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Project Title: Laboratory Studies of Processing of Carbonaceous Aerosols by Atmospheric Oxidants/Hygroscopicity and CCN Activity of Secondary & Processed Primary Organic Aerosols

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Executive Summary

The atmosphere is composed of a complex mixture of gases and suspended microscopic aerosol particles. The ability of these particles to take up water (hygroscopicity) and to act as nuclei for cloud droplet formation significantly impacts aerosol light scattering and absorption, and cloud formation, thereby influencing air quality, visibility, and climate in important ways. A substantial, yet poorly characterized component of the atmospheric aerosol is organic matter. Its major sources are direct emissions from combustion processes, which are referred to as primary organic aerosol (POA), or in situ processes in which volatile organic compounds (VOCs) are oxidized in the atmosphere to low volatility reaction products that subsequently condense to form particles that are referred to as secondary organic aerosol (SOA). POA and VOCs are emitted to the atmosphere from both anthropogenic and natural (biogenic) sources.

The overall goal of this experimental research project was to conduct laboratory studies under simulated atmospheric conditions to investigate the effects of the chemical composition of organic aerosol particles on their hygroscopicity and cloud condensation nucleation (CCN) activity, in order to develop quantitative relationships that could be used to more accurately incorporate aerosol-cloud interactions into regional and global atmospheric models. More specifically, the project aimed to determine the products, mechanisms, and rates of chemical reactions involved in the processing of organic aerosol particles by atmospheric oxidants and to investigate the relationships between the chemical composition of organic particles (as represented by molecule sizes and the specific functional groups that are present) and the hygroscopicity and CCN activity of oxidized POA and SOA formed from the oxidation of the major classes of anthropogenic and biogenic VOCs that are emitted to the atmosphere, as well as model hydrocarbons.

The general approach for this project was to carry out reactions of representative anthropogenic and biogenic VOCs and organic particles with ozone (O_3), and hydroxyl (OH), nitrate (NO_3), and chlorine (Cl) radicals, which are the major atmospheric oxidants, under simulated atmospheric conditions in large-volume environmental chambers. A combination of on-line and off-line analytical techniques were used to monitor the chemical and physical properties of the particles including their hygroscopicity and CCN activity. The results of the studies were used to (1) improve scientific understanding of the relationships between the chemical composition of organic particles and their hygroscopicity and CCN activity, (2) develop an improved molecular level theoretical framework for describing these relationships, and (3) establish a large database that is being used to develop parameterizations relating organic aerosol chemical properties and SOA sources to particle hygroscopicity and CCN activity for use in regional and global atmospheric air quality and climate models.

Comparison of Accomplishments with Project Goals and Objectives

The overall goal of this experimental research project was to conduct laboratory studies under simulated atmospheric conditions to investigate the effects of the chemical composition of organic aerosol particles on their hygroscopicity and cloud condensation nucleation (CCN) activity, in order to develop quantitative relationships that could be used to more accurately incorporate aerosol-cloud interactions into regional and global atmospheric models. The specific objectives of the portion of the project titled: “Laboratory Studies of Processing of Carbonaceous Aerosols by Atmospheric Oxidants” were to (1) identify and quantify the products of heterogeneous reactions of OH and NO₃ radicals, and O₃ with aerosol particles composed of selected organic compounds; (2) measure the rates of heterogeneous reactions of OH and NO₃ radicals and O₃ with aerosol particles composed of selected organic compounds; (3) investigate the effects of particle morphology and phase on the reactivity of organic aerosol compounds with OH and NO₃ radicals and O₃; and (4) investigate the effects of oxidation reactions on the hygroscopic properties of organic aerosol particles, whereas the specific objectives of the portion of the project titled: “Hygroscopicity and CCN Activity of Secondary & Processed Primary Organic Aerosols” were to (1) characterize the chemical composition of SOA formed from the oxidation of model hydrocarbons and anthropogenic and biogenic hydrocarbons, (2) evaluate the hygroscopicity and CCN activity of SOA formed from the oxidation of model hydrocarbons, (3) evaluate the hygroscopicity and CCN activity of SOA formed from the oxidation of anthropogenic and biogenic hydrocarbons, and (4) develop parameterizations relating hygroscopicity and CCN activity to organic composition and sources.

The research conducted by the UC Riverside, Colorado State, and North Carolina State research groups during the project period has largely accomplished the original research objectives. The heterogeneous reactions of OH, NO₃, Cl, and O₃ with aerosol particles are now understood to form products that are similar to those formed from gas phase reactions (which have been more thoroughly investigated over decades), with the major differences being the much reduced formation of products of alkoxy radical isomerization and decomposition in particle reactions. The kinetics of the heterogeneous reactions have been well quantified (other research groups have contributed significantly in this area over the duration of this project) and it is now understood that OH and Cl react with all compounds in particles at close to the collision rate, whereas O₃ and NO₃ radicals react predominantly with alkenes, and although they react more slowly than OH and Cl the rates are still sufficiently fast to be of importance in the atmosphere. It is now understood that particle morphology and phase effect the heterogeneous and multiphase reactions of organic aerosol compounds with OH, NO₃, Cl, and O₃, with the major difference being that for solid particles reactions are constrained to occur at the surface and this affects reaction pathways for radical intermediates and thus the reaction products and particle volatilization. It now appears that the heterogeneous oxidation of organic aerosol particles by OH, NO₃, Cl, and O₃ has relatively minor effects on particle hygroscopicity and CCN activity (and the conversion of POA from hydrophobic to hydrophilic), which are instead primarily determined by condensation of organics (SOA) and hydrophilic inorganic compounds such as sulfates and nitrates. Detailed chemical characterization of SOA formed in environmental chamber reactions of OH, Cl, NO₃, and O₃ with anthropogenic, biogenic, and model VOCs, conducted using particle mass spectrometry, chromatographic, and functional group analysis has determined many of the products and functional group compositions (which include mixtures of carbonyl, hydroxyl, carboxyl, peroxide, ester, and nitrate groups) of SOA

systems for comparison with their measured hygroscopicity and CCN activity. This has led to major improvements in understanding of the range of CCN activities of SOA compounds and their relationships to chemical composition. The results have provided an extensive database of hygroscopicity parameters (κ values) extracted from the data using κ -Köhler theory, which was developed by Professors Petters and Kreidenweis during this project and is now the standard form for representing aerosol hygroscopicity. Hygroscopicity parameters are widely used in regional and global models to describe aerosol-cloud interactions.

Summary of Project Activities and Accomplishments

1. Effect of chemical aging on CCN activity of primary organic aerosol

Carbonaceous aerosols comprise a large, sometimes dominant fraction of tropospheric aerosol mass and contribute to both scattering and absorption of solar radiation. However, the representation of emissions, transformations and removal pathways for organic particulate matter continues to be a major uncertainty in understanding many aerosol effects, from human health to global climate. In this study, we focused on primary organic aerosol (POA) emitted from combustion processes. Combustion-derived particles are generally very small (number mode diameters $< 0.1 \mu\text{m}$), and models and observations suggest that wet deposition is the dominant tropospheric sink for carbonaceous aerosol mass. The chemical constituents in POA are generally composed of non-polar high molecular weight hydrocarbons and are hydrophobic, whereas the rate of removal of particles by wet deposition depends strongly on their size and hydrophilicity, which influences their ability to act as cloud condensation nuclei (CCN). It follows that at least some hydrophobic organic particulate matter must be rendered hydrophilic, and thereby capable of being scavenged by cloud droplet nucleation followed by precipitation, during its atmospheric lifetime. Global models generally parameterize the hydrophobic-to-hydrophilic conversion of carbonaceous aerosol as an exponential turnover with an e-folding time of 1–2 days. Pathways for the hydrophobic-to-hydrophilic conversion of POA include condensation of hydrophilic species onto POA, which depends on the availability of condensable material such as sulfuric acid, nitric acid, or oxidized organic species; coagulation of POA with larger, more hydrophilic background particles; and “chemical aging”, which refers to oxidation reactions occurring on the surface or in the interior of POA particles.

In this study we performed laboratory experiments aimed at estimating time scales for hydrophobic-to-hydrophilic conversion due to heterogeneous chemical aging by the addition of functional groups to the condensed-phase carbon backbone using single-component particles composed of model, hydrophobic POA constituents: diethylhexyl sebacate (DEHS), oleic acid, and linoleic acid. DEHS is a C_{28} diester and oleic and linoleic acid are C_{18} monocarboxylic acids with one and two double bonds, respectively. The carbon number of these compounds is within the range typically found in primary particles. For both real and model POA, the chemical aging process corresponds to the conversion of hydrophobic CH_x units to hydrophilic oxygenated functional groups through oxidation reactions. In our experiments, carbonyl, hydroxy, nitrate, and carboxyl groups are added to the particles through controlled reactions with OH and NO_3 radicals. These functional groups are the primary ones expected for aged POA. The composition and hydrophilicity of the model particles are related to aged POA by estimating the time it would take atmospheric particles to add the same number of functional groups per carbon atom via known kinetics of atmospheric oxidation reactions. Chemical aging reactions were conducted in

a 7000 L Teflon environmental chamber by reacting aerosol with OH radicals formed by photolysis of methyl nitrite in the presence of NO_x and with NO_3 radicals formed by thermal decomposition of N_2O_5 . Particle chemical composition was monitored in real time using a thermal desorption particle beam mass spectrometer and unreacted and reacted particles were analyzed in a CCN counter to determine the relationships between dry particle diameter and the critical water vapor supersaturation required to activate the particle to a cloud droplet. Experimental results for CCN activity were parameterized using a single parameter, κ . The parameter κ provides a comparative measure of CCN activity, with larger values of κ correspond to increased CCN activities, with values ranging from $\kappa \sim 1$ for highly active inorganic compounds such as sodium chloride, to $\kappa = 0$ for non-hygroscopic but wettable species.

The chemical aging simulated in our laboratory experiments results in a measurable increase in CCN activity from $\kappa \sim 0$ to $\kappa \leq 0.01$. We therefore consider $\kappa = 0.01$ as an upper limit to what can likely be achieved in ~ 1 week of atmospheric chemical aging of POA occurring in the condensed phase. The experimental results show that initially hydrophobic POA particles measurably increase their CCN activity through chemical aging on reasonably short timescales. In order to determine if this increase is sufficient to enhance POA wet scavenging rates, indicating that chemical aging is their most important tropospheric hydrophobic-to-hydrophilic conversion pathway, we conducted model simulations of activation of particles in cloud updrafts to determine conditions for which a significant fraction of POA is incorporated into cloud water. The POA hydrophilicity (as represented by κ) and accumulation mode number concentration inputs captured conditions ranging from very clean background with only POA present to very polluted air. Based on these simulations we conclude that the typical increase in hydrophilicity due to chemical aging (as determined from our laboratory experiments) is insufficient to lead to efficient wet scavenging for sub-100 nm particles that are typically emitted from combustion sources. The absence of an efficient atmospheric oxidation pathway for hydrophobic-to-hydrophilic conversion suggests that the fate of carbonaceous aerosol is instead controlled by its interaction with more hydrophilic species such as sulfates, nitrates, and secondary organic aerosol, leading to longer lifetimes, higher burdens, and greater contributions to climate forcing in the free troposphere than are currently estimated. Future experiments should be conducted, however, to ensure that the degree, nature, and extent of organic oxidation in our experiments are fully representative of the atmosphere. These results were published in *Geophysical Research Letters*. As a result of this study and our conclusion that oxidative processing of POA was not an important process for converting low-volatility POA from hydrophobic to hydrophilic particles, we decided to direct more of our attention to measurements of the hygroscopicity and CCN activity of SOA particles, although we continued with studies of the composition of oxidized POA as an aid in interpreting results of chamber experiments.

2. Hygroscopicity and CCN activity of secondary organic aerosol

Atmospheric aerosols play an important role in the Earth's radiation budget. The direct effect derives from the light scattering and absorption properties of the particles themselves, whereas indirect effects arise from the ways in which aerosols affect the microphysical and radiative properties of the clouds they nucleate, including enhancements in cloud reflectivity and suppression of drizzle, or cloud formation. Organic moieties are commonly found in ambient aerosol, often accounting for 20–50% of fine particle mass over the continental mid-latitudes and up to 90% in tropical forests. POA is emitted directly in the condensed phase, while secondary

organic aerosol (SOA) forms when volatile organic compounds (VOCs) emitted from natural biogenic and anthropogenic sources are oxidized in the atmosphere to form highly oxygenated, lower vapor pressure products which partition into the particle phase. Although biogenic sources dominate global SOA formation, anthropogenic sources such as gasoline may dominate in more polluted areas. Numerous studies have explored the cloud condensation nuclei (CCN) activity of pure organic compounds, and a few have also investigated aerosol-water interactions of SOA formed under controlled conditions in an environmental chamber, which represent a step closer to ambient compositions. In this study we extended this work by simultaneously measuring water uptake below water saturation and CCN activation above water saturation from SOA generated in an environmental chamber. The SOA studied is formed from the oxidation of three monoterpenes that represent ~60% of estimated global monoterpene emissions, and toluene, a major component of vehicle emissions that is used here as a proxy for anthropogenic SOA.

SOA-forming reactions were conducted in a 7000 L Teflon environmental chamber by reacting monoterpenes with O₃ and toluene with OH radicals formed by photolysis of methyl nitrite in the presence of NO_x. SOA chemical composition was monitored in real time using a thermal desorption particle beam mass spectrometer, hygroscopic growth factors were measured using a humidified tandem differential mobility analyzer (HTDMA), and a CCN counter was used to determine the relationships between dry particle diameter and the critical water vapor supersaturation required to activate the particle to a cloud droplet. Experimental results for CCN activity were parameterized using a single parameter, κ . The parameter κ provides a comparative measure of CCN activity, with larger values of κ correspond to increased CCN activities, with values ranging from $\kappa \sim 1$ for highly active inorganic compounds such as sodium chloride, to $\kappa = 0$ for non-hygroscopic but wettable species. Results were also interpreted using a simulations conducted with a cloud parcel model. The main result from our study was the observation that the CCN activity of fresh SOA from low-molecular weight precursors could be modeled as $\kappa \sim 0.1$. This result that has now (2012) been shown to hold over a broad range of generation methods for the precursor α -pinene and thus has helped to better constrain its effect in global models.

Measured CCN activation was comparable for all of the types of SOA studied and occurred at humidity conditions that are readily attained in the atmosphere. Further, there was little variation in hygroscopic growth between SOA types. However, measured droplet activation conditions were inconsistent with hygroscopicity measured below water saturation and Köhler theory expressions based on Raoult's Law for several parameterizations for water activity. In the atmosphere, SOA may comprise a large fraction of atmospheric particulate matter and will often exist internally mixed with inorganic species. Using the results from this study we compared SOA to insoluble organic species to calculate CCN activation from mixed organic-sulfate particles for a range of atmospheric conditions. We find that droplet activation behavior of mixed particles containing SOA is the same as that of mixed particles for which the organic component is non-hygroscopic, except for cases in which there are low particle concentrations, low updraft velocities, and the aerosol composition is dominated by organics. The results of this study were published in *Journal of Geophysical Research*.

3. Measuring the critical diameter of CCN using mobility selected aerosol

Large uncertainties about the effect of carbonaceous and other types of particles on cloud microphysical properties have spawned intensive research on their ability to act as cloud

condensation nuclei (CCN). For example, several research groups have measured the critical diameter that must be exceeded before organic particles can serve as CCN when exposed to a fixed supersaturation inside a CCN instrument. In these activation experiments, a polydispersion of particles is charge equilibrated and made quasi-monodisperse in a differential mobility analyzer (DMA). Then the flow containing the quasi-monodisperse particle distribution is split, with equal concentrations being sent to a CCN counter sampling at fixed supersaturation and a condensation particle counter (CPC). For each mobility-selected size, the ratio of CCN to CPC concentration defines the so-called CCN active fraction. The diameter where 50% of the particles are CCN active (D_{50}) is generally interpreted as the critical dry diameter. Sometimes the critical diameter is defined as the *wet* critical diameter, i.e. the equilibrium diameter at the critical supersaturation. Here we define the critical diameter as the minimum *dry* diameter required for CCN activation at a specified supersaturation. Although most studies recognize the presence of multiply-charged particles, they do not quantitatively account for their contribution in determining D_{50} . Here we introduce a model that describes the transfer of polydisperse charge-equilibrated particles through an ideal DMA, followed by transit through an ideal CCN counter (CCNc). If the particles are internally mixed, have identical composition and surface tension is not a function of particle size, then Köhler theory predicts that all particles larger than D_c activate if the environmental supersaturation is held constant. In this work, we assume this idealized behavior for a quasi-monodisperse population, size selected for a single mobility diameter using a DMA. We also account for the presence of larger, multiply-charged particles when calculating the CCN active fraction. Repeating the calculation for several mobility-selected diameters produces the calculated CCNc response curve. These analyses were conducted on oxidized organic aerosol particles generated in an environmental chamber through reactions of dioctyl sebacate particles with OH radicals.

The model calculations demonstrate that multiply-charged particles may lead to a bias in estimation of the critical dry diameter and to nonmonotonic CCNc response when D_c is less than the mode diameter of the polydisperse size distribution. In addition, the model was used to determine the critical diameter of measured activation spectra that were evidently ‘contaminated’ with multiply-charged particles. We show that if the mode diameter of the polydisperse size distribution exceeds the critical diameter of the particles, multiply-charged particles may lead to nonmonotonic CCN counter response curves (plots of CCN-active fraction vs. mobility diameter) that exhibit multiple peaks, rather than a simple sigmoidally-shaped curve. Hence, determination of the 50% activation diameter is ambiguous. Multiply-charged particles significantly skew the CCNc response curves when sampling particles with critical diameters exceeding $0.1 \mu\text{m}$ from particle size distributions with mode diameters also larger than the critical diameter. Nonetheless, using the method for inversion of CCN counter data presented here, which takes multiple-charging effects into account, we demonstrate that our calculated CCN counter response curves are in good agreement with observations and can be used to infer the critical activation diameter for a specified supersaturation. The results of this study were published in *Aerosol Science and Technology*. Most CCN studies now recognize the importance of applying a multiple charge correction to properly interpret the results. We therefore believe that this study aided in reducing the uncertainty of CCN measurements, and thus indirectly of models that rely on laboratory and field data to initialize the simulations.

4. Role of molecular size in cloud droplet activation

Many organic compounds are water-soluble and therefore contribute to the hygroscopicity of the atmospheric aerosol, which in turn influences the ability of individual particles to serve as cloud condensation nuclei (CCN). By altering number and chemical composition of CCN populations, organic compounds also indirectly affect cloud droplet number concentrations and precipitation intensity, and in turn modify the Earth's radiation budget. It has been estimated that the organic aerosol indirect effect contributes $\sim -1 \text{ W m}^{-2} \text{ Tg}^{-1}$ cooling at the top of the atmosphere. This estimate is highly uncertain, however, because most of the organic aerosol has not been well characterized, making it difficult to assess the ability of organic aerosols to serve as CCN. The relationship between pure organic and inorganic compound properties and the water supersaturation that must be exceeded before a particle of known size activates as a CCN can be described using Köhler theory. The resulting relationship between the particle dry diameter and critical supersaturation depends on the dry particle chemical composition and indicates the efficiency with which a particle can serve as CCN in the atmosphere. More efficient CCN are those particles that activate at lower supersaturation when compared to another particle of equal diameter. In this framework, Raoult's law is commonly used to relate particle composition to water activity, in which case the chemical properties that determine the CCN efficiency are the molecular weight and density of the solute, the surface tension of the dilute aqueous solution and the ability of the compound to dissociate in solution. Raoult's law is not applicable to systems where solute molecules are much larger than solvent molecules, however, in which case Flory-Huggins theory is expected to be more appropriate. In this study we examined the observed relationships between molar volume (the ratio of molecular weight to density) and CCN activity for sufficiently soluble organic compounds found in atmospheric particulate matter and evaluated the validity of Raoult's law and Flory-Huggins theory in this modeling framework.

The data compilation employed in this study included our new CCN data for certain carbohydrates and oligoethylene glycols, as well as published data for organic acids, carbohydrates, synthetic oligomers, Suwanee river fulvic acid, and humic-like substances. We compared predictions of CCN activity using water activities based on Raoult's law and Flory-Huggins theory to observations. The results indicate that sufficiently soluble compounds with molar volumes exceeding $200 \text{ cm}^3 \text{ mole}^{-1}$ are more CCN active than anticipated by Raoult's law. The Flory-Huggins water activity expression, with an assumed surface tension of pure water, generally predicts CCN activity within a factor of two over the full range of molar volumes considered. CCN activity is only weakly dependent on molar volume for values exceeding $600 \text{ cm}^3 \text{ mole}^{-1}$, and the diminishing sensitivity to molar volume, combined with the significant scatter in the data, limits the accuracy with which molar volume can be inferred from CCN measurements. The results of this study were published in *Geophysical Research Letters*.

5. Heterogeneous ice nucleation of secondary organic aerosol

Although atmospheric aerosol effects on climate are typically considered in terms of their direct effect and indirect effects on liquid clouds, there is also a postulated indirect effect due to glaciation, in which changes in the number of particles that nucleate ice can alter precipitation and impact the radiative properties of clouds. Ice formation in the atmosphere occurs via homogeneous freezing involving aerosol with hygroscopic components, heterogeneous ice nucleation processes involving certain insoluble particles, and secondary processes initiated by pre-existing ice particles. At temperatures warmer than $-36 \text{ }^\circ\text{C}$, primary ice formation can only

occur by heterogeneous nucleation on some insoluble aerosol component, termed an ice nucleus (IN). Only a tiny fraction of particles serve as IN in the atmosphere, typically on the order of 1 in 100, although IN number concentrations can vary dramatically both spatially and temporally. Metal oxides and dust generally make up the largest percentage of heterogeneous IN by number. Contributions from soot and organic species have also been reported, with carbonaceous particles making up a significant fraction of ambient IN. However, organic compounds also have been shown to be anti-correlated with ice formation in atmospheric clouds presumably influenced by heterogeneous ice nucleation, and laboratory studies at cirrus temperatures have shown that condensation of secondary organic aerosol (SOA) from ozonolysis of α -pinene onto dust particles degrades their ice nucleation efficiency. Taken together, these data suggest that the composition of the carbonaceous material plays a critical role in determining the ability of particles to serve as IN. Although primary biological particles have been considered as potential ice nuclei, the ice nucleating ability of pure SOA has yet to be explored. The ability of organic compounds to promote ice nucleation is tied, in part, to the number and quality of functional groups, although the net impact of increasing functional groups on organic compounds is not known. In this study, we explored, for the first time, the ability of SOA formed from the oxidation of alkenes with ozone to serve as an IN at $-30\text{ }^{\circ}\text{C}$ and also investigated the effect of adding iodine vapor to the reaction mixture.

SOA-forming reactions were conducted in a 1000 L Teflon environmental chamber by reacting monoterpenes, sesquiterpenes, cyclic alkenes, substituted cyclic alkenes and linear alkenes with O_3 . Ozonolysis of these compounds leads to an array of multifunctional products containing various combinations of carbonyl, hydroxyl, carboxyl, hydroxperoxy, and peroxy groups. In addition, aerosol was formed from photolysis of diodomethane in the presence of O_3 to examine the potential IN activity of the resulting iodine oxides. A continuous flow diffusion chamber (CFDC) was used to characterize the ice nucleating characteristics of the aerosol particles. The CFDC permits observation of ice formation on a continuous stream of aerosol particles at controlled temperature and humidity. The CFDC is sensitive to deposition nucleation and condensation and immersion freezing. Contact freezing is not measured, but laboratory studies suggest that contact nucleation typically occurs at temperatures $4\text{--}5\text{ }^{\circ}\text{C}$ warmer than immersion freezing. For this study, the aerosol was exposed to $-30\text{ }^{\circ}\text{C}$ and water supersaturation. At these conditions, most IN which can impact ice formation in mixed-phase clouds are expected to nucleate.

For all of the systems studied, measured IN counts were mostly equal to or less than the measured background counts, and for cases in which sample counts exceeded background counts, signal-to-noise did not exceed unity and the maximum signal was 1 IN per 100 SOA particles. Such low values fall well within the noise of the measurements, and we conclude that none of the systems studied generated measureable concentrations of IN. This includes measurements on particles formed by photolysis of diodomethane in the presence of O_3 , a source of new particle formation in coastal areas, and ozonolysis of cyclopentene in the presence of iodine vapor. These data suggest that SOA formed by the ozonolysis of alkenes is unlikely to participate in heterogeneous ice nucleation in the atmosphere. The composition of SOA formed from other organic precursors and oxidants and in the presence of species such as NO_x are expected to differ significantly from the particles described here, however, and may exhibit different ice nucleation behavior. To our knowledge these are the first direct measurements of the ice nucleating ability of pure SOA particles. The results of this study were published in *Geophysical Research Letters*.

6. Hygroscopicity frequency distributions of secondary organic aerosols

Secondary organic aerosol (SOA) formed from the gas-phase oxidation of volatile organic compounds (VOCs) changes the distribution of particles that serve as cloud condensation nuclei (CCN) at prescribed supersaturations. This leads to indirect modification of cloud and precipitation spectra, which feeds back on the Earth's radiation budget and hydrological cycle. To better characterize these effects, a large number of studies have measured the CCN efficiency of some of the classes of compounds identified in ambient organic aerosol as well as SOA generated inside environmental chambers using a diverse assortment of VOCs and oxidants. One way to parameterize the results from these studies is to report the hygroscopicity parameter κ , which allows comparisons of CCN efficiency for different compounds or mixtures. Remarkably, the κ -values for SOA derived from the oxidation of isoprene, monoterpenes, and toluene, compounds representative of most of the major VOC classes, fall within the narrow envelope $\kappa = 0.1 \pm 0.04$, with SOA formation conditions appearing to exert only minor influences on the observed κ -values. Similarly, measurements also indicate that κ is near 0.1 for the organic fraction of ambient aerosol. These results are surprising, since SOA formed from VOC reactions is composed of many compounds with a large variety of structures and different H:C and O:C ratios and combinations of functional groups such as carbonyl, hydroxyl, carboxyl, hydroperoxy, and ester, and thus should have a large range of κ -values. In this study we attempted to determine why SOA composition appears to have such a minor effect on the κ -values of these complex SOA mixtures by measuring the κ -values of the fractionated components of these mixtures obtained using a new method we recently developed.

SOA was generated in a 1700 or 5900 L Teflon environmental chamber from reactions performed with a suite of VOCs and oxidants that were selected to result in a wide variety of chemical compositions and κ -values. The VOC-oxidant reactions included simple linear and cyclic alkenes with O_3 , linear and cyclic alkenes with NO_3 radicals generated by thermal decomposition of N_2O_5 , aromatics with OH radicals generated by photolysis of methyl nitrite in the presence of NO_x , and alkanes with Cl atoms generated by photolysis of Cl_2 or OH radicals generated by the reaction of tetramethylethene with O_3 in the absence of NO_x . Filter samples of SOA from the chamber experiments were extracted in ethyl acetate and fractionated by high performance liquid chromatography using gradient elution with acetonitrile and water. With this method, compounds elute from the column in the order of decreasing polarity. Eluate from the column was atomized to create an aerosol, the solvent was evaporated, and the resulting dried aerosol was then analyzed by high-resolution scanning flow CCN analysis to determine κ -values of mixture components.

The observed distributions of κ values reveal that the investigated SOA comprises a diverse array of products with hygroscopicities in the range $\sim 0 < \kappa < \sim 0.4$, with some product κ -values below the measurement envelope. Some SOA systems are composed of a few products with distinct κ -values while others exhibit a broad spectrum of component κ -values. For two selected systems we show that the distribution of SOA κ -values is consistent with current mechanistic understanding of SOA formation. Our results show that the distributions of constituent κ -values vary widely over a range of SOA systems. This is consistent with the range of chemical mechanisms and products that govern the formation of SOA from the different VOC and oxidant combinations. Most distributions are broad and consist of a continuum of κ -values rather than a pseudo-binary mixture of water-soluble and water-insoluble ($\kappa = 0$) compounds.

However, the CCN activity of the chamber SOA is less varied because of the averaging effect of the mixture. We demonstrate that SOA κ -values can be reconstructed from those of the constituents resolved by the HPLC separation. For the 24 systems studied here, the reconstructed κ -values agreed well with the SOA κ -values measured by direct sampling and analysis of chamber SOA ($R^2 = 0.66$, $n = 24$). Because SOA comprises many compounds with a broad spectrum of κ -values, and because the κ of the SOA is a volume-weighted average of these values, it is reasonable that SOAs formed from the reactions of hundreds of VOCs with OH radicals, O₃, and NO₃ radicals have relatively smaller variability in their net κ -value despite the different sources and compositions. The HPLC method separates compounds according to the polarity of the molecules, with less polar products eluting at later times. As expected, we found that κ -values decreased with increasing retention time and thus with decreasing polarity. However, the retention time did not unambiguously determine the κ -value, showing ~ 1 order of magnitude spread for any given retention time. Nevertheless, the relationship between a compound's κ -value and its polarity suggests that a relationship may exist between a compound's κ -value and its functional group composition and carbon number, which determine a compound's polarity. The resultant κ distributions are also useful for exploring mechanisms that relate changes in κ to chemical reactions such as chemical aging, as we demonstrated by contrasting different oxidation stages of SOA generated from the oxidation of *n*-decane and *n*-pentadecane. Future applications of this method could effectively combine modeling and chamber experiments to improve our understanding of the chemical mechanisms underlying the formation and evolution of organic aerosol composition and properties. The results of this study were published in *Journal of Geophysical Research*.

7. Development and application of functional group analysis methods

As part of this project a graduate student in the Ziemann group, Sukon Aimant, developed methods for functional group analysis and applied them to a variety of types of SOA that are of interest to this project. This research constituted the basis for her Ph.D. thesis, which she earned in 2012. Her research was supported by a fellowship from the Government of Thailand with supplemental summer support by this grant. These methods are being used on our current DOE-funded research on the relationship between organic aerosol composition and CCN activity.

Spectrophotometric methods were developed to quantify the concentrations of carbonyl, hydroxyl, carboxyl, and ester groups in collected samples of atmospheric organic matter. The methods employ derivatizing agents to convert each functional group to a characteristic colored derivative that is then quantified by measuring the absorbance using spectrophotometry. The effects of molecular structure on quantification have been evaluated by measuring calibration curves for a large variety of monofunctional and multifunctional compounds, and potential interferences from other compounds containing non-target functional groups have been determined and methods developed to eliminate these interferences. This means, for example, that under the conditions of these analyses carboxylic acids and alcohols do not form esters and esters do not hydrolyze to carboxylic acids and alcohols. Furthermore, formation of hemiacetals and peroxyhemiacetals by the reversible reactions of alcohols and hydroperoxides with carbonyls does not affect the quantification of any of these functional groups. For analysis of samples containing compounds with known structures, appropriate calibration curves can be prepared, whereas for samples containing unidentified compounds use of a simple monofunctional carboxylic acid, ketone or aldehyde, ester, and alcohol should give results that are within $\sim 30\%$

(and often much less) of the correct value, and at worst ~50%. Detection limits are approximately 0.01, 0.02, 0.03, and 0.1 μ moles for carbonyl, hydroxyl, carboxyl, and ester groups. A complete set of duplicate analyses (including peroxide and nitrate analysis by methods we developed previously) requires ~1 mg of sample and takes ~3 days, although additional samples can be analyzed in parallel. A manuscript describing this work will soon be submitted to *Aerosol Science and Technology*.

The functional group analysis methods were used to investigate the chemical composition of SOA formed in a 8300 L Teflon environmental chamber from the reaction of *n*-pentadecane with OH radicals in the presence and absence of NO_x and with Cl atoms in the absence of NO_x. OH radicals were generated in the presence of NO_x by photolysis of methyl nitrite, they were generated in the absence of NO_x by the reaction of tetramethylethene with O₃, and Cl atoms were generated by photolysis of Cl₂. Filter samples of SOA from the chamber experiments were extracted in ethyl acetate and analyzed using the functional group methods. SOA formed from reactions of OH radicals in the presence of NO_x contained carbonyl, hydroxyl, and nitrate groups from alkyl nitrates, hydroxynitrates, and hydroxycarbonyls, as well as ester and peroxide groups associated with carbonylestere and acyl peroxyxynitrate esters. SOA formed from the reactions of OH radicals in the absence of NO_x but in the presence and absence of O₃ and HNO₃ contained carbonyl, hydroxyl, peroxide, and carboxyl groups, and ester groups were also present in reactions with HNO₃. The major SOA products appear to be ketones, alcohols, and hydroperoxides as well as multifunctional cyclic hemiacetals, carboxylic acids, and esters that also contain carbonyl and hydroxyl groups. SOA formed from the reactions of Cl atoms in the absence of NO_x contained carbonyl, hydroxyl, peroxide, carboxyl, peroxyxycarboxyl, and ester groups associated with products similar to those formed from OH radical-initiated reactions. At high Cl exposures the average number of functional groups per molecule increased significantly, to ~3–4 for the conditions of these experiments. The results of all functional group analysis were also in good agreement with the results of elemental CHON analysis. These results demonstrate the value of these functional group analysis methods for SOA studies and lend additional support for the currently accepted mechanisms of SOA formation from reactions of alkanes with OH radicals and Cl atoms in the absence and presence of NO_x. A number of manuscripts describing these results are currently in preparation.

We have also used these methods as part of a continuing investigation to quantify the kinetics and products of reactions of NO₃ radicals with oleic acid aerosol particles, which is an excellent model system for understanding the role of heterogeneous oxidation in altering aerosol hygroscopicity, CCN activity, and particle lifetimes. The results show that self-reactions of peroxy radical intermediates formed by addition of NO₃ radicals to the oleic acid double bond form a pair of hydroxynitrate and carbonylnitrate products in equal amounts, and that these compounds then undergo multiphase reactions to form hemiacetals and acetals. Only about 2% of the peroxy radical self-reactions form alkoxy radicals, which then decompose to form a pair of products, one of which is volatile and evaporates to the gas phase. This result indicates that volatilization of particles via the formation and decomposition of alkoxy radicals occurs through surface peroxy radical self-reactions and not from those that occur in the bulk. This result provides a simple mechanism for describing aerosol heterogeneous/multiphase chemistry and the effect of particle phase, and strongly constrains the extent to which heterogeneous oxidation can lead to particle volatilization and thus impact particle lifetimes. A manuscript describing these results is currently in preparation for submission to *Journal of Physical Chemistry A*.

Technologies/Techniques Developed

1. Multiple charge correction for improving CCN activity

Our study dedicated to measuring the critical diameter of CCN using mobility selected aerosol (Petters et al., 2007) introduced a method to invert CCN data to correct them for potential artifacts introduced by using a differential mobility analyzer as part of the setup. This technique has been developed further (Petters, M. D., C. M. Carrico, S. M. Kreidenweis, A. J. Prenni, P. J. DeMott, J. L. Collett Jr., and H. Moosmüller (2009), Cloud condensation nucleation activity of biomass burning aerosol, *J. Geophys. Res.*, 114, D22205, doi:10.1029/2009JD012353.) and this or similar techniques are now widely used by the community to invert CCN data.

2. HPLC-CCN for interrogating the CCN activity of components in organic mixtures

Our recent study showing hygroscopicity frequency distributions of secondary organic aerosol (Suda et al., 2012) introduced a new technique that coupled reverse phase high performance liquid chromatography (HPLC) with scanning flow CCN analysis. This technique allows for fractionation of complex samples and thus the measurement of the kappa value of compounds in mixtures that would be very difficult if not impossible to obtain using previously available techniques.

3. Functional group analysis

During this project we developed a suite of derivatization-spectrophotometric methods for measuring carbonyl, hydroxyl, carboxyl, and ester functional groups, which we have employed with methods we developed previously for peroxide and nitrate analysis to characterize SOA and POA composition. These methods are being used in our ongoing DOE-funded research to determine relationships between organic aerosol composition and CCN activity and are likely to be of considerable interest to the aerosol community because they provide more quantitative results than Fourier transform infrared spectroscopy (the most widely used method) and require less sophisticated equipment.

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 study that examined the role of molecular size on cloud droplet activation (Petters et al., 2009) we developed a database that includes kappa values for a broad range of organic compounds. This database has been published as a supplement to that study and will be updated as new data become available.

Publications

Petters, M. D., A. J. Prenni, S. M. Kreidenweis, P. J. DeMott, A. Matsunaga, Y. B. Lim, and P. J. Ziemann. Chemical aging and the hydrophobic-to-hydrophilic conversion of carbonaceous aerosol, *Geophys. Res. Lett.* **33**, L24806, doi:10.1029/2006GL027249 (2006).

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