Cloud Nucleating Properties of Aerosols During TexAQS - GoMACCS 2006: Influence of Particle Size and Chemistry

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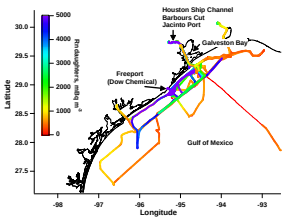
Introduction – Goals and Approach. During TexAQS – GoMACCS, the NOAA RV *Ronald H. Brown* encountered a wide variety of aerosol types ranging from marine near the Florida panhandle to urban and industrial in the Houston-Galveston area. This wide variability in aerosol sources provided an opportunity to investigate the role of chemistry and size in the activation of particles to form cloud droplets. Recently published papers have investigated the relative importance of size and chemistry but were limited by a narrow range of chemical composition [*Dusek et al.,* 2006] or a lack of composition measurements [*Hudson,* 2007]. Here we use a Cloud Condensation Nuclei (CCN) counter (DMT) to determine the fraction of particles that activate to form cloud droplets, an Aerosol Mass Spectrometer (Aerodyne Q-AMS) to quantify variability in chemical composition in the size range relevant for particle activation (<200 nm D_{vaero}), and a DMPS-APS (TSI, Inc.) to determine the aerosol size distribution.

We have sorted the large amount of data in two different ways (Figure 1). The first is based on geographical location and includes Barbours Cut, Freeport, Galveston Bay, Gulf of Mexico, Houston Ship Channel, Jacinto Port, and the Atlantic. The second is based on a combination of location and radon, a tracer of continental air. This approach yields three regimes: Gulf of Mexico – Southerly Flow, Inland Texas – Southerly Flow, and Northerly Flow.

Figure 1. Map of study area.



To investigate the degree to which aerosol composition affects particle activation we need a parameter to represent the observed variability in composition. We use the mass fraction of Hydrocarbon-like Organic Aerosol (HOA) for D_{vaero} < 200 nm as determined by the Q-AMS. For non-marine aerosol, HOA tends to dominate the mass in this size range over Oxidized Organic Aerosol (OOA) and sulfate (Figures 2 and 3).

Figure 2. Mass fraction of HOA and OOA relative to all aerosol mass measured by the Q-AMS for D_{vaero} < 200 nm.

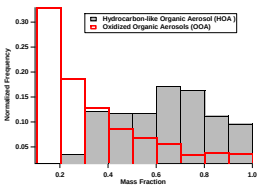
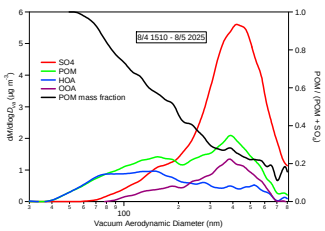


Figure 3. Size distribution of the chemical components measured by the Q-AMS on August 4th. This example shows the increasing POM mass fraction with decreasing size and dominance of the POM mass by HOA for diameters less than 200 nm vacuum aerodynamic.



The critical diameter for activation is defined here as the diameter at which

$$CCN_{measured} / CN_{integrated} = 1.0$$

where $CN_{integrated}$ is found by integrating the number concentrations from the largest diameter measured down to the point where the above equation is satisfied (Figure 4). A frequency distribution of critical diameters for the entire experiment reveals a size range of 60 to 160 nm (Figure 5).

Figure 4. Definition of critical diameter.

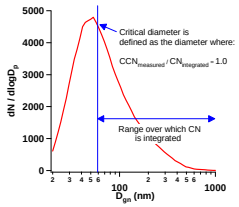
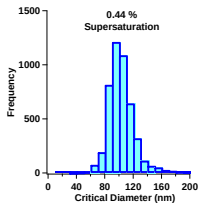
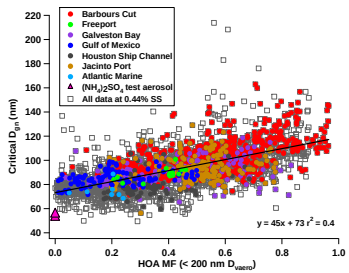


Figure 5. Frequency distribution of critical diameters calculated for all measurements made at 0.44% supersaturation.



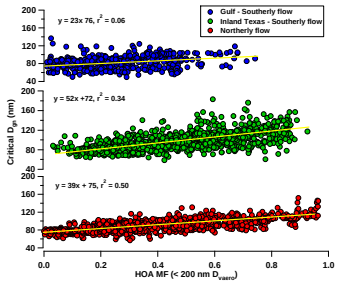
Measurement Results. For a given supersaturation, the critical diameter is a function of particle size and composition. Particles that are less than about 40 nm (geometric or D_{gn}) are too small to activate regardless of composition while particles greater than about 140 nm are large enough to activate regardless of composition. Within this size limit, composition contributes to a particle's cloud nucleating ability. Here, we use the correlation between variability in critical diameter and aerosol composition to quantify the effect of composition on particle activation. Figure 6 shows the HOA mass fraction for D_{vaero}- < 200 nm versus critical diameter for all data collected at 0.44% supersaturation and highlights Atlantic marine aerosol, locations within the Houston-Galveston region, and, for reference, $(NH_4)_2SO_4$ test aerosol. Based on the coefficient of determination of the fit, composition (defined in this way) explains 40% of the variance in the critical diameter.

Figure 6. HOA mass fraction of the Q-AMS mass for the size range <200 nm D_{vaero} vs. critical diameter measured at 0.44% supersaturation.



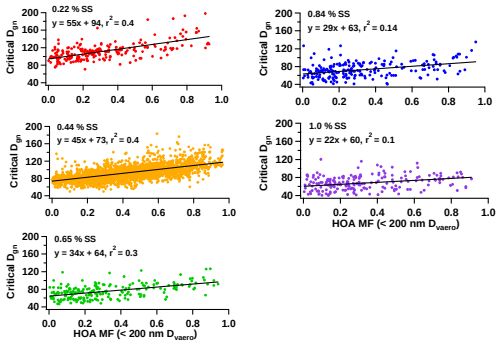
Positive slopes also are found for each of the three Radon-defined flow regimes although the degree of correlation varies (Figure 7). The r^2 value is largest for the Northerly Flow regime where HOA mass fractions vary between near zero and near one and concentrations are high so that the signal to noise ratio is high.

Figure 7. Similar to Figure 6 but for the three radon-defined flow regimes.



In Figure 8, we plot the HOA mass fraction versus critical diameter for all data collected during the experiment and for the five different supersaturation settings. There is a positive slope for each supersaturation but the magnitude of the slope decreases with increasing supersaturation. This change in slope is expected as composition (and size) becomes less critical with increasing supersaturation.

Figure 8. Dependence of the critical diameter on chemical composition as a function of supersaturation.



Modeled sensitivity of CCN concentration to observed variability in particle size and composition. A sensitivity study on the impact of size and composition on particle activation was performed based on the observed variability in size distribution and POM mass fraction and Köhler theory. To determine the sensitivity to composition, the size distribution was held constant with a geometric mean diameter of 60 nm, a standard deviation of 1.5, and a total number concentration of 3000 cm^{-3}. For this case, particle composition was varied between a POM mass fraction of 0.2 and 0.8, reflecting a conservative estimate of the measured variability. To determine the sensitivity to size, a particle composition of $(NH_4)_2SO_4$ was assumed and the mean geometric mean diameter was varied between 45 and 75 nm; again, a range that reflects the observed variability during TexAQS.

Figure 9 shows the comparison of the percent change in CCN concentration due to observed variability in size (top panel) and composition (bottom panel). In addition, the sensitivity of CCN concentration to the variability in composition reported in the *Dusek et al.* [2006] paper is shown. For the relative variability of size and composition observed during TexAQS, composition is the dominant factor in determining the degree of particle activation to form cloud droplets at each supersaturation setting. For example, at 0.44% SS, the observed variability in size distribution (D_{gn} =45 to 75 nm) resulted in an increase in CCN concentration by 55% while the observed variability in the POM mass fraction (0.2 to 0.8) resulted in a decrease in CCN concentration by 70%.

Figure 9. The percent change in CCN concentration due to the variability in the number size distribution observed during TexAQS (top panel). The bottom panel shows the change due to the variability in composition observed during TexAQS compared to that reported by *Dusek et al.* [2006].

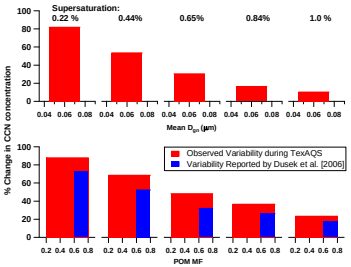
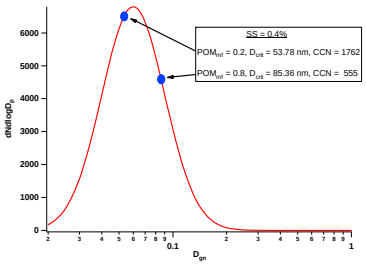


Figure 10 reinforces the importance of composition in determining particle activation for the range of variability observed during TexAQS. For a constant geometric mean diameter of 60 nm, a POM mass fraction of 0.2 yields 1800 CCN cm^{-3} while a POM mass fraction of 0.8 for the same size distribution yields a CCN concentration of around 560 cm^{-3}.

Figure 10. CCN concentration estimated for a constant size Distribution and POM mass fraction of 0.2 and 0.8.



Conclusion. For the variability of POM mass fraction observed during TexAQS-GoMACCS, composition plays a dominant role in determining the fraction of particles that are activated to form cloud droplets.

References
Dusek et al., *Science*, *312*, 1375 – 1378, 2006.
Hudson, *Geophys. Res. Lett.*, *34*, L08801, 2007.

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NOAA Climate Program Office
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