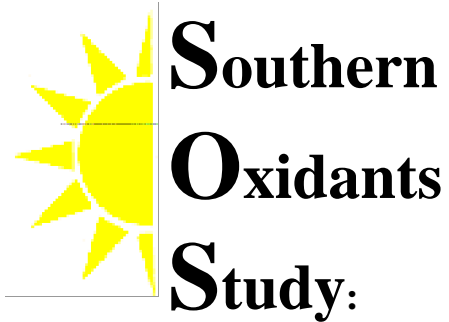


**The
State
Of The**



Research Accomplishments

&

Future Plans

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On Behalf of: The SOS Science Team

APRIL, 1995

The State of the
Southern Oxidants Study (SOS):

Policy-Relevant Findings In
Ozone Pollution Research
1988 - 1994

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The State of the Southern Oxidants Study (SOS):

Policy-Relevant Findings In Ozone Pollution Research 1988 - 1994

Policy and Executive Summary

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**POLICY SUMMARY:
THE MAJOR POLICY-RELEVANT FINDINGS OF SOS**

Ozone Abatement In the South:

- Ozone management strategies that focus on decreasing nitrogen oxide emissions will be more effective in decreasing ozone concentrations in the rural South and in Atlanta and similar urban centers than strategies that focus on decreasing anthropogenic emissions of volatile organic compounds.

Regional Chemical Climatology:

- No significant change was observed in the average ozone concentration in most rural and urban areas of the South from 1980 to 1992. This occurred despite the sizable investments made in volatile organic compound emissions controls in the region, and possibly because of the significant economic growth of the region over the period.
- During the summer months of many of these years, high concentrations of ozone occurred in rural as well as urban areas of the South.
- Ozone concentrations in rural areas of the South were not as high as in urban areas, but they frequently were high enough to inhibit photosynthesis in the region's extensive crops, forests, and ornamental plants.
- Because of these high rural ozone concentrations, revision of the current ozone standard, or promulgation of a secondary ozone standard based on a longer averaging time but a lower ozone concentration, could cause large portions of the rural South to be designated for ozone non-attainment.
- Because of the different temporal patterns of ozone episodes in rural and urban areas of the South, the promulgation of an ozone standard based on longer averaging times will tend to shift the regulatory focus in the South from urban centers to more rural areas.

Urban Non-Attainment:

- Maximum ozone concentrations in Atlanta can occur downwind of the city center but within power plant or similar point-source plumes as they emerge from the city. These point-source plumes occur within a more general urban ozone plume from biogenic, mobile, and other area sources, which, in turn, is embedded within a wide spread regional tide of enhanced ozone concentrations.
- This phenomenon of plume convergence suggests that ozone non-attainment events in the South can occur when enhanced ozone concentrations within the region, the urban plume, and smaller-scale point-source plumes intersect, producing a cumulative ozone concentration in excess of the standard.

POLICY SUMMARY (Cont'd)

Emissions:

- The primary source of nitrogen oxides in the South is the burning of fossil fuels in power plants, industrial boilers, motor vehicles, and other internal combustion engines. Nitrogen oxides also are emitted during the burning of biomass -- in open fields, recovery furnaces of pulp mills, other space and water heating furnaces stoves, incinerators, etc. and from well fertilized crop lands, pastures, and lawns. Under some meteorological conditions, nitrogen oxide production from lightning may be significant.
- Natural emissions from vegetation, principally trees, are the dominant source of volatile organic compounds in the rural South and a significant source of these compounds in many southern cities. Isoprene is typically the most significant biogenic ozone precursor.
- On-road measurements in two interstate highway tunnels indicate that the latest vehicle emissions models developed by EPA's Office of Mobile Sources (MOBILE 4.1 and MOBILE 5.0) provide reasonably good estimates of volatile organic compound, carbon monoxide, and nitrogen oxide emissions from a fleet of well maintained vehicles operating under highway conditions. It is therefore likely that these emissions models underestimate the emissions of the fleet of vehicles operating under urban conditions.
- On-road tests in Atlanta suggest that severe power enrichment caused by acceleration and other heavy engine loads is a major source of carbon monoxide and a significant source of volatile organic compound emissions from motor vehicles.

Attainment Demonstration For Atlanta Using UAM:

- Urban Airshed Model (UAM) simulations for the Atlanta metropolitan area using EPA State Implementation Plan guidelines suggest that a 90% decrease in nitrogen oxide emissions will be required to bring Atlanta into attainment with the present ozone standard. These simulations also suggest that complete elimination of anthropogenic volatile organic compounds emissions will decrease peak ozone concentrations in Atlanta, but still leave parts of the metropolitan area about 20 ppbv above the present ozone standard under some meteorological conditions.
- Analysis of the UAM simulations for the Atlanta metropolitan area using EPA State Implementation Plan guidelines indicates that the model, and/or its application following these guidelines, have significant technical deficiencies. These deficiencies include: An inability to simultaneously reproduce observed concentrations of ozone and its precursors, and an inaccurate representation of urban wind fields and thus an inaccurate reproduction of the direction, altitude, and dispersion of the urban ozone and precursor plumes. Because of these deficiencies, the conclusions drawn from UAM simulations using EPA State Implementation Plan guidelines cannot yet be viewed with confidence.

EXECUTIVE SUMMARY:

During the past 5 years, the Southern Oxidants Study (SOS) has developed and demonstrated the effectiveness of a new paradigm for policy-relevant, air-quality research in the United States. This new paradigm is based on a long-term commitment to improve scientific and public understanding of the fundamental chemical, meteorological, biological, and sociological processes that lead to the formation and accumulation of ozone (O₃) in the lower atmosphere of the earth. SOS uses the southern United States as a natural laboratory for systematic observation-based testing and evaluation of essentially every assumption undergirding EPA's present emissions-based thinking and modeling, an approach which has yet to achieve significant progress in the abatement of photochemical ozone pollution over the past 20 years.

The SOS Paradigm:

The progress SOS has made during the past five years has largely been a result of harnessing a diverse array of conceptual, scientific, financial, and organizational resources into a well coordinated scientific research and assessment program with the following characteristics:

1. Scientific and intellectual leadership from a select team of 24 skilled scientists and engineers from the university, industry, and federal and state government communities;
2. Significant financial and in-kind support provided by mutual agreement of 16 executive leaders from major stakeholders in the ozone air quality issue;
3. Technical oversight by a select group of internationally distinguished independent scientists;
4. Participation by nearly 200 research personnel from 20 states including:
 - More than 80 university scientists and engineers and 40 graduate students from 24 research universities; and
 - 75 government and industry scientists and engineers from 35 different federal, state, and industrial organizations, and public interest groups;
5. A common commitment to:
 - Developing climatologically as well as meteorologically relevant observation-based tools and models that complement emissions-based tools and models;
 - Formulating statements of scientific findings that are useful in public decision making and documenting these findings in the refereed journal literature;
 - Maintaining interactions between SOS and other regional air-quality research programs in the U.S. and abroad, especially the newly emerging North American Research Strategy for Tropospheric Ozone (NARSTO) and Photochemical Assessment and Monitoring Stations (PAMS);
 - Developing a proactive program of outreach and extension to federal, state, regional, and local air-quality managers, public interest groups, and the public at large; and
 - Increasing the number and ability of skilled air-quality professionals by providing opportunities for graduate education and research.

EXECUTIVE SUMMARY (Cont'd)

SOS Research Goals and Findings:

SOS was initiated in 1988 following *The Workshop on Atmospheric Photochemical Oxidants: A Southern Perspective*. In 1991, SOS entered into its first set of five-year Cooperative Agreements with the U.S. EPA. The resources provided by these Agreements, as well as other contracts, grants, and in-kind support from other agencies and organizations has fostered a comprehensive, university implemented research program focusing on understanding the causes of O₃ accumulation in the southern United States and developing tools needed to design and implement strategies to mitigate the harmful effects of O₃ accumulation in the South and in the nation as a whole.

Research efforts over the past five years have resulted in significant, policy-relevant scientific findings in the areas of:

- Chemical Climatology of the South;
- Role of Biogenic Hydrocarbon Emissions;
- Non-Traditional Sources of NO_x Emissions;
- Measurement Science;
- Development of an Observation-Based Paradigm for Elucidating Ozone Precursor Relationships and Evaluating Emission Inventories;
- Air Pollution Meteorology;
- 3-Dimensional Photochemical Grid Modeling; and
- Determining VOC- or NO_x-Limitation In Oxidant Formation

Studies from the SOS Regional Networks have shown the South to be a region where O₃ accumulates in high concentrations in both rural and urban areas. These rural O₃ concentrations frequently are high enough to inhibit photosynthesis in many of the region's extensive crops, forests, and ornamental plants. Because of the broad regional nature of these high rural concentrations of O₃, development of a secondary standard for ozone based on a longer averaging time could cause large parts of the rural South to be designated O₃ non-attainment areas. In contrast to the northeastern United States, regional episodes in the South are characterized by a disperse and spatially incoherent increase in oxidant concentrations, i.e., a "rising tide" of ozone, instead of the spatially coherent "river of ozone" -- a metaphor often (and appropriately) used to describe O₃ episodes in the northeast.

Observations in Atlanta indicate that maximum O₃ concentrations can occur downwind of the city center within a series of embedded plumes (i.e. a power plant or other similar point-source plume within a more general urban plume, which, in turn, is embedded within a wide spread regional "tide" of O₃). It is theorized that O₃ non-attainment episodes may occur in southern cities when these three regional, urban, and point-source plumes converge with each other, producing an additive or cumulative effect which raises the O₃ concentration above the current standard. If correct, this would imply that these peak O₃ concentrations are largely controlled by stochastic interactions between regionally dispersed processes and smaller-scale urban-plume and point-source plume phenomena.

EXECUTIVE SUMMARY (Cont'd):

These stochastic interactions, if they do indeed occur, will be difficult to simulate in the current generation of gridded air-quality models and probably also will be difficult to control using traditional pollution abatement strategies. For these reasons, SOS will test these hypotheses further in 1995 during its second major urban intensive in Nashville/Middle Tennessee. In the Nashville studies, SOS will use a series of research aircraft, supplemented by ground-based measurements, to investigate embedded plume phenomena in an urban setting.

Analyses of data gathered in SOS and calculations with both Emissions-Based Models (EBMs) and Observation-Based Models (OBMs) suggest that O₃ in the South is more sensitive to changes in anthropogenic nitrogen oxide emissions than to changes in anthropogenic VOC emissions. While still preliminary, these results suggest that strategies that focus on decreasing nitrogen oxide emissions may be more effective in abating regional and urban O₃ pollution than strategies that focus on decreasing anthropogenic VOC emissions. UAM simulations for the Atlanta area using EPA guidelines for State Implementation Plans (and thus are based on a worst-case meteorological scenario) indicate that a 90% decrease in NO_x emissions will be required to bring Atlanta into attainment with the National Ambient Air Quality Standard (NAAQS) for O₃. (According to these same simulations, even a 100% decrease in anthropogenic VOC emissions will still leave the city some 20 ppbv above the NAAQS for O₃.) However, comparisons of UAM-predicted concentration fields with SOS observations indicate some problem areas. For instance, the model does not appear to be able to simultaneously reproduce observed concentrations of ozone and isoprene.

In addition to elucidating the processes responsible for O₃ formation and accumulation in the South, SOS has focused and will continue to focus on developing the technological, intellectual, and human resources required by the nation and the southern region to effectively address the complex technical issues associated with air quality management today and in the future. Toward that end, SOS has:

- Implemented a three-tiered set of regional oxidant networks;
- Developed and evaluated a new generation of observation-based models; and
- Developed and field-tested state-of-the-science measurement techniques as well as devised protocols and sampling strategies for their effective use.

The Future of SOS in 1996 - 2000:

As this report is being prepared, the SOS Science Team begins the final year of its first five-year Cooperative Agreements with the U. S. EPA and the other federal, state, and industrial sponsors and has begun to develop a research agenda for a new set of Cooperative and Interagency Agreements for the years 1996-2000. In the near term, SOS will focus on implementing an Urban Intensive Field Measurement and Modeling Campaign in Nashville/Middle Tennessee during the summer of 1995. This will be followed by a period of thorough analysis and interpretation of data.

EXECUTIVE SUMMARY (Cont'd):

Looking toward the longer term, it is currently envisioned that the major scientific and policy-relevant research themes within SOS during the 1996-2000 time period are outlined below.

- Research Aimed At Elucidating Processes Responsible For Ozone Formation, Transport, and Accumulation in the South, including:
 - Continued and expanded interpretive use of the data from these networks and the SOS urban intensives in Atlanta and Nashville/Middle Tennessee;
 - Continued emphasis on chemical climatology, with expansion of the three-tiered regional oxidant networks to the west and north;
 - Implementation of one or two Intensive Field Studies;
 - Monitoring the impact of ozone management strategies in the South;

- Meeting National Needs Through Outreach, Tech Transfer, and Infrastructure Development, including:
 - Enhanced Observation-Based and Emissions-Based model development and evaluation;
 - Continuation of SOS's traditional focus on Measurements, Technology, and Standards;
 - Continuation of research on the improvement of methodologies used for developing emissions inventories;
 - Further collaboration and cooperation with other national and regional air quality studies in the United States and abroad, especially the North American Research Strategy for Tropospheric Ozone (NARSTO);
 - Outreach and technology transfer from SOS to federal, state, regional, and local air-quality managers, public interest groups, and the public at large (especially as it relates to PAMS); and
 - Continued graduate education of skilled air quality professionals.

- Research On Alternate Strategies For Implementing the CAAA of 1990 and Beyond, including:
 - Examination of underlying paradigms and methods used in current strategy;
 - Exploration of strategies based on alternate forms of the National Ambient Air Quality Standard for ozone; and
 - Exploration of feasibility and merits of alternate paradigms and strategies for managing O₃ pollution.

TABLE OF CONTENTS

Policy Summary	i
Executive Summary	iii
1. An Overview of SOS	1
1.1 Scientific Background that Led to SOS	5
1.2 South as a Natural Laboratory for the Study for Photochemical Oxidants	9
1.2.1 Defining the "South"	9
1.2.2 The Ozone Problem in the South	11
1.3 SOS Philosophy and Scientific Approach	13
1.3.1 A Policy-Relevant Theme: NO _x vs VOC Limitation	16
1.3.2 A Policy-Relevant Regional Context: Understanding Urban/Rural Coupling ..	19
1.3.3 A Policy-Relevant Temporal Context: Chemical Climatology	22
1.3.4 The Policy-Relevant But Robust Scientific Approach: Atmospheric Observations	23
1.3.5 The SOS Team	25
2. Major Scientific Findings of SOS: 1988-1994	29
2.1 Chemical Climatology of the South	30
2.1.1 The Climatology of Ozone	31
2.1.2 The Climatology of Ozone Precursors	33
2.1.3 Ozone/NO _y Relationships in the Rural South Suggest NO _x -Limitation	34
2.1.4 Spatial Inhomogeneities in Regional Ozone Episodes	35
2.1.5 Implications of Alternate Forms of Ozone Standard	36
2.1.6 The Southern Regional Ozone Episode - A "Rising Tide" of Ozone	37
2.1.7 Conclusion - Policy-Relevant Findings for Chemical Climatology of South ...	38
2.2 The Role of Biogenic Hydrocarbons	39
2.2.1 The Ubiquity of Biogenic Hydrocarbons	40
2.2.2 Improved Emission Estimates for Biogenic VOC	41
2.2.3 Elucidation of Isoprene Emission Mechanisms	43
2.2.4 Isoprene Emissions from Kudzu	44
2.2.5 Oxygenated VOC	45
2.2.6 Urban Forests, Biogenic Emissions, and the Urban Heat Island Effect	46
2.2.7 Conclusion - Policy-Relevant Findings for Biogenic VOC Emissions	47
2.3 Non-Traditional Sources of NO _x	48
2.3.1 Biogenic Emission from Soils	49
2.3.2 Production by Lightning	50
2.3.3 Conclusion - Policy-Relevant Findings for Non-Traditional NO _x Sources ...	51

Table Of Contents (Cont'd)

2.4	Measurement Science	52
2.4.1	Measurement of Mixing Height	52
2.4.2	The Measurement of Speciated Hydrocarbons Using Gas Chromatography	53
2.4.3	The Measurement of Carbonyls Using the DNPH Cartridge Method	55
2.4.4	Evaluation of Surface Sampling Strategy	56
2.4.5	Conclusion - The Policy-Relevant Findings in Measurement Science	57
2.5	Observation-Based Approach - Ozone Precursor Relationships	58
2.5.1	The Use of "Photochemical Indicators"	59
2.5.2	The Observation-Based Model For Urban Ozone	60
2.5.3	Conclusion - Policy-Relevant Findings for Observation-Based Approach: Ozone Precursor Relationships	61
2.6	Observation-Based Approach - Evaluating Emissions	62
2.6.1	Evaluation of Inventories Using Principal Component Analysis	62
2.6.2	Improved Motor Vehicle Emissions - The Tunnel Studies	63
2.6.3	Using Traffic Counters for Estimating Day-Specific Mobile Emissions	64
2.6.4	Power Enrichment In Mobile Source Emissions	65
2.6.5	Conclusion - Policy-Relevant Findings for Observation-Based Approach - Evaluating Emissions	65
2.7	Air Pollution Meteorology	66
2.7.1	Diurnal Wind-Structure and Pollutant Dispersion	66
2.7.2	Effects of Canopy Micrometeorology	67
2.7.3	Atlanta Non-Attainment As An Embedded Plume	68
2.7.4	Conclusion - Policy-Relevant Findings from Meteorological Studies	69
2.8	Evaluation and Improvements In Photochemical Grid Models	70
2.8.1	Development of Biogenic Emissions Inventory System (BEIS)	70
2.8.2	Evaluation of UAM Simulation of Atlanta	71
2.8.3	Evaluation of UAM Sensitivity To Specified Upper-Air Winds	72
2.8.4	Convective Cloud Parameterization In a Regional Model	73
2.8.5	Conclusion - Policy-Relevant Findings For 3-D Photochemical Grid Models	73
2.9	The VOC vs NO _x Question	74
2.9.1	The Role of the Radical Pool	74
2.9.2	The Global Perspective	75
2.9.3	The Regional Perspective	76
2.9.4	The Atlanta Perspective	77
2.9.5	Conclusion - The Policy-Relevant Finding for VOC - vs. NO _x -Limitation	79
3.	SOS In the Future	80
3.1	The Near-Term: The 1995 Nashville/Middle Tennessee Field Study	82
3.2	The Longer-Term	86
3.2.1	Research Aimed At Elucidating Processes	86
3.2.2	Meeting National Needs	89
3.2.3	Research on Alternate Strategies for Implementing CAAA-90	90
4.	Conclusion	94

1. AN OVERVIEW OF SOS

The Southern Oxidants Study (SOS) is a long-term, university-based research program aimed at expanding our understanding of the formation, accumulation, fate, and effects of ozone (O₃) and other photochemical oxidants in the southeastern United States (i.e., the South),

1. The three essential aspects of SOS:

- A study of the science of ozone pollution.
- A study focusing on the South.
- A study designed around a new paradigm in air quality research.

and developing scientifically robust methods for evaluating possible strategies for mitigation of the effects of photochemical oxidants in the South and in the nation as a whole. The SOS program grew out of a *Workshop on Atmospheric Photochemical Oxidants: A Southern Perspective*. This Workshop was held on the campus of the Georgia Institute of Technology in the Summer of 1988 at the request of the Southern Governors' Association. The major recommendation of the participants in this workshop was that a ... "study of ozone in the South and its control be undertaken" (Rodgers, and Chameides. 1988. Workshop Executive Summary, Georgia Tech, 33pp). On the basis of this recommendation, an ad hoc committee of interested university and government scientists was formed in the Fall of 1988 and the formulation of a research plan for SOS began in earnest.

After an approximate two-year planning phase that involved community-wide workshops, pilot studies, and demonstration projects, SOS initiated a five-year "PHASE I" program of research in 1990. Funding and in-kind support for these activities were provided by a number of agencies and private sponsors including the United States Environmental Protection Agency (U.S. EPA), the National Oceanic and Atmospheric Administration (NOAA), the Electric Power

Research Institute (EPRI), the Tennessee Valley Authority (TVA), the Department of Energy (DOE), and several state and local air quality regulatory agencies in the SOS region. Summaries of SOS financial support and major SOS milestones provided in Tables 1.1 and 1.2, respectively.

Funding Mechanism	Cooperative Agreements				Interagency Agreement	
	Ga Tech	Ga Tech	Univ. Alab. -Huntsville	N.Carol. State Univ.	NCAR	
Research Emphasis	Urban Obs. ⁽¹⁾	Regional Obs. ⁽¹⁾	Modeling ⁽²⁾	Emissions	MTS ⁽³⁾	SOS Total
Year						
1989						\$210,000
1990						\$440,000
1991	\$1,767,000	\$651,998	\$335,000	\$536,000	\$74,823	\$3,364,821
1992	\$2,232,000	\$851,388	\$405,000	\$730,000	\$150,372	\$4,368,760
1993	\$2,258,000	\$613,000	\$453,423	\$795,015	\$361,564	\$4,481,002
1994	\$1,097,000	\$1,220,000	\$756,000	\$1,205,000	\$283,362	\$4,561,382
1995 ⁽⁴⁾	\$835,000	\$1,015,000	\$709,000	\$920,000	\$171,000	\$3,650,000
1989 - '95	\$8,189,000	\$4,351,386	\$2,658,423	\$4,186,015	\$1,041,141	\$21,075,965
%	40%	21%	14%	20%	5%	100%
Notes: 1. Observations of chemical and meteorological parameters. 2. Modeling on urban and regional scales using emissions-based and observation-based models. 3. Measurement, Technology, and Standards. 4. 1995 funds are projections.						

Agency or Organization	Direct \$'s	In-kind \$'s	Total
U.S. EPA	\$4,468,760	\$1,000,000	\$5,468,760
Region IV of U.S. EPA		\$750,000	\$750,000
Electric Power Research Institute	\$1,500,000		\$1,500,000
Coordinating Research Council	\$400,000		\$400,000
U.S. Dep't of Energy	\$200,000	\$500,000	\$700,000
University Cost-Sharing		\$157,500	\$157,500
Nat'l. Atm. and Oceanic Admin.		\$1,300,000	\$1,300,000
Tenn. Valley Author.		\$1,000,000	\$1,000,000
Ga. Dep't. of Natural Resources		\$500,000	\$500,000
Other State Agencies in South		\$500,000	\$500,000
TOTAL	\$6,568,760	\$5,707,500	\$12,276,260

Table 1.2. SOS History and Milestones

1978	Atlanta cited for ozone non-attainment. TVA rural ozone stations established.
1980-88	Georgia spends \$750 million on VOC controls with no documented abatement in ozone.
Feb., '88	TVA-hosted meeting of Southeastern Monitoring Network Operators.
June, '88	Atlanta Workshop of Atmospheric Photochemical Oxidants: A Southern Perspective.
Aug., '88	Workshop Executive Summary presented to Southern Governors' Conference.
Fall, '88	Ad hoc SOS Steering Committee formulates science and management plan.
May, '89	Cooperative Agreement between EPA/AREAL and universities for SOS planning established.
June, '90	Cooperative Agreement between EPA/AREAL and universities for SOS Pilot Study Year.
Summer, '90	EPA conducts Atlanta Ozone Study and SOS conducts Atlanta Exploratory. SOS Rural Networks: SON becomes operational.; First SCION sites established; First major rural Intensive using SENIOR.
March, '91	Five year Cooperative Agreement between EPA/AREAL and universities established for SOS.
Summer, '91	SOS conducts Urban Pilot Studies/ Exploratories in Atlanta, Raleigh/Durham, Nashville, Tampa, Birmingham.
Dec., '91	SOS holds VOC Measurements Workshop at University of Miami.
April, '92	SOS Science Team chooses Nashville/Middle Tennessee for second Urban Intensive Field Study.
June, '92	SOS initiates interactions with LMOS, SJVAQS.
Summer, '92	SOS conducts First Urban Intensive Field Study in Atlanta. SOS Rural Networks: SON continued; SCION expanded; Second major rural Intensive using SENIOR.
October, '92	SOS Strategic Plan published.
Spring, '93	Texas, Louisiana, and EPA Region VI join SOS.
May, '93	SOS holds first SOS Data Analysis Workshop in Boulder, CO.
Nov., '93	San Diego AWMA Meeting: SOS initiates <u>International Intercomparison of 31 Regional Air Quality Studies in North America, Europe, and Japan.</u>
March, '94	SOS sponsors in collaboration with EPRI the International Plume-In-Grid Workshop in Atlanta.
June, '94	Report on <u>International Intercomparison</u> at meeting of 4th German/United States/European Union Workshop on Photochemical Oxidants, Charleston, S.C.
Summer, '94	SOS conducts Nashville Exploratory Field Study.
October, '94	Publication of <u>1993 SOS Data Analysis Workshop Report.</u>
Nov., '94	SOS Peer Review*.
January, '95	SOS holds second SOS Data Analysis Workshop in Raleigh/Durham, NC.
Summer, '95	SOS to undertake its second Urban Intensive Field Study in Nashville/Middle Tennessee.

* Time of preparation of this report

At the time of preparation of this report in the Fall of 1994, SOS is about to embark on the fifth year of its five-year "PHASE I" research program and to formulate a more detailed plan for a "PHASE II" research program that would take the study into the 21st century. As part of this process, this report on the "State of the Southern Oxidants Study" has been prepared to provide a review of the SOS research accomplishments to date and a brief summary of its future short-term and longer-term plans.

The report begins with a discussion of the salient scientific and regional aspects of the photochemical oxidant problem that gave rise to SOS and the philosophy and scientific approach that was adopted by the SOS Science Team to address these scientific and regional issues.

1.1. SCIENTIFIC BACKGROUND THAT LED TO SOS

Photochemical oxidants are a class of highly reactive chemicals produced in the earth's atmosphere. In the stratosphere, O₃, the most abundant of the photochemical oxidants, protects human, plant, and animal life from the harmful effects of ultraviolet light from the sun. In the lower atmosphere, paradoxically, O₃ and other photochemical oxidants can have adverse effects on plants, animals, and human health. In addition to O₃, photochemical oxidants include hydrogen peroxides, such as H₂O₂, organic nitrates, such as PAN (CH₃CO(O₂)NO₂), and numerous other reactive radicals.

Even though these chemical compounds are normally present only in very low concentrations, their health, economic, and ecological impact can be substantial. The Office of Technology Assessment of the U.S. Congress (OTA,

1988) estimated, for example, that high O₃ concentrations alone cost the United States \$1 - 5 billion annually in reduced crop yields and excess human health costs. Furthermore, the effects are not limited to the United States. Chameides et al. (1994, *Science*, 264:74-77) recently estimated that 10 to 35% of the world's total grain production occurs in regions of the northern

1.1. The Science of Ozone Pollution:

- O₃ produced from VOC & NO_x reactions.
- Environmental and economic impacts of O₃ pollution significant at urban, regional, and global scales.
- O₃ abatement efforts since 1970's largely ineffective.
- Numerous unresolved scientific and technical issues confound O₃ abatement efforts.
 - Complexities in chemistry
 - Natural precursor emissions
 - Regional/urban coupling
 - Meteorological influence on episodes
 - Uncertainties in emissions
 - Lack of reliable measurement technologies
 - Lack of comprehensive datasets
- Science community recommends long-term, policy-relevant regionally-focussed research programs to address these issues.

mid-latitudes where surface-level O_3 concentrations are high enough to decrease crop yields. The research of Jacobs et al. (1993. *J. Geophys. Res.* 98:14817-14826), Volz and Kley (1988. *Nature* 332:240-242) and others suggest that pollution from the United States and other industrially developed nations may be contributing significantly to a global increase in tropospheric O_3 concentrations. Because O_3 is an effective "Greenhouse Gas" when present in the upper troposphere, this O_3 increase may, in turn, be contributing to global warming.

A significant feature of atmospheric photochemical oxidants is the fact that they are secondary pollutants; that is, they are not emitted directly into the atmosphere, but are produced by photochemical reactions in the atmosphere. As illustrated in Figure 1.1A, these chemical reactions, referred to as the photochemical smog mechanism, involve hydrocarbons and other volatile organic compounds (VOC), nitrogen oxides ($NO_x = NO + NO_2$), and sunlight. VOC are oxidized by free radicals generated in sunlight; in the process, O_3 is produced from the peroxy radicals formed by oxidation of VOC, with NO_x acting as a catalyst (Figure 1.1B).

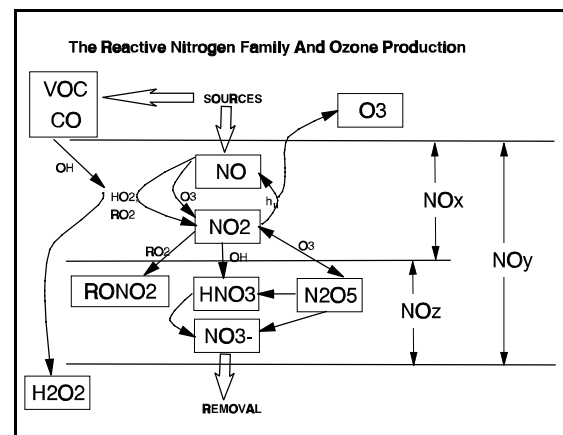
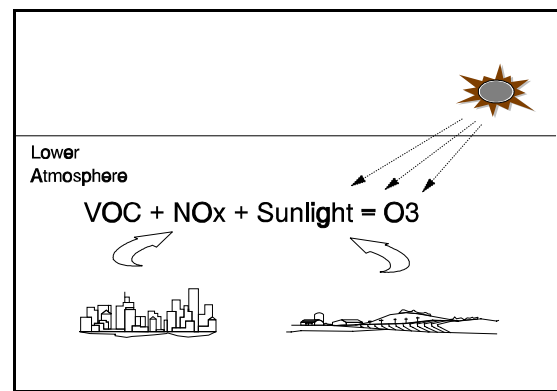


Figure 1.1A & B. Ozone is generated in the lower atmosphere from the photochemical smog mechanism involving the oxidation of volatile organic compounds (VOC), with nitrogen oxides (NO_x) acting as a catalyst in the presence of sunlight. Eventually the process is terminated when NO_x is oxidized to NO_z and removed by deposition to soils, vegetation, and surface waters or the VOC is exhausted.

Because O₃ can not be formed without VOC and NO_x, these two classes of compounds are often referred to as ozone precursors. In contrast to the photochemical oxidants, the ozone precursors are, for the most part, emitted directly into the atmosphere from a combination of natural and anthropogenic sources (i.e., they are primary pollutants). In principal therefore, high concentrations of O₃ and related photochemical oxidants can be decreased through the implementation of technological or institutional measures that limit emissions of VOC, NO_x, or both. In practice however, implementation of a strategy that actually results in lower O₃ concentrations has proven to be considerably more problematic. After more than 15 years of progressively tighter and tighter controls on emissions of ozone precursors (especially VOC), little documented progress has been achieved. As of August 1992, there were 97 ozone non-attainment areas in the United States and an estimated 70 million people living in these 97 areas (EPA. 1992. *National Air Quality and Emissions Trend Report*).

It would appear that attempts to decrease O₃ pollution in the United States have been confounded by a number of factors. These include:

1. Non-linearities and complexities in the photochemical smog mechanism that can, depending upon the relative concentrations of VOC and NO_x, make a VOC-based or a NO_x-based emission control strategy ineffective against O₃ pollution.
2. The non-negligible and often unaccounted for contributions of natural sources of ozone precursors (especially natural hydrocarbon from vegetation).
3. The long-range transport of O₃ and ozone precursors which effectively give rise to urban/rural and urban/urban interactions and exchange.
4. The strong influence of meteorology on the severity and frequency of short-term O₃ pollution episodes which confuse trend analysis and can mask the effects of pollution control measures or their lack of effect.
5. The large uncertainties associated with emissions inventories and the lack of ambient chemical data documenting the actual impact that controls and regulations have on these emissions.

6. The lack of reliable methods and dependable instrumentation for measuring speciated VOC and NO_y concentrations on a routine basis.
7. The lack of comprehensive chemical and meteorological datasets to test numerical and conceptual models of urban- and regional-scale photochemical smog formation.

In large measure, recognition of these technical complexities, as well as the lack of apparent progress in abating O₃ pollution through current regulations, led the members of the *1988 Workshop on Photochemical Oxidants: A Southern Perspective* to recommend initiation of a long-term research program on the accumulation and fate of oxidants in the southern United States (Rodgers and Chameides, 1988). A similar recommendation was strongly advocated three years later in a report of the National Academy of Sciences on *Rethinking the Ozone Problem in Urban and Regional Air Pollution* (NAS, 1991. National Academy Press, 500 pp). In this report it was recommended that "a coherent and focused national program should be established for the study of tropospheric ozone and related aspects of air quality in North America." The then fledgling SOS was specifically identified in the report as an example of the type of regional program that "should be developed" to address the complex scientific and technical issues surrounding the ozone pollution problem.

Thus, SOS was born out of recognition by the scientific community that, in spite of legislatively-mandated regulations and timetables for solving the ozone pollution problem in the United States, there were numerous unresolved technical and scientific issues surrounding the phenomenon of O₃ pollution, and that these unresolved issues hinder development of effective policies for managing the O₃ problem. The SOS Science Team took as its mandate development of a scientifically rigorous research program that can provide meaningful and useful input into a policy-making community faced with a very challenging environmental problem.

1.2. SOUTH AS A LABORATORY FOR STUDY OF PHOTOCHEMICAL OXIDANTS

The production, accumulation, transport, and eventual removal of O₃ and other photochemical oxidants within the atmospheric boundary layer generally occurs on regional scales; that is, over characteristic spatial scales that span several thousands of kilometers (Vukovich, et al. 1977. *Atm. Env.* 90:5687-5698; Logan, 1989. *J. Geophys. Res.* 94:8511-8532.). It follows, therefore, that a comprehensive study of the processes that control the formation, accumulation, and

1.2. Why a *Southern* Oxidants Study?

- O₃ pollution a fundamentally regional-scale phenomenon.
- SOS focusses on 10-state region of the southeastern United States. It is a:
 - Region with extensive regional O₃ pollution, and significant urban non-attainment.
 - Region that has unique characteristics that may render abatement strategy from other regions ineffective.
 - Region with characteristics that make it an excellent laboratory for studying photochemical mechanisms and atmospheric/biospheric interactions.

fate of photochemical oxidants must, at the very least, have a spatial coverage of similar regional magnitude. In this section we briefly review the characteristics of the southern region of the United States that induced the SOS Science Team to choose it for the focus of a scientific research program on photochemical oxidants.

1.2.1. Defining the "South"

Before beginning the discussion of the characteristics of the South, it is useful to develop a working definition for what is meant by "Southern" in the name "Southern Oxidants Study". The "South" is a not a very specific term; the exact portion of the United States it denotes varies considerably depending upon the context in which the term is used and the person or group using it.

The Congressional Sunbelt Caucus and Southern Governors' Association adopt rather expansive political definitions of the South that include states as far west as New Mexico and as far north as Missouri. Such a large spatial region would be unwieldy in a regional air quality study, and thus, a smaller portion of this region was identified for study in SOS. As illustrated in Figure 1.2, the SOS was initially designed to focus on eight southeastern states: Alabama, Florida, Georgia, Kentucky, Mississippi, North Carolina, South Carolina, and Tennessee. Together these states encompass the lowland areas of the Atlantic and Gulf Coast Plains, through the uplands areas of the Piedmont, to the high-elevation areas of the Appalachian Mountains. They also comprised U.S. EPA's Region IV jurisdictional area and thus represented a useful geographical unit of study from a regulatory point-of-view. In 1993, two states from EPA's Region VI, Louisiana and

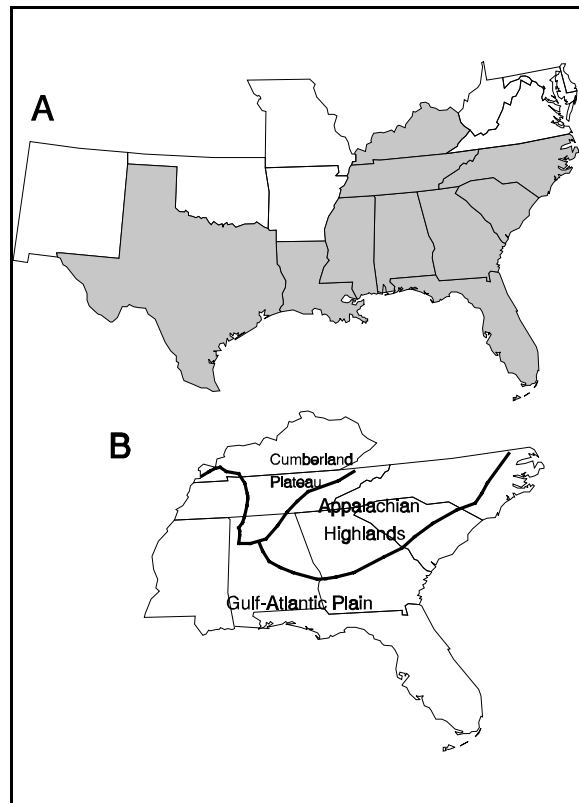


Figure 1.2. The Southern United States and the region focussed on by SOS. A. The states included in the Congressional Sunbelt Caucus with the 8-state region initially identified for study by SOS indicated by the dark shading and the two additional states added in 1993 by the light shadings. B. The major physiographic features of the SOS study region.

Texas were added to the program to broaden SOS' focus to include areas with larger impacts from the petrochemical industry. For the purposes of this report, we will use the "South" to denote the 10-state area currently included in the SOS program.

1.2.2. The Ozone Problem In The South

Like other regions of the United States, the lands and other natural resources of the South are used for a wide variety of human enterprises. A large portion of the land area of the South is currently used for agriculture (20 - 25%), but the majority of the region is covered by dense and highly productive forests (60 - 70%). However, the image of a largely rural South belies the fact that the region is also home to a number of densely populated metropolitan areas and areas of intense industrial activity. Moreover, the region has been and continues to experience significant growth in its urban population and industrial output as rural southerners relocate to urban locales and immigrants from other regions of the nation and other countries move to the South. This growth suggests that pollution problems in general are likely to become more critical in the South in the coming decades.

Given the South's rural and agricultural image, it is perhaps surprising that summertime O_3 in this region is, on average, among the highest in the U.S. Because of these high concentrations, and the fact that many of the agricultural and forest crops in the South are relatively susceptible to visible injury and economic damage from O_3 , the South bears a disproportionate share of the environmental and economic burden of regional-scale O_3 pollution (see Figure 1.3).

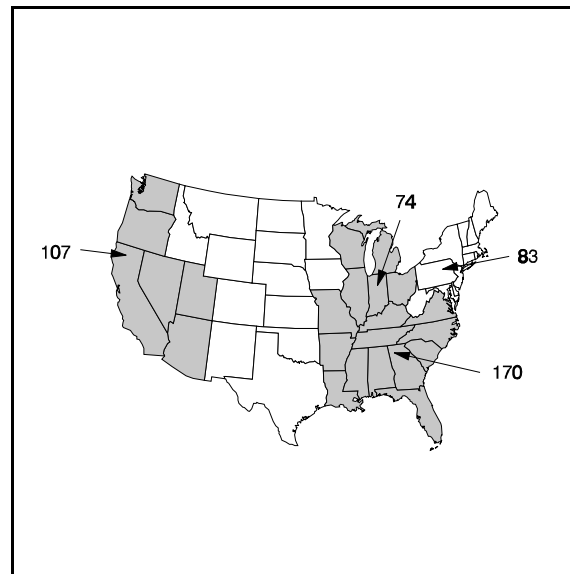


Figure 1.3. Thousands of acres of U.S. forests exposed to $O_3 > 120$ ppbv during 1987 and 1988 by region. Based on analysis of Lefohn (1991. *Surface Level Ozone Exposures and Their Effects on Vegetation*, Lewis Publishers, 31-84).

While perhaps not quite as critical as other regions of the nation, the urban O₃ pollution problem in the South is also extensive. There are currently twenty-eight O₃ non-attainment areas designated in the 10 state region that comprises the SOS focus area; of these twenty-eight, one (Houston) is designated as "severe", and five are designated as "serious".

In spite of the wide geographical distribution of the O₃ pollution problem in the South, the atmospheric chemistry of the region and of the region's urban centers were probably the least studied of any region of the United States prior to the implementation of SOS. Lack of data on the South's air quality was particularly vexing given the high probability that O₃ abatement strategies developed from air quality studies in other regions of the United States are not well-suited to the South because of the region's unique characteristics. These characteristics include:

1. A stagnant and hot summer climatology that inhibits dispersion of pollutants and favors O₃ accumulation near the ground; and
2. Dense vegetation which, when coupled with the high summertime temperatures, results in anomalously large emissions of isoprene and other natural hydrocarbons (Lamb et al., 1987. *Atm. Env.* 21:1695-1705).

On the other hand, the South has characteristics that make it an excellent laboratory for studying aspects of the O₃ pollution problem that are highly relevant to all regions of the nation. For example, because of the South's stagnant summertime climatology, field studies in the South are well-suited to elucidating photochemical pathways (Samson and Shi, 1989. OTA Report, 1989). The high-diversity of forest-types in the South, ranging from tropical in the most southerly coastal regions to boreal at the highest elevations of the Appalachian Mountains, makes the region ideal for studying biogenic emissions of ozone precursors, effects of O₃ and other oxidants on vegetation, and the interactions between the two.

1.3 SOS PHILOSOPHY AND SCIENTIFIC APPROACH

As described in preceding sections, very complex scientific and technical issues surround the problem of urban and regional oxidants and O₃ pollution in the nation in general, and in the South in particular. It is also true that, since the late 1970's, the nation has attempted to eliminate, or at least mitigate, the harmful effects of urban O₃ pollution through a process that involved very specific types of interactions between air quality research and the promulgation of standards, regulations, and emission controls. This process has had, at best, limited success throughout the nation and virtually no documentable success in the South. In undertaking to develop a research plan for

SOS, the SOS Science Team considered these facts and concluded that, in order to be successful, the program would need to be innovative. Toward that end, the SOS Science Team attempted to break with the traditions of research in air quality and develop a program that was based on new paradigms and approaches. The key aspects of this new approach are discussed in this section.

1.3. The SOS Research Paradigm

SOS strives to be a long-term, policy-relevant research program capable of informing the policy-making community on a continuous basis.

- Science Theme:
 - NO_x vs. VOC limitation
- Regional Context:
 - Urban/Rural coupling
- Temporal Context:
 - Chemical Climatology
- Research Approach:
 - Atmospheric Observations -
The organizing principal behind all studies.
- The Science Team:
 - University-based
 - Coalition of all science communities
 - Dedicated to building upon improved human resource base and sustainable economic development.

The scientific study of urban and regional air quality in the United States over the past two decades has been largely characterized by an environmental/policy-making paradigm that chronologically places research in front of policy-making and places the setting of regulations and emission controls as the final action in the process. Implicit in this paradigm is the assumption that air pollution problems can be essentially eradicated through the implementation of a narrowly-focused, scientific research program that provides technical input into a policy-making process that promulgates rules and regulations to limit critical emissions in the affected area. In order to meet specific legislatively mandated deadlines, the research program developed out of this paradigm usually has a relatively short time-horizon and is almost always terminated once the policy decisions have been made. A common example of this approach is a research program designed to develop and validate an air quality model that is then used by a local, state, or federal agency to evaluate various emission control options being considered to meet some specific air quality criteria or standard.

In principle, such an approach can be effective, but it requires that the research and related policy decision-making process be carried out in a linear fashion. It also presumes that the research/regulatory process can be expected to reach closure (i.e., success) at the point of implementation of the relevant policies and/or regulations. Experience has taught us, however, that this linear model of research and regulation is not appropriate for complex environmental problems, such as those rising from O₃ pollution. Because of the impossibility of completely understanding all the scientific and socio-economic issues involved, it is unlikely that a short-term, narrowly focused research program research will be able to adequately understand all the nuances of the problem. Moreover even if it did, these findings would soon become outdated by continuing population growth and changes in urban-industrial activities and land use patterns.

In the case of complex environmental problems like O₃ pollution, an iterative approach promises to be more effective. In an iterative approach, the goal is the long-term management and mitigation of pollution, rather than the (less realistic) total elimination of the problem through a one-time regulatory fix. However, such an iterative approach requires continuous feedback between on-going research programs and policy-making activities, so that policies and regulations can be periodically fine-tuned or altered as new technical information and data on the effectiveness of current regulations become available. To accomplish this iterative approach, the relevant research programs must adopt a longer-term, policy-relevant rather than policy-driven paradigm so that they can inform the policy community on a continuous and ever-improving basis.

SOS was developed and designed on the basis of this later paradigm. The SOS strives to be a long-term, policy-relevant research program capable of informing the policy-making process on a continuous basis. While cognizant of the mid-1990's regulatory deadlines for urban ozone pollution control mandated by the Clean Air Act Amendments (CAAA) of 1990, the SOS Science Team believes that ozone pollution will continue to plague many of our cities and rural areas long after the CAAA deadlines pass. SOS has therefore designed a program that will aid policy-making decisions in the mid-1990's and beyond. Five key aspects of the SOS program that epitomize this approach are described below.

1.3.1. A Policy-Relevant Theme: NO_x vs VOC Limitation

Despite the fact that the roles of VOC and NO_x as tropospheric O₃ precursors have been firmly established, the development of an effective strategy for abating O₃ pollution in the United States cities by decreasing anthropogenic emissions of these precursors has proven to be problematic (Chock, D.P., and J.M. Heuss. 1987. *Atm. Env.* 16:1146-1153; Friedman, R.M., et al. 1988. *New Clean Air Act Issues*, OTA Report; Lindsay, R.W., et al., 1989. *J. Air Poll. Contr. Assoc.* 39:40043; NAS, 1991. *ibid*). In spite of the ozone abatement strategies implemented in the early 1970's, an estimated 70 million Americans now live in areas that exceed the O₃ standard (EPA, 1992, *ibid*). Moreover, while the CAAA of 1990 prescribes specific VOC emission reduction targets in urban non-attainment areas, there is no firm scientific consensus on whether reducing VOC emissions or NO_x emissions is the most effective strategy for O₃ abatement (NAS, 1991, *ibid*).

It is difficult to imagine how our state and federal regulatory agencies will be able to design a successful, let alone cost-effective, O₃ abatement strategy if we are not able to definitively determine whether a VOC-based, or NO_x-based, or combined VOC-NO_x-based emission control strategy is needed. In recognition of this serious problem, SOS has chosen as its central scientific theme the development, evaluation, and implementation of research tools, procedures, and field experiments for assessing the relative importance of VOC and NO_x limitation on O₃ accumulation in a given airshed.

Much of the difficulty in addressing the problem of VOC vs NO_x limitation can be traced to O₃'s complex photochemistry. The rate of O₃ production is a non-linear function of the mixture of VOC and NO_x in the atmosphere. Depending upon the relative concentrations of VOC and NO_x and the specific mix of VOC present, O₃ production rates can be highly sensitive

to VOC and insensitive to NO_x or highly sensitive to NO_x and insensitive to VOC. Another difficulty arises from the presence of naturally produced hydrocarbons and/or NO_x (see Figure 1.4). Because these natural emissions can not be controlled, a strategy based on decreasing anthropogenic VOC (or NO_x) may not be effective even when O_3 production in the area is most sensitive to VOC (or NO_x) if natural emissions of these precursors are significant (Chameides, W.L. et al., 1988. *Science*, 241:1473-1475).

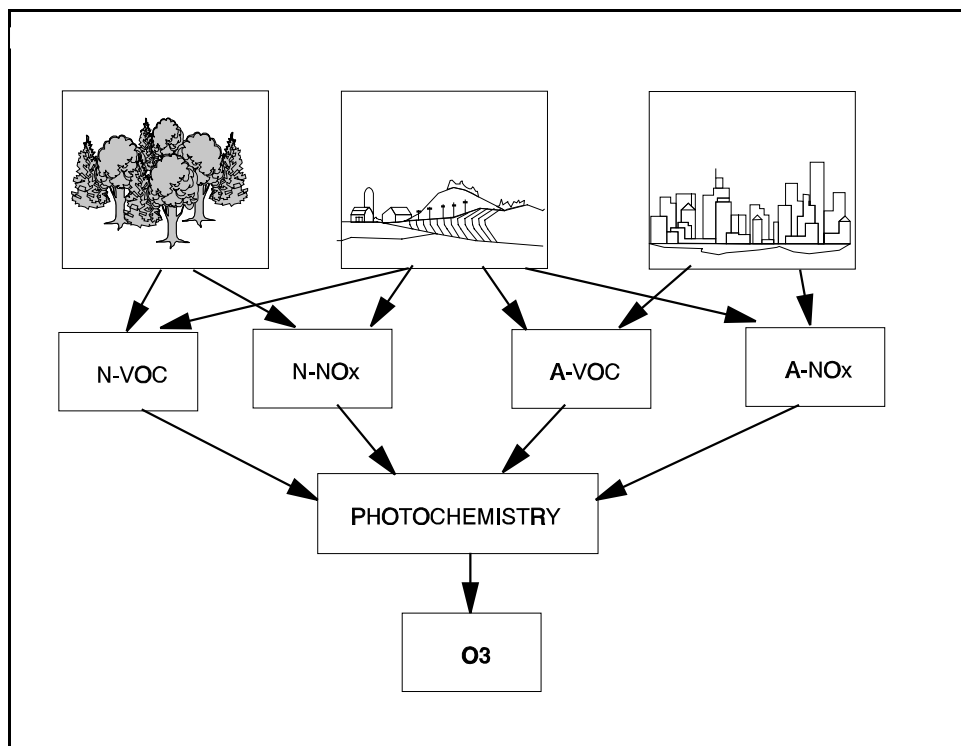


Figure 1.4. The evaluation of the effectiveness of VOC-based and NO_x -based strategies for ozone pollution abatement is confounded by the potential significant contribution of VOC and NO_x emissions from biogenic and other natural sources. In the Figure A-VOC and A- NO_x is used to denote anthropogenic VOC and NO_x , respectively, and N-VOC and N- NO_x is used to denote natural VOC and NO_x , respectively.

The determination of VOC and NO_x-limitation is thus a complex, technical issue that requires careful scientific research using advanced instrumentation and mathematical models. In SOS, this scientific theme has been addressed through a multi-tiered approach involving:

1. Development and testing of instrumentation capable of measuring the concentrations of VOC and NO_x compounds in urban and rural atmospheres (see Section 2.4).
2. Measurement of different VOC and NO_x species concentrations in urban and rural atmospheres (see Sections 2.1, 2.2, 2.3, 2.4).
3. Characterization of the magnitudes and relative importance of natural and anthropogenic sources of VOC and NO_x (see Sections 2.2, 2.3, 2.6).
4. Testing and evaluation of the photochemical oxidation mechanisms believed responsible for the degradation of VOC's in the O₃ photochemical smog mechanism (see Section 2.2, 2.9).
5. Development, evaluation, and implementation of prognostic and diagnostic models for inferring VOC and NO_x limitation (see Sections 2.5, 2.8).

1.3.2. A Policy-Relevant Regional Context: Understanding Urban/Rural Coupling

Because the current National Ambient Air Quality Standard (NAAQS) for O₃ is designed primarily for protection of human health, virtually all of the U.S. O₃ non-attainment areas are located in urban centers. For this reason, the relevant regulatory activities mandated by the CAAA have focused almost exclusively on the abatement of urban ozone pollution. In developing a strategy to accomplish this goal, it has been implicitly assumed that the most effective approach is one that limits O₃ precursor emissions within the urban non-attainment area. Air quality studies designed to assist in this process, have thus largely focussed on quantifying precursor emissions and their fate within urban non-attainment areas as well, with much less attention given to the non-urban and regional (i.e., suburban, rural and remote) aspects of the problem. This has been especially true in the southern United States, where O₃ air quality studies before SOS have been largely limited to short-term assessments of air pollution episodes in a handful of urban centers (eg., Houston, Dallas, Atlanta).

In contrast to the narrow, urban-core air quality studies described above, SOS has been designed to understand the regional characteristics of O₃ pollution in the Southern United States and how these regional characteristics are coupled to and influence O₃ concentrations in the urban centers of the region. This decision was based on two critical perceptions:

1. While not always severe enough to trigger non-attainment designations, O₃ pollution in rural areas, and especially in the southern United States, is sufficiently severe to cause significant environmental and economic losses through its effect on agricultural crops, forest and shade trees and other vegetation (Adams, et al. 1989. *J. Air Waste Manag.* 39:960-974; Runeckles, and Chevonne. 1992. *Surface Level Ozone Exposures and Their Effects on Vegetation*, Lewis Publishers, 189-270). For this reason, understanding the factors influencing the severity and frequency of rural O₃ pollution episodes is an important undertaking in its own right. In this regard, it is interesting to note that there is a distinct possibility that the U.S. EPA will modify the current NAAQS for O₃ or add a separate and distinct secondary standard in the near future (perhaps 1997) to address rural O₃ pollution and their effects.

2. As illustrated in Figure 1.5, there exists a significant coupling between rural and urban O_3 concentrations. For instance, Lindsay and Chameides (1988. *Environ. Sci. Technol.* 22:426-430) found that during a typical O_3 non-attainment episode in Atlanta, some 60 - 75% of the peak O_3 observed in the urban plume could be attributed to O_3 transported or advected into the Atlanta metropolitan area from its largely rural surroundings and other more distant urban, suburban, and rural areas of the South. Because of this urban/regional coupling, it seems likely that urban ozone pollution can be more easily understood and mitigated by accounting for this regional "background" O_3 pollution and taking regulatory steps to decrease its severity. Such an approach would, however, require a thorough understanding of the mechanisms that couple the regional and urban atmospheres.

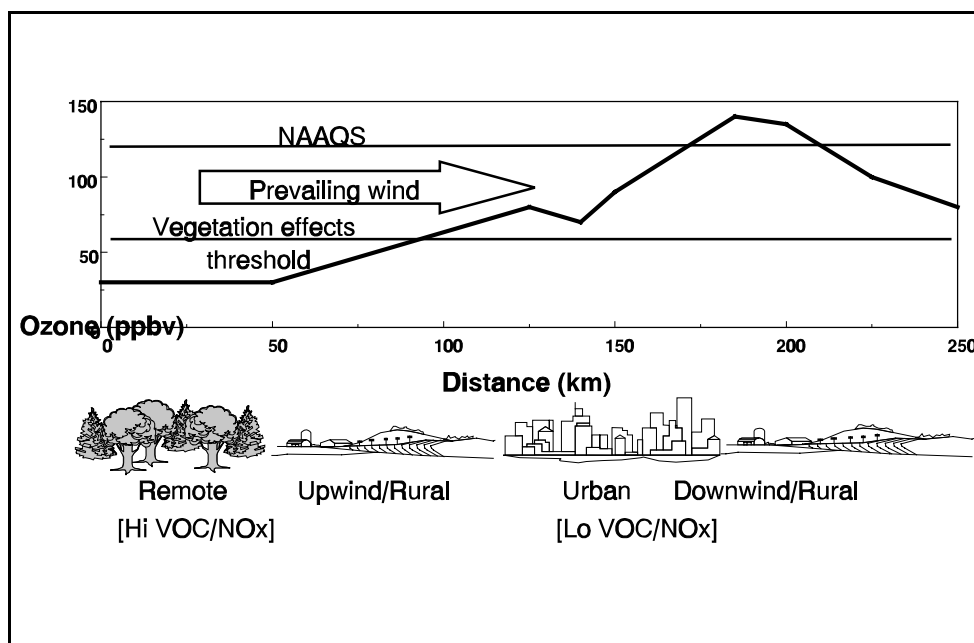


Figure 1.5. Studies indicate a degree of coupling between high O_3 concentrations in rural and urban areas. It is not uncommon for regional O_3 to contribute as much 50% or more to peak concentrations in urban areas that trigger non-attainment designations. By the same token transport of O_3 out of urban areas contributes to elevated concentrations of O_3 in rural areas located downwind of the urban core.

To understand the interaction between regional and urban O₃ pollution in the South, SOS has adopted a unique approach among air quality studies in the United States: Inclusion of simultaneous and interacting regional-scale and urban-scale air quality field experiments. To accomplish this, SOS has embedded intensive urban studies within the Southeastern Regional Oxidant Network (SERON). This regional network has been designed to achieve high spatial and temporal resolution, as well as state-of-the-science characterization of the chemistry of the air in the region by adopting a tiered approach, with three parallel sub-networks operating at different levels of spatial and temporal resolution and instrumental and technological sophistication. As illustrated in Figure 1.6, the network includes:

1. **The Spatial Ozone Network (SON)** for continuously monitoring surface O₃ concentrations at a large number of sites;
2. **The Southeastern Consortium Intermediate Oxidant Network (SCION)** for monitoring O₃, NO, NO_y, and speciated hydrocarbon concentrations at a smaller number of sites;
3. **The Southeastern Network for Intensive Oxidant Network (SENIOR)** for characterizing the detailed chemistry and chemical processes occurring at five rural sites in the region using state-of-the-science instrumentation.

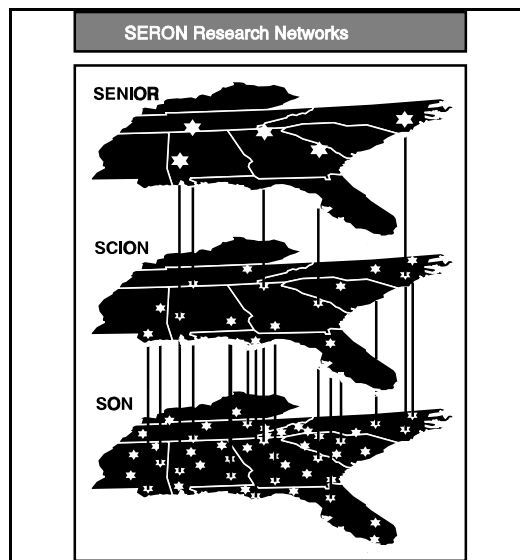


Figure 1.6. The 3-tier regional network (SERON) Network developed by SOS to establish chemical climatology of the region and elucidate the mechanisms responsible for oxidant generation on regional scales.

The insights gained thus far from SERON are discussed in Section 2.1

1.3.3. A Policy-Relevant Temporal Context: Chemical Climatology

Because the present NAAQS for O₃ is designed to address short-term, one-hour O₃ exceedances, air quality studies on O₃ pollution have focussed mostly on air pollution episodes. Since these episodes typically last 1-3 days, air quality studies have, by necessity, been dominated by a meteorological approach to understanding the relevant phenomena.

However, while short-term episodes are the current regulatory focus, longer term variability in O₃ may also be highly relevant. Factors that affect the seasonally averaged O₃ concentrations in a region, such as inter-annual shifts in climatology, can have a major impact on the severity and frequency of O₃ pollution episodes (cf., Lindsay et al., 1988, *ibid*). For this reason, it is conceivable that strategies focused on decreasing longer-term average O₃ concentrations would be effective in decreasing the frequency, duration, and peak concentrations of O₃ episodes. Indeed, consideration is currently being given to changing the NAAQS for O₃ to give weight to seasonally-averaged O₃ concentrations because of concern over the human health and vegetation effects of long-term exposures to moderately high O₃ concentrations (i.e., of the order of 60 ppbv or more). For this reason, SOS has sought to document and understand the seasonal and inter-annual chemical climatology of O₃ in the South and how this climatology affects regional and urban O₃ pollution episodes. To accomplish this, SOS has stressed:

1. Analysis of historical databases (see Section 2.1);
2. Development of a new database that can better characterize the chemical climatology of the region, through the implementation of SERON (see Sections 2.1, 2.2);
3. Development of analytical tools capable of investigating ozone photochemical relationships within a climatological as well as an episodic framework (see Sections 2.1, 2.5).

1.3.4. The Policy-Relevant But Robust Scientific Approach: Atmospheric Observations

In large part because of the past policy-driven (as opposed to policy-relevant) nature of air quality research in the United States, the central scientific themes in many of the nation's major air quality studies has been on:

1. Development of detailed emissions inventories; and
2. Evaluation of an emissions-based air quality model that uses the emission inventories developed in (1) to test the potential effectiveness of various emission control strategies.

While such an approach is essential in developing and implementing specific regulatory procedures, it is rarely productive in research, especially when dealing with complex scientific issues such as those that relate to O₃ accumulation and exposure.

SOS has endeavored to take a more scientifically rigorous approach that is *relevant to*, but not *driven by* the specific needs of the policy-making community. Our aim has been to provide robust input to the policy-making community by first elucidating the fundamental processes at work in the accumulation and dissipation of O₃ pollution and developing a hierarchy of models and analytical tools that are consistent with scientific understanding of these processes and useful in assessing a wide-range of policy-relevant technical issues. As illustrated in Figure 1.7, the foundation of this approach is ambient observations of the chemical and physical state of the atmosphere, since, in the final analysis, it is the chemistry and physics of the atmosphere itself that determines the frequency, duration, and intensity of air pollution and its effects. Because of the central role of observations, field measurements and, by extension the development, testing, and evaluation of the instrumentation used in these field measurements, have all played and will continue to play a central role in SOS research activities.

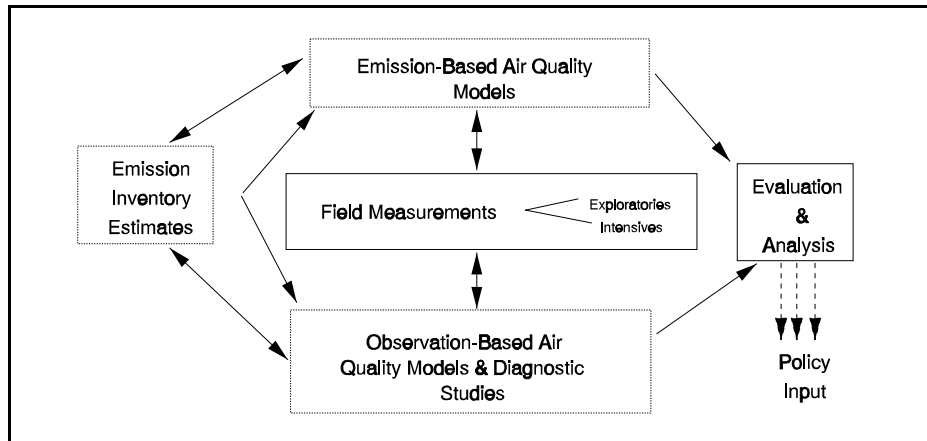


Figure 1.7. Atmospheric observations are the organizing principle for all research in SOS. Data obtained in field measurements are used to test, refine, and develop emission inventories, to test and refine emission-based air quality models, and to drive observation-based models and diagnostic studies. Since a hierarchy of emission-based and observation-based models, are used to address scientific questions, more robust input to policy decisions is possible.

The database developed from SOS field measurement campaigns have begun to provide the foundation for a host of different diagnostic and prognostic studies that address a variety of policy-relevant scientific questions. These diagnostic and prognostic studies include:

1. Evaluation of gridded, emissions-based air quality models (EBM's) typically used in regulatory processes (see Section 2.8).
2. Implementation of observation-based air quality models (OBM's) that are based on actual air concentrations rather than emissions inventories, and are therefore capable of providing independent assessments of O₃ precursor relationships and the efficacy of various emission control strategies (see Section 2.5).
3. Independent evaluation of emissions inventories from ambient data and the use of ambient data for assessing the accuracy of emissions inventories developed using the framework prescribed by regulatory agencies (see Section 2.6).
4. Evaluation and development of new algorithms for use in air quality models to simulate emissions, transport, and photochemistry (see Sections 2.2, 2.3, 2.7, 2.8).
5. Evaluation of instrumentation and field experiment designs that might be used in the future by national, regional, or state regulatory agencies for evaluating O₃ precursor and transport policy-relevant issues (see Section 2.4).

1.3.5. The SOS Team

A key feature of the SOS is the scientific team that provides leadership for the program as a whole. SOS is a university-based research program involving nearly 200 scientists from 40 different institutions; these institutions include 23 universities, as well as 17 government laboratories and private/industrial organizations (see Figure 1.8 and Table 1.3). The term "university-based" is used to denote a unique feature of SOS: The central role played by universities and their faculty in developing the research plans, procuring funds to support the activities called for in these plans, and overseeing the carrying out of the planned research.

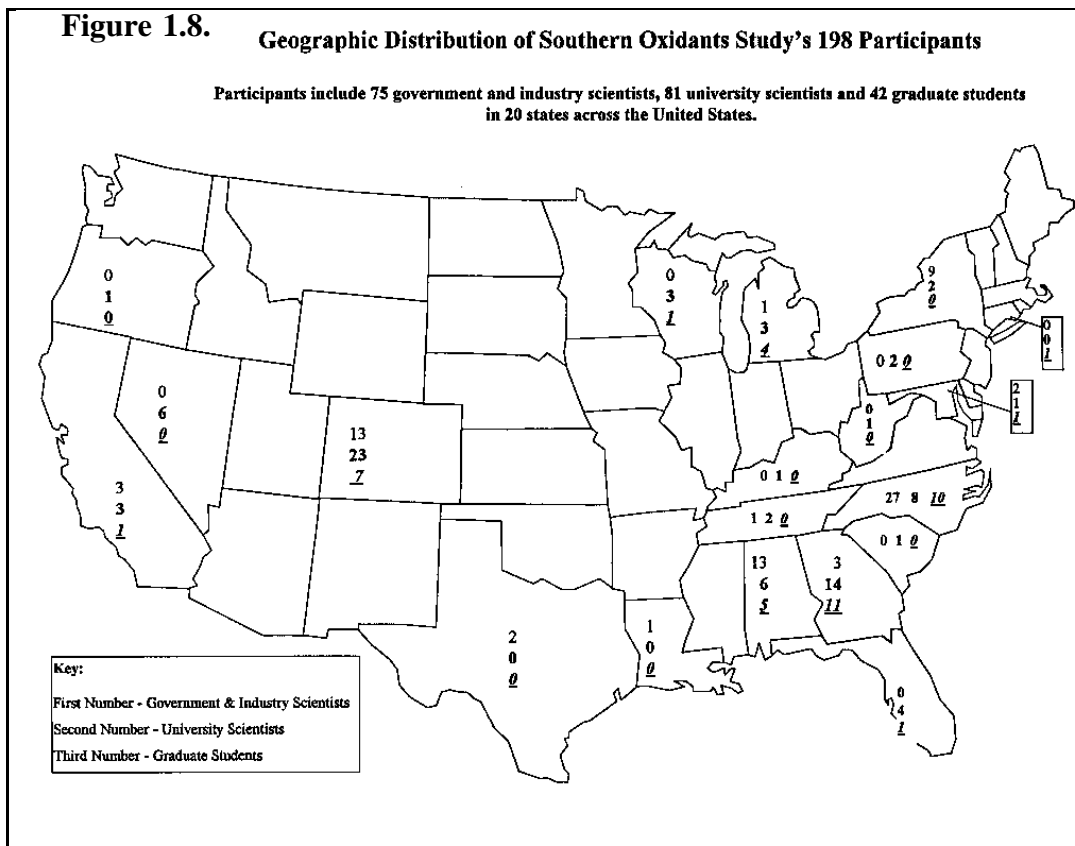


Table 1.3. The SOS Participants

Universities	Government and Private Industry
Appalachian State University	American Lung Association
Clemson University	Atlanta Regional Commission
Colorado State University	Brookhaven National Laboratory
Desert Research Institute	Computer Sciences Corporation
Duke University	Coordinating Research Council
Georgia Institute of Technology	DGA, Inc.
Harvard University	Duke Power Company
North Carolina State University	Electric Power Research Institute
Oregon Graduate Institute	Environmental Protection Agency
Pennsylvania State University	AREAL
State University of New York - Westberg Campus	AEERL
State University of New York at Albany	Office of Air Quality Planning and Standards
University of Alabama at Huntsville	Office of Mobile Sources
University of California at Riverside	Region 4
University of Colorado	Region 6
University of Denver	Environmental Science & Engineering, Inc.
University of Kentucky	General Motors Research Laboratory
University of Maryland	Georgia Department of Natural Resources
University of Miami	Georgia Power Company
University of Michigan	Metropolitan Health Department
University of North Alabama	Div. of Pollution Control, Nashville, Tennessee
University of Tennessee	National Center for Atmospheric Research
University of Wisconsin at Madison	National Oceanic and Atmospheric Administration
West Virginia University	National Institute for Environmental Health Services
	National Institute for Science and Technology
	National Park Service
	Natural Resources Defense Council
	North Carolina Supercomputing Center
	Science Applications International Corporation
	Southern Appalachian Mountain Initiative
	Southern Company Services
	Tennessee Air Pollution Control
	Tennessee Department of Environment & Conservation
	Tennessee Department of General Services
	Tennessee Valley Authority
	The Fleming Group
	University Corporation for Atmospheric Research

As illustrated in Figure 1.9, SOS is organized into 3 major groups. These groups are:

1. The SOS Coordinating Council, which provides general oversight of the program. The Council is comprised of 16 executive leaders, who represent each of the major federal and state governmental and industrial organizations that provide financial and in-kind support for SOS.
2. The SOS Scientific Advisory Committee, which provides scientific and technical advice to the Coordinating Council and SOS Science Team. The Committee is comprised of 9 internationally distinguished independent scientific experts.
3. The SOS Science Team, which provides scientific and technical leadership for SOS. The Team is led by the SOS Director, Dr. Ellis Cowling, and is divided into four task-group areas - Chemical and Meteorological Measurements, Models and Model Evaluation, Emissions and Effects, and Measurements, Technology, and Standards.

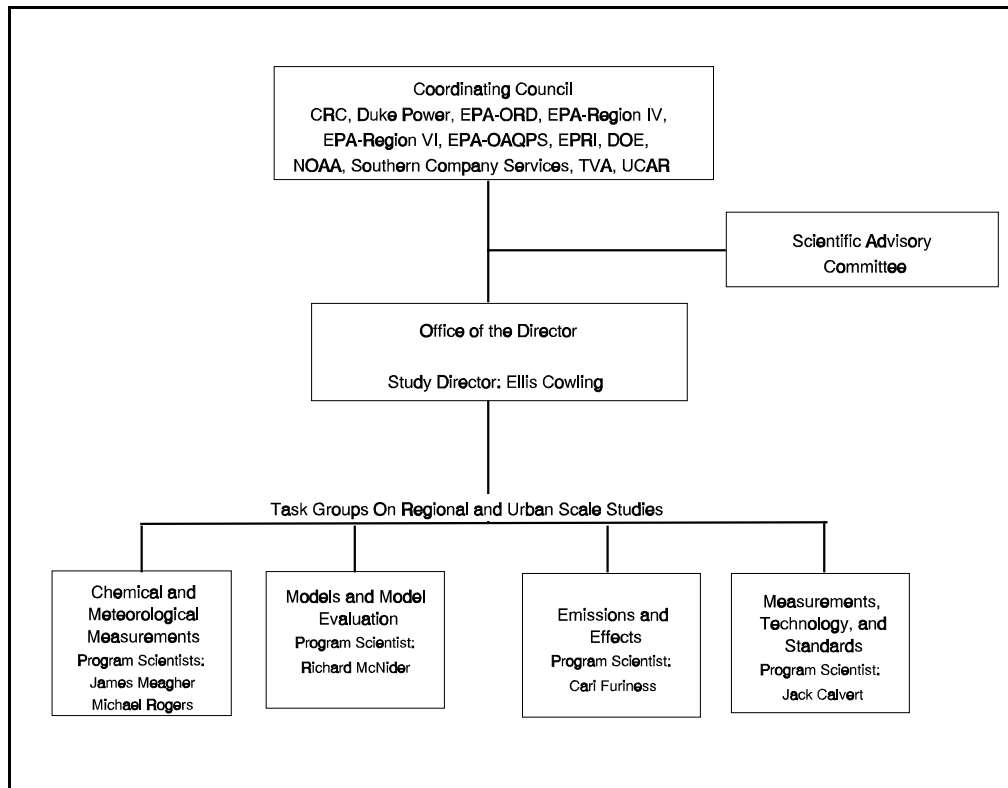


Figure 1.9. The SOS Organizational Chart.

The important features of the SOS Team approach include:

1. Inclusion of all stakeholders, including local, state, and federal government officials and scientists and administrators from the private sector in the selection of policy-relevant research themes and priorities.
2. Inclusion of university scientists and the advanced instrumentation and expertise that reside in the university community.
3. Leadership of the university community in the development of the scientific plan, including the setting of research priorities.
4. Building of the region's and nation's human resources in air quality research through the hands-on participation and education of graduate students and post-doctoral scientists within the university community.

As outlined in Table 1.1, most of U.S. EPA's support to SOS is supplied through Cooperative and Interagency Agreements with 3 southern universities (Georgia Institute of Technology, North Carolina State University, and University of Alabama - Huntsville), as well as the University Corporation for Atmospheric Research (UCAR). Other organizations also provide financial support; they include: The Electric Power Research Institute (EPRI) and its Tailored Collaboration partners (Duke Power Company, Georgia Power Company, Southern Company Services, and the Tennessee Valley Authority), the Coordinating Research Council of the Automobile and Petroleum Industries, and the U.S. Department of Energy. In addition, in-kind contributions to SOS projects have been provided by: The National Oceanographic and Atmospheric Administration (NOAA), Brookhaven National Laboratory, U.S. EPA Region IV, and several of the state regulatory and air quality agencies in the SOS region.

2. MAJOR SCIENTIFIC FINDINGS OF SOS: 1988 - 1994

At the time of the preparation of this report, the research projects and field studies implemented under the SOS multi-institutional umbrella have resulted in publication, acceptance, or submission of more than 100 peer-reviewed scientific and technical papers, completion and dissemination of numerous technical and outreach reports, presentation of more than 150 oral papers at national and international scientific meetings and symposia, and the completion of 18 Ph.D. dissertations or M.S. theses. Of the scientific and technical papers completed, roughly 20% were authored or co-authored by scientists from the U.S.

Environmental Protection Agency. A complete listing of the papers and documents produced by the SOS Science Team is included in Appendix A.

In the years since its initial inception following the Atmospheric Photochemical Oxidants Workshop in Atlanta in 1988, the SOS and its Science Team have addressed a broad spectrum of scientific and technical issues of relevance to the national, as well as the regional, regulatory community. In this Section, a summary of the major scientific findings of the research program and their policy-relevance is presented. This summary is largely based on the peer-reviewed publications listed in Appendix A.

2. Major Scientific Findings

- Chemical Climatology of the South
- Role of Biogenic Hydrocarbons
- Non-Traditional Sources of NO_x
 - Biogenic Soil Emissions
 - Production By Lightning
- Measurement Science
- The Observation-Based Paradigm
 - Ozone-Precursor Relationships
 - Emissions
- Air Pollution Meteorology
- Photochemical Grid Modelling
- The NO_x-vs-VOC Question

2.1 CHEMICAL CLIMATOLOGY OF THE SOUTH

SERON, the 3-tiered set of regional networks designed and implemented by SOS (see Figure 1.6), provides a unique and potentially powerful tool: a system for monitoring the spatial and long-term temporal trends in the rural concentrations of O₃ and its precursors on a regional scale. The scientific gains from a monitoring program are often greatest after a long-term dataset has been compiled. Since SERON did not become operational until the Summer of 1990 (see Table 1.1), the scientific

insights gained from the SOS regional network are still at a very preliminary stage. Nevertheless, they are of significance and interest. In this Section we summarize some of these insights.

2.1. Chemical Climatology of the South

- The Climatology of Ozone
- The Climatology of Ozone Precursors
- The Ozone-NO_z Relationship in the Region
- Inhomogeneities in Regional Ozone Episodes
- Implications for Alternate Forms of the Ozone Standard
- The Southern Regional Ozone Episode: A "Rising Tide" of Ozone

2.1.1. The Climatology of Ozone

Rural and suburban O₃ measurements obtained from the U.S. EPA's Aerometric Information Retrieval System (AIRS) for the years of 1981 to 1990 were combined with data from SOS' Spatial Ozone Network (SON) to develop an O₃ summertime climatology for the eastern two-thirds of the United States. Key characteristics of this climatology are listed below.

1. **Extensive Region of Enhanced O₃:** Over the 1981 to 1990 time period, much of the South and northeastern United States experienced average, summertime, diurnal- maximum O₃ concentrations in excess of 50 ppbv (see Figure 2.1)
2. **O₃ Exposure In the South Inhibits Photosynthesis:** O₃ concentrations are high enough to inhibit photosynthesis of crops, trees, and other plants during some portion of the growing season throughout the South (see Section 2.1.5).
3. **No Significant Trend:** Over the ten-year period O₃ concentrations in the South and in the northeast showed no significant temporal trend.

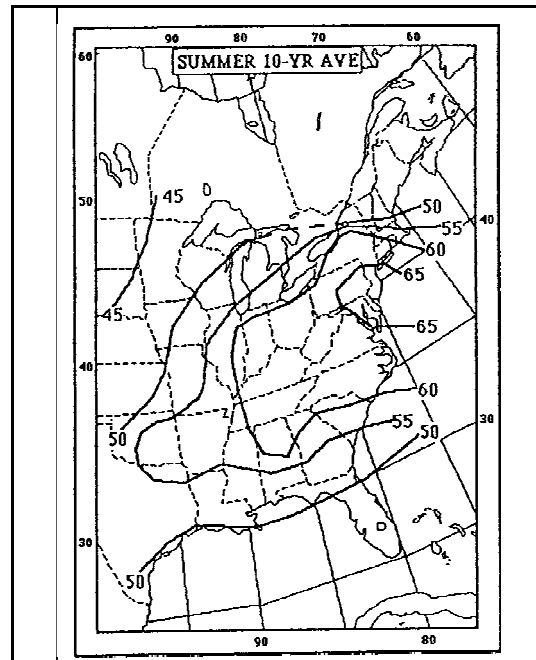


Figure 2.1. Ten-year average, daily maximum ozone concentration (ppbv). After Vukovich, 1994.

4. **O₃ Concentration Correlates With Temperature:** Anomalies in the annually-averaged, daily maximum O₃ correlated most strongly with temperature and sky cover. In the South, a strong anti-correlation was also found with precipitation (see Table 2.1).

Table 2.1. Correlation Coefficient Between Annual Anomaly In Diurnal Ozone Maximum and Selected Meteorological Parameters						
	Temperature	Dewpoint	Pressure	Wind Speed	Precipitation	Sky Cover
NE + South	0.89	0.52	-0.28	-0.22	-0.55	-0.84
South	0.91	0.31	0.33	-0.42	-0.91	-0.87

2.1.1. The Climatology of Ozone (Continued)

5. **Ozone in the South Is Decoupled From Ozone in Northeast:** O₃ episodes in the northeast were weakly correlated with those in the South ($r = 0.64$), suggesting that the processes that control O₃ concentrations in the two regions are significantly decoupled from each other (see Figures 2.2a and 2.2b).

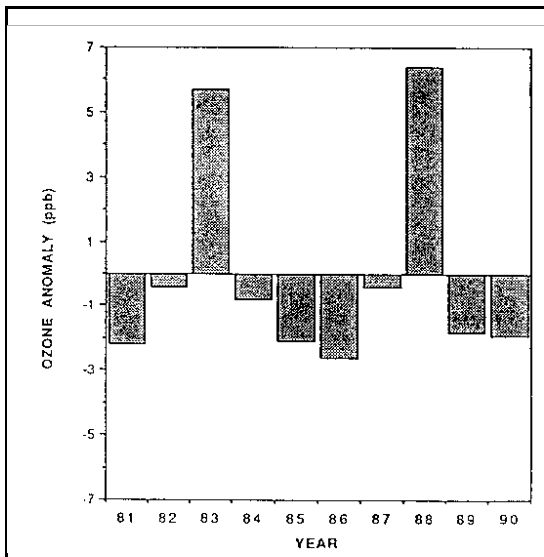


Figure 2.2a. Anomaly in surface ozone each summer over a 10-year period for the eastern two-thirds of the U.S. After Vukovich, 1994.

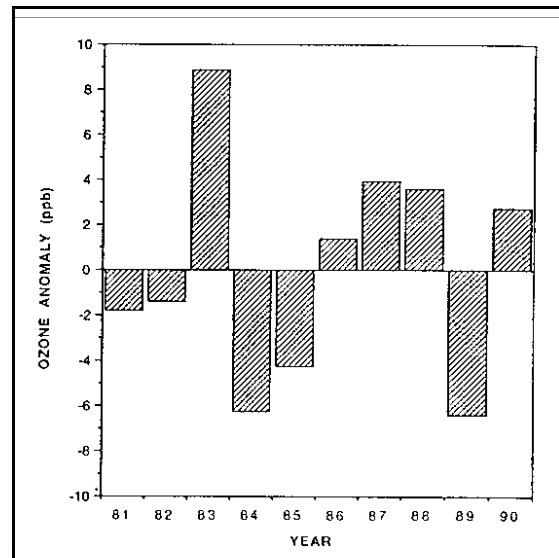


Figure 2.2b. Anomaly in surface ozone each summer over a 10-year period for the South. After Vukovich, 1994.

Key Citations:

Vukovich, F. M. 1994: Boundary layer ozone variations in the eastern United States and their association with meteorological variations: long-term variations. *J. Geophys. Res.*, 99, 16839-16850.

Lee, T., and E. B. Cowling. 1994. Spatial and temporal ozone concentrations in the southeastern United States: Implications for potential secondary standards. *J. Air Waste Manage. Assoc.* (Submitted).

2.1.2. Climatology of Ozone Precursors

One of the important outcomes of the SCION and SENIOR networks has been development of a database capable of characterizing the regional climatology of the precursors of O₃ as well as that of O₃ itself. Out of this climatology has emerged two important generalizations:

- 1. Isoprene Is The Dominant VOC:**
Biogenic isoprene dominates the daytime OH-reactivity of VOC during the summer in the rural South (see Table 2.2).
- 2. NO_y Abundances Are Low:**
Concentrations of reactive nitrogen (NO_y) are relatively low in the rural South and generally less than 4 ppbv (see Figure 2.3).

Table 2.2.
VOC fractional OH-reactivities at ROSE, 1200 Hours, 7/11/90. After Cantrell et al. 1992.

Compound	Fraction	Fraction, Total Sum from the First to the Compound Shown
Isoprene	0.710	0.711
Formaldehyde	0.08760	0.798
Carbon monoxide	0.03627	0.835
Methacrolein	0.03477	0.869
Methyl-vinyl-ketone	0.02981	0.899
α-Pinene	0.01773	0.917
Acetaldehyde	0.01520	0.932
Methane	0.01483	0.947
Nitrogen dioxide	0.01064	0.958
β-Pinene	0.01035	0.968
Methanol	0.00805	0.976
Sulfur dioxide	0.00514	0.981
Ethanol	0.00343	0.985
Myrcene	0.00333	0.988
Propane	0.00196	0.990
Isopentane	0.00140	0.991
n-Butane	0.00134	0.993
Acetone	0.00097	0.994
Isobutane	0.00078	0.994
Ethane	0.00074	0.995
Camphene	0.00069	0.996
Methyl-ethyl-ketone	0.00058	0.996
Nitric oxide	0.00058	0.997
p-Cymene	0.00053	0.997
n-Pentane	0.00053	0.998
n-Hexane	0.00037	0.998
m,p-Xylene	0.00035	0.999
3-Methylpentan	0.00025	0.999
2,3-Dimethylbutane	0.00017	0.999
o-Xylene	0.00013	0.999
Ethylbenzene	0.00009	0.999
Methylcyclohexane	0.00007	0.999
2,4-Dimethylpentane	0.00007	0.999
Toluene	0.00007	1.000
n-Octane	0.00003	1.000
Benzene	0.00001	1.000

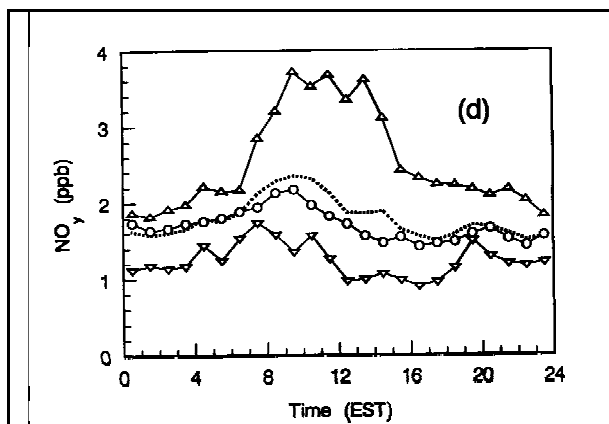


Figure 2.3. NO_y concentrations observed at Metter, Georgia in July and August, 1991. Dashed line is average for the period, triangles for days with high O₃, circles moderate O₃, and inverted triangles low O₃. After Kleinman et al., 1994.

KEY CITATIONS:

Cantrell, C. A., et al. 1992. Peroxy radicals in the ROSE experiment: Measurement and theory. *J. Geophys. Res.* 97D (18): 20, 671-20, 686.

Kleinman, L., et al. 1994. Ozone formation at a rural site in the southeastern United States. *J. Geophys. Res.* 99D (2): 3469-3482.

2.1.3. Ozone/ NO_y Relationships In the Rural South Suggest NO_x -Limitation

Simultaneous measurements of O_3 , NO_x , and NO_y at the rural SENIOR sites have revealed a fairly uniform relationship between daily maximum O_3 concentrations and the products of NO_x oxidation (i.e., $\text{NO}_z = \text{NO}_y - \text{NO}_x$). O_3 was found to vary linearly with the ambient concentration of NO_z with a slope of about 10 and an intercept of about 30 - 40 ppbv (see Figures 2.4a and 2.4b). These results suggest that:

1. **O_3 Is Limited By NO_x :** Rural O_3 concentrations throughout the South are largely limited by emissions of NO_x .
2. **Yield of O_3 From NO_x Is Relatively Large:** About 10 O_3 molecules are produced for each molecule of NO_x emitted in the SOS region.

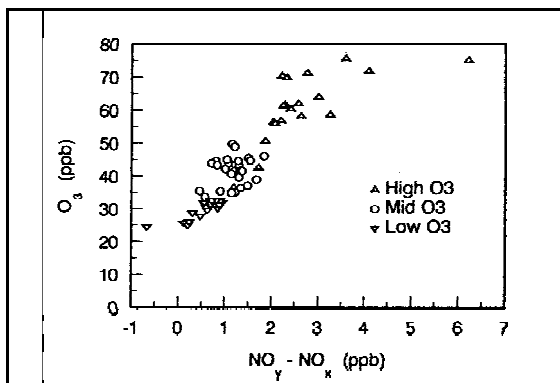


Figure 2.4a. Ozone vs. $\text{NO}_y - \text{NO}_x$ measured at Metter, GA in July and August of 1991. After Kleinman et al., 1994

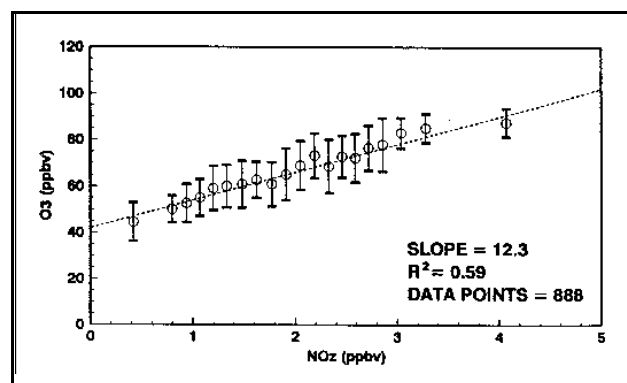


Figure 2.4b. Ozone vs. $\text{NO}_z = \text{NO}_y - \text{NO}_x$ measured in Giles County, TN, in the summer of 1991. After Olszyna et al., 1994

KEY CITATIONS:

- Trainer, M., et al.** 1993. Correlations of ozone with NO_y in photochemically aged air. *J. Geophys. Res.* 98: 2917-2915.
- Wang, T.,** 1992. Atmospheric Reactive Nitrogen Oxides and Their Relationship With Urban and Rural Ozone Formation, Ph.D. Thesis, Georgia Institute of Technology.
- Kleinman, L., et al.** 1994. Ozone formation at a rural site in the southeastern United States. *J. Geophys. Res.* 99D (2): 3469-3482.
- Olszyna, K. J., et al.,** 1994. O_3 and NO_y Relationships at a rural site. *J. Geophys. Res.* 99: 14557-14563.

2.1.4. Spatial Inhomogeneities in Regional Ozone Episodes

An analysis of ozone concentrations and meteorological conditions during seven regional ozone episodes revealed a number of unique features of the photochemical oxidant accumulation process in the South. While O₃ episodes in the South, like most other regions of the nation, are characterized by broad synoptic high-pressure systems, there is significant mesoscale variability with areas of deep moist convection interspersed within areas of subsidence and high insolation. Most likely as a result of this mesoscale variability, high O₃ concentrations within the region tend to lack spatial coherence (see Figure 2.5). These results suggest that:

- 1. Small-Scale Meteorological Phenomena Are Important:** Small-scale features, such as urban plumes, point-sources, and convective pumping, play an important role in determining the locations and magnitudes of the maximum O₃ concentrations in the SOS region.
- 2. High Resolution Models Are Needed:** Because of the importance of mesoscale variability, fine-scale grid resolutions may be required in regional models to adequately simulate the accumulation of O₃ in the South.

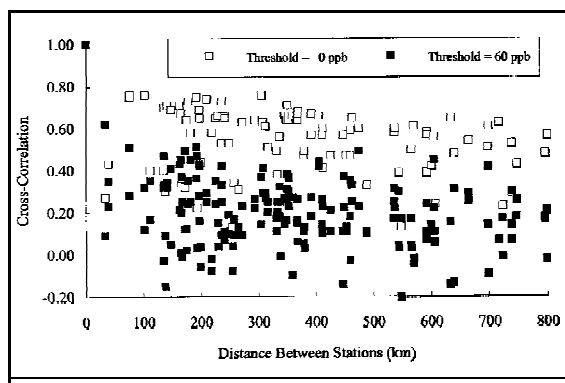


Figure 2.5. Spatial correlation of 1900 Hour O₃ among SON sites for all data (open squares) and for data with O₃ concentrations above 60 ppbv (solid squares). After McNider et al, 1994.

KEY CITATION:

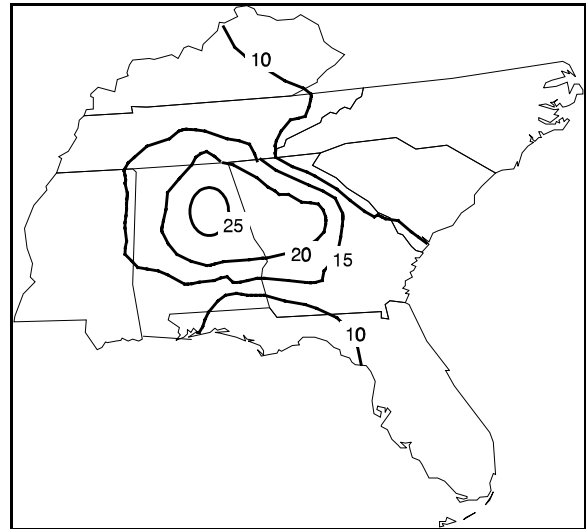
McNider, R.T., J. A. Song, and W. B. Norris. 1994. Regional meteorological characteristics during ozone episodes in the southeastern United States. *Transactions of Air and Waste Management Association - Photochemical Measurement and Modeling Studies*. (In press).

2.1.5. Implications of Alternate Forms of Ozone Standard

Data from the SON network were analyzed to determine what parts of the rural South are likely to be considered O₃ non-attainment areas if the secondary standard for O₃ was changed from its present 120 ppbv for one hour per year to one that more accurately reflected the sensitivity of vegetation to longer term O₃ exposures. Key findings of this analysis are summarized below.

- 1. Alternate Secondary Standard Could Affect Large Portions Of The South:** A switch to a secondary standard with a more moderate O₃ concentration (eg., 50-70 ppbv) but a longer averaging time (eg., 7 hours) would cause large portions of the rural South to be designated non-attainment areas (see Figure 2.6).
- 2. Longer-Time Averaging Of the Standard Moves Focus From Urban Centers To Rural Areas:** Because of the effects of NO-titration on evening, nighttime, and early-morning O₃, a standard with a longer time averaging tends to shift the focus of control from urban areas to rural areas (see Figure 2.6).

Figure 2.6. Number of days with 7-hour average O₃ at or above 70 ppbv during the period from April to September, 1990. After Lee and Cowling, 1994.



KEY CITATION:

Lee, T., and E. B. Cowling. 1994. Spatial and temporal ozone concentrations in the southeastern United States: Implications for potential secondary standards. *J. Air Waste Manage. Assoc.* (Submitted).

2.1.6. The Southern Regional Ozone Episode - A "Rising Tide" of Ozone

In 1977, George Wolff and colleagues published a seminal work on the regionality of O₃ episodes (Reference ??). Based on an analysis of data they proposed that O₃ episodes in the eastern United States were coupled through large-scale transport processes that produced "an ozone river" flowing over 1000-km scales. Analysis of meteorological and O₃ data collected in the South suggests a slightly different analogy for ozone episodes in the South. Because of the high level of stagnation coupled with mesoscale variability that characterizes the region during O₃ episodes, the distribution of O₃ in the South is more aptly described as a "rising tide" that swamps the entire region with high O₃ concentrations as opposed to a river that flows through the region (see Figure 2.7). Non-attainments appear in the region as small hotspots within this "rising tide" brought on by mesoscale variability in the regional meteorological pattern and enhanced levels of precursor emissions.

Figure 2.7 will be the ozone episode used on front cover of data workshop report.

2.1.7. Conclusion - Policy-Relevant Findings On The Chemical Climatology of South

SERON and other associated SOS studies on the chemical climatology of the South provide evidence for the following policy-relevant findings:

1. **Ozone Exposures:** Summertime O₃ concentrations in the South are sufficiently high to inhibit photosynthesis in vegetation throughout the region.
2. **No Discernible Trend:** Over the past decade, no statistically significant trend in regional O₃ concentrations are discernible. Since this period was one of substantial growth in human population and vehicle use, it is encouraging that no significant *increase* in average O₃ occurred in the SOS region. On the other hand, it is discouraging that no significant *decrease* occurred since substantial investments were made in the region in industrial VOC controls and cleaner (i.e., lower emission) vehicles. It appears that increased population and vehicle use may have largely offset the gains that had been bought from emission controls in the SOS region.
3. **Dominance of Biogenic VOC:** Over much of the rural South, VOC reactivity is dominated by biogenic isoprene.
4. **NO_x-Limitation:** On a regional scale, O₃ production in the South appears to be limited by NO_x as opposed to VOC.
5. **Rural South Affected By New Secondary Standard:** The promulgation of a new secondary standard with a longer time averaging may cause large portions of the South to be designated as non-attainment areas.
6. **A Regional Rising Tide of Ozone:** In contrast to the northeast, O₃ episodes in the South are characterized by a regionally-disperse, but spatially incoherent increase in oxidant concentrations punctuated on the mesoscale by "hot-spots" of high O₃ concentrations.

2.2. THE ROLE OF BIOGENIC HYDROCARBONS

Prior to the late 1980's, it was believed that biogenic hydrocarbons played little or no role in photochemical oxidant accumulation in either the rural or the urban atmosphere. The U.S. EPA, for example, recommended that biogenic hydrocarbons be neglected in developing State Implementation Plans (EPA. 1987. *Guidelines for Use of City-Specific EKMA in Preparing Post-1987 Ozone SIP's*, 56 pp). Two papers were pivotal in changing this viewpoint:

1. Trainer et al. (1987, *Nature*, 329:705-707) showed that biogenic hydrocarbons played a major role in rural O₃ episodes in the eastern United States; and
2. Chameides et al. (1988, *Science*, 241:1473-1475), showed that biogenic emissions represented a significant VOC source in Atlanta and that these emissions decreased the efficacy of a VOC-based O₃ abatement strategy (see Figure 2.8).

The findings of Trainer et al. and Chameides et al. were a major driving force behind the inception of SOS and, as a result, biogenic VOC was identified as a prominent research theme for the program. In this section, we outline some of the major findings of SOS with regard to these compounds.

2.2. The Role of Biogenic VOC

- The Ubiquity of Biogenic Hydrocarbons
- Improved Emissions Estimates for Biogenic VOC
- Isoprene Emissions Mechanisms
- Observations of Oxygenates
- Emissions From Kudzu
- The Urban Heat Island and Biogenic Emissions

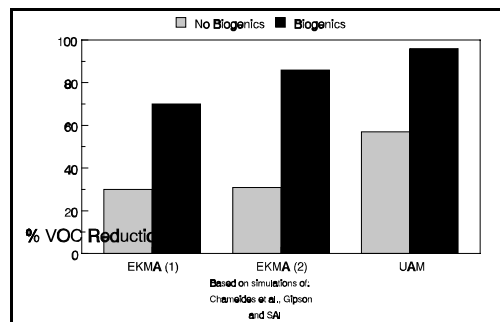


Figure 2.8. VOC reduction estimated for Atlanta O₃ attainment with and without biogenic VOC.

2.2.1. Ubiquity of Biogenic Hydrocarbons

Initial assessments of the role of biogenic VOC were largely based on emission inventories. In keeping with SOS's emphasis on an "observation-based" approach, an analysis of atmospheric measurements of speciated hydrocarbons was carried as an independent check on the conclusions drawn from these inventories. The findings, two of which are outlined below, tended to qualitatively confirm those based on emission inventories for biogenic VOC.

- 1. Isoprene Is of Biogenic Origin:** The variability of isoprene during the summer months, (eg., its anti-correlation with other hydrocarbons as illustrated in Figure 2.9, its diurnal profile, and its dependence on temperature), is consistent with it being dominantly of biogenic origin and not consistent with it being of anthropogenic origin.
- 2. Biogenic VOC Is a Significant Fraction of Total VOC-Reactivity:** Isoprene represents a significant fraction of total VOC reactivity in many urban as well as rural locales of the U.S. (see Figure 2.10 and Table 2.2).

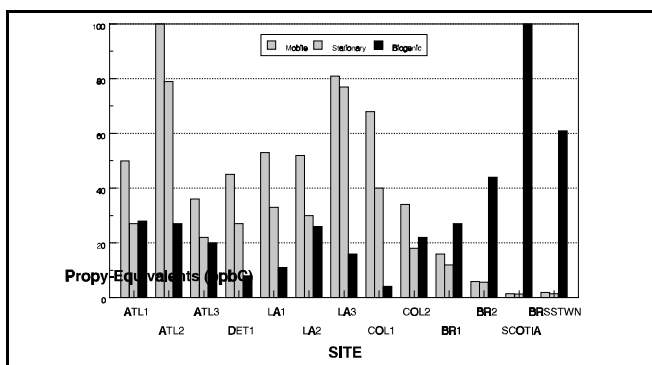


Figure 2.10. Propyl-Equivalent concentrations of VOC measured in urban and rural sites in U.S. After Chameides et al., 1992.

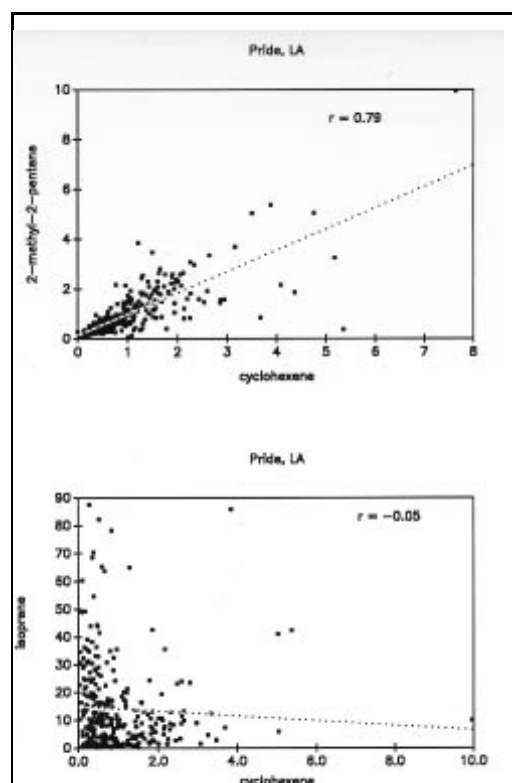


Figure 2.9. Scatterplots of VOC measured in Pride, LA. After Chameides et al., 1992.

KEY CITATION:

Chameides, W. L., et al. 1992. Ozone precursor relationships in the ambient atmosphere. *J. Geophys. Res.* 97D (5):6037-6055.

2.2.2. Improved Emission Estimates for Biogenic VOC

In order to provide better emission inventory inputs into air quality models, an improved system for calculating biogenic VOC emission rates was developed. The key features of this new and improved system for estimating biogenic VOC inventories include:

1. **Tree Genus-Specific Emission Factors:** Instead of foliar mass emission factors, the new system uses a newly derived and comprehensive database of genus-specific emission rate estimates for various genera of forest trees (eg., oaks, maples, sweetgum, etc.).
2. **Mechanistic Algorithms For Environmental Factors:** Effects of environmental conditions (i.e., temperature and light intensity) are accounted for in the new system through empirical algorithms based on mechanistic processes and a five-layer canopy model (see Figure 2.11).

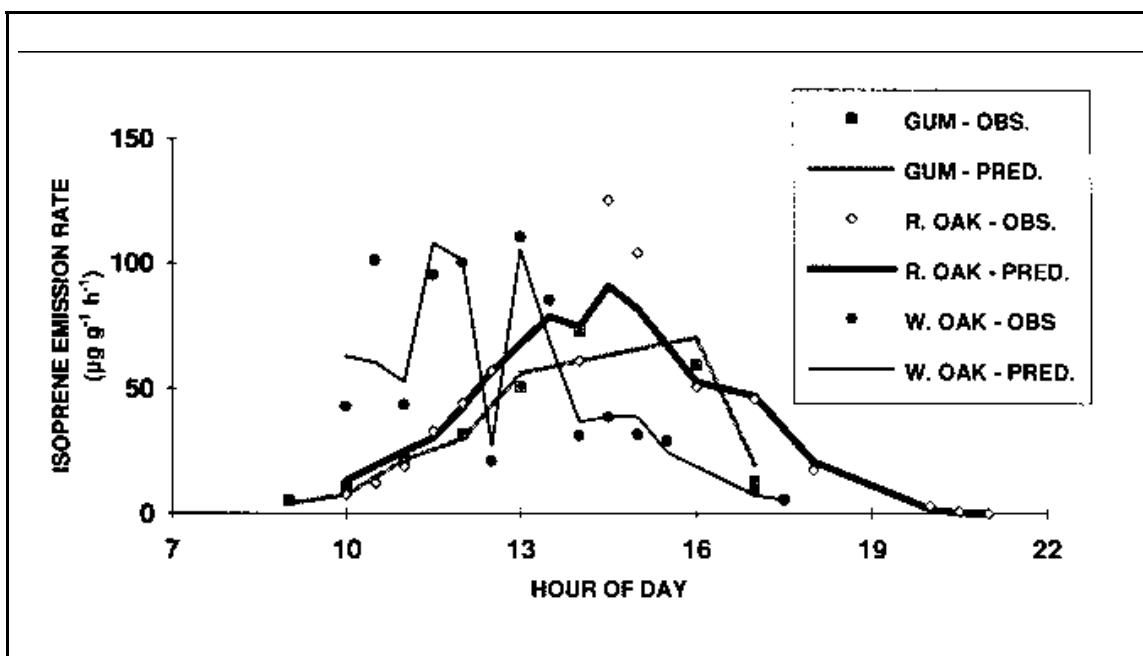


Figure 2.11. Isoprene emissions: observed (symbols) and predicted (lines) using mechanistic algorithms. After Guenther et al., 1993.

3. **Aggregation Into County-Level, Hourly Emissions:** Emission rates are aggregated into county-specific, hourly emission inventories for isoprene, monoterpenes, and other biogenic VOC using the U.S. Department of Agriculture, Forest Service Forest Inventory and Assessment Eastwide Database.

2.2.2. Improved Emission Estimates for Biogenic VOC (Cont'd)

- Higher Biogenic Emissions:** Use of the new system yields 5-10 times higher isoprene emission rates and 3-5 times higher total biogenic VOC emission rates than the system recommended by the U.S. EPA.
- Better UAM Agreement With Observations:** Incorporation of the new system into a UAM simulation for Atlanta yields significantly better agreement between calculated and measured isoprene concentrations during the daylight hours (see Figure 2.12).

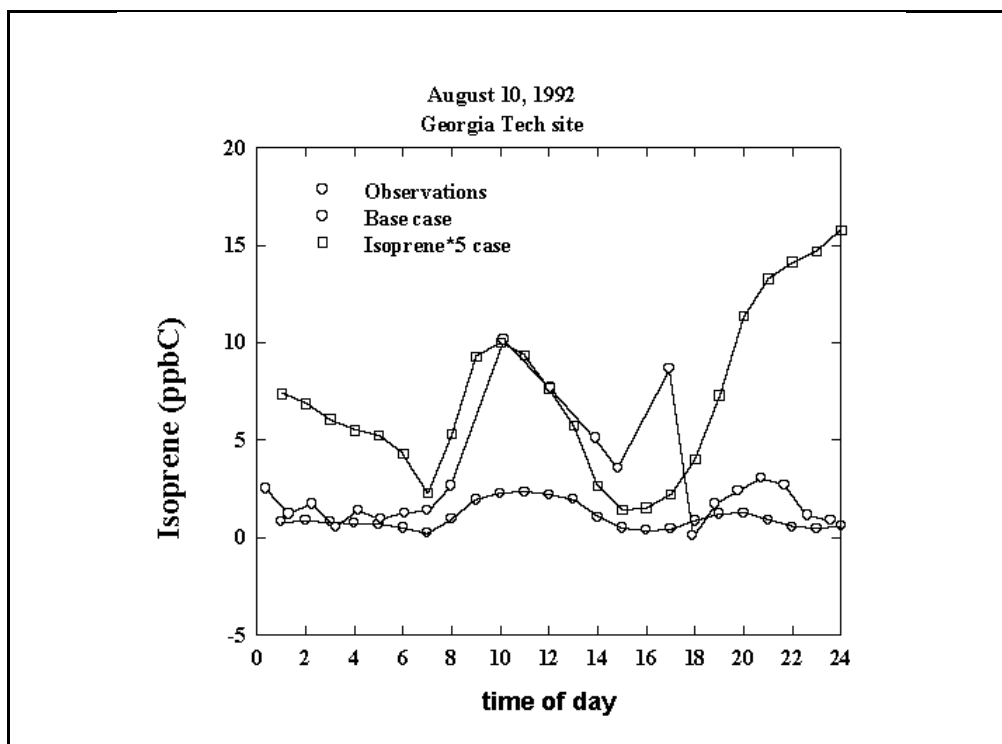


Figure 2.12. Isoprene in Atlanta: Observed and UAM-calculated with EPA-recommended inventory ("base case") and improved inventory ("Isoprene*5 case"). After Cardelino et al., 1994.

KEY CITATIONS:

- Cardelino, C, W.L. Chang, and M.E. Chang.** 1994. Comparison of emissions inventory and ambient concentrations of ozone precursors in Atlanta, Georgia, *AWMA International Conference on the Emission Inventory*.
- Geron, C. A. Guenther, and T. Pierce.** 1994. An improved model for estimating emissions of volatile organic compounds from forests in the eastern United States. *J. Geophys. Res.* 99:12773-12791.
- Guenther, A., P. Zimmerman, and P. Harley.** 1993. Isoprene and monoterpene emission rate variability: Model evaluations and sensitivity analyses. *J. Geophys. Res.* 98:12609-12617.
- Guenther, A., P. Zimmerman, and P. Harley.** 1994. Natural volatile organic compound emission rate estimates for U. S. woodland landscapes. *Atm. Env.* 28:1197-1210.

2.2.3. Elucidation of Isoprene Emission Mechanisms

Current systems for estimating biogenic VOC emissions include algorithms for relating emissions to environmental factors such as temperature and light intensity (see Section 2.2.2). However, the relationship between emissions and internal factors, such as plant development and growth regimes, remains poorly understood and thus, unaccounted for in emissions estimates. Nevertheless these internal factors can play a major role in determining the seasonal variations in biogenic emissions. To better understand how these internal factors might be incorporated into emission estimates, a study of the biological mechanisms controlling isoprene emissions from aspen was undertaken. The major findings of this study are outlined below.

- 1. Temperature Dependence Is Linked To Enzyme:** The temperature dependence of isoprene emissions arises from the temperature response of the enzyme isoprene synthase, a relationship that can be accurately modelled with the Arrhenius equation for the enzyme catalyzed reaction (see Figure 2.13).
- 2. Highest Emissions In Late Summer:** 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.

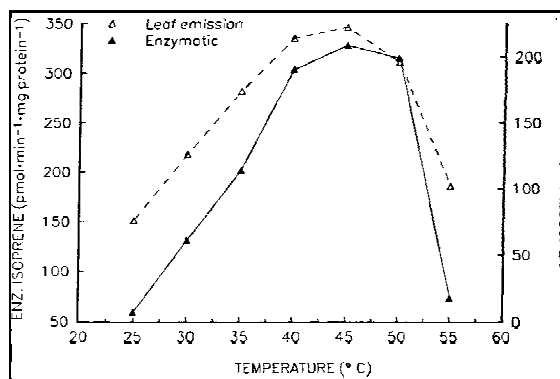


Figure 2.13. Temperature dependence of aspen leaf isoprene and isoprene synthase activity. Each symbol represents the mean of 2-4 replicates. After Monson, et al., 1992

KEY CITATIONS:

- Monson, R.K., et al., 1992. The relationships among isoprene emission rate, photosynthesis, and isoprene synthase activity as influenced by temperature, *Plant Phys.* 98:1175-1180
- Monson, R.K., et al., 1994. Environmental and developmental controls over the seasonal pattern of isoprene emission from aspen leaves. *Oecologia*: (In press).
- Monson, R. K., et al., 1994. Biological aspects of constructing volatile organic compound emissions inventories. *Atmos Env* (In press.)

2.2.4. Isoprene Emissions From Kudzu

In order to improve emission estimates for biogenic VOC, a number of studies were initiated that focussed on biogenic emissions from specific species whose VOC emissions had heretofore not been adequately characterized. One such study of particular relevance to the South focused on isoprene emissions from kudzu, a very rapidly-growing vine which forms large monospecific stands in disturbed areas of the southeastern United States. Measurements of isoprene emissions from the leaves of kudzu indicated:

- 1. Significant Emissions:** Isoprene emissions from kudzu typically represented a significant fraction of the total carbon fixed in photosynthesis; under conditions of high photon flux density and high temperature. This fraction was measured to be as much as 0.67 grams of isoprene per gram of C fixed (see Figure 2.14).
- 2. High Sensitivity to Temperature, Low Sensitivity to Water Stress:** Isoprene emissions from kudzu were more sensitive to temperature than that of other isoprene-emitting species (see inset in Figure 2.14), but tended to be less sensitive to water stress and continued after photosynthesis rates declined to near zero.

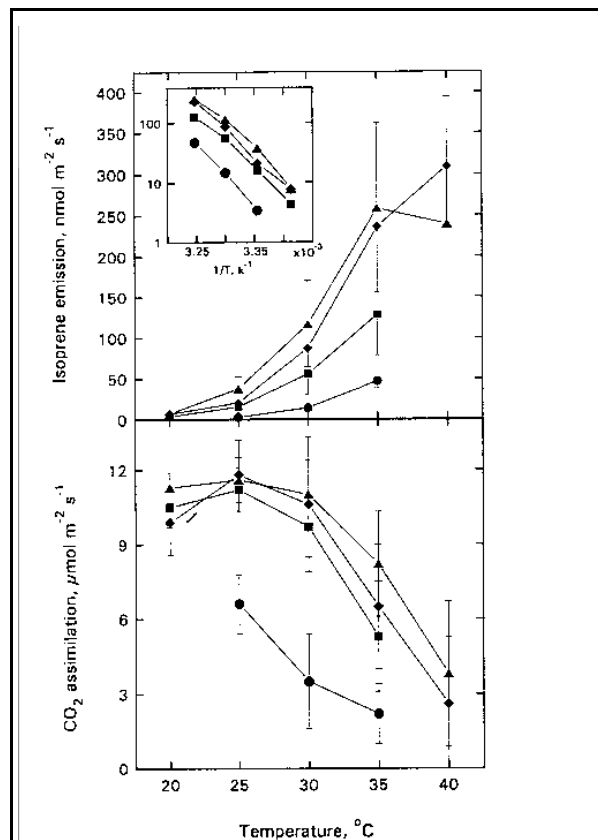


Figure 2.14. Isoprene emissions and CO₂ assimilation of kudzu leaves. After Sharkey and Loreto, 1993.

KEY CITATION:

Sharkey, T., and F. Loreto. 1993. Water stress, temperature, and light effects on the capacity for isoprene emission and photosynthesis of kudzu leaves. *Oecologia* 95:328-333.

2.2.5. OXYGENATED VOC

Oxygenated VOC arise primarily from the photochemical oxidation of hydrocarbons. Speciation and quantification of these compounds in the atmosphere is thus useful for corroborating laboratory-developed photochemical smog mechanisms, assessing the roles of secondary VOC in propagating radical chains, and diagnosing air mass history. Analyses of measurements of oxygenated VOC during SOS field experiments led to the three key findings outlined below.

- 1. Observation of Oxygenates Is Consistent With Isoprene Mechanism:** 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; the diurnal variations in MVK and MACR can be reasonably reproduced by a photochemical model (see Figure 2.15).

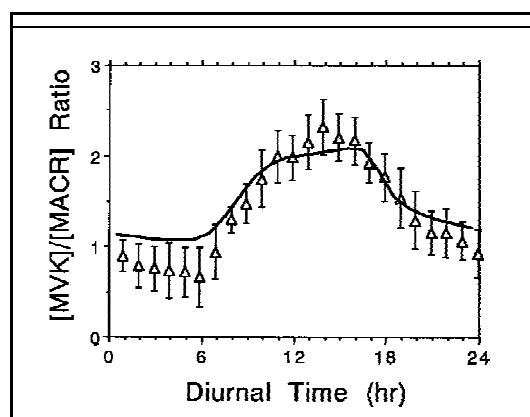


Figure 2.15. Observed (triangles) and model-calculated concentration ratios of MVK/MACR at a rural Alabama site. After Montzka et al., 1993.

- 2. Isoprene Provides a Major Local Source of PAN:** Analysis of measurements at a rural site in Georgia indicated that isoprene photooxidation provided a major local source of peroxyacetyl nitrate (PAN), this source arising from the production of the intermediates MVK and methylglyoxal and their subsequent oxidation to produce the peroxyacetyl radical (PA), the immediate precursor of PAN.

KEY CITATIONS:

Lee, Y-N., and X. Zhou. 1993. Method for determination of some soluble atmospheric carbonyl compounds. *Env. Sci. Techn.* 27:749-756.

Kleinman, L., et al. 1994. Ozone formation at a rural site in the southeastern United States. *J. Geophys. Res.* 99D (2): 3469-3482.

Montzka, S. A., et al. 1993. Isoprene and its oxidation products, methyl vinyl ketone and methacrolein, in the rural troposphere. *J. Geophys. Res.* 98D(1): 1101-1111.

2.2.6. Urban Forests, Biogenic Emissions, and the Urban Heat Island Effect

Forest trees are the largest source of biogenic VOC in the United States and isoprene is typically the most abundant of these. While isoprene emissions from trees increase sharply with increasing temperature, trees tend to decrease local temperatures through their regulation of evapo-transpiration rates. The result of these competing effects is a coupling between land-use patterns, local climate, and biogenic VOC emissions. This coupling can be most pronounced in urban areas, where urban developers replace forests with areas of concrete and asphalt that give rise to an urban heat island with increased temperatures. The implications of this coupling to efforts to control urban O₃ concentrations were investigated by SOS scientists in a modelling study using Atlanta as a case study. Major conclusions of the study are given below.

1. **Destruction of Urban Trees Can Increase Total VOC Emissions:** The destruction of approximately 20% of Atlanta's forests from 1979 to 1988 caused an approximate 2°C intensification of Atlanta's urban heat island and may have actually resulted in a net increase rather than decrease in Atlanta's total biogenic VOC emissions (see Table 2.2).
2. **Modulation of Urban Heat Island May Aid Ozone Attainment:** Practices that modulate the intensity of the urban heat island, through the placement of "green spaces" in the urban core and the use of high reflectivity building materials, may aid in O₃ pollution abatement by lowering urban temperatures and, thus, the emissions of biogenic (as well as anthropogenic, evaporative) VOC.

	<u>Isoprene Emissions (kg/km²)</u>
Pre-1979 emissions. (Summertime temperature of 28 °C and land coverage by forests of 57%.)	15
1988 emissions after 20% loss of Atlanta's forests with no effect on urban heat island.	12
1988 emissions after 20% loss Atlanta's forests with 2 °C intensification of urban heat island	22

KEY CITATION:

Cardelino, C. A., and W. L. Chameides. 1990. Natural hydrocarbons, urbanization and urban ozone. *J Geophys Res* 95: 13971-13979.

2.2.7. Conclusion - Policy-Relevant Findings For Biogenic VOC Emissions

SOS Research on biogenic VOC emissions have led to the following policy-relevant findings:

1. **Effect on Abatement Strategy:** Biogenic emissions can significantly reduce the efficacy of an anthropogenic VOC-based ozone abatement strategy.
2. **Ubiquity of Biogenic VOC:** Significant daytime concentrations of isoprene from biogenic sources are found in both rural and urban atmospheres during the summer months.
3. **Improvements in Biogenic VOC Inventories:** Inclusion of genus-specific emission factors and mechanistic-based algorithms for estimating the influence of environmental factors such as light intensity and temperature can improve the accuracy of biogenic emission inventories.
4. **Shortcomings In Biogenic Inventories:** Factors such as water stress, plant size, and age, that determine seasonal variations in VOC emissions from vegetation, are poorly understood and largely unaccounted for in present emission inventories.
5. **Coupling of Biogenic Emissions to Climate:** Local climatic conditions influence biogenic emission rates. Thus practices that lower summertime temperatures, for example by modulating the intensity of the urban heat island, can reduce biogenic VOC emissions and aid ozone abatement efforts.

2.3. NON-TRADITIONAL SOURCES OF NO_x

Realization that biogenic VOC could have a significant impact on O₃ abatement strategies was a significant, policy-relevant advance in our understanding of photochemical oxidant formation. As described in the previous section, SOS gave a high priority to the study of biogenic VOC and

their emissions. In addition, consideration was given to the potential role of similar, non-traditional sources of NO_x (i.e., sources that are known to exist but have heretofore been neglected in the development of urban and/or regional O₃ abatement strategies). Specifically, SOS undertook studies to better characterize the magnitude of NO_x emissions from soils and NO_x produced by lightning. The results of these studies are summarized in this section.

2.3. Non-Traditional Sources of NO_x

- Biogenic emissions from soils
- Production from lightning

2.3.1. Biogenic Emission From Soils

SOS sponsored a series of coordinated research projects to characterize the magnitude of and parameters that control biogenic emissions from soils. The major findings of these studies are summarized below.

- 1. Comparability of Techniques For Measuring Emissions:** A field inter-comparison of the flow-through and static soil chamber techniques for measuring soil NO emissions showed that both methods yielded similar emission rates.
- 2. Emissions Enhanced By Nitrate Fertilizers, High Temperatures:** Field measurements revealed that emissions increase exponentially with temperature, are highest in soils with enhanced nitrate concentrations, and often have a short-lived spurt after a light rainfall (see Figure 2.16).
- 3. Fertilizer-Induced Soil Emissions Significant:** Extrapolation of NO emission rates observed from fertilized soils indicates that these emissions represent a significant, regional source of NO_x to the South and probably other agricultural areas of the nation (see Figure 2.17).

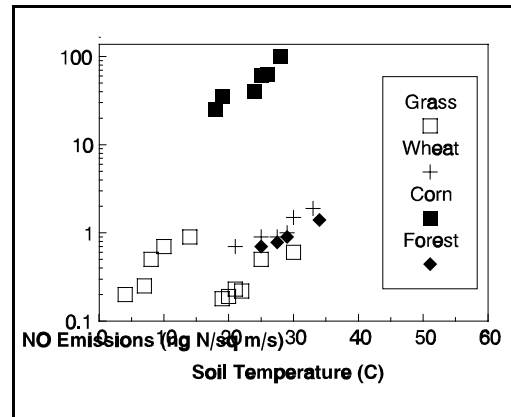


Figure 2.16. NO fluxes measured as a function of soil temperature. After Williams et al., 1991.

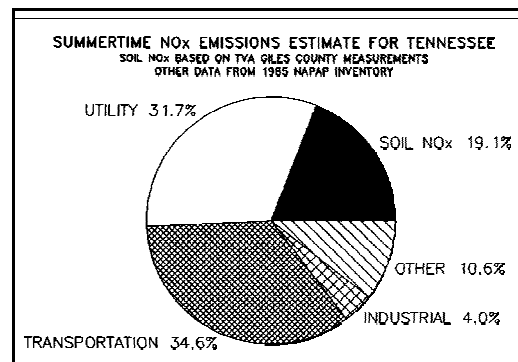


Figure 2.17. After Valente and Thornton, 1993.

KEY CITATIONS:

- Williams, E.J., and F.C. Fehsenfeld.** 1991. Measurement of soil nitrogen oxide emissions at three North American ecosystems. *J. Geophys. Res.* 96:1033-1042.
- Williams, E. J., A. Guenther, and F. C. Fehsenfeld.** 1992. An inventory of nitric oxide emissions from soils in the United States. *J. Geophys. Res.* 97:7511-7519.
- Valente, Ralph. J. and Frank. C. Thornton.** 1993. Emissions of NO from soil at a rural site in central Tennessee. *J. Geophys. Res.*, 98D(9): 16745-16753.
- Valente, R.J., F.C. Thornton, and E.J. Williams.** 1993. Field intercomparison of static and flow-through chamber techniques for measurement of soil NO_x emission. *J. Geophys. Res.* (In press).
- Kim, D.-S., V.P. Aneja, and W.P. Robarge.** 1994. Characterization of nitrogen dioxide fluxes from soil of fallow field in the central Piedmont of North Carolina. *Atm. Env.*, 28:1129-1137.

2.3.2. Production By Lightning

Re-evaluations of the production of NO from lightning indicated that:

- Lightning Appears to Be A Negligible Source Over Climatological Time-Scales:** On time-scales of weeks to months, the source of NO from lightning in the United States, appears to be over-shadowed by the large emissions from anthropogenic sources (see Figure 2.18).
- Potentially Significant Source Over Small Spatial and Temporal Scales:** Over short-time intervals and over small spatial areas, intense thunderstorm activity can produce bursts of NO production in excess of the local, time-averaged source of NO from anthropogenic sources (see Table 2.3).

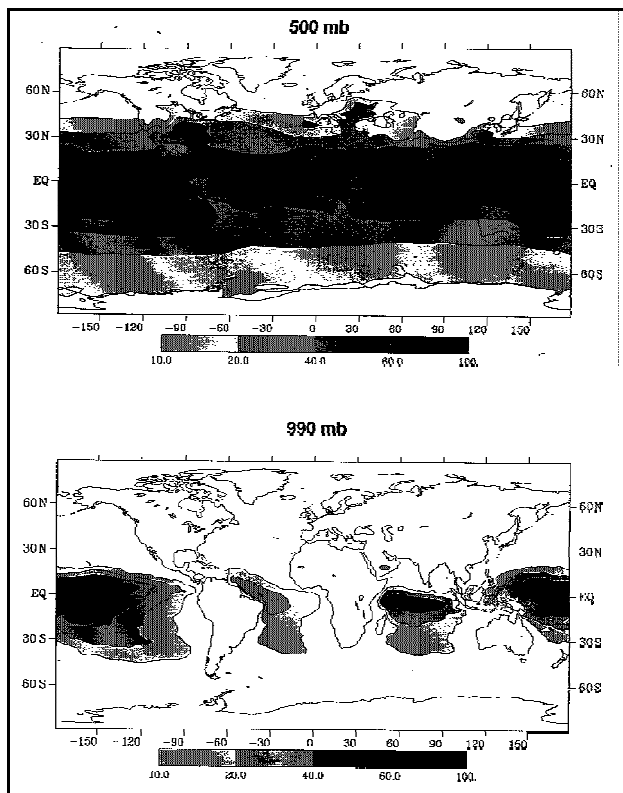


Figure 2.18. Annually averaged percent of NO_x at 500 and 990 mb arising from lightning. After Lawrence et al., 1994.

Table 2.3. Average number of times hourly NO production from lightning within a ~20km x 20km grid in the South exceeded the local anthropogenic NO source within the same grid. (After Biazar et al., 1994)

Month	# of times/month*
June, '89	29
July, '89	34
August, '89	21
June, '90	17
July, '90	28
August, '90	28
June, '91	27
July, '91	38
August, '91	24
June, '92	21
July, '92	30
August, '92	21
<hr style="border-top: 1px dashed black;"/>	
Average	26 ± 6
*Estimated using National Lightning Detection Network data and assuming yield of 4 x 10 ²⁶ NO molecules/flash.	

KEY CITATIONS:

Biazar, Arastoo P., and Richard T. McNider. 1994. Regional estimates of lightning production of nitrogen oxides. *J. Geophys. Res.* (In press).

Lawrence, M.G., et al., 1994. Lightning and atmospheric chemistry: The rate of atmospheric NO production, in *Handbook of Atmospheric Electrodynamics*, ed. by H. Volland, CRC Press. (In press).

2.3.3. Conclusion - Policy-Relevant Findings For Non-Traditional NO_x Sources

The study of non-traditional NO_x sources has led to the following policy-relevant findings:

1. **Fertilizer-Induced Biogenic Emissions From Soils Are Significant:** The emissions of NO from soils can represent a significant contribution to the regional budget of NO_x in areas of intensive agriculture.
2. **Agricultural Practices Are Relevant:** The application of nitrogen fertilizer to soils in agricultural and urban areas induces enhanced NO emissions from soils and can impact regional air quality.
3. **NO From Lightning Should Be Considered:** The intermittent, localized production of NO from lightning can represent a significant source of NO_x over short timescales and small space scales, and thus should not be neglected.

2.4. MEASUREMENT SCIENCE

The SOS research approach places a high premium on observations of the chemical and physical state of the atmosphere. This requires that the measurements be of the highest possible quality, both in terms of the accuracy and precision, as well as the strategy adopted for their use. For this reason, *the science of measurements in air quality* was given a high priority in SOS research. In fact,

as illustrated in Figure 1.9, a separate and independent program within SOS, entitled Measurements Technology and Standards (SOS-MTS), was initiated to facilitate rigorous evaluation of the measurement instruments and field experiment designs used in SOS field studies. Major findings of this facet of the SOS research program are summarized in this Section.

2.4.1. Measurement of Mixing Height

To assess the accuracy of remote sensing techniques for measuring mixing height, an intercomparison was carried out during the 1992 Atlanta Intensive between a rawinsonde system (NCAR CLASS), four radar acoustic sounding systems (RASS), and two lidar systems. The results of this intercomparison are summarized below.

- 1. Rawinsondes Provide The Most Accurate Mixing Height Measurements:** For most of the measurement period the various techniques provided reasonable consistent mixing heights. However, significant differences were obtained during the early morning hours, with the lidar and radar techniques tending to yield erroneously high mixing heights.

KEY CITATION:

Marsik, F. J., et al. 1994. Comparison of methods for estimating mixing height used during the 1992 Atlanta Field Intensive. *J. Appl. Met.* (Submitted).

2.4. Measurement Science

- Measurement of Mixing Height
- Measurement of Speciated Hydrocarbons
- Measurement of Carbonyls
- Evaluation of Surface Sampling Strategy For Hydrocarbons

2.4.2. Measurements of Speciated Hydrocarbons Using Gas Chromatography

A major objective of SOS field research has been documentation of ambient concentrations of the various hydrocarbon species that play a significant role in accumulation of photochemical oxidants in both urban and rural environments. To this end, the SOS-MTS program undertook to develop a protocol for measuring speciated hydrocarbons in the C₂ - C₁₀ range using the gas chromatographic/electron capture technique (GC/EC). Principal aspects of this activity are outlined below.

- 1. Priority Hydrocarbon List Developed:** After collection and analysis of exploratory hydrocarbon samples in various parts of the South and a review of speciated VOC emission inventories, a standard list of 60 C₂ - C₁₀ priority hydrocarbon compounds was identified by the SOS Science Team for standard quantification from chromatograms derived from whole air samples collected during both regional/rural and urban SOS field experiments. The list is presented in Table 2.3.

1. ethane	13. 3-methyl-butene	25. cyclopentane	37. methylcyclohexane	49. alpha-pinene
2. acetylene	14. isopentane	26. 2-methylpentane	38. 2,3,4-triethylpentane	50. n-propylbenzene
3. ethene	15. 1-pentene	27. 3-methylpentane	39. toluene	51. 1-ethyl-3-methylbenz.
4. 1,1-difluoroethane*	16. 2-methyl-butene	28. n-hexane	40. 3-fluorotoluene*	52. 1-ethyl-4-methylbenz.
5. propene	17. n-pentane	29. cis-3-hexene	41. n-octane	53. 1,3,5-trimethylbenz.
6. propane	18. isoprene	30. methylcyclopentane	42. perchloroethylene	54. 1-ethyl-2-methylbenz.
7. isobutane	19. trans-2-pentene	31. 2,4-dimethylpentane	43. ethylbenzene	55. beta-pinene
8. isobutene	20. cis-2-pentene	32. 1,1,1-trichloroethane	44. p-xylene	56. 1,2,4-trimethylbenz.
9. 1-butene	21. 2-methyl-2-butene	33. benzene	45. m-xylene	57. n-decane
10. n-butane	22. neohexane*	34. cyclohexane	46. styrene	58. limonene
11. trans-2-butene	23. 3-methyl-1-pentene	35. 2,3-dimethylbenzene	47. o-xylene	59. 1,3-diethylbenzene
12. cis-2-butene	24. 4-methyl-1-pentene	36. trichloroethylene	48. isopropylbenzene	60. n-butylbenzene

* Added as an internal standard.

- 2. Development and Promulgation of 55 Compound Standard Mixture:** A standard mixture of 55 priority compounds was developed and distributed to SOS hydrocarbon measurement teams to provide an elution time standard for chromatographs.
- 3. Evaluation of Stability Of Hydrocarbons In Canisters:** Hydrocarbon species stored in canisters with walls coated with inorganic polymers had no detectable loss of sample integrity over the course of a year, indicating the viability of canister sampling technique.

2.4.2. The Measurement of Speciated Hydrocarbons Using Gas Chromatography (Cont'd)

4. **Protocol Developed and Evaluated For Hydrocarbon Speciation:** A workshop involving independent hydrocarbon-measurement groups was held to evaluate and refine protocols for sampling, identification, and quantification of hydrocarbon species. Blind intercomparisons between different groups suggests that the GC/EC technique can quantify hydrocarbon species of interest to within a precision of about 10% (see Figure 2.19).

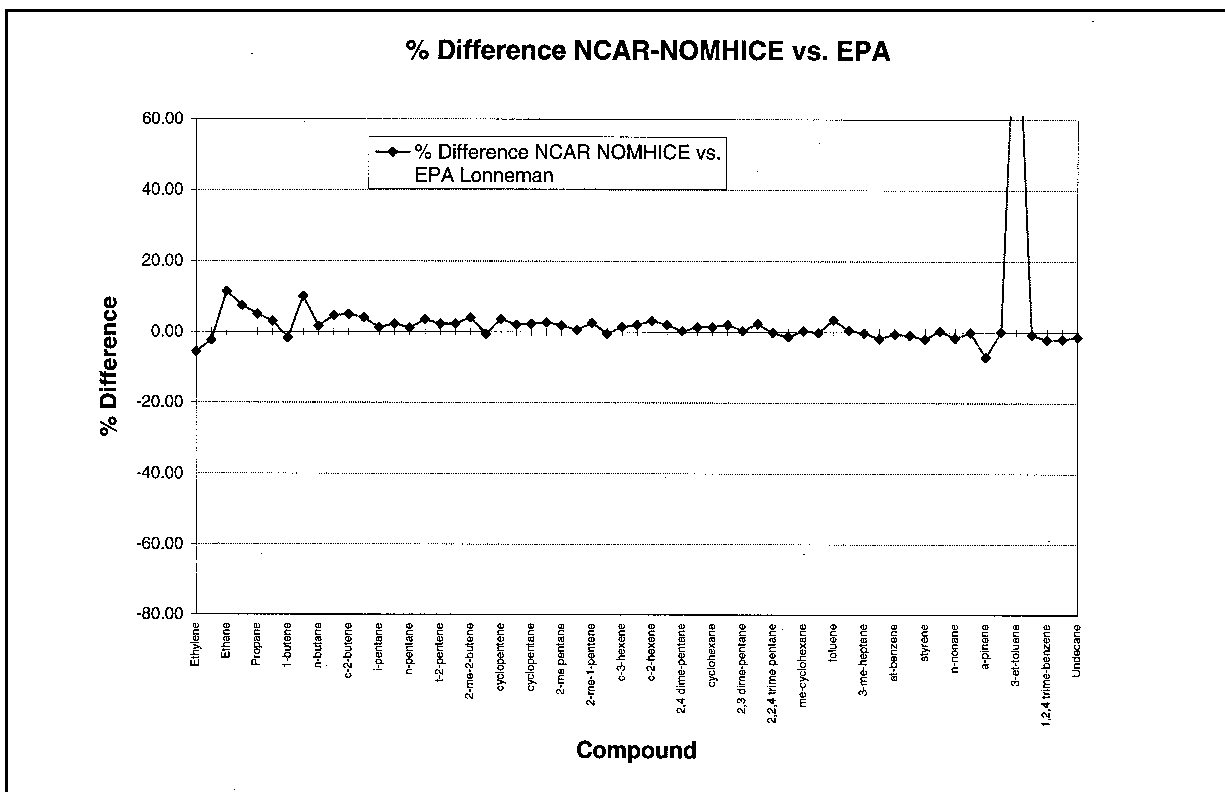


Figure 2.19. Comparison of hydrocarbon quantification by two groups (EPA and NCAR). After Apel, et al., 1994.

5. **Collection of Hydrocarbon Database From Atlanta:** The protocols developed by SOS-MTS were adopted during the 1992 Atlanta Intensive, when 3300 individual whole air samples were obtained and analyzed by three independent laboratories. Analysis of these chromatograms yielded a practical detection limit of 0.5 ppbC or less and an uncertainty of 20% for concentration > 3 ppbC and 35% for concentrations < 3 ppbC.

KEY CITATIONS:

Apel, E. C., J. G. Calvert, and F.W. Fehsenfeld. 1994. The non-methane hydrocarbon intercomparison experiment (NOMHICE): Tasks 1 and 2, *J. Geophys. Res.*99:16651-16664.

Bernado-Bricker, A., et al. 1993. Validation of speciated non-methane hydrocarbon data collected in Atlanta-1992 as part of the Southern Oxidants Study (SOS). Proceedings of the Air and Waste Management International Specialty Conference on Regional Photochemical Measurement and Modeling Studies.

Farmer, C.T., P.J. Milne, D.D. Riemer, and R.G. Zika. 1992. Continuous hourly analysis of C₂-C₁₀ non-methane hydrocarbon compounds in urban air. *Environ. Sci.Techn.* 28:238-245.

2.4.3. Measurement of Carbonyls Using The DNPH Cartridge Method

Atmospheric carbonyls, emitted or produced as intermediates from the oxidation of precursor hydrocarbons, play a pivotal role in the formation of photochemical oxidants. As a result, their measurement has been a high priority objective in many of the SOS field experiments. The DNPH cartridge method is a relatively common technique for measuring carbonyls and was the initial choice among the carbonyl-measurement groups in SOS. A series of tests, cross-calibrations, and inter-laboratory intercomparisons was undertaken in SOS-MTS to determine the adequacy of this technique. The major findings of these tests are outlined below.

1. Good Agreement Among Laboratories For Standard Solutions: The agreement between different laboratory analyses of standard solutions of the DNPH derivatives was good reflecting consistency of calibration standards and chromatographic separation procedures.

2. Poor Agreement For Ambient Air Samples: Large discrepancies were found among carbonyl concentrations reported by different laboratories analyzing equivalent air samples, with standard error of the means > 50% (see Figure 2.20). The sources of disagreement are unclear but may be related to the preparation and storage of the cartridges and the need for large blank corrections.

3. Second Intercomparison Planned: In view of these unsatisfactory results, a second intercomparison, that will include U.S. EPA's cartridge technique, a tunable diode laser technique, and several other methods, is planned for 1995.

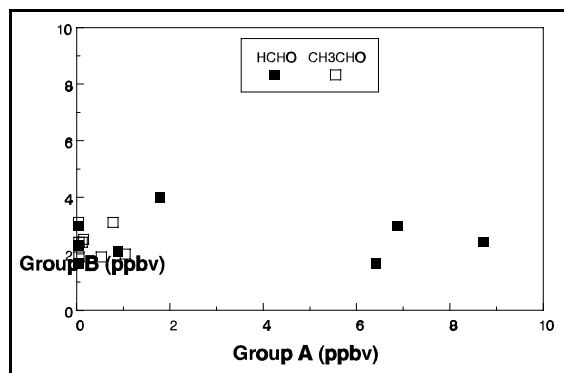


Figure 2.20. Results of blind intercomparison of carbonyl analyses of ambient air samples by two groups using the DNPH cartridge.

KEY CITATION:

Calvert, J.G., and E. Apel. 1994. Report on the MTS Carbonyl Intercomparison for the Southern Oxidants Study Programs During 1992-1994, Internal SOS Report.

2.4.4. Evaluation of Surface Sampling Strategy

Most of the nation's air quality monitoring networks, including the Photochemical Assessment Monitoring Stations (PAMS) network, largely depend on surface measurements to characterize the chemistry of the mixed layer of the atmosphere. In order to determine the extent to which vertical variability in concentrations of hydrocarbons limits the applicability of these surface networks, analyses were made of vertical profiles of hydrocarbons in rural and urban environments using a balloon sampling technique. The results of this study are summarized below.

1. **Complex Vertical Hydrocarbon Profiles Observed:** Vertical profiles for isoprene and other hydrocarbons were found to have complex structures with local maxima at heights between 100 and 300 m (see Figure 2.21).

2. **Complex Profiles Associated With Transient Meteorological Features:** The average of all profiles observed took the standard, monotonically decreasing shape, suggesting that the complex features are caused by transient meteorological phenomena that cancel out over longer time periods.

3. **Surface Measurements Are Not Well-Correlated With Boundary Layer Average:** Because of the transient features in hydrocarbon vertical profiles, measurements at the surface do not correlate as well with average concentrations in the boundary layer as do measurements at 40 to 100 m above the surface.

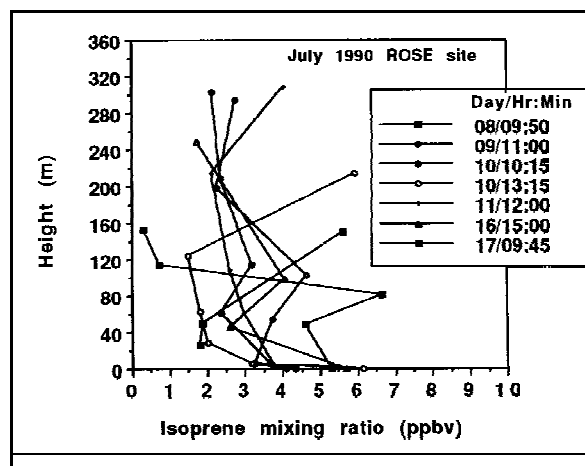


Figure 2.21. Complex vertical profiles of isoprene measured in rural Alabama. After Andronache, et al., 1994.

KEY CITATION:

Andronache, C., et al. 1994. Vertical distribution of isoprene in the lower boundary layer of the rural and urban southern United States. *J. Geophys. Res.* 99: 16989-16999.

2.4.5. Conclusion - The Policy-Relevant Findings In Measurement Science

The SOS program for Measurements Technology, and Standards developed the following policy-relevant findings:

- 1. Remote Sensing Measurements For Mixing Heights Are Accurate Except In Morning Hours:** Lidar and radar techniques for measuring mixing layer heights provide accurate estimate of mixing height, except during the early morning hours when the remote techniques tend to overestimate mixing heights.
- 2. Technology Exists For Accurate Measurements of Speciated Hydrocarbons:** The SOS Science Team has developed and evaluated a protocol for the accurate and precise quantification of C₂-C₁₀ hydrocarbons that can be used in an air quality monitoring network. (The protocol developed in SOS for speciated hydrocarbon measurements has been largely adopted in the EPA PAMS Networks.)
- 3. Serious Problems Identified In The DNPH Cartridge Technique For Carbonyls:** Blind intercomparisons have raised significant questions regarding to the ability of the DNPH cartridge technique for measuring atmospheric carbonyl compounds. (Depending on the outcome of the SOS carbonyl intercomparison scheduled for 1995, another technique may be required to meet the carbonyl requirements for the PAMS network as well as future SOS field experiments.)
- 4. Measurements At 30 - 60 m Above The Surface Provide More Representative Data:** Because of the vertical variability of hydrocarbon concentrations in the boundary layer, a measurement strategy involving sampling at a height of 30 - 60 m above the surface provides a more statistically robust measure of the average hydrocarbon abundance of the mixed layer than a surface sampling strategy.

2.5. OBSERVATION-BASED APPROACH - OZONE PRECURSOR RELATIONSHIPS

Ozone precursor relationships refer to the dependence of the O₃ photochemical formation rate on emissions or concentrations of the O₃ precursors, VOC and NO_x. Because these precursor relationships ultimately govern the response of O₃ concentrations to changes in local VOC and NO_x emission rates, their determination is essential in designing an effective O₃ abatement strategy. Traditionally, ozone precursor relationships have been inferred through model calculations that require the input of emission inventories (i.e., Emission-Based Models or EBMs).

2.5. Observation-Based Approach: Ozone Precursor Relationships

- Trainer Plots (see Section 2.1.3)
- Propy-Equivalents Method (see Section 2.2.1)
- Use of "Photochemical Indicators"
- The Observation-Based Model (OBM)

In keeping with SOS' emphasis on making atmospheric observations, the SOS Science Team developed a number of alternate and/or complementary observation-based methods that infer ozone precursor relationships using chemical observations rather than emission inventories. Two such methods developed by the SOS Science Team have already been discussed; these are the use of "Trainer plots", that relate O₃ to the amount of oxidized reactive nitrogen in the atmosphere (see Section 2.1.3) and the Propy-Equivalent Method that uses OH-reactivity and speciated hydrocarbon data to estimate the relative roles of specific hydrocarbons and/or classes of hydrocarbon species to the local rate of O₃ production (see Section 2.2.1). Two other observation-based approaches developed by the SOS Science Team are discussed in this Section.

2.5.1. Use of "Photochemical Indicators"

Use of ambient "photochemical indicators" to diagnose VOC- or NO_x-limitation is not a new idea; for many years it was believed that the morning VOC:NO_x ratio in an urban area could be used in this way. It is now apparent, however, that the VOC:NO_x ratio is not a reliable diagnostic of ozone precursor relationships (see for instance, Wolff, G.T., and P.E. Korsog. 1992. *J. Air Waste Man. Assoc.* 42:1173-1177). In order to determine if there are alternate photochemical indicators, a series of photochemical simulations were carried out using 3-dimensional Chemical Transport Models. Key results of this study are summarized below.

- 1. H₂O₂:HNO₃ Ratio Predicted To Be A Robust Indicator Of O₃ Sensitivity:** Model calculations indicate that O₃ sensitivity to VOC and NO_x correlates well with four photochemical indicators - NO_y, O₃/NO_z, (HCHO-5ppbv)/NO_z, and H₂O₂/HNO₃, with the last being most robust (see Figure 2.22).
- 2. Application of Photochemical Indicator Method To Atlanta Suggests NO_x-Limitation:** Data from the 1992 Atlanta Intensive suggest that Atlanta is close to the transition between VOC- and NO_x-limitation but was in fact in the NO_x-limited regime at the time of the measurements (see Section 2.9).

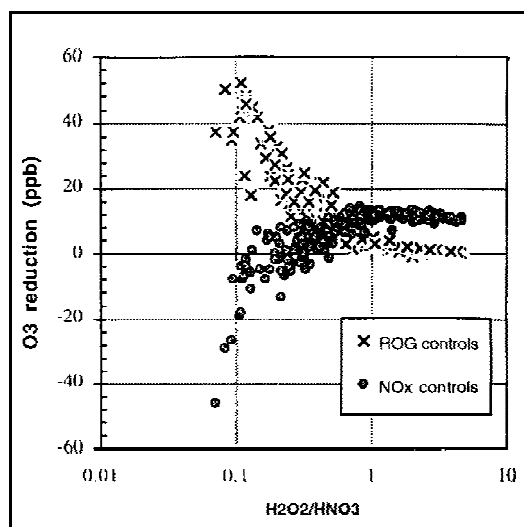


Figure 2.22. Predicted reduction in peak O₃ resulting from a 35% reduction in emissions of anthropogenic ROG (i.e., VOC) and NO_x as a function of local H₂O₂/HNO₃ ratio. After Sillman, 1994.

KEY CITATIONS:

- Milford, J.B., et al.** 1994. Total reactive nitrogen (NO_y) as an indicator of the sensitivity of ozone to reductions in hydrocarbon and NO_x emissions. *J. Geophys. Res.* 99:3533-3542.
- Sillman, S.** 1994. The use of NO_y, HCHO, H₂O₂ and HNO₃ as empirical indicators for ozone-NO_x-ROG sensitivity in urban locations. *J. Geophys. Res.* (In Press).

2.5.2. The Observation-Based Model For Urban Ozone

To provide an independent check on the precursor relationships predicted by Emission-Based Models (eg., the UAM), SOS developed an Observation-Based Model (OBM). The OBM uses in-situ atmospheric observations instead of emission inventories to drive a photochemical model and infer sensitivities of O₃ in an urban atmosphere to changes in the emissions of either VOC or NO_x (see Figure 2.23). Key features of the OBM are summarized below.

1. **OBM Yields Results Similar To UAM:** When concentration fields from the UAM are input into the OBM, the two models predict similar sensitivities to VOC and NO_x (see Figure 2.24).
2. **Application of OBM To Atlanta Suggests NO_x-Limitation On Average:** The application of the OBM with data from the 1990 Atlanta Study implies NO_x-limitation on average, but VOC-limitation for 1 episode (see Section 2.9). (Because of flaws in the dataset, however, these conclusions must be viewed as tentative.)

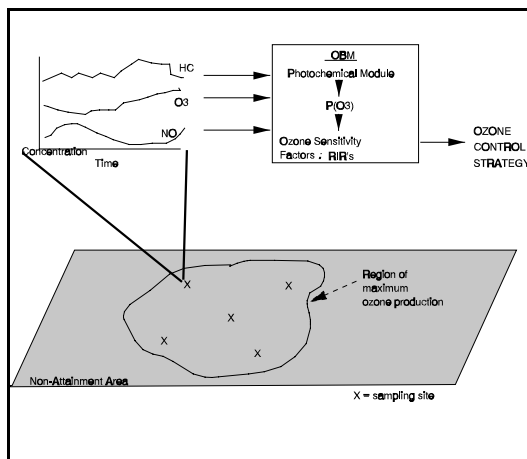


Figure 2.23. OBM uses ambient chemical data to infer ozone precursor relationships.

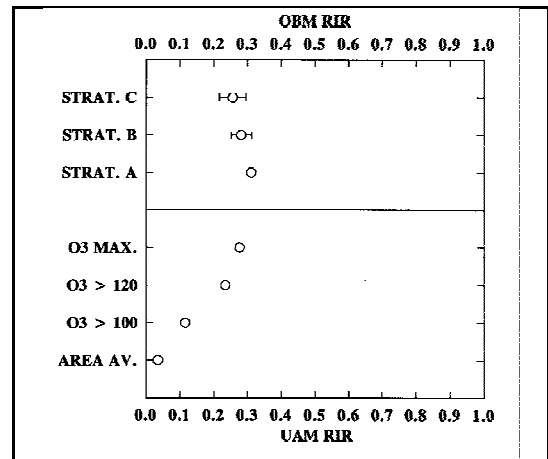


Figure 2.24. Comparison of OBM- and UAM-calculated sensitivity factors. After Cardelino and Chameides, 1994.

KEY CITATION:

Cardelino, C.A., and W.L. Chameides. 1994. An observation-based model for analyzing ozone precursor relationships in the urban atmosphere. *J. Air Waste Manag. Assoc.* (In press).

2.5.3. Conclusion - Policy-Relevant Findings For Observation-Based Approach: Ozone Precursor Relationships

Observation-based methods used for diagnosing ozone precursor relationships has yielded the following policy-relevant findings:

- 1. Observation-Based Approach Offers An Independent and Complementary Method For Evaluating Alternative Ozone Pollution Abatement Strategies:** Emission-based models (EBM's) such as the Urban Airshed Model (UAM) clearly must play a role in the regulatory implementation of O₃ abatement efforts. However, there remain very significant scientific uncertainties in the use of these EBM's. These uncertainties include the emission inventories and meteorological wind fields used to drive the model and derive concentration fields for O₃ and its precursors.

Because ozone precursor relationships are critically sensitive to the relative concentrations of VOC and NO_x, errors in calculating precursor concentration can cause EBM's to grossly misrepresent the sensitivity of O₃ to changes in VOC and/or NO_x emissions (see Section 2.6.4). For this reason, it is desirable to have alternate methods for diagnosing O₃ precursor relationships that do not depend upon emission inventories or meteorological parameterizations.

The observation-based methods developed by the SOS Science Team are intended to meet this need. Moreover, initial applications of these methods suggest that these methods can be used to provide an independent and (with the advent of the PAMS network) a cost-effective tool for inferring ozone-precursor relationships at both regional- and urban-scales.

2.6. OBSERVATION-BASED APPROACH - EVALUATING EMISSIONS

Just as observation-based approaches have the potential to provide an independent check on the ozone precursor relationships derived by EBMs, they can also provide an independent check on the emission inventories that drive the EBMs. In this section, SOS findings derived from observation-based evaluations of emissions inventories are summarized.

2.6.1. Evaluation of Inventories Using Principal Component Analysis

Concurrent measurements of NO_x , NO_y , CO, SO_2 , C_3H_8 , C_6H_6 , and O_3 at a rural site in Alabama were analyzed using Principal Component Analysis to identify the primary factors affecting the concentrations of ozone precursors in the rural South. Key findings of the analysis are outlined below:

- 1. Power Plants Are Confirmed To Be A Major NO_x Source And Biomass Burning Identified As Another Major Source:** The analysis indicated the presence of two major sources of reactive nitrogen - coal-fired power plants and either biomass burning or burning associated with pulp mills.
- 2. Inconsistencies Found With the NAPAP Inventory:** The data suggest that the NAPAP inventory overestimates the SO_2/NO_x emission ratio from coal-fired power plants and underestimates the CO/NO_x emission ratio from pulp mills.

KEY CITATION:

Buhr, M.B., et al. 1994. Evaluation of ozone precursor source types using principal component analysis of ambient air measurements in rural Alabama, *J. Geophys. Res.*, (Submitted).

2.6. Observation-Based Approach: Evaluating Emissions

- Biogenic Emissions:
Developing Mechanistic Algorithms (see Sections 2.2.2 and 2.3.1).
- Evaluation of Inventories
Using Principal Component
Analysis
- Motor Vehicle Emissions:
The SOS Tunnel Studies
- Motor Vehicle Emissions:
Using Traffic Counters for
Day-Specific Emissions

2.6.2. Improved Motor Vehicle Emissions - The Tunnel Studies

To evaluate EPA's motor vehicle emissions models (MOBILE 4.1 and MOBILE 5.0), direct on-road measurements of speciated VOC, NO_x, and CO emissions were made in the Fort McHenry Tunnel under the Baltimore Harbor and the Tuscarora Mountain Tunnel during the summer of 1992. These on-road measurements showed that:

- 1. Models Provide Reasonable Estimates For Highway Emissions:** MOBILE 4.1 and MOBILE 5.0 provide reasonably good estimates (i.e., from -40% to +160%) of the actual VOC, NO_x, and CO emissions from a fleet of well-maintained passenger cars and trucks using these two interstate highway tunnels (see Figure 2.25).
- 2. Roadway-Grade Effect Significant:** Roadway grade of 1 - 4% had a large effect on CO, VOC, and NO_x emissions, with uphill emissions as much as 100% greater than downhill emissions.

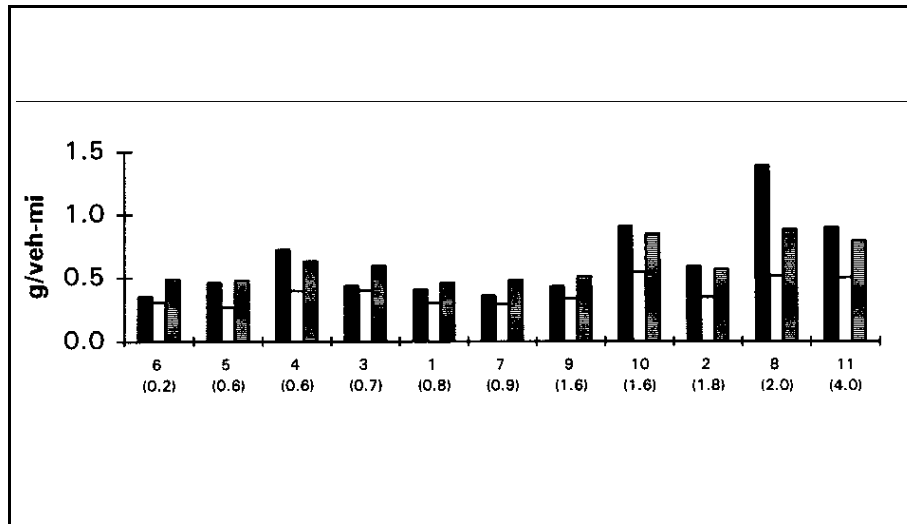


Figure 2.25 Observed (first bar) and MOBILE 4.1 and MOBILE 5.0 predicted (second and third bar) NMHC emissions in Fort McHenry Tunnel. After Pierson, et al., 1994

KEY CITATIONS:

- Bishop, G. A., et al.** 1994. Enhancements of Remote Sensing for Vehicle Emissions in Tunnels. *J. Air Waste Manag. Assoc.* 44: 169-175.
- Bishop, G. A., et al.** 1994. Method Comparisons of Vehicle Emissions Measurements in the Fort McHenry and Tuscarora Mountain Tunnels. *Atm. Env.* (Submitted).
- Pierson, W. R., et al.** 1994. Real-World Automotive Emissions -- Summary of Studies in the Fort McHenry and Tuscarora Mountain Tunnels. *Atm. Env.* (Submitted).

2.6.3. Using Traffic Counters For Estimating Day-Specific Mobile Emissions

As part of the activities of the SOS 1992 Atlanta Intensive, the Georgia Department of Transportation collected traffic data from 37 locations in the Atlanta Metropolitan Area. These data were used to develop day-specific, gridded mobile emissions estimates. The key findings of this study are summarized below.

- 1. Day-Specific Information Yields Significantly Different Emissions:** Use of day-specific traffic information resulted in significantly different mobile emissions estimates for Atlanta than those obtained using the defaults contained in the Emission Preprocessor System Version 2 (EPS2) of the UAM. As illustrated in Figure 2.26, these discrepancies included different temporal patterns of emissions as well as a different magnitude of total emissions. In general, the defaults tended to overestimate emissions, especially during the morning and evening rush hours.

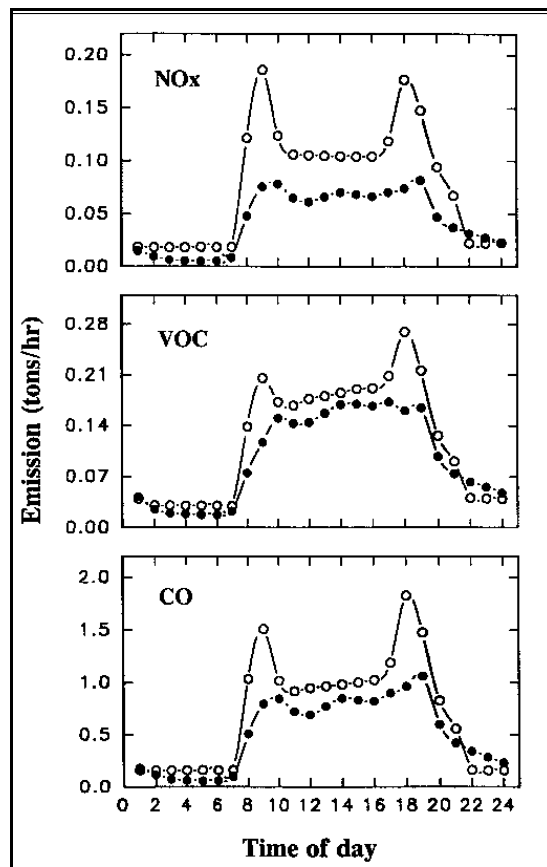


Figure 2.26. Comparison of grid-cell vehicular emissions using default traffic inputs (open circles) and day-specific information (closed circles). After Cardelino et al., 1994.

KEY CITATION:

Cardelino, C. A. et al. 1993. The use of traffic counters in the estimation of day-specific mobile emissions. Proceedings of the Air and Waste Management Association International Specialty Conference on Regional Photochemical Measurement and Modeling Studies. San Diego, California.

2.6.4. Power-Enrichment In Mobile Source Emissions

An evaluation of the effect of power-enrichment on emissions from motor vehicles was carried out by SOS scientists in Atlanta, Georgia. The key finding of the study is summarized below:

1. **Power-Enrichment Enhances Vehicular Emissions:** Acceleration and other heavy engine loads enhances emissions of CO and VOC from motor vehicles and likely represents a significant source of these compounds to the urban atmosphere.

KEY CITATION:

Rodgers, M.O. 1994. Mobile-source emissions. Estimation of power enrichment frequency through observations of velocity-acceleration profiles. Proceedings of Air and Waste Management Specialty Conference on Regional Photochemical Measurement and Modeling Studies. (In press).

2.6.5. Conclusion - Policy-Relevant Findings For Observation-Based Approach - Evaluating Emissions

Use of observation-based methods to evaluate emissions has resulted in the following policy-relevant findings:

1. **Biomass Burning Is A Major Source Of NO_x In The Rural South:** In addition to fossil fuels, the burning of biomass represents a major source of NO_x to parts of the rural South.
2. **Current Emissions Models Provide Reasonable Estimates for Highway Emissions:** Observations in two interstate highway tunnels indicate that the EPA-recommended mobile emissions models (MOBILE 4.1 and MOBILE 5.0) give reasonably good estimates for the emissions from well-maintained vehicles operating on interstate highways.
3. **Current Emissions Models Probably Underestimate Estimates Urban Emissions:** Because vehicular emissions are generally greater when operating under urban conditions than when operating under highway conditions, the tunnel-study observations suggest that the EPA-recommended MOBILE 4.1 and MOBILE 5.0 most likely underestimate emissions from the fleet of vehicles operating in urban areas.
4. **Engine Loads Enhance Vehicular Emissions:** Acceleration, roadway grades, and other engine loads significantly increase motor-vehicle emissions and should be accounted for when preparing mobile-source emissions inventories.
5. **Significant Day-to-Day Variation in Urban Emissions Inferred:** Inclusion of day-specific traffic information had a major impact on mobile source emissions estimates, suggesting that precursor emissions in Atlanta vary significantly from day-to-day.

2.7. AIR POLLUTION METEOROLOGY

While a major portion of the SOS research effort has been devoted to elucidating issues that relate most directly to photochemistry, meteorological issues have also been addressed. In fact, a number of findings that address air pollution meteorology have been discussed earlier in Section 2. These include study of the role of the urban heat island in fostering biogenic hydrocarbon emissions (see Section 2.2.6) and evaluation of in-situ and remote techniques for measuring mixing heights (see Section 2.4.3). In this section we review a few other key findings of SOS that relate to air pollution meteorology.

2.7. Air Pollution Meteorology

- Spatial Inhomogeneities in Ozone Episodes and Small-Scale Meteorological Variability (see Section 2.1.4)
- Biogenic Emissions and the Urban Heat Island (see Section 2.2.6)
- Evaluating Techniques For Measuring Mixing Height (see Section 2.4.3).
- Diurnal Wind-Structure and Pollutant Dispersion
- Effects of Canopy Micrometeorology
- Embedded Plumes

2.7.1. Diurnal Wind-Structure and Pollutant Dispersion

SOS used a coupled boundary-layer/Lagrangian particle model to investigate the role of boundary-layer shear on horizontal dispersion. Key findings of this study are summarized below.

1. **Latitude Affects Dispersion Rate:** Latitude was found to be an important parameter in determining horizontal dispersion rates.
2. **Ekman Solution Overestimates Wind Shear:** An analytical Ekman solution, based on a constant eddy diffusivity, produces too much shear compared to a more realistic numerical solution. A semi-empirical solution is needed to produce better results.

KEY CITATION:

McNider, R. T., M. P. Singh, and J. Lin. 1993. Diurnal wind-structure variations and dispersion of pollutants in the boundary layer. *Atm. Env.* 27a: 2199-2214.

2.7.2. Effects of Canopy Micrometeorology

During the SOS 1992 Atlanta Intensive, a 40 m micrometeorological tower was placed in the Fernbank Forest, a 65-acre urban, deciduous forest located a few miles northeast of the Atlanta's city center (see Figure 2.27). Measurements were made to determine the effects of the microclimate within this urban forest on turbulent vertical transport above and within the canopy. Key findings of the study are summarized below.

- 1. Large Eddies Cause Major Portion of Chemical Exchange Between Canopy and Boundary Layer:** A significant portion of the mass exchange between the atmosphere and canopy is caused by large, intermittent eddies.
- 2. Role of Large Eddies Increases With Stability:** The importance of large, intermittent eddies in transporting mass from the canopy to the atmosphere is greatest during periods of enhanced stability.
- 3. Transport By Large Eddies May Give Rise To Complex Vertical Profiles:** The transport of hydrocarbons aloft by large, intermittent eddies during stagnant conditions may be the cause of the complex vertical profiles, with local maxima above the surface, that have been observed during rural and urban SOS field experiments (see Section 2.4.4).

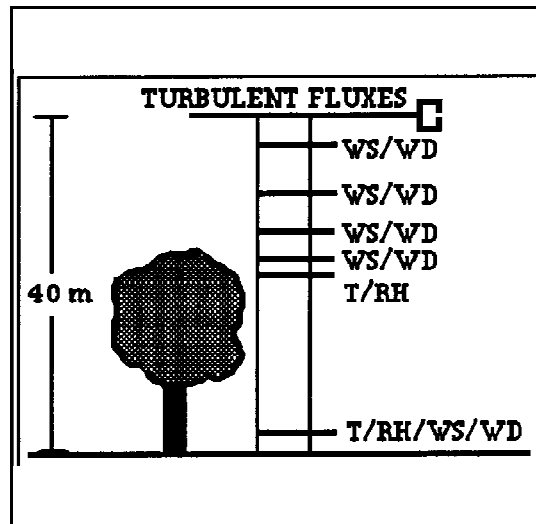


Figure 2.27. Fernbank Forest tower set-up. After Marsik and Samson, 1994

KEY CITATION:

Marsik, F. J. and P. J. Samson, 1994. Effects of canopy micrometeorology on the turbulent transport within an urban deciduous forest. Proceedings of the 21st Conference on Agricultural and Forest Meteorology, San Diego, CA. March 7-11.

2.7.3. Atlanta Non-Attainment As An Embedded Plume

During the 1992 SOS Atlanta Intensive Field Study, many helicopter flights were made to track air pollutants from urban sources as they were transported or advected downwind. One of the interesting insights gained from preliminary analysis of the data gathered from these measurements is summarized below.

- 1. Maximum Ozone Appears In An Embedded Plume:** Samples gathered from afternoon helicopter flights some 20 - 30 miles downwind of the urban core, suggest that maximum O_3 concentrations tend to appear within plumes that also contain high SO_2 and NO_x concentrations (see Figure 2.28). These observations suggest that peak O_3 concentrations in the Atlanta area may be found within plumes from power plants (or similar point sources), that are embedded within the broader urban plume, which is, in turn, embedded within the more amorphous, regional "tide" of high O_3 concentrations described in Section 2.1.6. If this inference is correct, it implies that O_3 non-attainment episodes in the Atlanta area occur when the sum total of O_3 that has accumulated within each of the plumes exceeds the NAAQS.

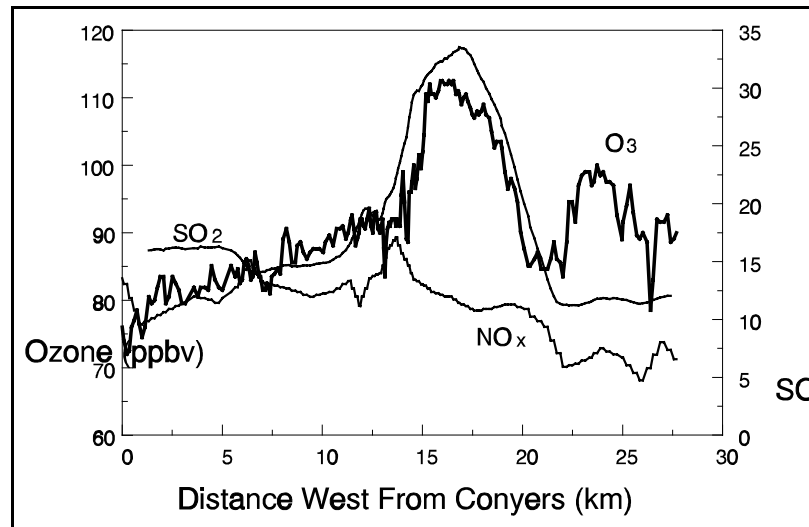


Figure 2.28. Concentrations of O_3 , NO_x , and SO_2 measured aboard the TVA helicopter as it traversed the Atlanta plume at about 1730 Hours on August 19, 1992. After Imhoff et al, 1994.

KEY CITATION:

Imhoff, R. E., et al. R. 1994. The production of O_3 in an urban plume: airborne sampling of the Atlanta urban plume. *Atm. Env.* (Submitted).

2.7.4. Conclusion - Policy-Relevant Findings In Air Pollution Meteorology

Meteorological studies carried out under SOS have resulted in the following policy-relevant findings:

1. **Large-Scale Eddies Play A Significant Role:** Large-scale eddies play a significant role in the transport and dispersion of airborne chemicals within the boundary layer in the South. Because these eddies are not resolved by mesoscale and urban-scale chemical transport models, their effects are likely not well-simulated in these models and this, in turn, may lead to significant biases in the simulation of oxidant photochemistry by these models.
2. **Non-Attainments As Embedded Plumes:** Maximum O₃ concentrations are found to appear downwind of the Atlanta city center as a series of embedded plumes from power plants (or similar point sources), general urban area sources, and the wide-spread "rising tide of O₃".

Other relevant conclusions in air pollution meteorology include #5 in Section 2.2 concerning Urban Heat Islands, #1 in Section 2.4 concerning the measurement of mixing heights using remote sensors, and #4 in Section 2.8 concerning the sensitivity of UAM simulations to the specification of upper-air meteorological data.

2.8. EVALUATION AND IMPROVEMENTS IN PHOTOCHEMICAL GRID MODELS

While the development and application of observation-based approaches was given a high priority in SOS, research on the development, evaluation, and application of 3-dimensional photochemical grid models (also called Chemical Transport Models or CTMs) was also a major priority for SOS. In this section, some of the key findings from this aspect of the SOS program are summarized.

2.8. Photochemical Grid Models

- Development of Biogenic Emissions Inventory System.
- Evaluating UAM Simulations of Atlanta.
- Parameterizing Convective Cloud Transport In A Regional Model.

2.8.1. Development of Biogenic Emissions Inventory System (BEIS)

The efficient incorporation of biogenic emissions into 3-D CTM's requires a numerical system that can relate land-use characteristics within the modeling domain with environmental and meteorological factors so that a gridded biogenic inventory coupled to the model's meteorology can be incorporated into the simulation in real time. Toward that end a Biogenic Emissions Inventory System (BEIS) was developed. The system estimates hourly emissions of isoprene and other biogenic hydrocarbons for any county in the United States as a function of specified temperature, relative humidity, wind speed, cloud cover, and genus and species of vegetation present in the relevant model grid.

KEY CITATION:

Pierce, T.E., and P.S. Waldruf. 1991. PC-BEIS: A personal computer version of the Biogenic Emissions Inventory System. *J. Air Waste Manage. Assoc.* 41: 937-941.

2.8.2. Evaluation of UAM Simulation of Atlanta

An important objective in SOS has been the evaluation of the performance of the UAM simulation of Atlanta's air pollution episodes. The intensive measurement campaigns in Atlanta during the summers of 1990 and 1992 have now made such an evaluation possible. Thus far, evaluations have been made with two versions of the UAM - the standard regulatory version with five layers in the boundary layer and a version with enhanced vertical resolution (i.e., 8 layers in the boundary layer). The major findings are summarized below.

1. **Vertical Resolution Affects Surface Concentrations:** Increasing UAM vertical resolution, increases the surface concentrations of reactive hydrocarbons (see Figure 2.29).

2. **UAM Underpredicts Isoprene:** UAM-calculated isoprene using the standard BEIS is systematically underpredicted at the surface and aloft (see Figure 2.29 and Figure 2.11).

3. **UAM Is Not Able To Simulate Isoprene and O₃ Simultaneously:** When the enhanced isoprene emissions of Geron et al. (1994) are used, reasonable agreement is obtained between observed and UAM-predicted isoprene (see Figure 2.11), however, O₃ is significantly overpredicted by the model, in this case.

4. **UAM Accurately Represents O₃-NO_y Correlations:** Intercomparison of airborne measurements of O₃ and NO_y from a helicopter during the SOS 1992 Atlanta Intensive and UAM simulations suggest that the model is able to represent the spatial and temporal relationships between O₃ and NO_y with reasonable accuracy.

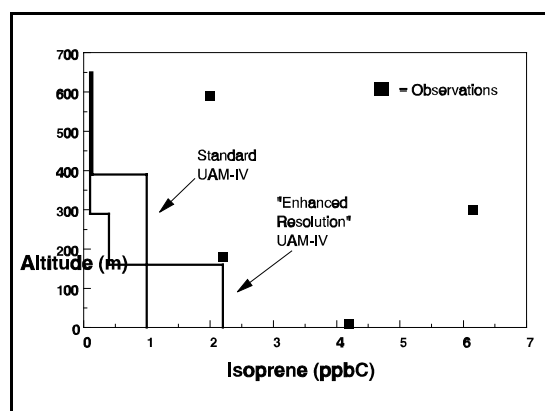


Figure 2.29. UAM-calculated and observed isoprene concentrations. After Sillman, 1994.

KEY CITATIONS:

Sillman, S., et al. 1994. Photochemistry of ozone formation in Atlanta, GA: models and measurements. *Atm. Env.* (Submitted).

Imhoff, R. E., et al. 1994. The production of O₃ in an urban plume: airborne sampling of the Atlanta urban plume. *Atm. Env.* (Submitted).

2.8.3. Evaluation of UAM Sensitivity To Specification of Upper Air Winds

During the 1992 SOS Atlanta Intensive, upper-air meteorological data were collected at different locations in the metropolitan area by a Cross-Lorain Atmospheric Sounding System (CLASS), two Lidar systems, and four radar wind profilers, all operated by the SOS measurement team. Meteorological data was also collected on the outer perimeter of the metropolitan area by rawinsondes operated by the National Weather Service. These data were used to investigate the sensitivity of UAM simulations to meteorological wind fields. Key findings of this investigation are summarized below.

- 1. UAM Sensitivity To Upper Wind Data Is Significant:** The use of upper-air data to specify wind fields in the UAM has a significant impact on the model-calculated concentration fields for O_3 and other chemicals (see Figure 2.30).
- 2. EPA-Approved Method Of Specifying UAM Wind Fields Using Rawinsonde Data Produces Significant Model Errors:** The model runs using only the rawinsonde data to specify the wind fields in the UAM gave the largest deviations in model-calculated O_3 and NO_y concentration fields (see Figure 2.30).

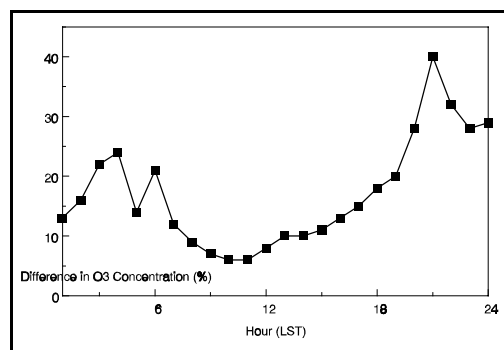


Figure 2.30. % difference in hourly O_3 concentrations calculated between two UAM-simulations for Atlanta: One using wind fields generated from the complete meteorological array deployed during the SOS Atlanta Intensive and one using wind fields generated only from rawinsonde data. After Al-Wali and Samson, 1994.

- 3. Improvements Can Be Obtained From Urban Core Measurements:** Significant improvements in UAM-simulations are obtained by using upper-air data obtained at or near the center of the emissions density. Thus priority should be given to the placement of upper-air measurements near the cores of urban areas where UAM simulations are planned.

KEY CITATION:

Al-Wali, K.I., and P.J. Samson. 1994. A preliminary sensitivity analysis of Urban Airshed Model simulations to the temporal and spatial availability of upper air measurements. *Atmos. Env.* (In press).

2.8.4. Convective Cloud Parameterization In a Regional Model

A parameterization of sub-grid scale convective cloud vertical mixing was developed by SOS and incorporated into the NOAA Aeronomy Laboratory 3-D Regional Chemistry Model.

Key findings are summarized below.

1. **Cloud Transport Is Significant:** Model results with and without cloud transport were found to differ significantly. This implies that cloud exchange is an important process in determining the vertical distribution of O₃ and its precursors.
2. **Agreement With Airborne Data Improved With Convective Parameterization:** The model results with the cloud parameterization tend to be in significantly better agreement with aircraft observations than those obtained without the parameterization.

KEY CITATION:

Lin, X. et al. 1994. A parameterization of subgrid scale convective cloud transport in a mesoscale regional chemistry model. *J. Geophys. Res.* (In Press).

2.8.5. Conclusion - Policy-Relevant Findings For 3-D Photochemical Grid Models

The SOS research efforts using 3-D Photochemical Grid Models have resulted in the following policy-relevant findings:

1. **UAM Can Be Improved By Increasing Vertical Resolution:** Numerical experiments with an enhanced version of UAM suggest that model performance can be improved by increasing its vertical resolution in the lowest portion of the boundary layer.
2. **UAM Has Difficulty Simultaneously Reproducing Observed Isoprene and O₃ Concentrations:** Comparison of the UAM-predicted concentrations with observations in the Atlanta Metropolitan Area indicate an inability of the model to simultaneously reproduce observed surface isoprene and ozone concentrations.
3. **UAM Is Able To Reproduce Observed Urban Relationship Between Ozone and NO_y:** Reasonable agreement was obtained between UAM-predicted and observed O₃ and NO_y concentrations aloft. This suggests that the model is simulating, with reasonable accuracy, the relationship between O₃ production and NO_x emissions and oxidation .
4. **UAM Sensitive To Method Used To Specify Upper-Air Wind Data:** Significant errors in the UAM simulations for Atlanta were inferred when the model was run using the EPA-approved method of specifying meteorological wind fields with data only from the standard, National Weather Service rawinsondes.

2.9. THE VOC vs NO_x QUESTION

As noted in Section 1.3.1, one of the major scientific questions addressed by SOS was the extent to which oxidant formation rates within the South could be characterized as being limited by VOC and/or by NO_x. While this is a complex and difficult question, and one that the SOS research is

not able to answer definitively for the entire region, significant insights have been gained during the Phase I research effort. These insights are summarized in this section.

2.9. The VOC vs NO_x Question

- The Role of the Radical Pool
- The Global Perspective.
- The Regional Perspective
- The Atlanta Perspective

2.9.1. The Role of the Radical Pool

Diagnostic analysis of the photochemical smog reactions has uncovered a fundamental property of the photochemical system that explains why the atmosphere switches from a VOC-limited and NO_x-limited regime as NO_x concentrations decrease. This shift reflects the two different ways in which the atmosphere processes emission inputs and the effect of the processes on the radical pool.

1. **The VOC-Limited Regime** has an excess of NO_x sources over free radical sources. This regime is thus characterized by an overabundance of NO_x and a deficiency of radicals and HNO₃ concentrations greater than H₂O₂ concentrations.
2. **The NO_x-Limited Regime** has an excess source of free radicals over NO_x sources. This regime is thus characterized by a deficiency of NO_x and an overabundance of radicals and H₂O₂ concentrations greater than HNO₃ concentrations.

KEY CITATION:

Kleinman, L.I. Low and high NO_x tropospheric photochemistry, *J. Geophys. Res.*, 99:16831-16838.

2.9.2. The Global Perspective

An analysis of O₃, NO_x, and speciated hydrocarbon concentrations measured in urban, suburban, and remote locations indicates:

- 1. NO_x-Limitation Implied Over Broad Spatial and Temporal Scales:** As one moves from remote forests to rural areas of the eastern and southern United States and then to urban areas, O₃ correlates well with NO_x but not with hydrocarbon reactivity. This suggests that, in the gross average, NO_x, and not hydrocarbons is the limiting factor in O₃ photochemical production and accumulation (see Figure 2.31).

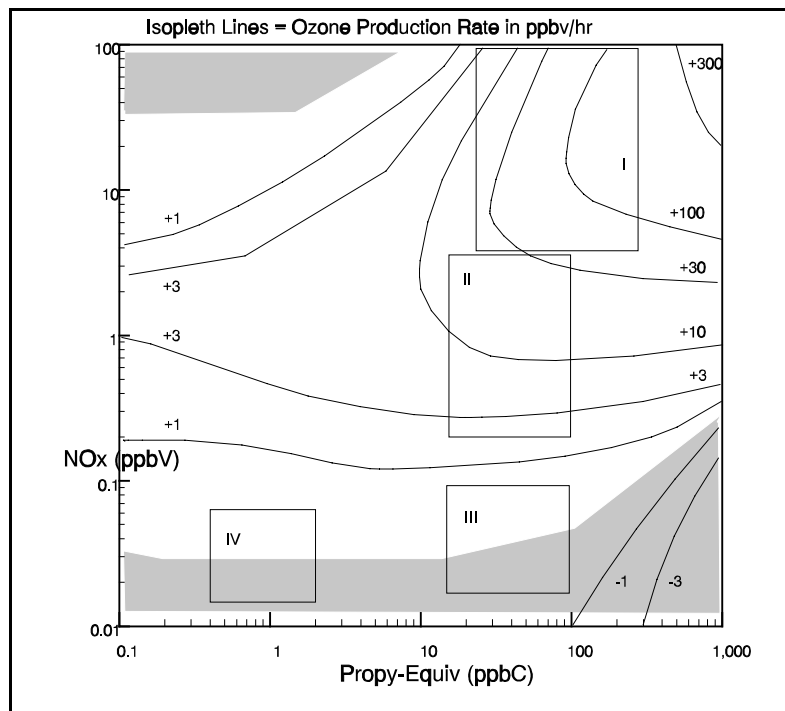


Figure 2.31. Summary of hydrocarbon/NO_x regimes: I = urban areas (high O₃), II = rural sites in eastern and southern United States (moderate O₃), III = remote tropical forests in Brazil (low O₃), and IV = remote marine atmosphere (low O₃). Shaded areas indicate regions where the net photochemical production is negative. After Chameides et al., 1992.

KEY CITATION:

Chameides, W. L., et al. 1992. Ozone precursor relationships in the ambient atmosphere. *J. Geophys. Res* 97D (5):6037-6055.

2.9.3. The Regional Perspective

Analyses of O_3 , NO_x , and NO_y measurements made in the rural South indicates that:

- 1. O_3 Correlates With Oxidized Products of NO_x :** Throughout much of the rural South, O_3 concentrations are well-correlated with $NO_z = NO_y - NO_x$ with a slope of about 10; thus it appears that about 10 O_3 molecules are produced for each NO_x molecule emitted in the region (see Figures 2.4 and 2.32).
- 2. Rural South Found To Be Most Often In NO_x -Limited Regime:** Observations indicate that the vast majority of air masses in the rural South have photochemical ages of 0.7 or greater (i.e., $NO_z/NO_y \geq 0.7$), an age which is consistent with NO_x -limitation. The term "photochemical age" here is defined as the fraction of the original NO_x emitted into an air mass that has been converted to NO_z (see Figure 1.1). Thus if all NO_x is converted to NO_z , then $NO_z/NO_y = 1$ and the photochemical age is 100%.

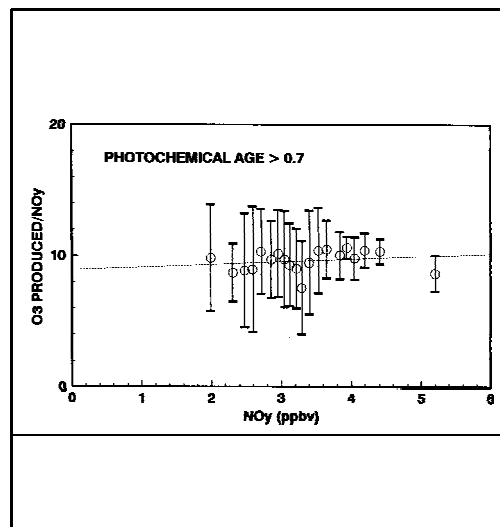


Figure 2.32. Observed ratios of $O_3:NO_y$ as a function of NO_y for air masses with photochemical ages of 70% or more. After Olszyna et al., 1994.

KEY CITATIONS:

Wang, T., 1992. Atmospheric Reactive Nitrogen Oxides and Their Relationship With Urban and Rural Ozone Formation, Ph.D. Thesis, Georgia Institute of Technology.

Kleinman, L., et al. 1994. Ozone formation at a rural site in the southeastern United States. *J. Geophys. Res.* 99D (2): 3469-3482.

Olszyna, K. J., et al. 1994. O_3 and NO_y Relationships at a rural site. *J. Geophys. Res.* 99: 14557-14563.

2.9.4. The Atlanta Perspective

The issue of VOC- vs NO_x -limitation in Atlanta has been addressed through a variety of prognostic and diagnostic tools. As summarized below, these tools all appear to yield a consistent result.

- 1. Photochemical Indicators Point To NO_x -Limitation:** Helicopter observations made during the 1992 SOS Atlanta Intensive suggest afternoon HCHO/NO_y and $\text{H}_2\text{O}_2/\text{NO}_y$ ratios in the urban plume about 30 km southeast of the city center of about 0.33 and 0.15-0.3, respectively. These ratios suggest NO_x -limitation on the basis of the photochemical indicator method, but lie close to the transition between NO_x - and VOC-limitation.
- 2. OBM Suggests O_3 Production Is More Sensitive To NO_x Than Anthropogenic VOC:** Analysis of six ozone exceedance days observed during the 1990 Atlanta Study using the OBM indicates that O_3 production is, on average, about 1.5 times as sensitive to NO_x than to anthropogenic hydrocarbons. However, data from one of the six exceedance days indicates greater sensitivity to anthropogenic hydrocarbons (see Figure 2.33). Moreover, flaws in the data used in the study (including uncertainties in afternoon NO concentrations and apparent contamination in some of the VOC measurements) render the results provisional.

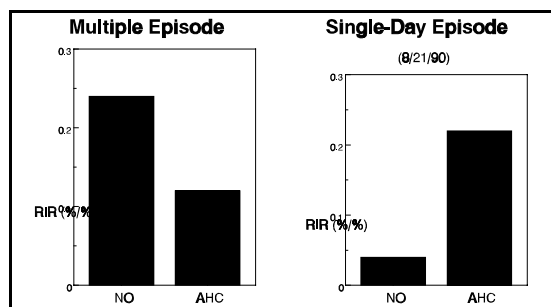


Figure 2.33. OBM-calculated RIRs (i.e., % O_3 reduction per % precursor reduction) for anthropogenic hydrocarbons (AHC) and NO . Results are shown for a six episode average and for the one episode with greater sensitivity to AHC. After Cardelino and Chameides, 1994.

- 3. The IER/Airtrak Approach Indicates NO_x -Limitation:** Analysis using the Integrated Empirical Rate (IER) Model with ambient data collected by the Airtrak instrument indicates a tendency toward NO_x -limitation in air parcels collected in the afternoon in Midtown Atlanta on days when the maximum O_3 concentration exceeded 100 ppbv (see Figure 2.34).

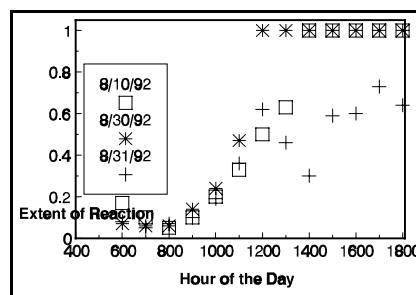


Figure 2.34. Extent of photochemical smog reaction inferred by IER/Airtrak System as a function of time of day for air parcels sampled on the Georgia Tech campus in Atlanta on days when maximum hourly O_3 exceeded 100 ppbv. Air parcels are NO_x -limited as the Extent of Reaction approaches 1. (After O'Neal, 1994.)

2.9.4. The Atlanta Perspective (Cont'd)

3. **UAM Simulation Suggests That Only NO_x Control Can Bring Atlanta Into Attainment:** Application of UAM-IV to 1999 projected emissions and "worst-case" scenario meteorological conditions for Atlanta (following U.S. EPA guidelines for developing a State Implementation Plan) indicates that a 100% decrease in anthropogenic VOC emissions reduces peak O₃ from 176 ppbv to 144 ppbv. UAM predicts O₃ attainment from a 90% decrease in anthropogenic NO_x emissions. However, decreases in NO_x emissions of less than 67% are predicted to cause an increase in peak O₃ concentrations of as much as 25%. (See Figure 2.35.)

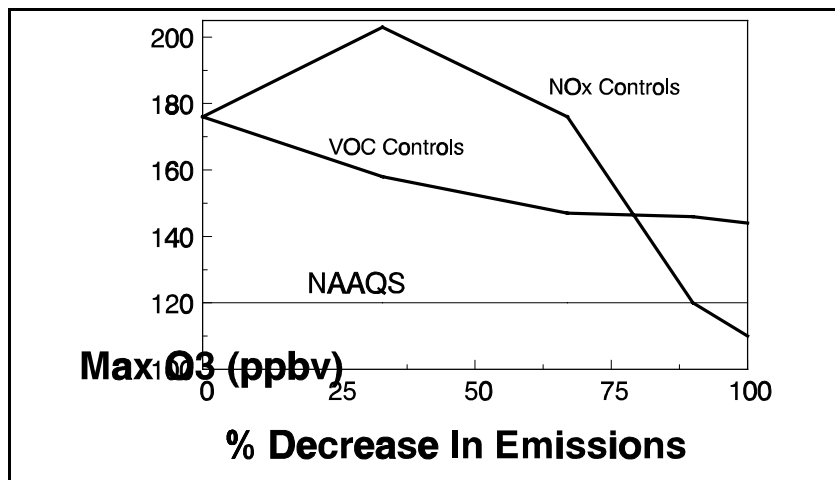


Figure 2.35. Peak O₃ concentrations predicted by the UAM in the Atlanta non-attainment area as a function of the percent decrease in base VOC and NO_x emissions for meteorological conditions encountered on July 31, 1987. Base emissions are those estimated for 1999 after accounting for projected economic and population growth of the area and the implementation of emission controls resulting from the Clean Air Act Amendment mandates for a 15% VOC Reduction Plan, Reasonable Available Control Technology (RACT) for major VOC and NO_x sources, Enhanced Inspection and Maintenance (I&M) for vehicles, and NO_x acid rain reductions.

KEY CITATIONS:

- Cardelino, C.A., and W.L. Chameides.** 1994. An observation-based model for analyzing ozone precursor relationships in the urban atmosphere. *J. Air Waste Manag. Assoc.* (In press).
- O'Neal, J.** 1994. *Assessing the Oxidative Potential of Urban Air Parcels.* M.S. Thesis, University of North Carolina, Chapel Hill, 101pp.
- Sillman, S.** 1994. The use of NO_y, HCHO, H₂O₂ and HNO₃ as empirical indicators for ozone-NO_x-ROG sensitivity in urban locations. *J. Geophys. Res.* (In Press).

2.9.5. Conclusion - The Policy-Relevant Finding For VOC- vs NO_x-Limitation

Analyses using a combination of observation- and emission-based approaches suggest that:

Ozone In South Is Limited By NO_x.

More specific conclusions include the following:

1. In the rural South, the data suggest conclusively that NO_x-limitation applies and that a decrease in the region's total NO_x emissions would bring about a decrease in rural O₃ concentrations.
2. The data and analyses for Atlanta also point to NO_x-limitation as being the dominant characteristic of most O₃ episodes. But this inference is not nearly as robust as that for the rural areas of the South.
3. The photochemical indicator method points to NO_x-limitation but the indicators lie very close to the critical values where the system switches over to VOC-limitation.
4. The OBM indicates NO_x-limitation, but the data used in the analyses were flawed and data for one of the six O₃ exceedance days studied pointed to VOC-limitation. One plausible interpretation is that some O₃ exceedances in Atlanta are characterized by NO_x-limitation and others by VOC-limitation.
4. The IER/Airtrak System usually indicates NO_x-limitation in air parcels sampled in Midtown Atlanta during the afternoon hours on days when the peak O₃ concentrations in the area exceeded 100 ppbv.
5. UAM simulations based on a "worst-case meteorological" scenario predict that decreasing NO_x emissions is the only way to bring Atlanta into attainment with the NAAQS. But attainment is predicted to require a large (i.e., 90%) reduction in NO_x emissions. Also more moderate reductions in NO_x emissions of less than 67% are predicted to bring about an **increase** in peak O₃ concentrations.

3. SOS IN THE FUTURE

SOS Phase I research during 1988 - 1994 confirms that the South is a region with significant rural and urban oxidant problems. These studies also indicate that these rural and urban air quality problems are coupled in a complex way that appears to reflect the unique summertime meteorology and diverse land-use patterns and industrial development of the region. In contrast to the northeast, whose O₃ episodes have been likened to an "ozone river", regional episodes in the South are more disperse and

spatially incoherent. This "rising tide" of O₃ is produced by photochemical reactions driven by ample amounts of biogenic hydrocarbons and a limited supply of nitrogen oxides. The nitrogen oxides, in turn, arise from a variety of sources - including fossil-fuel and biomass burning, and, to a lesser extent fertilizer-induced soil emissions, and, perhaps in some cases, lightning. Under the stagnant conditions that characterize the summertime South, the O₃ thus produced accumulates, giving rise to rural oxidant concentrations that affect human health, damage vegetation, limit crop production, and, as described below, promote the development of O₃ non-attainment episodes in the region's urban centers.

Observations during SOS field campaigns in and around Atlanta indicate that the maximum O₃ concentrations appear downwind in a series of embedded plumes. These plumes include power plant (or similar small point source) plumes advecting within a more general urban plume from area sources, which in turn is embedded within a geographically disperse

3. The Future

- PHASE I Findings Point Toward Future Scientific Directions.
- The Near-Term: Nashville /Middle Tennessee Intensive Ozone Study.
- The Longer-Term:
 - Data analysis and interpretation
 - Research To Facilitate The Effective Implementation of the CAAA
 - Meeting National Needs

regional "tide" of O₃, as described above. One working hypothesis developed from these observations is that O₃ non-attainment episodes in Atlanta, and perhaps other cities in the South, occur when the sum total of the O₃ that accumulated within each of these plumes exceeds the NAAQS. Hence the complex coupling of regional O₃ to urban O₃ non-attainment.

If correct, this hypothesis implies that peak O₃ concentrations in Atlanta, and other southern cities, are largely controlled by stochastic interactions between regionally dispersed processes and small-scale plume-type phenomena. As such, they will be difficult to simulate in the current generation of gridded air quality models and probably also difficult to control using traditional pollution-abatement practices that focus on limiting emissions in urban non-attainment areas. (Indeed, UAM-simulations for Atlanta that follow the EPA-guidelines indicate the necessity to eliminate virtually all of Atlanta's anthropogenic emissions to reach O₃ attainment.)

The SOS Science Team is now formulating a research plan to determine the applicability of the above hypothesis to the South and to explore the implications of this and related hypotheses on the region's ability to effectively manage its air resources, meet the statutory requirements of the CAAA, and continue to grow economically. In the near-term, SOS will examine sub-grid scale chemistry and meteorology (including plume-in-grid phenomena) in an urban intensive field-measurement campaign in Nashville/Middle Tennessee. This research will be done to better understand how plumes interact with each other chemically and with the regional and urban background. Over the longer term, SOS is planning to expand and enhance its regional program to better understand how small-scale, urban-scale, and mesoscale phenomena interact throughout the region and to investigate the viability of alternate strategies for managing O₃ pollution in the South and implementing the CAAA of 1990. These two aspects of SOS' planned activities (Near-Term and Long-Term) are briefly summarized below.

3.1. THE NEAR-TERM: THE 1995 SOS NASHVILLE/MIDDLE TENNESSEE INTENSIVE OZONE FIELD STUDY

The 1995 SOS Nashville/Middle Tennessee Intensive Ozone Field Study represents the culmination of several years' preparation by the SOS Science Team for a major Urban Intensive in the Nashville non-attainment area. This preparation has included a number of Exploratory Field Studies, the most recent having taken place in the Summer of 1994.

As a follow-up to the intriguing observations during the Atlanta Intensive, the primary objective of the Nashville/Middle Tennessee Intensive Ozone Field Study will be to:

Examine sub-grid scale chemistry and meteorological processes especially with regard to rural/urban, urban/rural, power plant/urban, and power plant/rural exchange.

From this study, it should be possible to improve our understanding of regional, urban, and point-source plumes and their interactions, and how these interactions affect O₃ formation, as well as the accumulation of peak O₃ concentrations on both urban and regional scales. In addition the study will aim to:

1. Characterize and quantify the chemical and climatological similarities/dissimilarities between the Nashville, Tennessee and Atlanta, Georgia metropolitan areas;
2. Better understand the role of biogenic emissions in accumulation of ozone in rural and urban areas of the Middle Tennessee region; and
3. Test and improve both emissions-based and observation-based air-quality models.

The Nashville/Middle Tennessee region is well suited for these process-oriented studies. It is sufficiently distant from other urban areas to permit characterization of distinct regional, urban, and point source regimes. Also, large TVA fossil-fuel power plants within the Nashville non-attainment area (Gallatin), and west (Johnsonville and Cumberland) and north (Paradise) of Nashville provide opportunities to study the influence of large point sources of nitrogen oxides on both regional and urban O₃ chemistry in essentially all wind directions.

The 1995 SOS Nashville/Middle Tennessee Intensive Ozone Study is scheduled for June 21 through July 28, 1995. The middle four weeks of this six-week study will focus on aircraft experiments. As shown in Figure 3.1, the following ground-level monitoring sites will be maintained during the entire six-week period:

- 1) One "Level 3" (i.e. state-of-science) chemistry site will be developed and maintained by the Georgia Institute of Technology at the New Hendersonville site just north of Hendersonville, Tennessee. This location was the site of the 1994 SOS NO/NO_y intercomparison study and historically experiences the highest O₃ concentrations in the Nashville area.
- 2) Five "Level 2" (i.e., moderately enhanced) chemistry stations will be operated by the Tennessee Valley Authority and related agencies. These sites will be located at Giles County, Downtown Nashville, and Cove Mountain in Tennessee, and Land Between the Lakes and Mammoth Cave in Kentucky. They will remain operational for the entire 1995 ozone season - April 1 through October 31, 1995 and will provide continuous high-sensitivity measurements of NO/NO_y, CO, SO₂, O₃, and canister VOCs.
- 3) Finally, more than 40 "Level 1" sites equipped with O₃ monitors will be maintained by cooperating state, local, and federal air-quality management organizations from across the east-central U.S. The data from Level 1 stations will be accessed daily by SOS and used for experimental planning.

In addition, six air-quality research aircraft will participate in the study, giving it one of the largest contingent of aircraft-sampling resources in the history of air quality research in the U.S. The planned research aircraft include:

- 1) A P-3 Orion from NOAA Aeronomy Laboratory
- 2) A Bell 205 Helicopter from TVA
- 3) A DOE G-1 aircraft sponsored by the Brookhaven National Laboratory
- 4) A Twin Otter aircraft sponsored by the NOAA-Air Resources Laboratory
- 5) A Casa 212 sponsored by the EPA/NOAA-Environmental Testing Laboratory, and
- 6) A second P-3 Orion aircraft sponsored by the NASA.

FIGURE 3.1 MAP OF NASHVILLE

The P-3 Orion and G-1 aircraft will provide airborne chemical research capabilities equivalent to a "Level 3" ground-based chemistry site. The Bell 205 helicopter and the Twin Otter will provide airborne enhanced chemistry platforms equivalent to the "Level 2" ground stations. The Casa 212 will provide an ozone/particle LIDAR system. The NASA P-3 will be flying a tropospheric emissions spectrometry system destined for use in the Earth Observing System satellite early in the 21st century.

To measure meteorological factors affecting ozone, seven radar profiler systems will be used during the intensive study - five operated by NOAA-ETL, one by the Georgia Institute of Technology, and one by the University of Alabama in Huntsville. Three sites will be located in and around the Nashville metropolitan area (New Hendersonville, Youth, Inc., Dickson County, or Old Hickory) and four will be regionally dispersed at the regional Level 2 ground stations (Giles County, Land Between The Lakes, Mammoth Cave, and Cove Mountain).

The 1995 Nashville/Middle Tennessee Ozone Study will be entering the final planning stage in the coming months. The current plans were presented to the SOS Science Team and larger SOS community at the SOS Annual Meeting/Data Analysis Workshop on January 10-14, 1995 in Raleigh, North Carolina. A final detailed plan is now under development and will be distributed to research groups who may wish to develop allied air quality studies in cooperation with SOS.

3.2. THE LONGER-TERM

Following the Nashville Intensive in 1995, SOS will enter Phase II of the program with funding required from a new set of Cooperative Agreements. The SOS Science Team has identified two major objectives of the research program during the second phase:

Objective 1: Make the South a model for effective management of ozone pollution through effective and innovative interaction of the scientific research and policy communities.

Objective 2: Use the research tools, technology, and expertise developed by SOS to aid in the national program aimed at cost-effective management of ozone pollution

To carry out these objectives, three research themes have been identified for Phase II, as described below.

3.2.1. Research Theme 1: Research Aimed At Elucidating Processes Responsible For Ozone Formation, Transport, and Accumulation in the South

As in Phase I, SOS will continue to develop a policy-relevant, regional air quality research program capable of continuously informing and guiding the policy-making community with useful, relevant, and scientifically-robust technical information. The SOS Science Team will therefore maintain its focus on the design and implementation of research projects related to Chemical and Meteorological Measurements, Emissions and Effects, Modeling, and Measurement Technology and Standards aimed at furthering our basic understanding of the processes responsible for the formation, accumulation, and transport of ozone on urban and regional scales in the southern United States. Toward these ends, the SOS Science Team will undertake the research activities outlined below.

3.2.1.1. Data Analysis and Interpretation

By the end of 1995, SOS and related regional air quality programs will have amassed an unprecedented set of chemical and meteorological data related to the O₃ pollution issue. These data include those gathered from:

- 1990-1995 SOS/SON monitoring
- 1990 EPA Atlanta Ozone Study
- 1990 and 1992 SOS/SENIOR Intensives
- 1991 SOS Atlanta Exploratory Study
- 1992-1995 SOS/SCION monitoring
- 1992 SOS Atlanta Intensive Study
- 1993-1995 PAMS monitoring data
- 1994 SOS Exploratory study in Nashville/Middle Tennessee
- 1995 SOS Nashville/Middle Tennessee Intensive Ozone Study
- And other databases from the
 - Southern Appalachian Mountain Initiative (SAMI)
 - Environmental Assessment of the Southeast (EASE)
 - Southern Global Change Program (SGCP)
 - Southern Commercial Forest Research Cooperative (SCFRC)
 - Southern Appalachian Man and Biosphere (SAMAB) Program
 - Other Regional Oxidant Programs in the United States and abroad.

While the SOS Science Team has already worked extensively on a number of these databases, the research is by no means exhaustive. Moreover, data from the 1995 study will only become available for analysis and interpretation in the 1996 and later timeframe. Thus, a major activity for Phase II research in SOS will be the analysis, interpretation, archiving, and policy-relevant assessment of many of the above-listed databases and information sources.

3.2.1.2. Chemical Climatology

SOS will maintain, integrate, and expand the existing 3-tiered SOS regional network (see Figure 1.6) to include carefully selected additional rural sites in the states of Louisiana, and Texas, and possibly also in Virginia, Maryland, Delaware, Arkansas, and Washington, D.C.

3.2.1.3. Urban Field Intensives

SOS will carry out one or two Intensive Field Studies embedded within the SOS regional networks. Possible scientific foci for these Intensives that are currently being considered by the SOS Science Team include:

- A "whole-city" emissions test;
- An intensive study in area impacted by sea-breeze (thus, providing a counterpoint to the Atlanta and Nashville Intensives);
- An intensive study in a dry climate (thus, less-likely to be impacted by biogenic VOC emissions and also providing a counterpoint to the Atlanta and Nashville Intensives);
- An intensive study in area impacted by the petro-chemical industry;
- A model-evaluation study.

Candidate sites for these studies include: Atlanta, Baltimore/Washington D.C., Dallas, El Paso/Juarez, Houston, Tampa, and the Piedmont Crescent of North Carolina (i.e., Raleigh/Durham). (Selection of Intensive sites in SOS is accomplished through a consensus-building process that involves preliminary paper studies and discussions led by designated "proponents" and limited Exploratory Field Studies. The selection process typically takes at least 1 year and is completed no less than 2 years prior to the implementation of an Intensive Field Study.)

3.2.1.4. Monitoring The Impact Of Ozone Management Strategies In the South

SOS will analyze data gathered from the SOS regional networks and field intensives to monitor "rule effectiveness" and evaluate the efficacy of regional and urban ozone abatement strategies and their implementation in various parts of the South.

3.2.2. Research Theme 2: Meeting National Needs Through Outreach, Tech Transfer, and Infrastructure Development

In order to help meet the South's and the nation's continuing need for a strong scientific and technical capability in the air quality area in general, and especially as it relates to O₃ pollution and abatement, SOS will:

- Continue efforts in model development and model evaluations including:
 - Development, evaluation, demonstration of operational feasibility of OBM's developed inside and outside SOS;
 - Evaluation of urban-scale EBM's using datasets gathered in SOS Intensives; and
 - Intercomparison and evaluation of regional EBM's using datasets gathered by SOS and others.
- Disseminate and assist in the transfer of improved analytical tools, technologies and methodologies for the accurate and precise quantification of chemical species and their fluxes - especially as these activities relate to successful implementation and enhancement of the Photochemical Assessment Monitoring Stations (PAMS) network.
- Disseminate and assist in the transfer of improved algorithms and methodologies for UAM applications.
- Disseminate and assist in the transfer of OBM's and other analytical tools capable of aiding in the design of effective ozone abatement strategies.
- Continue SOS' traditional focus on improved Measurements, Technology, and Standards.
- Increase collaboration and cooperation with other national and regional air quality studies in the United States and abroad, especially in connection with the emerging North American Research Strategy for Tropospheric Ozone (NARSTO).

3.2.3. Research Theme 3: Research On Alternate Strategies For Implementing the CAAA-90 and Beyond

As a result of the Phase I SOS research activities described in Section 2 of this report, a number of important new insights have been developed with regard to the ozone (O₃) non-attainment problem in Atlanta and its abatement. Specifically relevant to Atlanta's non-attainment problem it has been found that:

Because of the copious amounts of natural hydrocarbon emissions and the extremely low concentrations of NO encountered in Atlanta during afternoon hours, **ozone in the Atlanta metropolitan area appears to be more sensitive to anthropogenic emissions of nitrogen oxides (NO_x) than the anthropogenic emissions of volatile organic compounds.**

This finding, based upon analyses using the Urban Airshed Model, as well as observation-based methods developed by the SOS Science Team, suggests that a strategy based on reducing anthropogenic emissions of NO_x should provide an effective means of abating ozone pollution in the Atlanta metropolitan area.

However, the translation of this scientific finding into the regulatory arena has proven to be problematic. In the development of a State Implementation Plan (SIP) for Title I of the Clean Air Act Amendments of 1990 (CAAA-90), the State of Georgia has developed a disturbing result:

Urban Airshed Model (UAM) simulations for the Atlanta area following EPA guidelines for devising a State Implementation Plan (SIP) (based on "worst-case" meteorological scenarios), suggest that **unrealistically large NO_x-decreasing emission controls will be required to bring Atlanta into compliance with the NAAQS for O₃**; specifically, the simulations suggest that a 90% decrease in NO_x emissions will be required to bring peak O₃ in Atlanta below the present 120 ppbv O₃ standard and that complete elimination of anthropogenic emissions of volatile organic compounds will still leave the metropolitan areas some 20 ppbv over the present national standard.

This result implies that attainment of the present National Ambient Air Quality Standard for O₃ will require a virtual complete shut-down of Atlanta as an urban and economic center of the region and nation. (Similar conclusions are being reached for many of the other serious ozone non-attainment areas in the nation.) The economic as well as environmental implications of this result are profound. They suggest that there is a critical need for research to understand why the methods presently used in the SIP process generate such drastic control requirements, and to devise new approaches and methods that might yield more realistic and cost-effective O₃ control strategies. In recognition of this need, the SOS Science Team proposes to implement a new research initiative during the Phase II effort that will examine the present SIP process and explore the potential efficacy of alternate control paradigms and strategies. The key elements of this new initiative are described below.

3.2.3.1. The New Initiative

The new SOS research initiative will attempt to directly address the emerging needs of the policy-making community that is trying to meet the statutory requirements of Title I of the CAAA-90 while maintaining the economic vitality of the nation. Using the data and research tools at its disposal via Research Themes 1 and 2 outline above, the SOS Science Team will:

- Comprehensively examine the underlying paradigms and methods used in current O₃ control strategies;
- Explore the feasibility and merits of O₃ control strategies based on alternate air quality standards; and
- Explore the feasibility and merits of alternate and potentially more robust paradigms and strategies for controlling O₃ pollution that would allow metropolitan areas like Atlanta to manage their ozone pollution problems within statutory requirements while preserving their economic and cultural vitality.

The exploration of alternate control paradigms and strategies will be carried in the SOS initiative using Atlanta as a case study. Specific possible alternate control strategies will be posited and examined with regard to their ability to bring about compliance with present and possible future ozone standards and to minimize ozone exposures of humans, crops, forests, and other vegetation. Strategies that might be considered include:

- **A Regionally-Based Implementation Strategy;** i.e., a strategy that manages ozone in Atlanta by controlling emissions in a larger portion of, or throughout the South.
- **A Climatologically-Based Plan;** i.e., a strategy that uses climatological conditions rather than "worst-case scenario" meteorological conditions to design emission controls.
- **A Plan Based On The Application of Periodic Controls;** i.e., a strategy that uses a decision-making infrastructure (including a Regional Chemical Meteorology/Air Quality Prediction System) for implementing periodic institutional and technological controls on days most prone to air pollution episodes in Atlanta.

3.2.4. The SOS Research Matrix

The Phase II research effort combines SOS' traditional scientific research activities that focus on the processes responsible for O₃ formation, transport, and accumulation and the tools used for their study (under Research Themes 1 and 2), with a new integration and assessment activity that focusses on alternate O₃ control strategies (under Research Theme 3). In order to assure effective interaction and synergy between these complementary activities, SOS will adopt a matrix structure (see Table 3.1) that will facilitate a free flow of information between the research and assessment activities.

		Research Theme 3 → → → Assessment of Alternate Control Strategies → → →				
		Current Strategy	Alternate Standards	Regional Strategy	Climatological Strategy	Periodic Controls
↓ ↓ ↓ ↓ Research Themes 1 & 2 ↓ ↓ ↓ ↓	Observations	X	X	X	X	X
	Models	X	X	X	X	X
	Emissions	X	X	X	X	X
	MTS	X	X	X	X	X

Research Theme 1: Research On Ozone Formation, Transport, and Accumulation In the South
 Research Theme 2: Meeting National Needs Through Outreach, Tech Transfer, and Infrastructure Development
 Research Theme 3: Research On Alternate Strategies For Implementing CAAA-90 and Beyond

4. CONCLUSION

In the summer of 1988 a group of scientists and policy-makers gathered together in a workshop in Atlanta Georgia to discuss the problem of O₃ pollution in the South, its effects, and the possibilities for its effective mitigation. Out of that workshop grew a bold plan for a new kind of air quality research program - a program predicated on sound scientific principles and goals but dedicated to policy-relevance. In 1991, with the establishment of the SOS Cooperative Agreements with U.S. EPA, the plan formulated in 1988 was put into action and today, almost four years later, it is evident that the plan has, in fact, made significant progress from both a scientific and a policy-relevant point-of-view.

Nevertheless, much work remains. Ozone exceedances continue to plague Atlanta, Houston, Nashville, Tampa, and other cities of the South and the nation, in spite of the relatively mild summers of the past few years. Moreover, the preparation of the State Implementation Plans called for in the CAAA of 1990 has proven problematic for Georgia and many other states.

The stakes that the citizens of the nation confront with the O₃ pollution problem are high. They include the state of our air, the health of our citizenry, the vitality of our crops and forests, and ultimately, because of the threat of economic sanctions from the federal government, the economic viability of our cities. The SOS Science Team remains committed to applying its talents and resources to this complex environmental problem by continuously striving to provide accurate, timely, and relevant scientific and technical information to the policy-making community.