

Excerpts from
SOS NEWS YOU CAN USE
Scientific Findings from the
SOUTHERN OXIDANTS STUDY (SOS)
1988-2005:
Texas-Related Findings

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 upwind 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 (C)

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 volatile organic compounds [VOC] and nitrogen oxides [NO_x]), as well as PM_{2.5} (mainly VOC, NO_x, sulfur dioxide [SO₂], and ammonia [NH₃]).

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.

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 + CH₄ (Goldan et al., 2000)

ANO_x + AVOC + NVOC + NNO_x + ACO + CH₄ + N/ANH₃ + ASO₂ (Chameides et al., 1999)

A. Biogenic and Other Natural Sources of Ozone Precursors (BG)

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.

- 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.

B. Motor Vehicle and Other Anthropogenic Sources of Ozone Precursors (AN)

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.

- 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, SO₂, and CO₂ 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).

C. Emissions Inventories and Evaluation Methods

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.

IV. 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 through 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.

- 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).

B. Ozone Production Efficiencies of VOC and NO_x (OPE)

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).

V. 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 SO₂ 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, NO₂, 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)

- 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 µg m⁻³ to 15 µg m⁻³, which is close to the annual average NAAQS of 15 µg 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, SO₂, NO_x, and NH₃. Thus, management strategies aimed at decreasing air emissions of VOC, SO₂, NO_x, and NH₃ 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.

- 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).

VI. 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).

- 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.

VII. 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, Nashville, and Houston 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.

- OBM4. A wide range of values was observed for H₂O₂ and for summed NO_x reaction products (referred to as NO_z, or NO_y-NO_x), with no correlation between high H₂O₂ and high NO_z. There is a strong correlation between ozone and the sum NO_z+2H₂O₂, which appeared to be virtually identical between Nashville and Houston (Sillman, 2004).
- 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).

B. Emissions-Based Models (EBM)

- 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 1km² 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)
- 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 HNO₃ concentrations) during rapid ozone formation episodes in Houston. These reasonably good estimates of ozone concentrations and over-predictions of NO_z concentrations (and especially HNO₃ 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 chlorine-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).

VIII. 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.

A. Gas-Phase Methods (GPM)

- 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).

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.

IX. AIR QUALITY MANAGEMENT AND CONTROL (AQM)

- 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 SO₂/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).