TO: Texas Air Research Center

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SUBJECT: Annual Progress Report

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PROJECT TITLE: Experimental study of the production of PM2.5 in Southeast Texas clouds

PROJECT PERIOD: 9/1/13 – 8/31/15

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The specific objectives of the proposed work are i) to assess the in-cloud conversion efficiency of SO$_2$ and organic precursors under conditions representative of east Texas and ii) to quantify the sensitivities of those conversion rates to perturbations in trace gas concentrations, initial particle characteristics, and environmental parameters. For some experiments concentrations of all relevant species (e.g., SO$_2$, hydrogen peroxide, ammonia, ...) will be prescribed, while for others ambient air will be used as the baseline to which perturbations of one or more species will be used to assess sensitivity. Most or all of the experiments will be conducted at a site about 10 km south of the Texas A&M campus. The primary tools to be used for all of the experiments are the newly developed Captive Aerosol Growth and Evolution (CAGE) chambers. For each experiment, known size and known composition particles will be injected into both chambers. After an initial conditioning period during which gas phase photochemistry produces a representative distribution of soluble species, clouds will be generated and then dissipated over a period of ~30 min to mimic the experience of an air parcel rising through a boundary layer cloud. The size distribution, volatility, and hygroscopicity of the particles will be measured immediately before and immediately after the cloud cycle using a scanning mobility particle sizer (SMPS) and tandem differential mobility analyzer (TDMA). The observed growth and change in properties of the particles resulting from the cloud cycle reflect the addition of mass through aqueous phase reactions. The primary result of this project is the difference between the added masses in the baseline and perturbed chambers. By isolating the impact of specific perturbations, these results can be considered as neatly-posed problems for model development and testing. A partial list of perturbation types was provided in the original proposal.

Of the major efforts undertaken during the first year, the one that was originally planned was improvement of the software control and automation. The challenge is to control the 18 flow rates, 14 temperatures, 8 pressures, and 5 humidities within the CAGE and ancillary systems using 46 electrically-actuated control, on/off, and 3-way valves, 26 vacuum pumps, water pumps, and blowers, 11 heaters and a variable temperature chiller system, and 12 data acquisition cards. Feedbacks between many of the measured elements makes any level of manual control impractical. Portions of the software had been created and tested prior to the start of this project, but repeated problems and some resulting component failures made it clear
that the more robust and automated control was needed. The resulting improvements have been substantial and have resulted in far better experimental control and experimental results. The user interface couples graphical display of all of the relevant measured quantities and control signals with dynamic schematics that quickly show e.g. flow path and that help quickly identify problems. As just one example of the improvement that has resulted from the software revision, Figure 1 shows results of an earlier (left) and recent (right) attempt at creating the adiabatic expansion required for cloud formation. The black lines in both graphs represent the desired chamber pressure over the ~30 min cycle and the red lines represent that measured. Beyond the improved control that is evident in the comparison between the two, the recent experiment was entirely software-controlled, whereas the previous one required coordination among several people to turn on and off vacuum pumps and switch valves. We will continue to optimize control parameters and make small refinements to the Labview software, but the intensive effort is complete.

![Figure 1. Adiabatic expansion experiments conducted with the original software (left) and with the revised software (right).](image1)

Preliminary experiments conducted early in the project identified two major obstacles to successful completion of the planned experiments: 1) small leaks that were undetectable during standard operation with the chambers under only ~50 mbar vacuum, but became pronounced and
problematic during cloud cycles when the vacuum exceeds 200 mbar, and ii) contamination in
the chambers or tubing, valves, flow meters, etc. upstream of the chambers resulted in
unacceptable growth rates of injected particles when zero air was flushed behind the permeable
expanded PTFE membranes. Descriptions of these issues and of the steps taken to remedy them
are provided below.

As briefly discussed in the original proposal, the chambers are constructed of a
cylindrical section of 0.05 mm thick FEP Teflon film. They are surrounded by two additional
layers of the same material, resulting in three concentric layers with thin, flexible walls. The
FEP film is attached and sealed to end rings/caps using combinations of Teflon gasket and
tensioned Teflon-wrapped cable. The pressures within each of the layers must be precisely
controlled to maintain slight positive differential pressure in the innermost two while the
absolute pressure changes about two orders of magnitude more during a typical cloud cycle. In
addition to the seals at ends of the FEP layers, there are over a hundred tubing and pipe
connections in each chamber that must be leak free. The manifestation of a leak between the
chamber and the surrounding layer is a reduction of particle retention time below that expected
based on the rate at which sample is withdrawn and replaced with particle-free air. A leak
between the two outermost layers or between the outermost layer and the surrounding
environment becomes most evident only during cloud cycles as the vacuum in the chambers
increases significantly with the adiabatic expansion. Both of these problems were identified in
the preliminary experiments, the former resulting in particle loss rates of as much as 30% per
hour and the latter resulting in the need for additional vacuum pumps. The graduate students
involved in this project spent a considerable amount of time systematically working through all
potential leaks and devising approaches to reduce or eliminate them. Over a period of months
they redesigned and constructed improved seals for the FEP layers, replaced all flange gaskets,
and made numerous other modifications of components, tubing, and air flow ducts. To guide
them in identifying the sources and determining whether they had been sealed, they filled the
chambers with elevated levels of ozone using a high concentration generator they constructed
and then “sniffed” for leaks using a trace-level ozone analyzer. This effort has resulted in a
substantial improvement in particle retention and vacuum control.
The more challenging problem we have worked to resolve is contamination levels in the chambers that result in unexplained growth of injected particles even when the volumes behind the ePTFE membranes are flushed with zero air. The experimental approach taken with these chambers in which monodisperse particle populations are injected and their size tracked over time likely results in increased sensitivity and detectability of such contamination sources relative to the more conventional approach of injecting polydisperse particle populations and tracking their volume or mass concentration. Regardless, any unexplained particle growth must be smaller than the changes in particle size that will accompany cloud processing. The chambers are constructed only of Teflon and great care was taken during their construction and installation to avoid introducing any contamination. They were repeatedly conditioned by filling with several ppm of ozone and then exposing them to direct sunlight throughout the day. The injected ozone, and oxidants produced as it is photolyzed such as hydroxyl radical, react with sites on the Teflon surfaces and with potential contaminants that deposited on the walls. Though such conditioning reduced the unexplained particle growth rate, it was still unacceptably high in both chambers.

Based on our observation that the compounds condensing on the particles were likely organic, we next sampled air at dozens of points in the chambers, particle generation system, and gas conditioning system using a proton transfer reaction mass spectrometer (PTR-MS). Figure 2 shows results from a set of those measurements that suggest an array of VOCs were concentrated in the outermost layer of the chamber system, with substantially lower concentrations in the chambers. These experiments were valuable, but difficulty in identifying the VOCs associated with each m/z and the inability of the PTR-MS to detect many relevant compounds led us to develop the capability to directly measure particle mass production potential of the air throughout the chamber system. We designed and constructed the Potential Aerosol Mass system (e.g., Kang et al., 2007) depicted in Figure 3 and repeated the sampling process used with the PTR-MS. Through these tests we determined that a substantial source of contamination was the homemade heated catalyst system we had used in the zero air system. Even when this was turned off, residual contamination that had deposited in the tubing and components upstream of the chambers resulted in particle growth. We have since removed the impacted tubing and worked to clean or replace the impacted components. Despite the resulting reduction in
unexplained particle growth rate, it remains stubbornly high and we continue to work to achieve further reductions.

Figure 2. Example PTR-MS spectra measured in the chamber and surrounding layers.

Figure 3. Potential Aerosol Mass (PAM) system that was constructed to locate sources of contamination responsible for unexplained particle growth.

We recently conducted several experiments designed to test chamber performance and control and are now preparing to transition to the science experiments outlined in the initial proposal. Any experiments initially planned for the first summer that are not completed this fall will be conducted next summer. We have no competing demands for the chamber system next summer and will be able to use them for as much time as needed to complete the project.