SOS NEWS YOU CAN USE

Scientific Findings from the
SOUTHERN OXIDANTS STUDY (SOS)
1988-2005

I. GENERAL INTRODUCTION

During the first ten years of the SOS program, the major focus in research was on regional oxidant (especially ozone) pollution and the earliest objectives were to identify ozone-related chemical and meteorological factors that were unique to the SOS region – such as the large quantities of biogenic VOC emissions, greater frequencies of air stagnation days, and abundant NO_x-producing lightning strikes during summer thunderstorms. As the SOS program matured, however, the focus broadened to include both ozone and particulate matter (especially $PM_{2.5}$) pollution and more emphasis on quantitative comparisons regarding ozone and PM pollutant exposures with those in other regions of the US, Canada, and Mexico.

Thus, some of the research studies within SOS were designed to:

1) Identify and quantify many of the unique natural processes (including plant physiological and ecological processes, topographic features, and meteorological and climatological processes) that influence the formation and accumulation of ozone, other photochemical oxidants, and particulate matter (especially $PM_{2.5}$) pollution in the SOS region;
2) Identify and quantify some of the unique changes in human activities (agricultural, forestry, industrial, commercial development, and both demographic and land-use patterns) that influence ozone and PM exposures in the SOS region; and
3) Compare and contrast these natural processes in the atmosphere and human activities in the SOS region with those in other regions of the United States, Canada, and Mexico – especially with regard to development of optimal management strategies and tactics for efficient and cost-effective control of the accumulation of ozone, PM, and/or regional haze.

From the standpoint of ozone and PM management, it is very important to recognize the differences between *ozone formation* and *ozone accumulation*. The air concentration of ozone at a given location near the ground is the net result of the following six different processes in the atmosphere above that location:

1) The rate of ozone *formation* from chemical precursors emitted at or transported into that location,
2) The rate of ozone *destruction* by chemical reactions in the same air parcel,
3) The rate of *vertical transport* of ozone from the stratosphere (or from an ozone reservoir aloft, within the atmosphere) to ground level at that location,
4) The rate of *horizontal transport* of ozone from up-wind sources,
5) The rate of *atmospheric deposition* of ozone from the air to vegetation or other surfaces exposed to the air at that location, and
6) The rate of ozone atmospheric dispersion and dilution as a result of mixing with cleaner air during advection or when the height of the planetary boundary layer rises.

In essence, the air concentration of ozone is a kind of “algebraic sum” of all six of these processes:

1) increasing (+) if the ozone formation rate is high,
2) decreasing (-) if the ozone destruction rate is high,
3) increasing (+) if the rate of vertical transport of ozone is high,
4) decreasing (-) if the rate of horizontal transport of ozone is high,
5) decreasing (-) if the ozone deposition rate is high, and
6) decreasing (-) if the ozone dispersion (dilution) and/or advection rates are high.

The National Ambient Air Quality Standards (NAAQS) for ozone and PM are based on maximum air concentrations that are allowed to accumulate at ground level in the atmosphere at any given urban, suburban, rural, or remote location within a certain well-defined period of time. For example, the recently promulgated "8-hour NAAQS” for ozone requires that air concentrations of ozone be maintained below an average of 80 ppm over any eight-hour period on all but two allowable days during any three-year period.

II. CLIMATOLOGY OF OZONE AND OZONE PRECURSORS

The ozone climatology research program within SOS aimed at identifying the long-term weather-related characteristics of the southeastern region of the United States that influence the pollution climate of the southern states. The SOS region includes the states of Alabama, Florida, Georgia, Kentucky, Louisiana, Mississippi, North Carolina, South Carolina, Tennessee, and Texas. This region includes the warm and humid Atlantic Coast and Gulf Coastal Plains, the moderate elevation hilly Piedmont regions of all ten states, and the high-elevation, nearly boreal Appalachian Mountain areas within the states of North Carolina and Tennessee and foothill areas of Georgia, Alabama, and Mississippi. Much of this large region has a higher intensity of solar radiation and somewhat lower average wind speeds, and a higher frequency of air stagnation events than other parts of the eastern US and Canada.

It is well known that natural conditions such as solar radiation, temperature, relative humidity, and wind speed affect not only the photochemical processes that lead to ozone and particulate matter formation and accumulation in the atmosphere, but also influence the rate and magnitude of air emissions and dispersion of the chemical precursors of ozone and other oxidants (mainly VOC and NO_x), as well as $PM_{2.5}$ (mainly VOC, NO_x, SO_2, and NH_3).

To the extent that these conditions and their impacts in the SOS region are different from those in other regions, both the chemical climatology and optimal strategies for mitigating the photochemical ozone problem in the SOS region may be different from those in other regions. Thus, evidence generated in ozone climatology studies has critically important implications with respect to the possible value of region-specific rather than uniform across-the-country ozone control strategies.

The major results from SOS ozone climatology studies are summarized in the specific scientific findings and *policy implications* listed below.

- C1. The ozone pollution problems in rural and urban areas within the ten-state SOS region (NC, SC, KY, TN, GA, FL, AL, MI, LA, and TX) are somewhat different in character from that of the mid-Atlantic region (VA, MD, DL, NJ) and even more different in character from that of the midwestern (OH, IN, MI, IL, WI, IA, and MN) and the northeastern states (NY , MA, CN, VT, NH, and ME) and the southeastern provinces of Canada (Ontario, New Brunswick, Quebec, and Nova Scotia). Peak ozone concentrations in the SOS region are generally lower than those in the mid-Atlantic, northeastern states, and some of the eastern provinces of Canada. But minimum concentrations of ozone are generally higher. Furthermore, ozone accumulation in the SOS region is decoupled from ozone accumulation in the mid-Atlantic and northeastern states. The differences between these three regions are due in part to the greater frequency of weather-front passages in the mid-Atlantic and northeastern states and the greater frequency of air-stagnation events in the southeastern states (Vukovich, 1992, 1994).
- C2. In contrast to the northeastern states, ozone episodes in the SOS region are characterized by regionally dispersed, but spatially incoherent areas of high ozone concentration punctuated on the mesoscale by "hot spots" of high ozone concentrations (Chameides and Cowling, 1995).
- C3. Ozone concentrations throughout the SOS region are high enough (in excess of 60 ppbv) to inhibit photosynthesis of crops, forest and shade trees, and other plants during some portion of the growing season in essentially every year (Heck and Cowling, 1997).
- C4. Substantial year-to-year and month-to-month variability in daily maximum ozone concentrations was observed within the SOS region, and was attributed to climate fluctuations and variation in emissions, respectively (Vukovich, 1998).
- C5. The spatial variability of ozone concentrations in the SOS region suggests that multiple monitoring sites in urban, suburban, and rural sites may be necessary to detect maximum ozone concentrations in a reliable way (Imhoff and Valente, 1995).
- C6. Ozone concentrations in the SOS region are positively correlated with temperature and negatively correlated with amount of precipitation (Vukovich, 1994).
- C7. On a climatological scale, interannual variations in either temperature or cloud cover explained about 80 percent of the variability in daily maximum ozone concentrations during the time period 1981-1990 (Vukovich, 1998).
- C8. Multiple-regression models of ozone concentration with air temperature, wind speed, relative humidity, and ozone concentration during the previous 24 hours can provide a useful method for decreasing the effect of meteorological variability on the year-to-year ozone concentration trends (Vukovich, 1994).
- C9. In examining short-term (1-5 days) ozone episodes, the most persistent relationship between ground-level ozone concentrations and weather parameters was between ozone concentrations and wind speeds, with stagnation periods leading to the highest daily maximum ozone concentrations. When a 15-year-long time series of ozone concentrations was compared with the same 15-year-long time series of meteorological patterns, however, the most persistent relationship was between ozone and cloud cover. When days with ozone concentrations equal to or greater than 100 ppb were extracted from the 15-year time series and examined separately, only wind speed and cloud cover were important. Neither temperature nor dew point was important on these high ozone days (Vukovich, 1998).

- C10. Regional NO_x and/or VOC emission control strategies may decrease the frequency of ozone exceedance events, but episodic NO_x and/or VOC control strategies probably will be necessary to eliminate exceedance events completely (Vukovich, 1997).

These scientific findings (C1-C10 above) suggest that while the ozone problems in the ten SOS states and the mid-Atlantic and northeastern states and southeastern provinces of Canada have some common features, e.g., correlation of peak ozone with temperature and stagnation conditions, there also are significant differences that suggest application of different control strategies in the SOS region than in some other parts of the eastern US and southeastern Canada. Thus, concern in the northeastern and mid-Atlantic states and southeastern Canada logically should focus more often on short-term ozone episodes that generally are confined within urban areas and their effects on human health. In contrast, concern in the SOS region logically should focus more often on both short-term urban ozone episodes and also on the high and pervasive regional ozone concentrations and the effects on vegetation when ozone concentrations exceed 60 ppb). In terms of control strategies, emission controls in the mid-Atlantic and especially the northeastern states are justifiably limited mostly to NO_x *and VOC sources within the non-attainment area, whereas the situation in the SOS region suggests application of controls on both regional and urban scales.*

- C11. From 1982 to 2001, US national average ambient one-hour ozone concentrations decreased by about 18 percent and the corresponding 8-hour average ozone concentrations decreased by about 11 percent (USEPA, 2002). Also, one-hour exposures decreased for the nation as a whole from 1982 to 2001 on average by about 18 percent. The largest 20-year-trend decreases in ozone concentrations were observed in the northeastern states and the far western states (24-32 percent) and the smallest decreases were observed in the southeastern states and mid-Atlantic states (7-10 percent) (USEPA, 2002).

This scientific finding (C11 above) underscores the seriousness of the ozone problem in the SOS region and the need for a comprehensive research program addressed specifically to ozone problems in this region.

- C12. From 1982 to 2001, estimated annual emissions of VOC in the United States as a whole decreased by about 16 percent, but estimated annual emissions of NO_x increased in the United States as a whole by about 9 percent (USEPA, 2002).

Given the dual role of NO_x *in both the formation and in the destruction of ozone in the atmosphere, it is not clear whether it was the decrease in VOC emissions or the increase in* NO_x *emissions that caused the downward trend in ozone concentrations cited in C13 above.*

- C13. No significant improvement in total exposure to ozone was observed in either rural areas or urban areas of the SOS region between 1980 and 1992 (Vukovich, 1994; Meagher and Parkhurst, 1996).

This 12-year period was one of substantial growth in human population and vehicle use in the SOS region, but was also a period of substantial investment in VOC controls and cleaner (lower emission) vehicles. It is discouraging that no significant decrease in average ozone concentrations occurred despite these investments, but it is also encouraging that there were no ozone increases caused by the increased growth. Evidently, the increased growth in human population and vehicle use and the increased investment in ozone controls during that period have substantially offset each.

- C14. Air concentrations of reactive nitrogen (NO_y) (i.e., unreacted and reacted NO_x; or, to be more specific, mainly NO, NO_2, nitric acid, PAN, organic and inorganic nitrates, and occasionally nitrous acid) generally are relatively low in rural parts of the SOS region – usually less than 4 ppbv (Kleinman et al., 1994).

Because NO_y *concentrations generally were below 4 ppbv in rural areas of the SOS region, and also because both ozone and* NO_y *concentrations decrease with decreasing* NO_x*, concentrations, this scientific finding (C14 above) suggests that ozone production in rural parts of the SOS region generally are* NO_x*-limited. Thus, the optimum strategy for decreasing regional ozone accumulation in the SOS region is control of those* NO_x *sources that impact the SOS region's rural areas.*

- C15. The adverse effects of ozone on agricultural crops, forest and shade trees, and other natural vegetation when ozone concentrations exceed 60 ppbv indicate that a secondary (welfare-based) National Ambient Air Quality Standard (NAAQS) for ozone – a standard that would be different in form from the present one-hour or eight-hour primary (human health-based) NAAQS – would provide an increased margin of safety for agricultural crops, forest and shade trees, and natural vegetation against the injurious and economic-damaging effects of ozone on ecosystems. The often-proposed SUM06 secondary standard for ozone was the consensus choice recommended by ecologists who participated in an SOS workshop on a possible secondary standard for ozone (Heck and Cowling, 1997; Chameides et al., 1997).

Adoption of a secondary standard for ozone (such as the often proposed SUM06 standard) with a more moderate ozone concentration (e.g., 60 ppb) but a longer 3-month or growing-season long average time will cause large portions of the rural parts of the SOS region and other states to be designated non-attainment areas. These possible changes also will tend to shift the major focus of concern about ozone effects from public health alone, to human and ecological health. It also will tend to shift the major concern about precursor emission controls from urban areas alone, to include also both suburban and rural areas, as is already the case in the European Union.

- C16. The ozone concentration data in EPA's Aerometric Information Retrieval System (AIRS) are largely inadequate for identifying rural areas that would be in non- attainment if a welfare-based secondary standard such as SUM06 were adopted by the USEPA or any of the states in the US or eastern provinces of Canada. More appropriate data, covering rural areas, are those taken in SOS' Spatial Oxidants Network (SON) and EPA's Clean Air Status and Trends Network (CASTNet) (Chameides et al., 1997).

III. OZONE PRECURSOR EMISSIONS

Unlike other photochemical pollutants, including acid pollutants and aerosols, the precursors of ozone, VOC and NO_x, are peculiar in that they not only produce ozone but they also destroy it. As a consequence, ambient ozone does not depend linearly on either VOC or NO_x. Ozone accumulates in concentrations that affect human health (>80 ppb) and ecosystems (>60 ppb) when the ambient concentrations of the two precursors are at an optimum ratio and is suppressed when either one of the two precursors is in large excess relative to the other. For this reason, it is critically important that VOC and NO_x emissions in all non-attainment regions be characterized both with respect to their absolute rates and also with respect to the relative ambient concentration ratios they create in the atmosphere. Such characterizations are extremely difficult in the SOS region mainly because of the abundance of biogenic VOC emissions and of the complex influences on emissions of the unusually intensive solar radiation, temperature, and relative humidity conditions in that region. The SOS program aimed at collecting improved data mainly on concentrations and variability of the VOC and

NO_x emissions from motor vehicles and other anthropogenic sources, and from natural sources, with emphasis on VOC emissions from vegetation and NO_x emissions from well fertilized crops and pastures.

For this reason, it is important that VOC and NO_x emissions in non- attainment areas, and in vertically and horizontally upwind areas, be characterized both with respect to the absolute amounts of NO_x and VOC emissions and also with respect to the relative ambient concentration ratios they create in non-attainment atmospheres. Such characterizations are difficult to achieve in the SOS region mainly because of the abundance of highly reactive biogenic VOC emissions (such as isoprene) and also because of the complex influences on emission rates of the intensive solar radiation, temperature, and relative humidity conditions in the SOS region. The SOS research program was designed to produce improved data and information regarding the rates, amounts, sources, and ratios of VOC and NO_x emissions from natural biogenic sources, motor vehicle sources, electric utility sources, and other natural and anthropogenic sources.

During the years since initiation of SOS, the ozone and particulate matter precursors of concern and both natural (N) and anthropogenic (A) sources have become progressively more numerous:

ANO_x + AVOC (Haagen-Smit, 1952)
ANO_x + AVOC + NVOC (Chameides et al., 1988)
ANO_x + AVOC + NVOC + NNO_x (Valente & Thornton, 1993)
ANO_x + AVOC + NVOC + NNO_x + ACO (Daum et al., 2000b)
ANO_x + AVOC + NVOC + NNO_x + ACO + CH_4 (Goldan et al., 2000)
ANO_x + AVOC + NVOC + NNO_x + ACO + CH_4+ N/ANH_3 + ASO_2 (Chameides et al., 1999)

A. Biogenic and Other Natural Sources of Ozone Precursors

Investigation of the occurrence and role of biogenic and other natural precursors of ozone has been one of the two main research themes in the SOS research program (the other was the development and application of observational methods and observation- based models). Such emphasis was justified by: 1) The unusually large abundance of biogenic VOC in the SOS region, 2) The difficulty in obtaining reliable biogenic VOC emission inventory data, and 3) The extremely complex role that such organics play in the development of ozone control strategies – for example, the question of whether ozone attainment in an ozone non-attainment area should be pursued through VOC control or NO_x control is closely linked to the role of the biogenic VOC in the SOS region.

The SOS program included studies of nearly every aspect of biogenic VOC role in the photochemical ozone pollution problem including: 1) the extremely important issue of land use, 2) vegetation species identification, 3) biogenic VOC emission rates, 4) atmospheric chemistry of biogenic VOC – especially isoprene, and 5) the effect of biogenic VOC emissions on VOC or NO_x control requirements in ozone non-attainment areas. Given the fact that biogenic VOC are ubiquitous – they occur in urban areas in both the eastern and western regions of the US, Canada, Mexico, and other parts of the world – the biogenic research findings from the SOS should be of general interest to air quality managers.

The biogenic VOC compounds studied by SOS scientists included:

1) A wide variety of hydrocarbons including both alkanes and alkenes (especially isoprene from hardwood forest trees, ethylene from many different species of healthy and diseased plants, and methane from plant, animal, and insect sources);

2) Many aromatic VOC, especially alpha- and beta-pinenes from softwood (coniferous) trees, wind-downed and ice damaged conifers, and from harvesting, chipping, sawing, drying, and other processing of softwood timber in pulp, paper, lumber, and plywood manufacturing,

3) A large variety of oxygenated biogenic VOC including carbon monoxide from wild fires and controlled burning operations, aldehydes (especially formaldehyde), both saturated and unsaturated alcohols (especially methanol and ethanol), ketones, and organic acids, and

4) Alkyl sulfides.

- BG1. Vegetation is a major source of reactive volatile organic compounds (VOC) in both urban and rural areas throughout the SOS region (Chameides et al., 1988; Guenther et al., 1993, 1995, 1996a, 1996b; Guenther 1997).

- BG2. Biogenic hydrocarbons (mainly isoprene and monoterpenes) play a major role in ozone formation and accumulation in both urban and rural areas in large parts of the eastern United States, especially in the summertime (Chameides et al., 1988; Williams et al., 1997; Kleinman et al., 1997; Frost et al., 1998; Helmig et al., 1998; Roberts et al., 1998; Nouaime et al., 1998; Starn et al., 1998a, 1998b).

The implication of this finding is that pursuing an ozone abatement strategy that ignores the effect of natural VOC emissions can incur substantial error.

- BG3. Based on measurements made at the Rural Oxidants in the Southern Environment (ROSE) Site in 1990, isoprene was the largest OH-consumer VOC species (the fraction of OH reacting with isoprene was 0.71) (Cantrell et al., 1992).

The term "reactivity" in Finding BG3 is meant to describe reactivity in terms of reaction with the OH radical, and not reactivity in terms of ozone production efficiency. Isoprene has a very high ozone production reactivity, which it displays in VOC-limited atmospheres, but isoprene also has a very large ozone inhibition/destruction reactivity, which it displays in ozone-rich and NO_x*-deficient atmospheres.*

- BG4. Isoprene is mainly of biogenic origin and accounts for a large part of the total VOC reactivity in the SOS region. Various species of oaks are the most important biogenic sources of isoprene (Geron et al., 1994, 1995, 1997).

- BG5. The temperature dependence of isoprene emissions arises from the temperature response of the enzyme isoprene synthase. Due to the progressive effect of warm temperatures on the activation and stimulation of isoprene synthase, the highest emissions of isoprene occur in the late summer (Monson et al., 1994; Wildermuth and Fall, 1996)

- BG6. Water stress, temperature, and light intensity all have substantial effects on isoprene emissions from vegetation. These effects are especially notable in leaves of kudzu plants, which are very common in many parts of the SOS region. In kudzu, isoprene emissions typically represent a significant fraction of the total carbon fixed in photosynthesis (as much as 0.67 grams of isoprene per gram of carbon fixed). Also, isoprene emission rates in kudzu are more sensitive to temperature than that in other species of isoprene-emitting plants (Loreto and Sharkey, 1993a, 1993b; Sharkey and Loreto, 1993; Fang et al., 1996; Wildermuth and Fall, 1996).

- BG7. Isoprene shows large regional and seasonal variations in emission rates, especially on small temporal (e.g., diurnal) and spatial (e.g., a few km^2) scales. Because of the short lifetime of isoprene in the atmosphere, a few hours or less, these variations are important to predict accurately (Guenther et al., 2000).

- BG8. Concentrations of biogenic VOC decrease slowly with altitude in the mixed layer while surface layer concentrations show much more variability, based on tethered balloon measurements at ten North American sites and one Amazon site (Greenberg et al., 1999).
- BG9. Isoprene concentrations in the planetary boundary layer (mixed layer) of the atmosphere remain fairly constant in the middle of the day, in contrast to isoprene concentrations at canopy level, which continue to increase until evening. Daytime emissions, which increase with temperature and solar radiation, are balanced by changes in entrainment and oxidation (Greenberg et al., 1999).
- BG10. Measurements made at 40-100 meters above ground yield the most reliable measures of average boundary layer concentrations of reactive organics such as isoprene (Andronache et al., 1994).
- BG11. Estimates of isoprene emission fluxes based on ambient concentrations of isoprene and monoterpene emissions measured at two rural sites in Alabama and Georgia in 1990 were within a factor of two of fluxes predicted based on enclosure measurements and landscape data (Guenther et al., 1996b).
- BG12. Oxygenated organic compounds (mainly aldehydes and alcohols) also contribute significantly to air concentrations of VOC in the SOS region. The identification of oxygenates produced from isoprene photooxidation, such as methylvinylketone (MVK) and methacrolein (MACR), at rural sites is consistent with a photochemical mechanism involving their production from isoprene and their subsequent photooxidation. Photooxidation of isoprene is probably a major local source of peroxyacetyl nitrate (PAN) arising from production of MVK and methylglyoxal and their subsequent oxidation to produce peroxyacetyl radical, the immediate precursor of PAN (Lee and Zhou, 1993, 1994; Montzka et al., 1993; Kleinman et al., 1994; Lee et al., 1995, 1998; Stroud et al., 2001).
- BG13. Simultaneous measurements of peroxymethylacrylyl nitrate (MPAN), peroxypropionyl nitrate (PPN), and peroxyacetyl nitrate (PAN) provide a method for apportioning photochemically produced ozone into a fraction resulting from oxidation of biogenic VOC (mainly isoprene) and a fraction resulting from oxidation of anthropogenic VOC (Nouaime et al., 1998).
- BG14. The contribution of biogenic emission sources to ambient VOC concentrations can be determined quantitatively through radiocarbon (^{14}C) measurements (Lewis et al., 1999).

Scientific finding BG14 is extremely important because it identifies a reliable method for determining by direct measurements what fraction of the ambient VOC are from recently fixed carbon (and therefore biogenic sources), compared with historically fixed (and therefore fossil-fuel-based, anthropogenic sources) of carbon. Reliable measurement of ambient biogenic VOC helps to evaluate or obtain reliable biogenic VOC emission inventory data.

- BG15. Destruction of about 20% of the urban forests of Atlanta, GA from 1979-1988 caused an approximate 2° C intensification of Atlanta's urban heat island and may have resulted in a net increase rather than decrease in Atlanta's total biogenic emissions of isoprene (Cardelino and Chameides, 1990).

City planning and construction practices that modulate the intensity of urban heat islands, through placement of "green spaces " in the urban core of cities and use of highly light-reflective building materials, may aid in ozone pollution abatement by decreasing urban temperatures and thus decreasing emissions of biogenic (*as well as anthropogenic, evaporative) VOC.*

- BG16. More detailed studies of biogenic emissions of alkane and aromatic VOC, including research at SOS sites in Georgia, showed that biogenic emissions are much less than those reported in an earlier national inventory of emissions of these same classes of biogenic VOC. The primary factor in previous overestimates was misinterpretation of chromatographic data in the earlier study (Guenther et al., 2000; Zimmerman, 1979).

- BG17. Biogenic emissions of isoprene are more important to urban ozone production in Nashville, TN (Roberts et al., 1998) and Atlanta, GA (Chameides et al., 1992), than in Houston, TX (Wiedinmyer et al., 2001). The major differences in biogenic emissions between Houston and both Atlanta and Nashville may be explained in part by the greater abundance of isoprene-emitting trees (mainly oak forests) in the land cover of the suburban and rural areas surrounding Atlanta and Nashville than in similar rural areas near Houston.

- BG18. Much of the photochemically produced ozone in the southern part of the multi- state Nashville/Middle Tennessee study area resulted from oxidation of biogenic VOC. This percentage decreased from south to north within the study region (Goldan et al., 2000).

- BG19. Much of the spatial variability in air concentrations of isoprene and NO_x can be explained by differences in patterns of land use (mainly crop vs. forest), forest type (especially amount of oak), and meteorological conditions (mainly temperature and wind speed) (Thornton et al., 1997).

- BG20. NO emissions from well-fertilized soils used for row crops and intensively managed pasture lands are a significant regional source of NO emissions in parts of the SOS region which are dominated by agriculture. NO emission rates: 1) increase significantly after light rains, 2) increase exponentially with temperature, and 3) are highest in soils with high nitrate fertilizer application rates (Williams and Fehsenfeld, 1991; Williams et al., 1992; Meyers and Baldocchi, 1993; Valente and Thornton, 1993; Kim et al., 1994; Valente et a1., 1995; Thornton and Shurpali, 1996; Davidson and Kingerlee, 1997; Potter et al., 1997; Thornton et al., 1997).

- BG21. The average summertime contribution of soil NO to the overall NO inventory for nine states within the southeastern US (Alabama, Florida, Georgia, Kentucky, Mississippi, North Carolina, South Carolina, Tennessee, and Virginia) was 4.1 percent (Thornton et al., 1997).

The NO released from agricultural activities plays an important role in the photochemical air pollution problems; namely, it contributes significantly to regional build-up of ozone and particulate nitrates by reacting photochemically with biogenic VOC. Viewed in this respect, agricultural activities may be characterized as a quasi-anthropogenic source of pollution.

- BG22. Urban-metropolitan soils were not an important source of soil NO_x during the Nashville/Middle Tennessee Ozone Study (Thornton et al., 1997).

- BG23. For the middle Tennessee non-attainment area, soil biogenic NO_x contributed from 7 to 10 percent of the daily average NO_x budget during the months of June through August, 1995. But measurements made during the hottest days of July 1995 indicated that soil biogenic sources contributed more than 17 percent of the total NO_x emissions for the state of Tennessee (Thornton et al., 1997).

- BG24. NO emissions from lightning, although still highly uncertain in amount, cannot be ruled out as a source of ozone precursors in the SOS region. Lightning appears to be a negligible source of NO_x on large space (regional) and time (weeks to months) scales but can be a significant source of NO_x on smaller space and time scales in the SOS region (Biazar and McNider, 1995).

- BG25. Emissions from distant forest fires can contribute to regional concentrations of carbon monoxide and to regional accumulations of high ozone concentrations. This conclusion is based on measurements made during the Nashville/Middle Tennessee Ozone Study and back-trajectory modeling results for July 1995 that showed an influence of Canadian forest fires on CO and ozone concentrations in both the central and eastern US; ambient ozone concentrations were increased by 10-30 ppb (McKeen et al., 2002; Wotawa and Trainer, 2000).

The policy implication of this finding is that, in addition to local sources and regional sources of ozone precursors, occasionally far-distant sources of precursors can contribute to ozone accumulation in a given region.

B. Motor Vehicle and Other Anthropogenic Sources of Ozone Precursors

Motor vehicles are the most important source of VOC and NO_x emissions in most urban areas throughout the world. The National Academy of Science "1999 Rethinking" report expressed concerns about automobile emissions inventories and recommended both that tunnel studies of on-road motor vehicle emissions be conducted, and that remote sensing methods be used in such studies (NAS, 1999). The anthropogenic emissions part of the SOS program focused mainly on such tunnel studies, on refining methods for traffic volume measurement, on studies of driving pattern and roadway factors and their effects on motor vehicle emissions, and also on determining and characterizing other anthropogenic sources, especially power plants in the case of NO_x and other industrial emissions in the case of VOC.

Noteworthy scientific findings from SOS' anthropogenic emissions studies are presented below.

- AN1. Motor vehicles are a major human source of ozone precursor chemicals in urban and rural areas throughout the SOS region (LeBlanc et al., 1995).
- AN2. Direct on-road measurements of speciated VOC, NO_x, and CO emissions were made in the Fort McHenry Tunnel under Baltimore Harbor and the Tuscarora Tunnel on the Pennsylvania Turnpike during the summer of 1992. These on-road measurements showed that the MOBILE4.1 and MOBILE5.0 models provided reasonably good estimates (most of them within ± 50%) of actual VOC, NO_x, and CO emissions for the fleet of passenger cars and light-duty trucks as well as for the fleet of heavy-duty trucks (gasoline- and diesel-powered) using these two interstate highway tunnels (Gertler et al., 1996; Pierson et al., 1996; Robinson et al., 1996).

In interpreting this scientific finding (AN2), it should be recognized that neither the relatively new and well-maintained fleets of vehicles using these tunnels, nor the manner in which they were operated during these tunnel experiments (relatively constant interstate highway speeds), are fully representative of the total fleet and more variable conditions of operation of motor vehicles, especially in many urban areas of the United States.

- AN3. VOC emissions from light-duty passenger cars and trucks were very different from those emitted by heavy-duty gasoline-powered and diesel trucks. More than half the VOC from heavy-duty vehicles contained more than 10 carbon atoms per molecule, while only 10 to 20 percent of the VOC from light-duty vehicles contained more than 10 carbon atoms (Zielinska et al., 1996).

These differences in chemical composition of VOC described in AN3 above were not predicted by the MOBILE4.1 or MOBILE5.0 emissions models. It is also noteworthy that the high molecular weight VOC emitted by heavy duty vehicles have a smaller ozone production efficiency than the lower molecular weight VOC emitted by light-duty vehicles. But these high molecular weight VOC also produce larger amounts of photochemically induced particulate matter.

- AN4. Roadway grade had a large effect (uphill values were 100% greater than downhill values) on both the amount of CO, VOC, and NO_x emitted and on the composition of VOC emitted by passenger cars and light-duty and heavy-duty trucks (Pierson et al., 1996).

These large effects of roadway grade on the amount and chemical composition of motor vehicle emissions should not be ignored in developing the next generation of motor vehicle emissions models, or in using these models to prepare mobile source emissions inventories for use in State Implementation Plans.

- AN5. During the SOS intensive measurement campaign in 1992, traffic counters were found to be a very useful tool for developing day-specific estimates of mobile source emissions of VOC and NO_x. These day-specific estimates were significantly different from those obtained using the defaults contained in the Emissions Preprocessor System Version 2 (EPS2) of the Urban Airshed Model. These discrepancies included different temporal patterns of emissions as well as different magnitudes of total emissions. In general, the EPS2 defaults tended to overestimate emissions, especially during the morning and evening rush hours in Atlanta and Nashville (Cardelino, 1998).
- AN6. Acceleration, roadway grades, and other heavy engine loads leading to "power enrichment" significantly increased motor vehicle emissions and should be accounted for in mobile source emissions inventories. On-road tests on the urban vehicle fleet in Atlanta, GA indicate that power enrichment occurred about 1 percent of the fleet's total operating time and thus constituted a significant part of VOC emissions in the Atlanta metropolitan area (Fehsenfeld et al., 1994).
- AN7. In the Atlanta metropolitan area, the temporal distribution of motor vehicle emissions was strongly dependent on the area (urban or rural), the type of road (interstate, principal, secondary or local), and the day of the week during which the measurements were made. Motor vehicle emissions were substantially different on week days (Monday through Thursday) compared to weekend days (Friday through Sunday). However, ozone predicted by models with customary resolution did not reflect comparable variability (Cardelino, 1998).
- AN8. The vehicle classification distribution by road type obtained from traffic counters in Atlanta in 1992 was significantly different from the default distribution contained within the Mobile5a computer model. When applied to a specific-day inventory, the use of observed data, as opposed to default data, produced decreases in emissions that varied by 8 percent for VOC, 9 percent for CO, and 19 percent for NO_x in Atlanta (Cardelino, 1998).

- AN9. Compared to a typical summer day, the day-to-day range of mobile emission variability was 26 to 28% for urban areas and 13 to 19% for rural areas around Atlanta (Cardelino, 1998).

- AN10. The daily variability in point-source NO_x emissions was found to be as much as 24 percent with respect to typical summer day emissions in the Atlanta metropolitan area. The daily variability of point-source VOC emissions was as large as 28 percent, but their contribution to total VOC emissions in Atlanta was not very significant (W. Chang et al., 1996).

This substantial day-to-day variability of both the motor vehicle emissions and the point source emissions make it imperative that day-specific emission inventory data be used in modeling simulations of control strategies.

- AN11. Numerical simulations suggest that changes in point-source NO_x emissions can have either a positive or a negative effect on ambient ozone concentrations, depending on the geographical location of the NO_x sources (rural vs urban areas) (M. Chang et al., 1996).

The extremely important implication of this scientific finding (AN11) and findings from other studies is that because of the ozone-destruction effect of NO_x *under VOC-sensitive conditions and the widespread occurrence of such conditions (e.g., within intensely urbanized areas), air quality managers should view* NO_x *control with caution.*

- AN12. Use of day-specific roadway traffic information resulted in significantly different emissions estimates for motor vehicles in the 1992 SOS Intensive Field Study in Atlanta and the 1995 SOS Nashville/Middle Tennessee Ozone Study than those obtained using the defaults contained in the Emissions Preprocessor System Version 2 (EPS2) of the Urban Airshed Model. In general, the defaults tended to overestimate emissions especially during the morning and evening rush hours (Cardelino, 1998).

The important implication of this scientific finding (AN12) is that the emission inventory data used in model simulations of ozone and PM concentrations should be day-specific rather than default data.

- AN13. Observations of the amounts, types, and variability of CO, VOC, and NO_x emissions from motor vehicles in Houston, TX – including passenger cars, light-duty trucks, and both diesel-powered and gasoline-powered heavy duty trucks – were essentially identical to similar observations in other urban areas in the southern US such as Nashville, TN and Atlanta, GA (Allen and Durrenberger, 2003).

- AN14. VOC and NO_x emissions in industrial areas of Houston, Texas, showed substantial spatial and temporal variability (Allen and Durrenberger, 2003).

One important implication from this scientific finding (AN14) *is that model simulations of ozone problems in such areas should be conducted using high spatial and temporal resolution (i.e.,* 1 *km or less cell size, and 1-hr averaging time).*

- AN15. NO_x, SO_2, and CO_2 emissions from fossil-fueled power plants in eastern and central Texas were accurately estimated in inventories, but CO emissions show significant discrepancies between direct measurements and inventory estimates at some power plants (Nicks et al., 2003).

- AN16. The uniquely rapid formation and accumulation of ozone ("ozone spikes") in Houston, Texas was caused primarily by photochemical processing of industrial emissions (Daum et al., 2003; Ryerson et al., 2003; Allen and Durrenberger, 2003).

- AN17. Burning of biomass both in open fields and in pulp and paper mills was identified as an important source of NO_x in various rural parts of the SOS region (Buhr et al., 1995b).

An important consequence of scientific finding AN17 is the large contribution of such NO_x *to regional ozone accumulation.*

C. Emissions Inventories and Evaluation Methods (EIE)

Reliable ozone precursor emissions inventories are indispensable in the development and implementation of ozone management strategies. Such data are obtained either through direct measurement of precursor emission rates and amounts, or through calculations based on guidelines issued by the USEPA. Different applications of inventory data require different temporal and spatial resolutions, and such requirements are not always met. This latter problem is particularly serious in development of State Implementation Plans for ozone through use of three- dimensional grid models. SOS efforts in this arena were aimed at assessing and improving the reliability of emission inventory data.

Noteworthy scientific findings from SOS' emissions inventory improvement research studies are presented below.

- EIEl. Certain aspects of the guidance currently followed in developing emissions inventories of ozone precursor chemicals in rural and urban areas of the SOS region:
  1) Do not accurately reflect the land-use distributions in many southern cities;
  2) Are not consistent with direct observations of NO_x, VOC, and CO in rural and urban areas; and/or
  3) Do not properly quantify biogenic and other natural emissions of VOC and NO_x (Fehsenfeld et al., 1994).
- E1E2. The fraction of ozone produced from photooxidation of isoprene decreased from south to north during SOS' 1994-95 and 1999 field measurement campaigns in the multi-state area centered over the Nashville, TN Metropolitan area. This decrease was predicted by the BEIS2 emission model (Ryerson et al., 1998).
- EIE3. Ground-based measurements of biogenic emissions of NO_x from soils and isoprene emissions from vegetation agreed well with NO_x and isoprene emissions estimates provided by BEIS2, a second-generation mathematical model for estimating biogenic sources of VOC and NO_x (Geron et al., 1994; 1997).
- EIE4. Boundary layer concentrations of isoprene and NO_x varied greatly from one geographical locale near Nashville, Tennessee to another. BEIS2 estimates of this spatial variability agreed well with aircraft measurements of boundary layer isoprene concentrations when land use, forest type, canopy temperature, and wind speed above the canopy were considered (Pierce et al., 1998).
- EIE5. BEIS2 uses more temporally resolved environmental corrections (hourly versus monthly), more spatially resolved vegetative cover (county-level versus latitude/longitude grid cells), and more resolved vegetative emission factors (genus versus broad biome classes) than BEIS1. Higher isoprene emissions are obtained with BEIS2, which are about a factor of 5 higher than BEIS1 during warm, sunny conditions (Pierce et al., 1998).

- EIE6. When BEIS2 was used with the RADM model, areas of elevated concentrations of ozone went from being VOC-sensitive to NO_x-sensitive across much of the RADM modeling domain. The new system yielded better agreement with observations. Using BEIS2 in RADM resulted in mean near-surface isoprene predictions that were slightly lower (25%) than observed (Pierce et al., 1998).
- EIE7. Isoprene emissions derived from inverse modeling were 2 to 10 times higher than any of the accepted BEIS-based emission estimates for Atlanta (M. Chang et al., 1996, 1997).
- EIE8. Isoprene emissions significantly increased the concentration of ozone observed within the plumes of nitrogen oxides emitted from large point sources (M. Chang et al., 1996, 1997).
- EIE9. Uncertainties in mixing height were not likely to be responsible for underpredictions of isoprene in the Urban Airshed Model seen in a modeling study in Atlanta (M. Chang et al., 1996, 1997).
- EIE10. Inhomogeneities in the spatial distribution of emissions can severely limit the application of the inverse method for analysis of source-receptor relationships (M. Chang et al., 1996, 1997).

To the limitations of the "inverse method," described in scientific finding EIE10, one may add the uncertainties introduced by the fast disappearance of isoprene in air in reactions with OH and ozone.

- EIE1l. Correlations between SO_2, CO, and NO_y in the Nashville urban area indicated only a minor impact from power plant emissions. Plume-like excursions of high SO2 occurred less than 5% of the time during the Nashville-Middle Tennessee Ozone Study (Kleinman et al., 1998).
- EIE12. The 1990 NAPAP emission estimates for VOC and NO_x emissions can be brought into reasonable agreement with the values observed during the 1995 SOS Nashville Intensive if the VOC emission rate is decreased by 30 percent and the CO emission rate is increased by about 35 percent (Kleinman et al., 1998).

III. CHEMISTRY OF OZONE FORMATION

Unlike the traditional laboratory (smog chamber) approach to studying atmospheric chemistry, the approach taken in SOS' research program was use of direct field observational methods. Key atmospheric chemistry issues studied by SOS included:

1) The relative ozone-production efficiencies of VOC and NO_x in various environments – an issue that is linked to the relative ozone-management benefits associated with VOC and NO_x controls;
2) The existence of predictive relationships between ambient ozone concentrations and concentrations of VOC and NO_x photo-degradation products; and
3) The chemical mechanism of the atmospheric photooxidation of biogenic VOC, especially isoprene.

The SOS program was especially effective in developing innovative observational methods for:

1) Defining ambient condition-regimes for which decreases in ozone exposures should be pursued through VOC controls or though NO_x controls;
2) Determining the ozone-production efficiencies of NO_x from different types and sizes of sources, and

3) Evaluating the accuracy of atmospheric VOC-photooxidation mechanisms by determining both the identity and yield of photooxidation products.

A. General Features of Ozone Chemistry (OC)

General features of ozone chemistry studied by SOS included:

1) Dynamic variations of ozone and ozone precursor concentrations in urban plumes, power plant plumes, and rural or other well-vegetated areas in the SOS region,
2) Reactivities of the various types of VOC emissions,
3) Identity and abundance of reaction products from photooxidation processing of these emissions, and
4) Differences between these processes in the SOS region and other regions of the US and Canada,

These four aspects of the ozone chemistry were investigated by SOS scientists in the belief that scientific findings from these studies will provide valuable evidence regarding the causes of ozone non-attainment problems in the SOS region and other parts of the US, Canada, and Mexico.

Noteworthy scientific findings from SOS' studies of ozone chemistry are summarized below.

- OC1. In the SOS region, rates of ozone accumulation, and rates of NO_x removal from air near the ground, were more rapid than in other parts of the United States. These differences in rates were caused in part by the higher air concentrations of biogenic VOC in the SOS region than in other regions within the US (Fehsenfeld et al., 2003)

This scientific finding (OC1) suggests two conflicting effects of biogenic VOC on ozone: 1) a positive, direct effect that favors ozone production, and 2) a negative and indirect effect – removing NO_x (the *precursor that catalyzes the ozone formation) and thus inhibits ozone production. One important implication of these conflicting effects is that in atmospheres with abundant* NO_x*, biogenic VOC enhance ozone formation, whereas in* NO_x*-deficient or* NO_x*-depleted atmospheres, biogenic VOC inhibit ozone formation.*

- OC2. Various oxygenated species of VOC, including methylvinyl ketone (MVK), methacrolein (MACR), and peroxyacetyl nitrate (PAN), are produced as a result of photochemical oxidation of isoprene. Photochemical oxidation of isoprene is a major source of peroxyacetyl nitrate (PAN) in the SOS region (Lee and Zhou, 1993, 1994; Montzka et al., 1993; Kleinman et al., 1994; Lee et al., 1995, 1998).

- OC3. Maximum ozone concentrations in the Atlanta metropolitan area occur when plumes from power plants or other point sources are embedded in a broader urban plume which in turn is embedded in a regional "tide" of ozone resulting in part from the interaction of NO_x with the "sea" of isoprene in rural areas surrounding isolated metropolitan areas (Imhoff et al., 1995; St. John et al., 1998; St. John and Chameides, 2000).

- OC4. Isoprene chemistry dominated the formation of ozone in forested rural areas near Nashville, Tennessee during the 1995 study (Helmig et al., 1998; Starn et al., 1998a, 1998b; Roberts et al., 1998; Frost et al., 1998).

- OC5. The removal rate of VOC (rate of decrease in concentrations as the Nashville urban plume aged) was proportional to the reactivity of the VOC under consideration. Thus, highly reactive VOC (such as isoprene) showed more rapid rates of decrease in concentration as an urban plume aged than less reactive VOC (Nunnermacker et al., 1998).

- OC6. Anthropogenic VOC (including CO) accounted for about two-thirds of OH - VOC reactivity during the 1995 Nashville/Middle Tennessee Ozone Study (Daum et al., 2000b).

The OH- VOC reactivity is the reactivity of VOC with respect to their reaction with OH radicals. It is different from and unrelated to the ozone-production reactivity of VOC.

- OC7. Chlorine was shown to enhance ozone production in chamber experiments with captured Houston air, although it appears not to be the dominant mechanism of ozone formation in Houston (Tanaka et al., 2003a, 2003b).
- OC8. In the southeastern US, the highest ozone concentrations occur under stagnation conditions. Model calculations and observations show that stagnation conditions promote VOC sensitivity. In Nashville, the sensitivity of peak ozone concentrations is somewhere between the strongly VOC-sensitive condition typical of Los Angeles and the strongly NO_x-sensitive condition typical of rural areas in most US states. In all likelihood, a dual (NO_x and VOC) control strategy may be required for efficient and cost-effective management of ozone concentrations in the SOS region. Such a strategy will have to take into account the role of biogenic VOC emissions since their emissions cannot be controlled (Valente et al., 1998; Banta et al., 1998).
- OC9. Ozone photochemistry was rapid in the Nashville urban plume during the Nashville/Middle Tennessee Ozone Study. The urban plume examined on July 3 and on July 18, 1995 consumed about half of its NO_x and half its supply of anthropogenic hydrocarbons within two hours (Nunnermacker et al., 1998).
- OC10. Biogenic VOC became more important as the Nashville urban plume was advected into the rural surroundings during the 1995 Nashville/Middle Tennessee Ozone Study. As the urban plume moved into surrounding rural areas the biogenic VOC contribution to ozone production increased from about 25 percent to about 36 percent while the anthropogenic contribution to ozone production decreased from about 55 percent to about 44 percent (Nunnermacker et al., 1998; Luria et al., 2000).
- OC11. During a stagnation episode on July 18, 1995, lidar cross-sections and profiles and wind profiler data showed that the layer of ozone aloft over Nashville mixed out during the day and became part of the surrounding suburban and rural mixed layer during the next day (Banta et al, 1998).
- OC12. Measurements made at ground level at a suburban Tennessee site on July 1, 1994 showed that of the 120 ppbv of ozone recorded on that date, 80 ppb was due to vertical transport of ozone-rich air from aloft. This ozone-rich layer of air was a remnant of the previous day's photochemistry. An additional 40 ppb was added due to the current day's urban plume. These observations demonstrated that urban ozone can impact next day's ozone at downwind suburban locations (Baumann et al., 2000).

- OC13. Based on modeling studies of ozone formation within an urban plume as it advects and mixes with the background atmosphere, Duncan and Chameides (1998) made the following conclusions.
    1) A given day's photochemistry often builds on a regional background of ozone that was created in previous days.
    2) Regional background ozone almost always is NO_x-sensitive, and often cannot be attributed to a single NO_x source or even a single NO_x source region.
    3) Urban plume ozone, on the other hand, can be either NO_x-sensitive or VOC- sensitive.
    4) In stagnation episodes, the ozone formed in an urban plume during the first day of an ozone episode can be very VOC-sensitive, and even increase further in ozone concentration if NO_x emissions are decreased.
    5) Model calculations show that decreases of NO_x emissions in an urban area also decrease export of ozone from that urban area. This was true even in cases when the peak concentration of ozone accumulated during the ozone pollution episode is more effectively decreased by VOC emission controls than NO_x controls.
    6) Under advection conditions, decreases in NO_x emissions generally provided more effective control of ozone pollution in both rural and urban areas of the SOS region.
    7) Model calculations under advection conditions, also indicated a tendency for NO_x sensitivity to increase and VOC sensitivity to decrease as the meteorological situation shifts from the stagnation conditions typical of extreme ozone episodes to more typical advection conditions.
    8) Ozone production over the Nashville and/or Atlanta urban center can still be VOC-sensitive; but in contrast to stagnation episodes, however, the peak ozone concentration is more likely to occur downwind than in the urban core of the city.
    9) Thus, optimally efficient and effective management of urban ozone and regional background ozone often can require different ozone precursor emissions control measures (Duncan and Chameides, 1998).

An important policy implication from this set of scientific findings (OC13 above), is that control strategies aimed at decreasing emissions of NO_x from sources that impact rural areas, especially well-vegetated areas, always are beneficial in terms of decreasing ozone exposures in rural areas. By contrast, however, decreasing NO_x emissions in urban areas may be either beneficial or counter-beneficial, depending on whether the urban area of concern is VOC-sensitive or NO_x-sensitive.

B. Ozone Production Efficiencies of VOC and NO_x

Resolution of the issue of relative ozone production efficiencies of VOC and NO_x is perhaps the most important achievement of the SOS research and assessment program. Its importance lies, first, in the fact that the issue itself is critically important as it pertains to the relative merits of VOC and NO_x controls. Thus, air quality managers need reliable evidence regarding such efficiencies for the purpose of determining whether to focus control efforts on VOC emissions or on NO_x emissions (or on both).

Also, ozone production efficiencies of VOC and NO_x serve as bases for emission trade-off strategies. The SOS achievement is remarkable also because the scientific issue of ozone production efficiencies of VOC and NO_x is an extremely complex one, as the absolute and relative efficiencies of VOC and NO_x are subject to influences from numerous factors and that these influences are often conflicting. Please note in the findings described below, that ozone formation conditions are often referred to as "VOC-limited/sensitive" or "NO_x- limited/sensitive, meaning that, under such conditions, the VOC or the NO_x precursor, respectively, is the more efficient producer of ozone.

- OPE1. In the Houston-Galveston area of Texas during the month-long Texas 2000 Air Quality Study, ozone was produced very rapidly and very efficiently in downwind areas dominated by industrial sources. The rate of ozone formation in and around the industrial-source dominated areas in Houston was very high; ozone formation rates ranging between 50 ppbv/hr and 150 ppb/hour were measured on multiple days during the Texas 2000 Air Quality Study. These rates of ozone production are much greater than those observed in other urban areas in the US and Canada, which almost always are less than 40 ppb/hour (Daum et al., 2002).
- OPE2. In Houston, Texas, high rates and high efficiencies of ozone formation can be explained by co-located emissions of VOC and NO_x from industrial sources. High rates and high efficiencies of ozone production in the industrial plumes are driven by high concentrations of reactive hydrocarbons in the presence of NO_x. The industrial plumes exhibiting rapid and efficient ozone formation also tend to exhibit a complex spatial structure (Daum et al., 2002; Kleinman et al., 2002).
- OPE3. Ozone formation in the Nashville, Tennessee urban plume was VOC-limited during the extreme stagnation conditions observed in July 1995. Observed indicator ratios showed VOC-sensitive conditions within the Nashville urban core and NO_x-sensitive conditions by the edges of the urban plume and in the background air (Valente et al., 1998).
- OPE4. In Nashville under stagnation conditions, the urban plume started out being VOC-limited in the morning and remained that way for the remainder of high ozone days (Daum et al., 2000b).
- OPE5. In Nashville, the amount of ozone formed under stagnation and advective conditions was similar. The total amount of ozone formed in the Nashville urban plume could be approximated by multiplying the daily average NO_x emissions rate times the ozone production efficiency (OPE_x equals the number of molecules of ozone formed per molecule of NO_x that reacts). OPE_x under stagnation and advective conditions was observed to be about the same. The plume from small power plants such as the Gallatin plant, which had an average NO_x emission rate of 11,000 tons of NO_x per year, had an OPE_x similar to the Nashville urban plume (OPE_X of about 3.0). By contrast, large power plants such as the Paradise plant, which had an average NO_x emission rate of 120,000 tons of NO_x per year, had a lower OPE_x of about 2.0 (Nunnermacker et al., 1998; Daum et al., 2000a).
- OPE6. NO_y concentrations in rural areas of the SOS region are generally very low, i.e., less than 4 ppbv. Under such conditions, ozone accumulation is largely limited by emissions of NO_x (Kleinman, 1994).
- OPE7. The yield of ozone from NO_x is sometimes relatively large – as many as about 10 molecules of ozone being produced for each molecule of NO_x emitted (Trainer et al., 1993). In other situations, however, the yield of ozone per molecule of NO_x emitted can be relatively small, with as few as 1.0-7.0 molecules of ozone formed per molecule of NO_x emitted. Observations in SOS's Nashville/Middle Tennessee Ozone Study indicated that the ozone production efficiency is lower (OPE_x of 0.8 to 1.7 moles of ozone per mole of NO_x) for isolated large power plants than for isolated small power plants (OPE_x of 3.0 to 7.0). This difference in ozone production per unit of NO_x emissions appears to be related to rapid NO_y removal and may be associated with a more rapid conversion of NO_x to HNO_3 in power plant plumes than in urban plumes. Within 50 km from a small rural power plant, NO_x oxidation proceeded most rapidly when the NO_z:NO_y ratio was greater than 0.7 (Ryerson et al., 1998).

- OPE8. Measurements of total NO, and different chemical species of NO_y (NO, NO_2, nitric acid, PAN, organic and inorganic nitrates, and occasionally nitrous acid) provide significant insight into the chemical reactions that control the rate of ozone accumulation in many rural and some urban areas in the SOS region. It appears that a significant part of the variability in ozone concentrations from time to time and from place to place in the SOS region can be explained on the basis of variation in NO_x concentration, as inferred from variation in observed NO_y concentration (Trainer et al., 1993; Sillman and Samson, 1993; Trainer et al., 1995; Valente et al., 1998; Sillman et al., 1998; Nunnermacker et al., 1998, 2000; Daum et al., 2000a, 2000b).
- OPE9. SOS evaluations of a variety of "photochemical indicators" for use in identifying VOC-sensitive or NO_x-sensitive areas and conditions have indicated that the VOC:NO_x ratio is not a reliable diagnostic tool but that ozone sensitivity to VOC and NO_x correlates well with four other photochemical indicators: 1) NO_y concentration, 2) ozone:NO_z ratio, 3) (HCHO concentration - minus 5ppbv):NO_z ratio, and 4) H_2O_2:HNO_3 ratio, with the last being most robust (Milford et al., 1994; Kleinman et al., 1994, 1995, 1997; Sillman, 1995a, 1995b, 1999; Sillman et al., 1997; Tonnesen and Dennis, 2000a, 2000b).
- OPE10. Data from the 1992 SOS Intensive Field Study in Atlanta indicate that Atlanta is close to the transition between VOC-sensitivity and NO_x-sensitivity, but that the city was in fact in the NO_x-sensitive regime at the time of this 1992 Intensive Field Study (Imhoff et al., 1995; St. John et al., 1998; St. John and Chameides, 2000).
- OPE11. Diagnostic analyses of photochemical smog reactions have uncovered a fundamental property of the photochemical system that explains why the atmosphere switches from a VOC-sensitive and NO_x-sensitive regime as NO_x concentrations decrease. This shift reflects the two different ways in which the atmosphere processes emissions inputs and the effect of these processes on the pool of reactive free radicals {Kleinman, 1994; Weinstein-Lloyd et al., 1998):
    1) VOC-sensitive regimes within the atmosphere contain an excess of NO_x sources over free radical sources. Thus, such regimes are characterized by: a) an abundance of NO_x, b) a deficiency of free radicals, and c) HNO_3 concentrations greater than H_2O_2 concentrations.
    2) By contrast, NO_x-sensitive regimes within the atmosphere contain an excess of free radicals over NO_x sources. Thus such regimes are characterized by: a) a deficiency of NO_x, b) an abundance of free radicals, and c) H_2O_2 concentrations greater than HNO_3 concentrations.
- OPE12. During the summers of 1994 and 1995, the urban plume of Nashville, Tennessee showed a stronger tendency to VOC limitation than the urban plume of Atlanta, Georgia during the summers of 1990, 1991, and 1992, or that of Los Angeles, California (Sillman et al., 1997).
- OPE13. During the 1994-1995 Nashville/Middle Tennessee Ozone Study, power plant plumes typically decreased ozone concentration in the near field (0 to 20 km downwind) and increased ozone concentrations above the regional background further downwind (> 20 km). Ozone concentration increases as large as 50 ppb above the regional background were observed in these plumes. When the plume from a nearby power plant mixed with the Nashville urban plume on July 12, 1995, the power-plant contribution to the total increase on ozone concentration was estimated to be about 17 ppb or about 28 percent of the total increase in ozone concentration observed (Ryerson et al., 1998; Gillani et al., 1998a, 1998b).

- OPE14. Most of the largest utility sources of NO_x are found in rural areas of the SOS region, which have high emissions of biogenic VOC (USEPA, 1997).
- OPE15. Ozone production efficiency was observed to have an inverse relationship with NO_x emission rate at several coal-fired power plants in the SOS region during the summer of 1995. (Ryerson et al., 1998; Sillman, 2000; Nunnermacker et al., 2000).

The policy implication of scientific finding OPE15 is that, for large power plant sources, the benefits of decreasing emissions of NO_x *are partially offset by an increase in the efficiency with which ozone is formed.*

- OPE16. NO_y concentrations decreased very rapidly in summertime urban plumes and power plant plumes near Nashville, Tennessee. The rate of depletion of NO_y in these plumes was more rapid than can be accounted for by any known NO_y-removal process (Gillani et al., 1998a, 1998b).

The unexpectedly rapid rates of depletion described in scientific finding OPE16 suggest that either:
1) *These plumes produce an unknown reaction product that was not detected at any of the ground-based or aircraft-based* NO_y *measurement systems used in the Nashville/Middle Tennessee Ozone Study; or*
2) *Rates of deposition of* NO_y *to vegetation or other natural or man-made surfaces near the ground are much greater than have been reported before.*

The rapid rate of NO_y *depletion described in scientific finding OPE16 also implies that:*
1) *Ozone production rates based on ozone:*NO_y *or ozone:*NO_z *relationships may significantly overestimate the ozone production efficiency of both urban plumes and power plant plumes, or*
2) NO_x *emissions may not be transported as far as is commonly assumed in current air quality models such as UAM-IV, UAM-V, MM5, ROM; RADM, etc.*

- OPE 17. Peroxide concentrations were lower in both urban plumes and power plant plumes than in background air near Nashville, Tennessee. The lower rates of formation of peroxides within these plumes are believed to be the result of higher NO_x concentrations within than outside the plumes; this maximizes radical consumption by NO_2 to form nitric acid as opposed to radical combination reactions that form peroxides (Jobson et al., 1998; Weinstein-Lloyd et al., 1998).
- OPE18. Carbon monoxide and methane made significant contributions (~19 and ~3 percent, respectively) to ozone formation in regions where isoprene emissions were relatively small, i.e., in the Nashville urban plume (Nunnermacker et al., 1998).

The scientific finding described in OPE18 indicates that carbon monoxide and methane will need to be considered as more important precursors of ozone than has generally has been recognized in past ozone management strategies. The role of methane and carbon monoxide in ozone formation is expected to increase still further as air quality managers continue to decrease emissions of the more reactive anthropogenic VOC.

IV. OCCURRENCE, COMPOSITION, AND SOURCES OF PARTICULATE MATTER AND ITS PRECURSORS

The particulate matter in air consists of tiny bits of airborne liquid or solid matter that are either: 1) emitted directly into the air (primary particles), or 2) are formed in the atmosphere (secondary particles) by a wide variety of photochemical, condensation, and other atmospheric processes. The primary and secondary particles have a wide variety of environmental effects that range from direct impacts on human and animal health to regional haze that decreases visibility at airports and scenic vistas in wilderness areas.

SOS was selected by EPA to implement the Agency's first PM Program field research effort. The Atlanta Supersite Project consisted of a one-month intensive field program to compare advanced methods for measurement of $PM_{2.5}$ mass, chemical composition (including single particle composition) in real time, and aerosol precursor species. The Project was funded by EPA through a cooperative agreement with SOS. It included intercomparisons of results from filter-based time-integrated aerosol measurements, and continuous or semi-continuous measurement of mass and PM components and precursors. Special attention was paid to the semi-volatile PM constituents because of the analytical problems their on-filter volatilization posed.

The Atlanta Supersite Project took place during the month of August 1999 at the Jefferson Street Site near downtown Atlanta. This same site was operated since 1998 as part of the Southeastern Aerosol Research and Characterization Study (SEARCH), the Aerosol Research Inhalation Epidemiology Study (ARIES), and the Assessment of Spatial Aerosol Composition in Atlanta (ASACA) – all three of which were affiliated with SOS but funded by EPRI, the Southern Company, and the Georgia Power Company.

The photochemical processes that lead to formation of the secondary aerosols within $PM_{2.5}$ are essentially the same as those that produce ozone, except that they also include photooxidation of SO_2 and VOC into condensable products. Thus, the photochemical processes that lead to accumulation of ozone are very closely related to those that form $PM_{2.5}$. Unfortunately, however, air quality management approaches aimed at decreasing ozone accumulation in the air sometimes lead to increased accumulation of $PM_{2.5}$. Furthermore, management approaches aimed at decreasing $PM_{2.5}$ sometimes lead to increased accumulation of ozone. This strategy-conflict problem is not confined to the ozone and $PM_{2.5}$ problems, it exists among all photochemical pollution problems – namely, ozone, NO_2, PM, acid deposition, greenhouse effects, stratospheric ozone depletion, and secondary toxic pollution.

PM occurrence and characterization efforts, using methods well characterized during the Atlanta Supersite Program, also were conducted in Anderson, South Carolina, during SOS' Nashville '99 field research program, and in connection with both the Texas 2000 Air Quality Study in the Houston-Galveston area, and in southeastern Texas through the Texas Supersite Program.

A. Occurrence and Composition of Ambient PM (PMC)

- PMC1. In Atlanta, hourly $PM_{2.5}$ data from the 1999 Atlanta Supersite Program indicated two types of events – morning peaks dominated by carbonaceous material and afternoon events dominated by sulfate. Carbon and sulfate accounted for ~75% of aerosol mass during these peak events. Nitrate concentrations were generally low. However, the hourly data clearly indicated the temporal nature of nitrate, with nitrate concentrations peaking in the early morning before sunrise, when temperature was at its minimum (Weber et al., 2003b).
- PMC2. In Atlanta, significant semi-volatile organic material was present in $PM_{2.5}$ particles collected during the Atlanta Supersite Experiment (Solomon et al., 2003b).
- PMC3. In Atlanta, the composition of the ultrafine particles less than 100 nm particles was dominated by carbon compounds. The major composition classes (expressed as percentage of particle mass) were: organic carbon (~74%), potassium (~8%), iron (~3%), calcium (~2%), nitrate (~2%), elemental carbon (~1.5%), and sodium (~1%) (Solomon et al., 2003b).

- PMC4. In Atlanta, the total mass of ultrafine particles (<10 nm) was higher during traffic rush hours, while larger diameter particles (10-100 nm and 100-2000 nm) had higher concentrations at night than during the day, while also reaching their highest concentrations during traffic rush hours (Rhoads et al., 2003).
- PMC5. In Atlanta, organic matter and elemental carbon comprised ~40% and ~8%, respectively, of $PM_{2.5}$ mass on average during August 1999 (Lim and Turpin, 2002).
- PMC6. In Atlanta, the average air concentration of $PM_{2.5}$ mass during August 1999 was 31.3 µg m^{-3}, with a peak value of 47.2 µg m^{-3}. Thus, the 24-hour $PM_{2.5}$ standard was not exceeded. Interestingly, the 1-hr ozone standard was exceeded for multiple hours on several days during the Atlanta Supersite Study in August 1999. Sulfate and ammonium ion concentrations were well correlated with $PM_{2.5}$ mass; but organic carbon and elemental carbon concentrations were not very well correlated (Solomon et al., 2003b).
- PMC7. In Atlanta, light scattering by PM was dependent on a wide range of chemical components of the aerosols. Light absorption was most strongly linked to the elemental carbon component (Carrico et al, 2003).
- PMC8. The average direct aerosol radiative forcing properties estimated in the Atlanta Supersite Experiment was about minus 11 $\pm$ 6 watts m^{-2}; this value is about 10 times larger than global mean estimates for aerosols (Carrico et al., 2003).
- PMC9. The composition of particles measured during the Atlanta Supersite Study was generally internally mixed, with components of organic matter, sulfate, nitrate, ammonium and other constituents (Lee et al., 2002).
- PMC10. During the ASACA study, annual $PM_{2.5}$ mass concentrations measured from March 1999 to February 2000 exceeded the annual NAAQS of 15 µg m^{-3} at all four monitoring sites, with annual averages ranging from 19.3 to 21.2 µg m^{-3}. One site violated the daily $PM_{2.5}$ NAAQS of 65 µg m^{-3} (Butler et al., 2003).
- PMC11. ASACA data in Atlanta showed that most $PM_{2.5}$ constituents peaked during summer months; but nitrate, metals, and elemental carbon usually showed some enhancement during winter due mainly to lower inversion heights. Diurnally, there were discernible early morning and late night peaks that corresponded to rush-hour traffic patterns and inversion heights, respectively (Butler et al., 2003).
- PMC12. At a rural site near Anderson, SC, the average $PM_{2.5}$ mass during July 2001 was 20.9 µg m^{-3}, with a high of 41.2 µg m^{-3} on July 18 and a low of 4.4 µg m^{-3} on July 25. The overall average in January 2002 was 9.4 µg m^{-3}, with a high of 18.2 µg m^{-3} on January 18 and a low of 3.7 µg m^{-3} on January 25. Across all sampling events, the average annual mass concentration was 15.1 µg m^{-3}, just above the new NAAQS annual standard of 15 µg m^{-3} (Husain and Christoforou, 2003).
- PMC13. At a rural site near Anderson, SC, winter and summer data showed higher mass concentrations in summer than in winter. Sulfate ion and ammonium ion concentrations increased in summer, but nitrate ion concentrations decreased in summer. Comparison of these SC air concentration data with those for similar rural sites in GA and NC showed that the NC sites generally had higher and the GA sites generally had lower air concentrations of $PM_{2.5}$ mass during late 2001 and early 2002 (Husain and Christoforou, 2003).

- PMC14. Across southeast Texas, sulfate, ammonium ion (which neutralizes the sulfate ion), organic carbon, and elemental carbon are the major constituents of $PM_{2.5}$; the annual average concentrations of these major components were generally spatially homogeneous although localized events with high mass fractions of sulfate or carbon occurred frequently at many monitors in this region. When averaged over long time periods, $PM_{2.5}$ mass concentrations were spatially homogeneous throughout southeast Texas (Russell and Allen, 2004; Russell et al., 2004).
- PMC15. Throughout southeast Texas, a consistent and strong morning peak in $PM_{2.5}$ mass concentrations is observed and a weaker and slightly less consistent peak in mass concentration is observed in the late afternoon to early evening (Russell et al., 2004).
- PMC16. In southeast Texas, concentrations of sulfate were slightly higher in the spring and late fall than in the summer; carbon concentrations were highest in the late fall (Russell and Allen, 2004; Russell et al., 2004).
- PMC17. In southeast Texas, high organic-carbon to elemental-carbon ratios suggest that much of the carbonaceous material in $PM_{2.5}$ is not emitted directly, but is formed in the air through reactions involving both gaseous biogenic and anthropogenic VOC emissions (Russell and Allen, 2004; Russell et al., 2004).
- PMC18. Over wide regions of eastern and southeast Texas, annual average mass concentrations of $PM_{2.5}$ ranged from about 10 $\mu g\ m^{-3}$ to 15 $\mu g\ m^{-3}$, which is close to the annual average NAAQS of 15 $\mu g\ m^{-3}$ (Russell et al., 2004).
- PMC19. Data from both the Atlanta and Houston Supersite Programs indicate that secondary formation of organic aerosols tended to be large compared to primary emissions (Dechapanya et al., 2002; Lemire et al., 2002; Lim and Turpin, 2002). In some suburban and rural locations in SE Texas secondary aerosol formation is dominated by biogenic VOC reactions (Lemire et al, 2002).

Scientific findings PMC1-PMC19 indicate that $PM_{2.5}$ in the SOS region consists of directly emitted primary particles and secondary formation of aerosols produced from atmospheric chemical reactions involving VOC, SO_2, NO_x, and NH_3. Thus, management strategies aimed at decreasing air emissions of VOC, SO_2, NO_x, and NH_3 will be necessary to decrease both regional haze and human exposures to $PM_{2.5}$.

B. Sources and Emissions of Primary PM and Precursors of Secondary $PM_{2.5}$ (PMS)

The SOS program on emissions of PM constituents and precursors focused on identification of natural and human sources of primary PM and precursors of secondary PM and on source allocation of precursors of different sizes of particles.

- PMS1. In Atlanta, based on data collected between 1998 and 2000, airborne soil was the largest source of primary PM_{10} mass and sulfate-rich secondary aerosol was the primary contributor to Atlanta $PM_{2.5}$ mass (Kim et al., 2003).

- PMS2. In Atlanta, eight types of sources were identified as major emission sources for $PM_{2.5}$ constituents: 1) SO_4^{2-}-rich secondary aerosol sources (56 percent), 2) motor vehicle sources (22 percent), 3) wood smoke sources (11 percent), 4) NO_3^--rich secondary aerosol sources (7 percent), 5) mixed cement kiln and organic carbon sources (2 percent), 6) airborne soil sources (1 percent), 7) metal recycling facilities (0.5 percent), and 8) a miscellaneous source that includes bus stations and metal processing facilities (0.3 percent). Invariably, NH_4^+ (presumably mainly from agricultural sources) was associated with both the SO_4^{2-}-rich and NO_3^--rich secondary aerosols (Kim et al., 2003).
- PMS3. In Atlanta, five types of sources were identified as major emission sources for PM_{10}: 1) airborne soil sources (60 percent), 2) NO_3^--rich secondary aerosol sources (16 percent), 3) SO_4^{2-}-rich secondary aerosol sources (12 percent), 4) cement kiln facilities (11 percent), and 5) metal recycling facilities (1 percent) (Kim et al., 2003).
- PMS4. Point sources of primary PM_{10} particles are significant, but point-sources of primary $PM_{2.5}$ particles have not yet been quantified. Thus, additional research is needed to determine the importance, size distributions, and chemical compositions of these $PM_{2.5}$ primary emissions Texas (Allen, 2002; Brock et al., 2003; NOAA, 2003).
- PMS5. In Atlanta, using carbon monoxide as a tracer, motor vehicles were indicated as a primary emission source of elemental carbon. Elemental carbon concentrations tended to peak at 0600-0900 EST and had a much smaller peak during evening hours. These temporal patterns of variability are also indicative of motor vehicle emissions (Lim and Turpin, 2002).
- PMS6. In southeast Texas, wind-blown soil was a relatively minor source of $PM_{2.5}$ mass (Allen, 2002; Brock et al., 2003; NOAA, 2003).
- PMS7. In southeast Texas, when high concentrations of $PM_{2.5}$ mass, sulfate and organic carbon were observed throughout this region, back-trajectory analyses of these air parcels often indicated high concentrations of background sulfate and organic carbon in $PM_{2.5}$ that extend far upwind in an easterly direction. These observations suggest that much sulfate and carbonaceous aerosol is transported into southeast Texas elsewhere in eastern North America (Russell et al., 2004).
- PMS8. In southeast Texas, high concentrations of $PM_{2.5}$ mass and organic carbon sometimes are observed at isolated monitors. These observations suggest that local source contributions are important on some days (Russell et al., 2004).
- PMS9. In southeast Texas, mobile-source emissions account for about 25-35 percent of the primary particles in $PM_{2.5}$ mass. Sources of primary emissions of $PM_{2.5}$ in this area are diesel engines in heavy duty trucks, trains, and farm or construction equipment; gasoline engines in cars, trucks, boats, and hand tools; and jet-fueled aircraft (Allen, 2002; Brock et al., 2003; NOAA, 2003).
- PMS10. In southeast Texas, primary particle emissions from cooking of foods were significant in all urban areas. These emissions account for about 10-15 percent of $PM_{2.5}$ mass in urban areas (Allen, 2002; Brock et al., 2003; NOAA, 2003).
- PMS11. In southeast Texas, fires are a sporadic, but significant, source of primary $PM_{2.5}$ emissions. On an annual average basis, they contribute about 1-2% of the total mass of $PM_{2.5}$ particles in the Houston-Galveston area; but these emissions tend to be concentrated on specific days with fire events in Texas (Allen, 2002; Brock et al., 2003; NOAA, 2003).

- PMS12. Regional sources of $PM_{2.5}$ are primary contributors to fine PM mass amounts in the Southeast, but instances of long-distance transport of particles can have a noticeable influence on monthly PM mass concentration, as observed during a Central American fire event in 1998 (Tanner et al., 2001).

Given the identity of the $PM_{2.5}$ precursors, one might assume at first glance that the photochemically produced part of $PM_{2.5}$ could be controlled simply by decreasing emissions of all four precursors -- SO_2, NO_x, NH_3, and VOC. In actuality, however, as in the case of ozone, formation of sulfate, nitrate, and organic-carbon particles does not depend linearly on their precursors. Minimum formation of secondary aerosols occurs when the ratios among NO_x, VOC, and SO_2 precursors are least favorable for photochemical interactions. Regrettably, however, the ratios least favorable for secondary aerosol formation are not necessarily optimal for control of ozone formation.

V. METEOROLOGY AND ATMOSPHERIC DYNAMICS OF OZONE AND PM FORMATION AND ACCUMULATION (MD)

The SOS program on ozone- and PM-related meteorology and atmospheric dynamics consisted mainly of ambient monitoring studies to define meteorological conditions and scenarios associated with accumulation of high ozone concentrations. Given the extremely complex meteorology in various parts of the SOS region, the SOS studies were not merely a routine application of standard meteorological measurement methods. Substantial evaluation, adaptation, and further development of existing meteorological and atmospheric dynamics measurement methods were included in the SOS program. Furthermore, the findings listed below regarding meteorological conditions and scenarios within the SOS region, in themselves, have primarily local applicability and utility. Comparison of such conditions/scenarios with those in other US regions can only serve the purpose of explaining differences in pollutant climatology among regions. Nevertheless, there is one important implication that has general utility (see below).

- MD1. Small-scale features, such as urban plumes, point sources, and convective pumping, played important roles in determining the locations and magnitudes of the maximum ozone concentration in the SOS region (McNider et al., 1993). Because of this mesoscale variability, fine-scale grid resolutions probably will be required in regional models to adequately simulate accumulation of ozone in the SOS region (McNider, 1994).
- MD2. Temperature was confirmed to be a very important meteorological factor determining the rate of formation of ozone in many parts of the SOS region (Olszyna et al., 1997; Sillman and Samson, 1995).
- MD3. Vertical profiles of isoprene and other ozone precursor VOC with maximum concentrations at heights of 100-300 meters above ground level were observed in the SOS region and were associated with as yet uncertain transient meteorological phenomena. Because of this vertical variability of VOC concentrations in the boundary layer, a measurement strategy involving sampling at 30-60 meters above ground level provides a more robust measure of average hydrocarbon abundance in the mixed layer than a surface sampling strategy (Andronache et al., 1994; Lawrimore et al., 1995).

- MD4. A significant portion of the mass exchange between forest canopies and the atmosphere was caused by large, intermittent eddies. The importance of these large eddies in transporting biogenic VOC mass from the canopy into the atmosphere was greatest during periods of enhanced stability. These large intermittent eddies during stagnation conditions may be at least part of the cause of the complex vertical profiles with maximum precursor concentrations observed at 100-300 meters above ground level during rural and urban field experiments (see also finding MD3) (Marsik and Samson, 1994; Marsik et al., 1995).
- MD5. Latitude was found to be an important parameter in determining the rapidity of dispersion of power plant and urban plumes in the SOS region (McNider et al., 1993).
- MD6. The height of the mixed layer in the Nashville/Middle Tennessee region was strongly dependent on land-use patterns, with the lowest mixing-layer heights being observed over forested areas in this region and much higher mixing heights being observed over agricultural and urban areas in this region. This discovery of substantial land-use-controlled variation in mixing height was made using an airborne ozone LIDAR (White et al., 1999; Angevine et al., 2003).
- MD7. During the Nashville/Middle Tennessee Ozone Study in 1995, the typical regional ozone events were dominated by light and variable daytime and nocturnal winds, which were punctuated on many days by short-term, relatively localized convective storms, sometimes with lightning. Regional background concentrations of ozone varied from 40 to 80 ppbv; peak day-time concentrations of ozone in both rural and urban areas varied from about 75-90 ppbv, with some rural and urban areas reaching day-time peaks of 80 to more than 110 ppbv. Emissions leading to these moderately high regional ozone event days were derived from both distant and local sources – biogenic and anthropogenic – point, area, mobile, biogenic, and other natural sources (McNider et al., 1998; Banta et al., 1998).
- MD8. The episode that generated the highest ozone concentrations during the 1995 Nashville/Middle Tennessee Ozone Study (138 ppbv) occurred from July 11-15. This episode was dominated by an extraordinarily intense air stagnation event in which the Nashville urban plume was confined directly over the urban area of approximately 600 km^2. The regional background concentration during this period was only about 45-63 ppbv. Thus the 75-90 ppbv increase in ozone concentration over the regional background was the result of photochemical smog reactions that occurred within the immediate vicinity of the Nashville metropolitan area. On July 12, 1995 the plume from one of the power plants near Nashville merged with the urban plume (Valente et al., 1998).
- MD9. During stagnation conditions in the Nashville/Middle Tennessee Ozone study, nighttime winds tended to dominate pollutant transfer processes. These nighttime winds appeared to be the major mechanism for transporting ozone and its precursors into rural areas under these stagnant weather conditions (McNider et al., 1998, Banta et al., 1998).
- MD10. The average daytime ozone deposition velocity over rural areas unperturbed by urban plumes or power plant plumes, as measured by aircraft during the Nashville/Middle Tennessee Ozone Study, was uniformly about 0.5 cm/sec. This measured deposition velocity agrees well with the deposition velocity estimates used in many air quality models. By contrast, ozone deposition velocities measured from aircraft flying above urban areas were highly variable. This high variability in observed deposition velocity over urban areas suggests that current air quality models must be used with great caution in such areas (Meyers et al., 1998).

- MD11. The larger the radius, the more horizontally homogeneous the field of a specified wind variable became. The magnitude of the radius for a specified amount of change in a wind variable depends on the wind variable chosen. The radius computed for wind speed for a given location will, in general, not be the same as the radius computed for the u- or v-component. Each variable has its individual degree of degradation with distance from the base location (Norris, 2003).
- MD12. Under light wind conditions during the Nashville/Middle Tennessee Ozone Study, substantial (~40%) horizontal variations in daytime mixing height due to the urban-rural contrast in the surface energy balance (an “urban dome of ozone”) was observed over the city of Nashville. This dome allowed venting of urban emissions aloft, making them available for horizontal transport but unavailable for vertical mixing downwind of the dome during the day (Banta et al., 1998).
- MD13. Cumulus clouds vented pollutants from the boundary layer and reduced the sunlight available for photochemistry during the Nashville-Middle Tennessee Ozone Study. Because direct measurements of cumulus venting are difficult to obtain experimentally, this process was not quantified during SOS’ Nashville ‘95 and Nashville ’99 studies or during TexAQS 2000. Deep vertical mixing associated with convective storms may have resulted in some stratosphere/troposphere exchange (Banta et al., 1998).
- MD14. Synoptic-scale subsidence associated with high pressure strengthened the boundary-layer capping inversion during the Nashville/Middle Tennessee Ozone Study. This inhibited vertical transport of momentum and pollutants and cumulus convection. This behavior, combined with the stagnant conditions resulting from relaxation of the synoptic-scale pressure gradient, allowed pollutants to accumulate locally during the day (Banta et al., 1998).
- MD15. The morning transition caused photochemically aged NO_x and VOC and their reaction products from the residual layer to interact with pollutants emitted at night into the shallow nocturnal boundary layer. During the Nashville/Middle Tennessee Ozone Study, the breakup of the nocturnal inversion occurred at an urban site 1 to 2 hours earlier than at three rural sites. In the humid environment in the SOS field studies, surface water vapor mixing ratio was often an excellent meteorological tracer for the timing of the morning transition (White et al., 2002).
- MD16. At night during the Nashville/Middle Tennessee Ozone Study, the winds above a shallow (tens of meters) layer at the surface accelerated as the atmosphere decoupled from the surface (White et al., 2002).
- MD17. During the Nashville/Middle Tennessee Ozone Study, the nocturnal winds rotated in time in accordance with the principles of the inertial oscillation. McNider et al. (1998) demonstrated the persistent nature of this phenomenon using wind spectra obtained from deployed wind profilers. Under sufficiently weak synoptic forcing, the low-level jet and inertial oscillation dominated nocturnal transport. Trajectories derived from the wind profiler network deployed during this study demonstrated the combined effect of these important features.
- MD18. Vertical transport was suppressed at night during the Nashville/Middle Tennessee Ozone Study. In the absence of convective storms, the atmosphere stabilized at night and suppressed any significant vertical transport. In many cases, intermittent turbulence was observed in the nocturnal boundary layer, which may be linked to wind shear associated with a low-elevation jet. The effect of intermittent turbulence on pollutant concentrations at ground level is an important topic of SOS research (Banta et al., 1998; McNider et al., 1998).

- MD19. During the Nashville/Middle Tennessee Ozone Study, remote sensors provided reliable measurements of mixing height. A comparison of mixed-layer depth estimates deduced from wind profiler and airborne lidar data showed very good agreement under clear or partly cloudy conditions (White et al., 1999).

This result confirmed that radar wind profilers and lidars are well suited to measure the depth of the mixed layer and its variability.

- MD20. During the Nashville/Middle Tennessee Ozone Study, variations in mixing height were found to be related to differences in such ground-surface characteristics as soil and vegetation type as well as surface moisture. These different surface characteristics were reflected in varying energy, ozone, and carbon fluxes at ground level (White et al., 1999).
- MD21. During the Nashville/Middle Tennessee Ozone Study, differences in mixing height were most pronounced under light wind conditions. Under stagnant conditions, air parcels tended to dwell over regions of one surface type, which allows surface heating differences to express themselves as variations in mixing height. Stronger flow moves air parcels over many surface types, thus producing a more uniform mixing height (White et al., 1999).
- MD22. During the Nashville/Middle Tennessee Ozone Study, the strong differences observed in surface heating between the Nashville urban area and the surrounding agricultural and forested areas resulted in significantly deeper mixed layers over the city, especially under stagnant conditions. Urban mixing heights of 2 km or more were frequently observed; this was as much as 800 m deeper than the mixing heights over adjacent rural areas. (Angevine et al., 2003)
- MD23. During the Nashville/Middle Tennessee Ozone Study, mixing processes due to convective or mechanical turbulence acted to smooth out vertical inhomogeneities in the height of the daytime boundary layer (Banta et al., 1998).
- MD24. During the Nashville/Middle Tennessee Ozone Study, ozone tended to form horizontal layers or patches that often persisted throughout the night until they were mixed out by the growing boundary layer the next morning. This horizontal layering and patchiness of ozone was caused in large part by minimal vertical mixing under stagnant air conditions during nighttime hours (Banta et al., 1998).
- MD25. During the Nashville/Middle Tennessee Ozone Study in 1995, and again during SOS' Nashville '99 ozone study, ozone concentrations in the free troposphere were shown to be affected by long-range transport or stratosphere-troposphere exchange processes. Ozone sonde and aircraft measurements showed that concentrations of ozone and other pollutants in the free troposphere were highly variable and were primarily affected by regional to continental-scale advection of clean or polluted air masses. Another significant process contributing to high tropospheric ozone concentrations is the intrusion of stratospheric air. Through entrainment processes, pollutant concentrations in the lower free troposphere can impact the air quality in the atmospheric boundary layer and at ground level (Banta et al., 1998).
- MD26. During TexAQS 2000, synoptically driven winds were found to be the dominant daytime horizontal transport mechanism. Mesoscale circulations caused by topography or land use differences also contributed to daytime transport. Synoptic flow exported the Houston/Ship Channel and Texas City pollution plumes to rural, source-free areas, resulting in ozone concentrations well above the ozone standard far downwind of the Houston metropolitan area. Many of these ozone exceedances were not detected by the surface monitoring network because of the sparse distribution of monitoring sites in rural areas (Senff et al., 2002).

- MD27. During TexAQS 2000, peak ozone concentrations downwind of the Houston/Ship Channel were anti-correlated with mixing height. In the Houston area, mixing depth typically increases with distance away from the coast. Thus, transport of the pollution plume from the Houston Ship Channel to coastal areas tended to produce higher peak ozone concentrations than transport to inland areas (Senff et al., 2003).
- MD28. During TexAQS 2000, off-shore to on-shore flow reversal was observed very frequently in conjunction with high ozone concentration events. Severe ozone exceedances on flow-reversal days were linked to a combination of two meteorological factors: 1) Light wind conditions that facilitated the buildup of ozone plumes over strong VOC and NO_x emissions source areas during the middle of the day, followed by 2) Afternoon sea breeze phenomena that transported aged air masses back over source areas, thus increasing still further the already high ozone concentrations. The distribution of precursors and the severity of the ozone event depended on the morning offshore flow regime, the timing of the sea breeze onset, and the strength of the sea breeze flow reversal (Banta et al., 2005; Senff et al., 2002; Nielsen-Gammon, 2001).
- MD29. During TexAQS 2000, other high ozone events were associated with a coupling of the sea breeze flow reversal and the inertial oscillation. These two phenomena are nearly congruent at the latitude of Houston, where they produce a few hours of nearly calm winds during late morning or early afternoon when large-scale winds are light from the south or southeast. Large-scale mean winds must be lighter than a threshold value of about 3 meters per second for flow reversal to occur. On these occasions, flow reversal takes place almost simultaneously throughout the metropolitan area, not only in association with the sea breeze front. When winds are sufficiently light, the likelihood of an ozone exceedance is greater than 50%. Exceedances are also relatively likely when synoptic winds flow from northeast to southwest (Senff et al., 2002; Nielsen-Gammon, 2001; see also McNider et al, 1998).
- MD30. During TexAQS 2000, measurements made by the Baylor aircraft downwind of industrial sources in the fall of 2001 suggested that while some industrial plumes are well mixed, other plumes are spatially heterogeneous. The spatially heterogeneous plumes can contain regions with high concentrations of VOC, regions with high concentrations of NO_x and regions with high concentrations of both VOC and NO_x. Whether a plume is well mixed or heterogeneous is likely to depend on the distance from the source and atmospheric stability conditions (Daum et al., 2002).
- MD31. Observations made during TexAQS 2000 indicated that improper treatment of aerosols in mesoscale numerical weather prediction models (PSU-NCAR MM5 and NCEP Eta Models) contributed to forecast errors regarding the amount of solar radiation reaching the surface. Aerosol absorption and scattering decrease the amount of sunlight that reaches the Earth's surface. Solar irradiance estimates were in good agreement with observations for smaller aerosol optical depths (Zamora et al., 2005).

The important implication of scientific findings MD1-MD31, which has general applicability and utility both inside and outside the ten-state SOS region, is that a very long list of meteorological variables need to be measured for the purpose of understanding the meteorology and atmospheric dynamics of ozone formation, accumulation, and both vertical and horizontal distribution in the atmosphere. Such variables include: 1) mixing height and its spatial variation,2) atmospheric stability conditions (stagnation vs. advection), 3) variables related to day-time and night-time pollutant transport processes, 4) "heat island" phenomena as they are influenced by the structure and species composition of urban vegetation, land use patterns, and the structure and distribution of buildings, pavement, playgrounds, parks, etc., 5) synoptic scale subsidence,6) transport of biogenic emissions *from canopy to atmosphere, 7) pollutant effects on solar radiation (i.e., aerosols and their optical properties), and 8) off-shore and on-shore flow-reversal patterns in coastal areas.*

VI. MODELS AND MODEL EVALUATION

Air quality models are indispensable tools for studying some atmospheric processes, and for the development and evaluation of alternative air pollution management strategies. The earliest models used in air pollution research were emissions-based models (EBMs), i.e., photochemical Eulerian grid-type or Lagrangian models with requisite inputs of emissions data, horizontal and vertical boundary condition estimates, meteorology and atmospheric deposition submodules, and chemical transformation modules. All these required inputs are subject to considerable uncertainties. For this reason, EBMs had to be subjected to extensive evaluations before they were accepted for application and use in making air quality management decisions. Modeling advances in recent years have produced EBMs with great sophistication and improved accuracy. Nevertheless, uncertainties persist, especially regarding the quality of emissions inventories and meteorological inputs needed for some ozone non-attainment areas. Thus, emission uncertainties introduced by fugitive emissions, by automobile engine operation and traffic volume factors, and by factors affecting some VOC emissions from vegetation have resisted improvement efforts and are still substantial. Also, meteorological models simulating air flow reversal phenomena in coastal areas are still lacking in reliability.

In reaction to these persistent problems with existing EBMs, and in response to concerns expressed in the National Academy of Science’s 1999 “Rethinking” report suggesting that EPA’s VOC-control approach to attainment may be less effective than NO_x control in some non-attainment areas, SOS researchers undertook the development of new, more reliable methods, based on direct observation of air concentrations of ozone and each of its many VOC and NO_x precursors.

SOS scientists and engineers were convinced that:

1) Effective ozone management strategies can only be achieved if the plans are based on reliable meteorological models and the amounts of ozone precursors *actually observed to be present in the air* rather than on amounts of precursors *believed to be present in the air* on the basis of often-inadequate emissions inventories; and
2) A reliable air quality model must not only ‘*get the ozone right*’ but also ‘*get the precursors right*’ and the ‘*relationships between the ozone and the precursors right for the right reasons*.’

The end-result of these efforts was development of:

1) A series of observation-based methods of analysis and Observation-Based Models (OBMs) that were used to evaluate various existing EBMs, and
2) Recommendations for complementary use of both OBM and EBM models and approaches in making air quality management decisions.

The success of the SOS’ OBM studies in resolving the issue of relative impacts on ozone of VOC and NO_x controls, led to the decision to compare relative impact data obtained by OBMs with those obtained by EBM methods. Such comparisons were extremely useful in that it is, in essence, an evaluation of the EBMs’ predictive performance against real-world data.

Specific key findings in the OBM and EBM study areas are given in the two sections below. The OBM-related findings describe the various observational methods developed by the SOS team, and, also the application of such methods for studying the sensitivity of ozone production to VOC and NO_x within various atmospheres (e.g., power plant plumes and urban plumes), for testing chemical mechanisms, and for developing improved emission inventory data.

A. Observation-Based Models (OBM)

The OBM-related part of the SOS program consisted of three components: A series of extensive field campaigns in the Atlanta and Nashville regions, extensive analyses of the field data toward development of OBM methods, and a comprehensive effort to evaluate and develop the analytical methods needed in the field campaigns. Key findings in the first two components are summarized below.

- OBM1. SOS developed a series of observation-based methods and two major Observation-Based Models (OBMs), each of which uses in-situ atmospheric observations of NO_x and VOC instead of emissions inventories to drive a photochemical model and thus infer whether ozone in a given locality is more sensitive to decreases in NO_x emissions or to decreases in VOC emissions. When concentration fields from the OBM were used as inputs into the Urban Airshed Model, the two models predicted similar sensitivities to NO_x and VOC. These observation-based approaches offer an independent and complementary method for evaluating alternative ozone pollution abatement strategies (Kleinman, 1994, 2000; Cardelino and Chameides, 1995; Kleinman et al., 1994, 1995, 1997, 1998).
- OBM2. Biogenic VOC, primarily isoprene, represented a significant fraction of the total VOC reactivity in large parts of the SOS region and significantly decreased the efficacy of ozone management strategies that considered only anthropogenic VOC emission decreases as an ozone mitigation strategy (Cardelino and Chameides, 2000).
- OBM3. SOS investigators also have tested and evaluated the value of a wide variety of "chemical indicator species" which can be used to help determine if a given locality ozone is more sensitive to decreases in VOC emissions or to decreases in NO_x emissions (Milford et al., 1994; Kleinman et al., 1994, 1995, 1997; Sillman, 1995a, 1995b, 1999; Sillman et al., 1997; Tonnesen and Dennis, 2000a, 2000b).
- OBM4. A wide range of values was observed for H_2O_2 and for summed NO_x reaction products (referred to as NO_z, or NO_y-NO_x), with no correlation between high H_2O_2 and high NO_z. There is a strong correlation between ozone and the sum $NO_z+2H_2O_2$, which appeared to be virtually identical between Nashville and Houston (Sillman, 2004).
- OBM5. Consistency between different methods of determining ozone production rate ($P(O_3)$)is an important test of theoretical understanding and measurement procedures for ozone. ozone precursors, photooxidation products, and peroxy-radicals (Frost et al., 1998).
- OBM6. The SOS science community has developed two complementary ways of analyzing the local rate and sensitivity of ozone production to one or the other or both of its two major precursors – NO_x, VOC, or both: 1) By means of a radical budget, and 2) By means of radical propagation efficiency. These methods yield insights and useful formulae. Generalizations provided the basis for development of reliable Indicator Ratio Methods (Kleinman et al., 1997; Tonnesen and Dennis, 2000a, 2000b).
- OBM7. Photochemistry under NO_x-sensitive conditions preferentially formed peroxides; by contrast, under VOC-sensitive conditions, NO_z compounds are formed preferentially. The sensitivity of $P(O_3)$ to NO and VOC is given by a simple analytic function of "LN/Q," the fraction of free radicals removed by reacting with NO_x (Kleinman et al., 1997).

- OBM8. Ozone is formed in a chain reaction. A simple version of these reactions is:

  $OH + VOC \rightarrow HO_2$
  $HO_2 + NO \rightarrow OH + NO_2$
  $NO_2 + h\nu + O_2 \rightarrow O_3 + NO$

  Numerical calculations show that ozone yield is maximized when the chain reaction length is long. Radical loss processes limit the length of the chain of reactions that lead to ozone formation. At low NO_x, HO_2 radicals combine to form peroxides; at high NO_x, OH reacts with NO_2 forming HNO_3. The combination of these two loss reactions causes a maximum in $P(O_3)$ at a particular NO_x concentration. The ratio of the peroxide to HNO_3 production rate tells us whether the atmosphere is on the low or high NO_x side of the maximum (Tonnesen and Dennis, 2000b).

The above two findings (OBM7 and OBM8) are, in essence, a mechanistic explanation, and also justification of one "indicator species" OBM method for determining whether ozone formation is VOC- or NO_x*-limited. This explanation/justification reinforces the validity of the indicator species method.*

- OBM9. EBM models should be evaluated by determining how well they perform for two specific indicator ratios: 1) ozone/NO_z, and 2) H_2O_2/HNO_3, both of which are closely linked with NO_x- or VOC-sensitive chemistry. The evaluation should be based on measurements that are congruent with peak ozone concentrations during the ozone episode of interest. Evaluations of EBMs should be done for a series of plausible model scenarios that give different results for both NO_x–sensitive and VOC-sensitive ozone episodes (Sillman et al., 1997).

- OBM10. Afternoon NO concentrations in the SOS region typically fell to concentrations that were at or below the limit of detection of the instruments used in EPA's Photochemical Assessment Monitoring Stations (PAMS). As a result, it is not possible to determine from PAMS measurements, whether ozone was more sensitive to decreases in anthropogenic VOC emissions or to decreases in NO_x emissions (Cardelino and Chameides, 2000).

- OBM11. During TexAQS 2000, use of emissions estimates based on ambient observations compared to inventory emissions resulted in air quality forecast model (NOAA-FSL) results for ozone concentrations that agreed better with measurements from the NCAR Electra and from the surface regulatory network (NOAA, 2003).

- OBM12. Four-dimensional data assimilation coupling an inverse, error-minimizing algorithm with a photochemical air quality model (URM) was used to minimize differences between simulated and measured concentrations of gas-phase and aerosol species to assess biases in the emissions inventory for the eastern US. Anthropogenic SO_2, high-stack point-source NO_x, and biogenic VOC emissions were estimated reasonably well in inventories, while area-source anthropogenic NO_x, anthropogenic VOC, NH_3, and organic $PM_{2.5}$ emissions may be significantly biased and require revisions from the base-case inventories (Mendoza-Dominguez and Russell, 2001a).

- OBM13. Estimated adjustments to the Atlanta emissions inventory were made utilizing four-dimensional data assimilation coupling an inverse, error-minimizing algorithm with the CIT photochemical air quality model for a 1992 ozone episode. In order to match ozone model predictions, rural anthropogenic VOC emissions were approximately doubled, anthropogenic NO_x and BEIS2 biogenic VOC emissions remained close to their base case value, and CO emissions were decreased. (Mendoza-Dominguez and Russell, 2001b).

B. Emissions-Based Models (EBM)

- EBM1. Vertical profiles for isoprene and other VOC during SOS' 1992 Atlanta Intensive field campaign often had complex structures with local maxima at heights between 100 and 300 meters above the land surface. But the average of all vertical profiles often took the expected monotonically decreasing shape, suggesting that the complex vertical features sometimes observed are caused by transient meteorological phenomena that cancel out over longer periods of time. Because of these transient features, however, surface measurements of VOC and other ozone precursors often do not correlate well with average concentrations at 40 to 100 meters above the land surface (Andronache et al., 1994; Lawrimore et al., 1995).
- EBM2. Large-scale eddies play a significant role in the transport and dispersion of airborne chemicals within the boundary layer in the SOS region. Because these eddies are not resolved by mesoscale and urban-scale chemical transport models, their effects are likely not well-simulated in these models. This, in turn, may lead to significant biases in the simulation of oxidant photochemistry by these models (McNider et al., 1993, 1998).
- EBM3. Higher resolution models (with 1km rather than the usual 4 km grid squares and 1hr-long averaging times rather than typical summer day averaging times) were shown to greatly increase the accuracy and precision of both EBMs and OBMs (McNider et al., 1993).
- EBM4. The Urban Airshed Model was found to be very sensitive to the method used to specify upper-air wind data (Al-Wali, 1996; Al-Wali and Samson, 1996).
- EBM5. Numerical experiments with an enhanced version of the Urban Airshed Model (UAM-V) showed that model performance can be enhanced by increasing its vertical resolution in the lowest portion of the boundary layer (Sillman et al., 1995; Imhoff et al., 1995).
- EBM6. Urban Airshed Model results with and without cloud transport were found to differ significantly. Model results with cloud parameterization tended to be in significantly better agreement with aircraft observations of ozone and ozone precursors than those obtained without cloud parameterization (Lin et al., 1994).
- EBM7. The Urban Airshed Model had difficulty simultaneously reproducing observed isoprene and ozone concentrations in Atlanta in 1992 (Sillman et al., 1995).
- EBM8. The Urban Airshed Model was able to reproduce observed urban relationships between ozone and NO_y in Atlanta in 1992 (Imhoff et al., 1995).
- EBM9. Incorporation of BEIS2 into the Urban Airshed Model (either UAM IV or UAM-V) led to significantly better agreement with observed ozone concentrations than use of these UAM models without BEIS2 (Guenther et al., 1993; Geron et al., 1994).
- EBM10. SOS was one of the first air quality research programs to explore regional decreases in emissions of NO_x and VOC. While the ROM model has perhaps been supplanted by higher-resolution, newer-generation models, the basic results shown in this study probably still prevail and are consistent with regional observations carried out under SOS for rural NO_x sensitivity (Roselle and Schere, 1995).
- EBM11. Several SOS studies demonstrated the power of vertical concentration profiles, indicator ratios, and ozone production efficiencies in diagnosing model outputs. Simply achieving an acceptable statistical performance for ozone is not sufficient to ensure that control actions taken based on model results will have the desired effectiveness (Sillman et al., 1995, 1998).

- EBM12. Recent applications of CMAQ for $PM_{2.5}$ show that results can be sensitive to the parameterization of vertical mixing, and the minimum diffusivities that are often assumed. At present, there does not appear to be a universally optimal approach. This can be critical for current efforts by Regional Planning Organizations dealing with visibility assessments and related policy decisions (Nowacki et al., 1996).
- EBM13. During 1996-99, SOS undertook a special project on seasonal modeling of regional air quality and developed a Seasonal Model for Regional Air Quality (SMRAQ). This simulation model used a non-hydrostatic version of the Multiscale Air Quality Simulation Platform (MAQSIP). SMRAQ had 22 vertical layers over a 36-km horizontal grid spanning the eastern US. Meteorological inputs were provided by the Mesoscale Meteorological Model (MM5) reinitialized every 5 days for the entire 4-month ozone season in 1995. Chemistry was provided by Carbon Bond Mechanism version 4.2 as in OTAG. The model was run with the then most current national emissions inventory of anthropogenic sources developed by the Ozone Transport Assessment Group (OTAG) and BEIS2 for natural emissions (Kasibhatla and Chameides, 2000).
- EBM14. Model results were compared with actual measured values at 137 locations from Texas and North Dakota through Florida and Maine during the period from May 15-September 15, 1995. Across the 137 comparisons of modeled vs measured ozone concentrations, the SMRAQ model performed better in terms of simulating seasonal rather than episodic characteristics of the regional ground-level ozone distribution. These results suggest that a seasonal model of the SMRAQ type can be a valuable adjunct to the current paradigm of developing ozone control strategies mainly on the basis of episode-specific simulations (Kasibhatla and Chameides, 2000; Houyoux et al., 2000).
- EBM15. During the development of SMRAQ, together with “NARSTO-Northeast” – a sister air quality research organization – the SOS and NARSTO-NE modeling teams evaluated the MAQSIP model by comparing its predictions of ozone concentration with the actual ozone concentrations measured during July 1995 at EPA’s SLAMS, NAMS, and PAMS monitoring sites in all states east of 100th meridian. During this evaluation the SMRAQ model gave: 1) Very good predictions of ozone concentration at synoptic space scales throughout the eastern US, 2) Good predictions of the magnitude but only moderately good predictions of the amplitude of diurnal variability in ozone concentrations, and 3) relative poor predictions of the ozone concentrations on different high ozone episode days during July 1995. Since mesoscale characteristics of the multiple-day episodes observed during this one-month study period were not well replicated in the SMRAQ model, the SOS and NARSTO-NE modeling teams suggested that longer-term (seasonal) model simulations may be preferable for regulatory purposes than simulations based on modeling of only one or two selected ozone episodes (Kasibhatla and Chameides, 2000; Hogrefe et al., 2001).
- EBM16. Use of the Direct Decoupled Method (DDM) for computing the effects of emission controls on ozone concentrations is subject to error due to the “non-linearity problem.” This problem arises from the fact that the DDM method is accurate only for small changes in emissions, and is of consequence when controls of greater than about 50% are simulated. In each of the Georgia cities in which this study was made, local sources, on top of regional background sources had the major, if not dominating, role in the source-receptor relationships observed, but the make-up of other sources that impacted the cities was significantly different. On a ppb-of-ozone per ton of NO_x basis, local, ground-level sources tend to have the greatest effectiveness (Odman et al., 2002).

- EBM17. Results using the coupled LES chemical model show that the turbulence paradigm that most air quality models are based upon, i.e. first order closure, can be trusted even within the deep boundary layers of the Southeast. However, details on how the first order closures (K profiles) are formulated can make a difference in model results. Thus, additional research is needed to ensure that the K-profiles imposed on many current air quality models reflect the appropriate turbulent intensities and scales in real-world boundary layers (Herwehe, 2000).
- EBM18. Consideration of air quality impacts across multiple episodes increased the importance of local sources. Regional modeling of source impacts on air quality showed that while long-range transport of pollutants and their precursors can be very significant during any one episode, when viewed across multiple episodes and meteorological conditions, the impact of local emissions became more important. Different long-distance source regions affected an area under different conditions, while local sources tended to have a role on a day-in/day-out basis. Thus, local controls will still have benefits, even in areas that are impacted from more distant sources (Odman et al., 2002).
- EBM19. Ozone formation potentials of individual VOC were consistent between different “metrics” or “indices” of reactivity across wide geographical domains. As noted in other SOS-related research, VOC controls were potentially beneficial in many urban areas. However, individual VOC can have very different impacts on the amount of ozone formed. Currently, the regulatory structure developed by the USEPA treats all VOC as either reactive or non-reactive, not taking in to account the spectrum of variability among VOC with greater or lesser ozone production reactivity. Regional modeling showed that the use of relative reactivities led to consistent results for ozone reactivity, suggesting that such a scale should be used in regulatory policy setting (Hakami et al., 2004).
- EBM20. Results from box model simulations run under conditions based on Houston’s industrial regions suggest that emissions of as little as 100 pounds of light alkenes (ethylene, propylene, butenes, pentenes, butadiene) and aromatics can lead to >50 ppb enhancements of ozone concentrations per hour over a 1km^2 area. Ozone productivities of alkane emissions are generally significantly lower than for alkenes and aromatics. The box model simulations also indicate much higher ozone productivities under conditions that involve high concentrations of both VOC and NO_x, as opposed to conditions that involve high concentrations of VOC alone. (Daum et al., 2002)
- EBM21. Rapid rates of NO_y depletion imply that NO_x may not be transported as far as is commonly assumed in current air quality models including UAM-IV, UAM-V, MM5, ROM, RADM (Nunnermacker et al., 1998, 2000; Daum et al., 2000a, 2000b).
- EBM22. Photochemical models using the common Carbon Bond 4 chemical mechanism gave reasonably good estimates of ozone concentrations during rapid ozone formation episodes in Houston. These same models and mechanisms tended to over-predict NO_z concentrations (and especially HNO_3 concentrations) during rapid ozone formation episodes in Houston. These reasonably good estimates of ozone concentrations and over-predictions of NO_z concentrations (and especially HNO_3 concentrations) also were observed in recent applications of the Comprehensive Air Quality Model with Extensions (CAMx) photochemical model (Gillani and Wu, 2003b, 2003c).

- EBM23. Chemical reactions with chlorine can increase ozone in Houston. Chemical reactions involving chlorine were incorporated into the Comprehensive Air Quality Model with Extensions (CAMx) photochemical model. An inventory of chlorine sources in the Houston urban area also was developed. Results from the chorine-included CAMx model indicated that estimated ozone concentrations were increased by 5-15 ppb compared to model results without chlorine chemistry. This was true in both the Ship Channel area and in other areas of Houston (Allen, 2003).
- EBM24. Both temporal and spatial fluctuations in air turbulence and distances between major NO and VOC sources can change the effective rates of ozone formation reactions. Comparison of modeling results using both coarse-grid and fine-grid versions of the LES-Chem model show that:
  1) If NO and reactive VOC plumes are mixed by turbulent meteorological conditions soon after emission, rapid ozone formation will occur immediately and in close proximity to the NO and VOC emission sources; and conversely
  2) If NO and reactive VOC plumes occur under low-turbulence conditions, convergence of the two plumes can be delayed, and rapid ozone formation will occur at longer distances from emissions sources (Gillani and Wu, 2003a).
- EBM25. The web-based Lagrangian Particle Model (LPM) developed at UAH has proven to be a useful tool for visualizing the transport and dispersion of atmospheric emissions. Since the model uses particles only as massless tracers, it is equally applicable to either gaseous or fine particulate emissions. UAH modified the LPM so that it can be operated through a web-page interface. When the run is completed, the user is given access to a temporal sequence of particle-position snapshots depicting transport and dispersion of particles released from the sources (http://texaqs.nsstc.uah.edu) (McNider, 2004).

VII. ANALYTICAL METHODS FOR OZONE, PM, AND THEIR CHEMICAL PRECURSORS

Because of the heavy focus of the SOS research approach on observation-based methods of evaluation and development of Observation-Based Models (OBMs), it was also necessary to place heavy emphasis on the accuracy, precision, detection limits, stability, and field-worthiness of both the measurement instruments we used and scientist, engineers, graduate students and post-docs who calibrated, operated, and compared the performance and streams of measurement data produced by those instruments.

Thus, SOS gave significant attention to the selection and comparative evaluation of:

1) Instruments, methods, physical and chemical calibration standards, and operating protocols for direct measurements of ozone, PM, and their many precursors;
2) Direct and indirect methods for measurement of meteorological variables including horizontal and vertical wind speeds and directions, mixing height of the planetary boundary layer, air and soil temperatures, moisture content of soil, relative humidity, and their horizontal and vertical temporal and spatial variability;
3) Optimizing the deployment of instruments at ground-based monitoring sites and in various sizes and types of fixed-wing aircraft, and helicopter-based, balloon-based, and tower- or tall-building-based measurement platforms;
4) Integration, coordination, and deployment of personnel and measurement teams during carefully designed and intensive field measurement campaigns; and

5) Analysis, interpretation, visual display, intercomparison, and both temporary and permanent archiving of measurement data.

As shown by the scientific findings listed below, these analytical methods-development and improvement efforts consumed a significant part of SOS' creative energies and financial resources.

A. Gas-Phase Methods (GPM)

- GPM1. SOS developed a wide array of improved methods for measuring air concentrations of volatile organic compounds (VOC) from both human and natural sources (Lee et al., 1993; Lee and Zhou, 1993, 1994; Cantrell et al., 1993; Apel and Calvert, 1994; Das and Aneja, 1994a, 1994b; Farmer et al., 1994; Riemer et al., 1994; Lee et al., 1995, 1996; Fischer et al., 1995; Weinstein-Lloyd and Lee, 1995; Apel et al., 1994, 1995; Bernardo-Bricker et al., 1995; Buhr et al., 1995a; Gilpin et al., 1997; Alvarez et al., 1998; Apel et al., 1998a, 1998b; Daughtrey et al., 1998; Luke et al., 1998; Parrish et al., 1998; Tanner et al., 1998; Williams et al., 1998).
- GPM2. Improved methods were developed for measuring oxygenated organic compounds, mainly aldehydes and alcohols (Lee and Zhou, 1993; Lee et al., 1995, 1996, 1998; Apel et al., 1998b) and for measuring hydrocarbons containing more than 10 carbon atoms (Zielinska et al., 1996).
- GPM3. Based on studies first undertaken in Atlanta, Georgia and Nashville, Tennessee, in comparison with research-grade instruments, the commercially-available instruments commonly used for measuring NO_x concentrations in air are: 1) not sensitive enough to measure NO reliably, and 2) are not specific enough to measure NO_2 reliably (Fehsenfeld et al., 1998).
- GPM4. Field inter-comparisons between flow-through and chamber techniques for measuring soil NO emissions showed that both methods yielded similar emission rate estimates (Valente et al., 1995).
- GPM5. An inter-comparison between rawinsonde systems, radar acoustic sounding systems, and LIDAR systems for estimating the mixing height of the atmosphere showed that rawinsonde systems gave the most reliable estimates of mixing height especially during early morning hours in the Nashville area (Marsik et al., 1995).
- GPM6. SOS developed a high-priority list of 60 VOC compounds for field studies in the SOS region and developed a standard mixture of 55 of these compounds for use in determining elution time standards for chromatograms. SOS also showed that aluminum canisters with interior walls coated with inorganic polymers had no detectable loss of sample integrity over the course of a year, thus indicating the viability of the canister method for quantitative field sampling and measurement of high-priority VOC concentrations (Apel and Calvert, 1994; Apel et al., 1994, 1998a; Bernardo-Bricker et al., 1995).
- GPM7. SOS developed and evaluated a protocol for accurate and precise quantification of C_2-C_{10} VOC that can be used in air-quality monitoring networks. This protocol was largely adopted in the network of Photochemical Assessment Monitoring Stations (PAMS) initiated by the USEPA in 1994 (Apel and Calvert, 1994; Apel et al., 1994, 1998a).
- GPM8. Agreement among laboratories for VOC mixtures with concentrations of 1-30 ppbv was very good, provided high quality gas-phase standards are used and introduced in the measurement instrument in a similar manner as the air samples (Apel et al., 2000).

- GPM9. Blind intercomparisons between different groups of investigators showed that the gas-chromatography elution-time technique can be used to quantify hydrocarbon species of interest with a precision of about 10% (Apel et al., 2000).
- GPM10. Excellent agreement was found between measurements of ozone, NO_x, NO_z, NO, NO_2, and HNO_3 made in remote sensing aircraft, in-situ sensing aircraft, and different in-situ sensing aircraft flying side-by-side. Very good agreement also was found between ground-based and in-situ aircraft measurements for most of the chemical species listed above (Apel et al., 1998a, 1998b; Luke et al., 1998).
- GPM11. 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 various analysts using both measurement methods (Williams et al., 1998).
- GPM12. Despite very substantial agreement among ground-based NO_y measurements, much poorer agreement was found among the aircraft and between the aircraft and ground-based measurements of NO_y during the Nashville/Middle Tennessee Ozone Study (Luke et al., 1998).
- GPM13. Rigorous intercomparison of simultaneous field measurements of ambient VOC by different techniques and researchers is critically important in determining the veracity of ambient air concentration measurements. SOS scientists developed a series of rigorous internal consistency tests for this purpose (Parrish et al., 1998).
- GPM14. A CIMS (mass spectrometry with chemical ionization) instrument to measure gas-phase HNO_3 was developed and demonstrated to be sensitive with fast response (detection limit of approximately 15 pptv for 1 s integration), accurate, precise, and interference-free. It was tested in ground-based intercomparisons at the Green Mountain Mesa field site in Boulder, CO (Fehsenfeld et al., 1998; Huey et al., 1998).
- GPM15. CIMS techniques for measurement of HNO_3, isoprene, and ammonia were developed and tested in ground-based intercomparisons during the Nashville/Middle Tennessee Ozone Study. These techniques promise to provide sensitive and fast aircraft measurements of those species. The selectivity of the isoprene technique must be tested by comparison to other techniques (Fehsenfeld et al., 1998).
- GPM16. Several different instruments for measuring NO_y were deployed and intercompared during the Nashville/Middle Tennessee Ozone Study. Results indicated that NO_y can be measured reliably in urban and suburban environments with existing instrumentation (Williams et al., 1998).
- GPM17. SOS made the first continuous OH and HO_2 measurements in urban environments during the Nashville/Middle Tennessee Ozone Study. The measurements, when compared to models, test the fundamental atmospheric chemistry that underpins chemical transport models. For Nashville SOS' OH and HO_2 measurements agreed to within a factor of two with model calculations near midday, but tend to be larger than models in the evening, at night, and for periods when nitrogen oxides are especially abundant. These observations indicate unidentified HO_x sources and questions about HO_x- NO_x chemistry (Kovacs and Brune, 2000).

- GPM18. Total OH loss-rate measurement (TOHLM) tests were used to determine the completeness of measured VOC inventories during the Nashville/Middle Tennessee Ozone Study. The presence of unmeasured VOC is indicated if TOHLM-measured OH loss rates are greater than those calculated from the sum of VOC measurements and OH reaction rate coefficients. Preliminary Nashville observations indicate that OH loss rates are about twice those calculated, suggesting unmeasured VOC (Kovacs and Brune, 2000).
- GPM19. SOS took a leadership role in the atmospheric science community and has partnered with the NOAA Climate and Global Change Program in conducting “The Non Methane Hydrocarbon InterComparison Experiment” (NOMHICE). This experiment assessed the accuracy of analytical methods used to determine mixing ratios of atmospheric non-methane hydrocarbons (NMHC) (Apel et al., 2000, 2003).
- GPM20. Based on a blind intercomparison of six ambient formaldehyde measurement techniques in 1995, SOS concluded that gas-phase standards should be employed with any of the measurement techniques, and the cartridge measurement methods were limited by long collection periods, and were generally lower in precision. Airborne CH_2O measurements by two fast and sensitive techniques, tunable diode laser absorption spectroscopy (TDLAS) and coil/2,4-dinitrophenylhydrazine (CDNPH), indicated that, on average, both instruments measured identical ambient CH_2O concentrations to better than 0.1-ppbv over the 0 to 0.8-ppbv-concentration range. However, significant differences, larger than the combined 2σ total uncertainty estimates, were observed in 29% of data set. Careful attention must be paid to the behavior of CH_2O in the inlet for accurate airborne measurements (Gilpin et al., 1997).
- GPM21. SOS prepared the first quantified and verified carbonyl standards, which were prepared gravimetrically with both calibrated permeation sources and in specially treated aluminum cylinders. Techniques such as atomic emission detection (AED) and FTIR have been applied to verify the accuracy of these carbonyl standards (Apel et al., 1998a).
- GPM22. Intercomparisons of cartridge–based (Si-Gel and C_{18}) and GC-MS measurements of carbonyls by SOS investigators showed serious discrepancies, indicating that more research is needed to resolve these discrepancies (Apel et al., 1998b).
- GPM23. A relatively fast-response (15-minute cycle) GC-FID technique was developed to measure carbonyls and other oxygenates aboard aircraft. A GC-MS technique was also being developed to measure carbonyls with a 5-minute time response (Apel et al., 1998b).
- GPM24. A photolytic converter utilizing the focused UV output from a high-pressure mercury (Hg) arc lamp was developed and tested. The new configuration permitted simple and accurate retrieval of ambient NO_2 data at very high time resolution, was more specific, provided increased sensitivity, and was less expensive to operate than previous photolytic converter designs (Ryerson et al., 2000).
- GPM25. Rapid and quantitative sampling of NO_y species, including HNO_3, was demonstrated using a short, heated Teflon inlet. In flight, standard addition calibrations of HNO_3 at the aircraft inlet demonstrated freedom from significant surface adsorption of HNO_3, which has significantly compromised measurements through other aircraft inlets (Ryerson et al., 1999).

- GPM26. Intercomparisons of ground-based NO_2 and NO_y measurements demonstrated that laser-induced fluorescence, differential optical absorption spectroscopy, and photolysis-chemiluminescence techniques are all capable of accurately quantifying atmospheric NO_2 above 1 ppbv. Further, molybdenum oxide and gold converters were shown to be capable of accurately measuring NO_y above 2 ppbv in both urban and suburban environments typical of the SOS region. These studies also concluded that generation of reliable NO_2 or NO_y data still demands skilled operators and dedicated, critical oversight during the measurement process (Williams et al., 1998).
- GPM27. Gas chromatographic methods for peroxyacyl nitrates (PANs) were refined to provide rapid and sensitive measurements. Aircraft-based instrumentation was developed to measure four of the major compounds of interest – PAN, PPN, PiBN, and MPAN – every 3.5 minutes. The measurement of PANs by proton-transfer reaction mass spectrometry (PTR-MS) was deployed during the Nashville '99 Intensive (Hansel and Wisthaler, 2000). While still in the development stage, this method has the potential to provide rapid (10 sec) measurements of PAN aboard aircraft (Williams et al., 2000).
- GPM28. Two different calibration methods for PAN were developed: 1) a diffusion source method, and 2) a method based on photochemical production of PAN in acetone/air/CO/NO mixtures. The diffusion system relies on a NO_y measurement for calibration, while the photochemical source relies on a known, efficient conversion of an NO standard to PAN. The two methods were compared during the TexAQS 2000 study and were found to agree within 5% (Williams et al., 2000).
- GPM29. An automated system for measurement of the organic nitrates produced from OH radical attack on isoprene was developed and deployed at the Dickson site during SOS' Nashville '99 study. These compounds are produced when the peroxy radicals derived from OH reaction with isoprene, reacts with NO to produce a set of 8 isomeric $RONO_2$ species. The maximum concentrations of the sum of these species were in the 100-200 pptv range, much higher than observed in a previous study. Comparison of these two data sets provides a good opportunity to examine the NO_x-dependence of this aspect of isoprene photochemistry (Grossenbacher et al., 2001).
- GPM30. An instrument based on vacuum UV resonance fluorescence was developed that is capable of fast (~1 Hz), accurate (~5%), and precise (~1 ppbv) measurement of CO from an aircraft platform. Intercomparisons with other techniques demonstrate that this method is highly specific with no identified interferences (Holloway et al., 2000).

These scientific findings (GPM1-GPM30) underscore the comprehensiveness and success of the SOS analytical program. As a result, the data bases that resulted from the SOS field campaigns are of high quality and usefulness. It was also because of this success that EPA assigned to SOS the task of developing the "Atlanta PM Supersite Program" – a mostly analytical methods development and intercomparison project.

B. Particle-Phase Methods (PPM)

Most of SOS' analytical-method studies for PM were undertaken in connection with the Atlanta Supersite Program. The major objectives of the Atlanta Supersite Program were intercomparisons and development of PM measurement techniques, and the characterization of aerosols and aerosol patterns in the Atlanta region.

- PPM1. During SOS' Atlanta Supersite Program, integrated filter methods showed good agreement for $PM_{2.5}$ mass (most samplers within ±20 percent), and sulfate and ammonium (most samplers within 10 percent) (Solomon et al., 2003a).
- PPM2. Larger discrepancies between methods were found among integrated filter methods for measurement of nitrate (±3 0 to 35 percent), possibly due to the low ambient concentrations of this ion in the Atlanta metropolitan area. Higher variability also was found for the organic (OC) and elemental (EC) carbonaceous fractions of $PM_{2.5}$. For all integrated filter samplers the OC variability ranged between 35 and 45 percent. EC variability was also high between the different analytical methods used (Solomon et al., 2003a).
- PPM3. Based on a range of studies utilizing the PC-BOSS sampler, designed to quantify fine particle composition including semi-volatile compounds, it was estimated that 10 percent to 50 percent of the fine particulate mass was not measured with the $PM_{2.5}$ FRM sampler; this was attributed to the loss of semi-volatile organic material and ammonium nitrate during sampling (Eatough et al., 2003; Modey et al., 2001).
- PPM4. Secondary organic aerosol, which comprised about 46 percent of the measured organic carbon, was from a combination of in situ photochemical production and transport of more aged secondary organic aerosol during the Atlanta Supersite Study. This conclusion is based on diurnal patterns and correlations with ozone and carbon monoxide and estimates of the fraction of organic carbon (OC) from secondary organic aerosol formation processes from mean 1-hour fine particle OC and elemental carbon (EC) data collected by new semi-continuous instrumentation deployed during the study (Lim and Turpin, 2002; Lim et al., 2003; Weber et al., 2003a).
- PPM5. In spite of the large uncertainties inherent in measuring carbon-containing particulate matter, which is very complex in composition, and in utilizing different operational techniques for measurement, there was generally good agreement between measurement systems (Lim et al., 2003).
- PPM6. Transient $PM_{2.5}$ episodes in which particle mass rapidly rises and falls over a period of a few hours but which go undetected with traditional time-integrated measurements were ubiquitous during the Atlanta Supersite Project. Continuous highly time-resolved measurements of fine particle mass and chemical composition, revealed these transient episodes. Speciated composition data show that these events are driven by sudden increases of two specific aerosol chemical components that dominate at different times – carbonaceous events in the early morning, and sulfate events in late afternoon (Weber et al., 2003b).

Apart from providing insights into sources, the unique chemical nature of these transient events may have specific health effects that previous epidemiologic studies based on highly averaged aerosol data could not readily resolve.

- PPM7. Partitioning between the gaseous and condensed phases was in reasonable agreement with predictions of the ISORROPIA thermodynamic equilibrium model. Application of this model to near real-time measurements of fine particle sulfate, nitrate, and ammonium, and gas phase ammonia and nitric acid showed good agreement, with an indication of potential bias in estimates of acidity/alkalinity (Zhang et al., 2002).

- PPM8. During the Atlanta Supersite Project, particle sizes were measured most accurately with ATOFMS, RSMS-II, and AMS during a side-by-side comparison of four particle mass spectrometers. The RSMS-II system can obtain composition information on individual particles as small as 15 nm. The three systems that utilize laser desorption/ionization, (PALMS, ATOFMS, and RSMS-II), produced mass spectra that were qualitative and representative of individual particles. The AMS instrument, which uses a two-step volatilization on a heated surface and ionization by electron impact, produced quantitative results representative of the ensemble of particles measured (Drewnick et al., 2003).
- PPM9. Single-particle positive ion classifications obtained for the Atlanta Supersite data by laser-based instruments were broadly consistent and revealed similar trends as a function of size for organic, sulfate, and mineral particles. The AMS, which is the most quantitative of the mass spectrometers compared, had nitrate to sulfate molar ratios that were highly correlated with those of the semi-continuous instruments discussed above. Based on insights from the Atlanta study, subsequent studies, such as those undertaken at the New York EPA Supersite in the summer of 2002 (PEMTACS), demonstrated the quantitative measurement capabilities of the AMS. Overall, the strength and primary focus of the laser-based instruments are their ability to find associations between chemical species in individual particles with high time resolution (Middlebrook et al., 2003).
- PPM10. Particles measured during the Atlanta Supersite Project typically included a major mass peak with a density in the ~1.5 to 1.7 g cm^{-3} range at 3-6 percent relative humidity. These data agreed with calculated densities based on measured size-resolved composition within about 5 percent (McMurry et al., 2002)

VIII. AIR QUALITY MANAGEMENT AND CONTROL (AQM)

SOS' scientific findings in this area are distilled out of a first collective analysis and interpretation of the detailed findings described above. They pertain strictly to the air quality management aspects of the ozone problem.

- AQM1. In most rural areas of the SOS region, the rate of accumulation of ozone is limited by air concentrations of NO_x rather than VOC (Trainer et al., 1993; Williams et al., 1997; Roberts et al., 1998; Sillman, 2004).
- AQM2. The efficiency with which airborne VOC and NO_x are converted into ozone is greater in rural areas than in urban areas of the SOS region (Ryerson et al., 1998; Gillani et al., 1998b; St. John et al., 1998).
- AQM3. In urban areas within the SOS region, a large fraction (typically more than 50 percent) of the ozone contributing to exceedances of the National Ambient Air Quality Standard for Ozone was transported into the urban area from regions outside the metropolitan area in which the exceedance was observed (McNider et al., 1998; Banta et al., 1998).
- AQM4. Urban Airshed Model (UAM) simulations for Atlanta, Georgia suggest that ozone accumulation throughout the Atlanta metropolitan area is more sensitive to decreases in NO_x emissions than to decreases in VOC emissions (Sillman et al., 1995; St. John and Chameides, 2000).

- AQM5. The UAM also predicts, however, that other southern cities, with smaller emissions of biogenic VOC and/or higher afternoon concentrations of NOy, could be close to the "transition condition" where ozone is nearly equally sensitive to decreases in emissions of both NO_x and VOC (Sillman et al., 1998).
- AQM6. Observation-based air-quality methods and Observation-Based Models provide a promising complement and/or alternative to emissions-based models in evaluating alternative strategies and tactics for management of ozone and other oxidants near the ground (Kleinman, 1994, 2000; Cardelino and Chameides, 1995; Kleinman et al., 1994, 1995, 1997, 1998; Sillman et al, 1997, 1998; Sillman, 1995a, 2004).
- AQM7. Summertime ozone concentrations throughout the SOS region often are high enough to inhibit photosynthesis in vegetation (Heck and Cowling, 1997; Saylor et al., 1998).
- AQM8. Adoption of an ecologically based (secondary) standard for ozone, a standard different in form from the present 1-hour and 8-hour federally mandated primary standards for ozone, with a lower allowable ozone concentration and a 3-month-long (or growing-season-long) averaging time – will provide an increased margin of safety for agricultural crops, forest and shade trees, and natural vegetation from the injurious and yield-decreasing effects of ambient ozone. This kind of a secondary standard (such the often proposed SUM06 standard) – will result in many rural parts (instead of the present mainly urban parts) of the SOS region being designated ozone non-attainment areas (Heck et al., 1998; Chameides et al., 1997; Saylor et al., 1998).
- AQM9. Coal-fired power plants were confirmed in both the 1992 SOS Intensive Field Study in Atlanta and in the 1995 Nashville/Middle Tennessee Ozone Study to be major NO_x sources. But well-fertilized crop and pasture lands and biomass burning in wildfires, controlled burning of crop lands and forests, municipal incinerators, and pulp and paper mills were as identified as additional important sources of NO_x and carbon monoxide. The TexAQS2000 Air Quality Study indicated that some of these same sources of NO_x and CO were important in the Texas and Louisiana parts of the SOS region. In this connection, it is significant to recall that the 1985 and 1990 NAPAP inventories overestimate the SO_2/NO_x emission ratio for coal-fired power plants and underestimate the CO/NO_x emission ratio for pulp mills (Buhr et al., 1995b; M. Chang et al., 1996; Gillani et al., 1998b; Jobson et al., 1998; Ryerson et al., 1998; Senff et al., 1998; Luria et al., 2000; Nunnermacker et al., 1998, 2000; St. John and Chameides, 2000).
- AQM10. Maximum ozone concentrations in the Atlanta and Nashville metropolitan areas appeared to occur when plumes from coal-fired power plants or other major point sources that also contain high SO_2 and NO_x concentrations are embedded in a broader urban plume which in turn is embedded within the more amorphous regional background concentration of ozone (Imhoff et al., 1995; St. John et al., 1998; St. John and Chameides, 2000).

- AQM11. During SOS' 1992 Atlanta Intensive and the Nashville/Middle Tennessee Ozone Study, important interactions were found to occur among land use, urban heat islands, and biogenic VOC emissions. These interactions occur because natural, managed, and urban forest trees are the largest sources of biogenic VOC in the United States and they also tend to decrease local temperatures in rural and urban areas by increasing total evapotranspiration in landscapes wherever they occur. Since isoprene is typically the most abundant VOC emitted by trees and isoprene emissions increase sharply with increasing temperature, the result of these competing effects is coupling between the distribution of forest trees, variations in local climate, and biogenic VOC emissions. This coupling is most pronounced in urban and suburban areas, where city planners and developers replace forests with areas of concrete and asphalt that give rise to urban "heat islands" with increasing temperatures. Thus, destruction of trees in urban and suburban areas increased total VOC emissions. Conversely, urban planning and construction practices that modulate the intensity of urban heat islands (for example, through placement of "green spaces" within the urban core of cities and use of high-reflectivity building materials) aided in ozone pollution abatement by decreasing air temperatures in urban and suburban areas (Cardelino and Chameides, 1990; Meagher et al., 1998).
- AQM12. In rural areas of the SOS region, summertime ozone production is usually limited by NO_x rather than VOC (Trainer et al., 1993; St. John et al., 1998; Roberts et al., 1998; Ryerson et al., 1998; Weinstein-Lloyd et al., 1998).
- AQM13. In urban areas of the SOS region (such as downtown Nashville, Tennessee and Atlanta, Georgia), summertime ozone production often is near the transition point between NO_x and VOC sensitivity (Sillman et al., 1998, Meagher et al., 1998).

X. LESSONS THAT ARE AVAILABLE TO BE LEARNED FROM THE SOUTHERN OXIDANTS STUDY (LAL)

The last step in collective interpretation of SOS scientific findings is development of a series of general lessons that are available to be learned from SOS' research, assessment, outreach, and extension efforts during the past 17 years. Major differences in air-quality have been found among geographical regions within the continental United States. These important regional differences include differences in:

1) Average and peak concentrations of ozone and particulate matter,
2) Frequencies and duration of air stagnation events,
3) Proximity of urban centers to large lakes and/or coastal areas with frequent land-sea air flow reversal compared to inland urban areas where wind-flow reversal is not very common,
4) Seriousness of risks to public health, damage to crops, forests, and engineering materials, and enjoyment of scenic vistas in urban, suburban, rural, and wilderness areas because of regional haze, and
5) Management strategies and tactics required for optimally efficient and cost-effective management of ozone and PM pollution.

Most of these regional differences are related to differences in meteorology, biogenic emissions, and/or industrial emissions. For these reasons, selection and implementation of optimum ozone and PM management strategies in any region requires comprehensive understanding of- (or specific studies to determine) the chemical climatology, biogenic and industrial emissions patterns, and the meteorological climatology of the region.

- LAL1. Observation-Based Models and methods for understanding ozone and PM pollution problems are very effective – and, in many cases, they are also more reliable than currently available Emissions Based Models and methods – especially for determining the relative efficiency and cost effectiveness of VOC and NO_x controls in decreasing ambient ozone exposures.
- LAL2. The databases produced during SOS field measurement campaigns are very useful for comprehensive and reliable evaluation of Emissions Based Models, and, also, for supporting research on new or emerging scientific issues. This is true for two principal reasons:
  1) The veracity of the concept of Observation-Based Models, which is derived from their reliance on real-world, observational data. [Or stated in another way, it is not the chemical precursors BELIEVED to be present in the air on the basis of frequently inadequate emissions inventories, but rather the chemical precursors ACTUALLY OBSERVED to be present in the air, that lead to accumulation of injurious or damaging concentrations of ozone and particulate matter.]
  2) The careful attention paid by SOS scientists and engineers to obtaining high quality field measurements of ozone, PM, and each of the major chemical precursors of these pollutants.
- LAL3. In cases of unusually large spatial and temporal variability of emissions, it is preferable that day-specific and location-specific emission inventory data be used in Emissions-Based Models of ozone and particulate matter pollution problems – especially in selecting optimal emission-control strategies of ozone and/or PM.
- LAL4. Many ozone and PM exceedances in urban non-attainment areas are not caused by the non-attainment area's emissions alone. Contributions of precursors from the surrounding region (and at least occasionally from far-distant regions such as wild fires in Canada, Mexico, Louisiana, Idaho, or other places) can also be important. Thus, to achieve attainment in many non-attainment areas, emission controls may have to be extended to include regional background sources outside the borders of the designated non-attainment area.
- LAL5. Sources of regional ozone and PM pollution are mainly urban plumes traversing the region and regional emission sources (the free troposphere is another possible source but is relatively rare and usually of minor importance). Control of regional ozone or PM pollution, therefore, may require control of both urban sources and regional sources. Furthermore, and more importantly, the optimum control approach for local and the regional sources may have to be different – that is, VOC control for local source and NO_x control for regional sources, or vice versa, that is, NO_x control for certain local sources and VOC controls for regional sources.
- LAL6. Control of NO_x from point sources should be viewed with great caution. If ozone and/or PM formation conditions in the area impacted by an NO_x source are VOC-limited, then control of the NO_x sources may cause increased concentrations of ozone and/or PM in that area. This sometimes unexpected phenomenon is often referred to as "NO_x disbenefit."
- LAL7. Ozone accumulation is almost always VOC-limited in urban-core areas of large cities (population greater than about one million people), almost invariably NO_x-limited in rural areas, and certainly less VOC-limited and more NO_x-limited in downwind suburban areas.
- LAL8. Biogenic VOC emissions are extremely important in that they tend to create NO_x-limited conditions under which the effectiveness of VOC controls for decreasing ozone exposures is diminished. NO_x-limited conditions also are created within "aged" urban plumes (due to rapid depletion of NO_x), and by unusually large (or unusually reactive) VOC emissions from industrial sources such as the Houston Ship Channel adjacent to the Houston, Texas metropolitan area.

- LAL9. Even when modest amounts of biogenic VOC are being emitted, for example in city parks, the remarkably high reactivity of isoprene and other biogenic VOC makes it imperative that these emissions be taken into account in using Emissions-Based Models for State Implementation Plans (SIPs). This raises the important requirement that reliable biogenic VOC measurements be made in essentially all ozone and PM non-attainment areas. Such measurements are not simple. They should include detailed information on land use, vegetation species composition, and emission-rate determinations for each important species of vegetation as a function of ambient temperature and wind speed conditions that affect biogenic VOC emission rates. Also, calculated biogenic emission estimates should be checked against direct measurements of biogenic loading rates (see next item, below).
- LAL10. Given the extremely fast decreases of biogenic VOC concentrations in ambient air (caused by rapid chemical reactions with peroxy radicals (OH) and ozone in air, the most reliable method for measuring atmospheric loading rates of biogenic VOC is radiocarbon (^{14}C) measurement applied on both gas-phase and aerosol-filter samples. This method produces estimates of both biogenic and anthropogenic VOC in air.
- LAL11. Well-fertilized crop and pasture lands are significant “semi-anthropogenic” sources of NO_x emissions in rural areas. These biogenic sources of NO_x emissions in rural areas can be as large as (and sometimes even exceed) the NO_x emissions from motor vehicles and combustion sources in rural areas.
- LAL12. In emission trade-off deliberations, consideration should be given to the fact that ozone production potentials of VOC and NO_x emissions vary, depending on the environment within which the emissions are discharged (for example, ozone production efficiency of NO_x is much greater in regions with large vs small total emissions of biogenic VOC) and on other factors (for example, the size of the NO_x source).
- LAL13. Ozone production efficiency per unit of NO_x emissions from power plants often is inversely proportional to the magnitude of the NO_x source. Thus, smaller power plants produce more ozone per unit of NO_x emitted than large power plants.
- LAL14. The photochemical processes that lead to formation of the secondary aerosol fraction of ambient $PM_{2.5}$ from SO_2, NO_x, and VOC emissions are very similar to the photochemical processes that lead to ozone formation from NO_x and VOC in air. For this reason, the concentrations of secondary aerosols in $PM_{2.5}$ non-attainment areas, as in the case of ozone in ozone non-attainment areas, depend more on the ratios among the reactants and their relative reactivity than they do on the amounts of these three reactants in the non-attainment atmosphere. Unfortunately, however, the optimum NO_x:VOC ratio for decreasing ozone concentrations in ambient air are not always the same as those for decreasing secondary aerosol concentrations in ambient air. Thus, optimum control strategies designed to decrease secondary aerosol formation in $PM_{2.5}$ may make the ozone problem worse. Air quality managers need to be aware of these interactions and possible interferences between ozone-control strategies and secondary-aerosol-control strategies.
- LAL15. A significant part of $PM_{2.5}$ is ammonium sulfate and nitrate, and may include also semi-volatile organic compounds. This has two implications. First, because of partial on-filter volatilization of the ammonium nitrate and semi-volatile organic components of $PM_{2.5}$, care should be exercised in preserving the integrity of filter samples. Second, besides SO_2, NO_x, and VOC, NH_3 also is a significant $PM_{2.5}$ precursor, the emissions of which need to be measured and considered in developing optimum $PM_{2.5}$ control strategies.

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