

**Sensitivity of Simulated Chemistry in
Houston-Galveston Industrial Point-source Plumes to
Wind Speed, Precursor Emission Rates
and Chemical Mechanism**

FINAL REPORT

HARC Contract No. H6-B-Supplement-01

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. Eduardo Olaguer, Project officer
Houston Advanced Research Center
4800 Research Forest Drive
The Woodlands, TX 77381

June 2004

EXECUTIVE SUMMARY

This Report presents results of our research performed in Phase 2 of the HARC-H6B Project, and is based on work directly motivated by the findings of the work of Phase 1 (Gillani and Wu, 2003a). The focus here is on sensitivity analyses of the rapid chemistry (particularly ozone production) in industrial (petrochemical) point-source plumes in the Houston-Galveston area (e.g. Sweeny) to three important variables: wind speed (U); precursor emission rates of NO_x and RVOC (reactive VOC, particularly ethene, ETH and other alkenes, OLE); and, chemical mechanism. The sensitivity analyses have been performed using both the pioneering UAH-LESchem Eulerian model which resolves the fast chemistry occurring at the scale of large turbulent eddies, and the Lagrangian Reactive Plume Model (UAH-LRPM) which is an operational model that parameterizes subgrid-scale eddy diffusion. The first two sensitivity analyses are based on application of the LESchem and the third one is based on application of the LRPM. The analyses are focused on the Sweeny plume transport-chemistry scenario of 28 August 2000, for which observational information is available based on aircraft measurements in the plume and its background, and for which both LRPM and LESchem studies have been done by us before. The sensitivity analyses are relative to the “standard” case, which was the above observed scenario, with prevailing wind speed of U = 3.8 m/s, Sweeny emissions of Q_{NO_x} = 24.6 kmol/h, Q_{ETH} = 3.6 Q_{NO_x} and Q_{OLE} = 2.0 Q_{NO_x}, and simulations based on the CB4-CMAQ chemical mechanism.

Task 1 pertained to sensitivity of plume chemistry to wind speed (U). This was motivated by sharp differences in the results of our earlier LESchem study and that of Herwehe et al. (2002). Our study had produced results in keeping with the observations (peak plume ozone concentration of 63 ppb relative to background concentration of 38-40 ppb, at a downwind distance of 23 km after about 2h of transport) at a 125m x 125m horizontal spatial resolution, but the Herwehe et al. study had suggested that ozone concentrations as high as 400 ppb could occur in such an industrial plume under light wind conditions (U = 1 m/s), even when their VOC emissions were only 1/3 as reactive as in our “standard” case and their results were averaged over a much larger horizontal grid size (4km x 4km). Our simulation with the “standard” emissions and U = 1 m/s yielded a concentration of only 115 ppb when averaged similarly over 4km x 4km (corresponding to their ~400 ppb). We performed new LESchem simulations corresponding to nominal wind speeds of 1, 2 and 3.2 m/s (in addition to our previous run for U = 3.8 m/s) over a domain of 32.5km x 20km x 4.5km at a horizontal spatial resolution of about 125m, and found that plume chemistry is quite sensitive to wind speed in the range U = 1 to 3.2 m/s, with the secondary formations of ozone, nitric acid and formaldehyde all increasing inversely with wind speed, in a non-linear manner. For example, on a domainwide basis after two hours of continuous emission, the local-instantaneous peak ozone concentration ranged from 100 ppb for U = 3.2 m/s (~16 km downwind of the source) to 208 ppb for U = 1 m/s (~ 4 km downwind).

Task 2 pertained to sensitivity of plume chemistry to source emission rates of NO_x and RVOC (ETH, OLE). The sensitivity analysis for Q(NO_x) was performed for constant Q_{std}(RVOC) and the following three different values of Q(NO_x): 0.5, 1.0 and 2.0 times Q_{std}(NO_x). The sensitivity analysis for Q(RVOC) was performed for constant Q_{std}(NO_x) and the following three different values of Q(RVOC): 0, 0.5 and 1.0 times Q_{std}(RVOC). An attempt to make the run with 2 Q_{std}(RVOC) became numerically unstable. Sensitivity to Q(NO_x) is strongest and positive for HNO₃ production, significantly weaker for ozone, and weakest for HO₂, FORM and organic nitrates. By contrast, sensitivity to Q(RVOC) is strongest and positive for FORM, organic nitrates and HO₂, somewhat weaker for ozone, and weakest and inverse for HNO₃. Increasing Q(NO_x)

from Sweeny would produce much more HNO₃, somewhat more ozone, and there would be fuel left for more such production beyond 2h and 23 km (NO_x was mostly depleted at this time and location for the “standard” emission of NO_x). Increasing Q(RVOC), instead, would be more productive particularly for aldehydes and organic nitrates, and less so for ozone. The ozone production efficiency (OPE) varies inversely with Q(NO_x) and positively with Q(RVOC), i.e., it is positively correlated with Q(RVOC)/Q(NO_x). Thus, a VOC control strategy for such sources to control ozone production appears more beneficial. We also examined the sensitivity of eddy-scale chemistry to variations in Q(NO_x) and Q(RVOC). In general, eddy-scale effects on chemistry (neglected in operational models) are most concentrated near the emission source and here, they tend mostly to slow down the real chemistry relative to the way it is represented in the operational models. The persistence of such eddy effects in plume chemistry is quite sensitive to Q(NO_x) and Q(RVOC): in general, such persistence increases with the magnitude of Q(NO_x) and diminishes with the magnitude of Q(RVOC).

Task 3 pertained to sensitivity of point-source plume chemistry to chemical mechanism, based on two versions of the CB4 chemical mechanism, viz., CB4-CMAQ (the standard version used widely in a variety of operational photochemical models) and a recently upgraded version of it (CB4-2003), in which the changes are more focused on the inorganic chemistry. In a sensitivity analysis we had separately done with the same two mechanisms for a very large powerplant plume (of the Cumberland Steam Plant of TVA in NW Tennessee, with Q_{NO_x} of more than an order of magnitude greater than that of the Sweeny plant), we had found quite substantial reduction in the production of both ozone and HNO₃ with the CB4-2003. By contrast, the developers of CB4-2003 had found that, for an urban mixture, this mechanism produced significantly more ozone, but less HNO₃. Evidently, the sensitivity of plume chemistry to the mechanisms is itself sensitive to the precursor emission rates. For the Sweeny plume, the difference in the production of ozone and other secondary products for the two mechanisms was rather small, much less than that for the Cumberland plume. We also ran simulations for Sweeny with Q_{RVOC} = 0 (powerplant case). Overall, our observation is that the sensitivity of point-source plume chemistry to the two CB4 mechanisms, i.e., the difference in simulated plume chemistry with the two mechanisms, increases with Q_{NO_x}, and decreases with Q_{RVOC}. Based on simulations for the Tennessee and Texas plumes, we also found that the sensitivity of point-source plume chemistry to the mechanisms is itself also sensitive to other factors influencing photochemistry, e.g., background chemical composition and photolysis rate. Such sensitivity appears to be positively related to the intensity of these factors.

Based on these findings, we make the following recommendations pertinent to the Texas SIP process as far as industrial point-source emissions are concerned:

1. Light wind conditions are particularly conducive to high ozone production and deserve special attention.
2. Operational models ignore significant retardation of chemistry due to reactant segregation effects at the scale of turbulent eddies. Such eddy-scale chemistry effects are most significant in the near field. Since co-emission of substantial NO_x and RVOC from industrial point sources leads to rapid near-source chemistry, the significance of eddy scale chemistry is particularly important in the plumes of such sources and need to be included through their parameterizations in operational models. Such parameterizations do not currently exist and need to be developed first using LESchem simulations.

3. Ozone production is sensitive to the magnitudes of both precursor emissions (RVOC and NO_x), but ozone production efficiency correlates with Q(RVOC)/Q(NO_x). Thus, it would appear that an RVOC control strategy may be more effective in controlling ozone production in industrial point source plumes.
4. The use of CB4-2003 is recommended over CB4-CMAQ more for power plant plumes than for industrial point source plumes.