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DOE/SC-ARM-15-011

New Particle Formation Study Final Campaign Report

JN Smith
PH McMurry

January 2015

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CLIMATE RESEARCH FACILITY

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Office of Science, Office of Biological and Environmental Research

Executive Summary

The scientific foci of the New Particle Formation Study were the formation and evolution of atmospheric aerosols and the impacts of newly formed particles on cloud processes. Specifically, we planned to: (1) to identify the species and mechanisms responsible for the initial steps of new particle formation, i.e., the formation of thermodynamically stable clusters; (2) investigate the role of acid-base chemistry in new particle growth through measurements of ammonia and amines as well as organic and inorganic acids in both atmospheric nanoparticles and the gas phase; (3) investigate the contribution of other surface area or volume-controlled processes to nanoparticle formation and growth; (4) create a comprehensive dataset related to new particle formation and growth that can be used as input for our own thermodynamic models as well as the modeling efforts by our Department of Energy (DOE) Aerosol Life Cycle working group collaborators; (5) characterize the increase of the number and activity of cloud condensation nuclei (CCN) due to particle formation and growth; (6) determine the regional extent of new particle formation to address the role that atmospheric transport plays in determining the impacts, if any, of new particle formation on cloud number and properties.

Most measurements took place at the Atmospheric Radiation Measurement (ARM) Southern Great Plains Central Facility in the guest instrument facility from April 13 to May 24, 2013. During the 6-week campaign we observed several intense nucleation events. Coincident particle number-size distribution measurements performed at the ARM Purcell Boundary Site located 200 km south of the Central Facility show that events can span this distance, and thus have regional significance. In addition, tethered balloon measurements of the vertical profile of 10 to 20 nm diameter particles suggest that some new particle formation events are initiated aloft. These vertical distributions will aid in the interpretation of our ground-based measurements. Data analysis and modeling efforts are currently underway; already it appears that we have obtained our richest and most complete set of observations to date on the particles and gases associated with new particle formation events.

Acronyms and Abbreviations

AC	Augsburg College
AmPMS	Ambient Pressure Proton Transfer Mass Spectrometer
CCNc	Cloud Condensation Nucleus counter
DEG SMPS	Diethylene Glycol Scanning Mobility Particle Sizer
DMA-DTIMS	Differential Mobility Analyzer – Drift Tube Ion Mobility Spectrometer
Dual DEG	Dual Diethylene Glycol particle counters
MCC	Minnesota Cluster Chemical Ionization Mass Spectrometer
NAMS	Nano Aerosol Mass Spectrometer
Nano HTDMA	Nanometer Hygroscopicity Tandem Differential Mobility Analyzer
NCAR	National Center for Atmospheric Research
NCC	NCAR Cluster Chemical Ionization Mass Spectrometer
NPF	New Particle Formation
NPFS	New Particle Formation Study
PSD	Particle Size Distribution system
PTRMS	Proton Transfer Reaction Mass Spectrometer
SGP	ARM Southern Great Plains research site
TDCIMS	Thermal Desorption Chemical Ionization Mass Spectrometer
UDel	University of Delaware
UMN	University of Minnesota, Twin Cities

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1.0 Background

The scientific foci of the New Particle Formation Study (NPFS) were the formation and evolution of atmospheric aerosols and the impacts of these newly formed aerosols on cloud processes. Specifically, our objectives were to: (1) identify the species and mechanisms responsible for the initial steps of new particle formation, i.e., the formation of thermodynamically stable clusters; (2) investigate the role of acid-base chemistry in new particle growth through measurements of ammonia and amines as well as organic and inorganic acids in both atmospheric nanoparticles and the gas phase; (3) investigate the contribution of other surface area or volume-controlled processes to nanoparticle formation and growth; (4) create a comprehensive dataset related to new particle formation and growth that can be used as input for our own thermodynamic models as well as the modeling efforts by our DOE Aerosol Life Cycle working group collaborators; (5) characterize the increase of the number and activity of CCN due to particle formation and growth; (6) determine the regional extent of new particle formation to address the role that atmospheric transport plays in determining the impacts, if any, of new particle formation on cloud number and properties.

Most of the measurements took place at the ARM Southern Great Plains (SGP) Central Facility in the guest instrument facility. In addition, a tethered balloon system was used to measure the vertical profiles of the concentrations of newly formed particles with diameters from 10 to 20 nm. These observations will aid in the interpretation of our ground-based measurements. We also deployed an instrument to measure the particle number-size distribution at the Purcell boundary site located 200 km S of the Central Facility. Those observations will explore the regional extend of new particle formation events. Table I shows a list of measurements and the research teams responsible for each instrument.

Personnel arrived in Oklahoma on or soon after Saturday, April 13, 2013. We departed the SGP site on or about Friday, May 24, 2013. Thus, we occupied the guest instrument facility for six weeks altogether. SGP is an excellent site for this work because it is located within the Southern Great Plains. Data acquired at SGP is likely representative of the large, yet poorly studied, Great Plains region. This is scientifically interesting because the chemical properties of the atmosphere in this region are likely affected by complex interactions between atmospheric transport, transfer of constituents to and from the surface, etc. The processes we study affect concentrations of CCN and therefore likely affect cloud properties. Long-term routine TDMA measurements at the SGP site (0.012-0.75 μm aerosol size distributions; Don Collins, Texas A&M, Instrument Mentor) show that new particle formation (NPF) occurs routinely in April and May (Figure 1).

The co-PIs of the campaign are James Smith (NCAR) and Peter McMurry (UMN). The project was funded by the Department of Energy Atmospheric System Research program and the National Science Foundation.

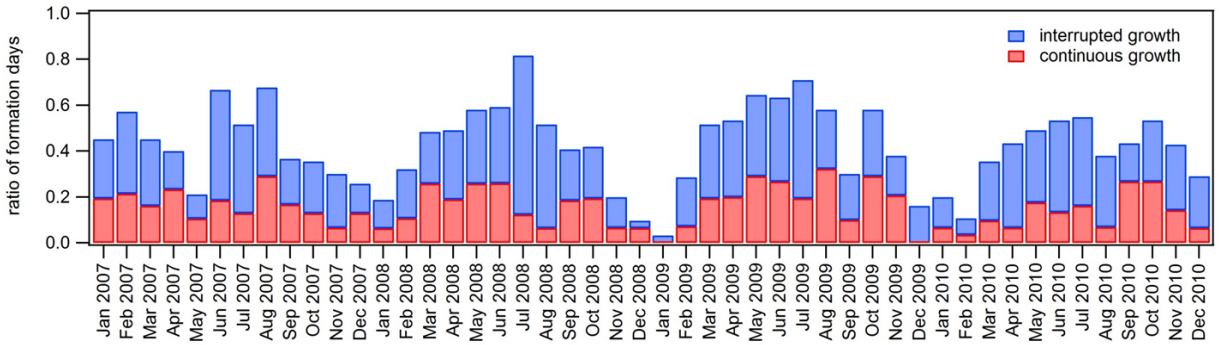

Figure 1. Ratio of days per month with new particle formation events, from observations by the ARM Tandem Differential Mobility Analyzer at the SGP Central Facility.

Table 1. Measurements and research teams participating in NPFS. For a list of acronyms refer to Page iv. Methods/instruments indicated with a * were protoytpes that were deployed for testing purposes; data from prototype instruments will not be uploaded to the ARM archive.

Central Facility measurements	method/instrument	investigator/institution
SO_2	Teco model 43C-TLE	Smith / NCAR
particle size distribution (3 - 1000 nm)	PSD	McMurry / UMN
nanoCN size distribution	DEG SMPS	McMurry / UMN
size-resolved nanoparticle hygroscopicity	Nano HTDMA*	McMurry / UMN
size-resolved nanoparticle hygroscopicity	DMA-DTIMS*	Hogan / UMN
gas phase amines	AmpMS	Hanson / AC
neutral cluster composition and sulfuric acid (NO3- reagent)	NCC	Smith / NCAR
neutral cluster composition (Acetate reagent)	MCC*	McMurry / UMN
gas phase organic acids	PTRMS	Smith / NCAR
nanoparticle molecular composition	HTOF-TDCIMS	Smith / NCAR
naoparticle elemental composition	NAMS*	Johnston / UDel
Satellite Facility measurements (Purcell site)		
particle size distribution (3 - 1000 nm)	SMPS	Smith / NCAR
Tethered Balloon measurements		
particle number concentration (10-20 nm diameter)	dual condensation particle counters	Smith / NCAR
meteorology	portable weather station	Smith / NCAR

2.0 Notable Events or Highlights

During the 36 days that our particle size distribution (PSD) system was operational we observed 13 regional new particle formation events. Figure 2 shows an example of one such event, which is characterized by the sudden appearance of particles at the minimum detected diameter of the PSD (3 nm) followed by subsequent growth of the size distribution over several hours. Most of the instruments operated properly. As typically occurs, difficulties were encountered for several prototype instruments, but valuable insights were gained as to how the design of those instruments might be revised to improve

performance. The tethered balloon measurements were also successful, having generated 50 vertical profiles of particle concentrations as high as 100 m above ground level. Atmospheric conditions varied significantly during the observation period. This included periods of severe weather, such as the storm system associated with the 2013 Moore tornado on 20 May 2013. Overall, we obtained our richest and most complete set of observations to date of particle and gas phase species that are believed responsible for new particle formation.

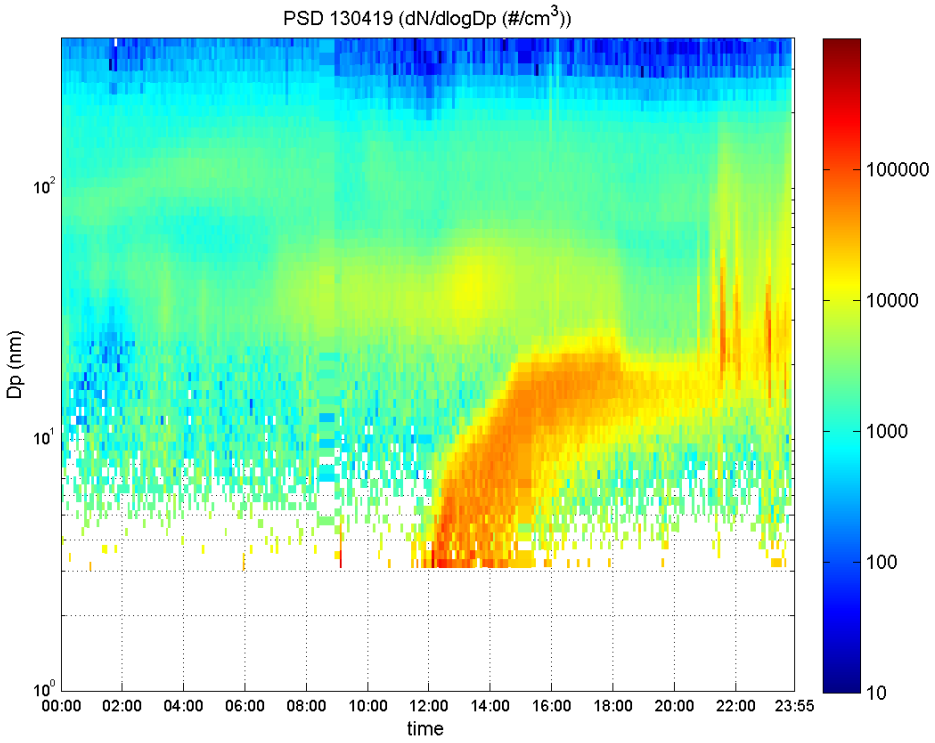

Figure 2. New particle formation event observed at the SGP Central Facility on 19 April 2013.

3.0 Lessons Learned

While overall the campaign was successful, we can nonetheless provide feedback as to what we feel went well, what went wrong, and some additional suggestions for ARM to consider for future campaigns. The following went well:

- The guest instrument facility provided an excellent base of operations. Although our instruments require a great deal of power, adequate power was available (although distribution with many long extension cords was required) and cooling was sufficient given the large number of heat-generating instruments in the building.
- SGP staff were very pleasant and supportive.
- The tethered balloon deployment was well-supported and provided important insights into the vertical extent of new particle formation.

- SGP cooperated with our request to postpone an infrastructure project adjacent to the Guest Instrument Facility. We appreciate this cooperation. If that work had continued, we would have lost all data from the best nucleation events during the entire study. Basically, we would have lost virtually all useful data from the intensive measurement campaign.
- NPFS was among our best intensive measurement campaigns because (i) SGP is located in an excellent location for our work; (ii) SGP provides excellent support personnel and facilities; (iii) our suite of instruments improves every year and functioned quite well during NPFS.

What went wrong:

- Prototype instruments occasionally fail during every intensive campaign. NPFS was no exception. Much of our effort focused on instrument repair.
- We were quite distressed that diesel engines were being operated adjacent to the guest instrument facility during our intensive measurement campaign. This destroyed our measurements during that period, and caused us to miss valuable data from some excellent nucleation events. This was unfortunate.

Areas that could be improved:

- Avoid scheduling any infrastructure projects that might interfere with scientific observations during intensive measurement campaigns.

4.0 Results

Post-processing and quality control of the measurement data have recently been completed, and the final dataset are being prepared for uploading to the ARM archive. Figure 3 shows an example of the type of data we acquired during a new particle formation event. Data such as these is essential for developing models for the formation and growth of nanometer-sized particles associated with these regional new particle formation events. The contour plot (c) shows measured aerosol number distributions down to ~1 nm.1 Similar measurements carried out in Atlanta (2009) allowed us to obtain size- and time-dependent growth rates for particles as small as 1 nm.2 Positive and negative ion spectra obtained with the TDCIMS (obtained using H3O+ and O2- as the reagent ions, which are employed alternately during a measurement sequence to detect different species in collected nanoparticles) are shown for 20 nm diameter particles formed during the NPF event. The positive TDCIMS spectrum (a) shows primarily basic compounds ammonium and amines, whereas the negative ion spectrum (b) shows deprotonated mono- and dicarboxylic acids as well as sulfate. These acidic and basic compounds may be among those that contribute to the formation of aminium salts.3 Cluster CIMS measurements of sulfuric acid vapor and sulfuric acid-containing clusters4 shown in plot (d) allow us to (i) quantify GRH2SO4, as described above, (ii) extend measurements of number distributions down to one molecule,5 and (iii) provide information about nucleation mechanisms.6 The Cluster CIMS also detects certain organic acids that likely affect GRother. (Obtaining concentration values for the organic compounds in plot (d) will require calibrations, which are in progress) The Ambient pressure Proton transfer Mass Spectrometer (AmPMS)7 detects gas-phase ammonia and a variety of other compounds including amines; these observations are shown in plot (e). Amines likely affect both nucleation and growth rates. The data in Figure 3 include information on species taken up by freshly nucleated particles as they grow, the concentrations of gas phase precursors that are likely contributing to growth, and measurements of

physical properties that allow *GR* to be determined as a function of size and time. Such data will provide the information required to understand the chemical mechanisms that determine GR_{other}, as described below in greater detail.

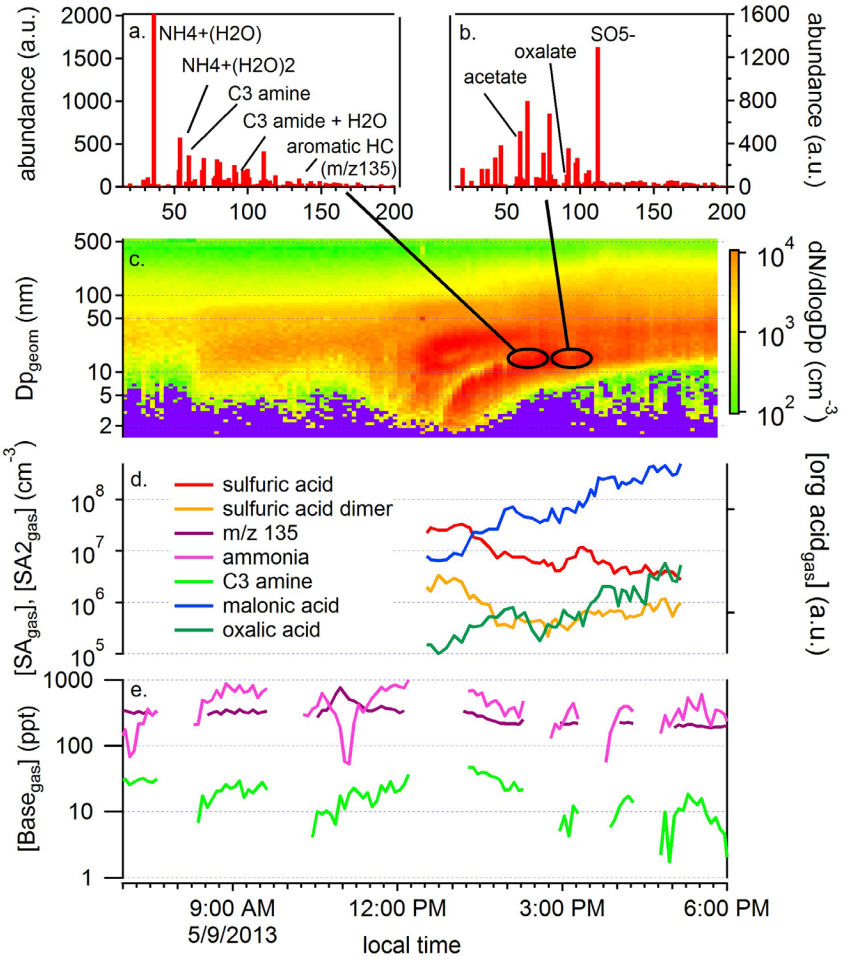

Figure 3. Observations of the composition of 20 nm diameter particles (a,b), the particle size distribution (c), the concentration of gas phase acids (d), and the concentration of select gas phase bases (e), measured on 9 May 2013 during NPFS. (*organic acid calibration will be performed after the campaign; data are presented uncalibrated).

Figure 4 shows an example of our observations of vertical profiles of 10-20 nm diameter particles. In the morning most of the 10-20 nm diameter particles are aloft, with highest concentrations at 500 m ASL; the afternoon was characterized by a well-mixed boundary layer, with nanoparticle concentrations relatively constant for the remainder of the event.

5.0 Public Outreach

No public outreach actions were associated with this campaign.

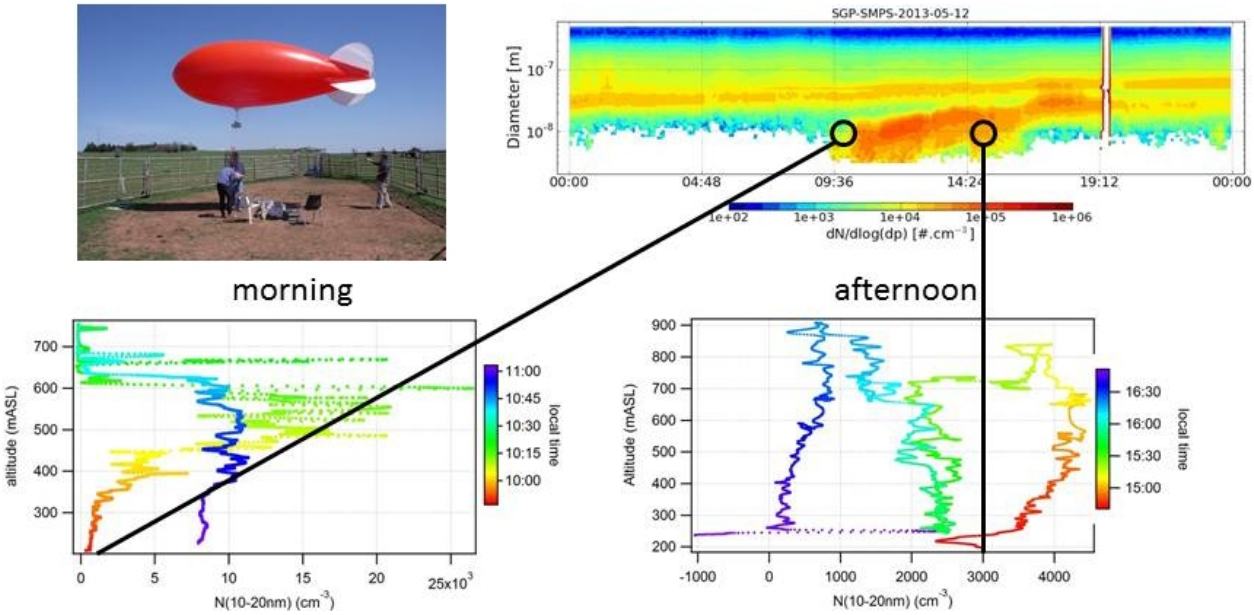

Figure 4. Tethered balloon data showing vertically resolved data on 10-20 nm diameter particle number concentrations during the NPFS.

6.0 NPFS Publications

6.1 Journal Articles/Manuscripts

Freshour, N., Carlson, K. K., Melka, Y. A., Hinz, S., Panta, B., & Hanson, D. R., 2014, "Amine Permeation Sources Characterized with Acid Neutralization and Sensitivities of an Amine Mass Spectrometer" *Atmospheric Measurement Techniques*, 7, 3611–3621.

Jiang, J., Kim, C., Wang, X., Stolzenburg, M. R., Kaufman, S. L., Qi, C., Sem, G. J., Sakurai, H., Hama, N. and McMurry, P. H., 2014, "Aerosol Charge Fractions Downstream of Six Bipolar Chargers: Effects of Ion Source, Source Activity, and Flowrate" *Aerosol Science and Technology*, 48:1207-1216. DOI: 10.1080/02786826.2014.976333

Zhao, J., J. Ortega, M. Chen, P. H. McMurry, and J. N. Smith, 2013, "Dependence of nucleation and growth on high molecular weight gas phase products during ozonolysis of a-pinene," *Atmospheric Chemistry and Physics,* 13: 7631–7644. doi:10.5194/acp-13-7631-2013.

6.2 Meeting Abstracts/Presentations/Posters

Lawler, MJ, et al., 2013. "Nanoparticle composition at two rural U.S. sites," *AGU Fall Meeting 2013*.

PH 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, Xi'an, China. (5/27/14)

PH 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. (6/6/14)

PH McMurry, University of Illinois, Urbana-Champaign, Department of Atmospheric Sciences departmental seminar. "New measurements of clusters and nanoparticles: Implications for atmospheric nucleation and growth models." (1/24/13)

PH McMurry, "New measurements of clusters and nanoparticles: Implications for atmospheric nucleation and growth models." Tsinghua University, Beijing, China. (2/26/13)

PH McMurry, AIST, Tsukuba, Japan. "New measurements of clusters and nanoparticles: Implications for atmospheric nucleation and growth models." (2/28/13)

PH McMurry, Atmospheric Chemistry Gordon Conference, Mt. Snow, Vermont. Invited Plenary Lecture. "Discoveries regarding nucleation and growth from new measurements of neutral molecular clusters and nanoparticles." (7/29/13)

PH McMurry, 11th UNU & GIST Joint Programme Symposium, Kota Kinabalu, Malaysia (Borneo), Invited Plenary Lecture, "Nucleation and growth of atmospheric aerosols." (10/23/13)

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

Smith, JN, 2014. Unraveling the mysteries of atmospheric new particle formation, *Clarkson University Seminar*, Potsdam, NY.

7.0 References

Chen, M, M Titcombe, J Jiang, C Jen, C Kuang, ML Fischer, FL Eisele, JI Siepmann, DR Hanson, J Zhao, and PH McMurry, An acid-base chemical reaction model for nucleation rates in the polluted atmospheric boundary layer. *Proceedings of the National Academy of Sciences*, 2012. 109(46).

Hanson, DR, PH McMurry, J Jiang, R Stickel, D Tanner, and LG Huey, Ambient Pressure Proton Transfer Mass Spectrometry: Initial Detection of Ammonia and Amines. *Environmental Science & Technology*, 2011. 45(20): p. 8881-8888.

Jiang, J, M Chen, C Kuang, M Attoui, and PH McMurry, Electrical Mobility Spectrometer using a Diethylene Glycol Condensation Particle Counter for measurements of aerosol size distributions down to 1 nm. *Aerosol Science and Technology*, 2011. 45: p. 510-521.

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Kuang, C, M Chen, J Zhao, JN Smith, PH McMurry, and J Wang, Size and time-resolved growth rate measurements of 1 to 5 nm freshly formed atmospheric nuclei. *Atmospheric Chemistry and Physics*, 2012. 12: p. 3573-3589.

Smith, JN, KC Barsanti, HR Friedli, M Ehn, M Kulmala, DR Collins, JH Scheckman, BJ Williams, and PH McMurry, Observations of aminium salts in atmospheric nanoparticles and possible climatic implications. *Proceedings of the National Academy of Sciences*, 2010. 107(15): p. 6634-6639.

Zhao, J, FL Eisele, M Titcombe, C Kuang, and PH McMurry, Chemical Ionization Mass Spectrometric Measurements of Atmospheric Neutral Clusters using the Cluster-CIMS *Journal of Geophysical Research*, 2010. 115: p. D08205.

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