and an inorganic-dominated phase co-exist within the particle prior to particle deliquescence at RH = 82.5%, at which point the two phases merge to a single phase. Only the detailed thermodynamic model that accounts for non-ideality and phase separations captures water-uptake behavior at low to moderate values of RH; however, measured and AIOMFAC-modeled growth factors approach the ideal assumption as particle water content increases and the separate phases merge to a single phase at high RH.

REFERENCES

Bertram, A.K., et al., 2011: Predicting the relative humidities of liquid-liquid phase separation, efflorescence, and deliquescence of mixed particles of ammonium sulfate, organic material, and water using the organic-to-sulfate mass ratio of the particle and the oxygen-to-carbon elemental ratio of the organic component. Atmos. Chem. Phys., 11, 10995 - 11006.

Cappa, C. D. et al., 2008: Evidence for liquid-like and nonideal behavior of a mixture of organic aerosol components. Proc. Natl. Acad. Sci., (105), 18687 - 18691.

Ciobanu, V. G., et al., 2009: Liquid-liquid phase separation in mixed-organic/inorganic aerosol particles. J. Phys. Chem. **113**: 10966 - 10978.

Koop, T., et al., 2011: Glass transition and phase state of organic compounds: dependency on molecular properties and implications for secondary organic aerosols in the atmosphere. Phys. Chem. Chem. Phys., (13), 19238 – 19255.

Krieger, U., et al., 2012: Exploring the complexity of aerosol particle properties and processes using single particle techniques. Chem. Soc. Rev., 41, 6631 - 6662.

Saukko, E., et al., 2012: Humidity-dependent phase state of SOA particles from biogenic and anthropogenic precursors. Atmos. Chem. Phys., 12**,** 7515 - 7529.

Song, M., et al., 2012: Liquid-liquid phase separation and morphology of internally mixed dicarboxylic acids/ammonium sulfate/water particles. Atmos. Chem. Phys., 12, 2691 - 2712.

Virtanen, A., et al., 2010: An amorphous solid state of biogenic secondary organic particles. Nature 467, 824 - 827.

You, Y., et al., 2012: Images reveal that atmospheric particles can undergo liquid–liquid phase separations. Proc. Natl. Acad. Sci., 109: 13188 - 13193.

Zuend, A., et al., 2008: A thermodynamic model of mixed organic-inorganic aerosols to predict activity coefficients. Atmos. Chem. Phys. 8, 4559 - 4593.

Zuend, A., et al., 2010: Computation of liquid-liquid equilibria and phase stabilities: implications for RH-dependent gas/particle partitioning of organic-inorganic aerosols. Atmos. Chem. Phys., 10, 7795 - 7820.

Zuend, A., et al., 2011: New and extended parameterization of the thermodynamic model AIOMFAC: calculation of activity coefficients for organic-inorganic mixtures containing carboxyl, hydroxyl, carbonyl, ether, ester, alkenyl, alkyl, and aromatic functional groups. Atmos. Chem. Phys. 2011: 11, 9155 - 9206.

Zuend, A., and J. H. Seinfeld, 2012: Modeling the gas-particle partitioning of secondary organic aerosol: the importance of liquid-liquid phase separation. Atmos. Chem. Phys., 12, 3857 - 3882.

Zuend, A., and J.H. Seinfeld, 2013: A practical method for the calculation of liquid–liquid equilibria in multicomponent organic–water–electrolyte systems using physicochemical constraints. Fluid Phase Equilibria, 337, 201 - 213.

IMPACT/APPLICATIONS

Potential future impact on the ability to predict properties of marine aerosols, especially those impacted by anthropogenic emissions, in atmospheric models.

RELATED PROJECTS

None.

PUBLICATIONS

Y.-C. Chen, M.W. Christensen, G.L. Stephens and J. H. Seinfeld, "Satellite-based estimate of global aerosol-cloud radiative forcing by marine warm clouds," *Nature Geoscience*, published online 3 August 2014; DOI 10.1038/NGEO2214. [Published; refereed]