Final Report: "Collaborative Project: Understanding the Chemical Processes That Affect Growth Rates of Freshly Nucleated Particles"

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Overview of achievements.

Our proposal for this project identified the following objectives. Our accomplishments are summarized along with the enumerated objectives.

Experimental Research

1) **We will carry out atmospheric observations of processes responsible for the growth of freshly nucleated particles at the Southern Great Plains (SGP) site. Included will be measurements of size distributions down to 1 nm, composition of freshly nucleated nanoparticles in the 8-50 nm size range, hygroscopicity and volatility of the freshly nucleated particles, and measurements of gas-phase precursors including amines, organic acids, and sulfuric acid.**

The SGP New Particle Formation Study (NPFS) took place on 13 April 2013 through 25 May 2013 at the DOE Southern Great Plains site and surrounding area. The foci of this study were the formation and evolution of atmospheric aerosols and the impacts of these newly formed aerosols on cloud processes. Data from the campaign have been finalized and are available, along with the final report, to the public on the DOE server (https://www.arm.gov/campaigns/sgp2013npfs). Observations from NPFS have created our best data set, to date, for understanding the species and mechanisms responsible for these frequent new particle formation events. A manuscript that integrates measurements and models from NPFS is in preparation and will be submitted to Atmospheric Chemistry and Physics Discussions during the next 2 months.

A proposed mechanism for nucleation arising from chemical reactions of sulfuric acid with various basic gases (ammonia, monoamines) is described by [1]. Subsequent laboratory research supported by NSF allowed us to understand more quantitatively the roles of ammonia and three monoamines (methylamine, dimethyl amine and trimethyl amine) at stabilizing sulfuric acid dimer [2]. Our DOE-supported measurements at SGP provided evidence for elevated concentrations of diamines, a new class of chemicals that has not been considered in studies of new particle formation. Based on these observations we returned to the laboratory to compare the stabilizing effects of three diamines and two monoamines: ethylene diamine (EDA, C2H4(NH2)2), tetramethylethylene diamine (TMEDA, ((CH3)2NCH2CH2N(CH3)2), and butanediamine (or putrescine, Put, (CH2)4(NH2)2), DMA ((CH3)2NH), and methylamine (MA, CH3NH) [3]. In all cases, the diamines were more potent nucleating agents. We hypothesis this is because diamine molecules have two amino groups that can each react with a sulfuric acid molecule, while monoamines have only one. We believe this is an important discovery.

In addition to the New Particle Formation Study, we collaborated with many other research groups to perform field measurements of new particle formation [4-6], and the impacts of newly formed particles on clouds and climate [7, 8]. This collaborative work will improve model representations of new particle formation events.

2) **We will carry out laboratory research aimed at understanding the relationship between nanoparticle growth rates and the concentrations of gas-phase precursors. These studies will be motivated by the atmospheric observations. Our first objective will be to**

understand the processes by which organic salts formed by reactions of organic acids (e.g., formic or acetic acid) and bases (e.g., methylamine, dimethylamine or trimethylamine) are taken up onto preexisting particles of known size.

A laboratory study of new particle formation and growth from reactions of biogenic VOCs with nitrate radical was carried out at the NCAR bioaerosol chamber during fall 2011 [9]. Results include: (1) measurements of aerosol yield from nitrate radical + BVOC chemistry for an important group of monoterpenes, including alpha and beta-pinene, delta-carene, limonene, and the sesquiterpene beta-caryophyllene; (2) direct measurements of the composition of growing nanoparticles, by TDCIMS; and (3) gas phase measurements of important oxidized VOCs and organonitrate compounds.

We collaborated with the University of Eastern Finland to study the impacts of secondary organic vapor condensation onto dust particles on the CCN activity of those particles [10]. We showed that secondary organic vapors can actually increase the hygroscopicity of dust.

Data Interpretation (applicable to both ambient and laboratory studies)

3) **From measurements of mobility distributions during new particle formation we will determine particle growth rates down to 1 nm. Measurements of growth rates of particles larger than ~5 nm have been possible for more than a decade, and we will continue to measure growth rates in that size range. However, measurements below 3 nm are new. The information on sub-3 nm growth rates promise to provide new information on the chemical processes responsible for growth at the earliest stages, when particle composition is easier to model than for larger particles that are inevitably more chemically complex.**

We developed a new approach for determining size-and time-resolved growth rates of freshly nucleated particles in the 1-3 nm range and applied it to measurements carried out in Atlanta (2009) with support from an earlier DOE Grant [11]. These analyses show clearly that in Atlanta, growth rates increased with increasing size in the 1-3 nm range. It was also our intent to apply this methodology to our 2013 SGP measurements. However, while clear evidence for extensive recent nucleation was observed at SGP, our measurements suggested that in most cases nucleation may have been occurring aloft rather than at ground level. Unlike our measurements in Atlanta where elevated concentrations of 1-2 nm particles were routinely evident, such particles were typically not observed at SGP. Therefore, we did not apply Dr. Chongai Kuang's analysis methods to the SGP data. Our observations at SGP reveal the need to study the dependence of nucleation and growth kinetics on altitude.

We also completed a laboratory study on bipolar charging. Bipolar charging is used to produce known charge distributions when aerosols are measured with Scanning Mobility Particle Spectrometers (SMPS) [12]. SMPS instrument systems are the instruments of choice for measuring size distributions from ~1 μm down to ~1 nm. During our measurements at SGP, we used three SMPS instrument systems: a conventional SMPS (we refer to it as the RSMPS; 23-528 nm); the Nano-SMPS (NSMPS; 2.8-47 nm) and the DEG SMPS [13] (1.9-13.9 nm). (Our RSMPS and NSMPS measurement methods are described by [14].) We carried out laboratory measurements aimed at understanding the ion source type, activity, and age, the neutralizer design, and aerosol flow rates [15]. This study provided information that allows us to better understand measurement uncertainties.

4) **We will look for dependencies of measured growth rates on measured concentrations of gas-phase precursors to determine empirical information on processes that contribute to growth.**

A study of the chemical composition of size-selected biogenic nanoparticles in the size range from 10 to 40 nm has been carried out. Particles were formed in a flow tube reactor by ozonolysis of alpha-pinene and analyzed with a Thermal Desorption Chemical Ionization Mass Spectrometer. While we found similar composition in 10 and 20 nm particles, the relative amounts of individual species varied significantly when compared to 40 nm particles. Smaller particles (10 and 20 nm) were characterized by enhancements in carboxylic acids and larger particles (40 nm) showed higher concentrations of carbonyl-containing compounds and low molecular weight organic acids. This composition change from smaller to larger size particles reflects a vapor pressure increase of the condensing vapors by 1-2 orders of magnitude indicating that the Kelvin effect plays a decisive role in the growth of biogenic nanoparticles. A manuscript describing this study has been published [16].

5) **We will compare HTOF-TDCIMS measurements of composition with empirical growth rate observations in an effort to achieve "closure" on chemical species that contribute to growth.**

A manuscript that reports on measurements of organic compounds that participate in nucleation during ozonolysis of alpha-pinene has been published [17]. This manuscript identifies the precursors to nanoparticle growth as high molecular weight, low volatility oxidized organic compounds. This was the first published observations of the neutral compounds that are now referred to as Extremely Low Volatility Organic Compounds (ELVOC). In that paper we demonstrate chemical closure between gas and particulate phases for the species responsible for growth.

In collaboration with Murray Johnston's group at University of Delaware, we performed HTOF-TDCIMS measurements at the Hyytiälä Research Station in Finland. We showed that particle phase sulfur and nitrogen increase just prior to new particle formation events, which future reinforces the important role of inorganic salt formation even in this biogenically-dominated site [18]. In another collaboration with the Johnston group, we combined TDCIMS measurements with the Nanoparticle Mass Spectrometer (NAMS) to show that carbonaceous matter can account for more than half of the mass growth of nanoparticles at a coastal site in Delaware. Nanoparticle composition is consistent with that expected for extremely low volatility organic compounds. An important novel finding is that the carbonaceous matter must contain a substantial amount of nitrogen, whose molecular identity is not fully understood [19].

We also analyzed data from a field campaign at Mace Head, Ireland, in which the TDCIMS performed measurements of ultrafine particle composition [20]. The data provides evidence for open ocean new particle formation events to the total concentration of ultrafine particles in this site. The observed events were correlated with the presence of benzoic acid in the particles and an increase in the number of lower hygroscopicity mode particles, which suggests that organic compounds may play an important role in nanoparticle growth.

Modeling

6) **We will develop a dynamic size-resolved partitioning model that describes nanoparticle growth due to H_2SO_4 and organics. The model will be based on current state-of-the-science thermodynamic equilibrium frameworks with added functionality to describe size-resolved growth rates.**

In collaboration with Prof. Ilona Riipinen (Stockholm University) and Dr. Taina Yli-Juuti (Univ. of Eastern Finland), we have developed a model for nanoparticle growth due to acid-base (including organic acids and bases) chemistry. That model, called Model for Acid-Base chemistry in Nanoparticle Growth (MABNAG), is described in [21]. This model is currently being amended to include growth due to the condensation of Extremely Low Volatility Organic Compounds (ELVOCs), and will form the basis for more sophisticated models in our current DOE-ASR funded project.

7) **We will work with Rahul Zaveri and others at PNNL to add an organic salt formation mechanism for nucleation and nanoparticle growth to the aerosol model MOSAIC (Model for Simulating Aerosol Interactions and Chemistry). The organic salt formation mechanism will be parameterized for all versions of MOSAIC. Several versions exist to allow aerosol modeling at multiple temporal and spatial scales.**

In collaboration with Dr. Alma Hodzic at the National Center for Atmospheric Research (NCAR), we modeled new particle formation events at the NCAR Manitou Experimental Forest Observatory using WRF-Chem. We concluded that, even at this remote site, sulfuric acid is responsible for the initiation of new particle formation. Monoterpene oxidation products are believed responsible for the growth of newly formed particles to CCN-relevant sizes. The model predicts that new particle formation could be responsible for as much as 67% of the surface Cloud Condensation Nuclei (CCN) at 0.5% supersaturation [22].

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Lectures that Acknowledged DE-SC0006861 or DE-SC0006762

Peter McMurry:

P. H. McMurry, “New Particle Formation: Atmospheric and Laboratory Evidence for Chemical Nucleation of Sulfuric Acid and Amines,” American Meteorological Society Annual Meeting, Plenary Lecture, Annual Meeting, Seattle, WA. January 26, 2011.

P. H. McMurry, “Tandem Measurements of Aerosol Properties,” Brazilian Association for Aerosol Research, Plenary Lecture, Rio de Janeiro, Brazil. August 1-5, 2011.

P. H. McMurry, “New Measurements of Clusters and Nanoparticles:Implications for Atmospheric Nucleation & Growth Models,” Columbia University, Department of Chemical Engineering, Departmental Seminar. November 15, 2011.

P. H. McMurry,” New Experimental Approaches to Studying the Formation and Growth of Atmospheric Particles,” International Atmospheric Modeling Algorithms (IAMA) Conference, UC Davis Conference Center, Davis, CA. November 30 – December 1, 2011.

P. H. McMurry, "New Measurements of Clusters and Nanoparticles:Implications for Atmospheric Nucleation & Growth Models." Earth Day Lecture. Washington University at St. Louis. April 20, 2012.

P. H. McMurry, "New Measurements of Clusters and Nanoparticles: Implications for Atmospheric Nucleation & Growth Models." Cambridge Particle Meeting, Cambridge University, UK. May 18, 2012.

P. H. McMurry, "Measurements of Clusters and Particles in the 1 nm Size Range." Cloud ITN Conference, Königstein KTC, Germany. May 22, 2012.

P. H. McMurry, "New Measurements of Clusters and Nanoparticles: Implications for Atmospheric Nucleation & Growth Models." Inaugural Donora Lecture (chosen by CMU graduate students), August 13, 2012.

P. H. McMurry, "An Acid-Base Chemical Reaction Model for Nucleation Rates in the Polluted Atmospheric Boundary Layer." Leadoff Lecture. Workshop on atmospheric aerosol formation and early growth, Hyytiälä, Finland. August 20, 2012.

P. H. McMurry, "New Measurements of Clusters and Nanoparticles: Implications for Atmospheric Nucleation & Growth Models." 21st Nisshin Engineering Particle Technology International Symposium. Kanazawa University, Japan. December 2-5, 2012.

P. H. McMurry, " New Measurements of Clusters and Nanoparticles:Implications for Atmospheric Nucleation & Growth Models." KIST and Sungkyunkwan University, Seoul, South Korea. December 6, 2012.

P. H. McMurry, "New measurements of clusters and nanoparticles: Implications for atmospheric nucleation and growth models." University of Illinois, Urbana-Champaign, Department of Atmospheric Sciences departmental seminar. January 24, 2013

P. H. McMurry, "New measurements of clusters and nanoparticles: Implications for atmospheric nucleation and growth models." Tsinghua University, Beijing, China. February 25, 2013.

P. H. McMurry, "New measurements of clusters and nanoparticles: Implications for atmospheric nucleation and growth models." AIST, Tsukuba, Japan. February 28, 2013.

P. H. McMurry, "Discoveries regarding nucleation and growth from new measurements of neutral molecular clusters and nanoparticles." Atmospheric Chemistry Gordon Conference, Mt. Snow, Vermont. Invited Plenary Lecture. July 28-31, 2013

P. H. McMurry, "Nucleation and growth of atmospheric aerosols." 11th UNU & GIST Joint Programme Symposium, Kota Kinabalu, Malaysia (Borneo), Invited Plenary Lecture, October 22-24, 2013

P. H. McMurry, "Perspectives based on work as Co-chair of *Particulate Matter Science for Policy Makers: A NARSTO Assessment*," 1st UMN_CAS Bilateral Seminar. PM2.5 Science, Health Effects, and Control Technology, Xian, China. May 27, 2014.

P. H. McMurry, "New measurements of precursor vapors, neutral clusters, and nanoparticles: Implications for mechanisms of nucleation in the atmosphere," International Workshop: Nucleation & Early Stages of Particle Formation, Friedrich-Alexander Universität, Erlangen-Nürnberg, Germany,.June 6, 2014.

P. H. McMurry, " Chemical Nucleation in the Atmosphere: Recent Discoveries Enabled by Instrument Development," Atmospheric Chemistry Group, University of Colorado at Boulder, February 18, 2015.

P. H. McMurry, "Chemical Nucleation by Acid-Base Reactions: Discoveries from Laboratory Experiments Enabled by Instrumental Development," American Chemical Society, Boston, MA. August 16-20, 2015.

James Smith

Smith, J., 2014: What are field (and lab) measurements telling us about the role of organics in new particle formation and growth? Telluride Workshop: Organic Particles in the Atmosphere: Formation Properties, Processing, and Impact, Telluride, CO.

Smith, J., 2014:Contributions of Organic Compounds to the Growth of Freshly Nucleated Atmospheric Nanoparticles, 2014 Users' Meeting, Environmental Molecular Sciences Laboratory, Richland, WA [plenary speaker]

Smith, J., 2013: Atmospheric Nanoparticles: Measurements and Observations, Tutorial Speaker, American Association for Aerosol Research Annual Conference, Portland, OR.

Smith, J., M. Lawler, P. Winkler, J. Zhao, and P. McMurry, 2013: Biogenic new particle formation and its potential impacts on climate, Goldschmidt2013 meeting, Florence, Italy [invited].

Smith, J., 2013: Biogenic new particle formation and its potential impacts on climate, Goldschmidt Conference, Florence, Italy.

Smith, J., 2013: Atmospheric Nanoparticles: Measurements and Observations, Dept. of Nanoengineering Seminar, Univ. of Calif., San Diego, CA.

Smith, J., 2013: The Roles of Nitrogen in Atmospheric Aerosol Formation and Growth, NSPIRE Distinguished Lecture Series, Wash. State Univ., Pullman, WA.

Smith, J., 2013: Recent insights into the chemical composition and spatial distribution of nanometer-sized particles formed from nucleation, Atmospheric Chemistry Seminar, Colorado State Univ., Ft. Collins, CO.

Smith, J., L. Hildebrandt, P. Winker, J. Ortega, and Mike Lawler, 2012: Recent insights into the chemical composition and spatial distribution of nanometer-sized particles formed from nucleation, Workshop on Atmospheric Aerosol Formation and Early Growth, Hyytiälä, Finland.

Smith, J., 2012: Chemical ionization mass spectrometry applied to the analysis of atmospheric nanoparticle composition, Chemical Ionization Mass Spectrometry Research Symposium, University of Colorado, Boulder, CO.

Smith, J., 2011: Insights into the role of organics in new particle formation and growth, CLOUD Open Workshop, Vienna, Austria.

Smith, J., 2011: Insights into the role of organics in new particle formation and growth, Forschungszentrum Juelich, Juelich, Germany.

Smith, J., P. Winkler, J. Zhao, and P. McMurry, 2011: Exploring the role of organics in atmospheric new particle formation with chemical ionization mass spectrometry, Fall Meeting of the American Chemical Society, Denver, CO, USA [invited].