

**EXAMINATION OF THE EFFECTS OF SEA SALT AEROSOLS ON
SOUTHEAST TEXAS OZONE AND SECONDARY ORGANIC
AEROSOLS**

An Undergraduate Scholars Thesis

by

MARK DAVID BENOIT

Submitted to Honors and Undergraduate Research

Texas A&M University

in partial fulfillment of the requirements for the designation as

UNDERGRADUATE RESEARCH SCHOLAR

Approved by

Research Advisor:

Dr. Don Collins

May 2013

Major: Meteorology

TABLE OF CONTENTS

	Page
TABLE OF CONTENTS.....	1
ABSTRACT.....	2
AKNOWLEDGEMENTS.....	4
NOMENCLATURE.....	5
CHAPTER	
I INTRODUCTION.....	6
II METHODS.....	10
III RESULTS AND CONCLUSIONS.....	15
REFERENCES.....	17
FIGURES.....	19

ABSTRACT

Examination of the Effects of Sea Salt Aerosols on Southeast Texas Ozone and Secondary
Organic Aerosol. (May 2013)

Mark David Benoit
Department of Atmospheric Sciences
Texas A&M University

Research Advisor: Dr. Don Collins
Department of Atmospheric Sciences

Despite decades of study, we still do not fully understand aerosols and their interactions among gases or other aerosols in the atmosphere. Among their impacts, they influence radiative transfer in the atmosphere and contribute to cloud formation. There are many different types of aerosols, including dust particles, soot particles, and microscopic particles containing inorganic compounds such as sulfates. Most of these particles have natural origins, but many are anthropogenic. The eventual purpose of this research is to examine sea salt aerosols and their impact on polluted environments. Sea salt aerosols act as Cloud Condensation Nuclei (CCN) as well as providing a surface for heterogeneous reactions. Such reactions have implications for trace gases such as ozone, reactive nitrogen, mercury, and sulfur containing compounds. Urban areas are most impacted by these trace gases, which is a concern because ozone especially affects the health of citizens. Experiments have three basic parts. First we generate mono-disperse

aerosols. That aerosol is then injected into the aerosol chambers with sea salt aerosols and prescribed concentrations of trace gases to characterize relevant interactions. However, those chambers are still under construction and not used during my study. The processed aerosols are then analyzed with a tandem differential mobility analyzer (TDMA) and other equipment. Different concentrations of sea salt aerosols, NO_x , O_3 , and other gases were planned to be introduced during the experiments. Concentrations of other gases and intensity of solar radiation would mimic those outside. Because these reactions have proved to increase localized concentrations of ozone in other work, this could have important implications. Future work will be designed to find study these interactions. This is important because the EPA has considered tightening the standards for both ozone and particulate matter. Industries would then need to reduce emissions or move farther from current sources of Cl or NO_x pollution.

ACKNOWLEDGEMENTS

Dr. Collins for all of your support, advice, and review of my thesis. I appreciate your willingness to put time and effort into my education.

To master's student Nathan Taylor for helping me get experiments started. You also explained many things that I did not fully understand. Also, thank you for helping me with the instruments at Geochemical Environmental Research Group (GERG) that were not familiar.

NOMENCLATURE

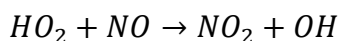
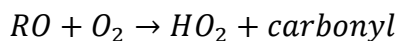
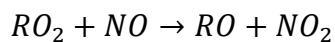
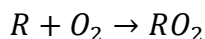
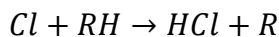
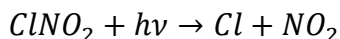
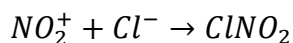
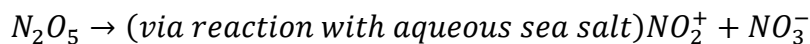
CCN	Cloud condensation nuclei
CPC	Cloud condensation nuclei counter
e-PTFE	Expanded polytetrafluoroethylene
HR-ToF-AMS	High-resolution time-of-flight mass spectrometer
HTDMA	Humidified Tandem Differential Mobility Analyzer
GHG	Greenhouse Gas
O_3	Ozone
PILS	Particle into liquid sampler
SMPS	Scanning mobility particle analyzer
VOCs	Volatile Organic Compounds

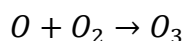
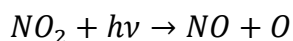
CHAPTER I

INTRODUCTION

Sea salt aerosols, as their name implies, originate from the sea. They are a major component of atmospheric aerosols globally and have a significant influence on cloud microphysics as well as heterogeneous chemistry. However, they still are not well understood. Research has been conducted to analyze sea salt particle effects on atmospheric radiative forcing (Ayash et al., 2008), where they appear to have major impacts on the atmospheric radiation budget as a source of cloud condensation nuclei (CCN). Sea salt aerosols are also a source of halogens, and because of their large size, provide a significant surface area on which heterogeneous reactions can take place, which affects the concentrations of trace gases such as ozone, reactive nitrogen, mercury, and sulfur containing compounds. This is a major concern for high pollution areas like Houston, TX where there are health concerns. Prior research was done to analyze some potentially important but poorly constrained impacts of sea salt aerosols. What was found was noteworthy. In the presence of NO_x , a common pollutant, reactions involving Cl atoms in the sea salt may lead to increased ozone production and removal of organics from the marine boundary layer (Oum et al., 1998). There is recognition of the importance of sea salt aerosols to atmospheric processes, but there remains a gap in research of the aging process of sea salt aerosols, their impact on a polluted environment, and their role in heterogeneous reactions of gas phase species. The evolution of sea salt aerosols in the atmosphere results from interactions with condensable and reactive gaseous species that exist in a given environment, the products of which can vary greatly with time and location.

As aforementioned, sea salt aerosols are a source of halogens, and as such, they can have a significant effect on the atmosphere. Most importantly, these aerosols contain chlorine and can provide a steady, yet small, source of reactive chlorine to the atmosphere. The reaction sequence starts first by the dissolution of N_2O_5 in an aqueous sea salt particle and its subsequent reaction with Cl to create $ClNO_2$. This is most significant at nighttime because N_2O_5 is and its precursors are photolyzed by sunlight. $ClNO_2$ that accumulates overnight is rapidly photolyzed after sunrise, generating reactive chlorine atoms. Recent evidence of the importance of this cycle comes from observed high concentrations of $ClNO_2$ in the subtropical marine boundary layer (Osthoff et al., 2008). Indeed, in recent research, it has been shown that $ClNO_2$ is an important part of chlorine cycling (Simon et. al., 2009). Often, the chlorine atom will act as a catalyst and recycle itself resulting in elevated concentrations. Active chlorine atoms can destroy ozone and some GHG through direct reaction, but can alternatively react with organics and accelerate ozone production if there are sufficient oxides of nitrogen (NO_x) (Oum et al., 1998). Ozone destruction, however, is unlikely in the morning since its concentration is low at sunrise. Oum also mentions that laboratory studies have identified possible photolyzable Cl containing compounds that form in the presence of O_3 and probably sunlight. The basic reactions described above are as follows:





From these reactions it can be seen that ozone production possibly could be enhanced, especially in the morning hours. When there are locally high concentrations of $ClNO_2$ and the sun is just coming up, it is rapidly disassociated, freeing the chlorine radicals to react with organics and eventually lead to a large change in ozone over a short period of time. In a study done in southeast Texas, it was shown that ozone concentrations increased at a rate of up to 70ppb per hour in the morning (Chang and Allen et. al., 2006). Also, it is worth noting that even though a hydroxyl radical is used in the process, one is also produced, thus allowing it to oxidize more VOCs. Not all ozone is harmful, for stratospheric ozone blocks many harmful UV rays that would destroy life as we know it. Ozone at ground level, however, can have negative health impacts in high concentrations on human health, causing premature death, upper and lower respiratory diseases such as asthma and bronchitis, heart attack, and other cardiovascular problems (Weinhold et. al., 2008). Plants are affected as well, as ozone influences photosynthesis, decreasing the economic yield of most plants (Kyoungwon, et al., 2011). Consequently there are standards imposed by the government for 8 hr. maximum concentrations of ozone. As of 2008, but enacted in 2012, the standard is 75ppb (parts per billion) averaged over 8 hrs., which is lower than the previous standard of 84ppb set in 1997. The government is presently having debate on whether to lower it ever further. Therefore, research on the topic of sea salt aerosols and their interaction with a polluted environment, particularly ozone, is paramount to future decisions. Southeast Texas is definitely an area that would be impacted by this chemistry and benefit from research in this area. It has plentiful sea salt aerosols from the gulf and Galveston Bay in addition to many industries that emit chlorine as a pollutant. Not only this, but they also have abundant organics and NO_x . Studies in southeast Texas have certainly

been of great importance, yet, specific laboratory experiments of these interactions have not been conducted.

CHAPTER II

METHODS

Experiments done for this project were conducted at the Geochemical and Environmental Research Group (GERG) site in south College Station, TX. A cargo trailer with instruments was to be used in conjunction with two large 1000 liter chambers that are on a large fifth wheel trailer (See Figure 1). The chambers are cylindrical as seen in Figure 2 and have two components. The inside chamber houses the experiments while the outside portion is circulated ambient air and moderates the temperature and pressure. Both walls are largely transparent to the solar radiation that drives relevant photochemistry. Both the outer and inner walls are made of fluorinated ethylene propylene (FEP) film that is very thin and allows most sunlight to penetrate. The ends of the chambers are made of expanded polytetrafluoroethylene (ePTFE), which acts as a permeable barrier separating ambient air behind it from the chamber air. The micro-porous structure of the ePTFE maintains efficient particle filtration while simultaneously allowing gases to readily pass through. The filtration efficiency is estimated at 96% for particles larger than 10nm. This makes it popular in various filtration and pharmaceutical applications (Wikol et al., 2008). This is a unique feature that allows conditions inside the chamber to approach those outside. Particle loss rates are minimized to the extent possible to permit long duration experiments. In addition, the chambers rotate at a rate of one revolution per minute to minimize the settling of any large aerosol particles such as sea salt.

Instrumentation

Since there are two chambers available for use, one is generally used as the control, while the other is perturbed in some manner. Though the chambers are partially operational, they are not

yet suitable for the planned experiments. Instead, my focus shifted to optimizing the aerosol generation and characterization steps that will be critical elements of the chamber experiments. The first step in our experiment was to generate aerosols to be injected into the chambers. This was done using an atomizer. In order to generate a narrow range of aerosol sizes, we used a DMA. Use of particles in a narrow size range is important for tracking the size evolution in the chambers. Following a period of several hours in the chambers the now larger particles will be sampled and analyzed. Bypassing the chambers, we used a humidified tandem differential mobility analyzer (HTDMA), a scanning mobility particle analyzer (SMPS), and a TSI, Inc. condensation particle counter (CPC) to measure the size distribution of the generated aerosol. When we conduct further experiments, we will do a full physical and chemical analysis. In the physical analysis, aerosol size distribution and concentration will be recovered, with an emphasis on minimizing the air volume drawn from the chambers during each experiment. They will enter the HTDMA to measure their hygroscopicity and then to the SMPS to retrieve a size distribution. For both the HTDMA and SMPS, separated particles are detected by the CPC counter, which exposes the particles to supersaturated butanol to activate them and grow them large enough to count optically. Complementary compositional analysis to be conducted in the future will employ an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS) and Brechtel Manufacturing, Inc. (BMI) particle-into-liquid sampler (PILS) with ion chromatography (IC, Dionex 1600). Chemical composition measurements are described in other work (DeCarlo et al., 2006), but the details are not relevant for discussion here. Species measured by the HR-ToF-AMS include sulfate, nitrate, chloride, ammonium, and organic material. Organic material can be separated into types based on mass spectral characteristics using statistical techniques (Canagaratna et al., 2007; De Haan et al., 2009). The BMI PILS

provides measurement of the composition of the water-soluble fraction of sampled particulate matter. The aerosol is collected in a water stream that is directed into a Dionex 1600 IC for ionic composition. With it we will be able to measure sulfate, nitrate, chloride, ammonium, potassium, magnesium, calcium, and sodium. Other analyses may also be conducted such as light absorption by organics or water-soluble organic carbon content.

Procedures

Experiments using these chambers are founded on controlled perturbations of conditions in one chamber from a baseline, identical configuration. The control chamber will just contain ambient air in most cases. Obviously, other baselines can be made by modifying this primary condition in both chambers. Again, this will be an outline of future work, since the chambers were incomplete. Most experiments would be constructed by creating perturbations in the injected aerosol, trace gas composition, or environmental conditions in one of the parallel chambers. Chambers would be set up to be in equilibrium initially, and then a perturbation would be applied. For example, sea salt aerosol of varying sizes may be injected in one of the chambers where both already contain NO_x and O_3 that was previously injected. Such experiments would take place both in the presence and absence of sunlight. Sunlight seemed to have a significant impact on studies done in the past. Replication of the observations, however, has not been done in a laboratory environment. During and after the experiment, it could then be assessed what impact the sea salt aerosols would have on composition within the two chambers. One important part of this process will be to equilibrate the gases and aerosols and characterize any losses to the side of the chambers or plumbing in the instruments. In a typical sample, 10L of the available 1000L is required from the chamber. The instrument required volume may be diluted to preserve the chamber sample.

Figure 3 highlights the three basic steps to this process of experimentation. First, generation of aerosols and other trace gases needed for the perturbation of the chambers. Second, reaction of gases in the chambers with introduced aerosols and added trace gases such as ozone. Third, analysis of the trace gas concentrations and particle size and properties from the chambers. Mono-disperse aerosols were generated in preparation for the experiments using the atomizer and the DMA. The middle and second step was omitted because the chambers were incomplete. After we generated the mono-disperse aerosols, we analyzed them with the HTDMA, CPC, and SMPS. This was done to assure that the atomizer and DMAs were performing properly and to optimize the generation procedure.

Size distributions typical of marine aerosols with a large sea salt fraction range from just above $1\mu m$ to around $20\mu m$ (Squires et al., 1958). Experiments would include size ranges that fit the distribution Squires found empirically, as well as differences to study variations in their evolution. Increased particle size increases the available surface area but also may reduce the efficiency with which chlorine is liberated. Droplet concentrations from 10 cm^{-3} to 200 cm^{-3} will be included over the relevant size range. These are also typical concentrations Squires found. The Gulf of Mexico near Houston, TX will be mimicked in experiments. However, high concentrations of aerosols typical of Houston will also be represented by the addition of aerosols to the chambers. Large concentrations upward of $10,000\text{ cm}^{-3}$ have been recorded in Houston, and these will be emulated. Trials will vary in number, ranging from 3 to 6 or more for each mono-disperse particle size and concentration. More experiments will be conducted with the most typical particle sizes and concentrations such as $5\mu m$ and 50 cm^{-3} respectively. Most of these trials will be conducted over 2-6 hours, with some being shorter or longer depending on the objective for that experiment. The measurements are expected to reveal

information on how interactions with NO_x and other pollutants influence the experiment end gas and particle phase characteristics. Change in levels of pollutants and characteristic aerosol sizes and concentrations will be measured.

CHAPTER III

RESULTS AND CONCLUSIONS

Unfortunately, as aforesaid, the chambers were not yet suitable for experimentation. Recently, work has been done and one chamber is basically complete as this paper is finishing. In the methods, we had three steps to our experiments. The middle step of using the chambers was omitted, but the other two were conducted. The first important step in our experiments was to create aerosols. This was described in our methods and involved the DMA to separate particles by size. Using the atomizer and a dilute sodium chloride solution, we generated salt aerosols. First, using the CPC and SMPS, we measured the atmospheric size and concentration distribution of the generated aerosols. This is seen in Figure 4. Next, testing the atomizer, we generated aerosols without using the DMA and then analyzed them. In Figure 5 it is evident that the concentrations overall were greater than in the atmosphere, but with a similar size distribution shape. Lastly, we wanted to create ranges of aerosols that were mono-disperse, which means concentrated in narrow bands of particle sizes. Using the DMA with the atomizer, we obtained a narrow range of particles seen in Figure 6. This is important because we will introduce multiple narrow bands of sizes into the chambers and track their evolution along with the other characteristics outlined in the methods.

We hoped in our experiments to gain some valuable insight into the interactions of sea salt aerosols and trace gases and pollutants in an environment like Houston. As discussed in the introduction, some modeling research studies suggested that in a marine environment such as that frequently entering the Houston airshed, spiked levels of ozone could result from rapid photolysis of $ClNO_2$. This frees the Cl radical and allows it to react with organics, which are

abundant in Houston, and produce spiked 1 hr. concentrations of ozone (Chang and Allen et. al., 2006). High levels of ozone are harmful to human health, causing premature death, upper and lower respiratory diseases (Weinhold et. al., 2008). Likewise, plants are affected (Kyoungwon, et al., 2011). The EPA standards enacted in 2012 allow for the 8 hr. concentration of ozone to be 75ppb, which is lower than the previous standard of 80ppb in 1997. If the EPA wishes to lower this level further, which has been debated, it could have huge implications to industry in such an area as Houston. Future work will continue this research and hopefully reach meaningful conclusions.

REFERENCES

1. Ayash, T. "Direct and indirect shortwave radiative effects of sea salt aerosols." *Journal of Climate* 21.13 (2008):3207-3220.
2. Canagaratna, M. R., et al. "Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer." *Mass Spectrometry Reviews* 26.2 (2007): 185-222.
3. Chang, Sunghye, and David T. Allen. "Atmospheric chlorine chemistry in Southeast Texas: Impacts on ozone formation and control." *Environmental science & technology* 40.1 (2006): 251-262.
4. Cho, Kyoungwon, et al. "Tropospheric ozone and plants: absorption, responses, and consequences." *Reviews of Environmental Contamination and Toxicology Volume* 212 (2011): 61-111.
5. DeCarlo, Peter F., et al. "Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer." *Analytical Chemistry* 78.24 (2006): 8281-8289.
6. De Haan, David O., Margaret A. Tolbert, and Jose L. Jimenez. "Atmospheric condensed-phase reactions of glyoxal with methylamine." *Geophysical Research Letters* 36.11 (2009): L11819.
7. Osthoff, Hans D., et al. "High levels of nitryl chloride in the polluted subtropical marine boundary layer." *Nature Geoscience* 1.5 (2008): 324-328.
8. Oum, K. W., et al. "Formation of molecular chlorine from the photolysis of ozone and aqueous sea-salt particles." *Science* 279.5347 (1998): 74-76.

9. Simon, H., et al. "Modeling heterogeneous $Cl(NO)_2$ formation, chloride availability, and chlorine cycling in Southeast Texas." *Atmospheric Environment* 44.40 (2010): 5476-5488.
10. Squires, P. "The microstructure and colloidal stability of warm clouds." *Tellus* 10.2 (1958): 262-271.
11. Wikol, Michael, et al. "Expanded Polytetrafluoroethylene Membranes and Their Applications." *DRUGS AND THE PHARMACEUTICAL SCIENCES* 174 (2008): 619.
12. Weinhold, Bob. "Ozone nation: EPA standard panned by the people." *Environmental health perspectives* 116.7 (2008): A302.

FIGURES

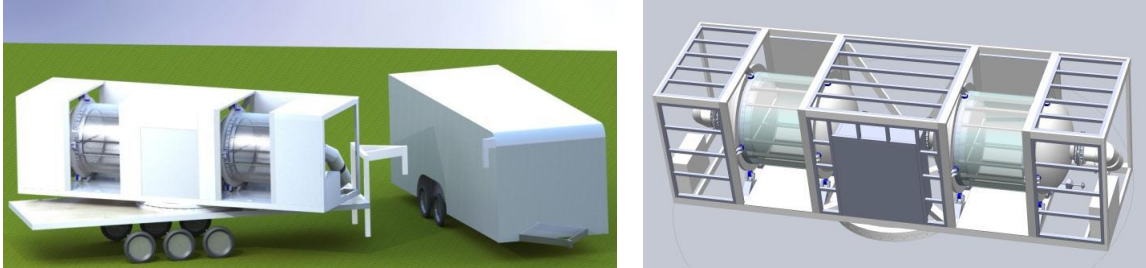


Figure 1 Left: Sun-tracking, trailer mounted chamber system and instrumentation trailer. Right: The exposed chambers.

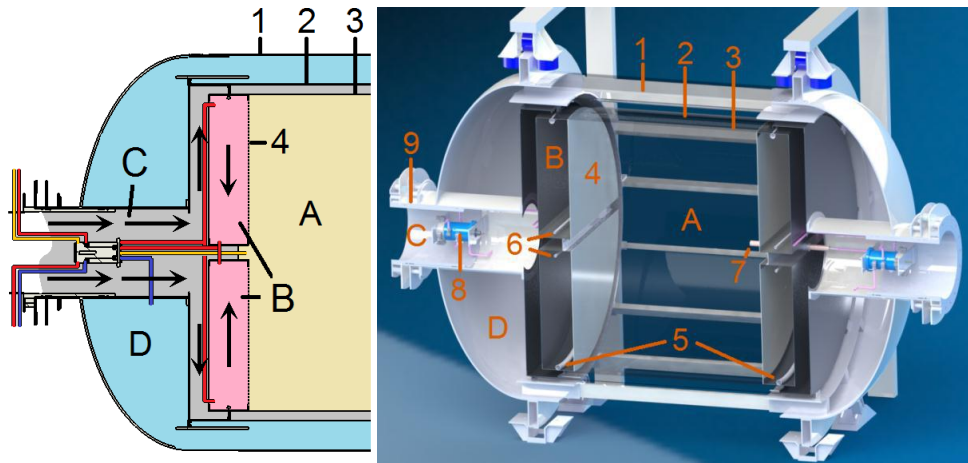


Figure 2: A. Aerosol Retention Volume, $1m^3$; B. Gas Exchange Circulation; C. Temperature Conditioning Flow; D. Stagnant Insulating Volume. 1. Outer FEP layer, 5 mil; 2. Middle FEP layer, 3 mil; 3. Inner FEP layer, 3 mil; 4. ePTFE gas exchange membrane; 5. Gas exchange volume, perforated injection line; 6. Gas exchange volume, perforated extraction line; 7. Retractable aerosol sample injection port (similar extraction port not shown); 8. Internal rotary union for sample line routing; 9. External rotary union for temperature conditioning flow.

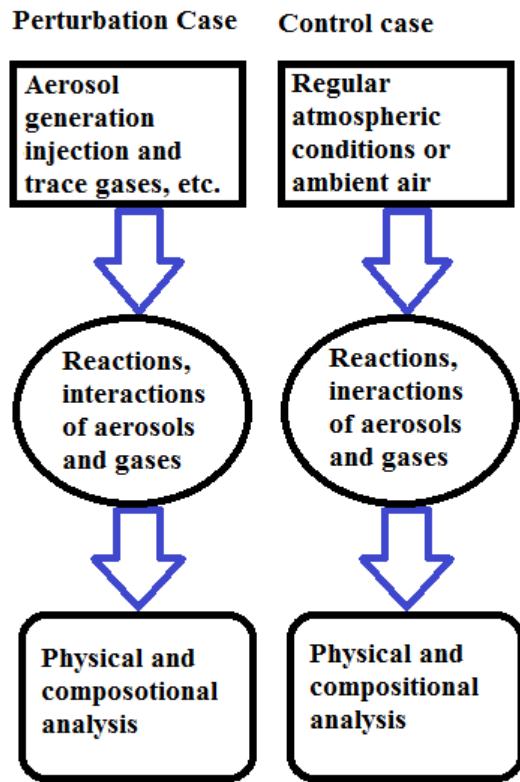


Figure 3: Steps in the experimenting process

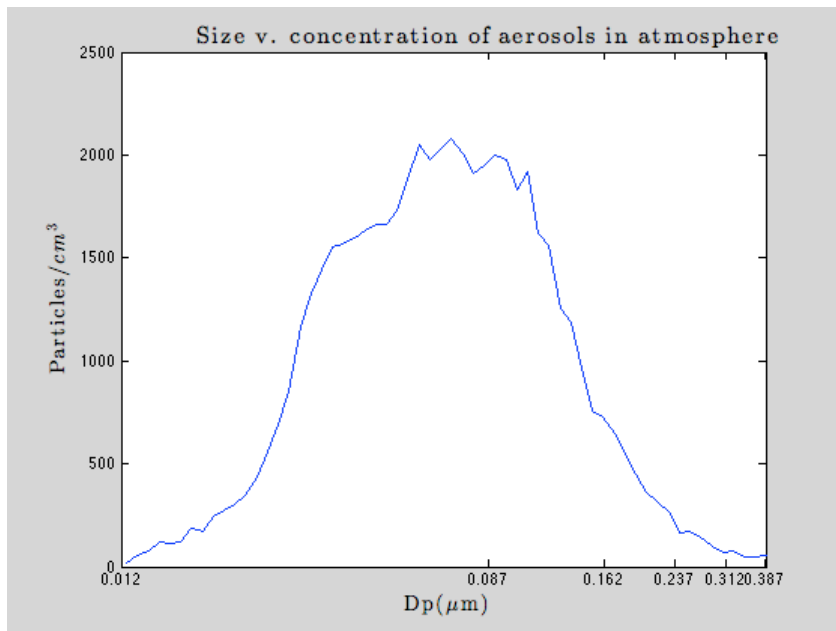


Figure 4: Atmospheric particle size and concentration distribution

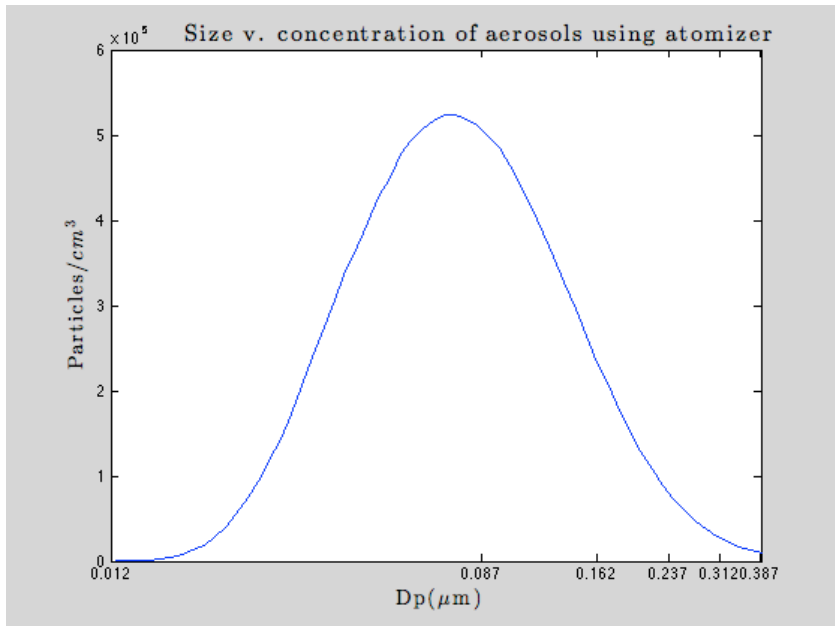


Figure 5: Atomizer generated particle size and concentration distribution

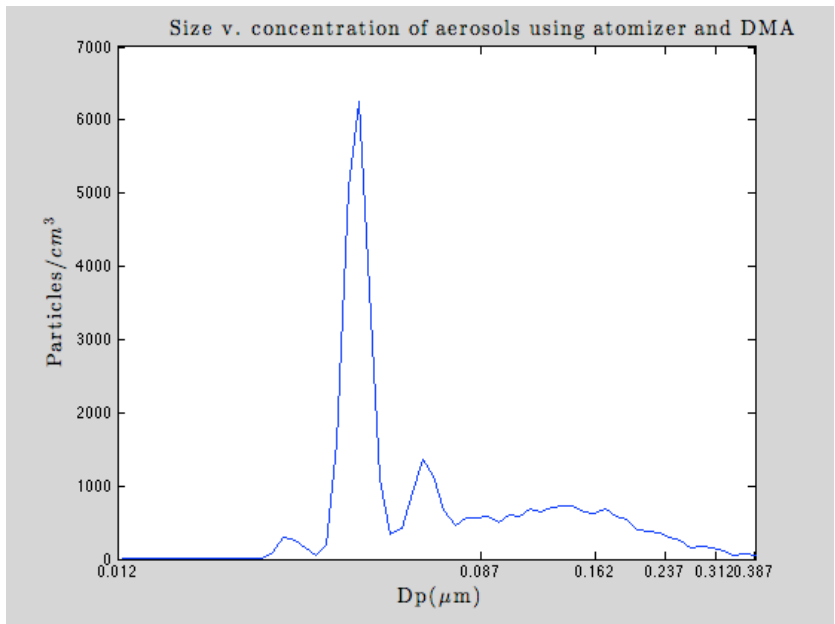


Figure 6: Mono-disperse aerosols using the atomizer and DMA