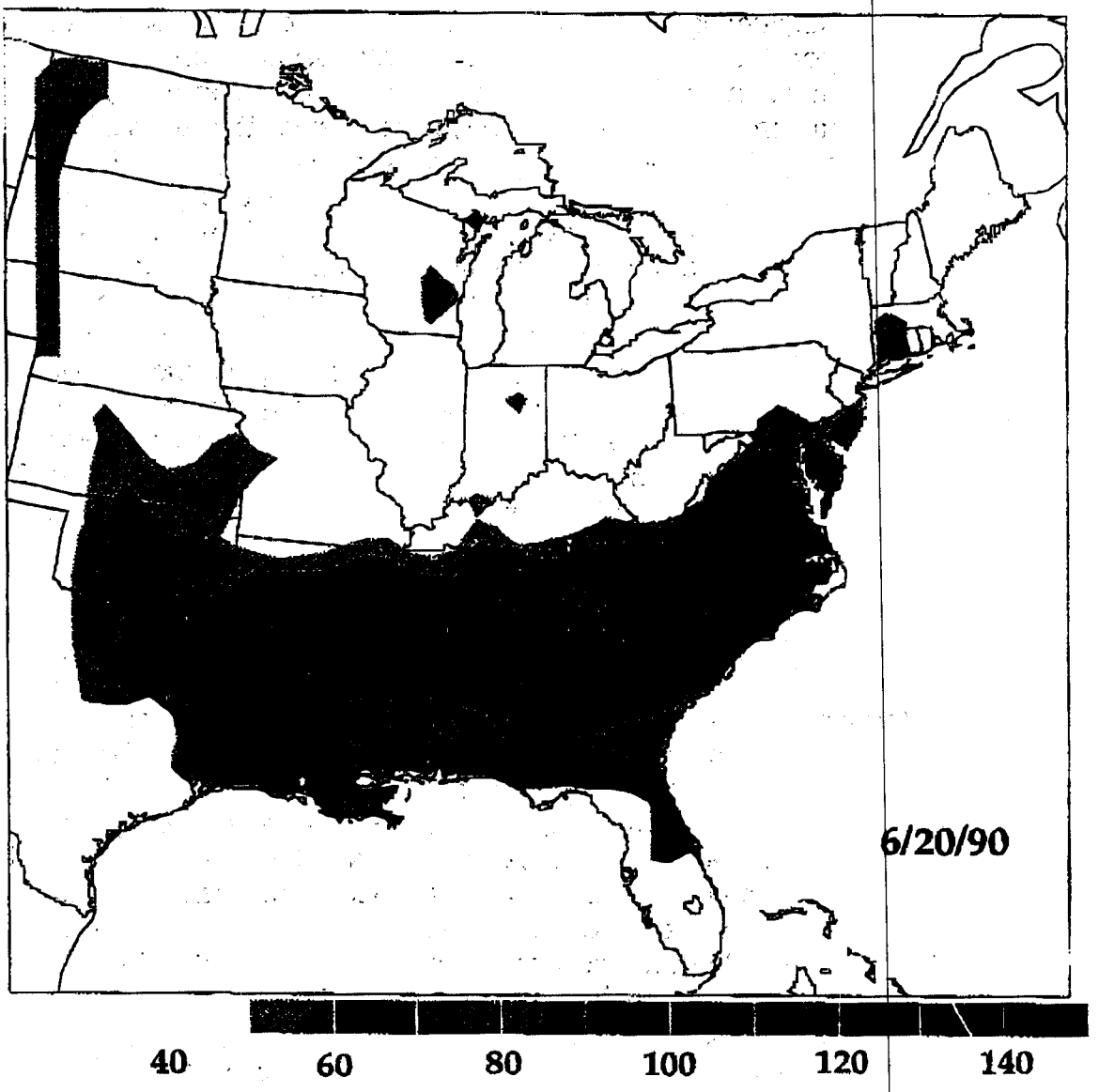
Southern Oxidants Study



1993 DATA ANALYSIS WORKSHOP REPORT

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EVALUATION OF THE RELATIVE CONTRIBUTION OF VOCs AND NO_x TO OZONE FORMATION IN RURAL AND URBAN AREAS

Is the production of ozone NO_x- or VOC- limited?

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III. Introduction

The photochemical precursors of ozone are the oxides of nitrogen (NO_x), carbon monoxide (CO), methane (CH_4), and nonmethane hydrocarbons (NMHC). Due to high reactivity and relatively large sources, NO_x and NMHC represent the most important ozone precursors in most areas of the United States.

Ozone formation is driven by the cycle of odd hydrogen radicals ($=OH+HO_2+RO_2$) in reactions that drive the oxidation of the NMHC and their oxidation by-products. In general, as many as two ozone molecules may be formed for each carbon atom in the original NMHC. In order to produce ozone, NO_2 must be formed in the oxidation of NO by peroxy radicals. The main source of radicals is the photolysis of ozone or carbonyls and the subsequent oxidation of

NMHC. The main sinks for radicals are the formation of hydrogen peroxide and organic peroxides that dominates at low NO_x and high HC/NO_x ratios, and the formation of nitric acid that dominates at high NO_x concentration and low HC/NO_x ratios. Nitric acid also represents the major sink for NO_x. Conversion of NO_x to PAN is as significant as conversion to nitric acid, but PAN represents a temporary reservoir that eventually returns to NO_x. The odd hydrogen cycle is important because the rates of ozone-forming reactions are governed by the availability of OH. NO_x conversion to HNO_3 is also governed by OH.

It is clear that elevated ozone concentrations are produced by meteorological conditions that favor high photochemical activity and transport of O_3 precursors from sources of those compounds. With this in mind, this aspect of the research is aimed at determining whether the availability of oxidizable VOCs or the catalyst NO_x limits the production of ozone in rural areas and urban areas in the Southeast.

Scientific topics that were addressed through SOS involve ozone formation in the southeastern United States in: (A) rural areas, and (B) urban areas.

IV. Findings

A. Ozone Formation in Rural Areas

1. Interpretation of measurements

Rural ozone formation is understood in terms of two questions: (1) How *efficient* is the chemical formation of ozone? (i.e., how much ozone is formed per unit of precursor removal?) (2) How *fast* is ozone formation? In order to answer the first question, ozone is related to various anthropogenic tracers and/or precursors. In this regard, it has been observed recently that the amount of O_3 formed in relation to the amount of NO_x removed serves to describe ozone formation at many rural locations. In the second case, it is found that the production of O_3 with time correlates strongly with the removal of NO_x with time. That is, in rural locations, $\Delta O_3/\Delta NO_x$ controls O_3 production. Together these two approaches indicate that the formation of ozone is NO_x-limited.

The dependence of ozone production efficiency on NO_y is illustrated by the correlation of O_3 with NO_y or various combinations of NO_y species (NO_y species include NO_x, peroxyacetyl nitrate, gaseous nitric acid, gaseous nitrous acid, all organic nitrates, and nitrate radicals). This dependence is illustrated by the results shown in Figure 5.1 that shows a plot of ozone concentration versus the oxidation products of NO_x (NO_y - NO_x). These results were taken from measurements made at Condor, North Carolina; Giles County, Tennessee; Kinterbish, Alabama; and Metter, Georgia. The measurements are compared with the results taken from a 3-D model simulation. The agreement between the measurements and the model are good.

For most measurements made within the Planetary Boundary Layer (PBL), estimates for $\Delta O_3/\Delta(NO_y-NO_x)$ range from 6 to 9, including estimates for urban sites (Los Angeles), rural locations (including rural sites in the Southeast), and smog chambers. Within the boundary layer the O_3/NO_y correlation is affected by: (1) titration of O_3 by direct NO_x emissions, which is important at night or in power plant plumes with very high NO_x concentrations; (2) daytime ozone production; (3) loss of ozone through reaction with NO and NO_2 at night; (4) different rates of removal for ozone and for NO_y; (5) mixing of air from the boundary layer with air from the free troposphere, which usually has a much higher O_3/NO_y ratio.

The titration effect was illustrated by a flight through Birmingham, which shows a pattern of increasing O_3 with NO_y in the urban plume, but a separate trend of *decreasing* O_3 with increasing NO_y where the aircraft intersected power plant plumes. During the daylight hours, ozone production per NO_x removal decreases at higher NO_y concentrations (Liu et al, 1987). This is largely due to the slow relative rate of conversion of NO_x to nitric acid at low NO_x concentrations that is associated with the attendant low OH to HO_2 ratios.

The ozone/NO_y correlations also can be analyzed in terms of the air mass "chemical age," as reflected in the parameter $1 - (NO_x/NO_y)$. This age parameter is zero for fresh, un-reacted NO_x emissions ($NO_y = NO_x$) and ~0.8 for highly aged air in which most of the NO_x has reacted to other forms of reactive nitrogen. This parameter represents the amount of chemical aging (not the chronological age) of the air mass.

The result from the measurements made at Giles County, Tennessee, shows that O_3/NO_y increases with chemical age, up to a "plateau" of $O_3/NO_y = 12$, and then remains constant as the age parameter increases beyond 0.70. This result, shown in measurements, is very similar to results obtained in smog chamber studies. The fact that O_3/NO_y is independent of the NO_y concentration when plotted in this format suggests that ozone is NO_x-limited.

From aircraft observations made within the planetary boundary layer during the ROSE study, ozone was observed consistently to increase with increasing NO_y-NO_x. The increase is especially steep as $NO_y - NO_x$ increases from 0 to 2 ppb. In flights on separate days, the correlation of O_3 with $NO_y - NO_x$ correlation shows a similar slope, but with a different intercept (40 ppb on one day, 60 ppb on the next), suggesting that photochemically produced ozone is being added on top of a different base of "background" ozone on the two days.

With NO_y - NO_x ranging from 1 to 4 ppb, the slope of O_3/NO_y - NO_x is 15 at Rose -- higher than at most other locations studied. A 1-D model shows a slope that matches these observations. When urban emissions are added to this model, NO_y increases and the slope of ozone to NO_y - NO_x decreases -- corresponding to conditions found in an urban plume. Hence, the efficiency of ozone production is higher in rural areas. As the urban plume ages, however, eventually the NO_x-converted-to-PAN will be re-converted to NO_x and produce additional ozone. When the urban air has aged long enough for the PAN to return to active NO_x, the O_3/NO_y curve may become steeper.

During a three-day episode with high concentrations of ozone at Birmingham, the curve of O_3 vs NO_y is observed to "bend over." That is, O_3 no longer increases with NO_y for NO_y mixing ratios greater than 10 ppbv. However, the curve of O_3 vs NO_y-NO_x does not bend over; it continues to increase. Removal rates for NO_x in the urban plume were deduced to be 20%-40% per hour from these aircraft measurements. This would imply a high OH concentration ($\approx 4X10^6$ molecules/sec). This estimate does not include NO_x-to-PAN conversion. Previous estimates for NO_x removal were lower, about 10%-15% per hour. However, those estimates were made in studies of plumes from larger metropolitan areas with more concentrated NO_x sources.

At the sites studied thus far, ozone concentrations correlates with CO and with SO_2. However, SO_2 is not a precursor of ozone, and it is unlikely that CO is the cause of high ozone (although it is a precursor). Most likely both CO from area sources, and SO_2 from industrial point sources, correlate with NO_y produced by those sources; and it is the NO_x from those sources that is driving ozone production. In this regard it should be noted that the SO_2 sources usually emit very small amounts of NMHCs. This indicates that there are enough NMHCs present in these air masses, probably in the form of biogenic NMHCs from forest trees to support considerable ozone production. This also was the conclusion of the factor analysis presented by Parrish and Buhr (c.f., Session 4).

2. Results of model simulations

An alternate approach to studying rural ozone formation, and the interaction between air masses of rural and urban origin, is through detailed model calculations. Provided the emissions and important processes determining boundary layer ozone are accurately represented, the models can be used to assess the impact of emission reductions for various primary ozone precursors. The relative importance of NO_x emissions reductions compared to NMHC or VOC reductions is of particular importance to those concerned with federally mandated ozone compliance requirements.

Independent results from two 3-D mesoscale photochemical modeling projects provide a reasonably consistent picture of the ozone response to both NO_x and NMHC reductions, despite considerable differences in the models' structure and simulation conditions. The EPA Regional Oxidant Model (ROM) has high horizontal resolution (~ 20 X 20 km^2), but a highly parameterized boundary layer structure. The National Oceanic and Atmospheric Administration (NOAA) Aeronomy Lab 3-D Eulerian model has lower horizontal resolution (60 X 60 km^2), but explicitly incorporates boundary layer physics and vertical exchange within its 16 vertical layer formulation. The domain of both models are similar (the eastern United States) and both models evaluated ozone changes due to 50% emissions reductions of either anthropogenic NO_x or NMHC, as well as a 50% reduction for both NO_x and NMHC emissions. However, the emission reductions studies were done for entirely different dates and synoptic conditions. Also, ozone differences predicted by the EPA ROM were based on the maximum ozone concentration occurring over a nine-day period, while the NOAA Aeronomy Lab model-evaluated ozone differences at a specific time and date.. During this period observed O_3 values exceeded 150 ppbv in the southeastern United States and 180 ppbv downwind of Chicago, Detroit, and along the Northeast United States Corridor. The following conclusions were made based on the model simulations:

- 50% NMHC reductions had little effect on episode maximum O_3 for most of the model domain, except near major NO_x source regions including the Texas-Gulf Coast area, the Chicago-Lake Michigan area, and near New York City. The average episode maximum O_3 decreased 3%.

- NO_x reductions decreased episode maximum O_3 nearly everywhere (a 16% domain average decrease), *except* for the limited locations where NMHC controls appeared more important. In the Texas-Gulf Coast region, Lake Michigan and Toronto areas NO_x reduction caused an increase in episode maximum O_3.

- 50% reductions in both NO_x and NMHC decreased episode maximum O_3 in most locations (a 17% domain average decrease). O_3 increased in a few locations near major NO_x sources, but the spatial extent was limited to a few grid cells.

- NMHC/NO_x concentration ratios were much lower in the Texas-Gulf Coast region and in urban cores (Chicago and New York), which were locations where NMHC emission reductions were most effective. The southern United States generally had higher NMHC/NO_x ratios than the rest of the eastern United States.

The NOAA Aeronomy Lab 3-D Eulerian model simulated a four-day episode (July 4-7, 1986) in which an O_3 episode occurred on July 6, 1986. The following conclusions were drawn from this study:

- Reducing anthropogenic NMHC emissions by 50% leads to domain averaged O_3 reduction of 3%, with larger reductions in urban areas and downwind of the Ohio valley.

- Reducing anthropogenic NO_x emissions by 50% leads to a domain averaged O_3 reduction of 11%. However, O_3 increases are found in some urban areas (~8% of the domain area).

- Reducing both NO_x and NMHC emissions by 50% leads to a domain averaged O_3 reduction of 12%.

- The crossover in the O_3 response to either NMHC or NO_x emission reductions occurs for mid-day NO_x-mixing ratios between 3 and 10 ppbv. At higher NO_x-mixing ratios, NMHC controls are more beneficial, and NO_x controls usually increase O_3 .

- Sensitivity studies indicate that with anthropogenic NMHC emissions increased by a factor of four, the 50% NO_x control results in O_3 reductions in all urban areas. The same result is found when biogenic NMHC emissions are increased by factor of four.

- O_3 control strategies are also altitude dependent: O_3 decreases are greatest close to the ground for both control strategies, but NO_x controls are more effective relative to NMHC as altitude increases.

- The ratio of NMHC to NO_x emissions within an urban grid square is a controlling factor that determines the O_3 response to NO_x emission reductions. Grid size can influence this emission ratio. Higher grid resolution is needed to adequately model the O_3 response in urban areas.

Despite the contrasting model formalisms, synoptic conditions, and definitions used in the O_3 response, the first three conclusions of both model studies are quite similar with respect to changes in average O_3, and the relative benefits of the three emission reduction possibilities.

B. Ozone Formation in Urban Areas

1. Model simulations

Analysis of urban ozone formation

The nature of ozone sensitivity to its photochemical precursors, NO_x and VOCs, can be represented in terms of isopleth plots, which show that peak production of ozone occurs at a given VOC/NO_x ratio. Ozone is sensitive to VOCs at lower VOC/NO_x ratios and sensitive to NO_x at higher ratios. In rural air in the Southeast, there are large sources of VOCs associated with emissions from forests that generally lead to large $VOCs/NO_x$ ratios. Consequently, as described in the preceding section, the rural areas of the South are expected to be NO_x-sensitive. In urban locations there tend to be relative large sources of NO_x in comparison with anthropogenic VOC sources. In addition, while the biogenic hydrocarbons emitted by trees may be important sources of VOCs, they are not dominant. However, urban air has widely varying photochemical age and, as an air mass ages, the $VOCs/NO_x$ ratio will increase as NO_x reacts away. Consequently, an aging urban air mass is likely to become NO_x-sensitive as it moves downwind. This effect has been demonstrated in smog chambers and in detailed urban simulations. Because of these competing influences on the $VOCs/NO_x$ ratio in cities, the sensitivity of ozone to VOCs and NO_x is more uncertain in the urban environments.

A less obvious effect of the photochemical aging process becomes obvious if you differentiate between the chemistry of air with very high precursor concentrations (due to high emissions density, lack of vertical mixing during the daytime, or both) and the chemistry of air with low or moderate precursor concentrations. The chemical reactions progress more rapidly when precursor concentrations are lower. Consequently, urban plumes under conditions of rapid dispersion are likely to evolve more rapidly and become NO_x-limited (within an eight-hour period). But, concentrated urban plumes evolve more slowly. Assuming that their emissions have VOC-sensitive chemistry, concentrated plumes are more likely to have HC-sensitive ozone even after eight hours of photochemical processing. [Referring to the "chemical age" parameter (discussed above), the concentrated and dispersed air masses may have the same chronological age, but the concentrated parcels are much younger in terms of chemical age.] The difference between concentrated and dispersed air is illustrated with simple air parcel calculations, in which air parcels are allowed to photochemically "cook" for an eight-hour period.

This difference also was illustrated with results from a simulation for the Lake Michigan airshed. In the simulation, ozone-NO_x-VOCs

sensitivity is shown to be correlated with NO_y at the time of the ozone peak (i.e., afternoon). Locations with high afternoon NO_y are almost all VOC-sensitive in the simulation. (These correspond to locations where the Chicago plume is trapped all day under the Lake inversion.) Locations with low NO_y are all NO_x-sensitive. The correlation between sensitivity and NO_y has been explored in simulations for several cities.

Results from the Atlanta UAM runs for August 10, 1992, are explained in this context. The entire UAM domain for Atlanta comes out NO_x-sensitive, and afternoon NO_y concentrations are much lower than in the VOCs-sensitive Chicago simulation. (Afternoon NO_x is below 15 ppbv.) It is argued that Atlanta comes out NO_x-sensitive in UAM simulations largely because Atlanta is a city with relatively low emission rates and with relatively vigorous vertical mixing (as opposed to lake- or ocean-induced daytime inversions). As expected in Atlanta, isoprene emissions have a large impact on the sensitivity of ozone concentrations to anthropogenic NO_x or VOCs reduction. However, the relative low emission density and vertical mixing also may be a significant factor in explaining the sensitivity of model simulation to NO_x.

The correlation of sensitivity with NO_y also provides a new way to obtain direct evidence for model accuracy (or lack thereof) concerning sensitivity. Several chemical species can be identified as "empirical indicators" for sensitivity, in that they consistently assume different values in VOCs-sensitive versus NO_x-sensitive locations in the simulations. The identified indicators are: afternoon NO_y (>20 ppbv for VOC-sensitive chemistry), afternoon $HCOH/NO_y$ (<0.27 for VOC sensitive chemistry) and H_2O_2/HNO_3 (<0.4 for VOCs-sensitive chemistry). If measured values for these indicators are in reasonable agreement with UAM predictions, there will be strong evidence in support of the UAM prediction that Atlanta ozone is NO_x-sensitive. Preliminary results from airborne measurements of O_3 and NO_y in Atlanta give measured peak ozone at 160 ppbv with 12 ppbv NO_y. This measurement is consistent with the UAM for Atlanta on August 10, which suggests that ozone is NO_x-sensitive but approaching the "transition" to VOCs-sensitivity.

Results from 1990 measurements suggested that air over Atlanta often is not well mixed, even during the daytime. The "standard" UAM assumes near-instantaneous vertical mixing. This has been corrected by exercising the UAM with eight vertical layers. The UAM internally calculates a vertical eddy diffusion coefficient of ~500 m^2/sec during the daytime, a value that may be too high. The UAM has been

modified to run with vertical diffusion coefficients of 200 m^2/sec and 50 m^2/sec. The 50 m^2/sec UAM simulation gives surface concentrations for reactive hydrocarbons (isoprene and xylene) that are higher than in the original UAM by a factor of three. This provides a much better agreement with 1990 measurements, based on one case so far (July 31). Previously the UAM overestimated daytime concentrations of all VOCs by a factor of two, and overestimated isoprene by a factor of ten. With reduced vertical mixing, a significant underestimate remains only for isoprene, and can be corrected by doubling the emission rate for isoprene. Other species, even xylene, do not appear to be underestimated. The resulting UAM still does not have a satisfactory agreement with measurements, but it does not provide evidence for large errors in the emission inventory.

Diagnostic Analysis: The use of the observational based model to determine effectiveness of VOC and NO_x control in Atlanta.

The observation-based model (OBM) makes the use of uncertain emission inventories unnecessary. The OBM calculates the O_3-forming potential based on relative incremental reactivities (RIR). The OBM was applied to the Atlanta area case study: for August, 1990. The OBM found RIRs of NO_x to be greater than the RIRs of anthropogenic NMHCs; mobile NMHCs were greater than stationary NMHCs that were, in turn, greater than biogenic HC, which were greater than CO. The OBM has also been used to investigate the variation of RIRs with location within the domain and test the RIRs of individual NMHCs. The OBM is simple and easy to use. It is inexpensive and complements Urban Airshed Model (UAM)

2. Interpretation of measurements

NO_y/ozone relation in the urban environment.

Vertical profiles of O_3 and NO_y mixing ratios were measured over Atlanta using helicopter-borne instruments during the SOS summer intensive in 1992. There was considerable difference between the correlation of O_3 and NO_y on various flights, reflecting the relative degree of chemical processing with increasing distance from the urban center. These results exhibited many of the features alluded to in the model simulation of the Atlanta scenario, above.

Ratio of Isoprene to NO_y in Atlanta

Preliminary analysis of the 1992 Atlanta data has focused on the "chemical reactivity" of air that was expressed in terms of the ratio of isoprene to NO_y at the different measurement sites. At most of the measurement sites in and around Atlanta, the isoprene mixing ratios were similar, but the [NO_y] varied considerably from site to site. As expected, the highest [NO_y] was observed inside Atlanta. There was a

systematic north-south gradient in the isoprene mixing ratio associated with a north-south gradient in land use: in the North there is more forest, in the South more agriculture.

This analysis indicated decreasing reactivity with increasing NO_y, probably due to the fact that the NMHC in these air masses were dominated by less reactive anthropogenic hydrocarbons. Isoprene to benzene ratio decreases from about 60 at a reasonably isolated rural site (Bird Mountain) to less than 5 inside Metropolitan Atlanta. A correlation was observed between benzene and either iso-pentane or iso-butane. The scatter in benzene/iso-pentane correlation is explained by the observation that benzene comes chiefly from auto exhausts while iso-pentane comes chiefly from evaporation of gasoline. At the urban site, NO_y mixing ratios were as large as 300 ppbv, NO_2 as large as to 100 ppbv. The diurnal variations in the relative concentration of the various NMHCs indicate mobile sources dominate in the morning, biogenic sources become increasing important during the afternoon.

Ozone trends in Atlanta

Based on long-term ozone network data in the Atlanta metropolitan area, an investigation was carried out that focused on the trends in ozone and the potential contribution by metropolitan Atlanta to these ozone concentrations. One factor of particular interest was the possible impact, if any, on ozone concentration changes associated with the mandatory lowering of gasoline vapor pressure, a major source of anthropogenic NMHC emissions. Analyzing O_3 data upwind and downwind of Atlanta (ΔO_3 30-35 ppbv) found no statistical significant difference, though differences in the meteorology might have masked trends. Other changes at that time include improvement of the freeway system and the substantial population growth. Further research will look in greater detail and include more analysis of meteorological influences.

V. Conclusions

The following conclusions can be drawn from the SOS results obtained to date:

- In rural areas of the Southeast, production of ozone in the planetary boundary layer is NO_x-limited. This conclusion is reached based on model results; comparison of model simulation with measurement of NO_x, NO_y, and VOCs; and statistical correlation between O_3, NO_y, NMHC and other precursor species.

- Ozone production and NO_x removal in the Southeast are relatively fast compared to other regions of the United States possibly due to large emissions of biogenic NMHCs.

- Ozone production in rural areas is more efficient than in urban areas. This suggests that more attention be paid to rural photochemical production of ozone.

- Current UAM simulations for Atlanta suggest that ozone is sensitive to NO_x rather than NMHC throughout the Atlanta metropolitan area. These predictions are supported by other methods of analysis (OBM, observed NO_y, etc.). However, the UAM predicts that other southern metropolitan areas with the lower emissions of NMHC and/or the higher afternoon NO_y mixing ratios, may be close to the "transition region" where ozone is sensitive to both NO_x and NMHC reduction.

VI. SOS Strategic Plan Reference

This report summarizes the progress made toward completion of the products and outputs outlined in Sections III-F-1 and III-F-3 of the 1992 Southern Oxidants Study Strategic Plan.

Section III-F-1. *Evaluation of the relative effectiveness of VOC and NO_x controls in achieving ozone reductions in cities studied by SOS. Evaluation to address the relative importance of various emission source types.*

Section III-F-3. *Evaluation of the relative contribution of VOCs and NO_x to the formation of ozone in rural areas in the South. Evaluation to address the relative importance of various source types to each precursor.*

VII. Unresolved Issues - Future Research

In selecting management strategies to decrease accumulation of ozone, it is critical to consider both the presence of natural NMHC and the nonlinear dependence of the ozone production on NO_x and NMHC concentrations. Current control efforts are directed toward reducing anthropogenic NMHC. The work presented here suggests that in the southeastern United States such efforts will not be effective in reducing rural ozone and probably less effective in reducing urban ozone. The preliminary results presented during the workshop suggest that in the Southeast control of the oxides of nitrogen will be more effective than control of the NMHCs in both the urban and most rural settings. However, before the tentative conclusions drawn above can be accepted, more measurements in this region must be done. These measurements should focus on determining scientifically-defensible answers to several key questions, including:

- Is the production of ozone NO_x limited in urban as well as rural areas of the Southeast?

- Are biogenic hydrocarbons as important as anthropogenic hydrocarbons in urban ozone production in all metropolitan areas of the South?

- How important is the regional scale photochemical production of ozone vis-a-vis local production in leading to ozone concentrations that exceed air quality standards?

- Can model predictions of the relative sensitivity of ozone concentrations to NO_x or VOCs reduction be verified by comparison of model simulations with accurate measurement of "indicator ratios" (e.g., $HCOH/NO_y$ or H_2O_2/HNO_3).

- Can better monitoring strategies be found to determine the relative effectiveness of controls on different sources of ozone precursor emissions?

- Are there measurements and/or sampling strategies that would be useful in terms of reducing uncertainties, or exposing inadequacies, within models designed to evaluate O_3 control strategies?

- Are the answers to these questions applicable to all urban and rural areas of the Southeast?