ACCELERATED SCIENCE EVALUATION of OZONE FORMATION IN THE HOUSTON-GALVESTON AREA:

Photochemical Air Quality Modeling

Daily Max O3 Conc (ppb) : Layer 1



February 17, 2002

Summary

This document summarizes key photochemical modeling issues that are being addressed in the Accelerated Science Evaluation of ozone formation in the Houston-Galveston area. Comprehensive photochemical models are important because they reveal whether current data and models for meteorological processes, chemical processes, and emissions are accurate representations of the region being modeled and because the models are used to assess the effectiveness of proposed air quality regulations.

The report focuses on the ability of current photochemical models to predict the magnitude, spatial distribution and temporal distribution of air pollutants in the Houston-Galveston (HG) area, and is organized into the following sections:

1.) *Previous applications of photochemical grid modeling in the HG area.* The results of previous modeling, the spatial and temporal scales used in the models, and the procedures used to describe emissions, chemistry and meteorology in the models are described. Performance evaluations of the modeling suggest that current photochemical models are capable of simulating ozone formation in most urban areas, and most ozone formation events in the HG area. However, certain types of rapid and efficient ozone formation that occur in the HG area are not well replicated in current models. Observational data collected during the 2000 Texas Air Quality Study (TexAQS) indicate that these rapid and efficient ozone formation events are primarily associated with areas of high industrial emissions containing high concentrations of hydrocarbons.

There is no clear scientific consensus concerning the reasons why current models are not able to replicate rapid and efficient ozone formation observed in the HG area, so a variety of hypotheses are being investigated. In this report, the hypotheses will be classified into three categories: data inputs to the model, chemical and physical processes described by the model and the computational structure of the model.

2.) *Model input data.* Photochemical air quality models require data on emissions, meteorology, and other parameters. As documented in the Accelerated Science Evaluation report on Emission Inventories, data from TexAQS suggest that the emissions of light hydrocarbons from industrial sources in the HG area are underrepresented in the models. If these emissions were adequately characterized in the models, it is possible that the rapid and efficient ozone formation might be replicated. A number of studies are underway to investigate this hypothesis.

Another possible reason for the inability of current models to replicate rapid and efficient ozone formation is that the meteorological data inputs are not adequately describing the mixing and dispersion of industrial plumes. For example, data collected during TexAQS indicated the presence, on some days, of low level jets. These phenomena have not yet been replicated by meteorological models applied on the days when jets were observed. If these, or other, meteorological phenomena cause mixing that promotes ozone formation, the accurate modeling of these

phenomena may allow the models to replicate the observed rapid and efficient ozone formation.

3.) *Chemical and physical processes.* As described in the Accelerated Science Evaluation report on Atmospheric Chemistry, current mechanisms describing the reactions that form ozone will accurately predict rapid and efficient ozone formation in laboratory experiments, if the concentrations of ozone precursors are sufficiently high. This does not necessarily mean that the chemical mechanisms are complete or entirely accurate. Certain chemistries that are not currently in the mechanisms may be significant in the HG area, however, it is unlikely that these chemistries are the dominant phenomena associated with most rapid and efficient ozone formation events.

In contrast, some of the models for physical processes (advection, diffusion, deposition) embedded in current gridded photochemical models appear to cause plumes to be dispersed more rapidly than observed during TexAQS. It is not yet clear if this is due to inaccurate meteorological inputs or inaccurate parameterizations of advection, turbulent diffusion processes, and deposition in the models. Studies currently underway will help to resolve this issue. It is clear, however, that if the model allows relatively high concentrations of ozone precursors to persist for periods of approximately an hour, and if upset emissions are included in the emissions inventory, then the chemistry will yield rapid and efficient ozone formation, similar to even the most extreme events that occur in the region.

4.) *Computational structure of the model* A number of issues associated with processing of information within comprehensive air quality models (e.g., numerical processing of the interfaces between nested grids, the conversion of meteorological model grids to photochemical model grids) are being investigated. These topics deserve attention but are unlikely to be the reason for the inability of the model to replicate observed rapid and efficient ozone formation events.

So, several hypotheses are being investigated to explain the inability of current photochemical models to replicate rapid and efficient ozone formation in the HG area. One set of hypotheses suggests that emission and meteorological inputs to the model may be inaccurate or may lack sufficient spatial or temporal resolution, and that if the input data are improved, the model will predict rapid and efficient ozone formation. A second group of hypotheses suggests that even if the input data are improved, the model will not predict rapid and efficient ozone formation, diffusion and/or deposition are incorrectly parameterized.

Ongoing projects should help to resolve these issues and subsequent versions of this document will describe relevant findings.

This report will build on other reports developed in the Accelerated Science Evaluation of ozone formation in the Houston-Galveston Area. Issues related to the chemistry used in the photochemical grid models in the HG area are covered in the report entitled

"Atmospheric Chemistry". Issues related to the emissions used in photochemical grid models in the HG area are covered in the report entitled "Emissions Inventories". Issues related to selection of episode days, and the development of meteorological parameters is covered in the report entitled "Meteorology".

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Background

Photochemical air quality models take data on meteorology and emissions, couple the data with descriptions of the physical and chemical processes that occur in the atmosphere, and mathematically and numerically process the information to yield predictions of air pollutant concentrations as a function of time and location. This flow of information in photochemical air quality models is shown conceptually in Figure 1.

Figure 1. (adapted from Russell and Dennis, 2000)



Photochemical air quality models provide predictions of air pollutant concentrations as a function of time and location and these predictions can be compared to ambient observations of air pollutant concentrations. The comparisons reveal whether current data and models for meteorological processes, chemical processes, and emissions are accurate representations of the region being modeled. The process of comparing model predictions to ambient observations is referred to as a performance evaluation and will be described at more length later in this report. Photochemical air quality models can also be used to assess the sensitivity of air pollutant concentrations to changes in meteorological and chemical models, or to changes in emissions.

There are two basic types of photochemical air quality models used in regulatory applications. The simplest type of photochemical model is a "box" model. This model places a three dimensional box over an area that is to be simulated and then calculates the temporal evolutions of air pollutant concentrations assuming the box is well mixed. This type of box modeling is frequently used to evaluate chemical mechanisms based on smog chamber experiments. A modification of the box model is the Empirical Kinetic Modeling Approach (EKMA) that has been used in the past by many states (California, Texas, New York, and others) for development of ozone control plans. More rigorous photochemical air quality modeling employs grid models. In this approach a fixed three-dimensional grid network is defined over the region to be modeled and all of the emissions, chemical processes and physical processes are accounted for in each grid cell. This is shown conceptually in Figure 2. Modeling is performed over a time period (episode) usually based on one hour increments for a period of several days. A reporting period of one hour is typically used for presenting photochemical modeling results to be consistent with monitoring data that is normally reported in one hour increments. For regions that do not meet the National Ambient Air Quality Standard (NAAQS) for ozone and that are designated as extreme, severe, or serious (this includes all of the ozone non-attainment areas in Texas), the Federal Clean Air Act Amendments for 1990 (FCAA, 1990) require that photochemical grid models be used in assessing the air quality benefits of emission reductions (FCAA, 1990). The FCAA allows areas that are classified as moderate to use the EKMA approach.



Figure 2. Eulerian (fixed grid) modeling approach

Photochemical grid models have been used over modeling domains of many sizes ranging from coverage of a city to coverage of the contiguous 48 states. Modeling is routinely performed with horizontal grid cell dimensions ranging from 1 km to 16 km or

more, depending on the size of the region to be modeled. Modeling with a horizontal grid cell smaller than 1 km has not been routinely performed in the past, but is being investigated.

Recently models have been developed that can use nested grids that cover a large area. Typically the urban area of interest is covered by a fine grid (4km). A larger area surrounding the urban grid may contain sources of interest that may impact the urban grid. This larger area is covered by a medium grid (12 to 16 km) that surrounds the urban area. In order to minimize the impact of boundary conditions, a large grid (32 to 36 km) is placed over the area surrounding the medium grid. With the nesting grid capability all of these areas can be modeled at the same time, instead of making separate model runs for each sized grid.

The use of a grid to characterize the region introduces an important set of spatial resolution questions. Within each grid cell, the atmosphere is assumed to be uniformly (well) mixed. Concentrations of air pollutants, wind speeds, wind directions, temperatures and other parameters used in model calculations represent an average value for the grid cell. As smaller and smaller grid cells are used, this assumption becomes more reasonable; however, use of small grid cells places enormous data and computational demands on the model. Emissions and other input data must be resolved at the same spatial scale as used in the grid cells. Achieving an appropriate balance between the accuracy of the model is one of the most difficult challenges in formulating photochemical grid models. In most regions, grid cells of 1-4 kilometers in horizontal dimension and 20 - 500 meters in vertical dimension are the smallest considered implementable. This spatial scale is clearly too large for characterizing some phenomena, such as air pollutant formation in plumes from point sources, so many grid models employ special approaches for selected sub-grid cell processes, such as plumes.

The selection of a spatial scale for a grid model also implicitly suggests a temporal scale. Grid models typically compute the temporal distribution of air pollutant concentrations using a computation time step and report results using a fixed reporting time. The length of the computation time steps depend on the time scales of the processes being modeled and size of the grid cells, but are generally less than one minute for urban modeling. The most frequently used reporting time periods have been 15 minutes to one hour based on sets of consecutive 24-hour days that have grouped into multi day episodes. Just as with concentrations, wind fields and other parameters are assumed to be constant over the spatial scale of a grid cell and these parameters are also assumed to be constant over a computation time step.

For each calculation time step in each grid cell the model calculates the time rate of change of air pollutant concentrations by evaluating the time derivative of the concentration. The sequence of the calculations varies with the model, but for the Comprehensive Air Quality Model with extensions (CAMx) used by the TNRCC the sequence is:

Time derivative (dC_i/dt) of the concentration = (Equation 1) change due to emissions + change due to advection (transport) in horizontal + change due to advection in vertical + change due to vertical diffusion + change due to horizontal diffusion + change due to removal processes + change due to chemical reactions

Over the computation time step, all of the pollution generation (addition) and pollution depletion (loss) processes are assumed to occur at constant rates, so dC_i/dt is constant over the time step. Concentrations in the grid cells in the next time steps are calculated by multiplying the time derivative by the length of the time step ($\Delta C = dC_i/dt *$ length of time step) and adding the result to the concentrations present at the start of the time step. The length of the time step varies based on a number of parameters, including meteorological conditions (mainly wind speeds) and chemical reaction rates. The exact formulation depends on the particular grid model being used.

Previous applications of photochemical grid models in the HG area

The goals for the application of a photochemical grid model to an area are to accurately predict ozone concentrations over the area in space in time and to accurately predict the sensitivity of ozone formation to changes in the magnitude, location and timing of emissions. Typically, the approach has been to develop a base case that replicates an historical episode. Using estimates of meteorological parameters and emissions based on historical data, the model must be able to accurately predict the air pollutant concentrations that were measured during the episode. Once it is established that the model can perform adequately, future emissions for a target attainment year are developed. Then proposed control strategies are applied to this future emissions inventory and the model run with the past meteorological conditions to determine the response of ozone to the reductions. Using this process in an iterative fashion, a set of control strategies are selected for a State Implementation Plan (SIP).

The EPA has designated the eight county HG area as a severe ozone nonattainment area, and therefore the TNRCC must develop and submit to EPA a SIP that shows how the area will attain the 1-hour ozone standard by 2007. The Federal Clean Air Act amendments of 1990 (FCAA) require that photochemical grid modeling must be used to develop the SIP. For the HG area the TNRCC has submitted ozone SIPs prior to 1988 and in 1994, 1998, 1999 and 2000. The photochemical grid modeling used in each of these SIPs is different and will be briefly described below.

EKMA

The Texas Air Control Board (TACB), one of the precursor agencies for the TNRCC, used the Empirical Kinetic Modeling Approach (EKMA) to develop State Implementation Plans (SIP) for ozone submitted to EPA prior to 1988. The EKMA approach is a simple box model with the carbon bond IV chemistry (EPA, 1981). This approach relates peak ozone levels to concentrations of reactive non-methane hydrocarbons (NMHC) and oxides of nitrogen (NO_x). The model develops ozone isopleths based on morning NMHC and NO_x concentrations, emissions of NMHC and NO_x, simple meteorological conditions, and a chemical mechanism to calculate ozone concentrations.

Prior to 1988, using the approach that EPA required at the time, the TACB submitted SIPs based on EKMA modeling. Days when the 1-hour ozone standard was exceeded were identified. Hourly emissions of ozone precursors were determined for the whole area being modeled (usually the county). For each day being modeled, morning levels of NMHC and nitrogen oxides (NO_x) were determined based on monitoring data or estimated based on NO_x levels and median values of the NMHC to NO_x ratios over the time period. Then it was assumed that at 8:00 am on the morning of each day being modeled, and then moved to the monitor site exceeding the standard. Calculations were made for each hour of the simulation, with the final hour being the hour that recorded the largest concentration on that day at the site being modeled. For each hour, the emissions from the area were added to the air parcel and the air parcel height grew with the mixing height for that hour. It was assumed that the air parcel volume was well mixed.

To use the results, the model was required to estimate the ozone concentration within 30 percent of the maximum monitored ozone concentration at that site for that day. The model developed an "EKMA" diagram relating the concentrations of NMHC and NO_x to ozone concentrations. From this diagram the user determined the percentage reduction of NMHC that was necessary to attain the standard. This modeling was performed for each day the standard was exceeded and the largest reduction to attain the standard for all days modeled was used for the SIP. The EKMA approach provides an estimate of the percent reduction of NMHC to attain the standard. The approach does not address the difference in reactivity of various components of NMHC, does not address the spatial distribution of the emissions, nor can it be used to predict ozone concentrations with emissions projected to a future year. The assumption for the advection from the center of the city to the monitor is not appropriate for most locations in Texas. In Texas, EKMA modeling was performed for the HG area, Dallas, Fort Worth, and El Paso.

UAM-IV

Early in the EKMA modeling it became evident that the EKMA process would be not be adequate to simulate the complex emissions and meteorological conditions found in all Texas nonattainment areas. In 1988 the TACB purchased the Urban Airshed Model version IV (UAM-IV) and had its staff trained to use the model. At that time the UAM-

IV was the state-of-the-science photochemical grid model and was listed by EPA in the "Guidelines on Air Quality Modeling" (EPA, 1986) as a preferred air quality model for ozone modeling. The TACB had a consultant use the UAM-IV to model the HG area with a set of historical data. One of the strong recommendations from that initial modeling was that a field study should be performed to obtain data to use in running and evaluating the performance of a photochemical grid model in the HG area. As a result, the TACB conducted the Coastal Oxidant Assessment for Southeast Texas (COAST Study) in 1993. The main purpose of this study was to collect data sets for use in photochemical modeling. The COAST study was performed in conjunction with a field study conducted by the US Minerals Management Service (MMS, 1995).

The 1990 FCAA required the TACB to submit, by 1994, a SIP based on photochemical grid modeling. It was not possible to develop modeling based on the COAST study in that time period, so TACB performed UAM-IV modeling with three historical episodes that occurred prior to 1993. The staff reviewed the meteorological and monitoring data for years prior to 1992 and identified three episodes to model. These were in May 1988, July 1990, and October 1991. The emissions were based on the 1990 emissions inventory (EI) that was developed as a part of the requirements of the 1990 FCAA.

The Colorado State University Mesoscale Model (CSUMM)(Kessler, 1989) prognostic meteorological model was used to develop the meteorological inputs for the UAM-IV model. The grid cells were 5 km x 5 km over a domain that covered the HG and Beaumont/Port Arthur areas as shown in Figure 3. This modeling used 5 layers in the vertical. The UAM-IV has vertical layers that change hourly in height based on the hourly rise and fall of the mixed layer. Two vertical cells were located below the mixing height and three were located above the mixing height. Boundary conditions came from national scale modeling that EPA conducted with the Regional Oxidants Model (ROM). In some cases boundary conditions and initial conditions were developed from monitoring conditions and "clean boundary" conditions defined by EPA (EPA, 1991).



Figure 3. Coast Modeling Domain

The May 1988 episode had marginal model performance, the July 1990 episode had performance that generally met EPA criteria, and the October 1991 episode had unacceptable model performance. Modeling from the May 1988 and July 1990 episodes was used for the SIP that was submitted in 1994 (TNRCC, 1994). The modeling followed the EPA recommendations in "Guideline for Regulatory Application of the Urban Airshed Model" (EPA, 1991). However, the TNRCC indicated that this was a temporary SIP to be replaced by one with modeling based on episodes that occurred during the COAST study period.

COAST

The COAST study was conducted in July and August 1993. During this period the number of surface monitoring sites continuously measuring ozone and meteorological parameters was increased. Radar profilers and acoustic sounders were installed to measure meteorological parameters in the upper air. On selected days airborne sampling was conducted. Continuous gas chromatographs were located at two sites where hourly

concentrations were measured for 55 hydrocarbon compounds. These measurements formed a robust data set that was used by TNRCC to provide inputs to run photochemical grid models and evaluate their performance.

For the time during the COAST study, the emissions inventory (EI) was enhanced beyond that normally developed by collecting activity data for the 14 area and non-road source categories that contributed most to the emissions. Estimates of biogenic emissions were enhanced with a survey of local vegetative species and biomass densities. Results from travel demand modeling were used to develop episode day-specific, link based, hourly on-road mobile emissions. For eight episode days, hourly, speciated point source emissions were developed based on actual emissions.

UAM-V

In addition to the robust COAST data set, a variable grid version (UAM-V) of the UAM was used. This enhanced photochemical grid model had a number of new features:

- 1. The grid structure for vertical cells was fixed in space and time.
- 2. The model could be run with nested horizontal grid cells of various sizes. In particular it was possible to run the model over part of the domain with a coarse grid of 16km x 16km, another part with a medium grid of 4km x 4km and a fine grid of 2km x 2km.
- 3. The model had the plume-in-grid (PIG) algorithm that allowed the plumes from a small number of point sources to be modeled separately until the plumes were uniformly mixed into the modeling grid.
- 4. The chemical mechanisms were modified to incorporate the latest results for reactions involving isoprene and radical termination.

Two sets of model runs were performed with the UAM-V. To set boundary conditions for the urban scale modeling domain, regional scale modeling was conducted over a large domain with a horizontal grid of 16km x 16 km. This domain is shown in Figure 4. The domain for the smaller urban scale modeling is shown in Figure 5.

Figure 4. Regional Modeling Domain for TNRCC Modeling with the COAST Data









Figure 6 shows the grid cell sizes used in the urban modeling domain that was used for UAM-V modeling. A large 16km x 16km grid covered the whole modeling domain. A 4km x 4km grid covered both the HG and BPA areas. Two 2km x 2km sub domains covered each of the HG and BPA nonattainment areas. A 4km x 4km grid covered the Victoria/Corpus Christi areas. Results from the regional modeling were used to define the initial conditions and boundary conditions for the urban scale modeling domain.

Figure 6. Subgrids Used for COAST UAM-V Modeling.



Following EPA guidance (EPA, 1991) four episodes were selected for base case development. These were October 24-25, 1992; August 18-20, 1993; September 1-2, 1993; and September 8-11, 1993. The Systems Applications International Meteorological Model (SAIMM)(Kessler and Douglas, 1993) was used to develop the meteorological parameters for UAM-V. SAIMM is a prognostic hydrostatic meteorological model, which is an enhancement of the CSUMM.

Initial base case development was performed for each of the four episodes. The October 1992 and August 1993 episodes did not meet performance criteria. After extensive examination and hundreds of sensitivity runs, these episodes were set aside. The September 1-2, 1993 episode, developed for the BPA area, met performance criteria. After additional analyses and emissions inventory enhancements the performance for the September 8-11, 1993 episode met the criteria in the HG and BPA areas. Initial sensitivity modeling indicated that it was not necessary to use the extra time and resources to model with the 2km x 2km grids, so almost all urban scale modeling was performed with a 4km x 4km grid spacing.

Results of modeling for the September 8-11, 1993 episode were used for the HG SIP submitted in 1998 (TNRCC, 1998)

CAMx

After the 1998 SIP was completed TNRCC began using version 1 of Comprehensive Air Quality Model with Extensions (CAMx)(CAMx, 2001) for photochemical modeling. There are three versions of this advanced photochemical grid model and TNRCC has consistently used the latest version available during the time that the modeling for SIP activities was being performed. CAMx has a number of features that are not all present in other similar models:

- 1. Two-way nested grid structures
- 2. Enhanced plume-in-grid algorithm
- 3. Ozone source apportionment technology (OSAT)
- 4. Option to use any one of three horizontal advection solvers

Version 3 has the following features:

- 1. Choice between SAPRC97 and four versions of CB-IV for gas phase chemistry (see Accelerated Science Evaluation document on Atmospheric Chemistry for a more complete description.)
- 2. Decoupled Direct Method (DDM) for source sensitivity analyses
- 3. Process Analysis for sensitivity analyses
- 4. Flexi-nesting that allows more flexibility for use of fine grids

Initially, the August 1993 episode was modeled with CAMx, but model performance still did not meet EPA criteria. The TNRCC continued to focus their modeling efforts on the

September 1-2, 1993 and September 8-11, 1993 episodes. Enhancements continued to be made to the EI, and when appropriate these were assimilated into the photochemical modeling. For example, updated non-road emissions based on the EPA NONROAD model were incorporated into the inventory, and updated emission factors and landcover were used to estimate biogenic emissions. Also, emissions from non-road categories for commercial marine traffic and diesel construction equipment were based on survey data.

With the nesting capability of CAMx, TNRCC moved from running two sets of models, regional and urban, to one model with a nested grid over the regional domain as shown in Figure 7. This has been denoted as the SuperCOAST domain. Merging the regional and COAST domains removed the necessity of first running a regional model, extracting boundary conditions, then running the urban scale model. It also allows regional controls to be evaluated directly rather than in a two-step fashion.

Figure 7. SuperCOAST modeling domain with grids used for photochemical modeling with CAMx.



Model Performance Evaluation

The continual improvements to the CAMx based modeling were reflected in SIPs submitted in 1999 and 2000. Since the 2000 SIP submission is the most recent, reflecting the most extensive updates, discussion of model performance will focus on the modeling done in support of that submission.

Version 2 of CAMx was used to develop the modeling performed for the HG SIP submitted in 2000 (TNRCC, 2000). While the model met overall performance goals defined in the EPA guidance (EPA, 1991), the model could not replicate measured ozone on several days at a number of sites. Figure 8 shows the time series from September 6 to September 11, 1993 for an old emissions inventory (93basA) and the most recent emissions inventory (aak93) for the monitoring site located at Smith Point on the eastern side of Galveston Bay. The first two days are the spin up days for the model application. On September 8 and September 9, the model could not replicate the maximum ozone measured. Measured concentrations on September 8 reached 214 ppb while the modeled maximum for that day at that site was about 150 ppb. On September 9 the model again significantly under estimated the measured concentration.

Figure 8. Ozone time series for the Smith Point Monitor for September 6-11, 1993 with CAMx. (<u>http://envpro.ncsc.org/projects/TNRCC-projects/HG/superC/aak93/</u>)



Figure 9 shows a time series similar to the one found in Figure 8, except the location is at the Croquet monitoring site in southwest Houston. For this site, the maximum predicted concentration on September 8, 1993 was 186 ppb, while the maximum measured concentration was about 120 ppb. In this case the model significantly over predicted the

measured concentration. This location is the site of the maximum modeled concentration for the episode. At this location on this day, when various emissions scenarios were modeled for the future year 2007, the ozone did not show much response to emission reductions of VOC and/or NOx. (TNRCC, 1998,2000)



Figure 10 shows a time series similar to the one found in Figure 8, but the location is the Clinton monitoring site. On September 10 and September 11, the model did not replicate the rapid rise and fall of the monitored ozone. These conditions have been called "rapid ozone formation events".

Figure 10. Ozone time series for the Clinton Monitor for September 6-11, 1993 with CAMx. (<u>http://envpro.ncsc.org/projects/TNRCC-projects/HG/superC/aak93/</u>)

The modeling for the TNRCC SIPs was based on meteorological modeling developed with the SAIMM model. The RAMS meteorological model and the MM5 model were both run to develop meteorological parameters for the September 8-11, 1993 episode. When these meteorological parameters were run in CAMx, the model produced similar results as those with SAIMM data. This indicates that simply using another meteorological model would not significantly improve CAMx model performance (ENVIRON, 2001).

A diagnostic tool recently added to CAMx (ENVIRON, 2001) is Process Analysis. This procedure allows the user to display rates of individual generation (increase) and depletion (loss) processes for air pollutants in individual grid cells. An example showing one of the outputs from process analysis tools is shown in Figure 11. This figure provides information on the generation and depletion rates predicted by CAMx for ozone at the Croquet site on September 8, 1993 (also see Figure 9, which shows that the ozone concentration is over predicted at this site on this date). There is an unexpected large amount of ozone advected down from the higher levels and the dry deposition rate appears to be very high (up to 100 ppb per hour)(Tonnesen, 2001). These data illustrate the potential value of process analysis but represent conditions for only one day in only one grid cell. Further investigation using process analysis is ongoing and these results will be described in more detail in later versions of this report.

Figure 11. Integrated Process Rate Analysis for September 8, 1993 at the Croquet monitor site. (Tonessen, 2001).

Preliminary results with the TexAQS data

Although photochemical modeling episodes for the Texas Air Quality Study period (August and September, 2000) are not yet available, some qualitative features of the phenomena observed during the TexAQS period can be compared to previous modeling results.

Data collected during TexAQS clearly indicate the rate of ozone production in and around the industrial source dominated areas in Houston can be very high, approaching 200 ppb/hr. Data showing estimated rates of ozone formation, based on aircraft measurements made throughout the study period are shown in Figure 12.

Figure 12. Very rapid ozone formation (>50 ppb/hr) is observed in the Houston area, particularly in the industrial corridor north and northwest of Galveston Bay (Daum, 2001)

Longitude

Data collected during TexAQS also indicate three distinctly different types of ozone presursor sources, that lead to different ozone formation efficiencies, where ozone efficiency characterizes the molecules of ozone formed per molecule of NO_x reacted. Measurements from plumes resulting from these three source types (isolated power plants, urban sources and petrochemical sources) are shown in Figure 14. The ozone formation efficiencies are given by the slopes of the ozone versus reacted NO_x ($NO_y - NO_x$) plots (Ryerson and Trainer, 2001).

The HG urban plume shown in Figure 13 is typical of other urban areas. The plume generated by isolated power plants (Parish power plant) is NO_x rich and VOC lean and is similar to plumes seen from power plants in other areas. In the power plant plume, ozone yield was less efficient (less ozone created per unit concentration of NO_z) than that found in the urban plume. The plumes from areas with refinery and chemical manufacturing sources in the HG area exhibited very high ozone yields, larger than any other plumes previously observed in the U.S. These yields seem to be correlated to high levels of ethylene, propylene, butadiene and other reactive hydrocarbons emitted from industrial sources.

It is not yet clear if the models will be able to replicate these ozone production efficiencies, but performance evaluations of TexAQS episodes should examine this issue.

Figure 13. Comparison of ozone productivities from data taken in power plant, urban and petrochemical plumes. The co-location of anthropogenic reactive VOC with NO_X leads to rapid ozone formation in very high yield [from Ryerson and Trainer, 2001]

In addition, data collected during the Texas Air Quality Study in 2000 (TexAQS) can be used to determine if the current use of a 4kmx4km horizontal grid with a 1-hour reporting time step is the best to use for modeling southeast Texas. For example, one of the lidar maps of spatial distribution of ozone concentrations is shown in Figure 14. The data suggest that there are very large gradients of ozone concentrations over relatively small distances (less than 4 km) in both the vertical and horizontal, and this implies that accurate replication of the temporal evolution of ozone concentrations (Figures 8-10) will require grid cell sizes smaller than 4 km.

Figure 14. Down looking LIDAR (Excimer UV-DIAL) ozone concentrations taken by the NOAA Environmental Technology Laboratory Aircraft flying west to east transects over Houston on August 30, 2000. (Data has a 10 second time resolution and a 90 meter vertical resolution, flying at 60-70 m/s)(Senff, et al, 2001)

Summary of past modeling

The performance evaluation of CAMx for the September 8-11, 1993 episode indicates that in the HG area photochemical grid models can replicate the normal urban ozone plume (modeling of the September 1993 episode meets EPA performance criteria for many monitors in the region). But, the model can not simulate events that are characterized by rapid and efficient ozone formation. As indicated in the Accelerated Science Evaluation Overview document (Accelerated Science Evaluation, 2002a), the rapid and efficient ozone formation events play a large role in the magnitude of the measured design value in the HG area. Since photochemical grid models are used to evaluate approaches to reduce ozone, it is necessary that these models be able to simulate such events. This leads to key science questions relating to photochemical grid modeling.

Structure of the report and key scientific issues

This brief summary of the history of photochemical air quality modeling for the HG area reveals that the models have been continually improved since their initial application more than a decade ago. However, these models have not been able to replicate rapid and efficient ozone formation that has been observed in the HG area. So, additional improvement continues to be needed. The most significant issues that need to be addressed in the Accelerated Science Evaluation are:

- 1. What temporal and spatial resolutions are necessary for the photochemical models to obtain better agreement with measured ozone concentrations in southeast Texas?
- 2. Can the cause of the photochemical model's difficulty in correctly simulating the temporal and spatial distribution of ozone in southeast Texas be identified and corrected?
- 3. How do the linkages between the photochemical models, the emissions inventory data, the meteorological data, and the chemical mechanisms effect model performance?

The remainder of this report will address these issues by examining

- Model input data
- Chemical and physical processes
- Computational structure of the model

Special attention will be given to how the robust data set from the Texas Air Quality Study (TexAQS), performed in the summer of 2000, can be utilized to address the scientific questions that have been identified.

Model Input Data

Emissions

As shown in equation 1, the first step performed by the model in calculating the rate of change of air pollutant concentrations is accounting for emissions in each grid cell for each calculation time step. To account for emissions, models generally use an emissions preprocessor that performs several functions:

- 1. The chemical composition of the emissions are specified and the reported chemical emissions are mapped into the chemical categories ("lumped species") used by the chemistry sub-model,
- 2. The spatial and temporal distributions of the emissions are specified by allocating the emissions to specific grid cells and specific time steps and
- 3. Emissions from multiple source categories are combined (point sources, on-road mobile sources, non-road mobile sources, area sources and biogenic sources.)

The focus of this section of the report will be on the second of the three functions listed above – specifying spatial and temporal distributions of emissions. The first function will be described in the section of this report that describes how the model handles chemical reactions. The individual source categories and the uncertainties associated with estimating those emissions are described in the Emission Inventory report issued as part of the Accelerated Science Evaluation (Accelerated Science Evaluation, 2002c).

The spatial and temporal distribution of many types of emissions have been extensively studied, and while uncertainties remain, it is likely that the spatial and temporal distribution of on-road mobile sources, non-road mobile sources, area sources and biogenic sources can be described with current modeling approaches. However, activities will continue to enhance these portions of the emissions inventory (EI). Examples of recent projects designed to improve emission estimates in these categories are evaluation of on-road mobile emissions with the tunnel data collected during the TexAQS study and projects to collect better activity data for area and non-road mobile sources, non-road mobile sources, area sources and biogenic sources are likely to require evolutionary improvements, it is likely the modeling of the temporal distribution of point source emissions will require much more dramatic change.

Temporal Issues

Current point source inventories used in photochemical modeling rely, in some cases, on annualized or daily emission inventories, and may or may not include non-routine releases. Use of daily average emissions and not including non-routine emissions may

seriously compromise the model's ability to predict ozone formation. Consider non-routine releases.

Table 1 shows a small subset of more than 200 upset reports that were submitted to TNRCC during the time period of the TexAQS study. For routine reporting purposes an "upset" is associated with plant startup, plant shutdown or an unplanned emission event with emissions greater than 5,000 pounds. For the emissions inventory for TexAQS smaller reporting levels were used in some cases in an attempt to quantify all significant emission sources during the study. Shown in Table 1 are the upset emissions, the duration of the upset and the ratio of upset emissions to the routine emissions, integrated over the period of the upset. The data indicate that an upset can result in emissions from a facility increasing by a factor of 1000 or more. These releases can range in length from under an hour to more than a week, and the temporal pattern of emissions in the longer events is not recorded in the upset reports.

	I I I I I I I I I I I I I I I I I I I		
Chemical	Release	Duration	Upset release to
	(lbs.)	(hr)	routine release ratio
Butadiene	1225	7	34
Cumene	6300	27.5	
Ethylene	5280	1	242
Ethylene	26700	14	87
Ethylene	25000	59	19
Ethylene	5000	19	5
Ethylene	20000	744	6
Isobutylene	581	0.5	
Propylene	1235	0.22	3036
Propylene	2680	4.3	52
Propylene	1295	3	38
Propylene	7108	48	25

Table 1. Selected sample of upset reports for the summer of 2000.

To assess the potential effect of this type of release on model predictions of ozone formation, the University of Texas performed box model calculations, employing the SAPRC '99 chemical mechanism. The horizontal dimensions of the box were 1 km by 1 km and the height of the box ranged from 250 m to 1250 m over the course of a day depending on estimates of the mixing depth. The box was given initial hydrocarbon and NO_x concentrations typical of those observed in the morning at LaPorte during TexAQS, and additional emissions were added to the box model over the course of a day to simulate routine emissions. The resulting base case led to maximum ozone concentrations of 95 ppb, predicted to occur at 5:30 PM. Upset emissions were added into this base case box model, and typical results for the third upset emission scenario reported in Table 1 are reported in Table 2. In this scenario, up to 5280 pounds of ethylene were added to the box during the 7AM-8AM time period. If just 5280 pounds of ethylene is added, then the maximum ozone concentration reached 298 ppb, and this

peak occurs at 11AM. If NO_x emissions are added into the upset (at a ratio of 1 pound of NO_x , which is 90% NO and 10% NO_2 , to 7 pounds of ethylene – a ratio typical of a well operated flare) the maximum ozone concentration reached 1180 ppb. As shown in Table 2, intermediate values of the upset emissions of ethylene and NOx were also considered.

Table 2. Maximum ozone concentrations (in bold) obtained in a box model; emissions representative of upsets were added, over a one hour period, to a base case of typical emissions

Ethylene upset emissions (lb/hr)	NOx upset emissions (lb/hr)				
	0	189	377	566	754
0	94.79	12.79	6.331	6.3	6.3
1320	278.1	506.1	558.7	572.4	588.3
2640	302.4	638.1	784.2	873.6	907.1
3960	303.9	673.7	876	1009	1085
5280	298.1	675.5	905	1059	1179

The results shown in Table 2 do not incorporate plume dispersion and hence are a high upper bound on the potential effects of upsets on maximum ozone concentrations. Nevertheless, the results indicate that, if confined to a volume similar to a grid cell, typical upset emissions can quickly generate very large amounts of ozone, especially if the upset involves the release of reactive hydrocarbons and NO_x in ratios typical of flares.

The data presented in Tables 1 and 2 indicate that non-routine releases from point sources have the potential to be very significant in ozone formation, but these emissions are not well accounted for the September 8-11, 1993 episode used in current modeling. These analyses indicate that if emissions similar those reported as upsets are assumed to remain undispersed, using a box model, it is possible to simulate rapid and efficient formation of ozone. Preliminary modeling of the same upsets using grid models (4 km grid resolution with the upset modeled as a plume in grid) generate much lower (0-30ppb) ozone enhancements due to the upsets. This suggests that the methods used by the grid models to disperse pollutants play an important role in the model's ability to simulate rapid and efficient ozone formation.

Spatial Issues

In the model, point sources are located at their exact geographic location, so their location is essentially independent of the grid structure.

However, an important spatial issue related to point sources is determining the proper vertical layer for their emissions. All point source plumes that are emitted at

temperatures greater than ambient temperature are subject to plume rise. Simple equations are used in the model to determine plume rise based on meteorological conditions (TNRCC, 1998)

As shown in Tables 1 and 2, episodic releases have the potential to rapidly generate significant quantities of ozone, potentially creating large gradients in ozone concentration. If processes that depend on concentration gradients, such as diffusion and deposition, are to be modeled correctly, it is essential that these emissions be placed in the correct vertical layer. Emissions from flares are likely to be particularly important since flare emissions are subject to plume rise, are a significant fraction of the routine emissions inventory and are likely to be a significant fraction of the upset emissions.

Meteorology

Meteorological imputs to photochemical grid models are developed using a meteorological model. The outputs from the meteorological model are used in photochemical grid models to charaterize advection, dispersion, temperatures, humidity and other critical parameters. The photochemical model must be able to use the meteorological inputs to accurately simulate the temporal and spatial movement of air parcels that contain ozone and ozone precursors. This section summarizes key meteorology issues that are addressed in the Meteorology report for Accelerated Science Evaluation of ozone formation in the Houston-Galveston area (Accelerated Science Evaluation, 2002d).

The Meteorology report focuses on the ability of current meteorological models (such as MM5) to predict parameters such as wind speed, wind direction, and temperature in the HG area. Issues discussed are the meteorological conditions correlated with measured high ozone concentrations in the HG area, previous applications of meteorological models in the HG area, and initial results from meteorological model simulations of the data from the TexAQS study.

The preliminary meteorological modeling done for the TexAQS period suggests that the meteorology correlated with high ozone concentrations is more complex that previously thought. Two regimes correlated to high ozone concentrations have been identified. The first regime involves a continuous shifting of wind direction in a circular pattern. Winds start in the early morning out of the west and northwest, then shift in a clockwise direction, and are from the southeast in the afternoon. The winds continue their rotation and are from the north again in the evening. This flow pattern involves complex interactions with land/sea breeze flows, but there is little wind shear in the vertical. Large-scale winds are onshore. The second regime includes a land/sea breeze flow, but a low level jet forms in the evening, with significant wind shear in the vertical. Large-scale winds are parallel to the shore. These findings will be used to revise the conceptual model for formation of high ozone concentrations in the HG area.

Further, the preliminary meteorological modeling with the fifth generation NCAR/Penn State Mesoscale Model (MM5) indicates that it is difficult for the model to properly replicate the time and location of the sea breeze flow patterns. It has been difficult to properly simulate the low level jet that forms in the second regime. Furthermore, the model tends to create regions of convective flow that have not been observed. Additional work with the model is ongoing. It has been found that land surface characteristics, model vertical grid structure, the algorithm used for parameterization of the planetary boundary layer, and incoming longwave and shortwave radiation will be among the more sensitive inputs for MM5. Additional model improvement activities underway are use of satellite data to refine the surface characteristics used in the meteorological model to better simulate heating cycles and the assimilation of upper air wind measurements to fine tune MM5 performance. Also underway are testing activities to determine the best approaches for defining MM5 vertical structure and the best algorithms for characterizing planetary boundary layer physics.

Land use, temperature, and cloud cover

A number of data sets are used for more than one aspect of development of the inputs to the photochemical model. It is imperative that the data values used for these common elements be consistent throughout the model. Three examples described below are land use, temperature and cloud cover.

Land use data is used in biogenic emissions modeling to spatially distribute leaf biomass densities for different forest types so that high emitting vegetation is properly located. For dry deposition (discussed later in the report) land use is used to spatially determine surface roughness. Area source emissions are spatially distributed over the modeling domain based on land use surrogates. Land use is also used in meteorological models to determine surface roughness, albedo, and soil moisture. Land use information is found in different sources, so extreme care must be used to insure that the data inputs for land use are appropriate for each of these applications and consistent between applications.

The hourly ambient temperature is used to calculate hourly biogenic emissions. Mobile source emissions are based on hourly temperatures. The rate of some reactions in the gas phase chemical mechanism depends on temperature. The results from the meteorological modeling are dependent on the temperature. The temperatures used in all of these applications should be carefully examined to insure that appropriate and consistent values are used. For example, biogenic emissions are very sensitive to temperature and are based on temperatures at the level of the foliage, typically up to 35 meters from the surface. Temperature data from the meteorological model (MM5) may differ from values interpolated from National Weather Service observations or from continuous monitor sites. For applications that rely on temperature, studies should be conducted with temperature data from various sources to establish the sensitivities and to establish the best set of data to use for each specific application.

Hourly data on cloud cover is needed to calculate biogenic emissions. The reaction rates for many reactions in the gas phase chemical mechanisms depend on the solar intensity. Cloud cover affects ambient temperatures. However, meteorological models normally can not accurately predict the location and time of cloud cover. Other mechanisms for determining cloud cover such as those based on satellite information may provide the accuracy needed. Studies should be performed to determine the best source for cloud cover information based on the application that requires this information.

Issues related to model input data

The point source emissions inventory must contain detailed information on the hourly diurnal pattern, location, magnitude and chemical speciation of all routine and non-routine releases.

The impact of the complex vertical structure of wind fields on ozone and ozone precursor transport and mixing should be examined.

Common data elements, such as land use, cloud cover and temperature, which are used in a variety of model calculations, should be assessed for appropriateness and consistency.

Chemical and physical processes

Chemical processes

In order for the photochemical model to predict the spatial and temporal distribution of ozone concentrations, the gas phase chemical mechanism used in the photochemical model must be able to accurately replicate atmospheric reaction processes. Since there are thousands of reactive compounds and therefore a large number of reactions that could describe the atmospheric reactions of these compounds, any chemical mechanism used for modeling must be based on assumptions that simplify the reactions and reduce the number of components involved in reactions.

There are several chemical mechanisms that can be used for photochemical modeling and these mechanisms are being investigated to determine which is the most appropriate for modeling the HG area. The completeness of the mechanisms (including the consideration of chlorine chemistry and heterogeneous reactions) and the accuracy of the rate parameters are being assessed. These topics are covered in detail in the Accelerated Science report on Atmospheric Chemistry (Accelerated Science Evaluation, 2002b).

Carbon Bond Mechanisms

The Carbon Bond Mechanism (CB) was one of the first chemical mechanisms used for photochemical modeling. There are several versions of this mechanism with a number of revisions. The basic approach is that the reactive hydrocarbons are partitioned (lumped) into reactivity classes and then the atmospheric chemical reactions are described by equations that involve these reactivity classes. For some compounds the mass of the emissions will be divided among different reactivity classes based on the functional groups of the compound. Depending on the version being used, the number of equations for most CB simulations are less than 100. The most often used version is CB-IV (for a summary, see Adelman, 1999), which was used in the UAM-IV and is available in CAMx. The version of CB-IV used in UAM-IV has some radical termination reactions that are inadequate in situations that are NO_x-limited. This is the situation in the HG area. CB-IV was later updated with improved radical termination reactions and better isoprene chemistry. This version of CB-IV is used in UAM-V and is available in CAMx. TNRCC modeling with UAM-IV used the earlier version on CB-IV and the modeling with UAM-V and CAMx used the latest version of CB-IV.

SAPRC97

The chemical mechanism developed by Bill Carter of the Statewide Air Pollution Research Center (SAPRC) in California contains a much more detailed representation of hydrocarbons than is available in CB-IV (Carter, 2001). The most recent version (SAPRC-99) contains explicit reaction mechanisms for several hundred hydrocarbon species, as well as more computationally efficient, lumped mechanisms. A version of SAPRC 97 has been added to CAMx. The latest version of SAPRC is currently being incorporated as an optional mechanism in CAMx. SAPRC has a larger number of reaction mechanisms than CB-IV and some important reactive hydrocarbons are treated separately instead of being lumped into a more general mechanism. This added detail would allow for more focused analyses on the role of specific compounds that have been identified in initial analyses of the TexAQS data as playing a major role in ozone formation in the HG area.

Since it is clear that specific reactive hydrocarbons and other ozone precursors significantly influence ozone formation in the HG area, it is very important that photochemical modeling sensitivity studies be performed with the CB-IV, CB-IV with chlorine, and SAPRC mechanisms.

Speciation Issues

Once a chemical mechanism is selected for use in the photochemical model, the hydrocarbon emissions must be divided into the reactivity classes used by the mechanism. While in theory this might appear straightforward, in practice it involves a significant degree of qualitative scientific judgment.

Major portions of the point source hydrocarbon emissions in the TNRCC emissions inventory are reported for individual hydrocarbon species. In other cases, the hydrocarbon emissions are reported as total VOC, so these emissions must be divided into hydrocarbon species. For some source categories, TNRCC has developed a Texas specific speciation profile that may be used to divide the VOC into separate species. In other cases, a more generic profile has been developed. For area, on-road mobile and non-road mobile sources, speciation profiles have been developed for specific source categories. Biogenic emissions have been reported for specific hydrocarbon species. For the TexAQS study period, TNRCC is preparing a highly detailed hourly, speciated emissions inventory. The companies that report their emissions supply the speciation of hydrocarbon point source emissions in the TNRCC emissions inventory. The quality of this information can vary from facility to facility and there has not been an independent verification of the data.

Once the emissions have been separated into individual hydrocarbon species, these emissions must be mapped to the chemical (reactivity) classes used by the chemical mechanism in the photochemical grid model. For example, to use the CB-IV mechanism, the hydrocarbon emissions must be distributed into the reactivity classes (lumped species) used by CB-IV.

Assuming that the chemical mechanisms are complete and rate parameters are accurate (see Accelerated Science Evaluation report on Atmospheric Chemistry) the critical modeling issues are the choice of mechanism and the mapping of the composition of emissions into "lumped" chemical species used in the models.

Plume in Grid

For most point source emissions, at the place they are emitted and for a significant distance downwind, the horizontal grid dimension is significantly larger than the width of the plume. To model plumes, that are at sub-grid cell dimensions, plume-in-grid (PIG) algorithms have been developed. However, there are two problems with existing PIG approaches. First the PIG algorithms account for only a small subset of the chemical reactions considered in the rest of the model (typically NO_x-ozone chemistry with no hydrocarbon reactions). In NO_x rich, VOC lean plumes this chemistry may be adequate, but in NO_x rich and VOC rich plumes from refineries and chemical manufacturing facilities, this simplified chemistry is likely to be inadequate. A second concern is that the PIG algorithms are developed for isolated plumes. A version of the PIG should be developed that can be used for a complex network of plumes that interact with each other and overlap. This is a challenging problem and is the topic of on-going projects, which will be described in future versions of this document.

Horizontal Advection and Diffusion

The methods used to describe advection and diffusion in photochemical models can have a significant impact on predictions of air pollutant concentrations. Before describing the state of current advection schemes in air quality models, including those used in the HG area, however, it is useful to define terminology.

Advection is the term commonly used to describe the bulk transport of pollutants due to winds. Consider a simple example involving the three grid cells shown below. At some initial time, air pollutants are concentrated in the first grid cell.

Initial condition

Assume that over one time step, winds transport the air parcels half the length of the grid cell. Accounting only for advection, assuming that the material moves as a "plug", the pollutants would be distributed as shown below.

After one time step

After a second time step, if the winds continue to advect the material half a grid cell per time step, the pollutants would have moved entirely to the second cell.

After two time steps

So, pure advection will result in material moving as a "plug" with the velocity of the wind. This situation is not precisely modeled by an approach that mixes pollutants in each cell at each time step (as is done in photochemical grid models). Consider again the simple example outlined above. The initial condition in each case remains the same.

Initial condition

In the first time step, the material is advected half the length of the grid cell; pure advection yields the situation on the left; advecting material, then mixing the contents of each grid cell yields the situation on the right. For the case on the right, the concentrations of the two cells are half the initial peak concentration.

After one time step

After one more time step, the pure advection of case (a) above yields the situation on the left; advecting case (b) above, then mixing the contents of each time step yields the situation on the right, where the concentrations in the cells are .25, .5 and .25 of the initial peak concentration.

After two time steps

Thus, grid models, which completely mix the contents of each cell at each time step, have an inherent difficulty in accounting for advection. Before describing how advection schemes account for this problem, it is useful to describe diffusion.

Consider again a simple three cell model. The initial condition is a high concentration of pollutant in the middle cell. After an infinite length of time, even in the absence of bulk fluid movement, random molecular motion will cause the concentrations in all three cells to become uniform (one third of the initial peak concentration). This process is referred to as molecular diffusion.

An infinite length of time later

Other types of diffusion, such as turbulent diffusion, are also accounted for in air quality models and are the result of processes that are both advective and diffusive. For the purposes of this report, however, advection and diffusion will be differentiated simplistically based on bulk flow. Advection is the transport of pollutants due to bulk air movement, while diffusion is the transport of pollutants in the absence of bulk air movement (but including transport due to fine scale turbulence in the atmosphere). Broadly interpreted, this is the distinction made in most photochemical models.

As shown in the simple, three grid-cell examples, advection models that mix the contents of cells at each time step have an intrinsic problem in modeling pure advection. Most advection schemes handle this difficulty by introducing a numerical diffusion to balance the inaccuracy of the advection scheme. Using parameterizations, material is artificially diffused to improve modeled advection. The effect of this artificial diffusion can be seen clearly in Figure 15. In the simulation reported in this Figure, a high concentration of pollutants was placed in a 6 by 6 grid cell block at the center of a larger grid. Only advection was assumed to occur for this numerical experiment – no true diffusion. Therefore the pollutants should remain stagnant in the center of the array, as shown by the plot in the upper left of the figure. Advection schemes introduce numerical diffusion, however, and therefore material is artificially diffused to surrounding grid cells. Results are shown for the three advection schemes commonly used in CAMx.

Figure 15. Predictions of three advection algorithms for concentration distributions under stagnant flow (CARB, 1996).

The magnitude of the uncertainty introduced by advection schemes (in this case, the horizontal advection scheme) has been assessed by the California Air Resources Board (CARB, 1996). The most rigorous test of a horizontal advection scheme is the "one-grid cell spike" test, in which material, initially present as a spike in one grid cell, is advected. The exact solution preserves the maximum concentration at its initial value, but advection algorithms introduce numerical diffusion, diluting peak concentration. Results of the one grid cell spike test for three horizontal advection schemes used in CAMx are shown in Table 3. As shown in the Table, the horizontal advection schemes preserve mass, but significantly reduce peak concentrations. The results shown in Table 3 are for a particularly difficult test case, nevertheless, they show the potential problems associated with the accurate advection of high, isolated spikes of concentration in current advection schemes.

Table 3. Results from a one-cell spike test of three advection algorithms used in CAMx. In the test, material initially present as a spike in one grid cell is advected (no true diffusion) a distance of 50 grid cells at a wind speed of 0.5 grid cell lengths per time step (100 time steps). Reported are the peak concentrations and the mass conservation properties of the advection schemes (CARB, 1996)

Advection Scheme	Peak concentration/ Peak concentration in exact solution	Total mass/ Total mass in exact solution
Bott	0.35	1.00
Piecewise Parabolic	0.24	1.00
Smolarkiewicz	0.24	1.00

The three advection schemes listed in Table 1 have different approaches to modeling advection, and while it is clear that all conserve mass, all have difficulty in preserving spikes in concentrations. Given the potential significance of narrow plumes with large gradients of pollutants in the HG area, the potential significance of the choice of horizontal advection algorithm, and the parameterization of numerical diffusion in that algorithm on ozone concentrations should be examined. In addition, the use of alternative advection schemes should be investigated.

Vertical diffusion and advection

The preceding discussion has focussed on horizontal advection. A related, but distinctly different problem is that of vertical advection. The problems of vertical advection arise both for the reasons outlined for horizontal advection, but also because of:

• difficulty in characterizing turbulent mixing in the vertical direction

• problems associated with matching the wind fields predicted by the meteorological models and the mass conservation properties required in the photochemical models. This is particularly complicated when the meteorological and photochemical models have different vertical grid cell dimensions (see discussion of the computational structure of the model later in this report).

These issues are encountered in all photochemical modeling, however, the complex vertical wind structure in certain types of ozone episodes in the HG area (see discussion of Regime II for the TexAQS period in the Meteorology report, Accelerated Science Evaluation, 2002d), may make these problems particularly acute.

Dry deposition

Dry deposition is the most important physical removal mechanism for pollutants during the ozone season in Texas. This is shown clearly in Figure 11, which indicates that for one of the critical regions in the September, 1993 SIP modeling, dry deposition rates had a large impact on local ozone concentrations.

"Dry deposition in CAMx is modeled as flow through a series of resistances with three processes, aerodynamic transport, diffusion across a quasi-laminar sub-layer, and surface uptake, determining the resistances. The dry deposition flux is modeled as

$$F_c = -V_d C_z$$
 (Equation 2)

where F_c is the dry deposition flux (ppbv cm/s), V_d is the dry deposition velocity (cm/s), and C_z is the concentration or mixing ratio at a reference height (ppbv). The reference height used in CAMx is generally 10 meters. The dry deposition velocity is calculated as the inverse of the sum of the resistances to deposition (eq 3):

$$V_d = (R_a + R_b + R_c)$$
 (Equation 3)

where R_a is the aerodynamic resistance (s/cm), R_b is the quasi-laminar sub-layer resistance (s/cm), and R_c is the bulk surface or canopy resistance (s/cm). Hourly, gridded meteorological data are used to calculate the aerodynamic resistance in each grid cell as a function of solar insolation, wind speed, surface roughness, and near-surface temperature lapse rate. The quasi-laminar sub-layer resistance is a function of a pollutant's molecular diffusivity. The bulk canopy resistance is divided into component resistances for vegetation, the lower canopy, and the ground." (McDonald-Buller, et al., 2001)

Dry deposition rates depend critically on the details of the wind fields near the surface, land surface characteristics, temperature, and molecular properties of the compound that deposits, but the sensitivity of deposition to these parameters is not well known in the HG area. Only limited studies have been done on the sensitivity of ozone deposition rates and ozone concentrations to the parameters used in the HG deposition calculations. McDonald-Buller, et al (2001) have examined the impact on ozone concentrations of using different land cover characterizations in deposition calculations. They found that relatively minor changes in land covers (USGS data versus a composite land cover used to estimate biogenic emissions) can cause changes (both positive and negative) of up to 10 ppb in ozone concentrations. Typical results are shown in Figure 16.

Figure 16. Predicted difference in 1-hour averaged ozone mixing ratios (ppbv) between the new land use data and the default USGS data ($O_{3(New)} - O_{3(USGS)}$) at 1800 on June 22, 1995.

This work suggests that collecting data on deposition velocities may be important, however, dry deposition is a difficult quantity to measure. Most studies of dry deposition have been conducted in rural areas where surface characteristics are somewhat uniform. Few studies of urban dry deposition rates of ozone, NO_x or VOC have been undertaken, so there are uncertainties involving the algorithm that is used and the correlation with the land use surrogates. Issues related to chemical and physical processes

Which chemical mechanisms are most appropriate for modeling ozone formation in the Houston-Galveston area and how should hydrocarbon species be mapped into the "lumped" reactivities used in the models?

Can modified Plume in Grid (PiG) algorithms be used to model ozone formation in VOC rich and NO_x rich plumes?

Which horizontal advection solver is most accurate for use in the HG area and how can numerical diffusion and other adjustable features in the solver be parameterized for optimal performance?

Which methods for characterizing vertical advection and diffusion are most accurate for use in the HG area and how can adjustable features in the models be parameterized for optimal performance?

Are current methods for estimating dry deposition of ozone and ozone precursors sufficiently accurate?

Computational structure of the model

Several aspects of the computational structure may be significant in improving model performance. These include the grid size and the interface between meteorological and photochemical models.

Grid cell size

One approach to modeling an area with a complex configuration of sources and complex meteorological flows is to use smaller nested grids in these areas. CAMx and other advanced photochemical models have the ability with "flexi-nesting" to add smaller grids at times and locations where needed. A small grid might allow for more accurate treatment of the interaction of a number of point source plumes, and would decrease inaccuracies of averaging concentrations over larger gird cells. It will be important to perform a series of evaluations to determine the best approach to use in complex industrial areas. These analyses should provide guidance on the size, location, and extent of such smaller grids. The analyses should also address the impact of utilizing smaller grid structures in situations where the wind flow regimes are complex and vary significantly over small horizontal and vertical scales. The TexAQS data set provides a robust data set for performing such studies. Several such studies are currently underway. For example, Tesche has recently run CAMx with flexi-nested grids at 200 meters in the HG area to assess the effect of grid cell size on the model's predictions of the impacts of

large point source releases. Results from these and related analyses will be reported in subsequent versions of this document.

Data transfer between meteorological and photochemical models

Advection or transport in the horizontal is simulated in photochemical models by using hourly values for the wind direction and wind speed for each grid cell. These data are developed by the meteorological model, but the photochemical model horizontal advection solver takes the data from the meteorological model and processes it for use in the photochemical model. To keep from having unrealistic values, the process must maintain mass conservation and mass consistency. Mass conservation insures that all sources and sinks of mass are accurately accounted for in the model. Mass consistency is the ability of the model to transport inert pollutant mass equivalent to the atmospheric momentum field input to the model. Mass consistency problems can be minimized (CAMx Users Guide) by

- 1. using the same grid structure for the meteorological and photochemical model
- 2. interpolating meteorological conditions for each computation time step between the reporting time steps,
- 3. supplying specific data for nested grids instead of interpolating from coarse grid data, and
- 4. supplying meteorological data developed with a prognostic meteorological model.

Prognostic meteorological models are frequently run with a large number (31 or more) of vertical layers. To minimize elapsed computation time, the photochemical models are normally run with significantly fewer (5 to 8) vertical layers. In such a case the meteorological data must be processed for use in the photochemical model with fewer vertical layers. Sensitivity studies should be performed to determine the optimal number of vertical layers to use in the photochemical model to balance elapsed run time with loss of vertical detail.

Issues related to the computational structure of the model

Examine the effect of grid structure (both horizontal and vertical, both the photochemical model and the meteorological model) on model performance.

Examine the sensitivity of model performance to calculation time steps for optimal grid structures.

Summary of key issues

Key issues related to model input data, chemical and physical processes, and the computational structure of the model are summarized below. In all of these issues, characterizing and, when necessary, developing methods for characterizing levels of uncertainty, should be a focus of on-going work.

Issues related to model input data

The point source emissions inventory must contain detailed information on the hourly diurnal pattern, location, magnitude and chemical speciation of all routine and non-routine releases.

The impact of the complex vertical structure of wind fields on ozone and ozone precursor transport and mixing should be examined.

Common data elements, such as land use, cloud cover and temperature, which are used in a variety of model calculations, should be assessed for appropriateness and consistency.

Issues related to chemical and physical processes

Which chemical mechanisms are most appropriate for modeling ozone formation in the Houston-Galveston area and how should hydrocarbon species be mapped into the "lumped" reactivities used in the models?

Can modified Plume in Grid (PiG) algorithms be used to model ozone formation in VOC rich and NO_x rich plumes?

Which horizontal advection solver is most accurate for use in the HG area and how can numerical diffusion and other adjustable features in the solver be parameterized for optimal performance?

Which methods for characterizing vertical advection and diffusion are most accurate for use in the HG area and how can adjustable features in the models be parameterized for optimal performance?

Are current methods for estimating dry deposition of ozone and ozone precursors sufficiently accurate?

Issues related to the computational structure of the model

Examine the effect of grid structure (both horizontal and vertical, both the photochemical model and the meteorological model) on model performance.

Examine the sensitivity of model performance to calculation time steps for optimal grid structures.

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