Final Report
HARC Project H-1

SENSITIVITY MODELING STUDY OF RAPID OZONE FORMATION EVENTS IN THE HOUSTON-GALVESTON AIRSHED

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EXECUTIVE SUMMARY

Ozone measurements in the H/G area during episodes in which 1-hour ozone standard is exceeded routinely capture several unique characteristics, including Rapid Ozone Formation Events (ROFEs) and Transient High Ozone Events (THOEs), in which ozone concentrations can fluctuate by as much as 100 ppb well within 1 hour. Several such ROFEs were captured by surface and aircraft measurement platforms during the TexAQS2000 field program. Consensus from many studies over the past several years indicate that a major potential source of these events are associated with sudden large releases of HRVOC from industrial sources along the ship channel. Whereas past modeling of H/G ozone episodes have not adequately accounted for the sources of these characteristics, the latest field and modeling research has attempted to quantify sources and effects of HRVOC events on ozone production efficiency during periods conducive to poor air quality.

It will continue to be particularly challenging for today's state-of-the-science numerical modeling platforms to adequately capture the nature of ROFEs and THOEs given the Eulerian (i.e., discretized) nature of their formulations. The current hypotheses that ROFE/THOEs may be caused by highly localized precursor and ozone plumes will make simulating these events very difficult even using grid spacing as low as 1 km. However, there is promise that given sufficient horizontal and vertical resolution, and the accurate characterization of the fine-scale meteorology and emissions, the current generation of photochemical grid models are capable of simulating the unique ozone events of the H/G area.

Under the HARC H-1 study, we have performed MM5, CMAQ, and CAMx sensitivity modeling of the H/G area for the August 22 – September 6 TexAQS2000 period with the explicit purpose of investigating the capacity of these models to replicate ROFE/THOEs. Additionally, the TCEQ expanded the MM5 meteorological applications to include August 16 – August 21, and added provisions to evaluate some of science features of MM5.

The goals of this study were twofold:

1. Undertake numerous high-quality MM5 experiments for a subset of days during which ROFE/THOEs occurred to determine sensitivity to meteorological model configuration for the H/G area. Based on the sensitivity tests and reviews of specific model algorithms, certain MM5 configurations were selected to develop four distinct meteorological realizations for the entire modeling period of August 16 – September 6, 2000. Several reports from ATMET have been developed that document the expanded meteorological modeling configuration, runs, and results.

2. Use the CAMx and Models-3/CMAQ photochemical grid models for the TexAQS2000 period of August 22 – September 6 to investigate the occurrences of ROFEs in the H/G area via numerous sensitivity analyses. A major goal of the project is to assess the ability of the air quality models to replicate ozone formation in highly reactive VOC plumes from industrial sources in the H/G area. A major goal of the project was to assess the ability of the air quality models to replicate ozone formation in highly reactive VOC plumes from industrial sources in the H/G area.

Emission inputs were taken from official model-ready inventories developed by the TCEQ for the H/G SIP mid-course review. To establish "base case" simulations, both CAMx and CMAQ were first run for the TexAQS period of August 22 – September 1 using the latest official TCEQ input fields and configurations. Emissions, meteorological, and initial/boundary condition inputs were mapped from CAMx formats to CMAQ formats with as little modification as possible. Following the modeling procedures used by TCEQ for the mid-course review, CAMx was run on the TCEQ 4-grid nested 36/12/4/1-km domain, where the finest mesh was "flexi-nested", i.e., high-resolution emissions were provided for the 1-km grid but the meteorological fields were interpolated from the 4-km inputs. CMAQ was run on the 3-grid TCEQ 36/12/4-km domain since it requires all emission and meteorological inputs to exist for all grids (no flexi-nesting capability is available). Both models were subjected to a detailed and comprehensive model performance evaluation using the extensive TexAQS2000 database.

Photochemical model sensitivity tests were designed and undertaken, commensurate with the capabilities of each platform, to evaluate model response to the alternative MM5 simulations generated by ATMET, and to investigate each model's ability to simulate highly concentrated ozone plumes through changes in model formulations and inputs. These tests included a specific inflated HRVOC release scenario to specifically test ROFE/THOE replication, based on information gleaned from project H-13 (Allen et al., 2004).

Simulations and Tests with MM5

ATMET produced several reports for Project H-1 (ATMET, 2003a,b,c,d). The first was an interim report detailing a number of idealized tests of the MM5 basic numerics, along with a large number of short-term (2-3 day) sensitivity runs. The second report provided the main documentation for the original H-1 scope of work, describing the results from three alternative MM5 simulations for the full August 16 – September 6, 2000 modeling period. The third and fourth reports described work specifically carried out by request for the TCEQ, including: modifications to the MM5 MRF boundary layer scheme and an associated fourth full MM5 run of the August 16 – September 6 period; and an review and assessment of the various boundary layer options available in MM5 that are based upon "turbulent kinetic energy" approaches. All of the major findings from these reports are summarized in Section 2 of this report and are not repeated here.

Simulations and Tests with CAMx

The CAMx simulation results completed under the HARC H-1 study are summarized as follows:

- We were able to successfully reproduce the TCEQ Base Case CAMx simulation for the H/G SIP modeling of August 22 – September 6, 2000; this was important to establish that the proper model inputs were used and the model was correctly configured to establish and "ground truth" against which sensitivity tests could be compared.

- The TCEQ Base Case simulation was reasonably successful at simulating the ROFE events, which occurred during the August 22 – September 1, 2000 episode period.

- We performed several sensitivity tests, and found that the CAMx output ozone fields were more sensitive to changes in meteorology than to the apparently small change associated with an update to the TCEQ Base Case emission inputs (version “5a” to “5b”). It was unclear if the TCEQ emissions update improved model performance.

- The magnitude, but not the distribution, of the CAMx ozone fields was sensitive to the change in vertical diffusivity. Meteorological fields other than the vertical diffusivity are also responsible for the differences between the ATMET meteorology and TCEQ Base Case runs. Use of the two “best” ATMET MM5 meteorological simulations led to generally degraded CAMx performance relative to the TCEQ/TAMU meteorology.

- Setting the horizontal diffusivity to zero had the expected effect of forcing pollutant plumes to remain more coherent and intense than they were with the standard K_h calculation. However, setting $K_h = 0$ did not have much effect on the ozone time series at most stations, and did not systematically improve the simulation of ROFEs.

- Correcting the staggered wind flag setting in the CAMx configuration to appropriately describe the input MM5 wind fields did not have a large impact.

- The use of super high resolution (200 m) produced more ozone in tighter plumes near the source areas in the Ship Channel. This showed that the model is capable of simulating the most extreme ozone rises observed during ROFEs. However, from these specific results, it was not obvious that the model’s performance in replicating the observations in the area improved. We conclude that there may be a need to further investigate the role of explicit horizontal diffusion, and that further improvements will be needed in the local time- and space-characterization of the input meteorological and emission fields.

- The simulation with a representative hypothetical upset event of HRVOC (in time, space, and frequency) located in the eastern Ship Channel indicated that up to 40 ppb ozone is generated locally near the source and ~10-20 ppb peak ozone increments can occur in the cloud as it passes over the NOx-rich Houston core, as represented in this modeling realization. Including known upset events into base year modeling inventories seems to be important for properly simulating ozone episodes in the H/G area.

Simulations and Tests with CMAQ

The CMAQ simulation results completed under the HARC H-1 study are summarized as follows:

- The CMAQ “Base Case”, which was configured as closely as possible to the TCEQ CAMx “Run 5a” application, performed reasonably well in replicating high ozone on several days and at several monitors in which ROFEs were observed. However, like CAMx, there were certain observed ROFEs that were not captured by CMAQ. Furthermore, CMAQ exhibited a much stronger tendency toward under predictions relative to the TCEQ CAMx base case, probably due to the deeper and more robust vertical mixing rates derived by MCIP from MM5 output, and the fact that all CMAQ modeling was performed on a 4-km horizontal grid mesh (rather than 1-km in CAMx).

- CMAQ did not consistently exhibit high ozone concentrations, or replicate the ROFE conditions, at monitoring sites located around the industrial Ship Channel area as were measured – however, the model did seem to adequately simulate the Houston ozone plume exiting the core urban area to the west. This suggests that the typical urban emissions are properly characterized, and that the combination of grid resolution, meteorology and potential HRVOC emission events need to be improved to properly capture ROFEs when and where they are observed.

- The EXPT3 and EXPT4 sensitivity tests suggest that CMAQ ozone fields are quite sensitive to the change in meteorology. From the statistical measures, it is difficult to say whether the alternative meteorology results in better performance relative to the base case; from time series plots, however, it is clear that these two runs performed worse than the base case.

- The CB-2002 mechanism predicted higher ozone in urban areas or areas with intense emissions. There was very little difference between the new and old CB-IV mechanism in rural areas. The CB-2002 mechanism appeared to result in a better simulation of the ROFE peaks, if only marginally.

- Operator splitting approximates the original three-dimensional equation through successive spatial decomposition. By applying the operator splitting to the continuity equation, the air quality model will solve the advection, diffusion, deposition, emissions, and chemistry processes independently of each other.

- The order in which emissions are updated in the operator splitting will affect the VOC-to-NOx ratio in each grid cell and subsequently affect the amount of ozone produced. In this case, the effect of increased NO_2 and radical scavenging by NO_2 outweigh the effects of higher VOC and NO_x concentrations and led to overall lower ozone concentration.

- Ozone chemistry intensified as we moved the emissions injection from the vertical diffusion routine into the chemistry process. In this case, the change resulted in lower ozone efficiency per NO_x and a higher percentage of NO_x was converted into nitric acid. Both time series plots and model performance statistics showed that CMAQ performed worse by releasing emissions in the chemistry process.

- Inverting the grid resolution dependence of horizontal eddy diffusivity did not make a significant impact on the model performance. It also did not improve the model's capability to simulate ROFEs.

- We showed that the model is capable of simulating a ROFE-like condition by injecting a "representative" short-term industrial HRVOC emissions event into the surface emissions; if ROFEs are commonly caused by such events during periods conducive to high ozone formation rates, then this shows that CMAQ should be able to reproduce such signals.

- The peak ozone signal within the HRVOC release with CMAQ was consistently smaller than seen in CAMx. This is most likely due to the more vigorous/deeper vertical mixing and coarser grid resolution employed in CMAQ. However, the way that CMAQ treats hourly emissions is likely to be partly responsible for the lower ozone signal. CMAQ interpolates emissions between the top of each hour, rather than using constant rates over the hour as is done in CAMx; this dilutes the hourly upset emissions by injecting them across two hours.

- The finest horizontal grid scale we used in these simulations was 4 km. It is difficult to say whether the model will perform better with improved resolution both horizontally and vertically, but given the apparent improvements seen in TCEQ CAMx simulations using a local 1 km grid, it is quite likely to be the case as well for CMAQ.

RECOMMENDATIONS

The CAMx and CMAQ modeling conducted under the HARC H-1 study has demonstrated conclusively that the two models are capable of simulating ROFEs in the H/G area given adequate meteorological and emissions inputs and sufficient grid resolution. However, the study stopped short in identifying the optimal model configuration for simulating ROFEs. Below are some recommended additional activities intended to improve the numerical simulation of ozone and ROFEs in the H/G area.

Use of Subgrid-Scale Plume-in-Grid Modules: The simulation of ROFEs due to HRVOCs could also be accomplished using full chemistry Plume-in-Grid (PiG) modules in addition to, or instead of, high resolution grids. The use of super high resolution grids (such as the 200 m test conducted with CAMx in this project) can lead to extremely long integration times, and are thus considered too inefficient for control strategy assessments in which numerous model simulations need to be conducted in a short period of time. Sensitivity tests using full-chemistry PiGs were not conducted in Project H-1 because the PiG modules in the current public release versions of CAMx and CMAQ are designed mainly for large NOx plumes. However, new PiG modules are being developed that include full organic chemistry that are appropriate for simulating HRVOC plumes. For example, the CAMx Incremental Reactions for Organics and NOx (IRON) PiG module is in the final stages of development and testing, and would be an appropriate tool for HRVOC ROFE analysis. The CMAQ Advanced Plume Treatment (APT), which incorporates the SCICHEM model and incremental chemistry, may also be appropriate for simulating HRVOCs. Additional sensitivity tests with the existing H-1 databases should be conducted using these new advanced full chemistry PiG modules.

Additional High Resolution Grid Modeling: The CAMx high resolution 1 km and 200 m flexi-nest modeling shows promise for better simulation of ROFEs. As CMAQ does not provide flexible grid nesting, similar experiments could not be conducted with CMAQ. Processors should be developed that can generate CMAQ inputs at 1 km and 200 m resolution so that similar high resolution grid modeling can be conducted with CMAQ. Further CAMx and CMAQ high resolution modeling should be conducted to determine optimal model resolution and configuration for simulating HRVOCs and ROFEs. In particular the role of the horizontal diffusion coefficient should be investigated as a function of resolution.

Updated Chemical Mechanism: The CMAQ experiments using the updated CB4-2002 chemical mechanism estimated higher ozone and marginally better simulation of ROFEs. Similar experiments should be conducted with CAMx. In addition, numerical experiments using the

SAPRC99 chemistry, which provides updated chemical kinetics and more detailed representation of hydrocarbon classifications, should be conducted. Such experiments could not be performed in the H-1 study due to the lack of SAPRC emission inventories. However, TCEQ is currently working on SAPRC emission inventories. SAPRC is generally a more reactive mechanism in heavily urban environments, so it has the potential to better represent ROFEs due to HRVOC releases. EPA is currently updating the CB4 mechanism, which should be ready in early 2005. The new CB mechanism should be considered for use when available.

<u>Refined VOC Upset Representations</u>: Further analysis of hypothetical HRVOC and VOC upsets should be conducted using different model configurations to identify the optimal configuration for simulating ROFEs. The Decoupled Direct Method (DDM) in CAMx should be used to further evaluate the sensitivity of ozone to HRVOC/VOC emissions from specific industrial source categories (fugitives, flares, cooling towers, etc.) in different geographic areas (Harris, Brazoria, Galveston Counties). The DDM results should be used for inverse modeling (as in HARC study H-6) to seek improved model performance and to evaluate whether emission caps should vary geographically.

<u>Higher Time-Resolved Inputs</u>: Both CMAQ and CAMx should be provided emissions and meteorological input fields at higher time resolution than one hour. This is especially important if such inputs are prepared on super high resolution grids (at or below 1 km) since resolving small-scale changes in time are as important as resolving their spatial variation. CAMx currently allows all inputs to be provided at frequencies higher than 1 hour; CMAQ (either the core transport model or its preprocessors), may need to be updated to allow for this.

<u>Additional Process Analyses</u>: The use of Process Analysis with CAMx and CMAQ should be further examined to explain ozone formation in the H/G area and the chemical processes within an HRVOC plume. Limitations in funding and schedule restricted in-depth analyses of CMAQ Process Analysis output.

<u>Treatment of Vertical Diffusion</u>: CMAQ differs from CAMx in its treatment of convective vertical mixing. Specifically, it utilizes the “Asymmetric Convective Mixing” (ACM) parameterization, which is a non-local transport scheme. In the ACM approach, mass can be distributed among several vertical layers each time step, based on the diagnosed intensity of vertical eddies, as apposed to the “K-theory” approach used in CAMx, which is analogous to molecular diffusion in that diffusive transfer can only occur between adjacent layers each time step. The differences resulting from adopting the Asymmetric Convective Mixing parameterization versus K-theory in the CMAQ vertical transport scheme should be compared.