

Final Report: "Collaborative Project: Contributions of organic compounds to  
the growth of freshly nucleated atmospheric nanoparticles"

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## Overview of achievements.

This is the final technical report for the portion of the project that took place at the National Center for Atmospheric Research, which covers approximately the first year of the period of performance. During this time we focused primarily on preparation for laboratory studies of individual processes that contribute to atmospheric new particle formation.

Our accomplishments to date are summarized along with the enumerated objectives.

### Analysis and modeling of DOE-funded observations

**Objective 1) We will perform growth-rate analyses and constrained box-model simulations of NPF from recent DOE field observations, including intensive observations such as the ARM-supported New Particle Formation Study (NPF2013) at the Southern Great Plains (SGP) site, the ASR-funded Nucleation and Cloud Condensation Nuclei (NCCN2009) study in Atlanta, and GoAmazon2014, as well as long-term observations from SGP.**

The 2013 ARM Southern Great Plains (SGP) New Particle Formation Study (NPF2013) held from April 13-May 24 provided an intensive look at formation and growth processes of aerosol particles as well as an opportunity to gain insight into the atmospheric chemistry in this understudied region of the United States. The 6-week campaign's objectives were to identify the species and growth mechanisms responsible for the region's new-particle formation and growth as well as create a comprehensive data set for use in both analysis and modelling efforts. Gas-phase aerosol precursors and particle-phase data were measured continuously throughout the campaign, including measurements of key acids (sulfuric and organic acids), bases (ammonia and amines), and VOCs; particle composition; and particle concentrations and size distributions. The measurements were primarily taken at the ARM Central Facility in Lamont, OK.

Throughout the 6-week campaign, several new-particle formation and growth events were observed. We identified three events, occurring on April 19, May 9, and May 11, respectively, that span over a range of chemical conditions and air-mass histories. Each day's event showed different dominant species in the growing particles: April 19 showed growth dominated by organics, May 9 showed growth dominated by ammonium sulfate, and May 11 showed growth dominated by sulfuric acid, amines, and organics. The Hysplit back-trajectories of the region's air masses for these days showed flow from the north through primarily agricultural regions for April 19 and May 11, and flow from the south through many urban and industrial regions of Texas for May 9.

We sought to determine if we could predict the variability of these growth events using our current knowledge of aerosol growth theories. We modelled these three days in the Model for Acid-Base chemistry in Nanoparticle Growth (MABNAG), developed by Yli-Juuti, et al. MABNAG simulates condensation, acid-base reactions, and oligomerization reactions leading to the growth of a single particle from nucleation size to CCN sizes. The inputs to MABNAG are gas-phase concentrations and properties of key atmospheric species that have been shown through field and lab measurements to strongly contribute to particle growth; the outputs are particle

growth and composition as a function of time. Our data set provided the gas-phase inputs to model condensation and acid-base reactions. On each day, the modelled particle growth rate falls within the observed growth rate and that the modelled particle composition shows the same dominant species contributing to growth as the observed particle composition shows. We find that growth by sulfuric acid, ELVOCs and organic acid-base reactions each contribute to growth to different degrees on each day.

The data collected at the ARM SGP site has given us unique and important insights to particle growth. By combining what we have learned from this campaign with ongoing laboratory growth experiments, we will create a computationally efficient parameterization for climate models. By using this parameterization in full aerosol-climate models, we will be able to estimate the climate impacts of new-particle growth and the importance of each growth mechanism as predicted by our detailed growth scheme.

In addition to the New Particle Formation Study, we collaborated with many other research groups to perform field measurements of new particle formation [1-3]. This collaborative work will improve model representations of new particle formation events.

#### Development of models for nanoparticle growth and composition

**Objective 2a) We will perform laboratory experiments focusing on the contribution of heterogeneous acid-base chemistry of semivolatile organic acids with ammonia and amines to nanoparticle growth. Results will be used to validate and improve the Model for Acid Base chemistry in NANoparticle Growth (MABNAG), which was recently developed by Prof. Ilona Riipinen and her students (Univ. of Stockholm) in collaboration with Prof. Kelley Barsanti of our research team.**

**Objective 2b) We will perform laboratory experiments focusing on nanoparticle growth due to particulate phase accretion reactions, initially focusing those involving the  $\alpha$ -dicarbonyl compound glyoxal. A model representing this chemistry will be developed based on particulate properties such as acidity as well as ambient temperature, RH, and other pertinent environmental conditions.**

**Objective 2c) We will quantify the contribution of the reversible condensation of low-volatility organic compounds to nanoparticle growth rates through integrated laboratory measurements and process level models. These studies will initially focus on the direct partitioning of pure vapors onto laboratory-generated seed particles, varying environmental conditions and aerosol loading. Results will be interpreted using a thermodynamic model that associates molecular structure with volatility.**

A major activity during the past year has been the preparation for laboratory studies of individual processes that contribute to atmospheric new particle formation. For our first experiments on the role of inorganic and organic salt formation on nanoparticle growth, we have constructed system capable of providing known concentrations of ammonia and alkyl amines at concentrations as low as 10 ppt. Permeation tubes were purchased from VICI Metronics (Poulsbo, WA) and were found to have more consistent amine delivery rates than permeation tubes constructed using the method of Freshour et al. [4] The compounds used for this were ammonia (NH<sub>3</sub>, MW=17), methyl amine (MA, MW=31), dimethyl amine (DMA, MW=45) and diethyl amine (DEA,

MW=73). The permeation tubes were placed in glass vials sealed with Teflon caps. Nitrogen gas from a liquid nitrogen dewar at  $100 \text{ ml min}^{-1}$  was passed through the glass vials which were perpetually maintained at  $30^\circ\text{C}$  using individual insulated temperature-controlled ceramic blocks. All fittings and tubing were PTFE. This method produced constant delivery rates between 30 and  $150 \text{ pmol s}^{-1}$  (depending on the amine). The delivery rates were verified using two independent methods. First, they were weighed once per week for 4 months to obtain a gravimetric measurement. By plotting the mass loss vs. time, a slope was generated that defined the delivery rate in pmoles per second. The 2nd method used acid neutralization by bubbling the flow of each individual amine into 50 ml of  $\sim 3.5$  pH solution of HCl as described by Freshour et al.[4] Results generally agreed within  $\sim 20\%$ .

The ppm-level amine concentrations were systematically reduced using a dilution system in order to obtain the ppt levels required for our experiments. An active dilution system consists of three separate dilution stages made from three pairs of mass flow controllers (MFC). In each stage, a certain portion (50-95%) of the incoming  $100 \text{ ml min}^{-1}$  flow is removed from the total flow, and the same amount of  $\text{N}_2$  flow is added shortly downstream. Using tubing of different diameters and inserting the smaller ones into the larger ones as shown ensures that the amine is only in contact with Teflon tubing from the perm cell to the mass spectrometer without ever contacting any other surface (including the mass flow controllers). All tubing was soaked in a 0.1 M NaOH solution to ensure that any acidic-impurities on tubing surfaces (left over from the manufacturing process) were passivated and minimized any non-reversible chemical losses of the alkaline amines. This technique can result in a total dilution factor of over 1000x. A final 100x dilution is performed by mixing the  $100 \text{ ml min}^{-1}$  with  $\sim 10 \text{ l min}^{-1}$  flow in the experiment chamber or flow tube apparatus.

The dilution system performance was verified using  $\text{CO}_2$  and an infrared gas analyzer (IRGA, LI-Cor, model 6262). The IRGA was calibrated from  $\sim 17$  to 6500 ppm  $\text{CO}_2$  and then used to verify single and multiple dilution steps. Because  $\text{CO}_2$  is a non-condensing and non-reactive gas, dilution stages could be checked fairly quickly ( $\sim 10$  minutes) before and after each amine test. The dilution checks were found to be necessary as small drifts in the dilution system flows (especially the vacuum flows) can result in large uncertainties in the overall dilution.

In addition to the ammonia/amine generation system, we have:

- Completed construction and testing of our  $10 \text{ m}^3$  aerosol reaction chamber. Calibrations are currently underway to quantify wall loss rates and residence time distributions.
- Constructed a flow tube reactor for generating nanoparticles of known composition. This flow tube is based on the design described in Zollner et al. [5]
- Built an AmPMS based on the instrument described in Hanson et al. [6]

**Objectives 3 (Development of a semi-empirical growth rate parameterization) and 4 (Regional and global modeling) are the focus of activities of our collaborator, Prof. Jeffrey Pierce at Colorado State Univ.). Therefore, a description of accomplishments of these objectives will not be included in this document.**

**The following is a list of manuscripts that have been published that made use of data from this project.**

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” *Atmos. Meas. Tech.*, 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 Sci. Technol.*, 48:1207-1216. DOI: 10.1080/02786826.2014.976333

References Cited that acknowledge DE-SC0011664:

1. Yu, F., et al., *Spring and summer contrast in new particle formation over nine forest areas in North America*. *Atmos. Chem. Phys.*, 2015. **15**(24): p. 13993-14003.
2. Zhou, L., et al., *Contribution from biogenic organic compounds to particle growth during the 2010 BEACHON-ROCS campaign in a Colorado temperate needleleaf forest*. *Atmos. Chem. Phys.*, 2015. **15**(15): p. 8643-8656.
3. You, Y., et al., *Atmospheric amines and ammonia measured with a chemical ionization mass spectrometer (CIMS)*. *Atmospheric Chemistry and Physics*, 2014. **14**(22): p. 12181-12194.

Other references cited above:

4. Freshour, N.A., et al., *Amine permeation sources characterized with acid neutralization and sensitivities of an amine mass spectrometer*. *Atmos. Meas. Tech.*, 2014. **7**(10): p. 3611-3621.
5. Zollner, J.H., et al., *Sulfuric acid nucleation: Power dependencies, variation with relative humidity, and effects of bases*. *Atmos. Chem. Phys.*, 2012. **12**: p. 4399-4411.
6. Hanson, D.R., et al., *Ambient Pressure Proton Transfer Mass Spectrometry: Initial Detection of Ammonia and Amines*. *Environmental Science & Technology*, 2011. **45**(20): p. 8881-8888.

Lectures that Acknowledged DE-SC0011664

Understanding the chemical processes that affect growth rates of atmospheric nanoparticles, *Berkeley Atmospheric Sciences Center Seminar*, UC Berkeley, Berkeley, CA, April 22, 2015.

Recent research and future plans involving Land Ecosystem Atmosphere Processes, *Land Ecosystem—Atmosphere Processes Workshop*, EMSL, Richland, WA, March 9., 2015.

What are GoAmazon measurements telling us about the sources of ultrafine aerosol particles in the Amazon? *GoAmazon Science Team Meeting*, Boston, MA, May 18, 2015.

Mechanisms for the formation and growth of nanometer-sized particles in the Amazon: Insights from GoAmazon2014 and the Tapajós Upwind Forest Flux Study (TUFFS), *AGU Fall Meeting*, San Francisco, CA, December 15, 2014.

What are field (and lab) measurements telling us about the role of organics in new particle formation and growth? *Telluride Meeting: Organic Particles in the Atmosphere: Formation, Properties, Processing, and Impact*, Telluride, CO, July 28, 2014.

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

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

Pierce, J.R., Anna Hodshire, Jim Smith, Peter McMurry, Jun Zhao, “New-particle formation and growth at the DOE Southern Great Plains field site in Oklahoma”, *DOE ASR meeting*, Washington D.C., 3/2015.