Top-down Emissions Verification for the Houston-Galveston Industrial Point Sources Based on TexAQS Data

FINAL REPORT
HARC Contract No. H62002B

Submitted by

Noor V. Gillani, PI
Yuling Wu, Co-I

Earth System Science Center
University of Alabama in Huntsville
Huntsville, AL 35899

Submitted to

Dr. Anne Brun, Project officer
Houston Advanced Research Center
4800 Research Forest Drive
The Woodlands, TX 77381

June 2003

EXECUTIVE SUMMARY

A diagnostic analysis, based on comparison of TexasAQS-2000 aircraft observations in the H-G area and corresponding simulations on multiple modeling platforms, has been carried out, principally to infer the accuracy of the NOx and VOC emissions inventory (EI) for major industrial point sources in the area. Previous studies have suggested that EIs of some reactive alkenes, in particular, may be far too low, leading to the failure of corresponding operational air quality modelS (OAQMS) to simulate the observed transient high ozone episodes (THOEs). The aircraft observations were made aboard the NCAR Electra. The modeling platforms included lagrangian and Eulerian modeling systems. The Lagrangian modeling system included U. of Alabama in Huntsville's UAH-PDM (Plume Dynamics Model) and the UAH-LRPM (Lagrangian Reactive Plume Model), in both their single-plume and multi-plume configurations. The Eulerian system was the UAH-LESchem (RAMS-LES with a generalized chemistry module added by UAH). All model simulations used the full CB-IV chemistry with the single-product isoprene mechanism. The bulk of the analyses presented here are based on applications of the lagrangian models. The motivation for the LES study was based on suspicion that large co-emissions of VOC and NOx may lead to strong positive correlations of the turbulent fluctuating components of reactant concentrations, which can enhance the corresponding reaction rates significantly in excess of those used in OAQMs (based on mean concentrations only). The LESchem study is the right approach to explore such enhancement, if any. Our LESchem study is of a pioneering nature and was applied only to an isolated single plume, corresponding to its sampling during a particular aircraft traverse on one of the case study days. A special effort was made to make the application case specific and realistic.

The diagnostic analyses were applied to five particular source clusters --- Sweeny, Freeport, Chocolate Bayou and Texas City in the southern part of the study domain, and the Ship Channel Complex between downtown Houston and the northern end of Galveston Bay. The particular point sources studied were aggregated into a total of 35 as follows: Sweeny (1), Freeport (3 = A, B, M), Bayou (2) and Texas City-SCC (29). Of these, the Sweeny, Freeport and Bayou source plumes of the case study days were isolated, requiring separate isolated plume analyses, and the Texas City-SCC plumes merged into a mega-plume for which separate multi-plume modeling was necessary. Two case studies were selected for their meteorological simplicity and low overall chemical reactivity --- August 27 and 28. On both days, the CBL transport winds were consistently from S-SE during the entire day, and fairly steady in the 3-5 m/s range. Both days had some broken clouds. The highest ground level measured ozone concentrations in the entire study domain were 87 ppb (8/27) and 112 ppb (8/28), both at the same site impacted by the SCC plume. We had performed an LRPM-based case study of 8/28 before. Here we have performed a similar study for 8/27, sought corroboration from the two viewed together, and have done an LESchem study of a particular subset of the 8/28 case study.

A very important and comforting finding of our study is that the results of the two case studies (8/27 and 8/28) are corroborating both qualitatively and even, quite satisfactorily, quantitatively. Where the quantitative differences are significant (e.g., both show that the EIs of ethene and propene are too low by 1-2 orders of magnitude, even though there are differences of a factor of 1-5 in the results of the two days), they provide a measure of day-to-day variability in the emissions or in the uncertainty of this kind of a study, using the available empirical data. The analyses have yielded the following major conclusions:

1. The industrial point sources in the H-G area are mostly concentrated in five complexes, three of which (Sweeny, Freeport and Chocolate Bayou) are more or less isolated, and the other two (Texas City and the Ship Channel Complex) have a fairly large number of sources in relatively close proximity such that their plumes tend to interact and form a mixed multi-plume complex.

2. For most of the sources, the NOx emission rates in the EI appear to be fairly accurate, most likely well within a factor of 2; there are some exceptions, however, specifically the Bayou sources and some sources in the western half of the SCC, for which the NOx emission rates appear to be a factor of 3 to 5 higher than their EI estimates.

3. Similarly, for almost all sources (except power plants), the ETH and OLE emission rates appear to be grossly underestimated in the EI, typically by 1 to 2 orders of magnitude, such that these emission rates are comparable to the co-emitted NOx emission rates. Such co-emissions of NOx and reactive VOCs lead to rapid nonlinear gas-phase chemistry, which produces large amounts of ozone and other secondary products (e.g., NOz, aldehydes) rather close to the source complexes, and appears to explain the development of THOEs observed before and during the TexasAQS-2000 study.

4. The CB4 chemical mechanism (and presumably also other state-of-the-art mechanisms, e.g., RADM2 and SAPRC99) is able to simulate the rapid observed chemistry adequately, making it unnecessary to invoke substantial contributions from other mechanisms such as chlorine chemistry, which are not part of CB4 ordinarily.

5. UAH-LRPM and its upgraded multi-plume version (M-LRPM) are able to simulate the high-resolution observations of primary and secondary species concentrations measured in the NCAR-Electra aircraft in the plumes of the H-G industrial point sources and their background. These models have performed very well as diagnostic tools to evaluate the EIs for these sources, and can be very useful also to perform a variety of other diagnostic tests (e.g., checking the relative differences between results of using different chemical mechanisms) for which regional or sub-regional Eulerian models would require much more intense resources.

6. Our application of LESchem was limited to a 4h simulation of the emissions from Sweeny between ~1130 and 1530. The results were compared with LRPM results and with aircraft measurements. Data-model comparisons were for the 1.7h old Sweeny plume sampled in traverse T2 of 8/28, at 23 km downwind from the source at about 1315. For the conditions of this plume, we found there to be no enhancement of the chemistry due to turbulence effects; indeed, quite the opposite --- there was, if anything, a little deceleration of the chemistry in the fresh plume compared to the mean chemistry. Such deceleration was pronounced very close to the source, and decreased with downwind distance. Such decrease in the turbulence effect on chemistry was significantly faster for the high-VOC case (high ethene and propene emissions as inferred from the LRPM study), with the rate returning to that of the mean chemistry within 5-15 km. For the low-VOC case (low EI values of the VOC), such return to the mean conditions was not yet quite complete at 25 km. Our results are in sharp contrast to the simulation of excessive ozone production and significant chemistry enhancement by the turbulence effect in the LESchem study of the same plume scenario by Herwehe et al. (2002), quite possibly due to an important difference in the input values of the mean transport wind speed ($\bar{u}$) in our simulations (3.2 m/s, based on profiler measurements) and in theirs (1

m/s, to keep the computational domain small). Our explanation of our result is that the initial sharp depletion of the oxidants (ozone and the free radicals) by the NOx emission creates an *anti*-correlation between the oxidants and the precursors, leading to a negative turbulence effect in their reactions. Later, when the radicals are recovered and build up in excess of the background (more rapidly in the high-VOC case), NOx is mostly spent, more or less shutting off the chemistry. It is possible that the same result will not hold for the ship channel complex, where new NOx emissions from downwind sources may provide the NOx to sustain the chemistry, now at a faster rate due to the turbulence effect. However, this needs to be tested.

7. In our application of LESchem to the Sweeny plume (~1130-1530), we made special effort to incorporate realistic physics based on the field measurements (e.g., $\bar{u} = 3.2$ m/s, variable mixing height), and were able to simulate the observed chemistry (peak ozone ~65 ppb over a background of ~35 ppb) reasonably closely, in contrast to the result of Herwehe et al. of production of up to 400 ppb of ozone in the plume. This discrepancy between our and their simulations suggests a possible important sensitivity of ozone production to wind speed, particularly for $\bar{u} < 3$ m/s. This issue needs to be further explored. Our post-processing was also designed to preserve the spatial detail of the plume simulations by performing the averaging over time rather than over distance (e.g., over 4km x 4 km horizontally in Herwehe et al, 2002).

8. One drawback of our LESchem study was that our computations were limited to a single 2.4 GHz Pentium-4 processor and 2 GB of memory, requiring about 20 days of CPU time for each run of the Sweeny simulation over a horizontal domain of 32 km x 20 km. The use of very low $\bar{u}$ by Herwehe et al (2002) was also motivated by this limitation. For application to the SCC plumes, we would need a significantly larger domain. This would not be practical on a single processor. What limits us to the single-processor application is that while RAMS-LES supports multi-processing, our new chemistry module in it does not. It would be most useful to parallelize this chemistry code also, and perform the LESchem studies in multi-processing mode.

9. The application of the LRPM has some physical limitations. In terms of plume dynamics, the LRPM is limited to applications under conditions when wind shear effects are not very significant, and it is also not the ideal tool for simulation of multiple interacting plumes, because it cannot apply differing turbulent diffusion rates that may exist in different parts of the lagrangian air parcel including fresh and aged sub-plumes. To include such complex effects as wind shear and multi-plume interactions more realistically in lagrangian modeling, it would appear that the new EPRI puff model SCICHEM may be more suitable (but it is much more computation-intensive).

10. In terms of simulation of the gas-phase chemistry, our study has revealed a consistent over-prediction of NOz (particularly HNO3) by CB4. This has also been observed in recent applications of CAMx with CB4 in the H-G area.

11. An important limitation of this study and of any diagnostic study for the H-G area aimed at top-down verification of the VOC and NOx EIs based on TexAQS-2000 database is the very sparse point-measurements of speciated VOCs in the Texas 2000 field study. There is a dire need for more continuous speciated VOC measurements, especially in the near-source

regime. It is our judgement that such capability would be the single most important way to reduce the uncertainty of our results and conclusions.

We wish to make the following specific recommendations:

LESchem

1. There is a need to perform more LESchem diagnostic analyses of the Sweeny plume, particularly to test the sensitivity of plume chemistry (both mean and turbulent) to precursor emission rates and to $\bar{u}$, particularly < 3 m/s.

2. There is a need to perform LESchem diagnostic analyses of the SCC plumes. This first requires that the computer code of the chemistry module be parallelized --- not a trivial task. However, the payoff would be considerable. We can determine if the role of the turbulence effect is important or not in the ship channel plumes.

3. If the turbulent chemistry is important, then LESchem would be the vital tool to use in developing parameterizations of the chemistry enhancement factor in terms of mean concentrations. With such a parameterization, we can incorporate the turbulence effect easily into the OAQMs (LRPM or CAMx, etc.). LESchem is an ideal research tool; it is not a tool for operational models.

LRPM

4. There is a need to test the applications of chemical mechanisms other than CB4 to simulate the chemistry of the H-G area, particularly with respect to simulation of NOz species, which appear to be consistently over-predicted by CB4. The LRPM is an ideal inexpensive tool for such tests, particularly for the important industrial point-source plumes.

5. The LRPM has important limitations with respect to realistically simulating such complex effects as significant wind shear and interacting multiple plumes with nonlinear chemistry. The case study day of the present study was an unusually simple scenario meteorologically. The application of Lagrangian modeling to scenarios with recirculations and much higher ozone production than on 28 Aug 2000 would be very useful to test effects related to fast chemistry in more intense ozone episodes. We recommend the application of SCICHEM for such applications. The satisfactory evaluation of SCICHEM has just been completed.

6. We recommend highly the application of UAH-LRPM to a similar case study for which higher density (ideally continuous) data are available of ethene and propene, such as the measurements made in the Baylor Twin Otter subsequent to the 2000 study.

7. We believe that, especially in the study of point-source plumes embedded in the urban soup, the UAH-LRPM is an ideal tool in many respects, especially once parameterizations of the turbulent chemistry effects have been built into it. Such studies may include those aimed at exploring different combined VOC-NOx control strategies. Future measurements must be planned with this analysis tool in mind.

Other

8. Finally, it is important that the substantial amount of new findings reported here be published in the open literature.