

**FY 2010 Third Quarter Report
Comparison of Aerosol and Cloud Condensation
Nuclei (CCN) Relationship Parameterizations
with Data Collected During the 2008 VAMOS
Ocean-Cloud-Atmosphere Land Study
(VOCALS) Field Campaign**

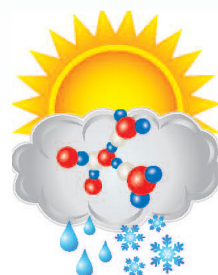
J Wang R McGraw
PH Daum AJ Sedlacek
LI Kleinman G Senum
YN Lee SR Springston

June 2010



U.S. DEPARTMENT OF
ENERGY

Office of Science



ASR

Atmospheric
System Research

DISCLAIMER

This report was prepared as an account of work sponsored by the U.S. Government. Neither the United States nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the U.S. Government or any agency thereof.

**FY 2010 Third Quarter Report
Comparison of Aerosol and Cloud
Condensation Nuclei (CCN)
Relationship Parameterizations with
Data Collected During the 2008 VAMOS
Ocean-Cloud-Atmosphere Land Study
(VOCALS) Field Campaign**

J Wang R McGraw
PH Daum AJ Sedlacek
LI Kleinman G Senum
YN Lee SR Springston

June 2010

Work supported by the U.S. Department of Energy,
Office of Science, Office of Biological and Environmental Research

Contents

1.0	Statement of the Metric	1
2.0	Introduction	1
3.0	Measurements.....	1
3.1	Aerosol Chemical Composition	1
3.2	Aerosol Size Distribution.....	2
3.3	Cloud Condensation Nuclei Concentrations	2
4.0	Data Analysis.....	2
5.0	Results	3
6.0	Summary.....	5
7.0	References	5

Figures

1	Comparison of calculated and measured N_{CCN} at supersaturations of (a) 0.2%, (b) 0.28%, and (c) 0.4%.....	3
2	Ratio of calculated to measured CCN concentration as a function of organics mass fraction for supersaturations of 0.20, 0.28, and 0.4%.....	4
3	Comparison of calculated and measured N_{CCN} at supersaturation of (a) 0.2%, (b) 0.28%, and (c) 0.4%.....	4

Tables

1	Archived data used in Fourth Quarter Metric.....	1
---	--	---

1.0 Statement of the Metric

Metric for Quarter 3: Report comparisons of aerosol/CCN relationship parameterizations with data collected in the first quarter and best parameterization for VOCALS data set.

2.0 Introduction

During October and November 2008, Brookhaven National Laboratory (BNL) participated in VOCALS (VAMOS Ocean-Cloud-Atmosphere Land Study), a multi-agency, multinational atmospheric sampling field campaign conducted over the Pacific Ocean off the coast of Arica, Chile. Support for BNL came from the U.S. Department of Energy's (DOE) Atmospheric Science Program (ASP), which is now part of the Atmospheric System Research (ASR) program following a merger with DOE's Atmospheric Radiation Measurement (ARM) Program. A description of the VOCALS field campaign can be found at:

<http://www.eol.ucar.edu/projects/vocals/>

Archived data products are at:

ftp://ftp.asd.bnl.gov/pub/ASP%20Field%20Programs/2008VOCALS/Processed_Data/

See the first-quarter metric report for a full description of the various files posted. Here we report the comparison of aerosol-CCN relationship parameterizations using data collected during the VOCALS field campaign. The measurements used in this metric report are listed in Table 1.

Table 1. Archived data used in Fourth Quarter Metric.

Data	Files	Last Modified
Aerosol chemical composition	Aerosol_Comp	5/14/2009
Aerosol size distributions	DMAPart	5/14/2009
Cloud condensation nuclei (CCN) concentrations	CCN_Edited	12/17/2009

3.0 Measurements

3.1 Aerosol Chemical Composition

The aerosol composition was measured using an Aerodyne C-ToF Aerosol Mass Spectrometer (AMS). A measurement cycle for acquiring a mass spectrum was typically 12 seconds. In this study we make use of AMS-derived mass concentrations of NO_3^- , SO_4^{2-} , NH_4^+ , and organics. As shown in the first-quarter metric report, the chemical composition of sub-micrometer aerosol measured below cloud level was remarkably uniform as a function of longitude as indicated by AMS data. Within a longitude grouping, there are only small fluctuations around an average composition of 45% H_2SO_4 , 45% NH_4HSO_4 , and 10% organics by mass.

3.2 Aerosol Size Distribution

Aerosol size distribution was measured by a Scanning Mobility Particle Sizer (SMPS) (Wang et al. 2003). The major components of the SMPS are a cylindrical Differential Mobility Analyzer (Model 3081, TSI Inc., Minneapolis, Minnesota) and a Condensation Particle Counter (Model 3010, TSI Inc., Minneapolis, Minnesota). Prior to measurements, the relative humidity (RH) of aerosol sample was reduced to about 15% inside a Nafion drier. Aerosol size distribution ranging from 15 nm to ~450 nm was measured every 60 seconds. The SMPS was calibrated using polystyrene latex standards. Data from the SMPS were reduced using the data inversion procedure described by Collins et al. (2002).

3.3 Cloud Condensation Nuclei (CCN) Concentrations

CCN concentrations at 0.2, 0.28, and 0.4% supersaturations were measured by a dual-column CCN counter and a single-column CCN counter (Droplet Measurement Technologies, Boulder, Colorado). Prior to VOCALS, the CCN counters were calibrated using ammonium sulfate particles. The CCN counters consist of cylindrical continuous-flow gradient diffusion chambers. A constant stream-wise temperature gradient is applied in the chamber such that the difference between water vapor mass diffusivity and air thermal diffusivity leads to a quasi-uniform centerline supersaturation. Cloud condensation nuclei, which are confined near the centerline, grow into super-micrometer droplets and are detected by an Optical Particle Counter downstream (Roberts and Nenes 2005). The CCN data during the descent and ascent of aircraft were excluded from this analysis, as the pressure change inside the CCN counter led to instability of sample flow and supersaturation.

4.0 Data Analysis

In this analysis, the particle-critical dry diameters (i.e., the minimum diameter of CCN at a given supersaturation) that correspond to activation at 0.2, 0.28, and 0.4% supersaturations were calculated using the “ κ Köhler theory” (Petters and Kreidenweis 2007), which uses a single parameter κ to describe the Raoult effect on CCN activation. In κ Köhler theory, the water vapor saturation ratio over the aqueous solution droplet, S , is given by:

$$S = \frac{D^3 - D_p^3}{D^3 - D_p^3(1 - \kappa)} \exp\left(\frac{4\sigma_w M_w}{RT\rho_w D}\right) \quad (1)$$

where D is the droplet diameter, D_p the dry diameter of the particle, M_w the molecular weight of water, σ_w the surface tension of aqueous solution, ρ_w the density of water, R the gas constant, and T the absolute temperature. For particles comprised of multiple components, the value of κ is given by a simple mixing rule (Petters and Kreidenweis 2007):

$$\kappa = \sum_i x_i \kappa_i \quad (2)$$

where x is the volume fraction and subscript i denotes species i . For soluble inorganic species, such as H_2SO_4 and NH_4HSO_4 , κ_i can be derived as:

$$\kappa_i = \nu_i \frac{\rho_i M_w}{\rho_w M_i} \quad (3)$$

where ρ is the density, M the molecular weight, and ν the van't Hoff factor. The van't Hoff factor takes into consideration the non-idealities of water activity, and the values used in study are 2.5 for both H_2SO_4 and NH_4HSO_4 .

Based on the AMS measurements, an average aerosol chemical composition of 45% H_2SO_4 , 45% NH_4HSO_4 , and 10% organics by mass are used to derive CCN concentrations. All species are treated as internally mixed. Organics are assumed to be non-hygroscopic with $\kappa=0$. Given the small contribution (i.e., 10%) to the overall aerosol mass, the calculated CCN concentrations (N_{CCN}) are expected to be insensitive to the κ of organics (Wang et al. 2008). The impact of using the average chemical composition is examined in the next section. Using the average composition, the critical dry particle activation diameter was calculated for all three supersaturations using the κ Köhler theory, and N_{CCN} was then derived from the measured size distribution as the integral of particles larger than D_{pc} . The derived N_{CCN} is then compared to concurrent measurements by the CCN counters onboard the DOE Gulfstream-1 aircraft.

5.0 Results

Comparison of calculated CCN concentrations to measured values at supersaturations of 0.2%, 0.28%, and 0.4% are shown in Figure 1. The calculated CCN concentrations agree well with the concurrent measurements, especially at 0.2 and 0.28% supersaturations. The ratios of calculated to measured CCN concentrations are derived through least-square fit, and are 0.94, 1.06, and 1.22, for supersaturations of 0.2, 0.28, and 0.4%, respectively. The correlation coefficient (R^2) of the fit is greater than 0.92 at all three supersaturations.

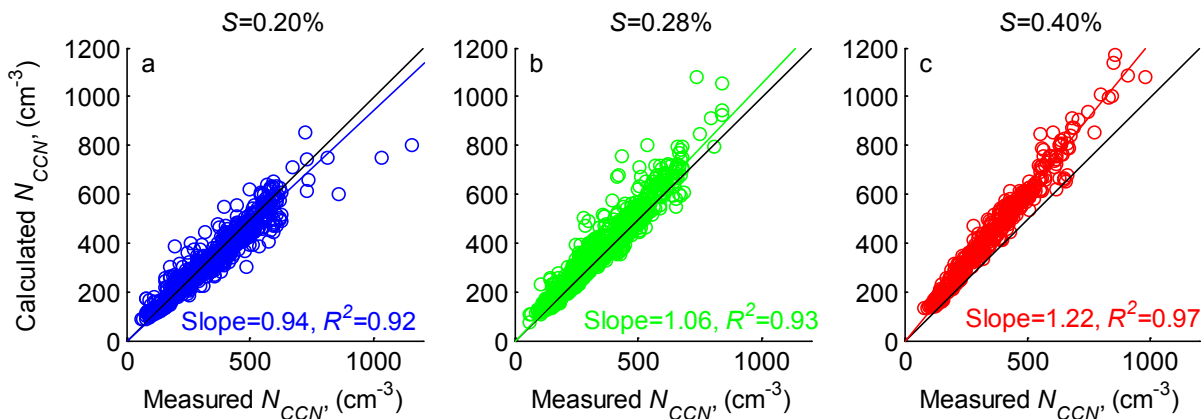


Figure 1. Comparison of calculated and measured N_{CCN} at supersaturations of (a) 0.2%, (b) 0.28%, and (c) 0.40%. The CCN concentrations were calculated using the averaged chemical composition of 45% H_2SO_4 , 45% NH_4HSO_4 , and 10% organics by mass.

As discussed earlier, the chemical composition of sub-micrometer aerosol measured below cloud level was remarkably uniform as a function of longitude, and the average composition is 45% H_2SO_4 , 45% NH_4HSO_4 , and 10% organics by mass. However, organics occasionally contributed to up to 40% of the

total aerosol mass. To examine the impact of using the average composition, CCN concentrations are derived with an organics mass fraction ranging from 0% to 40%. In these calculations, the sulfate remains as an equal mass mixture of H_2SO_4 and NH_4HSO_4 . Figure 2 shows that for aerosols observed during VOCALS, the calculated CCN concentration is insensitive to the assumed organics mass fraction. For all three supersaturations, the ratio of calculated to measured CCN concentration varies less than 10% when organic mass fraction increased from 0 to 40%.

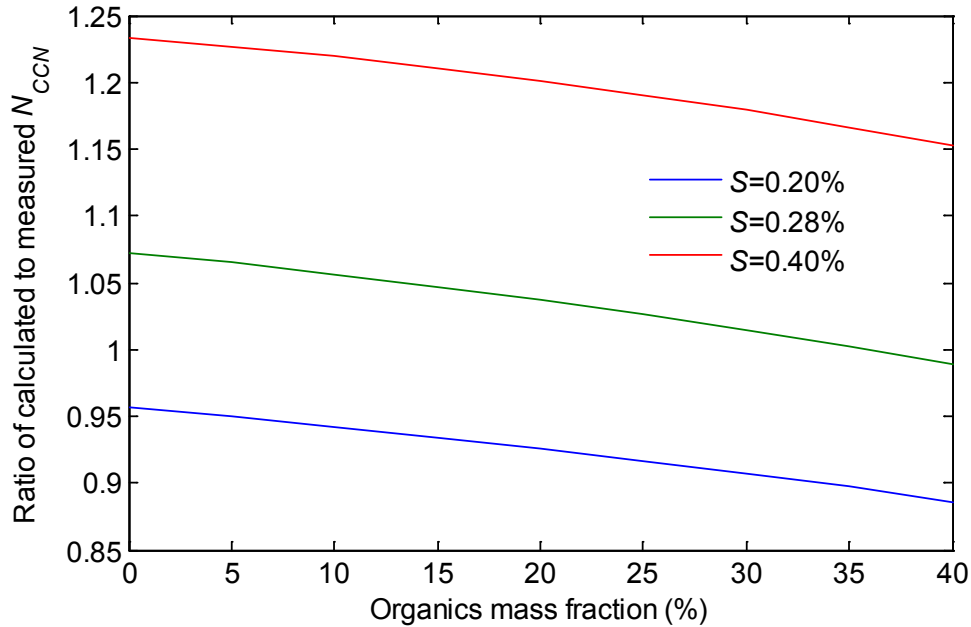


Figure 2. Ratio of calculated to measured CCN concentration as a function of organics mass fraction for supersaturations of 0.20, 0.28, and 0.4%.

The CCN concentrations were also calculated by assuming pure ammonium sulfate particles. Figure 3 shows that even with this greatly simplified composition, the calculated CCN concentration agrees with the measurements at all three supersaturations.

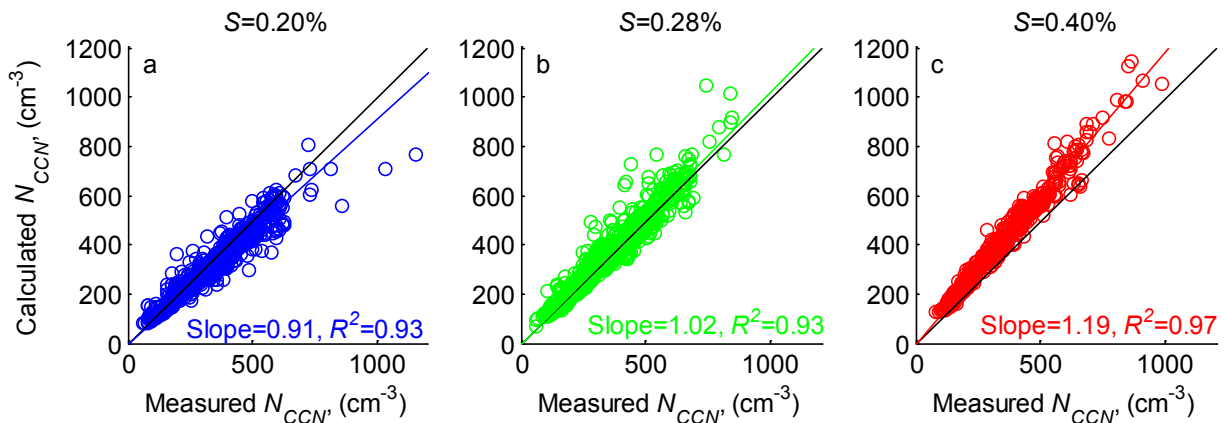


Figure 3. Comparison of calculated and measured N_{CCN} at supersaturation of (a) 0.2%, (b) 0.28%, and (c) 0.40%. The CCN concentrations were calculated assuming pure ammonium sulfate particles.

6.0 Summary

For aerosols observed during VOCALS, organics had a small contribution to the aerosol mass, and consequently, a negligible influence on the ability of aerosol to form cloud droplets at representative supersaturation of stratocumulus cloud. As a result, detailed chemical composition of aerosol particles is not necessary, and CCN concentration can be derived assuming pure ammonium sulfate particle for the aerosols observed over the Southeast Pacific.

7.0 References

Collins, DR, Flagan, RC, and Seinfeld, JH. 2002. "Improved inversion of scanning DMA data." *Aerosol Science and Technology* 36: 1–9.

Petters, MD, and Kreidenweis, SM. 2007. "A single parameter representation of hygroscopic growth and cloud condensation nucleus activity." *Atmospheric Chemistry and Physics* 7: 1961–1971.

Roberts, GC, and Nenes, A. 2005. "A continuous-flow streamwise thermal-gradient CCN chamber for atmospheric measurements." *Aerosol Science and Technology* 39: 206–221.

Wang, J, Flagan, RC, and Seinfeld, JH. 2003. "A differential mobility analyzer (DMA) system for submicron aerosol measurements at ambient relative humidity." *Aerosol Science and Technology* 37: 46–52.

Wang, J, Lee, YN, Daum, PH, Jayne, J, and Alexander, ML. 2008. "Effects of aerosol organics on cloud condensation nucleus (CCN) concentration and first indirect aerosol effect." *Atmospheric Chemistry and Physics* 8: 6325–6339.