NASHVILLE 1999 FIELD STUDY
SCIENCE PLAN

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TABLE OF CONTENTS

INTRODUCTION

The SOS Paradigm

The oxidant-management approaches being used during the 1980s were based largely on scientific findings, air quality models, and related air quality management tools from research conducted in southern California and the urban megalopolis in the northeastern United States. Few scientific studies had been conducted in the South. In the late 1980s, however, studies began to emerge that pointed to the South's unique air quality management problems. These problems included: 1) a high frequency of air mass stagnation, warm temperatures, high humidity, and intense solar insulation that characterize the region's summer climate; 2) abundant natural emissions of biogenic hydrocarbons from the South's ample rural and urban forests; and 3) an anthropogenic emission mix dominated by island cities and rural point sources. Because of these unique characteristics, it became apparent that air quality management approaches developed in other parts of the Nation might not be appropriate for the South. To address this concern, the Southern Oxidants Study (SOS) was formed in 1988.

The SOS is a coordinated, long-term research program focusing on the formation, accumulation, and management of photochemical oxidants in the South. Since its founding, the SOS has focused on two general purposes:

1. Using the southern United States as a natural laboratory for policy-relevant scientific investigations, improving scientific and public understanding of the chemical and meteorological processes that cause ozone and other photochemical oxidants to accumulate in the atmosphere near the ground; and

2. Evaluating alternative strategies by which leaders in various Federal, State, municipal, industrial, and commercial organizations can manage the accumulation of ozone and other photochemical oxidants in the atmosphere, and decrease the injurious effects of these airborne chemicals in various urban and rural areas.

SOS Research

Prior to the late 1980's, biogenic hydrocarbons were believed to play little or no role in ozone formation in either the rural or urban atmospheres. Two papers were pivotal in changing this viewpoint: 1) Trainer *et al.,* (Nature, 1987) showed that biogenic hydrocarbons played a major role in rural ozone episodes in the eastern United States; and 2) Chameides *et al.,* (Science, 1988) showed that biogenic emissions represented a significant source of volatile organic compounds (VOCs) in Atlanta and that these emissions decreased the efficacy of a VOC-based ozone abatement strategy. The findings of Trainer *et al.* and Chameides et al. were a major driving force behind the inception of SOS and, consequently, the study of the role of biogenic VOC in ozone formation was identified as a prominent research theme for the program.

Research conducted as part of the SOS program has been broad in scope, necessitated by the complex nature of the problem. The program participants have been responsible for significant advances in methods development, emissions characterization, model development and evaluation, and have provided important new insights into the processes that control ozone accumulation in the atmosphere (Fehsenfeld *et al.,* 1993; Chameides and Cowling, 1995).

Field programs conducted during the early years of SOS relied primarily on ground-based measurements in the rural environment and were focused on developing a better understanding of the role of

biogenic emissions in ozone formation and exploring ozone/NO_Y relationships. There were, however, two SOS studies that used highly instrumented aircraft to provide a more comprehensive view of regional ozone formation and transport. In each case, the instrumentation mounted on the aircraft were used to characterize the spatial variability of ozone and its precursors over the region. Further, the flight paths were designed to provide information on ozone formation in urban and power plant plumes. In 1990 an effort led by NOAA's Aeronomy Laboratory (Trainer *et al.*, 1995) made measurements around Birmingham Alabama while in 1992 the Tennessee Valley Authority participated in a major field program in Atlanta Georgia (Imhoff *et al.*, 1995)

The results of these studies demonstrated the extreme value of the three dimensional information provided by these kinds of platforms. The experience obtained in the conduct of these studies and the analysis of the data collected provided critical new information on ozone production efficiency in plumes and formed the basis for the Nashville/Middle Tennessee Ozone study that was conducted in 1994/1995.

Nashville/Middle Tennessee Ozone Study – 1994/1995

The SOS Nashville/Middle Tennessee Ozone Study was conducted in two phases. Phase I, a preparatory study, was conducted during a three-week period in the summer of 1994. During this period, four ground-based monitoring stations, two wind profilers, and two instrumented aircraft (the NOAA WP-3 and the TVA Bell-205 helicopter) were operational. This three-week period also provided opportunity for: 1) evaluation of protocols for the ground-based and aircraft-based measurements systems to be used in 1995; 2) accumulating baseline data to aid in planning and calibrating instruments for the 1995 study; and 3) a rigorous intercomparison of the NOy measurement methods employed by various SOS groups in the 1992 SOS Atlanta Intensive and SOS-SERON field studies during 1992-1994.

Phase II was carried out over a six-week period (June 19-July 28) in 1995. During this second phase a

three-tiered (Level I, II, and III) network of progressively more sophisticated surface chemistry stations was established. The 108 Level I surface monitoring stations, operated as part of various regulatory and research networks, provided broad spatial ozone coverage across the Nashville/Middle Tennessee region and parts of eleven neighboring states. Six Level II surface monitoring stations provided continuous short-term (1 to 5 minute), high-sensitivity measurements of ozone (O_3), sulfur dioxide (SO_2), nitric oxide (NO), total nitrogen oxides (NO_Y), and carbon monoxide (CO) along with temperature, relative humidity, wind speed, wind direction, and solar radiation. Integrated, one-hour, pressurized canister samples for VOC analysis were collected midday at each station. Two Level III stations, one located approximately 20 km NE and the other approximately 20 km SE of the Nashville urban center provided detailed research-grade photochemistry measurements (e.g., organic nitrates, peroxides, aldehydes, VOC speciation). A network of five wind profilers was also employed.

Six instrumented aircraft were employed during the study -- NOAA WP-3, DOE G-1, NOAA Twin Otter, TVA Bell 205, NOAA CASA 212, and NASA C-130. The first four of these aircraft made *in-situ* chemistry and meteorology measurements and the last two had remote sensing capabilities.

The six-week 1995 intensive study was structured around a series of five aircraft-based experiments:

1. *Urban Plume* - Measurements of ozone formation in the Nashville urban plume under free-flow and stagnation conditions.

2. *Power Plant Plume Studies* - Measurement of ozone destruction and production in fossil-fuel fired power plant plumes.

3. *Subregional Characterization* - Detailed atmospheric chemistry and meteorological characterizations to evaluate urban-rural interchange and provide a detailed observational data set for model evaluations.

4. _Regional Characterization_ – Measurements using instrumented aircraft that extended north to the Great Lakes, south to the Gulf of Mexico, west to Missouri and Arkansas, and east to the Appalachian mountains to provide context for and contrast to the measurements in the Nashville/Middle Tennessee area.

5 . _Aircraft Intercomparisons_ - Side-by-side intercomparisons for the _in-situ_ sampling aircraft and overflights for the remote-sensing aircraft supporting the quantitative assessment of data inter-comparability

Findings From the 1994/1995 Study

The analysis of the measurements that were made during the course of the 1994/1995 Nashville Middle Tennessee Ozone Study has already produced several important findings.

Air Stagnation produced high ozone concentrations in a very confined area
The episode that resulted in the highest observed ground-level, hourly surface ozone concentration (138 ppb) occurred during stagnation conditions (July 12, 1995). The Nashville urban plume remained localized directly over the urban area covering approximately 600 km^2. During this episode ozone concentrations outside the boundaries of the urban plume were in the 60 to 70 ppb range indicating that local production resulted in an ozone concentration increase of approximately 70 to 80 ppb over the background. Under stagnation conditions, the ozone produced over the Nashville urban area during the day was subsequently redistributed throughout the region by nighttime winds.

Ozone production efficiency scales inversely with NO$_X$ source strength
Ozone production per unit of NO$_X$ emission appears to be greatest for the Nashville urban plume and for power plants with smaller NO$_X$ emissions that are located in areas rich in natural VOC emissions. Ozone production was found to be less efficient for NO$_X$ emitted form rural power plants with higher NO$_X$ emissions.

Inefficient ozone formation in plumes
Cross-plume pollutant profiles obtained by the NOAA WP-3 were combined with detailed wind fields to investigate O$_3$ formation at various downwind distances for several pollutant sources with very different NO$_X$ emissions. The analysis of this data from the measurements made in 1994 and 1995 indicate that NO$_X$ removal occurred rather quickly and that O$_3$ production in these plumes was much less efficient than ozone production from more dispersed NO$_X$ sources.

Reduced formation of H$_2$O$_2$ in plumes
Peroxide concentrations were lower in urban and power plant plumes than in background air. The lower peroxide formation rates inside the plumes are thought to be a result of higher NO$_X$ concentrations that maximize radical consumption by NO$_2$ to form nitric acid as opposed to radical combination reactions that form peroxides.

Importance of biogenic VOCs
Isoprene chemistry dominated ozone formation in the forested rural areas of the Nashville / Middle Tennessee region. The simultaneous measurement of peroxymethacrylic nitric anhydride (MPAN), peroxypropionic nitric anhydride (PPN) and peroxyacetic nitric anhydride (PAN) provides an opportunity to apportion photochemically-produced ozone into a fraction resulting from oxidation of biogenic hydrocarbons (BHCs) and a fraction resulting from oxidation of anthropogenic hydrocarbons (AHCs). A significant portion of the photochemically-produced ozone in the southern portion of the study region resulted from oxidation of BHCs. The contribution of isoprene to rural ozone formation was found to decrease significantly with increasing latitude (i.e. from south to north). This decrease paralleled a similar decrease in isoprene emissions with latitude predicted by current biogenic emission inventories.

Role of carbon monoxide and methane in regional ozone formation
An analysis of the VOC data suggests that carbon monoxide and methane make a significant contribution to ozone formation in regions where isoprene levels are depressed (i.e. in the boundary

layer in urban plumes, in the upper Midwest and the free troposphere). The more reactive VOCs have high removal rates and their absence suggests a lack of nearby sources of these VOCs. The more limited contribution to ozone formation from the more reactive VOCs may also be due, in part, to the effectiveness of current emission abatement strategies that have targeted these compounds. The apparent importance of methane and carbon monoxide in O_3 formation in the regions described above necessitate their consideration in future ozone management strategies. The role of methane and carbon monoxide should be expected to be further enhanced as emission of more reactive VOCs continue to decline.

Intercomparison of measurements
A comprehensive intercomparison of ground-based NO_y measurement systems employing both gold/CO and molybdenum catalytic reduction systems indicated good agreement between the two methods and among the various groups making the NO_y measurements. Intercomparisons between aircraft and surface measurements indicated generally good agreement for O_3, SO_2, and CO. However, there were some significant differences in the NO_y measurements, both between aircraft flying parallel flight tracts and between airborne and ground-based NO_Y measurements.

These results, along with many others, are described in detail in a special section of Journal of Geophysical Research – Atmospheres Volume 103, No. D17. For an overview of the 1994/1995 Nashville / Middle Tennessee Ozone Study see Meagher *et al.*, 1998.

Changes in Air Quality Regulations

During 1997, EPA introduced three regulatory initiatives to address the most egregious air quality problems in the Nation.

1. The EPA implemented a new National Ambient Air Quality Standard (NAAQS) for ozone. The level of the new standard was set at 80 ppb, averaged over 8-hr. (U.S. EPA, 1997a). This action caps nearly three decades of effort to manage ozone with mixed results.

2. The EPA revised the NAAQS for particulate matter (PM) by adding a new annual $PM_{2.5}$ (particles with aerodynamic diameters less than 2.5 micrometers) standard set at 15 $\mu g/m^3$ and a new 24-hr $PM_{2.5}$ standard set at $65\mu g/m^3$. The annual PM_{10} (particles with aerodynamic diameters less than 10 micrometers) standard was retained and the form of the 24-hr PM_{10} standard was modified (U.S. EPA, 1997b). In taking this action, the EPA cited epidemiological evidence linking significant human health impacts (mortality, hospital admissions, and respiratory illness) to ambient particulate levels below the previous standard.

3. New Regional Haze Regulations have been proposed (U.S. EPA, 1997c). These regulations are designed to protect and improve visibility in the 156 mandated Class I areas (National Parks and Wilderness areas) of the country. The focus, once again, is on reducing $PM_{2.5}$ concentrations in these areas.

These actions are expected to result in a significant increase in the number of areas as nonattainment for ozone (Chameides *et al.*, 1997) and PM. This anticipated expansion in the number of nonattainment areas serves to heighten the need for effective ozone and PM management strategies, based on sound science.

SOS Science Questions

In response to the insights and events described above the SOS community has articulated a set of six policy-relevant science questions to serve as a focus for future SOS research. They are as follows:

1. By what specific aerosol measurement methods can SOS achieve maximally beneficial characterization of aerosols in both urban and rural areas of the SOS region?

2. What are the linkages (similarities and differences) between the chemical, biological, and meteorological processes that govern formation and accumulation of ozone and fine particulate aerosols?

3. What is the relative efficiency of production of ozone and fine particulate aerosol in urban plumes compared to that in power-plant plumes?

4. In what ways are the rates and efficiencies of ozone and fine particulate aerosol production and accumulation different in large urban areas compared to small urban areas -- especially in cases where an air mass spends an extended period traversing a very large urban area?

5. How do nighttime meteorological and chemical processes influence the rates, efficiencies, and areal extent of ozone and fine particulate aerosol formation and accumulation?

6. What meteorological and chemical factors determine the regionality and/or locality of ozone and fine particulate aerosol accumulation events? In particular:
a) How do the processes that govern ozone accumulation in isolated urban areas surrounded by high-isoprene-emitting forests differ from those in urban areas in which urban plumes overlap from one urban or non-forested area to another?
b) How important are urban heat-island phenomena in determining the regionality and or locality of ozone and fine particulate aerosol formation and accumulation processes?

PROPOSED RESEARCH

Study Overview

The ramifications of the conclusions from the SOS 1994/1995 Nashville Middle Tennessee Ozone Study for policies to control ozone on local and regional scales in the Southeastern United States and their applicability to other locales and regions in the United States require additional testing and verification. In addition, these unexpected conclusions force us to consider other factors that may influence the photochemical processing of these compounds. In particular, the role played by particulate matter (PM) in tropospheric chemistry needs to be addressed.

The expansion of our measurements to investigate PM and PM-related processes is timely. Aerosols participate in a variety of chemical and physical processes in the troposphere. On a regional scale, these processes are associated with regional air quality as related to visibility and the effects of fine particles on human health. In this regard, there is a natural synergism between the ozone-related research described previously and the study of processes leading to or involving fine particles. The new Federal air quality regulations force us to recognize that a basic scientific understanding of the chemistry and physics of the atmosphere is prerequisite to the design of effective control strategies for these pollutants and that the concentrations of the pollutants in the atmosphere are often co-dependent because of interacting chemical reactions.

With this in mind, we are proposing to expand the SOS measurements program to elucidate:

1. how chemical processing on aerosols influences ozone formation;

2. how the atmospheric oxidation leading to ozone formation leads to aerosol formation; and

3. how atmospheric chemistry influences the growth and/or the chemical composition of aerosols.

This expansion of SOS to include the study of the formation and fate of fine particles in the atmosphere is being led by SOS' affiliated Southern Center for Integrated Study of Secondary Air Pollutants (SCISSAP). The Nashville-99 field study will be closely coordinated with the SCISSAP measurement network (see Appendix D). The Field Study measurements will augment those of SCISSAP, providing process-level information on PM formation and distribution and an opportunity to evaluate emerging measurement technologies related to PM.

Study Themes

The past measurements and those that we propose below are intended to provide a better understanding of the basic chemical, meteorological, and transport processes that determine ozone and fine particle distributions and new information to assist policy-makers in devising optimal ozone and PM management strategies. These studies are encompassed in three broad themes.

Local vs. Regional – Regional Contrasts
The first area of investigation addresses whether ozone or fine particle pollution is a regional or a local problem. The range provided by the WP-3D and the G-1 allows the composition of the atmosphere in a particular location to be placed in a regional perspective. Even though the concentration of ozone and fine particles can be elevated over large areas, it is still an open question how much of either ozone or fine particles are produced locally and how much are produced remotely and then transported to a particular locale.

Although the study will be centered in the Nashville/Middle Tennessee area flights are planned for the Mountain West and the Upper Midwest where meteorological conditions and the mix of ozone and PM-precursor emissions are expected to be significantly different than in the Southeast. These measurements will build on previous NOAA studies in Colorado and the Midwest and the recent BNL study in Phoenix.

Ozone and PM formation in Plumes
The second area of investigation relates to if and how ozone or fine particles observed in a particular location can be attributed to a particular source of precursor compounds located among a complex matrix of precursor sources. An ideal setting to address this question is an isolated urban area set in a rural background with several large point sources of pollution (e.g., fossil fuel burning power plants) imbedded at various distances with a wide range of pollutant emission. Under certain general flow conditions the plumes of the power plants merge with each other and/or the urban plume; in others they don't. Hence, the synergism associated with the interaction of power plants plumes, urban plumes, and the regional background can be investigated under a variety of conditions and in various combinations. As the dimensions of the urban complex grows the magnitude of the problem becomes greater. A second aspect of interaction involves the relation of ozone pollution to fine particle pollution. To date, ozone pollution has been largely treated as a local or sub-regional problem, while fine particle pollution has been viewed as a local problem from the health-effects perspective and a regional problem from the visibility perspective. The co-variation of these pollutants has never been extensively investigated, particularly on the regional scale.

The study of the evolution of the pollutant mix in plumes is particularly useful in the determination of pollution formation kinetics. The advection of plumes into a reasonably uniform background airmass provides a convenient "clock" allowing the quantification of the chemical rates that are critical to model development and evaluation.

Diurnal Cycle in Chemistry and Meteorology
In the overwhelming majority of cases, intensive field studies have targeted the study of daytime chemistry and dynamics. This interest is driven by a recognition of the important role that photochemistry plays in secondary pollutant formation and a concern for the impacts associated with daytime pollution exposures for both humans and plants. The pollutant mix can be significantly affected by non-photochemical reactions that occur at night. The results of the 1995 SOS field study in Nashville highlighted the importance of nighttime mixing processes in the redistribution of pollution throughout the region.

This field study offers the opportunity to document the entire diurnal cycle of chemistry and meteorology over one or more complete consecutive diurnal cycles using both surface-based and airborne observations. Information will be developed on processes that are not well described in current models. The measurements will help us understand how rural daytime chemistry, which establishes the residual convective mixed layer above the nocturnal boundary layer, ultimately is coupled to the daytime urban photochemistry that establishes peak ozone and PM levels in urban areas. Similarly, we will learn how daytime urban pollution affects rural air quality on the following day.

Focus Areas

In order to address the scientific themes identified above, we propose a research program combining a comprehensive suite of aircraft and ground-based measurements of the chemical and dynamical properties of the PBL and lower free troposphere. The proposed study focuses on six research areas.

Primary PM and PM precursor emissions
The current research-grade ozone precursor inventory for the study area will be expanded to include both natural and anthropogenic sources of PM fine and PM precursors, with particular emphasis on animal and crop-agricultural sources of NH_3.

PBL dynamics
Studies are proposed to characterize the effects of vertical and horizontal transport on the concentrations of ozone and aerosols and their precursors.

Ozone production efficiency
The influence of NO_X source strength and ambient VOC distributions on ozone production efficiency (the number of molecules of ozone produced per NO_X molecule emitted) will be investigated through studies of urban and power plant plume chemistry.

Characterization of loss processes
Follow-on studies will be conducted to determine the source of the high NO_X loss rates observed during the 1995 field experiments. Both mass balance and tracer techniques will be employed.

VOC contribution to ozone and PM formation

The relative role of anthropogenic and biogenic VOCs in ozone and aerosol formation and aerosol composition will be investigated.

Fine particulate matter – formation and characterization
The effect of atmospheric chemistry on the composition and morphology of ambient aerosols will be investigated. The connections between the processes that control ozone and aerosol formation will be studied. The relative importance of primary and secondary aerosols, with their varied sources, to ambient aerosol mass will be determined.

Nighttime chemistry and dynamics
The processes that control the formation and distribution of ozone and aerosols during the daytime and nighttime will be contrasted. A particular effort will be made to characterize the fate of plumes from large power plants that are emitted above the nocturnal boundary layer.

PRIMARY PM AND PM PRECURSOR EMISSIONS

Emissions inventory improvement has been a hallmark of SOS research from its inception in 1988. Before 1988, ozone precursor emissions inventories consisted almost entirely of "typical summer day" estimates mainly of anthropogenic sources of "reactive hydrocarbons and nitrogen oxides." Natural emissions of isoprene and other reactive VOCs by forest trees, emissions of NO by soil microorganism in well-fertilized row crops and pastures, and lightning in thunderstorms in some states with high frequencies of lightning events, typically were omitted from ozone precursor inventories in many State Implementation Plans. Carbon monoxide emissions also were regarded as a separate environmental issue and thus not included in some ozone precursor inventories. Although the phrase "nonmethane hydrocarbons" was commonplace in ozone-management circles, the SOS Nashville/Middle Tennessee Ozone Study and other SOS investigations have demonstrated conclusively that both CO and methane, and oxygenated as well as non-oxgenated VOCs, must be recognized in ozone precusor inventories that are to be used especially in small-grid-scale atmospheric modeling studies and other research projects. Thus, SOS has developed the notion of "research grade emissions inventories" which need to be compound specific, hourly and spatially resolved, grid based, environmentally corrected, and arranged to include <u>all</u> **natural** sources and **anthropogenic** sources of precursor emissions. Furthermore, the research grad inventories should not be based on unrealistic assumptions about "negligibly reactive compounds" or "negligible sources."

As SOS and SOS-SCISSAP have been preparing for the transition from an essentially "ozone only" program to an "ozone and PM_{fine}" program, the array of natural and anthropogenic precursor species of concern has had to be augmented still further to include sulfur dioxide (mainly from point sources) and gaseous ammonia (mainly from animal agriculture, but also including use of anhydrous ammonia in crop-based farming operations, and human waste treatment plants). Thus, Carlos Cardelino of the Georgia Institute of Technology, who has led SOS efforts to develop research grade emissions inventories for SOS' since 1992, is joining with Patrick Zimmerman of the South Dakota School of Mines, Lowry Harper of the USDA-Agricultural Research Service in Georgia, Wayne Robarge of North Carolina State University who is responsible for the "Nitrogen Budget Project" for the State of North Carolina, the Census of Agriculture in Washington DC, and the Departments of Agriculture in the 10 states of the SOS region in developing more accurate quantitative estimates of ammonia, amine, and volatile amino acid emissions from a wide range of crop and animal agrcultural operations.

These studies are based largely on domestic and wild animal and insect (especially termite) population estimates for the several southern states. So far, the work has been mainly a literature survey based on published scientific studies and official records of animal waste treatment "permits" approved by state regulatory agencies. These studies include both published and as yet unpublished estimates of emissions factors for volatile emissions from both European and North American animal rearing facilities, animal waste storage lagoons and other animal waste treatment facilities, and land applications of animal manures.

Ammonia Emission Estimates

Of the atmospheric gases that are part of the nitrogen cycle, ammonia is the one that is more close related to agricultural systems. Current estimates indicate that livestock wastes and fertilizer losses are the dominant ammonia sources in the U.S. They represent about 75% of all NH_3 emissions (NAPAP, 1990). To estimate livestock waste emissions we will use activity data from the States Statistician (USDA, 1996) and from the 1992 Census of Agriculture

published by the Department of Commerce (DOC)(DOC, 1995). In agricultural publications by DOC, the number of head of cattle and calves, poultry, sheep, pigs and hogs, horses, goats, and mink are reported at the county level. The most recent livestock waste emission factors were published as a report for EPA (Battye et al., 1994). This report contains ammonia emission factors in lb. NH_3 per head.

To estimate fertilizer loss emissions we will use activity data from the Agriculture statisticians office of the states involved or from the Commercial Fertilizer Data Base compiled by the Tennessee Valley Authority (TVA, 1990). Fertilizer databases contain fertilizer usage at the county level for a variety of fertilizers among which are those that emit NH_3. Activity levels of fertilizers that emit NH_3 are reported in tons of Nitrogen. As with the livestock waste factors, the most recent emission factors for fertilizer losses appeared in the 1994 report (Battye et al., 1994). In this case, the emission factors are reported as Kg of NH_3 per ton of Nitrogen.

During the coming year, we propose to derive ammonia emission estimates for the SMRAQ modeling domain with a grid resolution of 54 kilometers. In addition, we propose to develop a more detailed ammonia emission inventory (with a grid resolution of a few kilometers), for the Nashville/Middle Tennessee modeling domain.

PBL DYNAMICS

Pollutant concentrations at the surface are strongly influenced by the physical behavior of the atmosphere, particularly the planetary boundary layer (PBL). Polluted air may exist in a "reservoir" layer above the immediate PBL and be entrained as the PBL grows, increasing pollutant concentrations near the surface ("fumigation"); conversely, the overlying layer may be clean and entrainment may dilute the concentrations near the surface. The reservoir layers themselves are created by the collapse of the PBL upwind on the previous afternoon or by venting of polluted air out of the PBL by clouds and other detrainment mechanisms. Pollutants are transported at all levels, both within and above the PBL, and travel considerable distances even during periods of relative stagnation at the surface. In the daytime, vertical transport (entrainment and venting) tends to dominate, especially during stagnation episodes; at night, horizontal transport is dominant. ***The overall objective of the PBL dynamics component of the field study is to understand the effects of vertical and horizontal transport through the diurnal cycle on the concentrations of ozone and its precursors.***

Vertical Transport and Mixing

Vertical transport can be broken down into entrainment, detrainment, and venting. Entrainment is the capture of overlying air by the growing convective PBL, this air is then mixed throughout the depth of the PBL. Detrainment describes the opposite process, where air is left behind by the collapsing PBL in the afternoon or is transported horizontally out of the PBL when the PBL depth decreases downwind. Venting is the ejection of air from an active PBL by clouds. Entrainment is better understood than detrainment and venting.

Another important process is vertical mixing within the daytime mixed layer. Although potential temperature is constant in the daytime mixed layer, other species such as water vapor, or ozone may not be 'well mixed,' (i.e., constant with height). During Nashville-99, both the gradient of ozone in the mixed layer and the turbulence energy, as well as the surface fluxes driving the mixing processes will be measured.

Objective: Entrainment / morning transition
Description: Quantify the contribution of entrainment to the concentrations of pollutants near the surface.
Measurements:

> Profilers - continuous, uniform daytime operation at high resolution for z_i; half-hourly 4-5 minute high-resolution RASS
> Doppler lidar - VAD scans for high resolution wind profiles
> Ozone lidar - continuous daytime operation, staring vertically, for vertical ozone and aerosol profiles
> Ceilometers - continuous operation
> Airborne in-situ - constituent profiles during the morning as available; turbulence intensity as available
> Airborne ozone lidar - ozone profiles during the morning as available; horizontal distribution of ozone as available

Entrainment is quantified as fluxes of heat, moisture, and chemical constituents at the BL top. Since these fluxes cannot be directly measured, they must be inferred from other measurements. Two basic approaches are available, using entrainment velocity coupled with a constituent profile or using budget methods. Both approaches have large uncertainties and both have limitations, but they are complementary. The approaches and some results are discussed by Angevine *et al.* (1998).

For the entrainment velocity method, measurements of BL height z_i and its rate of change dz_i/dt are key.

These will be provided by the profiler network. Profiles of temperature and water vapor will be taken from the Nashville NWS soundings. Profiles of ozone and other constituents will be provided by the ground-based and airborne ozone lidars and by the airborne in-situ chemistry measurements. The cloud altitudes measured by the ceilometers help to remove ambiguities in the profiler z_i measurements. The primary uncertainty in the entrainment velocity method is the rate of subsidence at the BL top, which as a small mean of a strongly fluctuating velocity is quite difficult to measure. The profiler network and models may provide some estimates of subsidence.

The budget method requires measurements of the BL-mean value of a quantity and of its sources and sinks. For temperature, these are provided by the profiler/RASS network and by the surface flux network. Key uncertainties are direct radiative heating and advection, both of which can be estimated by models. Since reliable surface flux estimates over the urban area will be unavailable, the budget method can only be applied to the rural surroundings. The ozone budget can also be computed using measurements from the ground-based ozone lidar, but reducing the uncertainties in the source terms to acceptable levels may be quite difficult.

Objective: Detrainment & venting / evening transition
Description: Characterize the processes by which pollutants are removed from the active PBL and made available for horizontal transport.
Measurements:
> Profilers - continuous, uniform daytime operation at high resolution for z_i and residual reflectivity layers
> Surface flux network - half-hourly estimates of surface flux through the afternoon and evening
> Doppler lidar - VAD scans for high resolution wind profiles
> Ozone lidar - continuous operation through the afternoon and evening for vertical ozone and aerosol profiles
> Ceilometers - continuous operation

> Airborne in-situ - constituent profiles in the residual layer during the evening as available
> Airborne ozone lidar - ozone profiles during the evening as available; horizontal distribution of ozone as available

Losses of PBL pollutants can occur by detrainment of boundary layer air into the free troposphere either 1) during the evening transition when the CBL collapses or 2) through horizontal transport in regions where the mixing depth decreases downwind. Another loss mechanism is penetrative convection that vents the PBL of pollutants either temporarily, if air parcels settle back into the PBL, or permanently, if air parcels are detrained through cloud boundaries. Airborne chemistry measurements are also important in determining the mix of species that remains aloft, from which the origin and time of emission may be determined.

Detrainment during the evening transition is to first order approximated by assuming that the BL is well-mixed to its maximum height, and that all the air between that height and some nominal nocturnal BL height is detrained and available for horizontal transport by 1800 LST. A greater level of detail of the transition is needed, however. Wind and turbulence profiles from the profiler network and the Doppler lidar during the afternoon will show the evolution of vertical mixing and the time and space scales of its decay. The surface flux network will provide estimates of the decay of the surface fluxes, which may be modulated by clouds. The ground-based ozone lidar will show the formation of layers of differing ozone content. Airborne in-situ measurements and the airborne ozone lidar may also be used to show the formation and evolution of these layers if the aircraft can be flown well into the evening hours.

Venting of the active daytime BL by clouds is extremely difficult to estimate. The amount of cloud is shown by the ceilometers. Budget methods as described above for entrainment may be feasible. If a strong contrast exists between the BL and above-BL values of some constituent, airborne in-situ measurements may be used to derive a budget of that constituent in the free atmosphere immediately above

the BL. Residual boundary-layer traces may be detected by backscatter measurements from radar wind profilers and by aerosol and ozone lidars.

Objective: Daytime PBL characterization
Description: Document the height and intensity of mixing of the PBL during the day, including its spatial variation.
Measurements:

> Profilers - continuous, uniform daytime operation at high resolution for z_i and residual reflectivity layers
> Surface flux network - half-hourly estimates of surface flux through the afternoon and evening
> Ceilometers - continuous operation
> S-band profiler - continuous, uniform daytime operation for cloud top and precipitation characterization
> Doppler lidar - primarily vertical staring
> Airborne in-situ - constituent profiles in and above the PBL as available
> Airborne ozone lidar - ozone profiles as available; horizontal distribution of ozone as available

It is now recognized that vertical mixing processes often dominate the diurnal cycle of ozone in the PBL (Kleinman *et al*., 1994; Neu *et al*., 1994). Losses by dry deposition at the surface and through the top of the mixed layer by detrainment are regulated by vertical mixing. Gains due to sources, production, and advection are distributed in the vertical by mixing processes during the day. Therefore, the need exists to measure the temporal evolution of the boundary layer and understand its role in the production and modulation of ozone and precursor gases. The growth of the morning convective layer allows the chemical composition of the residual layer from the previous day, and perhaps from a different location, to mix to the surface at the same time that photochemical production of ozone is beginning. Ultimately, the growth rate of the PBL, local emissions emitted within the PBL, and the chemical composition of the residual layer all contribute to determining whether there is net production or destruction of ozone in the PBL. For example, because of the parabolic relationship between ozone production and NO, a slower growing boundary layer can result in either increasing ozone by limiting the vertical dilution of precursor concentrations or decreasing ozone by titration if NO is in excess. After the morning inversion is broken, the rapid growth of the midday boundary layer can cause ozone concentration to decrease even as the photochemical production rate is reaching a maximum. Later in the afternoon, when ozone concentration often reaches its peak in the diurnal cycle, the mixing depth may become quasi-steady through the competing effects of subsidence and entrainment. The maximum mixing depth that is achieved depends both on surface forcing (land use, topography, partitioning of latent and sensible heat fluxes) and aloft processes (entrainment, subsidence, advection).

Another important parameter controlling pollutant concentrations is the mixed layer depth. The mixing depth depends both on surface forcing (land use, topography, partitioning of latent and sensible heat fluxes) and processes occurring aloft (entrainment, subsidence, advection). One of the interesting results from SOS-95 was the horizontal variability in mixing depth observed in lidar transects and by the wind profiler array. In particular, Banta *et al*. (1998) speculated that the gradient in the peak afternoon mixing depths from the northwest to the southeast of Nashville was due to a difference in vegetation characteristics (forest versus open agricultural fields) and that the impact of these varying surface characteristics was strongest under stagnant conditions. A further, possible explanation for the variability in mixing depth observed during the mid-July stagnation episode was nocturnal advection of the urban residual layer toward the southeast, which led to less stability over a deeper layer downstream of the city and, ultimately, a deeper daytime mixed layer in the southeast region (White *et al*., 1998a). Another encouraging result from SOS-95 was that the mixing depths determined by analyzing aerosol backscatter profiles from the airborne lidar and reflectivity profiles from the ground-based wind profilers were in good agreement, indicating that the turbulence interpretation of the mixing depth provided by the profilers is the correct interpretation for air pollution applications (White *et al*., 1998b).

Additional factors affecting chemistry in the PBL arise when cumulus convection occurs. Clouds serve two potentially important roles in the PBL (Neff, 1998). First, clouds present an environment in which aqueous-phase chemistry can occur. Second, penetrative convection vents the PBL of pollutants either temporarily, if air parcels are recirculated into the PBL, or permanently, if air parcels are detrained through cloud boundaries. Clouds provide special challenges for remote sensors, for example, by inhibiting the performance of lidars and complicating the clear-air interpretation of radar returns. For Nashville-99 we propose to increase the number of cloud sensing devices including commercially available laser ceilometers and a new, vertically pointing 3-GHz radar (White *et al.*, 1998c).

As can be seen from these descriptions, a variety of measurement systems are necessary to characterize the full boundary layer evolution, including high-resolution, short-range instruments for the nocturnal PBL as well as the morning and evening transition periods, and long-range instruments for the daytime PBL. In addition, to study the horizontal distribution of mixing depth and to characterize the influence of inhomogeneous surface conditions, a network of surface-based integrated observing systems supplemented by aircraft is required. The network of wind profilers and the airborne ozone/aerosol lidar will be used to monitor the temporal and spatial evolution of the mixing depth. Aircraft with gust probes (e.g. G-1) will fly beneath the airborne ozone lidar to obtain simultaneous measurements of mixed layer depth and turbulence. Surface flux measurements at the profiler sites will help to determine to which extent the horizontal inhomogeneity in mixing depth observed during the SOS-95 campaign in the Nashville area depends on surface forcing. The ground-based and airborne ozone lidars will give a detailed picture of the temporal evolution and spatial distribution of ozone concentration from near the surface to the lower free troposphere. The profiler network as well as the Doppler lidar will provide continuous monitoring of the wind field. In addition, the Doppler lidar will yield important turbulence quantities, such as profiles of momentum flux, TKE, and vertical velocity variance. The combination of highly resolved ozone lidar data

with vertical wind speed measurements from the Doppler lidar offers the opportunity to determine the turbulent ozone flux within the PBL directly using the eddy correlation method. Unfortunately, direct measurements of subsidence, entrainment, and cloud venting are extremely difficult to obtain experimentally. Divergence fields derived from SOS-95 profiler data were useful in predicting the sign of the mesoscale vertical motion, but questions regarding quantitative accuracy still remain (White *et al.*, 1998a). One of the reasons for the planned profiler configuration in Nashville-99 (see Section III) is to minimize errors in the profiler divergence calculations. Recent work applying Large Eddy Simulation (LES) models and lidar observations of turbulence statistics shows promise in using the lidar observations to tune the model, then applying the model to estimate parameters that are not easily observed, such as entrainment.

Horizontal Transport

Objective: Daytime horizontal transport
Description: Document the spatial and temporal variation of horizontal winds during the day.
Measurements:

> Profilers - continuous, uniform daytime operation at high resolution for z_i and residual reflectivity layers
> Airborne *in-situ* - horizontal distribution of winds in and above the PBL as available
> Airborne ozone lidar - ozone profiles as available; horizontal distribution of ozone as available

The spatial and temporal variation of the horizontal winds in the daytime mixed layer control peak pollutant concentrations and the direction of transport of urban and power-plant plumes. Some specific issues include: causes of the narrowness of the urban plume (not sampled at the New Hendersonville site), changes from NO_x to VOC sensitivity over the urban area at low wind speeds, and transport aloft of ozone and its precursors.

Wind profilers and the airborne systems (in situ and ozone lidar) will document the spatial and temporal

variation of horizontal winds and pollutant transport during the day. The airborne ozone lidar will traverse power-plant plumes farther downstream than during the SOS-95 campaign, to characterize the ozone enhancement region of the plume and study its effect on background concentrations.

Objective: Nighttime horizontal transport
Description: Characterize the vertical and horizontal variation of winds at night, with special emphasis on the low-level jet and transport above the nocturnal PBL.
Measurements:

> Profilers - continuous, uniform daytime operation at high resolution for z_i and residual reflectivity layers
> Doppler lidar - VAD and shallow angle RHI scans
> Ceilometers - continuous operation to define cloud layers
> S-band profiler - continuous, uniform nighttime operation for cloud top and precipitation characterization

During periods of high ozone and/or aerosol loading, the ability to document processes affecting horizontal transport, including recirculation and stagnation, is critical. Of particular importance is the transport aloft of ozone and its precursors (Bigler-Engler and Brown, 1995; Trainer *et al.*, 1995). Wind profilers were invaluable in assessing transport patterns during SOS-95. For example, in addition to describing the general meteorological conditions for the 1995 field campaign, McNider *et al.* (1998) used a combination of wind profiler data, GOES imagery, conventional sondes, and Lagrangian particle models to describe the evolution of ozone episodes. The effects of inertial oscillations can be seen in the generation of azimuthal shear with height of the horizontal wind which leads to enhanced dispersion (McNider *et al.*, 1993) as well as in the generation of the classical low-level jets at nighttime that can produce enhanced trapping near the surface in the presence of stable lapse rates (Neff, 1990). The importance of the nighttime low-level jet accelerations to pollutant transport on days with light synoptic forcing, demonstrated during the SOS-95 campaign will again be a focus for 1999. The previous study showed that

the location of pollutant layers could be determined from trajectories derived from hourly profiler winds. Specific issues include: significance of the inertial oscillation on nights of somewhat stronger winds, documentation of the purging of the urban pollution 'dome' overnight during stagnation periods, plume shape and diffusion at night as a function of wind speed, mixing time scales versus reaction rates, maintenance of vertical shear in the "residual layer", the magnitude and interpretation of vertical gradients of pollutant species, especially those subjected to dry deposition, the horizontal variability of the flow near the surface and aloft in the low-level jet, and the role of nighttime transport in maintaining or contributing to background pollution levels.

Historically, horizontal transport has been characterized using two approaches (Neff, 1998). The first approach is routine monitoring of the flow field using arrays of instruments that are commonly available, cost effective, and operate unattended or are already part of operational networks. Presently, this includes sodars, wind profilers, rawinsondes, and surface meteorological stations. However, the technique of using NEXRAD data to derive VAD winds (Michelson and Seaman, 1998) may eventually be used to supplement the sparse wind observing network currently in place in the U.S. The second approach is required for detailed process studies and involves using research-grade instruments that may require special attention such as lidars, scanning radars, and supplemental sounding systems including rawinsondes, tethered sondes, and aircraft. Both approaches were used in SOS-95 and will be used again in Nashville-99. An additional focus of Nashville-99 will be nocturnal transport, which was not documented completely in SOS-95. We propose to deploy a scanning Doppler lidar and a high-resolution Doppler sodar to measure velocity profiles and a tethered sounding system to measure temperature and perhaps other scalar profiles at a site favorable for studying nocturnal boundary-layer phenomena. The lidar will provide both VAD and RHI scans.

Modelling Data base

Mesoscale meteorological models are key tools in the analysis of the meteorological and chemical results of the field campaign. They provide the ability to fill in for missing data with physically consistent fields, initialize chemical models, and predict unmeasured variables and cases. There are two objectives under this heading, the measurement data base and the external model database.   The actual model verification and use objectives are beyond the scope of this science plan.

Objective: Measurement database
Description: Produce a set of meteorological data that will allow for the verification and improvement of mesoscale meteorological models to represent the measured behavior of the atmosphere during the campaign and to predict unmeasured variables and cases.
Measurements: All

Still at issue is the proper balance between models and observations for air-quality assessment (Seaman, 1998), where in many cases, the observations are used to initialize and then nudge prognostic models back to "reality." This issue assumes greater importance as meteorological models are run with finer resolution

and used as pre-processors for photochemical grid models (Lyons *et al.*, 1995).   The instruments deployed during Nashville-99 will provide a comprehensive set of measurements for detailed comparisons of numerical simulations with observations. The data set will also serve in testing and improving the PBL parameterization schemes contained within the models (e.g., Zamora *et al.*, 1998). Forecasts of the mixed layer depth are most important. Realistic modelling of mixed layer depths requires a detailed specification of the mesoscale subsidence rate and the surface energy budget.

Objective: External model database
Description: Archive fields from runs of MM5 and Eta models and analyses made by outside organizations for future use as initial and boundary conditions and as verification for our own modeling efforts.
Measurements:
  NCEP Eta analysis
  MM5 analysis

Mesoscale numerical models such as the Colorado State University RAMS system, the NCEP Eta model and the Penn State/NCAR MM5 system are all capable of providing the necessary inputs to both the chemical and dispersion models.

OZONE PRODUCTION EFFICIENCY

Ground-Based Measurements

Much of the research that has been conducted to investigate the relationship between O_3 production and NO_x and VOC levels has taken place in rural or remote areas, that is where the mixing ratios of NO_x are only a few ppbv or less. The results of this research have demonstrated a number of key points. Photochemical production of O_3 cannot occur in the absence of NO_x; indeed, at very low levels of NO_x photochemistry destroys O_3. At somewhat higher levels of NO_x it has been determined that O_3 production becomes highly non-linear with respect to NO_x and that O_3 production peaks and then falls off (Liu *et al*., 1987; Lin *et al*., 1988). The level of NO_x where this roll-off occurs also appears to depend on the levels and relative composition of the VOC species present. Much less research has focused on investigating O_3 photochemistry for high NO_x, that is in urban plumes and point source (power plant) plumes. Modeling studies indicate that O_3 production efficiency, that is the amount of O_3 produced per NO_x oxidized, should be reduced at high loading of NOx due to scavenging by NOx of the radical species that are required for O_3 production. In fact, some previous research (Ryerson *et al*., 1998) indicates that the O_3 production efficiency can be large for urban plumes and for small power plant plumes, while for much larger power plants (and consequently much larger NO_x emission rates) O_3 production efficiency appears to be sizably lowered. Since the exact mechanism that causes this latter effect is unknown at present, these observations clearly demonstrate that our understanding of the photochemistry that occurs in these high NO_x environments is incomplete. Given that the air quality standard for O_3 has recently been made more stringent, it becomes imperative that the processes that lead to O_3 production be well understood in order to implement effective control strategies.

The multi-year study of O_3 photochemistry in the southeastern United States by the Southern Oxidants Study has focused on the contribution of rural areas to large scale O_3 pollution episodes, especially with respect to the impact that biogenic emissions of NOx and VOC have on production of O_3 in urban areas. More recently, studies of suburban and power plant plume chemistry in the Middle Tennessee region surrounding Nashville have been conducted, principally from aircraft platforms. These measurements have been valuable for probing photochemistry over a wide spatial and temporal domains, and under some conditions there has been sufficient data collected at high NO_x to explore O_3 production. Unfortunately, those ground measurements that have been taken have lacked the data at high NO_x because the measurement sites have been too far away from the urban "center". This was true, in particular, for the two Nashville intensive studies in 1994 and 1995. On those infrequent occasions when the urban plume did pass over the site at Hendersonville, the photochemistry had already peaked with respect to O_3 production. For the 1999 Nashville field study, in addition to the aircraft measurements, ground-based sampling will be conducted in order to acquire a data record of sufficient length at a location that has been chosen to have a high probability of near-field exposure to the outflow from the urban environment for a large fraction of the measurement period. The site and the proposed suite of measurements are described elsewhere in this document.

A number of approaches for the determination of the O_3 production rate (as a function of NO_x and VOC) are proposed for the ground-based portion of the 1999 study. Determination of the O_3 production rate requires the measurement of NO and the radical species that oxidize NO to NO_2, which in turn is

photolyzed to produce O_3. High quality measurements of NO are routinely made, but determination of the peroxy radical species is very difficult. We intend to obtain data that will allow comparison of estimated HO_x and RO_2 (via modeling) to those from direct and indirect measurements.

1. One direct measurement of these species that will be performed is the Chemical Amplifier (CA) technique. This instrument utilizes the cycling that occurs between OH and HO_2 when the peroxy radical oxidizes NO in the presence of CO to produce an "amplification" in the amount of NO_2 produced, which is then sensitively determined. An improved CA instrument will be provided and operated by personnel from TVA.

2. Measurements of OH and HO_2 will also be taken during the study. While this is not a determination of the complete suite of peroxy radicals, reliable HO_2 data can provide a lower limit to the rate of O_3 production. These measurements are based on the laser-induced fluorescence detection of OH, where HO_2 is measured as OH after being titrated by an excess of NO in the instrument inlet system. This instrument will be provided and operated by personnel from the Pennsylvania State University.

3. In many cases an indirect determination is made that infers the radical levels by calculating the deviation of the ratio of NO_2 to NO from the expected photochemical steady state (PSS) ratio that is induced with O_3 as the sole NO oxidant under given conditions of light intensity. This approach requires, in addition to NO data, high quality measurements of NO_2, O_3, and the photolysis rate of NO_2. The suite of measurements that are proposed for the Level III site can provide the necessary data.

4. Photochemical models can be used to derive the peroxy radical levels by estimating the concentration of radicals produced from known photochemical reactions of VOC species that are measured at the site. This approach requires a considerably larger suite of measurements than that of the PSS above, but the results are generally

more robust (Frost *et al.*, 1998). Many of the measurements required by the model that we intend to use will be available from the urban ground site.

It is expected that the above approaches for estimating the peroxy radical levels will be synergistic in that the more truly independent methods that are used to determine a given quantity, the more robust will be the result. At the least, redundant measurements are more likely to result in useful data should any given instrument fail.

Aircraft measurements

Important new information on the transformation and loss of pollutants in urban and power plant plumes was obtained during the 1995 Nashville/Middle Tennessee Ozone Field Study. As discussed above, analyses of these data indicate rapid removal of NO_X in power plant plumes and ozone production efficiencies that were much lower than previously reported. By making detailed chemical measurements at multiple down-wind distances using highly-instrumented aircraft it was possible to describe the evolution of the pollutant mix to a degree that had not previously been possible. Two methods were used to correct for concentration changes resulting from non-chemical processes (plume dilution, venting, surface deposition etc.). These methods have been described in detail by Ryerson *et al.* (1998).

1. Mass balance
The mass balance approach for NO_x conversion and O_3 production uses the integral of trace species of interest over the entire volume section of the plume at each flight transect. The change in the integrated amount is determined from plots of net mixing ratio in the plume (plume minus surrounding background levels) versus distance (or time) downwind from the source. Knowledge of the emission rates (assumed constant) from the source, measurements of the wind field affecting plume transport, and estimates of deposition (via calculation) and venting loss processes (estimated from longer-lived species, e.g., SO_2) are used with the measured change from the plot to

estimate the conversion of NO_x as a residual. The production of O_3 is determined in a like manner. Comparison of NO_x conversion and O_3 production for different points on a plume and among different plumes provides insight into the efficiency by which O_3 is generated by the different NO_x sources, the ozone production efficiency, or OPE. In addition to OPE determinations, the mass balance approach can determine effective boundary layer removal rates for various trace gases. An improvement expected for the 1999 study over previous studies will be the in situ aircraft measurement of NO_2 rather than derivation of NO_2 from PSS calculations.

2. Pollutant ratios

During the transport of plumes, mixing effects within the boundary layer significantly alter the plume composition downwind. These mixing effects can be taken into account by using the ratio of the level of that species (minus the background) to that of a co-emitted tracer species. Measurements of the ratio as a function of downwind distance (or time) provide a determination of the removal of one species relative to the other. When a longer-lived species, such as SO_2, is used for the tracer compound, then the ratio of O_3 to SO_2 versus the ratio of NO_x to SO_2 provides information about the photochemical change of O_3 relative to NO_x which yields the OPE. In contrast to the mass-balance approach described above where estimates of loss rates are needed, the concentration ratio method accounts for these effects explicitly, depending on the nature of the tracer.

In 1999 both of the above approaches will be used. However, since the meteorological requirement for the successful application of the mass balance approach are quite restrictive it is desirable that a tracer be available to allow for the quantification of lifetimes of plume constituents. Current plans call for the use of two types of tracers: 1) tracers of opportunity and 2) artificial tracers.

1. Tracers of opportunity

These are compounds that are present in either the urban or power plant emissions in sufficient abundance that they can be accurately quantified far downwind (>50 km). These are semi-conserved tracers whose deposition and transformation rates are sufficiently low and well quantified that their measurement provides a means for normalizing the concentrations of more reactive pollutants. The successful application of this method also requires that the emission ratios be well quantified and that the time response characteristics of the aircraft instrumentation be well characterized. Three tracers of opportunity are being considered: SO_2, CO and CO_2. The characteristics of each are described below.

SO_2 - This compound can be used as a tracer for power plant plumes. Large power plants are required to make continuous in-stack measurements of SO_2 with their Continuous Emission Measurement Systems (CEMS). The deposition velocity and atmospheric oxidation rate for SO_2, although low (~1 cm sec^{-1} and 0.01-0.05 hr^{-1} respectively) are nevertheless significant and make SO_2 a less than ideal tracer. However, lifetimes calculated using SO_2 as a tracer compared favorably with estimates using the mass balance approach (Ryerson, *et al.*, 1998).

CO - This compound can be used as a tracer for urban plumes. Urban emissions are reasonably well quantified and measurements of CO and NO_Y made in the Nashville urban core during 1995 agreed well with the expected emission ratio based on available inventory data. Carbon monoxide has a very low deposition velocity (< 0.1 cm sec^{-1}) and photochemical production and loss are expected to have only a minor effect on the measured concentration.

CO_2 - This compound can be used for either power plant or urban plumes but application to power plant plumes appears most promising. This compound is also monitored on a continuous basis with the CEMS in large power plants. Fast response instrumentation are available to quantify this compound with sufficient sensitivity and precision to detect it in power plant plumes above the very large background (~360 ppm) that is present in the atmosphere. Background variability may

be a greater problem in the use of CO_2 as a tracer.

2. Artificial tracer
During the Nashville 1999 field campaign the use of the above tracers of opportunity will be augmented by the use of an artificial tracer. The tracer will be introduced into TVA's Cumberland power plant at a rate proportional to plant emissions. Canister samples collected on the NOAA WP-3 will be analyzed for the tracer, providing a direct measure of plume dilution.

To be useful for this purpose the tracer must have the following characteristics:
- The tracer must have low atmospheric reactivity and surface deposition rates.
- The tracer must be detected with high sensitivity and selectivity.

- The tracer must be safe to handle and environmentally benign.

Tracers that have been traditionally used for atmospheric dispersion studies (SF_6 and perfluorocarbons) were not considered since these compounds have long atmospheric lifetimes and significant global warming potentials.

A hydrofluorocarbon, HFC 152a (1,1,-difluoroethane) has been selected for use and this application is undergoing safety review by TVA. This compound appears to satisfy all of the above criteria. It has an expected atmospheric atmospheric lifetime, based on removal by reaction with hydroxyl radical, of approximately 1.5 years and a small global warming potential.

CHARACTERIZATION OF LOSS PROCESSES

Analysis of power plant and urban plume data for the measurements made in 1994 and 1995 suggests that NO_x is rapidly depleted in these plumes in the Southeast. Cross-plume pollutant profiles obtained by the NOAA WP-3D were combined with detailed wind fields to calculate NO_x fluxes as a function of downwind distances for multiple plumes and indicated that NO_x removal rates were significantly larger than those expected from model simulations based on the best available knowledge. This implies that either the plume chemistry results in a NO_x reaction product that cannot be effectively detected with the NO_y measurement systems employed or that surface deposition, boundary layer venting and/or uptake of NO_y species on aerosols may be occurring at a rate much faster than presently predicted.

Ozone is a by-product in the oxidation of natural and anthropogenic hydrocarbons in the presence of nitrogen oxides ($NO_x = NO + NO_{2)}$. NO_x acts as a catalyst in this process. In the study region, the southeastern United States, NO_x is mainly directly emitted of from combustion sources and thus of anthropogenic origin. Through photochemistry the primary emitted NO and NO_2 are oxidized and can be converted into reservoir species. Those are compounds as organic nitrates that are less reactive and therefore have a longer lifetime in the atmosphere. Enhanced stability allows the transport of reactive nitrogen over long distances to the remote atmosphere where these species can be reconverted to more photochemically active forms. In this way even remote regions without any local pollution sources can be effected. The ultimate fate of the reactive nitrogen oxides is the conversion to HNO_3 or nitrate aerosol and their removal from the atmosphere through dry deposition or washout by rain.

A goal of the SOS ozone research is to gain the ability to attribute the local ozone abundances to the different precursor sources. The precursor distributions are shaped by emissions, photochemical conversions that either produce or remove these trace gases from active photochemistry, other losses like wet deposition or rainout and transport. Any reliable assessment of how the ozone production can attributed to different precursor sources is dependent on how well one can account for the precursor distributions.

The local ozone production is dependent on the availability of the catalyst. Measurements from prior SOS experiments suggest that throughout most of the southeastern U.S. the production of ozone is NO_x limited. Therefore, it is most important to understand what happens to the NOx emitted. How long that is for how many oxidation cycles are the nitrogen oxides available as catalyst? This, combined with the above cited preliminary result from SOS 94/95 - more rapid loss of NO_x than presently understood - pose a severe question that needs to be addressed in the upcoming SOS 99 study. Is the observed rapid loss real and if so, what is the cause of the rapid loss of NO_x that we do not understand at this time?

Several potential causes need to be considered for a seemingly too rapid loss:

- Measurement artifact
- Incorrectly quantified physical removal of NO_x from airmass (deposition, venting of PBL)
- Loss on aerosol

Measurements of the nitrogen oxides are made by widely accepted techniques (chemiluminescence detection of NO, photolysis of NO_2 to NO combined with chemiluminescence detection of NO, conversion of all reactive nitrogen component species to NO combined with chemiluminescence detection of NO). In the laboratory and in ground based measurements these instruments have been challenged with the compounds that are thought to be the major components of NO_y (ie NO, NO_2,

HNO$_3$, PAN, PPN, and other organic nitrates). Many of the individual species have been measured concurrently in filed studies. By comparison with the measurement of total NO$_y$ the budget and with it the current understanding can be tested. With the rich, complex hydrocarbon mix present in these atmospheres a variety of organic nitrates can be expected, and indeed, a number of nitrates have been identified and measured in the southeast. The air mix though is much to complicated to account for all the hydrocarbon precursors and reaction products. This leaves the possibility that unidentfied reaction products may be formed that are specific to this region.

SOS sponsored in 1994 at Nashville a ground based intercomparison of these techniques with generally good agreement (Williams et al., in press). Together with the results of other ground-based intercomparisons (NASA GTE, Fehsenfeld *et al*, Fehsenfeld et al.) one has to conclude that these are the best measurements available and that they have been thoroughly tested.

The inflight intercomparison of NO$_y$ measurements during SOS-95 though, revealed significant differences. Therefore, it has to be investigated whether the deployment of these instrument from aircraft in the southeastern US with its complex air matrix can lead to yet unappreciated measurement artifacts. Sampling of reactive trace gases from an aircraft is a difficult task and the impact of the used inlets on the sampled airmass thoroughly evaluated. Another explanation for the seemingly fast loss could be the removal of NO$_x$ through physical processes, either deposition or cloud venting at the top of the Planetary Boundary Layer (PBL). Trace gas deposition velocities for nitrogen oxides have been measured and agree reasonably well. Venting at the top of the boundary layer is difficult to quantify (see above) but was thought not to significantly exchange air from the PBL to LFT during the observations of SOS 1994/5. Ambient aerosol might supply enough surface area for reactions or uptake and help removal or conversion of nitrogen oxides from the plumes.

Objectives

- Make measurements of reactive nitrogen oxides
- Validate them by intercomparison and support measurements
- Investigate whether loss of nitrogen oxides in urban and power plant plumes is in agreement with current understanding
- Investigate whether loss can be attributed to higher deposition or more effective venting of PBL
- Investigate whether loss correlates with aerosol loading

Plans for 1999

A first step is the verification of the rapid NO$_x$ depletion that was indicated in the SOS 94, 95 measurements. Measurements will be made by multiple investigators and thoroughly compared. In addition, two of the platforms will attempt to assess the reactive nitrogen oxide budget by measuring the major individual species (NO, NO$_2$, HNO$_3$, PAN , organic nitrates) and total reactive nitrogen oxides (NO$_y$). It is planned to measure under various meteorological conditions and to contrast the measurements in Tennessee with the Midwestern region north of the Ohio river and measurements in the Mountain West. Tracers will also be employed as has been described above.

The measurements on the NOAA WP-3D will be enhanced by the deployment of a new instrument to make fast in-situ measurements of HNO$_3$ by chemical ionization mass spectrometry. This will allow to follow the downwind evolution of the primary gases (NO$_x$) and its photooxidation product.

The possibility of lidar measurements on the NOAA WP-3D to determine the local PBL depths is being evaluated.

More emphasis will be put on investigating the vertical structure of plumes downwind. Crosswind profiles of plumes at various heights will show how far vertical mixing leads to constant volume mixing

ratios through the full PBL height. Overflight of the plumes just above the PBL top will indicate whether venting will effectively remove gases from a plume that travels in the PBL into the lower free troposphere.

The addition of two instruments that measure the aerosol size distribution from the nanometer (nm) to micrometer (μm) range will allow to follow the development of the aerosol surface area that could be available for surface reactions in plumes. Any uptake of reactive nitrogen species should result in a modification of the aerosol distributions in the plumes along the downwind distance.

VOC CONTRIBUTION TO OZONE AND PM FORMATION

Volatile organic compounds (VOCs) play a key role in the formation of ozone and PM. Emissions of anthropogenic VOCs have declined significantly during the last two decades (U.S. EPA, 1997d) due to emission management programs that target these compounds. As anthropogenic emissions have decreased biogenic emissions of reactive VOCs, such as isoprene and terpenes, play a greater role in ozone and PM formation especially in heavily vegetated areas such as the Southeast. Analysis of VOC data collected during the 1995 SOS study indicated that carbon monoxide and methane can also make a significant contribution to VOC reactivity, especially in rural areas without significant biogenic emissions (Figure 1). These latter compounds are usually not included in VOC emission management programs because of their low reactivity. A better understanding of the relative role of anthropogenic, biogenic and low reactivity VOCs (i.e. methane and CO) to atmospheric reactivity is essential to the development of effective pollutant management strategies.
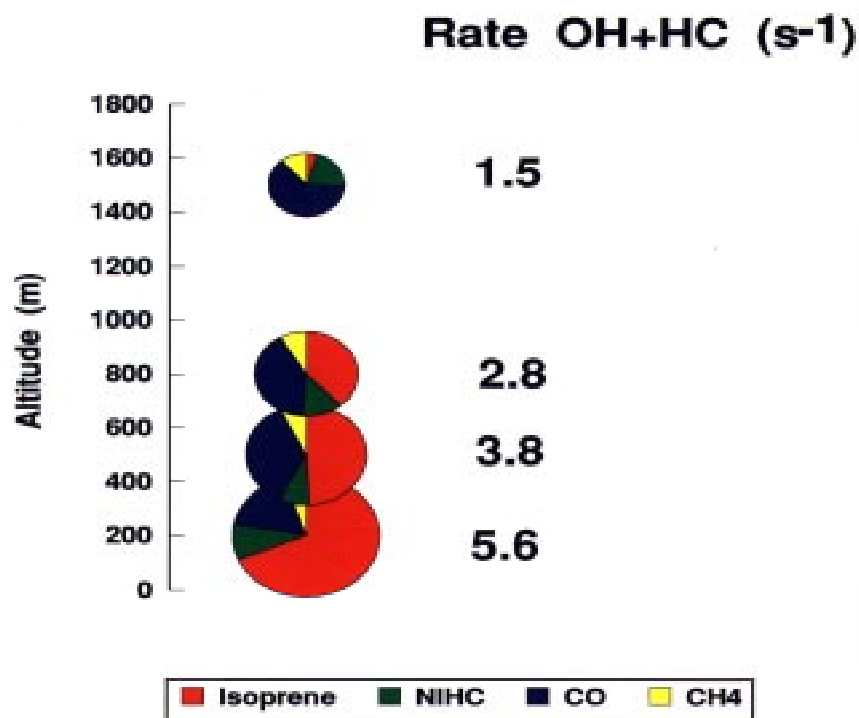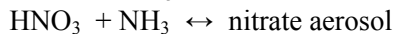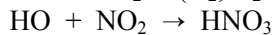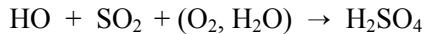

Figure 1. VOC reactivity distribution as a function of altitude. Data are from canister samples collected aboard the DOE/BNL, G-1 during the 1995 Nashville/Middle Tennessee field study. Figure provided by L. Kleinman.

Although the role of VOCs in ozone formation is well understood their role in PM formation is less appreciated. VOCs can contribute to PM formation in two ways:

1. **Generation of free radicals** – Obviously VOCs are a key ingredient in the pollutant mix responsible for sustaining the atmospheric population of free radicals such as HO and HO_2.

The radicals can oxidize SO$_2$ and NO$_2$ directly, with subsequent formation of sulfate and nitrate aerosols.

$$HO + SO_2 + (O_2, H_2O) \rightarrow H_2SO_4$$
$$HO + NO_2 \rightarrow HNO_3$$
$$H_2SO_4 + NH_3 \rightarrow \text{sulfate aerosol}$$
$$HNO_3 + NH_3 \leftrightarrow \text{nitrate aerosol}$$

These radicals also influence the formation of ozone and peroxide compounds that are responsible for the oxidation of SO$_2$ in clouds, which is an additional source of sulfate aerosols.

2. **Formation of organic aerosols** – Low vapor pressure products of atmospheric photo-oxidation contribute to fine aerosol mass in the atmosphere through condensation onto pre-existing particles. The aromatic compounds found in gasoline have been shown (Odum et al., 1997) to react under atmospheric conditions to form aerosols. Biogenic VOCs are another potential source of atmospheric aerosols. Laboratory studies suggest that isoprene photoxodation does not lead to significant aerosol formation. However, pinenes and other monoterpenes form aerosols through reaction with ozone and hydroxyl radicals (U.S. EPA, 1996).

During the 1999 field campaign the role of various classes of VOCs (anthropogenic, biogenic, low reactivity) in promoting the formation of ozone and PM will be evaluated using the approaches described below. Both ground-based and airborne sampling will be employed. The airborne measurement capability will afford the opportunity to conduct measurements in different regions (Southeast, Midwest, Mountain West) with a variety of VOC pollutant regimes.

Quantification of VOC Emissions
The accurate quantification of VOC emissions is crucial to the successful interpretation of ambient measurements performed during the study. The VOC emission mix contained in the Nashville emission inventory will be evaluated against data collected during a tunnel study conducted in the Nashville urban area during the 1995 field campaign. Additional checks on the VOC emission mix and

source strength will be provided by VOC samples collected in the urban core during the 1999 study. VOC canister samples will be collected daily at the downtown sampling site, located on top of an 18-storey building. In addition, canister samples will be collected for VOC analysis at several elevations above the city center using the TVA helicopter. These vertical profiles will be repeated several times during the study.

Ambient VOC reactivity
Ambient VOC concentrations will be determined by several means during the study. 1) Daily canister samples (1-hr integrated) will be collected and analyzed for VOCs at the upwind, background site (Dixon) the downwind urban site (Cornelia Fort) and the downtown site (Polk Building). 2) The TVA helicopter, the DOE G-1 and the NOAA WP-3 will each collect canister samples for VOC analysis. 3) The DOE G-1 and the NOAA WP-3 will be equipped with systems (atmospheric pressure mass spectrometry and gas chromatography respectively) for real-time VOC analysis.

The VOC data from the sources described above will be used to evaluate the contribution the various VOCs measured to ozone formation. The contribution of individual compounds to overall VOCs reactivity can be estimated in several ways:

1. **HO reactivity** – The rate of reaction with the HO radical provides a convenient measure of the contribution of a particular VOC to propagation of the free radical chain that is responsible for ozone formation.

2. **Incremental reactivity** – The use of ozone reactivity scales for VOCs (Carter, 1994) provides a more direct means of weighting the contribution of individual components of a VOC mix with respect to ozone formation.

3. **Model simulations** – Photochemical grid models can be used to determine the relative sensitivity of ozone formation to the concentration of indivudal VOCs.

Biogenic/anthropogenic contribution to ozone formation:

Recent analyses (Roberts *et al.*, in press) have demonstrated the use of relationships between observed photochemical products, PAN (peroxyacetic nitric anhydride) and PPN (peroxypropionic nitric anhydride) and MPAN (peroxy-methacrylic nitric anhydride) and ozone to estimate the contribution of anthropogenic and biogenic VOCs to regional ozone production. In this approach MPAN is used as a marker for chemistry driven by biogenic VOCs and PPN as a marker for chemistry driven by anthropogenic VOCs.

Measurements of these organic nitrates will be performed at the downwind urban site (Cornelia Fort)

and onboard the NOAA WP-3. Analysis of these data will provide a measure of the contribution of biogenic and anthropogenic VOCs to regional ozone formation independent of source estimates or chemical mechanisms.

VOC Contribution to Aerosol Mass

The careful measurement of the organic fraction of the fine aerosol mass will provide a direct measure of the VOC contribution to aerosol formation. These measurements will be performed at the downwind urban site (Cornelia Fort) and are described in more detail in the section "Fine Particulate Matter – Formation and Characterization".

FINE PARTICULATE MATTER
FORMATION AND CHARACTERIZATION

Airborne particles may have many sources and contain hundreds of inorganic and thousands of organic components. Atmospheric particles are distributed by size into fine and coarse modes with a split at about 2.5μm. Course mode particles in the range 2.5-10 μm are largely deposited in the nasal-pharyngeal areas of the respiratory system, whereas particles smaller than 2.5 μm are more likely to reach the lungs. Fine mode particles, principally those in the 0.1-1.0 μm range, scatter visible light efficiently and are major contributors to the regional haze that is prevalent in the Southeast during the summer.

The atmospheric particles that populate the fine and coarse modes are characterized by different sources, composition, and atmospheric behavior. Coarse Mode particle mass is dominated by primary particles such as fugitive dust and fly ash. In contrast, much of the fine particle mass in the atmosphere is formed through the chemical transformation of gaseous precursors such as SO_2 and NH_3. Aerosol studies conducted during the field study will focus on improving our understanding of the processes that control the formation and distribution of fine particles in the atmosphere.

Chemical Composition and Morphology of Atmospheric Aerosols

The careful characterization of atmospheric aerosols in terms of chemical composition and morphology not only provides important clues regarding their sources and possible mechanisms of formation but also provides valuable information for those studying health effects of particulate matter (PM).
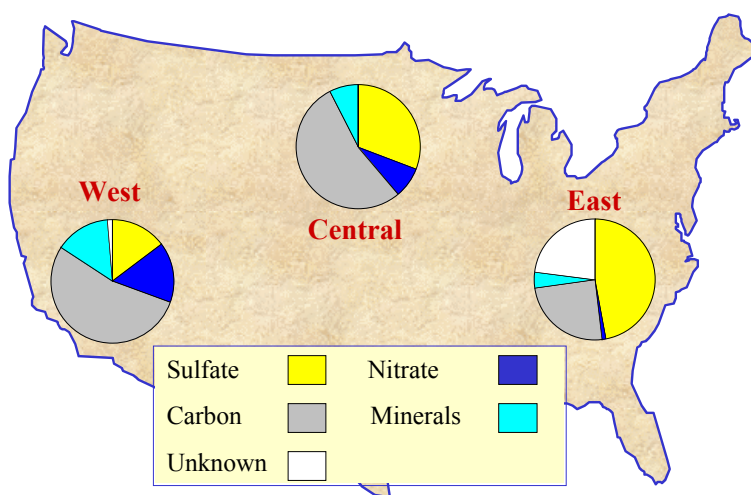

Figure 2. Composition of $PM_{2.5}$ aerosol mass in the U.S. Source U.S. EPA, 1996.

The chemical composition of ambient $PM_{2.5}$ aerosol mass varies significantly across the country (Figure 2). Sulfate constitutes a significant fraction of the fine particle mass in the East with nitrate and carbon

(elemental and organic) playing lesser roles. In the West, on the other hand, the fine particle mass is dominated by nitrate and carbon with sulfate making a smaller contribution. While carbon-containing aerosols comprise only about 25% of $PM_{2.5}$ mass in the East they are the dominant fraction of $PM_{2.5}$ in the Central and West regions of the country. These differences in the chemical composition of $PM_{2.5}$ reflect differences in emissions in the two regions. As the regulations lower the emission limits for SO_2 and NO_x, carbon-containing aerosols will represent an increasingly larger fraction of $PM_{2.5}$ throughout the country.

For aerosol samples collected in the eastern U.S., a significant fraction (typically 20-30%) of the $PM_{2.5}$ mass cannot be readily identified. This "missing" mass is believed to be comprised of semivolatile materials such as water, ammonium nitrate and organics (Andrews et al., submitted for publication). Of particular concern are the semi-volatile organics, which are not efficiently captured by traditional filter techniques. Eatough et al. (1995) estimated that between 20 and 60% of the fine particle organic mass is lost when these techniques are employed. The proper quantification of these materials is particularly important in light of their potential health impacts.

Another issue of concern in the determination of fine particle chemical composition is the length of time over which the sample is taken. Filter samples are typically collected over a 24-hr period, which diminishes their usefulness for source apportionment due to the variation in transport winds that can occur over such an extended period. In addition, chemical compositions determined from such samples may not accurately reflect the makeup of coexisting aerosols.

Thus, being cognizant of these issues, systems have been selected that permit the determination of fine particle chemical composition with: 1) a time resolution compatible with air mass trajectory analysis, and 2) under conditions that allow the reliable quantification of the organic fraction of the aerosol mass. The sample sizes necessary for speciation of the organic fraction will require longer (6-12hr) sampling times.

Filter-based samplers
These will be deployed both at the ground sites and on the *in situ* sampling aircraft. The airborne particle samplers will operate with short sampling times (<30 min./sample) to produce useful spatial resolution for regional background, and plume studies. Long-term averages (24-hr) will be obtained at the surface sites through collaboration with the Southern Center for the Study of Secondary Air Pollutants (SCISSAP) program. These latter samplers will employ the Federal Reference Method (FRM) sampler and the filters will be used for both $PM_{2.5}$ mass determinations and chemical analysis. At the "super" chemistry site filter samples will be taken with greater frequency and accompanied by a gaseous ammonia measurement to examine the sulfate/nitrate/ammonia equilibrium dynamics.

Sampling of organic aerosols (including semi-volatiles)
The sampling and characterization of organic aerosols is particularly challenging. The organic material in the atmosphere is present in both the gaseous and aerosol phases. These two phases are coupled by a fragile equilibrium that can be easily disturbed during sampling. Atmospheric aerosols may contain thousands of organic compounds with a wide range of properties (polarity, solubility, vapor pressure etc.) making the chemical characterization equally difficult. Two separate systems, specifically designed to reduce positive and negative artifacts in the sampling of organic aerosols, will be deployed at the super chemistry site. Both systems employ a denuder/filter/denuder or sorbent bed array. The Particle Concentrator BYU Organic Sampling System PC BOSS system developed by Eatough and coworkers (Eatough et al., 1993; Pang et al., 1997) uses charcoal-impregnated surfaces to collect gas-phase organics both in front of and behind a quartz filter. The Integrated Organic Gas And Particle Sampler (IOGAPS) developed by Gundel and co-workers (Gundel and Lane, 1998; Lane and Gundel, 1996) uses a similar arrangement with the exception that XAD resin is used as a denuder material. One advantage of using XAD resin as the denuder material is that it provides the option of extraction and speciation of the absorbed organic material, which is not possible for the PC BOSS system. Samples will

be analyzed using both gas chromatography/mass spectrometric and liquid chromatography/mass spectrometric techniques.

Particle Analysis by Laser Mass Spectrometry (PALMS)

PALMS is a real-time in-situ technique for analyzing the chemical composition of individual atmospheric aerosol particles (Murphy et al., 1995; Murphy et al., 1998). PALMS has the unique feature of detecting a wide variety of elemental and chemical species in individual particles. The advantage of deploying PALMS at the "super" chemistry site is that it can be used to estimate the contribution of different particle classes (i.e. sulfate, nitrate, organic material, soot, sea salt, crustal material, and/or metals) to the overall population and the extent of internally-mixed particles. By placing a differential mobility analyzer or a PM $_{2.5}$ impactor in front of the PALMS inlet, compositional differences as a function of particle size can also be investigated. After completion of the field campaign, the individual particle spectra may be grouped according to sampling conditions such as time of day, meteorological conditions, and trace gas concentrations and compared with other particle composition measurements. Two limitations of this technique are that quantitative information of the components present and molecular speciation of organic compounds is not obtained. However, the techniques described above will be used to provide speciation of the organic fraction of the fine particulate mass. Thus, PALMS provides important complementary information to traditional bulk compositional analysis of atmospheric particles.

Aerosol Formation Rates

As stated above, particulate matter formed as a result of gas-to-particle conversion represent a significant fraction of the fine particle mass. Most notable, are the ammonium salts of sulfuric and nitric acid. These materials result from the oxidation of SO_2 and NO respectively and the subsequent reaction of the acids formed with gaseous ammonia. Understanding the factors that control the formation of these, and other secondary particles, is critical to the development of viable PM management programs.

The study of the chemical evolution of urban and power plant plumes as they are advected downwind provides an opportunity to measure the rate of aerosol formation in these environments. The varied emission strengths and mixes (NO_X, SO_2, and VOCs) that are represented by the Nashville Urban area and the various power plants in the region permit the study of aerosol formation in a variety of chemical and meteorological environments. The contribution of biogenic VOCs to aerosol formation can be evaluated by contrasting these rate measurements with similar measurements performed in less heavily vegetated areas such as the upper Midwest and the mountain west.

The conversion of gaseous SO_2 to aerosol sulfate in power plant plumes has been studied extensively (see for example review by Newman, 1981). Daytime conversion rates during the summer are typically 1-5% per hour and are consistent with a photochemical mechanism with oxidation by the hydroxyl radical. Model simulations have qualitatively reproduced the sulfate aerosol formation rates observed in power plant plumes (see for example Gillani, 1986). However, the model performance has not been adequately evaluated since these early measurements provided only limited NO_Y speciation and no credible VOC measurements.

The proposed sampling strategy calls for the use of instrumented aircraft equipped with fast time response aerosol probes capable of characterizing particle number and size distribution in these plumes. By selecting meteorological conditions with reasonably uniform flow and moderate (3-7 m/s) wind speeds it will be possible to construct cross-wind profiles of gaseous pollutants and aerosol parameters at several downwind distances (transport times). The change in aerosol volume with transport time provides a measure of aerosol production. The measurement of aerosol size distribution and number allows the study of dynamics of aerosol formation and growth. An example of the evolution of fine mode aerosol in the plume of the Cumberland power plant plume is provided in Figure 3.
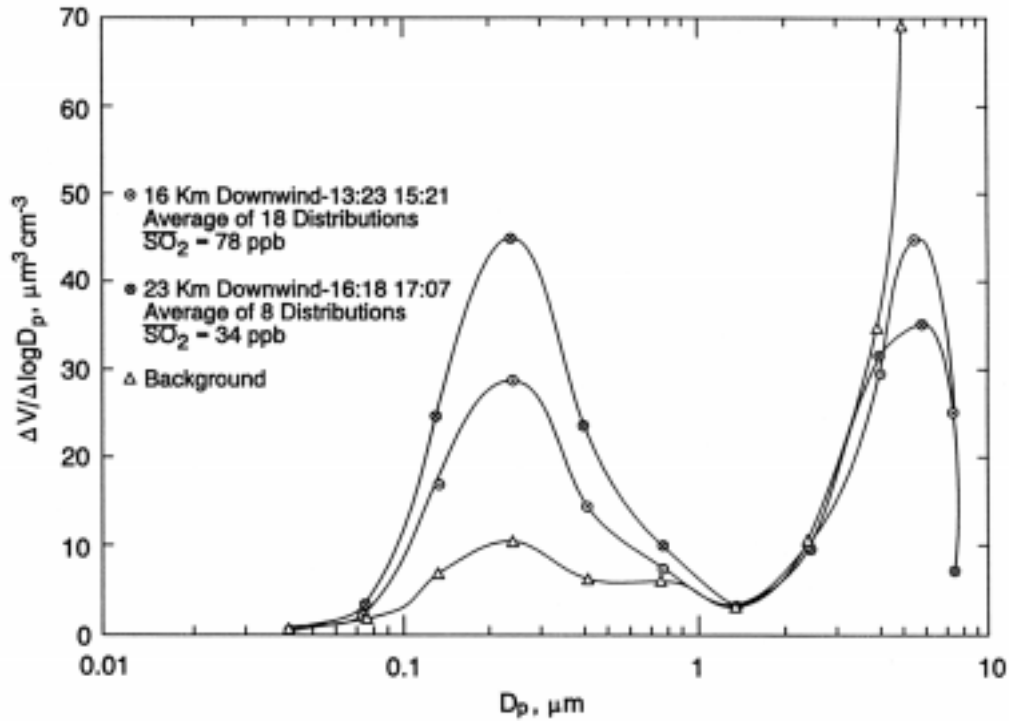
Figure 3. Volume-size distribution taken in the plume of the Cumberland power plant in Tennessee. Source McMurry et al., 1981.

Aerosol Measurement Networks in the Study Region

The measurements described above will benefit substantially from other aerosol measurement programs operating in the study region. Data collected as part of these ongoing programs will serve to extend the spatial and temporal coverage of the measurements planned for the field intensive providing valuable context for those measurements. Many of these efforts are being integrated through SCISSAP, which is managed through the SOS program. Each of the programs is described briefly below. A more detailed description is provided in the Appendices.

Southern Center for the Study of Secondary Air Pollutants (SCISSAP) – The center operates collaborative programs that seek to integrate information on the formation and distribution of fine particles and other secondary air pollutants with a focused model development and application effort.

Interagency Monitoring of Protected Visual Environments (IMPROVE) – There are three IMPROVE sites operating in the study region: Great Smoky Mountain National Park, TN, Mammoth Cave National Park, KY and Sipsey Wilderness Area, AL. At these sites visibility measurements (b_{scat} and visual range) are made on a continuous basis, and filter collections for fine and coarse particle chemical composition (24-hr) are performed every sixth day.

SEARCH – This network of aerosol and gaseous monitoring stations has been established as a series of rural/urban pairs throughout Mississippi, Alabama, and Georgia in a collaborative effort between the Southern Company and the Electric Power Research Institute. Several of these sites have an extensive array of state-of-the-art gaseous pollutant and aerosol measurements. The availability of high quality, fast response (<15 min,) measurements of aerosol parameters will be particularly useful in the interpretation of data collected during the intensive.
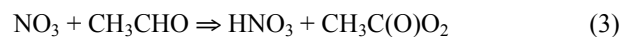
TVA, DOE, NPS Collaboration – This group will be operating a three site network in northeastern Tennessee. The program calls for the augmentation of two existing sites operated by the National Park Service on the border of the Great Smokey Mountain National Park and a suburban/rural site operated by TVA near Knoxville Tennessee.
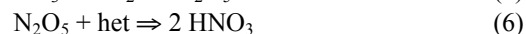
NIGHTTIME CHEMISTRY AND DYNAMICS

After sunset photochemistry, by definition, shuts off; however, it is well known that radical chemistry proceeds during the night provided sufficient O_3 is present (Finlayson-Pitts and Pitts, 1986, and references therein; Seinfeld, 1986, and references therein). Furthermore, because nighttime boundary layers are typically shallow with strong temperature inversions, deposition losses of chemical species to surfaces tends to be an important process in the relatively quiescent surface layer but of little consequence for the free tropospheric air aloft. A question posed here is whether significant chemical processing occurs at night, especially near urban areas where emission sources can be important throughout the night. Moreover, if such nocturnal chemical processing is significant, how might this affect the total export of urban emissions to larger spatial scales and over longer temporal scales. A second question is to what extent chemical processing occurs in the very high NO_x environment of power plant plumes and to what extent does plume transport/dispersion in the free tropospheric environment during the night affect the chemistry.

The reaction of O_3 and NO_2 produces the nitrate radical, NO_3, but it is only during the nighttime hours that this species can build to measureable levels due to the absence of a high photolytic loss rate (Platt et al., 1980). This highly reactive NO_3 species is capable of reacting with a number of VOC compounds and in so doing can promote many of the reactions that are observed during daylight conditions. For example, NO_3 can abstract H atoms from aldehyde compounds which then results in the production of peroxy-type radicals. Oxidation of NO to NO_2 can then occur. Another significant reaction of NO_3 is the addition reaction to alkenes which results in formation of nitrated peroxy species.
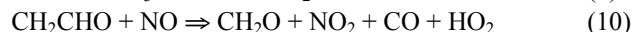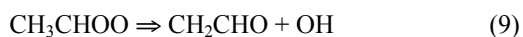
$$NO + O_3 \quad \Rightarrow \quad NO_2 + O_2 \qquad (1)$$
$$NO_2 + O_3 \quad \Rightarrow \quad NO_3 + O_2 \qquad (2)$$

$$NO_3 + CH_3CHO \Rightarrow HNO_3 + CH_3C(O)O_2 \qquad (3)$$
$$NO_3 + CH_3CHCH_2 \Rightarrow CH_3CH(O_2)CH_2ONO_2 \qquad (4)$$

In addition to VOCs, NO_3 can react with NO_2 to form N_2O_5 which can be scavenged by aerosols, as can NO_3 itself, to form HNO_3.

$$NO_3 + NO_2 \Leftrightarrow N_2O_5 \qquad (5)$$
$$N_2O_5 + het \Rightarrow 2\ HNO_3 \qquad (6)$$
$$NO_3 + het \Rightarrow HNO_3 \qquad (7)$$

The overall result of these latter reactions converts NO_x to NO_y but without the concomitant production of O_3 that occurs during the day. Estimates from 3-D model calculations (S. McKeen, personal communication) suggest that nighttime production of N_2O_5 could be responsible for as much as 30% of the diurnally averaged conversion of NO_x to NO_y. This process may represent a sizable sink of reactive nitrogen if aerosol uptake of N_2O_5 and subsequent deposition losses are significant in the quiescent nocturnal boundary layer. Further, if the size of this NO_x sink is as suggested, then the prediction of regional O_3 production based on estimated NO_x emission rates and O_3 production efficiency estimates will be greatly exaggerated, especially considering the concurrent homogeneous chemical loss of O_3 during the nighttime hours.

Another source of radicals during the night may be O_3 reactions with alkene compounds, especially those that contain internal double bonds. Both OH and HO_2 are expected to be formed from these reactions. A modeling study (Paulson and Orlando, 1996) has suggested that trace amounts of unsaturated VOC compounds can produce these HOx, as well as RO2, species in quantities comparable to O_3 photolysis or NO_3 reactions at certain times during the diurnal cycle, especially in urban areas.

$$CH_3CHCHCH_3 + O_3 \Rightarrow \quad CH_3CHO + CH_3CHOO \quad (8)$$

$$CH_3CHOO \Rightarrow CH_2CHO + OH \qquad (9)$$
$$CH_2CHO + NO \Rightarrow CH_2O + NO_2 + CO + HO_2 \qquad (10)$$

As noted above, these radicals undergo similar chemistry at night as would be expected during the day, but without O_3 formation. Thus with sufficient HO_x production at night, OH oxidation of NO_2 and formation of HNO_3 (with subsequent loss to surfaces or aerosols) may be significant.

Finally, it is reasonable to expect that PAN decomposition could be a source of free radical species at night, especially in urban environments. PAN is a thermally unstable species that undergoes unimolecular decomposition with a lifetime that is dependent on temperature (Roberts, 1990). This reaction is more specifically characterized as an equilibrium since re-association of the decomposition products, peroxyacetyl (PA) radical and NO_2, can occur. However, the re-association is strongly dependent on the NO_2-to-NO ratio since the reaction of PA radical and NO is fast. One of the products of this latter reaction is methylperoxy radical which can also oxidize NO (producing HO_2) or it can form peroxide species (e.g., CH_3OOH), as can the PA radical (e.g., $CH_3C(O)OOH$).

$$CH_3C(O)OONO_2 \Leftrightarrow CH_3C(O)O_2 + NO_2 \qquad (11)$$
$$CH_3C(O)O_2 + NO \Rightarrow NO_2 + CO_2 + CH_3O_2 \qquad (12)$$
$$CH_3O_2 + NO \Rightarrow NO_2 + CH_2O + HO_2 \qquad (13)$$
$$CH_3O_2 + HO_2 \Rightarrow CH_3OOH + O_2 \qquad (14)$$
$$CH_3C(O)O_2 + HO2 \Rightarrow CH_3C(O)OOH + O_2 \qquad (15)$$
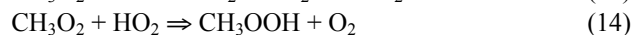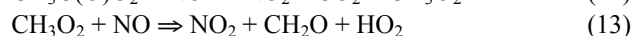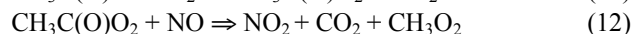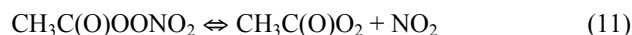
In an urban environment it is likely that NO_2-to-NO ratios will be low enough that irreversible PAN loss could occur which can be viewed as a radical source process, again with HNO_3 production as a result. This process could be enhanced by import of PAN from relatively cooler, NO-poor rural areas surrounding the urban environment.

Aerosol formation rates may be significant during the night, as well, due to production of radicals and subsequent reaction with species such as SO_2 or aromatic VOCs. Whether or not this is an important process with respect to primary particle emissions remains to be determined. An accurate assessment rests critically on the determination of radical production rates during the night. On the other hand,

it is also possible that significant scavenging of radicals by aerosols can happen. For example, it is known that peroxyacetyl radicals can be partitioned into fog droplets with reasonable efficiency (Villalta et al., 1996), and the same may be true for other peroxy radicals. If this is an important loss process for radicals, then the significance of nighttime chemical processing (except for NO_3 reactions) may be somewhat lessened. The consequence is that heterogeneous chemistry cannot be ignored, especially during the nighttime hours when the relative humidity can frequently approach 100%. This effect influences both the aerosol size distribution and composition.

The diurnal cycle of the growth and decay of the planetary boundary has profound effects on the chemical composition of the atmosphere near the surface. One of the most significant aspects of the cycle is the formation of a strong temperature inversion that results when the ground is no longer subject to solar heating near sundown. This temperature inversion effectively isolates the layer of atmosphere near the surface from that above, where the surface layer is on the order of 100 m thick. Moreover, since surface heating has ceased, convection and turbulent mixing in the vertical also are severely curtailed and the nocturnal surface layer becomes generally quiescent. However, the formation of nocturnal jets aloft is a common occurrence and, depending on conditions, mechanical mixing via wind shear generation may be strong enough to induce mixing in the surface layer or between the surface layer and the residual daytime boundary layer immediately above. The consequence of this is that emissions are reasonably constrained to the surface layer such that nighttime levels of pollutants such as NO_x and CO can be considerably greater than during the day. This, of course, has a profound impact on the chemistry that may occur. For example, with strong local sources of NO (e.g., in urban areas) O_3 can be titrated completely and nighttime chemistry would be suppressed. However, nocturnal jets can mix down air from the residual boundary layer aloft which can replenish O_3. Thus chemistry during the night is strongly dependent both on location (i.e., emission source strengths) and dynamics.

With respect to plumes from power plants, one

consequence of the formation of the nocturnal boundary layer is the plume dispersion that occurs with the onset of the inertial oscillation. This phenomenon is a result of the virtual elimination of surface drag effects on airflow aloft when the strong nighttime temperature inversion isolates the surface layer from the free troposphere. Because the winds accelerate and change direction, considerable shear can be introduced which results in plume dispersal during that period. Later in the night the effects of the inertial oscillation become negligible, and the plume is transported along the mean flow. The chemistry that occurs in the plume during these different periods may be quite different. With dispersion comes mixing with the ambient environment and whatever O_3-promoted chemistry that occurs in the absence of sunlight. Nitrate radical chemistry is not expected to be significant, especially near the stack, since titration of NO_3 with NO is very fast and NO levels can be quite high near the source. Downwind, the chemistry will be modified as NO is diluted and reacted with O_3. This regime may be similar to that expected for the urban situation. When the inertial oscillation has died away dispersion of the plume is likely to be lessened as the plume is transported along with the mean flow. Under these conditions chemistry at the plume perimeter will be influenced by the local environment (i.e., O_3) while inside the plume a wholly different chemical regime may be in place. For example, in the high NO_x plume interior, reactions that would not normally occur such as those that are second-order in NO_x may be expected to proceed.

$$NO + NO_2 + H_2O \Rightarrow 2HONO \qquad (16)$$
$$2NO_2 + H_2O \Rightarrow HNO_3 + HNO_2 \qquad (17)$$
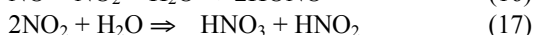
Thus, non-negligible NO_x to NO_y conversion may occur. Heterogeneous chemistry may also be important, especially on acid-containing aerosols. Plume chemistry will be examined by direct encounters with the aircraft as well as with the remote sensing instruments, especially the airborne O_3 and aerosol lidars.

There are two main areas of inquiry that we wish to explore during the 1999 Nashville field study with respect to nighttime chemistry. The first is an examination of the importance of nighttime conversion of NO_x to NO_y relative to that which occurs from photochemistry during the day. The second is an assessment of the occurrence of chemistry that produces free radicals during the night.

1. The first of these objectives will be assessed via modelling using the NOx, PAN, peroxides, NO_y, O_3, and other data collected at the ground stations as well as from the aircraft. There is a possibility of direct ground-based NO_3 measurements from a new instrument developed by NOAA/AL, but this instrument has not yet been field tested. Data from the airborne platforms may provide an interesting contrast to that from the ground stations since the effects of surface emissions are not likely to have an influence on the chemistry aloft except near power plant plumes. In an analysis of the evolution of chemical profiles in the nocturnal boundary layer, Galmarini (1997) found that very little of the NO emitted at the surface was transported above 10% of the boundary layer depth due to the reduced turbulent activity and to the fast chemical reaction with ozone. As a result, NO influences on the overall chemical processes were minimal. As noted earlier, the strong temperature gradients in the lower atmosphere at night will be of chemical significance since the concentrations of N_2O_5 and NO_3 are temperature-dependent. The ratio of N_2O_5 to NO_3 increases by a factor of 20 going from 20°C to 0°C (Dentener and Crutzen, 1993). With proper flight planning nighttime flights could provide information on NO_x to NO_y conversion in the atmosphere both within and above the NBL. Previous SOS research during the ROSE experiment (Ridley et al., 1998) indicated measurable conversion of NO_x within the NBL during the night. Important information on transition periods (morning and evening) could also be obtained with nighttime flights. For example, observations during the 1995 Southern Oxidants Study showed an order of magnitude increase in isoprene levels aloft with the onset of turbulent mixing shortly after sunrise (Berkowitz and Shaw, 1997). There are, however, some difficulties of making nighttime aircraft measurements. For example, very close coordination between aircraft and crew are required simply as a result of the fatigue factor

and the additional restrictions of flying at night. In many cases, restrictions on duty days for the pilots, among other reasons, make it impossible for the crew involved in the nighttime flight to participate in flights the next day. A possible solution would be to combine aircraft capabilities, where one of the aircraft makes a post-sunset sampling mission followed by another aircraft making a pre-sunrise mission. An additional, critical, requirement here would be close coordination on data comparability (i.e., aircraft instrument intercomparisons).

2. The second objective stated above will be directly tested by measurements of OH, HO_2, and RO_2 from instruments fielded by coworkers from TVA and Penn. State Univ. The LIF HO_x instrument has been field tested on aircraft and on the ground. The RO_2 instrument is an improved version of the well-known chemical amplifier technique. There will be an extensive suite of remote-sensing chemical and meteorological measurements to probe the evolution and structure of the boundary layer. These are described in detail elsewhere in this document. The combined sets of measurements, including aerosol data, with the addition of modeling support, will provide a high-quality data set with which to examine nighttime chemistry.

INSTRUMENTED AIRCRAFT

This section describes the workplace for the aircraft program of the 1999 SOS-Nashville Field Study. The aircraft program will build upon the results and experience of the 1995 study. Again the SOS Nashville Study will be a process-oriented study in which extensive coordinated airborne measurements will be made aboard five instrumented aircraft under a wide range of ambient conditions. Three of the aircraft will make *in situ* measurements mainly in the atmospheric boundary layer; two other aircraft will make remote-sensing measurements from above the boundary layer.

Four aircraft, having a wide range of capabilities, will participate. Three of these aircraft will be equipped with an array of instrumentation for study of O_3 chemistry. Two of those have sufficient range and endurance to survey larger areas. This gives also the opportunity to contrast the pollutant mix and meteorology in vicinity of Nashville to that of the Midwestern U.S. A helicopter can obtain detailed chemistry measurements over the urban area and in power plant plumes. The remaining two aircraft are equipped with instrumentation to remotely sense ozone and aerosols. The aircraft participating in the study are listed below along with the affiliations of the groups providing the aircraft and the instrumentation.

Participating Aircraft
In-situ:

- **Lockheed WP-3D Orion:** NOAA Aircraft Operations Center / NOAA Aeronomy Laboratory
  trace species for ozone photochemistry

- **Grumman G1:** DOE Pacific Northwest National Laboratory
  trace species for ozone photochemistry

- **Bell 205 Helicopter:** TVA Environmental Research Center
  trace species for ozone photochemistry

Remote Sensing:

- **CASA 212-200:** Private vendor /NOAA Environmental Technology Laboratory
  ozone and aerosol backscatter vertical profiles

The three aircraft making *in situ* measurements will be the Grumman G1 Gulfstream operated by the Department of Energy, the Lockheed WP-3D Orion operated by the NOAA Aeronomy Lab, and the TVA Bell 205 helicopter. The G1 and the WP-3D are relatively large, high-speed (~200 knots) aircraft with an endurance of more than 6 hrs. The helicopter is the smallest and slowest with typical sampling speed of 60 knots and endurance ~2 hrs. Its slow speed, however, makes it an ideal platform for detailed plume studies. Table 1 summarizes the principal aircraft specifications and capabilities.

Table 1: Aircraft specifications and capabilities

Platform	Endurance	Ceiling	Payload	Research Speed
WP-3D Orion	< 10 hrs	7.6 km	2700 kg	100-150 m/s
Grumman G1	6 hrs	3.5 km*	1300 kg	100 m/s
CASA 212-200	4.5 hrs	3.5 km*	< 2700 kg	65-100 m/s
Bell 205	2 hrs	2.5 km*	500 kg	40-50 m/s

* Aircraft operated with unpressurized cabin

NOAA AOC WP-3D Orion / NOAA Aeronomy Lab

Over the last few years the Aeronomy Lab has developed and integrated a set of in-situ instrumentation to study ozone photochemistry on airborne platforms. Measurements of particular interest include the quantification of ozone, its precursors, and the by-products of the photochemistry that lead to ozone formation. Those by-products can be used as indicators or diagnostic species to help interpret comparisons made between measurements and model simulations.

The most important by-products are the oxidation products of the precursors: the nitrogen oxides ($NO_x = NO + NO_2$) and the volatile organic compounds (VOCs). Tracer measurements help to determine the sources of the compounds and the transport processes that distribute them throughout the atmosphere. Of course the meteorological parameters that pertain to chemistry and transport, are recorded too. In extension of the gas phase measurement aerosol measurement will be added to investigate the interaction of aerosols and ozone pollution. The measurement package is described in Table 2.

Table 2 . Aircraft Instrument Package for the NOAA WP-3D Orion

Parameter	Time Resolution	Method	Det. Limit
Ozone (O3)	10 seconds	UV Absorption	1 ppbv
Fast O3 (FO3)	1 second	NO/O3 Chemiluminescence	0.2 ppbv
Fast CO (FCO)	1 second	VUV Resonance Fluorescence	25 ppbv
Sulfur Dioxide (SO2)	2 seconds	UV Pulsed Fluorescence	1 ppbv
Nitric Oxide (NO)	1 second	NO/O3 Chemiluminescence	30 pptv
Nitrogen Dioxide (NO2)	3 seconds	Photolysis NO/O3 Chem.	100 pptv
Total Nitrogen Ox.ides (NOy)	1 second	Au Converter. NO/O3 Chem.	50 pptv
In-situ VOCs	5 min./every 15 mins.	Cryo Collection, GC/FID	‹ 10 pptv
Canister VOCs	5 min. at selected times	Canister Sampling, GC/FID	‹ 10 pptv
PAN	30 sec / every 5 min	Dir. Injection., GC/ECD	‹ 5 pptv
PPN	30 sec / every 5 min	Dir. Injection., GC/ECD	‹ 5 pptv
MPAN	30 sec /every 5 mins	Dir. Injection., GC/ECD	‹ 5 pptv
CH2O	20 sec out of every minute	Tunable Diode Laser Absorption Spectrometry	30 pptv
Peroxides (incl. H2O2)	1 minutes	Dual Enzymatic / Fluorimeter	30 pptv
Aerosol size distribution	1 second	NMASS	µm
Aerosol size distribution	1 second	FCAS	µm
UV Radiation	1 second	300-400 nm, Zenith & Nadir	
UV Radiation	~ 10 second	Spectral radiometer, 295-480 nm, Zenith & Nadir	1 nm
Water Vapor (H2O)	1 second	Lyman Alpha Absorption	
Air Temperature	1 second	Platinum Thermistor	
Dewpoint/Frostpoint	≤ 3 seconds	Dew/Frostpoint Hygrometer	
Wind Speed	1 second	Derived from INE	
Wind Direction	1 second	Derived from INE	
Altitude	1 second	Barometric	
Position	1 second	GPS, INE	
Air Speed	1 second	Barometric	
Atmospheric Reflectivity		C Band Radar	

Objectives

The study on the NOAA Orion WP-3D focuses on addressing nine major themes:

1. Aircraft instrumentation development and validation;
2. Contrast the chemistry and distribution of O_3 and O_3 precursors, aerosol and aerosol precursors in regions having very different precursor mixes and meteorologies;
3. Apportionment of VOCs, CO, SO_2 , NH_3, and NO_x among the various anthropogenic sources;
4. Determining the importance of natural VOCs, CO and NO_x relative to man-made VOCs, CO and NO_x in photochemical ozone production;
5. Obtain more information concerning the relative importance of VOCs, SO_2 , NH_3, HNO_3 and wind blow dust in the formation of fine particles;
6. Determination of the ways that chemical processing on aerosols can influence ozone formation;
7. Investigation into the correlations between ozone formation and aerosol formation;
8. How does atmospheric chemistry influence the growth and/or the chemical composition of aerosols; and
9. Study the effects of dynamic factors (mixing and transport) on the observed concentrations.

DOE/PNNL Grumman G1

The Gulfstream-1 twin turboprop aircraft is capable of measurements to altitudes approaching 30,000 feet (7.5 km) over ranges up to 1500 nautical miles (2,800 km), and can be operated at speeds that enable both relatively slow sampling and rapid deployment to field sites throughout the world. The aircraft accommodates a variety of external probes for aerosol and turbulence measurements and internal sampling devices for a wide range of measurements. The G-1 has sufficient cabin volume, electrical power and payload capacities, and flight characteristics to accommodate a variety of instrument systems and experimental equipment configurations.

The primary sampling goals of the G-1 are:

1. to make measurements in the residual mixed layer for investigating nitrogen reactions on the surfaces of aerosols at night, and

2. to quantify chemical processes as a function of atmospheric mixing, with an emphasis on the breakup of the nocturnal boundary layer.
3. The G-1 will also be deployed in support of the broader objectives of the SOS '99 Field Campaign.

Table 3. Aircraft Instrument Package for the DOE G-1

Gas Phase Species

Species	Instrument/Technique	Range
NOy, NO	**Teco Model 42S/Chemiluminescence**	**0.3 to 200ppb**
NO2	**LMA-3; luminol chemiluminescence**	**15-15,000ppt**
HNO3 HONO	**API-365 MS/MS; mass spectrometer**	**100=100,000ppt (both)**
PAN	**Shimadzu (modified); GC-EDC**	**20-20,000ppt**
Hydrocarbons	**Canisters, GC/FID**	**0.1-100ppb**
Ozone	**Teco 49/UV-abs**	**25-500ppb**

The G1 standard meteorology package consists of the following instruments; obviously the radiation instruments will receive limited use during nighttime flights!

Meteorology

Temp., Press.	Rosemount Instrument	
Dewpoint	Cooled mirror	-75C to 50C
UV Radiation	Eppley, 295 to 385 nm	295-385 nm
Short-wave irradiance	Eppley PSP	285-2800 nm
Long-wave irradiance	Eppley PIR	4-50 microns
Vector Winds	Inertial navigation	
Turbulence	Gust probe, differential global positioning system	

Research Issues of Interest to PNNL:

A major uncertainty in understanding ozone chemistry is associated with the thermal and chemical structure of the nighttime atmosphere and the morning mixing process. Repeated *in situ* observations of both the chemistry and thermal/turbulent structure of the boundary layer will elucidate not only the effects of mixing and transport, but also the relation between thermally sensitive reactions and the resulting chemical composition of the PBL.

Also, as noted earlier, a key issue in nighttime chemistry is the conversion of NO_x to NO_y without the concomitant production of O_3. There are very few measurements of NO_y, NO_x, organic compounds or ozone aloft at night. NO_x/aerosol chemistry and the thermal structure of the nighttime PBL are two inter-linked aspects of nighttime chemical/dynamic processes to be investigated by the G-1 aircraft

within the broader focus areas of the SOS-99 Field Campaign.

Within this subset of research for the field campaign, PNNL hopes to work with other investigators in collecting several diurnal cycles of measurements within a slowly moving air mass. Such measurements would include chemical and meteorological characterization of the selected air mass during both the daytime and nighttime. Although the scientific pay-off will be high, it poses significant logistical problems including flight and scientific crew fatigue and restrictions on pilot duty hours. Success will come only by close cooperation between multiple aircraft teams having strong surface chemistry and meteorology support. It is anticipated that these criteria will be met during the SOS-99 Field Campaign.

Several sampling strategies for the G-1 are being considered within the broad objective of characterizing the chemistry and thermal structure of an air mass over several day/night cycles. We propose the following sampling strategy in the vicinity a ground-based air chemistry/profiler site:

- *In situ* measurements of NO_y (HNO_3, HONO, PAN, NO, NO_2), hydrocarbons, CO, ozone and aerosols (size and composition) over a limited domain by the G-1 at three altitudes,

- At the same time, and over the same location that the G-1 is making *in situ* measurements, we suggest

the CASA be used to characterize the aerosol and ozone loading in the PBL.

- Sampling by the WP-3D over a wider geographic area in the vicinity of the G1/CASA. And

- the Bell 205, with its lower minimum altitude, be used to complete the desired set of airborne measurements, also in close proximity to the G-1/CASA site.

TVA Bell Helicopter / TVA Environmental Research Center

The Bell 205 helicopter carries instruments for the in-situ measurement of photochemically active trace gases. The measurement package is described in Table 4. With its high maneuverability the helicopter is especially well suited to fly close to point sources and investigate plume evolution close in.

Their are two sets of science goals for TVA's instrumented Bell 205 helicopter campaign for 1999. First, the helicopter will conduct the second phase of the Cumberland Visible Emissions Study (CVES) whenever plume conditions are suitable, using up to 8 flight days conducting cross-plume traverses from a few km downwind to as far as 100 km ((7-10 hours of transport) with the principal objective being the acquisition of a particle formation data set from an isolated power plant plume that can be use to validate a dynamic plume chemistry and transport model.

Table 4. Instrument Package of the TVA Bell 205 Helicopter

PARAMETER	MANUFACTURER AND MODEL	RANGE
particle-sized sulfate, nitrate and ammonium ions	Andersen 1 ACFM Cascade Impactor	<0.43 (m; 0.43 - 0.65 (m; 0.65 - 1.1 (m; 1.1 - 2.1 (m
number of particles per optical particle size bin[*]	Particle Measuring Systems model PCASP particle size instrument	0.17 - 3.0 microns
light scattering of blue, green and red	3-wavelength Nephelometer, TSI Model 3550	$0.1 - 100 \times 10^{-4}$ m^{-1}
Sulfate, nitrate, H$^{(}$ and ammonium in particles; SO$_2$, HNO$_3$ on backup	Filter Sampler	1 - 100 (g/m3 (1-100 nmole/m3 for H$^{(}$)
NO$_y$ (NO + NO$_2$ + other odd nitrogen species) concentration	Thermo Electron Model 42S Nitrogen Oxides Analyzer	0 - 200 ppbv (plume & background)
NO$_y^*$ (NO + NO$_2$ + other odd nitrogen species less HNO$_3$+NO$_3^-$) conc'n.	Thermo Electron Model 42S Nitrogen Oxides Analyzer	0 - 200 ppbv (plume & background)
NO$_2$ concentration	Thermo Electron Model 42C Nitrogen Oxides Analyzer with upstream photolytic cell	0 - 5 ppmv (multiple ranging)
NO concentration	Thermo Electron Model 42C Nitrogen Oxides Analyzer.	0 - 5 ppmv (multiple ranging)
O$_3$ concentration	Thermo Electron Model 42 Nitrogen Oxides Analyzer modified for fast response O$_3$ measurement	0 - 200 ppbv
SO$_2$ concentration	Thermo Electron Model 43S Sulfur Dioxide Analyzer.	0 - 200 ppbv
CO$_2$ concentration	Licor NDIR CO$_2$ Analyzer	0-1000 ppmv
Latitude and Longitude		+/- 100 meters
Temperature		
Dewpoint		

The secondary objective of the CVES plume study will be to improve estimates of ozone production efficiency in power plant plumes and address enhanced NO$_Y$ loss rates exceeding those of SO$_2$. The flight plans, involving plume traverses at multiple altitudes in a semi-Lagrangian mode, are optimized to study the particle and ozone formation and growth and NO$_Y$ loss, foci of the study.

A second set of science goals pertain to obtaining airborne measurements of aerosol composition and related gaseous data above the sites of the SCISSAP Nashville urban-rural sampler pair. For exposure considerations, surface measurements are critical, but to understand the transport and potentially the transformation of fine particles and their precursors, the vertical distribution of particle composition must be probed. The TVA goals for the use of the

helicopter package are to characterize the near-surface boundary layer and urban plume chemistry under conditions of transport from an upwind background location through the downtown, high-emissions area to the downwind chemistry site, linking the precise locations to measurements of gaseous species at the proposed enhanced surface monitoring stations, and of particulate and related gaseous species being measured by the SCISSAP urban-rural pair samplers. Vertical structure will be probed using spirals to the top of the boundary layer before and after near-surface characterization.

CASA 212-200 Private Vendor / NOAA Environmental Technology Lab

The CASA 212-200 carries the NOAA-ETL LIDAR measurement package whose capabilities are described in Table . The downward looking LIDAR system measures the vertical distributions of ozone and aerosol backscatter below the flight path. Ozone concentrations are derived from the measurement of differential absorption signals. The aircraft usually flies at constant altitude (~3000 m above mean sea level (msl).

Design and specification of subcomponents (overlap of outgoing LIDAR beam and field-of-view of the optics; large though limited range of backscatter amplitude that can be recorded) limit the availability of useful data from approximately 800 -1000 m below the aircraft to 100 -200 m above ground level depending on terrain and cloud cover. Since the UV and visible radiation used for the LIDAR does not penetrate clouds there are no data below clouds. The aircraft will operate above the mixed layer and provides profile information to the surface with primary focus on mapping the Nashville urban plume and providing additional information on power plant plume structure and mapping regional ozone levels to provide a context for interpretation of the detailed chemical measurements made by the other aircraft.

Table 5: Aircraft Instrument Package for the NOAA CASA 212-200

| Parameter	Time/Space Resolution	Method	Det. Limit
Ozone (O_3)	3-8 secs / 200-520 m horizontal, 15 m vertical	differential absorption LIDAR	5 ppbv
Aerosol Backscatter	3-8 secs / 200-520 m horizontal, 15 m vertical	LIDAR	5×10^{-7} $m^{-1}sr^{-1}$

Flightplans

NOAA WP-3D

Example 1:

Urban plume study
An example of a flight plan aimed at investigating the chemical processing and evolution of the urban plume is shown in Figure 2. This is plan was followed in a flight of the WP-3D on July 2, 1994. The wind was reasonably constant in speed and direction during the course of the day. The flight track is shown as the green trace, the urban plume interceptions are indicated by the color coding. The flight plan allowed the plumes from Nashville to be investigated over a day within a fully developed planetary boundary layer. Flights such as of this will, also, be undertaken during the 1999 study.

July 2, 1994 – WP – 3D flight track
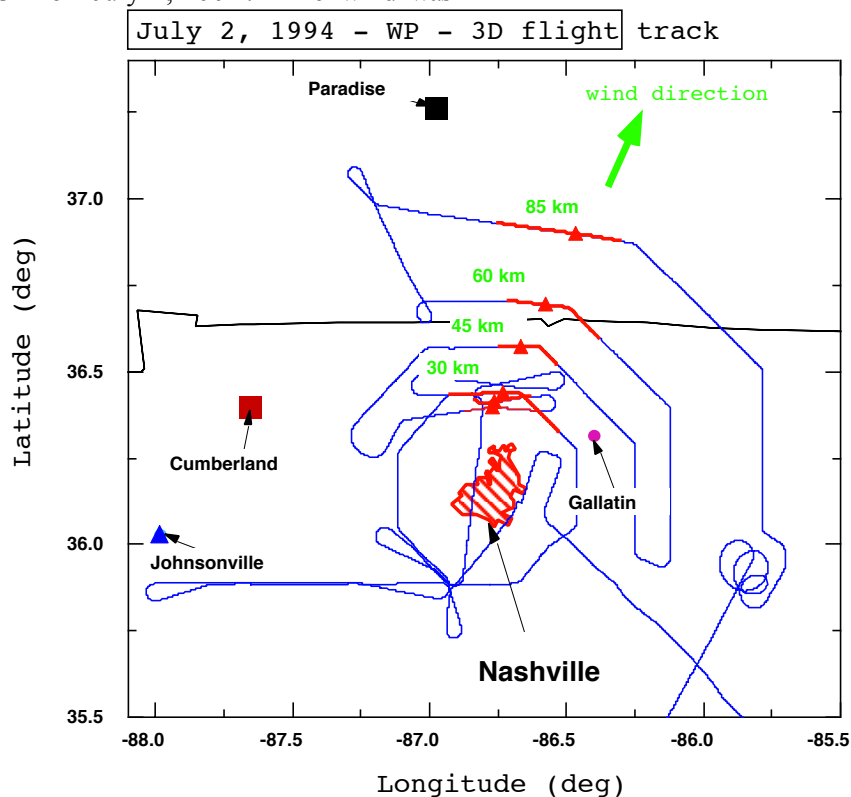
Example 2:

Metropolitan Complexes: the urban region
 Several urban complexes in the United States are now reaching cross-metropolitan dimensions of fifty kilometers or more. For example, in the Southeastern region Atlanta and Houston have grown to such dimensions. In our previous studies, we have concentrated on following urban plumes for transport times of about five hours or a distance of approximately 90 km at wind speeds of 5 m/s. For a city the size of Nashville, it takes one to two hours to cross the metropolitan under these circumstances. However, as the urban centers become larger and more dispersed, the urban area may become sufficiently large that locally emitted pollution undergoes substantial photochemical processing before it leaves the urban domain. This picture is very different from plume studies involving powerplants or smaller cities where we can assume quasi-point-source emissions followed by photochemistry and dilution as the air parcel travels downwind form the source. Hence, it would be very desirable to investigate an extensive urban complex where the sequential additions of pollution from the matrix of sources containing many different ozone and fine particle precursors would influence the rate and extent of ozone and fine particle formation.

An initial scoping flight to investigate the urban region is planned for the 1999 Study. An illustration of such a flight plan is indicated in Fig. 4 that shows a proposed flight over the Atlanta metropolitan area. The flight would follow a zipper pattern flown perpendicular to the prevailing wind in the planetary boundary layer covering the metropolitan area. According to the plan proposed here the flight involves the systematic crossing of the urban area at a constant altitude of approximately 500 m AGL. The crossing would proceed at approximately 0.1 degree intervals (11 km latitude, 9 km longitude). It would be highly desirable to cross the urban center one or two additional times at different altitudes following a similar pattern to establish the vertical distribution of trace gases over the city. In addition, an onboard lidar instrument would be useful to determine in-situ the height of the boundary layer and whether any layering occurs within the PBL.

Four different flight patterns can be prepared (N to S, W to E, NW to SE and SW to NE) and modified according to FAA restrictions for the given urban area prior to the study. For the given flight day one of these plans could be selected according to the prevailing wind direction. This flight plan is intended to sample the variations in the distribution of O_3 and the O_3-precursors as the flight unfolds. As was the case for the nighttime flights described in the preceding section, for safety reasons these extended urban flight plans must be carefully coordinated between the AOC and Air Traffic Control.

Outline of Atlanta Metropolitian Area
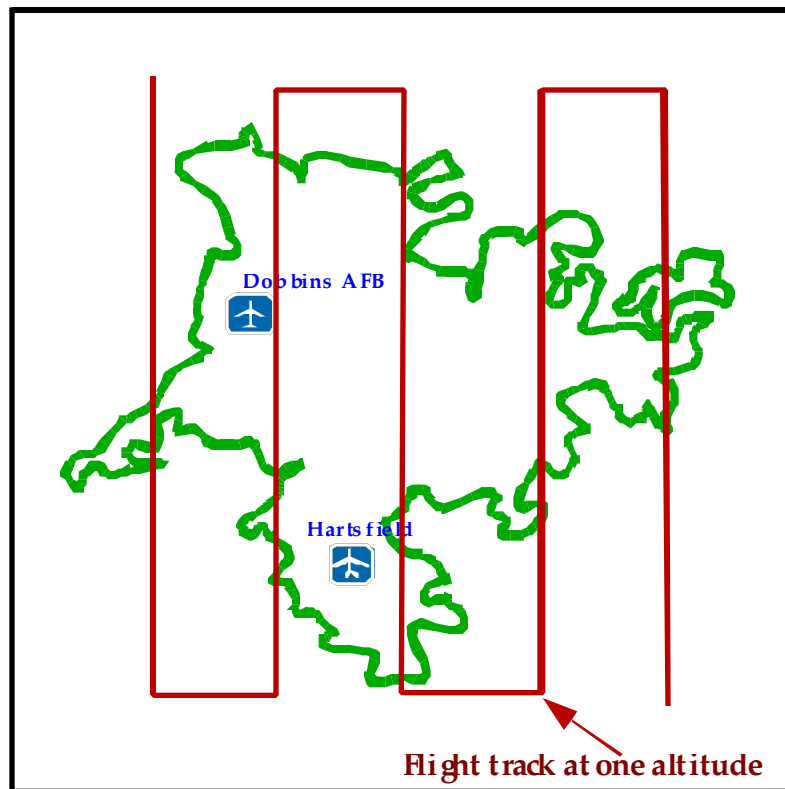
Example 3:

Powerplant plume study

An example of a typical flight plan aimed at investigating the chemical processing and evolution of powerplant plumes is shown in Figure 6. This plan was followed in a flight of the WP-3D on July 7, 1995. The wind was reasonably constant in speed and direction during the course of the day. The flight track is shown as the green trace and the plume-paths and the aircraft interceptions of the plumes of the four power plants is indicated by the color coding. The flight plan allowed the plumes from four powerplants to be resolved from each other and from the Nashville plume and to be investigated over a ten hour daytime period with a fully developed planetary boundary layer. The differences in the NO_x emissions from the four plants, ranging over approximately an order of magnitude, allowed the processes to be studied over an exceptionally wide range. Several flights such as this will be undertaken during the 1999 study.
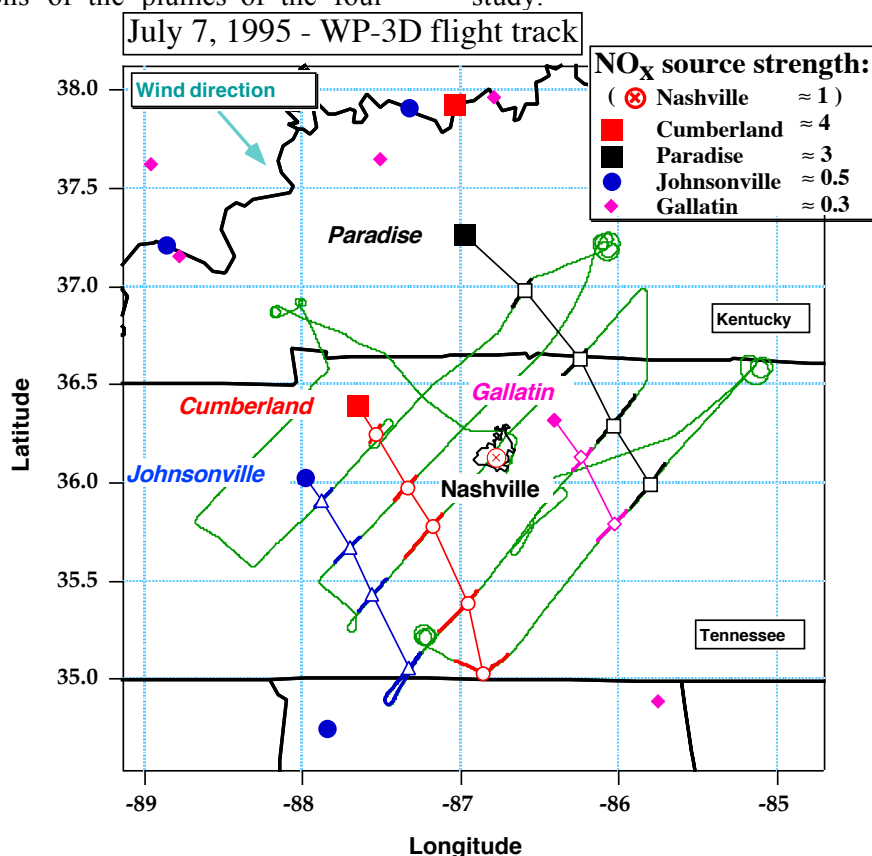

Figure 6: The flight track of the WP-3D on July 7, 1995 making measurements of power plant plumes in the Nashville region. The estimated relative NOx source strength of the various sources are listed in the box. The color code identifies the flight track of the WP-3D (green) and the various point sources in the region, the direction of their plumes and the plume-crossing by the WP-3D.

Example 4:

### Regional Contrasts: Regionality of pollution

A separate aspect of this study would be to determine the distribution of compounds observed during regional flights. Such a flight that was flown in the 1995 Nashville study is shown in Figure . During the flight, measurements were made of the

mixing ratios of NO_y, CO, VOCs. The measured mixing ratios in the boundary layer reflect the emission rates of these compounds from their sources.

The measurements of isoprene from the flight shown in Fig. 7, when compared to other anthropogenic hydrocarbons and CO, indicated that over heavily forested regions, isoprene oxidation dominated photochemical ozone formation. In the free troposphere, over the whole region and in the rural regions of the upper midwest CO and CH_4 are the most significant oxidizable O_3-precursors. These measurements will be made during the 1999 flights along with the addition of the size-resolved concentration of fine particles. This will allow the comparison of the measured concentrations of the two co-pollutants, ozone and fine particles, along with a suite of their gas-phase precursors.
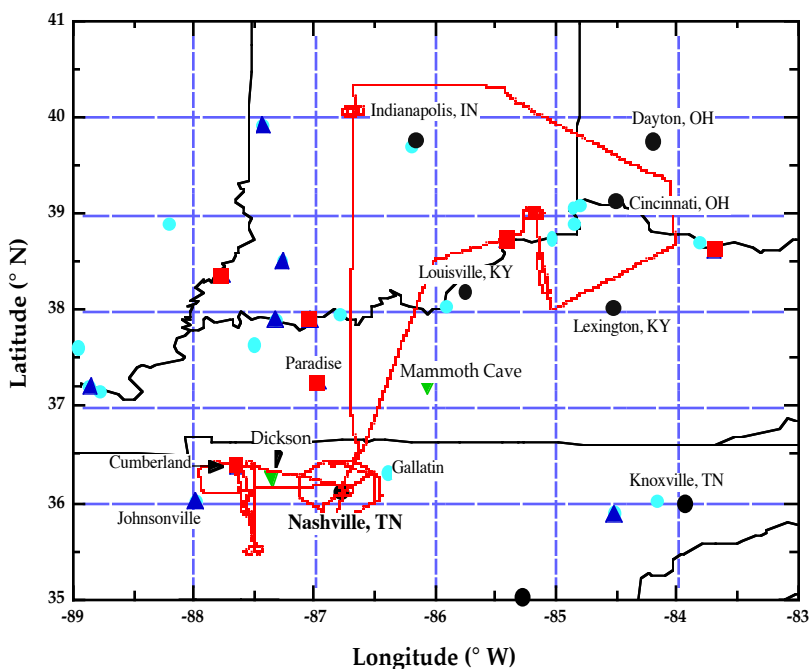

TVA Bell 205 Helicopter

CUF Visible Emissions Study
The flight plan for the CUF Visible Emissions Study are based on a total of up to 8 missions of approximately 4 hours total duration each (plus refueling stops) performed over the period of the SOS 1999 intensive, in June-July, 1999. It is anticipated that multiple cross-plume traverses will be conducted at a minimum of three downwind distances on most or all of the missions. Multiple passes at 2 or more altitudes serves two purposes. Relevant to the $PM_{2.5}$ issue, the use of multiple passes allows the accumulation of sufficient mass to permit accurate determination of chemical composition of total quartz filter samples from the high-volume sampler (and, if used, from size segregated samples from a cascade impactor) which require a minimum of 20 min sampling time (30 min if possible). It will also be of advantage to have particle size data from the PCASP active scattering probe for multiple passes to determine if size distributions across the plume remain roughly the same as a function of altitude. Concerning the ozone issue, the use of multiple passes may provide an opportunity to do "flux-across-a-plane" calculations, but will certainly permit an improved determination of the uncertainties in calculation of plume-excess ozone and nitrogen oxides as a function of downwind distance, a critical consideration in the estimation of NO_Y loss rates from the plume.

Helicopter Flight Plan
Cumberland Plume Characterization (Isolated)
Upwind Verticle Profile with Multiple Downwind Transects
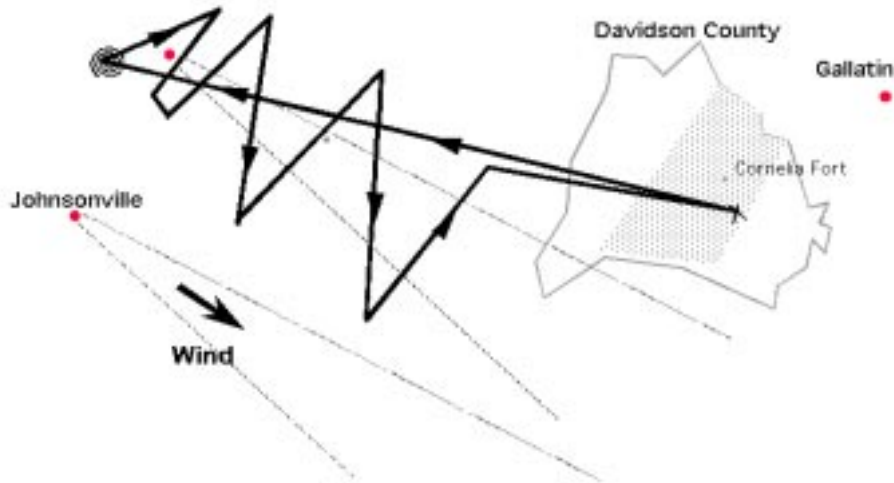
The selection of plume distances at which to sample will depend on the meteorological conditions, but will be made based on the following considerations. The close-in sampling will be done at a point at which the plume is still in Stage 1, that is, in which ozone formation at the wings is still insufficient to bring the ozone concentration above that of surrounding "background" air. This will likely be in the 5-15 km downwind range, and will serve as "initial conditions" traverses with respect to particle formation and growth within the plume. The second traverse distance will be chosen to be in late stage 2 or early stage 3 with respect to ozone formation, with estimated travel times since release of 3 to 5 hours. This should give sufficient time (for summertime conditions) for of the order of 10% of the SO_2 to be converted in plume to sulfate, and should be near the maximum concentration of "nitrate" as determined by the difference in the NO_Y and NO_Y^* signal. The third distance, sampling at which may not always be possible under more dispersive conditions, will be in full stage 3 plume conditions and at estimated travel times of the order of 7 to 10 hours.

Helicopter Flight Plan
Point Source/Urban Plume Interatction Characterization
Upwind Verticle Profile with Multiple Downwind Transects
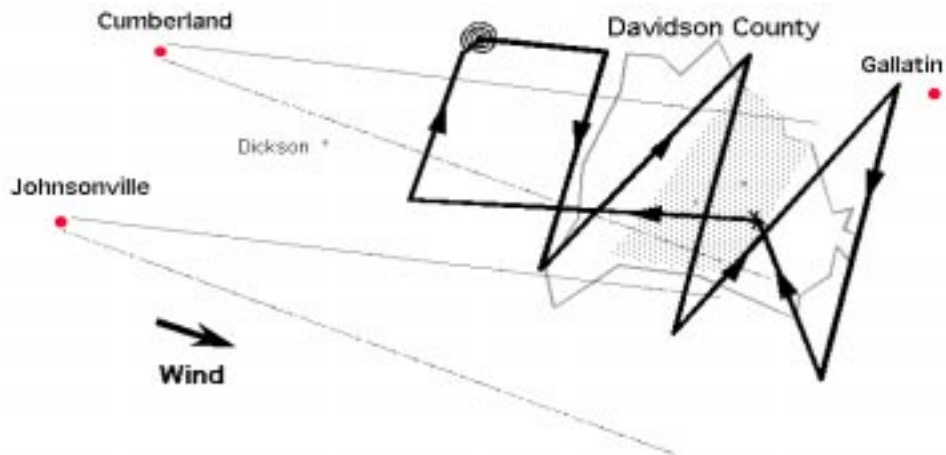
Meteorological conditions for flying include all those for which reasonable transport conditions can be determined. This excludes periods of thunderstorms or general rain, periods during frontal passage in which the air mass (hence plume) trajectories are expected to change significantly during the period of the mission. It also excludes periods of stagnation in which light and variable winds are expected, and days in which highly dispersive conditions in which we would not expect to be able to follow the plume for at least 5 hr. Cloudy conditions are not excluded a priori if good wind fields from the radar profiler are available.

Boundary Layer-Urban Plume Characterization
The second goal of the TVA helicopter sampling program is to obtain airborne measurements of aerosol composition and related gaseous data above the sites of the SCISSAP urban-rural sampler pair in and near Nashville. Flight plans for the helicopter package are designed to characterize the near-surface boundary layer and urban plume chemistry under conditions of transport from an upwind background location through the downtown, high-emissions area to the downwind chemistry site, linking the precise locations to measurements of gaseous species at the proposed Level 2 stations, and of particulate and related gaseous species being measured by the SCISSAP urban-rural pair samplers. Vertical structure will be probed using spirals to the top of the boundary layer before and after near-surface characterization. The attached figure

Helicopter Flight Plan
Upwind-Urban-Downwind Traverses with Urban Vertical Profile
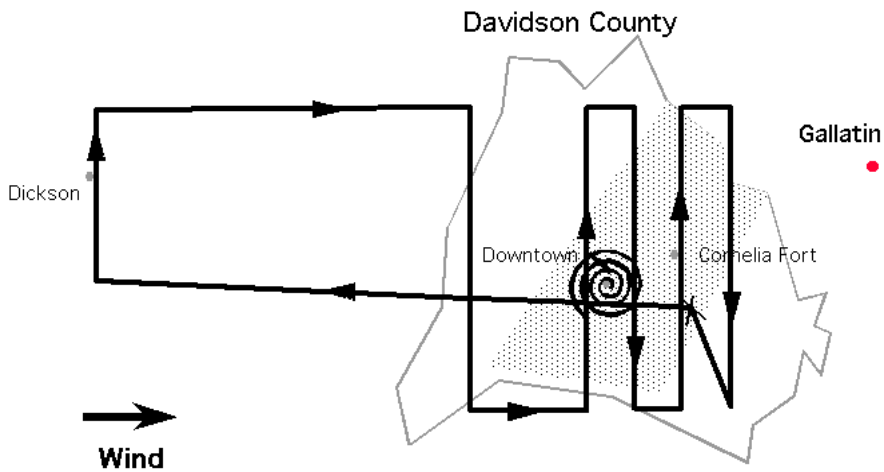
serves to illustrate the general flight plan for this characterization, typically a spiral near downtown at about the time of the mid-morning breakup up the surface layer, followed by an upwind transect in which the helicopter overflies the Dickson site, then cross-urban plume transects in the vicinity of downtown, followed by of the order of 2 or 3 transects downwind of the urban area, at least one of which would be in the vicinity of the proposed NOAA chemistry site. If time permits, a second spiral over the down town area would be conducted to complete the mission. The flight plan would be conducted only under conditions of predominantly west to east flow, and is designed to document the horizontal and vertical extent of the urban plume, the extent of excess particulate mass and ozone levels in the urban plume, and to provide intercalibration data with respect to surface air sampling at the surface monitoring sites.

CASA 212-200

1. Nashville urban plume

The airborne ozone lidar deployed on the CASA 212 will be used to define the Nashville urban plume based on ozone and aerosol characteristics. We will document the horizontal and vertical extent of the urban plume and characterize the 3-dimensional ozone and aerosol distribution associated with the plume. A box-type flight pattern covering the Nashville urban area (as shown below) seems to be best suited to achieve these objectives. By flying the box pattern repeatedly the spatial characteristics of the urban plume as well as its evolution with time can be monitored. Given the range of the CASA of about 1600 km and the size of the Nashville metro area (~30 km) the box pattern could be flown 3 to 4 times per flight. The data gathered with the airborne lidar during these flights can also be used to estimate the ozone budget in the urban plume (in conjunction with ground-based lidars, profiler network, and surface flux stations).

Flight pattern: Box pattern covering the Nashville urban area
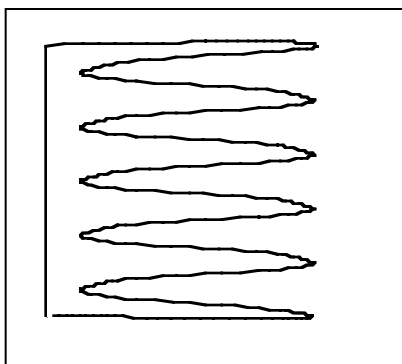
2. Power plant plumes

Data from the airborne ozone lidar will be used to identify power plant plumes, determine their size and shape, and estimate ozone production rates in the plumes. To study power plant plumes the CASA will fly zig-zag patterns downwind of the power plants. Data gathered during SOS95 showed that the airborne ozone lidar needs to sample power plant plumes out to greater downwind distances (> 50 km) in order to clearly document ozone enhancement in the plume. In addition, the coordination between the power plant plume missions flown by the CASA and the other aircraft will be improved during the Nashville 1999 campaign. One goal of the Nashville 1999 experiment is to investigate the fate of power plant plumes during nighttime. Due to its 3-dimensional ozone and aerosol mapping capabilities the airborne lidar will be very useful in locating power plant plumes at night and directing the other aircraft.

Flight pattern: Multiple plume crossings downwind of the power plant
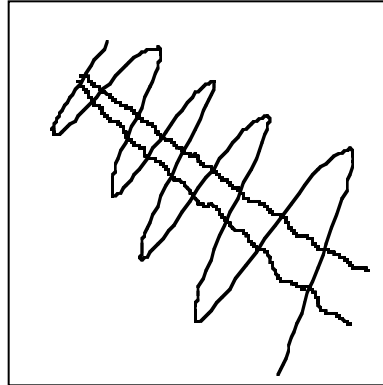
3. Mixed-layer depth, ozone-aerosol linkages

A third objective of the CASA lidar measurements is to document the depth of the mixed layer and its spatial variability in the greater Nashville / Middle Tennessee area. A typical flight pattern would be a butterfly pattern (see below) that encompasses the Nashville urban area and adjacent rural areas with different land use characteristics. Flying the same pattern repeatedly will add information on the temporal evolution of the mixed layer depth. In addition, we will use the airborne lidar measurements to investigate the relationship between mixed layer depth and ozone/aerosol concentrations and study possible linkages between ozone and aerosol distributions.

Flight pattern: Butterfly pattern covering Nashville and adjacent rural areas
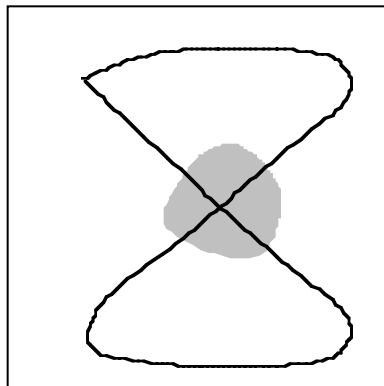
Aircraft Inflight Intercomparisons:

The use of four aircraft and the wide variety of the instrumentation flown on these platforms make a thorough intercomparison of the various instruments/measurements mandatory. This intercomparison is especially important since the aircraft resources will be used complementary manner. We envision staggered deployment of some platforms (either on the same day and/or by flying alternating platforms on consecutive days) in order to extend the time coverage of the measurements.

Objectives--A series of intercomparisons will verify the validity of the accumulated data sets and also assure the compatibility of the data collected on the various platforms.

The intercomparison is envisioned in several stages including a standards exchange, pre-intensive intercomparison and in-flight intercomparison exercises interspersed at several times during the 1999 Nashville intensive. A standard exchange will help insure that the different measurements are tied to comparable standards. A pre-intensive intercomparison will enable a correction of any detected problems prior to the science flights. The repeated in-flight intercomparisons throughout the campaign will give the maximum possible confidence that the data sets are comparable throughout a wide range of various environmental conditions and that any possible problems are identified and resolved as soon as possible.

In addition to the measurements from the airborne platforms ground based measurements will be made over a large region and a combined data set will be used for modeling studies. Therefore, the data sets from the two domains need to be tied together through overflights of the ground stations.

Aircraft Resources--The in-flight intercomparisons will involve at least two platforms at a time but no more than three during a certain flight interval. More platforms would seem inappropriate because of the logistical difficulties and the concern for air safety. The goal is to integrate the intercomparisons within flight plans towards other science objectives to maximize the benefits from each flight. Obvious pairings of the aircraft are derived from the suite of common instruments and or the operating characteristics of the aircraft and their instrumentation.

DOE G1, NOAA WP-3B, TVA Bell 205: common suite of in situ instruments.

NOAA CASA 212 and DOE G1 or NOAA P3: comparison of in-situ measurements with remote sensing results.

Overview of Flight Scenarios--DOE G1 and NOAA P3 will fly side by side at four different altitudes on north/south tracks over rural Tennessee west of Nashville (overflight by NOAA CASA 212 possible). The altitudes legs will each be about 90 km long (15 min. flighttime) and spaced between 1000 and 3000 ft apart depending on meteorological conditions.

In an intercomparison of either the G1 or P3 with a smaller and slower aircraft (TVA helicopter) the larger aircraft will fly the above described pattern while the smaller platforms will fly an equivalent pattern with horizontal offset but its north/south flight tracks co-located to the center of the flight tracks of the large aircraft.

A main concern is that the various platforms are operated at their standard parameters to be able to compare representative measurements.

Each aircraft should be involved in three in-flight intercomparisons throughout the study.

Meteorological Conditions—
In-flight intercomparisons will be conducted under conditions suitable to the experiment to be conducted. Conditions to be avoided include low clouds, precipitation and low visibility. Well mixed conditions will produce the most uniform concentration fields and, therefore, are the most desirable.

Critical Support Needs--Good communications between the aircraft are essential. Furthermore, rapid turnaround of data in the field ($\leq$ 24 hrs..) will be needed to detect any problems in a timely manner.

In addition to the in-flight intercomparisons, Standards will be exchanged among the in-situ aircraft to allow comparability among calibration standards. NIST traceable gas standards for NO, CO, and SO2 will be exchanged.

Data Management and Analysis--Data collected during the in-flight intercomparisons will be exchanged and reviewed as soon as possible after the intercomparison flights so any problems/issues can be resolved. A more comprehensive analysis will be presented at a data analysis workshop to be held approximately 6 to 8 months after the measurement program is complete.

Meteorological Forecasting 1999 Nashville Field Campaign

The meteorological forecasting for the 1999 Nashville Program will build upon the 1995 experience. The following describes the forecasting plans and schedules including a description of the special and routine products to be utilized.

The Meteorological Forecasting Plan has several major goals.

1. Provide two to five-day forecast outlooks to carry out advanced planning for the aircraft operations and other special observational deployments. This will be included as a part of the daily weather briefings.

2. Provide immediate daily forecasts for times encompassing actual flight operations or other deployments. This would validate, negate or refine previously defined operational plans and would be the focus of the morning briefings.

3. Provide current meteorological information to help interpret on-going experiments and preliminary results.

4. Develop a real-time archive of meteorological data and operational products that will be a part of the post-analysis process.

Development of Forecasts

Meteorologists and other interested scientists will discuss weather products and forecast products to come to a consensus on the forecast presentation. This will be accomplished during the prior day with a relatively intensive data gathering and discussion in the early morning (6:00 am to 7:30am)

Weather Forecast Briefings

Forecast briefings will be held every operational day during the Nashville 1999 Intensive. A formal morning briefing (nominally at 7:30am) will be held in which weather forecast products and their air pollution implications will be discussed. Attendees at this meeting would include scientific mentors, aircraft operations and other scientists. The briefing would characterize the immediate weather expected for that day and the forecast for the next day. In addition a longer-range outlook for the next five to seven days would be provided so as to put current and future weather into perspective. This meeting would also serve as a springboard for a discussion on flight plans and experiment selection.

A more informal weather discussion would be held in the late afternoon to examine that day's weather and to make some judgement in whether that morning's forecast for the next day is holding up. At this point some relatively hard decision would be upheld concerning the next day's activities.

Special Weather Products

In addition to the standard weather products listed below several special products will be used in the forecast preparation and briefings. These are:

1. High Resolution Mesoscale Model Products. UAH , TVA and NASA are carrying out real-time forecasts for the Tennessee Valley Region at relatively high resolution. These models are the Regional Spectral Model (20 km) and MM5 (35) models. These will be used to supplement the standard ETA and other NCEP models.

2. Long-range trajectory models. As in Nashville 95 we will employ the trajectory models developed by ARL. These will be used to look at air mass origin in both forward and back trajectory modes.

3. Profiler Driven Lagrangian Plume Models. Using the profiler network winds will be assimilated into a one –dimensional boundary layer model to drive a Lagrangian plume model. These representations in 1995 were very useful in defining where power plant plumes and urban plumes might be located on flight days. Post analysis of these trajectories indicate they were accurate so more credence and use of this tool will take place in Nashville 1999.

4. Lagrangian Particle Model Prediction. The same plume model employed above will also be employed by using wind and turbulence data from the MM5 model forecast to also give possible plume trajectories.

5. Statistical Models. Regression type models will be employed using forecast meteorological data to test ozone forecast capability. These will be used as information in the daily briefings.

Standard Weather Products

Meteorological data for research activities is available via the internet, free of charge, through UCAR/UNIDATA. These data include the NOAA Family of Services data sets which include hourly surface observations, rawinsonde data (available either twice or four times daily) and the output from various NCEP numerical models. These models include the ETA, NGM, and NGM-MOS outputs. Other data, such as lightning and radar data

may be received through UNIDATA if fees are provided to the data originator. Other data such as that from profilers and aircraft reports organic to the field experiment will also be available. Additionally, other data are available on the internet from a variety of sources. (Note: The UNIDATA feed is subject to the limitations of internet reliability, and no guarantees are implied. However, this network is fairly robust, with a wide variety of possible data pathways, and its reliability has generally compared favorably with other sources)

Using UNIDATA provided software a variety of products can be prepared for use in daily mission planning. These include surface and upper air analyses and prognostic charts, analyses and forecasts of vertical profiles and various stability indices, Time cross sections of observations and/or forecast data. Upon coordination between the requestors and project meteorologists, products can be delivered in either text or image format either on electronic or paper media.

Coordination to determine which products will be routinely produced for the campaign will be determined by project scientists and the forecast team. For general information: Upper air sounding data are routinely available by 07:00 AM and 07:00 PM CST daily. NCEP model output data are generally available by 11:00 AM and 11:00 PM CST daily.

GROUND-BASED MEASUREMENTS

Chemistry Measurements

There are a number of O_3 monitoring stations already in place in the Middle Tennessee region (and beyond) which are operated within certain regulatory and research networks. These networks (SLAMS, NAMS, NDDN, CASTNet, IMPROVE, SEARCH, and SCISSAP) are described in detail elsewhere in this document. Depending on the network with which they are associated, the more than 100 ground stations are capable of monitoring long-term one or two (e.g., at least O_3) air quality parameters to a majority of trace gas and aerosol measurements.

In addition to these monitoring networks that are already in place in the Middle Tennessee study region, three additional sites will be selected for the 1999 field intensive study period that will have more extensive measurement capabilities. In keeping with previous nomenclature, these sites will be designated as either Level II (two locations) or Level III (or "Super Chemistry"; one location). The two Level II sites will be instrumented and maintained by personnel from TVA. These sites will measure NO, NO_2 (via photolysis/NO-O_3 chemiluminescence), NO_y (via conversion to NO on molybdenum), O_3, CO, SO_2, standard meteorological variables, and $PM_{2.5}$ aerosol data via TEOM. There will also be a measurement of peroxy radicals via the chemical amplifier technique at one of the Level II sites. The Level III site will have an expanded measurement capability over the Level II sites. In addition to NO, NO_2, NOy, O_3, CO, SO_2, and meteorological measurements, the Level III location will (depending on availability of funds and the time/resource constraints of the PIs associated with the measurements) provide data on the following chemical and aerosol parameters:

1. HNO_3, aerosol nitrate, aerosol sulfate, aerosol ammonium (and possibly other cationic aerosol species) via Teflon/Nylon filter pair sampling and analysis by ion chromatography (conducted by Aeronomy Laboratory personnel)
2. photolysis rates (principally jO_3, jNO_2, and jCH_2O, but others as well) by means of a spectral radiometer provided and operated by personnel from NCAR
3. concentrations of OH and HO_2 by a laser-induced fluorescence instrument provided and operated by personnel from the Pennsylvania State University
4. peroxyacetic nitric anhydride, or PAN, and analogs of PAN measured via a gas chromatograph (GC) provide and operated by personnel from Western Michigan University
5. VOC measurements via GC provided and operated by personnel from Ohio University, EPA will provide additional VOC analyses
6. isoprene (and its oxidation products) measured with a GC-mass spectrometer provided and operated by personnel from Purdue Univ.
7. 3-dimensional profiles of O_3 in the boundary layer measured by an O_3 lidar system provided and operated by personnel from NOAA/ETL
8. aerosol data measured by personnel from EPA will include the following:
   - particle size distribution (0.02-30 um, mobility analyzer)
   - visible range (nepheleometer, aethaleometer)
   - sulfate and liquid water content
   - fine - coarse size fractionation /collection (Moudi impactor)
   - organic/elemental carbon content (filters; 6 hour sample)
   - fine particle (<2.5 um) organics
   - 24 hour samples for scanning electron microscope analysis
9. 3-dimensional aerosol profiles in the boundary layer measured by an aerosol lidar provided and operated by personnel from NOAA/ETL
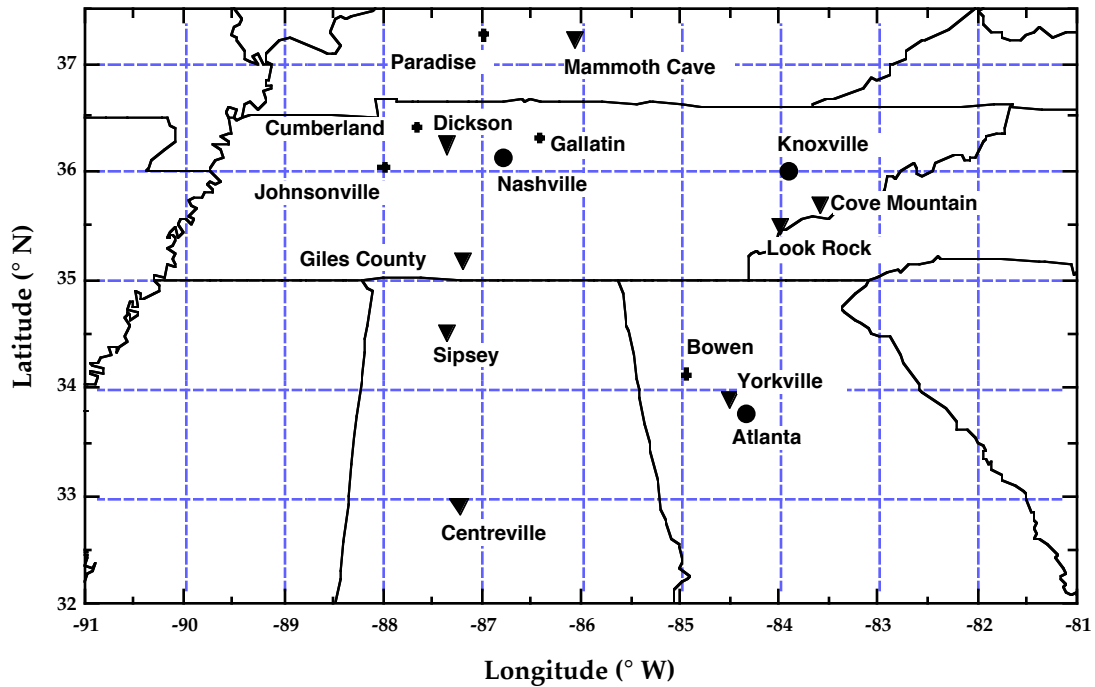
Figure 4. Regional map of study area with selected cities (filled circles), power plants (crosses) and regional measurement sites (triangles) indicated.
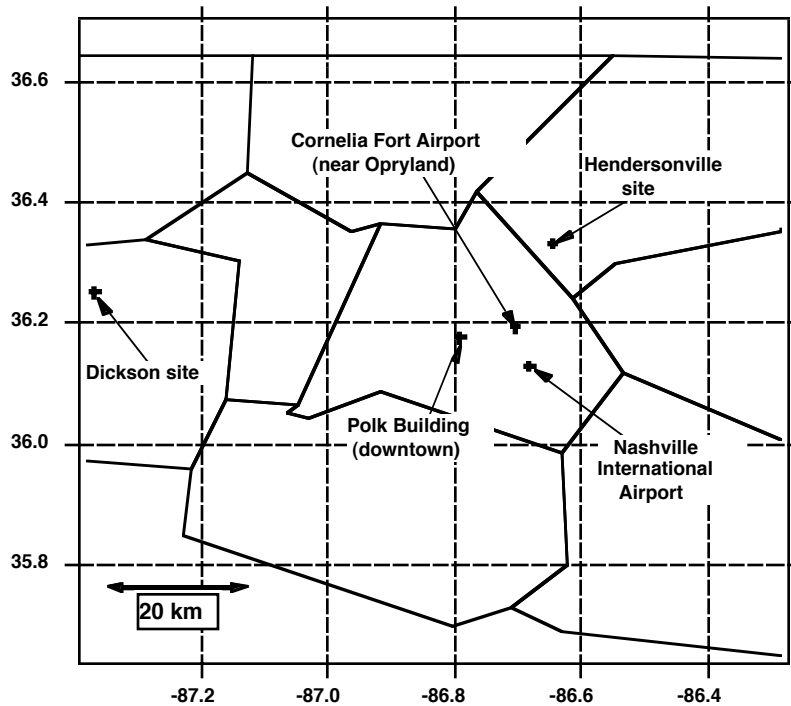

Figure 5. Outline map of counties around Nashville. Potential sampling sites for Level II/LevelII measurements are indicated.

The locations of the sites are tentatively the following (Figures 4 and 5 above):

1. One Level II site will be the top of the Polk office building in downtown Nashville. This building is 14 stories tall, but the sampling point will be on a tower 10 meters above the roof. This site will provide data on the levels of emission precursors at the center of the urban area.

2. One Level II site will be located approximately midway between the urban Nashville area and the two large power plants (Johnsonville and Cumberland) to the west of Nashville. The site is located ~18 km north of the city of Dickson, TN, near the top of a ridgeline in partly forested/partly agricultural terrain. There are no nearby sources (towns, highways, etc.) of anthropogenic pollution; however, the site occasionally comes under the influence of the Johnsonville power plant plume (60 km to the SW) and the Cumberland power plant plume (30 km to the NW). It is unlikely, though not impossible, that the site will be influenced by the urban plume from Nashville (53 km to the east) due to the westerly/southwesterly prevailing winds in the summer. This site was chosen because 1) it is suitable as a measuring point for air masses that are advected into the Nashville urban area (i.e, upwind site) and 2) the influence of the power plant plumes results in wide dynamic range of the important oxidant-producing species NOx. This in turn provides a more robust data set for modelling studies of photochemical oxidat production.

3. The Level III site will be located in the prevailing downwind direction from the Nashville urban center in order to capture as much as possible the conditions that allow examination of photochemical oxidant production at high levels of precursor species, principally NO_x at levels between 5 and 20 ppbv. However, the exact location of this site is a difficult issue to resolve since one of the most important emission sources in the Nashville region is mobile sources and the highways that are principal traffic routes are virtually everywhere in the area. On the one hand, the sampling location cannot be so far away from these highways that dilution and photochemistry reduce the NOx burden in the observed air masses to unacceptably low levels. But, on the other hand, the site cannot be located such that the only air masses sampled are those containing fresh emissions where little photochemistry has occurred. Thus, a site must be selected that will be close enough to the sources without being constantly overwhelmed by them. The tentative site chosen is at the Cornelia Fort airport which is 8-9 km to the northeast of the Polk office building site. The nearest major roads from the prevailing wind direction (SW) are 4-6 km away, which represents 1-2 hours of photochemical processing (and mixing) time. However, easterly wind will bring air from a major thoroughfare (SH 155) that is only 1 km distant. The airport is privately owned, serves mostly small private aircraft, and encompasses a large area adjacent to the Cumberland River. The area is mostly open and flat with some small stands of forest interspersed. There is more than sufficient room to accommodate all of the potential gas-sampling instruments as well as all of the remote sampling RADAR and LIDAR instruments. The open nature of the site also is a plus with respect to the siting requirements of the LIDAR instruments which require adequate sight lines down to low angles off the horizon for all directions of the compass. The other normal requirements of access, security, power availability, etc. also appear to represent no major difficulties.

Meteorological Measurements

Profiler network

The profiler network will consist of at least four profilers: AL (Angevine) will deploy one at a close-in site (preferably Cornelia Fort airport) for at least several months before, during, and after the campaign. ETL will deploy three in a roughly equilateral triangle surrounding Nashville. One of the ETL profilers will be at

Dixon. Several of these sites will also have laser ceilometers.

The profiler network will address all of the PBL dynamics objectives. The profilers will operate at 60 m resolution in space and approximately 30 s resolution in time. Vertical beam measurements will be emphasized, with a vertical beam every third measurement (every 90 s). RASS will be run for 5 minutes every half hour. The profilers will operate in the same mode at all times around the clock, unless some sites require that RASS not be run at night.

Surface flux

At least three surface flux measurement systems will be deployed. One site will be on each of the significant land use types (forest, agriculture, grassland). The sites will be the best available for surface flux measurements independent of other considerations. The full surface energy balance will be measured at each site. It would be desirable to have these sites running for some time before and after the intensive campaign.

The surface flux network will address the objectives of daytime PBL characterization, detrainment & venting / evening transition, and modelling database. The primary data product will be hour-average surface energy balance terms for each site. The goal is a continuous data set at least during the day; all routine maintenance will be done at night.

Doppler lidar

The mini-MOPA scanning Doppler lidar will be deployed at a close-in site (preferably Cornelia Fort airport). A variety of scanning strategies may be employed for different objectives and different times of day. The Doppler lidar will address all of the PBL dynamics objectives. It is the key instrument for the nighttime horizontal transport objective. Some specific strategies are as follows:
- Wind - profiles, vertical structure/shear, horizontal variability (mesoscale flows), nighttime layering
- Turbulence - effectiveness of vertical transports, dilution/entrainment, transports to surface (control on DD)

- Flow structures - gravity waves, low-level jets, drainage winds
- Aerosol profiles - time dependence of profiles, layers, well-mixed?
- Water-vapor profiles -- promising

Characteristics of the system are: wavelength 10.59 m (adjustable from 9 to 11.5 m), measures radial wind velocity at 75-90-m spatial and 1-s temporal resolutions, and velocity accuracy of $\sim$ 30 cm s^{-1}. Full scanning capabilities in azimuth and elevation. VAD scans yield vertical profiles of horizontal wind, TKE, and momentum flux in the layer between $\sim$100 m and 2-4 km AGL.

Ground-based ozone lidar

The ground-based ozone lidar will provide continuous profiling of ozone and aerosol from near the surface to the lower free troposphere (about 3 km AGL). The ozone lidar can be scanned within a vertical plane, thus providing a detailed picture of the spatial distribution of ozone in the scan direction. Shallow-angle scans will be particularly useful to study the evolution of ozone concentrations in the nocturnal stable boundary layer. Typical resolutions of the ground-based ozone lidar during routine operation are 90 m in range and a few minutes in time. For process studies the ozone lidar data can be processed at higher time resolution. The lidar will be collocated with the Mini-MOPA Doppler lidar and the AL wind profiler (preferably at Cornelia Fort airport). Combination with Mini-MOPA will permit direct measurement of ozone fluxes in the PBL.

Airborne measurements

Instruments on the airborne platforms are primarily targeted at chemistry measurements. Flight patterns, etc. are defined above. Nonetheless, some vital PBL dynamics information will come from the airborne instruments. The most important piece is the mixing depth measurements from the airborne ozone DIAL system, which will add to our understanding of the horizontal distribution of mixing height. Aircraft equipped with gust probes (e.g., the G-1) will be able to provide valuable turbulence measurements (e.g., TKE) below the airborne O_3 DIAL to relate to the

variations in mixing height. The airborne in-situ chemical measurements may help to define the vertical profile of pollutants above the morning PBL, useful for entrainment and vertical transport studies, and may observe detrainment and venting if the right opportunities present themselves.

TRACER RELEASE

Another significant addition to the 1999 SOS field intensive will be the intentional release of a tracer species from two power plant stacks. The reasoning behind these releases is discussed in the Ozone Production section of this document; the logistics are discussed here.

As discussed above, HFC 152a (1,1,-difluoroethane) has been selected for this application and is currently under safety review by TVA. HFC 152a is a flammable liquefied gas. It has a boiling point of -25 ^{o}C. When a cylinder of this material is opened and the gas is released to the atmosphere, evaporation occurs, and the temperature of the system drops. This can significantly lower the vapor pressure in the tank and can result in changes in the release rate. The tank must be heated to maintain a constant vapor pressure during the release. The cooling also affects the performance of pressure regulators, flow regulators, and flow metering devices. It is difficult to release large quantities of a liquefied gas at a controlled rate using only vapor pressure as the driving force of the release. These difficulties will be avoided by releasing the tracer as a liquid.

The tracer release will be accomplished by driving the 152a in liquid state from the storage tank with compressed air. The tank is equipped with two external fittings attached to tubes that extend into the interior of the tank. The first ends at the top of the tank and is used to introduce compressed air into the tank. The second fitting ends near the bottom of the tank and is the exit for liquid 152a. The liquid flow rate will be measured with a turbine meter and regulated with a metering valve that is manually adjusted based on flow meter reading. After the metering valve, the liquid 152a is at atmospheric pressure will begin to vaporize. A flexible stainless steel line with a one-inch inside diameter will be used to transport the tracer to a nozzle mounted in power plant stack. The storage tank will be mounted on load cells that will continuously measure the weight of the tank as a check on the turbine meter. Data from the flow meter and load cells will be collected by the CR-10 data logger and recorded and displayed on a laptop computer. The data collection rate is 4 Hz.

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APPENDIX A
SOUTHERN CENTER FOR THE INTEGRATED STUDY OF SECONDARY AIR POLLUTANTS - SCISSAP

1.1 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 _m ($PM_{2.5}$) 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.

At the end of the 3-year period it is expected that SCISSAP will have:

1. Added significantly to the existing data base on $PM_{2.5}$ and their relationship to photochemical oxidant chemistry in the southern United States;

2. Better defined the sources and precursors of $PM_{2.5}$ and O_3 in contrasting urban and rural locales in the southern United States;

3. Improved understanding of the mechanisms that couple O_3 and $PM_{2.5}$ and incorporated these into a variable mesh Chemical Transport Model (CTM);

4. Developed and applied more rigorous methods for evaluating CTMs used in air quality applications; and

5. Provided data, improved instrumentation, modeling tools, and scientific insights critical to the design of an integrated control strategy for O_3 and $PM_{2.5}$ pollution in the southern United States.

To meet these objectives, SCISSAP will undertake the development and evaluation of Chemical Transport Models (CTMs) and the collection of ambient data through field measurements. The field measurements will, in turn, be carried out under two distinct research activities: (i) An augmented Urban/Rural Monitoring Network for $PM_{2.5}$, Oxidants, and their Precursors (hereafter referred to as the Urban/Rural Monitoring Network); and (ii) Intensive Field Measurements. This Quality Integrated Work Plan (QIWP) will address the activities to be conducted under the Urban/Rural Monitoring Network. A QIWP for activities related to the CTM has been developed and submitted to U.S. EPA under separate cover. Finally, to the extent that measurement instrumentation, data quality objectives, and protocols for activities during the Intensive Field Measurements diverge from those developed for the Urban/Rural Monitoring Network, a separate QIWP for these activities will be prepared and submitted to the U.S. EPA before these activities are initiated.

1.2 Background – SCISSAP Organization

The SCISSAP research activities will be coordinated through two collaborating, multi-institutional teams from Duke University, the Universities of Minnesota, Alabama-Huntsville, New Hampshire, and Miami as well as Georgia Tech and the larger Science Team of the Southern Oxidants Study (SOS). Figure 1.1 illustrates the organizational structure for the teams and their relationship with the larger SOS community.

As illustrated in Figure 1.1, SCISSAP will function in collaboration with the Southern Oxidants Study (SOS) and the universities, government laboratories, and private sector entities that comprise the SOS Science Team. Through this collaboration SCISSAP will benefit from the considerable technological and human resources of the SOS Science Team. By developing an independent research team with its own unique expertise team, SCISSAP will provide a mechanism for undertaking a new and broader scientific objective: the integrated study of secondary air pollutants. This will be accomplished via a case study approach that focuses on subsets of secondary air pollutants and their interactions within the South.

The SCISSAP Numerical Modeling Team will focus on the further development and evaluation of variable-mesh, eulerian chemical transport models (CTMs) for simulating photochemical O_3 and $PM_{2.5}$ on regional and urban scales, using data collected by SCISSAP and related field studies. Specific emphasis will be given to the definition of a framework and procedure for evaluating CTMs, and then applying these to 3 CTMs, including a Models-3 prototype. An evaluation of modules for treating $PM_{2.5}$ and the incorporation of these modules into Models-3 and other CTMs will also be undertaken.

The SCISSAP Field Measurements Team will undertake two major tasks. One task will be the implementation of Intensive Field Measurements in collaboration with the larger SOS community. In the summer of 1999, the SCISSAP Field Measurements Team will collaborate with the larger SOS research community Science Team on an Intensive Field Study. This study will have two major components: (i) in the Nashville/Middle Tennessee Area area, a coordinated surface and airborne investigation of the evolution of secondary pollutants in power plant and urban plumes will be undertaken; and (ii) in the Atlanta Metropolitan Area, a testing, intercalibration, and evaluation of existing and new technologies for characterizing the chemical and physical characteristics of $PM_{2.5}$ will be carried out. In the summer of 2000, the SCISSAP Field Measurements Team may provide ancillary surface measurements for an SOS Intensive Field Program in East Texas.

The other major task of the SCISSAP Field Measurements Team will be to design, and help implement and coordinate an Urban/Rural Monitoring Network for $PM_{2.5}$ and its chemical composition and O_3 and its precursors in the southeastern United States. As envisioned, this network would augment surface monitoring activities of state and federal regulatory agencies with those of the Tennessee Valley Authority, Southern Company, and SCISSAP. SCISSAP's participation in this network will include carrying out $PM_{2.5}$ and trace gas measurements at 3 monitoring sites and maintaining a website/database

for the Urban/Rural Network. As noted earlier it is this aspect of the SCISSAP research plan (i.e., that related to the Urban/Rural Network) that is addressed in this QIWP.
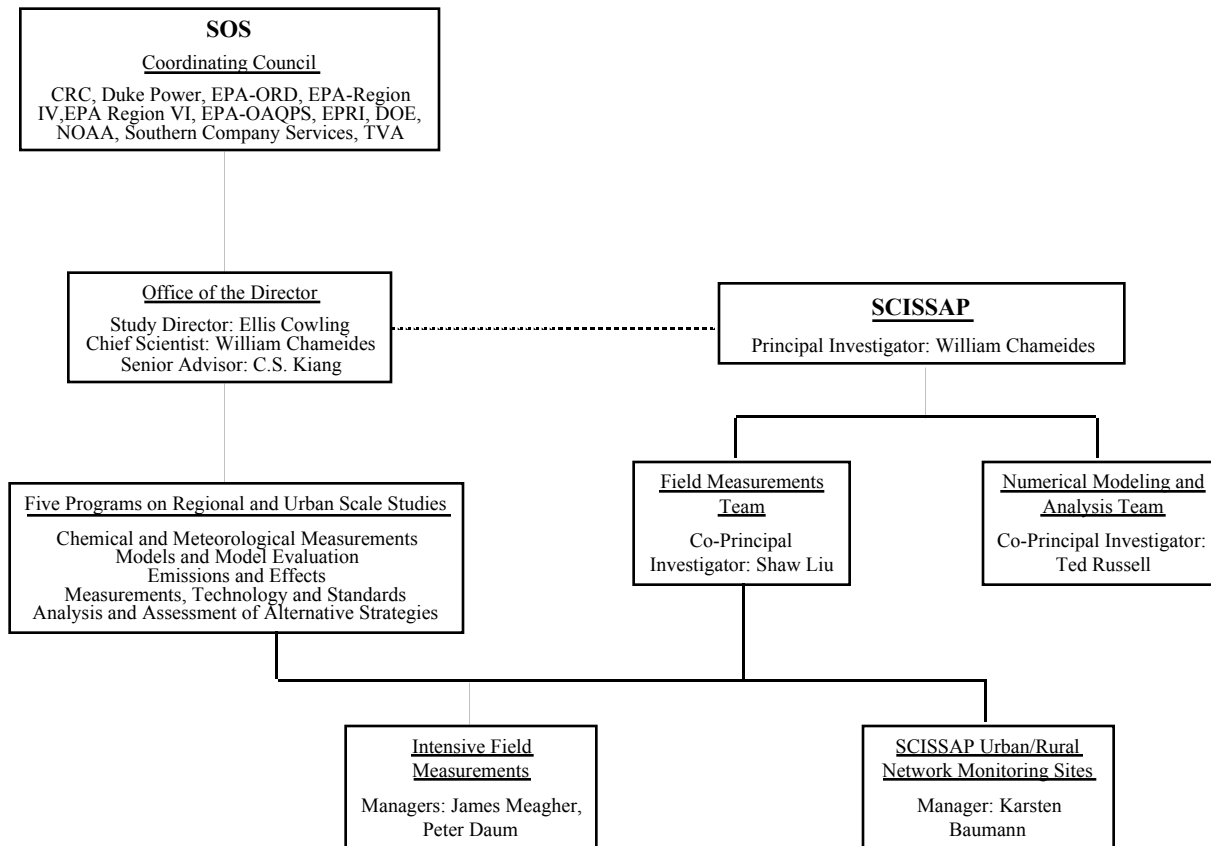
Figure 1.1. Organizational Structure for SCISSAP and its relationship to the larger SOS Science Team.

1.3 The Urban/Rural Monitoring Network: Project Scope and Work Objectives

Four major and interrelated scientific questions have been identified for SCISSAP's research focus over the next three years:

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?

These questions represent an increasingly complex order of progression. The first two questions focus on the morphology and sources of PM_{fine} and can be addressed through the collection and statistical analysis of ambient data. The third question focuses on mechanistic issues while the fourth addresses the issue of an integrated management strategy for O_3 and PM_{fine}.

As previously mentioned this QIWP addresses the field measurements associated with SCISSAP's participation in an Urban/Rural Monitoring Network for $PM_{2.5}$, O_3, and its precursors. The objectives of this network are to: (i) provide the data necessary to address Questions 1 and 2 of the SCISSAP scientific focus; (ii) identify mechanistic uncertainties related to Questions 3 and 4 that could be addressed during SCISSAP/SOS Intensive Field Experiments; and (iii) elucidate the technical issues related to the monitoring of particle composition using filter pack systems and the interpretation of data collected with these systems. Clearly to meet these objectives, it will be essential for SCISSAP to provide data from its Urban/Rural Monitoring sites of known and documentable quality. The purpose of this QIWP is to provide a framework and mechanism for ensuring the quality of this data.

To meet the objectives stated above, SCISSAP will partner with the Atmospheric Sciences Division of the Environmental Research Center of the Tennessee Valley Authority (TVA), the Southern Company (SC) and Atmospheric Research and Analysis, Inc. (ARA). Collectively, these organizations will augment the existing and planned Federal/State Regulatory Network for $PM_{2.5}$ with: (i) monitoring sites in rural as well as urban locales; and (ii) detailed particle composition and precursor species measurements at both urban and rural sites. The specific activities and responsibilities of the SCISSAP Science Team in the implementation of the Urban/Rural Monitoring Network are described in detail in Section 2 of the report.

When fully implemented and integrated with existing federal and state agency $PM_{2.5}$ sites, the Urban/Rural Monitoring Network will consist of three types of monitoring sites:

Level 0 sites with Federal Reference Method for $PM_{2.5}$ and largely consisting of state-operated NAMS/SLAMS sites;

Level 1 sites with measurement of particle composition for $PM_{2.5}$ and ozone and consisting of state-operated sites, IMPROVE sites operated by the National Parks Service and the U.S. EPA, sites operated by SC/ARA and TVA; and

Level 2 sites with measurements of particle composition, ozone, and gaseous precursors (VOC, NO, NO_y, NH_3, SO_2) and consisting of sites operated by SCISSAP, SS/ARA/, and TVA.

The proximate locations for these sites and the organizations responsible for maintaining and operating these sites are illustrated in Figure 1.2. The specific Data Quality Objectives for the SCISSAP-operated (level 2) Urban/Rural Monitoring Network sites are listed by parameter in Table 1.1.

Atlanta

Nashville

Level 2
\# NC/AQ
' SC/ARA
% SC ISSAP
$ TVA
% TVA/IMPROVE
% TVA/SC ISSAP
Level 1
& GA DNR
% GIT
] NPS/IMPROVE
' SC/ARA
& TN/APCD
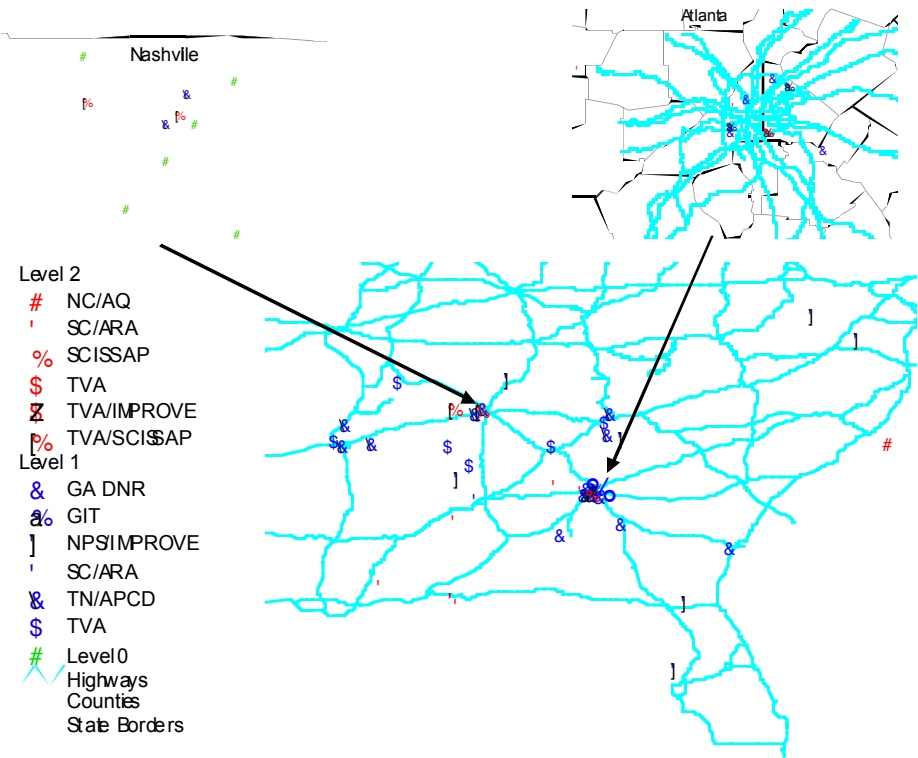$ TVA
\# Level 0
Highways
Counties
State Borders

Figure 1.2. Anticipated locations of sites in the Augmented Urban/Rural Monitoring Network for PM$_{2.5}$, O$_3$, and Precursors.

Table 1.1. Data Quality Objectives for SCISSAP Urban/Rural Network Monitoring Sites

I. Measurements Using PM$_{2.5}$ Particle Composition Monitoring System - (24-hr Integrated samples) [1]
  (*GIT-Baumann responsible for filter/denuder prep, and mounting of filter/denuder systems at Atl. Site. TVA responsible for mounting of filter/denuder systems at urban and rural Tennessee sites.*

Measurement/ (*Responsible Org.*)	Frequency [2]	Detection Limit	Accuracy	Precision	Completeness	Method
Mass (*GIT-Baumann*)	X	0.5 μg m^{-3}	± 10%	±10%	90%	Gravimetric analysis on Teflon filter
SO$_4$$^{2-}$ (*GIT-Baumann*)	X	*0.2 μg m^{-3}*	± 10%	±10%	90%	IC analysis on Teflon, Nylon, or Na$_2$CO$_3$ filter
NO$_3$$^-$ (*GIT-Baumann*)	X	*0.2 μg m^{-3}*	± 10%	±10%	90%	IC on Nylon or Na$_2$CO$_3$ filter
Cl$^-$ (*GIT-Baumann*)	X	*0.2 μg m^{-3}*	90-110%	±10%	90%	IC analysis on Teflon, Nylon, or Na$_2$CO$_3$ filter
Organic Acid (*GIT-Baumann*)	EXP	TBD	TBD	TBD	EXP	IC analysis on Teflon, Nylon, or Na$_2$CO$_3$ filter
NH$_4$$^+$ (*GIT-Baumann*)	X	*0.3 μg m^{-3}*	± 20%	±20%	90%	IC analysis on Nylon filter + citric acid impregnated filter
Na$^+$ (*GIT-Baumann*)	X	*0.3 μg m^{-3}*	± 10%	±10%	90%	IC analysis on citric acid impregnated filter
(HNO$_3$)$_g$ (*GIT-Baumann*)	X	*0.1 ppbv*	± 15%	±15%	90%	A. IC analysis on: (i) Na$_2$CO$_3$ coated denuder ; or (ii) difference of Nylon or Na$_2$CO$_3$ filters with and without denuder
(SO$_2$)$_g$	X/2	*0.1 ppbv*	± 15%	±15%	85%	IC analysis of: (i) Na$_2$CO$_3$ coated denuder; or (ii) difference of Nylon or Na$_2$CO$_3$ filters with and without denuder
(NH$_3$)$_g$ (*GIT-Baumann*)	X	*0.4 ppbv*	± 20%	±20%	85%	IC analysis of: (i) citric acid coated denuder; or (ii) difference of Nylon or citric acid impregnated filters with and without denuder
Soluble Trace Elements (*GIT-Froelich*)	X	See Part II	See Part II	See Part II	50%	ICP-MS analysis on Teflon filter
Elemental and organic C (*GIT-Baumann*)	Y$_1$	0.3 μg m^{-3}	± 20%	± 20%	85%	Thermal/FID-on quartz filter

Total C, ^{13}C,
Total N, ^{15}N,
^{14}C

(1) (*GIT-Jahren*) Y$_2$

   Y$_{2a}$ 1.5 μg m^{-3} ± 20% ± 20% 85% Sealed-tube combustion w/ stable isotope MS analysis on quartz filter   Particulate Organic species (POC) [3]

   (*UMiami – Zika* Y$_{EXP}$ TBD TBD TBD EXP GC/MS, GC/MS/ECD, LC/MS on quartz filter Trace Elements

   (*GIT-GTRI*) TBD 0.02 μg m^{-3} ± 20% ± 20% 85% Xray fluorescence   DQO's subject to revision on the basis of findings during the Shake-Down Phase.
(2) X to be determined and will be either (2 days)$^{-1}$ or (3 days)$^{-1}$, with X = Y$_1$ + Y$_2$ + Y$_{EXP}$ and Y$_{2a}$ < Y$_2$ to be determined when ^{14}C data deemed to be of interest. Y$_{EXP}$ denotes "experimental activity" with variable sampling frequency and operating procedure.
(3) The individual POC species to be quantified will be determined during Year 1. These measurements will become operational during Year 2 and Year3.

Table 1.1. Data Quality Objectives for SCISSAP Urban/Rural Network Monitoring Sites

II. Listing of Soluble Trace Elements To Be Quantified Using ICP/MS (see Part I) [1]

Element	Detection Limit ($\mu g/gPM_{2.5}$) [2]	Accuracy	Precision
Vanadium (V)	10	± 15%	±15%
Manganese (Mn)	10	± 15%	±15%
Iron (Fe)	100	± 15%	±15%
Copper (Cu)	10	± 15%	±15%
Platinum (Pt)	1	± 15%	±15%
Lead (Pb)	1	± 15%	±15%
Thorium (Th)	1	± 15%	±15%
Uranium (U)	1	± 15%	±15%

(1) List and quantities are subject to revision on the basis of findings during the Shake-Down Phase.
(2) Detection limits presented assume analysis on filter extraction with 10 ml distilled,.

Table 1.1. Data Quality Objectives for SCISSAP Urban/Rural Network Monitoring Sites

III. Measurements Using Independent Gas Sampling Systems [1]

Measurement	Frequency	Detection Limit	Accuracy	Precision	Completeness	Method
Ozone *(GIT-Baumann for Atl site, TVA for Tenn sites)*	1 min	2.00 ppbv	±2 ppbv	±2 ppbv	90%	Dasibi
NO *(GIT-Baumann for Atl site, TVA for Tenn sites)*	10 s	20 pptv	± 15%	± 10%	90%	Chemiluminescent
NO_y *(GIT-Baumann for Atl site, TVA for Tenn sites)*	10 s	100 pptv	± 25%	± 20%	90%	Chemiluminescent w/gold tube converter
Speciated $(VOC)_g$ (4, 12, 24-hr integrated sample) *see Part IV (UMiami – Zika)*	Y_{EXP} [2]	0.5 ppbC	TBD	TBD	90%	GC-FID on whole-air grab samples
T, $T_{dew\ point}$ *(Data gathered by PCM)*	$(5\ min)^{-1}$	NA	± 10%	±10%	90%	Standard Met

(1) DQO's subject to revision on the basis of findings during the Shake-Down Phase.
(2) Speciated $(VOC)_g$ measurements will occur whenever POC measurements are made. See Part 1.

Table 1.1. Data Quality Objectives for SCISSAP Urban/Rural Network Monitoring Sites

IV. List of (VOC)$_g$ Species To Be Quantified Using GC/FID Analysis on Whole-Air Grab Samples [1]

	Hydrocarbons				Oxygenated Volatiles	
1	Ethene	36	2,3-Dimethylpentane	1	Acetaldehyde	
2	Acetylene	37	Trichloroethylene	2	Propanal	
3	Ethane	38	Heptane	3	Butanal	
4	1,1-Difluoroethane (IS)	39	Methylcyclohexane	4	Pentanal	
5	Propene	40	2,3,4-Trimethylpentane	5	Hexanal	
6	Propane	41	Toluene	6	Heptanal	
7	Isobutane	42	3-Fluorotoluene (IS)	7	Octanal	
8	Isobutene	43	n-Octane	8	Nonanal	
9	1-Butene	44	Perchloroethylene	9	Decanal	
10	n-Butane	45	Ethylbenzene	10	Methanol	
11	Trans-2-butene	46	p-Xylene	11	Ethanol	
12	Cis-2-butene	47	m-Xylene	12	1-Butanol	
13	3-Methyl-1-Butene	48	Styrene	13	Methacrolein	
14	Isopentane	49	o-Xylene	14	Methyl ethyl ketone	
15	1-Pentene	50	Nonane	15	Methyl vinyl ketone	
16	2-Methyl-1-Butene	51	Isopropylbenzene	16	2-Butanone	
17	n-Pentane	52	a-Pinene	17	2-Pentanone	
18	Isoprene	53	n-Propylbenzene	18	Benzaldehyde	
19	Trans-2-pentene	54	1-Ethyl-3-Methylbenzene			
20	Cis-2-pentene	55	1-Ethyl-4-Methylbenzene			
21	2-Methyl-2-Butene	56	1,3,5-Trimethylbenzene			
22	2,2-Dimethylbutane	57	1-Ethyl-2-Methylbenzene			
23	1-Chloropropane (IS)	58	b-Pinene			
24	3-Methyl-1-Pentene	59	1,2,4-Trimethylbenzene			
25	4-Methyl-1-Pentene	60	n-Decane			
26	Cyclopentane	61	Limonene			
27	2-Methylpentane	62	1,3-Diethylbenzene			
28	3-Methylpentane	63	n-Butylbenzene			
29	n-Hexane	64	Undecane			
30	Cis-3-hexene	65	Decalin (IS)			
31	Methylcyclopentane	66	Dodecane			
32	2,4-Dimethylpentane	67	1,3,5-Triethylbenzene			
33	1,1,1-Trichloroethane	68	1,2,4-Triethylbenzene			
34	Benzene	69	Tridecane			
35	Cyclohexane					

(1) List subject to change on the basis of findings during the Year1 tests.

1.4 The Urban/Rural Monitoring Network: Project Implementation

Figure 1.3 illustrates the major milestones for the development and implementation of the Urban/Rural Network and the relationship of these milestones to the other research activities in SCISSAP. These activities are to be carried out in phases, each briefly outlined below.

1.4.1. The Start-Up Period is scheduled to encompass the first ~5 months of the project and will be devoted to instrument procurement, initial testing of Standard Operating Procedures and preparation of the Quality Integrated Work Plan (Revesion No. 0).[1] A key aspect of this activity was the convening of a joint SCISSAP/SOS Aerosol Measurements Workshop in July 21, 1998 in Raleigh,North Carolina. At this workshop, experts in aerosol measurements were invited to review and comment on SCISSAP's proposed methods for $PM_{2.5}$ mass and composition measurements. A report of the Workshop will be made available to the community on the SCISSAP WebSite (http://www-wlc.eas.gatech.edu/scissap/).

1.4.2. The Shake-Down Period will cover the next six months of the project and will be devoted to a detailed testing and assessment of the instrumentation and standard operating procedures identified in the QIWP for particle composition measurements by SCISSAP in the Urban/Rural Monitoring Network. These tests will be carried out at a sampling site located in the rear of the parking lot behind the SCISSAP 14th Street Analytical Laboratory in Atlanta, Georgia. This phase of the project will also include at least two informal field intercalibrations with particle composition measurements being carried out by other organizations in the region (e.g., SC/ARA). (At this time, it is envisioned that the intercalibrations will occur in the late summer and winter at an urban site in Atlanta and a rural site outside of Atlanta. An external review committee, headed by Dr. Roger Tanner of TVA and supported by the SOS Office the Director, will provide guidance on the design and interpretation of these intercalibrations.) To the extent indicated to be necessary by these tests, assessments, and intercalibrations, the QIWP will be altered at the end of this phase to ensure maximal precision and accuracy of the SCISSAP measurements. The altered QIWP (i.e., Revision 1) will then be resubmitted to the U.S. EPA for review and approval before implementation.

1.4.3. Implementation of the SCISSAP Urban/Rural Monitors will begin at the end of the Shake-Down period (i.e., on or about March, 1999) and continue throughout the remaining months of the 3-year project. SCISSAP's participation in this network will include carrying out $PM_{2.5}$ and trace gas measurements (see Table 1.1) at 3 "Level 2" monitoring sites and maintaining a website/database for the Urban/Rural Network. As illustrated in Figure 1.2, the three SCISSAP sites will be located at O_3, PM_{10}, and/or $PM_{2.5}$ NAMS or SLAMS sites in Atlanta, Georgia, Nashville, Tennessee, and Dixon Tennessee. More detailed descriptions of the SCISSAP site locations, instrumentation, and analytical procedures are included in subsequent sections of this QIWP.

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[1] At the time of preparation of this QIWP, the project is currently in the later stages of the Start-Up Period, and it is anticipated that the QIWP (Revision No. 0) will be submitted to the U.S. EPA for review at the end of this period.

Analysis of the Urban/Rural Network Data will commence almost immediately after implementation of the SCISSAP monitoring network and also continue throughout the remainder of the 3-year project. As indicated in Figure 1.3, this activity will be carried out in close collaboration with the SCISSAP Modeling Team. Moreover as outlined in Section 8 (on Data Management), a key aspect of this activity will be the development of an Urban/Rural Monitoring Network Database and the maintenance of this database on the SCISSAP WebSite (http://www-wlc.eas.gatech.edu/scissap/).

1.5   Personnel Qualifications and Training

The senior personnel involved in the SCISSAP Urban/Rural Monitoring Network include: Dr. W.L. Chameides as Project P.I., Dr. S.C. Liu as Field Measurements Team Leader, Dr. J. St John as Data Quality Officer and Archive Manager, and Dr. K. Baumann as SCISSAP Network Director, Atlanta Site Manager, Analytical Laboratory Manager. All have Ph.D.'s and considerable experience in atmospheric chemistry, air pollution meteorology, and/or field measurements. Abbreviated cirriculum vitae for all senior personnel are included in Appendix A.

In addition to the above senior personnel, it is envisioned that a number of individuals will be engaged in the SCISSAP Urban/Rural Network operations. These include laboratory directors for analytical procedures carried out outside the SCISSAP Analytical Laboratory (see Section 3); all have Ph.D.'s and extensive research experience in the appropriate area of expertise. Non-senior SCISSAP personnel will also include a number of individuals working in a supportive capacity as laboratory technicians, field monitor specialists, and so forth. All of these individuals will be thoroughly apprised of the SCISSAP standard operating procedures and protocols and periodically audited for compliance with these procedures.

Figure 1.3 Milestones for the 3-Year SCISSAP Project
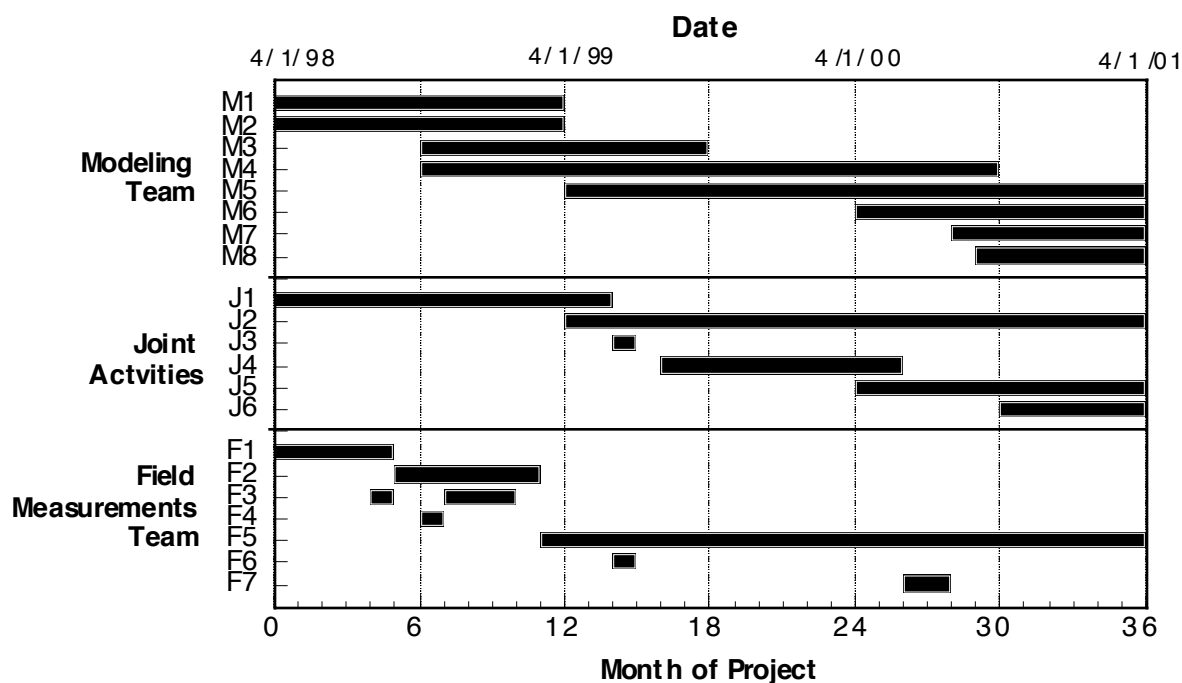
Legend:

M1 – Multi-model evaluation using SOS/SEAVS/NARSTO-NE data
M2 – Particulate algorithm intercomparison
M3 – Emissions inventory assessment
M4 – Development of SCISSAP Chemical Transport Model (CTM)
M5 – Mechanistic/diagnostic studies
M6 – Application of SCISSAP CTM to Intensive data
M7 – SCISSAP CTM uncertainty analysis
M8 – Control strategy analysis

J1 – Plan 1999 SCISSAP/SOS Intensive Field Experiment in Nashville, TN
J2 – Analyze Urban/Rural Network data
J3 – Real-time forecasts during 1999 SCISSAP/SOS Intensive Field Experiment in Nashville, TN
J4 – Plan 2000 SOS Intensive Field Experiment in Houston/Dallas, TX
J5 – Analyze Intensive data
J6 – Prepare Final Report

F1 – Start-up (e.g., instrument procurement, preparation and submittal of QIWP, version 1.0)
F2 – Shake-Down (e.g., testing of procedures, intercomparisons, submittal QIWP, version 2.0))
F3 – Intercalibration of Particle Composition Monitoring with Southern Company instrumentation
F4 – Intercalbration of NH_3 measurements in Boulder, CO
F5 – Implement SCISSAP Urban/Rural Network monitors
F6 – Participate in 1999 SCISSAP/SOS Intensive Field Experiment in Nashville, TN, and Atlanta, GA
F7 – Participate in 2000 SOS Intensive Field Experiment in Houston/Dallas, TX

1.6   Communication Plan

The organizational structure for SCISSAP illustrated in Figure 1.1 describes the formal communication pathways for the project. In general information and data will flow to and from the Urban/Rural Network Monitoring Sites Sub-Team headed by Dr. K. Baumann to the SCISSAP Field Measurements Team and then the larger SOS Science Team via the SCISSAP P.I. (W.L. Chameides). The convening of annual joint SOS/SCISSAP Science Team Meeting will further facilitate these communications; since these meeting are held in the Raleigh area, they will also facilitate communication and participation of U.S. EPA scientists.

Within the Urban/Rural Network Monitoring Sites Sub-Team there will be a variety of communication pathways.   The Sub-Team will hold weekly status meetings on the Georgia Tech campus, with conference call capability to allow for participation of distant participants when deemed necessary.

Monthly Quality Assurance Reports (see Sections 8 and 9) will be generated by the Data Quality Officer and shared with all senior personnel. Archived data will be placed on the SCISSAP WebSite within 30 days after receipt by the Data Office and made available to all members of the SCISSAP Science Team. Quality Assurance checks on the data will continue in an iterative fashion over an approximate 12-month period. We anticipate a release of data to the larger scientific community on an annual basis; on March 1 of each year, all data that is more than 12 months old will be moved to a data archive on the SCISSAP WebSite that is universally accessible. It is also anticipated that at the same time this data will be submitted to the NARSTO Data Archive.

Communication of SCISSAP data and results to the U.S. EPA will be accomplished through the submission of annual reports and a Final Report.

The ultimate avenue for communication of SCISSAP data and results to the scientific community will be via the submission and publication of scientific papers in the peer-reviewed literature (e.g, *Journal of Geophysical Research, Environmental Science and Technology*).   All of these publications will contain an acknowledgement of the support of the U.S. EPA's Office of Research and Development.

APPENDIX B
THE NATIONAL PARK SERVICE
ENHANCED MONITORING NETWORK

The National Park Service (NPS) operates three sites in the SOS study region as part of the Interagency Monitoring of Protected Environments (IMPROVE) network. The sites are located in Great Smoky Mountain National Park, located on the Tennessee/North Carolina border, Mammoth Cave National Park in south central Kentucky and the Sipsey Wilderness Area located in northwestern Alabama. Two of the sites have an extensive array of continuous gaseous measurements in addition to the standard IMPROVE aerosol sampling protocol. The location of the sites is shown in figure 1.

National Park Service Enhanced Monitoring Sites in the SOS Study Region
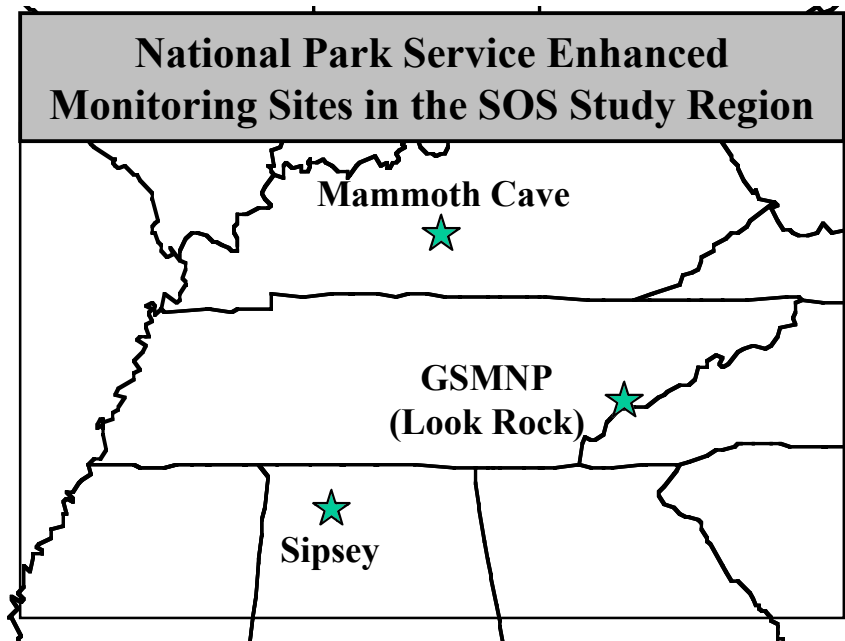
The IMPROVE Network

The National Park Service (NPS) and other Federal Land Managers are required by the Clean Air Act to protect visibility at Class I areas, which include most national parks and wilderness areas. This is being accomplished through the IMPROVE program. IMPROVE has representatives from the National Park Service (NPS), the Forest Service (USFS), the Bureau of Land Management, the Fish and Wildlife Service (FWS), the Environmental Protection Agency (EPA), and regional-state organizations. The IMPROVE program includes the characterization of haze by photography, the measurement of optical extinction with transmissometers and nephelometers, and the measurement of the composition and concentration of the fine particles that produce the extinction and the tracers that identify emission sources. The IMPROVE particulate monitoring sites are funded by the following agencies: the

IMPROVE committee, the NPS, the USFS, the FSW, the Tahoe Regional Planning Agency, the Department of Energy (DOE), the Northeast States Cooperative Air Use Management (NESCAUM), the State of Vermont, and the Regional District of Fraser Cheam (British Columbia). The sites are operated by University of California, Davis.

The standard IMPROVE sampler has four sampling modules: modules A, B, and C collect fine particles (0-2.5: um), and D collects PM10 particles (0-10: um). Module A Teflon is the primary filter, providing most of the fine particle data. Module B, with a denuder before the nylon filter to remove acidic gases, is used primarily for nitrate. Module C, with tandem quartz filters, measures carbon in eight temperature fractions. At many sites, the Module A or D Teflon filter is followed by a quartz filter impregnated with K_2CO_2 that converts SO_2 gas to sulfate on the filter. Some sites have a single Module A Teflon filter. Each week two 24-hour samples (Wednesdays and Saturdays) are collected. The filter cassettes are changed weekly and shipped to Davis for processing and analysis. Further detailed documentation is provided by Crocker Nuclear Laboratory, Air Quality Group, University of California, Davis, and by Air Resource Specialists Inc. Colorado. The recovery rate for validated data, since 1991, has
been 96%.

Great Smoky Mountains National Park

Objectives:

The enhanced monitoring program at Great Smoky Mountains National Park, Big Meadows, is a multiple-year cooperative program designed to measure and understand air pollutants that impact the park. The general objectives of the program are to: 1) characterize ozone trends and precursors, 2) identify source regions and source types, 3) determine proportions of local vs. transported ozone, 4) to understand ozone production limiting factors (NO_x- or VOC-limited, seasonal changes), and 5) observe S and N species trends (related to acidic deposition)..

Comments:
The site is cooperatively operated by NPS and TVA. Funding has been primarily by NPS and TVA. The Southern Oxidant Study used the site and data during the SOS Nashville Intensive. The high elevation and location makes the station useful for determining regional ozone concentrations. Nearby at the Look Rock monitoring station there are visibility measurements that have complimentary measurements and objectives

Site Information:

Site name: Cove Mountain
Location: Great Smoky Mountains National Park   Lat: 35° 41" 48'   Long: 83° 36" 35'
Elevation: 1243 m (MSL)
Measurement height: 10 m
AIRS number: 471550101

Instrumentation:

Parameter/measurement	Date Started	Sensitivity/time resolution	Comments
O3	5/83	2 ppb / 1-min, 1-hr	Hourly data submitted to AIRS
SO2	5/95	50 ppt / 1-min	
CO	5/95	15 ppb / 1-min	Modified TECO
NOy	5/95	50 ppt / 1-min	Mo catalyst converter, external
NO	5/95	30 ppt / 1-min	
NO2	5/97	50 ppt / 1-min	Photolysis converter with TECO 42s
Wind direction	5/95		
Wind speed	5/95		
Ambient temperature	5/95		
Relative humidity	11/95		
Precipitation	11/95		
Solar radiation	12/95		
UV radiation	5/95		
Barometric pressure	4/96		
VOC (cannisters)	5/95		GC speciatation of 60+ cmpds

Mammoth Cave National Park

Objectives:

The enhanced monitoring program at mammoth Cave National Park, Big Meadows, is a multiple-year cooperative program designed to measure and understand air pollutants that impact the park. The general objectives of the program are to: 1) characterize ozone trends and precursors, 2) identify source regions and source types, 3) determine proportions of local vs. transported ozone, 4) to understand ozone production limiting factors (NO_x- or VOC-limited, seasonal changes), and 5) observe S and N species trends (related to acidic deposition)..

Comments:
The site is cooperatively operated by NPS and TVA. Funding has been primarily by NPS and TVA. The Southern Oxidant Study used the site and data during the SOS Nashville Intensive.

Site Information:

Site name: Mammoth Cave
Location: Mammoth Cave National Park   Lat: 37° 13" 04'   Long: 86° 04" 25'

Elevation: 219 m (MSL)
Measurement height: 10 m
AIRS number: 210610500

Instrumentation:

Parameter/measurement	Date Started	Sensitivity/time resolution	Comments
O3	5/83	2 ppb / 1-min, 1-hr	Hourly data submitted to AIRS
SO2	5/95	50 ppt / 1-min	
CO	5/95	15 ppb / 1-min	Modified TECO
NOy	5/95	50 ppt / 1-min	Mo catalyst converter, external
NO	5/95	30 ppt / 1-min	
Wind direction	11/88		
Wind speed	11/88		
Ambient temperature	11/88		
Relative humidity	1/89		
Precipitation	11/88		
Solar radiation	11/88		
Barometric pressure	2/96		
VOC (cannisters)	6/95		GC speciatation of 60+ cmpds
IMPROVE	3/88		Elements, mass, PM10, PM2.5, SO4, NO3, organics (A,B, C modules)
Nephelometer	3/93		
Transmissometer	12/88		

APPENDIX C
TVA/EPRI/DOE/NPS ENHANCED MONITORING SITE
GREAT SMOKEY MOUNTAINS

Objectives

One of the most important issues in the mid-south region in which TVA operates is the composition of $PM_{2.5}$ mass, and the degree to which the emissions of sulfur and nitrogen oxides from TVA's power plants contribute to the mass of fine particles ($PM_{2.5}$) and to regional haze. The development of a fully equipped monitoring site in or near the largest Class I area in the southeast, the Great Smoky Mountains National Park (GSMNP), which is also located within the sphere of influence of major urban areas and point sources of sulfur and nitrogen oxides, will provide a unique platform for methods testing and special purpose monitoring of the physical properties and chemical composition of fine particles. The results from this site will aid significantly in evaluating the precision and accuracy of mass data from EPA's $PM_{2.5}$ monitoring networks, in improving models to identify sources of $PM_{2.5}$, and eventually in developing improved control strategies. It also complements other monitoring efforts being conducted or proposed by other groups in the southeast region.

Instrumentation and Deployment Strategy

Following development of a proposal with approved funding from TVA, EPRI, and the Department of Energy, discussions were held with personnel from the National Park Service. Plans which are being developed on the basis of those discussions include the following.

Location

- The Look Rock site - on the foothills parkway along Chilhowee Mountain immediately west of the GSMNP - will be the **primary** monitoring site. This decision is based on a number of considerations which include the following:

  - year-round site accessibility;

  - modest costs for site modification, including existing infrastructure to support site expansion;

  - the presence of considerable existing NPS air/quality/particle/visibility monitoring resources (Look Rock is the site of an existing IMPROVE network sampler, and data on ozone concentrations, ambient light scattering and basic met conditions are also collected year-round).

- The Cove Mountain station will be a **secondary** monitoring station. It will be possible to do a limited amount of gaseous and particulate sampling within the constrained infrastructure of this

station, sufficient to provide data for comparision with the Look Rock station (which is 28 kilometers west and about 1500 feet lower elevation than Cove Mountain).

Supersite Monitoring Triad
TVA, DOE, EPRI, and NPS
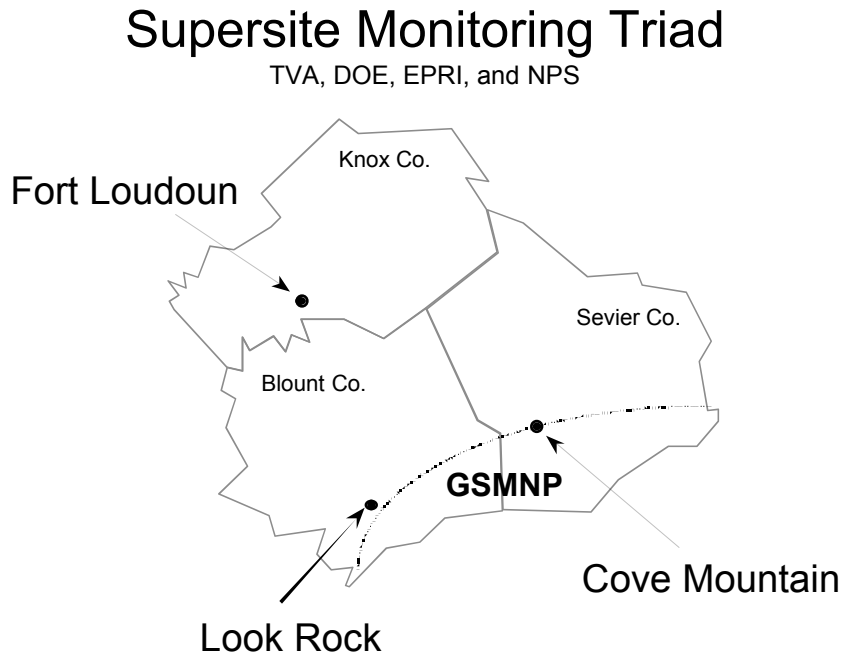
Instrumentation

- TVA will supplement existing Look Rock monitoring equipment by adding high-sensitivity NO-NO$_y$, SO$_2$, and CO instruments and an FRM PM$_{2.5}$ sampler for routine operation, and provide a trailer/platform for this purpose. The FRM PM$_{2.5}$ sampler may be deployed year-round as one of the State of Tennessee's network sites. TVA will also consider deploying the TEOM ("conventional" 30 C operation with a 2.5um inlet) routinely for extended periods of time at Look Rock. Sufficient workspace will be provided for the campaign-oriented deployment of the continuous PM2.5 TEOM (possibly with some inlet modifications to be provided by NPS), an upgraded PC-BOSS (for semi-volatile organics and nitrates), and possibly other gaseous and particulate samplers.

- TVA staff have proposed the Look Rock site for intercalibration activities for various network sampling being performed or proposed in the Southeast region.

- Local NPS staff at GSMNP will assist TVA in providing routine support for the additional instrumentation at both Cove Mountain and Look Rock stations.

There are attractive opportunities to use the existing Knoxville PM2.5/PM10 monitoring station at the UT Ag Experiment Center for some Valley/Mountain comparisons.

Schedule

The proposed schedule is to upgrade the Look Rock site with a trailer and platform for additional routinely operated gas-phase and particulate instrumentation in the early part of FY99. Additional instrumentation proposed for The Cove Mountain site would be installed and operations begun at the beginning of the 1999 ozone season (approximately April, 1999). The first "sampling campaign" for testing of more sophisticated particulate sampling equipment at the Look Rock site would take place during the summer months of 1999.

APPENDIX D
DESCRIPTION OF THE SEARCH PARTICULATE COMPOSITION MONITOR

Eric S. Edgerton, Atmospheric Research & Analysis, Inc.

Introduction

The Southeastern Aerosol Research and Characterization study (SEARCH) operates a 7 station air monitoring network designed to characterize aerosol concentration and composition at a number of rural and urban locations across the southeastern United States (see Figure 1). Continuous (1-minute average) measurements at rural sites currently include a variety of trace gases (O_3, NO, NO_2, NO_y, HNO_3, CO and SO_2) and particle mass (modified TEOM). Research is underway to expand the list of continuous measurements to include NH_3 and major aerosol components (e.g., ammonium, nitrate and sulfate). Discrete (i.e., 24 hour average) measurements at rural and urban sites include $PM_{2.5}$ mass (Federal Reference Method), PM_{10} mass and composition (dichotomous sampler), and $PM_{2.5}$ composition. This presentation addresses the design and operation of the $PM_{2.5}$ speciation sampler used in SEARCH. A brief description of the sampler follows.

Description of $PM_{2.5}$ Speciation Sampler

The SEARCH speciation sampler, hereafter referred to as a particulate composition monitor (PCM), is a 4-channel system designed to collect 24-hour integrated samples for analysis of mass, major ions, trace/crustal elements, organic and elemental carbon and semi-volatile organics in the $PM_{2.5}$ size range (see Figure 2). Key features of the PCM include a variety of denuders for selective removal of interferent gases, multiple filters in series for evaluation of volatilization losses, independent mass flow control (16.7 lpm at 760 mm and 298 K) on each channel and capabilities for multi-day operation. The PCM is controlled by a data acquisition system, which activates sampling, sequences filters from one day to the next, controls and logs sample flow.

Ambient air enters each channel of the PCM through a cyclone with a nominal cutpoint of 10 microns. The purpose of the cyclone is not to provide a precise size fraction, but to prevent large particles (e.g., pollen, road dust and fog droplets) from entering and depositing within the system. Sample air then flows through one or more annular denuder, a WINS impactor (without impaction oil) and, finally, through the sampling media. The WINS provides a relatively sharp size cut at 2.5 microns aerodynamic diameter. An attractive feature of the WINS is a deep impaction well, which reduces particle bounce and provides a substantial capacity for retained particles. This allows the sampler to operate for several

days (probably longer in rural areas) between visits. Descriptions of individual channels and target analytes are provided below.

Channel 1 (3-stage filter pack) – This channel is used for quantification of $PM_{2.5}$ mass, volatile-nitrate, volatile-ammonium, water-soluble metals and trace/crustal elements. Air is pulled through two annular denuders in series coated with sodium carbonate and citric acid, then through a 3-stage filter pack. The denuders remove acidic and basic gases (primarily HNO_3, SO_2 and NH_3) which might otherwise contaminate sample filters. Sample then flows through a 47 mm filter pack containing Teflon, nylon and a citric acid impregnated filters in series. All Teflon filters are analyzed gravimetrically for $PM_{2.5}$ mass and roughly one-third are analyzed for extractable metals (ICP-MS), trace/crustal elements (XRF). Nylon and citric acid filters are extracted in deionized water and analyzed for volatile-nitrate and volatile-ammonium, respectively.

Channel 2 (single-stage nylon filter pack) – This channel is used for quantification of sulfate, nitrate and ammonium. Air is pulled through carbonate and citrate denuders and then through a 47 mm nylon filter. The nylon filter is extracted in deionized water and analyzed for ions via IC and colorimetry.

Channel 3 (dual quartz filter pack) – This channel is used for quantification of organic and elemental carbon. Air is pulled through a carbon paper denuder based on the design of Eatough (Atmos. Envir., 27A, 1213-1219, 1993), then through tandem pre-fired quartz filters (37 mm). It is assumed that the denuder effectively removes gas phase organics in the volatility range that could interfere with OC measurements. Tests on the efficiency and capacity of the carbon denuder are currently underway. Both quartz filters are analyzed for organic and elemental carbon using the thermal-optical reflectance method. Organic carbon on the backup filter may be interpreted as volatilization loss from the first filter. Since the sampling conditions favor volatilization of semi-volatiles from both quartz filters, the OC signal is probably a lower limit on the actual ambient composition.

Channel 4 (quartz filter-PUF/XAD cartridge) – This channel is used for quantification of semi-volatile organic compounds. Given the diversity of semi-volatile organics in the ambient atmosphere, the purpose of this channel will be to: 1) provide gross characterization of organics based on polarity; and 2) quantify marker compounds for various source categories (e.g., wood smoke and diesel exhaust); and 3) estimate biases (positive or negative) in organic carbon measurements which use the traditional quartz filter approach. Air is pulled through a carbon paper denuder (same as channel 3), then through a sorbent sandwich of polyurethane foam and XAD resin(other sorbents may be used as time goes by). The choice of sorbent will depend, among other things, on sampling conditions and target analytes. Samples will be analyzed for extractable carbon using a multiple solvent extraction scheme similar to that developed by Barbara Turpin. Selected samples will also be extracted and analyzed for target species via GC-MSD or LC-MSD.

SEARCH Particulate Composition Monitor