09:25:15 OCA PAD AMENDMENT - PROJECT HEADER INFORMATION 07/29/96 Active **Cost share #**: G-35-327 Rev #: 16 Project #: G-35-609 OCA file #: Center # : 10/24-6-R7292-0A0 Center shr #: 10/22-1-F7292-0A0 Work type : RES Contract#: CR 818690-01-0 Mod #: 03-3 Document : AGR Contract entity: GTRC Prime #: CFDA: 66.501 Subprojects ? : Y PE #: CNMA1E Main project #: Project unit: E & A SCI Unit code: 02.010.140 Project director(s): KIANG C S E & A SCI (404)894-3896 Sponsor/division names: ENVIRON PROTECTION AGENCY / EPA RES TRIANGLE PARK-NC Sponsor/division codes: 129 / 003 Award period: 910813 960930 (performance) to 961231 (reports) Sponsor amount New this change Total to date 19,999.00 4,286,995.00 Contract value Funded 19,999.00 4,286,995.00 · Cost sharing amount 245,773.00 Does subcontracting plan apply ?: Y Title: SOUTHEASTERN REGIONAL OXIDANT NETWORK FIELD PROGRAM ACTIVITIES **PROJECT ADMINISTRATION DATA** OCA contact: Anita D. Rowland 894-4820 Sponsor technical contact Sponsor issuing office BASIL DIMITRIADES ALICE K. CHI (919)541-2706 (202)260-9285 ATMOSPHERIC RES. & EXP. ASSES. LAB GRANTS OPERATIONS BRANCH U.S. ENVIRON. PROTECTION AGENCY GRANTS ADMIN. DIVISION (PM-216F) RESEARCH TRIANGLE PARK, NC 27711 U.S. ENVIRON. PROTECTION AGENCY Security class (U,C,S,TS) : U ONR resident rep. is ACO (Y/N): N supplemental sheet Defense priority rating : Equipment title vests with: Sponsor GIT X >1,000 REQUIRES APPROVAL; >1,000-EPA MAY ELECT TITLE Administrative comments -

AMEND 03-3 ADDS \$19999 (C/S \$1053) INCREMENTAL FUNDS. BUDGETED INTO SUB (X50) AND REQUIRES SEPARATE FINANCIAL REPORTING, REF. EPA'S 5.8.96 LETTER, ATT.

CA	8	1	2	0	

Georgia Institute of Technology Office of Contract Administration 09-MAY-1997 11:31 PROJECT CLOSEOUT - NOTICE

Y

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Closeout Notice Date 09-MAY-1997 Project Number G-35-609 Doch Id 44513 Center Number 10/24-6-R7292-0A0 Project Director KIANG, CHIA Project Unit E & A SCI Sponsor ENVIRON PROTECTION AGENCY/EPA RES TRIANGLE PARK-NC Division Id 3476 Contract Number CR 818690-01-0 Contract Entity GTRC Prime Contract Number Title SOUTHEASTERN REGIONAL OXIDANT NETWORK FIELD PROGRAM ACTIVITIES

Effective Completion Date 30-SEP-1996 (Performance) 31-DEC-1996 (Reports)

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

Comments

Distribution Required:

Project Director/Principal Investigator	Y
Research Administrative Network	Y
Accounting	Y
Research Security Department	N
Reports Coordinator	Y
Research Property Team	Y
Supply Services Department	Y
Georgia Tech Research Corporation	Y
Project File	Y

NOTE: Final Patent Questionnaire sent to PDPI

PROGRESS REPORT

1991 - 1992

PROGRESS REPORT

SOUTHEASTERN REGIONAL OXIDANT NETWORK (SERON)

Re: USEPA Cooperative Agreement No. CR-818690-01-0

INTRODUCTION

Under the referenced cooperative agreement, the U.S. Environmental Protection Agency provided funding in support of the Southeastern Regional Oxidant Network (SERON). The SERON research is comprised of two inter-related activities: 1) Field Program Activities, and 2) Modeling Activities. The period of performance addressed is April 1, 1991 through September 30, 1992 and is submitted along with our request for a continuation of the cooperative agreement. Funding levels for the first two years (CY91/92) of the SERON project were as follows: CY91 ;\$987K, CY92 ;\$978K. Additionally, funds in the amount of \$154K in supplemental funding were provided in late CY92. This report will address, on a task by task basis, progress to date within the SERON Program.

SERON MANAGEMENT

Under the general task of SERON Management resides the day to day coordination, facilitation and execution of this very complex research initiative. The Program Scientist, along with the Program Manager, choreographs the day to day activities required to keep the program vital and moving. In addition to required administrative and logistical support, many planning and strategy meetings were conducted. Periodic meetings for the purpose of SCION Network Coordination, Science Team and SERON Program Committee reviews were conducted. Briefings and presentations to ensure full integration of SERON research into the broader perspective Southern Oxidants Study were conducted along with SOS Workshop Participation. (Associated Tasks: Program Scientist, Meetings)

REGIONAL FIELD STUDIES

SERON-SORP-EE COOPERATIVE RESEARCH

Late in calendar year 1991, \$130,000 was provided to NCSU to further research under the SORP-EE Program. Dr. Ellis B.Cowling, is the Principal Investigator and progress on this effort will be included in reports submitted under that program - funded under a separate cooperative agreement with the USEPA.

SON COORDINATION/SON ARCHIVE

The Spatial Ozone Network (SON) is designed to address rural ozone formation, and provide information that will ultimately address effective regional ozone control strategies for both urban and rural areas. These sites provide high spatial resolution measurements of regional ozone patterns. Recent network designs, including SERON, aim to achieve both high spatial and temporal resolution. The major purpose of these sites will be to provide information on the regional extent and coherence of ozone episodes.

The SON has been designed from the outset as a cooperative venture between numerous organizations representing a broad range of interests. State and federal regulatory agencies, public utility companies, private research organizations, and public and private universities have all been involved at one stage or another in planning and implementation of SON.

The SON project management center and data archive are located at the Tennessee Valley Authority (TVA) in Muscle Shoals, Alabama. The objectives of the SON project are:

- o manage and coordinate the establishment of the SON network with the USEPA, state and local air pollution control agencies, Federal agencies, public utilities and universities.
- o develop and assure continued adherence to acceptable monitor siting criteria.
- o define consistent sampling protocols and quality assurance criteria and documentation.
- o manage, coordinate, and operate the development of the SON data acquisition and archive.
- o provide data to SOS participants.
- o provide operational analysis in the form of data reports and publications.
- o coordinate training and operational comments.

All stations fully included in the network are operated according to State and Local Air Monitoring Station (SLAMS) criteria as outlined in 40 CFR, Part 58. Many stations operate year round, and others during various monthly periods that constitute the EPA prescribed monitoring period for that state. A majority operate only during the "ozone season" (April-October). The SON data archive will house data for all network periods.

1991:

The first year of SON monitoring commenced in the Spring of 1991 with 26 regional scale (i.e., no major urban or point source within 50 kilometers of the site) stations, some of which were already operational, and others were being added at the request of

SON and EPA Region IV in Atlanta. Most of the stations included in SON during 1991 were part of the EPA National Dry Deposition Network (NDDN), and others were operated by the Georgia Department of Natural Resources, the North Carolina Department of Natural Resources, the South Carolina Department of Health and Environment, the National Park Service, TVA, Appalachian State University, Clemson University and the Georgia Institute of Technology. Instrumentation at three of these sites were not operated according to the minimum SLAMS criteria, and have been annotated to advise the user that data from these stations may be suspect. The SON data system computers were installed, and programming completed to archive and provide data in all popular formats to data users in the fall of 1991. Data from 23 of the 26 stations were obtained by January, 1992 and stored in the SON data archive and have been provided on request to SON data users. SON data products in the form of station listings, graphical mapping of station locations, descriptive statistics, and data availability charts have been provided to SERON participants.

1992: Prior to the 1992 monitoring season, nine additional stations (increasing network size to 35 regional scale sites) were installed and operated as part of SON and other programs in SERON by the Alabama Department of Natural Resources, Tennessee Division of Air Pollution Control and Southern Company Services. The SON management center and data system have been augmented with personnel and computer capabilities to perform more detailed statistical analysis and isoplethic/kriging modeling to provide more advanced data products listed above. Analysis of these data are ongoing and are directed toward understanding the spatial and temporal impact of ozone levels on a seasonal, monthly, and episodic basis.

Recently, to facilitate the formation of a data base that will serve the needs of all projects in the SOS, the SON was expanded to include all ozone monitoring (micro, middle, urban, and neighborhood scale) stations operated by state and local programs in the states of EPA Region IV, along with the states of Arkansas, Louisiana, Virginia and the eastern part of Texas. This will add some additional two hundred sites to the network. Prior to obtaining these data from the EPA Aerometric Information Retrieval System (AIRS), and admission of these data to the SON data system, extensive evaluation of these sites will be performed to determine the appropriate scale (above) for modeling purposes, since this information is not provided in AIRS.

SCION FIELD SUPPORT

During 1991-1992 the SCION portions of the ROSE, ROME and SONIA sites were operated by Auburn University, GIT/Georgia Southern University, North Carolina State University/ESE respectively. The scope of this effort included the operation and maintenance of the SCION portion of the aforementioned sites during both intensive and non-intensive periods. In addition to sample collection, the sites were maintained via the replacement of items consumed by instrumentation, calibration of instruments was performed and telephone and electrical service were maintained. Operators participated in intercalibrations and exchange of challenge standards. These sites also underwent QA/QC systems audits during 1992. Since the SCION sites operate in conjunction with the SENIOR sites, many of the comments and accomplishments discussed under that latter heading are germane to the SCION Network.

SCION NETWORK COORDINATOR

During the growth years of the SCION Network (1991-1992) a great deal of coordination was required to ensure proper siting, outfitting and operation of each site. Frequent meetings and workshops were conducted to enhance training and communication throughout the network. As a result, spatial and temporal coverage seems to be consistent with modeling goals and good quality QA/QC'd data is now being captured within the network.

SENIOR

ROME/SHARP (BNL)

In 1991 and 1992 scientists from Brookhaven National Laboratory (BNL) spent a month in Metter, GA, measuring trace atmospheric gases and meteorological parameters related to the formation of ozone and other oxidants.

The site operated by BNL is one of five sites (not all operated at once) located in regions remote from large emission sources which measure an extensive suite of chemical substances pertinent to understanding the causes of ozone formation. chemical measurements at Metter included NO, NO₂, NO_y, NO_y* (NO_y less HNO₃ and particulate NO₃⁻ wrapped on a nylon filter), PAN, O₃, H₂O₂, organic peroxides, CO, SO₂, HCHO and other carbonyl compounds, hydrocarbons and aerosol particle scattering. Meteorological measurements included total solar UV irradiance, temperature, dew point, rainfall rate, and wind speed and direction.

Reduction of data from the 1991 campaign is complete; analysis of the chemical data is in varying stages of completion. A paper on peroxide measurements (Lee, J.H., D.F. Leahy, I.N. Tang, and L. Newman, *Measurement and Speciation of Gas-phase Peroxides in the Atmosphere*, JGR) and a paper on the methodology for measuring soluble carbonyl compounds (Lee, Y.N. and S. Zhou, *A Method for the Determination of Some Soluble Atmospheric Carbonyl Compounds*, EST) have been submitted. Ozone measurements and measurements of ozone precursors are being examined with the objective of determining factors upon which ozone production depends. Preliminary results of that analysis are described below. Concentrations of trace gases measured in Metter, GA, during a 22-day period in the summer of 1991 are consistent with the relative remoteness of this site from major NO_x and SO_2 emission sources. The measurement site is located in a mixed deciduous, evergreen forest and this is reflected in the concentrations of isoprene and pinenes (average values of 6.0 and 2.3 ppbc, respectively). Midday maximum ozone levels (1 hour averages) ranged between 32 and 75 ppb. These ozone values are somewhat lower than expected based on previous years' measurements in similar forested rural locations n GA and AL, but nevertheless, indicate an active photochemistry.

In order to determine the causes of variability in O_3 and the reasons why high concentrations are occasionally recorded, the data set was split into subsets having high, medium and low maximum O_3 values. Trace gas concentration data were examined for differences between subsets and for diurnal trends within a subset. It was found that:

This fit is similar to that found for other rural sites in eastern North America (Trainer *et al, Correlation of Ozone With NO_y in Photochemically Aged Air,* submitted to JGR) and indicates a background O₃ level of approximately 30 ppb; values higher than 30 ppb are due to photochemical production in the recent past (the last several days). Based on a 30 ppb background, O₃ production varied from near zero to 45 ppb.

2. An *in-situ* rate for chemical production of O_3 was calculated from observed concentrations of NO and free radical precursors. Calculated diurnal trends in O_3 production were dominated by the usual diurnal variability in solar intensity and by variations in NO. Highest NO concentrations were approximately 200 ppt and occurred between 0800 hours and 0900 hours. By the afternoon, NO concentrations were much lower (average value between 1200 hours and 1600 hours, 50 ppt), and in consideration of the ample amounts of hydrocarbons, were a limiting factor for the formation of O_3 .

3. A comparison of calculated dO_3/dt based on *in-situ* chemistry with the observed O₃ time trends reveals a systematic bias toward underprediction in the AM which is particularly apparent on high O₃ days. In addition, there is poor correlation between hourly values of predicted and observed dO_3/dt , except for the low O₃ days. These features point towards an important role for vertical motions in determining hour-to-hour variation in O₃ concentration. Approximately 2/3 of the steep increase in O₃ in the AM for high O₃ days is attributable to entrainment and 1/3 is due to *in-situ*

chemical production. Additional evidence for the role of vertical transport in controlling the hour-to-hour changes in O₃ is found in the diurnal cycles of SO₂ and HNO₃ (defined as NO_y-NO_y*) which also have rapid increases in the morning due to entrainment of dirty air aloft by the growing convective boundary layer.

4. Differences between high, medium, and low O_3 cases may be due in part to weather conditions. High O_3 days were characterized by high pressure systems and near maximum solar insolation conducive to enhanced vertical mixing. In contrast, low O_3 days occurred during frontal passages and experienced rain on 4 or 5 occasions. However, according to the *in-situ* calculations, difference in solar intensity were not great enough to cause the observed variation in O_3 . solar intensity on high and medium days were nearly identical.

5. A back trajectory model predicts the correct magnitude for NO_y at Metter and identifies the period with highest NO_y as being due to emission from near Atlanta, GA and Birmingham, AL. Day-to-day changes in trajectory location *vis-a-vis* emission sources cause variations in NO_y at Metter. Inasmuch as NO_x concentrations are low in the peak photochemical period, the NO_y at Metter consists mainly of the oxidation products of NO_x . According to previous studies and the relation found here between NO_y and O_3 , upwind NOx emissions are an important determinant of midday O_3 levels.

ROME /SHARP (GIT)

During the funding period, GIT participated as part of the ROME/SHARP study at the George L. Smith State Park near Metter, GA. During both 1991 and 1992 SENIOR intensives, GIT provided canister analysis of NMHC concentrations at this site. In 1991, samples were collected on either three or four hour intervals. In 1992 samples were collected on alternate hours between 7:00 am and 7:00 pm. During both meausrement periods, all samples were tansported to Atlanta and analyzed within seven days of collection.

Additonal NMHC samples were collected on six day intervals coincident with the SCION sampling protocol. In total, approximately 75% coverage for the summer of 1991 was achieved. Measurements were also conducted for NO, NO, O₃ and SO₂ at the site. These intstruments were intercompared in 1991 with similar intrumentation from BNL anD showed good agreement. Significant logistical problems were encountered in operating this site (about 350 km from Atlanta) and, thus, data recovery was limited to about 50%. To ease these problems during 1992, Dr. Robert Mauldin of Georgia Southern University was recruited to operate the Metter site with assistance from GIT personnel.

ROSE

Ground-based Measurements at Kinterbish, Alabama in 1990 and 1992: ROSE I &II

Extensive sets of chemical and dynamical measurements were made in 1990 and 1992, as part of the SOS/SERON/ROSE effort, at the Kinterbish Wildlife Management Area, near Jachin Alabama. The objectives of these studies were to obtain a detailed set of measurements of the precursors, participants and products of oxidant photochemistry, and to quantify transport and deposition processes. These measurements are being used to answer key questions pertaining to regional photchemical oxidant formation and transport processes. Ambient measurements are being used to identify episodes during which various sources were dominant, and to test the self-consistency of the emissions inventories for those sources. The photchemical oxidation of biogenic hydrocarbons is being studied through relationships of two co-emitted compounds. The importance of biogenic emissions of oxygenated organics is being examined. Contrasts in the day/night relationships of hydrogen peroxide and ozone reveal differences in their formation chemistry and relative deposition rates. The measurements of NO_V and constituent species reveals the extend of conversion of NO_x products and the relative importance of the product species PAN and HNO₃. Unique chemical signatures are being used to discern the degree of photchemical processing that air-masses have undergone. Future work will involve comparing and contrasting the data sets from the two years, and in depth examination of the photchemistry occurring under the variety of meteorological conditions experienced during these studies.

Aircraft Measurements during the SOS/SERON/ROSE-Air II Experiment

The purpose of the SOS/SERON/ROSE II aircraft measurement campaign was to determine and quantify the processes responsible for the transport of ozone and ozone precursors (NO_y) vertically (1) through the planetary boundary layer, (2) between the planetary boundary layer and the free troposphere, and (3) through the free troposphere, as well as the horizontal transport of these compounds. The aircraft employed was the NCAR King Air, equipped with fast response chemical sensors for NO_y, O₃, CO2, and H₂O, as well as slow response sensors for CO and O₃, and a complete suite of fast response meteorological instrumentation. Approximately 40 research hours were flown from Meridian, Mississippi, during which primary focus of the flight planning was collection of an eddy correlation flux data base. An additional 20 research hours were flown from Chattanooga, Tennessee, during which the primary flight planning objective was to obtain a chemical survey over a wider region of the Southeastern U.S. Results obtained during the experiment will be presented and compared to the results obtained during the 1990 ROSE-Air experiment. In addition,

the results obtained thus far will be discussed in terms of enhancing the design of future aircraft experiments in the Southeastern U.S.

A Comparison of Model Results with Observation from the 1990 ROSE-I Field Campaign

As part of the SOS/SERON effort, 3-dimensional regional scale photchemical models provide a means of comparison between observed photochemical conditions and what one would expect based on current understanding of the emissions, transport and transformations of oxidants and their precursors inherent to the 3-D model formulation. An important issue associated with such models concerns their ability to adequately describe photochemical conditions over large rural areas within the regional model's domain. This is largely due to the paucity of data with sufficient detail and accuracy necessary to make objective model evaluations for specific episodes. Observations of photchemical oxidants, nitrogen oxide and NMHC compounds collected by the NOAA Aeronomy Laboratory and other collaborating institutions during the 1990 SOS/SERON/ROSE campaign in western Alabama (June 5 to July 21, 1990) provide a unique and complete data-set particularly suited for detailed comparison with results from 3-D photochemical models.

A one week period (June 24-30, 1990) has been simulated using the NOAA Aeronomy Lab 3-D regional oxidant model. Within this time period and elevated pollutant episode related to regional scale transport was observed, followed by the passage of a cold front and associated "clean" conditions. Several aspects of the comparison between model results and the detailed photchemistry observed at this site are addressed. First is the model's ability to simulate the temporal patterns of several key gas-phase species n response to the regional scale meteorological forcing. As a test of more localized forcing factors, the diurnal dependence of ozone precursors, the partitioning of NO_y species, quantities related to the photohemical signatures defined by relationships between individual species are compared to qualitatively assess the applicability of the model's chemical mechanism for this rural setting.

REACT/TVA

The Tennessee Valley Authority prepared and operated a SENIOR network site at a rural location in Giles county, Tennessee. In addition to the funds provided by EPA for the SOS, TVA funds were also used for operation of the REACT site. Intensive field studies were conducted from July 22 to September 1. 1991 and from June 10 to July 18, 1992. TVA used a 40-foot trailer that has been modified into a mobile lab equipped with a wide variety of instruments which include high sensitivity gas phase monitors and standard meteorological monitors. A tethered balloon was used to acquire vertical profiles of temperature, relative humidity, wind speed and direction, and concentrations of ozone and isoprene. A wind profiler was used to estimate mixing

heights and ground based inversion heights. Ozone, ozone precursors, and meteorological parameters were monitored at Giles County during the summer studies of 1991 and 1992. Table 1 lists the parameters measured at the Giles County SENIOR site.

The diurnal pattern for O_3 at Giles Country is similar to that observed at other rural sites. A median midday ozone value of 75 ppb was observed at this site during 1991. The ozone levels were significantly lower in 1992 compared to 1991. The temperature was also significantly lower in 1992 compared to 1991. The lower temperature was the result of atypical synoptic conditions. The unusual weather conditions may be the reason for the lower ozone levels at Giles County during the 1992 study season.

The temporal behavior of the speciated nitrogen oxides was obtained during the 1991 and 1992 studies. There was no significant diurnal variability for NO_y . The median NO_y concentration ranged between 3 and 3.5 ppb. NO_2 is the major NO_y species at night. The NO₂ comprises more than 65% of the NO at daybreak. Since the sum of the individually measured NO_y species, i.e., NO, NO_2 , PAN, HNO₃, and NO_3 aerosol, do not account for all the NO_y measured, the unknown species are designated as XS when a diurnal plot is made. The diurnal profile for the XS species, which is similar to that for PAN and HNO₃, suggests photochemical production. These species are believed to be organic nitrates and PAN homologues produced from peroxyl and acylperoxyl radical reactions with NO_x .

The 1991 field data were analyzed to assess the importance of NO_x emissions in controlling rural O₃ levels. If NO_x emissions are an important factor controlling rural O₃ levels, then an association between O₃ levels and the NO_x oxidation products would be expected. The ambient levels of NO_x oxidation products is obtained by subtracting the observed NO_x species. The NO_x oxidation products, NO_y - NO_x , are sorted by concentration and then plotted vs. O₃. The field data was sorted into 20 equal bins to reduce the amount of scatter in the plots. Data suggests a strong association between O₃ and observed NO_x oxidation products.

Measurements were made of ambient levels of formaldehyde, CO, and hydrocarbons ranging in size from 2 to 10 carbon atoms. Midday concentrations of hydrocarbons and formaldehyde, isoprene, and the alkanes make the largest contributions to midday concentration. Reactivities were calculated and summed by VOC class. The reactivity plots show that (1) reactivity during midday hours is dominated by isoprene, and (2) formaldehyde makes a significant contribution to reactivity during midday hours. Formaldehyde is a significant contributor to the odd hydrogen budget, competing with ozone photolysis in the morning for radical production.

Table 1 Parameters Which Were Monitored during REACT, 1991 and 1992

Gas-Phase Species

O₃ PAN NO₂ NO NO_y HNO₃ Hydrocarbons containing 2 to 10 carbon atoms CH₂O CO

Meteorological Parameters

Temperature Relative Humidity Wind Speed and Direction Precipitation Barometric Pressure Solar UV Radiation

Ions in particulate material

 NO_{3}^{-} SO_{4}^{-} NH_{4}^{+} Na^{+} K^{+}

Vertical Profiles

Wind Speed and Direction Temperature Relative Humidity Ozone Isoprene

Initial Findings in 1991-1992

- The midday median O₃ levels were about 75 ppb at the Giles County rural site during 1991 but only about 53 ppb during 1992.
- o There is a strong relationship between O_3 and NO_x oxidation products.
- o At night, about 10% of the NO_y species is unknown. During the daylight hours up to 25% of the NO_y species is unknown.
- o VOC reactivity is dominated by isoprene. Formaldehyde and carbon monoxide make smaller but significant contributions.

The strong association between O_3 and NO_x oxidation products suggest that NO_x emissions are a major factor in O_3 production at the Giles County SENIOR site. However, a better understanding of the role of VOC's in the local production of O_3 is still needed. The data suggest that emphasis should be placed on determining the contribution of oxygenated VOC's to rural ozone formation.

The results from TVA's REACT/SENIOR program will be used in a collaborative effort to produce SERON products (e.g., 4 peer reviewed scientific publications and 4 paper presentations at the AWMA Conference in San Diego, California in November 1993).

SONIA (NCSU)¹.

Principal Accomplishments in 1991-1992

During the summer (i.e., May, June and July for about 5 weeks) of 1991 and 1992, intensive measurements were made of ozone, other photochemical oxidants and their precursors, and meteorology. These measurements were made at the SERON SONIA Site located in Candor, North Carolina. The measurements made were:

a. Gaseous Pollutants

 O_3 NO, NO₂, NO_y, PAN, PPN, HNO₃ SO₂ CO H_2O_2 Continuous ambient measurements of C2-C10 speciated HC's Carbonyls

^{1.} The University of Maryland withdrew from operation of the SCION portion of the SONIA site and the work was taken over by NCSU as reported below.

b. Aerosol Pollutants

 $SO_4 = 2$, NO_3^- , CI^- , major cations

- c. NO_x Emission Flux Measurements from soils and its characterization
- d. Meteorological Parameters: wind speed, direction, temperature, dew point, pressure and rainfall amount
- e. Precipitation chemistry and rainfall rate

Data recovery from 1991 was limited by available personnel. 1992 recovery was much improved due to having a more experienced field team. It is anticipated that most of the analysis of SONIA data will depend on 1992 field observations.

Initial Findings in 1991-1992

- o Ozone concentrations did not exceed NAAQS during the measurement period at the SONIA site.
- o NO emission flux from soils ranges from 0.1 to approximately 2.5 ng N m⁻²S⁻¹
- 0 NO₂ emission flux from, and deposition to soils was observed.
- o NO emission maxima from soil appears to be coincident with the ambient NO maxima in the mid morning.
- o Gaseous H₂O₂ and peroxyacetyl nitrate range from level of detection to about 2 ppbv and follow photochemical cycle during the measurement period.

Two graduate thesis and two published articles have resulted from this early work.

HYDROCARBON QA/QC and INSTRUMENT DEVELOPMENT

During 1991-1992, GIT provided operator training and method development for the SCION measurement program. In 1991, five training programs were conducted with three additonal workshops conducted in 1992. These workshops included manufacturer sponsored training for commercial instrumentation and operator training for hydrocarbon sampling apparatus. The SCION sampling protocol was developed in early 1991 at GIT under the instrument development program.

In 1992 GIT, TVA and NCSU participated in a joint SERON/SORP-ONA hydrocarbon measurement workshop in Miami, FL. where a common SOS measurement protocol was established. This work resulted in a modified grab samplecollection protocol which was introduced during the SOS Atlanta intensie and tested at the Burnt Mountain site. This protocol will be instituted network- wide in November of 1992. GIT also developed a sample tracking protocol now used SOS- wide for hydrocarbon canister samples.

1992 SUPPLEMENTAL FUNDING

The reallocation of one hundred thirty thousand dollars from SERON Field Activities to support cooperative research with the Southern Oxidants Research Program on Emissions and Effects (SORP-EE) left SERON management with the decision to shut down one of its planned SENIOR intensive sites. Fortunately, One hundred fifty-four thousand dollars was provided by the USEPA as supplemental funding late in 1992. These funds were provided to support the operation of the ROME SENIOR site, Hydrocarbon Analysis for the Burnt Mountain Site, and start up funds for a Public Outreach Program for the SOS.

The **ROME** site was operated by the Brookhaven National laboratory and has been previously addressed.

Georgia Institute of Technology, received nine thousand dollars to provide hydrocarbon collection and analysis for the **Burnt Mountain** site in cooperation with the SOS Atlanta intensive study. All funds were expended in providing this service.

Ten Thousand dollars were provided, under subcontract, to Cabot-Smethurst and Associates for **Public Outreach** "start up". All funds have been expended. Principal accomplishments:

- o An Outreach Steering Committee, comprised of key participants and sponsors of the SOS, was established to provide critical review of all outreach activities. A media subcommittee was formed to deal with anticipated media interested generated by the intensive studies conducted during the summer of 1992.
- o An SOS brochure and two fact sheets were produced and printed in lots of 5,000. To date, approximately 500 sets of materials have been distributed to individuals, sponsors, and media. Additionally, a list of over 100 key Georgia people and organizations and addresses has been prepared.
- o The Atlanta intensive press conference was planned and implemented with 300 invitations sent to key publics and 100 attendees at the press

conference. Senator Wyche Fowler and EPA Regional Administrator, Greer Tidwell, were keynote speakers. Approximately 8 members of the press attending resulting in good media coverage of the event. The consultant provided assistance to the Georgia Tech Office of Media Relations in the preparation of three press releases.

SERON DELIVERABLES

Appendix A lists some fifty products, publications and deliverables to be derived from this research.

SERON ACTIVITIES/PRODUCTS/DELIVERABLES

As deve	eloped during	SERON Science Team Meeting		
Septem	ber 09-10, 19	92 Research Triangle Park, NC		
ITEM	ACTIVITY	DESCRIPTION	RESPONSILE	DUE
SON AF	RCHIVE			
1	Product	For SON Archive: Thru user contact, develop list of desired products	Lee, Deakin	92OCT01
2	Product	Develop Descriptive Matrix of site criteria. Include definition/class of site. Include urban influenced and high elevation sites. Thru Central FL,KY,and Region VI to Western ROM Boundary.	Lee, Edgerton, Schere, Vukovich, Deakin	November Workshop
3	Product	Annual descriptive statistics of SCION data by station (including frequency distribution)	Edgerton	920CT01
SCION	DATA BASE			
4	Product	Recommendation concerning opportunities to combine aspects of Model/SCION Archives. Look at usefulness/cost of other "SCION-like data".Revisit time interval of SCION data.	Schere, Edgerton,Lee, Deakin,Aneja Vukovich	November Workshop
5	Product	Describe platforms supporting McIdas & mechanisms for acquiring available data.	McNider	92OCT01
	RCHIVES			
6	Product	Hard copy of satellite imagery for modeling period to modeling archives	McNider	7-10 days after request
7	Product	Gridded insolation to modeling archives.	Mc Nider	7-10 days after request
8	Product	Include NCC data in modeling archives.	Schere	6-8 mos lag
9	Product	Event Selection list for study. Include ATL Study datasets, 90&91 data, 92 Quicklook for ATL O3. Consider as task in detailed workplan for SOS 93.	Model Team plus Meagher	93JAN20
10	Product	Look at how well we can characterize O3 field with available data & analysis techniques. Generate chemical climatology of South using SON data.	Vukovich, Lee, McNider	920CT01

11	Product	Evaluate spatial and temporal representativeness of SENIOR data. Discuss regional characteristics of O3 precursors using SENIOR/SCION databases.	Aneja (lead), Edgerton, Meagher, McKeen,Kleine- man	92OCT01
SCIENT	FIC DELIVER	ABLES: CY 90&91 DATA		
12	Journal	Elevated Site Study : Atmos. Env.	McNider (UAH/UK)	93FEB
13	Journal	Convective Contributions: Atmos. Env.	Pielke (UAH.CSU)	93FEB
14	Journal	Satellite Insolation Methods: AWMA	Song (UAH)	92NOV17
15	Journal	Sensitivity of O3 Production/Natural NOx-Lightning: Atmos. Env.	McNider (UAH,TVA)	93MAY
16	Journal Sensitivity of O3 Production/Natural NOx-Soil: Atmos. Env.		McNider (UAH,TVA)	93NOV
17	Journal	Climatology of O3 in Eastern 2/3 of U.S. & SOS Region: Atmos. Env.	Vukovich	93FEB
18	Journal	Changes in Meteorology: High vs. Low Ozone Seasons: JGR	Vukovich	93MAY
19	Journal	4 Dimensional Assimilation of NOAA Model: JGR (?)	Seaman (PSU,NOAA)	93NOV
20	Journal	1988 Base Case ROM Emission Reduction Scenarios: JGR	Roselle	93NOV
21	Report	Model Intercomparison: Internal Report	Schere	93NOV
22	Journal	Carobonyl Speciation: EST	Murthy	93FEB
23	Journal	PAN Data: JGR	Roberts et al	In Press
24	Journal	Hydrogen Peroxide: JGR	Claiborne (NCSU)	93FEB
25	Journal	Intercomparison: Denuder/Fileterpack Techniques for HNO3 and Aeresols:EST	Aneja (NCSU,GIT)	93FEB
26	Journal	Ozone Photochemical Production: JGR	Wang (GIT)	93MAY
27	Journal	Ozone Photostationary Study: JGR	Rodgers (GIT)	93MAY
28	Journal	NOy Speciation: JGR	Wang (GIT)	93MAY
29	Journal	Hydrocarbon Speciation: JGR	TVA	93MAY
30	Journal	Chemical Climatology of Giles County Site: JGR	TVA	93MAY
31	Journal	Ozone/Nitrogen Relationships:	Trainer	In Press
32	Journal	NOy Speciation:	Parrish	In Press

SERON ACTIVITIES/PRODUCTS/DELIVERABLES

PAPER	S FOR PRESEN	TATION: AWMA CONFERENCE SAN DIEGO, CA		
33	Conference	SENIOR Overview	Rodgers	93NOV
34	Conference	Meteorological Framework	McNIder	93NOV
35	Conference	Metter Site Operations	Springston	93NOV
36	Conference	Giles County Site Operations	Bailey	93NOV
37	Conference	Candor Site Operations	Aneja	93NOV
38	Conference	NMHC: AWMA San Diego	TVA	93NOV
39	Conference	Nitrogen Speciation	NL	93NOV
40	Conference	NOx Photostationary State	GIT	93NOV
41	Conference	Ozone Production	TVA	93NOV
42	Conference	Hydrogen Peroxide	BNL	93NOV
43	Conference	Carbonyls	BNL	93NOV
44	Conference	Events	NCSU	93NOV
DOCU	MENTATION			
45	Document	Approved QA/QC Plan: Comments to Rodgers	Science Team	92NOV01
46	Document	Site Descriptions: Existing Sites	ALL	93FEB
47	Document	Site Descriptions: New Sites	ALL	93MAY
48	Document	Data Plan	Schere	92NOV
49	Document	SON/SCION Standard Operating Procedures: Status Check	Lee,Edgerton	92NOV17
50	Document	SON/SCION Standard Opetating Procedures: Completed	Lee,Edgerton	93NOV

6-35-607 *I*Z

SERON Field Program Cooperative Agreement 1993

Reference: CR 818690-02

Semiannual Report

Period Covered: January 1 - June 30, 1993

Submitted By:

Drs. C. Cardelino, W.L. Chameides, C.S. Kiang, and A.W. Stelson School of Earth and Atmospheric Sciences Georgia Institute of Technology Atlanta, GA 30332-0340

Submitted To:

Dr. Basil Dimitriades U.S. Environmental Protection Agency Research Commons 79 Alexander Drive Building 4201, Room 306 Research Triangle Park, NC 27709

August 31, 1993

Report Components

	Page No.
Overview	1
Observation-Based Modeling (MME-5-93)	2
UAM Sensitivity Modeling (MME-6-93)	4
Emission Inventory Coordination (EE-1-93)	6
Isoprene Emissions Estimates (EE-2-93)	8
Recommendations and Conclusions	9

OVERVIEW

This document contains semiannual status reports for four components of the Southern Oxidant Study. These components of research are being performed at the Georgia Institute of Technology under the direction of Drs. C. Cardelino, W.L. Chameides, C.S. Kiang and A.W. Stelson. In addition, Dr. C.S. Kiang provides assistance to Dr. Ellis Cowling of North Carolina State University in direction of the Southern Oxidant Research Program.

Dr. Kiang has assisted Dr. Ellis Cowling, Director of the Southern Oxidants Study, in the following activities:

- 1. Assisted the new Study Director in development of overall SOS strategic implementation plan, preparation of budgets, and preparation for the Nashville Intensive Study during the period January-March, 1993.
- 2. Served as a liason between the Sunbelt Institute and the Office of the Director of SOS and the Science Team, from April to May, 1993.
- 3. Established new efforts in the participation of EPA Region VI, Texas Air Control Board, etc., for a collaborative role with SOS.
- 4. Established initial contact with industries such as Pulp and Paper and Petrochemical to be involved in future collaboration with SOS.

For future activities there will be emphasis on the interaction with industry, EPA Region VI and other regions of the USA.

OBSERVATION-BASED MODELING: (MME-5-93)

Highlights of Research Performed

Research activities during the period focussed on 1. The development and application of an observation-based model for analyzing ozone precursors relationships in the urban atmosphere; 2. An analysis of vertical distribution of isoprene in the lower boundary layer of the rural and urban southern United States; 3. The development of a iterative procedure to estimate emission inventories uncertainties; and 4. An analysis of the impact of the heat island effect on biogenic emissions and ozone concentrations.

Conclusions thus far:

1. A comparison of a series of simulations of the Atlanta metropolitan area between the Observation-Based Model (OBM) and the Urban Airshed Model (UAM) showed that the OBM can adequately characterize urban ozone photochemistry. An application of the OBM to a dataset obtained from the 1990 Atlanta Ozone Study showed a) the importance of biogenic hydrocarbons produced from urban vegetation; b) The potential flaw in using early morning VOC/NOx to infer whether ozone production is limited by VOC or NOx; c) The critical need for high-sensitivity NO measurements to quantify the sub-ppbv concentrations of NO during the afternoon hours; and d) The need to consider a number of ozone episodes in designing a control strategy because of the possibility that the degree of VOC- and NOx-limitations may vary from one episode to another.

2. A convective air-parcel model is used to simulate the ascent of a spherical bubble of air under the chemical and meteorological conditions observed at an urban site in Georgia and a rural site in Alabama. The model calculations indicate that air parcels will tend to be trapped and dispersed at altitudes close to the observed local maxima and suggest that these local maxima arise from an injection of isoprene-rich air from the surface via convection.

3. Output simulations from an air quality model and observed concentrations of ozone precursors are used to modify the emission estimates that are a critical component of the air quality model input. At predetermined time increments, the residual error P(observed) - P(model predicted), where P is a precursor concentration, is minimized. Since the residual error is a function of the different emission inventory categories, the minimization technique reduces the residual error by modifying the emission in each category. New P(model predicted) are calculated by running the air quality model again with the new emission values. This approach was tested successfully using the air quality model OZIPM4.

Anticipated Research

1. The OBM and the convective air-parcel model will be used to analyze the conditions of the Atlanta urban atmosphere during the Atlanta Intensive of 1992.

2. The iterative method to estimate emissions uncertainties will be used to simulations done by the Urban Airshed Model and observational data obtained during the 1992 Atlanta Intensive.

3. The effect of the heat island in Atlanta photochemistry will be studied by UAM simulations. Spatial and temporal temperature fields are represented based on land use patterns typical to the modeling domain together with measured ambient temperatures.

UAM SENSITIVITY MODELING: (MME-6-93)

Highlights of Research Performed

Graphics and Visualization

Two previously UAM modeled ozone episodes (June 3-4, 1984 and July 30-31, 1987) were used to develop visualization techniques with the AVS 5 software. The temporally and spatially allocated emissions (area, mobile, biogenic, and point) and winds have been extracted from the model input data and successfully displayed. Further, visual graphics of temporal and spatial predictions of pollutant and precursor concentrations have also been demostrated. Several techniques were used to convey the emission and concentration information. They are 2-D and 3-D color meshing or tiling (area, mobile, and biogenic emissions; all species concentrations), contour plotting (all species concentrations), isosurface rendering (all species concentrations), and bubble rendering (point sources). Bv observation, volume visualization of concentration data was not considered an effective data communication technique due to limitations in the hardware and software. Hedgehog (vector rendering) and particle advection were used to visualize the wind fields.

Using a preliminary SOS emissions inventory (Atlanta, Georgia, August 9-10, 1992), results of our efforts in scientific visualization will be presented at the Air and Waste Management Association's Conference on "Regional Photochemical Measurement and Modeling Studies" on November 7-12,1993 in San Diego, California. Some of the scientific visualization techniques will be displayed in a poster presentation titled, "Integrating Scientific Visualization and Photochemical Grid Modeling to Investigate the Impact of the Heat Island Effect on Biogenic Emissions and Ozone Concentrations." Further, in cooperation with the SOS emission modelers, direct application of visualization to the field of emission modeling will be presented in three other papers: "The Use of Traffic Counters in the Estimation of Day-specific Mobile Emissions," "A Comparison of Emission Estimates and its Effect of Ozone Concentrations Between Survey Data and Surrogate Data for the Atlanta Metropolitan Area," and "The Impact of the Heat Island Effect on Biogenic Emissions and Ozone Concentrations."

Reconciling Ambient Measurements with Model Predictions

We are currently in the early stages of concept development. Preliminary ideas revolve around using geostatistics and ambient measurements of pollutants and precursors to calculate urbandomain wide, spatial averages of pollutant and precursor concentrations. This technique will be incorporated into the visualization environment to facilitate analysis.

Tagging and Tracking of Precursors in the UAM

Efforts thus far have primarily concentrated on assisting with the creation of the 1992 emissions inventory. Once the emissions inventory is completed, UAM modeling will be conducted to distinguish power plant NOx from mobile source NOx. The SO2/NOx signal is an indicator of power plant NOx. It is believed that the spatial and temporal distribution of this ratio should be correlated with the spatial and temporal distribution of theoretical massless particles released from the power plant sources and advected by the mean winds throughout the domain. Strong, positive correlation should confirm the spatial and temporal extent of power plant emissions and hence their contribution to ozone production.

Using measured SO2/NOx ratios and measured wind fields, the contribution of power plants to Atlanta urban air quality was determined. This technique was successful in determining the average contribution of power plants to ambient urban NOx in Atlanta and the results agreed with two other predictions. In addition, specific power plant's contributions were identifiable by their SO2/NOx ratios. The results of this effort will be presented at the "Regional Photochemical Measurement and Modeling Studies Conference" with a platform talk entitled "Estimated Contributions of Power Plants to the Urban Plume of Atlanta, Georgia: August, 1992."

Anticipated Research

This effort will continue to train two Doctoral students and help facilitate the publication of their work. Though the smallest of this group of projects, the students and researchers efforts are commendable. The majority of the effort in the next six months will be spent documenting and reporting results via five papers at the AWMA International Specialty Conference entitled "Regional Photochemical Measurement and Modeling Studies." In addition, precursor tracking modeling studies will be performed and compared to measurements to evaluate the predictive capabilities of the Urban Airshed Model and its input data.

EMISSIONS INVENTORY COORDINATION (EE-1-93)

Highlights of Research Performed

Research activities during the period focussed on 1. Collection and analysis of data obtained during the Atlanta Intensive of 1992; 2. Data reduction to conform with the file structure required by the EPA-developed computer model EPS2 (Emissions Preprocessor System Version 2); and 3. Development of emission inventories for a typical summer day of 1992 for the Atlanta Metropolitan Area, and emission inventories for specific days (August 9 and August 10) during the Atlanta Intensive of 1992.

The work done addressed the following points:

1. Roads Mobile Sources

Data analysis and data reduction of estimates of VMT (vehicle miles traveled) for 43 Georgia counties, by road classification and by type of vehicles. Data analysis and data reduction of traffic data from 31 urban traffic counters and 12 rural traffic counters collected by the Georgia Department of Transportation during July and August of 1992 to obtain traffic volume, vehicle mix, and speed traffic for specific days of the Atlanta Intensive of 1992.

2. Non-Road Mobile Sources

Data analysis and data reduction of files received from the Environmental Protection Agency containing non-road mobile sources of VOC, NOx and CO for 18 Georgia counties. This 1990 emissions inventory was updated for 1992 using data from the Bureau of Economic Activities (BEA).

3. Area Sources

Data analysis and data reduction of files received from the Georgia Department of Natural Resources containing 55 area sources for the 43 counties within the Atlanta Metropolitan Area modeling domain. This 1990 emissions inventory was updated for 1992 using data from BEA.

4. Point Sources

Data analysis and data reduction of 537 point sources of 1992 emissions of VOC, NOx and CO for the 43 counties within the modeling domain.

5. Biogenic Sources

Meteorological data for specific days and land use patterns derived from satellite data are used to produce day specific biogenic emissions of isoprene, monoterpenes and NO. Three different algorithms that describe isoprene dependence on temperature and light intensity, those derived by Tingey (1981), Guenther (1991) and Guenther (1993), are incorporated into the UAM-BEIS section of EPS2.

6. Link definitions

Road mobile emissions are defined by road links. Using a Geographical Information System (GIS) all interstate and principal roads within the modeling domain are defined as links by their specific UTM coordinates.

7. Questionnaire surveys

Analysis of questionnaires of emission estimates and operational logs of levels of activity for autobody painting and graphic arts facilities within the modeling domain.

8. EPS2 improvements

As a consequence of the application of EPS2 to the Atlanta datasets, several sections of the computer code of EPS2 were improved. These improvements were communicated to Chet Wayland from the Model Application Section of the Office of Air Quality Planning and Standards of EPA.

Anticipated Research

1. Sensitivity analysis of emission inventories to estimate the relative contribution of day-specific emissions with respect to emissions obtained for a typical summer day.

2. Study of the impact of day-specific emission inventories on ozone concentrations and on ozone precursors concentrations, using the UAM to simulate the chemical and meteorological conditions of days during the 1992 Atlanta Intensive.

ISOPRENE EMISSIONS ESTIMATES (EE-2-93)

Highlights of Research Performed

The method by which isoprene emissions into the urban Atlanta atmosphere are estimated was evaluated to determine the sensitivity of the results to vegetation coverage, vegetation speciation, amount of kudzu and mobile source contributions. The main evaluation criteria was to determine how analytically determined isoprene fluxes compare with predicted fluxes based on landuse, vegetation and mobile sources. The analytically determined isoprene fluxes were too large to be due solely to vegetation emissions. When automobile emissions were incorporated into the analysis, the measured fluxes could be predicted.

The first six months of this study determined mobile sources may contribute between 9 and 73 % of urban Atlanta ambient isoprene and mobile emission factors are consistent when evaluated using several different criteria. Specifically, this analysis has focussed on Fort McPherson, the location of the highest measured isoprene fluxes in the 1990 Ozone Precursor Study.

Technical products during the first six months include submission of one technical note to "Atmospheric Environment Part B: Urban Atmospheres" entitled "Does Isoprene Come from Biogenic Sources or Automobiles?" and the training of two graduate students, one in pursuit of a Master's degree and the other working on a Doctorate.

Anticipated Research

During the next six months, this study will be expanded to evaluate other sampling sites and Urban Airshed Modeling grids to see whether similar results are obtained. Hopefully, aerial photographs can be obtained to determine spatial distributions of vegetation and mobile sources. In addition, surface field studies will be performed to greater clarify the aerial views.

RECOMMENDATIONS AND CONCLUSIONS

During the first six months of this contract, much progress has occurred in elucidating mechanisms and reasons for ozone nonattainment in the Atlanta urban airshed. Many diagnostic techniques have been developed and applied to State and specific episode data. These tools will be well-suited for application to the Nashville Intensive Data. In addition, further application to the more extensive Atlanta air quality dataset would be desirable. Thus, it is proposed to continue Atlanta studies and expand into the Nashville arena.

	SISTANCE		11/11/7	4	V4+++++++++	
TYPE OF SUBMISSION: Application Construction Construction		DATE RECEIVED BY	STATE	State Application Identifier		
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APPLICANT INFORMATI						
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Georgia Tech	Research Co	rporati	on		Earth & Atmospheric Scien	ces
Address (give city, count	y, state, and zip code)	k			ne number of the person to be contacted on mett	ers involving
Georgia Inst	itute of Tec	hnology	,	this application (g		
Atlanta, Ful	ton, GA 303	32-0420	I		Michael O. Rodgers 4) 853-3094 /	
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OME Approval No. 0348-0044

BUDGET INFORMATION — Non-Construction Programs

	SECTION A - BUDGET SUMMARY								
Grant Program Catalog of Federal Function Domestic Assistance		Estimated Unot	aligated Funds	New or Revised Budget					
	or Activity Number (a) (b)		Federal (c)	Non-Federal (d)	Federal (e)	Non-Federal (f)	Total (g)		
1.			\$	\$	\$	\$	\$		
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			SE	TION B - BUDGET CATEGOR					
6 0	bject Class Categorie	\$	m1/1/93-12/31/93	GRANT PROGRAM, FU (2)1/1/93-12/31/93	(3)1/1/94-12/31/94	(4)1/1/94-12/31/94	Total (5)		
•	. Personnel		\$ 23,500	\$ 23,200	s 149,400	\$ 45,700	\$ 241,800		
b	. Fringe Benefits		5,984	1,415	30,845	4,678	42,922		
c	. Travel		9,839	_	15,916	-	25,755		
d	. Equipment		3,651		6,100		9,751		
•	. Supplies		7,783		17,250	-	25,033		
1.	Contractual		529,868		1,041,624		1,571,492		
9	. Construction						_		
h	. Other					-			
i.	Total Direct Charg	ges (sum of 6a - 6h)	580,625	24,615	1,261,135	50,378	1.916.753		
j.	Indirect Charges		32,375	11,053	114,503	22,620	180,551		
	. TOTALS (sum of (ii and 6j)	\$ 613,000	\$ 35,668	\$ 1,375,638	\$ 72,998	\$ 2,097,304		
т. Р	rogram income		\$	S	S	5	50		
· · ·	- 3								

FISCAL DATA SHEET

The following pertains to your CURRENT hudget period (Federal and non-Federal). This page must be completed and submitted with your continuation application.

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ETROM: 4-01-91	тикока	: 12-31-92	ASSI	stance number: C	R 818690-01-
APPROVED BUILTET CATELORIES	CURRENT BUDGET (1)	ACTUAL EXPEND- ITURES THROUGH 9-30-92 (Insert Date) (2)	ESTIMATED ADDITIONAL EX- PENDITURES FOR REMAINDER OF CURRENT HUDGET PERIOD (3)	TOTAL ESTIMATED EXPENDITURES (Columns 2 & 3) (4)	ESTIMATED UNEX- PENDED FUNDS (Subtract Col.4 from Col. 1) (5)
PERSONNEL	114,883	84,414	30,469	114,883	Ø
FRIME RENEFITS	19.329	7,693	11,634	19.329	Ø
TPAVEL	15,182	904	3,570	4,474	10,708
EUTTEMENT	13,305	ø	3,500	3,500	9.805
SUPPLIES	16,515	13,463	2,747	16,210	305
CONTRACTUAL SERVICES	1,080,526	1,080,526	Ø	1,080,526	ø
CONSTRUCTION ·	Ø	Ø	Ø	ø	Ø
COPERATIVE OTHER RESEARCH	130,000	130,000	ø	130,000	ø
SUMUTALS	1, 389,740	1,317,002	51,920	1,368,922	20,818
INDIRECT (USTS (Show Rate Used) 62.58 61.5 R	118,502	81.854	33,335	115,189	3,313
TUTAL (Federal and Non- Federal)	1,508,242	1,3 98,856	85,255	1,484,111	24,131
TUPAL APPROVED GRANT AMOUNT (Federal Only)	1, 418,996	1,309,610	85,255	1,394,865	24,131



OFFICE OF THE CHIEF OF NAVAL RESEARCH ARLINGTON, VIRGINIA 22217-5000

IN REPLY REFER TO 26 August 1992

UNILATERAL RATE DETERMINATION

TITUTION: Georgia Institute of Technology Georgia Tech Research Corporation Atlanta, GA 30332

S AGREEMENT SUPERSEDES THE UNILATERAL RATE DETERMINATION EXECUTED 29 JUNE 1992

: Indirect Cost Rate(s) and Fringe Benefit Rate(s) contained herein are for use grants and contracts with all Federal Agencies in accordance with the cost inciples mandated by Office of Management and Budget (OMB) Circular A-21. These invisional rates shall be used for forward pricing and billing purposes for the ititution's fiscal year 1993 until amended and are subject to the conditions itained in Section II.

TION I:	RATES							
INDIRECT RATES								
<u>)e</u> pvisional	<u>From</u> 7/1/92	<u>To</u> 6/30/93	<u>Rate</u> 49.0%	<u>Base</u> (a)	<u>Applicable To</u> (d)All programs	Location GTRI		
ovisional	7/1/92	6/30/93	46.6%	(a)	(e)All programs	GTRI		
ovisional	7/1/92	6/30/93	55.2%	(a)	(d)All programs	All other units		
ovisional	7/1/92	6/30/93	44.9%	(a)	(e)All programs	All other units		
ovisional	7/1/92	6/30/93	33.0%	(a)	All programs	Public Service		

(d) applicable to awards effective prior to July 1, 1992(e) applicable to awards effective on or after July 1, 1992

DISTRIBUTION BASE

) Modified Total Direct Cost Base consisting of salaries and wages, fringe benefits, materials and supplies, services, travel and subcontracts and subgrants up to \$25,000.00 each.

FRINGE BENEFIT RATES

<u>pe</u> ovisional	<u>From</u> 7/1/92	<u>To</u> 6/30/93	<u>Rate</u> 27.2 %	<u>Base</u> (b)	<u>Applicable To</u> All programs	<u>Location</u> GTRI
ovisional	7/1/92	6/30/93	27.2%	(b)	All programs	All other units
ovisional	7/1/92	6/30/93	2.88	(c)	All programs	GTRI
ovisional	7/1/92	6/30/93	2.8%	(c)	All programs	All other units

DISTRIBUTION BASE

Salaries and wages of (i) regular full-time faculty, (ii) principal investigators, (iii) professional and administrative staff, (iv) joint staff, (v) temporary academic or research professionals covered by the Teachers Retirement System (TRS) and group health and life insurance, (vi) bi-weekly permanent employees and (vii) part-time employees who work 50 percent but less than 100 percent of a full-time work schedule.

Salaries and wages of employees who participate in the social security program but do not participate in TRS or group health and life insurance plans. This rate covers (i) temporary classified persons, (ii) temporary academic or research professionals not eligible for TRS or group health or life insurance coverage and (iii) part-time employees employed for less than 50 percent of a full work schedule.

NOTE: Fringe benefits are not applicable to student employees.

TION II: GENERAL

<u>AITATIONS</u>: Use of the rates contained in this Determination are subject to any Atutory or administrative limitations and are applicable to a given contract or Ant consistent with the limitation of cost provisions contained therein.

For the Government

Michael D. Karp Administrative Contracting Officer

te: <u>236 - 5+ 14</u>72

r information contact: Office of Naval Research Resident Representative Georgia Institute of Technology 206 O'Keefe Building Atlanta, Georgia 30332-0490 (404) 347-4213

CERTIFICATION REGARDING LOBBYING

CERTIFICATION FOR CONTRACTS, GRANTS, LOANS, AND COOPERATIVE AGREEMENTS

The undersigned certifies, to the best of his or her knowledge and belief, that:

(1) No Vederal appropriated funds have been or will be paid, by or on behalf of the undersigned, to any person for influencing or attempting to influence an officer or employee of any agency, a Member of Congress, an officer or employee of Congress, or an employee of a Member of Congress in connection with the awarding of any Vederal contract, the making of any Vederal grant, the making of any Vederal loan, the entering into of any cooperative agreement, and the extension, continuation, reneval, amendment, or modification of any Vederal contract, grant, loan, or cooperative agreement.

(2) If any funds other than Federal appropriated funds have been paid or will be paid to any person for influencing or attempting to influence an officer or employee of any agency, a Member of Congress, or an employee of a Member of Congress in connection with this Federal contract, grant, loan, or cooperative agreement, the undersigned shall complete and submit Standard Form-LLL, "Disclosure Form to Report Lobbying," in accordance with its instructions.

(3) The undersigned shall require that the language of this certification be included in the award of documents for all subawards at all tiers (including subcontracts, subgrants, and contracts under grants, loans, and cooperative agreements) and that all subrecipients shall certify and disclose accordingly.

This certification is a material representation of fact upon which reliance was placed when this transaction was made or entered into. Submission of this certification is a prerequisite for making or Thtering into this transaction imposed by Section 1352, Title 31, U.S. Code. Any person who fails to file the required certification shall be subject to a civil penalty of not less than \$10,000 and not more than \$100,000 for each such failure.

R. Dennis Farmer, Contracting Officer

TYPED NAME & TITLE OF AUTHORIZED REPRESENTATIVE

11/11/92 DATE

SIGNATURE OF AUTHORIZED REPRESENTATIVE

EPA Project Control Number



United States Environmental Protection Agency Washington, DC 20450 Certification Regarding Debarment, Suspension, and Other Responsibility Matters

The prospective participant certifies to the best of its knowledge and belief that it and its principals:

- (a) Are not presently debarred, suspended, proposed for debarment, declared ineligible, or voluntarily excluded from covered transactions by any Federal department or agency;
- (b) Have not within a three year period preceding this proposal been convicted of or had a civil judgement rendered against them for commission of fraud or a criminal offense in connection with obtaining, attempting to obtain, or performing a public (Federal, State, or local) transaction or contract under a public transaction; violation of Federal or State antitrust statutes or commission of embezziement, their, forgery, bribery, faisification or destruction of records, making false statements, or receiving stolen property;
- (c) Are not presently indicted for or otherwise criminally or civily charged by a government entity (Federal, State, or local) with commission of any of the offenses enumerated in paragraph (1)(b) of this certification; and
- (d) Have not within a three-year period preceding this application/proposal had one or more public transactions (Federal, State, or local) terminated for cause or default.

I understand that a false statement on this certification may be grounds for rejection of this proposal or termination of the award. In addition, under 18 USC Sec. 1001, a false statement may result in a fine of up to \$10,000 or imprisonment for up to 5 years, or both.

R. Dennis Farmer, Contracting Officer

rped Name & Trise of Authorized Representative

gnature of Authorized Representative

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I am unable to certify to the above statements. My explanation is attached.

PA Form \$700-49 (13-66)

SEPA

PPLICANT'S NAME

GEORGIA TECH RESEARCH CORPORATION

ASSISTANCE APPLICATION NUMBER

PPLICANT'S ADDRESS

CENTENNIAL RESEARCH BUILDING, ROOM 246 GEORGIA INSTITUTE OF TECHNOLOGY ATLANTA, GEORGIA 30332-0420

SECTION 1 - INSTRUCTIONS

The applicant must complete and submit a copy of this form with each application for EPA Assistance. If the applicant has certified its procurement system to EPA within the past 2 years and the system has not been substantially revised, complete Part A in Section II, then sign and date the form. If the system has not been certified within the past 2 years, complete Part B, then sign and date the form.

SECTION II - CERTIFICATION	
Y's summing the obligations within the best 7 Ages certified to ELW tugt its biochigment	MONTH/YEAR
system complies with 40 Crn rart 33 and that the system meets the requirements in 40]
CFR Part 33. The date of the applicant's latest certification is:	

3. Based upon my evaluation of the applicant's procurement system, I, as authorized representative of the applicant: (Check one of the following:)

1. CERTIFY that the applicant's procurement system will meet all of the requirements of 40 CFR Part 33 before undertaking any procurement action with EPA assistance

Please furnish citations to applicable procurement ordinances and regulations

		-
2. DO NOT CERTIFY THE APPLICANT'S PROCUREMENT SYSTEM. The applicant agrees to follow the requirements of 40 CFR Part 33, including the procedures in Appendix A, and		
allow EPA preaward review of proposed procurement actions that will use EPA assistance.		
TYPED NAME AND TITLE	SIGNATURE	DATE
R. Dennis Farmer CONTRACTING OFFICER		11/11/92

EPA Form \$700-48 (Rev. 5-84) Previous edition is obsolete.

ASSURANCES --- NON-CONSTRUCTION PROGRAMS

: Certain of these assurances may not be applicable to your project or program. If you have questions, please contact the awarding agency. Further, certain Federal awarding agencies may require applicants to certify to additional assurances. If such is the case, you will be notified.

e duly authorized representative of the applicant I certify that the applicant:

las the legal authority to apply for Federal ssistance, and the institutional, managerial and mancial capability (including funds sufficient to ay the non-Federal share of project costs) to nsure proper planning, management and comletion of the project described in this application.

Vill give the awarding agency, the Comptroller Jeneral of the United States, and if appropriate, he State, through any authorized representative, access to and the right to examine all records, works, papers, or documents related to the award; and will establish a proper accounting system in accordance with generally accepted accounting standards or agency directives.

Will establish safeguards to prohibit employees rom using their positions for a purpose that constitutes or presents the appearance of personal or organizational conflict of interest, or personal gain.

Will initiate and complete the work within the applicable time frame after receipt of approval of the awarding agency.

Will comply with the Intergovernmental Personnel Act of 1970 (42 U.S.C. §§ 4728-4763) relating to prescribed standards for merit systems for programs funded under one of the nineteen statutes or regulations specified in Appendix A of OPM's Standards for a Merit System of Personnel Administration (5 C.F.R. 900, Subpart F).

Will comply with all Federal statutes relating to nondiscrimination. These include but are not limited to: (a) Title VI of the Civil Rights Act of 1964 (P.L. 88-352) which prohibits discrimination on the basis of race, color or national origin; (b) Title IX of the Education Amendments of 1972, as amended (20 U.S.C. §§ 1681-1683, and 1685-1686), which prohibits discrimination on the basis of sex; (c) Section 504 of the Rehabilitation Act of 1973, as amended (29 U.S.C. § 794), which prohibits discrimination on the basis of handicaps; (d) the Age Discrimination Act of 1975, as amended (42 U.S.C.§§ 6101-6107), which prohibits discrimination on the basis of age; (e) the Drug Abuse Office and Treatment Act of 1972 (P.L. 92-255), as amended, relating to nondiscrimination on the basis of drug abuse; (f) the Comprehensive Alcohol Abuse and Alcoholism Prevention, Treatment and Rehabilitation Act of 1970 (P.L. 91-616), as amended, relating to nondiscrimination on the basis of alcohol abuse or alcoholism; (g) §§ 523 and 527 of the Public Health Service Act of 1912 (42 U.S.C. 290 dd-3 and 290 ee-3), as amended, relating to confidentiality of alcohol and drug abuse patient records; (h) Title VIII of the Civil Rights Act of 1968 (42 U.S.C. § 3601 et seq.), as amended, relating to nondiscrimination in the sale, rental or financing of housing; (i) any other nondiscrimination provisions in the specific statute(s) under which application for Federal assistance is being made; and (j) the requirements of any other nondiscrimination statute(s) which may apply to the application.

- 7. Will comply, or has already complied, with the requirements of Titles II and III of the Uniform Relocation Assistance and Real Property Acquisition Policies Act of 1970 (P.L. 91-646) which provide for fair and equitable treatment of persons displaced or whose property is acquired as a result of Federal or federally assisted programs. These requirements apply to all interests in real property acquired for project purposes regardless of Federal participation in purchases.
- Will comply with the provisions of the Hatch Act (5 U.S.C. §§ 1501-1508 and 7324-7328) which limit the political activities of employees whose principal employment activities are funded in whole or in part with Federal funds.
- Will comply, as applicable, with the provisions of the Davis-Bacon Act (40 U.S.C. §§ 276a to 276a-7), the Copeland Act (40 U.S.C. § 276c and 18 U.S.C. §§ 874), and the Contract Work Hours and Safety Standards Act (40 U.S.C. §§ 327-333), regarding labor standards for federally assisted construction subagreements.

Authorized for Local Reproduction

PROGRESS REPORT

1991 - 1992

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PROGRESS REPORT

SOUTHEASTERN REGIONAL OXIDANT NETWORK (SERON)

Re: USEPA Cooperative Agreement No. CR-818690-01-0

INTRODUCTION

Under the referenced cooperative agreement, the U.S. Environmental Protection Agency provided funding in support of the Southeastern Regional Oxidant Network (SERON). The SERON research is comprised of two inter-related activities: 1) Field Program Activities, and 2) Modeling Activities. The period of performance addressed is April 1, 1991 through September 30, 1992 and is submitted along with our request for a continuation of the cooperative agreement. Funding levels for the first two years (CY91/92) of the SERON project were as follows: CY91 ;\$987K, CY92 ;\$978K. Additionally, funds in the amount of \$154K in supplemental funding were provided in late CY92. This report will address, on a task by task basis, progress to date within the SERON Program.

SERON MANAGEMENT

Under the general task of SERON Management resides the day to day coordination, facilitation and execution of this very complex research initiative. The Program Scientist, along with the Program Manager, choreographs the day to day activities required to keep the program vital and moving. In addition to required administrative and logistical support, many planning and strategy meetings were conducted. Periodic meetings for the purpose of SCION Network Coordination, Science Team and SERON Program Committee reviews were conducted. Briefings and presentations to ensure full integration of SERON research into the broader perspective Southern Oxidants Study were conducted along with SOS Workshop Participation. (Associated Tasks: Program Scientist, Meetings)

REGIONAL FIELD STUDIES

SERON-SORP-EE COOPERATIVE RESEARCH

Late in calendar year 1991, \$130,000 was provided to NCSU to further research under the SORP-EE Program. Dr. Ellis B.Cowling, is the Principal Investigator and progress on this effort will be included in reports submitted under that program - funded under a separate cooperative agreement with the USEPA.

SON COORDINATION/SON ARCHIVE

The Spatial Ozone Network (SON) is designed to address rural ozone formation, and provide information that will ultimately address effective regional ozone control strategies for both urban and rural areas. These sites provide high spatial resolution measurements of regional ozone patterns. Recent network designs, including SERON, aim to achieve both high spatial and temporal resolution. The major purpose of these sites will be to provide information on the regional extent and coherence of ozone episodes.

The SON has been designed from the outset as a cooperative venture between numerous organizations representing a broad range of interests. State and federal regulatory agencies, public utility companies, private research organizations, and public and private universities have all been involved at one stage or another in planning and implementation of SON.

The SON project management center and data archive are located at the Tennessee Valley Authority (TVA) in Muscle Shoals, Alabama. The objectives of the SON project are:

- o manage and coordinate the establishment of the SON network with the USEPA, state and local air pollution control agencies, Federal agencies, public utilities and universities.
- o develop and assure continued adherence to acceptable monitor siting criteria.
- o define consistent sampling protocols and quality assurance criteria and documentation.
- o manage, coordinate, and operate the development of the SON data acquisition and archive.
- o provide data to SOS participants.
- o provide operational analysis in the form of data reports and publications.
- o coordinate training and operational comments.

All stations fully included in the network are operated according to State and Local Air Monitoring Station (SLAMS) criteria as outlined in 40 CFR, Part 58. Many stations operate year round, and others during various monthly periods that constitute the EPA prescribed monitoring period for that state. A majority operate only during the "ozone season" (April-October). The SON data archive will house data for all network periods.

1991:

The first year of SON monitoring commenced in the Spring of 1991 with 26 regional scale (i.e., no major urban or point source within 50 kilometers of the site) stations, some of which were already operational, and others were being added at the request of

SON and EPA Region IV in Atlanta. Most of the stations included in SON during 1991 were part of the EPA National Dry Deposition Network (NDDN), and others were operated by the Georgia Department of Natural Resources, the North Carolina Department of Natural Resources, the South Carolina Department of Health and Environment, the National Park Service, TVA, Appalachian State University, Clemson University and the Georgia Institute of Technology. Instrumentation at three of these sites were not operated according to the minimum SLAMS criteria, and have been annotated to advise the user that data from these stations may be suspect. The SON data system computers were installed, and programming completed to archive and provide data in all popular formats to data users in the fall of 1991. Data from 23 of the 26 stations were obtained by January, 1992 and stored in the SON data archive and have been provided on request to SON data users. SON data products in the form of station listings, graphical mapping of station locations, descriptive statistics, and data availability charts have been provided to SERON participants.

1992: Prior to the 1992 monitoring season, nine additional stations (increasing network size to 35 regional scale sites) were installed and operated as part of SON and other programs in SERON by the Alabama Department of Natural Resources, Tennessee Division of Air Pollution Control and Southern Company Services. The SON management center and data system have been augmented with personnel and computer capabilities to perform more detailed statistical analysis and isoplethic/kriging modeling to provide more advanced data products listed above. Analysis of these data are ongoing and are directed toward understanding the spatial and temporal impact of ozone levels on a seasonal, monthly, and episodic basis.

Recently, to facilitate the formation of a data base that will serve the needs of all projects in the SOS, the SON was expanded to include all ozone monitoring (micro, middle, urban, and neighborhood scale) stations operated by state and local programs in the states of EPA Region IV, along with the states of Arkansas, Louisiana, Virginia and the eastern part of Texas. This will add some additional two hundred sites to the network. Prior to obtaining these data from the EPA Aerometric Information Retrieval System (AIRS), and admission of these data to the SON data system, extensive evaluation of these sites will be performed to determine the appropriate scale (above) for modeling purposes, since this information is not provided in AIRS.

SCION FIELD SUPPORT

During 1991-1992 the SCION portions of the ROSE, ROME and SONIA sites were operated by Auburn University, GIT/Georgia Southern University, North Carolina State University/ESE respectively. The scope of this effort included the operation and maintenance of the SCION portion of the aforementioned sites during both intensive and non-intensive periods. In addition to sample collection, the sites were maintained via the replacement of items consumed by instrumentation, calibration of instruments was performed and telephone and electrical service were maintained. Operators participated in intercalibrations and exchange of challenge standards. These sites also underwent QA/QC systems audits during 1992. Since the SCION sites operate in conjunction with the SENIOR sites, many of the comments and accomplishments discussed under that latter heading are germane to the SCION Network.

SCION NETWORK COORDINATOR

During the growth years of the SCION Network (1991-1992) a great deal of coordination was required to ensure proper siting, outfitting and operation of each site. Frequent meetings and workshops were conducted to enhance training and communication throughout the network. As a result, spatial and temporal coverage seems to be consistent with modeling goals and good quality QA/QC'd data is now being captured within the network.

SENIOR

ROME/SHARP (BNL)

In 1991 and 1992 scientists from Brookhaven National Laboratory (BNL) spent a month in Metter, GA, measuring trace atmospheric gases and meteorological parameters related to the formation of ozone and other oxidants.

The site operated by BNL is one of five sites (not all operated at once) located in regions remote from large emission sources which measure an extensive suite of chemical substances pertinent to understanding the causes of ozone formation. chemical measurements at Metter included NO, NO₂, NO_y, NO_y* (NO_y less HNO₃ and particulate NO₃⁻ wrapped on a nylon filter), PAN, O₃, H₂O₂, organic peroxides, CO, SO₂, HCHO and other carbonyl compounds, hydrocarbons and aerosol particle scattering. Meteorological measurements included total solar UV irradiance, temperature, dew point, rainfall rate, and wind speed and direction.

Reduction of data from the 1991 campaign is complete; analysis of the chemical data is in varying stages of completion. A paper on peroxide measurements (Lee, J.H., D.F. Leahy, I.N. Tang, and L. Newman, *Measurement and Speciation of Gas-phase Peroxides in the Atmosphere*, JGR) and a paper on the methodology for measuring soluble carbonyl compounds (Lee, Y.N. and S. Zhou, *A Method for the Determination* of Some Soluble Atmospheric Carbonyl Compounds, EST) have been submitted. Ozone measurements and measurements of ozone precursors are being examined with the objective of determining factors upon which ozone production depends. Preliminary results of that analysis are described below. Concentrations of trace gases measured in Metter, GA, during a 22-day period in the summer of 1991 are consistent with the relative remoteness of this site from major NO_x and SO_2 emission sources. The measurement site is located in a mixed deciduous, evergreen forest and this is reflected in the concentrations of isoprene and pinenes (average values of 6.0 and 2.3 ppbc, respectively). Midday maximum ozone levels (1 hour averages) ranged between 32 and 75 ppb. These ozone values are somewhat lower than expected based on previous years' measurements in similar forested rural locations n GA and AL, but nevertheless, indicate an active photochemistry.

In order to determine the causes of variability in O_3 and the reasons why high concentrations are occasionally recorded, the data set was split into subsets having high, medium and low maximum O_3 values. Trace gas concentration data were examined for differences between subsets and for diurnal trends within a subset. It was found that:

1. There is strong correlation between O₃ and the quantity $NO_V - NO_X$

 $O_3(ppb) = 29 + 0.9 * (NO_v(ppb) - NO_x(ppb)), R^2 = 0.74$

This fit is similar to that found for other rural sites in eastern North America (Trainer *et al, Correlation of Ozone With NO_y in Photochemically Aged Air*, submitted to JGR) and indicates a background O₃ level of approximately 30 ppb; values higher than 30 ppb are due to photochemical production in the recent past (the last several days). Based on a 30 ppb background, O₃ production varied from near zero to 45 ppb.

2. An *in-situ* rate for chemical production of O_3 was calculated from observed concentrations of NO and free radical precursors. Calculated diurnal trends in O_3 production were dominated by the usual diurnal variability in solar intensity and by variations in NO. Highest NO concentrations were approximately 200 ppt and occurred between 0800 hours and 0900 hours. By the afternoon, NO concentrations were much lower (average value between 1200 hours and 1600 hours, 50 ppt), and in consideration of the ample amounts of hydrocarbons, were a limiting factor for the formation of O_3 .

3. A comparison of calculated dO_3/dt based on *in-situ* chemistry with the observed O_3 time trends reveals a systematic bias toward underprediction in the AM which is particularly apparent on high O_3 days. In addition, there is poor correlation between hourly values of predicted and observed dO_3/dt , except for the low O_3 days. These features point towards an important role for vertical motions in determining hour-to-hour variation in O_3 concentration. Approximately 2/3 of the steep increase in O_3 in the AM for high O_3 days is attributable to entrainment and 1/3 is due to *in-situ*

chemical production. Additional evidence for the role of vertical transport in controlling the hour-to-hour changes in O₃ is found in the diurnal cycles of SO₂ and HNO₃ (defined as NO_y-NO_y*) which also have rapid increases in the morning due to entrainment of dirty air aloft by the growing convective boundary layer.

4. Differences between high, medium, and low O_3 cases may be due in part to weather conditions. High O_3 days were characterized by high pressure systems and near maximum solar insolation conducive to enhanced vertical mixing. In contrast, low O_3 days occurred during frontal passages and experienced rain on 4 or 5 occasions. However, according to the *in-situ* calculations, difference in solar intensity were not great enough to cause the observed variation in O_3 . solar intensity on high and medium days were nearly identical.

5. A back trajectory model predicts the correct magnitude for NO_y at Metter and identifies the period with highest NO_y as being due to emission from near Atlanta, GA and Birmingham, AL. Day-to-day changes in trajectory location vis-a-vis emission sources cause variations in NO_y at Metter. Inasmuch as NO_x concentrations are low in the peak photochemical period, the NO_y at Metter consists mainly of the oxidation products of NO_x . According to previous studies and the relation found here between NO_y and O_3 , upwind NOx emissions are an important determinant of midday O_3 levels.

ROME /SHARP (GIT)

During the funding period, GIT participated as part of the ROME/SHARP study at the George L. Smith State Park near Metter, GA. During both 1991 and 1992 SENIOR intensives, GIT provided canister analysis of NMHC concentrations at this site. In 1991, samples were collected on either three or four hour intervals. In 1992 samples were collected on alternate hours between 7:00 am and 7:00 pm. During both meausrement periods, all samples were tansported to Atlanta and analyzed within seven days of collection.

Additonal NMHC samples were collected on six day intervals coincident with the SCION sampling protocol. In total, approximately 75% coverage for the summer of 1991 was achieved. Measurements were also conducted for NO, NO, O₃ and SO₂ at the site. These intstruments were intercompared in 1991 with similar intrumentation from BNL anD showed good agreement. Significant logistical problems were encountered in operating this site (about 350 km from Atlanta) and, thus, data recovery was limited to about 50%. To ease these problems during 1992, Dr. Robert Mauldin of Georgia Southern University was recruited to operate the Metter site with assistance from GIT personnel.

ROSE

Ground-based Measurements at Kinterbish, Alabama in 1990 and 1992: ROSE I &II

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Extensive sets of chemical and dynamical measurements were made in 1990 and 1992, as part of the SOS/SERON/ROSE effort, at the Kinterbish Wildlife Management Area, near Jachin Alabama. The objectives of these studies were to obtain a detailed set of measurements of the precursors, participants and products of oxidant photochemistry, and to quantify transport and deposition processes. These measurements are being used to answer key questions pertaining to regional photchemical oxidant formation and transport processes. Ambient measurements are being used to identify episodes during which various sources were dominant, and to test the self-consistency of the emissions inventories for those sources. The photchemical oxidation of biogenic hydrocarbons is being studied through relationships of two co-emitted compounds. The importance of biogenic emissions of oxygenated organics is being examined. Contrasts in the day/night relationships of hydrogen peroxide and ozone reveal differences in their formation chemistry and relative deposition rates. The measurements of NO_v and constituent species reveals the extend of conversion of NO_x products and the relative importance of the product species PAN and HNO3. Unique chemical signatures are being used to discern the degree of photchemical processing that air-masses have undergone. Future work will involve comparing and contrasting the data sets from the two years, and in depth examination of the photchemistry occurring under the variety of meteorological conditions experienced during these studies.

Aircraft Measurements during the SOS/SERON/ROSE-Air II Experiment

The purpose of the SOS/SERON/ROSE II aircraft measurement campaign was to determine and quantify the processes responsible for the transport of ozone and ozone precursors (NO_y) vertically (1) through the planetary boundary layer, (2) between the planetary boundary layer and the free troposphere, and (3) through the free troposphere, as well as the horizontal transport of these compounds. The aircraft employed was the NCAR King Air, equipped with fast response chemical sensors for NO_y, O₃, CO2, and H₂O, as well as slow response sensors for CO and O₃, and a complete suite of fast response meteorological instrumentation. Approximately 40 research hours were flown from Meridian, Mississippi, during which primary focus of the flight planning was collection of an eddy correlation flux data base. An additional 20 research hours were flown from Chattanooga, Tennessee, during which the primary flight planning objective was to obtain a chemical survey over a wider region of the Southeastern U.S. Results obtained during the experiment will be presented and compared to the results obtained during the 1990 ROSE-Air experiment. In addition,

the results obtained thus far will be discussed in terms of enhancing the design of future aircraft experiments in the Southeastern U.S.

A Comparison of Model Results with Observation from the 1990 ROSE-I Field Campaign

As part of the SOS/SERON effort, 3-dimensional regional scale photchemical models provide a means of comparison between observed photochemical conditions and what one would expect based on current understanding of the emissions, transport and transformations of oxidants and their precursors inherent to the 3-D model formulation. An important issue associated with such models concerns their ability to adequately describe photochemical conditions over large rural areas within the regional model's domain. This is largely due to the paucity of data with sufficient detail and accuracy necessary to make objective model evaluations for specific episodes. Observations of photchemical oxidants, nitrogen oxide and NMHC compounds collected by the NOAA Aeronomy Laboratory and other collaborating institutions during the 1990 SOS/SERON/ROSE campaign in western Alabama (June 5 to July 21, 1990) provide a unique and complete data-set particularly suited for detailed comparison with results from 3-D photochemical models.

A one week period (June 24-30, 1990) has been simulated using the NOAA Aeronomy Lab 3-D regional oxidant model. Within this time period and elevated pollutant episode related to regional scale transport was observed, followed by the passage of a cold front and associated "clean" conditions. Several aspects of the comparison between model results and the detailed photchemistry observed at this site are addressed. First is the model's ability to simulate the temporal patterns of several key gas-phase species n response to the regional scale meteorological forcing. As a test of more localized forcing factors, the diurnal dependence of ozone precursors, the partitioning of NO_y species, quantities related to the photostationary state, and hydrocarbon abundances are also compared. Lastly, the photchemical signatures defined by relationships between individual species are compared to qualitatively assess the applicability of the model's chemical mechanism for this rural setting.

REACT/TVA

The Tennessee Valley Authority prepared and operated a SENIOR network site at a rural location in Giles county, Tennessee. In addition to the funds provided by EPA for the SOS, TVA funds were also used for operation of the REACT site. Intensive field studies were conducted from July 22 to September 1. 1991 and from June 10 to July 18, 1992. TVA used a 40-foot trailer that has been modified into a mobile lab equipped with a wide variety of instruments which include high sensitivity gas phase monitors and standard meteorological monitors. A tethered balloon was used to acquire vertical profiles of temperature, relative humidity, wind speed and direction, and concentrations of ozone and isoprene. A wind profiler was used to estimate mixing

heights and ground based inversion heights. Ozone, ozone precursors, and meteorological parameters were monitored at Giles County during the summer studies of 1991 and 1992. Table 1 lists the parameters measured at the Giles County SENIOR site.

The diurnal pattern for O₃ at Giles Country is similar to that observed at other rural sites. A median midday ozone value of 75 ppb was observed at this site during 1991. The ozone levels were significantly lower in 1992 compared to 1991. The temperature was also significantly lower in 1992 compared to 1991. The lower temperature was the result of atypical synoptic conditions. The unusual weather conditions may be the reason for the lower ozone levels at Giles County during the 1992 study season.

The temporal behavior of the speciated nitrogen oxides was obtained during the 1991 and 1992 studies. There was no significant diurnal variability for NO_y . The median NO_y concentration ranged between 3 and 3.5 ppb. NO_2 is the major NO_y species at night. The NO₂ comprises more than 65% of the NO at daybreak. Since the sum of the individually measured NO_y species, i.e., NO, NO_2 , PAN, HNO₃, and NO_3 aerosol, do not account for all the NO_y measured, the unknown species are designated as XS when a diurnal plot is made. The diurnal profile for the XS species, which is similar to that for PAN and HNO₃, suggests photochemical production. These species are believed to be organic nitrates and PAN homologues produced from peroxyl and acylperoxyl radical reactions with NO_x .

The 1991 field data were analyzed to assess the importance of NO_x emissions in controlling rural O₃ levels. If NO_x emissions are an important factor controlling rural O₃ levels, then an association between O₃ levels and the NO_x oxidation products would be expected. The ambient levels of NO_x oxidation products is obtained by subtracting the observed NO_x species. The NO_x oxidation products, NO_y - NO_x , are sorted by concentration and then plotted vs. O₃. The field data was sorted into 20 equal bins to reduce the amount of scatter in the plots. Data suggests a strong association between O₃ and observed NO_x oxidation products.

Measurements were made of ambient levels of formaldehyde, CO, and hydrocarbons ranging in size from 2 to 10 carbon atoms. Midday concentrations of hydrocarbons and formaldehyde, isoprene, and the alkanes make the largest contributions to midday concentration. Reactivities were calculated and summed by VOC class. The reactivity plots show that (1) reactivity during midday hours is dominated by isoprene, and (2) formaldehyde makes a significant contribution to reactivity during midday hours. Formaldehyde is a significant contributor to the odd hydrogen budget, competing with ozone photolysis in the morning for radical production. **Gas-Phase Species**

O₃ PAN NO₂ NO NO_y HNO₃ Hydrocarbons containing 2 to 10 carbon atoms CH₂O CO

Meteorological Parameters

Temperature Relative Humidity Wind Speed and Direction Precipitation Barometric Pressure Solar UV Radiation

Ions in particulate material

$$NO_{3}^{-}$$

$$SO_{4}^{-}$$

$$NH_{4}^{+}$$

$$Na^{+}$$

$$K^{+}$$

Vertical Profiles

Wind Speed and Direction Temperature Relative Humidity Ozone Isoprene

- o The midday median O₃ levels were about 75 ppb at the Giles County rural site during 1991 but only about 53 ppb during 1992.
- o There is a strong relationship between O_3 and NO_x oxidation products.
- o At night, about 10% of the NO_y species is unknown. During the daylight hours up to 25% of the NO_y species is unknown.
- VOC reactivity is dominated by isoprene. Formaldehyde and carbon monoxide make smaller but significant contributions.

The strong association between O_3 and NO_x oxidation products suggest that NO_x emissions are a major factor in O_3 production at the Giles County SENIOR site. However, a better understanding of the role of VOC's in the local production of O_3 is still needed. The data suggest that emphasis should be placed on determining the contribution of oxygenated VOC's to rural ozone formation.

The results from TVA's REACT/SENIOR program will be used in a collaborative effort to produce SERON products (e.g., 4 peer reviewed scientific publications and 4 paper presentations at the AWMA Conference in San Diego, California in November 1993).

SONIA (NCSU)^{1.}

Principal Accomplishments in 1991-1992

During the summer (i.e., May, June and July for about 5 weeks) of 1991 and 1992, intensive measurements were made of ozone, other photochemical oxidants and their precursors, and meteorology. These measurements were made at the SERON SONIA Site located in Candor, North Carolina. The measurements made were:

a. Gaseous Pollutants

O₃ NO, NO₂, NO_y, PAN, PPN, HNO₃ SO₂ CO H_2O_2 Continuous ambient measurements of C₂-C₁₀ speciated HC's Carbonyls

^{1.} The University of Maryland withdrew from operation of the SCION portion of the SONIA site and the work was taken over by NCSU as reported below.

b. Aerosol Pollutants

 $SO_4 = 2$, NO_3^- , CI^- , major cations

- c. NO_x Emission Flux Measurements from soils and its characterization
- d. Meteorological Parameters: wind speed, direction, temperature, dew point, pressure and rainfall amount
- e. Precipitation chemistry and rainfall rate

Data recovery from 1991 was limited by available personnel. 1992 recovery was much improved due to having a more experienced field team. It is anticipated that most of the analysis of SONIA data will depend on 1992 field observations.

Initial Findings in 1991-1992

- Ozone concentrations did not exceed NAAQS during the measurement period at the SONIA site.
- o NO emission flux from soils ranges from 0.1 to approximately 2.5 ng N m⁻²S⁻¹
- o NO₂ emission flux from, and deposition to soils was observed.
- o NO emission maxima from soil appears to be coincident with the ambient NO maxima in the mid morning.
- Gaseous H₂O₂ and peroxyacetyl nitrate range from level of detection to about 2 ppbv and follow photochemical cycle during the measurement period.

Two graduate thesis and two published articles have resulted from this early work.

HYDROCARBON QA/QC and INSTRUMENT DEVELOPMENT

During 1991-1992, GIT provided operator training and method development for the SCION measurement program. In 1991, five training programs were conducted with three additonal workshops conducted in 1992. These workshops included manufacturer sponsored training for commercial instrumentation and operator training for hydrocarbon sampling apparatus. The SCION sampling protocol was developed in early 1991 at GIT under the instrument development program.

In 1992 GIT, TVA and NCSU participated in a joint SERON/SORP-ONA hydrocarbon measurement workshop in Miami, FL. where a common SOS measurement protocol was established. This work resulted in a modified grab samplecollection protocol which was introduced during the SOS Atlanta intensie and tested at the Burnt Mountain site. This protocol will be instituted network- wide in November of 1992. GIT also developed a sample tracking protocol now used SOS- wide for hydrocarbon canister samples.

1992 SUPPLEMENTAL FUNDING

The reallocation of one hundred thirty thousand dollars from SERON Field Activities to support cooperative research with the Southern Oxidants Research Program on Emissions and Effects (SORP-EE) left SERON management with the decision to shut down one of its planned SENIOR intensive sites. Fortunately, One hundred fifty-four thousand dollars was provided by the USEPA as supplemental funding late in 1992. These funds were provided to support the operation of the ROME SENIOR site, Hydrocarbon Analysis for the Burnt Mountain Site, and start up funds for a Public Outreach Program for the SOS.

The ROME site was operated by the Brookhaven National laboratory and has been previously addressed.

Georgia Institute of Technology, received nine thousand dollars to provide hydrocarbon collection and analysis for the **Burnt Mountain** site in cooperation with the SOS Atlanta intensive study. All funds were expended in providing this service.

Ten Thousand dollars were provided, under subcontract, to Cabot-Smethurst and Associates for Public Outreach "start up". All funds have been expended. Principal accomplishments:

- o An Outreach Steering Committee, comprised of key participants and sponsors of the SOS, was established to provide critical review of all outreach activities. A media subcommittee was formed to deal with anticipated media interested generated by the intensive studies conducted during the summer of 1992.
- o An SOS brochure and two fact sheets were produced and printed in lots of 5,000. To date, approximately 500 sets of materials have been distributed to individuals, sponsors, and media. Additionally, a list of over 100 key Georgia people and organizations and addresses has been prepared.
- The Atlanta intensive press conference was planned and implemented with 300 invitations sent to key publics and 100 attendees at the press

conference. Senator Wyche Fowler and EPA Regional Administrator, Greer Tidwell, were keynote speakers. Approximately 8 members of the press attending resulting in good media coverage of the event. The consultant provided assistance to the Georgia Tech Office of Media Relations in the preparation of three press releases.

SERON DELIVERABLES

Appendix A lists some fifty products, publications and deliverables to be derived from this research.

SERON ACTIVITIES/PRODUCTS/DELIVERABLES

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SERON	ACTIVITIES/P	UBLICATIONS		
As deve	eloped during S	SERON Science Team Meeting		
Septem	ber 09-10, 19	92 Research Triangle Park, NC		
ITEM	ACTIVITY	DESCRIPTION	RESPONSILE	DUE
SON A	RCHIVE			
1	Product	For SON Archive: Thru user contact, develop list of desired products	Lee, Deakin	92OCT01
2	Product	Develop Descriptive Matrix of site criteria. Include definition/class of site. Include urban influenced and high elevation sites. Thru Central FL,KY,and Region VI to Western ROM Boundary.	Lee, Edgerton, Schere, Vukovich, Deakin	November Workshop
3	Product	Annual descriptive statistics of SCION data by station (including frequency distribution)	Edgerton	920CT01
SCION	DATA BASE			
4	Product	Recommendation concerning opportunities to combine aspects of Model/SCION Archives. Look at usefulness/cost of other "SCION-like data".Revisit time interval of SCION data.	Schere, Edgerton,Lee, Deakin,Aneja Vukovich	November Workshop
5	Product	Describe platforms supporting McIdas & mechanisms for acquiring available data.	McNider	920CT01
MET A	RCHIVES			
6	Product	Hard copy of satellite imagery for modeling period to modeling archives	McNider	7-10 days after request
7	Product	Gridded insolation to modeling archives.	Mc Nider	7-10 days after request
8	Product	Include NCC data in modeling archives.	Schere	6-8 mos lag
9	Product	Event Selection list for study. Include ATL Study datasets, 90&91 data, 92 Quicklook for ATL O3. Consider as task in detailed workplan for SOS 93.	Model Team plus Meagher	93JAN20
10	Product	Look at how well we can characterize O3 field with available data & analysis techniques. Generate chemical climatology of South using SON data.	Vukovich, Lee, McNider	92OCT01

11	Product	Evaluate spatial and temporal representativeness of SENIOR data. Discuss regional	Aneja (lead),	92OCT01
		characteristics of O3 precursors using SENIOR/SCION databases.	Edgerton,	
			Meagher,	
			McKeen,Kleine-	
			man	
SCIENT	IFIC DELIVER	ABLES: CY 90&91 DATA		
12	Journal	Elevated Site Study : Atmos. Env.	McNider	93FEB
			(UAH/UK)	
13	Journal	Convective Contributions: Atmos. Env.	Pielke (UAH.CSU)	93FEB
14	Journal	Satellite Insolation Methods: AWMA	Song (UAH)	92NOV17
15	Journal	Sensitivity of O3 Production/Natural NOx-Lightning: Atmos. Env.	McNider	93MAY
			(UAH,TVA)	
16	Journal	Sensitivity of O3 Production/Natural NOx-Soil: Atmos. Env.	McNider	93NOV
			(UAH,TVA)	
17	Journal	Climatology of O3 in Eastern 2/3 of U.S. & SOS Region: Atmos. Env.	Vukovich	93FEB
18	Journal	Changes in Meteorology: High vs. Low Ozone Seasons: JGR	Vukovich	93MAY
19	Journal	4 Dimensional Assimilation of NOAA Model: JGR (?)	Seaman	93NOV
			(PSU,NOAA)	
20	Journal	1988 Base Case ROM Emission Reduction Scenarios: JGR	Roselle	93NOV
21	Report	Model Intercomparison: Internal Report	Schere	93NOV
22	Journal	Carobonyl Speciation: EST	Murthy	93FEB
23	Journal	PAN Data: JGR	Roberts et al	In Press
24	Journal	Hydrogen Peroxide: JGR	Claiborne (NCSU)	93FEB
25	Journal	Intercomparison: Denuder/Fileterpack Techniques for HNO3 and Aeresols:EST	Aneja	93FEB
			(NCSU,GIT)	
26	Journal	Ozone Photochemical Production: JGR	Wang (GIT)	93MAY
27	Journal	Ozone Photostationary Study: JGR	Rodgers (GIT)	93MAY
28	Journal	NOy Speciation: JGR	Wang (GIT)	93MAY
29	Journal	Hydrocarbon Speciation: JGR	TVA	93MAY
30	Journal	Chemical Climatology of Giles County Site: JGR	TVA	93MAY
31	Journal	Ozone/Nitrogen Relationships:	Trainer	In Press
32	Journal	NOy Speciation:	Parrish	In Press

SERON ACTIVITIES/PRODUCTS/DELIVERABLES

PAPER	S FOR PRESEN	TATION: AWMA CONFERENCE SAN DIEGO, CA		
33	Conference	SENIOR Overview	Rodgers	93NOV
34	Conference	Meteorological Framework	McNider	93NOV
35	Conference	Metter Site Operations	Springston	93NOV
36	Conference	Giles County Site Operations	Bailey	93NOV
37	Conference	Candor Site Operations	Aneja	93NOV
38	Conference	NMHC: AWMA San Diego	TVA	93NOV
39	Conference	Nitrogen Speciation	NL	93NOV
40	Conference	NOx Photostationary State	GIT	93NOV
41	Conference	Ozone Production	TVA	93NOV
42	Conference	Hydrogen Peroxide	BNL	93NOV
43	Conference	Carbonyls	BNL	93NOV
44	Conference	Events	NCSU	93NOV
DOCUM	MENTATION			
45	Document	Approved QA/QC Plan: Comments to Rodgers	Science Team	92NOV01
46	Document	Site Descriptions: Existing Sites	ALL	93FEB
47	Document	Site Descriptions: New Sites	ALL	93MAY
48	Document	Data Plan	Schere	92NOV
49	Document	SON/SCION Standard Operating Procedures: Status Check	Lee,Edgerton	92NOV17
50	Document	SON/SCION Standard Opetating Procedures: Completed	Lee,Edgerton	93NOV