

DOE Award Number: DE-SC000663

Recipient: University of California, Riverside

Project Title: Quantifying the Relationship between Organic Aerosol Composition and Hygroscopicity/CCN Activity

Principal Investigator: Paul J. Ziemann

Co-Principal Investigators: Sonia Kreidenweis (Colorado State University), Markus Petters (North Carolina State University)

Executive Summary

Aerosol indirect forcing, a measure that quantifies the effect of aerosol-cloud interactions on the climate system, represents one of the main uncertainties in climate projections, and reducing this uncertainty requires improved understanding of the life cycle of aerosol particles, including aging and cloud nucleating properties. In this project we investigated the relationships between the chemical composition of organic aerosol particles, which are known to be important components of atmospheric particulate matter, and their ability to serve as cloud condensation nuclei (CCN). In particular, we generated organic aerosol compounds that were tailored to span a broad range of molecules having different carbon chain length and functional groups, with the emphasis to measure, parameterize, and predict the relationship between the organic compounds' molecular structure and its cloud nucleating properties.

The overall objective for this project was to provide the data and underlying process level understanding necessary to facilitate the dynamic treatment of organic aerosol CCN activity in future climate models. The specific objectives were as follows: (1) employ novel approaches to link organic aerosol composition and CCN activity, (2) evaluate the effects of temperature and relative humidity on organic aerosol CCN activity, and (3) develop parameterizations to link organic aerosol composition and CCN activity.

We created complex secondary organic aerosol (SOA) mixtures similar to those formed in the atmosphere by reacting volatile organic compounds with O_3 , OH , or NO_3 in an environmental chamber over a wide range of temperature and humidity. We used derivatization-spectrophotometric methods we developed for functional group analysis along with particle mass spectrometry to characterize the SOA, and also employed a new on-line method we developed to measure the CCN activity of specific components of SOA and tailor-made organic mixtures after these components have undergone fractionation using high performance liquid chromatography. The combination of capabilities for creating realistic atmospheric organic aerosol for CCN analysis, either as single compounds with known, selectable structures, or in complex mixtures, provided unprecedented opportunities for unraveling the relationships between organic aerosol composition and CCN activity. We also extended our experimental studies to colder temperatures more typical of most of the lower troposphere, a step urgently needed to gain confidence in simulations that model aerosol-cloud climate interactions, and began development of a framework for modeling SOA CCN activity.

Although excellent progress was made on the project, not all originally planned research was completed because the award was terminated after less than two years due to the upcoming move of Dr. Ziemann, the PI on project, to the University of Colorado, Boulder in August 2013. A renewal proposal has been submitted for the original Year 3 funding, and we will also submit a request for supplementary funding equal to the amount of unexpended funds from Years 1 and 2 that are being returned to DOE in accordance with DOE policy, and which are in large part a result of work delays caused by this move. The combination of the renewal award and supplementary funds will allow us to complete the full scope of originally planned work.

The results from our studies will lead to parameterizations for relating organic aerosol properties to particle CCN activity for use in atmospheric models. In one, the input will be SOA sources, which can be calculated by current models that employ SOA yield parameterizations to predict SOA mass concentration, while in the other the input will be organic aerosol chemical composition, which can be predicted by state-of-the-art atmospheric chemistry models that can be included in regional scale simulations. The successful achievement of our objectives will help constrain one of the most significant remaining uncertainties in climate projections.

Comparison of Accomplishments with Project Goals and Objectives

The overall objective for this project was to provide the data and underlying process level understanding necessary to facilitate the dynamic treatment of organic aerosol CCN activity in future climate models. The specific objectives were as follows: (1) employ novel approaches to link organic aerosol composition and CCN activity, (2) evaluate the effects of temperature and relative humidity on organic aerosol CCN activity, and (3) develop parameterizations to link organic aerosol composition and CCN activity.

In the less than two-year duration of this project we made significant progress on all aspects of the proposed research. This is described in more detail below. Experiments were conducted that significantly enhanced our database of measurements of the CCN activity of organic aerosol particles formed from single compounds and chemically characterized complex mixtures. These studies of the effects of composition on CCN activity showed that the addition of hydroxyl and carboxyl groups significantly increase CCN activity, while the addition of hydroperoxide, nitrate, and methylene groups does not. These functional groups include most of the major ones that are present in atmospheric organic aerosol, and our results can be used to quantify these effects for model development. Our work on the effects of temperature and humidity on CCN activity yielded a validated methodology to accurately perform CCN measurements over the temperature range from 0° to 40°C, revealed the relative importance of the principle physical factors controlling the temperature dependence of CCN activity, and helped to extend the CCN modeling framework to correctly account for temperature dependence for model simulations. We also further developed the hygroscopicity tandem differential mobility analyzer technique to be able to better understand the relative influences of water activity and surface tension on CCN activity, and conducted experiments to better constrain the role of surfactants in pure and internally mixed particles on CCN activity. These studies are needed to build a robust parameterization of hygroscopicity of organic aerosol. We have also begun to develop a framework for modeling aerosol CCN activity.

Summary of Project Activities and Accomplishments

Because our current project did not officially start until September 1, 2011, we did not conduct joint studies at UCR as originally planned. Instead, those studies were conducted in the summer of 2012. Furthermore, because Dr. Ziemann will be moving the University of Colorado, Boulder and re-establishing his laboratory during the second half of 2013, we have requested that this grant be terminated as of June 30, 2013, and have submitted a renewal proposal to continue the research originally scheduled for Year 3. We will also be submitting a request during the upcoming year for supplementary funding and a no-cost extension, which will allow us to complete the full scope of work originally planned for the project.

1. Low temperature CCN measurements

During Year 1 we completed a series of CCN experiments exploring the dependence of temperature on the relationship between critical supersaturation and dry diameter for single component organic aerosol (maleic acid, glucose, glutamine, ketoglutaric acid, polyethylene glycol 600, methane sulfonic acid, adipic acid, sodium dodecyl sulfate), as well as for secondary organic aerosol generated from the ozonolysis of α -pinene. The specific objectives of our work were (1) to design a calibrated method with viable temperature control that will be used during

the upcoming joint study period at UC Riverside, (2) to measure the temperature dependent CCN activity for a variety of organic compounds that serve as proxies for atmospheric organic aerosol, and (3) to better understand the temperature dependence of the critical supersaturation - dry diameter relationship. Our efforts (1) yielded a validated methodology to accurately perform CCN measurements over the temperature range from 0° to 40°C; (2) revealed the relative importance of the principle physical factors controlling the temperature dependence of the supersaturation - dry diameter relationship, which in decreasing order of importance these are: surface tension (most important), solubility in water (moderately important), activity coefficients, and dissociation constants (weakly important/negligible); and (3) helped to extend the kappa modeling framework to correctly account for temperature dependence for model simulations in general and our functional group parameterization in particular. This initial work was performed by graduate student Sara Christensen at NCSU and formed the core of her M.S. thesis. She defended June, 2012 and the work was published in *Journal of Physical Chemistry A*.

2. Cold and warm T CCN experiments with on-line chemical characterization of model hydroxynitrates, hydroxyketones, terpenes, and Cl oxidation experiments

In Year 1 we conducted our first joint experiment at UCR in June–July 2012, with the focus being HPLC/scanning flow CCN measurements and cold temperature CCN experiments. The warm/cold temperature experiments included both cold chemistry and cold CCN measurements on some model SOA systems. No significant changes in kappa – consistent with the water- soluble model compounds reported in Christensen and Petters (2012) – were observed. We thus focused on the HPLC/CCN experiments. These were performed on designed model systems that allow systematic investigation of the influence of the number and location of particular functional groups on the organic aerosols' kappa value. Organic compounds were synthesized via gas-phase and liquid-phase reactions. Aerosol products from gas-phase reactions were collected on filters, extracted using ethyl acetate, and fractionated by reversed-phase high-performance liquid chromatography using gradient elution with acetonitrile and water. The eluate was atomized, the solvent was removed by evaporation, and the residual aerosol particles were analyzed as a function of retention time using high-resolution scanning flow CCN analysis. Individual organic compounds eluting from the synthesized mixture were identified using thermal desorption particle beam mass spectrometry. These experiments yielded changes in kappa that can be attributed to the addition of one or more hydroxyl, nitrate, carboxyl, aldehyde, hydroperoxide, and methylene functional groups while otherwise maintaining the structure of the organic molecule. Our results show that the addition of hydroxyl and carboxyl groups can significantly increase a particle's kappa value, while the addition of hydroperoxide, nitrate, and methylene groups does not. A snapshot of these results is summarized in Figure 1. A manuscript summarizing the results is currently in preparation.

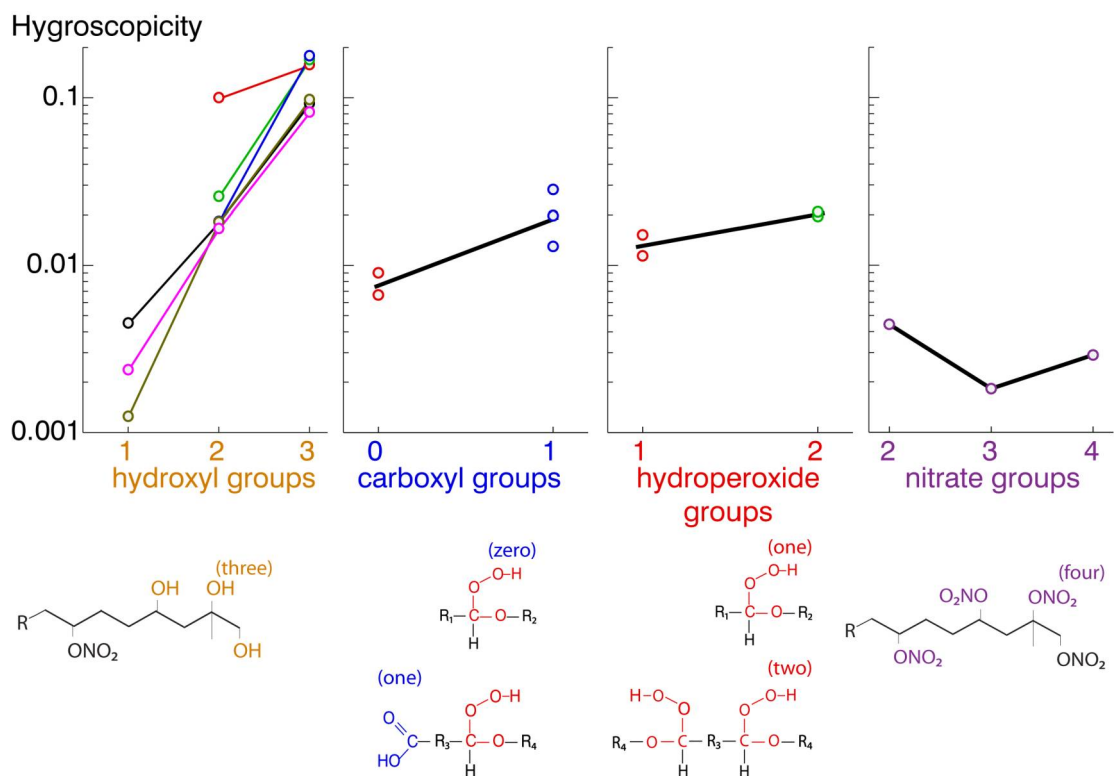


Figure 1. Influence of functional groups on the effective hygroscopicity (parameterized relationship between critical supersaturation and dry diameter). Results are for designed model systems varying carbon number (hydroxyl groups) and location of particular functional group on the carbon backbone of the organic molecule.

3. Functional group analysis, aerosol aging, and ozone reaction studies

In Year 1 the functional group analysis methods developed as part of our previous DOE/ASR project were evaluated and used in a series of environmental chamber studies to quantify the functional group composition of secondary organic aerosol formed over a range of reaction conditions and compositions. These data are necessary for developing parameterizations for relating the functional group composition of organic aerosol to the aerosol hygroscopicity and CCN activity. The methods quantify carbonyl (C=O), hydroxyl (CHOH), carboxyl (C(O)OH), ester (C(O)OR), peroxide (ROOH), and nitrate (CHONO₂) groups, which are the major functional groups expected to be present in organic aerosol. Experiments were conducted for reactions of *n*-pentadecane, a C₁₅ alkane, with OH radicals in the presence and absence of NO_x, O₃, and HNO₃, and with Cl radicals, which react similar to OH radicals but allow for more extensive oxidation. For OH reactions with NO_x carbonyl, hydroxyl, ester, and nitrate functional groups were detected and quantified, with the total average number per C₁₅ secondary organic aerosol molecule ranging from 2–2.5 with higher values from greater OH exposure. For OH reactions without NO_x and without and with HNO₃, carbonyl, hydroxyl, ester, carboxyl, and peroxide functional groups were detected and quantified, with the total average number per C₁₅ secondary organic aerosol molecule ranging from 1.4–2.4, and with the larger values occurring when HNO₃ was added to catalyze heterogeneous reactions that lead to the formation of additional carbonyl, ester, and peroxide groups. For Cl reactions without NO_x carbonyl,

hydroxyl, ester, carboxyl, and peroxide functional groups were detected and quantified, with the total average number per C₁₅ secondary organic aerosol molecule ranging from 2.0–3.5, with higher values for greater CI exposure, including especially large increases in carbonyl and carboxyl groups. These controlled reactions yielded a useful range of compositions and concentrations of functional groups for comparisons with measured aerosol hygroscopicity and CCN activity. The development of the functional group analysis methods and the applications described here comprised the PhD thesis work of Sukon Aimanant, who was supported by our DOE/ASR grant during summer months. She graduated from UC Riverside in March 2012. A paper describing the functional group methods and a paper describing the application of these methods to SOA aging have been published in *Aerosol Science & Technology*, and two more are in preparation.

During the last joint intensive study of our previous project conducted at UCR in 2010 we had pursued experimental studies on the 1-alkene + O₃ system followed by reaction of the stabilized Criegee intermediate (SCI) with water, alcohols and aldehydes. In our experiments we systematically varied the carbon chain length as well as SCI reactants. For identical carbon chain length we were able to identify a sorting of kappa-values according to the different functional groups formed during the reaction, with kappa(hydroxyl-hydroxyperoxide) > kappa(alkoxy-hydroxyperoxide) > kappa(peroxyhemiacetal). This identification involved two months of experiments conducted during Year 1 with the CSU reactor, which allowed us to continuously vary the fraction of hydroxyl-to-hydroxyperoxide groups. Combined with our HPLC/CCN analysis to determine the hygroscopicity of individual compounds in the complex organic aerosol (Suda et al., 2012), we were able to further analyze and explore the effect of the presence of water vapor during SOA formation on the resultant SOA kappa values. A manuscript summarizing the results from this system is currently in preparation.

4. Improved HTDMA technique

During Year 2 we further developed the HTDMA technique to be able to better understand the relative influences of water activity and surface tension on the relationship between critical supersaturation and dry diameter. To this end we have designed and implemented a new HTDMA system with improved temperature and RH control. Temperature stability in the second DMA was achieved to $\pm 0.02^\circ\text{C}$ tolerance by implementing active control using thermoelectric heat exchangers and PID control loops. The DMA size resolution was increased by operating high-flow DMA columns at a sheath:sample flow ratio of 15:0.5. This improved size resolution allowed for improving the accuracy of the RH sensors by interspersing ammonium sulfate reference scans at high frequency. We obtained growth factor data for pure compounds at RH up to 99% and compared the data to theoretical values and to available bulk water activity data. With this HTDMA instrument and method, the osmotic coefficients of spherical, non-volatile aerosols of known composition between 30 and 200 nm in diameter can be determined within $\pm 20\%$. We expect that data from this instrument will lead to an improvement of aerosol water content models by contributing to the understanding of aerosol water uptake at high RH. Knowledge of osmotic coefficients near water saturation is needed to better constrain the relative roles of water activity, solubility, and surface tension for CCN activation. This work has been published in the journal *Aerosol Science & Technology*.

5. Understanding the role of surface tension

During Year 2 we also conducted experiments to better constrain the role of surfactants in pure and internally mixed particles on the relationship between critical supersaturation and dry diameter. These studies are needed to build a robust parameterization of hygroscopicity of organic aerosol. During these studies, two foci emerged, which are discussed below.

The role of dynamic surface tension. Dynamic surface tension relates to kinetic limitations of droplets reaching equilibrium surface tension. To test for the potential influence on kinetic limitations we examined the cloud droplet forming abilities of two-component particles that contain the surfactant sodium dodecyl sulfate and sodium chloride or ammonium sulfate. The experiments were designed to test specific predictions made by Köhler theory modified to include the reduction of surface tension and the partitioning of the surfactant between the interior and the surface of the droplet. We also introduced a pre-humidification step followed by a six minute time delay to test whether dynamic surface tension may lead to kinetic limitations on the partitioning process. Our results confirm previous studies that show surfactants do not enhance cloud droplet activation relative to what would be predicted from water activity alone. The data obtained with and without time delay were indistinguishable within measurement uncertainty, suggesting that dynamic surface tension does not need to be considered in Köhler theory. This work has been summarized as extended abstract and will be published by AIP in the conference proceedings of the 19th International Conference on Nucleation & Atmospheric Aerosols.

The effect of solute-solute interactions and surfactants present in internally mixed particles. Application of our proposed parameterization of hygroscopicity of organic aerosol requires extension to internally mixed particles, either organic/organic or organic inorganic. Our initial work (Petters and Kreidenweis, 2007) showed that a linear mixing rule could predict the relationship between critical supersaturation and dry diameter within measurement uncertainties. However, we also pointed out that (1) relative measurement errors were surprisingly large, often exceeding +/-100% for retrieved kappa values (c.f. their Figures 3 and 5) and (2) that surprisingly few data points for internal mixtures are available. To address these issues we placed emphasis on improving our methodology to reduce this error to kappa +/-5% for laboratory studies. We also improved the time resolution of the measurements so we are able to measure the relationship between critical supersaturation and dry diameter in more detail than was previously possible. We are currently applying this technique to internal mixtures of organic/inorganic particles, and organic/organic particles that contain surfactants. Figure 2 illustrates a few examples of the new measurements. A manuscript summarizing the results is currently in preparation.

6. Development of hygroscopicity model framework

During Year 2 we also began work on developing a framework for modeling aerosol hygroscopicity. Our initial approach was to robustly incorporate the observed influences of temperature and surface tension into the model framework.

Surface Tension. To account for the presence of surface active compounds on the relationship between critical supersaturation and dry diameter we extended the single parameter hygroscopicity equations. The revised framework is a hybrid model that accounts for partitioning between the bulk and surface phases in the context of single parameter representations of CCN activity. The presented formulation incorporates analytical approximations of surfactant partitioning to yield a set of equations that maintain the conceptual and mathematical simplicity of the single parameter framework. The resulting set of equations allows users of the single

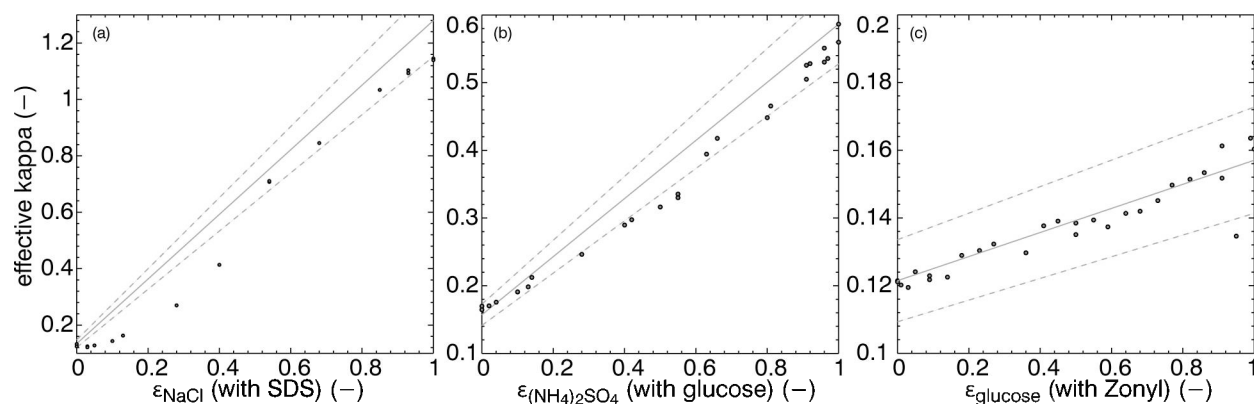


Figure 2. CCN activity of internal mixtures of organic and inorganic compounds. Each point represents a fresh mixture. Dashed lines correspond to $\pm 10\%$ variability around the linear mixing rule (solid line). Measurement accuracy for pure glucose is $\pm 5\%$ within the prediction based on water activity. Combinations are (a) ionic surfactant sodium-dodecyl sulfate and sodium chloride, (b) glucose and ammonium sulfate, (c) glucose with zonyl, a water-soluble nonionic organic and highly potent surfactant.

parameter model to account for surfactant partitioning by applying minor modifications to already existing code. This work is published in *Atmospheric Chemistry and Physics*.

In addition we found that accounting for the temperature dependence of the surface tension of pure water in the theory is required to extend laboratory studies at ambient temperature to cold conditions. Not accounting for this effect may lead to an estimated erroneous indirect forcing of 0.2 W m^{-2} . Fortunately the correction is simple and the appropriate revised equations accounting for temperature are published in Christensen and Petters (2012) and included in the revised framework of Petters and Kreidenweis (2013).

Functional groups. Parameterization of the influence of functional groups is ongoing and a major focus of Year 3 activities. Our main objective is to express $\kappa_{effective} = \sum_i f(MW_i, T, n_{i,j})$ where f is a function that predicts the effective hygroscopicity (the critical supersaturation and dry diameter relationship) of a molecule i that is described by MW_i : molecular weight; T : temperature; and $n_{i,j}$: number of functional groups of type j . Our combined work suggests that the transitions from low-to-high kappa seen are primarily caused by particle phase (e.g. the transition from insoluble to sparingly soluble to sufficiently soluble for CCN activation). This solubility transition is qualitatively captured by the semi-empirical UNIFAC (Universal Functional Group Activity Coefficients) framework, which already underlies important atmospheric thermodynamic models such as E-AIM. Traditionally UNIFAC has been applied over a wide range of water activities and functional group coefficients are not tuned to capture the solubility transition with high accuracy. Towards the development of our parameterization we have implemented a UNIFAC-based testbed that predicts the solubility transition.

Technologies/Techniques Developed

1. Low temperature CCN measurements

We designed and validated a calibrated method with viable temperature control to accurately perform CCN measurements over the temperature range from 0° to 40°C (Christensen and

Petters 2012). This method makes it possible to measure the temperature dependent CCN activity of atmospheric aerosol in order to better understand the temperature dependence of the relationship between critical supersaturation and dry diameter.

2. Improved HTDMA technique

We further developed the HTDMA technique for measuring water uptake by aerosol particles by designing and implementing a new HTDMA system with improved temperature and RH control. This technique makes it possible to better measure the relative influences of water activity and surface tension on the relationship between critical supersaturation and dry diameter.

Other Products, such as Data or Databases, Physical Collections, Audio or Video, Software or Netware, Models, Educational Aid or Curricula, Instruments or Equipment

1. Database of kappa values (hygroscopicity parameters)

As part of our previous DOE/ASR research study that examined the role of molecular size on cloud droplet activation we developed a database that includes kappa values for a broad range of organic compounds. The database was published as a supplement to that study and will be updated with new data obtained in this project.

Publications

Christensen, S. I. and M. D. Petters. The role of temperature in cloud droplet activation. *J. Phys. Chem A* 116, 9706-9717, doi:10.1021/jp3064454 (2012).

Aimanant, S. and P. J. Ziemann. Development of spectrophotometric methods for the analysis of functional groups in oxidized organic aerosol. *Aerosol Sci. Technol.* 47, 581-591 (2013).

Aimanant, S. and P. J. Ziemann. Chemical Mechanisms of Aging of Aerosol Formed from the Reaction of n-Pentadecane with OH Radicals in the Presence of NO_x. *Aerosol Sci. Technol.* 47, 979-990 (2013).

Petters, M. D., S. R. Suda, and S. I. Christensen. The role of dynamic surface tension in cloud droplet activation, AIP Conf. Proc. 1527, pp. 801-807, doi:http://dx.doi.org/10.1063/1.4803393, (2013).

Petters, M. D. and S. M. Kreidenweis. A single parameter representation of hygroscopic growth and cloud condensation nucleus activity - Part 3: Including surfactant partitioning. *Atmos. Chem. Phys.* 13, 1081-1091, doi:10.5194/acp-13-1081-2013 (2013).

Suda, S. R. and M. D. Petters. Accurate determination of aerosol activity coefficients at relative humidities up to 99% using the hygroscopicity tandem differential mobility analyzer technique. *Aerosol Sci. Technol.* 47, 991-1000 (2013).