Final Report

"Nucleation and Growth of Atmospheric Aerosols"
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Research Overview

Research that was supported by this contract has contributed substantially to progress in our understanding of new particle formation in the atmosphere. Objectives included the development of new measurement methods, the application of those new instrument systems in atmospheric field studies, and the interpretation of results from those studies. All objectives were achieved and have been (or will soon be) described in the peer reviewed archival literature.

Development of New Measurement Methods
(Reference citations apply to archival journal articles mentioned previously)

We developed the "Nano TDMA" to measure the hygroscopicity and volatility of 4-20 nm particles (Sakurai et al., 2003). We used this instrument system to characterize properties of atmospheric particles in the Atlanta atmosphere in July/August 2002 (Sakurai et al, 2005) as well as to study properties of diesel exhaust particles (Sakurai et al, 2003).

We also developed the thermal desorption chemical ionization mass spectrometer (TDCIMS) to measure the chemical composition of nanoparticles as small as 7 nm with a time resolution of 10-20 minutes (Voisin et al, 2003; Smith et al, 2004). The TDCIMS is currently the only instrument that can perform such measurements. A paper that described the performance of the unipolar charger that is used to charge particles as they enter the TDCIMS is in the final stages of preparation (Ghimire et al., 2005).

Atmospheric Field Measurements

Atmospheric field measurements were carried out in Atlanta (July/August 2002; we refer to this as the ANARChE study) and in Boulder, CO (2003/04). The Atlanta study we operated more or less in a routine manner, 24 hours/day throughout the study. The Boulder study is being conducted over more extended periods of time, and involves more work on technique refinement than was done in Atlanta. Data from the University of Minnesota instrumentation are downloaded on a daily basis. Routine maintenance operations on Minnesota equipment are conducted by the NCAR personnel.

Results of the ANARChE study have been written up in four papers that should appear as a Topical Collection in JGR-Atmospheres. These papers describe the results of nano-TDMA (Sakurai et al, 2005) and TDCIMS measurements (Smith et al., 2005) on freshly nucleated particles. They also summarize our efforts to reconcile measured and calculated growth rates of

freshly nucleated particles. Two of the papers focus on interpretation of particle formation and growth rates (see below).

We also carried out laboratory studies on the properties of diesel exhaust particles in the Center for Diesel Research at the University of Minnesota (Sakurai et al., 2003). We found that diesel exhaust particles that were formed by nucleation in the exhaust plume had properties similar to lubricating oils (i.e., C28-C32 alkanes). In contrast, freshly nucleated particles measured in Atlanta were found to have hygroscopicity and volatility that was similar to laboratory-generated ammonium sulfate.

Interpretation of Data from Atmospheric Field Measurements

The Minnesota-NCAR team carried out an intensive DOE-supported study of new particle formation in Atlanta, GA (July/August, 2002; ANARChE study). In this study we measured, for the first time, the composition of freshly nucleated particles as small as 7 nm using the TDCIMS. The ANARChE study also included the first nano-TDMA measurements of the volatility and hygroscopicity of freshly nucleated particles as small as 4 nm. Other parameters that were measured included particle size distributions (3 nm-2 μm), and sulfuric acid and ammonia concentrations. Papers on this work have recently been submitted for publication (McMurry et al., 2005; Sakurai et al., 2005; Smith et al., 2005; Stolzenburg et al, 2005). Several key discoveries were made during ANARChE, among these are:

•McMurry et al. (2005) demonstrate a criterion that determines whether or not nucleation occurs on any given day. A single dimensionless parameter, L, which gives the relative rates at which clusters are lost by coagulation scavenging to preexisting particles and at which they are lost by condensational growth to the next larger size, determines whether or not nucleation can occur. We found that, consistent with theory, nucleation occurred when L was less than 1, and that nucleation almost never occurred when L was significantly greater than 1. We also showed that the number of new particles produced was equal to or less than the theoretical maximum number that could have been produced if nucleation were collision-controlled.

•Smith et al. (2005) analyzed TDCIMS measurements during ANARChE. These results can be summarized as follows. During the period in which the TDCIMS was operating and properly calibrated, 9 individual nucleation events were characterized for the chemical composition of size-selected particles in the 7 to 13 nm diameter range. Prior to a new particle plume impact or regional growth event, the concentration of ammonium and sulfate in 7 to 13 nm diameter particles is lower than that which would be expected for a pure ammonium sulfate aerosol, with ammonium and sulfate comprising 25 to 50% by volume. A new particle formation event always coincided with an increase in volume fractions of these compounds, usually to values of equal to or slightly exceeding 100%. Following these events, sulfate volume fraction in 13 nm diameter particles returned to values smaller than 100%. This suggests that the sulfur-enriched air mass that encouraged new particle formation probably passed by the sampling site after new particles were formed. The observations of ammonium following nucleation events showed the same general trends as sulfate, but are probably also closely correlated with the mixing of air masses of different

origins. With one exception, higher concentrations of ammonium were observed in 7 nm diameter particles compared to 13 nm diameter particles. These measurements suggest that freshly nucleated particles consisted primarily of ammonium sulfate during this study.

•Sakurai et al. (2005) measured water uptake and volatility of freshly nucleated particles. They found that freshly nucleated particles in Atlanta have hygroscopicity and volatility similar to that of ammonium sulfate, but that nanoparticles sampled before or after nucleation events are less hygroscopic and more volatile. Consistent with the composition measurements reported by Smith et al. (2004), these measurements support the conclusion that freshly nucleated particles in Atlanta during ANARChE consisted primarily of ammonium sulfate.

•Stolzenburg et al. (2005) compared growth rates of freshly nucleated particles during ANARChE with expected values assuming that sulfuric acid vapor was the primary growth species. Reasonable agreement between measured and calculated growth was found for growth rates observed in the mornings when particles were still smaller than ~20 nm, provided that the effects of intermodal and intramodal coagulation are taken into account. Observed growth rates at midday when particles were larger than ~20 nm, however, were typically significantly greater (~5X) than calculated rates, suggesting that a species in addition to sulfuric acid was contributing to growth. Again, this paper is consistent with the results of Smith et al. (2004) and Sakurai et al (2004): if sulfuric acid is the primary growth species when particles are smaller than 20 nm, then the freshly nucleated particles should consist primarily of sulfates. We do not yet understand why particles grow as fast as they do later in the day.

This contract also supported TDCIMS and aerosol physical property measurements performed at NCAR's Mesa Laboratory in Boulder, CO, intermittently since the Spring of 2002. The TDCIMS measurements were made on sub-20 nm diameter atmospheric particles, and have uncovered many intriguing questions that warrant further investigation (Smith et al, 2004). For example, unlike the case in Atlanta where primarily ammonium was observed in the positive ion spectrum for ambient aerosol, Boulder aerosols appear to be composed of a variety of compounds most of which have not been identified. In the negative ion spectrum, Boulder sub-20 nm diameter particles are characterized by large nitrate peaks, with integrated areas up to 3 orders of magnitude greater than aerosol sulfate. While it is true that a directly evaporated compound such as nitrate would be observed more sensitively than sulfate that originates from ammonium sulfate, the large nitrate peaks are nonetheless significant. Laboratory-generated pure ammonium nitrate aerosol at diameters smaller than 20 nm were seen to quickly volatilize in the TDCIMS electrostatic precipitator, thus suggesting the presence of cations other than NH_4^+ in the ambient aerosol in order to stabilize the observed nitrate. Nitrate was continuously monitored in Atlanta during ANARChE, however it was not observed in the particles in significant amounts. It is also interesting to note that both sulfate and nitrate are minor constituents in the aerosol at times corresponding to the peak in volume concentration (noon to 4:00 pm).

Refereed Journal Articles

Published:

Hanson, D. R., F. L. Eisele, S. M. Ball, P. H. McMurry, 2002, "Sizing small sulfuric acid particles with an ultrafine particle condensation nucleus counter," Aerosol Sci. Technol. 36(5):554-559.

Voisin, D., J. N. Smith, H. Sakurai, P. H. McMurry, F. L. Eisele, 2003, "Thermal desorption chemical ionization mass spectrometer for ultrafine particle chemical composition," Aerosol Sci. Technol., 37:471-475.

Sakurai, H. K. Park, P. H. McMurry, D. D. Zarling, D. B. Kittelson, P. J. Ziemann, 2003, "Size-dependent mixing charactistics of volatile and non-volatile compositions in diesel exhaust aerosols" Environ. Sci. Technol., **37**:5487-5495.

Smith, J. N., K. F. Moore, P. H. McMurry, F. L. Eisele, 2004, Atmospheric measurements of sub-20 nm diameter particle chemical composition performed using thermal desorption chemical ionization mass spectrometry, Aerosol Sci. Technol. **38(2)**: 100:110.

Kulmala, M., H. Vehkamaki, T. Petajda, M. dal Maso, A. Lauri, V.-M. Kerminen, W. Birmili, P. H. McMurry, 2004, Formation and growth of ultrafine atmospheric particles: A review of observations, J. Aerosol Sci., **35(2)**:143-176.

Dunn, M., J. L. Jimenez, D. Baumgardner, T. Castro, P. H. McMurry, J. N. Smith, 2004, Observations of Mexico City nanoparticle size distributions: Observations of new particle formation and growth, Geophysical Research Letters **31**:L10102.

Accepted or Under Review (We anticipate that the following four articles will be published together in a JGR "Topical Collection"):

Smith, J. N., K. F. Moore, F. L. Eisele, D. Voisin, A. K. Ghimire, H. Sakurai, P. H. McMurry, 2005, "The chemical composition of atmospheric nanoparticles during nucleation events in Atlanta," Journal of Geophysical Res. Atmospheres, Accepted.

McMurry, P. H., M. Fink, H. Sakurai, M. R. Stolzenburg, R. L. Mauldin III, J. Smith, F. Eisele, K. Moore, S. Sjostedt, D. Tanner, L. G. Huey, J.B. Nowak, E. Edgerton, D. Voisin, 2005, "A criterion for new particle formation in the sulfur-rich Atlanta atmosphere," Journal of Geophysical Res. Atmospheres, Accepted.

Stolzenburg, M. R., P. H. McMurry, H. Sakurai, J. Smith, R. L. Mauldin III, F. L. Eisele, C. F. Clement, 2005, "Growth rates of freshly nucleated particles in Atlanta," Journal of Geophysical Res. Atmospheres, Accepted.

Sakurai, H., M. A. Fink, P. H. McMurry, L. Mauldin, K. F. Moore, J. N. Smith, F. L. Eisele, 2005, Hygroscopicity and volatility of 4-10 nm particles during atmospheric nucleation events in summer in urban Atlanta," Journal of Geophysical Res. Atmospheres, in Review.

In Preparation:

Ghimire, A. K. Smith, J. Smith, F. L. Eisele, P. H. McMurry, 2004, “Aerosol charge distributions produced by a unipolar charger,”

Theses

Melissa Ann Fink, “Hygroscopicity and Volatility of Ultrafine Particles from Controlled Diesel Exhaust,” M.S. Project Defended May 4, 2005.

Hyo-Kuen Ahn, “Numerical Analysis of Particle Collection with Electrostatic Precipitator in TDCIMS,” MS Project Defended May 26, 2005.

Ajaya Ghimire, “Aerosol charge distributions produced by a unipolar charger,” MS Project to be completed during summer 2005.

Other Archival Articles

McMurry, P. H., K. S. Woo, R. Weber, D.-R. Chen, D. Y. H. Pui (2003) “Size distributions of 3-10 nm atmospheric particles: Implications for nucleation mechanisms,” in Ultrafine Particles in the Atmosphere, L.M. Brown, N. Collings, R. M. Harrison, A. D. Maynard, R. L. Maynard, Editors, Imperial College Press, London.

Smith, J. N., Moore, K. F., Eisele, F. L., Ghimire, A. K. and McMurry, P. H. (2003). Recent insights into the formation and chemical composition of atmospheric nanoparticles from the aerosol nucleation and realtime characterization experiment, Abstr. Pap. Am. Chem. Soc. **225**:U984-U984.

Invited Lectures (P. H. McMurry)

P. H. McMurry, "Formation and Properties of Tropospheric Nanoparticles," Engineering and Applied Sciences, Atmospheric Chemistry Division, Harvard University, 1/25/01.

P. H. McMurry, "Nucleation and Growth of Atmospheric Particles," Department of Physics, Tartu University, Estonia, 3/5/02.

P. H. McMurry, "Atmospheric Nanoparticles: Measurement and Observations Pertinent to Nucleation and Growth," International Aerosol Conference, Taipai, Taiwan, 9/9/02.

P. H. McMurry, “Nucleatation and growth of atmospheric nanoparticles,” Centre of Excellence Research Unit on Physics, Chemistry and Biology of Atmospheric Composition and Climate Change, Hyytiala, Finland, 3/14/03.

J. N. Smith "Recent insights into the formation and chemical composition of atmospheric nanoparticles from the Aerosol Nucleation and Realtime Characterization Experiment," Aeronomy Laboratory, National Oceanographic and Atmospheric Administration, Boulder, CO, 4/2/03.

P. H. McMurry, "Physical and Chemical Properties of Atmospheric Aerosols," PM2003, Pittsburgh, PA, 4/2/03. Invited Plenary Lecture

J. N. Smith, "Atmospheric Measurements of Sub-20 nm Diameter Particle Chemical Composition Performed Using Thermal Desorption Chemical Ionization Mass Spectrometry," Analytical Chemistry Department, Purdue University, 5/2903.

P. H. McMurry, "Observations of New Particle Formation and Growth Rates in the Atmosphere," Invited Plenary Lecture, Department of Chemistry and Biochemistry, University of Maryland, 10/3/03

P. H. McMurry, "Observations of New Particle Formation and Growth Rates in the Atmosphere," Invited Plenary Lecture, AAAR Annual Meeting, Anaheim, CA, 10/21/03

P. H. McMurry, "Observations of New Particle Formation and Growth Rates in the Atmosphere," Invited Plenary Lecture, Department of Mechanical Engineering, Yale University, 11/5/03

P. H. McMurry, "Observations of New Particle Formation and Growth Rates in the Atmosphere," Invited Plenary Lecture, Department of Mechanical Engineering, Carnegie Mellon University, 11/7/03

P. H. McMurry, "Observations of New Particle Formation and Growth Rates in the Atmosphere," Tsukuba, Japan, National Institute for Environmental Sciences, 1/20/04.

P. H. McMurry, "Observations of New Particle Formation and Growth Rates in the Atmosphere," Carleton College, Department of Chemistry, 1/23/04.

P. H. McMurry, "Observations of New Particle Production During ANARChE," ARIES, Atlanta, GA, 3/9/04.

P. H. McMurry, "Factors that Influence Rates of Atmospheric Particle Production," Cambridge University, England, 4/13/04.

P. H. McMurry, "Nucleatation and growth of atmospheric nanoparticles," Centre of Excellence Research Unit on Physics, Chemistry and Biology of Atmospheric Composition and Climate Change, Hyytiala, Finland, 4/15/04.

P. H. McMurry, Particulate Matter Measurement and Modeling Workshop , United Nations ECE EMP Workshop on Particulate Matter Measurement, New Orleans, LA, 4/20/04.

J. N. Smith, “Recent insights into the formation, growth, and composition of atmospheric nanoparticles,” University of California at Riverside, Environmental Toxicology Seminar Series, 5/5/04.

P. H. McMurry, PNL, “The Need for New Experimental Approaches for Understanding Nucleation Kinetics in the Atmosphere,” 10/20/04

P. H. McMurry, "Atmospheric Nanoparticles: Measurement, Formation and Properties," NSF-ACS-Brazil Atmospheric Aerosol Chemistry Workshop, Rio de Janeiro, Brazil, 12/7/04.

P. H. McMurry, “Ion-Induced Nucleation in Boulder, CO,” Center of Excellence, Centre of Excellence Research Unit on Physics, Chemistry and Biology of Atmospheric Composition and Climate Change, Pallas, Finland.

P. H. McMurry, “Observations of new particle formation and growth rates in the atmosphere,” Brookhaven National Laboratory Atmospheric Chemistry Series, 5/19/05.

P. H. McMurry, “Atmospheric Aerosols: Measurement, Processes and Effects” Annual meeting of the Air and Waste Management Association, Minneapolis, MN., Breakfast talk to educators, 6/22/05.

Other Conference Presentations

J. N. Smith, K. F. Moore, P. H. McMurry, F. L. Eisele, "Chemical Composition Measurements of Sub-20 nm Atmospheric Aerosols," 10/8/02, American Association for Aerosol Research, Charlotte, NC.

K. F. Moore, J. Smith, F. Eisele, P. H. McMurry, “Direct Observations of the Composition of Sub-20 Nanometer Ambient Aerosol,” American Geophysical Union, December 9, 2002, San Francisco, CA

Sakurai, H,, K. Park, H. J. Tobias, P. J. Ziemann, D. B. Kittelson, P. H. McMurry, “On-line measurements of volatility, hygroscopicity, composition and mixing characteristics of diesel particles,” 6th International Aerosol Conference, pp 821-822, September 9-13, 2002, Taipei, Taiwan

J. N. Smith, K. Moore, F. Eisele, A. Ghimire, P. H. McMurry, “Recent insights into the formation and chemical composition of atmospheric nanoparticles from the Aerosol Nucleation and Realtime Characterization Experiment,” ACS Special Symposium on Nanotechnology and the Environment, March 25-28, 2003.

J. N. Smith, K. F. Moore, D. Voisin, L. Mauldin, A. K. Ghimire, H. Sakurai, M. A. Fink. P. H. McMurry, F. L. Eisele, “The chemical composition of atmospheric ultrafine

particles during nucleation events," Annual Meeting Abstracts, American Association for Aerosol Research, Anaheim, CA, October 20-24, 2003.

J. N. Smith, M. Dunn, J.-L. Jimenez, H. Sakurai, A. Ghimire, P. H. McMurry, F. L. Eisele, T. Castro, D. Baumgardner, "Measurement of Mexico City Ultrafine aerosol size distributrions: Observations of new particle formation and growth," Annual Meeting Abstracts, American Association for Aerosol Research, Anaheim, CA, October 20-24, 2003, p. 53.

K. F. Moore, J. Smith, F. Eisele, A. Ghimire, P. H. McMurry, "Chemical composition of sub-20 nm atmospheric aerosol in Boulder, CO," Annual Meeting Abstracts, American Association for Aerosol Research, Anaheim, CA, October 20-24, 2003.

H. Sakurai, A. Ghimire, M. Fink, P. H. McMurry, J. Smith, L. Mauldin, K. Moore, F. Eisele, D. Voisin, "Hygroscopicity and volatility of atmospheric ultrafine particles during nucleation events in Atlanta, Georgia," American Association for Aerosol Research, Anaheim, CA, October 20-24, 2003.

P. H. McMurry, "Recent insights into the formation and chemical composition of atmospheric nanoparticles from the Atlanta Aerosol Nucleation and Realtime Characterization Experiment (Atlanta-ANARChE)," DOE Atmospheric Sciences Program Meeting, Orlando, FL, March 4-5, 2003.

M. J. Dunn, K. Moore, F. L. Eisele, J. N. Smith, A. Ghimire, M. Stolzenberg, P. H. McMurry, Measurement of the size distribution and chemical composition of rural atmospheric nanoparticles," AAAR Annual Conference, Atlanta, GA October 4-8, 2004.

A. Ghimire, M. R. Stolzenburg, P. H. McMurry, J. Smith, K. Moore, H. Sakurai, "Size-dependent charging efficiencies and charge distributions for nanoparticles downstream of a unipolar charger: Application to size-dependent sampling," AAAR Annual Conference, Atlanta, GA October 4-8, 2004.

M. R. Stolzenburg, P. H. McMurry, M. Fink, C. F. Clement, H. Sakurai, F. L. Eisele, J. N. Smith, R. L. Mauldin, E. Kosciuch, K. F. Moore, "Growth of the atmospheric nanoparticle mode: Comparison of measurements and theory," AAAR Annual Conference, Atlanta, GA October 4-8, 2004.

M. Fink, D. B. Kittelson, P. H. McMurry, J. Savstrom, M. R. Stolzenburg, "Hygroscopicity and volatility of ultrafine particles from filtered diesel exhaust aerosols," AAAR Annual Conference, Atlanta, GA October 4-8, 2004.

K. F. Moore, J. N. Smith, M. Dunn, F. L. Eisele, P. H. McMurry, M. Fink, M. R. Stolzenburg, "Size-dependent chemical composition of sub-20 nm atmospheric aerosol," AAAR Annual Conference, Atlanta, GA October 4-8, 2004.