



SCIENCE PLAN

DRAFT

October 1999

FOREWORD

A consortium of researchers from universities, private industry, and federal laboratories is joining the Texas Natural Resource Conservation Commission (TNRCC) and local communities in planning a major photochemical oxidant and aerosol field study in the eastern half of Texas in the late summer of 2000. While the Houston-Galveston area will be a focus of the study significant work throughout the eastern half of the state is also planned. Resources for this program include a monitoring network for O₃ and aerosols augmented by at least one highly instrumented super-site, a surface meteorology network including wind profilers, two aircraft carrying a comprehensive suite of chemical instruments, a third aircraft for remotely sensing O₃ and aerosol vertical profiles, and a fourth for source region characterization. The Texas 2000 field program is one in a series of oxidant/aerosol studies which the National Oceanic and Atmospheric Administration (NOAA), the Department of Energy, and a number of university scientists have cooperatively conducted under the umbrella of the Southern Oxidants Study (SOS) in affiliation with NARSTO. The location was selected because the eastern half of Texas includes major urban areas with significant ozone pollution problems and possible difficulties meeting new national particulate matter standards, and because of the unique chemical and meteorological features in this area that make it important from a scientific perspective. The goal of the study is to provide a better understanding of the basic chemical, meteorological, and atmospheric transport processes that determine ozone and fine particle distributions, and to develop new scientific understanding that will assist policy-makers in devising optimal ozone and PM management strategies.

This document describes the scientific objectives that will be addressed in the Texas 2000 program. It presents generic plans for acquiring observations and performing model calculations. The task that remains is to formulate a detailed operational plan that reconciles the scientific objectives with available resources.

INTRODUCTION

Air quality in the eastern half of Texas has shown substantial improvement over the last twenty years in spite of a dramatic increase in the population of its major urban areas. However, within the past few years the trend of improving air quality has flattened, and several of the major urban/industrial centers in the state still do not meet either the 1 hr, or the new 8 hr NAAQS for O_3 . A recent sensitivity study for the Houston-Galveston area using the CAMx model suggests that dramatic reductions (65-85%) in nitrogen oxide emissions will be required to meet the standard. Similar results were obtained from a sensitivity study of the Dallas-Fort Worth area. Other major metropolitan areas within the country face a similar situation. With the new eight-hour ozone standard, and the new PM_{2.5} standard being implemented over the next several years, states will have to devise strategies for meeting these new requirements. A significant issue is whether sufficient scientific understanding of either the ozone or the aerosol problems exists, to develop strategies to meet either the existing or the new NAAQS, in an effective, cost-efficient way. The Texas 2000 field study will provide much needed information about the chemistry, physics, and meteorology that control the formation and accumulation of ozone and PM_{2.5} in the eastern half of Texas, and provide fundamental scientific knowledge that can be applied to other areas of the country with similar problems.

A significant portion of the atmospheric emissions in eastern Texas originates in the two largest urban centers, the Dallas-Fort Worth (DFW) Metroplex and the Houston-Galveston area. Each of these urban complexes extends over 100 kilometers and has a population of approximately four million people. The eastern half of Texas also has a network of large coal-fired power plants that emit substantial quantities of sulfur dioxide (SO_2), nitrogen oxides (NO_x), and fine particles. The upper Texas Gulf Coast is home to scores of petroleum refineries and synthetic organic chemical manufacturing plants. These industrial activities all emit volatile organic compounds (VOCs) and NO_x , and some release SO_2 and fine particles. The extensive vegetation and warm temperatures that are typical of this region result in large emissions of biogenic VOCs. Agricultural emissions of ammonia (NH_3) are expected to be important in the formation of ammonium sulfate and ammonium nitrate particles in the region.

A number of unusual chemical and meteorological features distinguish this region from others with similar problems. These features include a mix of sources that leads to an observed VOC/ NO_x ambient concentration for the Houston area, which is significantly larger than the ratio derived from emissions inventories, and is also much higher than typically observed in most urban areas. There has been a suggestion that chlorine chemistry, due to the admixture of urban emissions and sea-salt aerosol from the Gulf of Mexico, or to direct industrial emissions of molecular chlorine (Cl_2), or to both, may have an influence on ozone formation. This unusual precursor mix will undoubtedly influence the rate and efficiency of ozone formation relative to other

urban areas and implies that a special set of strategies may be required to control ozone and PM concentrations.

The unique meteorological component of the Houston O_3 problem is illustrated by Figure 1 which shows the effect of land-sea breeze flow reversal on the O_3 concentration. The data are from the 1993 Coastal Oxidant Study for Southeast Texas (COAST) when there was a radar wind profiler at the airport on Galveston Island. Wind measurements recorded by this profiler, were used to separate the days during the mid-July to mid-September, 1993, COAST intensive period into those with wind flow reversal and those without. Figure 1 shows that all 20 exceedances during this period occurred under conditions where there was a land/sea breeze flow reversal.

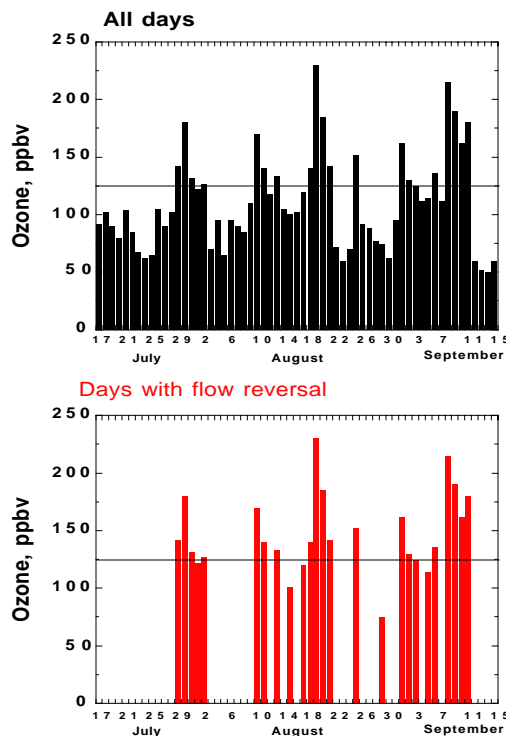


Figure 1. Ozone concentrations in Houston during the 1993 Coast Study. Upper panel shows ozone concentrations for all days. Lower panel shows concentrations on days when flow reversal occurred. Horizontal line is the 1 hr NAAQS for O_3 .

The region also affords the opportunity to study interesting and important aspects of aerosol formation and transport. Fine aerosol mass in the region is dominated by sulfate, as it is in the Southeast. However, semi-volatile organic aerosols are also important. Additionally, near the coast marine aerosols can act as nucleation centers producing internal

mixtures with significantly different properties from those formed in urban and power plant plumes.

Inter- and interregional transport may have an important role in the air quality of the region. Transport along the Gulf coast from Louisiana and farther east often defines the ozone and particulate matter background in the Houston area. Transport from the Houston-Galveston, Beaumont-Port Arthur area may have a significant effect on air quality in Dallas-Fort Worth and on Northeast Texas.

Study Themes

Diversity of Chemical Environments

Within the east Texas study area there are a diverse range of chemical environments driven by a corresponding diversity of emission sources and geographic features. Houston/Galveston and Dallas/Fort Worth are major metropolitan regions with an emission mixture dominated by transportation sources. Nearby to these cities are large power plants and petrochemical complexes providing point source emissions of NO_x and VOCs. Many of the power plants are located in the lignite belt, which is also a region of very high isoprene emissions. The Gulf Coast is a source of marine aerosols and possibly reactive chlorine.

This field study offers the opportunity to study photochemistry and aerosol production under a wide range of precursor conditions. Plume studies will be useful in determining how source types differ in their O_3 and PM forming potential, and hence the relative benefits of controlling different categories of emissions. Interactions of biogenic and anthropogenic pollutants can be quantified. Box model calculations driven by observed concentration fields will help us understand how production rates of O_3 and PM vary from place to place and what the sensitivities of these rates are to precursor concentrations.

Process Representation in Models

Development of useful and cost effective strategies to control O_3 requires the use of photochemical-transport models so that potential control strategies can be examined. A goal of the Texas 2000 Field Study is to improve model performance by providing a detailed set of observations for model inputs, a comprehensive data base against which model performance can be evaluated, and data to judge the adequacy of the meteorological and chemical representations used in these models. This latter effort goes beyond the usual model validation criteria by developing tests targeted at specific model components. Thus, spatial patterns and vertical distributions of trace gases with varying lifetimes can provide a ground truth for the model's ability to simulate transport and vertical dispersion. For the simulation of high O_3 episodes it is particularly important that the coastal flow reversal and the attendant "double dose" of pollutants be accurately represented. Ratios of oxidation products provide an "Indicator" for NO_x and VOC limited conditions that can be compared with model

predictions. Oxidation rates can be tested by comparing observed and predicted ratios such as for NO_x/NO_y . Ratios of primary pollutants in source regions can be compared with emission inventories.

Specific objectives

In order to focus the planning activities on these thematic concerns, a set of specific scientific objectives have been formulated. These are presented in 5 sections, segregated along traditional discipline lines, namely:

- Atmospheric Dynamics and Transport
- Ozone Formation and Distribution
- Fine Particulate Matter - Formation and Distribution
- Emission Inventories
- Modeling

In each section there is a brief discussion of general issues and their relation to the specifics of eastern Texas. Scientific objectives (An organized list of scientific questions is included in Appendix A) are intermingled with thoughts on how those objectives can be implemented. Instrumentation needs are identified. In the course of putting together a field operation plan, it is expected that some objectives will be discarded as being impractical to implement and others will be assigned low priority. It is also expected that new ideas will emerge.

I. Atmospheric Dynamics and Transport

Pollutant concentrations at the surface are strongly influenced by the physical behavior of the atmosphere, particularly the planetary boundary layer (PBL). Polluted air may exist in a "reservoir" layer above the immediate PBL and be entrained as the PBL grows, increasing pollutant concentrations near the surface. This phenomenon is often referred to as fumigation. Conversely, the overlying layer may be cleaner and entrainment may dilute the concentrations in the PBL. The reservoir layers themselves are created by the separation of the PBL upwind on the previous afternoon or by venting of polluted air out of the PBL by clouds and other detrainment mechanisms, including the sea breeze front. Pollutants can be transported at all levels, both within and above the PBL, and can travel considerable distances even during periods of relative stagnation at the surface. In the daytime vertical transport (entrainment and venting) tends to dominate, especially during stagnation episodes; at night horizontal transport is dominant. Because Houston is reasonably close to the Gulf coast, pollutant transport is also influenced by sea-breeze circulations. The overall objective of the PBL dynamics component of the Texas 2000 field study is to understand the effects of vertical and horizontal transport through the diurnal cycle on the concentrations of ozone, fine particulate matter, and their precursors. In the Houston area there will be special emphasis on the role of the land/sea-breeze circulation. The interaction of regional pollutant concentrations and sources with ozone and PM_{2.5} in the Dallas-Fort Worth area is another important consideration.

Specific objectives are listed below.

1. Quantify the contribution of entrainment to the concentrations of pollutants near the surface.

Entrainment is the capture of overlying air by the growing convective PBL and the mixing of this air and its contaminants throughout the depth of the PBL. Entrainment is quantified as fluxes of heat, moisture, and chemical constituents at the top of the PBL. Since these fluxes cannot be directly measured, they must be inferred from other measurements. Two basic approaches are available: (1) using an entrainment velocity coupled with a constituent profile or (2) using budget methods. Both approaches have large uncertainties and both have limitations, but they are complementary. The approaches and some results are discussed by Angevine et al. (1998).

2. Characterize the processes by which pollutants are removed (detrained) from the active PBL and made available for horizontal transport.

Losses of PBL pollutants can occur by detrainment of boundary layer air into the free troposphere either (1) during the evening transition when the CBL collapses or (2) through horizontal transport in regions where the mixing depth decreases downwind. Another loss mechanism is penetrative convection that vents

the PBL of pollutants either temporarily, if air parcels settle back into the PBL, or permanently, if air parcels are detrained through cloud boundaries.

Detrainment during the evening transition is to first order approximated by assuming that the PBL is well-mixed to its maximum height and that all the air between that height and some nominal nocturnal PBL height is detrained and available for horizontal transport by 1800 LST. Budget methods similar to the ones used to examine entrainment may be feasible.

3. Document the height and intensity of mixing of the PBL during the day, including its spatial variation.

It is now recognized that vertical mixing processes often dominate the diurnal cycle of ozone in the PBL (Kleinman et al., 1994; Neu et al., 1994). Losses by dry deposition at the surface and through the top of the mixed layer by detrainment are regulated by vertical mixing. Gains due to sources, production, and advection are distributed in the vertical by mixing processes during the day. For this reason the need exists to measure the temporal evolution of the boundary layer and understand its role in the production and modulation of ozone, fine PM, and precursor gases. The growth of the morning convective layer allows the chemical composition of the residual layer from the previous day, and perhaps from a different location, to mix to the surface at the same time that photochemical production of ozone is beginning. Ultimately, the growth rate of the PBL, local emissions released within the PBL, deposition to the surface, and the chemical composition of the residual layer all contribute to determining whether there is net increase or decrease of ozone and fine PM in the PBL.

Another important parameter controlling pollutant concentrations is the mixed layer depth. The mixing depth depends both on surface forcing (land use, topography, partitioning of latent and sensible heat fluxes) and processes occurring aloft (entrainment, subsidence, advection). Additional factors affecting chemistry in the PBL arise when cumulus convection occurs. Clouds serve two potentially important roles in the PBL (Neff, 1998). First, clouds present an environment in which aqueous-phase chemistry can occur. Second, penetrative convection vents the PBL of pollutants either temporarily, if air parcels are recirculated into the PBL, or permanently, if air parcels are detrained through cloud boundaries..

4. Document the spatial, temporal and diurnal variation of horizontal winds.

The spatial and temporal variation of the horizontal winds in the daytime mixed layer control peak pollutant concentrations and the direction of transport of pollutants and their precursors. During periods of high ozone and/or aerosol loading, the ability to document processes affecting horizontal transport, including recirculation and stagnation, is critical. A special feature of the Texas 2000 study is the role of the land/sea-breeze circulation on the formation transport and dispersion of ozone in the Houston-Galveston area.

The importance of the nighttime low-level jet accelerations to pollutant transport on days with light synoptic forcing has been demonstrated. Specific issues include: significance of the inertial oscillation on nights of somewhat stronger winds; documentation of the purging of the urban pollution overnight during stagnation periods; plume shape and diffusion at night as a function of wind speed; mixing time scales versus reaction rates; maintenance of vertical shear in the residual layer; the magnitude and interpretation of vertical gradients of pollutant species, especially those subjected to dry deposition; the horizontal variability of the flow near the surface and aloft in the low-level jet, and; the role of nighttime transport in maintaining or contributing to background pollution levels.

5. Produce a set of meteorological data that will allow for the verification and improvement of mesoscale meteorological models.

Mesoscale meteorological models are key tools in the analysis of the meteorological and chemical results of the field campaign. They provide the ability to fill in for missing data with physically consistent fields, initialize chemical models, and predict variables that are not measured. There are two objectives under this heading, the measurement data base and the external model database. The actual model verification and use objectives are beyond the scope of this science plan.

Measurement Requirements

A variety of measurements are required to address the above objectives. They include high-resolution, short-range instruments to characterize the nocturnal PBL as well as the morning and evening transition periods and long-range instruments for the daytime PBL. In addition, to study the horizontal distribution of mixing depth and to characterize the influence of inhomogeneous surface conditions, a network of surface-based integrated observing systems supplemented by aircraft is required. A network of wind profilers in combination with airborne measurements of chemical species is required to document the spatial and temporal variation of horizontal winds and pollutant transport. A Doppler lidar to provide monitoring of wind fields as well as important turbulence quantities such as profiles of momentum flux, turbulent kinetic energy, and vertical velocity variance is highly desirable. Ground based and airborne ozone and aerosol lidars to provide a detailed picture of the temporal evolution and spatial distribution of the ozone and aerosol concentrations from near the surface to the lower free troposphere would also be highly desirable. A network of ceilometers to define cloud cover and its variability would be very useful for studies of cloud venting.

Summary of Required Instruments

Profiler network - continuous, uniform daytime operation at high resolution for z_i , and residual reflectivity layers.

Surface flux network - half-hourly estimates of surface flux through the afternoon and evening.

Ceilometers network - continuous operation

Doppler lidar - primarily vertical pointing

Ozone lidar - continuous operation for vertical ozone and aerosol profiles

Airborne ozone lidar - ozone and aerosol profiles as available; horizontal distribution of ozone and aerosol profiles as available

Airborne in-situ - airborne winds, and trace constituent measurements as available

II. Ozone Formation and Distribution

A major driver for the Texas 2000 field study is development of an understanding of the combined chemical and meteorological processes that lead to the high levels of O₃ and fine PM that are formed in the greater Houston area under episodic conditions. Photochemical O₃ production requires sunlight, NO_x, and VOCs. The VOCs act as a fuel. The reaction of VOCs with hydroxyl radical OH and to a lesser extent O₃ and NO₃ initiates a sequence of reactions with the net effect that O₃ is formed and the initial VOC compounds are converted into oxidation products. These products can themselves be oxidized, forming more O₃. Because CO has a similar role in O₃ production, it is useful to consider it along with the VOCs.

For regulatory purposes the principal question is whether peak O₃ concentrations are limited by the availability of NO_x or hydrocarbons, and the extent to which HC or NO_x emissions, or both, need to be controlled in order to achieve regulatory compliance with NAAQS limits for the maximum allowable O₃ concentration. A significant question is whether the models used to develop control strategies represent either the chemical or meteorological processes involved in O₃ formation with sufficient fidelity to be used to develop such strategies. Specific issues related to the meteorological component of this problem are covered in Chapter I. Here we detail plans for examination of the processes that control the rate, efficiency, and amount of O₃ that is formed.

Because of the size of the Houston-Galveston metropolitan area and the diversity of sources contained within this area, O₃ formation is expected to occur under a much different set of conditions than it does in a medium sized, isolated city such as Nashville. The greater Houston-Galveston area is one of the urban complexes in the US that have reached dimensions of 50-100 km or more. These dimensions are sufficiently large that locally emitted pollution undergoes substantial photochemical processing before it leaves the urban domain. Thus, O₃ is formed under conditions where O₃ precursors are continually renewed as air travels over the region. It is possible that much of the O₃ that is produced by Houston urban emissions will occur under conditions where O₃ production rates and efficiencies are very different from those in the urban plumes emanating from smaller cities, particularly those that are isolated from other large urban/suburban areas. The situation is further complicated by the presence of intense point sources of NO_x and VOCs that add to the urban mix as air travels across the region. Emissions from these point sources may substantially affect the rate, efficiency, and amount of O₃ that is formed, especially under episodic conditions..

Objectives for the study of O₃ formation chemistry in the Texas 2000 field study can be divided into groups by scale. Some of the objectives focus on obtaining a process level understanding of the chemistry and require detailed measurements on a local scale. Other objectives focus on chemical processes occurring over extended periods of time and over larger spatial scales. In many cases, the strategies required to address the

two classes of objectives are the same, since an overall perspective of O₃ formation can be constructed by combining observations comprising the study of local scale phenomena. The objectives are outlined below.

1. Characterize the concentration fields of O₃, O₃ precursors, and photochemical product species and their evolution as an air mass advects over the Houston-Galveston Region.

A first order objective of this study is to provide a description of the concentrations of O₃, O₃ precursors, and pertinent photochemical product species as a function of time and location. A particular emphasis will be on conditions where it is suspected that exceedances of the NAAQS for O₃ will occur. Achieving this objective will require detailed measurements of the chemistry at the surface at number of locations and detailed and extensive measurements of the concentration fields by aircraft as a function of time, location, and altitude. This characterization of the concentration fields needs to be accompanied by an equally detailed characterization of the meteorology including boundary layer growth, vertical mixing, and horizontal wind fields.

2. Determine the spatial distribution of VOCs in relation to the locations of emission sources and O₃ generating regions.

In comparison with other regions where intensive field programs have been conducted, the upper Texas Gulf Coast, including the Houston-Galveston area and the Beaumont-Port Arthur area, has an unmatched diversity of large VOC sources. Major contributors are source emissions from transportation, point source emissions from refineries, and biogenic emissions from nearby forested regions. The fact that observed VOC to NO_x ratios are a factor of 2 greater than predicted from emission inventories suggests that emissions from one or more of these source categories are not fully represented in the available inventories. Overestimation of NO_x emissions in the inventory may also contribute to this discrepancy. In view of the large biogenic isoprene source, it is possible that VOC reactivity could remain very high outside of urban and industrialized regions. The formulation of O₃ and PM control strategies will have to take into account the unique chemical environments created by the various ways of mixing NO_x point source plumes, VOC point source plumes, NO_x and VOC containing urban air, and isoprene containing rural air.

To fulfill this objective, VOC concentrations will be determined at surface sites and also from airborne platforms, including at least the DOE G-1 and NOAA WP-3 aircraft and hopefully a helicopter, the latter to obtain low altitude measurements directly over source regions. The aircraft will collect canister samples, at a frequency of about 10 - 20 per flight. In addition the NOAA P-3 (and possibly also, the DOE G-1) will be equipped for real time VOC analysis. CO and formaldehyde (HCHO) which are important contributors to VOC reactivity will also be measured from these two aircraft.

It is important that VOC samples be collected in background air, within source regions, and in processed air where the highest O₃ and PM concentrations are expected. Within the Houston region there are sub-regions with distinct VOC signatures. Some combination of airborne and surface sampling will be needed to characterize high isoprene forested regions; inputs from the Gulf including recirculated air; and the composition and range of influence of industrial areas including refineries.

3. Determine the reactivity of the ambient mixture of VOCs.

Several approaches have been used to deduce reactivity from observations of VOC concentration. The simplest approach is to sum the rates at which the individual VOCs react with OH. More complicated approaches (i.e., incremental reactivity scales of Carter, 1994) take into account the multiple effects that each VOC has on the photochemistry. In contrast to OH reactivity, incremental reactivity scales are not just functions of the individual VOCs but depend on the entire photochemical mixture.

An important component of this activity is to apportion reactivity among the major categories of VOCs. These include anthropogenic NMHCs, CO, CH₄, HCHO, isoprene, other biogenic VOCs, and other oxygenated species. A similar exercise has been conducted for Nashville area and New York City. In Nashville it was found that on average, most of the VOC-OH reactivity was coming from isoprene. It was also found that the spatial variability of the apportionment was so high that it was misleading to only look at averages. Reactivity OH radical in the New York City plume about 100 km downwind of the city is compared with reactivity upwind of the city in Figure 2. Reactivity is actually greater in the background air because of higher concentrations of isoprene.

4. Quantify the relative contributions of anthropogenic and biogenic VOCs to O₃ formation.

While OH reactivity is an easily implemented way of determining the effects of biogenic VOCs on O₃ formation it can only give information on the instantaneous rate of O₃ production. By itself it does not fully address the question of where does the O₃ come from? In the Nashville study "tracer" methods were developed to distinguish the contributions of biogenic and anthropogenic VOC to O₃. One such method (Roberts et al., 1998) depended on relationships between O₃, PAN (mixed origin), PPN (anthropogenic origin), and MPAN (biogenic origin).

5. Characterize the instantaneous rates and efficiencies of O₃ formation as a function of time, location, and precursor concentrations.

Measurements of concentration fields by themselves (Objective 1), while useful for model evaluation and for estimating the overall rates and efficiencies of O₃ production, do not provide a time-

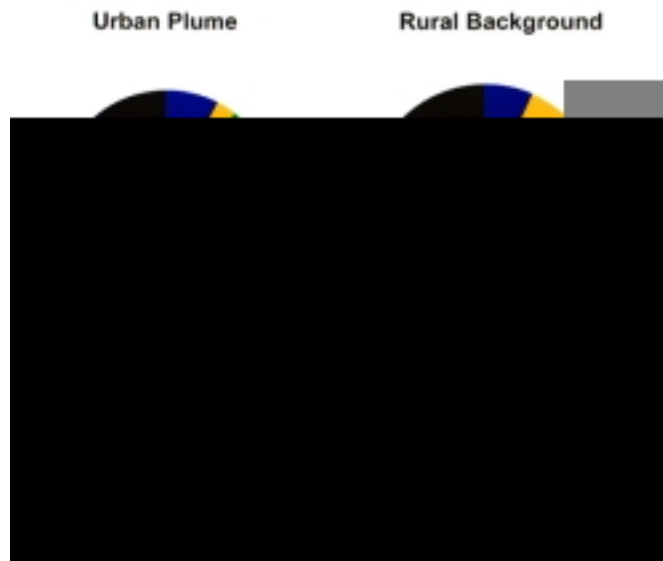


Figure 2. Comparison of the Apportionment hydrocarbon reactivity in the New York City Urban Plume and in the rural background surrounding the city.

dependent picture as they do not include the free radicals directly responsible for O₃ formation. Neither do they provide production and loss rates of O₃ and other key species such as peroxides and nitrates as a function of time and location. Although these quantities are not directly observable, they can be calculated using a photochemical box model in which the concentrations of stable species including O₃, NO, CO, and VOCs are constrained to their observed values. These calculations can yield: (1) concentrations of transient species including hydroxyl radical (OH) and peroxy radicals; (2) chemical rates of change, for example the instantaneous production and loss rates of O₃ and product species including peroxides and nitrates; (3) reaction pathway information including the sources and sinks of free radicals; and, (4) instantaneous efficiencies of ozone production with respect to NO_x and VOCs. In combination with measurements of concentration fields these calculations provide a powerful tool for understanding the quantities controlling the overall rate, efficiency, and factors limiting the total amount of O₃ produced in the Houston urban plume. Thus, we plan to develop aircraft measurement strategies for the specific purpose of gathering the data required for such calculations over a range of conditions.

6. Compare instantaneous O₃ formation rates, calculated by measurement of radical concentrations and NO, to the rates determined by calculation of radical concentrations.

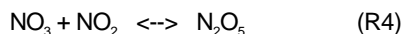
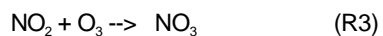
This objective constitutes a closure experiment to test our ability to calculate the instantaneous O₃ formation rate P(O₃). Under many conditions P(O₃) is well approximated by the rate at which NO is oxidized to NO₂ by peroxy radicals, i.e., that

$$P(O_3) = k_t ([HO_2] + [RO_2])[NO]$$

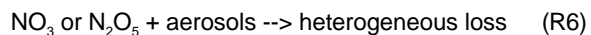
where $[HO_2] + [RO_2]$ is the total peroxy radical concentration and k_t is the weighted average rate constant for reaction of HO₂ and RO₂ with NO. Calculation of the P(O₃) thus requires the measurement of NO and some estimate of the quantity $[HO_2] + [RO_2]$. The closure experiment consists of comparing P(O₃) calculated using measured concentrations of $[HO_2] + [RO_2]$ to concentrations of $[HO_2] + [RO_2]$ estimated using various approximations. Possible ways of calculating radical concentrations include inferring the radical concentrations by calculating the deviation of the ratio of NO₂ to NO from the expected photochemical steady state (PSS) ratio that is induced with O₃ as the sole NO oxidant under given conditions of light intensity. This approach requires, in addition to NO data, high quality measurements of NO₂, O₃, and the photolysis rate of NO₂. We also plan to estimate peroxy radical concentrations by calculating the concentration of radicals using a box model constrained by measured concentrations of stable photochemical species. This approach requires a considerably larger suite of measurements than that of the PSS above, but the results are generally more robust.

7. Look for evidence for the nighttime oxidation of NO_x.

Although ozone production proceeds only during the daylight hours when photolysis rates are high, nighttime processes may also have an important effect on O₃ concentrations. Power plants, industrial facilities, and mobile sources continue to emit NO_x during the night. How much of this NO_x is available for production of O₃ the next day depends on how efficiently it is processed and removed at night. It is known that NO₂ can be oxidized to NO₃ and N₂O₅ at night (e.g., Heintz et al., 1996),



Subsequent reactions of NO₃ and N₂O₅ include:



Reaction (R3) is generally rate limiting. For many conditions the removal rate of NO_x will be of order 10% h⁻¹. Nighttime reactions can thereby severely limit the amount of NO_x that is available for the next day's photochemistry.

To accomplish this goal a significant number of coordinated nighttime observations will be required, particularly aircraft flights, since it is suspected that night time chemistry is most important in the residual layer above the nocturnal surface layer and this is generally not accessible by surface measurements. Material in this layer mixes with the surface level air the following morning and may be an important determinant of the next day's photochemistry.

Compounds of interest include those associated with the conversion of NO₂ to NO₃ and ultimately to HNO₃, organic nitrates, and aerosol products. Included are HCHO, terpenes, and other compounds that react rapidly with NO₃ and provide a pathway for removal of NO_x.

Nighttime flights for this purpose will focus on tracking the chemical evolution of the plume from an urban area or an isolated power plant or other large NO_x source. A useful strategy may be to look for evidence for the nighttime oxidation of NO_x by using either CO or SO₂ as an inert tracer and by looking for changes in the ratio of NO₂ to NO_y as a function of distance downwind of the source region. Since NO₃ is the key species in nighttime chemistry, a method for its direct measurement from an aircraft is highly desirable.

8. Determine the evolution of VOCs and oxidants from a discrete VOC emissions point source.

The tactic of making crosswind measurements at different downwind distances from a power plant plume has provided kinetic information on the oxidation of primary pollutants (i.e., NO_x and SO₂); the deposition rate of plume constituents, and the chemical production rate of O₃ and PM (Ryerson et al., 1998). There are large VOC point sources in the Houston area which should be amenable to the same observation tactic. A necessary step will be determining which of the large VOC sources do not have large NO_x sources associated with them. One possible source type is large commercial tank farms. VOC plume observations will show the effects of mixing a concentrated VOC source into a dilute NO_x containing background. Downwind traverses of the plume and adjacent background regions will provide a measure of the O₃ and PM which can be ascribed to the VOC point source. By following several VOCs with different OH reactivities it should be possible to deduce an ambient OH concentration [Parrish et al., 1992; McKeen et al., 1996]. VOC ratios determined near the stack can be compared with predictions from emission inventories. A high resolution emission inventory will be needed to locate a suitable plume, which would need to be as isolated as possible from other sources.

9. Assess the effect of concentrated source regions imbedded in the Houston-Galveston area on the rate and efficiency of ozone formation.

The Houston Galveston area includes areas of concentrated industrial activity that may emit large quantities of NO_x and VOCs. Of particular interest are regions that may emit large quantities of VOCs because O₃ formation in urban areas is usually hydrocarbon limited and the addition of large quantities of reactive hydrocarbons will increase both the rate, efficiency, and presumably the amount of O₃ that is formed, relative to the conventional mix of urban emissions which are typically dominated by transportation sources. The effect of these emissions sources may be particularly important under episodic conditions, which are frequently associated with land/sea breeze flow circulation, because of the presence of significant industrial activity to the east and to the south of Houston.

10. Examine the role of chlorine chemistry in O₃ formation.

Molecular chlorine released into the atmosphere will rapidly photolyze creating free radicals that can react with hydrocarbons and participate in the formation of O₃. In the Houston ship channel region it is estimated that about 2500 gram-moles of molecular chlorine are released per day. Under a reasonable set of assumptions regarding boundary layer height, this corresponds to a radical source strength of approximately 10⁹/cm³/day. Although this source radicals is small relative to radical production from other sources such as photolysis of ozone or formaldehyde, it may be important on a local scale. Thus, we plan to sample in the vicinity of regions with potential chlorine emissions and examine the data for the presence of species indicating the occurrence of chemical processes involving chlorine as a precursor. If Cl is an important oxidant of VOCs, the ratio of VOCs downwind from their source should reflect their relative rate constants for reaction with Cl. Alternately, the ratios would reflect the relative OH + VOC rate constants. Recent work by Mckeen et al (1996) has shown how these ratios should be interpreted when mixing processes are also affecting VOC concentrations.

11. Examine the role of regional background, urban plumes, and rural emissions in impacting regional haze and ozone that affect PM2.5 and ozone concentrations in the Dallas-Fort Worth area.

Regional photochemical grid modeling indicates that regional background, urban plumes, and rural emissions all play a role in affecting ozone concentrations in the Dallas-Fort Worth area. Refining information about the way these factors interact to impact upwind ozone and ozone in the urban area is an objective of this study.

Measurement requirements

A least two aircraft equipped with a comprehensive array of instrumentation for measuring the concentrations of ozone, ozone precursors, and photochemical product species (see list below). These aircraft would be employed for comprehensive boundary layer measurements over the sampling domain. It is also necessary to have an airborne platform capable of low altitude measurements over source regions, including downtown, and an aircraft equipped with an O₃/aerosol lidar for remote sensing of the horizontal and vertical distribution of these substances over large areas. These airborne measurements would need to be supplemented by a network of surface sites all of which measure the basic complement of O₃ and O₃ precursors, and smaller number which measure a much more comprehensive array of chemical species. It is also envisioned that the study would have a "supersite" which would include all of the basic chemical and meteorological measurements and in addition those instrument so scarce or costly to use, that they can only be deployed at a small number of sites. Examples of such instruments include O₃ aerosol lidars, single, particle mass spectrometers, and instruments that measure hydroxy and peroxy radicals.

Species that need to be measured include:

Nitrogen Oxides (NO, NO₂, NO_y, HNO₃, PAN)
 Ozone
 Sulfur dioxide
 Carbon monoxide
 VOCs
 Oxygenated hydrocarbons (including formaldehyde)
 Speciated peroxides
 NO₃
 Nitrous acid
 HO₂, RO₂, OH
 NH₃

III. Fine Particulate Matter - Formation and Characterization

In contrast to the other criteria pollutants, aerosol particles are not a single substance, but instead are mixtures of inorganic ions, organic compounds, pollen and plant waxes, soot, crustal materials, and marine salts. Particles have a wide range of sizes ranging from newly formed clusters of molecules a few thousandths of a micrometer (μm) in size to diameters of 10s of μm . Environmental effects depend on particle size and composition. Human health effects are the motivation behind the recent Federal standard for PM_{2.5}. It is an open question as to what physical properties or chemical component(s) of PM_{2.5} causes the increased mortality and morbidity seen in epidemiological studies.

Sub-micron size particles account for most of the visibility reduction in haze events. Large particle (several micron diameter) tend to be mainly crustal material such as wind blown dust and fly ash over land and marine salts over the ocean. Measurements of size distributions show, in general, that large and small particles are distinct sub-populations.

There are two families of sources for aerosol particles, direct emission (or primary) and gas to particle conversion (or secondary). Large particles tend to be from primary emissions, while small particles are formed largely by the condensation of non-volatile products of atmospheric photochemistry and to a lesser extent by the condensation of low volatility materials that were emitted in the vapor phase at high temperature. In many parts of the U.S. east of the Mississippi half or more of the small particle loading consists of sulfates, which are formed by the aqueous phase oxidation of SO₂ to sulfate, largely in non precipitating clouds or by the gas phase oxidation of SO₂ producing low volatility H₂SO₄. New particles can be formed from the heterogeneous nucleation of H₂SO₄, H₂O, and probably NH₃. Most of the H₂SO₄ condenses on pre-existing particles, which will subsequently take up H₂O and NH₃ from the atmosphere in order to maintain their equilibrium. The condensation of low volatility organic compounds can be another significant contributor to PM_{2.5}. The photochemistry that produces low volatility organic compounds is not well understood but is receiving increasing attention by the research community (e.g., Odum et al., 1997)

The atmospheric lifetime of PM_{2.5} is relatively long as the only effective removal mechanism is by precipitation. Regional haze events can cover regions that are many hundreds of km in extent and transport distances can be 1000 km or more. An important question is therefore the extent to which a given area is affected by the regional background.

Objectives

1. Characterize large-scale spatial distributions.

A measurement strategy is needed to distinguish the impacts of local sources from the baseline contributed by regional haze events. Surface observations of

PM_{2.5} are needed within the areas directly affected by local emissions and also in upwind background areas. Aircraft observations of particle number concentration would be useful in mapping out the distribution of accumulation mode particles within a several hundred kilometer region. Regional haze events, however, can have much larger dimensions, with significant impacts due to sources located 1000 km or farther away. Monitoring networks can provide data over this size domain. Qualitative information on intense regional haze episodes can be obtained under cloud-free conditions from GOES satellite pictures. Images are available every 30 minutes, thereby giving a sense of movement and source location. Airport visibility information is also useful for tracking regional haze episodes that reduce visibility to less than seven miles.

2. Characterize the evolution of an aerosol downwind of a point source.

Point source plumes afford an opportunity to study the chemistry and microphysics of the aerosol formation process by making measurement within the plume at different downwind distances. Wind speed is used to convert the known downwind distance to a atmospheric residence time, which allows determination of formation and removal rates. This type of study has yielded information on the oxidation rates of NO_x and SO₂ in power plant plumes.

Observation of the chemical constituents of the point source plumes is problematic. It is difficult to site surface stations so that they intercept a narrow point source plume. Aircraft traverses are typically too rapid to collect a large enough filter sample for analysis.

Gas phase precursor compounds can be measured with adequate spatial resolution. Measurements as a function of processing time would yield the oxidation rates of the particle precursors. The particle probes on the aircraft give size resolved information on aerosol number concentration over a range of sizes from less than 10 nm (i.e., .010 μm) to about 10 μm , and therefore could provide kinetic data on particle growth. Plume studies should be done for discrete VOC sources as well as power plants.

3. Determine the downwind influence of an urban area.

Downwind of an urban area there will be a plume containing elevated concentrations of aerosol particles due to primary emissions of aerosol in the urban area and (secondary) aerosol formed by gas to particle conversion. Comparisons with upwind measurements will show the extent to which the aerosol problem is local as opposed to regional. This comparison will also provide an identification of the chemical constituents that the urban area is contributing.

In contrast to the point source plumes, the urban plume is large enough so that there is a reasonable chance of seeing it with a surface station, and under favorable conditions it can be sampled with filters from the aircraft. If the urban plume is advected away from its source, into a relatively clean region, it should be

possible to do the types of kinetic experiments suggested for point source plumes. However, if the flows are complicated (e.g., a sea breeze or recirculation), it will be difficult to define a unique source region or processing time.

4. Characterize conditions under which new particles are formed.

It is not known whether new particle formation is an atmospherically important process in polluted regions or whether low volatility material formed by gas phase reactions is almost entirely added to existing particles. On the one hand, concentrations of particle precursors are high, so there is ample material for new particle formation. On the other hand the concentration of pre-existing particles is also high and therefore condensation of precursors on existing particles might be favored over nucleation.

The signature for new particle formation is high concentrations of ultra-fine particles. The G-1 (and P-3) will be equipped with instrumentation that will allow for the measurement of particles down to .003 μm . The first question to address is where and when are small particles observed. Areas to look at are the urban plume, forested regions, and the free troposphere. Ancillary measurements of precursors (i.e., SO_2 , VOCs) and meteorological conditions will improve our understanding of mechanisms.

5. Determine whether aerosol particles are a sink for NO_y .

A observation made by several research groups in the 1995 Nashville intensive study was rapid loss of NO_y from power plant and urban plumes (Gillani et al., 1998; Ryerson et al., 1998; and Nunnermacker et al., 1999). Loss rates were too fast to be explained by dry deposition. A possible explanation is that gas phase NO_y is being incorporated into large aerosol particles, which do not pass through the aircraft inlet systems. Gas phase plume observations should be analyzed to see if there is a similar rapid loss of NO_y in the Houston area and throughout the rural areas of the eastern half of Texas. Aircraft based plume measurements of particle concentrations and composition would allow testing the hypothesis of NO_y "loss" by gas to particle conversion.

6. Determine the role of local VOC emissions in forming $\text{PM}_{2.5}$.

VOCs with low vapor pressure can contribute to the fine PM concentrations by condensing on pre-existing particles or by forming new particles. Low vapor pressure VOCs can be emitted directly into the atmosphere, but more often they are a result of oxidation reactions in which VOCs are oxidized to form lower volatility products. The chemical mechanisms that lead to the formation of organic PM are not well understood. Preliminary observations in Houston indicate that organic carbon constitutes 20% or more of the $\text{PM}_{2.5}$ mass. An excess of organic $\text{PM}_{2.5}$ in a VOC source region relative to background could indicate a local contribution. A difficulty is distinguishing primary (i.e.,

directly emitted) organic carbon $\text{PM}_{2.5}$ from $\text{PM}_{2.5}$ formed from atmospheric reactions of VOCs. Use of tracers of opportunity can be helpful for this purpose. Tracers have been worked out for fat from cooking, for wood smoke from soft wood and from hard wood, for diesel vehicles, and for gasoline vehicles. Having tracers alone is not sufficient. Source profiles usable for the area of the study are also necessary to establish the ratio of organic $\text{PM}_{2.5}$ mass to the mass of the tracer. Source profiles for the eastern half of Texas are not currently available. Obtaining them and using them together with ambient samples to determine the contribution of source categories to $\text{PM}_{2.5}$ concentrations is an objective of this study.

Measurements at increasing downwind distance from the source areas would help distinguish between primary and secondary sources. Gas phase VOC observations would indicate possible precursors of the organic fraction. This data set will not reach its full potential immediately following the field program, as much laboratory and modeling work needs to be done to draw the connection between the gas and particle phase.

Measurement Requirements

In addition to the list of trace gas species given under measurement requirements in Chapter II, the required measurements include:

1. Continuous vertical profiles of aerosol extinction at one or more sites in the project area (i.e., lidar measurements).
2. Measurements of chemical composition on the aircraft and at multiple surface sites in the project area. Chemical composition to include at least EC, OC, and major inorganic species.
3. Measurements by aircraft and at one or more surface sites of the number concentration and size distribution of particles from .003 μm to 3 μm .
4. Measurements of single particle chemical composition at one or more surface sites.
5. Continuous measurement of aerosol mass at multiple surface sites.

IV. Emission Inventories

An accurate emission inventory is an essential input to photochemical grid models used to evaluate the effectiveness of control strategies. For predicting O_3 levels it is crucial to know the absolute emission rates of NO_x and speciated VOCs. If results of work in progress indicate that molecular chlorine (Cl_2) may have a significant impact on O_3 formation, a similar emission inventory for Cl_2 will also be necessary. Prediction of PM requires emission rates of primary and precursor compounds (i.e., SO_2 , NO_x , VOCs, NH_3). Significant attributes of the inventories include geographic distribution, time dependence, breakdown by source category, and the relative importance of anthropogenic and biogenic sources. Because of the importance of biogenic emissions in the formation of ozone in the eastern half of Texas, and the uncertainties inherent in estimating biogenic emissions, it is especially important to have field measurements that can evaluate the performance of the biogenic emission inventory, and determine the importance of these emissions in forming ozone and aerosol particles

It is widely felt that poor quality emission inventories are a major source of discrepancies between model predictions and observations. As such, emission errors can confound the task of evaluating other model components. This section includes a description of on-going activities by TNRCC directed at improving the accuracy of the emission inventories needed for modeling the east Texas region. The Texas 2000 field study will provide observations needed for emission inventory evaluation.

Specific objectives are to:

1. Develop an episode specific emission inventory for the period of the Texas 2000 field study.

Develop a speciated, geographically distributed, point source emission inventory including (a) the emission parameter information needed for modeling and (b) the information on hour by hour variation from standard emission rates typical of the study period. Develop an area source emission inventory relying to the extent possible on bottom-up approaches rather than allocation of national or regional estimates. Develop a mobile source emission inventory with hourly diurnal patterns for each day of the week for summer vacation and for school in session traffic patterns. Collect information on unusual traffic patterns caused by major disruptions including traffic accidents, construction, and weather.

2. Improve the accuracy of the anthropogenic emissions inventory.

Inaccuracies in the existing inventory were demonstrated in the COAST field program. Observed VOC/ NO_x ratios were a factor of 2 higher than emission estimates. The TNRCC has been contracting for significant work to improve both the VOC and the NO_x emission inventories. There are projects completed or underway to improve emission estimates for gasoline

refueling, construction equipment, and ship emissions while in port. During the summer of 1999 the TNRCC will have contract work underway to improve VOC and semi-volatile organic compound (S-VOC) source profiles for gasoline, mobile sources, the Ship Channel, and some categories of area sources in the Houston area. This work will include S-VOC ambient sampling and chemical mass balance analysis to evaluate the performance of the current emission inventories in estimating the contribution of the various source categories to VOCs and S-VOCs in the Houston area. There are substantial additional sources for which emission estimates need to be improved.

3. Evaluate the accuracy of the anthropogenic emissions inventory.

Ratios of CO, NO_y , and VOCs observed in source regions will be compared with the corresponding quantities derived from emission estimates. Surface samples and low altitude aircraft samples will be used.

4. Assess the possibility that large, unscheduled, and undocumented VOC releases may be involved in some unusually high ozone events near the Ship Channel.

The TNRCC is preparing to test a system for taking canister samples for VOCs in response to high ozone concentrations and in response to high VOC concentrations. The canisters will be analyzed to determine whether there are unusual concentrations or unusual VOC species present, which might indicate unusual releases. The limitation of this work is that fewer than 100 specific chemicals can be identified and quantified using the available analytical procedures. The scope of this activity will be enlarged during the field intensive by aircraft sampling and possibly by the detection of additional compounds.

5. Improve the accuracy of the biogenic inventory

Data from the COAST experiment indicates that biogenic VOC emissions in the Houston area may have been overestimated by a factor of three. The TNRCC has been working, to the extent its resources have allowed, to resolve the uncertainties. New biogenic emission inventories have been prepared for the eastern part of Texas using resources available to the TNRCC and the near-nonattainment areas in the state. The data on plant species and biomass density are being assembled into a single database. In the summer of 1998 the TNRCC supported combined university-National Center for Atmospheric Research (NCAR) check of the inventory in a number of locations by measuring the flux of emitted biogenic compounds. In the summer of 1999 the TNRCC will be supporting an observation-based approach to checking the accuracy of the biogenic emission estimates: measuring products of isoprene reactions to determine how much of the ozone in the air being sampled is the result of isoprene reactions.

V. Modeling

The TNRCC is charged with the task of using photochemical grid models to evaluate steps needed to bring regions into compliance with the NAAQS for O₃. Photochemical models and the associated meteorological drivers will also be used by a broader research community to study processes. These two types of applications can, of course, overlap.

Regulatory calculations have been done by the TNRCC using the mesoscale chemical grid models, UAM-IV, UAM V, and CAMx with the meteorological fields provided by CSUM, RAMS, and SAIMM. Model performance for regulatory applications is judged by a series of graphical and statistical comparisons between observed and predicted values for O₃. For the Dallas-Fort Worth area and for the eastern part of the state, model performance was judged to be satisfactory. It was also satisfactory for some types of episodes in the Houston area. However, the models do not perform adequately for the type of flow reversal episodes over the Ship Channel that typically produce the highest ozone in Houston.

It is an overall goal of the Texas 2000 field study to improve model performance by providing an enhanced set of observations for model inputs. Performance will also be improved by using the field observation to test model components and to diagnose problems. An enhanced set of meteorological and chemical observations will be useful for both the regulatory models and for other more process oriented applications. An important output from the evaluations will be determination whether the chemical mechanisms currently available for ozone and for PM_{2.5} grid modeling are adequate to deal with processes in the upper Texas Gulf coast and the eastern half of Texas.

Specific objectives are:

1. Assemble model inputs using the enhanced observations.

The MM5 model will be used to improve simulation of the complex vertical and horizontal flows found along the coast and around Galveston Bay and the barrier islands. Extra soundings will be used as input to MM5 with the expectation that this will produce a better representation of the coastal re-circulation and of mixing heights. Recognizing the fact that an enhanced sounding network is not always available, it may be possible to test the value of such observations by running MM5 with and without the extra soundings. Chemical measurements over the Gulf and above the boundary layer will help define initial and boundary conditions. It should be recognized, however, that aircraft observations are sparse in relation to the data needed to define a concentration field over the modeling domain. Hence the aircraft observations are best used to determine characteristic boundary and initial conditions rather than exact realizations.

2. Conduct a model-observation comparison for O₃ and its precursors following the usual graphical and statistical criteria.

As part of this activity questions will be addressed regarding effects of emission controls and regarding the apportionment of the O₃, PM_{2.5}, and regional haze to local and to regional sources.

3. Determine whether chemical and mixing processes are accurately represented in the models.

Measurements of precursors, chemical intermediates, and products of photochemical reactions are needed to determine whether the current chemical mechanisms and mixing algorithms in the regulatory photochemical grid models are adequate to simulate the Houston-Galveston area and other large urban areas that extend over many miles. Measurements will have to be taken both at the surface and aloft. Points of comparison between predictions and observations will include: 1) spatial patterns of chemicals reflecting their dispersion and chemical removal; 2) vertical profiles reflecting the competition between mixing and chemical transformation; 3) nighttime concentration fields reflecting transport and transformation in the nocturnal boundary layer 4) ratios of product species (i.e., O₃/NO₂, H₂O₂/NO₂) reflecting chemical pathways, 5) ratios of primary species (i.e., HC/NO_x, CO/NO_x) reflecting emission rates; 6) ratios of oxidation products (i.e., PAN, PPN, and MPAN) reflecting biogenic vs. anthropogenic sources of O₃; 7) other indicators of biogenic oxidation including HCHO; and 8) concentrations of aerosols and aerosol precursors.

The flow reversal that is associated with the highest ozone events in the Houston area involves rapid addition of fresh VOC and NO_x emissions into an aged photochemical mixture. Evaluate existing chemistry mechanisms in the models to determine whether they need to be modified to simulate this situation adequately.

Of particular importance is the correct representation of oxidation rates by OH and other oxidants. Ratios of primary compounds and oxidation products (i.e., NO_x/NO_y) along with VOC ratios will be used to test model predictions.

Chlorine chemistry is not included in regulatory models but may be significant. The TNRCC has contracted for university laboratory and field work to evaluate the possible impact of molecular chlorine (Cl₂) on ozone formation in the Houston area. Preliminary outdoor smog chamber runs using a VOC/NO_x mixture designed to be typical of the Houston urban area suggest the following effects: Addition of less than 1 part per billion (ppb) of Cl₂ increases the rate of ozone formation but does not increase the maximum amount of ozone produced (approximately 100 ppb). Addition of over 10 ppb Cl₂ both increases the rate of ozone formation and doubles the concentration of ozone produced. The next steps in this work are first, to attempt to identify chlorinated chemical products that indicate the participation of chlorine in the reactions that

lead to ozone formation. Second, to analyze ambient air samples to determine whether such chlorinated products are present in ambient air downwind of Cl_2 sources in the Houston area.

4. Compare model predictions of the sensitivity of O_3 to emission changes to other indicators of O_3 sensitivity.

Ozone control measures are conventionally evaluated using an emissions based photochemical model. Another approach is that of observational based analysis (Sillman, 1995; Cardelino and Chameides, 1995; Kleinman et al., 1997, Daum et al., 1999) in which observed concentrations are used to make predictions about O_3 formation. An advantage of the latter approach is that there is less reliance on estimates of emissions. A limitation is the accuracy of the ambient measurements. Under the general heading of observational based methods are procedures for deducing O_3 formation rates and sensitivities from a set of observations such as can be made from an aircraft at a single point in time. Also, there are indicator species methods in which NO_x or VOC sensitivity is related to the ratio of two photochemical products, e.g., $\text{H}_2\text{O}_2/\text{NO}_z$ or O_3/NO_z . These techniques are particularly useful when they are used to evaluate Eulerian model results (Sillman, 1995).

5. Address questions relating to aerosol sources and effects of control measures.

The modeling of aerosol formation is not as advanced as that for O_3 control and thus the use of the PM data set in calculations will likely lag behind that for

oxidants. However, in view of the fact that initial PM_{2.5} measurements indicate that PM_{2.5} concentrations in some areas of Houston may exceed the annual standard and that the Dallas-Fort Worth area will be close to the standard, several questions can be posed:

- 1) If sulfur dioxide emissions are reduced in the Houston area to reduce ammonium sulfate concentrations, what is the relationship of ammonium sulfate reductions to sulfur dioxide reductions? What is the relationship between regional reductions in sulfur dioxide emissions and reductions in sulfate in the Houston and Dallas-Fort Worth areas?
- 2) If sulfur dioxide emissions are reduced to reduce ammonium sulfate concentrations, how much will ammonium nitrate concentrations increase because of increased ammonia available to react with nitric acid to produce ammonium nitrate?
- 3) Do the industrial emissions of volatile organic compounds (VOCs) and semi-volatile organic compounds (S-VOCs) in the Houston area lead higher concentrations of particulate phase organic compounds than in urban areas that do not have these emissions?
- 4) Is the amount of PM_{2.5} formed locally by atmospheric reactions in the Houston area strongly dependent on the amount of photochemical activity, or is it mainly dependent on emissions of precursors and on dispersion conditions?

REFERENCES

Angevine, W.M., A.W. Grimsdell, S.A., McKeen, and J.M. Warnock, Entrainment results from the Flatland boundary layer experiments., *J. Geophys. Res.*, 103, 13,689-13,702, 1998.

Cardelino, C.A. and W.L. Chameides, An observation-based model for analyzing ozone precursor relationships in the urban atmosphere, *J. Air Waste Manage. Assoc.*, 45, 161-180, 1995.

Carter, W.P.L., Development of ozone reactivity scales for volatile organic compounds, *J. Air Waste Manage. Assoc.*, 44, 881-899, 1994.

Daum, P.H., et al., Analysis of the processing Nashville urban emissions on July 3 and July 18, 1995, *J. Geophys. Res.*, accepted, 1999.

Gillani, N.V., M. Luria, R.J. Valente, R.L. Tanner, R.E. Imhoff, and J.F. Meagher, Loss rate of NO_y from a power plant plume based on aircraft measurements, *J. Geophys. Res.*, 103, 22,585-22,592, 1998.

Kleinman, L.I., et al., Dependence of ozone production on NO and hydrocarbons in the troposphere, *Geophys. Res. Letters*, 24, 2299-2302, 1997.

Kleinman, L.I., et al., Ozone formation at a rural site in the southeastern United States, *J. Geophys. Res.*, 99(D2), 3469-3482, 1994.

Neu, U., T. Kuenzle, and H. Warner, On the relation between ozone storage in the residual layer and daily variation in near-surface ozone concentration - a case study, *Bound. Layer Meteor.*, 69, 221-247, 1994.

McKeen, S.A., S.C. Liu, E.-Y. Hsie, X. Lin, J.D. Bradshaw, S. Smyth, G.L. Gregory, and D.R. Blake, hydrocarbon ratios during PEM-WEST A: A model perspective, *J. Geophys. Res.*, 101, 2087-2109, 1996.

Odum, J.R., T.P.W. Jungkamp, R.J. Griffin, R.C. Flagan, and J.H. Seinfeld, The atmospheric aerosol-forming potential of whole gasoline vapor, *Science*, 276, 96-99, 1997.

Parrish, D.D., C.J. Hahn, E.J. Williams, R.B. Norton, F.C. Fehsenfeld, H.B. Singh, J.D. Shetter, B.W. Gandrud, and B.A. Ridley, Indications of the photochemical histories of Pacific air masses from measurements of atmospheric trace species at Point Arena, California, *J. Geophys. Res.*, 97, 15,883-15,901, 1992.

Roberts, J.M., et al., Measurements of PAN, PPN and MPAN, made during the 1994 and 1995 Nashville intensives of the Southern Oxidants Study: Implications for regional ozone production from biogenic hydrocarbons, *J. Geophys. Res.* ????

Ryerson, T.B., et al., Emissions, lifetimes and ozone formation in power plant plumes, *J. Geophys. Res.*, 103, 22,569-22,584, 1998.

Sillman, S., The use of NO_y , HCHO , H_2O_2 and HNO_3 as indicators for ozone- NO_x -hydrocarbon sensitivity in urban locations, *J. Geophys. Res.*, 100, 14,175-14,188, 1995.

APPENDIX 1. SCIENTIFIC QUESTIONS

The following is as list of scientific questions that has driven the construction of this document. They are organized according to the titles of the chapters that they correspond to.

Atmospheric Dynamics and Transport

- What is the fate of plumes during the night and day/night transitions Transport?
- How does the sea-breeze influence the peak/duration of urban O₃/PM concentrations?
- How does the sea-breeze circulation affect regional O₃/PM concentrations?
- How does entrainment/detrainment influence the concentration of pollutants near the surface?
- How far are precursors transported overnight?
- What factors control the height and intensity of mixing of the PBL? Do these factors vary between urban and rural areas?

Ozone Formation and Distribution

- What is the influence of biogenic VOCs on production/evolution of O₃/PM on emissions from point sources?
- How is O₃/PM formation/evolution altered when point sources are in the urban plume?
- What is the influence of biogenic emissions on evolution of O₃/PM in Dallas/Fort Worth versus the Houston urban plume?
- What effect does Cl₂ chemistry have on odd hydrogen production and overall reactivity?
- What are the relative rates/contribution of anthropogenic and biogenic VOCs?
- Does the rate of photochemical formation of O₃/PM change with wind direction over the urban regions of Houston or Dallas/Fort Worth?
- What is the fate of NO_x in urban and power plant plumes during the night time transport? How much NO_y is removed/converted during the night? How much is available to participate in photochemistry the following day
- What is the spatial distribution of pollutants sources? What does this say about source receptor relationships?
- What are the factors that control the rate and amount of O₃ and PM in urban and power plant plumes? How fast? How much? How efficient?
- What is the effect of intense point sources of VOC and NO_x on the rate and efficiency of PM formation.

Aerosol Formation, growth, and distribution

- What are the factors that control the formation, characteristics, and distribution of PM_{2.5} in eastern Texas?
- What is the chemical composition of PM_{2.5} in rural and urban areas.
- How is the composition and morphology of PM_{2.5} influenced by transport in the marine boundary layer? What is the role of marine aerosols?
- What is the relationship between secondary aerosol and ozone formation?
- Are their differences in the rate, efficiency and amount of PM in urban and power plant plumes?
- What factors control aerosol nucleation, and growth, and size distributions?
- What is the influence of natural and anthropogenic VOCs on the formation and optical properties of PM_{2.5}?
- How well is the organic fraction of PM_{2.5} mass quantified by the FRM?
- Where do high regional backgrounds of O₃ and PM_{2.5} come from?

Emission Inventories

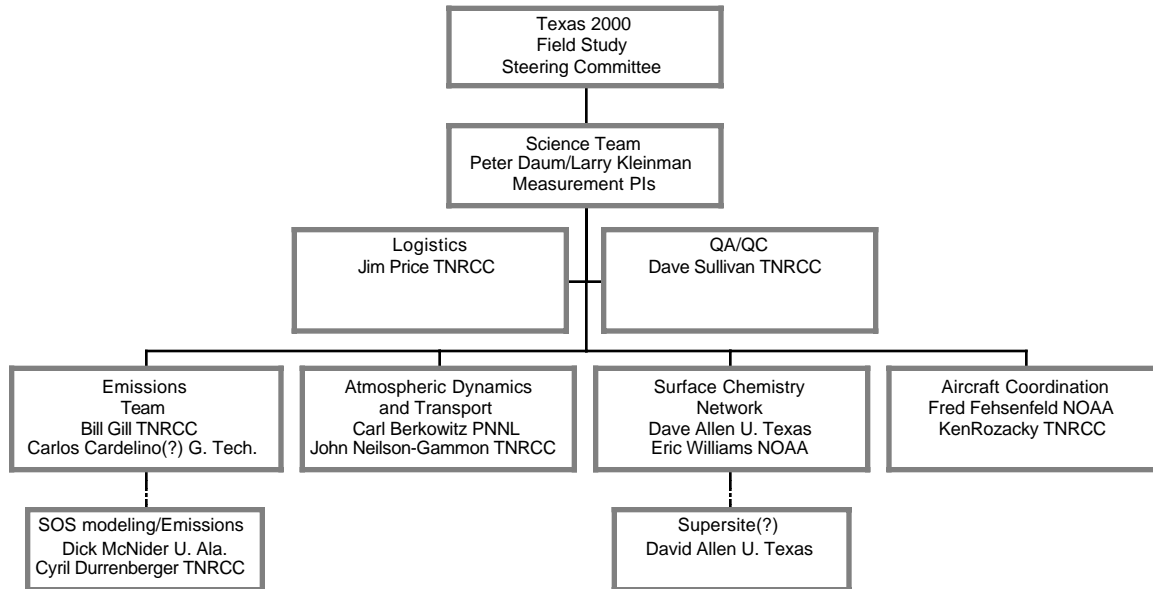
- What are the primary aerosol sources and how do they compare with inventories?
- Are the high values of observed VOC/NO_x ratios due to inaccuracies in the emissions inventories of hydrocarbons, NO_x, or both?
- Are large, unscheduled, and undocumented VOC releases involved in unusually high ozone events near the Ship Channel?
- How well are biogenic emissions represented in the inventories?

Modeling

- How well do current Air Quality models represent the concentrations and physical distribution of pollutants in the atmosphere?
- Do regional NO_x, SO₂, VOC, CO measurements compare well with model predictions?
- Are chemical and mixing processes accurately represented in models?
- How well do model predictions of the sensitivity of O₃ to emissions changes compare to other indicators of O₃ sensitivity?

APPENDIX 2. ORGANIZATIONAL STRUCTURE

The preliminary organizational structure for the Texas 2000 Field study is shown the chart below.



Texas 2000 Field Campaign Organizational Structure