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(NEW)

# Southern Center For The Integrated Study of Secondary Air Pollutants (SCISSAP)

## Progress Report

For

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Submitted By:

W.L. Chameides, P.I.
School of Earth and Atmospheric Sciences
Georgia Tech
Atlanta, GA 30332

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# Introduction

The long-term mission of the Southern Center for the Integrated Study of Secondary Air Pollutants (SCISSAP) is:

> *The development of the scientific understanding and analytical tools that underpin the design and implementation of an effective and integrated control strategy for secondary air pollutants, using the atmosphere of the southern United States as a natural laboratory.*

This mission is based on the premises that a basic understanding of the chemistry and physics of the atmosphere are a prerequisite for designing effective control strategies for secondary air pollutants; and that the concentration of secondary air pollutants in the atmosphere are often codependent because of interacting chemical reactions.

Over a three-year period beginning on April 1, 1998, SCISSAP has chosen to focus on an integrated study of ground-level ozone ($O_3$) and particulate matter with diameters less than 2.5 μm ($PM_{2.5}$) in the South. The central scientific objectives of this focus will be to provide a better understanding of:

(i) The sources and dynamics of $O_3$ and $PM_{2.5}$ in the southern United States;
(ii) The physical and chemical processes, and emissions that couple $O_3$ and $PM_{2.5}$; and
(iii) The combined effects of various emissions control strategies on $O_3$ and $PM_{2.5}$.

Specifically, four major and interrelated scientific questions will be addressed:

***Question 1:*** What is the concentration and composition of $PM_{2.5}$ in urban and rural locales in the South and to what extent do temporal and spatial variations in these parameters correlate with those of $O_3$ and its precursor compounds?

***Question 2:*** What are the major precursor compounds and sources for $PM_{2.5}$ in urban and rural locales in the South and to what extent do these compounds and sources correspond to/correlate with the sources of natural and anthropogenic $O_3$ precursors (i.e., VOC and $NO_x$)?

***Question 3:*** How are the formation rates and concentrations of $O_3$ and $PM_{2.5}$, as well as the $PM_{2.5}$ composition affected by the relative emissions and concentrations of $NO_x$, $SO_x$, $NH_3$, and VOC species?; and What are the mechanisms responsible for these relationships?

***Question 4***: To what extent do the mechanisms elucidated above affect the formulation of an integrated control strategy for $O_3$ and $PM_{2.5}$?; and Do our findings suggest an "optimum" strategy for addressing both pollutants?

In the process, SCISSAP will work on the development, evaluation, and application of analytical tools, methods, and models that can ultimately become available to the regulatory communities tasked with the management of secondary air pollutants.

## First Year Activities - Developing Standard Operating Procedure for PCM

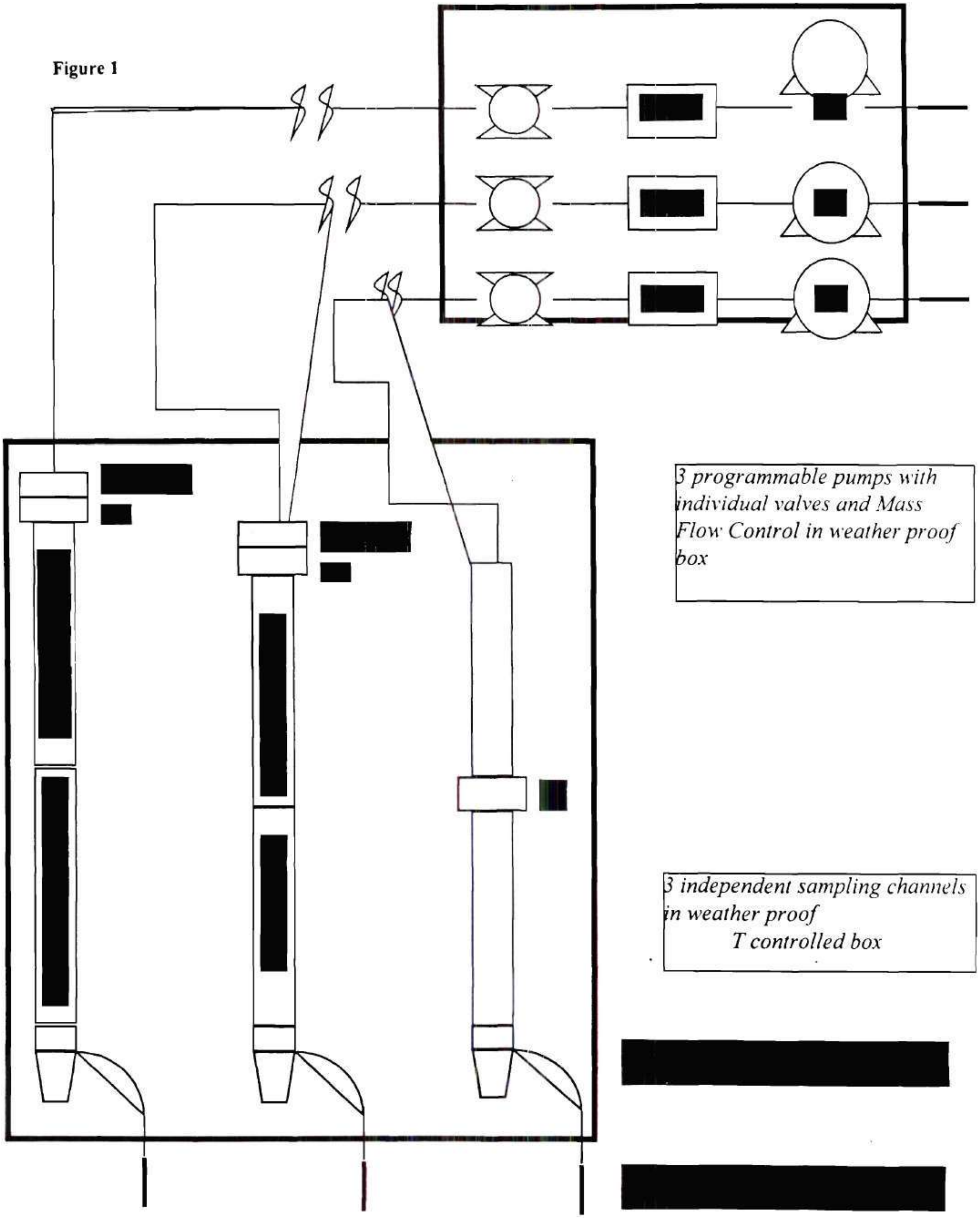
One of the major goals of SCISSAP is its participation in the Urban/Rural Monitoring Network for $PM_{2.5}$, $O_3$, and its precursors, as well as scientifically field intensives that might occur in the region. To meet this objective, SCISSAP's first task was to develop, test, and quality assure instrumentation and associated procedures for documenting the mass concentration and chemical composition of $PM_{2.5}$, as well as its associated gaseous precursors. This task was the primary focus for SCISSAP during the fist year of its 3-year grant and has been completed on schedule.

SCISSAP's $PM_{2.5}$ measurements will be carried out using a 3-channel denuder/filter pack Particle Composition Monitor (PCM) designed to quantify $PM_{2.5}$ mass, sulfate, nitrate, ammonium, organic carbon, elemental carbon, and trace metal concentrations using the Standard Operating Procedures in the attached document. As illustrated in Figure 1, the PCM has three separate channels each equipped with a Teflon-coated cyclone that provides a nominal cut of 2.5 μm at a flow rate of 10 liter $min^{-1}$. Upward flows are maintained with pumps and flow controllers for each channel and the filters and denuders are housed in a temperature controlled box.

## Plans for Future Field Measurements

The SCISSAP $PM_{2.5}$ measurements become operational on June 1, 1999 when two PCM's will be deployed in the Nashville area. Initially, these PCM's will operate initially as part of the SOS 1999 Nashville/Middle Tennessee Field Study and then following the completion of this study in mid-July will assume monitoring mode in the Urban/Rural Monitoring Network for $PM_{2.5}$, $O_3$, and its precursors. In August SCISSAP will participate in the 1999 Atlanta SuperSite Experiment. Following this experiment, SCISSAP monitoring in the Atlanta area will commence.

**Figure 1**



3 programmable pumps with individual valves and Mass Flow Control in weather proof box

3 independent sampling channels in weather proof T controlled box

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**GEORGIA INSTITUTE OF TECHNOLOGY**

**SOUTHERN CENTER FOR THE INTEGRATED STUDY OF SECONDARY AIR POLLUTANTS**

School of Earth and Atmospheric Sciences
221 Bobby Dodd Way, OCE 205
Atlanta, GA 30332-0340

# Standard Operating Procedure (SOP) for the Particle Composition Monitor (PCM)

## at

## 829 Jefferson St

Revised 2 August 1999

| *contact* | *phone* | *fax* | *email* |
|---|---|---|---|
| Karsten Baumann | (404) 385-0583 | 894-1779 | kb@eas.gatech.edu |
| ***SCISSAP-Lab*** | ***(404) 385-0438*** | ***385-0795*** | |
| Danny DiPasquale | | | dd65@prism.gatech.edu |
| Wes Younger | | | wy8@prism.gatech.edu |
| Jing zhi Zhao | | | jing.zhao@eas.gatech.edu |

# Jefferson Str – Field SOP Outline

1) Bring empty and full coolers to the site
2) Empty PCM
    a. Locate labeled bags to hold specific caps and plugs
    b. Disconnect sample channel 1 from cyclone
        1. separate into denuder and filter pack
        2. store in proper layer
    c. Disconnect sample channel 2
        1. separate into denuder and filter pack
        2. store in proper layer
    d. Disconnect blank channel 1
        1. store in proper layer
    e. Disconnect blank channel 2
        1. store in proper layer
    f. Disconnect sample channel 3
        1. separate XAD denuder from filter pack
        2. store in proper layer
3) Fill PCM
    a. Locate labeled bags containing caps and plugs
    b. Sample channel 3
        1. assemble filter pack and XAD denuder
        2. couple chain with cyclone in sampling box
    c. Blank channel 2
        1. Just clip in to box
        2. or couple blank to cyclone in sampling box
    d. Blank channel 1
        1. Just clip into box
        2. Or couple chain to cyclone in sampling box
    e. Sample channel 2
        1. couple chain to cyclone in sampling box
    f. Sample channel 1
        1. couple chain to cyclone in sampling box
    g. Attach correctly labeled sampling hose to each sample channel
4) Complete Traveler for PCM
5) Leak Check
6) PCM Traveler

# 1. GENERAL

Thank you for your involvement and interest in our urban/rural network measurements! Your work is most important to obtain high quality data for scientific analyses and interpretation through our Southern Center for the Integrated Study of Secondary Air Pollutants (SCISSAP). If you have access to the internet, you can retrieve more information about these ongoing studies at

*www-wlc.eas.gatech.edu/scissap/.*

Please read the following directions thoroughly (as many times as necessary) before attempting any process, and feel free to contact us at any time if you have questions.

In preparation for going out to the site you will always need coolers. One has to be empty (except for the ice packs, Traveler, and the caps/plugs that were removed during assembly) for unloading and transporting back the sampling media that are currently out there. The other one is the new cooler containing the unsampled media. There will always be samples out in the field to be removed, and those should always be removed and stored in the empty cooler before assembling the new samples. **Please handle all sample media with great care! The 1" diameter tubes (6" and 10" long) containing glass annuli and the 2.5" diameter, 11" long cylinders made completely of glass are extremely fragile! Please also be aware that a human body is a potential source for contamination of the samples; therefore, wash your hands thoroughly prior to handling samples, hold them away from your body and do not smoke during assembly and disassembly. Do not breathe directly onto any disconnected sample medium, and cap ends as quickly as possible.**

The Traveler is extremely important paper work that helps acquire and sort out the data that is to be collected. The Traveler is in a sealed bag that serves two purposes. The first is to protect the Traveler from liquid (possibly from condensation from the ice packs during transportation; possibly from some rampaging soda can bent on the destruction of the Traveler); and the second is to protect the Traveler from wind. Under no circumstances should the Traveler come to any harm or loss. Section 6 will explain step by step how to fill out the Traveler. For now it is only important to know what and where it is.

The ice packs will be stored, frozen, at the sampling station.

The sampling channel consists of the individual media of each assembly. We operate 3 sampling channels inside a temperature controlled sampling box. Blanks consist of the same media as the sample channels and are carried along for quantification of any contamination that is eventually induced during operation. **Figure 2** depicts a fully assembled sampling box with the door open. We provided a bungie cord to hold this swinging door open allowing relatively little motion during assembly and disassembly. The following is a nomenclature of the media used in each channel.

| | |
|---|---|
| inlet arm.. | 0.55" ID, 12" long Teflon coated Al curved tube |
| cyclone… | cuts off particles with aerodynamic diameter > 2.5 µm, Teflon coated Al |
| denuder… | 6" or 10" long, 1" OD diffusion tube with 3 glass annuli inside |
| chain… | two denuders, or one denuder and a filter pack coupled together |
| filter pack… | Teflon holder with Teflon membrane and paper, or quartz fiber filter |
| CA… | Citric Acid coating solution applied to 1" OD denuder or paper filter |
| SC… | Sodium Carbonate solution applied to 1" OD denuder or paper filter |
| XAD… | specially ground resin applied to 2.5" OD, 12" long 8-annuli denuder |
| PUF… | polyurethane foam inside a 6" long, 1" OD glass tube |
| cap…. | ~2" diameter white (Delrin) or red (Teflon lined) with #30 female thread |
| plug…. | ~1.5" dia white with #30 male thread or 0.5" dia red w/out thread |

## 2. DISASSEMBLY

It is required that the current sampling media be disassembled, packed, and logged before the next (unsampled) media are assembled. The cooler should be emptied of the top three layers of foam, and the foam should be placed conveniently and safely around the cooler.

Make sure that there are three PE zip-lock bags containing different caps and plugs that were removed from specific sampling media during installation. The bags are labeled "CA caps/plugs", "SC caps/plugs", and "XAD caps/plugs", and are meant to be left at the site. The specific use of each bag is described in the assembly Section 4.

The first step in disassembly is to remove the sampling hose. This is the hose that connects the pump to the sampling chain. There should be three hoses connected to sample channels 1, 2 and 3. Each hose has a quick-connect fitting that snaps into the top of each sample channel.

### 2.1 Sample Channel 1

Sample channel 1 is the first chain from the left on the back wall of the swinging door of the sampling box (see Figure 2). Disconnect the quick-connect fitting from the chain (filter pack) and replace the fitting with the small red plug that was removed during installation. If the installation directions were followed, then the red plug should be in the PE zip-lock bag labeled "CA caps/plugs". The next step is to remove the sampling chain from the sampling box. This requires that the chain be uncoupled from a cyclone. First, remove one white cap from the bag labeled "CA caps/plugs". Safely place the cap (open end down) somewhere that it can be reached after the sampling chain has been uncoupled, e.g. on the bottom ledge inside the sampling box. With the cap in place, uncouple sample channel 1 from the cyclone. When uncoupling, make sure that the black coupler remains on the cyclone and not the chain. Use the spare cap to cover the open end of the denuder.

Now the chain needs to be broken into two components. For the Jefferson Street site, this step should be preformed in the lab.

### 2.2 Sample Channel 2

Repeat this exact procedure for sample channel 2. Sample channel 2 is the second chain from the left on the back wall of the swinging door of the sampling box. For sample chain 2, the caps will be coming out of the bag labeled "SC caps/plugs". To remove sample chain 2, get a white cap. Uncouple the chain from the cyclone. Cap the open end.

### 2.3 Blank Channels 1 and 2

Now sample channel 1 and 2 have been removed and stored for shipment. It is time to remove and store blank channels 1 and 2. For now, the sampling box that is being used in Jefferson St does not have the ability to store blanks open. Blanks are instead left closed in the sampling box. In the future, a sampling box will be used that stores the blanks in an identical manor to the samples. For now just remove the blanks from the sampling box and put them in the cooler. When the new box is in operation use the following procedure.

Get another white cap from the "CA caps/plugs" bag into position. Remove the red plug at the top of the filter pack and re-plug immediately to simulate the short exposure of the sample channel during removal of sampling hose (see "Sample Channel 1" above). Uncouple blank channel 1 from the cyclone, making sure that the black coupler remains on the cyclone. Cap the open end of the denuder. Remove the chain from the box and bring it to the foam. Unscrew the filter pack from the 10" denuder, and place the filter pack open end down in the foam groove where a PE bag labeled "Blank-FP" has been left after assembly. Taking the last white cap from the CA caps/plugs bag, cover the open end of the 10" denuder and place the denuder into the foam. Next, use the last white plug from the "CA caps/plugs" bag to close the open end of the filter pack. Put the closed filter pack inside the PE zip-lock bag labeled "Blank-FP", seal, and place it back into the foam.

No amount of care is too much. If something is going to be broken on accident, the chances are highest that it will be broken during this stage.

Now Blank channel 2, a single 10" SC denuder, can be removed. Get the last white cap from the "SC caps/plugs" bag ready, and remove the denuder from the cyclone. Cap the open end of the denuder. Uncap the other end of the denuder briefly to simulate the exposure the sample chain experienced when the filter pack was removed. Then place it directly into the foam.

At this stage, the operator gets a break. Go rest for a moment in the shelter, and bring back two frozen ice packs. Insert them into the slots made in layers of foam.

### 2.4 Sample Channel 3

There are now only one chain left at the back wall of the sampling box. Now two thirds of disassembly has been completed. Place the empty layer of foam in the cooler on top of the full layers. To disassemble the sample channel 3 chain, make ready two white caps and a red plug that were removed during the installation of channel 3 and kept in a sealed bag labeled "XAD caps/plugs". Sample channel 3 is mounted on the right side of the fixed back wall of the sampling box. Disconnect the sampling hose at the top of the filter pack and seal open end with red plug. Using all due care (and both hands) remove, i.e. unscrew the complete XAD denuder assembly from the cyclone. Cap the open end of the denuder and disconnect the white filter pack from the larger XAD denuder. Use the plug to cover the open end of the XAD denuder and the cap to cover the open end of the filter pack. Place the filter pack into the groove in the foam.

## 3. CLEANING CYCLONE HEADS AND INLET ARMS

Before assembly of new sampling media, all cyclone heads and inlet arms need to be cleaned with canned air that we have provided at the site. Please note that especially the inlet arms of the blank channels offer convenient shelter for bugs and insects. It is therefore necessary to check and clean all three cyclones as follows. Remove bottom plug of cyclone, rotate it by 90 degrees and shoot air through the bottom (now un-plugged) end and the inlet arm. Rotate back 180 degrees and shoot air through the top of the cyclone head with the coupler attached. Dry-clean the plug separately. We recommend such "dry cleaning" before each sampling. However, if the cleaning could not be performed for more than 5 consecutive samplings (e.g. due to severe weather conditions), a more thorough cleaning should be performed by rinsing with distilled de-ionized water (DDW) prior to dry-cleaning.

## 4. ASSEMBLY

You should have the blue Igloo cooler from the Atlanta Lab. The cooler should not be opened until it is time to assemble the new media. This means that the old sampling media should be completely removed, and the cyclone heads and inlet arms cleaned. Three empty bags labeled "CA caps/plugs/plugs", "SC caps/plugs/plugs", and "XAD caps/plugs" should be kept at the site. As you remove the caps and plugs from the sampling media you will need to place these in the appropriately labeled bag.

Take these bags and the cooler up to the sampling box. When you open the cooler, remove the 'warm' ice packs from the top layer of foam and move them out of the way (e.g. into the freezer if available at the site).

### 4.1 Sample Channel 3

The first chain to be installed in the sampling box is channel 3. Remove the XAD denuder from inside the foam groove and place it down securely. Leave bubble wrap on around the denuder for protection. Take the filter pack out of the bag in labeled "Sample PP". Leave the empty bag in the groove.

Remove the white cap from the filter pack and the white plug from the XAD denuder, and screw the male threads of the filter pack into the female threads of the denuder. Leave open ends disconnected as briefly as possible. Place the removed cap and plug in the bag labeled "XAD caps/plugs". Congratulations! You have just assembled channel 3. The goal when connecting the two sections is to eliminate as many possible sources of contamination as possible. Without compromising safety (please do not rush the process), the filter pack should be attached to the XAD denuder as quickly as possible. This chain shall be placed into right most fittings of the swinging door.

To install sample channel 3, slide the cyclone on the left side of the back wall a bit to the right, slip the XAD denuder down through the white clip. Now remove the plug from the bottom end of the XAD denuder. Place the plug down on the inside ledge of the sampling box face down. Screw the female end of the XAD denuder directly onto the cyclone. Make sure that the chain is safely in place before you remove your hands. Place the cap inside the bag labeled "XAD caps/plugs". Remove red cap at top of filter pack and connect the sample hose to the sample channel.

### 4.2 Blank Channel 3

The single filter pack which contains the quartz filter for the field blank will be placed in the sampling box during the sampling date, however the XAD denuder blank will be taken every 10 samples.

### 4.3 Blank Channels 1 and 2

Currently no modification have been made to the Jefferson St sampling box to allow blanks to be stored in the same manor as sample material. This is acceptable for now, as long as the sampling material stays in the sampling box for as little time as possible before sampling. For the summer intensive media will be installed at 6:30 AM for a 7:00 AM start time; and be removed before 8:00 AM for a 7:00 AM stop time. So for now simply remove the blanks from the cooler, open them briefly (to mimic loading of the sampled material), and place them in the sampling box on the clips of the fixed wall. When the new sampling box is in operation follow the following instructions.

Install the blank channel 2 to the very right of the inside wall of the swinging. Remove the denuder from the foam groove with the SC Blank. Look at the number that is written on the side of the denuder. The number will read left to right. Remove the cap from the left end of the denuder and couple the denuder onto the far right cyclone. Place that cap in to the bag labeled "SC caps/plugs". Briefly uncap the top end of the denuder to simulate connection of the sample hose.

From the exposed layer 1 remove the filter pack labeled "Blank-FP". Take it out of the PE bag and store this bag inside the groove. Remove the white plug from the bottom of the filter pack and place the pack open end down on the ledge of the sampling box. Take the plug and place it in the bag labeled "CA caps/plugs". Now remove the CA Blank denuder labeled from its groove in the foam. Again orient the denuder so that the number printed on its side can be read from left to right. Remove the cap from the right side of the denuder and couple the open end of the 3-stage filter pack to the open end of the denuder. Remove the cap at the other end of the denuder and couple it to the cyclone that is second from the right on the back wall of the swinging door, assigned for blank channel 1. Make sure that the chain is secure before removing your hands. Now place both caps from the CA blank denuder into the bag labeled "CA caps/plugs". Remember that the goal is to eliminate all possible sources of contamination when the sampling medium is open. Briefly remove the red plug at the top to simulate exposure experienced by the sample channel, and re-plug.

### 4.4 Sample Channel 2

Now it is time to assemble sample channel 2. First, remove the filter pack from the foam groove in a bag labeled "SC-FP ". Take it out of the PE bag and store the bag inside the groove. Remove the white plug from the bottom of the filter pack. Place the plug in the bag labeled "SC caps/plugs", and place the filter pack open end down on the ledge of the sampling box. Remove the coupled 6" and 10" denuders from the layer 2 groove labeled "SC Chain" on the diagram. Remove the white cap from the end of the 6" (shorter one on the right), and couple the open end of the denuder to the open end of the filter pack. Place the cap in the bag labeled "SC caps/plugs". Now sample channel 2 is assembled and ready for installation. It will be coupled to the cyclone second from the left on the back wall of the swinging door. Uncap the remaining capped end of the denuder and couple the chain to the cyclone. Remove the red plug at the top and connect the sampling hose with the quick-connect fitting labeled "2". Put the white cap and the red plug into the bag labeled "SC caps/plugs".

### 4.5 Sample Channel 1

The last chain to be assembled is sample channel 1. Using the coupled denuders from the layer 1 groove labeled "CA Chain" on the diagram, and the filter pack from the layer 1 groove in a bag labeled "CA-FP"; repeat the process used for assembling sample channel 2. Unplug the bottom of the filter pack, uncap the right end of the 6" denuder, place the white cap and plug in the "CA caps/plugs" bag, and couple the filter pack to the denuders. Uncap the final cap from the left end of the denuder, and attach this assembly to the only uncoupled cyclone remaining- the first to the far left on the back wall of the swinging door of the sampling box. Remove the red plug at the top and connect the sampling hose with the quick-connect fitting labeled "1". Put the white cap and the red plug into the bag labeled "CA caps/plugs".

### 4.6 Closing Sampling Box

Use extreme care when closing the door. There is not much clearance between the top of sample channel 3 and the top wall of the box. The sampling hose may have a tendency to kink or get caught when closing the door. Before closing up, take one last glance over your work and make sure everything seems right. Verify that the "Auto/Man" switch on the temperature controller is still on Auto (the Heat/Cool switch position is unimportant).

## 5. LEAK CHECK

Cap the 3 inlet arms of the channels that are being sampled (and therefore connected to the suction tubes) with the red caps stored inside the sampling box. Locate the pump box and turn rear switch to "Local". All three pressure gauges should read 20" Hg vacuum within 10 seconds.

When breaking the vacuum seal after leak testing, make sure to remove the red caps very slowly. Gently let the air vent back into the sampling chain. If done correctly, no pressure pulse will be created. If a violent pressure pulse is created; filters will rupture. Replace caps from inlet arms in the bag inside sampling box.

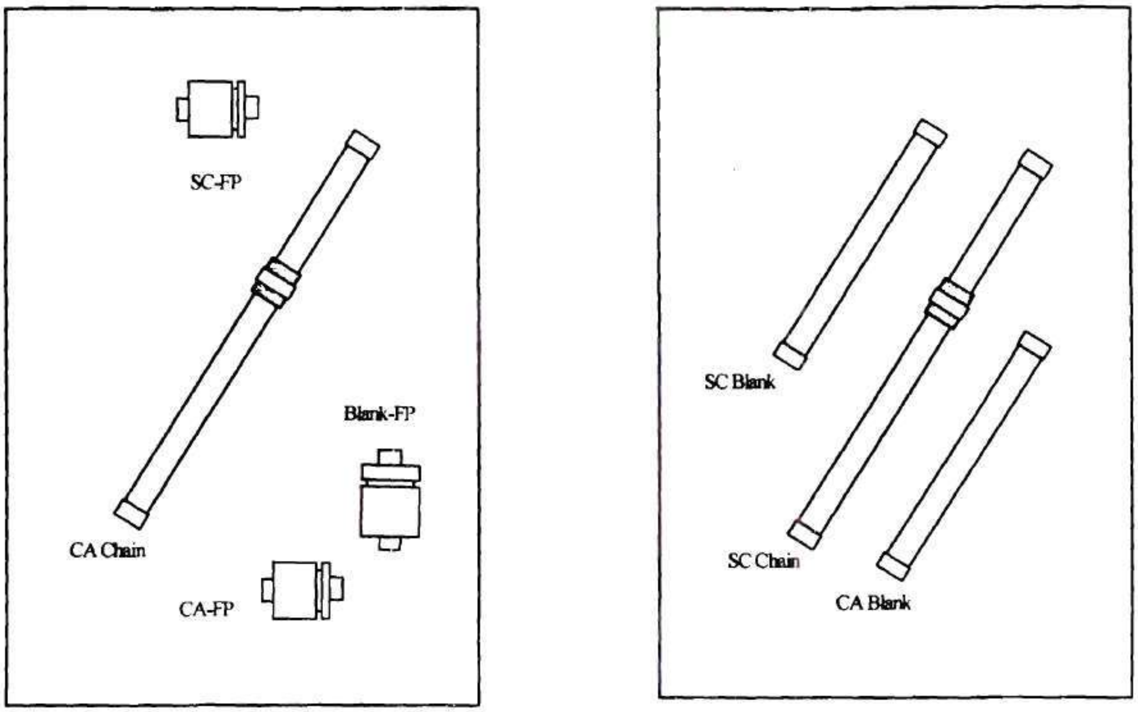
If this is NOT the case, first verify that all three inside pump switches are on and that all three pumps are running and retest. If the test fails again, identify the channel that might have a leak, turn off all pumps, and re-tighten all connections between the sampling media of the problematic channel. Then redo the leak test. Once the leak check was performed successfully, begin filling out the Traveler described in the next Section.

## 6. PCM TRAVELER

Most of this Traveler was completed at the Lab in Atlanta. This form carries important information in reference to our lab analyses and needs to be filled out carefully after the leak check and before the actual sampling. On Page 1 of the Traveler the first thing to fill out is the Location, sampler ID, and sampler Inlet. The location is "JST" and the sampler ID should be filled in with "URG PCM". The sampler Inlet refers to the type of cyclone used. The sampler was installed with a long arm, Teflon coated, 16 lpm cyclone. You will be made aware of any changes to that information. The next slot to fill out is Date/Time Installed. That would be the date and time when you installed the sampling chain; use the local time of your watch.

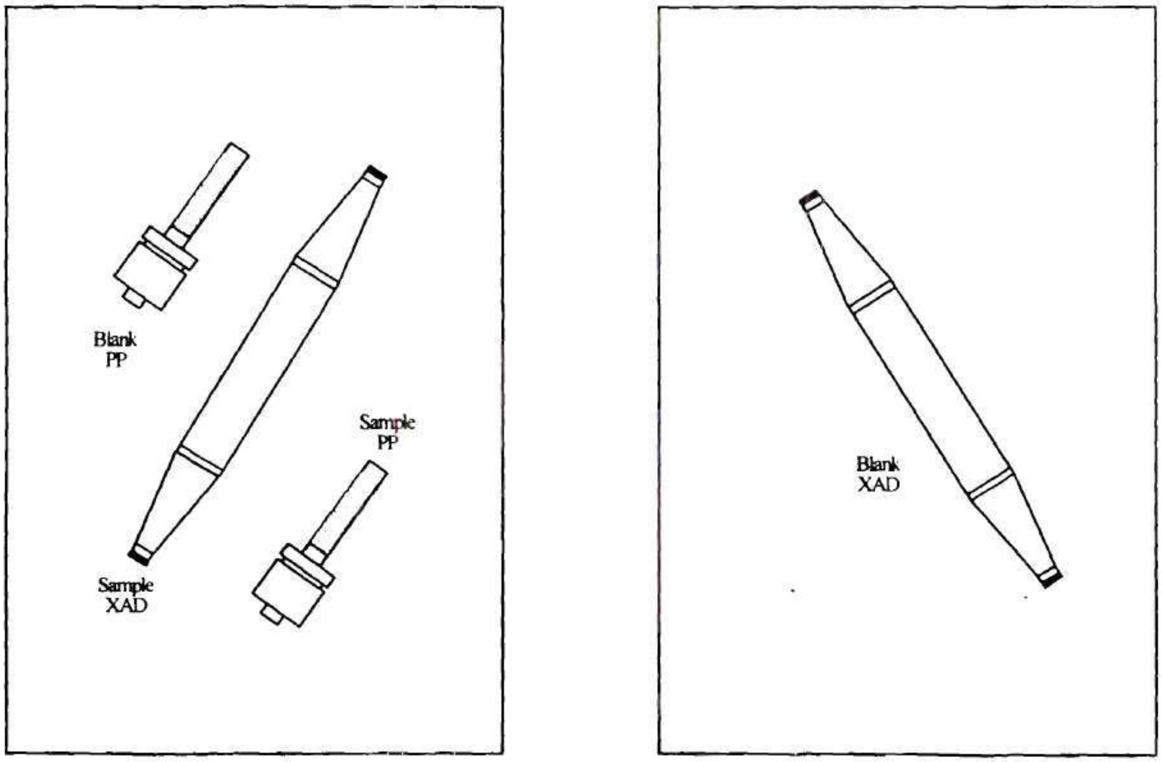
Now you will notice several pages that describe the chain in each of the channels. The only part to fill in is the Sampling Date. As you write that date on each line, check to make sure that the number written down on the "Sampled S/N" matches the serial number of the denuder or filter pack. There should be only one of two reasons for any discrepancy. First is that there was some mix-up during installation. If this is the case, then there should be some corresponding component out of place. Simply correct the mistake. If there is not such apparent mix-up, simply write over the incorrect number with the actual number. The mistake was probably made in our lab.

Page Three of the PCM Traveler is the Sampling Record. You will be responsible for filling out the first four lines of the record, as well as the last line. Meteorological Conditions should be filled out before and after sampling. After sampling you should comment on the weather the day of sampling as well as the condition while removing the sampling medium.



Layer one

Layer two



Layer three

Layer four

**Figure 1:** Foam layers of shipping box containing all sampling media required for one complete sample run. CA… citric acid, SC… sodium carbonate, PP… PUF pack

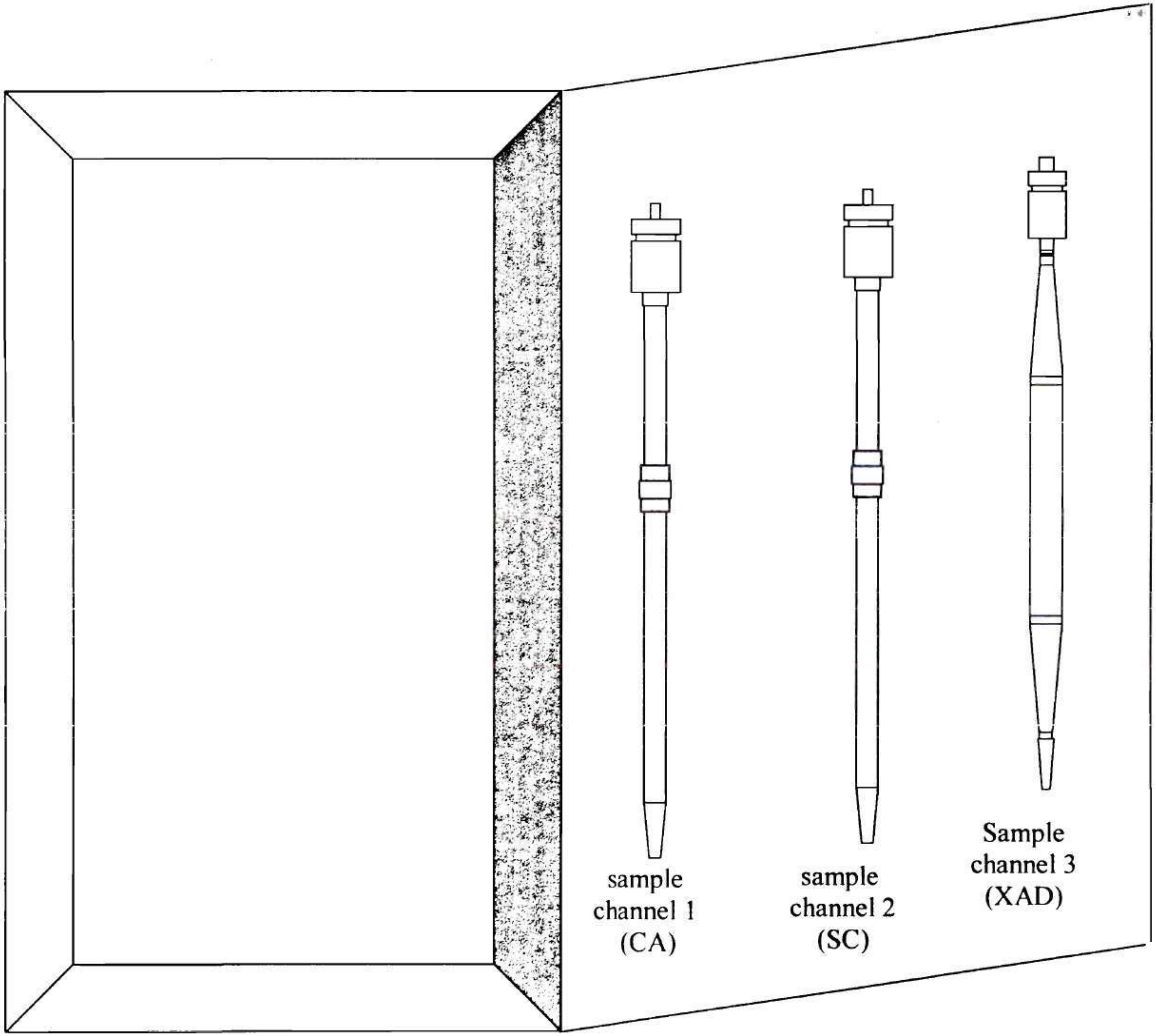


**Figure 2:** Georgia Tech's 3-channel Particle Composition Monitor

# 7. Filters and Denuders

In order to obtain useful information about atmospheric aerosol composition, multiple sampling media are used simultaneously. We operate a total of three different channels to measure concentrations of gaseous and particle-bound chemical species as well as particle mass. Each channel is configured differently in that different gas species are separated from the aerosol sample. This is achieved by application of specifically coated diffusion tubes (hence called denuders) upstream of particle filters. Filter media are round, 47mm diameter membrane or fiber disks. Denuders are placed upstream of Teflon filters with paper filters downstream of the Teflon filters. The paper filters sever to capture volatilization losses of the Teflon filters. The specific selectivity of the media requires special preparation. The following information is the standard operating procedure for preparing and analyzing each type of medium.

## 7.1 Coating Solutions

In general, two different coating solutions are applied to cellulose fiber (paper) filters and denuders that are intended to collect specific gaseous compounds. One solution contains sodium carbonate ($Na_2CO_3$) and the other citric acid ($C_6H_8O_7$). Sodium carbonate, as a base, is especially selective for $HNO_3$ (but also for HCl, $HNO_2$, and $SO_2$). and citric acid for $NH_3$. Special tests may involve sodium chloride (NaCl) as a replacement agent for $Na_2CO_3$. The same solution that is used to coat a denuder is used for a paper filter. Coating solutions are applied as close to the day of shipping as possible, most often the same day.

Sodium Carbonate Coating Solution

Assuming a sample volume of 1250 ml, 500ml of distilled deionized water (DDW) is added to 20ml of glycerol and 20g $Na_2CO_3$ in a clean PE vial. After the Sodium Carbonate is completely dissolved in the DDW, add 750 ml of methanol (MeOH). When the solution is fully mixed the vial is labeled, sealed and refrigerated.

Citric Acid Coating Solution

Assuming a sample volume of 250 ml, 250ml of methanol (MeOH) is added to 5ml of glycerol and 10g Citric Acid in a clean PE vial. When the solution is fully mixed the vial is labeled, sealed and refrigerated.

## 7.2 Field Blanks

A field blank for every filter and denuder is also prepared in the exact same fashion and same time as the sampling filter or denuder. Field Blanks are serialized, labeled, and stored and shipped in accordance with the SOP for storage and shipping.

Once in the field, field blanks are attached to a cyclone designated for this purpose and installed in the same sampling box side-by-side with the sampling train.

### 7.3 Denuders

The denuders used are made by University Research Glassware (URG; 116 S Merritt Mill Road, Chapel Hill, NC 27516; 919-942-2753) and have 3 annuli with a 1mm separation, etched quartz glass surfaces. The denuders for citric acid as well as sodium carbonate are 24.2cm long.

Denuders are prepared and coated in a controlled environment inside dedicated gloveboxes (one for CA, one for SC). The Glove boxes are Plas-Labs Analytical Balance Chamber (Fisher Scientific Catalog Number 11-389-6), and each is supplied with filtered air. Ambient air is dried and pumped through a cartridge that contains activated carbon and then one that contains either monohydrate citric acid or monohydrate sodium carbonate depending on the specific glove box. The glove boxes are cleaned regularly, and have the volume exchanged with filtered air prior to use.

The following procedure for preparation and handling is the same for both the citric acid and sodium carbonate coated denuders:

1. Cleaned denuders are placed in the glove boxes anti chamber.
2. The glove box air is exchanged with filtered air.
3. The denuders are placed in the main section of the glove box. Coating solution is filled into both (sample and blank) denuders and ends are capped. It is possible to contaminate the sample with spilled coating solution. The coating solution (especially CA) is sticky and can build up on the glove box gloves. The coating solution can be transported then to the outside of the denuder and caps. Contamination can come from the coating solution (Sodium from coating solution showing up as sampled sodium on a CA denuder) or from things sticking to the outsides or caps of the denuders and eventually being “extracted”. Care should be taken to reduce spillage and to clean the gloves as often as necessary.
4. Filled denuders are serialized and entered into the glove box’s logbook. A few quick shakes are given to the denuder to agitate the coating solution. Start and stop coating times are recorded, as well as date and denuder serial number.
5. After a minimum of one hour, the denuders are drained and left to drip-dry for approximately 180 minutes. The glove box is equipped with a special rack that can hold 18 denuders vertically to aid drying. Then the denuders are removed from the glove box.
6. Denuders are stored in accordance with the SOP for storage.
7. When the denuders are ready to be moved to the sampling site the shipment procedure follows in accordance with SOP for shipping.
8. Once the denuders have reached the sampling site extreme care is used to ensure that the absolute minimal amount of contamination occurs; e.g. denuders are held “upwind” from operator and are exposed to the ambient air for the briefest of time while loaded into the sampling unit. Field blanks are treated as described in section C.1.2 above.
9. The sampling unit is set to run.

10. While the sampling unit is running all denuder caps must be completely cleaned. Washing in a sonic bath for 10 min is more than sufficient.
11. After the run is complete the denuders as well as the field blanks are removed and all disconnected (open) ends are recapped. All denuders are recapped with spare caps (ones not removed from the denuder originally) that have been cleaned and sealed in the laboratory. Denuders are stored and shipped in accordance to the SOP for storage and shipping (see section C.4 below).

Extraction of Citric Acid Denuder

The citric acid denuders (sample and field blank) are extracted with 30ml DDW under a specially filtered air laminar flow hood. The extraction is done in two steps, first 15ml of DDW is pipetted into the denuder. The pipetter used to deliver the extraction DDW is a Labsystems Finnpipette Stepper Pipetter. Used on the 5ml step, the pipett has an accuracy of ± 0.5%and a precision of ± 0.3%. The denuder is capped again and shaken vigorously on a shaker table. Again, care must be taken to avoid cross contamination between denuders. Sodium from a SC coated denuder would show up as sampled sodium if the SC denuder cap is placed on the CA coated denuder. It is necessary to not mix up the denuder caps while they are removed to add DDW. The extract is emptied from the denuder and filled into a PE 30ml, amber wide mouthed bottle (Nalgene Company) that has been pre-cleaned and labeled. Next a second 15ml extraction is done the same way and added to the first. Finally the total 30ml extract is analyzed for $NH_4^+$ and $Na^+$ via Ion Chromatography following corresponding SOP.

Extraction of Sodium Carbonate Denuder

The sodium carbonate denuders (sample and field blank) are extracted with 30ml DDW under a specially filtered air laminar flow hood. The extraction is done in two steps, first 15ml of DDW is pipetted in to the denuder. The denuder is capped again and shaken vigorously on a shaker table. Again, care must be taken to avoid cross contamination between denuders. Sodium from a SC coated denuder would show up as sampled sodium if the SC denuder cap is placed on the CA coated denuder. It is necessary to not mix up the denuder caps while they are removed to add DDW. The extract is emptied from the denuder and filled into a PE 30ml, amber wide mouthed bottle (Nalgene Company) that has been pre-cleaned and labeled. Again, a second 15ml DDW extraction is performed. This extraction is added to the first. Then the extraction is shaken to try and ensure a homogeneous mix. A 15ml sample is taken from the 30ml total and stored in a second wide mouthed bottle. To this second bottle about three drops of $H_2O_2$ is added to convert $SO_3^-$ to $SO_4^{-2}$. The extracts are then analyzed for $Cl^-$, $NO_2^-$, $NO_3^-$ and $SO_4^{-2}$ via Ion Chromatography following corresponding SOP.

## 7.4 Teflon Filters

A Gelman Teflon-membrane filter (Zeflour™ P5PJ047) is used for determining PM-mass. The filter has a 2µm pore size, and a 47mm diameter. Each filter is given sufficient time (at least one month) to equilibrate to constant levels of relative humidity (35% ±5%) and temperature (21°C ±1°C) inside a controlled clean air room, that has the micro-balance installed. The clean air room is part of the SCISSAP analytical laboratory in Atlanta, and is kept under slightly positive pressure by temperature and humidity controlled filtered air. Positive pressure is maintained by introducing a small amount of ambient air into the otherwise closed-loop circulation. The air is filtered by citric acid and activated charcoal beds and enters the room via a membrane diffusion ceiling plenum creating a near-laminar flow at the work surface. The following procedure applies for further preparation and handling of equilibrated Teflon filters:

1. Mass of filters is determined using SOP for mass determination (section C.3).
2. Once mass has been determined, both field blank and sample Teflon filters are serialized and placed into pre cleaned 50mm perti dishes with completely covering the bottom, but not snapped shut.
3. Filters are stored in the clean room until shipment date. At which time they are removed from the petri dish and place unto a URG 2-stage filter holder. Special care must be taken to ensure that the filter is placed in the filter holder with the correct orientation. The Teflon filters that are used are PTFE backed, and sampling should be not done on this side. A difference can be viewed by the naked eye, the "smoother" side is the sampling side. If a trained eye is unavailable, pull slightly on an excess filter until separation occurs. The sampling side is the section that is the thin Teflon membrane.
4. All filters are shipped in accordance to the SOP for shipping (section C.4).
5. Once the filters have reached the sampling site extreme care is used to ensure that the absolute minimal amount of contamination occurs. Sampling media is exposed to the ambient air for the briefest of time while loaded into the sampling unit. Field blanks are treated as described in section C.1.2 above.
6. The sampling unit is set to run.
7. While the sampling unit is running all filter pack caps must be completely cleaned. Washing in a sonic bath for 10 min is more than sufficient
8. After the run is complete the filter packs are removed and all disconnected (open) ends are recapped. Field blanks are treated as described in section C.1.2 above. Filters are stored and shipped in accordance to the SOP for storage and shipping (see section C.4 below).
9. Once the filters have returned to the lab they are weighed according to SOP for mass determination (section C.3).
10. After weighing, the sample and field blank filters are extracted. Each filter is placed in a 30 ml bottle that has been pre-cleaned in the sonic bath for 30 minutes with heat. After the filter has been placed in the bottle, 30 ml of DDW is added. The bottle is labeled, and placed in the sonic bath for 30 minutes. The extract is then analyzed via the Ion Chromatography SOP for cations and anions.

### 7.5 Citric Acid (CA) Coated Cellulose Filter Filters

A CA coated Whatman 41 cellulose fiber (paper) filter is used for determining volatile particulates coming off of the Teflon filter. The filters are 47mm in diameter and are stored independently in a petri dish inside the refrigerator. Each petri dish is marked with a blank piece of tape. The filters are then moved to an $NH_3$-free glove box for coating. The following describes the procedure for preparing and handling a CA coated paper filter:

1. CA coating solution (section C.1.1) is applied to both sample and field blank filters by a 60 minute long soak inside the glove box.
2. The filters are then dried under vacuum inside the glove box. The filters take approximately 30 minutes to dry at room temperature under vacuum.
3. After the filters are dried, both field blank and sample filters are placed back into their petri dish serialized with the coating date and lot number.
4. Filters are stored in refrigeration until the date of shipping.
5. On the date of shipping the filters are removed from refrigeration and placed in the clean room. In the clean room the filters are placed in a URG 2-stage filter pack behind a Teflon filter. The loaded filter packs are then shipped to the sampling site in accordance with the SOP for shipping.
6. At the sampling site extreme care is used to ensure that the absolute minimal amount of contamination occurs. Sampling media is exposed to the ambient air for the briefest of time while loaded into the sampling unit. Field blanks are treated as described in section C.1.2 above.
7. The sampling unit is set to run.
8. While the sampling unit is running all filter pack caps must be completely cleaned. Washing in a sonic bath for 10 min is more than sufficient
9. After the run is complete the filters are removed and all disconnected (open) ends are recapped. Field blanks are treated as described in section C.1.2 above. Filters are stored and shipped in accordance to the SOP for storage and shipping (see section C.4 below).
10. The paper filters (blank included) undergo a two step 10ml DDW extraction under an $NH_3$-free laminar flow hood. The paper filter is placed in the bottom of a 100ml Nalgene beaker and 10ml of DDW is added. After agitation and time (usually 10 to 15 minutes), the extraction is poured off, and the process is repeated. The extract is then analyzed via the Ion Chromatography SOP for cations.

### 7.6 Sodium Carbonate (SC) Coated Cellulose Filter Filters

A SC coated Whatman 41 cellulose fiber (paper) filter is used for determining volatile particulates coming off of the Teflon filter. The filters are 47mm in diameter and are stored independently in a petri dish inside the refrigerator. Each petri dish is marked with a blank piece of tape. The filters are then moved to a $HNO_3$-free glove box for coating. The following describes the procedure for preparing and handling a SC coated paper filter:

1. SC coating solution (section C.1.1) is applied to both sample and field blank filters by a 60 minute long soak inside the glove box.
2. The filters are then dried under vacuum inside the glove box. The filters take approximately 6 hours to dry at room temperature under vacuum.
3. After the filters are dried, both field blank and sample filters are placed back into their petri dish serialized with the coating date and lot number.
4. Filters are stored in refrigeration until the date of shipping.

5. On the date of shipping the filters are removed from refrigeration and placed in the clean room. In the clean room the filters are placed in a URG 2-stage filter pack behind a Teflon filter. The loaded filter packs are then shipped to the sampling site in accordance with the SOP for shipping.
6. At the sampling site extreme care is used to ensure that the absolute minimal amount of contamination occurs. Sampling media is exposed to the ambient air for the briefest of time while loaded into the sampling unit. Field blanks are treated as described in section C.1.2 above.
7. The sampling unit is set to run.
8. While the sampling unit is running all filter pack caps must be completely cleaned. Washing in a sonic bath for 10 min is more than sufficient
9. After the run is complete the filters are removed and all disconnected (open) ends are recapped. Field blanks are treated as described in section C.1.2 above. Filters are stored and shipped in accordance to the SOP for storage and shipping (see section C.4 below).
10. The paper filters (blank included) undergo a two step 10ml DDW extraction under an $NH_3$-free laminar flow hood. The paper filter is placed in the bottom of a 100ml Nalgene beaker and 10ml of DDW is added. After agitation and time (usually 10 to fifteen minutes), the extraction is poured off, and the process is repeated. The extract is then analyzed via the Ion Chromatography SOP for cations.

### 7.7 Quatrz Filter

A Pallflex #2500 QAT-UP Quartz fiber filter is used to measure C, N, isotopes, and metals. The filter has a 1µm pore size and 47mm diameter. Quartz filters are pre-baked at 700°C for about one hour. Initially Quartz filters are purchased pre-treated from Sunset Labs in Forest Grove, OR: but will later be prepared in house once the method is confirmed. A step by step process for preparing a Quartz filter:

1. Once pre-treatment is complete, both field blank and sampling filters are then serialized and placed into filter holders. To avoid contamination these filter holders are the very same holders that will be mounted into the PCM. Both filters are stored and shipped in accordance to the SOP for storage and shipping.
2. Once the filters have reached the sampling site extreme care is used to ensure that the absolute minimal amount of contamination occurs. Sampling media is exposed to the ambient air for the briefest of time while loaded into the sampling unit. All actions preformed to the sampling media are similarly preformed to the field blank.
3. The sampling unit is set to run from midnight to midnight.
4. After the run is complete the filters are removed. Filters are stored and shipped in accordance to the SOP for storage and shipping. Make sure to recap the disconnected ends inside of the PCM.
5. The Quartz filters are not dedicated to one particular type of analysis, as are the other filters and denuders. Instead these filters are going to be used by different groups to measure a variety of species using different methods. Each method has its own SOP detailed else where; but here is a brief summary:

A. Thermal-Optical analysis for elemental carbon, organic carbon. and total carbon.
B. Inductively coupled plasma/mass spectrometry for soluble trace metals. Total trace metals will be analyzed on an experimental basis.
C. Stable Isotope mass spectrometry for total carbon, nitrogen, carbon-13, and nitrogen-15 via sealed tube combustion.
D. X-ray fluorescence
E. Analysis of speciated particulate organics on an experimental basis.

### 7.8 XAD denuder coating

1. Prepare hexane-XAD-4 slurries: Weigh 1.30 g ground XAD-4 resin into a clean 400 mL beaker. Use a dust mask that filters out particles down to 0.5 micrometers. Take the beaker to the hood, add 200 mL UV (pesticide analysis) grade hexane. Cover with clean Al foil or a large clean inverted petri dish. Place the beaker into the sonic bath and turn it on. Sonicate at room temperature for at least 30 min. It is OK if the bath water gets warm (to 40 oC) from the heat of the sonicator's continuous operation. The slurry must be suspended in order to coat the denuder surfaces evenly. While the slurries are sonicating, clean the end pieces, the Teflon-coated aluminum connectors that attach the denuders to the VAPS. Prepare one slurry for each denuder. Label the slurry beaker with its denuder ID. If the denuders have not been labeled or numbered by the manufacturer, use a black permanent marker to label them with unique numbers or alphanumeric identification strings.

2. Before coating any denuders that have removable end pieces: Practice attaching the metal end pieces. Use a foam cradle or similar cushion for support of the midsection of the denuder. Each end piece will have two Teflon o-rings of about 5 cm diameter inside the wider end. To attach, be careful to keep the end piece and denuder co-axial. Wet the o-rings with a small amount of hexane. Slide the end piece on gently, with slight twisting, if necessary, to minimize bumping the glass denuder end into the aluminum step of the end piece. With careful attention to pressure sensations in the fingers that hold the end cap and denuder, notice the ease of sliding the piece on until it makes contact with the first o-ring. Sliding over the first -ring requires a little more effort until the glass reaches the second o-ring. Even more effort is required to move the glass over the second o-ring. Practice caution because it is possible to overdo this and bang the glass into the step at the end of the end piece barrel. Careful attention and slight twisting while pushing helps to minimize this impact.

3. Use the ruler or scale to measure the depth of the denuder inside the end cap. Record this length. Attach the other end piece.

4. Before coating any denuders that have removable end pieces: Practice removing the end pieces. *[This section may change as experience is gained with Teflon o-rings that are to be used starting in mid-Feb 1999.]* Put a foam cushion section,

about 10 cm in length, such as used for pipe insulation, around the middle of the denuder. Pull the end pieces off gently, one at a time. By monitoring the force needed to move the end piece, it is possible to sense the glass passing over the first and then the second o-rings. Avoid jerky motions to prevent damage to the glass ends of the denuders. If the end piece is difficult to remove, twist while pulling, so as to minimize sudden increase in pressure or banging the metal and glass together.

5. When the end pieces need to be cleaned (for example, between coatings of different denuders that need to share end pieces): Remove the end pieces from the denuder. *[This section may change as experience is gained with Teflon o-rings that are to be used starting in mid-Feb 1999.]* Remove the 5 cm diameter inner o-rings by carefully pulling/rolling, one at a time, so that the bulging o-ring can be rolled out by hand. Alternately, wedge them out one at a time, using blunt-end tweezers or the round end of a scoop. Do not use tweezers or forceps with pointed ends, as they will scratch the end pieces or damage the Teflon coated aluminum surface of the end piece. Wipe out the o-ring grooves with a Kimwipe; follow with another that has been prewet with hexane. Remove the small o-ring from the smaller diameter end only when the end piece is to be cleaned with hexane.

6. With o-rings and gaskets removed, the end pieces can be sonicated in hexane, air dried, and then sonicated again in methanol or other solvent. At a minimum, rinse each end piece with hexane from a squirt bottle and air dry. Air dry on the clean area in the hood. Wrap with clean aluminum foil if the end piece is to be stored.

7. Wipe the Teflon o-rings with Kimwipes that have been wet with hexane. Check for nicks, dust, grit, XAD resin or other visible contamination.

8. Attach the end pieces to the denuders, making sure that the second o-ring has reached the glass. Check the depth of the denuder inside the end cap. If the depth is greater by 5 mm than the depth measured in step 3, gently rotate the end cap while applying pressure so that the o-rings will slide smoothly over the glass.

9. Rinse the assembled denuder twice with hexane: Pour 500 mL hexane into a clean beaker. Put a threaded Teflon plug into the open end of one end cap. Hold the denuder vertical, resting on the end cap, and support it in a padded clamp attached to a ring stand. To avoid hexane contact with the small o-ring in the end piece, put a clean glass rod into the open end of the denuder, past the small o-ring, and use it to guide hexane into the denuder annuli. Fill about half way. The volume depends on the design of the end piece. (The denuder designed for the VAPS in 1998 has an internal volume of about 180 mL. This requires about 500 mL for the denuders and end pieces available in November 1998.) Cap the denuder end piece. Carefully unclamp the denuder and support it with one hand at each end. Invert 20 times (10 complete revolutions) with one quarter turn axial rotation for each inversion. Remove one end cap and pour out the hexane rinse into a waste beaker while supporting and rotating the denuder. Remove the other Teflon end plug and

air dry the denuder (horizontally) in the hood. (Keep the end pieces in place on the denuder).

10. Apply slurries to the annuli: When the denuder is dry, as indicated by the movement of the solvent front through the denuder, put a Teflon plug on one end piece and support the denuder in the ringstand. Carefully place the clean glass rod into the opening of the end piece, so that it rests on the denuder annuli. Make sure the slurry is still sonicating. Turn off the sonicator, remove the beaker, touch the underside of the beaker to a paper towel or tissue to remove water from the sonic bath. Let the slurry settle, but for no more than 15 sec before pouring it along the glass rod into the denuder. Add about 80% of the slurry volume to the denuder. The remainder should be reserved in the beaker. (If all the slurry is added, a streaky, uneven coating may result because of the presence of larger than optimal particles.) Cap the top end of the denuder, remove the denuder from the clamp, support in both hands and invert 20 times.

11. Decant the slurry into its beaker by pouring while rotating the denuder. Rotate the denuder to minimize the formation of streaks in the coating. Top up the slurry volume to 200 mL with clean hexane, cover the beaker with clean Al foil and return it to the sonicator. Continue to sonicate between coating steps.

12. Remove the second white cap from the denuder. Place the denuder on the bench of the hood so that it is perpendicular to the back wall, about two inches from the wall. Dry the denuder in the laboratory hood between coatings. Air drying will take about 10 minutes. As the solvent front evaporates the appearance of the denuder changes. Rotate the denuder once or twice while the hexane is evaporating. Alternately, clean (ultrapure) dry nitrogen can be used to dry the denuder between coatings. However, the source purity needs to be verified before routine use for denuder drying, because the XAD coating will adsorb any organic impurities from the drying gas.

13. Re-apply the slurry. Repeat steps 10-12 at least 7 times. Collect the slurry residue and let the hexane evaporate. Dry used XAD from all the denuders should be saved and returned to L. Gundel or D. Lane for re-grinding.

14. After the final coating step, rinse the coated denuder twice with clean hexane to remove loose resin particles. Put the white cap on one end. Add about 200 mL hexane to the denuder when it is mounted vertically in the ringstand. Attach the other cap, remove from the ringstand and invert 20 times with twisting, as in denuder coating. Pour the rinse to waste while turning the denuder. Air dry and repeat.

15. Before the denuder has dried completely after the second rinse remove the end pieces, using the techniques that were practiced in step 4. Wet a Kimwipe with hexane and wipe the outside of the denuder ends.

16. Remove coating from the last 0.5 cm of each end of the denuder. The purpose of this step is to make sure that the adhesive joints between the inner tubes do not have patches of XAD resin that could flake off during sampling. Use a beaker that is wide enough to fit the cross section of the exposed glass end of the denuder. Add hexane to the beaker to about 1 cm depth. Put the beaker into the sonicator and turn it on. Carefully hold the exposed end of the denuder into the beaker so that just the bottom 0.5 cm is below the hexane level, but do not let the denuder rest on the bottom of the beaker. Sonicate for 15 sec. Lift the denuder up to inspect the end. Repeat. Apply the same procedure to the other end of the denuder. Air dry the denuder. It should be possible to see where the coating has been removed from each end.

17. When the denuder is dry, carefully cap the exposed ends with clean aluminum foil and wrap the whole denuder twice with aluminum foil. Roll the denuder with bubble wrap and put it into a cardboard box for storage before shipment. When Teflon end caps become available these should be used instead of the aluminum foil. (Before use caps should be cleaned with hexane after the o-rings have been removed and the grooves wiped clean with Kimwipes.

## 7.9 XAD denuder extraction:

1. Prepare 3 liters of 1:1:1 (v:v:v) dichloromethane (DCM):methanol (MEOH): hexane (HEX) by mixing 1 liter of each solvent in a clean 4 liter bottle. Use the 1 L graduated cylinder for measuring each solvent. Keep bottle capped when not in use. Label the bottle.
2. Record the denuder number and sample identification on the appropriate log sheet and in the laboratory notebook.
3. Using a syringe add appropriate amounts of internal standards to the glass surface of the denuder. Add 200 ng D10-Phenanthrene and 50 ng D10-Fluoranthene; 1 □g each of $C_{16}D_{34}$, succinic acid D6 and myristic acid D 37. Apply the solution onto several areas of the coated glass surface of the denuder, avoiding the metal end pieces. Allow the denuder to dry for 10 min to evaporate the solvent. Record the amounts of internal standards added.
4. Carefully cap one end of the denuder with a glass plug or Teflon-lined cap. Carefully clamp the denuder in a ring stand and add the 125 mL of (v:v:v) dichloromethane (DCM): methanol (MEOH): hexane (HEX) using a clean funnel and glass rod.
5. Carefully cap the open end of the denuder. Carefully unclamp the denuder and support it with one hand at each end. Invert 20 times (10 complete revolutions) with one quarter turn axial rotation for each inversion. Remove one end cap and pour out the solvent rinse into a clean 400 mL beaker. Rotate the denuder to remove as much solvent as possible. Carefully cap each end of the denuder with a glass plug or Teflon-lined cap.
6. Assemble the extract filter system with a new Millipore FHUP filter and apply vacuum to rinse with 50 mL of 1:1:1 (v:v:v) dichloromethane (DCM): methanol

(MEOH): hexane (HEX). Discard this solvent. Now filter the denuder extract from step 5. Collect the filtrate in a clean 250 mL pear shaped flask.

7. Transfer the flask to the rotary evaporator.
8. Rotary evaporation procedure. Add solution to be evaporated to the pear shaped flask but fill to no more than half the capacity. Cover any extract remaining in the beaker. Have the temperature of the bath between 20-25□C. Slowly increase the vacuum keeping the solution from rapidly boiling and flashing out of the pear shape flask. Slowly increase the vacuum to 400 Torr and the temperature of the bath to 30_C. When the solution is evaporated to ~10 mL cool the bath to 20_C, add the remainder of the extract and repeat the procedure.
9. Carefully clamp the denuder in a ring stand and add the 200 mL of 1:1:1 (v:v:v) dichloromethane (DCM): methanol (MEOH): hexane (HEX) to the denuder using a clean funnel and glass rod.
10. Repeat step 5. (Perform a second extraction of the denuder.)
11. Discard this solvent. Collect the filtrate in the same 250 mL pear shaped flask as used for the first extraction, step 6.
12. Transfer the flask to the rotary evaporator and evaporate the sample per step 8 to 5-10 mL. Cool flask to room temperature.
13. Add the appropriate amount of $C_{24}D_{50}$ to the pear flask and mix in flask. Measure the extract volume with a syringe and record in log sheet the volume of the extract and color. Transfer to a clean 25 mL brown bottle with narrow neck and Teflon lined cap.
14. Label bottle with appropriate identification and place a mark on the bottle at the bottom of the solvent meniscus. Store the bottle in a freezer at -30□C.

### 7.10 Denuder blank

Each denuder will have two blank extractions. The "pre-use" blank is determined from the final rinse of the coating procedure, described in the SOP for coating denuders; the "post-use" blank is described here. Since the denuders are being used 10 times between re-coatings, the "post-use" blank of from the first sampling period will be the "pre-use" blank of the second sampling period, and so-on.

1. Add the same amounts of internal standards to the denuder as used in extraction of the denuder, step 3 above. Dry in air for 10 min to evaporate the solvent.
2. Cap one end of the denuder with a Teflon-lined or glass plug. Carefully clamp the denuder in a ring stand and add the 200 mL of 1:1:1 (v:v:v) dichloromethane (DCM): methanol (MEOH): hexane (HEX) to the denuder using a clean funnel and glass rod. Cap the open end of the denuder.
3. Carefully unclamp the denuder and support it with one hand at each end. Invert 20 times (10 complete revolutions) with one quarter turn axial rotation for each inversion. Remove one end cap and pour out the solvent rinse into a clean 400 mL beaker.
4. In the hood, dry the denuder with ultrapure $N_2$. Alternatively, air dry in the hood with both end plugs removed. The denuder can rest on its side.

5. Assemble the extract filter system with a new Millipore FHUP filter and rinse with 50 mL of 1:1:1 (v:v:v) dichloromethane (DCM): : hexane (HEX) . Discard this solvent. Collect the blank filtrate in a clean 250 mL pear shaped flask.
6. Transfer the flask to the rotary evaporator and evaporate the sample to 5-10 mL as in step 8 above. Cool flask to room temperature.
1. Add the appropriate amount of $C_{24}D_{50}$ to flask and mix in flask. Measure the final volume with a 10 mL syringe and record in log sheet the amount of extract and color. Transfer to a clean 25 mL brown bottle with narrow neck and Teflon lined cap. Label bottle with appropriate identification and place a mark on the bottle at the bottom of the solvent meniscus.
2. Label the bottle as denuder blank with appropriate identification. Store the bottle in a freezer at -30□C.

### 7.11 QA/QC

1. Every 10th sample or a minimum of 3 samples per study which ever is larger: when extracting the denuder do not combine the first and second extract but keep them separate. This will provide information on extraction efficiencies.

2. Each time a new batch of solvent is made, save 200 mL and rotary evaporate the sample to 5-10 mL as in step 8, **Extraction**, above. Cool flask to room temperature. Measure with a syringe and record in log sheet the amount of extract and color. Transfer to a clean 25 mL brown bottle with narrow neck and Teflon lined cap. Label the bottle with appropriate identification and place a mark on the bottle at the bottom of the solvent meniscus. Label the bottle as solvent blank with appropriate identification. Store the bottle in a freezer at -30_C.

## 8. ION CHROMATOGRAPH

Ion Analysis from the sampled media is preformed by means of an Ion Chromatograph (IC). The specific IC used in the lab is the *Dionex* DX 500 Chromatography System. The system consists of four main pieces and several accessories.

### 8.1 Main Pieces

1. GP50 Gradient Pump
2. LC30 Chromatography Oven
3. CD20 Conductivity Detector
4. EG40 Eluent Generator

## 8.2 Accessories

1. Ionpac AG11-HC Guard Column (for Anion Detection)
2. Ionpac AG11-HC Analytical Column (for Anion Detection)
3. Anion Self-Regenerating Suppressor-II
4. Ionpac CS12A Guard Column (for Cation Detection)
5. Ionpac CS12A Analytical Column (for Cation Detection)
6. Cation Self-Regenerating Suppressor-II

## 8.3 Eluent

The EG40 is an automatic high-purity eluent generator that can create KOH or MSA eluent, depending on the cartridge. Eluent concentration from 0.1 to 100 mM is controlled by adjusting the current across the generator. Pure DDW is created using a Barnstead E-Pure and fed directly to the EG40. The E-Pure delivers DDW with a resistance of 17.5 ±5 MΩ or better. Degassing is preformed on-line immediately after the eluent is added to the DDW.

## 8.4 Helium Gas

Helium gas is used to operate the solenoid valve that controls the Rheodyne injection port. The pressure is controlled with a two stage standard tank regulator with a high and low pressure reading.

## 8.5 Standards

A standard solution is prepared for each ion that is being examined. A total of six different standard concentrations are prepared. The concentrations are prepared so that their concentrations lie on either side of the expected ion sample concentration. For example, a very typical Sulfate sample concentration is 15 μg/ml. The standard concentrations that are used to calibrate the IC are:

| | | |
|---|---|---|
| Standard 1 | 0 μg/ml | (DDW) |
| Standard 2 | 5 μg/ml | |
| Standard 3 | 10 μg/ml | |
| Standard 4 | 15 μg/ml | |
| Standard 5 | 20 μg/ml | |
| Standard 6 | 25 μg/ml | |
| Standard 7 | 30 μg/ml | |
| Standard 8 | 35 μg/ml | |
| Standard 9 | 24 μg/ml | |
| Standard 10 | 23 μg/ml | |

A calibration plot is generated, and the produced data is adjusted for the actual additional check, as well as for archiving purposes, all calibration curves are reproduced in Excell and saved.

### 8.6 Sampling

Once the standards have been run, 1 - 2 milliliters of sample are injected into the IC for testing. Since the standards have already been run, and the peak range for specific ions has already been recorded in the computer, all that remains is to read the *PeakNet* output. The output gives the concentration of each ion in ppm, i.e. µg/ml. Section _____: Sample Calculations gives a detailed description of how the *PeakNet* output is converted into reported values.

## 9. MASS DETERMINATION

Mass must be recorded before a filter has been sampled as well as after. And because of the nature of the filter material humidity must be controlled. The following information is the standard operating procedure for making mass measurements.

1. Filters are removed from their original packaging in lots of twenty to fifty. The filters are removed using Teflon tweezers in the clean room.
2. They are placed into small individual partially open cassettes. These cassettes are labeled and numbered a piece of masking tape.
3. The filters remain in a climate-controlled clean air room, where they are unsealed, for no less than one month. The humidity inside the room is maintained at 35 ±5%, the temperature at 21 ±1°C.
4. The filters are serialized. Each subset of filters consists of the filter to be weighed on a particular day. The piece of tape is marked with the weighing date and lot number. The filter is now serialized.
5. Masses are determined using a Mettler Toledo MT5 Electronic Balance. Each time that the balance is turned on, an internal automatic calibration is preformed. Immediately after the balance is zeroed, two standards are each weighed twice. If the weighed standards lie outside of the accepted precision of the balance; then the internal calibration and zeroing procedure is repeated and the standards are weighed again. Now each filter is weighed three consecutive times, alternating between pairs.
6. NOTE: The balance is activated with nothing on the scale after every second filters final weighing. If the weight of the balance is not zero, then the balance is rezeroed.
7. At the entrance to the balance chamber a radioactive strip has been placed to minimize the amount of static electricity. The strip is oriented so that when each filter is placed in to the balance chamber the strip is close enough to act on the filter; but not to hinder the filter.
8. Each filter is placed in its own filter holder and stored and shipped in accordance with the SOP for storage and shipping (see section C.4 below).

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#2

# Southern Center For The Integrated Study of Secondary Air Pollutants (SCISSAP)

## Progress Report

## For

## 2nd Year of 3-Year U.S. EPA Grant
(Grant R826372)

Submitted By:

W.L. Chameides, P.I.
School of Earth and Atmospheric Sciences
Georgia Tech
Atlanta, GA 30332

June 28, 2000

## Introduction

The long-term mission of the Southern Center for the Integrated Study of Secondary Air Pollutants (SCISSAP) is:

> *The development of the scientific understanding and analytical tools that underpin the design and implementation of an effective and integrated control strategy for secondary air pollutants, using the atmosphere of the southern United States as a natural laboratory.*

This mission is based on the premises that a basic understanding of the chemistry and physics of the atmosphere are a prerequisite for designing effective control strategies for secondary air pollutants; and that the concentration of secondary air pollutants in the atmosphere are often codependent because of interacting chemical reactions.

Over a three-year period beginning on April 1, 1998, SCISSAP has chosen to focus on an integrated study of ground-level ozone ($O_3$) and particulate matter with diameters less than 2.5 μm ($PM_{2.5}$) in the South. The central scientific objectives of this focus will be to provide a better understanding of:

(i) The sources and dynamics of $O_3$ and $PM_{2.5}$ in the southern United States;
(ii) The physical and chemical processes, and emissions that couple $O_3$ and $PM_{2.5}$; and
(iii) The combined effects of various emissions control strategies on $O_3$ and $PM_{2.5}$.

Specifically, four major and interrelated scientific questions will be addressed:

***Question 1:*** What is the concentration and composition of $PM_{2.5}$ in urban and rural locales in the South and to what extent do temporal and spatial variations in these parameters correlate with those of $O_3$ and its precursor compounds?

***Question 2:*** What are the major precursor compounds and sources for $PM_{2.5}$ in urban and rural locales in the South and to what extent do these compounds and sources correspond to/correlate with the sources of natural and anthropogenic $O_3$ precursors (i.e., VOC and $NO_x$)?

***Question 3:*** How are the formation rates and concentrations of $O_3$ and $PM_{2.5}$, as well as the $PM_{2.5}$ composition affected by the relative emissions and concentrations of $NO_x$, $SO_x$, $NH_3$, and VOC species?; and What are the mechanisms responsible for these relationships?

***Question 4*:** To what extent do the mechanisms elucidated above affect the formulation of an integrated control strategy for $O_3$ and $PM_{2.5}$?; and Do our findings suggest an "optimum" strategy for addressing both pollutants?

In the process, SCISSAP works on the development, evaluation, and application of analytical tools, methods, and models that can ultimately become available to the regulatory communities tasked with the management of secondary air pollutants.

## Second Year Activities

### 1. Field Measurments

#### 1.1. SCISSAP PCM Measurements

The field-measurements portion of the project during the second year has focused its efforts on the deployment of a Particle Composition Monitor (PCM) (see Figure 1) and related instruments. This deployment was implemented in two modes: (i) a monitoring mode in which the PCM was operated at a site on 2-3 samples/week basis in order to characterize the general properties and concentration of $PM_{2.5}$; and (ii) an intensive mode in which the PCM and ancillary equipment housed in a Mobile Laboratory (Figure 2) were operated on a continuous basis in conjunction with other instrumentation from other institutions to obtain mechanistic information concerning the formation, accumulation, and transport of $PM_{2.5}$ and its components. Our efforts in this regard were focused on two regions of the southeast: Nashville, Tennessee, and Atlanta, Georgia.

#### 1.1.1. Measurements in Nashville, Tennessee

In June, 1999, we placed two PCM's in the Nashville, Tennessee metropolitan area: one at a site typically located upwind of Nashville and the other downwind of Nashville. During a 6-week period from June to mid-July the PCM's were operated in an intensive mode as part of the SOS 1999 Nashville/Middle Tennessee Ozone Field Study. From Mid-July through April 2000 the PCM's were operated in a monitoring mode to obtain a longer-term data set on the $PM_{2.5}$ concentration and composition in the Nashville area.

#### 1.1.2. Measurements in Atlanta, Georgia

Operational sampling in Atlanta was initiated in May, 1999. From May to the end of July, the sampling was carried in monitoring mode. In August, we participated and hosted the 1999 Atlanta SuperSite Experiment in which a wide array of $PM_{2.5}$ measurement technologies were deployed at a single site in Atlanta to assess the current state-of-the-science in $PM_{2.5}$ measurement. During this period we sampled in intensive mode. Following the SuperSite Experiment, sampling returned to monitoring mode.

#### 1.1.3. Data Analysis

Figures 3 and 4 present a sampling of the preliminary results of our analysis of the data collected during the reporting period. These preliminary results were presented at the SOS Data Analysis Workshop in Raleigh, North Carolina in March 2000. We anticipate a more complete presentation of our results at a Special Session devoted to the 1999 SOS field experiments at the Fall, 2000 American Geophysical Union, followed by a comprehensive discussion in a paper to be submitted to a Special Issue of the Journal of Geophysical Research devoted to the SOS 1999 field experiments.

### 1.2. University of Minnesota Measurements

As part of the SCISSAP project, a research group from the University of Minnesota and headed by Dr. Peter McMurry developed a new method for measuring the material density of atmospheric particles during SCISSAP. This technique involved selecting particles of known mobility equivalent size with a differential mobility analyzer (DMA) and measuring their mass with an aerosol particle mass analyzer (APM). The APM is a new instrument that has not been used previously for atmospheric studies. These measurements showed that atmospheric particles of a given mobility equivalent diameter often include a variety of particle types with different densities. Based on aerosol composition measured by other groups and on water uptake measured by the University of Minnesota team, we believe the most abundant particle type consists of an internal mixture of sulfates and organic carbon. The measured densities of these particles (~1.6-1.8 g/cm3)is within about 5% of the density calculated from the measured aerosol composition. The aerosol often included particles with densities that were both higher and lower than this. We believe the low density particles probably consisted of chain agglomerate soot particles. The more dense particles may have been soil dust.

Professor McMurry will present the results of this work in an invited plenary lecture at the International Conference on Nucleation and Atmospheric Aerosols to be held in Rolla, MO (August 7-11, 2000) and at the meeting of the American Association for Aerosol Research in St. Louis, MO (Nov. 6-10, 2000).

## 2. Model Development/Evaluation

During 1999-2000, we have continued development and application of the SCISSAP particulate and photochemical oxidant model. In particular, we have installed a new, state of the science aerosol thermodynamics routine, and are now applying the updated model to an August 1999 period during which the Atlanta SuperSite measurements were being conducted. As part of this, we are developing an updated emissions inventory, and obtaining day-specific emissions for the major sources in the primary region of interest (e.g., around the north Georgia area that has the most direct impact on PM levels at the Supersite). In addition to the SuperSite measurements, we also have the total mass measurements, IMPROVE measurements and PM measurements from the ASACA network. This set provides the most extensive set of measurements available for model evaluation. Of note, the period being studied had both very high PM and ozone levels, and also a period where a front moved through, significantly reducing pollutant levels in the area.

In related studies being directed at Duke Univeristy by Dr. Prasad Kasibhatla we have completed an analysis of regional air quality model performance over an entire seasonal simulation period:

> Kasibhatla, P., and W.L. Chameides: "Seasonal modeling of regional ozone pollution in the eastern United States," Geophys. Res. Lett. 27:1415-1418, 2000;

and an analysis of algorithms used to simulate the formation and growth of secondary aerosols:

> Capaldo, K.P., P. Kasibhatla, S.N. Pandis: "Is aerosol production within the remote marine boundary layer sufficient to maintain observed concentrations?" J. Geophys. Res. 104: 3483-3500, 1999

**Plans for Year 3 of Project**

1. During the summer of 2000 we will undertake two field intensive measurement campaigns. In June and July we will carry out measurement in cities in southern Georgia to better characterize the spatial variability of $PM_{2.5}$ in the southeast. In August we will participate in the 2000 SOS Texas Air Quality Study;
2. The remainder of the project period will be devoted to completing our data analysis and model simulations and documenting our results in papers to be submitted to technical, peer-reviewed journals.

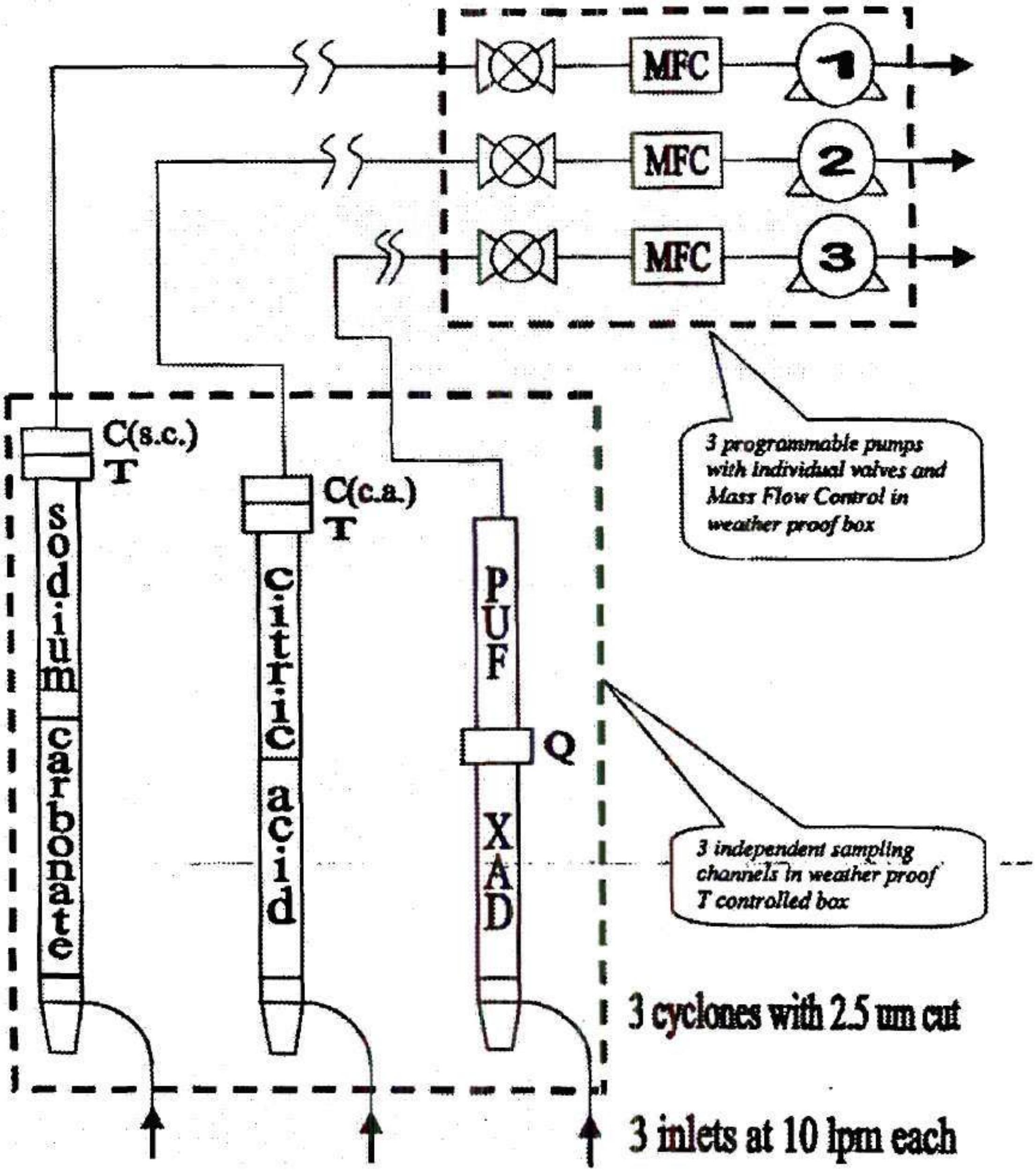
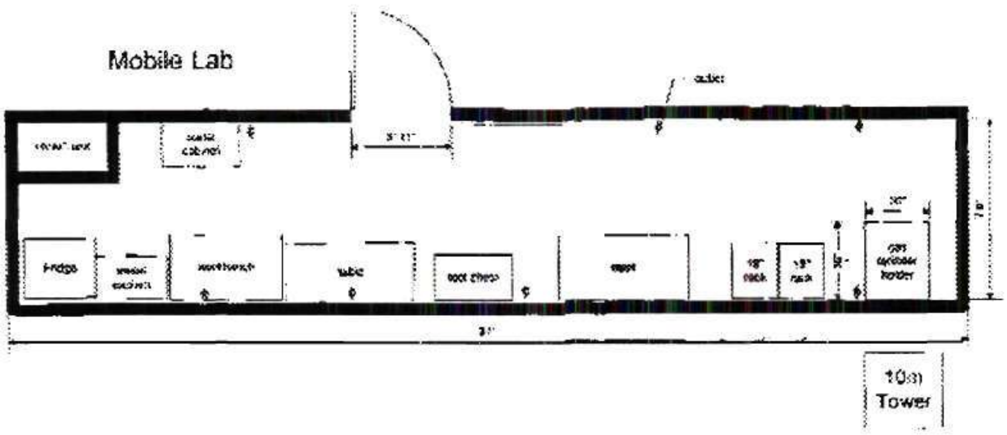


Figure 1. Schematic of the SCISSAP 3-channel, filter-dehuder pack Particle Compisition Monitor.



### Measurements

| Measurement | Instrument | Sensitivity | | Accuracy | Other |
|---|---|---|---|---|---|
| Air T/ ΔT | RM Young RTDs (2) | | | ±0.05 °C | |
| RH | Vaisala | | | ±2% RH (0-90%) | T depend.: 0.05% RH °C$^{-1}$ |
| WS/WD | RM Young | 0.4 m s$^{-1}$ | | ±0.2 m s$^{-1}$; ±3° | |
| Global Rad | LI-COR 400-1100 nm | 0.2 kW m$^{-2}$ mV$^{-1}$ | | | T depend.: 0.15% °C$^{-1}$ |
| UV Radiation | YES 280-320 nm | 1.97 W m$^{-2}$ V$^{-1}$ | | | ±5% for 0-60° solar zenith |
| | | Det. Limit | Precision | | |
| P | Vaisala 800-1060 hPa | | ±0.03 hPa | ±0.3 hPa overall | |
| Rain | Texas Electronics | 0.3 mm | | ±1% for < 10 mm hr$^{-1}$ | |
| NO | Air Quality Design | 3 pptv | ±10% | ±15% | |
| $NO_y$ | Air Quality Design | > 3 pptv | ±20% | ±25% | Well-characterized converter |
| $O_3$ | TEI 49C | 1 ppbv | ± 1 ppbv | ± 1 ppbv | |
| CO | TEI 48C-TL | 13 ppbv | ±10% | ±15% | Highly modified |
| $SO_2$ | TEI 43C-TL | 150 pptv | ±10% | ±15% | Modified |
| $PM_{2.5}$ | PRGS: 3 channels with individual cyclone heads; mass flow controlled denuder/filter pack systems | | | | |
| | TEOM- 1400a with Rupprecht & Patashnick 2.5 micron sharp cutpoint cyclone inlet | | | | |

### National Instruments Data Acquistion System

AT_MIO-64E-3 Multifunction I/O card
Analog: 32 differential inputs, 12-bit resolution, 500 kHz; 2 12-bit outputs
Digital: 8 TTL lines, 2 counter/timers, 24 bits, 20 MHz maximum source frequency

AT-DIO-24- Digital I/O card; 24 TTL lines used to switch valves through relay pods

6B-series- Distributed Signal Conditioning System
Inputs: Thermocouple, RTD, mV to ±50V, ±0-20mA.
Signaling range 1200 m; up to 256 modules; samples 16 bit resolution @ 9 Hz.

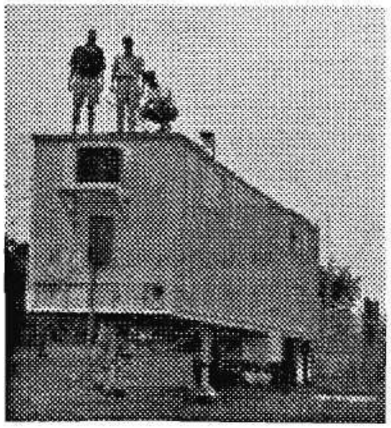
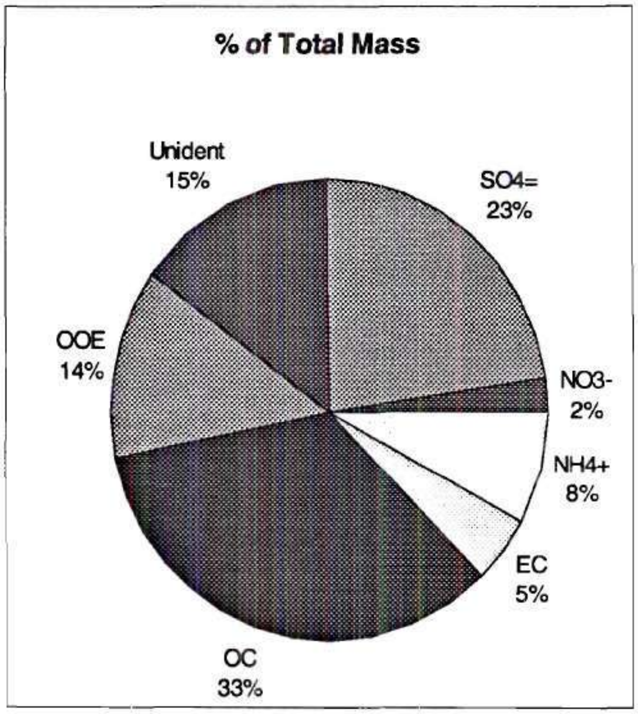


Figure 2. The SCISSAP Mobile Laboratory. Top panel: schematic of laboratory layout. Right panel: Photograph on laboratory as deployed at the 1999 Atlanta SuperSite Expeirment.

Monthly Averaged SCISSAP PCM DATA
Site: Jefferson Street, Atlanta, GA
Measurement Period: 5/15/99 - 6/15/99
# of samples: 9

$PM_{2.5}$ Averaged Composition



$PM_{2.5}$ average mass: 29 μg $m^{-3}$

GAS-PHASE CONCENTRATIONS

| | |
|---|---|
| $SO_2$: | 6.7 ppbv |
| $HNO_3$: | 0.8 ppbv |
| $NH_3$: | 2.0 ppbv |

Figure 3. Typical monthly-averaged data obtained from SCISSAP PCM operated under monitoring mode.

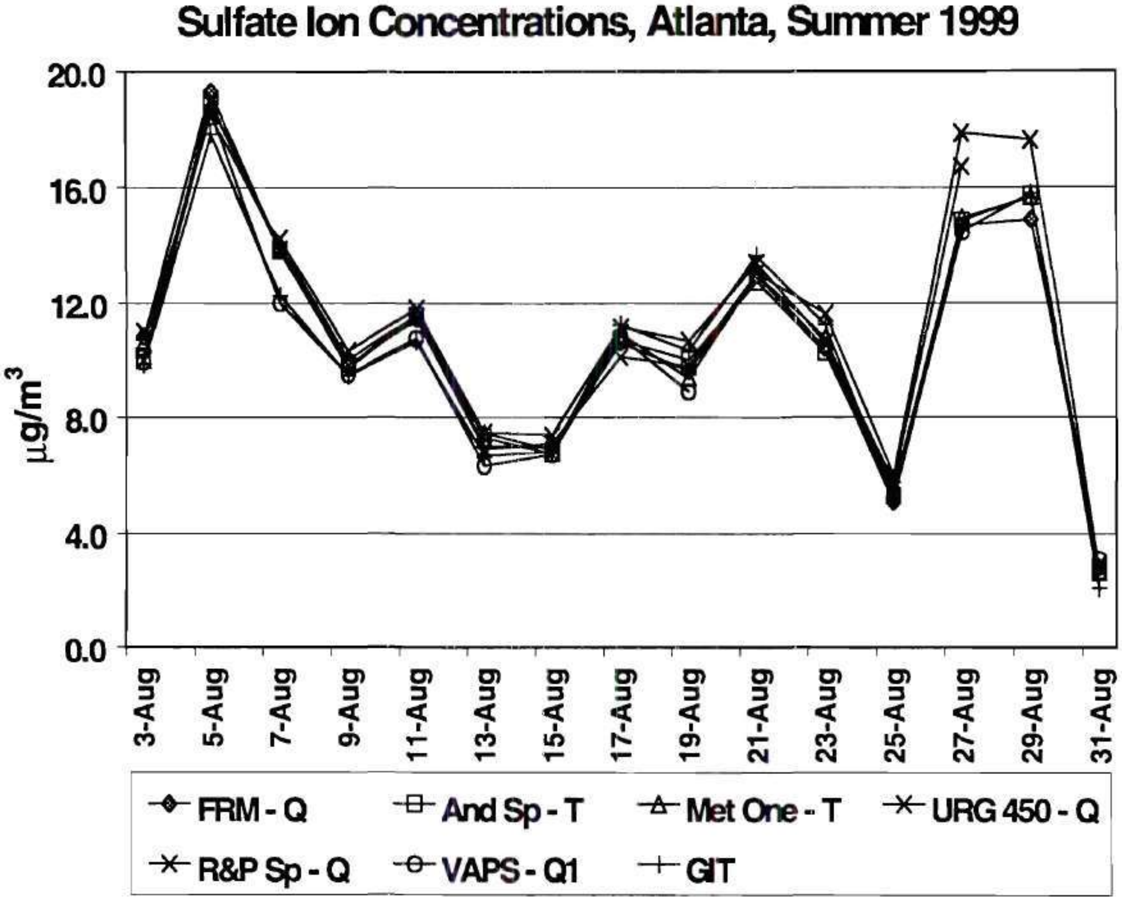


Figure 4. Illustrative result from 1999 Atlanta SuperSite Expeirment: comparison of $PM_{2.5}$ sulfate measurements. GIT represents results from SCISSAP PCM and others are from EPA-operated insturmentation. (After Solomon, Personal Communication, 2000).

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## 1. INTRODUCTION

In this report we summarize the major activities, accomplishments, and findings of a four-year research project funded by U.S. EPA's National Center for Environmental Research (NCER) through STAR Grant R826372 and carried out by the Southern Center for the Integrated Study of Secondary Air Pollutants (SCISSAP) at the Georgia Institute of Technology. The project funds were awarded to the Georgia Tech Research Corporation with Dr. W.L. Chameides, Smithgall Chair and Regents' Professor of Atmospheric Sciences in the School of Earth and Atmospheric Sciences at the Georgia Institute of Technology serving as the Principal Investigator. Dr. A.G. Russell of the School of Civil and Environmental Engineering at Georgia Tech served as a Co-Investigator (and leader of the modeling effort in the project). Subcontracts were awarded from Georgia Tech to the University of Minnesota (P. McMurry as Co-I), the University of Miami (R. Zika as Co-I), Duke University (P. Kasbhatla as Co-I), and the University of Alabama at Huntsville (D. McNider as Co-I).

The mission of the Southern Center for the Integrated Study of Secondary Air Pollutants (SCISSAP) is:

> *The development of the scientific understanding and analytical tools that underpin the design and implementation of an effective and integrated control strategy for secondary air pollutants, using the atmosphere of the southern United States as a natural laboratory.*

This mission is based on the premises that a basic understanding of the chemistry and physics of the atmosphere are a prerequisite for designing effective control strategies for secondary air pollutants; and that the concentration of secondary air pollutants in the atmosphere are often codependent because of interacting chemical reactions.

Over a four-year period beginning on April 1, 1998, SCISSAP was funded by U.S. EPA the NCER/STAR extramural funding program to focus on an integrated study of ground-level ozone ($O_3$) and particulate matter with diameters less than 2.5 μm ($PM_{2.5}$) in the South. Specifically, four major and interrelated scientific questions were addressed:

***Question 1:*** What is the composition and size distribution of fine particles in urban and rural locales in the southern United States and to what extent do temporal and spatial variations in these parameters correlate with those of ozone and its precursor compounds?

***Question 2:*** What are the major precursor compounds and sources for fine particles in urban and rural locales in the southern United States and to what extent do these compounds and sources correspond to/correlate with the sources of natural and anthropogenic ozone precursors (i.e., VOC and $NO_x$)?

***Question 3:*** To what extent, if any, is the chemical composition and abundance of fine particles in urban and rural locales in the southern United States affected by the concentration of natural and anthropogenic ozone precursors and/or ozone?

***Question 4:*** To what extent is the concentration of ground-level ozone in urban and rural locales in the southern United States affected by the concentration and composition of fine particles and/or the concentration of the precursors of fine particles?

To address these questions the SCISSAP Science Team adopted two tangential and interrelated lines of inquiry:

- **Instrumentation Development, Evaluation, and Implementation:** one line of investigation focused first on the development and testing of a mobile capability to measure $PM_{2.5}$, ozone, and their precursors, and then its subsequent application to large-scale, multi-investigator field experiments, as well as longer-term regional monitoring in the southeast;
- **Modeling:** the other focused on the development, evaluation and application of a regional scale air quality for conducting integrated studies of ozone and particulate matter: the "Urban-to-Regional, Multiscale Model: One Atmosphere"

(URM-1ATM), with one atmosphere used to denote an integrated approach to treating the physics and chemistry of ozone, acid deposition and particulate matter simultaneously.

## 2. SUMMARY OF MAJOR ACCOMPLISHMENTS:

During the 4-years of support for SCISSAP from NCER the SCISSAP Science Team successfully developed a facility for measuring $PM_{2.5}$ concentrations and composition as well as ozone and ozone- and fine particle gaseous precursors – a unique capability in the southeastern United States. This facility played a central role in a number of major regional air quality field experiments, most particularly in the 1999 Atlanta Supersite Experiment. The Science Team was also able to develop, evaluate, and apply a new multi-scale, multi-pollutant regional modeling system. Both the measurement facility and modeling system continue to serve a resource for the scientific and policy-making communities in the south and other regions of the United States.

Specific accomplishments are outlines below:

- Developed, field tested, intercompared, and implemented a Particle Composition Monitor (PCM) and related laboratory analytical techniques for measuring the mass and composition of $PM_{2.5}$ as well as its precursor compounds using the filter-denuder technique
- Developed, field tested, intercompared, and implemented a Differential Mobility Analyzer - Aerosol Particle Mass Analyzer (DMA - APM) for *in situ* measurements of particle mass as a function of mobility (i.e., size).
- Developed, field tested and implemented a system for quantifying *in situ* concentrations of oxygenated volatile organic compounds (OVOC).
- Participated in the 1999 SOS Nashville/Middle Tennessee Ozone Study; carried out first measurements of $PM_{2.5}$ vertical gradient within the boundary layer.
- Hosted, and provided analytical laboratory and meeting facilities for the 1999 Atlanta Supersite Experiment; also participated in the experiment.

- Participated in the 2000 Texas Air Quality Study.
- Operated urban and rural $PM_{2.5}$ monitoring sites in Tennessee and Georgia
- Developed an on-going regional center for air quality field measurements with a mobile measurement capability in the southeastern United States; this capability has played a key role in the State of Georgia supported Fall-line Air Quality Study and will provide vital data for a locally-supported field experiment in Pensacola Florida during the Summer of 2002.
- Helped develop and evaluate a regional-scale air quality model (URM-1ATM); this model played a critical role in the Southern Appalachians Mountains Initiative (SAMI) to address specific policy questions and many of the critical components of the model are now being migrated to EPA's Models 3.

## 3. SUMMARY OF MAJOR FINDINGS FROM EXPERIMENTAL PORTION OF THE PROGRAM

In addition to developing and evaluating new and improved instrumentation and analytical techniques for characterizing air pollutant concentrations and characteristics, SCISSAP endeavored to use this technology in field experiments to test various hypotheses with regards to the characteristics and processes that control the characteristics of $PM_{2.5}$ in the southeast. Specific findings and their policy-relevant implications are outlined below.

**Finding 1.** $PM_{2.5}$ composition (at the 24-hour integrated sampling time used in the study) was found to show little variability across the sites operated from Nashville, Tennessee, to Atlanta Georgia, to Houston Texas (see Figure 3.1). In virtually all cases more than 60% of the $PM_{2.5}$ mass was found to arise from sulfate (and the ammonium associated with it) and organic carbon (and the other organic elements assumed to be associated with the organic carbon). Thus pollution mitigation aimed at simply lowering $PM_{2.5}$ mass in the southeast would be most effective if they sought to lower the emissions of particulate sulfate and organic carbon and their precursors. (However, note finding #x below.)

**Finding 2.** $PM_{2.5}$ mass, sulfate, nitrate, and ammonium concentrations were found to have a positive vertical gradient between 4 and 42 m altitude at a suburban site in Tennessee.

**Finding 3.** The daily variations in the chemical components of $PM_{2.5}$ exhibited little of no correlation with their gaseous precursors, and $PM_{2.5}$ mass was not well-correlated with local ozone concentrations..

**Finding 4.** $PM_{2.5}$ mass concentrations showed only moderate increases as one moves from rural to suburban to urban locales.

**Policy-relevant Implication:** Collectively findings 1 – 4 suggest that the source for fine particles is regionally distributed with perhaps direct emissions of $PM_{2.5}$ and its precursors and/or secondary formation of $PM_{2.5}$ occurring aloft as opposed to at the surface.

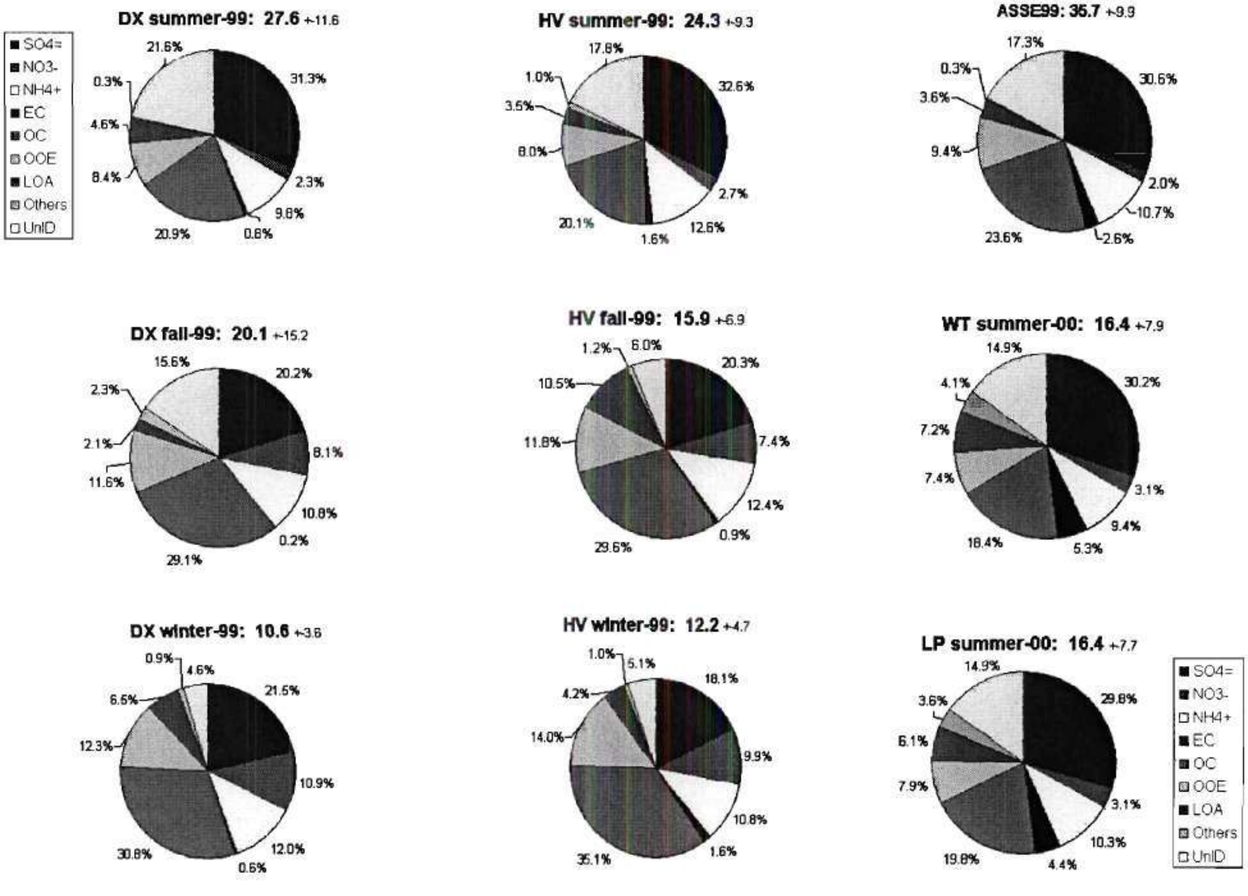

**Figure 3.1**. Average $PM_{2.5}$ mass (indicated in $mg/m^3$ next to the site descriptor above each pie chart) and percentage composition as a function of season at rural Dixon, Tennessee (DX), and suburban Hendersonville (HV) near Nashville, TN, metropolitan Atlanta (ASSE99) and two Houston, Texas sites, LaPorte (LP) and Williams Tower (WT). Note: OOE denoted other organic elements other than C associated with organic C particulate matter (OC), LOA denoted light organic acids.

**Finding 5.** Different instrumentation designed to measure the mass and composition of $PM_{2.5}$ with 12- or 24-hour integrated sampling will generally yield comparable results with each other and with more sophisticated continuous and semi-continuous methodologies.

**Finding 6.** Under highly humid conditions (e.g., Atlanta in the summer) significant artifacts in the measurement of $PM_{2.5}$ mass using the filter technique can arise from the presence of solid hydrates on the filter.

**Finding 7.** Negative artifacts in the measurement of OC can arise from the liberation of semi-volatile organics from the particulate phase when using the filter-denuder technique. Assuming OOE from the denuded quartz front filter to equal 60 % of OC, these semi-volatile organics showed lower OOE, indicating more volatile features of less polar and less water soluble species, see Baumann et al, 2002.

**Policy-relevant Implication**: While the denuder-filter technique can yield reasonably robust measurements of $PM_{2.5}$ mass and composition the method is subject to artifacts and thus thorough QA/QC procedures and self-consistency checks must be adopted with this technique. For example, accurate estimates of total organic mass requires development and application of methods for quantifying and correcting for artifacts arising from liberation of semi-volaite organics.

**Finding 8.** Atmospheric particles of 100 nm and 300 nm in Atlanta at ~3-6% relative humidity typically had two distinct densities: $1.6 \pm 0.1$ g $cm^{-3}$ and $0.45 \pm 0.20$ g $cm^{-3}$.

**Finding 9.** Effective densities of diesel exhaust particles decrease with increasing size. At 50 nm, densities are about $1.1 \pm 0.1$ g $cm^{-3}$, while at 300 nm densities are about $0.3 \pm 0.05$ g $cm^{-3}$.

**Policy-relevant Implication:** The "low density" particles observed in the Atlanta atmosphere have densities similar to diesel exhaust particles of the same mobility size. The densities of "high density" particles are consistent with values calculated from measured composition, assuming that they consist primarily of organic carbon and sulfates.

**Finding 10.** The DMA-APM technique can measure the mass and density of spherical particles to within 5%.

**Finding 11.** The DMA-APM technique can measure the mass and "effective densities" of nonspherical particles.

**Policy-relevant Implication:** The DMA-APM provides a precise and accurate technique for measuring particle density thereby enabling a determination of the definitive relationships between aerodynamic and mobility equivalent diameters. This relationship helps to reconcile measurements based on different physical principles. Also, the new, in-situ technique for direct measurement of mass size distributions and concentrations will provide insights into the accuracy of filter-based measurements of mass concentrations, such as are used in EPA's FRM network.

**Finding 12.** Diagnostic analysis of measurements of $PM_{2.5}$ composition and related gas-phase concentrations in Atlanta tend to support the notion that the amount of ammonium nitrate found in $PM_{2.5}$ is controlled by thermodynamic equilibrium between the $PM_{2.5}$ and gas-phase ammonia and nitric acid.

**Finding 13.** $PM_{2.5}$ in the southeast is generally slightly acidic with relatively small amounts of nitrate.

**Policy-relevant Implication:** In the southeast, there is generally an inadequate amount of ammonia to neutralize sulfate and hence $PM_{2.5}$ is slightly acidic and this in turn limits the amount of particulate nitrate that can form. Thus $PM_{2.5}$ mitigation efforts based on reducing particulate sulfate by decreasing $SO_2$ emissions may be offset, to some extent, by a concomitant increase in particulate nitrate.

**Finding 14**. A positive correlation was found between simultaneously measured OVOC concentrations and speciated, size-segregated particulate OC abundances in Atlanta. Calculation of the hourly new particle production potential from hourly OVOC measurements suggest that gas to particle conversion is a significant source of new organic aerosols. This calculation of new particle production predicts approximately half of the measured $PM_{2.5}$ total organic carbon observed.

**Policy-relevant Implication:** Controls on the gaseous emissions of OVOC and their precursors could have a significant impact on reducing $PM_{2.5}$ mass concentrations in Atlanta.

## 4. MAJOR POLICY-RELEVANT SCIENTIFIC FINDINGS

In addition to addressing the scientific and policy-relevant issues outlined above, the data gathered by SCISSAP and related programs were used to evaluate the URM-1ATM, being developed by the SCISSAP Modeling Team. Once successfully evaluated, the model was then used to comprehensively address the four major scientific questions SCISSAP set out to answer in its original proposal. Our findings are summarized below.

**Question 1:** What is the concentration and composition of $PM_{2.5}$ in urban and rural locales in the South and to what extent do temporal and spatial variations in these parameters correlate with those of $O_3$ and its precursor compounds?

**Findings**: While ozone and elemental carbon exhibit significant variations between urban and rural regions, most of the other components of $PM_{2.5}$ have relatively uniform concentrations between urban and rural areas, though certain regions have higher sulfate than others. On the other hand on urban scales there is a tendency for ozone and PM to be highest in or just downwind of urban areas.

**Question 2**: What are the major precursor compounds and sources for PM2.5 in urban and rural locales in the South and to what extent do these compounds and sources correspond to correlate with the sources of natural and anthropogenic $O_3$ precursors (i.e., VOC and $NO_x$)?

**Findings:** The major precursors for $PM_{2.5}$ in the southeast are $SO_2$ (largely from coal fired power plants) and organic carbon, from a myriad of sources including biogenic (e.g., biomass burning and secondary conversion of higher organics) and anthropogenic (automobiles, cooking, etc.). Nitrate plays less of a role at present since the aerosol is so acidic that much of the ammonia that is necessary for ammonium nitrate formation is tied up as ammonium sulfate. Ammonia, largely from animal waste and fertilizer use acts to form a fraction of the PM mass, but is important as it is the primary neutralizing agent. For ozone, the two primary precursors are $NO_x$ and, again, organics. Automobiles appear to play a major role, followed by electrical generating units in terms of ozone formation due to $NO_x$ emissions. Automotive (in urban areas) and biogenic (most everywhere else) sources, as well as solvent usage, have the most impact on forming ozone from the VOC perspective.

Sensitivity maps show that both ozone and sulfate have similar source-impact patterns. Thus, one would expect that controls for precursors of both pollutants would have benefits over the same general area.

**Question 3**: How are the formation rates and concentrations of O3 and $PM_{2.5}$, as well as the $PM_{2.5}$ composition affected by the relative emissions and concentrations of $NO_x$, $SO_x$, NH3, and VOC species, and what are the mechanisms responsible for these relationships?

**Findings:** Over most of the domain, ozone formation is $NO_x$-limited, though not always in urban areas where there can be a greater sensitivity to VOC emissions. Outside of primary emissions of particulate matter, $SO_x$ appears to be the most sensitive precursor for PM formation since it also captures ammonia and water. Sulfate appears to be formed primarily via gas phase oxidation, though aqueous phase reactions are important. Organic PM appears to be split between primary emissions and oxidation of biogenic emissions. Nitrate is formed from oxidation of $NO_2$, which takes place both during the day and at night, followed by reaction with ammonia. Ammonia acts as a neutralizing agent for sulfate and nitrate. The nitrate is highest, at least during the summer, in the early morning hours when the air is cooler and more humid, promoting condensation.

We do find that elevated NOx sources are less efficient at forming ozone than ground level sources, as has been found from aircraft studies as well. Increased emissions, while increasing ozone, can decrease the "ozone production efficiency" (OPE). We see a much more linear response in $SO_2$ emissions.

**Question 4**: To what extent do the mechanisms elucidated above affect the formulation of an integrated control strategy for $O_3$ and $PM_{2.5}$?; and Do our findings suggest an "optimum" strategy for addressing both pollutants?

**Findings:** Strategies to reduce $NO_x$ and $SO_2$ simultaneously will be effective in reducing ozone and PM at the same time. For example, using new, combined cycle gas turbines (or coal gasification), could lower both pollutants effectively. On the other hand, one could envision controls that only go after one of the precursors alone. We did not do an economic optimization to find which would be best. Also of importance, both ozone and

PM share a largely uncontrollable source, biogenics such as trees, which will limit the effectiveness of controls. For example, there will be a limit on how low PM levels can go since the biogenic fraction appears to be substantial on stagnant and hot days. Further, in the Southeast, VOC controls primarily will be effective only in and around urban areas, at least on high ozone days.

Our model results show (and as indicated by the measurements) that, at times, reducing $SO_2$ emissions, and hence PM sulfate, can be offset by increased nitrate aerosol as ammonium is no longer tied up neutralizing the sulfuric acid. The extent of this was quite varied over the region. In some cases, this led to a very small impact, though at other times and locations upwards of about 50% of the reduction in sulfate could be lost by an increase in ammonium nitrate. It was also found that this result will change in the future as $SO_2$ emissions are reduced due to acid rain controls and ammonia emissions may increase due to increased agricultural operations. In such cases, the effect of reduced sulfate leading to increased nitrate becomes more significant. We also found that there is a seasonal dependence. As part of a separate project, using URM-1ATM, we found that over a synthetic year that the replacement phenomena led to a relatively small reduction in the overall benefits of $SO_2$ control, on the order of 10%.

## 5. Summary of Quality Assurance/Control Activities

The SCISSAP Science Team is and has been committed to the production of high quality and reliable data, modeling products, and outputs. As a result Quality Integrated Work Plans for the experimental and modeling portions of the project were developed and submitted to U.S. EPA for review, comment, and ultimate approval during the summer of 1998. Assessment of data quality involved field audits by U.S. EPA personnel as well as systematic calibrations, zero spans, and careful and complete documentation (on record in the SCISSAP 14th Street laboratory facility). Quality assurance on the modeling side involved algorithm testing and intercomparisons between Georgia Tech and Duke University personnel as well as comprehensive evaluations using pseudo and real data. However, the ultimate quality assurance of our activities has been the submission and publication of our work in the peer-reviewed literature. A listing of the peer-reviewed articles currently published, in press, or under peer-review is provided in Appendix I.

## 6. SCISSAP PM, $O_3$, and PRECURSOR MEASUREMENTS[1]

SCISSAP's main objective over the past four years has been to advance our understanding of the physical and chemical processes that couple the formation of secondary air pollutants, in particular $O_3$ and $PM_{2.5}$ in the Southeastern United States by contrasting measurements in rural, suburban, and urban-metropolitan sites. Within this framework, a **Particle Composition Monitor (PCM)** was developed for discrete measurements of $PM_{2.5}$ mass and composition including relevant gas-phase species. The main species quantified and reported are the particle phase sodium ($Na^+$), potassium ($K^+$, since 2000), calcium ($Ca^{2+}$), ammonium ($NH_4^+$), fluoride ($F^-$, starting in 2000), chloride ($Cl^-$), nitrate ($NO_3^-$), sulfate ($SO_4^=$), formate ($HCOO^-$), acetate ($CH_3COO^-$), and oxalate ($C_2O_4^=$), as well as elemental and organic carbon (EC, OC). In addition to the particle-bound species, the PCM also measures the important gas-phase species $NH_3$, HCl,

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[1] *Prepared by: Karsten Baumann, School of Earth and Atmospheric Sciences, Georgia Tech*

HONO, $HNO_3$, $SO_2$, and the light organic acids (LOA) HCOOH, $CH_3COOH$, and $(COOH)_2$ over discrete sampling time intervals.

As part of the Southern Oxidants Study (SOS), long-term measurements were conducted at two sites in the Nashville, Tennessee area, and intensive measurements were made during August 1999 as part of the Atlanta Super Site Experiment (ASSE99), and in August and September 2000 in Houston, as part of the Texas Air Quality Study (TexAQS2k), where measurements were conducted at LaPorte, and at Williams Tower, 254 m above ground. During the SOS field experiment conducted on a multi-institutional level during June and July 1999, measurements at the two Tennessee sites, the more rural Dickson, and the suburban Hendersonville, were intensified as well. The facilities at the suburban Hendersonville site allowed daytime-nighttime separated measurements of vertical gradients (between 42 and 4 m agl) of $PM_{2.5}$ mass and major ions concentrations, as well as temperature, relative humidity, wind speed, and direction, as illustrated in Figure 6.1. Vertical gradients of the basic meteorological parameters allowed certain characterization of atmospheric stratification and mixing. The following Table 6.1 summarizes all locations, site names, characters and periods for which PCM measurements were made.

Table 6.1: SCISSAP site names, locations, characters and periods

| **Site name** | **Coordinates lat.(N)/long.(W)/el.(masl)** | **Character** | **Period** |
|---|---|---|---|
| Dickson, TN | 36.161/87.298/225 | rural | 07/02/99 – 04/05/00 |
| Hendersonville, TN | 36.298/86.653/143 | suburban | 07/02/99 – 04/05/00 |
| *Atlanta, GA* | | | |
| East Rivers ES | 33.820/84.389/251 | urban | 06/25/98 – 09/19/98 |
| Jefferson Street | 33.777/84.414/265 | urban | 02/16/99 – 09/26/99 |
| 14th Street | 33.787/84.406/298 | urban | 09/28/99 – 06/02/00 |
| *Houston, TX* | | | |
| LaPorte Airport | 29.671/95.069/ 8 | urban | 08/15/00 – 09/14/00 |
| Williams Tower | 29.750/95.475/284 | urban | 08/15/00 – 09/13/00. |

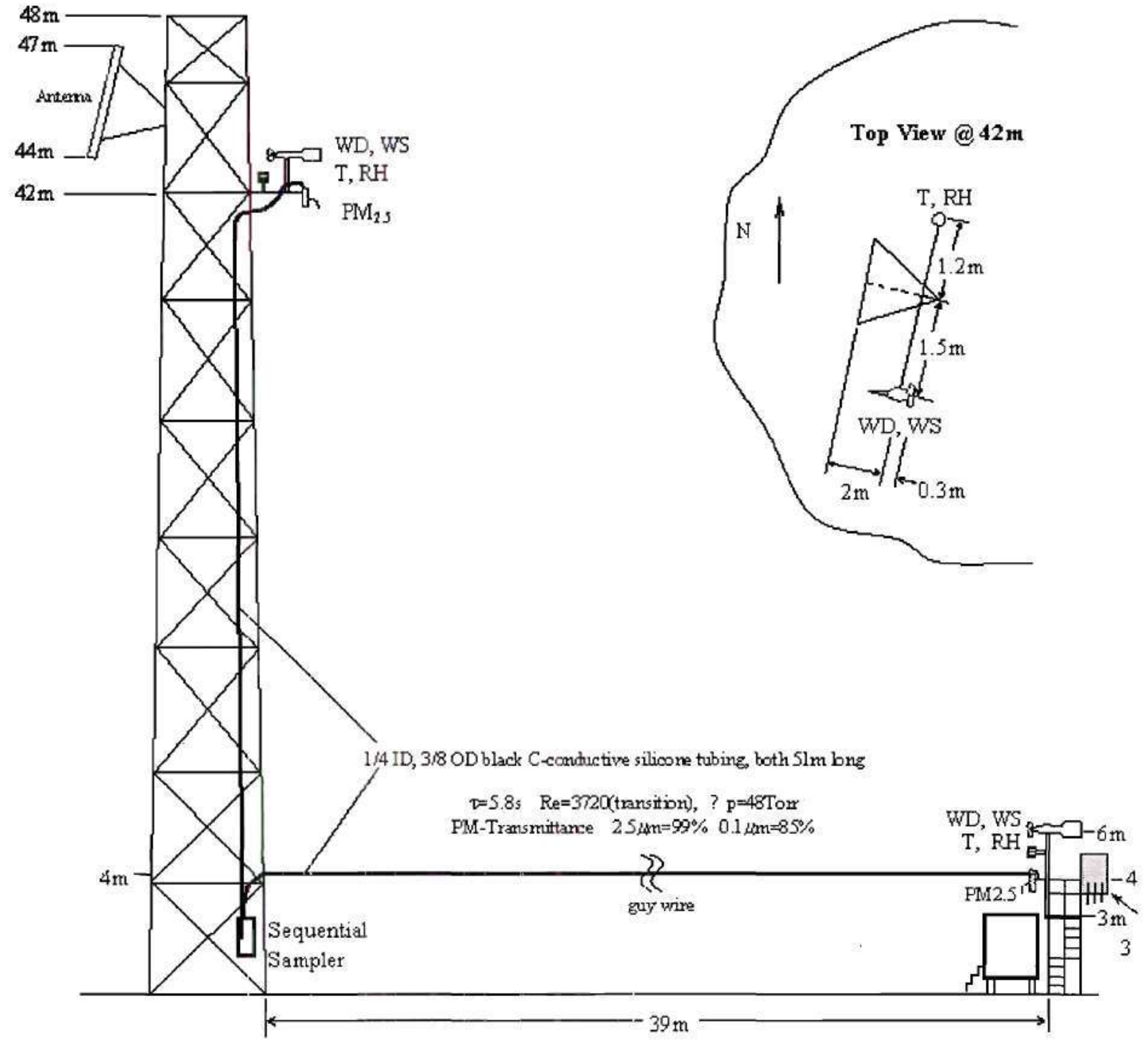

**Figure 6.1:** Use of 48 m tall tower at Hendersonville site for measuring vertical gradients (42 vs 4 m agl) of meteorological parameters, $PM_{2.5}$ mass and major ions concentrations.

The sampling frequency usually was about one 24h sample per week, however, more frequent sampling, up to 3 samples per day, has been conducted during the above mentioned collaborative research intensives. During these intensive periods, the SCISSAP team carried out tower-based meteorological and continuous gas measurements, in addition to its discrete $PM_{2.5}$ mass and composition measurements, involving the deployment of the Center's Air Quality Research Trailer (AQRT). In addition to serving as measurement platform, the AQRT hosted up to three additional research groups during those field intensives:

- Aerodyne Research Inc., lead by Dr. Doug Worsnop (TexAQS2k only);
- Particles in Liquid Solution (PILS) measurement group, lead by Prof. Rodney Weber;
- Aerosol Optical Properties (AOP) measurement group, lead by Prof. Mike Bergin.

### 6.1. PCM Sample Collection and Analysis

Details of the PCM operational characteristics are described in *Baumann et al.* [2001] and are briefly summarized here. The PCM is a bottom-up type sampler consisting of three channels as illustrated in Figure 6.2. Each channel follows the same principle of successive separation of particles larger than 2.5 microns aerodynamic diameter, followed by the separation of gaseous species prior to $PM_{2.5}$ collection on inert substrates with absorbing backup filters. Particles larger than 2.5 microns aerodynamic diameter are separated by standard, Teflon coated cyclone heads (URG, 116 S Merrit Mill Rd, Chapel Hill, NC 27516) with an estimated $D_{50}$ cut-off value for 50% aerosol penetration of 2.46 ±0.015 μm (1-sigma), and a "sharpness" $(D_{16}/D_{84})^{0.5}$ of 1.45. The sample air passes through a 30 cm long inlet tube with 14 mm ID prior to entering the cyclone. Tubes and cyclones are coated with two 25 μm thick layers of polytetrafluorethylene (PTFE) and perfluoroalkoxy (PFA) monomers. Special tests performed in comparison with fused silica coated inlets and cyclones showed the Teflon coat having superior characteristics for the transmission of $NH_3$ and $HNO_3$ gases. The transmission efficiency of new, cleaned surfaces varied between 82 and 99%, and would slightly increase with increased use for ambient air sampling, pointing to possible surface passivation effects, particularly for gaseous $NH_3$ and $HNO_3$.

As illustrated in Figure 6.2, two of the three PCM channels are dedicated for the determination of ionic species following sample analysis via ion chromatography (IC), while the third channel yields quantitative analysis of the elemental and organic carbon (EC, OC) content of the $PM_{2.5}$ samples using the thermal optical transmittance (TOT) method of *Birch and Cary* [1996]. Alkaline gases like $NH_3$ are removed in the first channel, and acidic gases such as HONO, $HNO_3$ etc. are removed in the second channel by means of 3-annuli denuders (concentrically arranged etched glass tubes, URG Corp.) coated with a 200 mM citric acid and a 150 mM sodium carbonate solution, respectively. The same coating solutions are applied to Whatman 41 cellulose fiber filters placed downstream of the Teflon filters (Zeflour™ P5PJ047, Gelman, Ann Arbor, MI, 2μm nominal pore size, and 47mm diameter), in order to capture volatilization losses that occur as a result of the altered gas/solid phase equilibrium after removal of gaseous species in the denuders.

Artifact reactions involving $NO_2$, $O_3$, and water vapor are particularly important in the HONO and $HNO_3$ denuder measurements. Using a tandem denuder set-up allowed the investigation of secondary surface induced $O_3$ reaction, which was found to potentially overcorrect the nitrite to nitrate oxidation step on the denuder walls, underestimating [$HNO_3$] and correspondingly overestimating [HONO]. Therefore, the ambient [$HNO_3$] and [HONO] were simply calculated from the differences in nitrite and nitrate found on the 1st and 2nd denuder, considering the combined disproportionation reaction ($2\ NO_2 + H_2O \rightarrow HNO_3 + HONO$), plus the reductive surface conversion of $NO_2$ to nitrate ($NO_{2g} + Na_2CO_3\text{-wall} \rightarrow NO_2^-{}_{surface}$), but neglecting the secondary $O_3$ oxidation step ($NO_2^-{}_{surface} + O_3 \rightarrow NO_3^-{}_{surface} + O_2$). Denuder breakthrough was insignificant for $NH_3$ and $SO_2$, but not so for the light organic acids.

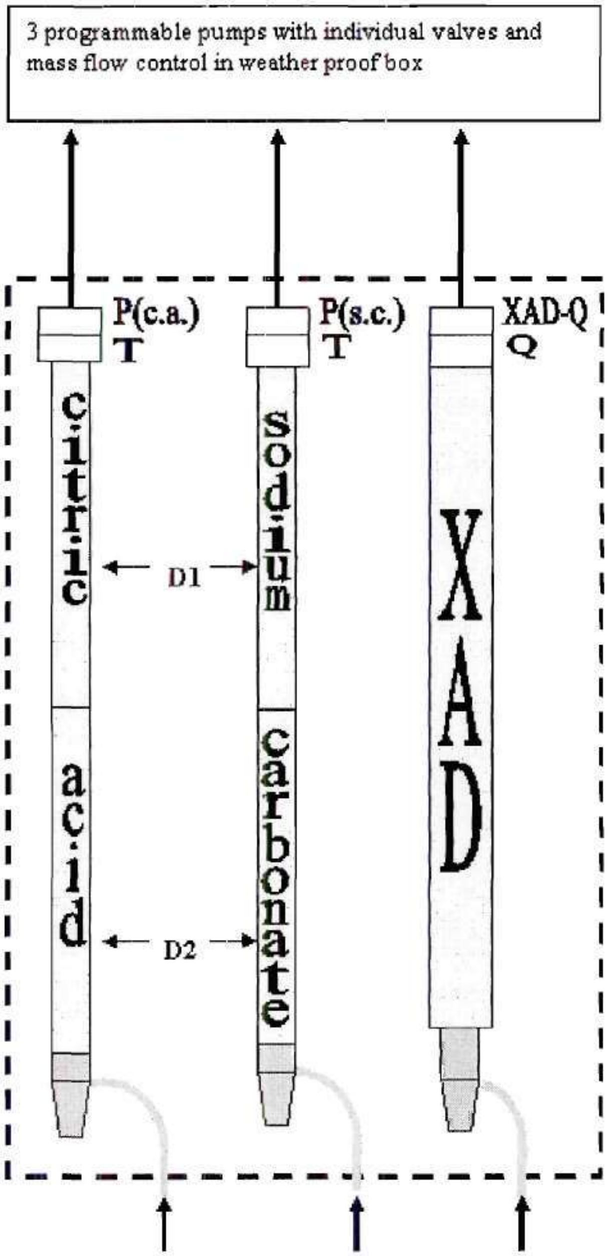

**Figure 6.2:** Standard PCM setup with three independent sampling channels in a weather proof, temperature controlled box. The 30 cm long Teflon coated inlets (ID= 1.4 cm) are attached to cyclones with 50% cutpoint efficiency for 2.46 μm aerodynamic diameter at 16.7 l min$^{-1}$ flow rate, resulting in a filter face velocity of 20 cm s$^{-1}$. *D1, D2*... 3-annuli denuder tandem $Na_2CO_3$ / $C_6H_8O_7$ coated, 24 and 15 cm long, 0.1 and 0.06 s sample residence time under plug flow (Re=295), respectively; *XAD*...8-annuli coated denuder, 28.5 cm long 0.8 s residence time; *T*...Teflon filter, 2 μm Zeflour™; *P*...paper filter, Whatman 41, $Na_2CO_3$ / $C_6H_8O_7$ coated; *Q*...quartz filter, pre-baked; *XAD-Q*...XAD coated quartz filter.

The coating solutions for both denuders and paper filters were prepared and applied in dedicated glove boxes under clean, filtered air micro-environments, in order to keep laboratory contamination, and therefore field blank levels at a minimum (see data quality section). The alkaline coated denuders of 15 and 24 cm lengths were found near 100% effective in retaining the particularly "sticky" gaseous species $NH_3$ and $HNO_3$, respectively. The actual efficiency with which the denuders retained less sticky species, e.g. light organic acids, was governed, however, by the adsorption efficiency of the coated surface, and was determined experimentally via a tandem set-up with two denuders in series. The sample residence times through the triple-annuli portion of each denuder, assuming plug flow at Re = 295, were 0.06 s and 0.1 s, respectively.

Extractions were performed under a laminar flow hood with a mixed filter-bed of activated carbon and citric acid. Each denuder was subject to a two-step extraction assuming a total volume of 30 ml DDW. Field blanks for each sample medium type (i.e., denuders, Teflon and coated paper filters) were carried together with each sample. These blanks were handled the same way as the actual samples and served two purposes, taking into account possible contaminations as a result of handling/mounting/dismounting the samples, and determination of the detection limits for each species investigated.

The Teflon and paper backup filters from channel 1 were dedicated for particle-phase cations $Na^+$, $Ca^{2+}$, and $NH_4^+$, while particle bound concentrations of $Cl^-$, $NO_3^-$, $SO_4^{2-}$, as well as formate, acetate, and oxalate were determined from the channel 2 samples. Only ammonium nitrate and the organic acids were considered subject to possible volatilization loss off the Teflon filters (negative artifact). All filters were 47 mm in diameter and experienced a face volicity of ~20 cm $s^{-1}$ at nominal sample flow rates of 16.7 lpm. The gravimetric mass of the sampled $PM_{2.5}$ was determined from the Teflon filters, after an equilibration process as described later. Once the Teflon filter mass had been determined, the filters were extracted via 30 minute sonication in 30 ml heated DDW. The paper filters (blank included) underwent a two-step 20ml DDW extraction under a laminar flow hood supplied with a bed of activated carbon and citric acid providing contaminant-free air.

IC analysis was used to determine the soluble ion content of the various extracts applying a dual-channel Dionex DX-500 ion chromatograph with two separate EG40 eluent generators; KOH for anions, methane-sulfonic acid (MSA) for cations, controllable to within 0.5 and 50 mM, and IonPac analytical columns AG11-HC for anions and CS12A for cations, both in the 2 mm ID microbore format. Each channel operates a self-regenerating SRS-ULTRA suppresor in external DDW regeneration mode, a CD20 conductivity detector, and a GP50 gradient pump. The applied micro-bore system allows economical analyte flow rates of 0.25 ml/min for cations, and 0.35 ml/min for anions. DDW is supplied by a Barnstead E-Pure at a resistivity of 18.0 ±0.3 MΩ and fed directly to the EG40. Degassing is performed on-line immediately after the eluent is added to the DDW well upstream of the injector.

In order to minimize the artifacts induced by semi-volatile organic compounds (SVOC) that exist in the atmosphere in equilibrium between the gas and particle phases, the sampling principle applied to channels 1 and 2 was also applied to channel 3, by use of an XAD-coated denuder upstream of the (pre-baked) sample quartz filters (Pallflex #2500 QAT-UP). This denuder was a downsized version of the one used in the IOGAPS, and identical to what has been reported as the Versatile Air Pollution Sampler (VAPS) by *Stevens et al.* [1993] and *Pinto et al.* [1998]. The effective coating material was finely ground XAD-4 resin, a porous macroreticular, nonpolar, polystyrene-divinylbenzene resin, which is insensitive to highly volatile organic compounds (VOC) but was selected as the sorbent because of its high surface area (725 $m^2/g$) for adsorption of a wide range of gas phase SVOC from the airstream [*Lane et al.,* 2000]. Also similar to channels 1 and 2, the application of an XAD-denuder upstream of the quartz filter disturbs the gas-particle equilibrium of the condensable organics, potentially enhancing losses of semi-volatiles from the collected particles (negative artifact), therefore requiring the use of an appropriate adsorber downstream of the main $PM_{2.5}$ filter substrate, in order to adequately account for volatilization losses of semi-volatile compounds. A XAD-coated quartz filter was used as the backup adsorber and analyzed for (operationally defined) SVOC via a specially modified TOT program run. In contrast to the conventional TOT analysis program [*Birch and Cary*, 1996], where EC is measured in a 5.24 % $O_2$ atmosphere after the $O_2$-free OC-stage, the evolving carbon here is being oxidized exclusively by surface catalysis (using the $MnO_2$ bed at 900°C) in a pure He atmosphere. The oven temperature at the punch is stepped up to 176 °C from ~50 °C within ~1 min and held constant at 176

°C for a period of ~3 min. In contrast to a regular, uncoated quartz filter run, no $O_2$ is introduced to the oven and no EC is generated or measured. The split point between OC and EC, which is usually determined by the point where the same amount of laser light is being transmitted through the punch as before the sample run, is made here meaningless and set before the internal $CH_4$ calibration. As for all sample media, field blanks were carried and analyzed for each XAD-coated quartz sample filter as well.

### 6.2. $PM_{2.5}$ Mass Determination

Due to the disturbance of the gas/particle phase equilibria imposed on the particles collected on the Teflon filters by use of denuders, *blow off* of semi-volatile species had to be accounted for. The semi-volatile fractions of $NH_4^+$, $NO_3^-$, and the light organic acids retrieved from the adsorbing paper backup filters (considering blanks and denuder efficiencies) were added to the gravimetric mass determined from the Teflon sample filter. Mostly due to their relatively high volatility, the light organic acids were undetectable via the TOT analysis on quartz filters.

The total $PM_{2.5}$ mass concentration was determined gravimetrically from the Teflon filters prior to IC extraction using a Mettler Toledo MT5 Electronic Balance in a temperature (21 ±1 °C) and humidity (35 ±3 %) controlled class 1000 clean room. The micro-balance maintained a linear range between 0 and 500 mg to within ±0.0004% and a detection limit of 0.37 ±0.7 μg for all measurements subject to this report.

During the ASSE99, a sub-set of Teflon filter samples was investigated further to quantify the level of mass artifact introduced by hydrates formed from water vapor attracted by the hydrophylic components of the sampled particles and incorporated in a matrix of molecules or ions. Therefore, if the water concentration is not high enough to yield a liquid solution, water molecules will be incorporated into the solid phase compounds and result in hydrates. In order to accelerate the dehydration process, the sub-set of Teflon filters was placed in a desiccator using anhydrous calcium sulfate (97% $CaSO_4$, 3% $CoCl_2$, W.A. Hammond Drierite Co. Ltd., Xenia, OH), which resulted in an acceleration of the dehydration rate of up to 9-fold compared to simple exposure in the clean room. The dehydration process was determined to be complete when subsequent weighings yielded a change within ±10 %, which was typically the case after ~4 weeks of clean room exposure. The sub-set of these Teflon filters was also used to verify that the observed loss of mass is not due to losses of any of the identified ionic species. Corresponding IC analyses showed that the change in ion content after dehydration was indeed below the determined level of precision of the measurement. Therefore, the mass loss is assumed to be predominantly caused by condensed water vapor in the form of hydrates. Figure 6.3 shows the final mass after dehydration versus the initial mass weighed after the samples had been exposed in the controlled clean room environment for ~24 to 48 h. As shown by the slope of the linear regression (0.774 ±0.028 standard error), the water vapor induced mass artifact is on average ~20 % ($r^2$=0.94, n=11), and the 1-sigma variation of the individually determined artifacts is ±8 %.

In consequence of this finding, all Teflon filter samples collected after ASSE99 were dehydrated by either prolonged exposure in the clean room or more commonly (since more effectively) by desiccation prior to gravimetric mass determination. The gravimetric $PM_{2.5}$ mass concentrations determined from all ASSE99 Teflon filter samples as well as from all samples collected at Dickson and Hendersonville, TN, that had not been actively dehydrated were retro-corrected by the above factor of 0.774.

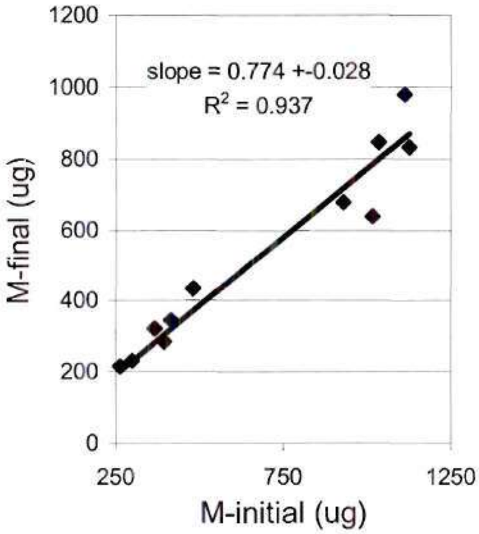

**Figure 6.3:** Absolute mass lost due to dehydration from regression of the final desiccated $PM_{2.5}$ mass ($M_{final}$) versus the initial gravimetric $PM_{2.5}$ mass ($M_{initial}$) of a sub-set of 11 Teflon sample filters from ASSE99.

### 6.3. Continuous Measurements of Gaseous Tracers

As mentioned above, the AQRT served as a mobile platform for auxiliary meteorological and gas phase measurements (NO, $NO_x$, $NO_y$, $O_3$, CO, $SO_2$, UVB and global radiation, wind speed and direction, relative humidity, various air and soil temperatures and ambient pressure), besides hosting research collaborators for joint intensive field studies. The following briefly describes the most important features of the continuous gas phase measurements.

$O_3$ was measured using a pressure and temperature compensated commercial UV absorption instrument (model TEI 49-C, TEI, Inc., Franklin, MA), being absolutely calibrated by the known absorption coefficient of $O_3$ at 254 nm. The linearity and precision of the analyzer was checked on average once every 22 hours. Precision check mixing ratios of 0, 90, 180, 270, and 360 ppbv were provided by a primary standard calibrator with active feedback control (model TEI 49C-PS). The calibrator was supplied with $O_3$-free (zero) air from a cartridge of activated carbon that effectively removed $O_3$ from the ambient air. Each precision check resulted in a 5 point linear regression. Assuming normal distribution of the regressions' intercepts, the $O_3$ analyzer's detection limit was and typically is 1.0 ppbv; whereas the slopes of the linear regressions yielded ±4 % precision. The accuracy is estimated to be the same. The same type analyzer was deployed at Williams Tower during TexAQS2k and was subjected to the primary standard calibration procedure before and after the study yielding a similar level of quality.

CO was measured by gas filter correlation, nondispersive infrared absorption (model TEI 48C-TL with a hand-selected PbSe detector matched with an optimal preamplifier, and an absorption cell with gold-plated mirrors). The signal output was pressure compensated while the absorption cell temperature was controlled at 44 $\pm 0.1\ ^{o}C$. A zero trap of 0.5 % Pd on alumina catalyst bed (type E221 P/D, Degussa Corp.) kept at 180 $^{o}C$ quantitatively oxidized CO to $CO_2$ at an efficiency greater 99 %, and allowed the switching of zero modes every 11 min for 2 min. NIST traceable calibration gas of 405 ±4 ppmv CO in $N_2$ (Scott-Marrin Inc., Riverside, CA) was introduced into the sample stream by mass flow controlled standard addition and dynamic dilution at the instrument inlet for 2 min approximately every 11 h. The detection limit for a 1 min average based on the 1 Hz data was ~107 ppbv, and ~23 ppbv for a 1 h average. The instrument's precision, determined from the standard addition span checks, was ±9 % at ~570 ppbv. The accuracy was estimated as the RMS error of uncertainties in the calibration tank concentration (2 %), the mass flow controllers (4 % each MFC), the background variation (4 %), and potential inaccuracies from interpolation of the measured ambient CO during span checks (15 %). Thus, the total uncertainty in the CO measurement is estimated at ±17 % for the entire measuring range. The instrument's linearity within its 5000 ppbv range was determined from all calibrations performed during each study (zero excluded), and revealed an $r^2$ of 0.98.

$SO_2$ was measured by use of a commercial, pulsed UV fluorescence instrument (model TEI 43C-TL) with pressure and temperature compensated signal output. It's response time was ~45 s and therefore, required longer zeroing and calibration periods compared to the CO instrument: zero for 4 min once every 55 min; calibration - via mass flow controlled standard addition of 30.6 ±0.3 ppmv $SO_2$ in $N_2$ NIST traceable calibration gas (Scott-Marrin Inc.) and dynamic dilution at the instrument inlet - was performed for 4 min once every 11 hours. Zero [$SO_2$-free] air was produced by passing ambient air through a HEPA glass fiber in-line filter (Balston) impregnated with a 0.15 molar $Na_2CO_3$ solution. At a flow rate of 0.9 slm, the filter removed >99 % of the $SO_2$ in the sample. Calibrations were performed and evaluated analogous to the CO measurements resulting in a detection limit of 4.3 ppbv for 1 min, and 0.08 ppbv for 1 h averages, and a precision of ±4 % at 60-130 ppbv. Since the instrument's measurement principle is known to be sensitive to organic hydrocarbons (HC), the efficiency of the internal HC removal through a semi-permeable wall was enhanced by introducing an activated carbon trap into the flow of the low-[HC]-side of the wall, and thereby further increasing the [HC] gradient across the wall. NO is known to be another interferent, and its level of interference was examined by standard addition of NO calibration gas, resulting in a 2-3 % increase of signal. The $SO_2$ data were not corrected for this relatively small interference. The accuracy was estimated as the RMS error of uncertainties in the calibration tank concentration (2 %), the mass flow controllers (4 % each MFC), the background variation (12 %), the NO interference (2 %), and potential inaccuracies from interpolation of the measured ambient $SO_2$ during span checks (10 %).

Thus, the total uncertainty in the $SO_2$ measurement is estimated at ±17 % for the entire measuring range. The instrument's linearity within its 200 ppbv range was determined from all calibrations during the study, and revealed an $r^2$ of 0.99.

Proto-type Air Quality Design (AQD, Golden, Colorado) NO/$NO_y$ and NO/$NO_x$ analyzers were deployed for the measurement of NO, $NO_x$, and total reactive nitrogen oxides ($NO_y$) that include NO, $NO_2$, $NO_3$, $N_2O_5$, HONO, $HNO_3$, aerosol nitrate, PAN and other organic nitrates. The $NO_y$ measurements were based on the principal method of metal-surface induced reduction of the more highly oxidized species to NO, and its subsequent chemiluminescence detection (CLD) with excess ozone. The metal surface here was a 35 cm long, 0.48 cm ID MoO tube (Rembar Co., Dobbs Ferry, NY), temperature controlled at 350 ±2 °C, and housed inside an inlet box mounted to the met tower ~9 m above ground. The NOx measurements made 4.5 m agl, utilized a Xe/Hg photolysis system with an average $NO_2$ conversion fraction of 12 ±3 % at 1 s sample residence time. The data quality of all the gas-phase measurements are summarized on the basis of 1 min averages in Table 6.2.

**Table 2:** Detection limits (DL), precision, and accuracy for the continuous measurement of $O_3$, CO, $SO_2$, NO, $NO_x$, and $NO_y$

| | $O_3$ | CO | $SO_2$ | NO | $NO_x$ | $NO_y$ |
|---|---|---|---|---|---|---|
| DL (ppbv) | 1 | 23* | 0.08* | 0.003 | 0.5 | 0.4 |
| Precision (%) | ±4 | ±9 | ±4 | ±10 | ±15 | ±15 |
| Accuracy (%) | ±4 | ±17 | ±17 | ±15 | ±25 | ±20 |

* based on a 1 h average.

The sample air was drawn continuously through a 15 cm long 0.64 cm OD SS tube, which extended ~5 cm to the outside bottom of the box and was coupled to two SS crosses, where the flow was diverted to a MoO converter tube for the $NO_y$ and a bypass PFA tube of same length for the NO measurement, at 1 slm respectively. All SS components were Teflon coated and temperature controlled at 40 °C. A stream selector assembly with mass flow controllers (MFC) housed inside the inlet box, which reduced the sample residence time inside the PFA tubing between the inlet box on the tower and the CLD unit inside the mobile lab at the ground to < 0.2 s. NO and $NO_y$ measure modes were switched every 2 minutes. Automated calibrations were performed via a programmed set of NO, $NO_2$, n-propyl nitrate (NPN), and $HNO_3$ standard additions to the sample inlet on average 2 times per day in ambient air, and about once per day in zero air. The calibrations allowed the determination of specific parameters that are relevant for the assessment of the overall instrument performance, such as sensitivity, artifacts, detection limits, and conversion efficiencies of the MoO tube.

In summary, the NO detection limit for a 1 min integration time was 3 ±0.5 pptv in ambient air and 2 ±0.1 pptv in zero air at a signal-to-noise ratio of 2, respectively. The instrument's overall sensitivity to ambient NO (S_NO) averaged to 3.57 ±0.6 Hz $pptv^{-1}$ in ambient air and 4.39 ±0.15 Hz $pptv^{-1}$ in zero air. A difference in signal was present when sampling zero air in NO measure mode versus NO zero mode, displaying a NO artifact (A_NO), which was 28 ±4 pptv. A_NO was interpolated between calibrations and subtracted from the ambient NO measurements. Since the zero volume efficiency was less than 100 %, i.e. on average 97 ±3 %, the instrument's zero varied with ambient NO and $NO_y$ levels, respectively. Thus, during low level periods sporadically occurring at night, the NO_zero signal counts typically averaged 1300 Hz ±2 %. The accuracy of the NO measurements had uncertainty due to variations in instrument zeroes, sensitivities, MFC calibrations, and the level of calibration standard used. The MFC calibrations before and after the study were within 2 %. The biggest contributor to the overall uncertainty was the variable level of ambient NO before and after the standard addition and the interpolation necessary for the S_NO determination, which is estimated here at ±13 %. Therefore, the overall uncertainty of the NO measurement is estimated at ±15 % as RMS error of all the above potential inaccuracies.

Each calibration cycle allowed the determination of the instrument's sensitivity to $NO_2$, NPN, and $HNO_3$. The $NO_2$ sensitivity (S_$NO_2$) in ambient air averaged 3.72 ±0.44 Hz $pptv^{-1}$ revealing a $NO_2$ conversion efficiency Q_$NO_2$ of 94 ±8 %. With each calibration cycle the conversion efficiencies for NPN and $HNO_3$, species that are typically harder to convert than $NO_2$, were also determined via standard addition. NPN cal gas was delivered mass flow controlled to the converter inlet from a NIST traceable compressed air tank of 3.88 ±0.19 ppmv NPN in $O_2$-free $N_2$ (Scott-Marrin Inc.). $HNO_3$ was supplied from a permeation tube (Kin-Tek) inside an oven controlled at 40 ±0.1 °C via a critical orifice controlled zero air flow of ~10 sccm. The permeation rate was verified before and after each study via dissolution of $HNO_3$ using a small scale impinger and subsequent IC analysis of $NO_3^-$. The conversion efficiencies for both NPN and $HNO_3$ in ambient air were 87 ±18 % and 80 ±53 %, respectively, suggesting that $NO_2$ is typically converted the easiest and $HNO_3$ the hardest. The variability and relative differences in conversion efficiencies of these three $NO_y$ species add uncertainty to the $NO_y$ measurement as considered below. The $NO_y$ zeroes averaged 1450 Hz ±10 %, and an artifact A_NOy was present when sampling zero air. This artifact varied with time and level of converter decay, and was therefore considered in a time-dependent manner; it averaged 0.39 ±0.17 ppbv. Based on measured variations in $NO_y$ over 2 – 3 h periods, the precision of our $NO_y$ measurements ranged between ±10 and ±15 %. In addition to the potential uncertainties that contributed to the NO inaccuracies described above, our estimate for the overall accuracy of the $NO_y$ measurements include the uncertainties in the GPT derived $NO_2$ calibration gas, and the unequal MoO converter efficiencies for $NO_2$, NPN, and $HNO_3$ resulting in an RMS error of ±20 %.

### 6.4. $PM_{2.5}$ Data Quality

A thorough QA/QC protocol [see Quality Integrated Work Plan submitted to the U.S. EPA in August 1998 in fulfillment of requirement for Quality Assurance Plans for environmental data operations, and Standard Operating Procedures listed therein] ensures highest quality of the suite of species that are analyzed and reported. From our extensive experience with the analysis of data from beforementioned field intensives, it has been found to be imperative to do thorough QA/QC and self-consistency checks of the data prior to reporting. This extended QA/QC protocol involves mass and charge balance evaluations and interpretations, and critical review of each sample result under the aspects of atmospheric processes and evolution.

Field blanks for each sample medium type (i.e., denuders, Teflon, paper, quartz, XAD-coated quartz filters) were carried together with the samples on every sampling day. Detection limits were determined assuming a two-tailed student's *t*-distribution and a confidence level of 95 %. For particulate species concentrations with semi-volatile character that were derived from a combination of Teflon and coated paper backup filter values ($NH_4^+$, $NO_3^-$, acetate, formate, and oxalate), a combined *DL*, based on the root mean square, was calculated. Table 6.3 summarizes the *DL*s for each species as part of the general data quality indicators determined for two major field campaigns, the ASSE99 and TexAQS2k.

Special side-by-side runs of identical set-ups were performed on various occasions in between intensives, allowing an assessment of the measurements precision based on the evaluation of bias. Similar tests investigating the quality of our EC,OC measurements were performed as well. No data quality indicators are reported for certain species, particularly oxalic acid (no *D-eff*), sodium, calcium, and chloride (no $P_n$), since their values remained below *DL* for all side-by-side runs.

Accuracy is assessed for $SO_2$, $PM_{2.5}$ mass, EC, and OC concentrations. $SO_2$ was also measured continuously by use of a modified commercial, pulsed UV fluorescence instrument (model TEI 43C-TL), as described above. A least squares linear regression with the continuous measurements averaged over the discrete sampling periods, indicates a relative deviation of the denuder-derived $SO_2$ of 0.91 ±0.03 at an offset of -0.10 ±0.15 ppbv (below *DL*) and an $r^2 = 0.99$ for ASSE99, while the same type regression yielded 0.73 ±0.03, 0.00 ±0.08 ppbv and $r^2 = 0.99$ for TexAQS2k, respectively.

The accuracy of our reported gravimetric $PM_{2.5}$ mass concentration is assessed by comparing the dehydrated Teflon filter mass (related to the ambient sample volumes) with the corresponding averages from a commercial Tapered Element Oscillating Monitor (TEOM, R&P Co., Inc., Albany, NY). The instrument was operated at constant 50 % relative humidity and 60 min integration. The Teflon filters from the first 9 samples corrected for hydrates according to the procedure mentioned earlier, and combined with the successive 11 samples that had been dehydrated, were linearly regressed with the TEOM data. The least squares linear fit (slope = 1.06 ±0.07, intercept = 0.43 ±2.1 $\mu g\ m^{-3}$) indicated a thus interpreted accuracy of +6 % at $r^2 = 0.93$. Although the semi-volatiles determined from the paper backup filters have a combined uncertainty of ±25 %, the error propagation analysis yields an average uncertainty of the reported total gravimetric mass concentration of +7 % for ASSE99, and +1 % for LaPorte and -4 % for Williams Tower during TexAQS2k, respectively.

The accuracy estimates for EC (+9 %) and OC (-10 %) listed in **Table 3**, were derived from comparison measurements sending punches of three different quartz filter samples to the National Institute for Standards and Technology for analysis (NIST). The least squares linear fit with the NIST measurements being the independent variables, resulted in a slope of 1.09 ±0.43 ($r^2$= 0.87) and an intercept of 0.34 ±0.56 µg $m^{-3}$ for EC, which is below the *DL*, whereas the OC regression had to be forced through zero, since the OC values ranged between a relatively narrow span of 13 and 20 µg $m^{-3}$ yielding a slope of 0.90 ±0.02 at a coefficient of determination ($r^2$) of 0.97. Note, that these are uncertainties related only to the principle of quartz sample analyses, and that uncertainites arising from intrinsic sampling errors such as positive and negative artifacts, specificity and efficiency of XAD-coated denuders and backup adsorbers are much harder to assess. Probably the biggest uncertainty in the EC determination arises from the pyrolysis correction, which Chow et al. [2001] report to be between a factor of 1.2 and 10 too low, with urban samples at the lower and rural samples at the higher end

*Lewtas et al.* [2001] showed that trace-level VOC potentially released from residual solvent (hexane, dichlormethane, acetone) used for denuder extractions between sample runs, were not causing a significant artifact OC signal on the quartz filters downstream, demonstrating that these solvents' vapor pressures are too high to allow condensation onto the quartz fibers under ambient sampling conditions. It should be noted, that instead of acetone, the slightly less volatile methanol was used here in the last extraction/cleaning step. The XAD denuder efficiency was found to be better than 95% for Atlanta air, and a negligible amount (between 0.14 to 0.29 µg $m^{-3}$) of VOC being part of the sample air or possibly released by the denuder itself, or gas phase SVOC that is not being retained by the denuder, is captured by the XAD coated backup adsorber. Hence, we have reason to assume that the XAD resin whether applied as a coating on the denuder walls or on the quartz filter fibers retained the same species of gas phase SVOC, and therefore did not change the adsorbing characterisitics and affinity toward certain species. Nevertheless, the data quality indicators stated for XAD quartz filters in **Table 3**, DL= 1.5 and 0.5 µg $m^{-3}$ (ASSE99 and TexAQS2k, respectively) and ±25 % precision, indicate that the use of XAD coated quartz filters bear great potential for contamination during the entire sampling and analysis process.

**Table 6.3a:** Data quality indicators (denuder efficiencies, D-eff; detection limits, DL; biases; and accuracies) for gas and particle phase species measured via the PCM during the ASSE99. The data were derived from the different sampling media, i.e., citric acid or sodium carbonate coated denuders (D(ca)/D(sc), respectively), Teflon filters (T), paper filters (P), quartz filters (Q), and XAD coated quartz filters (XQ). A denuder efficiency of 100% was assumed for nitric acid (see text).

| | $NH_3$ | $HNO_3$ | $SO_2$ | HCl | HCOOH | $CH_3COOH$ | $(COOH)_2$ |
|---|---|---|---|---|---|---|---|
| Retrieved from | D (ca) | D (sc) | D (sc) | D(sc) | D (sc) | D (sc) | D (sc) |
| D-eff [%] | 99±1 | 100* | 99±3 | 90 | 89±2 | 83±7 | - |
| DL [ppbv] | 0.14 | 0.05 | 0.18 | 0.20 | 0.10 | 0.47 | 0.02 |
| BIAS [%] | 10 | 11 | 6 | 14 | 6 | 12 | 20 |
| Accuracy [%] | | | -11 | | | | |

| | $NH_4^+$ | $NO_3^-$ | $SO_4^{2-}$ | EC | OC | SVOC | $M_{tot}$ |
|---|---|---|---|---|---|---|---|
| Retrieved from | T+P | T+P | T | Q | Q | XQ | T+P |
| DL [$\mu g\ m^{-3}$] | 0.29 | 0.32 | 0.21 | 0.31 | 0.42 | 1.50 | 1.44 |
| BIAS [%] | 8 | 24 | 6 | 7 | 5 | 25 | 12 |
| Accuracy [%] | -6 ±5 | | -16 ±2 | +9 | -10 | | +7 |

| | $Na^+$ | $Ca^{2+}$ | $Cl^-$ | $HCOO^-$ | $CH_3COO^-$ | $C_2O_4H^=$ |
|---|---|---|---|---|---|---|
| Retrieved from | T | T | T | T+P | T+P | T+P |
| DL [$\mu g\ m^{-3}$] | 0.49 | 0.16 | 0.29 | 0.55 | 1.10 | 0.12 |
| BIAS [%] | - | - | - | 17 | 11 | 55 |

The results of the major ions sulfate, ammonium, and nitrate determined by the discrete PCM method during both field studies, are also compared with the higher-resolved Particle-In-Liquid-Solution technique (PILS), see *Weber et al.* [2002] for more details. Accuracy is here assessed assuming the PILS data to be the independent variable, although significant discrepancies existed among various newly developed semi-continuous aerosol measurement techniques during ASSE99, where differences in nitrate were particularly large. Besides its innovative nature, ASSE99 was especially designed as a platform to compare and evaluate discrete chemical speciation samplers that have been historically used according to EPA's $PM_{2.5}$ Federal Reference Method (FRM, see *EPA* [1997]) as well. A detailed analysis and comparison of the various discrete sampling methods employed during ASSE99 is provided by *Solomon et al.* [2002], and Table 6.4 summarizes the performance of our PCM by comparison with the "relative reference values" obtained from the average of all discrete samplers operated.

**Table 6.3b:** Data quality indicators (denuder efficiencies, D-eff; detection limits, DL; biases; and accuracies) for gas and particle phase species measured via the PCM during the TexAQS2k. A 122 mM phosphorous acid solution (pa) replaced citric acid as coating solution for denuders and backup adsorbers; everything else remained the same as for ASSE99.

| | **Site** | **$NH_3$** | **$HNO_3$** | **HONO** | **$SO_2$** | **HCl** | **HCOOH** | **$CH_3COOH$** | **$(COOH)_2$** |
|---|---|---|---|---|---|---|---|---|---|
| Retrieved from | | D (pa) | D (sc) | D (sc) | | | D (sc) | D (sc) | D (sc) |
| D-eff [%] | LP | 91±18 | 100* | 91±8 | 87±19 | 97±6 | 83±10 | 81±18 | 78±17 |
| | *WT* | 92±22 | 100* | 88±9 | 91±18 | 96±17 | 83±11 | 89±19 | 73±21 |
| DL [ppbv] | LP | 0.49 | 0.33 | 0.03 | 0.07 | 0.18 | 0.08 | 0.21 | 0.01 |
| | *WT* | 1.40 | 0.36 | 0.04 | 0.20 | 0.15 | 0.11 | 0.28 | 0.02 |
| Accuracy [%] | *LP* | | | | -28<br>±2 | | | | |

| | **Site** | **$NH_4^+$** | **$NO_3^-$** | **$SO_4^{-2}$** | **EC** | **OC** | **SVOC** | **$M_{tot}$** |
|---|---|---|---|---|---|---|---|---|
| Retrieved from | | T+P | T+P | T | Q | Q | XAD-Q | T |
| DL [$\mu g\ m^{-3}$] | LP | 0.23 | 0.09 | 0.06 | 0.42 | 0.80 | 0.51 | 1.1 |
| | WT | 0.22 | 0.10 | 0.05 | 0.59 | 0.93 | 0.51 | 1.1 |
| BIAS [%] | LP | 12 | 33 | 13 | | | | |
| | WT | 13 | 19 | 3 | | | | |
| Accuracy [%] | LP/ WT | -6 ±3 | +2 ±9 | -7 ±2 | +9 | -10 | | -1 / +4 |

| | **Site** | **$Na^+$** | **$K^+$** | **$Ca^{2+}$** | **$Cl^-$** | **$F^-$** | **$HCOO^-$** | **$CH_3COO^-$** | **$C_2O_4H^{=}$** |
|---|---|---|---|---|---|---|---|---|---|
| Retrieved from | | T | T | T | T | T | T+P | Q | Q |
| DL [$\mu g\ m^{-3}$] | LP | 0.15 | 0.10 | 0.18 | 0.07 | 0.02 | 0.88 | 1.71 | 0.18 |
| | WT | 0.10 | 0.07 | 0.14 | 0.07 | 0.02 | 0.84 | 0.84 | 0.16 |
| BIAS [%] | LP | 20 | 35 | 17 | | | | | 25 |
| | WT | 22 | 37 | 26 | | | | | 27 |

**Table 6.4:** Performance characteristics of our PCM expressed as regression slopes for 0 intercept and calculated regression intercepts (± standard errors) relative to the standard reference values from the averages of all discrete samplers operated during ASSE99; adapted from Solomon et al. [2002].

| | slope | intercept<br>$\mu g\ m^{-3}$ | $r^2$ |
|---|---|---|---|
| Mass | 1.06 ±0.02 | 1.2 ±2.9 | 0.91 |
| $SO_4^{=}$ | 1.02 ±0.01 | -0.1 ±0.3 | 0.99 |
| $NO_3^-$ | 1.27 ±0.11 | -0.6 ±0.3 | 0.50 |
| $NH_4^+$ | 1.02 ±0.02 | 0.4 ±0.2 | 0.95 |
| OC | 1.02 ±0.04 | -1.1 ±1.3 | 0.80 |
| EC | 0.78 ±0.05 | -0.1 ±0.2 | 0.57 |

### 6.5 Major Findings

It was found that the $PM_{2.5}$ problem is much more regional than initially believed, and that the source for fine particles and one of their main compositions, sulfate, is more regionally distributed, indicating a secondary formation of such particles in the atmosphere rather than primary emission. The vertical gradient measurements made between 42 and 4 m agl at Hendersonville, TN, from 16 June to 22 July 1999, (see Figure 6.1) showed positive vertical gradients for 60-70 % of all daytime, and 70-80 % of all nighttime samples of $PM_{2.5}$ mass, sulfate, nitrate, and ammonium, see Figure 6.4. This is in agreement with the thermodynamic stratification of the lower atmosphere as indicated by the simultaneously (and continuously) measured vertical temperature gradients. It is evident from Figure 6.4 that the larger the difference in temperature gradient, i.e. negative during daytime, and positive during nighttime, indicating convective mixing and nocturnal stratification, respectively, the larger the reciprocal difference in relative humidity gradient, i.e. positive during daytime and negative during nighttime. This was particularly the case at the beginning and towards the end of this measurement period, coinciding with the days when the gradients in $PM_{2.5}$ mass and major ions were mostly positive and especially large. During the center period (6/24 to 7/8 1999), the temperature and humidity gradients were relatively small, both absolutely and relative to the time of day, pointing to the influence of labile meteorological conditions with frontal passages and other synoptic disturbances. and furthermore points to direct emissions of $PM_{2.5}$ precursors into and secondary formation of $PM_{2.5}$ within those layers aloft. seasons at suburban Hendersonville and rural Dickson, TN, and for TexAQS2k at Houston, i.e. LaPorte and Williams Tower.

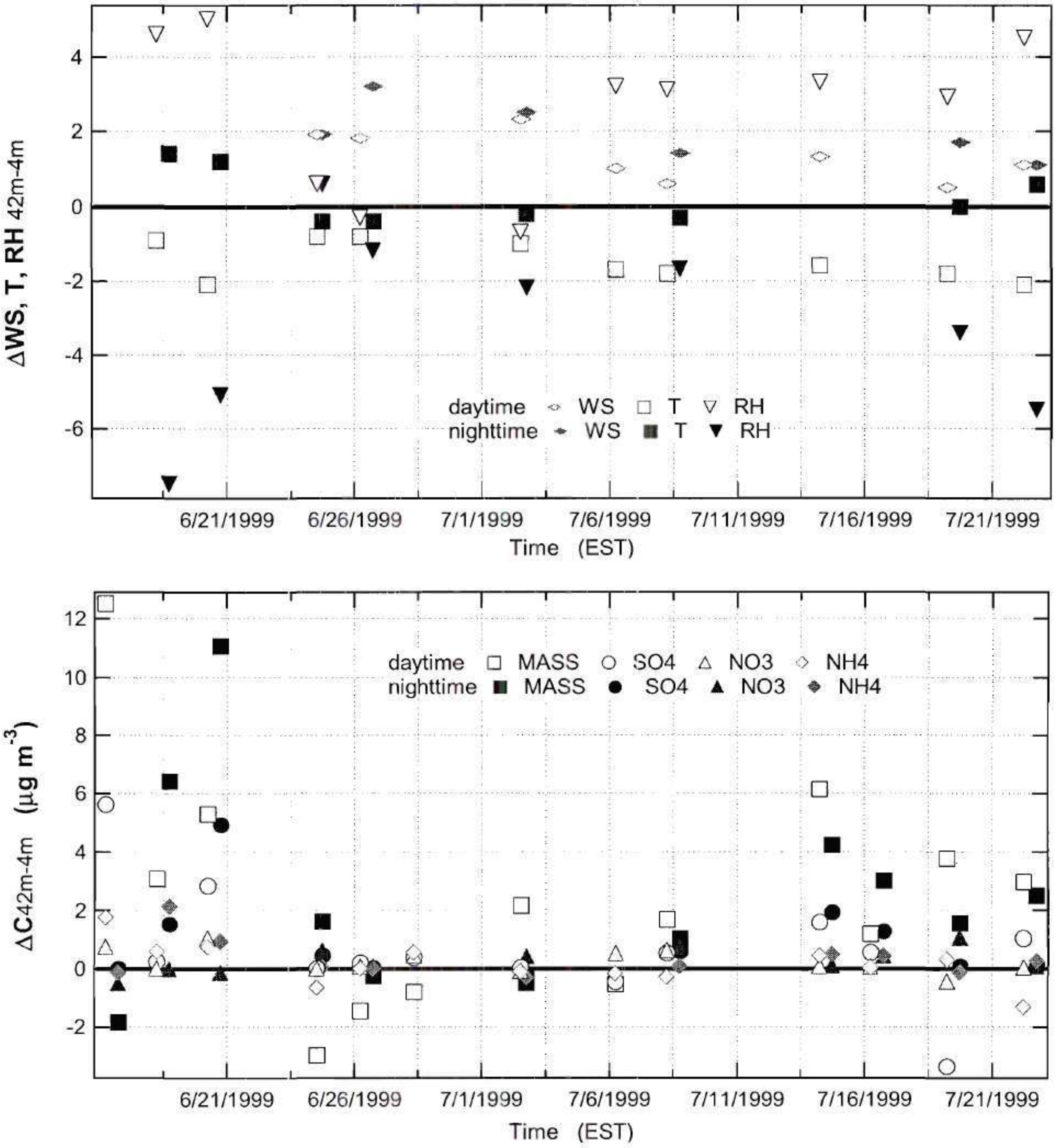

**Figure 6.4:** Vertical gradients, expressed as difference between 42 and 4 m agl, of wind speed, temperature and relative humidity (top), and $PM_{2.5}$ mass, sulfate, nitrate and ammonium concentrations (bottom).

Figure 6.5 illustrates that the gaseous precursors for gas-to-particle conversion, i.e., $NH_3$, $HNO_3$, and $SO_2$ are highest in urban environments where also highest $PM_{2.5}$ are seen. Furthermore, acidic gases exhibit a seasonal trend with lowest values in winter. This is particularly obvious for formic and acetic acids (summed as LOA in Figure 6.5), which show a factor of 3 to 4 lower mixing ratios in winter. A similar seasonal pattern is shown with respect to total fine mass ($PM_{2.5}$) with averages being highest during the summer (ranging from 24 to 36 $\mu g\ m^{-3}$) and dropping significantly during fall and winter (16 to 20 $\mu g\ m^{-3}$ and 11 to 12 $\mu g\ m^{-3}$, respectively). $PM_{2.5}$ mass concentrations averaged for the summer and fall periods tend to be systematically higher at Dickson than at Hendersonville, despite the relative close proximity of the two sites that are ~50 miles apart. This can be attributed to the different surrounding environment of the two locations, and the specific sampling strategy, that emphasized the capturing of the Nashville urban plume at the Hendersonville site, whereas the Dickson site is surrounded by dense forests typical of more rural sites in the SE-US. From various studies within the framework of SOS and other research projects, it is known that the planetary Boundary Layer (BL) over forests remains more shallow and less mixed during sunny daytime periods (release of more latent heat due to vegetative evapotranspiration), compared with urban and sub-urban areas, where more intense surface heating typically forms a deeper, convectively well-mixed BL. This difference in BL height may be the main reason for the observed difference in $[PM_{2.5}]$.

The absolute sulfate mass concentrations and even its fraction of the total fine mass, as depicted in Figure 3.1 in form of pie-charts, also show this seasonal trend with 30-33 % in summer, and 18-22 % in fall and winter. Formic, acetic, and oxalic acids, the latter being mostly below the denuder derived DL, are summed up and depicted as light organic acids (LOA). The group of "Others" consists of all minor ions, i.e. $Na^+$, $K^+$, $Ca^{2+}$, $F^-$, and $Cl^-$. Organic carbon (OC) concentration shows less seasonal variation, and due to lower total mass concentrations during fall and winter, the relative contribution of total organic mass (i.e. the sum of 1.4*OC + LOA) to the total fine mass concentration increases significantly, from between 29 and 35 % in summer to between 48 and 52 % in fall and winter. The third largest contributer to total fine mass, especially in summer, is the unidentified fraction (grey area), and is discussed later.

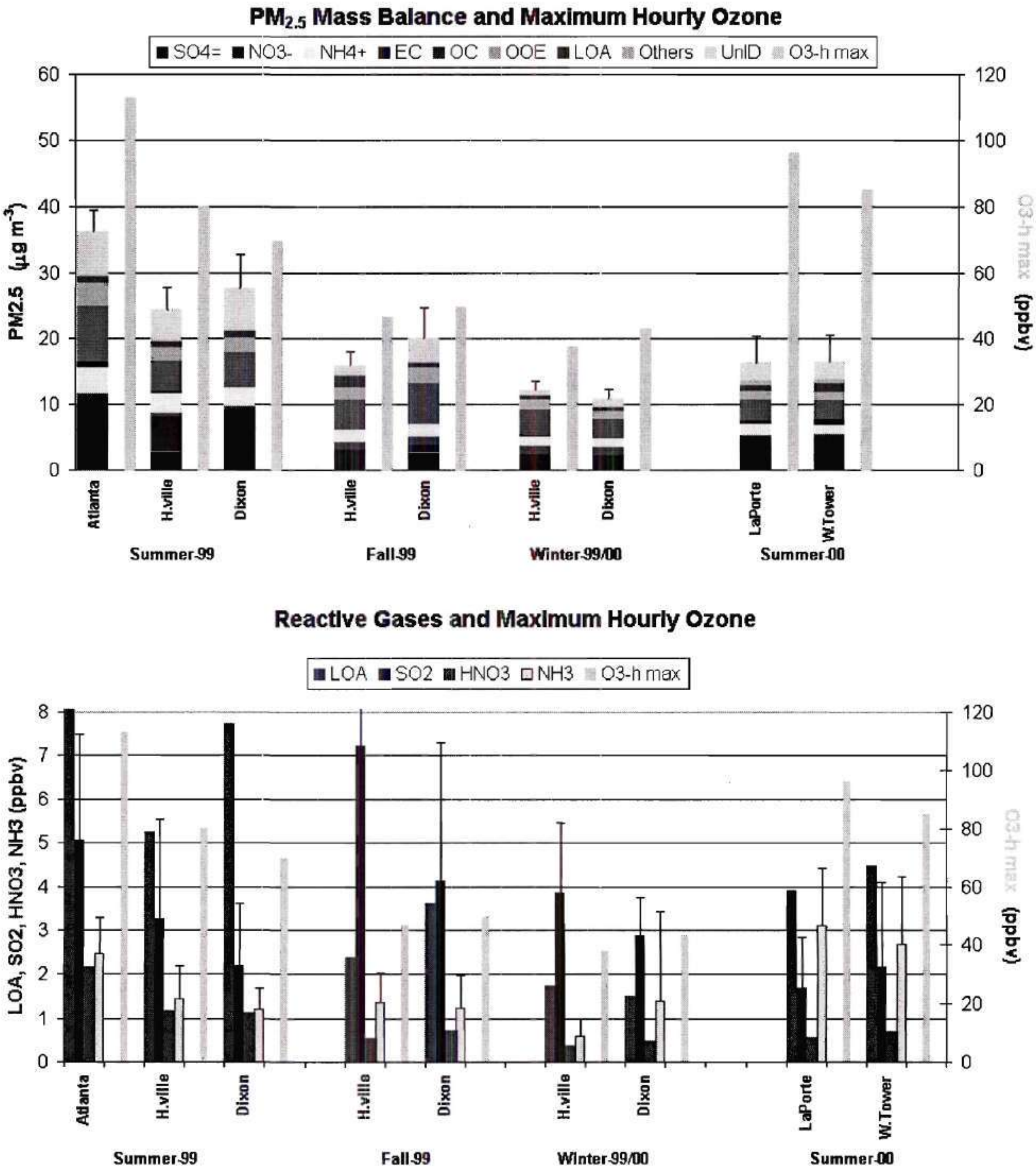

**Figure 6.5:** $PM_{2.5}$ mass balance, average maximum hourly $O_3$, and average daily $NH_3$, $HNO_3$, $SO_2$ and light organic acids (mainly formic and acetic) for ASSE99 and different

Measurements made in the Houston, TX area during the TexAQS2k field experiment at LaPorte, and at Williams Tower, 254 m above ground, provided an interesting contrast to the results found in GA and TN. LaPorte, for example, was influenced predominantly by a strong land-sea breeze circulation with veering wind directions, causing periodic short-term impacts of plumes from nearby sources with significantly reduced (titrated) nighttime ozone levels. Although $O_3$ was formed rapidly in this VOC-rich environment, rich particularly in alkenes, the $PM_{2.5}$ mass concentrations were only ~16 $\mu g\ m^{-3}$, and not significantly different between the two sites. While LaPorte experienced generally higher ozone levels during the day, the elevated site at Williams Tower showed systematically higher levels at night, pointing to effects of nocturnal stratification and redistribution of previous days' ozone. LaPorte was impacted by exceptionally high ozone only on two consecutive days, August 30 and 31, with maximum hourly averages of 219 and 196 ppbv, respectively. At the same time, the elevated site at Williams Tower saw only ~50% lower ozone maxima, because the plume did not reach the site. The difference in [$PM_{2.5}$], however, was insignificant between the two sites regionally and temporaly compared to the neighboring days and for the entire study period (as seen in Figuress. 6.5 and 3.1), which makes these plumes very rapid and efficient ozone producers without significant fine particle formation. With exception of the 08/30-31 episode, however, the $PM_{2.5}$ mass and sulfate concentrations generally followed the trends in daily ozone maxima similar to the observations made in GA and TN. Similar to these other sites, the aerosol was slightly acidic on the basis of $NH_4^+/SO_4^=/NO_3^-$, as seen in Figure 6.6, pointing to a certain importance of other nitrate-forming mechanisms and possible role of organic nitrates.

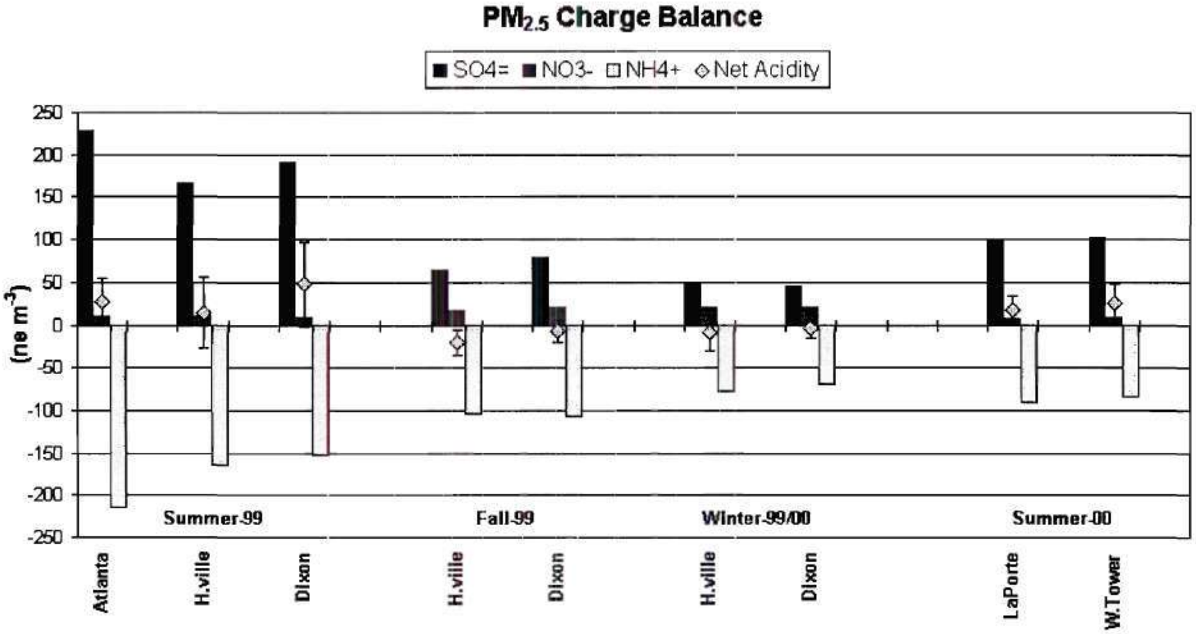

**Figure 6.6:** PM2.5 charge balance on the basis of $NH_4^+/SO_4^=/NO_3^-$ for ASSE99 and different seasons at sub-urban Hendersonville and rural Dixon, TN, and for TexAQS2k at Houston, i.e. LaPorte and Williams Tower.

As mentioned above, when other organic elements (OOE) are taken into account as 0.4*OC, the third largest "contributor" to the total gravimetric mass in summertime is the unidentified mass fraction. Note that for all mass balance closure approaches, the dehydrated or hydrate-corrected gravimetric mass concentration was considered. The average organics molecular weight to carbon weight ratio (OM/OC) of 1.4 that has been widely used in the past, originates from very limited theoretical and laboratory studies from more than 20 years ago, suggesting it to be the lowest reasonable estimate for urban aerosols [*White and Roberts*, 1977; *Countess et al.*, 1980; *Japar et al.*, 1984]. A more recent investigation by *Turpin and Lim* [2001], however, suggests a factor of 1.6 ±0.2 to be more accurate in an urban environment. When other organic elements (OOE) from the denuded quartz front filter are taken into account as 0.6*OC for the ASSE99 data set for example, an average percent fraction unidentified mass of 13 ±10 % relative to the total reported mass concentration would still remain. If then semi-volatile OC captured downstream from denuded quartz filters were considered, its OOE would result in ~0.4

for mass closure (corresponding OM/OC= 1.4). It seems reasonable to assume that enhanced water solubility based on polar functional groups result in reduced volatility as a consequence of stronger intermolecular interactions, and that more volatile compounds are captured on the XAD quartz backup filter, which have lower OOE factors than the less volatile ones captured on the quartz front filter.

Using the $PM_{2.5}$ mass balance closure approach on dehydrated Teflon filters to solve for the organics mass to carbon ratio OM/OC and applying it to the different data sets, reveals a trend of larger OM/OC towards more rural locales, as seen in **Table 5** between Atlanta (2.1), Hendersonville (2.4), and Dickson (2.9), with values clearly greater 1.6. Even during the fall period, Dickson would require an OM/OC of 2.2 to achieve mass closure, versus 1.7 at Hendersonville. This can be interpreted with the photochemical aging and processing of air masses under clear-sky summertime conditions when relatively high levels of reactive radicals, particularly OH·, drive the formation and processing of secondary aerosols. Compared to the relative stagnant conditions in Atlanta during ASSE99, the TexAQS2k measurements at Houston one year later, were characterized by distinct land-sea-breeze circulations, and a rather "rich" mix of VOC emissions, especially alkenes, from large agglomerations of petrochemical facilities that are unique to Houston, adding to the mobile and power plant sources that are more common for metropolitan areas. At both TexAQS2k sites, the OM/OC yields an average 3.5 for closure but largely variable due to the closeness of these different sources and events, such as a dominant influence from large biomass burning activities in NE-Texas and Louisiana early September. When SVOC are included from the XAD-coated quartz backup filter, and no distinction was made between the possible different volatility, i.e. polarity and governing functional groups as was done for ASSE99, then the average OM/OC {svoc} factors as shown in Table 5 would be significantly lower than without SVOC. Contrasting Atlanta 1999 with Houston 2000, and furthermore considering the episodal character of largely different OM/OC ratios during TexAQS2k, it may be concluded that photochemically well-aged and well-mixed air masses contain particulate organic compounds with more highly oxygenated and less volatile functional groups, whereas under more stagnant conditions, particle phase organics might be less oxygenated and therefore more volatile.

**Table 6.5:** Organic mass to carbon mass ratio OM/OC needed to achieve $PM_{2.5}$ mass closure for different metro areas (Atlanta vs Houston) at different summers, i.e. ASSE99 vs TexAQS2k, and for different seasons comparing suburban Hendersonville with rural Dickson, TN.

| | | **OM/OC for closure** | | **OM/OC {svoc} for closure** | |
|---|---|---|---|---|---|
| | | **AVG** | STD | **AVG** | STD |
| **Summer-99** | **Atlanta** | **2.1** | 0.7 | **1.5** | 0.3 |
| | **H.ville** | **2.4** | 0.7 | | |
| | **Dickson** | **2.9** | 1.8 | | |
| **Fall-99** | **H.ville** | **1.7** | 0.5 | | |
| | **Dickson** | **2.2** | 0.9 | | |
| **Winter-99/00** | **H.ville** | **1.6** | 0.3 | | |
| | **Dickson** | **1.6** | 0.4 | | |
| **Summer-00** | **LaPorte** | **3.5** | 3.8 | **2.3** | 2.6 |
| | **W.Tower** | **3.5** | 3.2 | **2.4** | 2.3 |

## 6.6. Summary

- A positive artifact due to hydrates was determined from ASSE99 denuded Teflon filter samples and quantified at ~20 ±8 %; this finding prompted a general change in the standard operating procedure (SOP) of our Teflon filter treatment, adding a 24 to 48 hour desiccation period.
- Our tower measurements at Hendersonville, TN revealed positive vertical gradients (42 vs 4 m agl) of $PM_{2.5}$ mass and major ions, especially sulfate, pointing to atmospheric aerosol formation.
- We found insignificant regional differences in $PM_{2.5}$ composition, but noticeable seasonal differences, esp. in the $SO_4^{=}$ fraction, variing from >30 % in summer to ~20 % in winter, which is likely due to higher $SO_2$ emissions and photochemical activity in summer.
- Based on $SO_4^{=}/NO_3^{-}/NH_3^{+}$ system, $PM_{2.5}$ in SE-US is slightly alkaline in winter but more acidic in summer, leaving i) sulfate only partly neutralized as $(NH_4)HSO_4$ or ii) possibly other neutralizing acting species undetected.
- The organic mass to carbon fraction OM/OC= 1.4 seems mostly too low but is highly variable, reflecting certain influence from different air masses.

- Applying mass closure to dehydrated mass concentrations, requires greater OM/OC factors in summer possibly due to more oxygenated species from photochemistry.
- General trend for higher factors away from urban areas point to secondary atmospheric processes.
- Different factors might have to be applied for OC from quartz front and XAD backup filters due to different volatilities, as shown for ASSE99 (see *Baumann et al.* 2002).

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## 7. MEASUREMENT OF PARTICLE DENSITY DURING SCISSAP[2]

This portion of the SCISSAP project involved the development and use of the Aerosol Particle Mass Analyzer (APM; (Ehara et al., 1996)) for *in situ* measurements of particle mass. All of the measurements carried out in this project involved first classifying particles with a differential mobility analyzer (DMA; (Liu and Pui , 1974; Knutson and Whitby, 1975)) and them measuring their mass with the APM. Therefore, we refer to this new technique as the DMA-APM technique. Our work has involved studies with laboratory-generated aerosols of known composition to evaluate measurement accuracy, measurement of atmospheric particles during the Atlanta Supersite Project in 1999, and measurements of diesel exhaust particles done in collaboration with Professor David Kittelson in the Center for Diesel Research at the University of Minnesota. Our major findings are:

(1) The DMA-APM technique can measure the mass and density of spherical particles to within 5%.
(2) The DMA-APM technique can measure the mass and "effective densities" of nonspherical particles.
(3) "Effective densities" measured by the DMA-APM technique can be used to determine the relationship between mobility equivalent diameter and aerodynamic diameter. This relationship is valid for particles of arbitrary shape and composition.

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[2] *Prepared by: Peter H. McMurry, Department of Mechanical Engineering University of Minnesota*

(4) Effective densities of diesel exhaust particles decrease with increasing size. At 50 nm, densities are about 1.1±0.1 g $cm^{-3}$, while at 300 nm densities are about 0.3±0.05 g $cm^{-3}$.

(5) Atmospheric particles of 100 nm and 300 nm in Atlanta at ~3-6% relative humidity typically had two distinct densities: 1.6±0.1 g $cm^{-3}$ and 0.45±0.20 g $cm^{-3}$.

(6) The "low density" particles observed in the Atlanta atmosphere have densities similar to diesel exhaust particles of the same mobility size. The densities of "high density" particles are consistent with values calculated from measured composition, assuming that they consist primarily of organic carbon and sulfates.

(7) The fractal-like dimension of diesel exhaust particles measured in this study ranged from 2.33±0.02 to 2.41±0.03, with the higher values observed at lower engine loads or with fuels having higher sulfur content. We believe this is because the particles produced at low loads or with higher sulfur fuel contain more liquid content, and are therefore more compact and more nearly spherical. (The fractal dimension of spheres is 3.0.)

(8) The DMA-APM technique enables the direct measurement of aerosol mass distributions as a function of either mobility-equivalent size or aerodynamic size. Mass distributions of laboratory and diesel exhaust particles measured with the DMA-APM technique are in very good agreement with mass distributions measured with a nano-MOUDI impactor, although the impactor data show evidence of bounce in the smallest size ranges.

(9) Mass distributions measured with the DMA-APM technique can be integrated to obtain mass concentrations.

(10) Mass concentrations of laboratory-generated DOS, NaCl and diesel exhaust particles obtained with the DMA-APM technique are typically in good agreement (±15%) with mass concentrations measured gravimetrically using filters or impactors. Adsorption or volatilization artifacts that can be significant with impactors and filters, however, do not affect the DMA-APM measurements.

(11) We have not yet extended DMA-APM measurements to particles above 500 nm, although in principle this should be possible.

Two of these results represent significant advances in the science of aerosol measurement. The development of a precise and accurate technique for measuring particle density enables determining definitive relationships between aerodynamic and mobility equivalent diameters. This relationship helps to reconcile measurements based on different physical principles. Also, the new, in-situ technique for direct measurement of mass size distributions and concentrations will provide insights into the accuracy of filter-based measurements of mass concentrations, such as are used in EPA's FRM network. In the following sections the principle of DMA-APM measurements are briefly summarized, and some illustrative results are provided. A summary of publications and graduate students who have been supported by the project is given at the end of the report.

## 7.1 Principle of the DMA-APM Measurements

A schematic diagram of the DMA-APM system is shown in Figure 7.1. Particles are classified according to electrical mobility with a DMA before they enter the APM where their mass is measured. A CPC is located downstream of the DMA-APM apparatus to enable detecting particles that penetrate through the DMA or the DMA-APM. A schematic diagram of the APM is shown in Figure 7.2. The instrument consists of two coaxial cylinders that rotate together about their common axis at an angular speed $\omega$. The outer cylinder is grounded while a voltage is applied to the inner cylinder. Aerosol flows axially through the thin annular gap between the two cylinders from the inlet to the outlet while it simultaneously rotates with the cylinders. Particles that enter the APM from the DMA are electrically charged. Therefore, as particles flow through the APM they experience an electrical force that draws them radially inwards, and a centrifugal force that is radially outwards. When these two forces balance, the particles will be transported through the APM to the CPC detector located downstream. The equation that describes this force balance is:

$$m\omega^2 r = neE_{APM} \qquad [1]$$

where m is particle mass, r is radial distance of the particle from the axis of rotation, n is the number of elementary charges carried by the particle, e is the unit electrical charge, and $E_{APM}$ is the local electric field in the annular gap (which varies in proportion to the voltage applied to the inner cylinder.) The width of the annular gap between the cylinders is much smaller than r. Therefore, it is reasonable to assume that r and $E_{APM}$ are approximately constant within the annular gap. Furthermore, we operate in a size range where there are few multiply charged particles, so n=1. It follows that the only unknown in Equation [1] is particle mass, m. When this force balance is satisfied, particles do not move relative to the mass flow. It follows that the APM classifies particles according to mass regardless of their shape or composition. This is in contrast to the DMA, which classifies particles according to electrical mobility, which depends upon particle shape (but not on particle density).

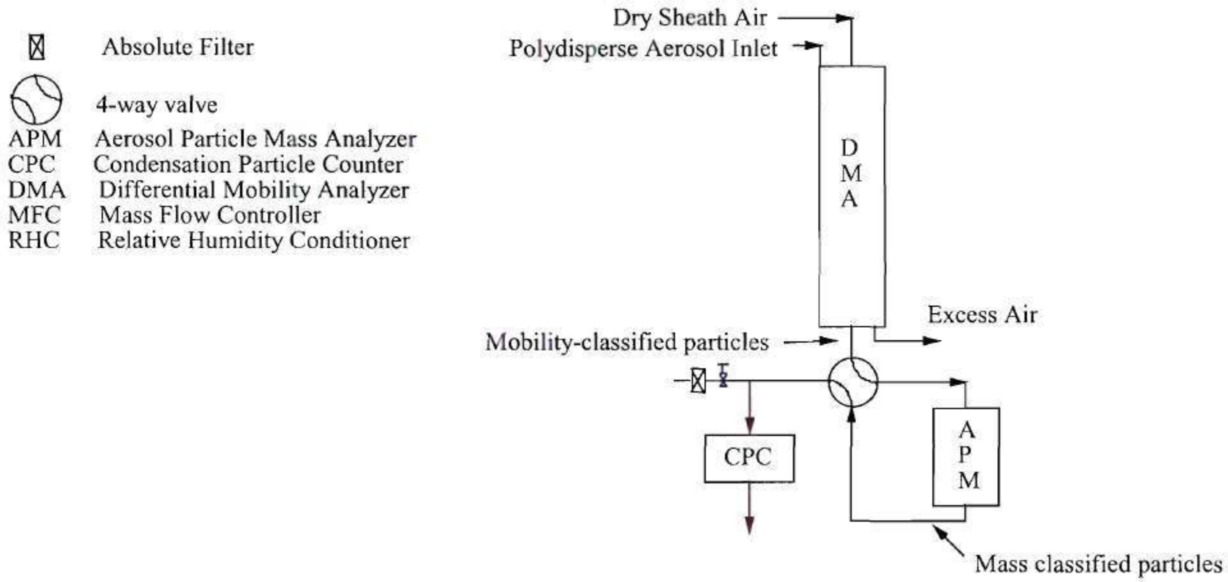

Figure 7.1: Schematic of DMA-APM system.

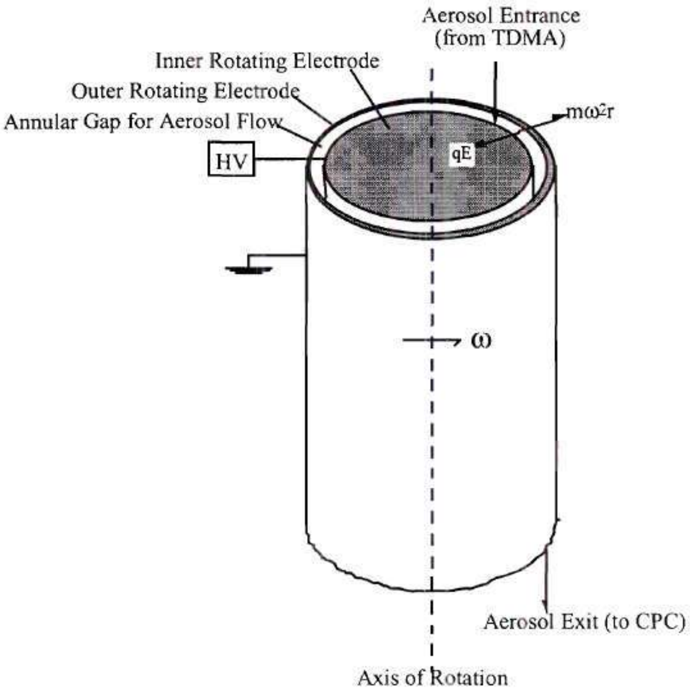

Figure 7.2: APM Schematic.

By using the DMA and APM in tandem it is possible to learn a great deal about particle properties. The DMA classifies particles according to electrical mobility, Z. For spherical particles, the electrical mobility equivalent diameter, $d_{me}$, equals the geometric or Stokes diameter and is independent of particle density. For nonspherical particles the electrical mobility depends on the dynamic shape factor, $\chi$, which is defined by (e.g.,(Kasper, 1982)):

$$Z = \frac{neC_c(d_{me})}{3\pi\mu d_{me}} = \frac{neC_c(d_{ve})}{3\pi\mu d_{ve}\chi} \qquad [2]$$

where n is the number of elementary charges per particle, e is the unit electric charge, $C_c$ is the Cunningham slip correction factor (Allen and Raabe, 1982), $d_{me}$ is the mobility equivalent diameter for spherical particles, $\mu$ is the absolute viscosity of air, $\chi$ is the dynamic shape factor, and $d_{ve}$ is the diameter of a sphere having the same volume as the irregularly shaped particle. For spherical particles $\chi = 1$ and $d_{me} = d_{ve}$ while for nonspherical particles $\chi > 1$ and $d_{me} > d_{ve}$. Note that the mobility equivalent diameter is independent of particle density. Thus by measuring Z with the DMA and m with the APM for the same particles it is possible to determine the relationship between mass and mobility equivalent diameter. For spherical particles, the true density can be inferred directly:

$$\rho_{\text{true (spherical particles)}} = \frac{m}{\frac{\pi d_{ve}^3}{6}} = \frac{m}{\frac{\pi d_{me}^3}{6}} \qquad [3]$$

For nonspherical particles the technique provides an "effective density" which is equal to (McMurry et al., 2002):

$$\rho_{\text{effective}} = \rho_{\text{true}} \frac{d_{ve}^3}{d_{me}^3} \qquad [4]$$

Because $d_{me} > d_{ve}$ for nonspherical particles, the densities of nonspherical particles obtained in this way are less than the true material densities. The relationship between aerodynamic diameter, $d_{ae}$, and mobility equivalent diameter is (McMurry et al., 2002):

$$d_{ae}^2 C(d_{ae}) = \frac{1}{\chi}\frac{\rho_{true}}{\rho_0} d_{ve}^2 C(d_{ve}) = \frac{\rho_{eff}}{\rho_0} d_{me}^2 C(d_{me})$$

[5]

In all of our measurements of density or effective density we carried out sequential measurements of the "unknown" aerosol (i.e., atmospheric particles or diesel exhaust particles) and of polystyrene spheres (PSL) of exactly the same mobility equivalent size. The DMA was first adjusted to achieve maximum penetration of the PSL, and the masses of the unknown particles were then measured with the APM keeping the DMA flow rates and classifying voltage fixed. With this approach, it can be shown from Equation [1] that:

$$\rho_{\mathrm{true\ (spherical\ \ particles)}} = \rho_{\mathrm{PSL}} \frac{V_{\mathrm{APM\ \text{"unknown"}}}}{V_{\mathrm{APM\ \ PSL}}}$$

[6]

and, for nonspherical particles,

$$\rho_{\mathrm{effective}} = \rho_{\mathrm{PSL}} \frac{{}_{\mathrm{A}}V_{\mathrm{PM\ \text{"unknown"}}}}{V_{\mathrm{APM\ \ PSL}}}$$

[7]

where the density of PSL, $\rho_{\mathrm{PSL}}$, equals 1.054 g $\mathrm{cm}^{-3}$. The use of PSL as a reference standard improves the accuracy of measured densities. The alternative would be to calcualte densities with Equation [3], where the mobility equivalent diameter is inferred from the DMA operating conditions. Unless extraordinary care is taken to control DMA flow rates and voltages, sizing errors of ~2% are typical. Because mass varies with the cube of diameter, this results in typical uncertainties of 6% for measured densities. The use of Equations [6] and [7] to infer density leads to uncertainties of less than 5%. Based on experiments with laboratory aerosols of known composition we found that most of our density measurements were accurate to within 3%.

The use of the scanning mobility particle spectrometer (SMPS; (Wang and Flagan, 1990)) to measure aerosol mobility distributions is well established. SMPS measurements involve measuring the concentration downstream of a DMA as the DMA classifying voltage is scanned from 0 to a maximum value of about 10,000 V. By using an APM to measure the mass of the mobility-classified particles, it is possible to use the DMA-APM system to directly measure aerosol mass distributions as a function of mobility diameter. The following equation shows the relationship between the mass distribution (left side of equation) and the number distribution measured with the SMPS:

$$\frac{dc_m}{d\log(d_{me})} = m \cdot \frac{dN}{d\log(d_{me})} \qquad [8]$$

where m is the mass of individual particles measured with the APM, and $c_m$ is the mass concentration of particles. Equation [5] enables converting these to distributions as a function of aerodynamic diameter. It follows that the total aerosol mass concentration is:

$$c_m = \int_{-\infty}^{\infty} \frac{dc_m}{d\log(d_{me})} d\log(d_{me}) \qquad [9]$$

Because the APM measurements of mass are valid for particles of arbitrary shape or composition, no assumptions about particle properties are required to obtain mass concentrations in this manner.

## 7.2 Illustrative Results

Figure 7.3 shows an example of data measured in Atlanta during the August 1999 Atlanta Supersite study. During these measurements the DMA was used to select polystyrene spheres or atmospheric particles of 309 nm mobility equivalent diameter. The penetration through the APM as a function of the APM classifying voltage was then measured with the CPC. Note that the PSL penetration through the APM peaked at 160 v, while the penetration of atmospheric particles peaked at 67 and 246 v, indicating that two types of particles having distinct masses were present. The particle densities for these measurements, obtained with Equation [6] or [7] are 0.44 g $cm^{-3}$ (low mass particles) and 1.62 g $cm^{-3}$.

Figure 7.4 shows the relationship between the effective density of diesel exhaust particles and mobility size. Note that 50 nm particles have an effective density of about 1 g $cm^{-3}$, while the density decreased to ~0.3 g $cm^{-3}$ for 300 nm particles. Average effective densities for 107 nm and 309 nm particles measured in Atlanta are also shown in Figure 4. Note that the atmospheric "low density" particles have effective densities that are similar to values measured for diesel exhaust particles. We examined the diesel particles by scanning electron microscopy to examine morphological properties as a function of size. We found that 50 nm particles tended to be compact and nearly spherical, while larger particles consisted of chain agglomerates. We believe this explains the reason for the observed size-dependent density: the large, fluffy particles have a large mobility equivalent size due to their large dynamic shape factors (see Equation [2]). The dynamic shape factors for ~50 nm particles should be close to unity, since these particles are nearly spherical. It follows that the mobility equivalent diameter for these particles is much more nearly equal to their volume equivalent diameter. The effective density of the 50 nm particles should, therefore, be much closer to the inherent material density for diesel exhaust particles than would be the case for the 309 nm particles.

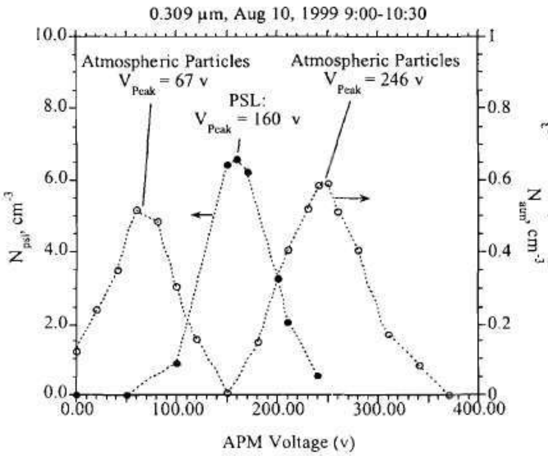

Figure 7.3. Number concentration downstream of APM as a function of the APM classifying voltage for 309 nm polystyrene latex (PSL) particles, and for 309 nm mobility-classified atmospheric particles. Note that two distinct peaks were observed for the atmospheric particles.

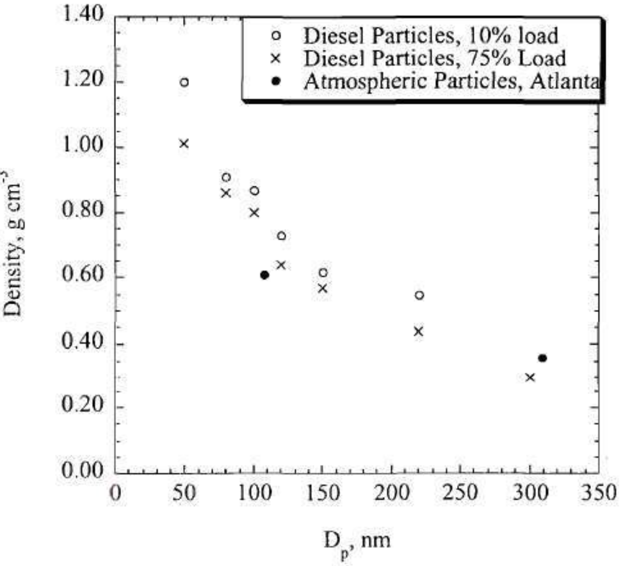

Figure 7.4. Effective density of diesel exhaust particles versus mobility diameter. Note that the effective densities of diesel particles produced at high engine loads are somewhat smaller than those of particles produced at low loads, presumably because

Figure 7.5 shows the relationship between mass distributions of diesel exhaust particles measured with a nano MOUDI impactor and the DMA-APM. The nano-MOUDI data were converted from aerodynamic to mobility-equivalent diameter using Equation [4] for this comparison. Note that the total mass concentrations (areas under the curves) measured by the two techniques are in good agreement. The mass mean diameter measured by the two instruments is in good agreement, but the nano-MOUDI detected more mass in the small size ranges. We hypothesize that the observed shift of the MOUDI mass distributions to smaller sizes is due to the bounce of particles from upper stages (Stein et al., 1994). If this is correct, then virtually all of the mass collected on the bottom stages of the nano-MOUDI for these particles was due to bounce. If so, any measurements of composition for particles collected on the bottom nano-MOUDI stages would lead to erroneous information about nanoparticle composition.

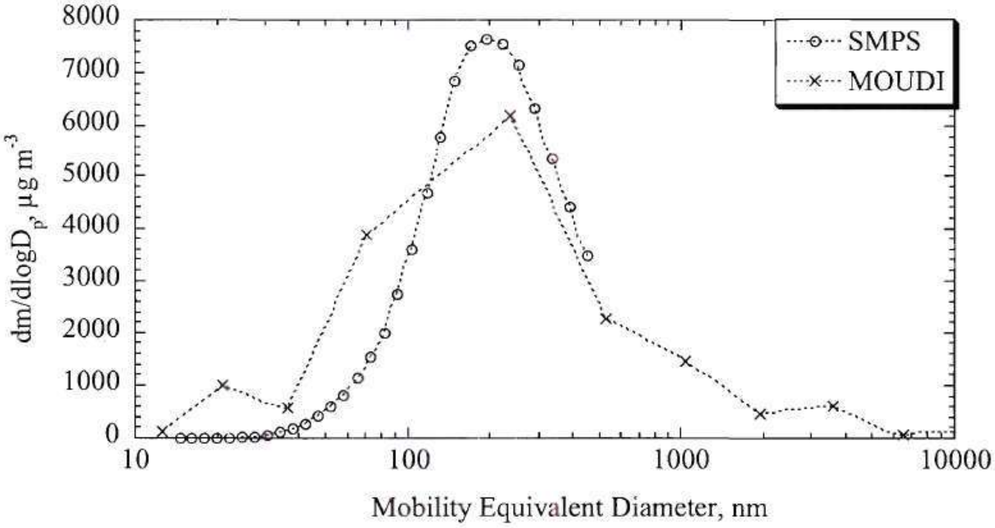

Figure 7.5. Comparison of mass distributions measured with the DMA-APM and a nano-MOUDI.

Figures 7.6 and 7.7 compare filter and DMA-APM measurements of aerosol mass concentrations for NaCl and diesel exhaust aerosols, respectively. Mass concentrations were calculated using Equation [9]. In order to keep filter sampling times reasonable short, measurements were made at high mass concentrations. However, because the DMA-APM technique involves single particle measurements, it works well for mass concentrations that are well below typical ambient levels.

Note that except for the measurements made at 10% engine load, the gravimetric mass concentrations agree with DMA-APM measurements to within about 15%. We believe the discrepancies at low load occur because the engine emits more unburned hydrocarbons that can adsorb to the filter under these conditions. Therefore, we believe it is likely that the DMA-APM measurements under these conditions are more accurate.

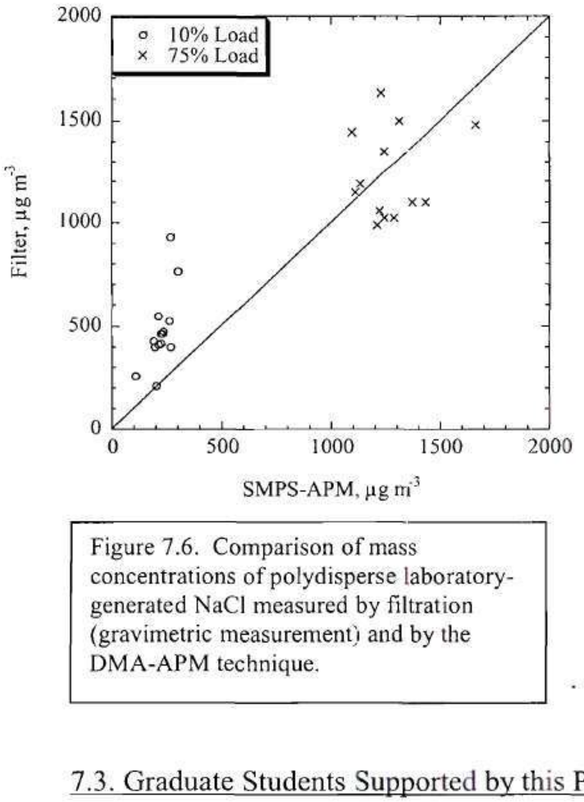

Figure 7.6. Comparison of mass concentrations of polydisperse laboratory-generated NaCl measured by filtration (gravimetric measurement) and by the DMA-APM technique.

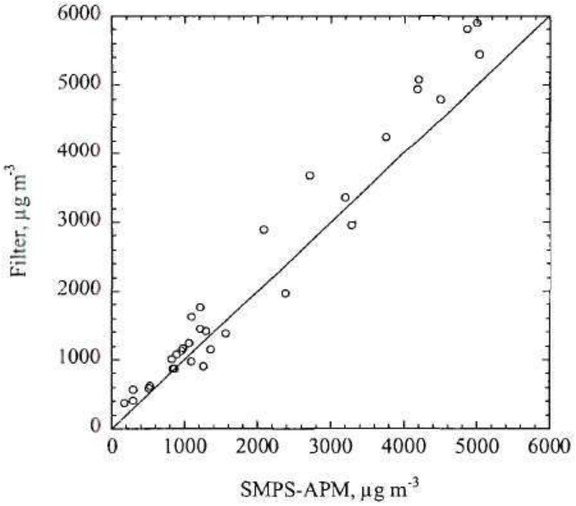

Figure 7.7 Comparison of mass concentrations of diesel exhaust aerosols measured by filtration (gravimetric measurement) and by the DMA-

## 7.3. Graduate Students Supported by this Project

The M.S. research of Ms. Xin Wang was entirely supported by this project. Ms. Wang carried out the initial laboratory measurements that documented the accuracy with which density can be measured with particles of known composition with the DMA-APM technique. She also carried out measurements of atmospheric aerosol composition in Atlanta during the August 1999 Supersite Study. Subsequent to completing her M.S., Ms. Wang entered a Computer Science graduate program at Stanford University.

Mr Kihong Park, a doctoral student, was supported by this grant for the past three years. He has done all of the diesel exhaust particle studies, and has documented the ability of the DMA-APM technique to measure mass distributions and mass concentrations.

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## 8. ADVANCED ORGANIC CARBON MEASUREMENTS[3]

This portion of the SCISSAP project, carried out at the University of Miami, consisted of:

1- Providing ambient volatile organic compounds (VOCs) concentration in Atlanta.
2- Providing organic composition of fine particulate matter in Nashville and Atlanta.
3- Providing organic composition of size segregated particulate matter in Atlanta.
4- Participating in laboratory intercomparison for organic contaminants in PM2.5
5- Data analysis and results dissemination in peer reviewed journals

### 8.1 Sample collection and analysis

*8.1.1. VOCs:* Hourly concentrations of ambient VOCs in Atlanta (Jefferson Street site) were measured from 08/04/99 to 08/31/99. A total of 448 one-minute time integrated samples were taken at the beginning of the hour. A unique collection and concentration system incorporating highly inert surfaces, Teflon and Silicosteel, coupled with state-of-the-art GC-MS provided detection limits in the range of 2 to 28 parts per trillion (ppt) for 100ml ambient air samples. The 84 quantified VOCs are listed in Table 8.1. The data acquired was submitted to the SCISSAP database in early June 2000.

*8.1.2 $PM_{2.5}$ Organic Composition:* PM2.5 samples acquired in Nashville and Atlanta were provided to us by Georgia Tech. Table 8.2 lists the sample information (dates and sample numbers). All samples were solvent extracted by mild sonication using a mixture of dichloromethane/acetone/hexane (2:3:5 by vol.) and analyzed for organic composition using a GC/MS. Table 8.3 lists the compounds quantified. The data is available from the University of Miami. This data set along with the data from the size-segregated sampling are being use for a student dissertation at UM-RSMAS.

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[3] **Prepared by:** PRod Zika, Rosenstiel School of Marine and Atmospheric Sciences, University of Miami

Table 8.1. VOCs target list for SCISSAP study

| | | |
|---|---|---|
| Freon-12 | Butanal | 1,2-Dibromoethane |
| Freon-114 | Methyl Vinyl Ketone (MVK) | Hexanal |
| Chloromethane | Chloroform | Methyl Butyl Ketone (MBK) |
| Vinyl Chloride | Ethyl Acetate | Chlorobenzene |
| Propylene | 1,1,1-Trichloroethane | Ethylbenzene |
| 1,3-Butadiene | Cyclohexane | m&p-Xylene |
| Bromomethane | Methyl Ethyl Ketone (MEK) | o-Xylene |
| Acetaldehyde | Tetrahydrofuran (THF) | Styrene |
| Chloroethane | Carbon Tetrachloride | Bromoform |
| Methanol | Benzene | α-Pinene |
| Freon-11 | 1,2-Dichloroethane | Heptanal |
| Isoprene | 2-Butanol | 1,1,2,2-Tetrachloroethane |
| 1,1-Dichloroethene | Heptane | 4-Ethyltoluene |
| Freon-113 | Trichloroethylene | β-Pinene |
| Carbon Disulfide | 1,2-Dichloropropane | 1,3,5-Trimethylbenzene |
| Propanal | 1-Butanol | 2-Ethyl-1-Hexanal |
| Ethanol | Pentanal | Benzealdehyde |
| Methylene Chloride | Bromodichloromethane | 1,2,4-Trimethylbenzene |
| trans-1,2-Dichloroethene | 2-Pentanone | 1,3-Dichlorobenzene |
| Acetone | Methyl Methacrylate | Limonene |
| Isopropyl Alcohol | 1,4-Dioxane | 1,4-Dichlorobenzene |
| Hexane | trans-1,3-Dichloropropene | Octanal |
| 1,1-Dichloroethane | Toluene | Benzyl Chloride |
| Methyl tertbutyl ether (MT | Methyl Isobutyl Ketone (MI | 1,2-Dichlorobenzene |
| Methacrolein (MACR) | cis-1,3-Dichloropropene | Nonanal |
| Vinyl Acetate | 1,1,2-Trichloroethane | 1,2,4-Trichlorobenzene |
| cis-1,2-Dichloroethene | Tetrachloroethylene | Hexachloro-1,3-Butadiene |
| 3-Methyl furan | Dibromochloromethane | Decanal |

Table 8.2. Sample information for PM2.5 samples

| | **Sampling date** | **Samples received and analyzed** |
|---|---|---|
| Nashville (Hendersonville) | | |
| PUF Samples | 6/16/99 to 8/1/99 | 2 samples + 2 blanks |
| QFF Samples | | 16 samples + 16 blanks |
| **Nashville (Dickson)** | | |
| PUF Samples | 6/15/99 to 8/1/99 | 3 samples + 3 blanks |
| QFF Samples | | 15 samples + 15 blanks |
| *Atlanta (Jefferson)* | | |
| ***QFF Samples*** | 7/28/99 to 8/04/99 | 6 samples + 7 blanks |

Table 8.3. Target compounds for organic speciation of PM2.5

| Alkanes | PAH | Organic acids |
|---|---|---|
| | | |
| n-C10, Decane | Napthalene | n-C4 Carboxylic acid |
| n-C11, Undecane | Acenaphthylene | n-C5 Carboxylic acid |
| n-C12, Dodecane | Acenapthene | n-C6 Carboxylic acid |
| n-C13, Tridecane | Fluorene | n-C7 Carboxylic acid |
| n-C14, Tetradecane | Phenanthrene | n-C8 Carboxylic acid |
| n-C15, Pentadecane | Anthracene | n-C9 Carboxylic acid |
| n-C16, Hexadecane | Fluoranthene | n-C10 Carboxylic acid |
| n-C17, Heptadecane | Pyrene | n-C12 Carboxylic acid |
| n-C18, Octadecane | Chrysene | n-C13 Carboxylic acid |
| n-C19, Nonadecane | Benzo(a)anthracene | n-C14 Carboxylic acid |
| n-C20, Eicosane | Benzo(b)fluoranthene | n-C15 Carboxylic acid |
| n-C21, Heneicosane | Benz(k)fluoranthene | n-C16 Carboxylic acid |
| n-C22, Docosane | Benzo(e)pyrene | n-C17 Carboxylic acid |
| n-C23, Tricosane | Benzo(a)pyrene | n-C18 Carboxylic acid |
| n-C24, Tertacosane | Perylene | n-C19 Carboxylic acid |
| n-C25, Pentacosane | Indeno(1,2,3-cd)pyrene | n-C20 Carboxylic acid |
| n-C26, Hexacosane | Dibenzo(ah)anthracene | n-C21 Carboxylic acid |
| i-C27, *iso*-Heptacosane | Benzo(ghi)perylene | n-C22 Carboxylic acid |
| a-C27, *anteiso*-Heptacosane | | n-C23 Carboxylic acid |
| n-C27 Heptacosane | Other | n-C24 Carboxylic acid |
| i-C28, *iso*-Octacosane | | |
| a-C28, *anteiso*-Octacosane | Pristane | |
| n-C28, Octacosane | Dibenzothiophene | |
| i-C29, *iso*-Nonacosane | Phytane | |
| a-C29, *anteiso*-Nonacosane | | |
| n-C29, Nonacosane | | |
| i-C30, *iso*-Triacontane | | |
| a-C30, *anteiso*-Triacontane | | |
| n-C30, Triacontane | | |
| i-C31, *iso*-Hentriacontane | | |
| a-C31, *anteiso*-Hentriacontane | | |
| n-C31, Hentriacontane | | |
| i-C32, *iso*-Dotriacontane | | |
| a-C32, *anteiso*-Dotriacontane | | |
| n-C32, Dotriacontane | | |
| i-C33, *iso*-Tritriacontane | | |

*8.1.3 Size Segregated Particulate Matter Organic Composition:* Size segregated particulate matter samples were collected by UM-RSMAS using a MOUDI (Micro Orifice Uniform Deposit Impactor). A total of 8 sampling periods (72 hours) were collected each having a QFF backup, 9 size cuts of aluminum impactor discs, and a

PUF plug. The aluminum impactor discs were extracted using the same procedure as the QFF media. New analytical methods had to be developed in order to detect the compounds of interests. A Programmable Temperature Vaporization (PTV) inlet was used allowing injection volumes of 50 ul. The compounds quantified are the same as for PM2.5 listed in Table 3. Data is available from the University of Miami. This work has also been used as preliminary work in preparation for the May 2002 BRACE (Bay Regional Atmospheric Chemistry Experiment in Tampa, Fl) funded by Florida Department of Environmental Protection and involving USEPA. This data

*8.1.4. Laboratory Intercomparison:* At the request of EPA, Dr. Zika's group became involved in NIST (National Institute of Standards and Technology) Intercomparison Exercise Program for Organic Contaminants in PM2.5 Air Particulate Matter. This intercomparison program includes the laboratories that are involved in the various national Supersite studies. Its goal is to compare extraction and analysis methods for organic contaminants in PM2.5. During phase 1, unknown neat PM2.5 material and unknown PM2.5 extracts were analyzed using the same methods as for SCISSAP samples. Our results agreed extremely well with certified values. Phase 2 is currently under progress.

## 8.2 Results and Findings

*8.2.1.Evaluation of an Automated OVOC Sampling and Analysis System:* During August 1999, an analysis targeting 84 OVOCs was undertaken as part of the EPA SCISSAP program at the Atlanta SuperSite. The sampling manifold consisted of glass pipe with the inlet at approximately 11 meters above ground level. Ambient air was pulled through the manifold with a regenerative blower at a rate of approximately 2000 liters/minute. Teflon tubing was inserted into the flow stream of the manifold and air was drawn into the laboratory through this tubing at a flow rate of at least 2 liters/minute. An ambient air sample was collected from this tubing every hour and was sampled at a flow rate of 100 ml/minute. The sample was concentrated using a cryotrapping, cryofocussing system developed in our laboratory for automated, unattended analysis of OVOCs. It consisted of a 25 liter liquid Nitrogen dewar, into which the traps were assembled. A Teflon cap was machined to fit the top of the dewar that held two square channels that extended to almost the bottom of the dewar. The cap also contained 4 ports, one for the introduction of liquid nitrogen, one for pressurizing the dewar, and two for venting the dewar. On top of the Teflon cap, a cover plate was attached, which held the two traps that were used. One, the cryotrap, was used to collect the ambient air and was made of 1/16" silcosteel tubing. The second, the cryofocusser, was used to further concentrate the sample and was made of 0.53 mm id silcosteel tubing. Valves and other electronics used to control the trapping of the sample were housed in two enclosures. Software was developed using National Instruments LabView to control the entire concentration process, and to initiate the gas chromatographic analysis. The GC system was a Hewlett-Packard 6890 GC with a Hewlett-Packard 5973 MSD detector. The system ran approximately 23 hours per day throughout the study, with the remaining hour used to refill the dewar for the next day's analysis. Gas standard mixtures were analyzed routinely and an evaluation of the overall performance of the system will be discussed in terms of the precision and accuracy of the analytical results obtained.

*8.2.2. Urban Air Characterization Using Measurements of Hourly Oxygenated Volatile Organic Compounds During the Atlanta Supersite Experiment 1999:* An extensive gas phase urban air sampling and characterization study was conducted during the Atlanta Supersite 1999 Experiment to determine gas phase oxygenated volatile organic compound (OVOC) concentrations. A fully automated OVOC system consisting of a two stage cryogenic sampler connected directly to a Hewlett-Packard 6890 GC with a Hewlett-Packard 5973 MS detector was used for the sample analysis. This system collected and analyzed one 100 ml sample of ambient air per hour. On average 20 samples a day were run during the month of August,1999 at the Supersite. The remaining 4 hours each day were used for running standards and other system operations. A total of 696 samples were analyzed for 84 OVOCs that included, in addition to the EPA TO-15 standard, a series of primarily biogenic compounds of interest. Hourly analysis permitted monitoring of diel variations in concentration and speciation. A positive correlation between ozone concentrations and methyl methacrylate, 2-pentanone, and propanal indicate a relationship between these compounds and air quality. Further analysis revealed a positive relationship amongst CO, benzene, and MTBE indicating similar sources for these compounds. The relative proportion of biogenic to anthropogenic compounds in the total OVOC budget will be determined. Further work will include the use of ratios of specific anthropogenic compounds as markers to differentiate between gas and diesel emissions and give relative contributions of each on an hourly basis. This data will be made available in the Supersite combined data to be used in evaluating relationships between OVOCs and particulate organic compounds.

*8.2.3. The Size Distribution and Interrelationships of Speciated Organic Compounds, Aerosol Organic Carbon and Elemental Carbon:* Aerosol samples were collected for analysis of organic and elemental carbon (EC/OC) and speciated organic compounds using non-rotating Micro Orifice Uniform Deposit Impactors (MOUDI) during the month of August 1999 at the Atlanta Super Site as part of the SCISSAP Project. Aerosols were collected on aluminum foil impactor stages with a quartz fiber after filter. Both foils and filters were precombusted at $>$ 500 C. The aerodynamic cut diameters of the stages used were: 1.78, 0.97, 0.56, 0.32, 0.18, 0.098, and 0.056 um. Two different sampling durations were used: 9.5h for total EC/OC analysis and 84h for speciated organic compound analysis (SOC). EC/OC samples were collected daily, nominally 08:30 to 18:00 and 19:30 to 06:00 EST, in order to sample possible diel variability. Organic and elemental carbon analyses were performed using the Desert Research Institute Thermal/Optical Reflectance Carbon Analysis System. Samples for SOC were extracted using dichloromethane:hexane:acetone and the extracts were analyzed on a Hewlett-Packard 6890 GC with a Hewlett-Packard 5573 MSD Total elemental carbon concentrations ranged from 0.5 to 4.7 and averaged 1.7 ug m-3. An unpaired t-test indicated the probability that day and night time elemental carbon concentrations were different was 0.80. The EC and OC distribution did change over the course of the month, but no diel trend was apparent. On average, 43 percent of the total organic carbon collected was located on the quartz fiber after filter. This is very unlike elemental carbon where the after filter contained only 9 percent of the total. Volatile and semi-volatile organic compounds may have adsorbed on the after filter. The total organic carbon concentration for the aluminum foil stages ranged from 1.7 to 9.9 and averaged 4.5 ug m-3. Nighttime organic carbon concentrations were greater than those during the day (probability of 0.984). SOC analysis provided semi-quantitative information for a series a n-alkanes (C17 to C34) and polycyclic aromatic hydrocarbons (PAH) such as pyrene, fluoranthene and benzo(b,k)fluoranthene. Preliminary results indicate that nearly all the compounds detected are present in all the size fractions. Different distributions among the size fractions for the n-alkanes and the PAHs extracted were observed. The distribution of specific markers (diesel, gasoline, wood burning, etc.) with different size fractions and with OC/EC content and aerosol number density will be discussed.

*8.2.4. Evidence for a Correlation Between Gas Phase Organic Compounds and Particle Formation During the Atlanta Supersite Study in 1999:* Analysis of hourly ambient air samples for 84 oxygenated volatile organic compounds (OVOCs) in Atlanta, GA during the EPA Supersite field study August 1999 are presented. A unique collection and concentration system incorporating highly inert surfaces, Teflon and Silicosteel, coupled with state-of-the-art GC-MS provided detection limits in the range of 2 to 28 parts per trillion (ppt) for 100ml ambient air samples. A relationship was observed between OVOCs and particulate phase organic carbon concentration, $PM_{2.5}$ total organic carbon, as well as particle number. Calculation of the hourly new particle production potential from our hourly OVOC determination shows that gas to particle conversion is a significant source of new organic aerosols. This calculation of new particle production predicts approximately half of the measured $PM_{2.5}$ total organic carbon observed. A correlation was observed between the variation of predicted organic particle concentration over time and the measured $PM_{2.5}$ total organic carbon however there is a variable time lag between these two values. Reaction mechanisms in the literature propose a branching during the oxidation of OVOCs where one route leads to lower volatility compounds capable of particle production and the other leads to higher volatility products. The higher volatility oxidized organic compounds were investigated as an indicator of organic particle co-production. A strong correlation was observed for acetone to number of particles in the Aitken nuclei range. Combined with improved knowledge of organic particle production potential, gas phase data may serve as a predictive tool for air quality in urban regions.

## 9. MODELING[4]

As presented in the proposal, one of the major activities associated with SCISSAP was to develop, apply and evaluate a regional scale air quality for conducting integrated studies of ozone and particulate matter, and to use that model for inverse modeling for assessing emissions inventories. As such, we developed a model called URM-1ATM: the "Urban-to-Regional, Multiscale Model: One Atmosphere". In this case, one atmosphere refers to the integrated approach to modeling the physics and chemistry of ozone, acid deposition and particulate matter treating them as part of "one atmosphere." In the past, models have been applied separately for ozone, particulate matter and acid deposition. Another important aspect of this model is that it has, built in, a direct sensitivity analysis technique which is used for source apportionment and inverse modeling.

As documented in the paper by Boylan et al. (2002) (see Appendix), URM-1ATM has the capability to simulate the emissions, transport, chemical and physical conversion and deposition (wet and dry) of gaseous and condensed phase pollutants. Being built upon a multiscale model, this is done efficiently across urban and regional domains (Figure 9.1). Outputs of the model are simulated concentration fields for ozone, other gases, and the major particulate matter species (e.g., sulfate, ammonium, elemental and organic carbon and crustals) (Table 9.1). Also, the integrated sensitivity analysis

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[4] ***Prepared by:*** *A.G. Russell, School of Civil and Environmental Engineering, Georgia Tech*

capability provides the means to show how specific source regions impact other regions (Figure 9.2).

As proposed, we have utilized the model, with the integrated sensitivity analysis capability to simulate the pollutant dynamics during the period of SCISSAP (and also Supersite) measurements. As noted in Figures 9.3 and 9.4, the performance was very good. This application is discussed in more detail in the thesis of Alberto Mendoza-Dominguez. (The thesis structure is that most of the internal chapters are published manuscripts, the publications appearing in *Journal of Geophysical Research, Environmental Science and Technology* and *Waste Management and Atmospheric Environment*.) As part of this work, a new approach to inverse modeling for emissions estimation was developed. Based upon Ridge-Regression, the method utilizes the direct sensitivity analysis to rapidly provide estimates of biases in the emissions estimates. As applied to the SCISSAP/Supersite measurements, and shown in Table 9.2, it was found that while some of the emissions estimates in the inventory appear very accurate (e.g., $SO_2$), others (e.g., VOCs) appear significantly biased.

We were presented, during the course of this project, with the opportunity to integrate the science developed as part of this study with a policy-driven study: the Southern Appalachians Mountains Initiative (SAMI). We used the model to address specific policy questions, not unlike the issues being addressed as part of SCISSAP, though on a much different timeline. This provided a unique opportunity for the research team to bridge between the two communities, and have the development of the research tools have a more focused flavor.

At this point, it should be noted, we plan to move the products of the SCISSAP modeling to EPA's Models 3. We agree with the tenet that a community model can provide a more effective approach to advancing the state of the science in air quality modeling, though the SCISSAP model has advantages over the current version of Models 3, including the sensitivity analysis, inverse modeling, chemical mechanism and aerosol thermodynamics. Under other funding, these products of the SCISSAP modeling, and other projects, are being migrated to Models 3, and that model is being used in current studies.

As noted above, four overarching questions were to be addressed during the SCISSAP project. They are listed below, along with brief findings developed from the SCISSAP modeling. More detailed findings can be found in the papers cited in the Appendix and related attachments.

Question 1: What is the concentration and composition of $PM_{2.5}$ in urban and rural locales in the South and to what extent do temporal and spatial variations in these parameters correlate with those of $O_3$ and its precursor compounds?

Findings: Our modeling results suggest a significant variation in the concentration of some of the species between urban and rural regions, e.g., ozone and the elemental carbon fraction of the PM. On the other hand, sulfate concentrations are relatively uniform between urban and rural areas, though certain regions have higher sulfate than others. For example, we find greater sulfate in the Southeast than in the Midwest and Northeast. This tends to be true for ozone, but to a lesser extent. Ozone and PM are highest in or just downwind of urban areas.

Question 2: What are the major precursor compounds and sources for PM2.5 in urban and rural locales in the South and to what extent do these compounds and sources correspond to correlate with the sources of natural and anthropogenic $O_3$ precursors (i.e., VOC and $NO_x$)?

Findings: The major precursors for $PM_{2.5}$ in the southeast are $SO_2$ (largely from coal fired power plants) and organic carbon, from a myriad of sources including biogenic (e.g., biomass burning and secondary conversion of higher organics) and anthropogenic (automobiles, cooking, etc.). Nitrate plays less of a role at present since the aerosol is so acidic that much of the ammonia that is necessary for ammonium nitrate formation is tied up as ammonium sulfate. Ammonia, largely from animal waste and fertilizer use acts to form a fraction of the PM mass, but is important as it is the primary neutralizing agent. For ozone, the two primary precursors are $NO_x$ and, again, organics. Automobiles appear to play a major role, followed by electrical generating units in terms of ozone formation due to $NO_x$ emissions. Automotive (in urban areas) and biogenic (most everywhere else) sources, as well as solvent usage, have the most impact on forming ozone from the VOC perspective.

Sensitivity maps show that both ozone and sulfate have similar source-impact patterns. Thus, one would expect that controls for precursors of both pollutants would have benefits over the same general area.

Question 3: How are the formation rates and concentrations of O3 and $PM_{2.5}$, as well as the $PM_{2.5}$ composition affected by the relative emissions and concentrations of $NO_x$, $SO_x$, NH3, and VOC species, and what are the mechanisms responsible for these relationships?

Findings: Over most of the domain, ozone formation is $NO_x$-limited, though not always in urban areas where there can be a greater sensitivity to VOC emissions. Outside of primary emissions of particulate matter, $SO_x$ appears to be the most sensitive precursor for PM formation since it also captures ammonia and water. Sulfate appears to be formed primarily via as phase oxidation, though aqueous phase reactions are important. Organic PM appears to be split between primary emissions and oxidation of biogenic emissions. Nitrate is formed from oxidation of $NO_2$, which takes place both during the day and at night, followed by reaction with ammonia. Ammonia acts as a neutralizing agent for sulfate and nitrate. The nitrate is highest, at least during the summer, in the early morning hours when the air is cooler and more humid, promoting condensation.

We do find that elevated NOx sources are less efficient at forming ozone than ground level sources, as has been found from aircraft studies as well. Increased emissions, while increasing ozone, can decrease the "ozone production efficiency" (OPE). We see a much more linear response in $SO_2$ emissions.

Question 4: To what extent do the mechanisms elucidated above affect the formulation of an integrated control strategy for $O_3$ and $PM_{2.5}$?; and Do our findings suggest an "optimum" strategy for addressing both pollutants?

Findings: Strategies to reduce $NO_x$ and $SO_2$ simultaneously will be effective in reducing ozone and PM at the same time. For example, using new, combined cycle gas turbines (or coal gasification), could lower both pollutants effectively. On the other hand, one could envision controls that only go after one of the precursors alone. We did not do an economic optimization to find which would be best. Also of importance, both ozone and PM share a largely uncontrollable source, biogenics such as trees, which will limit the effectiveness of controls. For example, there will be a limit on how low PM levels can go since the biogenic fraction appears to be substantial on stagnant and hot days. Further, in the Southeast, VOC controls primarily will be effective only in and around urban areas, at least on high ozone days.

Table 9.1. Species Used in the URM-1ATM Model.

| Transported Gas-Phase Species | Transported Gas-Phase Species | Transported Gas-Phase Species | Transported Aerosol Species | Steady-State Species |
|---|---|---|---|---|
| NO$^{b}$ - Nitric Oxide | RRP - RO2-RO2-Product | M2BT - 2- Methyl -2- Butene | SOD$X^{a,b}$ - Sodium | OSD - O*1D2, O Singlet D |
| NO2$^{b}$ - Nitrogen Dioxide | RHP - RO2-HO2-Product | AAR1$^{b}$ - General Alkane and Aromatics | HYD$X^{a}$ - Hydrogen | O - Oxygen Atom |
| O3 - Ozone | OLRI - OLD-RI, O Atom Reactions with Olefins | AAR2$^{b}$ - General Alkane and Aromatics | AMN$X^{a}$ - Ammonium | HO - Hydroxyl Radical |
| HONO - Nitrous Acid | O3SB - O3OL-SB, Represents Conversion of SO2 TO SO3 | AAR3$^{b}$ - General Alkane and Aromatics | NIT$X^{a,b}$ - Nitrate | CCO - CCO-O2 Radical |
| HNO3 - Nitric Acid | MEOH$^{b}$ - Methanol | OLE1$^{b}$ - General Alkenes | CHL$X^{a}$ - Chloride | C2CO - C2CO-O2 Radical |
| HNO4 - Peroxynitric Acid | ETOH$^{b}$ - Ethanol | OLE2$^{b}$ - General Alkenes | SUL$X^{a,b}$ - Sulfate | BCO2 - BZ-CO-O2 Radical |
| N2O5 - Nitrogen Pentoxide | GLY - Gluoxal | NH3$^{b}$ - Ammonia | WAT$X^{a}$ – Water | RO2N - Alkyl Nitrate RO2 Radical |
| NO3 - Nitrate Radical | RNO3 - Organic Nitrates | SO2$^{b}$ - Sulfur Dioxide | CAR$X^{a,b}$ - Elemental Carbon | RO2X - RO2-XN Radical |
| HO2 - Hydroperoxy Radical | GPAN - Glyoxyl Developed PAN | SO3 - Sulfur Trioxide, Rapidly forms H2SO4 | ORG$X^{a,b}$ - Organics | RO2P - RO2-NP, Phenol RO2 Radical |
| CO$^{b}$ - Carbon Monoxide | PHEN - Phenol | APNE$^{b}$ - $\alpha$-Pinene | CRM$X^{a,b}$ - Magnesium | RO2R - General RO2 #1 Radical |
| HCHO$^{b}$ - Formaldehyde | TOLU$^{b}$ - Toluene | UNKN - Unknown | CRK$X^{a,b}$ - Potassium | R2O2 - General RO2 #2 Radical |
| MEK$^{b}$ - Methlyethyl Ketone | BALD – Benzaldehyde | PRPA - Propane | CRC$X^{a,b}$ - Calcium | COCO - HCOCO-O2 Radical |
| MGLY - Methyl Glyoxyl | PBZN - Peroxy Benzoyl Nitrate | MARC - Methracloin | PM$X^{a,b}$ - Other PM | HCO3 - HOCOO Radical |
| PAN - Peroxyacetyl Nitrate | AFG1 - Aromatic Ring Fragments 1 | MVK - Methyl Vinyl Ketone | | BZO - Phenoxy Radical |
| MPAN - Methly Peroxyacetyl Nitrate | AFG2 - Aromatic Ring Fragments 2 | IPRD - Isoprene Reaction Prods. | | BZNO - BZ(NO2)-O |
| RO2 - Alkyl Peroxy Radicals | CCHO$^{b}$ - Acetaldehyde | MRC3 - Methly Peroxyacetyl Radical | | |
| RCO3 - Peroxyacyl Radical | RCHO - Propionaldehyde and all higher Aldehydes | AIR - Air | | |
| ETHE$^{b}$ - Ethene | ACET$^{b}$ - Acetone | INRT - Inert | | |
| CRES - Cresols and Other Alkyl Phenols | PPN - Peroxy Propionyl Nitrate | HCL - Hydrochloric Acid | | |
| NPHE - Nitrophenols | PRPE – Propene | ORGG - Gas Phase Condensable Organics | | |
| HO2H - Hydrogen Peroxide | M1BT - 2-Methyl-1-Butene | | | |
| C - Carbon Atoms | ISOP$^{b}$ - Isoprene | | | |
| LN - Lost Nitrogen Atoms | | | | |
| OOH - Lumped Hydroperoxy Species | | | | |

[a] $X$ represents the different aerosol size bins: $X = 1$ represents aerosols $< 0.156\ \mu m$, $X = 2$ represents aerosols from 0.156 - 0.625 μm, $X = 3$ represents aerosols from 0.625 - 2.5 μm, and $X = 4$ represents aerosols from 2.5 - 10.0 μm.

[b] Emission species generated by EMS-95.

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|  | Emission scaling factor |  |  |
|---|---|---|---|
| Source | August 1999 | SAMI July 1995 | SAMI May 1995 |
| **Total CO** | 1.01 | 1.08 | 1.26 |
| Total $SO_2$ | 0.92 | 1.13 | 1.08 |
| Area source $NO_x$ | 1.62 | 1.77 | 1.50 |
| Elevated point source $NO_x$ | 1.48 | 1.31 | 1.24 |
| Anthropogenic VOC | 2.47 | 2.21 | 2.84 |
| Biogenic VOC | 1.11 | 1.24 | 1.17 |
| Total $NH_3$ | 0.56 | 0.52 | 0.59 |
| Total fine OC PM | 1.10 (0.60) | 0.49 | 0.62 |
| Total fine EC PM | 0.56 | N/C | N/C |

Table 9.2. Estimated relative emissions biases developed using URM-1ATM and inverse modeling.

Figure 9.1: Multiscale Grid Capability used during SCISSAP modeling. Finest resolution is in the areas of greatest interest (the Southeast areas with high ozone and PM).

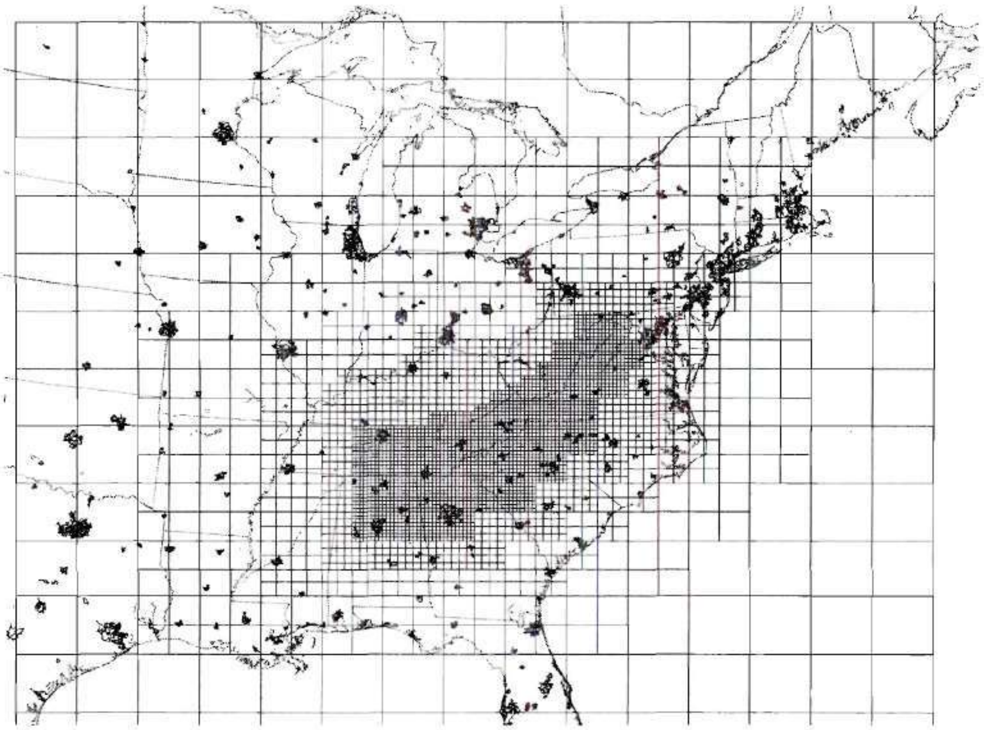


Figure 9.2. Ozone Sensitivity to mobile source NOx emissions in Atlanta, GA (ppb increase per % decrease).

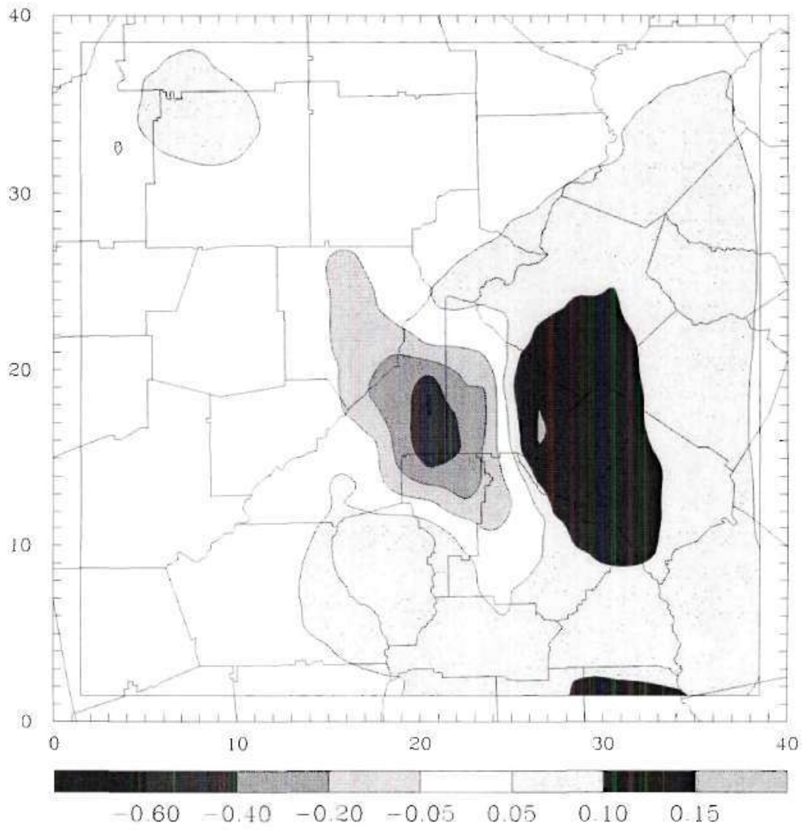
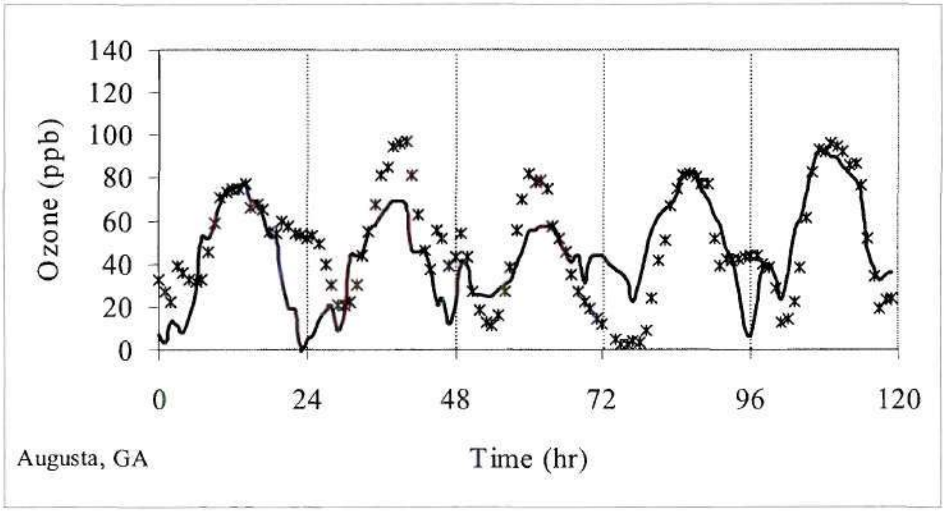
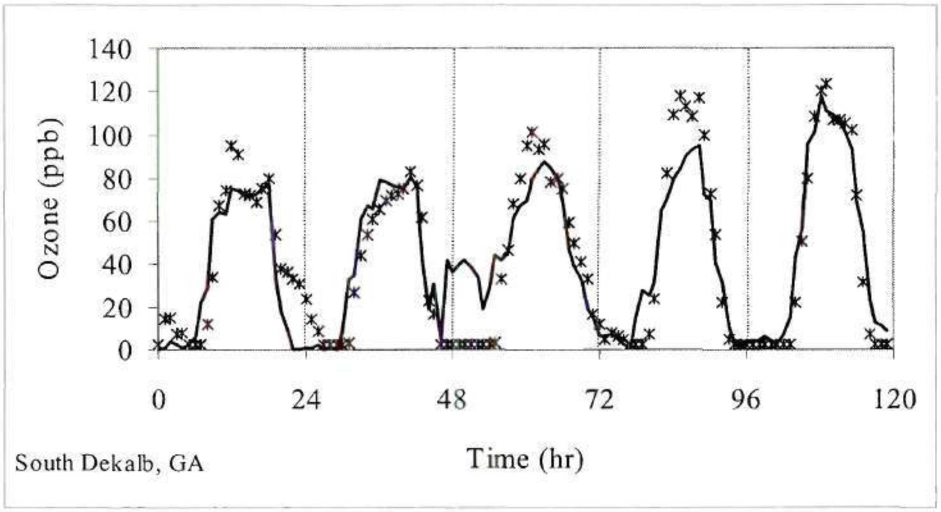


Figure 9.3: Simulated and observed ozone at two locations at two locations during the SCISSAP measurement period.





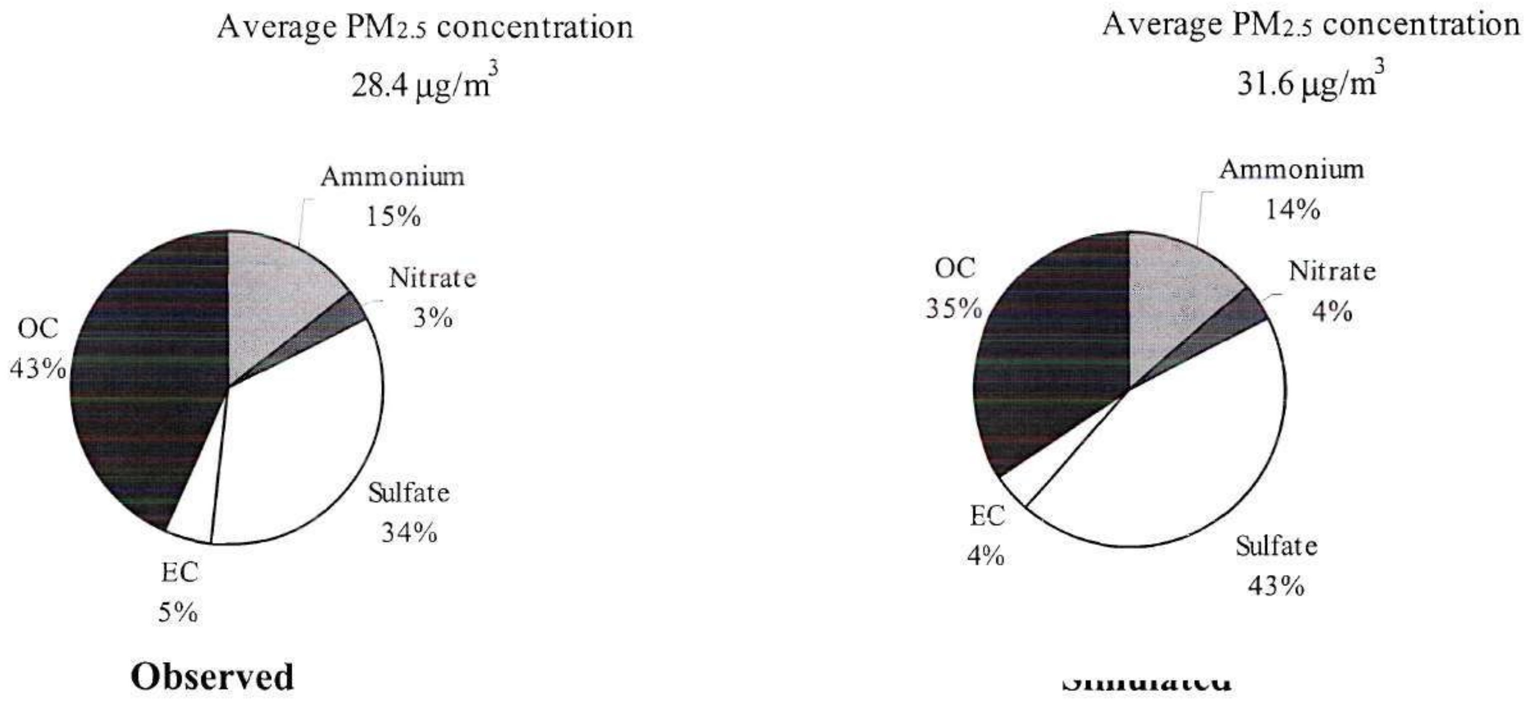
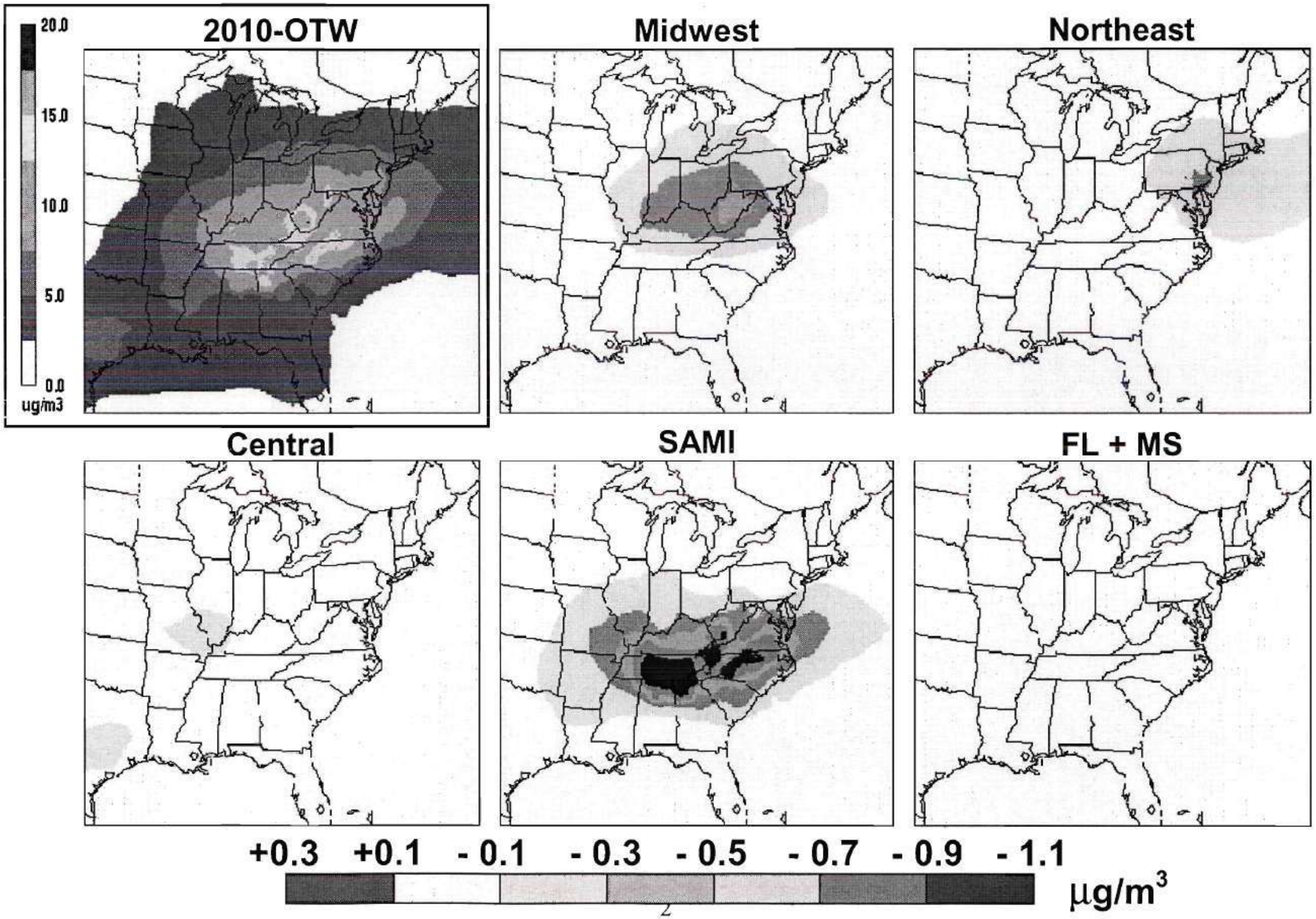


Figure 9.4: Simulated and observed PM2.5 by species during the SCISSAP measurement period.

Figure 9.5: Impact of source regions on sulfate aerosol..



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APPENDIX I. List of Peer-Reviewed Publications

Baumann K, F Ift, JZ Zhao, MH Bergin, and AG Russell, Measurement of trace gases and PM$_{2.5}$ mass and composition near the ground and at 254 m agl during TexAQS 2000, *Proceedings of the 4th Conference on Atmospheric Chemistry: Urban, Regional, and Global-Scale Impacts of Air Pollutants, Orlando, FL, Amer. Meteor. Soc.*, 242-247, 2002.

Baumann K, F Ift, JZ Zhao, and WL Chameides, Discrete measurements of reactive gases and fine particle mass and composition during the 1999 Atlanta SuperSite Experiment, *J. Geophys. Res.*, in press, 2002.

Baumann, K, F Ift, JZ Zhao, and WL Chameides, Investigating the adsorption artifact during aerosol sampling of semi-volatile organic carbon, *J. Geophys. Res.*, in revision 2002.

Carrico, CM, MH Bergin, J Xu, K Baumann, and H Maring, Urban aerosol radiative properties: Measurements during the Atlanta SuperSite 1999 Experiment, *J. Geophys. Res.*, in press, 2002.

Dasgupta PK, Z Genfa, BE Hartsell, S Slanina, K Baumann, CB Boring, PAC Jongejan, and ES Edgerton, Measurement of atmospheric nitric and nitrous acids during the 1999 Atlanta SuperSite Experiment, *J. Geophys. Res.*, in revision 2002.

McMurry, P. H., Wang, X., Park, K., Ehara, K, The relationship between mass and mobility for atmospheric particles: A new technique for measuring particle density, *Aerosol Sci. Technol.* 36:227-238, 2002

Solomon, PA, K Baumann, ES Edgerton, R Tanner, D Eatough, W Modey, H Maring, D Savoie, S Natarajan, MB Meyer, and G Norris, Comparison of integrated samplers for mass and composition during the 1999 Atlanta-Supersites Project, *J. Geophys. Res.*, in press, 2002.

Solomon, P.A., W. Chameides, R.W. Weber, A. Middlebrook, C.S. Kiang, A.G. Russell, A. Butler, , Turpin, B., D. Mikel, R. Scheffe, E. Cowling, E. Edgerton, J. St. John, J. Jansen, P. McMurry, S. Hering, and T. Bahadori, "Overview of the 1999 Atlanta Supersites Project, *J.Geophys. Res.*, in press, 2002

Weber RJ, D Orsini, Y Duan, K Baumann, CS Kiang, WL Chameides, YN Lee, F Brechtel, P Klotz, P Jongejan, H ten Brink, S Slanina, PK Dasgupta, SA Hering, M Stolzenburg, E Edgerton, B Hartsell, PA Solomon, and R Tanner, Intercomparison of near real-time monitors of PM2.5 of nitrate and sulfate at the EPA Atlanta Supersite, *J. Geophys. Res.*, in press, 2002.

Weber, R., D. Orsini, A. Sullivan, M. Bergin, K. Carrico, C. S. Kiang, M. Chang, Y.N. Lee, P. Dasgupta, J. Slanina, B. Turpin, E. Edgerton, S. Hering, G. Allen, P. Solomon, W. Chameides Short-term temporal variation in pm$_{2.5}$ mass and chemical composition during the atlanta supersite experiment, 1999, J. Air Waste Manag., In review, 2002.

Yang, Y.-J., Wilkinson, J.G., Odman, M.T., and Russell, A.G., Ozone Sensitivity and Uncertainty Analysis Using DDM-3D in a Photochemical Air Quality Model, in: *Air Pollution Modelling and Its Application XII*, S.-E. Gryning and E. Batchvarova eds., Kluwer Academic/Plenum Publishers, New York, 183-194, 2000.

Zhang, J., W.L. Chameides, R. Weber, G. Cass, D. Orsini, E. Edgerton, P. Jongejan, J. Slanina An evaluation of the thermodynamic equilibrium assumption for fine particulate composition: Nitrate and ammonium during Atlanta '99 Supersite Experiment, *J. Geophys. Res.* in review, 2002.

## Final Report Executive Summary

**Period Covered by the Report:** April 1, 1998 - March 31, 2002
**Date of Final Report**: June 15, 2002
**EPA Agreement Number:** Grant R826372
**Title:** Southern Center For The Integrated Study of Secondary Air Pollutants
**Investigators:** W.L. Chameides (PI), A.G. Russell (Co-PI), P. McMurry (Co-I), R. Zika (Co-I)
**Institution:** Georgia Institute of Technology (primary), University of Minnesota (sub-contractor), University of Miami (sub-contractor)
**Research Category:** Special Opportunity in Tropospheric Ozone
**Project Period:** April 1, 1998 - March 31, 2002

**Objective(s) of the Research Project:** The mission of the Southern Center for the Integrated Study of Secondary Air Pollutants (SCISSAP) is:

> *The development of the scientific understanding and analytical tools that underpin the design and implementation of an effective and integrated control strategy for secondary air pollutants, using the atmosphere of the southern United States as a natural laboratory.*

This mission is based on the premises that a basic understanding of the chemistry and physics of the atmosphere are a prerequisite for designing effective control strategies for secondary air pollutants; and that the concentration of secondary air pollutants in the atmosphere are often codependent because of interacting chemical reactions.

Over a four-year period beginning on April 1, 1998, SCISSAP was funded by U.S. EPA the NCER/STAR extramural funding program to focus on an integrated study of ground-level ozone ($O_3$) and particulate matter with diameters less than 2.5 μm ($PM_{2.5}$) in the South. Specifically, four major and interrelated scientific questions were addressed:

***Question 1:*** What is the composition and size distribution of fine particles in urban and rural locales in the southern United States and to what extent do temporal and spatial variations in these parameters correlate with those of ozone and its precursor compounds?

***Question 2:*** What are the major precursor compounds and sources for fine particles in urban and rural locales in the southern United States and to what extent do these compounds and sources correspond to/correlate with the sources of natural and anthropogenic ozone precursors (i.e., VOC and $NO_x$)?

***Question 3:*** To what extent, if any, is the chemical composition and abundance of fine particles in urban and rural locales in the southern United States affected by the concentration of natural and anthropogenic ozone precursors and/or ozone?

***Question 4:*** To what extent is the concentration of ground-level ozone in urban and rural locales in the southern United States affected by the concentration and composition of fine particles and/or the concentration of the precursors of fine particles?

To address these questions the SCISSAP Science Team adopted two tangential and interrelated lines of inquiry:

- one line of investigation focused on first on the development and testing of a mobile capability to measure $PM_{2.5}$, ozone, and their precusors, and then its subsequent application of this to large-scale, multi-investigator field experiments, as well as longer-term regional monitoring in the southeast;
- the other focused on the development, evaluation and application of a regional scale air quality for conducting integrated studies of ozone and particulate matter: the "Urban-to-Regional, Multiscale Model: One Atmosphere" (URM-1ATM), with one atmosphere used to denote an integrated approach to treating the physics and chemistry of ozone, acid deposition and particulate matter simultaneously.

**Summary of Major Accomplishments:**

- Developed, field tested, intercompared, and implemented a Particle Composition Monitor (PCM) and related laboratory analytical techniques for measuring the mass and composition of $PM_{2.5}$ as well as its precursor compounds using the filter-denuder technique
- Developed, field tested, intercompared, and implemented an Differential Mobility Analyzer - Aerosol Particle Mass Analyzer (DMA - APM) for *in situ* measurements of particle mass as a function of mobility (i.e., size).
- Helped develop and field test a system for quantifying *in situ* concentrations of oxygenated volatile organic compounds (OVOC).
- Participated in the 1999 SOS Nashville/Middle Tennessee Ozone Study; carried out first measurements of $PM_{2.5}$ vertical gradient within the boundary layer.
- Hosted, and provided analytical laboratory and meeting facilities for the 1999 Atlanta Supersite Experiment; also participated in the experiment.
- Participated in the 2000 Texas Air Quality Study.
- Operated urban and rural $PM_{2.5}$ monitoring sites in Tennessee and Georgia
- Developed an on-going regional center for air quality field measurements with a mobile measurement capability in the southeastern United States; this capability has played a key role in the State of Georgia supported Fall-line Air Quality Study and will provide vital data for a locally-supported field experiment in Pensacola Florida during the Summer of 2002.
- Helped develop and evaluate a regional-scale air quality model (URM-1ATM); this model played a critical role in the Southern Appalachians Mountains Initiative (SAMI) to address specific policy questions and the many of the critical components of the model are now being migrated to EPA's Models 3.

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1. $PM_{2.5}$ composition (at the 24-hour integrated sampling time used in the study) was found to show little variability across the sites operated from Nashville, Tennessee, to Atlanta Georgia, to Houston Texas (see Figure 1). In virtually all cases more than 60% of the $PM_{2.5}$ mass was found to arise from sulfate (and the ammonium associated with it) and organic carbon (and the other organic elements assumed to be associated with the organic carbon).

Thus pollution mitigation aimed at simply lowering $PM_{2.5}$ mass in the southeast would be most effective if they sought to lower the emissions of particulate sulfate and organic carbon and their precursors. (However, note finding #x below.)

2. $PM_{2.5}$ mass, sulfate, nitrate, and ammonium concentrations were found to have a positive vertical gradient between 4 and 42 m altitude at a suburban site in Tennessee.
3. The daily variations in the chemical components of $PM_{2.5}$ exhibited little of no correlation with their gaseous precursors, and $PM_{2.5}$ mass was not well-correlated with local ozone concentrations..
4. $PM_{2.5}$ mass concentrations showed only moderate increases as one moves from rural to suburban to urban locales.

**Implication:** Collectively findings 1 – 4 suggest that the source for fine particles is regionally distributed with perhaps direct emissions of $PM_{2.5}$ and its precursors and/or secondary formation of $PM_{2.5}$ occurring aloft as opposed to at the surface.

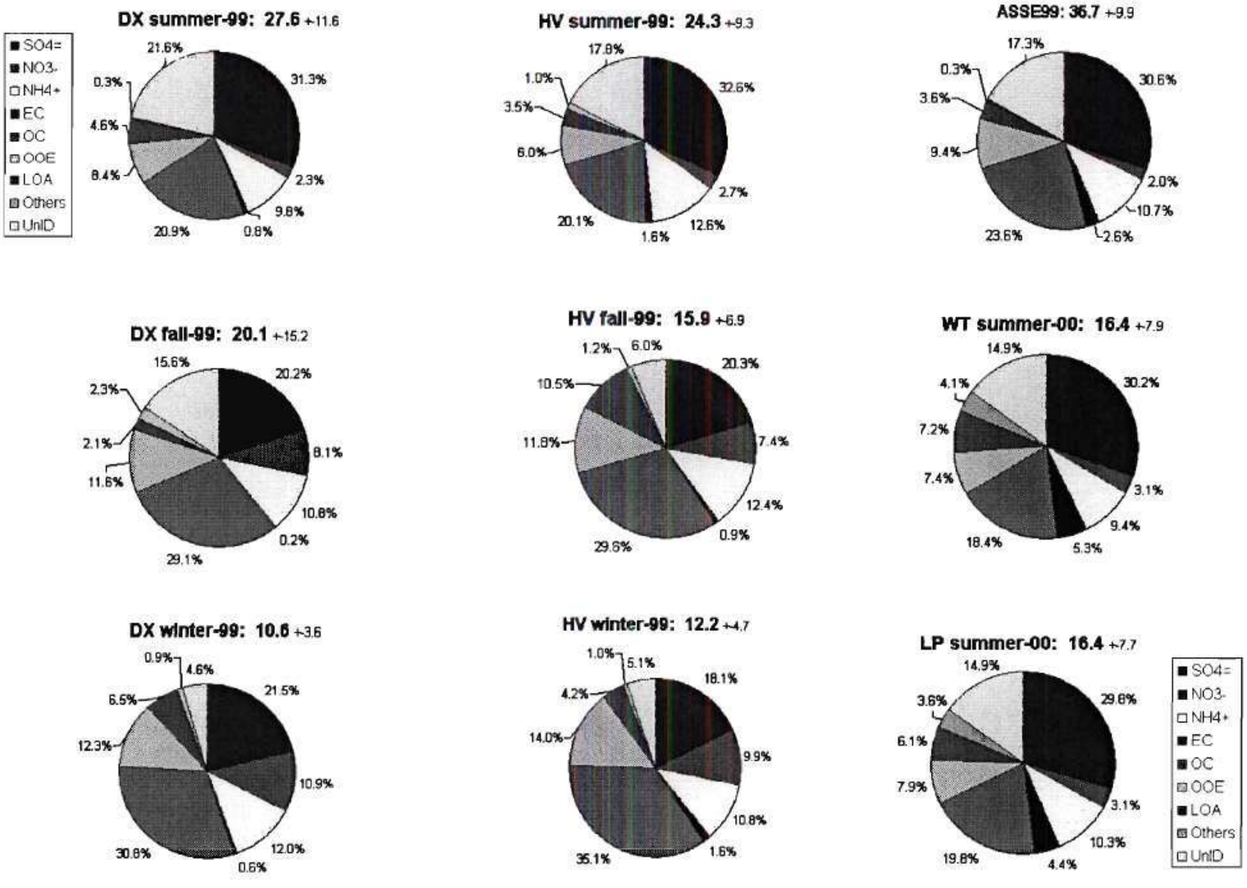

**Figure 1**. Average $PM_{2.5}$ mass (indicated in $mg/m^3$ next to the site descriptor above each pie chart) and percentage composition as a function of season at rural Dixon, Tennessee (DX), and

suburban Hendersonville (HV) near Nashville, TN, metropolitan Atlanta (ASSE99) and two Houston, Texas sites, LaPorte (LP) and Williams Tower (WT). Note: OOE denoted other organic elements other than C associated with organic C particulate matter (OC), LOA denoted light organic acids.

5. Different instrumentation designed to measure the mass and composition of $PM_{2.5}$ with 12- or 24-hour integrated sampling will generally yield comparable results with each other and with more sophisticated continuous and semi-continuous methodologies.
6. Under highly humid conditions (e.g., Atlanta in the summer) significant artifacts in the measurement of $PM_{2.5}$ mass using the filter technique can arise from the presence of solid hydrates on the filter
7. Negative artifacts in the measurement of OC can arise from the liberation of semi-volatile organics from the particulate phase when using the filter-denuder technique. Assuming OOE from the denuded quartz front filter to equal 60 % of OC, these semi-volatile organics showed lower OOE, indicating more volatile features of less polar and less water soluble species, see Baumann et al, 2002.

**Implication**: While the denuder-filter technique can yield reasonably robust measurements of $PM_{2.5}$ mass and composition the method is subject to artifacts and thus thorough QA/QC procedures and self-consistency checks must be adopted with this technique. For example, accurate estimates of total organic mass requires development and application of methods for quantifying and correcting for artifacts arising from liberation of semi-volaite organics.

8. Atmospheric particles of 100 nm and 300 nm in Atlanta at ~3-6% relative humidity typically had two distinct densities: $1.6\pm0.1$ g cm$^{-3}$ and $0.45\pm0.20$ g cm$^{-3}$.
9. Effective densities of diesel exhaust particles decrease with increasing size. At 50 nm, densities are about $1.1\pm0.1$ g cm$^{-3}$, while at 300 nm densities are about $0.3\pm0.05$ g cm$^{-3}$.

**Implication:** The "low density" particles observed in the Atlanta atmosphere have densities similar to diesel exhaust particles of the same mobility size. The densities of "high density" particles are consistent with values calculated from measured composition, assuming that they consist primarily of organic carbon and sulfates.

10. The DMA-APM technique can measure the mass and density of spherical particles to within 5%.
11. The DMA-APM technique can measure the mass and "effective densities" of nonspherical particles.

**Implication:** The DMA-APM provides a precise and accurate technique for measuring particle density thereby enabling a determination of the definitive relationships between aerodynamic and mobility equivalent diameters. This relationship helps to reconcile measurements based on different physical principles. Also, the new, in-situ technique for direct measurement of mass size distributions and concentrations will provide insights into the accuracy of filter-based measurements of mass concentrations, such as are used in EPA's FRM network.

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found in $PM_{2.5}$ is controlled by thermodynamic equilibrium between the $PM_{2.5}$ and gas-phase ammonia and nitric acid.

**13.** $PM_{2.5}$ in the southeast is generally slightly acidic with relatively small amounts of nitrate
**Implication:** In the southeast, there is generally an inadequate amount of ammonia to neutralize sulfate and hence $PM_{2.5}$ is slightly acidic and this in turn limits the amount of particulate nitrate that can form. Thus $PM_{2.5}$ mitigation efforts based on reducing particulate sulfate by decreasing $SO_2$ emissions may be offset, to some extent, by a concomitant increase in particulate nitrate.

14. A positive correlation was found between simultaneously measured OVOC concentrations and speciated, size-segregated particulate OC abundances in Atlanta. Calculation of the hourly new particle production potential from hourly OVOC measurements suggest that gas to particle conversion is a significant source of new organic aerosols. This calculation of new particle production predicts approximately half of the measured $PM_{2.5}$ total organic carbon observed.
**Implication:** Controls on the gaseous emissions of OVOC and their precursors could have a significant impact on reducing $PM_{2.5}$ mass concentrations in Atlanta.

## Summary of Findings from Modeling Portion of the Program

After using the data gathered by SCISSAP and related programs to evaluate the URM-1ATM, this model was then used to comprehensively address these questions. Our findings are summarized below.

**Question 1:** What is the concentration and composition of $PM_{2.5}$ in urban and rural locales in the South and to what extent do temporal and spatial variations in these parameters correlate with those of $O_3$ and its precursor compounds?

Findings: While ozone and elemental carbon exhibit significant variations between urban and rural regions, most of the other components of $PM_{2.5}$ have relatively uniform concentrations between urban and rural areas, though certain regions have higher sulfate than others. On the other hand on urban scales there is a tendency for ozone and PM to be highest in or just downwind of urban areas.

**Question 2**: What are the major precursor compounds and sources for PM2.5 in urban and rural locales in the South and to what extent do these compounds and sources correspond to correlate with the sources of natural and anthropogenic $O_3$ precursors (i.e., VOC and $NO_x$)?

Findings: The major precursors for $PM_{2.5}$ in the southeast are $SO_2$ (largely from coal fired power plants) and organic carbon, from a myriad of sources including biogenic (e.g., biomass burning and secondary conversion of higher organics) and anthropogenic (automobiles, cooking, etc.). Nitrate plays less of a role at present since the aerosol is so acidic that much of the ammonia that is necessary for ammonium nitrate formation is tied up as ammonium sulfate. Ammonia, largely from animal waste and fertilizer use acts to form a fraction of the PM mass, but is important as it is the primary neutralizing agent. For ozone, the two primary precursors are $NO_x$ and, again, organics. Automobiles appear to play a major role, followed by electrical generating units in terms of ozone formation due to $NO_x$ emissions. Automotive (in urban areas) and biogenic (most everywhere else) sources, as well as solvent usage, have the most impact on forming ozone from the VOC perspective.

Sensitivity maps show that both ozone and sulfate have similar source-impact patterns. Thus, one would expect that controls for precursors of both pollutants would have benefits over the same general area.

**Question 3**: How are the formation rates and concentrations of O3 and $PM_{2.5}$, as well as the $PM_{2.5}$ composition affected by the relative emissions and concentrations of $NO_x$, $SO_x$, NH3, and VOC species, and what are the mechanisms responsible for these relationships?

Findings: Over most of the domain, ozone formation is $NO_x$-limited, though not always in urban areas where there can be a greater sensitivity to VOC emissions. Outside of primary emissions of particulate matter, $SO_x$ appears to be the most sensitive precursor for PM formation since it also captures ammonia and water. Sulfate appears to be formed primarily via gas phase oxidation, though aqueous phase reactions are important. Organic PM appears to be split between primary emissions and oxidation of biogenic emissions. Nitrate is formed from oxidation of $NO_2$, which takes place both during the day and at night, followed by reaction with ammonia. Ammonia acts as a neutralizing agent for sulfate and nitrate. The nitrate is highest, at least during the summer, in the early morning hours when the air is cooler and more humid, promoting condensation.

We do find that elevated NOx sources are less efficient at forming ozone than ground level sources, as has been found from aircraft studies as well. Increased emissions, while increasing ozone, can decrease the "ozone production efficiency" (OPE). We see a much more linear response in $SO_2$ emissions.

**Question 4**: To what extent do the mechanisms elucidated above affect the formulation of an integrated control strategy for $O_3$ and $PM_{2.5}$?; and Do our findings suggest an "optimum" strategy for addressing both pollutants?

Findings: Strategies to reduce $NO_x$ and $SO_2$ simultaneously will be effective in reducing ozone and PM at the same time. For example, using new, combined cycle gas turbines (or coal gasification), could lower both pollutants effectively. On the other hand, one could envision controls that only go after one of the precursors alone. We did not do an economic optimization to find which would be best. Also of importance, both ozone and PM share a largely uncontrollable source, biogenics such as trees, which will limit the effectiveness of controls. For example, there will be a limit on how low PM levels can go since the biogenic fraction appears to be substantial on stagnant and hot days. Further, in the Southeast, VOC controls primarily will be effective only in and around urban areas, at least on high ozone days.

Our model results show (and as indicated by the measurements) that, at times, reducing SO2 emissions, and hence PM sulfate, can be offset by increased nitrate aerosol as ammonium is no longer tied up neutralizing the sulfuric acid. The extent of this was quite varied over the region. In some cases, this led to a very small impact, though at other times and locations upwards of about 50% of the reduction in sulfate could be lost by an increase in ammonium nitrate. It was also found that this result will change in the future as $SO_2$ emissions are reduced due to acid rain controls and ammonia emissions may increase due to increased agricultural operations. In such cases, the effect of reduced sulfate leading to increased nitrate becomes more significant. We also found that there is a seasonal dependence. As part of a separate project, using URM-1ATM, we found that over a synthetic year that the replacement phenomena led to a relatively small reduction in the overall benefits of SO2 control, on the order of 10%.

**Peer-Reviewed Publications:**

Baumann K, F Ift, JZ Zhao, MH Bergin, and AG Russell, Measurement of trace gases and $PM_{2.5}$ mass and composition near the ground and at 254 m agl during TexAQS 2000, *Proceedings of the 4th Conference on Atmospheric Chemistry: Urban, Regional, and Global-Scale Impacts of Air Pollutants, Orlando, FL, Amer. Meteor. Soc.*, 242-247, 2002.

Baumann K, F Ift, JZ Zhao, and WL Chameides, Discrete measurements of reactive gases and fine particle mass and composition during the 1999 Atlanta SuperSite Experiment, *J. Geophys. Res.*, in press, 2002.

Baumann, K, F Ift, JZ Zhao, and WL Chameides, Investigating the adsorption artifact during aerosol sampling of semi-volatile organic carbon, *J. Geophys. Res.*, in revision 2002.

Carrico, CM, MH Bergin, J Xu, K Baumann, and H Maring, Urban aerosol radiative properties: Measurements during the Atlanta SuperSite 1999 Experiment, *J. Geophys. Res.*, in press, 2002.

Dasgupta PK, Z Genfa, BE Hartsell, S Slanina, K Baumann, CB Boring, PAC Jongejan, and ES Edgerton, Measurement of atmospheric nitric and nitrous acids during the 1999 Atlanta SuperSite Experiment, *J. Geophys. Res.*, in revision 2002.

McMurry, P. H., Wang, X., Park, K., Ehara, K, The relationship between mass and mobility for atmospheric particles: A new technique for measuring particle density, *Aerosol Sci. Technol.* 36:227-238, 2002

Solomon, PA, K Baumann, ES Edgerton, R Tanner, D Eatough, W Modey, H Maring, D Savoie, S Natarajan, MB Meyer, and G Norris, Comparison of integrated samplers for mass and composition during the 1999 Atlanta-Supersites Project, *J. Geophys. Res.*, in press, 2002.

Solomon, P.A., W. Chameides, R.W. Weber, A. Middlebrook, C.S. Kiang, A.G. Russell, A. Butler, , Turpin, B., D. Mikel, R. Scheffe, E. Cowling, E. Edgerton, J. St. John, J. Jansen, P. McMurry, S. Hering, and T. Bahadori, "Overview of the 1999 Atlanta Supersites Project, *J.Geophys. Res.*, in press, 2002

Weber RJ, D Orsini, Y Duan, K Baumann, CS Kiang, WL Chameides, YN Lee, F Brechtel, P Klotz, P Jongejan, H ten Brink, S Slanina, PK Dasgupta, SA Hering, M Stolzenburg, E Edgerton, B Hartsell, PA Solomon, and R Tanner, Intercomparison of near real-time monitors of PM2.5 of nitrate and sulfate at the EPA Atlanta Supersite, *J. Geophys. Res.*, in press, 2002.

Weber, R., D. Orsini, A. Sullivan, M. Bergin, K. Carrico, C. S. Kiang, M. Chang, Y.N. Lee, P. Dasgupta, J. Slanina, B. Turpin, E. Edgerton, S. Hering, G. Allen, P. Solomon, W. Chameides Short-term temporal variation in $pm_{2.5}$ mass and chemical composition during the atlanta supersite experiment, 1999, J. Air Waste Manag., In review, 2002.

Yang, Y.-J., Wilkinson, J.G., Odman, M.T., and Russell, A.G., Ozone Sensitivity and Uncertainty Analysis Using DDM-3D in a Photochemical Air Quality Model, in: *Air Pollution Modelling and Its Application XII*, S.-E. Gryning and E. Batchvarova eds., Kluwer Academic/Plenum Publishers, New York, 183-194, 2000.

Zhang, J., W.L. Chameides, R. Weber, G. Cass, D. Orsini, E. Edgerton, P. Jongejan, J. Slanina An evaluation of the thermodynamic equilibrium assumption for fine particulate composition: Nitrate and ammonium during Atlanta '99 Supersite Experiment, *J. Geophys. Res.* in review, 2002.

**Supplemental Keywords:**

**Media:** air, ambient air, atmosphere, ozone
**Risk Assessment:** exposure
**Scientific Disciplines:** environmental chemistry
**Methods/Techniques:** modeling, monitoring, measurement methods
**Geographic Areas:** southeast, EPA Region 4

**Relevant Web Sites:**

www.wlc.eas.gatech.edu/scissap/
www.wlc.eas.gatech.edu/supersite/

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## Final Report Executive Summary

**Period Covered by the Report:** April 1, 1998 - March 31, 2002
**Date of Final Report**: June 15, 2002
**EPA Agreement Number:** Grant R826372
**Title:** Southern Center For The Integrated Study of Secondary Air Pollutants
**Investigators:** W.L. Chameides (PI), A.G. Russell (Co-PI), P. McMurry (Co-I), R. Zika (Co-I)
**Institution:** Georgia Institute of Technology (primary), University of Minnesota (sub-contractor), University of Miami (sub-contractor)
**Research Category:** Special Opportunity in Tropospheric Ozone
**Project Period:** April 1, 1998 - March 31, 2002

**Objective(s) of the Research Project:** The mission of the Southern Center for the Integrated Study of Secondary Air Pollutants (SCISSAP) is:

> *The development of the scientific understanding and analytical tools that underpin the design and implementation of an effective and integrated control strategy for secondary air pollutants, using the atmosphere of the southern United States as a natural laboratory.*

This mission is based on the premises that a basic understanding of the chemistry and physics of the atmosphere are a prerequisite for designing effective control strategies for secondary air pollutants; and that the concentration of secondary air pollutants in the atmosphere are often codependent because of interacting chemical reactions.

Over a four-year period beginning on April 1, 1998, SCISSAP was funded by U.S. EPA the NCER/STAR extramural funding program to focus on an integrated study of ground-level ozone ($O_3$) and particulate matter with diameters less than 2.5 μm ($PM_{2.5}$) in the South. Specifically, four major and interrelated scientific questions were addressed:

***Question 1:*** What is the composition and size distribution of fine particles in urban and rural locales in the southern United States and to what extent do temporal and spatial variations in these parameters correlate with those of ozone and its precursor compounds?

***Question 2:*** What are the major precursor compounds and sources for fine particles in urban and rural locales in the southern United States and to what extent do these compounds and sources correspond to/correlate with the sources of natural and anthropogenic ozone precursors (i.e., VOC and $NO_x$)?

***Question 3:*** To what extent, if any, is the chemical composition and abundance of fine particles in urban and rural locales in the southern United States affected by the concentration of natural and anthropogenic ozone precursors and/or ozone?

***Question 4:*** To what extent is the concentration of ground-level ozone in urban and rural locales in the southern United States affected by the concentration and composition of fine particles and/or the concentration of the precursors of fine particles?

To address these questions the SCISSAP Science Team adopted two tangential and interrelated lines of inquiry:

- one line of investigation focused on first on the development and testing of a mobile capability to measure $PM_{2.5}$, ozone, and their precusors, and then its subsequent application of this to large-scale, multi-investigator field experiments, as well as longer-term regional monitoring in the southeast;
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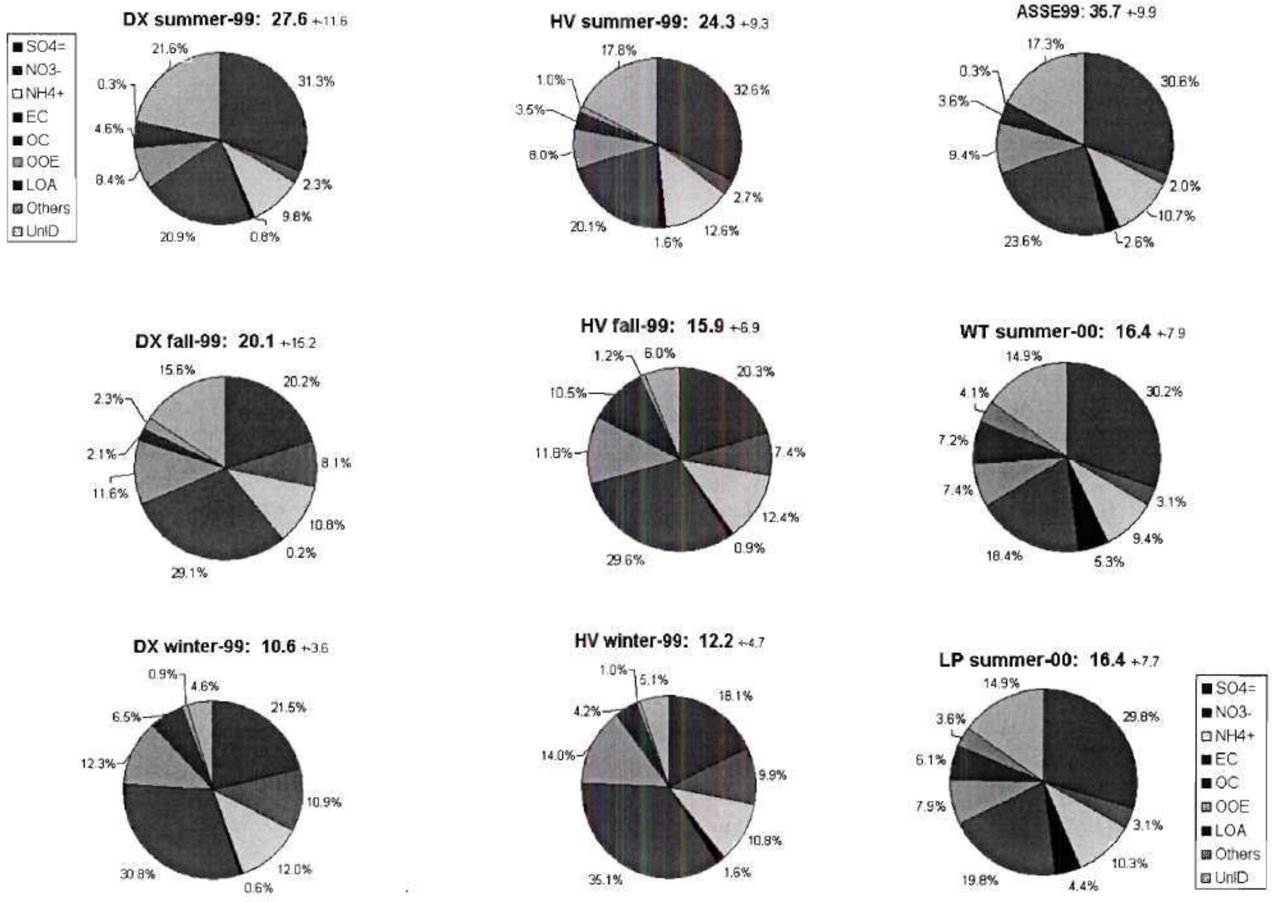

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Findings: Over most of the domain, ozone formation is $NO_x$-limited, though not always in urban areas where there can be a greater sensitivity to VOC emissions. Outside of primary emissions of particulate matter, $SO_x$ appears to be the most sensitive precursor for PM formation since it also captures ammonia and water. Sulfate appears to be formed primarily via gas phase oxidation, though aqueous phase reactions are important. Organic PM appears to be split between primary emissions and oxidation of biogenic emissions. Nitrate is formed from oxidation of $NO_2$, which takes place both during the day and at night, followed by reaction with ammonia. Ammonia acts as a neutralizing agent for sulfate and nitrate. The nitrate is highest, at least during the summer, in the early morning hours when the air is cooler and more humid, promoting condensation.

We do find that elevated NOx sources are less efficient at forming ozone than ground level sources, as has been found from aircraft studies as well. Increased emissions, while increasing ozone, can decrease the "ozone production efficiency" (OPE). We see a much more linear response in $SO_2$ emissions.

**Question 4**: To what extent do the mechanisms elucidated above affect the formulation of an integrated control strategy for $O_3$ and $PM_{2.5}$?; and Do our findings suggest an "optimum" strategy for addressing both pollutants?

Findings: Strategies to reduce $NO_x$ and $SO_2$ simultaneously will be effective in reducing ozone and PM at the same time. For example, using new, combined cycle gas turbines (or coal gasification), could lower both pollutants effectively. On the other hand, one could envision controls that only go after one of the precursors alone. We did not do an economic optimization to find which would be best. Also of importance, both ozone and PM share a largely uncontrollable source, biogenics such as trees, which will limit the effectiveness of controls. For example, there will be a limit on how low PM levels can go since the biogenic fraction appears to be substantial on stagnant and hot days. Further, in the Southeast, VOC controls primarily will be effective only in and around urban areas, at least on high ozone days.

Our model results show (and as indicated by the measurements) that, at times, reducing SO2 emissions, and hence PM sulfate, can be offset by increased nitrate aerosol as ammonium is no longer tied up neutralizing the sulfuric acid. The extent of this was quite varied over the region. In some cases, this led to a very small impact, though at other times and locations upwards of about 50% of the reduction in sulfate could be lost by an increase in ammonium nitrate. It was also found that this result will change in the future as $SO_2$ emissions are reduced due to acid rain controls and ammonia emissions may increase due to increased agricultural operations. In such cases, the effect of reduced sulfate leading to increased nitrate becomes more significant. We also found that there is a seasonal dependence. As part of a separate project, using URM-1ATM, we found that over a synthetic year that the replacement phenomena led to a relatively small reduction in the overall benefits of SO2 control, on the order of 10%.

**Peer-Reviewed Publications:**

Baumann K, F Ift, JZ Zhao, MH Bergin, and AG Russell, Measurement of trace gases and $PM_{2.5}$ mass and composition near the ground and at 254 m agl during TexAQS 2000, *Proceedings of the 4th Conference on Atmospheric Chemistry: Urban, Regional, and Global-Scale Impacts of Air Pollutants, Orlando, FL, Amer. Meteor. Soc.*, 242-247, 2002.

Baumann K, F Ift, JZ Zhao, and WL Chameides, Discrete measurements of reactive gases and fine particle mass and composition during the 1999 Atlanta SuperSite Experiment, *J. Geophys. Res.*, in press, 2002.

Baumann, K, F Ift, JZ Zhao, and WL Chameides, Investigating the adsorption artifact during aerosol sampling of semi-volatile organic carbon, *J. Geophys. Res.*, in revision 2002.

Carrico, CM, MH Bergin, J Xu, K Baumann, and H Maring, Urban aerosol radiative properties: Measurements during the Atlanta SuperSite 1999 Experiment, *J. Geophys. Res.*, in press, 2002.

Dasgupta PK, Z Genfa, BE Hartsell, S Slanina, K Baumann, CB Boring, PAC Jongejan, and ES Edgerton, Measurement of atmospheric nitric and nitrous acids during the 1999 Atlanta SuperSite Experiment, *J. Geophys. Res.*, in revision 2002.

McMurry, P. H., Wang, X., Park, K., Ehara, K, The relationship between mass and mobility for atmospheric particles: A new technique for measuring particle density, *Aerosol Sci. Technol.* 36:227-238, 2002

Solomon, PA, K Baumann, ES Edgerton, R Tanner, D Eatough, W Modey, H Maring, D Savoie, S Natarajan, MB Meyer, and G Norris, Comparison of integrated samplers for mass and composition during the 1999 Atlanta-Supersites Project, *J. Geophys. Res.*, in press, 2002.

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Weber RJ, D Orsini, Y Duan, K Baumann, CS Kiang, WL Chameides, YN Lee, F Brechtel, P Klotz, P Jongejan, H ten Brink, S Slanina, PK Dasgupta, SA Hering, M Stolzenburg, E Edgerton, B Hartsell, PA Solomon, and R Tanner, Intercomparison of near real-time monitors of PM2.5 of nitrate and sulfate at the EPA Atlanta Supersite, *J. Geophys. Res.*, in press, 2002.

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Zhang, J., W.L. Chameides, R. Weber, G. Cass, D. Orsini, E. Edgerton, P. Jongejan, J. Slanina An evaluation of the thermodynamic equilibrium assumption for fine particulate composition: Nitrate and ammonium during Atlanta '99 Supersite Experiment, *J. Geophys. Res.* in review, 2002.

**Supplemental Keywords:**

**Media:** air, ambient air, atmosphere, ozone
**Risk Assessment:** exposure
**Scientific Disciplines:** environmental chemistry
**Methods/Techniques:** modeling, monitoring, measurement methods
**Geographic Areas:** southeast, EPA Region 4

**Relevant Web Sites:**

www.wlc.eas.gatech.edu/scissap/
www.wlc.eas.gatech.edu/supersite/

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## Final Report Executive Summary

**Period Covered by the Report:** April 1, 1998 - March 31, 2002
**Date of Final Report**: June 15, 2002 (Submission of revised report: April 22, 2003)
**EPA Agreement Number:** Grant R826372
**Title:** Southern Center For The Integrated Study of Secondary Air Pollutants
**Investigators:** W.L. Chameides (PI), A.G. Russell (Co-PI), P. McMurry (Co-I), R. Zika (Co-I)
**Institution:** Georgia Institute of Technology (primary), University of Minnesota (sub-contractor), University of Miami (sub-contractor)
**Research Category:** Special Opportunity in Tropospheric Ozone
**Project Period:** April 1, 1998 - March 31, 2002

**Objective(s) of the Research Project:** The mission of the Southern Center for the Integrated Study of Secondary Air Pollutants (SCISSAP) is:

> *The development of the scientific understanding and analytical tools that underpin the design and implementation of an effective and integrated control strategy for secondary air pollutants, using the atmosphere of the southern United States as a natural laboratory.*

This mission is based on the premises that a basic understanding of the chemistry and physics of the atmosphere are a prerequisite for designing effective control strategies for secondary air pollutants; and that the concentration of secondary air pollutants in the atmosphere are often codependent because of interacting chemical reactions.

Over a four-year period beginning on April 1, 1998, SCISSAP was funded by U.S. EPA the NCER/STAR extramural funding program to focus on an integrated study of ground-level ozone ($O_3$) and particulate matter with diameters less than 2.5 µm ($PM_{2.5}$) in the South. Specifically, four major and interrelated scientific questions were addressed:

***Question 1:*** What is the composition and size distribution of fine particles in urban and rural locales in the southern United States and to what extent do temporal and spatial variations in these parameters correlate with those of ozone and its precursor compounds?

***Question 2:*** What are the major precursor compounds and sources for fine particles in urban and rural locales in the southern United States and to what extent do these compounds and sources correspond to/correlate with the sources of natural and anthropogenic ozone precursors (i.e., VOC and $NO_x$)?

***Question 3:*** To what extent, if any, is the chemical composition and abundance of fine particles in urban and rural locales in the southern United States affected by the concentration of natural and anthropogenic ozone precursors and/or ozone?

***Question 4:*** To what extent is the concentration of ground-level ozone in urban and rural locales in the southern United States affected by the concentration and composition of fine particles and/or the concentration of the precursors of fine particles?

To address these questions the SCISSAP Science Team adopted two tangential and interrelated lines of inquiry:

- one line of investigation focused on first on the development and testing of a mobile capability to measure $PM_{2.5}$, ozone, and their precusors, and then its subsequent application of this to large-scale, multi-investigator field experiments, as well as longer-term regional monitoring in the southeast;
- the other focused on the development, evaluation and application of a regional scale air quality model for conducting integrated studies of ozone and particulate matter: the "Urban-to-Regional, Multiscale Model: One Atmosphere" (URM-1ATM), with one atmosphere used to denote an integrated approach to treating the physics and chemistry of ozone, acid deposition and particulate matter simultaneously.

## SUMMARY OF MAJOR ACCOMPLISHMENTS:

During the 4-years of support for SCISSAP from NCER the SCISSAP Science Team successfully developed a unique capability in the southeastern United States: a facility for measuring $PM_{2.5}$ concentrations and composition as well as ozone and ozone- and fine-particle-gaseous precursors. This facility played a central role in a number of major regional air quality field experiments, most particularly in the 1999 Atlanta Supersite Experiment. The Science Team was also able to develop, evaluate, and apply a new multi-scale, multi-pollutant regional modeling system. Both the measurement facility and modeling system continue to serve a resource for the scientific and policy-making communities in the south and other regions of the United States.

Specific accomplishments are outlined below:

- Developed, field tested, intercompared, and implemented a Particle Composition Monitor (PCM) and related laboratory analytical techniques for measuring the mass and composition of $PM_{2.5}$ as well as its precursor compounds using the filter Denuder technique
- Developed, field tested, intercompared, and implemented a Differential Mobility Analyzer - Aerosol Particle Mass Analyzer (DMA - APM) for *in situ* measurements of particle mass as a function of mobility (i.e., size).
- Developed, field tested and implemented a system for quantifying *in situ* concentrations of oxygenated volatile organic compounds (OVOC).

- Participated in the 1999 SOS Nashville/Middle Tennessee Ozone Study; carried out first measurements of $PM_{2.5}$ vertical gradient within the boundary layer.

- Hosted, and provided analytical laboratory and meeting facilities for the 1999 Atlanta Supersite Experiment; also participated in the experiment.

- Participated in the 2000 Texas Air Quality Study.

- Operated urban and rural $PM_{2.5}$ monitoring sites in Tennessee and Georgia

- Developed an on-going regional center for air quality field measurements with a mobile measurement capability in the southeastern United States; this capability has played a key role in the State of Georgia supported Fall-line Air Quality Study As well as a locally-supported field experiment in Pensacola Florida during the Summer of 2002.

- Helped develop and evaluate a regional-scale air quality model (URM-1ATM);

- Used the URM-1ATM in the Southern Appalachians Mountains Initiative (SAMI) to address specific policy questions;

- Migrated many of the critical components of URM-1ATM to EPA's Models 3.

## SUMMARY OF MAJOR FINDINGS

### Findings from the Experimental Programs

In addition to developing and evaluating new and improved instrumentation and analytical techniques for characterizing air pollutant concentrations and characteristics, SCISSAP endeavored to use this technology in field experiments to test various hypotheses with regards to the characteristics and processes that control the characteristics of $PM_{2.5}$ in the southeast. Specific findings and their policy-relevant implications are outlined below.

**Finding 1.** $PM_{2.5}$ composition (at the 24-hour integrated sampling time used in the study) was found to show little variability across the sites operated from Nashville, Tennessee, to Atlanta Georgia, to Houston Texas (see Figure 3.1). In virtually all cases more than 60% of the $PM_{2.5}$ mass was found to arise from sulfate (and the ammonium associated with it) and organic carbon (and the other organic elements assumed to be associated with the organic carbon).

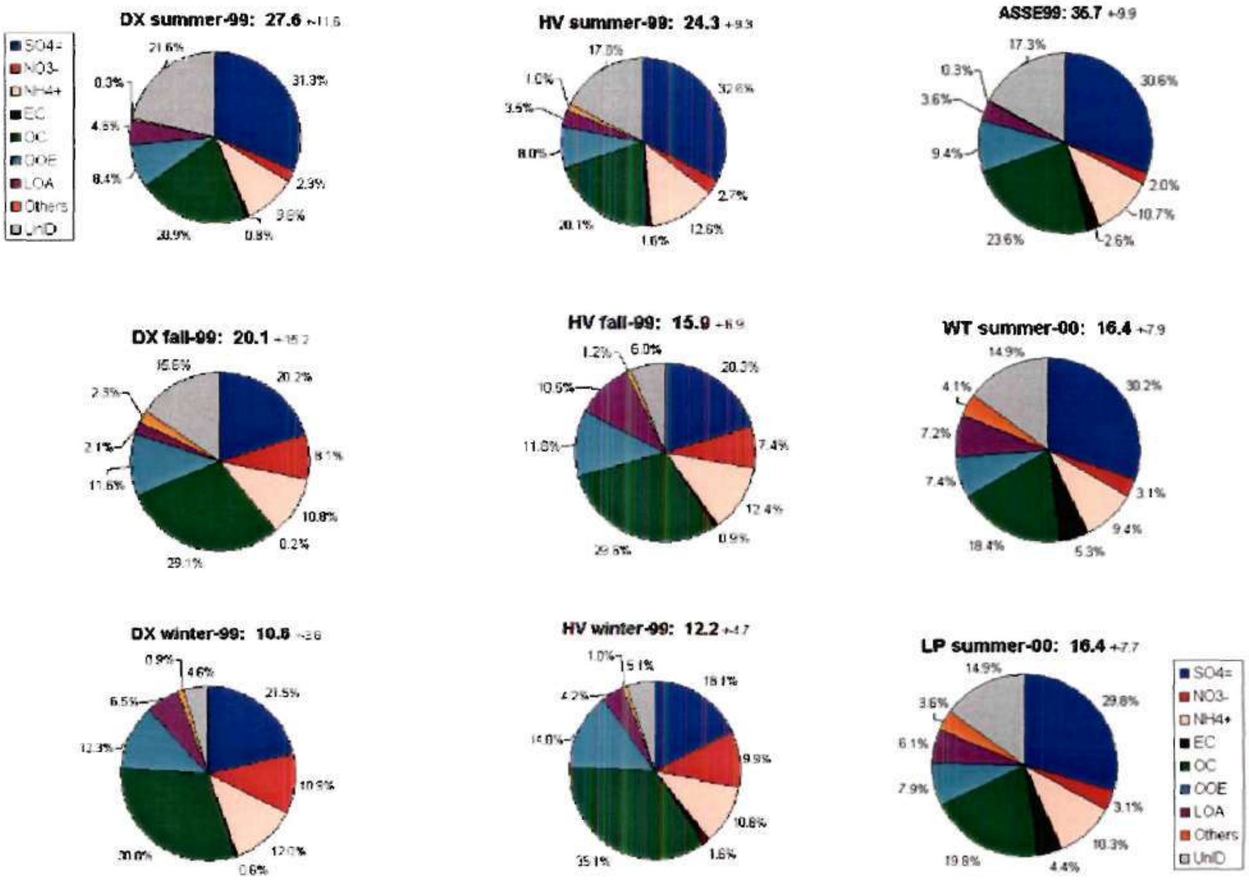

**Figure 3.1**. Average $PM_{2.5}$ mass (indicated in $mg/m^3$ next to the site descriptor above each pie chart) and percentage composition as a function of season at rural Dixon, Tennessee (DX), and suburban Hendersonville (HV) near Nashville, TN, metropolitan Atlanta (ASSE99) and two Houston, Texas sites, LaPorte (LP) and Williams Tower (WT). Note: OOE denotes other organic elements other than C associated with organic C particulate matter (OC), LOA denoted light organic acids.

**Finding 2.** $PM_{2.5}$ mass, sulfate, nitrate, and ammonium concentrations were found to have a positive vertical gradient between 4 and 42 m altitude at a suburban site in Tennessee.

**Finding 3.** The daily variations in the chemical components of $PM_{2.5}$ exhibited little of no correlation with their gaseous precursors, and $PM_{2.5}$ mass was not well-correlated with local ozone concentrations..

**Finding 4.** $PM_{2.5}$ mass concentrations showed only moderate increases as one moves from rural to suburban to urban locales.

**Finding 5.** Different instrumentation designed to measure the mass and composition of $PM_{2.5}$ with 12- or 24-hour integrated sampling will generally yield comparable results with each other and with more sophisticated continuous and semi-continuous methodologies.

**Finding 6.** Under highly humid conditions (e.g., Atlanta in the summer) significant artifacts in the measurement of $PM_{2.5}$ mass using the filter technique can arise from the presence of solid hydrates on the filter.

**Finding 7.** Negative artifacts in the measurement of particulate organic carbon (OC) using EPA's FRM filter-denuder technique can arise as a result of the liberation of semi-volatile organics from the filter during the sampling.

**Finding 8.** Atmospheric particles of 100 nm and 300 nm in Atlanta at ~3-6% relative humidity typically had two distinct densities: $1.6\pm0.1$ g $cm_{-3}$ and $0.45\pm0.20$ g $cm_{-3}$.

**Finding 9.** Effective densities of diesel exhaust particles decrease with increasing size. At 50 nm, densities are about $1.1\pm0.1$ g $cm_{-3}$, while at 300 nm densities are about $0.3\pm0.05$ g $cm_{-3}$.

**Finding 10.** The DMA-APM technique can measure the mass and density of spherical particles to within 5%.

**Finding 11.** The DMA-APM technique can measure the mass and "effective densities" of non-spherical particles.

**Finding 12.** Diagnostic analysis of measurements of $PM_{2.5}$ composition and related gas- phase concentrations in Atlanta tend to support the notion that the amount of ammonium nitrate found in $PM_{2.5}$ is controlled by thermodynamic equilibrium between the $PM_{2.5}$ and gas-phase ammonia and nitric acid.

**Finding 13.** $PM_{2.5}$ in the southeast is generally slightly acidic with relatively small amounts of nitrate.

**Finding 14.** A positive correlation was found between simultaneously measured OVOC concentrations and speciated, size-segregated particulate OC abundances in Atlanta. Calculation of the hourly new particle production potential from hourly OVOC measurements suggest that gas to particle conversion is a significant source of new organic aerosols. This calculation of new particle production predicts approximately half of the measured $PM_{2.5}$ total organic carbon observed.

Findings from the Modeling Program – Addressing Overarching Questions

In addition to addressing the scientific and policy-relevant issues outlined above, the data gathered by SCISSAP and related programs were used to evaluate the URM- 1ATM, being developed by the SCISSAP Modeling Team. Once successfully evaluated, the model was then used to comprehensively address the four major scientific questions SCISSAP set out to answer in its original proposal. Our findings are summarized below.

**Question 1:** What is the concentration and composition of $PM_{2.5}$ in urban and rural locales in the South and to what extent do temporal and spatial variations in these parameters correlate with those of $O_3$ and its precursor compounds?

**Finding 15**: While ozone and elemental carbon exhibit significant variations between urban and rural regions, most of the other components of $PM_{2.5}$ have relatively uniform concentrations between urban and rural areas, though certain regions have higher sulfate than others. On the other hand on urban scales there is a tendency for ozone and PM to be highest in or just downwind of urban areas.

**Question 2**: What are the major precursor compounds and sources for PM2.5 in urban and rural locales in the South and to what extent do these compounds and sources correspond to or correlate with the sources of natural and anthropogenic $O_3$ precursors (i.e., VOC and $NO_x$)?

**Finding 16:** The major precursors for $PM_{2.5}$ in the southeast are $SO_2$ (largely from coal fired power plants) and organic carbon, from a myriad of sources including biogenic (e.g., biomass burning and secondary conversion of higher organics) and anthropogenic (automobiles, cooking, etc.). Nitrate plays less of a role at present since the aerosol is so acidic that much of the ammonia that is necessary for ammonium nitrate formation is tied up as ammonium sulfate. Ammonia, largely from animal waste and fertilizer use acts to form a fraction of the PM mass, but is important as it is the primary neutralizing agent. For ozone, the two primary precursors are $NO_x$ and, again, organics. Automobiles appear to play a major role, followed by electrical generating units in terms of ozone formation due to $NO_x$ emissions. Automotive (in urban areas) and biogenic (most everywhere else) sources, as well as solvent usage, have the most impact on forming ozone from the VOC perspective.

**Finding 17:** Sensitivity maps show that both ozone and sulfate have similar source-impact patterns. Thus, one would expect that controls for precursors of both pollutants would have benefits over the same general area.

**Finding 18:** Inverse modeling suggests that the inventory of anthropogenic VOC emissions in the eastern United States is too low by a factor of ~2.

**Question 3**: How are the formation rates and concentrations of O3 and $PM_{2.5}$, as well as the $PM_{2.5}$ composition affected by the relative emissions and concentrations of $NO_x$, $SO_x$, NH3, and VOC species, and what are the mechanisms responsible for these relationships?

**Finding 19:** Over most of the domain, ozone formation is $NO_x$-limited, though not always in urban areas where there can be a greater sensitivity to VOC emissions. Outside of primary emissions of particulate matter, $SO_x$ appears to be the most sensitive precursor for PM formation since it also captures ammonia and water. Sulfate appears to be formed primarily via gas phase oxidation, though aqueous phase reactions are important. Organic PM appears to be split between primary emissions and oxidation of biogenic emissions. Nitrate is formed from oxidation of $NO_2$, which takes place both during the day and at night, followed by reaction with ammonia. Ammonia acts as a neutralizing agent for sulfate and nitrate. The nitrate is highest, at least during the summer, in the early morning hours when the air is cooler and more humid, promoting condensation.

**Finding 20:** We do find that elevated NOx sources are less efficient at forming ozone than ground level sources, as has been found from aircraft studies as well. Increased emissions, while increasing ozone, can decrease the "ozone production efficiency" (OPE). We see a much more linear response in $SO_2$ emissions.

**Question 4**: To what extent do the mechanisms elucidated above affect the formulation of an integrated control strategy for $O_3$ and $PM_{2.5}$?; and Do our findings suggest an "optimum" strategy for addressing both pollutants?

**Finding 21:** Strategies to reduce $NO_x$ and $SO_2$ simultaneously will be effective in reducing ozone and PM at the same time. For example, using new, combined cycle gas turbines (or coal gasification), could lower both pollutants effectively. On the other hand, one could envision controls that only go after one of the precursors alone. We did not do an economic optimization to find which would be best. Also of importance, both ozone and PM share a largely uncontrollable source, biogenics such as trees, which will limit the effectiveness of controls. For example, there will be a limit on how low PM levels can go since the biogenic fraction appears to be substantial on stagnant and hot days. Further, in the Southeast, VOC controls primarily will be effective only in and around urban areas, at least on high ozone days.

**Finding 22:** Our model results show (and as indicated by the measurements) that, at times, reducing $SO_2$ emissions, and hence PM sulfate, can be offset by increased nitrate aerosol as ammonium is no longer tied up neutralizing the sulfuric acid. The extent of this was quite varied over the region. In some cases, this led to a very small impact, though at other times and locations upwards of about 50% of the reduction in sulfate could be lost by an increase in ammonium nitrate. It was also found that this result will change in the future as $SO_2$ emissions are reduced due to acid rain controls and ammonia emissions may increase due to increased agricultural operations. In such cases, the effect of reduced sulfate leading to increased nitrate becomes more significant. We also found that there is a seasonal dependence. As part of a separate project, using URM-1ATM, we found that over a synthetic year that the replacement phenomena led to a relatively small reduction in the overall benefits of $SO_2$ control, on the order of 10%.

## 4.3 Policy-relevant Implications of Scientific Findings

*A. Emission control strategies:*

1. As is the case for ground-level ozone pollution, $PM_{2.5}$ pollution in the southeastern United States is regional in extent. The fine particle sources appear to be regionally distributed with perhaps direct emissions of $PM_{2.5}$ and its precursors and/or secondary formation of $PM_{2.5}$ occurring aloft as opposed to at the surface; and therefore

2. Mitigation of $PM_{2.5}$ pollution in the southeastern United States will likely require the development and implementation of regional as opposed to urban-scale emission control and pollution prevention strategies.

3. $PM_{2.5}$ mass in the southeastern United States is dominated by OC and sulfate, and therefore control strategies that aim to reduce total fine particle mass concentrations will require emission reductions in organic carbon and sulfur oxides ($SO_x$); however,

4. In the southeast, there is generally an inadequate amount of ammonia to neutralize sulfate and hence $PM_{2.5}$ is slightly acidic and this in turn limits the amount of particulate nitrate that can form. Thus $PM_{2.5}$ mitigation efforts based on reducing particulate sulfate by decreasing $SO_2$ emissions may be offset, to some extent, by a concomitant increase in particulate nitrate; and therefore

5. It would be prudent to consider implementation of controls on $NO_x$ and $NH_3$ emissions at the same time that $SO_x$ controls are implemented. Controls on $NO_x$ emission will have the added benefit of mitigating regional ground-level ozone pollution.

6. Controls on the gaseous emissions of OVOC and their precursors could have a significant impact on reducing $PM_{2.5}$ mass concentrations in Atlanta.

7. Controls on particulate emissions from diesel engines may lead to the elimination of a unique class of "low density" particles that were observed in the Atlanta atmosphere.

*B. Fine Particle Monitoring*

8. While the US EPA-approved denuder-filter technique can yield reasonably robust measurements of $PM_{2.5}$ mass and composition, the method is subject to artifacts and thus thorough QA/QC procedures and self-consistency checks must be adopted with this technique. For example, accurate estimates of total organic mass require development and application of methods for quantifying and correcting for artifacts arising from liberation of semi-volatile organics.

9. The DMA-APM provides a precise and accurate technique for measuring particle density thereby enabling a determination of the definitive relationships between aerodynamic and mobility equivalent diameters. This relationship helps to reconcile measurements based

on different physical principles; Also

10. In-situ techniques for semi-continuous, direct measurement of mass size distributions and concentrations can provide insights into the accuracy of filter-based measurements of mass concentrations, such as are used in EPA's FRM network, as well as the health impacts of short-term variations in fine particle mass and composition.

## CONCLUSION

As a result of EPA finding of SCISSAP, a new scientific and technical capability for air quality research, management, and policy formulation has been developed in the southeastern United States. This new capability encompasses a state-of-the-science mobile facility for measuring gaseous and particulate pollutants as well as a state-of-the-science multi-scale multipollutant air quality modeling system.

During the course of the project, the tools described above were used to address a number of policy-relevant scientific issues related to: (1) understanding causes and remedies to fine particle and ground-level ozone pollution in the southeastern United States and (2) the monitoring of fine particles in the atmosphere. With regard to the mitigation of fine particle pollution in the South, our studies confirmed the importance of organic carbon and sulfur oxide emissions and the need to control these emissions on regional rather than urban scales. However, because of thermodynamic interactions between sulfate, ammonium, and nitrate, our studies also suggest that control of nitrogen oxide and ammonium emissions may be desirable at the same time that organic carbon and sulfur oxide emission controls are implemented.

With regard to instrumentation for measuring particulates, our studies suggest that the EPA FRM using the filter-denuder technique can yield accurate data on the mass and overall composition of fine particles. However, the possibility of artifacts, especially for organic carbon persists. Further work and development of denuders, filters, and extraction techniques is probably needed. Our studies also suggest that a wealth of additional information on particulate composition, density, and short-term variability can be obtained with the use of a new and emerging class of semi-continuous particulate monitors. The information and data that can be generated by these new monitors may prove to be especially useful in epidemiological and medical effects research aimed at uncovering the specific components of fine particles that are responsible for the adverse health effects in humans.

The new capabilities developed in SCISSAP are now being used within the region to support both air quality research and management. The mobile monitoring facility is now playing a central role in a variety of local and regional air quality studies funded by local and state agencies, as well as the US EPA. Most notable among these studies is the Georgia Fall Line Air Quality Study (FAQS) which seeks to identify the sources of pollutants and pollutant precursors, and recommend solutions to realized and potential poor air quality in the Augusta, Macon, and Columbus metropolitan areas of Georgia (see url http://cure.eas.gatech.edu/faqs/) . We envision that the mobile facility will continue to represent a valuable resource for the region in the coming years.

The URM-1ATM modeling system developed SCISSAP has made contributions beyond SCISSAP. The modeling system was used in the Southern Appalachian Mountain Initiative to assess the air quality benefits of various possible pollution control scenarios, and is now being migrated to EPA's Models3.

## PUBLICATIONS, PRESENTATIONS, THESES

### 1. List of Peer-Reviewed Publications

Baumann K, F Ift, JZ Zhao, MH Bergin, and AG Russell, Measurement of trace gases and $PM_{2.5}$ mass and composition near the ground and at 254 m agl during TexAQS 2000, *Proceedings of the 4th Conference on Atmospheric Chemistry: Urban, Regional, and*

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www.wlc.eas.gatech.edu/scissap/
www.wlc.eas.gatech.edu/supersite/

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# Final Report

**To:**
National Center for Environmental Research
Office of Research and Development
U.S. Environmental Protection Agency

**From:**
Georgia Tech Research Corporation

**Subject:**
STAR GRANT: R826372

# Southern Center For The Integrated Study of Secondary Air Pollutants

| | |
|---|---|
| **Investigators:** | W.L. Chameides (PI)<br>A.G. Russell (Co-PI)<br>P. McMurry (Co-I)<br>R. Zika (Co-I)<br>P. Kasibhatla (Co-I)<br>D. McNider (Co-I) |
| **Institutions:** | Georgia Institute of Technology (primary)<br>University of Minnesota (sub-contractor)<br>University of Miami (sub-contractor)<br>Duke University (subcontractor)<br>University of Alabama – Huntsville (subcontractor) |

**Research Category:** Special Opportunity in Tropospheric Ozone
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## Table of Contents

## 1. INTRODUCTION

In this report we summarize the major activities, accomplishments, and findings of a four-year research project funded by U.S. EPA's National Center for Environmental Research (NCER) through STAR Grant R826372 and carried out by the Southern Center for the Integrated Study of Secondary Air Pollutants (SCISSAP) at the Georgia Institute of Technology. The project funds were awarded to the Georgia Tech Research Corporation with Dr. W.L. Chameides, Smithgall Chair and Regents' Professor of Atmospheric Sciences in the School of Earth and Atmospheric Sciences at the Georgia Institute of Technology serving as the Principal Investigator. Dr. A.G. Russell of the School of Civil and Environmental Engineering at Georgia Tech served as a Co-Investigator (and leader of the modeling effort in the project). Subcontracts were awarded from Georgia Tech to the University of Minnesota (P. McMurry as Co-I), the University of Miami (R. Zika as Co-I), Duke University (P. Kasbhatla as Co-I), and the University of Alabama at Huntsville (D. McNider as Co-I).

In the Section 2 we provide a brief overview of SCISSAP – its goals, the approaches taken to achieve these goals, and its organizational structure. In the Section 3 we summarize the major accomplishments achieved by the program as a result of EPA funding. In Section 4 we review the major scientific findings of the project and the policy-implications of these findings. Section 5 provides describes the related quality control/quality assurance activities. In Sections 6 – 9 more detailed discussions are presented of the individual subprojects undertaken with EPA funds. Finally, a concluding Section 10 provides an overview of the project's accomplishments and the future research direction to be undertaken following the EPA funding.

## 2. AN OVERVIEW OF SCISSAP

The mission of the Southern Center for the Integrated Study of Secondary Air Pollutants (SCISSAP) is:

> *The development of the scientific understanding and analytical tools that underpin the design and implementation of an effective and integrated control strategy for secondary air pollutants, using the atmosphere of the southern United States as a natural laboratory.*

This mission is based on the premises that a basic understanding of the chemistry and physics of the atmosphere are a prerequisite for designing effective control strategies for secondary air pollutants; and that the concentration of secondary air pollutants in the atmosphere are often codependent because of interacting chemical reactions.

Over a four-year period beginning on April 1, 1998, SCISSAP was funded by U.S. EPA the NCER/STAR extramural funding program to focus on an integrated study of ground-level ozone ($O_3$) and particulate matter with diameters less than 2.5 μm ($PM_{2.5}$) in the South. Specifically, four major and interrelated scientific questions were addressed:

***Question 1**:* What is the composition and size distribution of fine particles in urban and rural locales in the southern United States and to what extent do temporal and spatial variations in these parameters correlate with those of ozone and its precursor compounds?

***Question 2**:* What are the major precursor compounds and sources for fine particles in urban and rural locales in the southern United States and to what extent do these compounds and sources correspond to/correlate with the sources of natural and anthropogenic ozone precursors (i.e., VOC and $NO_x$)?

***Question 3**:* To what extent, if any, is the chemical composition and abundance of fine particles in urban and rural locales in the southern United States affected by the concentration of natural and anthropogenic ozone precursors and/or ozone?

***Question 4**:* To what extent is the concentration of ground-level ozone in urban and rural locales in the southern United States affected by the concentration and composition of fine particles and/or the concentration of the precursors of fine particles?

To address these questions, two interrelated lines of inquiry were undertaken:

- **Instrumentation Development, Evaluation, and Implementation:** one line of investigation focused first on the development and testing of a mobile capability to measure $PM_{2.5}$, ozone, and their precursors, and then its subsequent application to large-scale, multi-investigator field experiments, as well as longer-term regional monitoring in the southeast;
- **Modeling:** the other focused on the development, evaluation and application of a regional scale air quality model for conducting integrated studies of ozone and particulate matter: the "Urban-to-Regional, Multiscale Model: One Atmosphere" (URM-1ATM), with one atmosphere used to denote an integrated approach to treating the physics and chemistry of ozone, acid deposition and particulate matter simultaneously.

### 2.1. SCISSAP Organization

The SCISSAP organizational approach closely paralleled the research paradigm for air quality research that has been developed by the Southern Oxidants Study (SOS) and led to significant advances in our understanding of photochemical oxidant pollution. It is based on the gathering of relevant chemical and meteorological data in carefully planned and coordinated field experiments, followed by comprehensive and multi-faceted analysis of the data using a combination of observation-based and emissions-based numerical tools in order to develop a self-consistent and rigorously tested set of conclusions (see for example, the relevant documentation available at url http://www2.ncsu.edu/ncsu/CIL/southern_oxidants/docs/state.html). The planning and implementation of these activities are carried out by a team of scientists and engineers from university, government, industry, and federal and state government institutions and agencies. While funds from U.S. EPA are typically used to support the university-based portion of the study, significant leveraging of these funds is obtained from the financial and in-kind support obtained from other governmental and industrial entities.

The SCISSAP research was coordinated by two collaborating teams: (i) A Field Measurements Team; and (ii) A Numerical Modeling Team, each a conjoining of university scientists (supported by EPA funds) and scientists from federal and state agencies and laboratories (supported by non-EPA funds). The Field Measurements Team Leader was Dr. W.L. Chameides and the Numerical Modeling Team Leader was Dr. A. G. Russell, both of the Georgia Institute of Technology. Dr. Chameides also served as Project Scientist with responsibility for overall coordination and integration of the project. From an even larger perspective, the SCISSAP's research activities were coordinated and integrated into the research functions and activities of SOS at no cost by the SOS Project Director's Office at North Carolina State University. In addition the SOS Executive Committee served as ad hoc scientific advisory committee.

## 3. SUMMARY OF MAJOR ACCOMPLISHMENTS:

During the 4-years of support for SCISSAP from NCER the SCISSAP Science Team successfully developed a unique capability in the southeastern United States: a facility for measuring $PM_{2.5}$ concentrations and composition as well as ozone and ozone- and fine-particle-gaseous precursors. This facility played a central role in a number of major regional air quality field experiments, most particularly in the 1999 Atlanta Supersite Experiment. The Science Team was also able to develop, evaluate, and apply a new multi-scale, multi-pollutant regional modeling system. Both the measurement facility and modeling system continue to serve a resource for the scientific and policy-making communities in the south and other regions of the United States.

Specific accomplishments are outlined below:

- Developed, field tested, intercompared, and implemented a Particle Composition Monitor (PCM) and related laboratory analytical techniques for measuring the mass and composition of $PM_{2.5}$ as well as its precursor compounds using the filter Denuder technique
- Developed, field tested, intercompared, and implemented a Differential Mobility Analyzer - Aerosol Particle Mass Analyzer (DMA - APM) for *in situ* measurements of particle mass as a function of mobility (i.e., size).
- Developed, field tested and implemented a system for quantifying *in situ* concentrations of oxygenated volatile organic compounds (OVOC).
- Participated in the 1999 SOS Nashville/Middle Tennessee Ozone Study; carried out first measurements of $PM_{2.5}$ vertical gradient within the boundary layer.
- Hosted, and provided analytical laboratory and meeting facilities for the 1999 Atlanta Supersite Experiment; also participated in the experiment.
- Participated in the 2000 Texas Air Quality Study.
- Operated urban and rural $PM_{2.5}$ monitoring sites in Tennessee and Georgia
- Developed an on-going regional center for air quality field measurements with a mobile measurement capability in the southeastern United States; this capability has played a key role in the State of Georgia supported Fall-line Air Quality Study As well as a locally-supported field experiment in Pensacola Florida during the Summer of 2002.
- Helped develop and evaluate a regional-scale air quality model (URM-1ATM);
- Used the URM-1ATM in the Southern Appalachians Mountains Initiative (SAMI) to address specific policy questions;
- Migrated many of the critical components of URM-1ATM to EPA's Models 3.

## 4. SUMMARY OF MAJOR FINDINGS

### 4.1. Findings from the Experimental Programs

In addition to developing and evaluating new and improved instrumentation and analytical techniques for characterizing air pollutant concentrations and characteristics, SCISSAP endeavored to use this technology in field experiments to test various hypotheses with regards to the characteristics and processes that control the characteristics of $PM_{2.5}$ in the southeast. Specific findings and their policy-relevant implications are outlined below.

**Finding 1.** $PM_{2.5}$ composition (at the 24-hour integrated sampling time used in the study) was found to show little variability across the sites operated from Nashville, Tennessee, to Atlanta Georgia, to Houston Texas (see Figure 3.1). In virtually all cases more than 60% of the $PM_{2.5}$ mass was found to arise from sulfate (and the ammonium associated with it) and organic carbon (and the other organic elements assumed to be associated with the organic carbon).

**Finding 2.** $PM_{2.5}$ mass, sulfate, nitrate, and ammonium concentrations were found to have a positive vertical gradient between 4 and 42 m altitude at a suburban site in Tennessee.

**Finding 3.** The daily variations in the chemical components of $PM_{2.5}$ exhibited little of no correlation with their gaseous precursors, and $PM_{2.5}$ mass was not well-correlated with local ozone concentrations..

**Finding 4.** $PM_{2.5}$ mass concentrations showed only moderate increases as one moves from rural to suburban to urban locales.

**Finding 5.** Different instrumentation designed to measure the mass and composition of $PM_{2.5}$ with 12- or 24-hour integrated sampling will generally yield comparable results with each other and with more sophisticated continuous and semi-continuous methodologies.

**Finding 6.** Under highly humid conditions (e.g., Atlanta in the summer) significant artifacts in the measurement of $PM_{2.5}$ mass using the filter technique can arise from the presence of solid hydrates on the filter.

**Finding 7.** Negative artifacts in the measurement of particulate organic carbon (OC) using EPA's FRM filter-denuder technique can arise as a result of the liberation of semi-volatile organics from the filter during the sampling.

**Finding 8.** Atmospheric particles of 100 nm and 300 nm in Atlanta at ~3-6% relative humidity typically had two distinct densities: $1.6 \pm 0.1$ g $cm_{-3}$ and $0.45 \pm 0.20$ g $cm_{-3}$.

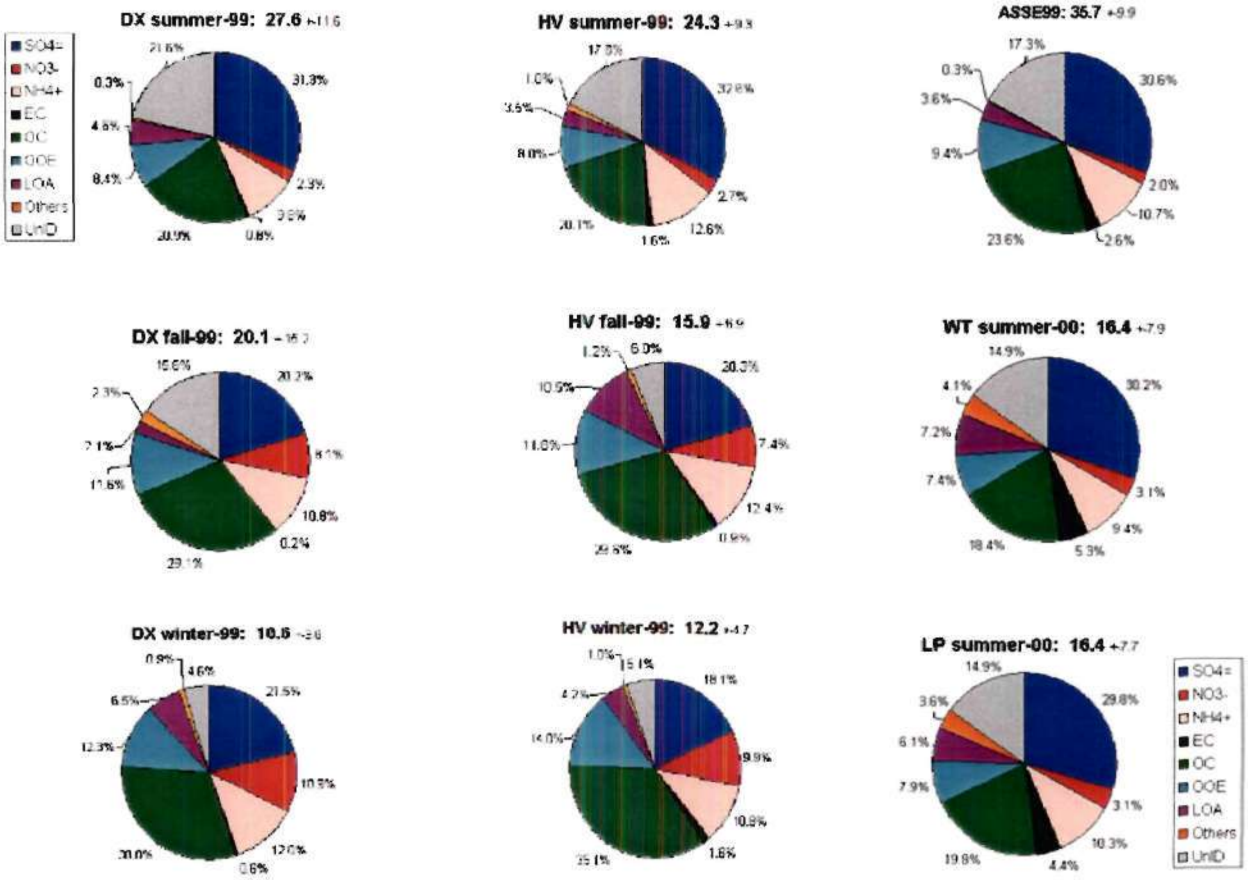

**Figure 3.1**. Average PM2.5 mass (indicated in mg/m$^3$ next to the site descriptor above each pie chart) and percentage composition as a function of season at rural Dixon, Tennessee (DX), and suburban Hendersonville (HV) near Nashville, TN, metropolitan Atlanta (ASSE99) and two Houston, Texas sites, LaPorte (LP) and Williams Tower (WT). Note: OOE denotes other organic elements other than C associated with organic C particulate matter (OC), LOA denoted light organic acids.

**Finding 9.** Effective densities of diesel exhaust particles decrease with increasing size. At 50 nm, densities are about 1.1±0.1 g cm$_{-3}$, while at 300 nm densities are about 0.3±0.05 g cm$_{-3}$.

**Finding 10.** The DMA-APM technique can measure the mass and density of spherical particles to within 5%.

**Finding 11.** The DMA-APM technique can measure the mass and "effective densities" of non-spherical particles.

**Finding 12.** Diagnostic analysis of measurements of PM2.5 composition and related gas-phase concentrations in Atlanta tend to support the notion that the amount of ammonium nitrate found in $PM_{2.5}$ is controlled by thermodynamic equilibrium between the $PM_{2.5}$ and gas-phase ammonia and nitric acid.

**Finding 13.** $PM_{2.5}$ in the southeast is generally slightly acidic with relatively small amounts of nitrate.

**Finding 14**. A positive correlation was found between simultaneously measured OVOC concentrations and speciated, size-segregated particulate OC abundances in Atlanta. Calculation of the hourly new particle production potential from hourly OVOC measurements suggest that gas to particle conversion is a significant source of new organic aerosols. This calculation of new particle production predicts approximately half of the measured $PM_{2.5}$ total organic carbon observed.

## 4.2 Findings from the Modeling Program – Addressing Overarching Questions

In addition to addressing the scientific and policy-relevant issues outlined above, the data gathered by SCISSAP and related programs were used to evaluate the URM-1ATM, being developed by the SCISSAP Modeling Team. Once successfully evaluated, the model was then used to comprehensively address the four major scientific questions SCISSAP set out to answer in its original proposal. Our findings are summarized below.

**Question 1:** What is the concentration and composition of $PM_{2.5}$ in urban and rural locales in the South and to what extent do temporal and spatial variations in these parameters correlate with those of $O_3$ and its precursor compounds?

**Finding 15**: While ozone and elemental carbon exhibit significant variations between urban and rural regions, most of the other components of $PM_{2.5}$ have relatively uniform concentrations between urban and rural areas, though certain regions have higher sulfate than others. On the other hand on urban scales there is a tendency for ozone and PM to be highest in or just downwind of urban areas.

**Question 2**: What are the major precursor compounds and sources for PM2.5 in urban and rural locales in the South and to what extent do these compounds and sources correspond to or correlate with the sources of natural and anthropogenic $O_3$ precursors (i.e., VOC and $NO_x$)?

**Finding 16:** The major precursors for $PM_{2.5}$ in the southeast are $SO_2$ (largely from coal fired power plants) and organic carbon, from a myriad of sources including biogenic (e.g., biomass burning and secondary conversion of higher organics) and anthropogenic (automobiles, cooking, etc.). Nitrate plays less of a role at present since the aerosol is so acidic that much of the ammonia that is necessary for ammonium nitrate formation is tied up as ammonium sulfate. Ammonia, largely from animal waste and fertilizer use acts to form a fraction of the PM mass, but is important as it is the primary neutralizing agent. For ozone, the two primary precursors are $NO_x$ and, again, organics. Automobiles appear to play a major role, followed by electrical generating units in terms of ozone formation due to $NO_x$ emissions. Automotive (in urban areas) and biogenic (most everywhere else) sources, as well as solvent usage, have the most impact on forming ozone from the VOC perspective.

**Finding 17:** Sensitivity maps show that both ozone and sulfate have similar source-impact patterns. Thus, one would expect that controls for precursors of both pollutants would have benefits over the same general area.

**Finding 18:** Inverse modeling suggests that the inventory of anthropogenic VOC emissions in the eastern United States is too low by a factor of ~2.

**Question 3**: How are the formation rates and concentrations of O3 and $PM_{2.5}$, as well as the $PM_{2.5}$ composition affected by the relative emissions and concentrations of $NO_x$, $SO_x$, NH3, and VOC species, and what are the mechanisms responsible for these relationships?

**Finding 19:** Over most of the domain, ozone formation is $NO_x$-limited, though not always in urban areas where there can be a greater sensitivity to VOC emissions. Outside of primary emissions of particulate matter, $SO_x$ appears to be the most sensitive precursor for PM formation since it also captures ammonia and water. Sulfate appears to be formed primarily via gas phase oxidation, though aqueous phase reactions are important. Organic PM appears to be split between primary emissions and oxidation of biogenic emissions. Nitrate is formed from oxidation of $NO_2$, which takes place both during the day and at night, followed by reaction with ammonia. Ammonia acts as a neutralizing agent for sulfate and nitrate. The nitrate is highest, at least during the summer, in the early morning hours when the air is cooler and more humid, promoting condensation.

**Finding 20:** We do find that elevated NOx sources are less efficient at forming ozone than ground level sources, as has been found from aircraft studies as well. Increased emissions, while increasing ozone, can decrease the "ozone production efficiency" (OPE). We see a much more linear response in $SO_2$ emissions.

**Question 4**: To what extent do the mechanisms elucidated above affect the formulation of an integrated control strategy for $O_3$ and $PM_{2.5}$?; and Do our findings suggest an "optimum" strategy for addressing both pollutants?

**Finding 21:** Strategies to reduce $NO_x$ and $SO_2$ simultaneously will be effective in reducing ozone and PM at the same time. For example, using new, combined cycle gas turbines (or coal gasification), could lower both pollutants effectively. On the other hand, one could envision controls that only go after one of the precursors alone. We did not do an economic optimization to find which would be best. Also of importance, both ozone and PM share a largely uncontrollable source, biogenics such as trees, which will limit the effectiveness of controls. For example, there will be a limit on how low PM levels can go since the biogenic fraction appears to be substantial on stagnant and hot days. Further, in the Southeast, VOC controls primarily will be effective only in and around urban areas, at least on high ozone days.

**Finding 22:** Our model results show (and as indicated by the measurements) that, at times, reducing $SO_2$ emissions, and hence PM sulfate, can be offset by increased nitrate aerosol as ammonium is no longer tied up neutralizing the sulfuric acid. The extent of this was quite varied over the region. In some cases, this led to a very small impact, though at other times and locations upwards of about 50% of the reduction in sulfate could be lost by an increase in ammonium nitrate. It was also found that this result will change in the future as $SO_2$ emissions are reduced due to acid rain controls and ammonia emissions may increase due to increased agricultural operations. In such cases, the effect of reduced sulfate leading to increased nitrate becomes more significant. We also found that there is a seasonal dependence. As part of a separate project, using URM-1ATM, we found that over a synthetic year that the replacement phenomena led to a relatively small reduction in the overall benefits of $SO_2$ control, on the order of 10%.

### 4.3 Policy-relevant Implications of Scientific Findings

*A. Emission control strategies:*

1. As is the case for ground-level ozone pollution, $PM_{2.5}$ pollution in the southeastern United States is regional in extent. The fine particle sources appear to be regionally distributed with perhaps direct emissions of $PM_{2.5}$ and its precursors and/or secondary formation of $PM_{2.5}$ occurring aloft as opposed to at the surface; and therefore

2. Mitigation of $PM_{2.5}$ pollution in the southeastern United States will likely require the development and implementation of regional as opposed to urban-scale emission control and pollution prevention strategies.

3. $PM_{2.5}$ mass in the southeastern United States is dominated by OC and sulfate, and therefore control strategies that aim to reduce total fine particle mass concentrations will require emission reductions in organic carbon and sulfur oxides ($SO_x$); however,

4. In the southeast, there is generally an inadequate amount of ammonia to neutralize sulfate and hence $PM_{2.5}$ is slightly acidic and this in turn limits the amount of particulate nitrate that can form. Thus $PM_{2.5}$ mitigation efforts based on reducing particulate sulfate by decreasing $SO_2$ emissions may be offset, to some extent, by a concomitant increase in particulate nitrate; and therefore

5. It would be prudent to consider implementation of controls on $NO_x$ and $NH_3$ emissions at the same time that $SO_x$ controls are implemented. Controls on $NO_x$ emission will have the added benefit of mitigating regional ground-level ozone

pollution.

6. Controls on the gaseous emissions of OVOC and their precursors could have a significant impact on reducing $PM_{2.5}$ mass concentrations in Atlanta.

7. Controls on particulate emissions from diesel engines may lead to the elimination of a unique class of "low density" particles that were observed in the Atlanta atmosphere.

*B. Fine Particle Monitoring*

8. While the US EPA-approved denuder-filter technique can yield reasonably robust measurements of $PM_{2.5}$ mass and composition, the method is subject to artifacts and thus thorough QA/QC procedures and self-consistency checks must be adopted with this technique. For example, accurate estimates of total organic mass require development and application of methods for quantifying and correcting for artifacts arising from liberation of semi-volatile organics.

9. The DMA-APM provides a precise and accurate technique for measuring particle density thereby enabling a determination of the definitive relationships between aerodynamic and mobility equivalent diameters. This relationship helps to reconcile measurements based on different physical principles; Also

10. In-situ techniques for semi-continuous, direct measurement of mass size distributions and concentrations can provide insights into the accuracy of filter-based measurements of mass concentrations, such as are used in EPA's FRM network, as well as the health impacts of short-term variations in fine particle mass and composition.

## 5. Summary of Quality Assurance/Control Activities

The SCISSAP Science Team is and has been committed to the production of high quality and reliable data, modeling products, and outputs. As a result Quality Integrated Work Plans for the experimental and modeling portions of the project were developed and submitted to U.S. EPA for review, comment, and ultimate approval during the summer of 1998. Assessment of data quality involved field audits by U.S. EPA personnel as well as systematic calibrations, zero spans, and careful and complete documentation (on record in the SCISSAP 14th Street laboratory facility). Quality assurance on the modeling side involved algorithm testing and intercomparisons between Georgia Tech and Duke University personnel as well as comprehensive evaluations using pseudo and real data. However, the ultimate quality assurance of our activities has been the submission and publication of our work in the peer-reviewed literature. A listing of the peer-reviewed articles currently published, in press, or under peer-review is provided in Appendix I.

## 6. SCISSAP PM, $O_3$, and PRECURSOR MEASUREMENTS[1]

SCISSAP's main objective over the past four years has been to advance our understanding of the physical and chemical processes that couple the formation of secondary air pollutants, in particular $O_3$ and $PM_{2.5}$ in the Southeastern United States by contrasting measurements in rural, suburban, and urban-metropolitan sites. Within this framework, a **Particle Composition Monitor (PCM)** was developed for discrete measurements of $PM_{2.5}$ mass and composition including relevant gas-phase species. The main species quantified and reported are the particle phase sodium ($Na^+$), potassium ($K^+$, since 2000), calcium ($Ca^{2+}$), ammonium ($NH^{4+}$), fluoride ($F_-$, starting in 2000), chloride ($Cl^-$), nitrate ($NO_3^-$), sulfate ($SO_4^{=}$), formate ($HCOO^-$), acetate ($CH_3COO^{-)}$, and oxalate ($C_2O_4^{-}$), as well as elemental and organic carbon (EC, OC). In addition to the particle bound species, the PCM also measures the important gas-phase species $NH_3$, HCl, HONO, $HNO_3$, $SO_2$, and the light organic acids (LOA) HCOOH, $CH_3COOH$, and $(COOH)_2$ over discrete sampling time intervals.

As part of the Southern Oxidants Study (SOS), long-term measurements were conducted at two sites in the Nashville, Tennessee area, and intensive measurements were made during August 1999 as part of the Atlanta Super Site Experiment (ASSE99), and in

August and September 2000 in Houston, as part of the Texas Air Quality Study (TexAQS2k), where measurements were conducted at LaPorte, and at Williams Tower, 254 m above ground. During the SOS field experiment conducted on a multi-institutional level during June and July 1999, measurements at the two Tennessee sites, the more rural Dickson, and the suburban Hendersonville, were intensified as well. The facilities at the suburban Hendersonville site allowed daytime-nighttime separated measurements of vertical gradients (between 42 and 4 m agl) of $PM_{2.5}$ mass and major ions concentrations, as well as temperature, relative humidity, wind speed, and direction, as illustrated in Figure 6.1. Vertical gradients of the basic meteorological parameters allowed certain characterization of atmospheric stratification and mixing. The following Table 6.1 summarizes all locations, site names, characters and periods for which PCM measurements were made.

**Table 6.1**: SCISSAP site names, locations, characters and periods

| **Site name** | **Coordinates lat.(N)/long.(W)/el.(masl)** | **Character** | **Period** |
|---|---|---|---|
| Dickson, TN | 36.161/87.298/225 | rural | 07/02/99 – 04/05/00 |
| Hendersonville, TN | 36.298/86.653/143 | suburban | 07/02/99 – 04/05/00 |
| *Atlanta, GA* | | | |
| East Rivers ES | 33.820/84.389/251 | urban | 06/25/98 – 09/19/98 |
| Jefferson Street | 33.777/84.414/265 | urban | 02/16/99 – 09/26/99 |
| 14th Street | 33.787/84.406/298 | urban | 09/28/99 – 06/02/00 |
| *Houston, TX* | | | |
| LaPorte Airport | 29.671/95.069/ 8 | urban | 08/15/00 – 09/14/00 |
| Williams Tower | 29.750/95.475/284 | urban | 08/15/00 – 09/13/00. |

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[1] **Prepared by**: Karsten Baumann, School of Earth and Atmospheric Sciences, Georgia Tech

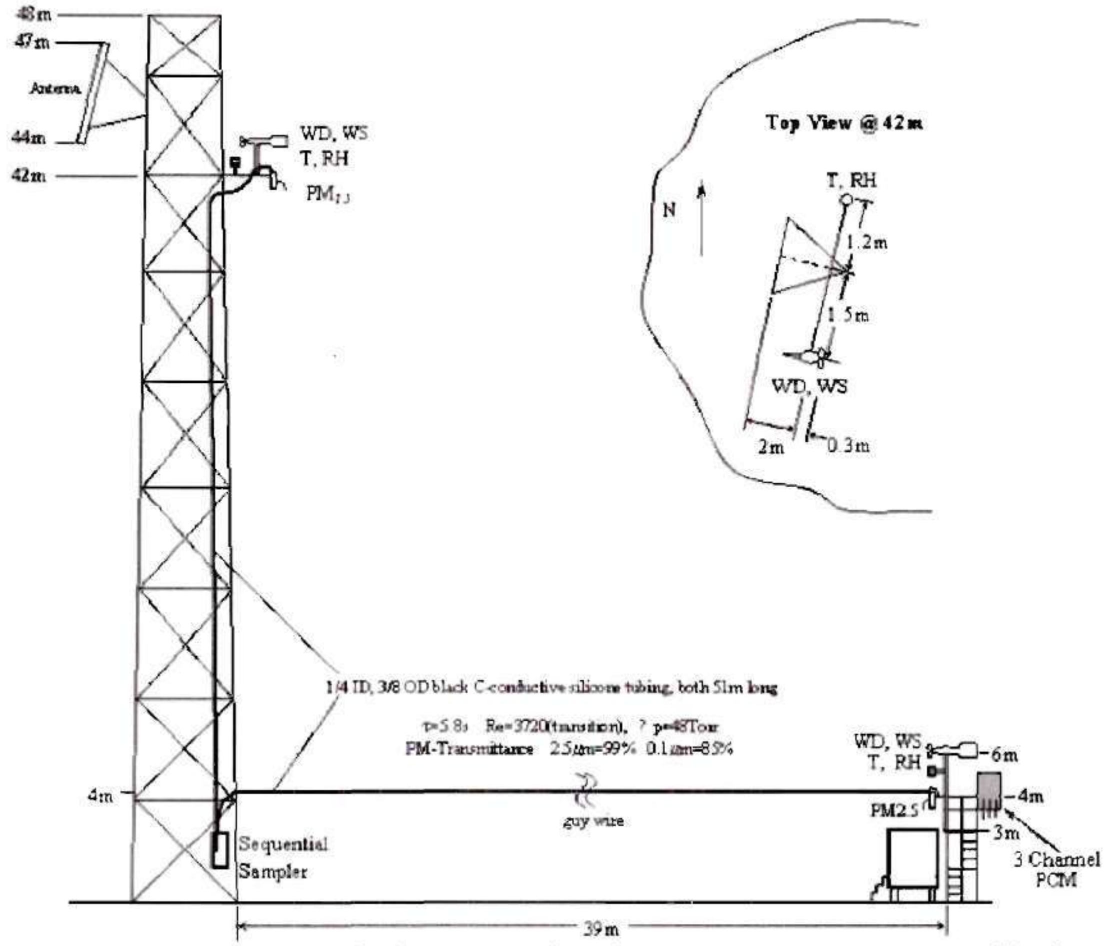

**Figure 6.1:** Schematic showing instrumentation of 48 m tall tower at Hendersonville site used to measure vertical gradients (42 vs 4 m agl) of meteorological parameters, $PM_{2.5}$ mass and major ions concentrations.

The sampling frequency usually was about one 24h sample per week, however, more frequent sampling, up to 3 samples per day, has been conducted during the above mentioned collaborative research intensives. During these intensive periods, the SCISSAP team carried out tower-based meteorological and continuous gas measurements, in addition to its discrete $PM_{2.5}$ mass and composition measurements, involving the deployment of the Center's Air Quality Research Trailer (AQRT). In addition to serving as measurement platform, the AQRT hosted up to three additional research groups during those field intensives:

- Aerodyne Research Inc., lead by Dr. Doug Worsnop (TexAQS2k only);
- Particles in Liquid Solution (PILS) measurement group, lead by Prof. Rodney Weber;
- Aerosol Optical Properties (AOP) measurement group, lead by Prof. Mike Bergin.

### 6.1. PCM Sample Collection and Analysis

Details of the PCM operational characteristics are described in *Baumann et al.* [2003] and are briefly summarized here. The PCM is a bottom-up type sampler consisting of three channels as illustrated in Figure 6.2. Each channel follows the same principle of successive separation of particles larger than 2.5 microns aerodynamic diameter, followed by the separation of gaseous species prior to $PM_{2.5}$ collection on inert substrates with absorbing backup filters. Particles larger than 2.5 microns aerodynamic diameter are separated by standard, Teflon coated cyclone heads (URG, 116 S Merrit Mill Rd, Chapel Hill, NC 27516) with an estimated $D_{50}$ cut-off value for 50% aerosol penetration of 2.46 ±0.015 μm (1-sigma), and a "sharpness" $(D_{16}/D_{84})_{0.5}$ of 1.45. The sample air passes through a 30 cm long inlet tube with 14 mm ID prior to entering the cyclone. Tubes and cyclones are coated with two 25 μm thick layers of polytetrafluorethylene (PTFE) and perfluoroalkoxy (PFA) monomers. Special tests performed in comparison with fused silica coated inlets and cyclones showed the Teflon coat having superior characteristics for the transmission of $NH_3$ and $HNO_3$ gases. The transmission efficiency of new, cleaned surfaces varied between 82 and 99%, and would slightly increase with increased use for ambient air sampling, pointing to possible surface passivation effects, particularly for gaseous $NH_3$ and $HNO_3$.

As illustrated in Figure 6.2, two of the three PCM channels are dedicated for the determination of ionic species following sample analysis via ion chromatography (IC), while the third channel yields quantitative analysis of the elemental and organic carbon (EC, OC) content of the $PM_{2.5}$ samples using the thermal optical transmittance (TOT) method of *Birch and Cary* [1996]. Alkaline gases like $NH_3$ are removed in the first channel, and acidic gases such as HONO, $HNO_3$ etc. are removed in the second channel by means of 3-annuli denuders (concentrically arranged etched glass tubes, URG Corp.) coated with a 200 mM citric acid and a 150 mM sodium carbonate solution, respectively. The same coating solutions are applied to Whatman 41 cellulose fiber filters placed downstream of the Teflon filters (Zeflour P5PJ047, Gelman, Ann Arbor, MI, 2∝m nominal pore size, and 47mm diameter), in order to capture volatilization losses that occur as a result of the altered gas/solid phase equilibrium after removal of gaseous species in the denuders.

Artifact reactions involving $NO_2$, $O_3$, and water vapor are particularly important in the HONO and $HNO_3$ denuder measurements. Using a tandem denuder set-up allowed the investigation of secondary surface induced $O_3$ reaction, which was found to potentially overcorrect the nitrite to nitrate oxidation step on the denuder walls, underestimating [$HNO_3$] and correspondingly overestimating [HONO]. Therefore, the ambient [$HNO_3$] and [HONO] were simply calculated from the differences in nitrite and nitrate found on the 1st and 2nd denuder, considering the combined disproportionation reaction ($2\ NO_2 + H_2O \rightarrow HNO_3 + HONO$), plus the reductive surface conversion of $NO_2$ to nitrate ($NO_{2g} + Na_2CO_3\text{-wall} \rightarrow NO_{2\,surface}$), but neglecting the secondary $O_3$ oxidation step ($NO_{2\ surface}^{-} + O_3 \rightarrow NO_{3\ surface}^{-} + O_2$). Denuder breakthrough was insignificant for $NH_3$ and $SO_2$, but not so for the light organic acids.

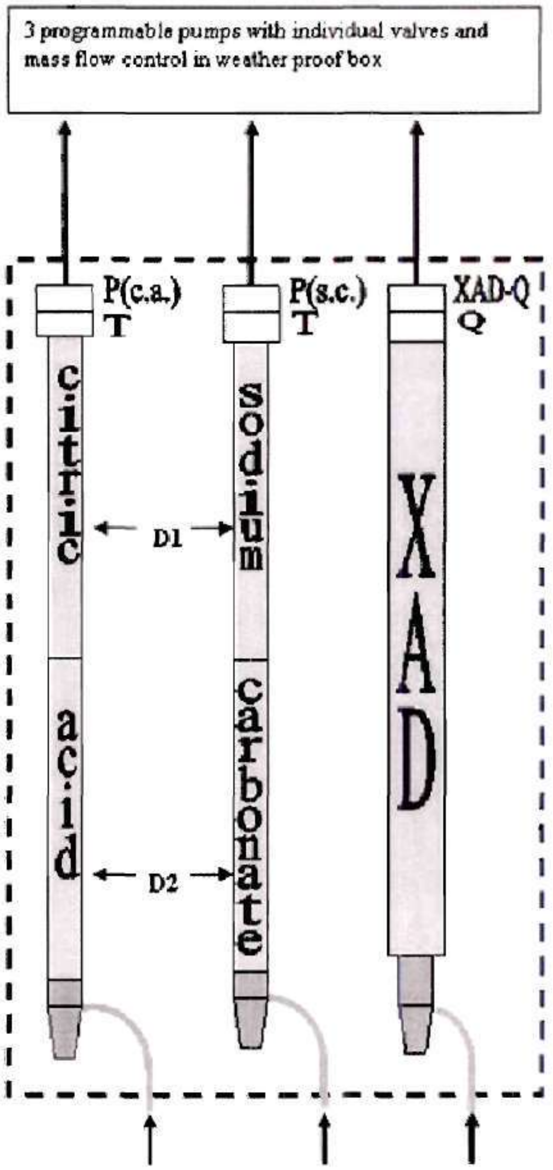

**Figure 6.2:** Standard PCM setup with three independent sampling channels in a weather proof, temperature controlled box. The 30 cm long Teflon coated inlets (ID= 1.4 cm) are attached to cyclones with 50% cutpoint efficiency for 2.46 ∝m aerodynamic diameter at 16.7 l $min^{-1}$ flow rate, resulting in a filter face velocity of 20 cm $s^{-1}$. *D1, D2*… 3-annuli denuder tandem $Na_2CO_3$ / $C_6H_8O_7$ coated, 24 and 15 cm long, 0.1 and 0.06 s sample residence time under plug flow (Re=295), respectively; *XAD*…8-annuli coated denuder, 28.5 cm long 0.8 s residence time; *T*…Teflon filter, 2 ∝m Zeflour™; *P*…paper filter, Whatman 41, $Na_2CO_3$ / $C_6H_8O_7$ coated; *Q*…quartz filter, pre-baked;
*XAD-Q*…XAD coated quartz filter.

The coating solutions for both denuders and paper filters were prepared and applied in dedicated glove boxes under clean, filtered air micro-environments, in order to keep laboratory contamination, and therefore field blank levels at a minimum (see data quality section). The alkaline coated denuders of 15 and 24 cm lengths were found near

100% effective in retaining the particularly "sticky" gaseous species $NH_3$ and $HNO_3$, respectively. The actual efficiency with which the denuders retained less sticky species, e.g. light organic acids, was governed, however, by the adsorption efficiency of the coated surface, and was determined experimentally via a tandem set-up with two denuders in series. The sample residence times through the triple-annuli portion of each denuder, assuming plug flow at Re = 295, were 0.06 s and 0.1 s, respectively.

Extractions were performed under a laminar flow hood with a mixed filter-bed of activated carbon and citric acid. Each denuder was subject to a two-step extraction assuming a total volume of 30 ml DDW. Field blanks for each sample medium type (i.e., denuders, Teflon and coated paper filters) were carried together with each sample. These blanks were handled the same way as the actual samples and served two purposes, taking into account possible contaminations as a result of handling/mounting/dismounting the samples, and determination of the detection limits for each species investigated.

The Teflon and paper backup filters from channel 1 were dedicated for particle-phase cations $Na^+$, $Ca_2^+$, and $NH_4^+$, while particle bound concentrations of $C^-$, $NO_3^-$, $SO_4^{2-}$, as well as formate, acetate, and oxalate were determined from the channel 2 samples. Only ammonium nitrate and the organic acids were considered subject to possible volatilization loss off the Teflon filters (negative artifact). All filters were 47 mm in diameter and experienced a face volicity of ~20 cm $s_{-1}$ at nominal sample flow rates of 16.7 lpm. The gravimetric mass of the sampled $PM_{2.5}$ was determined from the Teflon filters, after an equilibration process as described later. Once the Teflon filter mass had been determined, the filters were extracted via 30 minute sonication in 30 ml heated DDW. The paper filters (blank included) underwent a two-step 20ml DDW extraction under a laminar flow hood supplied with a bed of activated carbon and citric acid providing contaminant-free air.

IC analysis was used to determine the soluble ion content of the various extracts applying a dual-channel Dionex DX-500 ion chromatograph with two separate EG40 eluent generators; KOH for anions, methane-sulfonic acid (MSA) for cations, controllable to within 0.5 and 50 mM, and IonPac analytical columns AG11-HC for anions and CS12A for cations, both in the 2 mm ID microbore format. Each channel operates a self-regenerating SRS-ULTRA suppresor in external DDW regeneration mode, a CD20 conductivity detector, and a GP50 gradient pump. The applied micro-bore system allows economical analyte flow rates of 0.25 ml/min for cations, and 0.35 ml/min for anions. DDW is supplied by a Barnstead E-Pure at a resistivity of 18.0 ±0.3 M and fed directly to the EG40. Degassing is performed on-line immediately after the eluent is added to the DDW well upstream of the injector.

In order to minimize the artifacts induced by semi-volatile organic compounds (SVOC) that exist in the atmosphere in equilibrium between the gas and particle phases, the sampling principle applied to channels 1 and 2 was also applied to channel 3, by use of an XAD-coated denuder upstream of the (pre-baked) sample quartz filters (Pallflex #2500 QAT-UP). This denuder was a downsized version of the one used in the IOGAPS, and identical to what has been reported as the Versatile Air Pollution Sampler (VAPS) by *Stevens et al.* [1993] and *Pinto et al.* [1998]. The effective coating material was finely ground XAD-4 resin, a porous macroreticular, nonpolar, polystyrene-divinylbenzene resin, which is insensitive to highly volatile organic compounds (VOC) but was selected as the sorbent because of its high surface area (725 $m_2$/g) for adsorption of a wide range of gas phase SVOC from the airstream [*Lane et al.*, 2000]. Also similar to channels 1 and 2, the application of an XAD-denuder upstream of the quartz filter disturbs the gas-particle equilibrium of the condensable organics, potentially enhancing losses of semivolatiles from the collected particles (negative artifact), therefore requiring the use of an appropriate adsorber downstream of the main $PM_{2.5}$ filter substrate, in order to adequately account for volatilization losses of semi-volatile compounds. A XAD-coated quartz filter was used as the backup adsorber and analyzed for (operationally defined) SVOC via a specially modified TOT program run. In contrast to the conventional TOT analysis program [*Birch and Cary*, 1996], where EC is measured in a 5.24 % $O_2$ atmosphere after the $O_2$-free OC-stage, the evolving carbon here is being oxidized exclusively by surface catalysis (using the $MnO_2$ bed at 900°C) in a pure He atmosphere. The oven temperature at the punch is stepped up to 176 $_o$C from ~50 $_o$C within ~1 min and held constant at 176 °C for a period of ~3 min. In contrast to a regular, uncoated quartz filter run, no $O_2$ is introduced to the oven and no EC is generated or measured. The split point between OC and EC, which is usually determined by the point where the same amount of laser light is being transmitted through the punch as before the sample run, is made here meaningless and set before the internal $CH_4$ calibration. As for all sample media, field blanks were carried and analyzed for each XAD-coated quartz sample filter as well.

### 6.2. $PM_{2.5}$ Mass Determination

Due to the disturbance of the gas/particle phase equilibrium imposed on the particles collected on the Teflon filters by use of denuders, *blow off* of semi-volatile species had to be accounted for. The semi-volatile fractions of $NH_4^+$, $NO_3^-$, and the light organic acids retrieved from the adsorbing paper backup filters (considering blanks and denuder efficiencies) were added to the gravimetric mass determined from the Teflon sample filter. Mostly due to their relatively high volatility, the light organic acids were undetectable via the TOT analysis on quartz filters.

The total $PM_{2.5}$ mass concentration was determined gravimetrically from the Teflon filters prior to IC extraction using a Mettler Toledo MT5 Electronic Balance in a temperature (21 ±1 $_{o}$C) and humidity (35 ±3 %) controlled class 1000 clean room. The micro-balance maintained a linear range between 0 and 500 mg to within ±0.0004% and a detection limit of 0.37 ±0.7 ∝g for all measurements subject to this report.

During the ASSE99, a sub-set of Teflon filter samples was investigated further to quantify the level of mass artifact introduced by hydrates formed from water vapor attracted by the hydrophylic components of the sampled particles and incorporated in a matrix of molecules or ions. Therefore, if the water concentration is not high enough to yield a liquid solution, water molecules will be incorporated into the solid phase compounds and result in hydrates. In order to accelerate the dehydration process, the sub-set of Teflon filters was placed in a desiccator using anhydrous calcium sulfate (97% $CaSO_4$, 3% $CoCl_2$, W.A. Hammond Drierite Co. Ltd., Xenia, OH), which resulted in an acceleration of the dehydration rate of up to 9-fold compared to simple exposure in the clean room. The dehydration process was determined to be complete when subsequent gravimetric measurements yielded a change within ±10 %, which was typically the case after ~4 weeks of clean room exposure. The sub-set of these Teflon filters was also used to verify that the observed loss of mass is not due to losses of any of the identified ionic species. Corresponding IC analyses showed that the change in ion content after dehydration was indeed below the determined level of precision of the measurement. Therefore, the mass loss is assumed to be predominantly caused by condensed water vapor in the form of hydrates. Figure 6.3 shows the final mass after dehydration versus the initial mass weighed after the samples had been exposed in the controlled clean room environment for ~24 to 48 h. As shown by the slope of the linear regression (0.774 ±0.028 standard error), the water vapor induced mass artifact is on average ~20 % ($R^2$=0.94, n=11), and the 1-sigma variation of the artifacts is ±8 %.

In consequence of this finding, all Teflon filter samples collected after ASSE99 were dehydrated by either prolonged exposure in the clean room or more commonly (since more effectively) by desiccation prior to gravimetric mass determination. The gravimetric $PM_{2.5}$ mass concentrations determined from all ASSE99 Teflon filter samples as well as from all samples collected at Dickson and Hendersonville, TN, that had not been actively dehydrated were retro-corrected by the above factor of 0.774.

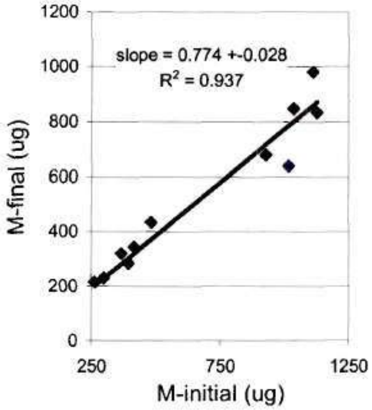

**Figure 6.3:** Absolute mass lost due to dehydration from regression of the final desiccated $PM_{2.5}$ mass ($M_{final}$) versus the initial gravimetric $PM_{2.5}$ mass ($M_{initial}$) of a sub-set of 11 Teflon sample filters from ASSE99.

## 6.3. Continuous Measurements of Gaseous Tracers

As mentioned above, the AQRT served as a mobile platform for auxiliary meteorological and gas phase measurements (NO, $NO_x$, $NO_y$, $O_3$, CO, $SO_2$, UVB and global radiation, wind speed and direction, relative humidity, various air and soil temperatures and ambient pressure), besides hosting research collaborators for joint intensive field studies. The following briefly describes the most important features of the continuous gas phase measurements.

$O_3$ was measured using a pressure and temperature compensated commercial UV absorption instrument (model TEI 49-C, TEI, Inc., Franklin, MA), being absolutely calibrated by the known absorption coefficient of $O_3$ at 254 nm. The linearity and precision of the analyzer was checked on average once every 22 hours. Precision check mixing ratios of 0, 90, 180, 270, and 360 ppbv were provided by a primary standard calibrator with active feedback control (model TEI 49C-PS). The calibrator was supplied with $O_3$-free (zero) air from a cartridge of activated carbon that effectively removed $O_3$ from the ambient air. Each precision check resulted in a 5 point linear regression. Assuming normal distribution of the regressions' intercepts, the $O_3$ analyzer's detection limit was and typically is 1.0 ppbv; whereas the slopes of the linear regressions yielded ±4 % precision. The accuracy is estimated to be the same. The same type analyzer was deployed at Williams Tower during TexAQS2k and was subjected to the primary standard calibration procedure before and after the study yielding a similar level of quality.

CO was measured by gas filter correlation, nondispersive infrared absorption (model TEI 48C-TL with a hand-selected PbSe detector matched with an optimal preamplifier, and an absorption cell with gold-plated mirrors). The signal output was pressure compensated while the absorption cell temperature was controlled at 44 ±0.1 $_o$C. A zero trap of 0.5 % Pd on alumina catalyst bed (type E221 P/D, Degussa Corp.) kept at 180 C quantitatively oxidized CO to $CO_2$ at an efficiency greater 99 %, and allowed the switching of zero modes every 11 min for 2 min. NIST traceable calibration gas of 405 ±4 ppmv CO in $N_2$ (Scott-Marrin Inc., Riverside, CA) was introduced into the sample stream by mass flow controlled standard addition and dynamic dilution at the instrument inlet for 2 min approximately every 11 h. The detection limit for a 1 min average based on the 1 Hz data was ~107 ppbv, and ~23 ppbv for a 1 h average. The instrument's precision, determined from the standard addition span checks, was ±9 % at ~570 ppbv. The accuracy was estimated as the RMS error of uncertainties in the calibration tank concentration (2 %), the mass flow controllers (4 % each MFC), the background variation (4 %), and potential inaccuracies from interpolation of the measured ambient CO during span checks (15 %). Thus, the total uncertainty in the CO measurement is estimated at ±17 % for the entire measuring range. The instrument's linearity within its 5000 ppbv range was determined from all calibrations performed during each study (zero excluded), and revealed an $R^2$ of 0.98.

$SO_2$ was measured by use of a commercial, pulsed UV fluorescence instrument (model TEI 43C-TL) with pressure and temperature compensated signal output. It's response time was ~45 s and therefore, required longer zeroing and calibration periods compared to the CO instrument: zero for 4 min once every 55 min; calibration - via mass flow controlled standard addition of 30.6 ±0.3 ppmv $SO_2$ in $N_2$ NIST traceable calibration gas (Scott-Marrin Inc.) and dynamic dilution at the instrument inlet – was performed for

4 min once every 11 hours. Zero [$SO_2$-free] air was produced by passing ambient air through a HEPA glass fiber in-line filter (Balston) impregnated with a 0.15 molar $Na_2CO_3$ solution. At a flow rate of 0.9 slm, the filter removed >99 % of the $SO_2$ in the sample. Calibrations were performed and evaluated analogous to the CO measurements resulting in a detection limit of 4.3 ppbv for 1 min, and 0.08 ppbv for 1 h averages, and a precision of ±4 % at 60-130 ppbv. Since the instrument's measurement principle is known to be sensitive to organic hydrocarbons (HC), the efficiency of the internal HC removal through a semi-permeable wall was enhanced by introducing an activated carbon trap into the flow of the low-[HC]-side of the wall, and thereby further increasing the [HC] gradient across the wall. NO is known to be another interferent, and its level of interference was examined by standard addition of NO calibration gas, resulting in a 2-3 % increase of signal. The $SO_2$ data were not corrected for this relatively small interference. The accuracy was estimated as the RMS error of uncertainties in the calibration tank concentration (2 %), the mass flow controllers (4 % each MFC), the background variation (12 %), the NO interference (2 %), and potential inaccuracies from interpolation of the measured ambient $SO_2$ during span checks (10 %). Thus, the total uncertainty in the $SO_2$ measurement is estimated at ±17 % for the entire measuring range. The instrument's linearity within its 200 ppbv range was determined from all calibrations during the study, and revealed an $R^2$ of 0.99.

Proto-type Air Quality Design (AQD, Golden, Colorado) NO/$NO_y$ and NO/$NO_x$ analyzers were deployed for the measurement of NO, $NO_x$, and total reactive nitrogen oxides ($NO_y$) that include NO, $NO_2$, $NO_3$, $N_2O_5$, HONO, $HNO_3$, aerosol nitrate, PAN and other organic nitrates. The $NO_y$ measurements were based on the principal method of metal-surface induced reduction of the more highly oxidized species to NO, and its subsequent chemiluminescence detection (CLD) with excess ozone. The metal surface here was a 35 cm long, 0.48 cm ID MoO tube (Rembar Co., Dobbs Ferry, NY), temperature controlled at 350 ±2 $_o$C, and housed inside an inlet box mounted to the met tower ~9 m above ground. The NOx measurements made 4.5 m agl, utilized a Xe/Hg photolysis system with an average $NO_2$ conversion fraction of 12 ±3 % at 1 s sample residence time. The data quality of all the gas-phase measurements are summarized on the basis of 1 min averages in Table 6.2.

**Table 6.2:** Detection limits (DL), precision, and accuracy for the continuous measurement of $O_3$, CO, $SO_2$, NO, $NO_x$, and $NO_y$

| | $O_3$ | CO | $SO_2$ | NO | $NO_x$ | $NO_y$ | |
|---|---|---|---|---|---|---|---|
| DL (ppbv) | 1 | 23* | 0.08* | 0.003 | 0.5 | 0.4 | |
| Precision (%) | | ±4 | ±9 | ±4 | ±10 | ±15 | ±15 |
| Accuracy (%) | | ±4 | ±17 | ±17 | ±15 | ±25 | ±20 |

* based on a 1 h average.

The sample air was drawn continuously through a 15 cm long 0.64 cm OD SS tube, which extended ~5 cm to the outside bottom of the box and was coupled to two SS crosses, where the flow was diverted to a MoO converter tube for the $NO_y$ and a bypass PFA tube of same length for the NO measurement, at 1 slm respectively. All SS components were Teflon coated and temperature controlled at 40 $_o$C. A stream selector assembly with mass flow controllers (MFC) housed inside the inlet box, which reduced the sample residence time inside the PFA tubing between the inlet box on the tower and the CLD unit inside the mobile lab at the ground to < 0.2 s. NO and $NO_y$ measure modes were switched every 2 minutes. Automated calibrations were performed via a programmed set of NO, $NO_2$, n-propyl nitrate (NPN), and $HNO_3$ standard additions to the sample inlet on average 2 times per day in ambient air, and about once per day in zero air.

The calibrations allowed the determination of specific parameters that are relevant for the assessment of the overall instrument performance, such as sensitivity, artifacts, detection limits, and conversion efficiencies of the MoO tube.

In summary, the NO detection limit for a 1 min integration time was 3 ±0.5 pptv in ambient air and 2 ±0.1 pptv in zero air at a signal-to-noise ratio of 2, respectively. The instrument's overall sensitivity to ambient NO (S_NO) averaged to 3.57 ±0.6 Hz pptv$_{-1}$ in ambient air and 4.39 ±0.15 Hz pptv$_{-1}$ in zero air. A difference in signal was present when sampling zero air in NO measure mode versus NO zero mode, displaying a NO artifact (A_NO), which was 28 ±4 pptv. A_NO was interpolated between calibrations and subtracted from the ambient NO measurements. Since the zero volume efficiency was less than 100 %, i.e. on average 97 ±3 %, the instrument's zero varied with ambient NO and $NO_y$ levels, respectively. Thus, during low level periods sporadically occurring at night, the NO_zero signal counts typically averaged 1300 Hz ±2 %. The accuracy of the NO measurements had uncertainty due to variations in instrument zeroes, sensitivities, MFC calibrations, and the level of calibration standard used. The MFC calibrations before and after the study were within 2 %. The biggest contributor to the overall uncertainty was the variable level of ambient NO before and after the standard addition and the interpolation necessary for the S_NO determination, which is estimated here at ±13 %. Therefore, the overall uncertainty of the NO measurement is estimated at ±15 % as RMS error of all the above potential inaccuracies.

Each calibration cycle allowed the determination of the instrument's sensitivity to $NO_2$, NPN, and $HNO_3$. The $NO_2$ sensitivity (S_$NO_2$) in ambient air averaged 3.72 ±0.44 Hz pptv$^{-1}$ revealing a $NO_2$ conversion efficiency Q_$NO_2$ of 94 ±8 %. With each calibration cycle the conversion efficiencies for NPN and $HNO_3$, species that are typically harder to convert than $NO_2$, were also determined via standard addition. NPN cal gas was delivered mass flow controlled to the converter inlet from a NIST traceable compressed air tank of 3.88 ±0.19 ppmv NPN in $O_2$-free $N_2$ (Scott-Marrin Inc.). $HNO_3$ was supplied from a permeation tube (Kin-Tek) inside an oven controlled at 40 ±0.1 C via a critical orifice controlled zero air flow of ~10 sccm. The permeation rate was verified before and after each study via dissolution of $HNO_3$ using a small scale impinger and subsequent IC analysis of $NO_3^-$. The conversion efficiencies for both NPN and $HNO_3$ in ambient air were 87 ±18 % and 80 ±53 %, respectively, suggesting that $NO_2$ is typically converted the easiest and $HNO_3$ the hardest. The variability and relative differences in conversion efficiencies of these three $NO_y$ species add uncertainty to the $NO_y$ measurement as considered below. The $NO_y$ zeroes averaged 1450 Hz ±10 %, and an artifact A_NOy was present when sampling zero air. This artifact varied with time and level of converter decay, and was therefore considered in a time-dependent manner; it averaged 0.39 ±0.17 ppbv. Based on measured variations in $NO_y$ over 2 – 3 h periods, the precision of our $NO_y$ measurements ranged between ±10 and ±15 %. In addition to the potential uncertainties that contributed to the NO inaccuracies described above, our estimate for the overall accuracy of the $NO_y$ measurements include the uncertainties in the GPT derived $NO_2$ calibration gas, and the unequal MoO converter efficiencies for $NO_2$, NPN, and $HNO_3$ resulting in an RMS error of ±20 %.

### 6.4. $PM_{2.5}$ Data Quality

A thorough QA/QC protocol [see Quality Integrated Work Plan submitted to the U.S. EPA in August 1998 in fulfillment of requirement for Quality Assurance Plans for environmental data operations, and Standard Operating Procedures listed therein] ensures highest quality of the suite of species that are analyzed and reported. From our extensive experience with the analysis of data from aforementioned field intensives, it has been found to be imperative to do thorough QA/QC and self-consistency checks of the data prior to reporting. This extended QA/QC protocol involves mass and charge balance evaluations and interpretations, and critical review of each sample result under the aspects of atmospheric processes and evolution.

Field blanks for each sample medium type (i.e., denuders, Teflon, paper, quartz, XAD-coated quartz filters) were carried together with the samples on every sampling day. Detection limits were determined assuming a two-tailed student's *t*-distribution and a confidence level of 95 %. For particulate species concentrations with semi-volatile character that were derived from a combination of Teflon and coated paper backup filter values ($NH_4^+$, $NO_3^-$, acetate, formate, and oxalate), a combined *DL*, based on the root mean square, was calculated. Table 6.3 summarizes the *DL*s for each species as part of the general data quality indicators determined for two major field campaigns, the ASSE99 and TexAQS2k.

Special side-by-side runs of identical set-ups were performed on various occasions in between intensives, allowing an assessment of the measurements precision based on the evaluation of bias. Similar tests investigating the quality of our EC,OC measurements were performed as well. No data quality indicators are reported for certain species, particularly oxalic acid (no *D-eff*), sodium, calcium, and chloride (no $P_n$), since their values remained below *DL* for all side-by-side runs.

Accuracy is assessed for $SO_2$, $PM_{2.5}$ mass, EC, and OC concentrations. $SO_2$ was also measured continuously by use of a modified commercial, pulsed UV fluorescence instrument (model TEI 43C-TL), as described above. A least squares linear regression with the continuous measurements averaged over the discrete sampling periods, indicates a relative deviation of the denuder-derived $SO_2$ of 0.91 ±0.03 at an offset of -0.10 ±0.15 ppbv (below *DL*) and an $R^2$= 0.99 for ASSE99, while the same type regression yielded 0.73 ±0.03, 0.00 ±0.08 ppbv and $R^2$= 0.99 for TexAQS2k, respectively.

The accuracy of our reported gravimetric $PM_{2.5}$ mass concentration is assessed by comparing the dehydrated Teflon filter mass (related to the ambient sample volumes) with the corresponding averages from a commercial Tapered Element Oscillating Monitor (TEOM, R&P Co., Inc., Albany, NY). The instrument was operated at constant 50 % relative humidity and 60 min integration. The Teflon filters from the first 9 samples corrected for hydrates according to the procedure mentioned earlier, and combined with the successive 11 samples that had been dehydrated, were linearly regressed with the TEOM data. The least squares linear fit (slope = 1.06 ±0.07, intercept = 0.43 ±2.1 μg $m_{-3}$) indicated a thus interpreted accuracy of +6 % at $R^2$= 0.93. Although the semi-volatiles determined from the paper backup filters have a combined uncertainty of ±25 %, the error propagation analysis yields an average uncertainty of the reported total gravimetric mass concentration of +7 % for ASSE99, and +1 % for LaPorte and -4 % for Williams Tower during TexAQS2k, respectively.

The accuracy estimates for EC (+9 %) and OC (-10 %) listed in Table 6.3, were derived from comparison measurements sending punches of three different quartz filter samples to the National Institute for Standards and Technology for analysis (NIST). The least squares linear fit with the NIST measurements being the independent variables, resulted in a slope of 1.09 ±0.43 ($R^2$= 0.87) and an intercept of 0.34 ±0.56 µg m$_{-3}$ for EC, which is below the *DL*, whereas the OC regression had to be forced through zero, since the OC values ranged between a relatively narrow span of 13 and 20 ∝g m$_{-3}$ yielding a slope of 0.90 ±0.02 at a coefficient of determination ($R^2$) of 0.97. Note that these are uncertainties related only to the principle of quartz sample analyses, and that uncertainties arising from intrinsic sampling errors such as positive and negative artifacts, specificity and efficiency of XAD-coated denuders and backup adsorbers are much harder to assess. Probably the biggest uncertainty in the EC determination arises from the pyrolysis correction, which Chow et al. [2001] report to be between a factor of 1.2 and 10 too low, with urban samples at the lower and rural samples at the higher end.

*Lewtas et al.* [2001] showed that trace-level VOC potentially released from residual solvent (hexane, dichlormethane, acetone) used for denuder extractions between sample runs, were not causing a significant artifact OC signal on the quartz filters downstream, demonstrating that these solvents' vapor pressures are too high to allow condensation onto the quartz fibers under ambient sampling conditions. It should be noted, that instead of acetone, the slightly less volatile methanol was used here in the last extraction/cleaning step. The XAD denuder efficiency was found to be better than 95% for Atlanta air, and a negligible amount (between 0.14 to 0.29 µg m$_{-3}$) of VOC being part of the sample air or possibly released by the denuder itself, or gas phase SVOC that is not being retained by the denuder, is captured by the XAD coated backup adsorber. Hence, we have reason to assume that the XAD resin whether applied as a coating on the denuder walls or on the quartz filter fibers retained the same species of gas phase SVOC, and therefore did not change the adsorbing characteristics and affinity toward certain species. Nevertheless, the data quality indicators stated for XAD quartz filters in Table 6.3, DL= 1.5 and 0.5 µg $m^{-3}$ (ASSE99 and TexAQS2k, respectively) and ±25 % precision, indicate that the use of XAD coated quartz filters bear great potential for contamination during the entire sampling and analysis process.

**Table 6.3a:** Data quality indicators (denuder efficiencies, D-eff; detection limits, DL; biases; and accuracies) for gas and particle phase species measured via the PCM during the ASSE99. The data were derived from the different sampling media, i.e., citric acid or sodium carbonate coated denuders (D(ca)/D(sc), respectively), Teflon filters (T), paper filters (P), quartz filters (Q), and XAD coated quartz filters (XQ). A denuder efficiency of 100% was assumed for nitric acid (see text).

| | $NH_3$ | $HNO_3$ | $SO_2$ | HCl | HCOOH | $CH_3COOH$ | $(COOH)_2$ |
|---|---|---|---|---|---|---|---|
| Retrieved from | D (ca) | D (sc) | D (sc) | D(sc) | D (sc) | D (sc) | D (sc) |
| D-eff [%] | 99±1 | 100 | 99±3 | 90 | 89±2 | 83±7 | - |
| DL [ppbv] | 0.14 | 0.05 | 0.18 | 0.20 | 0.10 | 0.47 | 0.02 |
| BIAS [%] | 10 | 11 | 6 | 14 | 6 | 12 | 20 |
| Accuracy [%] | | | -11 | | | | |

| | $NH_4^+$ | $NO_3^-$ | $SO_4^{2-}$ | EC | OC | SVOC | $M_{PM}$ |
|---|---|---|---|---|---|---|---|
| Retrieved from | T+P | T+P | T | Q | Q | XQ | T+P |
| DL [µg $m^{-3}$] | 0.29 | 0.32 | 0.21 | 0.31 | 0.42 | 1.50 | 1.44 |
| BIAS [%] | 8 | 24 | 6 | 7 | 5 | 25 | 12 |
| Accuracy [%] | -6 ±5 | | -16 ±2 | +9 | -10 | | +7 |

| | $Na^+$ | $Ca^{2+}$ | $Cl^-$ | $HCOO^-$ | $CH_3COO^-$ | $C_2O_4H^-$ |
|---|---|---|---|---|---|---|
| Retrieved from | T | T | T | T+P | T+P | T+P |
| DL [µg $m^{-3}$] | 0.49 | 0.16 | 0.29 | 0.55 | 1.10 | 0.12 |
| BIAS [%] | - | - | - | 17 | 11 | 55 |

The results of the major ions sulfate, ammonium, and nitrate determined by the discrete PCM method during both field studies, are also compared with the higher resolved Particle-In-Liquid-Solution technique (PILS), see *Weber et al.* [2002] for more details. Accuracy is here assessed assuming the PILS data to be the independent variable, although significant discrepancies existed among various newly developed semi-continuous aerosol measurement techniques during ASSE99, where differences in nitrate were particularly large. Besides its innovative nature, ASSE99 was especially designed as a platform to compare and evaluate discrete chemical speciation samplers that have been historically used according to EPA's $PM_{2.5}$ Federal Reference Method (FRM, see *EPA* [1997]) as well. A detailed analysis and comparison of the various discrete sampling methods employed during ASSE99 is provided by *Solomon et al.* [2003], and Table 6.4 summarizes the performance of our PCM by comparison with the "relative reference values" obtained from the average of all discrete samplers operated.

**Table 6.3b:** Data quality indicators (denuder efficiencies, D-eff; detection limits, DL; biases; and accuracies) for gas and particle phase species measured via the PCM during the TexAQS2k. A 122 mM phosphorous acid solution (pa) replaced citric acid as coating solution for denuders and backup adsorbers; everything else remained the same as for ASSE99.

| | Site | $NH_3$ | $HNO_3$ | HONO | $SO_2$ | HCl | HCOOH | $CH_3COOH$ | $(COOH)_2$ |
|---|---|---|---|---|---|---|---|---|---|
| Retrieved from | | D (pa) | D (sc) | D (sc) | | | D (sc) | D (sc) | D (sc) |
| D-eff [%] | LP | 91±18 | 100 | 91±8 | 87±19 | 97±6 | 83±10 | 81±18 | 78±17 |
| | *WT* | 92±22 | 100* | 88±9 | 91±18 | 96±17 | 83±11 | 89±19 | 73±21 |
| DL [ppbv] | LP | 0.49 | 0.33 | 0.03 | 0.07 | 0.18 | 0.08 | 0.21 | 0.01 |
| | *WT* | 1.40 | 0.36 | 0.04 | 0.20 | 0.15 | 0.11 | 0.28 | 0.02 |
| Accuracy [%] | *LP* | | | | -28<br>±2 | | | | |

| | Site | $NH_4^+$ | $NO_3^-$ | $SO_4^{-2}$ | EC | OC | SVOC | $M_{tot}$ |
|---|---|---|---|---|---|---|---|---|
| Retrieved from | | T+P | T+P | T | Q | Q | XAD-Q | T |
| DL [$\mu g\ m^{-3}$] | LP | 0.23 | 0.09 | 0.06 | 0.42 | 0.80 | 0.51 | 1.1 |
| | WT | 0.22 | 0.10 | 0.05 | 0.59 | 0.93 | 0.51 | 1.1 |
| BIAS [%] | LP | 12 | 33 | 13 | | | | |
| | WT | 13 | 19 | 3 | | | | |
| Accuracy [%] | LP/ WT | -6 ±3 | +2 ±9 | -7 ±2 | +9 | -10 | | -1 / +4 |

| | Site | $Na^+$ | $K^+$ | $Ca^{2+}$ | $Cl^-$ | $F^-$ | $HCOO^-$ | $CH_3COO^-$ | $C_2O_4H^-$ |
|---|---|---|---|---|---|---|---|---|---|
| Retrieved from | | T | T | T | T | T | T+P | Q | Q |
| DL [$\mu g\ m^{-3}$] | LP | 0.15 | 0.10 | 0.18 | 0.07 | 0.02 | 0.88 | 1.71 | 0.18 |
| | WT | 0.10 | 0.07 | 0.14 | 0.07 | 0.02 | 0.84 | 0.84 | 0.16 |
| BIAS [%] | LP | 20 | 35 | 17 | | | | | 25 |
| | WT | 22 | 37 | 26 | | | | | 27 |

**Table 6.4:** Performance characteristics of our PCM expressed as regression slopes for 0 intercept and calculated regression intercepts (± standard errors) relative to the standard reference values from the averages of all discrete samplers operated during ASSE99: adapted from Solomon et al. [2002].

| | slope | intercept $\mu g\ m^{-3}$ | $r^2$ |
|---|---|---|---|
| Mass | 1.06 ±0.02 | 1.2 ±2.9 | 0.91 |
| $SO_4^{=}$ | 1.02 ±0.01 | -0.1 ±0.3 | 0.99 |
| $NO_3^{-}$ | 1.27 ±0.11 | -0.6 ±0.3 | 0.50 |
| $NH_4^{+}$ | 1.02 ±0.02 | 0.4 ±0.2 | 0.95 |
| OC | 1.02 ±0.04 | -1.1 ±1.3 | 0.80 |
| EC | 0.78 ±0.05 | -0.1 ±0.2 | 0.57 |

## 6.5 Major Findings

It was found that the $PM_{2.5}$ problem is much more regional than initially believed, and that the source for fine particles and one of their main compositions, sulfate, is more regionally distributed, indicating a secondary formation of such particles in the atmosphere rather than primary emission. The vertical gradient measurements made between 42 and 4 m agl at Hendersonville, TN, from 16 June to 22 July 1999, (see Figure 6.1) showed positive vertical gradients for 60-70 % of all daytime, and 70-80 % of all nighttime samples of $PM_{2.5}$ mass, sulfate, nitrate, and ammonium, see Figure 6.4. This is in agreement with the thermodynamic stratification of the lower atmosphere as indicated by the simultaneously (and continuously) measured vertical temperature gradients. It is evident from Figure 6.4 that the larger the difference in temperature gradient, i.e. negative during daytime, and positive during nighttime, indicating convective mixing and nocturnal stratification, respectively, the larger the reciprocal difference in relative humidity gradient, i.e. positive during daytime and negative during nighttime. This was particularly the case at the beginning and towards the end of this measurement period, coinciding with the days when the gradients in $PM_{2.5}$ mass and major ions were mostly positive and especially large. During the center period (6/24 to 7/8 1999), the temperature and humidity gradients were relatively small, both absolutely and relative to the time of day, pointing to the influence of labile meteorological conditions with frontal passages and other synoptic disturbances and the role of direct emissions of $PM_{2.5}$ precursors and secondary formation of $PM_{2.5}$ within those layers aloft.

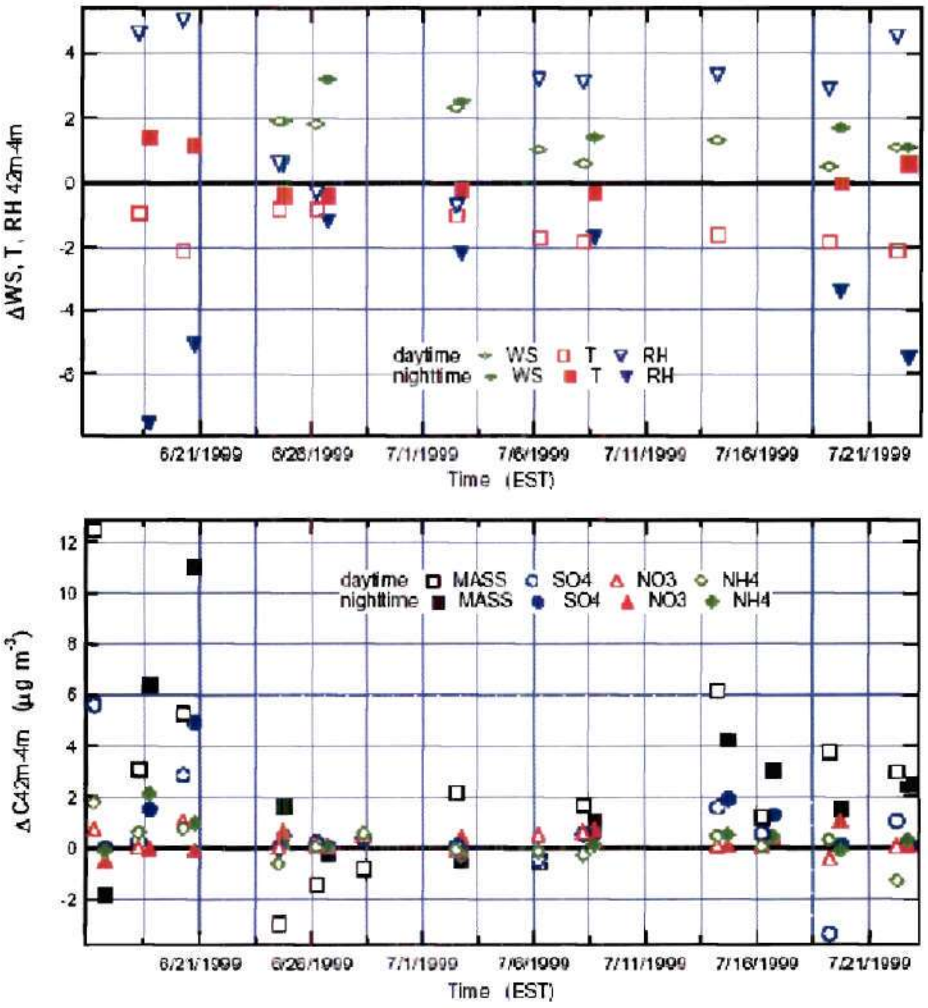

**Figure 6.4:** Vertical gradients, expressed as difference between 42 and 4 m agl, of wind speed, temperature and relative humidity (top), and $PM_{2.5}$ mass, sulfate, nitrate and ammonium concentrations (bottom).

Figure 6.5 illustrates that the gaseous precursors for gas-to-particle conversion, i.e., $NH_3$, $HNO_3$, and $SO_2$ are highest in urban environments where also highest $PM_{2.5}$ are seen. Furthermore, acidic gases exhibit a seasonal trend with lowest values in winter. This is particularly obvious for formic and acetic acids (summed as LOA in Figure 6.5), which show a factor of 3 to 4 lower mixing ratios in winter. A similar seasonal pattern is shown with respect to total fine mass ($PM_{2.5}$) with averages being highest during the summer (ranging from 24 to 36 μg $m^{-3}$) and dropping significantly during fall and winter (16 to 20 μg $m^{-3}$ and 11 to 12 μg $m^{-3}$, respectively). $PM_{2.5}$ mass concentrations averaged for the summer and fall periods tend to be systematically higher at Dickson than at Hendersonville, despite the relative close proximity of the two sites that are ~50 miles apart. This can be attributed to the different surrounding environment of the two locations, and the specific sampling strategy, that emphasized the capturing of the Nashville urban plume at the Hendersonville site, whereas the Dickson site is surrounded by dense forests typical of more rural sites in the SE-US. From various studies within the framework of SOS and other research projects, it is known that the planetary Boundary Layer (BL) over forests remains shallower and less mixed during sunny daytime periods (release of more latent heat due to vegetative evapotranspiration), compared with urban and sub-urban areas, where more intense surface heating typically forms a deeper, convectively well-mixed BL. This difference in BL height may be the main reason for the observed difference in [$PM_{2.5}$].

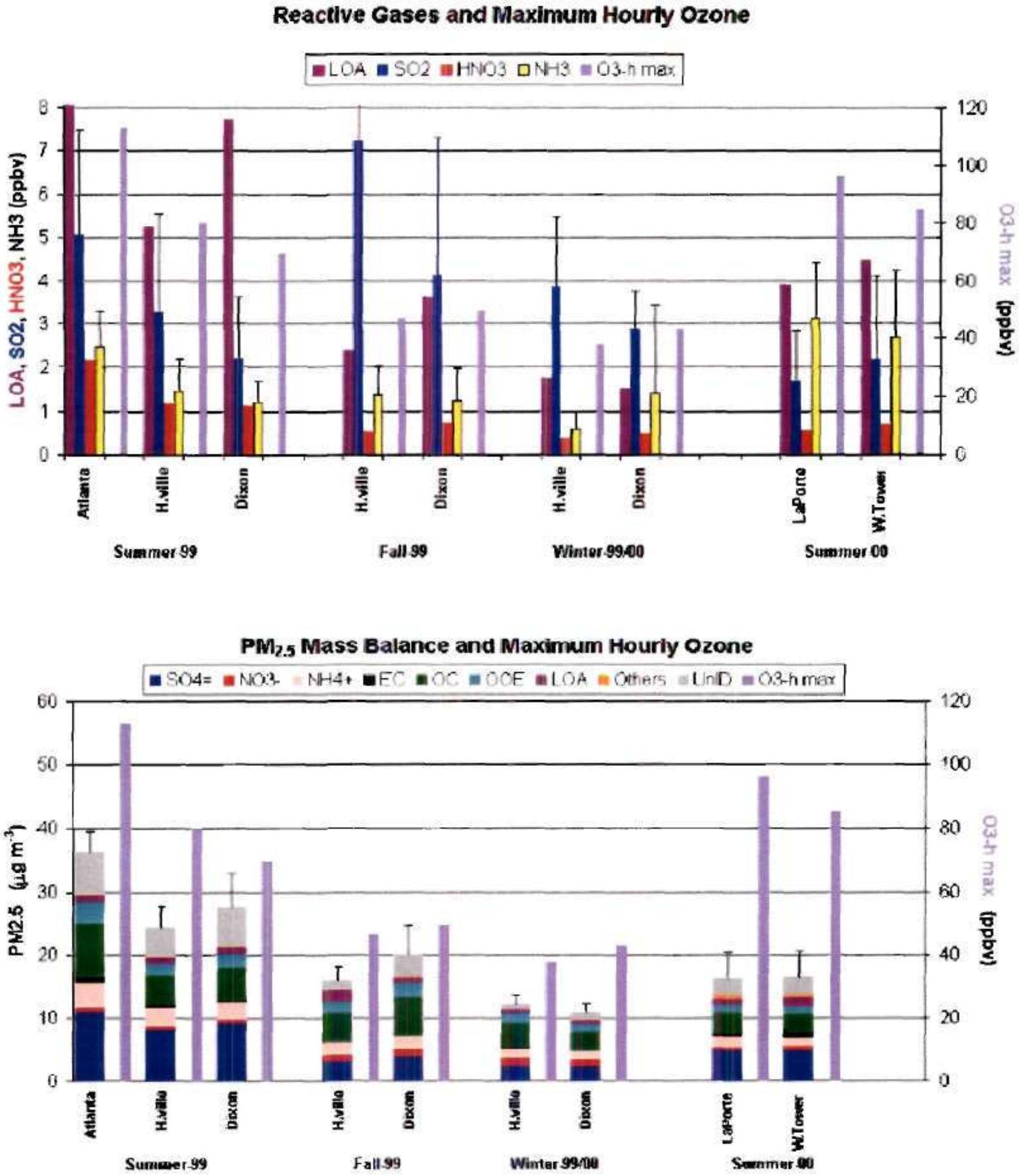

**Figure 6.5:** $PM_{2.5}$ mass balance, average maximum hourly $O_3$, and average daily $NH_3$, $HNO_3$, $SO_2$ and light organic acids (mainly formic and acetic) for ASSE99 and different seasons at suburban Hendersonville and rural Dickson, TN, and for TexAQS2k at Houston, i.e. LaPorte and Williams Tower.

The absolute sulfate mass concentrations and even its fraction of the total fine mass, as depicted in Figure 3.1 in form of pie-charts, also show this seasonal trend with 30-33 % in summer, and 18-22 % in fall and winter. Formic, acetic, and oxalic acids, the latter being mostly below the denuder derived DL, are summed up and depicted as light organic acids (LOA). The group of "Others" consists of all minor ions, i.e. $Na^+$, $K^+$, $Ca_2^+$, $F^-$, and $Cl^-$. Organic carbon (OC) concentration shows less seasonal variation, and due to lower total mass concentrations during fall and winter, the relative contribution of total organic mass (i.e. the sum of 1.4*OC + LOA) to the total fine mass concentration increases significantly, from between 29 and 35 % in summer to between 48 and 52 % in fall and winter. The third largest contributor to total fine mass, especially in summer, is the unidentified fraction (grey area), and is discussed later.

Measurements made in the Houston, TX area during the TexAQS2k field experiment at LaPorte, and at Williams Tower, 254 m above ground, provided an interesting contrast to the results found in GA and TN. LaPorte, for example, was influenced predominantly by a strong land-sea breeze circulation with veering wind directions, causing periodic short-term impacts of plumes from nearby sources with significantly reduced (titrated) nighttime ozone levels. Although $O_3$ was formed rapidly in this VOC-rich environment, rich particularly in alkenes, the $PM_{2.5}$ mass concentrations were only ~16 $\mu g\ m^{-3}$, and not significantly different between the two sites. While LaPorte experienced generally higher ozone levels during the day, the elevated site at Williams Tower showed systematically higher levels at night, pointing to effects of nocturnal stratification and redistribution of previous days' ozone. LaPorte was impacted by exceptionally high ozone only on two consecutive days, August 30 and 31, with maximum hourly averages of 219 and 196 ppbv, respectively. At the same time, the elevated site at Williams Tower saw only ~50% lower ozone maxima, because the plume did not reach the site. The difference in [$PM_{2.5}$], however, was insignificant between the two sites regionally and temporally compared to the neighboring days and for the entire study period (as seen in Figures. 6.5 and 3.1), which makes these plumes very rapid and efficient ozone producers without significant fine particle formation. With exception of the 08/30-31 episode, however, the $PM_{2.5}$ mass and sulfate concentrations generally followed the trends in daily ozone maxima similar to the observations made in GA and TN. Similar to these other sites, the aerosol was slightly acidic on the basis of $NH_4^+/SO_4^{2-}/NO_3^-$, as seen in Figure 6.6, pointing to a certain importance of other nitrate-forming mechanisms and possible role of organic nitrates.

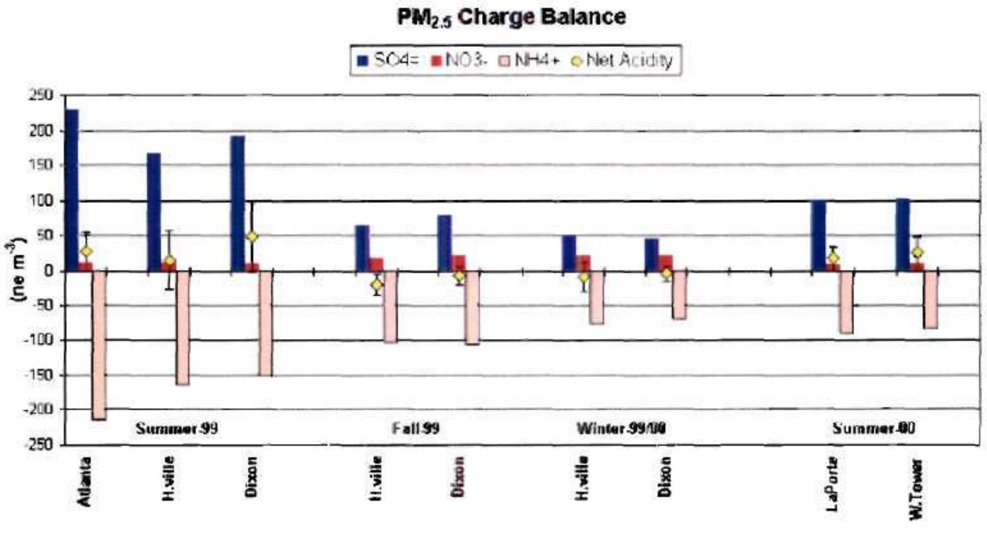

**Figure 6.6:** PM2.5 charge balance on the basis of $NH_4^+/SO_4^{2-}/NO_3^-$ for ASSE99 and different seasons at sub-urban Hendersonville and rural Dixon, TN, and for TexAQS2k at Houston, i.e. LaPorte and Williams Tower.

As mentioned above, when other organic elements (OOE) are taken into account as 0.4*OC, the third largest "contributor" to the total gravimetric mass in summertime is the unidentified mass fraction. Note that for all mass balance closure approaches, the dehydrated or hydrate-corrected gravimetric mass concentration was considered. The average organics molecular weight to carbon weight ratio (OM/OC) of 1.4 that has been widely used in the past, originates from very limited theoretical and laboratory studies from more than 20 years ago, suggesting it to be the lowest reasonable estimate for urban aerosols [*White and Roberts*, 1977; *Countess et al.*, 1980; *Japar et al.*, 1984]. A more recent investigation by *Turpin and Lim* [2001], however, suggests a factor of 1.6 ±0.2 to be more accurate in an urban environment. When other organic elements (OOE) from the denuded quartz front filter are taken into account as 0.6*OC for the ASSE99 data set for example, an average percent fraction unidentified mass of 13 ±10 % relative to the total reported mass concentration would still remain. If then semi-volatile OC captured downstream from denuded quartz filters were considered, its OOE would result in ~0.4 for mass closure (corresponding OM/OC= 1.4). It seems reasonable to assume that enhanced water solubility based on polar functional groups result in reduced volatility as a consequence of stronger intermolecular interactions, and that more volatile compounds are captured on the XAD quartz backup filter, which have lower OOE factors than the less volatile ones captured on the quartz front filter.

Using the $PM_{2.5}$ mass balance closure approach on dehydrated Teflon filters to solve for the organics mass to carbon ratio OM/OC and applying it to the different data sets, reveals a trend of larger OM/OC towards more rural locales, as seen in **Table 5** between Atlanta (2.1), Hendersonville (2.4), and Dickson (2.9), with values clearly greater 1.6. Even during the fall period, Dickson would require an OM/OC of 2.2 to achieve mass closure, versus 1.7 at Hendersonville. This can be interpreted with the photochemical aging and processing of air masses under clear-sky summertime conditions when relatively high levels of reactive radicals, particularly OH·, drive the formation and processing of secondary aerosols. Compared to the relative stagnant conditions in Atlanta during ASSE99, the TexAQS2k measurements at Houston one year later, were characterized by distinct land-sea-breeze circulations, and a rather "rich" mix of VOC emissions, especially alkenes, from large agglomerations of petrochemical facilities that are unique to Houston, adding to the mobile and power plant sources that are more common for metropolitan areas. At both TexAQS2k sites, the OM/OC yields an average 3.5 for closure but largely variable due to the closeness of these different sources and events, such as a dominant influence from large biomass burning activities in NE-Texas and Louisiana early September. When SVOC are included from the XAD-coated quartz backup filter, and no distinction was made between the possible different volatility, i.e. polarity and governing functional groups as was done for ASSE99, then the average OM/OC {svoc} factors as shown in Table 5 would be significantly lower than without SVOC. Contrasting Atlanta 1999 with Houston 2000, and furthermore considering the episodic character of largely different OM/OC ratios during TexAQS2k, it may be concluded that photochemically well-aged and well-mixed air masses contain particulate organic compounds with more highly oxygenated and less volatile functional groups, whereas under more stagnant conditions, particle phase organics might be less oxygenated and therefore more volatile.

**Table 6.5:** Organic mass to carbon mass ratio (OM/OC) needed to achieve $PM_{2.5}$ mass closure for at sites in Atlanta, Nashville and Houston during various summer intensive campaigns.

| | | OM/OC for closure | | OM/OC {svoc} for closure | |
|---|---|---|---|---|---|
| | | AVG | STD | AVG | STD |
| **Summer-99** | **Atlanta** | **2.1** | 0.7 | **1.5** | 0.3 |
| | **H.ville** | **2.4** | 0.7 | | |
| | **Dickson** | **2.9** | 1.8 | | |
| **Fall-99** | **H.ville** | **1.7** | 0.5 | | |
| | **Dickson** | **2.2** | 0.9 | | |
| **Winter-99/00** | **H.ville** | **1.6** | 0.3 | | |
| | **Dickson** | **1.6** | 0.4 | | |
| **Summer-00** | **LaPorte** | **3.5** | 3.8 | **2.3** | 2.6 |
| | **W.Tower** | **3.5** | 3.2 | **2.4** | 2.3 |

## 6.6. Summary

- A positive artifact due to hydrates was determined from ASSE99 denuded Teflon filter samples and quantified at ~20 ±8 %; this finding prompted a general change in the standard operating procedure (SOP) of our Teflon filter treatment, adding a 24 to 48 hour desiccation period.
- Our tower measurements at Hendersonville, TN revealed positive vertical gradients (42 vs 4 m agl) of $PM_{2.5}$ mass and major ions, especially sulfate, pointing to atmospheric aerosol formation.
- We found insignificant regional differences in $PM_{2.5}$ composition, but noticeable seasonal differences, esp. in the $SO_4^{2-}$ fraction, varying from >30 % in summer to ~20 % in winter, which is likely due to higher $SO_2$ emissions and photochemical activity in summer.
- Based on $SO_4^{2-}/NO_3^-/NH_4^+$ system, $PM_{2.5}$ in SE-US is slightly alkaline in winter but more acidic in summer, leaving i) sulfate only partly neutralized as

$(NH_4)HSO_4$ or ii) possibly other neutralizing acting species undetected.

- The organic mass to carbon fraction OM/OC at the sites sampled in this work is highly variable but most likely greater than the value of 1.4 commonly assumd by most investigators.
- Applying mass closure to dehydrated mass concentrations, requires greater OM/OC factors in summer possibly due to more oxygenated species from photochemistry.
- The general trend for higher OM/OC factors away from urban areas possibly points to the importance secondary atmospheric processes producing oxygenated OC.
- Different factors might have to be applied for OC from quartz front and XAD backup filters due to different volatilities, as shown for ASSE99 (see *Baumann et al.* 2003).

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## 7. MEASUREMENT OF PARTICLE DENSITY DURING SCISSAP[2]

This portion of the SCISSAP project involved the development and use of the Aerosol Particle Mass Analyzer (APM; (Ehara et al., 1996)) for *in situ* measurements of particle mass. All of the measurements carried out in this project involved first classifying particles with a differential mobility analyzer (DMA; (Liu and Pui , 1974; Knutson and Whitby, 1975)) and them measuring their mass with the APM. Therefore, we refer to this new technique as the DMA-APM technique. Our work has involved studies with laboratory-generated aerosols of known composition to evaluate measurement accuracy, measurement of atmospheric particles during the Atlanta Supersite Project in 1999, and measurements of diesel exhaust particles done in collaboration with Professor David

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[2] **Prepared by**: Peter H. McMurry, Department of Mechanical Engineering, University of Minnesota

Kittelson in the Center for Diesel Research at the University of Minnesota. Our major findings are:

1. The DMA-APM technique can measure the mass and density of spherical particles to within 5%.
2. The DMA-APM technique can measure the mass and "effective densities" of nonspherical particles.
3. "Effective densities" measured by the DMA-APM technique can be used to determine the relationship between mobility equivalent diameter and aerodynamic diameter. This relationship is valid for particles of arbitrary shape and composition.
4. Effective densities of diesel exhaust particles decrease with increasing size. At 50 nm, densities are about 1.1±0.1 g $cm^{-3}$, while at 300 nm densities are about 0.3±0.05 g $cm^{-3}$.
5. Atmospheric particles of 100 nm and 300 nm in Atlanta at ~3-6% relative humidity typically had two distinct densities: 1.6±0.1 g $cm^{-3}$ and 0.45±0.20 g $cm\text{-}^{3}$.
6. The "low density" particles observed in the Atlanta atmosphere have densities similar to diesel exhaust particles of the same mobility size. The densities of "high density" particles are consistent with values calculated from measured composition, assuming that they consist primarily of organic carbon and sulfates.
7. The fractal-like dimension of diesel exhaust particles measured in this study ranged from 2.33±0.02 to 2.41±0.03, with the higher values observed at lower engine loads or with fuels having higher sulfur content. We believe this is because the particles produced at low loads or with higher sulfur fuel contain more liquid content, and are therefore more compact and more nearly spherical. (The fractal dimension of spheres is 3.0.)
8. The DMA-APM technique enables the direct measurement of aerosol mass distributions as a function of either mobility-equivalent size or aerodynamic size. Mass distributions of laboratory and diesel exhaust particles measured with the DMA-APM technique are in very good agreement with mass distributions measured with a nano-MOUDI impactor, although the impactor data show evidence of bounce in the smallest size ranges.
9. Mass distributions measured with the DMA-APM technique can be integrated to obtain mass concentrations.
10. Mass concentrations of laboratory-generated DOS, NaCl and diesel exhaust particles obtained with the DMA-APM technique are typically in good agreement (±15%) with mass concentrations measured gravimetrically using filters or impactors. Adsorption or volatilization artifacts that can be significant with impactors and filters, however, do not affect the DMA-APM measurements.
11. We have not yet extended DMA-APM measurements to particles above 500 nm, although in principle this should be possible.

Two of these results represent significant advances in the science of aerosol measurement. The development of a precise and accurate technique for measuring particle density enables determining definitive relationships between aerodynamic and mobility equivalent diameters. This relationship helps to reconcile measurements based on different physical principles. Also, the new, in-situ technique for direct measurement of mass size distributions and concentrations will provide insights into the accuracy of filter-based measurements of mass concentrations, such as are used in EPA's FRM network. In the following sections the principle of DMA-APM measurements are briefly summarized and some illustrative results are provided. A summary of publications and graduate students who have been supported by the project is given at the end of the report.

### 7.1 Principle of the DMA-APM Measurements

A schematic diagram of the DMA-APM system is shown in Figure 7.1. Particles are classified according to electrical mobility with a DMA before they enter the APM where their mass is measured. A CPC is located downstream of the DMA-APM apparatus to enable detecting particles that penetrate through the DMA or the DMAAPM. A schematic diagram of the APM is shown in Figure 7.2. The instrument consists of two coaxial cylinders that rotate together about their common axis at an angular speed $\omega$. The outer cylinder is grounded while a voltage is applied to the inner cylinder. Aerosol flows axially through the thin annular gap between the two cylinders from the inlet to the outlet while it simultaneously rotates with the cylinders. Particles that enter the APM from the DMA are electrically charged. Therefore, as particles flow through the APM they experience an electrical force that draws them radially inwards, and a centrifugal force that is radially outwards. When these two forces balance, the particles will be transported through the APM to the CPC detector located downstream. The equation that describes this force balance is:

$$M\omega^2 r = neE_{APM} \qquad [7.1]$$

where m is particle mass, r is radial distance of the particle from the axis of rotation, n is the number of elementary charges carried by the particle, e is the unit electrical charge, and $E_{APM}$ is the local electric field in the annular gap (which varies in proportion to the voltage applied to the inner cylinder.) The width of the annular gap between the cylinders is much smaller than r. Therefore, it is reasonable to assume that r and $E_{APM}$ are approximately constant within the annular gap. Furthermore, we operate in a size range where there are few multiply charged particles, so n=1. It follows that the only unknown in Equation [1] is particle mass, m. When this force balance is satisfied, particles do not move relative to the mass flow. It follows that the APM classifies particles according to mass regardless of their shape or composition. This is in contrast to the DMA, which classifies particles according to electrical mobility, which depends upon particle shape (but not on particle density).

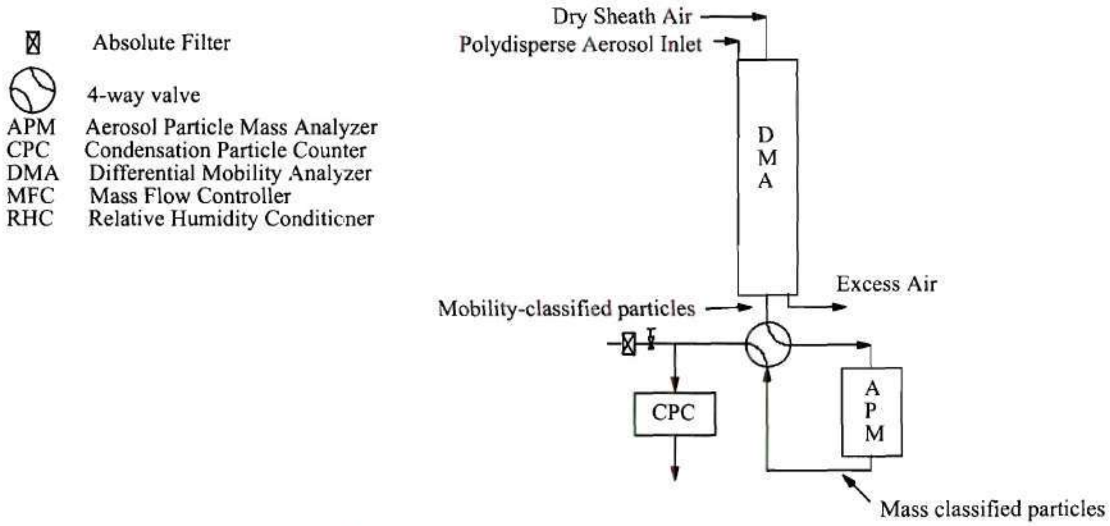

**Figure 7.1.** Schematic of DMA-APM system.

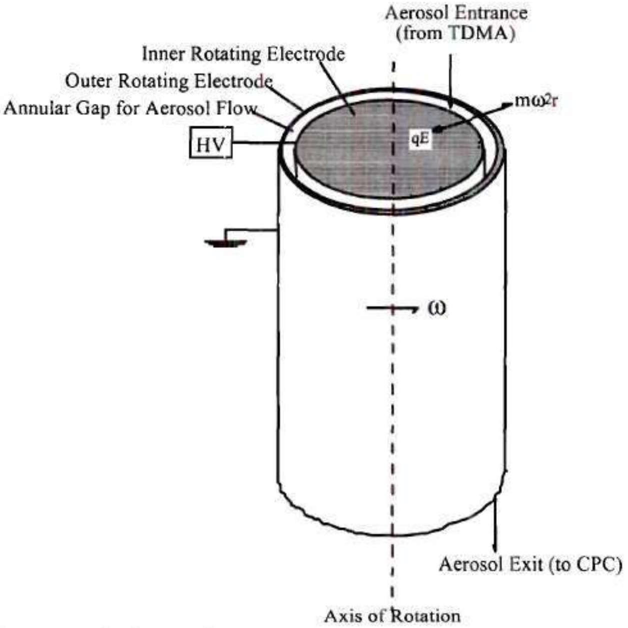

**Figure 7.2**. APM Schematic.

By using the DMA and APM in tandem it is possible to learn a great deal about particle properties. The DMA classifies particles according to electrical mobility, Z. For spherical particles, the electrical mobility equivalent diameter, $d_{me}$, equals the geometric or Stokes diameter and is independent of particle density. For nonspherical particles the electrical mobility depends on the dynamic shape factor, |, which is defined by (e.g.,(Kasper, 1982)):

$$Z = \frac{neC_c(d_{me})}{3\pi\mu d_{me}} = \frac{neC_c(d_{ve})}{3\pi\mu d_{ve}\chi} \qquad [7.2]$$

where n is the number of elementary charges per particle, e is the unit electric charge, $C_c$ is the Cunningham slip correction factor (Allen and Raabe, 1982), $d_{me}$ is the mobility equivalent diameter for spherical particles, $\mu$ is the absolute viscosity of air, $\chi$ is the dynamic shape factor, and $d_{ve}$ is the diameter of a sphere having the same volume as the irregularly shaped particle. For spherical particles $\chi = 1$ and $d_{me} = d_{ve}$, while for nonspherical particles $\chi > 1$ and $d_{me} > d_{ve}$. Note that the mobility equivalent diameter is independent of particle density. Thus by measuring Z with the DMA and m with the APM for the same particles it is possible to determine the relationship between mass and mobility equivalent diameter. For spherical particles, the true density can be inferred directly:

$$\rho_{\text{true (spherical particles)}} = \frac{m}{\frac{\pi d_{ve}^3}{6}} = \frac{m}{\frac{\pi d_{me}^3}{6}} \qquad [7.3]$$

For nonspherical particles, the technique provides an "effective density" which is equal to (McMurry et al., 2002):

$$\rho_{\text{effective}} = \rho_{\text{true}} \frac{d_{ve}^3}{d_{me}^3} \qquad [7.4]$$

Because $d_{me} > d_{ve}$ for nonspherical particles, the densities of nonspherical particles obtained in this way are less than the true material densities. The relationship between aerodynamic diameter, $d_{ae}$, and mobility equivalent diameter is (McMurry et al., 2002):

$$d_{ae}^2 C(d_{ae}) = \frac{1}{\chi} \frac{\rho_{\text{true}}}{\rho_0} d_{ve}^2 C(d_{ve}) = \frac{\rho_{\text{eff}}}{\rho_0} d_{me}^2 C(d_{me}) \qquad [7.5]$$

In all of our measurements of density or effective density we carried out sequential measurements of the "unknown" aerosol (i.e., atmospheric particles or diesel exhaust particles) and of polystyrene spheres (PSL) of exactly the same mobility equivalent size. The DMA was first adjusted to achieve maximum penetration of the PSL, and the masses of the unknown particles were then measured with the APM keeping the DMA flow rates and classifying voltage fixed. With this approach, it can be shown from Equation [7.1] that:

$$\rho_{\text{true (spherical particles)}} = \rho_{\text{PSL}} \frac{V_{\text{APM "unknown"}}}{V_{\text{APM PSL}}} \qquad [7.6]$$

and, for nonspherical particles,

$$\rho_{\text{effective}} = \rho_{\text{PSL}} \frac{V_{\text{APM "unknown"}}}{V_{\text{APM PSL}}} \qquad [7.7]$$

where the density of PSL, $\rangle_{\text{PSL}}$, equals 1.054 g cm$_{-3}$. The use of PSL as a reference standard improves the accuracy of measured densities. The alternative would be to calculate densities with Equation [3], where the mobility equivalent diameter is inferred from the DMA operating conditions. Unless extraordinary care is taken to control DMA flow rates and voltages, sizing errors of ~2% are typical. Because mass varies with the cube of diameter, this results in typical uncertainties of 6% for measured densities. The use of Equations [6] and [7] to infer density leads to uncertainties of less than 5%. Based on experiments with laboratory aerosols of known composition we found that most of our density measurements were accurate to within 3%.

The use of the scanning mobility particle spectrometer (SMPS; (Wang and Flagan, 1990)) to measure aerosol mobility distributions is well established. SMPS measurements involve measuring the concentration downstream of a DMA as the DMA classifying voltage is scanned from 0 to a maximum value of about 10,000 V. By using an APM to measure the mass of the mobility-classified particles, it is possible to use the DMA-APM system to directly measure aerosol mass distributions as a function of mobility diameter. The following equation shows the relationship between the mass distribution (left side of equation) and the number distribution measured with the SMPS:

$$\frac{dc_m}{d\log(d_{me})} = m \cdot \frac{dN}{d\log(d_{me})} \qquad [7.8]$$

where m is the mass of individual particles measured with the APM, and $c_m$ is the mass concentration of particles. Equation [7.5] enables converting these to distributions as a function of aerodynamic diameter. It follows that the total aerosol mass concentration is:

$$c_m = \int_{-\infty}^{\infty} \frac{dc_m}{d\log(d_{me})} d\log(d_{me}) \qquad [7.9]$$

Because the APM measurements of mass are valid for particles of arbitrary shape or composition, no assumptions about particle properties are required to obtain mass concentrations in this manner.

## 7.2 Illustrative Results

Figure 7.3 shows an example of data measured in Atlanta during the August 1999 Atlanta Supersite study. During these measurements the DMA was used to select polystyrene spheres or atmospheric particles of 309 nm mobility equivalent diameter. The penetration through the APM as a function of the APM classifying voltage was then measured with the CPC. Note that the PSL penetration through the APM peaked at 160 v, while the penetration of atmospheric particles peaked at 67 and 246 v, indicating that two types of particles having distinct masses were present. The particle densities for these measurements, obtained with Equation [7.6] or [7.7] are 0.44 g $cm^{-3}$ (low mass particles) and 1.62 g $cm^{-3}$.

Figure 7.4 shows the relationship between the effective density of diesel exhaust particles and mobility size. Note that 50 nm particles have an effective density of about 1 g $cm^{-3}$, while the density decreased to ~0.3 g $cm^{-3}$ for 300 nm particles. Average effective densities for 107 nm and 309 nm particles measured in Atlanta are also shown in Figure 7.4. Note that the atmospheric "low density" particles have effective densities that are similar to values measured for diesel exhaust particles. We examined the diesel particles by scanning electron microscopy to examine morphological properties as a function of size. We found that 50 nm particles tended to be compact and nearly spherical, while larger particles consisted of chain agglomerates. We believe this explains the reason for the observed size-dependent density: the large, fluffy particles have a large mobility equivalent size due to their large dynamic shape factors (see Equation [7.2]). The dynamic shape factors for ~50 nm particles should be close to unity, since these particles are nearly spherical. It follows that the mobility equivalent diameter for these particles is much more nearly equal to their volume equivalent diameter. The effective density of the 50 nm particles should, therefore, be much closer to the inherent material density for diesel-exhaust particles than would be the case for the 309 nm particles.

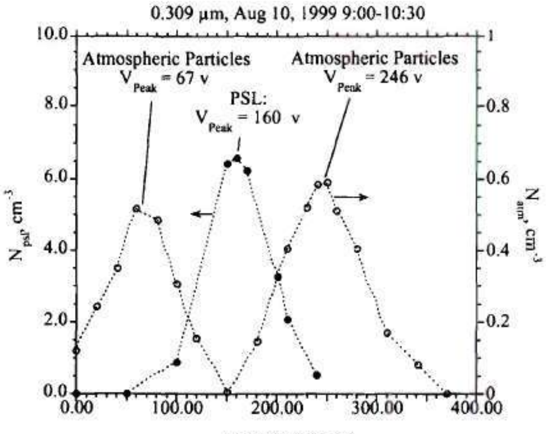

**Figure 7.3.** Number concentration downstream of APM as a function of the APM classifying voltage for 309 nm polystyrene latex (PSL) particles, and for 309 nm mobility-classified atmospheric particles. Note that two distinct peaks were observed for the atmospheric particles.

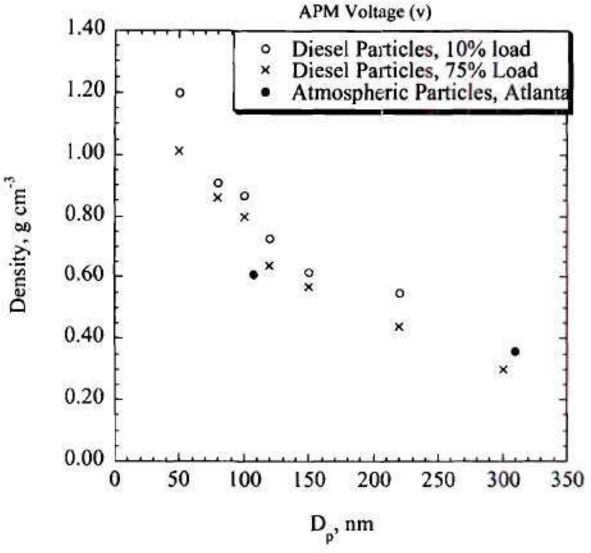

**Figure 7.4.** Effective density of diesel-exhaust particles versus mobility diameter. Note that the effective densities of diesel particles produced at high engine loads are somewhat smaller than those of particles produced at low loads, presumably because they contain less condensed mass.

Figure 7.5 shows the relationship between mass distributions of diesel exhaust particles measured with a nano MOUDI impactor and the DMA-APM. The nano-MOUDI data were converted from aerodynamic to mobility-equivalent diameter using Equation [7.4] for this comparison. Note that the total mass concentrations (areas under the curves) measured by the two techniques are in good agreement. The mass mean diameter measured by the two instruments is in good agreement, but the nano-MOUDI detected more mass in the small size ranges. We hypothesize that the observed shift of the MOUDI mass distributions to smaller sizes is due to the bounce of particles from upper stages (Stein et al., 1994). If this is correct, then virtually all of the mass collected on the bottom stages of the nano-MOUDI for these particles was due to bounce. If so, any measurements of composition for particles collected on the bottom nano-MOUDI stages would lead to erroneous information about nanoparticle composition.

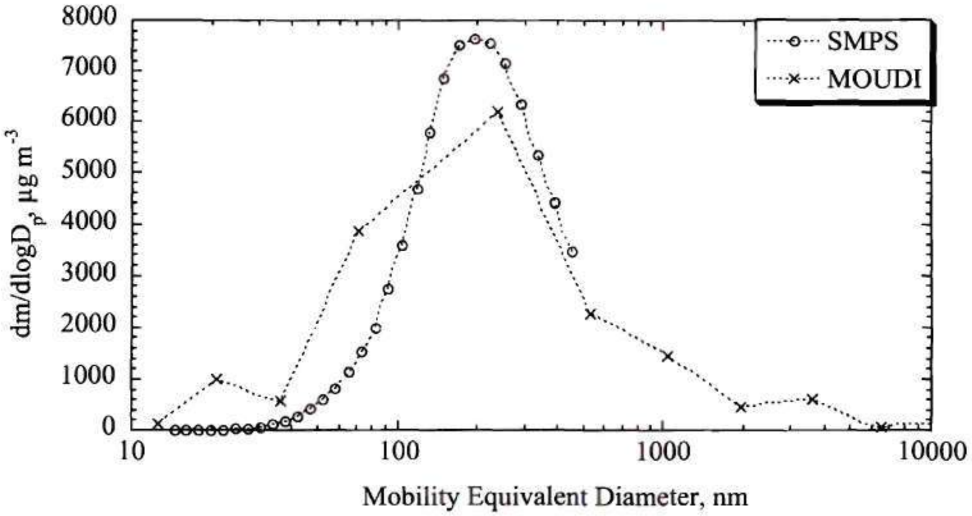

**Figure 7.5.** Comparison of mass distributions measured with the DMA-APM and a nano-MOUDI.

Figures 7.6 and 7.7 compare filter and DMA-APM measurements of aerosol mass concentrations for NaCl and diesel exhaust aerosols, respectively. Mass concentrations were calculated using Equation [7.9]. In order to keep filter sampling times reasonable short, measurements were made at high mass concentrations. However, because the DMA-APM technique involves single particle measurements, it works well for mass concentrations that are well below typical ambient levels. Note that except for the measurements made at 10% engine load, the gravimetric mass concentrations agree with DMA-APM measurements to within about 15%. We believe the discrepancies at low load occur because the engine emits more unburned hydrocarbons that can adsorb to the filter under these conditions. Therefore, we believe it is likely that the DMA-APM measurements under these conditions are more accurate.

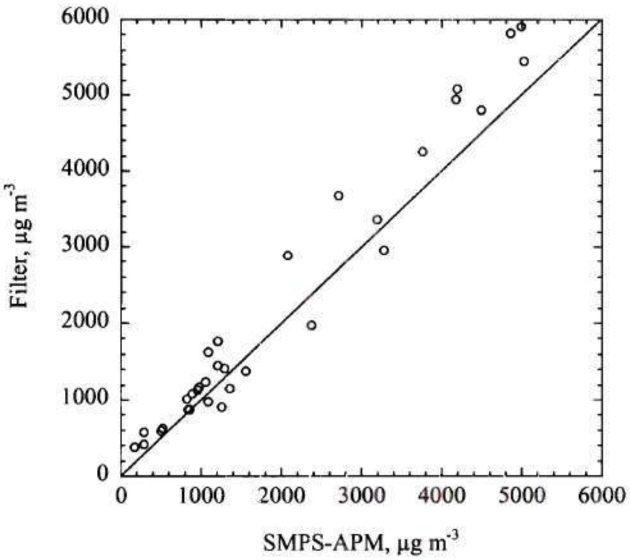

**Figure 7.6.** Comparison of mass concentrations of polydisperse laboratory-generated NaCl measured by filtration (gravimetric measurement) and by the DMA-APM technique.

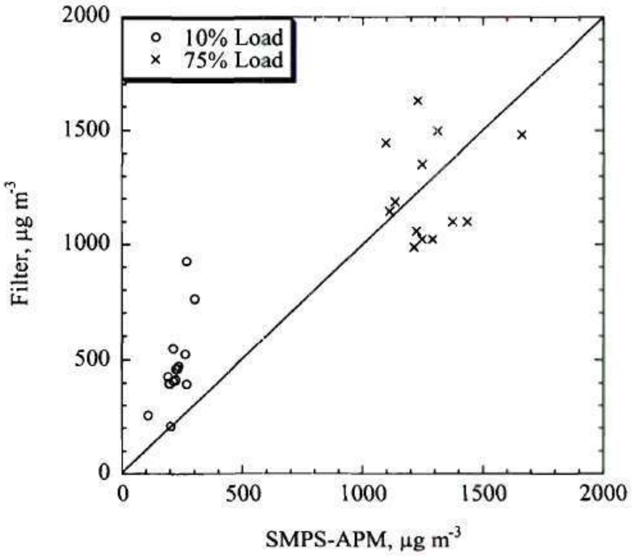

**Figure 7.7.** Comparison of mass concentrations of diesel exhaust aerosols measured by filtration (gravimetric measurement) and by the DMA-APM technique.

## 7.3. Graduate Students Supported by this Project

The M.S. research of Ms. Xin Wang was entirely supported by this project. Ms.Wang carried out the initial laboratory measurements that documented the accuracy with which density can be measured with particles of known composition with the DMA-APM technique. She also carried out measurements of atmospheric aerosol composition in Atlanta during the August 1999 Supersite Study. Subsequent to completing her M.S., Ms. Wang entered a Computer Science graduate program at Stanford University.

Mr Kihong Park, a doctoral student, was supported by this grant for the past three years. He has done all of the diesel exhaust particle studies, and has documented the ability of the DMA-APM technique to measure mass distributions and mass concentrations.

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## 8. ADVANCED ORGANIC CARBON MEASUREMENTS [3]

This portion of the SCISSAP project, carried out at the University of Miami, consisted of:

1. Providing ambient volatile organic compounds (VOCs) concentration in Atlanta.
2. Providing organic composition of fine particulate matter in Nashville and Atlanta.
3. Providing organic composition of size segregated particulate matter in Atlanta.
4. Participating in laboratory intercomparison for organic contaminants in $PM_{2.5}$
5. Data analysis and results dissemination in peer reviewed journals

### 8.1 Sample collection and analysis

*8.1.1. VOCs:* Hourly concentrations of ambient VOCs in Atlanta (Jefferson Street site) were measured from 08/04/99 to 08/31/99. A total of 448 one-minute time integrated samples were taken at the beginning of the hour. A unique collection and concentration

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[3] **Prepared by:** Rod Zika, Rosenstiel School of Marine and Atmospheric Sciences, University of Miami

system incorporating highly inert surfaces, Teflon and Silicosteel, coupled with state of the-art GC-MS provided detection limits in the range of 2 to 28 parts per trillion (ppt) for 100ml ambient air samples. The 84 quantified VOCs are listed in Table 8.1. The data acquired was submitted to the SCISSAP database in early June 2000.

*8.1.2 $PM_{2.5}$ Organic Composition:* PM2.5 samples acquired in Nashville and Atlanta were provided to us by Georgia Tech. Table 8.2 lists the sample information (dates and sample numbers). All samples were solvent extracted by mild sonication using a mixture of dichloromethane/acetone/hexane (2:3:5 by vol.) and analyzed for organic composition using a GC/MS. Table 8.3 lists the compounds quantified. The data is available from the University of Miami. These data set along with the data from the size-segregated sampling are being used for a student dissertation at UM-RSMAS.

Table 8.1. VOCs target list for SCISSAP study

| | | |
|---|---|---|
| Freon-12 | Butanal | 1,2-Dibromoethane |
| Freon-114 | Methyl Vinyl Ketone (MVK) | Hexanal |
| Chloromethane | Chloroform | Methyl Butyl Ketone (MBK) |
| Vinyl Chloride | Ethyl Acetate | Chlorobenzene |
| Propylene | 1,1,1-Trichloroethane | Ethylbenzene |
| 1,3-Butadiene | Cyclohexane | m&p-Xylene |
| Bromomethane | Methyl Ethyl Ketone (MEK) | o-Xylene |
| Acetaldehyde | Tetrahydrofuran (THF) | Styrene |
| Chloroethane | Carbon Tetrachloride | Bromoform |
| Methanol | Benzene | α-Pinene |
| Freon-11 | 1,2-Dichloroethane | Heptanal |
| Isoprene | 2-Butanol | 1,1,2,2-Tetrachloroethane |
| 1,1-Dichloroethene | Heptane | 4-Ethyltoluene |
| Freon-113 | Trichloroethylene | β-Pinene |
| Carbon Disulfide | 1,2-Dichloropropane | 1,3,5-Trimethylbenzene |
| Propanal | 1-Butanol | 2-Ethyl-1-Hexanal |
| Ethanol | Pentanal | Benzealdehyde |
| Methylene Chloride | Bromodichloromethane | 1,2,4-Trimethylbenzene |
| trans-1,2-Dichloroethene | 2-Pentanone | 1,3-Dichlorobenzene |
| Acetone | Methyl Methacrylate | Limonene |
| Isopropyl Alcohol | 1,4-Dioxane | 1,4-Dichlorobenzene |
| Hexane | trans-1,3-Dichloropropene | Octanal |
| 1,1-Dichloroethane | Toluene | Benzyl Chloride |
| Methyl tertbutyl ether (MT | Methyl Isobutyl Ketone (MI | 1,2-Dichlorobenzene |
| Methacrolein (MACR) | cis-1,3-Dichloropropene | Nonanal |
| Vinyl Acetate | 1,1,2-Trichloroethane | 1,2,4-Trichlorobenzene |
| cis-1,2-Dichloroethene | Tetrachloroethylene | Hexachloro-1,3-Butadiene |
| 3-Methyl furan | Dibromochloromethane | Decanal |

Table 8.2. Sample information for PM2.5 samples

| | **Sampling date** | **Samples received and analyzed** |
|---|---|---|
| Nashville (Hendersonville) | | |
| PUF Samples | 6/16/99 to 8/1/99 | 2 samples + 2 blanks |
| QFF Samples | | 16 samples + 16 blanks |
| **Nashville (Dickson)** | | |
| PUF Samples | 6/15/99 to 8/1/99 | 3 samples + 3 blanks |
| QFF Samples | | 15 samples + 15 blanks |
| *Atlanta (Jefferson)* | | |
| ***QFF Samples*** | 7/28/99 to 8/04/99 | 6 samples + 7 blanks |

Table 8.3. Target compounds for organic speciation of PM2.5

| Alkanes | PAH | Organic acids |
|---|---|---|
| | | |
| n-C10, Decane | Napthalene | n-C4 Carboxylic acid |
| n-C11, Undecane | Acenaphthylene | n-C5 Carboxylic acid |
| n-C12, Dodecane | Acenaphthene | n-C6 Carboxylic acid |
| n-C13, Tridecane | Fluorene | n-C7 Carboxylic acid |
| n-C14, Tetradecane | Phenanthrene | n-C8 Carboxylic acid |
| n-C15, Pentadecane | Anthracene | n-C9 Carboxylic acid |
| n-C16, Hexadecane | Fluoranthene | n-C10 Carboxylic acid |
| n-C17, Heptadecane | Pyrene | n-C12 Carboxylic acid |
| n-C18, Octadecane | Chrysene | n-C13 Carboxylic acid |
| n-C19, Nonadecane | Benzo(a)anthracene | n-C14 Carboxylic acid |
| n-C20, Eicosane | Benzo(b)fluoranthene | n-C15 Carboxylic acid |
| n-C21, Heneicosane | Benz(k)fluoranthene | n-C16 Carboxylic acid |
| n-C22, Docosane | Benzo(e)pyrene | n-C17 Carboxylic acid |
| n-C23, Tricosane | Benzo(a)pyrene | n-C18 Carboxylic acid |
| n-C24, Tertacosane | Perylene | n-C19 Carboxylic acid |
| n-C25, Pentacosane | Indeno(1,2,3-cd)pyrene | n-C20 Carboxylic acid |
| n-C26, Hexacosane | Dibenzo(ah)anthracene | n-C21 Carboxylic acid |
| i-C27, *iso*-Heptacosane | Benzo(ghi)perylene | n-C22 Carboxylic acid |
| a-C27, *anteiso*-Heptacosane | | n-C23 Carboxylic acid |
| n-C27 Heptacosane | Other | n-C24 Carboxylic acid |
| i-C28, *iso*-Octacosane | | |
| a-C28, *anteiso*-Octacosane | Pristane | |
| n-C28, Octacosane | Dibenzothiophene | |
| i-C29, *iso*-Nonacosane | Phytane | |
| a-C29, *anteiso*-Nonacosane | | |
| n-C29, Nonacosane | | |
| i-C30, *iso*-Triacontane | | |
| a-C30, *anteiso*-Triacontane | | |
| n-C30, Triacontane | | |
| i-C31, *iso*-Hentriacontane | | |
| a-C31, *anteiso*-Hentriacontane | | |
| n-C31, Hentriacontane | | |
| i-C32, *iso*-Dotriacontane | | |
| a-C32, *anteiso*-Dotriacontane | | |
| n-C32, Dotriacontane | | |
| i-C33, *iso*-Tritriacontane | | |

*8.1.3 Size Segregated Particulate Matter Organic Composition:* Size segregated particulate matter samples were collected by UM-RSMAS using a MOUDI (Micro Orifice Uniform Deposit Impactor). A total of 8 sampling periods (72 hours) were collected each having a QFF backup, 9 size cuts of aluminum impactor discs, and a PUF plug. The aluminum impactor discs were extracted using the same procedure as the QFF media. New analytical methods had to be developed in order to detect the compounds of interests. A Programmable Temperature Vaporization (PTV) inlet was used allowing injection volumes of 50 µl. The compounds quantified are the same as for PM2.5 listed in Table 8.3. This work served as the basis for the University of Miami participation in BRACE (Bay Regional Atmospheric Chemistry Experiment) carried out in Tampa, FL in May 2002 with the support of the Florida Department of EnvironmentAL Protection as well as the US EPA.

*8.1.4. Laboratory Intercomparison:* At the request of EPA, Dr. Zika's group became involved in NIST (National Institute of Standards and Technology) Intercomparison Exercise Program for Organic Contaminants in PM2.5 Air Particulate Matter. This intercomparison program includes the laboratories that are involved in the various national Supersite studies. Its goal is to compare extraction and analysis methods for organic contaminants in PM2.5. During phase 1 of the NIST Program, unknown neat PM2.5 material and unknown PM2.5 extracts were analyzed using the same methods as for SCISSAP samples. Our results agreed extremely well with certified values. Phase 2 of the NIST Program is currently under progress.

## 8.2 Results and Findings

*8.2.1. Evaluation of an Automated OVOC Sampling and Analysis System:* During August 1999, an analysis targeting 84 OVOCs was undertaken as part of the EPA SCISSAP program at the Atlanta SuperSite. The sampling manifold consisted of glass pipe with the inlet at approximately 11 meters above ground level. Ambient air was pulled through the manifold with a regenerative blower at a rate of approximately 2000 liters/minute. Teflon tubing was inserted into the flow stream of the manifold and air was drawn into the laboratory through this tubing at a flow rate of at least 2 liters/minute. An ambient air sample was collected from this tubing every hour and was sampled at a flow rate of 100 ml/minute. The sample was concentrated using a cryotrapping, cryofocussing system developed in our laboratory for automated, unattended analysis of OVOCs. It consisted of a 25 liter liquid Nitrogen dewar, into which the traps were assembled. A Teflon cap was machined to fit the top of the dewar that held two square channels that extended to almost the bottom of the dewar. The cap also contained 4 ports, one for the introduction of liquid nitrogen, one for pressurizing the dewar, and two for venting the dewar. On top of the Teflon cap, a cover plate was attached, which held the two traps that were used. One, the cryotrap, was used to collect the ambient air and was made of 1/16" silcosteel tubing. The second, the cryofocusser, was used to further concentrate the sample and was made of 0.53 mm id silcosteel tubing. Valves and other electronics used to control the trapping of the sample were housed in two enclosures. Software was developed using National Instruments LabView to control the entire concentration process, and to initiate the gas chromatographic analysis. The GC system was a Hewlett-Packard 6890 GC with a Hewlett-Packard 5973 MSD detector. The system ran approximately 23 hours per day throughout the study, with the remaining hour used to refill the dewar for the next day's analysis. Gas standard mixtures were analyzed routinely and an evaluation of the overall performance of the system will be discussed in terms of the precision and accuracy of the analytical results obtained.

*8.2.2. Urban Air Characterization Using Measurements of Hourly Oxygenated Volatile Organic Compounds during the Atlanta Supersite Experiment 1999:* An extensive gas phase urban air sampling and characterization study was conducted during the Atlanta Supersite 1999 Experiment to determine gas phase oxygenated volatile organic compound (OVOC) concentrations. A fully automated OVOC system consisting of a two stage cryogenic sampler connected directly to a Hewlett-Packard 6890 GC with a Hewlett-Packard 5973 MS detector was used for the sample analysis. This system collected and analyzed one 100 ml sample of ambient air per hour. On average 20 samples a day were run during the month of August,1999 at the Supersite. The remaining 4 hours each day were used for running standards and other system operations. A total of 696 samples were analyzed for 84 OVOCs that included, in addition to the EPA TO-15 standard, a series of primarily biogenic compounds of interest. Hourly analysis permitted monitoring of diel variations in concentration and speciation.

A positive correlation between ozone concentrations and methyl methacrylate, 2-pentanone, and propanal indicate a relationship between these compounds and air quality. Further analysis revealed a positive relationship amongst CO, benzene, and MTBE indicating similar sources for these compounds, and suggests that with further refinement this technique could be used to assess the relative proportion of biogenic to anthropogenic compounds in the total OVOC budget.

*8.2.3. The Size Distribution and Interrelationships of Speciated Organic Compounds, Aerosol Organic Carbon and Elemental Carbon:* Aerosol samples were collected for analysis of organic and elemental carbon (EC/OC) and speciated organic compounds using non-rotating Micro Orifice Uniform Deposit Impactors (MOUDI) during the month of August 1999 at the Atlanta Super Site as part of the SCISSAP Project. Aerosols were collected on aluminum foil impactor stages with a quartz fiber after filter. Both foils and filters were precombusted at $>$ 500 C. The aerodynamic cut diameters of the stages used were: 1.78, 0.97, 0.56, 0.32, 0.18, 0.098, and 0.056 um. Two different sampling durations were used: 9.5h for total EC/OC analysis and 84h for speciated organic compound analysis (SOC). EC/OC samples were collected daily, nominally 08:30 to 18:00 and 19:30 to 06:00 EST, in order to sample possible diel variability. Organic and elemental carbon analyses were performed using the Desert Research Institute Thermal/Optical Reflectance Carbon Analysis System. Samples for SOC were extracted using dichloromethane:hexane:acetone and the extracts were analyzed on a Hewlett-Packard 6890 GC with a Hewlett-Packard 5573 MSD Total elemental carbon concentrations ranged from 0.5 to 4.7 and averaged 1.7 ug m$^{-3}$. An unpaired t-test indicated the probability that day and night time elemental carbon concentrations were different was 0.80. The EC and OC distribution did change over the course of the month, but no diel trend was apparent. On average, 43 percent of the total organic carbon collected was located on the quartz fiber after filter. This is very unlike elemental carbon where the after filter contained only 9 percent of the total. Volatile and semi-volatile organic compounds may have adsorbed on the after filter. The total organic carbon concentration for the aluminum foil stages ranged from 1.7 to 9.9 and averaged 4.5 ug m$^{-3}$. Nighttime organic carbon concentrations were greater than those during the day (probability of 0.984). SOC analysis provided semi-quantitative information for a series a n-alkanes (C17 to C34) and polycyclic aromatic hydrocarbons (PAH) such as pyrene, fluoranthene and benzo(b,k)fluoranthene. Preliminary results indicate that nearly all the compounds detected are present in all the size fractions. Different distributions among the size fractions for the n-alkanes and the PAHs extracted were observed. The distribution of specific markers (diesel, gasoline, wood burning, etc.) with different size fractions and with OC/EC content and aerosol number density suggest that they could be used in detailed OC/EC source apportionment studies.

*8.2.4. Evidence for a Correlation Between Gas Phase Organic Compounds and Particle Formation During the Atlanta Supersite Study in 1999:* Analysis of hourly ambient air samples for 84 oxygenated volatile organic compounds (OVOCs) in Atlanta, GA during the EPA Supersite field study August 1999 are presented. A unique collection and concentration system incorporating highly inert surfaces, Teflon and Silicosteel, coupled with state-of-the-art GC-MS provided detection limits in the range of 2 to 28 parts per trillion (ppt) for 100ml ambient air samples. A relationship was observed between OVOCs and particulate phase organic carbon concentration, $PM_{2.5}$ total organic carbon, as well as particle number. Calculation of the hourly new particle production potential from our hourly OVOC determination shows that gas to particle conversion is a significant source of new organic aerosols. This calculation of new particle production predicts approximately half of the measured $PM_{2.5}$ total organic carbon observed. A correlation was observed between the variation of predicted organic particle concentration over time and the measured $PM_{2.5}$ total organic carbon however there is a variable time lag between these two values. Reaction mechanisms in the literature propose a branching during the oxidation of OVOCs where one route leads to lower volatility compounds capable of particle production and the other leads to higher volatility products. The higher volatility oxidized organic compounds were investigated as an indicator of organic particle co-production. A strong correlation was observed for acetone to number of particles in the Aitken nuclei range. Combined with improved knowledge of organic particle production potential, gas phase data may serve as a predictive tool for air quality in urban regions.

## 9. MODELING[4]

As presented in the proposal, one of the major activities associated with SCISSAP was to develop, apply and evaluate a regional scale air quality for conducting integrated studies of ozone and particulate matter, and to use that model to address four specific scientific questions (see Section 4.2) and to assess emissions inventories using inverse modeling. As such, we developed a model called URM-1ATM: the "Urban-to-Regional, Multiscale Model: One Atmosphere". In this case, one atmosphere refers to the integrated approach to modeling the physics and chemistry of ozone, acid deposition and particulate matter treating them as part of "one atmosphere." In the past, models have been applied separately for ozone, particulate matter and acid deposition. Another important aspect of this model is that it has, built in, a direct sensitivity analysis technique which is used for source apportionment and inverse modeling.

The URM-1ATM has the capability to simulate the emissions, transport, chemical and physical conversion and deposition (wet and dry) of gaseous and condensed phase pollutants. Being built upon a multiscale model, this is done efficiently across urban and regional domains (Figure 9.1). Outputs of the model are simulated concentration fields for ozone, other gases, and the major particulate matter species (e.g., sulfate, ammonium, elemental and organic carbon and crustals) (Table 9.1), as well as the output from the model's "integrated sensitivity analysis;" these outputs indicate how the concentrations of

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[4] **Prepared by:** A.G. Russell, School of Civil and Environmental Engineering, Georgia Tech

a given primary or secondary pollutant in one region are affected by emissions from that region and other regions of the model domain (see for example, Figure 9.2).

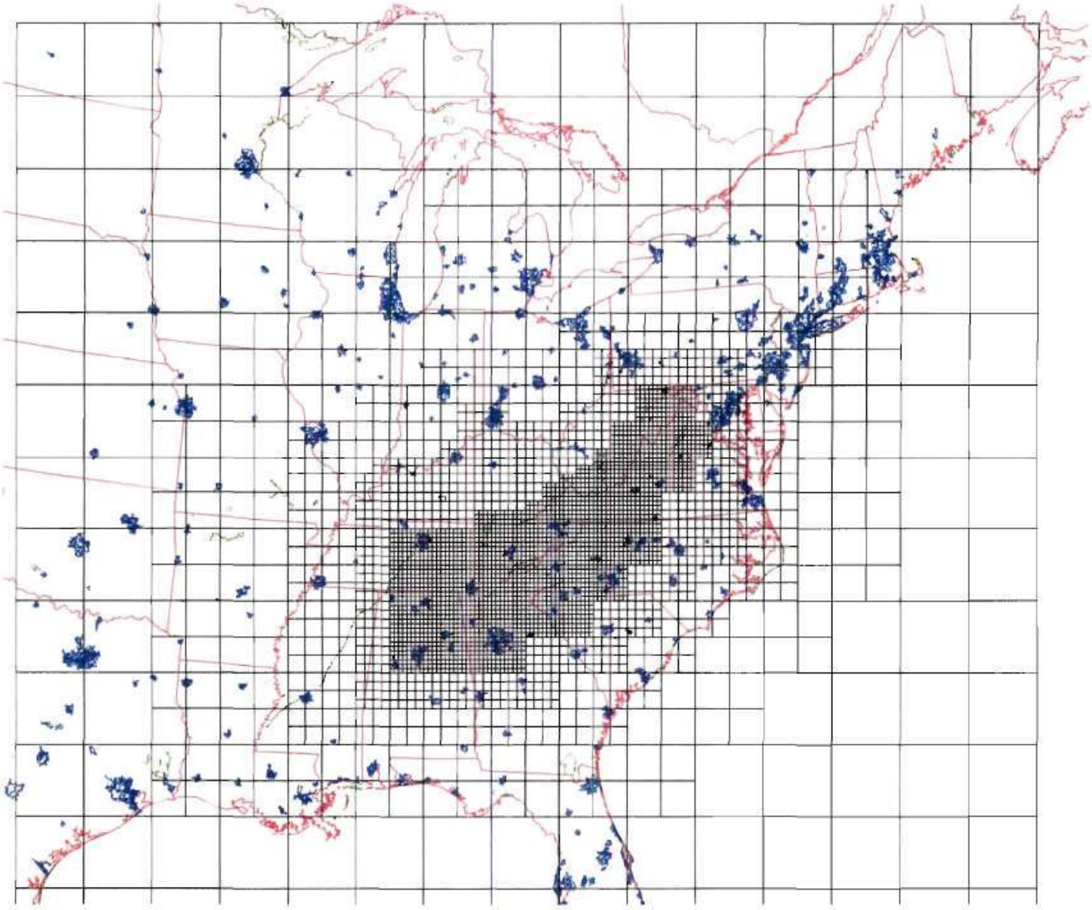


**Figure 9.1.** Multiscale grid used in the URM for the SCISSAP modeling project. Finest resolution was used for those areas of greatest interest (i.e., the areas of the Southeast areas with high ozone and PM cocentrations).

Table 9.1. Species Used in the URM-1ATM Model.

| Transported Gas-Phase Species | Transported Gas-Phase Species | Transported Gas-Phase Species | Transported Aerosol Species | Steady-State Species |
|---|---|---|---|---|
| NO[b] - Nitric Oxide | RRP - RO2-RO2-Product | M2BT - 2- Methyl -2- Butene | SOD$X$[a,b] - Sodium | OSD - O* 1D2, O Singlet D |
| NO2[b] - Nitrogen Dioxide | RHP - RO2-HO2-Product | AAR1[b] - General Alkane and Aromatics | HYD$X$[a] - Hydrogen | O - Oxygen Atom |
| O3 - Ozone | OLRI - OLD-RI, O Atom Reactions with Olefins | AAR2[b] - General Alkane and Aromatics | AMN$X$[a] - Ammonium | HO - Hydroxyl Radical |
| HONO - Nitrous Acid | O3SB - O3OL-SB, Represents Conversion of SO2 TO SO3 | AAR3[b] - General Alkane and Aromatics | NIT$X$[a,b] - Nitrate | CCO - CCO-O2 Radical |
| HNO3 - Nitric Acid | MEOH[b] - Methanol | OLE1[b] - General Alkenes | CHL$X$[a] - Chloride | C2CO - C2CO-O2 Radical |
| HNO4 - Peroxynitric Acid | ETOH[b] - Ethanol | OLE2[b] - General Alkenes | SUL$X$[a,b] - Sulfate | BCO2 - BZ-CO-O2 Radical |
| N2O5 - Nitrogen Pentoxide | GLY - Glyoxal | NH3[b] - Ammonia | WAT$X$[a] - Water | RO2N - Alkyl Nitrate RO2 Radical |
| NO3 - Nitrate Radical | RNO3 - Organic Nitrates | SO2[b] - Sulfur Dioxide | CAR$X$[a,b] - Elemental Carbon | RO2X - RO2-XN Radical |
| HO2 - Hydroperoxy Radical | GPAN - Glyoxyl Developed PAN | SO3 - Sulfur Trioxide, Rapidly forms H2SO4 | ORG$X$[a,b] - Organics | RO2P - RO2-NP, Phenol RO2 Radical |
| CO[b] - Carbon Monoxide | PHEN - Phenol | APNE[b] - α-Pinene | CRM$X$[a,b] - Magnesium | RO2R - General RO2 #1 Radical |
| HCHO[b] - Formaldehyde | TOLU[b] - Toluene | UNKN - Unknown | CRK$X$[a,b] - Potassium | R2O2 - General RO2 #2 Radical |
| MEK[b] - Methlyethyl Ketone | BALD – Benzaldehyde | PRPA - Propane | CRC$X$[a,b] - Calcium | COCO - HCOCO-O2 Radical |
| MGLY - Methyl Glyoxyl | PBZN - Peroxy Benzoyl Nitrate | MARC - Methacrolein | PM$X$[a,b] - Other PM | HCO3 - HOCOO Radical |
| PAN - Peroxyacetyl Nitrate | AFG1 - Aromatic Ring Fragments 1 | MVK - Methyl Vinyl Ketone | | BZO - Phenoxy Radical |
| MPAN - Methly Peroxyacetyl Nitrate | AFG2 - Aromatic Ring Fragments 2 | IPRD - Isoprene Reaction Prods. | | BZNO - BZ(NO2)-O |
| RO2 - Alkyl Peroxy Radicals | CCHO[b] - Acetaldehyde | MRC3 - Methly Peroxyacetyl Radical | | |
| RCO3 - Peroxyacyl Radical | RCHO - Propionaldehyde and all higher Aldehydes | AIR - Air | | |
| ETHE[b] - Ethene | ACET[b] - Acetone | INRT - Inert | | |
| CRES - Cresols and Other Alkyl Phenols | PPN - Peroxy Propionyl Nitrate | HCL - Hydrochloric Acid | | |
| NPHE - Nitrophenols | PRPE – Propene | ORGG - Gas Phase Condensable Organics | | |
| HO2H - Hydrogen Peroxide | M1BT - 2-Methyl-1-Butene | | | |
| C - Carbon Atoms | ISOP[b] - Isoprene | | | |
| LN - Lost Nitrogen Atoms | | | | |
| OOH - Lumped Hydroperoxy Species | | | | |

[a] $X$ represents the different aerosol size bins: $X = 1$ represents aerosols $< 0.156\ \mu m$, $X = 2$ represents aerosols from 0.156 - 0.625 μm, $X = 3$ represents aerosols from 0.625 - 2.5 μm, and $X = 4$ represents aerosols from 2.5 - 10.0 μm.

[b] Emission species generated by EMS-95.

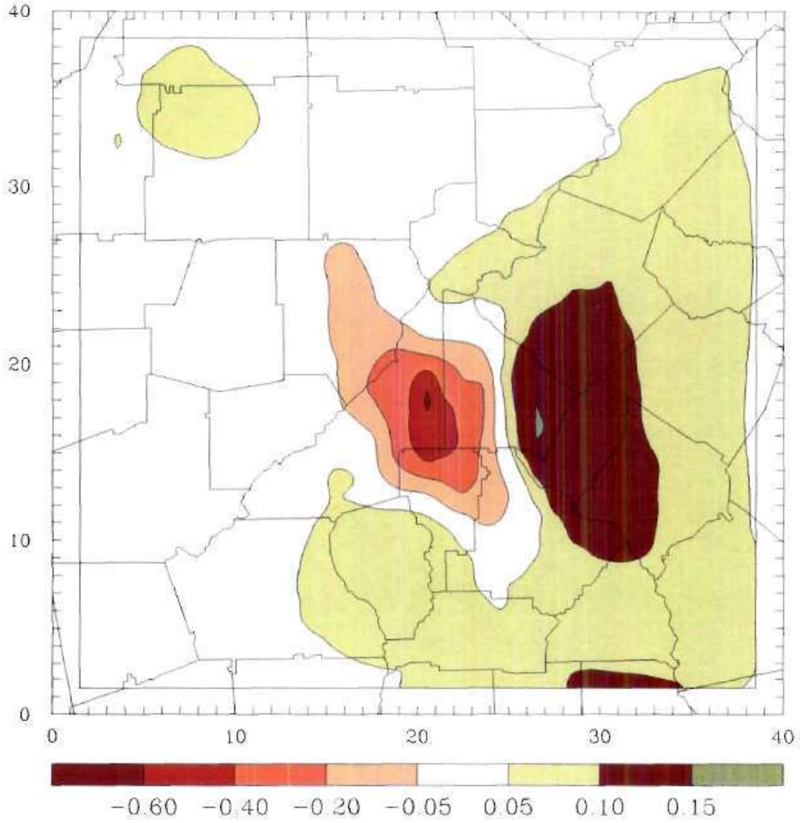


**Figure 9.2.** Model-calculated sensitivity of ozone to mobile source NOx emissions in Atlanta, GA obtained from URM's integrated sensitivity analysis package. (Units are ppbv increase in $O_3$ per % decrease in emissions).

To evaluate model performance, we ran the model, with the integrated sensitivity analysis capability, during the period of SCISSAP (and also Supersite) measurements. As indicated in Figures 9.3 and 9.4, the performance was very good. As part of this work, a new inverse modeling capability was added to the URM to assess the consistency between emissions inventories used to drive air quality models and observed pollutant concentrations. Based upon Ridge-Regression, the method utilizes the direct sensitivity analysis to rapidly provide estimates of biases in the emissions estimates. As applied to the SCISSAP/Supersite measurements, and shown in Table 9.2, it was found that while some of the emissions estimates in the inventory appear very accurate (e.g., $SO_2$), others (e.g., VOCs) appear significantly biased.

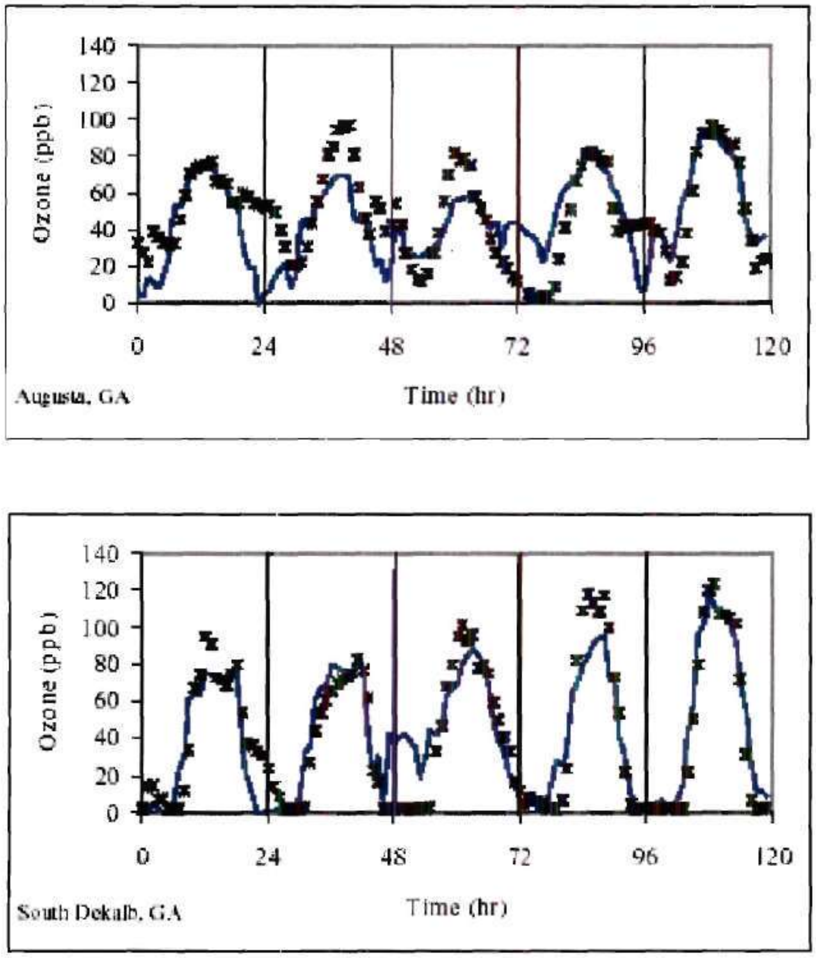
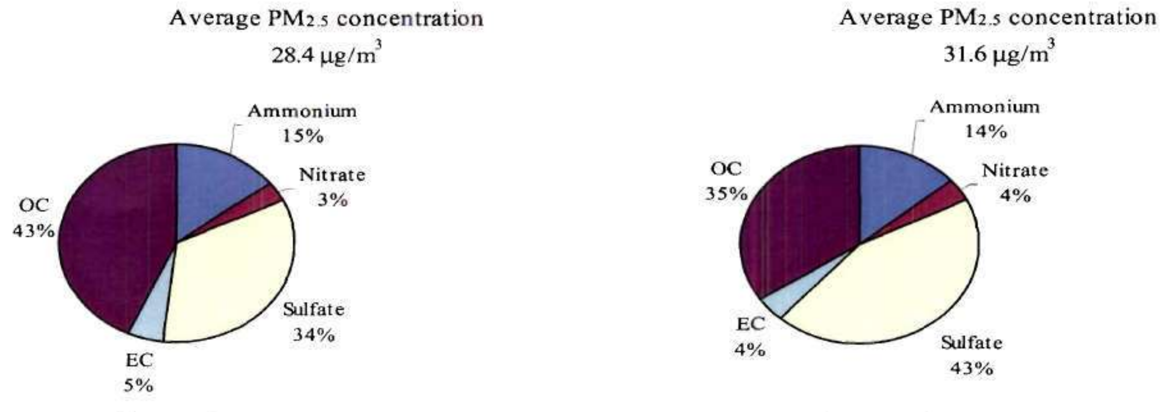


**Figure 9.3.** Simulated and observed ozone at two locations during the SCISSAP measurement period.



observed simulated

**Figure 9.4.** Simulated and observed $PM_{2.5}$ by species during the SCISSAP measurement period.

**Table 9.2.** Estimated relative emissions biases developed using URM-1ATM and inverse modeling.

| | Emission scaling factor | | |
|---|---|---|---|
| Source | August 1999 | SAMI July 1995 | SAMI May 1995 |
| Total CO | 1.01 | 1.08 | 1.26 |
| Total $SO_2$ | 0.92 | 1.13 | 1.08 |
| Area source $NO_x$ | 1.62 | 1.77 | 1.50 |
| Elevated point source $NO_x$ | 1.48 | 1.31 | 1.24 |
| Anthropogenic VOC | 2.47 | 2.21 | 2.84 |
| Biogenic VOC | 1.11 | 1.24 | 1.17 |
| Total $NH_3$ | 0.56 | 0.52 | 0.59 |
| Total fine OC PM | 1.10 | 0.49 | 0.62 |
| Total fine EC PM | 0.56 | N/C | N/C |

During the course of the SCISSAP project, we were presented with the opportunity to integrate the science developed as part of this study with a policy-driven study: the Southern Appalachians Mountains Initiative (SAMI). The SCISSAP modeling system was used in SAMI to address specific policy questions identified by SAMI; not surprisingly the questions the model was used to address for SAMI were quite similar to those listed above for SCISSAP. This provided a unique opportunity for the research team to interact directly with the policy-making community in the southeast and thereby provide a direct policy focus to the research tools being developed under SCISSAP. (The modeling runs for SAMI using the SCISSAP modeling system have now been completed and are currently being used as input into a more comprehensive integrated assessment of the environmental and economic costs and benefits of various emission scenarios projecting to 2010 and 2040; the results of these assessment will then be available to policy makers within the region. For more information see url http://www.saminet.org/aboutsami.html.)

Finally it should be noted, we plan to move the products of the SCISSAP modeling to EPA's Models 3. We agree with the tenet that a community model can provide a more effective approach to advancing the state of the science in air quality modeling, though the SCISSAP model has advantages over the current version of Models 3, including the sensitivity analysis, inverse modeling, chemical mechanism and aerosol thermodynamics. Under other funding, these products of the SCISSAP modeling, and other projects, are being migrated to Models 3, and that model is being used in current studies.

## 10. CONCLUSION

As a result of EPA finding of SCISSAP, a new scientific and technical capability for air quality research, management, and policy formulation has been developed in the southeastern United States. This new capability encompasses a state-of-the-science mobile facility for measuring gaseous and particulate pollutants as well as a state-of-the-science multi-scale multipollutant air quality modeling system.

During the course of the project, the tools described above were used to address a number of policy-relevant scientific issues related to: (1) understanding causes and remedies to fine particle and ground-level ozone pollution in the southeastern United States and (2) the monitoring of fine particles in the atmosphere. With regard to the mitigation of fine particle pollution in the South, our studies confirmed the importance of organic carbon and sulfur oxide emissions and the need to control these emissions on regional rather than urban scales. However, because of thermodynamic interactions between sulfate, ammonium, and nitrate, our studies also suggest that control of nitrogen oxide and ammonium emissions may be desirable at the same time that organic carbon and sulfur oxide emission controls are implemented.

With regard to instrumentation for measuring particulates, our studies suggest that the EPA FRM using the filter-denuder technique can yield accurate data on the mass and overall composition of fine particles. However, the possibility of artifacts, especially for organic carbon persists. Further work and development of denuders, filters, and extraction techniques is probably needed. Our studies also suggest that a wealth of additional information on particulate composition, density, and short-term variability can be obtained with the use of a new and emerging class of semi-continuous particulate monitors. The information and data that can be generated by these new monitors may prove to be especially useful in epidemiological and medical effects research aimed at uncovering the specific components of fine particles that are responsible for the adverse health effects in humans.

The new capabilities developed in SCISSAP are now being used within the region to support both air quality research and management. The mobile monitoring facility is now playing a central role in a variety of local and regional air quality studies funded by local and state agencies, as well as the US EPA. Most notable among these studies is the Georgia Fall Line Air Quality Study (FAQS) which seeks to identify the sources of pollutants and pollutant precursors, and recommend solutions to realized and potential poor air quality in the Augusta, Macon, and Columbus metropolitan areas of Georgia (see url http://cure.eas.gatech.edu/faqs/) . We envision that the mobile facility will continue to represent a valuable resource for the region in the coming years.

The URM-1ATM modeling system developed SCISSAP has made contributions beyond SCISSAP. The modeling system was used in the Southern Appalachian Mountain Initiative to assess the air quality benefits of various possible pollution control scenarios, and is now being migrated to EPA's Models3.

## APPENDIX I. PUBLICATIONS, PRESENTATIONS, THESES

### 1. List of Peer-Reviewed Publications

Baumann K, F Ift, JZ Zhao, MH Bergin, and AG Russell, Measurement of trace gases and $PM_{2.5}$ mass and composition near the ground and at 254 m agl during TexAQS 2000, *Proceedings of the 4th Conference on Atmospheric Chemistry: Urban, Regional, and Global-Scale Impacts of Air Pollutants, Orlando, FL, Amer. Meteor. Soc.*, 242-247, 2002.

Baumann K, F Ift, JZ Zhao, and WL Chameides, Discrete measurements of reactive gases and fine particle mass and composition during the 1999 Atlanta SuperSite Experiment, *J. Geophys. Res.*, **108**, doi: 10.1029/2001JD001210, 2003.

Baumann, K, F Ift, JZ Zhao, and WL Chameides, Investigating the adsorption artifact during aerosol sampling of semi-volatile organic carbon, *J. Geophys. Res.*, **108**, doi:10.1029/2001JD001210, 2003.

Boylan J.W., Odman M.T., Wilkinson J.G., Russell A.G., Doty K.G., Norris W.B. and McNider R.T. Development of a comprehensive, multiscale "one atmosphere" modeling system: Application to the Southern Appalachian Mountains. *Atmos. Environ.*, in press, 2003.

Capaldo, K.P., P. Kasibhatla, S.N. Pandis: "Is aerosol production within the remote marine boundary layer sufficient to maintain observed concentrations?" J. Geophys. Res. 104: 3483-3500, 1999

Carrico, CM,MH Bergin, J Xu, K Baumann, and H Maring, Urban aerosol radiative properties: Measurements during the Atlanta SuperSite 1999 Experiment, *J. Geophys. Res.*, *108*, doi:10.1029/2001JD001222, 2002.

Farmer, C.T., Stabenau, E.R., and Zika, R.G. Evaluation of an automated OVOC sampling and analysis system. *J. Geophys. Res.*, in press, 2003.

Kasibhatla, P., and W.L. Chameides: "Seasonal modeling of regional ozone pollution in the eastern United States," Geophys. Res. Lett. 27:1415-1418, 2000

McMurry, P. H., Wang, X., Park, K., Ehara, K, The relationship between mass and mobility for atmospheric particles: A new technique for measuring particle density, *Aerosol Sci. Technol.* 36:227-238, 2002

Mendoza-Dominguez A. and Russell A.G. Estimation of emission adjustments from the application of four-dimensional data assimilation to photochemical air quality modeling. *Atmos. Environ.* 35, 2879-2894, 2001.

Mendoza-Dominguez, A.; Russell, A.G. "Iterative Inverse Modeling and Direct Sensitivity Analysis of a Photochemical Air Quality Model," Environ. Sci. Technol. 34, 4974-4981, 2000.

Mendoza-Dominguez, A.; Wilkinson, J.G.; Yang, Y.-J.; Russell, A.G. "Modeling and Direct Sensitivity Analysis of Biogenic Emissions Impacts on Regional Ozone Formation in the Mexico-U.S. Border Area," J. of the Air & Waste Management Association. 50, 21-31, 2000.

Park, K., F. Cao, D. B. Kittelson, and P. H. McMurry, "Relationship between particle mass and mobility for diesel exhaust particles," Environ. Sci. Technol., 37(3) 577-583, 2003

Park. K., D. B. Kittelson, and P. H. McMurry, 2003, "A Closure Study of Aerosol Mass Concentration Measurements: Comparison of Values Obtained with Filters and by Direct Measurements of Mass Distributions," Atmospheric Environment, Special Issue of AE in honor of Jim Lodge, in press, 2003.

Solomon, PA, K Baumann, ES Edgerton, R Tanner, D Eatough, W Modey, H Maring, D Savoie, S Natarajan, MB Meyer, and G Norris, Comparison of integrated samplers for mass and composition during the 1999 Atlanta-Supersites Project, *J.Geophys. Res*108, doi:10.1029/2001JD001218, 2003.

Solomon, P.A., W. Chameides, R.W. Weber, A. Middlebrook, C.S. Kiang, A.G. Russell, A. Butler, , Turpin, B., D. Mikel, R. Scheffe, E. Cowling, E. Edgerton, J. St. John, J. Jansen, P. McMurry, S. Hering, and T. Bahadori, "Overview of the 1999 Atlanta Supersite Project, *J.Geophys. Res.*, **108**, doi:10.1029/2001JD001458, 2003.

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Yang, Y.-J., Wilkinson, J.G., Odman, M.T., and Russell, A.G., Ozone Sensitivity and Uncertainty Analysis Using DDM-3D in a Photochemical Air Quality Model, in: *Air Pollution Modelling and Its Application XII*, S.-E. Gryning and E. Batchvarova eds., Kluwer Academic/Plenum Publishers, New York, 183-194, 2000.

Zhang, J., W.L. Chameides, R. Weber, G. Cass, D. Orsini, E. Edgerton, P. Jongejan, J. Slanina, An evaluation of the thermodynamic equilibrium assumption for fine particulate composition: Nitrate and ammonium during Atlanta '99 Supersite Experiment, *J. Geophys. Res. 108*, doi:10.1029/2001JD001592, 2002.

2. List of Presentations

Baumann, K., et al. Measurement of trace gases and PM2.5 mass and composition near the ground and at 254 m agl during TexAQS 2000 and comparison with other regions, 82nd Annual Conference of the American Meteorological Society, Orlando, FL, January 2002.

Baumann, K. et al. Measurements of trace gases and $PM_{2.5}$ species and mass at LaPorte (LP) and Williams Tower (WT), TexAQS 2000 Science Meeting, Austin, TX, August 2001.

Baumann K, ES Edgerton, BE Hartsell, and WL Chameides, Trace gas concentrations during the 1999 Atlanta Supersite Experiment, *Eos Transactions, Amer. Geophys. U. 81*, A11B-04, 2000.

Bergin MH, J Xu, CM Carrico, ES Edgerton, K Baumann, and H Maring, Measurement of aerosol radiative properties during the Atlanta Supersite Study. *Eos Transactions, Amer. Geophys. U. 81*, A72C-09, 2000.

Bergin M.S., Boylan, J.W., Wilkinson J.G., Odman M.T. and Russell A.G. (2001) Regional multiscale atmospheric modeling: comparison of model performance for aerosol simulations using two grids. Poster presentation. *American Association for Aerosol Research Conference*. Portland, OR.

Edgerton, ES, BE Hartsell, JJ Jansen, J StJohn, and K Baumann, Chemical and meteorological characteristics of the Jefferson Street Monitoring Site, *Eos Transactions, Amer. Geophys. U. 81*, A11B-02, 2000.

Farmer CT, ER Stabenau and RG Zika, "Evaluation of an Automated OVOC Sampling and Analysis System", Eos Trans. AGU, 81 (48), Fall Meet. Suppl., Abstract A11B-05, 2000.

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Ift F, K Baumann, WL Chameides, DD DiPasquale, RJ Weber, JZ Zhao, C Baxter, MH Bergin, and ES Edgerton, Discrete measurements of PM2.5 mas and composition by use of the three-channel Particle Composition Monitor (PCM), *Eos Transactions, Amer. Geophys. U. 81*, A11B-10, 2000.

McMurry, P. H., Dick, W. D., Wang, X., "Novel Measurements of atmospheric aerosol properties," (Invited plenary lecture) Proceedings of the 15th International Conference on Nucleation and Atmospheric Aerosols, Rolla, MO, ,August 6-11, AIP Conference Proceedings Volume 534: 699-710, 2000.

McMurry, P. H. and X. Wang, "Precise measurements of the density of atmospheric particles by a novel technique," American Geophysical Union, San Francisco, CA, December 15-19.

Russell AG, A Butler, ES Edgerton, K Baumann, and PA Solomon, Local and regional representativeness of the Jefferson Street site, *Eos Transactions, Amer. Geophys. U. 81*, A11B-03, 2000.

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Stabenau ER, RT Tremblay, CT Farmer and RG Zika, "Urban Air Characterization Using Measurements of Hourly Oxygenated Volatile Organic Compounds During the Atlanta Supersite Experiment 1999", Eos Trans. AGU, 81 (48), Fall Meet. Suppl., Abstract A11B-06, 2000.

Tremblay RT, H Maring, DL Savoie, PJ Milne, ER Stabenau and RG Zika, "The Size Distribution and Interrelationships of Speciated Organic Compounds, Aerosol Organic Carbon and Elemental

Wang, X, P. H. McMurry, K. Ehara, "Measurements of density of atmospheric particles using the TDMA-APM technique," p. 443, American Association for Aerosol Research, St. Louis, MO, November 6-10, 2000.

3. List of Theses

M.S.

Xin Wang, 2000, "Measurement of particle density using the TDMA/APM technique" Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN. Defended September 9, 2000

Ph.D.

Kihong Park, 2003, "In-Situ measurements of physical properties of 50-500 nm particles: Mass-mobility relationship." Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN Defended April 10, 2003

Mendoza-Dominguez, A. "A Four-Dimensional Data Assimilation Method for Air Quality Modeling." School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, GA, 2000.

CA8120 Georgia Institute of Technology Page: 1
Office of Sponsored Programs 17-JAN-2003 08:30
PROJECT CLOSEOUT - NOTICE

PeopleSoft Project Id 3506W62 Closeout Notice Date 17-JAN-2003

PeopleSoft Fund R1013

Project Number G-35-W62 Doch Id 48104

Center Number 10/24-6-R1013-0A0

Project Director CHAMEIDES, WILLIAM

Project Unit EARTH AND ATM SCI

Sponsor ENVIRONMENTAL PROTECTION AGENCY/EPA/ DC

Division Id 3481

Contract Number R 826372 Contract Entity GTRC

Prime Contract Number

Title SOUTHERN CENTER FOR INTEGRATED STUDY OF SECONDARY AIR POLLUTANTS (SCISSAP)

Effective Completion Date 31-MAR-2002 (Performance) 30-JUN-2002 (Reports)

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| Closeout Action: | Y/N | Date Submitted |
|---|---|---|
| Final Invoice or Copy of Final Invoice | Y | |
| Final Report of Inventions and/or Subcontracts | Y | |
| Government Property Inventory and Related Certificate | N | |
| Classified Material Certificate | N | |
| Release and Assignment | N | |
| Other | N | |

Comments

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Distribution Required:

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| GTRI Accounting | N |
| Research Security Department | N |
| Reports Coordinator | Y |
| Research Property Team | Y |
| Supply Services Department/Procurement | Y |
| Research Communications Team | N |
| Georgia Tech Research Corporation | Y |
| Project File | Y |
| OSP/OOD | N |
| Office of Legal Affairs | N |

NOTE: Final Patent Questionnaire sent to PDPI

# MEMORANDUM

## GEORGIA INSTITUTE OF TECHNOLOGY
## OFFICE OF SPONSORED PROGRAMS

**TO:** LIBRARY/ARCHIVES
MAIL CODE: 0900

**FROM:** DISTRIBUTION CENTER/OSP

**SUBJECT:** MISSING DELIVERABLES

AFTER REVIEWING THE FOLLOWING TERMINATED PROJECT NUMBER G-35-W62
IT HAS BEEN DETERMINED THAT THERE ARE MISSING DELIVERABLES (REPORTS):

| | |
|---|---|
| DELIVERABLE NUMBER: 5 | DELIVERABLE NUMBER: ________ |
| DELIVERABLE NUMBER: ________ | DELIVERABLE NUMBER: ________ |
| DELIVERABLE NUMBER: ________ | DELIVERABLE NUMBER: ________ |
| DELIVERABLE NUMBER: ________ | DELIVERABLE NUMBER: ________ |

EVERY EFFORT WILL BE MADE TO LOCATE THE MISSING ONES, HOWEVER, WE ARE STILL SENDING THE REPORTS TO YOUR DEPARTMENT FOR THE CLOSE-OUT PROCEDURES.

IF YOU HAVE ANY QUESTIONS, PLEASE DO NOT HESITATE TO CALL.

THANKS.

CA8030

Georgia Institute of Technology - Office of Contract Administration
Deliverable Schedule Project #: G-35-W62

Page 1
16-APR-1998 13:00

Document Header Id #: 48104
Sponsor: ENVIRON PROTECTION AGENCY/EPA - DC
Award Document: GRANT Contract #: R 826372
Project Director(s): CHAMEIDES WILLIAM L Contract thru: GTRC
Unit: E & A SCI
Initiation Date: Termination Perf Date: 31-MAR-2001 Termination Rpts Date: 30-JUN-2001
Project Title: SOUTHERN CENTER FOR INTEGRATED STUDY OF SECONDARY AIR POLLUTANTS (SCISSAP)

| Rev No (1) | Description of Deliverable | Deliv Id No (2) | Period | Covered | Due Date to Sponsor (3) | Copies Reqd | Date Mailed (4) |
|---|---|---|---|---|---|---|---|
| | ANNUAL PROGRESS RRPORT | 1 | 01-APR-1998 | 31-MAR-1999 | 30-APR-1999 | 2 | 25-AUG-1999✓ |
| | ANNUAL PROGRESS RRPORT | 2 | 01-APR-1999 | 31-MAR-2000 | 30-APR-2000 | 2 | 05-JUL-2000✓ |
| | FINAL TECHNICAL REPORT - DRAFT | 3 | 01-APR-1998 | 31-DEC-2000 | 31-DEC-2000 | 2 | |
| | FINAL TECHNICAL REPORT - APPROVED | 4 | 01-APR-1998 | 31-MAR-2001 | 30-JUN-2001 | 2 | |

PLEASE NOTE:

1. An asterisk denotes this deliverable was changed or added by this mod.
2. The Deliverable Id No will remain associated with its originally assigned deliverable for the duration of the project. Modifications to the project will no longer cause this number to be sequentially renumbered.
3. Blanks in 'Due Date to Sponsor' indicate 'as appropriate' or 'as required'.
4. Blanks in 'Date Mailed' indicate that neither delivery nor notification of delivery has been accomplished through OCA/CSD.

Prepare reports in accordance with:
REFERENCE ITEM 9

PD/PI CONCUR: ____________________
SIGNATURE & DATE

If not returned, OCA assumes
concurrence with deliverable schedule.

CA8030

Georgia Institute of Technology - Office of Sponsored Programs
Deliverable Schedule P/S Project #: 3506W62
Old Project #: G-35-W62

28-JUN-2002 11:46

Document Header Id #: 48104
Sponsor: ENVIRON PROTECTION AGENCY/EPA/ DC
Award Document: GRANT Contract #: R 826372
Project Director(s): CHAMEIDES WILLIAM L Contract thru: GTRC
Unit: EARTH AND ATM SCI
Initiation Date: 01-APR-1998 Termination Perf Date: 31-MAR-2002 Termination Rpts Date: 30-JUN-2002
Project Title: SOUTHERN CENTER FOR INTEGRATED STUDY OF SECONDARY AIR POLLUTANTS (SCISSAP)

| Rev No (1) | Description of Deliverable | Deliv Id No (2) | Period | Covered | Due Date to Sponsor (3) | Copies Reqd | Date Mailed (4) |
|---|---|---|---|---|---|---|---|
| | ANNUAL PROGRESS RRPORT | ✓1 | 01-APR-1998 | 31-MAR-1999 | 30-APR-1999 | 2 | 25-AUG-1999 |
| | ANNUAL PROGRESS REPORT | ✓2 | 01-APR-1999 | 31-MAR-2000 | 30-APR-2000 | 2 | 05-JUL-2000 |
| | ANNUAL PROGRESS REPORT | 5 | 01-APR-2000 | 31-MAR-2001 | 30-APR-2001 | 2 | 19. Jun 02 |
| | FINAL TECHNICAL REPORT - DRAFT | ✓3 | 01-APR-1998 | 31-DEC-2001 | 31-DEC-2001 | 2 | 19-JUN-2002 |
| | FINAL TECHNICAL REPORT - APPROVED | ✓4 | 01-APR-1998 | 31-MAR-2002 | 30-JUN-2002 | 2 | 19-JUN-2002 ~ SF. 6.28.02 |
| | | | | | ✓ Revised ✓ Final Rpt ... | | 14-APR-2003 |

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1. An asterisk denotes this deliverable was changed or added by this mod.
2. The Deliverable Id No will remain associated with its originally assigned deliverable for the duration of the project. Modifications to the project will no longer cause this number to be sequentially renumbered.
3. Blanks in 'Due Date to Sponsor' indicate 'as appropriate' or 'as required'.
4. Blanks in 'Date Mailed' indicate that neither delivery nor notification of delivery has been accomplished through OSP/CSD.

Prepare reports in accordance with:
REFERENCE ITEM 9

✓ APR. 24, 2003 P.I. submitted another Final Rpt. 4-1-98 – 3/31/02 14-APR-2003.
(Revised version).

**Kamie Cunningham**

---

**From:** Laura Cederquist

**Sent:** Friday, June 28, 2002 4:36 PM

**To:** Kamie Cunningham

**Subject:** RE: SCISSAP Final Report

Kamie,

This is it for the project. It termed as of Mar 31, 2002. This is the last report Dr. Chameides will do for this project.

Laura

At 11:43 AM 6/28/2002 -0400, you wrote:

> Hi Laura,
>
> According to our database records Dr. Chameides have an Annual Report dated: Apr.01-00 Mar.-31-01. Due Apr. 30.
>
> Is this report also included in the reports that you forwarded to us. There is a new deliverable schedule and I would be happy to fax it to you.
>
> Thanks,
>
> Kamie
>
> -----Original Message-----
> **From:** Laura Cederquist
> **Sent:** Friday, June 28, 2002 2:13 PM
> **To:** ocareports
> **Subject:** Fwd: SCISSAP Final Report
>
> A signed "Research Report Approval Sheet" is being routed to OSP-REATT.
>
> Laura

X-Sender: wcham@eas.gatech.edu
X-Mailer: QUALCOMM Windows Eudora Version 5.1
Date: Wed, 19 Jun 2002 16:52:59 -0400
To: Shapiro.Paul@epamail.epa.gov
From: William Chameides <wcham@eas.gatech.edu>
Subject: SCISSAP Final Report
Cc: kb@eas.gatech.edu, mcmurry@me.umn.edu, rod Zika <rzika@rsmas.miami.edu>

Dear Paul,

I am herewith submitting to you the following:
1. A final version of the Executive Summary of our Final Report for web publication
2. A draft version of the complete Final Report, for you review and comment.

Thanx.

```
--

BILL Chameides

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>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>><<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<
|>>>>>> W.L. Chameides, Smithgall Chair and Regents Professor<<<<<<
<<<<<<<<<<<<
>>>>>>>>>Acting Chairperson for Earth and Atmospheric
Scences<<<<<<<<<<<<<<<<<<<
>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>><<<<<
|>> Earth and Atmospheric Sciences          email:wcham@eas.gatech.edu<<<<<<<<<<
|>> Georgia Tech                           PHONE:  (404) 385 - 1548<<<<<<<<<<<<<
|>> Atlanta, GA 30332                        FAX:(404) 894 - 5638<<<<<<<<<<<<<<<
|>> USA www-wlc.eas.gatech.edu<<<<<<<<<<<<<<<
>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>><<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<
```

Laura D. Cederquist
Financial Manager I
Earth and Atmospheric Sciences
Phone: (404) 894-0275
Fax: (404) 894-5638

...... You're caught up in the Internet

You think it's such a great asset
But you're wrong, wrong, wrong

All that fiber optic gear
Still cannot take away the fear
Like an island song..... J. Buffett

Laura D. Cederquist
Financial Manager I
Earth and Atmospheric Sciences
Phone: (404) 894-0275
Fax: (404) 894-5638

...... *You're caught up in the Internet*
*You think it's such a great asset*
*But you're wrong, wrong, wrong*

*All that fiber optic gear*
*Still cannot take away the fear*
*Like an island song..... J. Buffett*

2

**GEORGIA INSTITUTE OF TECHNOLOGY** OFFICE OF CONTRACT ADMINISTRATION

*RESEARCH REPORT APPROVAL SHEET*

(Please see Instructions on back)

31

Project No. G35-W62

EAS
Lab/School

I. **GENERAL**

A. Report Title Southern Center for the Integrated Study of Secondary Air Pollutants (SCISSAP)

B. Author(s) and/or PD/PI William L. Chameides Phone 404-894-1749/1747

C. Period Covered 4/1/98 - 3/31/99 Due Date 4/30/99

4 Copies staple

II. **REPORT IDENTIFICATION**

A. Deliverable Line No. 1 (from Deliverable Schedule)

B. Type Report:

☐ Monthly ☐ Quarterly ☐ Semi -Annual
☒ Annual ☒ Progress ☐ Cost & Performance
☐ Contract Mgt. ☐ Final ☐ Other ________ (Specify)

C. Draft Copy for Sponsor Approval ☐

D. Approval Copy for Distribution:

1. ☒ Send Copy to Sponsor
2. ☐ Send Master to Sponsor
3. ☒ Return Master to PD/PI ✓

III. **SECURITY CLASSIFICATION**

☒ Unclassified ☐ Secret ☐ In Confidence (Specified Industrial Contracts Only)
☐ Confidential ☐ Top Secret ☐ Other ________ (Specify)

IV. **DATA RESTRICTIONS** ☐ Yes ☒ No

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99-08-24 A08:51 IN

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☐ Spiral Bind ☐ Velobind ☐ Other ________

D. Cover Desired:

☐ Standard ☐ Sponsor-Prescribed
☒ None ☐ Special Design (VPR/OCA Approval Required) ________
☐ White ☐ Other Color (Specify) ________

E. Approval of Check Copy by School/Lab before binding: ☐ Yes ☒ No (If Yes, Phone ________ )

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☐ Lab/School ☒ OCA Contracting Support Division

1. If distribution made by lab/school, attach transmittal letter and 2 copies of report for archives. Indicate date mailed: ________ . (This is the mailing date OCA/CSD will enter into the database).

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266B/6/3040

VI. **APPROVALS**

A. PD/PI ________ DATE 8/16/99
B. Div. Chief/Branch Head ________ ________
C. Lab/School Director ________ ________
(Required on Finals)
D. Coordinator Log Entry: ________ ________

Georgia Institute of Technology

**Office of Sponsored Programs**
Research Administration, Compliance,
Training, and Technologies (ReACTT)
Atlanta, Georgia 30332-0420 U.S.A.
PHONE 404•894•6944
FAX 404•894•5285

**August 25, 1999**

**In reply refer to: G-35-W62**

**Deran Pashayan**
**Office of Research and Development (8723R)**
**U.S. EPA**
**Washington, DC 20460**

**Subject: Annual Progress Report**
**Project Director(s): William Chameides**
**Telephone No.: (404)894-1747**
**Contract No.: R 826372**
**Prime No.: N/A**
**"SOUTHERN CENTER FOR INTEGRATED STUDY OF SECONDARY AIR POLLUTANTS (SCISSAP)"**
**Period Covered: 4/1/98 – 3/31/99**

The subject report is forwarded in conformance with the contract/grant specifications.

Should you have any questions or comments regarding this report(s), please contact the Project Director or the undersigned at 404-894-4763.

/tw

Sincerely,

Thelma Woods
Customer Service Representative

**Distribution:**
**Addressee: 2 copies**

G-35-W62
#1
(NEW)

# Southern Center For The Integrated Study of Secondary Air Pollutants (SCISSAP)

## Progress Report

## For

## 1st Year of 3-Year U.S. EPA Grant
## (Grant R826372)

Submitted By:

W.L. Chameides, P.I.
School of Earth and Atmospheric Sciences
Georgia Tech
Atlanta, GA 30332

August 16, 1999

07/05/00

**GEORGIA INSTITUTE OF TECHNOLOGY** OFFICE OF CONTRACT ADMINISTRATION

## *RESEARCH REPORT APPROVAL SHEET*

(Please see Instructions on back)

9

18

Project No. G35 W62

EAS
Lab/School

## I. GENERAL

A. Report Title Southern Center for the Integrated Study of ... (SCISSAP)
B. Author(s) and/or PD/PI Dr. WL Chameides
Phone 4-1749
C. Period Covered 4/1/99 - 3/31/00
Due Date 4/30/2000

2 Copies Staple

## II. REPORT IDENTIFICATION

A. Deliverable Line No. 2 (from Deliverable Schedule)

B. Type Report:

| | | |
|---|---|---|
| ☐ Monthly | ☐ Quarterly | ☐ Semi-Annual |
| ☑ Annual Progress Rept. | ☐ Progress | ☐ Cost & Performance |
| ☐ Contract Mgt. | ☐ Final | ☐ Other ________ (Specify) |

C. Draft Copy for Sponsor Approval ☐

D. Approval Copy for Distribution:

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3. ☐ Return Master to PD/PI

## III. SECURITY CLASSIFICATION

| | | |
|---|---|---|
| ☑ Unclassified | ☐ Secret | ☐ In Confidence (Specified Industrial Contracts Only) |
| ☐ Confidential | ☐ Top Secret | ☐ Other ________ (Specify) |

## IV. DATA RESTRICTIONS ☐ Yes ☑ No

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C. Binding Desired: ☑ Staple ☐ Staple & Tape ☐ Spiral Bind ☐ Velobind ☐ Other ________

D. Cover Desired:

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|---|---|
| ☑ Standard | ☐ Sponsor-Prescribed |
| ☐ None | ☐ Special Design (VPR/OCA Approval Required) ________ |
| ☐ White | ☐ Other Color (Specify) ________ |

E. Approval of Check Copy by School/Lab before binding: ☐ Yes ☑ No (If Yes, Phone ________ )

F. Distribution to be by:
☐ Lab/School ☑ OCA Contracting Support Division

1

1. If distribution made by lab/school, attach transmittal letter and 2 copies of report for archives. Indicate date mailed: ________. (This is the mailing date OCA/CSD will enter into the database).

2. If distribution made by OCA/CSD, the signature of employee handling the report and the mailing date are shown here: Distributed by: JW Date mailed: 05-JUL-00

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DISTRIBUTION CENTER
2000 JUL 3 PM 1 15

## VI. APPROVALS

| | |
|---|---|
| A. PD/PI ________ | DATE 6/30/00 |
| B. Div. Chief/Branch Head ________ | ________ |
| C. Lab/School Director ________ (Required on Finals) | ________ |
| D. Coordinator Log Entry: ________ | |

2 Copies to sponsor per Del. Sch.

Georgia Institute of Technology

**Office of Sponsored Programs**
Research Administration, Compliance,
Training, and Technologies (ReACTT)
Atlanta, Georgia 30332-0420 U.S.A.
PHONE 404•894•6944
FAX 404•894•5285

**July 5, 2000**

**In reply refer to: G-35-W62**

**Dr. Deran Pashayan**
**Office of Research & Development**
**(8723R)**
**US EPA**
**Washington, DC 20460**

**Subject: Annual Progress Report**
**Project Director(s): Dr. W.L. Chameides**
**Telephone No.: (404)894-1749**
**Contract No.: R 826372**
**Prime No.: N/A**
**"SOUTHERN CENTER FOR INTEGRATED STUDY OF SECONDARY AIR POLLUTANTS (SCISSAP)"**
**Period Covered: 4-1-99 – 3-31-00**

The subject report is forwarded in conformance with the contract/grant specifications.

Should you have any questions or comments regarding this report(s), please contact the Project Director or the undersigned at 404-894-4763.

/tw

Sincerely,

Thelma Woods
Customer Service Representative

**Distribution:**
**Addressee**: **2 copies**

G-35-W62
#2

# Southern Center For The Integrated Study of Secondary Air Pollutants (SCISSAP)

## Progress Report

For

2nd Year of 3-Year U.S. EPA Grant
(Grant R826372)

Submitted By:

W.L. Chameides, P.I.
School of Earth and Atmospheric Sciences
Georgia Tech
Atlanta, GA 30332

June 28, 2000

6.35.W62
3,4

Hi Laura,

According to our database records Dr. Chameides have an Annual Report dated: Apr.01-00 – Mar.-31-01. Due Apr. 30.
Is this report also included in the reports that you forwarded to us. There is a new deliverable schedule and I would be happy to fax it to you.

Thanks,
Kamie

-----Original Message-----
**From:** Laura Cederquist
**Sent:** Friday, June 28, 2002 2:13 PM
**To:** ocareports
**Subject:** Fwd: SCISSAP Final Report

A signed "Research Report Approval Sheet" is being routed to OSP-REATT.

Laura

X-Sender: wcham@eas.gatech.edu
X-Mailer: QUALCOMM Windows Eudora Version 5.1
Date: Wed, 19 Jun 2002 16:52:59 -0400
To: Shapiro.Paul@epamail.epa.gov
From: William Chameides <wcham@eas.gatech.edu>
Subject: SCISSAP Final Report
Cc: kb@eas.gatech.edu, mcmurry@me.umn.edu, rod Zika <rzika@rsmas.miami.edu>

6.28.02

Dear Paul,

I am herewith submitting to you the following:
1. A final version of the Executive Summary of our Final Report for web publication
2. A draft version of the complete Final Report, for you review and comment.

Thanx.

--

BILL Chameides

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<<<<<<<<<
|>>>>>> W.L. Chameides, Smithgall Chair and Regents Professor<<<<<<
<<<<<<<<<<<<
>>>>>>>>>Acting Chairperson for Earth and Atmospheric
Scences<<<<<<<<<<<<<<<<<<
>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
>>><<<<<<
|>> Earth and Atmospheric Sciences
email:wcham@eas.gatech.edu<<<<<<<<<
|>> Georgia Tech                       PHONE:  (404) 385 -
1548<<<<<<<<<<<<
|>> Atlanta, GA 30332                    FAX:(404) 894 -
5638<<<<<<<<<<<<<<
|>> USA www-wlc.eas.gatech.edu<<<<<<<<<<<<<<
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<<<<<<<<<
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Laura D. Cederquist
Financial Manager I
Earth and Atmospheric Sciences
Phone: (404) 894-0275
Fax: (404) 894-5638

...... *You're caught up in the Internet*
*You think it's such a great asset*
*But you're wrong, wrong, wrong*

*All that fiber optic gear*
*Still cannot take away the fear*
*Like an island song..... J. Buffett*

DRAFT: 06/19/02

# Final Report

**To:**
National Center for Environmental Research
Office of Research and Development
U.S. Environmental Protection Agency

**From:**
Georgia Tech Research Corporation

**Subject:**
STAR GRANT: R826372

## Southern Center For The Integrated Study of Secondary Air Pollutants

**Investigators:**
W.L. Chameides (PI)
A.G. Russell (Co-PI)
P. McMurry (Co-I)
R. Zika (Co-I)
P. Kasibhatla (Co-I)
D. McNider (Co-I)

**Institutions:**
Georgia Institute of Technology (primary)
University of Minnesota (sub-contractor)
University of Miami (sub-contractor)
Duke University (subcontractor)
University of Alabama – Huntsville (subcontractor)

**Research Category:** Special Opportunity in Tropospheric Ozone

**Project Period:** April 1, 1998 - March 31, 2002

**Period Covered by the Report:** April 1, 1998 - March 31, 2002

**Date of Final Report**: July 1, 2002

## Table of Contents

**GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF SPONSORED PROGRAMS**
**Office of Research Administration, Compliance, Training & Technologies (ReACTT)**
**RESEARCH REPORT APPROVAL SHEET**

Project No. G35W62
Lab/School/Center: EAS

**1. GENERAL**
A. Report Title Southern Center for the Integrated Study of Secondary
B. Author(s) and/or PD/PI Dr. William L. Chameides Phone 4-3893
C. Period Covered: 4/1/98 - 3/31/02 Due Date 6/30/02

**2. REPORT**
A. Deliverable Line Number (from Deliverable Schedule) 4
B. Type of Report:
☐Monthly ☐Contract Mgt. ☐Progress ☐Semi-Annual ☐Cost & Performance
☐Annual ☐Quarterly ☑Final Report ☐Other
C. Draft Copy for Sponsor Approval ☐ → Emailed to ocareports
D. Approval Copy for Distribution ☐Send Copy to Sponsor ☐Send Master to Sponsor ☐Return Master to PD/PI

**3. SECURITY CLASSIFICATION**
☑Unclassified ☐Publication Delayed Until______ (Specified industry contracts only)
☐Confidential ☐Secret ☐Top Secret *Note: Classified reports are not to be emailed under any circumstances.*
☐Other______ (i.e. ITAR, export controlled, etc.)

**4. DATA RESTRICTIONS** ☐Yes ☑No
Proprietary Data (Confidential Disclosure); Export License; Trade Secret; Copyright or Publishing Restrictions; Patentable Technology *Note: If yes, contact OFFICE OF LEGAL AFFAIRS, 404 / 894-4812*

**5. PRINTING and DISTRIBUTION INSTRUCTIONS TO OSP/ReACTT**
(Unless otherwise indicated, printing charges will be assessed against project number. If the project has been terminated, charge number to use:______

A. Number of copies to be printed: N/A
[____]Sponsor [____]School / Lab [____]Other [____]Total
B. Printing Desired ☐One-Sided ☐Two-Sided
C. Binding Desired: ☐Staple ☐Staple & Tape ☐Spiral Bind ☐Velobind ☐Other______
D. Cover Desired: ☐Standard White ☐Other Color (Specify)______ ☐None
E. Approval of Check Copy by School/Lab before binding: ☐No ☐Yes ( If yes, phone:______)

OSP/ReACTT will retain one copy of each report throughout the life of the project.. When the project is closed, OSP/ReACTT will make an additional copy of all reports and forward both sets to the campus library archives.

**6. DISTRIBUTION BY:**

☑Lab/School/Center

*Paper copies*: If distribution by lab/school**, attach transmittal letter. Date mailed: 6/19/02
(This is the date that OSP/ReACTT will enter into the database).
*NOTE: Due to storage constraints, only one copy is to be provided to OSP / ReACTT. When the project is closed, ReACTT will make the required second copy for the library archives and circulation.*

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***Final reports require the approval of the Lab/School/Department/Center head. A Research Report Approval Sheet bearing that person's signature must be forwarded to ReACTT before the final report ship date will be entered into the database:*

*ReACTT*
*Office of Sponsored Programs*
*Centennial Research Building, Room 117A*
*Mail Code 0420 Campus*

☐OSP/ReACTT

If distribution by OSP/ReACTT, the signature of the ReACTT employee handling the report and the mailing date are to be entered here:
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2002 JUN 28 PM 2 47

**7. SIGNATURES and APPROVALS**

A. PD/PI ______ Date 6/30/02
B. Division Chief or Branch Head ______ Date 6/29/02
C. Lab/School/Department/Center Head ______ Date______
*(Required for final reports)*
D. MAPS / RAN ______ Date______

X-Sender: wcham@eas.gatech.edu
X-Mailer: QUALCOMM Windows Eudora Version 5.1
Date: Wed, 19 Jun 2002 16:52:59 -0400
To: Shapiro.Paul@epamail.epa.gov
From: William Chameides <wcham@eas.gatech.edu>
Subject: SCISSAP Final Report
Cc: kb@eas.gatech.edu, mcmurry@me.umn.edu, rod Zika <rzika@rsmas.miami.edu>

Dear Paul,

I am herewith submitting to you the following:
1. A final version of the Executive Summary of our Final Report for web publication
2. A draft version of the complete Final Report, for you review and comment.

Thanx.

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    BILL Chameides

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|>>>>>> W.L. Chameides, Smithgall Chair and Regents Professor<<<<<< <<<<<<<<<<<<<
>>>>>>>>>>Acting Chairperson for Earth and Atmospheric Scences<<<<<<<<<<<<<<<<<<<
>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>><<<<<<
|>> Earth and Atmospheric Sciences          email:wcham@eas.gatech.edu<<<<<<<<<
|>> Georgia Tech                           PHONE:   (404) 385 - 1548<<<<<<<<<<<<
|>> Atlanta, GA 30332                        FAX:(404) 894 - 5638<<<<<<<<<<<<<<
|>> USA www-wlc.eas.gatech.edu<<<<<<<<<<<<<<
>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>><<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<
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SCISSAP.Final Report_Executive Summary.pdf

SCISSAP Final Report_draft.pdf

## GEORGIA INSTITUTE OF TECHNOLOGY OFFICE OF SPONSORED PROGRAMS
## Office of Research Administration, Compliance, Training & Technologies (ReACTT)
## RESEARCH REPORT APPROVAL SHEET

Project No.__G-35-W62________
Lab/School/Center:____EAS_____

**1. GENERAL**

A. Report Title_Final Report Executive Summary________________________________
B. Author(s) and/or PD/PI__Dr. William L. Chameides____________________Phone__5-1548________________
C. Period Covered:___4/1/98-3/31/02____________________________Due Date_____6/30/02____________

**2. REPORT**

A. Deliverable Line Number (from Deliverable Schedule)________~~3~~ #4 Final Rpt. is #4 Not. #3. (JW)__________
B. Type of Report:

[ ]Monthly [ ]Contract Mgt. [ ]Progress [ ]Semi-Annual [ ]Cost & Performance
[ ]Annual [ ]Quarterly [X]Final Report [ ]Other ______________________

C. Draft Copy for Sponsor Approval [ ]
D. Approval Copy for Distribution [ ]Send Copy to Sponsor [ ]Send Master to Sponsor [ ]Return Master to PD/PI

**3. SECURITY CLASSIFICATION**

[X]Unclassified [ ]Publication Delayed Until_____________________ (Specified industry contracts only)
[ ]Confidential [ ]Secret [ ]Top Secret *Note: Classified reports are not to be emailed under any circumstances.*
[ ]Other_________________________________ (i.e. ITAR, export controlled, etc.)

**4. DATA RESTRICTIONS** [ ]Yes [X]No

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**5. PRINTING and DISTRIBUTION INSTRUCTIONS TO OSP/ReACTT**

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A. Number of copies to be printed:
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B. Printing Desired [ ]One-Sided [ ]Two-Sided

C. Binding Desired: [ ]Staple [ ]Staple & Tape [ ]Spiral Bind
[ ]Velobind [ ]Other ______________

D. Cover Desired: [ ]Standard White [ ]Other Color (Specify) ______________ [ ]None

E. Approval of Check Copy by School/Lab before binding: [ ]No [ ]Yes ( If yes, phone:______________)

**6. DISTRIBUTION BY:**

[X]Lab/School/Center

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*Emailed reports*: Send email copy** to ocareports@oca.gatech.edu.

***Final reports require the approval of the Lab/School/Department/Center head. A Research Report Approval Sheet bearing that person's signature must be forwarded to ReACTT before the final report ship date will be entered into the database:*

*ReACTT*
*Office of Sponsored Programs*
*Centennial Research Building, Room 117A*
*Mail Code 0420 Campus*

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APR 24 AM 7 49

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Date mailed:____________________

[ ]Research Security

If distribution by Research Security, the signature of the Research Security employee handling the report and the mailing date are to be entered here:
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Date mailed: ____________________

**7. SIGNATURES and APPROVALS**

A. PD/PI ______________________________ Date 4/23/03
B. Division Chief or Branch Head ______________________________ Date ______________
C. Lab/School/Department/Center Head_____ ______________________________ Date 4/23/03
*(Required for final reports)*
D. MAPS / RAN ______________________________ Date ______________

OSP Form 05-0400 Page 1 of 1

Revised Version per attached E-mail 4/24/03 JW

X-Sender: wcham@eas.gatech.edu
X-Mailer: QUALCOMM Windows Eudora Version 5.1
Date: Mon, 14 Apr 2003 21:26:18 -0400
To: bcampbel@scgcorp.com
From: Bill Chameides <wcham@eas.gatech.edu>
Subject: Final Technical Report Executive Summary
Cc: Shapiro.Paul@epamail.epa.gov

Dear Sir or Madam.

Attached please find as a pdf-file, the Final Technical Report Executive Summary for EPA Grant R82672. The current version of the Executive Summary represents a revised version of a summary submitted to Dr. Solomon last year,
and has been revised in accordance with the instructions from Dr. Solomon.

I would appreciate it if you would acknowledge by return e-mail receipt of the Summary and your ability to open and read the file.

Thank you.

G35W62

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BILL Chameides

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|>>>>>> W.L. Chameides, Smithgall Chair and Regents Professor<<<<<< <<<<<<<<<<<<
|>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>><<<<<<
|>> Earth and Atmospheric Sciences email:wcham@eas.gatech.edu<<<<<<<<<
|>> Georgia Tech PHONE: (404) 894 - 1749<<<<<<<<<<<<
|>> Atlanta, GA 30332 FAX:(404) 894 - 5638<<<<<<<<<<<<<<
|>> USA www-wlc.eas.gatech.edu<<<<<<<<<<<<<<
>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>><<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

Final Report.Executive Summary.Grant R826372.pdf

X-Sender: wcham@eas.gatech.edu
X-Mailer: QUALCOMM Windows Eudora Version 5.1
Date: Mon, 14 Apr 2003 21:27:45 -0400
To: Shapiro.Paul@epamail.epa.gov
From: Bill Chameides <wcham@eas.gatech.edu>
Subject: Revised Final Technical Report
Cc: laura.cederquist@eas.gatech.edu

Paul,

Attached as a pdf-file, is the revised version of the Final Technical Report on EPA Grant R826372.
All revisions that you requested have been made.

I would appreciate it if you would acknowledge by return e-mail receipt of the Summary and your ability to open and read the file.

Thank you.

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         BILL Chameides

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>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>><<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<
|>>>>>> W.L. Chameides, Smithgall Chair and Regents Professor<<<<<< <<<<<<<<<<<<
|>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>><<<<<<
|>> Earth and Atmospheric Sciences          email:wcham@eas.gatech.edu<<<<<<<<<
|>> Georgia Tech                          PHONE:   (404) 894 - 1749<<<<<<<<<<<<
|>> Atlanta, GA 30332                       FAX:(404) 894 - 5638<<<<<<<<<<<<<<
|>> USA www-wlc.eas.gatech.edu<<<<<<<<<<<<<<
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Final Report.Grant R826372.pdf

G-35-W62
#4

## Final Report Executive Summary

**Period Covered by the Report:** April 1, 1998 - March 31, 2002
**Date of Final Report**: June 15, 2002 (Submission of revised report: April 22, 2003)
**EPA Agreement Number:** Grant R826372
**Title:** Southern Center For The Integrated Study of Secondary Air Pollutants
**Investigators:** W.L. Chameides (PI), A.G. Russell (Co-PI), P. McMurry (Co-I), R. Zika (Co-I)
**Institution:** Georgia Institute of Technology (primary), University of Minnesota (sub-contractor), University of Miami (sub-contractor)
**Research Category:** Special Opportunity in Tropospheric Ozone
**Project Period:** April 1, 1998 - March 31, 2002

**Objective(s) of the Research Project:** The mission of the Southern Center for the Integrated Study of Secondary Air Pollutants (SCISSAP) is:

> *The development of the scientific understanding and analytical tools that underpin the design and implementation of an effective and integrated control strategy for secondary air pollutants, using the atmosphere of the southern United States as a natural laboratory.*

This mission is based on the premises that a basic understanding of the chemistry and physics of the atmosphere are a prerequisite for designing effective control strategies for secondary air pollutants; and that the concentration of secondary air pollutants in the atmosphere are often codependent because of interacting chemical reactions.

Over a four-year period beginning on April 1, 1998, SCISSAP was funded by U.S. EPA the NCER/STAR extramural funding program to focus on an integrated study of ground-level ozone ($O_3$) and particulate matter with diameters less than 2.5 μm ($PM_{2.5}$) in the South. Specifically, four major and interrelated scientific questions were addressed:

***Question 1:*** What is the composition and size distribution of fine particles in urban and rural locales in the southern United States and to what extent do temporal and spatial variations in these parameters correlate with those of ozone and its precursor compounds?

***Question 2:*** What are the major precursor compounds and sources for fine particles in urban and rural locales in the southern United States and to what extent do these compounds and sources correspond to/correlate with the sources of natural and anthropogenic ozone precursors (i.e., VOC and $NO_x$)?

***Question 3:*** To what extent, if any, is the chemical composition and abundance of fine particles in urban and rural locales in the southern United States affected by the concentration of natural and anthropogenic ozone precursors and/or ozone?

***Question 4:*** To what extent is the concentration of ground-level ozone in urban and rural locales in the southern United States affected by the concentration and composition of fine particles and/or the concentration of the precursors of fine particles?

G-35-W02
#4

# Final Report

**To:**
National Center for Environmental Research
Office of Research and Development
U.S. Environmental Protection Agency

**From:**
Georgia Tech Research Corporation

**Subject:**
STAR GRANT: R826372

## Southern Center For The Integrated Study of Secondary Air Pollutants

**Investigators:** W.L. Chameides (PI)
A.G. Russell (Co-PI)
P. McMurry (Co-I)
R. Zika (Co-I)
P. Kasibhatla (Co-I)
D. McNider (Co-I)

**Institutions:** Georgia Institute of Technology (primary)
University of Minnesota (sub-contractor)
University of Miami (sub-contractor)
Duke University (subcontractor)
University of Alabama – Huntsville (subcontractor)
**Research Category:** Special Opportunity in Tropospheric Ozone
**Project Period:** April 1, 1998 - March 31, 2002
**Period Covered by Report:** April 1, 1998 - March 31, 2002
**Date of Final Report Submission**: July 1, 2002
**Date of Revised Final Report Submission:** April 22, 2003

CAS160

Georgia Institute of Technology
Office of Contract Administration
OCA PAD AMENDMENT - PROJECT HEADER INFORMATION

07-APR-1999 16:22

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Document Header Id #: 48104 ACTIVE
Project #: G-35-W62
Cost Share #: G-35-387
Rev #: 2
Center #: 10/24-6-R1013-0A0
Center Shr #: 10/22-1-F1013-0A0
PeopleSoft Project Id:
PeopleSoft Cost Share Id:
OCA file #:
Project type: RES

Contract #: R 826372
Mod #: 2
Award type: GRANT
Prime #:
Contract entity: GTRC
Contract type: CRNF
(Cost Reimbursement)

CFDA: 66.500
PE #:

Project unit: E & A SCI
Unit code: 33
Project director(s):
PDPI- CHAMEIDES W L EAS (404)894-1749

---

Sponsor : ENVIRON PROTECTION AGENCY/EPA/ DC
Division Id: 129 / 3481
Award period: 01-APR-1998 to 31-MAR-2001 (performance) 30-JUN-2001 (reports)

| Sponsor amount | New this change | Total to date |
|---|---|---|
| Contract value: | 0.00 | 3,000,000.00 |
| Funded: | 1,000,000.00 | 3,000,000.00 |
| Cost sharing amount: | 161,253.00 | 844,213.00 |

Does subcontracting plan apply? N

Title: SOUTHERN CENTER FOR INTEGRATED STUDY OF SECONDARY AIR POLLUTANTS (SCISSAP)

---

PROJECT ADMINISTRATIVE DATA

OCA contact: Janis L. Goddard (404) 894-4820

Sponsor technical contact:
DERAN PASHAYAN
OFFICE OF RESEARCH AND DEVELOPMENT (8723R)
US EPA

WASHINGTON DC
20460
Phone: (202) 564-6913
Fax:
Email:

Sponsor issuing office:
FRANK ROTH
U.S. ENVIRONMENTAL PROTECTION AGENCY
GRANTS ADMINISTRATION DIVISION
401 M STREET, SW, (3903R);ROOM 51288
WASHINGTON D.C.
20460
Phone: 202.564.5329
Fax: 202.565.2469
Email: roth.francis@epamail.epa.gov

Security class (U,C,S,TS): U
ONR resident rep is ACO (Y/N): N
Defense priority rating :
Supplemental sheet:

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Equipment title vests with: SPON

Administrative comments -
This modification adds $1,000,000 to the project.

CA8140

Georgia Institute of Technology
Office of Contract Administration
OCA PAD AMENDMENT
Amendment Distribution

07-APR-1999 16:22

Project #: G-35-W62 Document Id: 48104 Mod: 2 Rev: 2

PeopleSoft Project Id:

Project Director: William L Chameides
From CO: Janis L. Goddard Phone: (404) 894-4820

Attached is the revision package for project G-35-W62
The following noted items are attached:

| | Admin | Bud | Fin | Deliv | Suppl | T & C |
|---|---|---|---|---|---|---|
| Project Director/Principal Investigator | Y | Y | ~~Y~~ | ~~Y~~ | ~~Y~~ | ~~Y~~ |
| Research Administrative Network | Y | Y | ~~Y~~ | ~~Y~~ | ~~Y~~ | ~~Y~~ |
| Accounting | Y | Y | ~~Y~~ | ~~N~~ | ~~Y~~ | ~~Y~~ |
| Research Security Department | Y | N | ~~N~~ | ~~N~~ | ~~N~~ | ~~Y~~ |
| Reports Coordinator | Y | N | ~~N~~ | ~~Y~~ | ~~N~~ | ~~Y~~ |
| Research Property Team | Y | Y | ~~Y~~ | ~~N~~ | ~~N~~ | ~~Y~~ |
| Supply Services Department/Procurement | Y | Y | ~~Y~~ | ~~N~~ | ~~Y~~ | ~~Y~~ |
| Research Communications Team | Y | N | ~~N~~ | ~~N~~ | ~~N~~ | ~~N~~ |
| Georgia Tech Research Corporation | Y | Y | ~~Y~~ | ~~N~~ | ~~N~~ | ~~N~~ |
| Library | Y | N | ~~N~~ | ~~N~~ | ~~N~~ | ~~N~~ |
| Project File | Y | Y | ~~Y~~ | ~~Y~~ | ~~Y~~ | ~~Y~~ |
| OCA/CSD | Y | N | ~~N~~ | ~~Y~~ | ~~N~~ | ~~N~~ |
| Office of Legal Affairs | Y | N | ~~N~~ | ~~N~~ | ~~N~~ | ~~N~~ |
| C. GIBSON | Y | N | N | N | N | N |

| CO | SEC | |
|---|---|---|
| — | | 1. Deliverable schedule attachment sheet |
| — | | 2. Include supplemental information sheet |
| ✓ | | 3. Copy of grant/contract agreement document distribution indicated |
| ✓ | | 4. Copy of proposal budget to distribution indicated |
| ✓ | | 5. Copy of cost sharing approval forms to distribution indicated |
| — | | 6. Copy of research project questionnaire to PD |
| — | | 7. Patent report record/stamp onto folder |
| — | | 8. Other ____________________ |

Completed by CO FOR JLG 4/8/99

Completed by SEC ____________________

CA8160

Georgia Institute of Technology
Office of Contract Administration
OCA PAD AMENDMENT - PROJECT HEADER INFORMATION

02-JUN-1998 18:13

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Document Header Id #: 48104 ACTIVE

Project #: G-35-W62 Cost share #: G-35-387 Rev #: 1
Center #: 10/24-6-R1013-0A0 Center shr #: 10/22-1-F1013-0A0
OCA file #: Project type: RES

Contract #: R 826372 Mod #: 1 Award type: GRANT
Prime #: Contract entity: GTRC
Contract type: CRNF

CFDA: 66.500
PE #:

Project unit: E & A SCI Unit code: 33
Project director(s):
PDPI- CHAMEIDES W L E & A SCI (404)894-1749

---

Sponsor : ENVIRON PROTECTION AGENCY/EPA - DC
Division Id: 129 / 3481
Award period: 01-APR-1998 to 31-MAR-2001 (performance) 30-JUN-2001 (reports)

| Sponsor amount | New this change | Total to date |
|---|---|---|
| Contract value: | 0.00 | 3,000,000.00 |
| Funded: | 1,000,000.00 | 2,000,000.00 |
| Cost sharing amount: | 0.00 | 682,960.00 |

Does subcontracting plan apply? N

Title: SOUTHERN CENTER FOR INTEGRATED STUDY OF SECONDARY AIR POLLUTANTS (SCISSAP)

---

PROJECT ADMINISTRATIVE DATA

OCA contact: Anita D. Rowland (404) 894-4820

Sponsor technical contact:
DERAN PASHAYAN
OFFICE OF RESEARCH AND DEVELOPMENT (8723R)
US EPA

WASHINGTON DC
20460
Phone: (202) 564-6913
Fax:
Email:

Sponsor issuing office:
FRANK ROTH
U.S. ENVIRONMENTAL PROTECTION AGENCY
GRANTS ADMINISTRATION DIVISION
401 M STREET, SW, (3903R);ROOM 51288
WASHINGTON D.C.
20460
Phone: 202.564.5329
Fax: 202.565.2469
Email: roth.francis@epamail.epa.gov

Security class (U,C,S,TS): U
Defense priority rating :

ONR resident rep is ACO (Y/N): N
Supplemental sheet:

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Equipment title vests with: SPON

Administrative comments -
Adds $1,000,000

CA8140

Georgia Institute of Technology
Office of Contract Administration
OCA PAD AMENDMENT
Amendment Distribution

03-JUN-1998 08:30

Project #: G-35-W62　Document Id: 48104　Mod: 1　Rev: 1
Project Director: William L Chameides
From CO: Anita D. Rowland　Phone: (404) 894-4820

Attached is the revision package for project G-35-W62
The following noted items are attached:

| | Admin | Bud | Fin | Deliv | Suppl | T & C |
|---|---|---|---|---|---|---|
| Project Director/Principal Investigator | Y | Y | ~~Y~~ | ~~Y~~ | ~~Y~~ | ~~Y~~ |
| Research Administrative Network | Y | Y | ~~Y~~ | ~~Y~~ | ~~Y~~ | ~~Y~~ |
| Accounting | Y | Y | ~~Y~~ | ~~N~~ | ~~Y~~ | ~~Y~~ |
| Research Security Department | Y | N | ~~N~~ | ~~N~~ | ~~N~~ | ~~Y~~ |
| Reports Coordinator | Y | N | ~~N~~ | ~~Y~~ | ~~N~~ | ~~Y~~ |
| Research Property Team | Y | Y | ~~Y~~ | ~~N~~ | ~~N~~ | ~~Y~~ |
| Supply Services Department/Procurement | Y | Y | ~~Y~~ | ~~N~~ | ~~Y~~ | ~~Y~~ |
| Research Communications Team | Y | N | ~~N~~ | ~~N~~ | ~~N~~ | ~~N~~ |
| Georgia Tech Research Corporation | Y | Y | ~~Y~~ | ~~N~~ | ~~N~~ | ~~N~~ |
| Library | Y | N | ~~N~~ | ~~N~~ | ~~N~~ | ~~N~~ |
| Project File | Y | Y | ~~Y~~ | ~~Y~~ | ~~Y~~ | ~~Y~~ |
| OCA/CSD | Y | N | ~~N~~ | ~~Y~~ | ~~N~~ | ~~N~~ |
| Office of Legal Affairs | Y | N | ~~N~~ | ~~N~~ | ~~N~~ | ~~N~~ |
| C. GIBSON | Y | N | ~~N~~ | ~~N~~ | ~~N~~ | ~~N~~ |

| CO | SEC | |
|---|---|---|
| | | 1. Deliverable schedule attachment sheet |
| | | 2. Include supplemental information sheet |
| ✓ | | 3. Copy of grant/contract agreement document distribution indicated |
| ✓ | | 4. Copy of proposal budget to distribution indicated |
| | | 5. Copy of cost sharing approval forms to distribution indicated |
| | | 6. Copy of research project questionnaire to PD |
| | | 7. Patent report record/stamp onto folder |
| | | 8. Other ______ |

Completed by CO 6-3-98

Completed by SEC

98-06-04 A09:54

CA8160

Georgia Institute of Technology
Office of Contract Administration
OCA PAD INITIATION - PROJECT HEADER INFORMATION

16-APR-1998 13:00

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Document Header Id #: 48104 ACTIVE
Project #: G-35-W62 Cost share #: G-35-387
Center #: 10/24-6-R1013-0A0 Center shr #: 10/22-1-F1013-0A0
OCA file #: Project type: RES

Contract #: R 826372 Award type: GRANT
Prime #: Contract entity: GTRC
Contract type: CRNF

CFDA: 66.500
PE #:

Project unit: E & A SCI Unit code: 33
Project director(s):
PDPI- CHAMEIDES W L E & A SCI (404)894-1749

---

Sponsor : ENVIRON PROTECTION AGENCY/EPA - DC
Division Id: 129 / 3481
Award period: 01-APR-1998 to 31-MAR-2001 (performance) 30-JUN-2001 (reports)

| Sponsor amount | New this change | Total to date |
|---|---|---|
| Contract value: | 3,000,000.00 | 3,000,000.00 |
| Funded: | 1,000,000.00 | 1,000,000.00 |
| Cost sharing amount: | 682,960.00 | 682,960.00 * |

Does subcontracting plan apply? N

Title: SOUTHERN CENTER FOR INTEGRATED STUDY OF SECONDARY AIR POLLUTANTS (SCISSAP)

---

PROJECT ADMINISTRATIVE DATA

OCA contact: Anita D. Rowland (404) 894-4820

| Sponsor technical contact: | Sponsor issuing office: |
|---|---|
| DERAN PASHAYAN | FRANK ROTH |
| OFFICE OF RESEARCH AND DEVELOPMENT (8723R) | U.S. ENVIRONMENTAL PROTECTION AGENCY |
| US EPA | GRANTS ADMINISTRATION DIVISION |
| | 401 M STREET, SW, (3903R);ROOM 51288 |
| WASHINGTON DC 20460 | WASHINGTON D.C. 20460 |
| Phone: (202) 564-6913 | Phone: 202.564.5329 |
| Fax: | Fax: 202.565.2469 |
| Email: | Email: roth.francis@epamail.epa.gov |

Security class (U,C,S,TS): U
Defense priority rating :

ONR resident rep is ACO (Y/N): N
Supplemental sheet:

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Equipment title vests with: SPON

Administrative comments -
INITIATION OF 3-YR* EFFORT. INCREMENTALLY FUNDED.

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Document Header Id #: 48104
Project No: G-35-W62

LIMITATION OF COST clause applies N
LIMITATION OF FUNDS clause applies Y

If Y is shown in either of the above blocks, sponsor notification is required in writing when, within the next 60 days, total costs incurred will exceed 75% of the total funding obligated to date.

---

Patent Rights: Patent report Y Retained Y Sold N Sold fee 0.00
License nonexclusive N License exclusive N Exclusive license option N
Comment:

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License nonexclusive Y License exclusive N Exclusive license option N
Comment:

Copyright Ownership Rights: Retained Y Sold N Sold fee 0.00
Comment:

Publication Restrictions N DD254 - no information released without approval N
Comment:
Ref.item 9,d. Submit article to Technical Officer

Georgia Institute of Technology

**Office of Contract Administration**
Program Administration Division
Atlanta, Georgia 30332-0420 U.S.A.
PHONE 404•894•4820
FAX 404•894•5945

April 16, 1998

**MEMORANDUM**

**TO:** **William L. Chemeides, E&A Sci**

**FROM:** Anita D. Rowland, OCA/PAD

**SUBJECT:** Deliverable Schedule for Project Number G-35-W62

Attached is the **DELIVERABLE SCHEDULE** for the subject project along with instructions for submitting reports and other deliverables. Please review this schedule for accuracy. If it does not represent your understanding of the reporting requirements under the terms of your project agreement, make the appropriate corrections or notations on a copy and return the copy to OCA/PAD, CRB ROOM 245 within TWO WEEKS of the date of this memo. If you agree that the deliverable requirements shown are correct, please sign and return the extra (OCA FILE) copy of the deliverable schedule to OCA/PAD.

*In the absence of any reporting requirement for a sponsored research project, it is Georgia Tech's policy to require, and include on the official deliverable schedule, a final project report, no matter how brief. Part of our mission, as a tax-exempt, non-profit educational institution, is to disseminate information to the public. One test that is used by the IRS (for the purposes of determining our tax exempt status) is to examine whether or not we have generated income that is unrelated to our mission. If the results of our research projects are not published and made available to the public (by way of placing them in the library), the income is considered unrelated to our mission and therefore jeopardizes our tax exempt status.*

**RECEIPT OF YOUR CONFIRMATION THAT THE SCHEDULE IS CORRECT WILL COMPLETE THE INITIATION OF YOUR SPONSORED PROJECT.**

Attachments

# PROCEDURES FOR SUBMITTING REPORTS AND OTHER DELIVERABLES

1. Submit reports and other deliverables to the OCA Reports Coordinator, Contracting Support Division, CRB Room 117A (Phone 894-4764). Copies will be reproduced and distributed according to the deliverable schedule and any other special instructions identified by the project director or contained in the project contract/agreement. A copy of the appropriate shipping document is required for deliverable items other than reports. The mail date and/or status comment is recorded for each deliverable item submitted.

2. Attach a completed **RESEARCH REPORT APPROVAL SHEET** (OCA Form 09-0996) to each deliverable. The report title, period covered, and deliverable line number must match the deliverable schedule listing. A copy of the form is enclosed for your use.

3. If a deliverable is submitted directly to a sponsor, two copies of the item must be provided to the Reports Coordinator with the completed **RESEARCH REPORT APPROVAL SHEET** for the OCA file and library archives. OCA will enter into the database the date provided by the PD/PI as the date the report was sent to the sponsor.

4. If special financial reports are prepared by the accounting office and submitted directly to a sponsor, a copy of each transmittal letter must be provided to the Reports Coordinator.

5. **CLASSIFIED REPORTS** are submitted to Research Security for control purposes along with a completed **RESEARCH REPORT APPROVAL SHEET**. The controlled document is delivered to OCA/CSD for reproduction, and all copies are delivered to the Research Security Department. Research Security distributes in accordance with the deliverable schedule and any special instructions either from the project director or contained in the project contract/agreement. NOTE: You may copy the **RESEARCH REPORT APPROVAL SHEET** for your use or order quantities from Central Supply or the GTRI Warehouse.

6. **E-MAIL REPORTS** may be sent directly by the PD/PI to the sponsor if allowed or required by the contract/grant. Additional hard copy versions of the report will be submitted by OCA/CSD to other locations as required by the contract/grant. Please cc: your e-mail reports to OCA's Reports Coordinator (wanda.simon@oca.gatech.edu or thelma.woods@oca.gatech.edu). First time e-mail submittals for each project copied to OCA must include the following identifiers: Project Number; Lab/School/Center; Report Title; Period Covered; Deliverable Number. Subsequent e-mail copies to OCA must include the following identifiers: Project Number; Deliverable Number; Period Covered; any changes to previous identifying information. Please be aware that FINAL REPORTS will still need the approval of the Lab/School/Center Director prior to submittal. A signed copy of the **RESEARCH REPORT APPROVAL SHEET** must be forwarded to OCA/CSD before the FINAL REPORT will be entered into the OCA database. NOTE: **Classified reports or those containing any type of data restriction should not be e-mailed under any circumstances.**

EORGIA INSTITUTE OF TECHNOLOGY | OFFICE OF CONTRACT ADMINISTRATION

## *RESEARCH REPORT APPROVAL SHEET*

(Please see Instructions on back)

Project No. ____________________

____________________
Lab/School/Center

**I. GENERAL**

A. Report Title ____________________

B. Author(s) and/or PD/PI ____________________ Phone ____________________

C. Period Covered ____________________ Due Date ____________________

**II. REPORT IDENTIFICATION**

A. Deliverable Line No. ____________________ (from Deliverable Schedule)

B. Type Report:

☐ Monthly ☐ Quarterly ☐ Semi-Annual
☐ Annual ☐ Progress ☐ Cost & Performance
☐ Contract Mgt. ☐ Final ☐ Other ____________ (Specify)

C. Draft Copy for Sponsor Approval ☐

D. Approval Copy for Distribution:

☐ Send Copy to Sponsor ☐ Return Master to PD/PI
☐ Send Master to Sponsor

**II. SECURITY CLASSIFICATION**

☐ Unclassified ☐ Secret ☐ Publication Delayed Until ________ (Date) (Specified Industrial Contracts Only)
☐ Confidential ☐ Top Secret ☐ Other ____________________ (i.e., ITAR, export controlled, etc.)

**V. DATA RESTRICTIONS** ☐ Yes ☐ No

Proprietary Data (Confidential Disclosure); Export License; Trade Secret; Copyright or Publishing Restrictions; Patentable Technology

NOTE: If "Yes", contact Office of Legal Affairs, Ext. 4-4812

**I. PRINTING/DISTRIBUTION INSTRUCTIONS** Unless otherwise indicated, printing charges will be assessed against project number. If project has been terminated, indicate charge number to use: ____________________

A. No. Copies to be Printed/Distributed

Sponsor ____ ; OCA 2 ; Lab/School/Center ____ ; Other ____ ; Total ____________

B. Printing Desired: ☐ One-side only ☐ Two sides

C. Binding Desired: ☐ Staple ☐ Staple & Tape ☐ Other ____________
☐ Spiral Bind ☐ Velobind

D. Cover Desired:

☐ Standard ☐ Sponsor-Prescribed
☐ None ☐ Special Design (OCA Approval Required) ____________
☐ White ☐ Other Color (Specify) ____________

E. Approval of Check Copy by Lab/School/Center before binding: ☐ Yes ☐ No (If Yes, Phone ____________ )

F. Distribution to be by:

☐ Lab/School/Center ☐ OCA Contracting Support Division ☐ Research Security

1. If distribution made by Lab/School/Center, attach transmittal letter and 2 copies of report for archives. Indicate date mailed: ____________________ . (This is the mailing date OCA/CSD will enter into the database).

2. If distribution made by OCA/CSD, the signature of employee handling the report and the mailing date are to be entered here: Distributed by: ____________________ Date mailed: ____________

3. If distribution made by Research Security, the signature of employee handling the report and the mailing date are to be entered here: Distributed by: ____________________ Date mailed: ____________

**I. APPROVALS**

| | DATE |
|---|---|
| A. PD/PI ____________________ | ____________ |
| B. Div. Chief/Branch Head ____________________ | ____________ |
| C. Lab/School/Center Director ____________________ (Required on Finals) | ____________ |
| D. MAPS/RAN Coordinator Log Entry: ____________________ | ____________ |

EPA OFFICIAL FILE COPY
RETURN AFTER SIGNATURE

EPA OFFICIAL FILE COPY
RETURN AFTER SIGNATURE

# U.S. ENVIRONMENTAL PROTECTION AGENCY
## EPA ASSISTANCE AGREEMENT / AMENDMENT
### PART I - ASSISTANCE NOTIFICATION INFORMATION

**1. ASSISTANCE ID NO.** R 826372-01-0

**2. LOG NUMBER**

**3. DATE OF AWARD** MAR 16 1998

**4. MAILING DATE** MAR 23 1998

**5. AGREEMENT TYPE**

| | |
|---|---|
| Cooperative Agreement | |
| Grant Agreement | X |
| Assistance Amendment | |

**6. PAYMENT METHOD**

☐ Advance ☐ Reimbursement ☒ ACH # 5096

Send Payment Request to: LAS VEGAS, FINANCIAL MANAGEMENT CENTER

**7. TYPE OF ACTION** NEW PROJECT

**RECIPIENT ORG**

**8. RECIPIENT** G-35-W62/CHAMEIDES/EAS
GEORGIA TECH RESEARCH CORPORATION
CENTENNIAL RES BUILDING, ROOM 246
GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GA 30332-0420

**EIN NO.** 580603146

**CONGRESSIONAL DISTRICT** 05

**9. PAYEE**
VICE PRESIDENT/GENERAL MANAGER
GEORGIA TECH RESEARCH CENTER
CENTENNIAL RESEARCH BUILDING, #270
ATLANTA, GA 30332-0415

**10. RECIPIENT TYPE** PUBLIC COLLEGE OR UNIVERSITY

**11. PROJECT MANAGER AND TELEPHONE NO.** (404) 894-1749
CHAMEIDES, WILLIAM
SCHOOL OF EARTH AND ATMOS. SCIENCES
221 BOBBY DODD WAY
ATLANTA, GA 30332-0340

**12. ADMINISTERING OFFICE / LAB**
ORD/NCERQA G-35-W62/CHAMEIDES/EAS

**EPA CONTACT**

**13. ISSUING OFFICE (CITY / STATE)**
WASHINGTON, DC 20460

Grant Specialist for this project:
FRANK ROTH
(202) 564-5329

**14. EPA PROJECT / STATE OFFICER AND TELEPHONE NO.**
PASHAYAN, DERAN (8723R)
OFFICE OF RESEARCH AND DEVELOPMENT
US ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, DC 20460
(202) 564-6913

**15. EPA CONGRESSIONAL LIAISON & PHONE** BARBARA BROOKS, (202) 260-5660

**16. STATE APPL ID (Clearinghouse)** N/A

**17. SCIENCE FIELD** 39

**18. PROJECT STEP (WWT Construction Grants Only)** N/A

**19. STATUTORY AUTHORITY** CLEAN AIR ACT: SEC. 103

**20. REGULATORY AUTHORITY** 40 CFR PTS 30 AND 40
-COPIES ATTACHED TO DR. CHAMEIDES

**21. STEP 2 + 3 & STEP 3 (WWT Construction Grants Only)**

| | |
|---|---|
| a. Treatment Level | |
| b. Project Type | N/A |
| c. Treatment Process | |
| d. Sludge Design | |

**22. PROJECT TITLE AND DESCRIPTION** SOUTHERN CENTER FOR THE INTEGRATED STUDY OF SECONDARY AIR POLLUTANTS(SCISSAP)-- To provide a better understanding of (1) the sources and dynamics of ozone and PM in the southern U.S.; (2) the atmospheric physical/chemical processes that couple ozone and fine PM; and (3) the combined effects of various emission control strategies on ozone and PM.

**23. PROJECT LOCATION (Areas Impacted by Project)**

| City / Place | County | State | Congressional District |
|---|---|---|---|
| ATLANTA | FULTON | GA | 05 |

**24. ASSISTANCE PROGRAM (CFDA Program No. & Title)** 66.500 CONSOLIDATED RESEARCH GRANTS

**25. PROJECT PERIOD** 04/01/98 - 03/31/01

**26. BUDGET PERIOD** 04/01/98 - 03/31/01

**27. COMMUNITY POPULATION (WWT Construction Grants Only)** N/A

**28. TOTAL BUDGET PERIOD COST** $1,366,359

**29. TOTAL PROJECT PERIOD COST** $3,658,410

| FUNDS | FORMER AWARD | THIS ACTION | AMENDED TOTAL |
|---|---|---|---|
| 30. EPA Amount This Action | $0 | $1,000,000 | $1,000,000 ✓ |
| 31. EPA In-Kind Amount | 0 | 0 | 0 |
| 32. Unexpended Prior Year Balance | 0 | 0 | 0 |
| 33. Other Federal Funds | 0 | 0 | 0 |
| 34. Recipient Contribution | 0 | 366,359 | 366,359 ✓ |
| 35. State Contribution | 0 | 0 | 0 |
| 36. Local Contribution | 0 | 0 | 0 |
| 37. Other Contribution | 0 | 0 | 0 |
| 38. Allowable Project Cost | $0 | $1,366,359 | $1,366,359 |

**39. FISCAL**

| Site Name | Document Control Number | FY | Approp. | Budget Organization | Program Element | Object Class | Site/Project | Cost Organization | Obligation / Deobligation |
|---|---|---|---|---|---|---|---|---|---|
| | T8KA26 | 9798 | C | 26T00E2 | C1X | 41.41 | | | 1,000,000 |

XC: CHAMEIDES, CEDERQUIST, GEC ACCTG, REP. COORD., KIRCHOFFER/RPM, FILE ( PP)

EPA Form 5700-20A (Rev. 5-82). Replaces previous editions and EPA Forms 5700-1A,B,C, and D, all of which are obsolete.

| TABLE A - OBJECT CLASS CATEGORY (Non-construction) | TOTAL APPROVED ALLOWABLE BUDGET PERIOD COST |
|---|---|
| 1. PERSONNEL | $298,894 |
| 2. FRINGE BENEFITS | 57,047 |
| 3. TRAVEL | 10,500 |
| 4. EQUIPMENT | 243,000 |
| 5. SUPPLIES | 38,806 |
| 6. CONTRACTUAL | 400,000 |
| 7. CONSTRUCTION | 0 |
| 8. OTHER | 41,000 |
| 9. TOTAL DIRECT CHARGES | $1,089,247 |
| 10. INDIRECT COSTS: RATE 49.02 % BASE MTDC | 277,112 |
| 11. TOTAL (Share: Recipient 26.00 % Federal 74.00 %.) | $1,366,359 |
| 12. TOTAL APPROVED ASSISTANCE AMOUNT | $1,000,000 |
| **TABLE B - PROGRAM ELEMENT CLASSIFICATION (Non-construction)** | |
| 1. | |
| 2. | |
| 3. | |
| 4. | |
| 5. | |
| 6. | |
| 7. | |
| 8. | |
| 9. | |
| 10. | |
| 11. | |
| 12. TOTAL (Share: Recipient ______ % Federal ______ %.) | |
| 13. TOTAL APPROVED ASSISTANCE AMOUNT | |
| **TABLE C - PROGRAM ELEMENT CLASSIFICATION (Construction)** | |
| 1. ADMINISTRATION EXPENSE | |
| 2. PRELIMINARY EXPENSE | |
| 3. LAND STRUCTURES, RIGHT-OF-WAY | |
| 4. ARCHITECTURAL ENGINEERING BASIC FEES | |
| 5. OTHER ARCHITECTURAL ENGINEERING FEES | |
| 6. PROJECT INSPECTION FEES | |
| 7. LAND DEVELOPMENT | |
| 8. RELOCATION EXPENSE | |
| 9. RELOCATION PAYMENTS TO INDIVIDUALS AND BUSINESS | |
| 10. DEMOLITION AND REMOVAL | |
| 11. CONSTRUCTION AND PROJECT IMPROVEMENT | |
| 12. EQUIPMENT | |
| 13. MISCELLANEOUS | |
| 14. TOTAL (Lines 1 thru 13) | |
| 15. ESTIMATED INCOME (if applicable) | |
| 16. NET PROJECT AMOUNT (Line 14 minus 15) | |
| 17. LESS: INELIGIBLE EXCLUSIONS | |
| 18. ADD: CONTINGENCIES | |
| 19. TOTAL (Share: Recipient ______ % Federal ______ %.) | |
| 20. TOTAL APPROVED ASSISTANCE AMOUNT | |

## TERMS AND CONDITIONS

1. In accordance with Section 2(d) of the Prompt Payment Act (P.L. 97-177), Federal funds may not be used by the recipient for the payment of interest penalties to contractors when bills are paid late nor may interest penalties be used to satisfy cost sharing requirements. Obligations to pay such interest penalties will not be obligations of the United States.

BILLING

2. By accepting this agreement for the electronic method of payment through the Automated Clearing House (ACH) network using the EPA-ACH payment system, the recipient agrees to:

   (a) Request funds based on the recipient's immediate disbursement requirements by presenting an EPA-ACH Payment Request to your EPA Servicing Finance Office (see EPA-ACH Payment System Recipient's Manual for additional information).

   (b) Provide timely reporting of cash disbursements and balances in accordance with the EPA-ACH Payment System Recipient's Manual; and

   (c) Impose the same standards of timing and reporting on subrecipients, if any.

   Failure on the part of the recipient to comply with the above conditions may cause the recipient to be placed on the reimbursement payment method.

ACCTG

3. As required by EPA regulations, the recipient agrees to submit a Financial Status Report (FSR) (Standard Form 269) within 90 days after the end of this budget period to the following address:

   U.S. Environmental Protection Agency
   Las Vegas Financial Management Center
   P.O. Box 98515
   Las Vegas, Nevada 89193-8515

   When the recipient submits their final FSR, they will in one of the following ways make an adjustment for the amount of Federal funds, if any, received in excess of the EPA share of the reported total budget period costs:

   (a) If the recipient is paid through EPA-ACH, they shall, in accordance with the enclosed payment guidance dated May 1995, refund excess assistance funds by either submitting a credit on a current EPA-ACH Payment Request or by sending a check to the lockbox address: U.S. Environmental Protection Agency, Las Vegas Financial Management Center, P.O. Box 371293M, Pittsburgh, Pennsylvania 15251.

   (b) If the recipient is paid by treasury check, they shall, in accordance with the enclosed payment guidance dated May 1995, refund excess assistance funds by submitting a check to the lockbox address in (a) above.

If funds are due to the recipient at the time of submission of the final FSR, the recipient shall follow the procedures as outlined on the enclosed payment guidance to request the appropriate amount of funds from EPA.

INCREMENTALLY FUNDED

4. EPA is partially funding this budget period and will consider funding the balance of the budget request contingent upon satisfactory progress as certified by the EPA Project Officer, the availability of funds, and EPA priorities. It is understood that the scope of work will be renegotiated to reflect the amount awarded if additional funds are not available.

5. EPA participation in the salary rate (excluding overhead) paid to individual consultants is limited to the maximum daily rate for a Level IV of the Executive Schedule, which is currently $453.85.

*6. Acceptable Quality Assurance Documentation must be submitted to the EPA Project Officer within 120 days of the acceptance of this agreement. No work involving environmental measurements or data generation shall be initiated under this project until the EPA Project Officer has approved the quality assurance documentation. (See 40 CFR 30.54 or 31.45 as appropriate)

7. In accordance with EPA guidance and OMB Circular No. A-21 or A-122, as appropriate, the recipient agrees that it will not use assistance funds (Federal or non-Federal share) for lobbying or political activities.

8. In accordance with applicable EPA regulations [40 CFR 31.40(d) for State, local and Indian tribal governments; 40 CFR 30.51(f) for other recipients], the recipient agrees to notify the EPA Award Official immediately in writing of any indication or allegation of research misconduct involving research activities that are supported in whole or in part with EPA funds under this project. EPA defines research misconduct as fabrication, falsification, or plagiarism in proposing, performing, or reviewing research, or in reporting research results. The term does not include honest errors in constructing the scientific record or honest differences in interpretation or judgments of data.

REPORTS/DELIVERABLES

9. By accepting this assistance agreement, the recipient agrees to:

a) Submit annual progress reports to the EPA Project Officer within 30 calendar days after each reporting period ends. The reporting period begins at the project start date, or, for subsequent years, on the annual anniversary of the start date. These reports shall include brief statements covering work status, work progress, preliminary data results, and evaluations made during the reporting period. They will address difficulties encountered, remedial actions taken, and a statement of activity anticipated during the subsequent reporting period, including a description of equipment, techniques, and materials to be used or evaluated. Each report will also include any changes of key personnel concerned with the project and a discussion of expenditures along with a comparison of the percentage of the project completed to the project schedule, and address how the quality of data is being assured when environmental measurements or data generation are involved. The report should generally not exceed five 8 1/2" x 11" pages.

b) Attendance by the Principal Investigator or Co-Investigator at annual EPA Research Grant Seminars, if asked by EPA, to present and discuss the project.

c) Provide a final technical report in accordance with 40 CFR 40.160-5. Therefore, the recipient shall submit a draft of the final report for review no later than 90 days prior to the end of the approved project period. The report shall document project activities over the entire period of funding and shall describe the recipient`s achievements with respect to stated project purposes and objectives. The report shall set forth in complete detail all technical aspects of the project, both negative and positive, the recipient`s findings, conclusions, and results, including the associated quality assurance results. The report should include, as applicable, an evaluation of the technical effectiveness and economic feasibility of the methods or techniques investigated or demonstrated. The final report is due within 90 calendar days after the end of the project period.

Publication d) Provide copies of any peer reviewed journal article(s) resulting from this research, in addition to the final technical report. The recipient shall submit three copies of each article to the EPA Project Officer. EPA encourages the independent publication of the results of its grant research in appropriate scientific journals. Any journal article so published, however, must contain the following statement:

* "Although the research described in this article has been funded wholly or in part by the United States Environmental Protection Agency through (grant number) to ( recipient`s name), it has not been subjected to the Agency`s required peer and policy review and therefore does not necessarily reflect the views of the Agency and no official endorsement should be inferred."

e) Provide final and annual reports in both hardcopy and electronic form. The electronic version must be on a DOS-formatted diskette that is compatible with EPA word processing software (i.e., WordPerfect™ 5.1/6.1). Also, the recipient is encouraged to provide the reports in native format as well, if different.

10. The Director, Grants Administration Division, has approved a deviation from 40 CFR 40.125-1(a) to allow the budget period to coincide with the project period. This permits the budget period to have a duration beyond the Agency's current regulatory limits.

11. The recipient agrees to comply with the MBE/WBE terms and conditions outlined in Attachment One.

**SPECIAL CONDITIONS** (continued)

## PART IV

**NOTE:** The Agreement must be completed in duplicate and the Original returned to the Grants Administration Division for Headquarters awards and to the appropriate Grants Administration Office for State and local awards within 3 calendar weeks after receipt or within any extension of time as may be granted by EPA.

Receipt of a written refusal or failure to return the properly executed document within the prescribed time, may result in the withdrawal of the offer by the Agency. Any change to the Agreement by the recipient subsequent to the document being signed by the EPA Award Official, which the Award Official determines to materially alter the Agreement, shall void the Agreement.

### OFFER AND ACCEPTANCE

The United States of America, acting by and through the U.S. Environmental Protection Agency (EPA), hereby offers assistance/amendment to the GEORGIA TECH RESEARCH CORPORATION (RECIPIENT ORGANIZATION) for 74.00 % of all approved costs incurred up to and not exceeding $ 1,000,000 (ASSISTANCE AMOUNT) for the support of approved budget period effort described in application (including all application modifications) cited in Item 22 of this Agreement

Signed: 07/14/97; Revised 1/9/98 (DATE AND TITLE), included herein by reference.

| ISSUING OFFICE (Grants Administration Office) | AWARD APPROVAL OFFICE |
|---|---|
| ORGANIZATION / ADDRESS<br>GRANTS ADMINISTRATION DIVISION<br>US ENVIRONMENTAL PROTECTION AGENCY<br>WASHINGTON, DC 20460 | ORGANIZATION / ADDRESS<br>OFFICE OF RESEARCH AND DEVELOPMENT<br>US ENVIRONMENTAL PROTECTION AGENCY<br>WASHINGTON, DC 20460 |

### THE UNITED STATES OF AMERICA BY THE U.S ENVIRONMENTAL PROTECTION AGENCY

| SIGNATURE OF AWARD OFFICIAL | TYPED NAME AND TITLE | DATE |
|---|---|---|
| for | MILDRED LEE<br>CHIEF, GRANTS OPERATIONS BRANCH 3903R | 3/16/98 |

This agreement is subject to applicable U.S. Environmental Protection Agency statutory provisions and assistance regulations. In accepting this award or amendment and any payments made pursuant thereto, (1) the undersigned represents that he is duly authorized to act on behalf of the recipient organization, and (2) the recipient agrees (a) that the award is subject to the applicable provisions of 40 CFR Chapter I, Subchapter B and of the provisions of this agreement (Parts I thru IV), and (b) that acceptance of any payments constitutes an agreement by the payee that the amounts, if any found by EPA to have been overpaid will be refunded or credited in full to EPA.

### BY AND ON BEHALF OF THE DESIGNATED RECIPIENT ORGANIZATION

| SIGNATURE | TYPED NAME AND TITLE | | DATE |
|---|---|---|---|
| | R. DENNIS FARMER<br>ASST. TO GENERAL MANAGER | Jilda Diehl Carton<br>Associate Vice Provost for Research and General Manager | 3/27/98 |

CA8140

Georgia Institute of Technology
Office of Contract Administration
OCA PAD INITIATION
Initiation Distribution

16-APR-1998 13:00

Project #: G-35-W62 Document Id: 48104
Project Director: William L Chameides
From CO: Anita D. Rowland Phone: (404) 894-4820

B

Attached is the initiation package for project G-35-W62
The following noted items are attached:

| | Admin | Bud | Fin | Deliv | Suppl | T & C |
|---|---|---|---|---|---|---|
| Project Director/Principal Investigator | Y | Y | Y | Y | ~~Y~~ | Y |
| Research Administrative Network | Y | Y | Y | Y | ~~Y~~ | Y |
| Accounting | Y | Y | Y | N | ~~Y~~ | Y |
| Research Security Department | Y | N | N | N | ~~Y~~ | Y |
| Reports Coordinator | Y | N | N | Y | ~~N~~ | Y |
| Research Property Team | Y | Y | Y | N | ~~Y~~ | N |
| Supply Services Department/Procurement | Y | Y | Y | N | ~~Y~~ | N |
| Research Communications Team | Y | N | N | N | ~~N~~ | N |
| Georgia Tech Research Corporation | Y | Y | Y | N | ~~N~~ | N |
| Library | Y | N | N | N | ~~N~~ | N |
| Project File | Y | Y | Y | Y | ~~Y~~ | Y |
| OCA/CSD | Y | N | N | Y | ~~N~~ | N |
| Office of Legal Affairs | N | N | N | N | ~~N~~ | N |

| CO | SEC | |
|---|---|---|
| ✓ | | 1. Deliverable schedule attachment sheet |
| — | | 2. Include supplemental information sheet |
| ✓ | | 3. Copy of grant/contract agreement document distribution indicated |
| ✓ | | 4. Copy of proposal budget to distribution indicated |
| ✓ | | 5. Copy of cost sharing approval forms to distribution indicated |
| — | | 6. Copy of research project questionnaire to PD |
| — | | 7. Patent report record/stamp onto folder |
| — | | 8. Other ______ |

Completed by CO adr 4-16-98

Completed by SEC ______