

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

FINAL REPORT

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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 $Q_{\text{NO}_x} = 24.6$ kmol/h, $Q_{\text{ETH}} = 3.6 Q_{\text{NO}_x}$ and $Q_{\text{OLE}} = 2.0 Q_{\text{NO}_x}$, 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 $Q(\text{NO}_x)$ was performed for constant $Q_{\text{std}}(\text{RVOC})$ and the following three different values of $Q(\text{NO}_x)$: 0.5, 1.0 and 2.0 times $Q_{\text{std}}(\text{NO}_x)$. The sensitivity analysis for $Q(\text{RVOC})$ was performed for constant $Q_{\text{std}}(\text{NO}_x)$ and the following three different values of $Q(\text{RVOC})$: 0, 0.5 and 1.0 times $Q_{\text{std}}(\text{RVOC})$. An attempt to make the run with 2 $Q_{\text{std}}(\text{RVOC})$ became numerically unstable. Sensitivity to $Q(\text{NO}_x)$ is strongest and positive for HNO₃ production, significantly weaker for ozone, and weakest for HO₂, FORM and organic nitrates. By contrast, sensitivity to $Q(\text{RVOC})$ is strongest and positive for FORM, organic nitrates and HO₂, somewhat weaker for ozone, and weakest and inverse for HNO₃. Increasing $Q(\text{NO}_x)$

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.

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1. INTRODUCTION

This 3-Task project was motivated by our results of the HARC H6B project of 2002-03 (Gillani and Wu, 2003a; henceforth, GW03a), in which both the UAH-LRPM (Lagrangian Reactive Plume Model) and the UAH-LESchem (Large Eddy Simulation with detailed chemistry) were applied in diagnostic mode to the Sweeny petrochemical complex plume scenario of 28 August 2000, corresponding to plume sampling by the NCAR-Electra aircraft during TexAQS 2000. That project was part of a larger effort aimed at top-down verification of emissions from industrial point sources in the Houston-Galveston area (H-G) based on use of ambient data. The application of UAH-LESchem (a pioneering modeling tool) in that project was, more or less, its first realistic application to an industrial plume, in that the model inputs and outputs were both close to observed conditions. A previous study of ours of top-down emissions verification of H-G industrial point sources had been performed based on diagnostic analyses of the 8/28/00 measurements using the LRPM only (Gillani and Wu, 2003b).

As stated above, our application of LESchem to the Sweeny plume of 8/28/00 under rather steady southerly prevailing wind conditions was quite realistic (GW03a), for a mean observed wind speed of about 3.8 m/s over the first two hours or so of plume transport in the convective boundary layer (CBL). The observed (aircraft) background ozone concentration was about 38-40 ppb, and the instantaneous observed peak plume concentration at plume age of about 1.7h at a downwind distance from the source of about 23 km and at the height of the aircraft traverse in the mixing layer was about 63 ppb. Our LES simulation gave the peak at about 70 ppb (temporally averaged in a 125m x 125m x 106m cell), and the discrepancy was mainly because the simulated plume width was somewhat narrower than that of the observed plume (GW03a), most probably because we had forced a constant domainwide input mean horizontal wind (spatially-temporally uniform), thus suppressing the wind shear of the real situation. Other than that, the meteorological and chemical simulations were quite realistic. A separate, more idealized LESchem study by Herwehe et al (2002; henceforth, H-02) of the same plume scenario used considerably lower emission rates of reactive VOCs (RVOC), but still obtained simulated peak ozone concentrations (spatially averaged over boxes of 4km x 4km x 200m) approaching 300 ppb two hours after commencement of continuous emissions (4-8 km downwind of the source), and about 400 ppb after four hours (8-12 km downwind), compared to observed local and instantaneous peak values of about 63 and 54 ppb, respectively, at 23 and 50 km downwind, at plume ages of about 2h and 4h. A major departure of H-02 from prevailing conditions was that it used a mean wind speed of just 1 m/s (to keep the domain size and amount of computation limited), as compared to the prevailing wind speed of 3-4 m/s. It raised concern whether ozone levels as high as 400 ppb were indeed even possible in such plumes under light wind conditions. The sharp contrast in the two results (H-02 vs. GW03a) raised the possibility that there may be a strong sensitivity of ozone production in the plume to wind speed between 1 and about 4 m/s. Our Task 1 was, therefore, aimed at exploring such sensitivity of plume ozone production to wind speed, and at investigating the likelihood of ozone levels as high as 400 ppb under light wind conditions.

In industrial plumes, since both ozone precursors (RVOC and NO_x) are co-emitted in large quantities, the chemistry starts out rapid. In our application of LESchem to the Sweeny plume in the earlier study (GW03a), a goal had been to test, in cases of such co-emissions of RVOC and

NO_x, if the resolution of large-eddy-scale correlation of RVOC and NO_x would *increase* the ozone production rate, as suspected (and as suggested by H-02), over that of the LRPM simulations (or, for that matter, of any operational model simulations, e.g., CAMx), in which the eddy-scale chemistry is not resolved, hence ignored. The finding of GW03a was the opposite, that in early plume transport (first half hour or so in the case of Sweeny), there was actually a *decrease* in ozone production due to an *anti*-correlation between the oxidants (O₃, OH, HO₂), on the one hand, and ozone precursors (RVOC, NO_x), on the other hand. These are the principal reactants in the key reactions of such smog chemistry. The anti-correlation continued until OH (more rapidly), and the peroxy radicals (less rapidly), were recovered in the plume after their initial depletion by reaction with large concentrations of NO_x. Thereafter, plume OH remained near background level, but the peroxy radicals continued to rise above background level, thereby supporting increased ozone production. However, by the time the plume was 2 hours old, plume NO_x was more or less depleted, thereby limiting much further possibility of ozone production. An important related question was: how would the eddy-scale correlation between the oxidants and both RVOC and NO_x change and affect ozone production for higher or lower emission rates of RVOC and NO_x? This shaped our Task 2, which is related to the sensitivity of plume ozone production to RVOC and NO_x emissions, *with* resolution of eddy-scale chemistry. Our intention in Tasks 1 and 2 was to include the role of eddy-scale chemistry effects in the simulations (hence LESchem).

Another important observation in GW03a and GW03b was that the use of CB4-CMAQ chemical mechanism (the standard form of CB4 used widely in photochemical modeling) in Lagrangian plume models tended to result in over-production of HNO₃, when simulation of ozone and other secondary products (e.g., HCHO) was relatively good. Other studies in TexAQS based on application of the Eulerian model CAMx had also found that. Recently, a new version of CB4 (CB4-2003) was developed with enhancement, particularly, of the inorganic chemistry. For urban mixtures in smog-chamber studies, CB4-2003 gave reduced production of HNO₃ and somewhat increased production of ozone. Gillani and Wu (2004) compared simulations of the chemistry in a very large power plant plume based on both CB4-CMAQ and CB4-2003 and found significantly lower production of both HNO₃ and ozone with CB4-2003, and providing much improved match with observations for both species. Our Task 3 was focused on exploring the sensitivity of Sweeny plume ozone production to different chemical mechanisms (CB4-CMAQ and CB4-2003), based on the LRPM as the modeling tool. We are now ready to state our three specific study objectives and Tasks.

2. SPECIFIC OBJECTIVES AND TASKS OF THE STUDY

- Objective/Task 1:* Test the sensitivity of ozone production in an industrial point-source plume (Sweeny) to wind speed between 1 and 4 m/s (LESchem study);
- Objective/Task 2:* Test the sensitivity of ozone production in an industrial point-source plume (Sweeny) to source emission rates of RVOC and NO_x (LESchem study);
- Objective/Task 3:* Test the sensitivity of ozone production in an industrial point-source plume (Sweeny) to chemical mechanism used in the model (LRPM study).

Before delving into the details of each Task, an overview of the sensitivity parameters, their values in the “standard” run, and their range of variability in the sensitivity studies, is presented in Table 1 below.

Table 1. Summary of Sensitivity Variables and Their Explored Variabilities

Task #	Sensitivity Variable	“Standard” Run Value	Variability Explored	Model
1	Wind speed, U*	3.8 m/s	1, 2, 3.2 m/s	LESchem
2	Precursor emission rates**			LESchem
	Q _{NOx}	Q _{std} = 24.6 kmol/h	(0.5, 1, 2) Q _{std}	
	Q _{ETH}	Q _{std} = 3.6 (Q _{NOx}) _{std}	(0, 0.5, 1) Q _{std}	
	Q _{OLE}	Q _{std} = 2.0 (Q _{NOx}) _{std}	(0, 0.5, 1) Q _{std}	
3	Chemical mechanism	CB4-CMAQ	CB4-CMAQ and CB4-2003	LRPM

* In the LESchem runs, $\mathbf{V} = (U, 0, 0)$, and U was held constant in time and space during the run

** For the Sweeny Plant in Brazoria CO, southwest of Houston TX. In this study, the Sweeny source was treated as a single point source with effective stack height of 150m in LRPM, and as a source of one grid cell size (125m x 125m x 61m) in the layer between 139m and 200m in LESchem.

Table 2 below summarizes the basic numerical variables of the two models used in this study, UAH-LESchem and UAH-LRPM.

Table 2. Basic Numerical Parameters of the Models (LESchem and LRPM)

<i>Model name:</i>	<u>UAH-LESchem</u>	<u>UAH-LRPM</u>
<i>Model framework:</i>	Eulerian	Lagrangian
<i>Model domain:</i>	32km (x) x 20km (y) x 4.5km (z) (261 x 161 x 40) cells	Open (x) x 60km (y) x 2.5km (z)
<u><i>Spatial resolution</i></u>		
<i>Horizontal</i>	125m x 125m	Variable: $W_p(t)/20$ *
<i>Vertical</i>	Staggered: 40m near ground, then increasing stepwise by 15% to a max of 125m	Variable: 10m near ground, then increasing gradually to a constant 100m above Z_i

* $W_p(t)$ = expanding plume width

3. TASK 1: SENSITIVITY OF PLUME CHEMISTRY TO WIND SPEED

3.1 Background and Motivation

As was shown by GW03a, the role of eddy-scale chemistry not resolved in the operational model LRPM is important only in early plume transport, up to 2h at most in the case of Sweeny. Most LESchem analysis in this section is, thus, limited to 2h of plume transport from the source. Two important features of the 8/28/00 scenario from the point of view of top-down emissions verification were: (1) that the daytime winds in the study area were rather steady and southerly for many hours, and (2) that the ozone chemistry was relatively subdued for a late summer day, with maximum measured surface-level ozone concentration anywhere in the Houston-Galveston area being only 112 ppb (downwind of the Houston ship channel).

The Sweeny plant (see Figure 1.1) is about 50km inland from the Gulf of Mexico, rather isolated from urban or other major source complexes, being more than 75 km SW of downtown Houston. A detailed description of the environmental conditions during the aircraft measurement scenario of the Sweeny plume of 28 August 2000 was given in GW03b. During the daytime, a sharp spatial gradient of the mixing height existed from the shoreline inland, and had reached the maximum well before Sweeny. Temporally, the inland mixing height downwind of Sweeny peaked at ~ 2000m in the early afternoon, about the time of the aircraft sampling of the Sweeny plume between 1300 and 1400 CDT. At the time, scattered clouds prevailed in the region. The winds were fairly steady throughout the afternoon from a southerly direction, with the mean wind speed of 3 – 4 m/s. The aircraft sampling of the Sweeny plume included plume traverses at downwind distances of about 23 and 50 km from the source, at plume ages estimated at ~ 1.7 and 3.7h, respectively.

Figure 1.2 (adapted from GW03a) shows the observed crosswind plume profiles of NO_y, ozone (measured continuously), formaldehyde (FORM in CB4, measured semi-continuously), and olefins (OLE in CB4, alkenes other than ethylene, aggregated from batch-mode measurement of speciated VOC) at the 23 km aircraft traverse, as compared with the corresponding profiles based on our LRPM and LESchem simulations. The plume was sampled by the aircraft in a crosswind plume traverse at about 1310 CDT, and was estimated (based on lagrangian particle modeling) to have been released from Sweeny (treated as a point source) at about 1130 CDT (see GW03b for determination of the details of plume transport scenario). In the LRPM simulation (GW03b), the plume spread rate (external input) was constrained to match the observed plume width at sampling, and the NO_y emission rate was adjusted (as 1.66 times the emission inventory value of ~15 kmol/h, or 24.6 kmol/h) to match the observed NO_y information. A previous diagnostic LRPM study of the Sweeny plume scenario of 28 August 2000 by Trainer (2001) had determined that the RVOC species emitted in significant quantities from Sweeny were ethylene (ETH in CB4) and propylene (main component of OLE), and that their emission rates, Q(ETH) and Q(OLE), respectively, were inferred to be Q(ETH) ~ 3.6 Q(NO_x) and Q(OLE) ~ 2 Q(NO_x). In our own more rigorous diagnostic study of the same Sweeny plume scenario based on UAH-LRPM (GW03b), and on data-model comparisons of ETH, OLE, ozone and FORM, we also inferred the same emission rates of ETH and OLE relative to Q(NO_x). The LRPM results shown in Fig. 1.2 are based on use of such emission rates and the *observed* PBL and plume dynamics as inputs in the simulations. The excellent comparisons between the observations and the LRPM

results are, thus, not surprising. However, in the LESchem simulation (taken from GW03a), we used the same species emission rates, but the plume spread evolved based on the simulated PBL turbulence. We adjusted the surface energy fluxes and further constrained the growth of the daytime mixing layer from above (by prescribing an elevated inversion layer) such that our mean mixing layer dynamics closely matched the corresponding observations based on a variety of observational information (see GW03b). Our specification of the mean wind field in LESchem, however, was somewhat idealized: it had about the right mean horizontal wind speed ($U = 3.8$ m/s) as observed, but no spatial-temporal variability --- U was constant in time during model spin-up and the 2h simulation after plume release, and also spatially uniform throughout the model domain, including vertically. Thus, there was no mean wind shear present in the LES simulation. As a result, the LES plume spread was *less* than the observed (and LRPM) spread. This is evident in the simulated LESchem crosswind concentration profiles. By mass conservation, therefore, the peak species concentrations are somewhat *greater* than the observed (and LRPM) values (about 70 ppb for LESchem ozone peak compared to about 63 ppb observed peak). Thus, the simulations, both LRPM and LESchem, are close to the observed plume chemistry.

In sharp contrast, Figure 1.3 shows results taken from the LESchem simulations of Herwehe et al. (2002). That study (H-02), also motivated by the Trainer (2001) study of the Sweeny plume of 28 August 2000, was substantially more idealized than our LESchem study (GW03a). H-02 used $Q(\text{ETH}) = 3.6 Q(\text{NO}_x)$ and the emission inventory value of $Q(\text{NO}_x) = 15$ kmol/h, but they used $Q(\text{OLE}) = 0$. Thus, their VOC reactivity with OH in the plume was about 1/3 of that used by us and by Trainer (2001). Like us, they also used the CB4-CMAQ chemical mechanism. Based on the difference in stack emissions alone, one would have expected O₃ and FORM production in the H-02 simulations to be significantly *less* than in our simulations. Yet, their simulation showed *much higher* production of ozone. Possibly, this was due to substantial idealization in their simulation of PBL physics also. In order to limit the domain size to 20km alongwind x 10km crosswind (LES computations are very computer resource-intensive), they used a constant and uniform mean wind speed of just 1 m/s (instead of the actual value closer to 3.8 m/s), with the wind direction being westerly instead of the actual southerly (of no particular consequence, because the surface emissions of VOC and NO_x were artificially selected to provide approximately the observed background ozone). Furthermore, H-02 did not constrain the mixing height growth from above, and generated mixing layer height growth from ~1200m at 1100 CDT to ~2600m at 1500 CDT, somewhat higher than observed values (peak ~ 2000m). Consequently, the intensity of turbulence in their LES simulation was greater than in ours, as was also their plume spread. They also assumed clear-sky conditions and used significantly higher species photolysis rates (J-values). Another significant difference between the H-02 and GW03a LES simulations was in model spatial resolution. H-02 used a horizontal grid size (Δ_h) of 200m and a vertical grid size (Δ_v) of 100m; GW03a (and this study) used $\Delta_h = 125$ m and a staggered Δ_v varying from 40m near the surface to a maximum of 125m, increasing by 15% from layer to layer until 125m is reached (in layer 10 around 700m). Higher up, Δ_v is held constant at 125m. The two simulations used fairly similar numerical time steps in the dynamical simulations (3s in H-02 and 2.5s in GW03a). Another relatively minor difference was in the effective stack height: GW03a and this study have used 150m, while H-02 used 350m. H-02 also used continuous and constant release of NO_x and ETH from the point source at the rates specified earlier, while our continuous and constant emissions also included OLE. One additional,

possibly significant, difference between the LES models themselves, of H-02 and GW, is that, while both models are based on the RAMS-LES meteorological model, H-02 used an earlier version of RAMS (v.3.2b) while we used the latest v.4.2.

Returning to Figure 1.3 of the H-02 results, the vertical profiles of ozone shown are based on horizontal *spatial* averaging in 4km x 4km layered boxes. Laterally, there were three such juxtaposed boxes: the center ones (C_i , i increasing away from the source along the downwind direction) were along plume centerline and extending to 2km on either side of it; the boxes to the left (north, hence N_i) and right (south, hence S_i) of C_i had a 1km overlap with C_i and extended 3km farther to the side (since the lateral domain size was only 10km). Figure 1.3 shows the spatially averaged vertical profiles of ozone in the plume in the central boxes C_1 , C_2 , C_3 at 1100 CDT (background level, just before plume release started), at 1300 CDT (2h after start of plume release), and at 1500 CDT (4h after start of plume release). For $U = 1$ m/s, the plume transported downwind at the speed of 3.6 km/h. Thus, at $t = 2$ h (1300), the forward edge of the plume centerline was at about 7 km (in box C_2), and the 1300 ozone profile peaks in C_2 . At $t = 4$ h (1500), the forward edge of plume centerline has transported about 14 km (in box C_4 , not shown), and the highest concentrations shown occur in C_3 at 4h. In the 1300 results ($t = 2$ h), the peak ozone concentrations are in C_2 , and even after substantial spatial averaging, are as high as about 280 ppb. At 1500 ($t = 4$ h), the peak ozone in C_3 is close to 400 ppb (spatially-averaged).

Intrigued by these very high values of ozone in the H-02 simulations, we made a run with our LESchem in which we modified our inputs of the stack emissions and the wind speed (the two inputs most obviously different between the H-02 and the GW03a simulations) to match those of H-02 exactly, i.e., we used $U = 1$ m/s and reduced the stack emissions to those used by H-02 (no OLE). Our results of that simulation are presented in Figure 1.4. Even with the emissions and the wind speed the same, the results of H-02 in Figure 1.3 and ours in Figure 1.4 are very substantially different. Our results are of the horizontal (upper panels) and vertical (lower panels) spatial distributions of NO_2 and O_3 for $t = 2$ h, and must be compared to the Figure 1.3 curves for 1300. In our Figure 1.4, the lower right panel for the vertical instantaneous distribution of near-surface ozone shows an *instantaneous and spatially unaveraged* peak of only 102 ppb, as compared to instantaneous but spatially-averaged (4km x 4km) ground level peak value of about 250 ppb in Figure 1.3. This is a very large discrepancy, and can be attributed either to differences in the two models (H-02 and GW03a), or to their remaining differences in inputs. We wanted to run our model with the exact same inputs as those used by H-02, but our attempts to acquire their inputs were futile. We, therefore, decided to perform our own systematic sensitivity analyses of ozone production in an isolated industrial point-source plume such as Sweeny. The sensitivities to be explored were to wind speed (Task 1), source emissions (Task 2), and chemical mechanisms (Task 3). Some very important questions were raised by the results in Figures 1.1-1.4; the most intriguing of them being, “Are concentrations of ozone as high as 400 ppb (even after averaging to 4km x 4km boxes) realistic in the Houston area, in light wind conditions, about 10km downwind of industrial point sources?”

3.2 Results and Discussion

The results here pertain to simulations based on our LESchem model, which involves the RAMS (v. 4.2) LES base model into which we built in an on-line detailed chemistry module, here using the CB4-CMAQ chemical mechanism (the current widely used version), with the chemical

integrations being performed by the SMVGEAR numerical scheme. The simulation domain size was 32km x 20km x 4.5 km (261 x 161 x 40 grid cells), and the spatial-temporal resolution was as specified before. Our Sweeny release started at 1130 and was maintained continuous and constant. Prior to that, we performed a 2-hour spin-up (0900 – 1100 CDT) of the LES physics model (RAMS-LES) only (no chemistry), followed by a 1/2h spin-up of the background chemistry. We ran our LESchem model three times in Task 1, nominally for CBL mean horizontal wind speeds (U) of 1, 2, 3.2 m/s (to complement our original run in GW03a at $U \sim 3.8$ m/s). The choice of 3.2 m/s gives a transport distance of ~ 23 km (the aircraft traverse location) at $t = 2$ h. The PBL physics initialization (at 0900 CDT) of horizontally uniform vertical profiles of potential temperature (θ) and mean wind speed component in the x-direction (U) is shown in the top panels of Figure 1.5 for the “ $U = 1$ m/s run”. In the model run, the evolution of the mixing layer height was approximately matched to that observed based on surface energy fluxes from day-specific MM5 simulations, and additional control from the top by imposing an elevated inversion such that the peak afternoon mixing height reached about 2000m. Simulation results of key physics variables at 1130, 1230 and 1330 CDT are shown in the lower panels of Figure 1.5. Figures 1.6 and 1.7 are similar to Figure 1.5, except that they are, respectively, for the “ $U = 2$ m/s” and “ $U = 3.2$ m/s” runs. Figure 1.8 shows a plot of the time evolution of the values of U for the three simulations. In this plot, U represents the domain-wide spatially and temporally averaged value of the transport wind speed in the CBL (below the elevated inversion and over the entire 32km x 20km horizontal domain).

Background chemistry was initiated at 1100 CDT, based on chemical initialization derived from our previous LRPM simulations (GW03b) and surface emissions of NO_x and VOC (including isoprene) also as in LRPM (surface gridded emissions inventory values adjusted to give the observed background concentrations of the measured species in the CBL at different times). Into this physical-chemical background, a continuous and constant release of NO_x ($Q_{\text{NO}_x} = 24.6$ kmol/h), ETH ($Q_{\text{ETH}} = 3.6 Q_{\text{NO}_x}$) and OLE ($Q_{\text{OLE}} = 2.0 Q_{\text{NO}_x}$) was maintained, starting at 1130 CDT, at the location of the Sweeny plant into the grid cell at about 150m elevation above ground level. LESchem then performed an Eulerian physical-chemical simulation in the transporting plume and its background.

Figure 1.9 shows selected simulated chemical information over the model domain at $t = 2$ h, i.e., two hours after the commencement of the Sweeny plant emissions, thus at 1330 CDT. Figures 1.9, 1.10, 1.11 are similar, but for the three different cases of U -values (1, 2, 3.2 m/s, respectively). Each figure shows a pair of 6-panel plots: the left 6-panel set is for domain-wide instantaneous concentration distributions of six selected species (NO_x , OLE+ETH, OH, O_3 , HNO_3 and FORM) over the horizontal (x - y) plane through $z = 150$ m (effective height of the Sweeny point-source emissions); and, the right set is for the corresponding instantaneous concentration distributions of the same species over the vertical (x - z) plane through plume centerline. The species $(\text{OLE+ETH})_{\text{eq}}$ is the propyl-equivalent representation of the alkenes. In the framework of the plots, the Sweeny point source was placed at $x = 1$ km. The concentration distribution in each panel is shown in the form of color-coded areas between contour lines; the color-coding legend is depicted in the bar charts below each panel. Above each species panel, the chemical species is identified at the left, and the maximum species concentration in the whole plane shown is also specified quantitatively. Thus, for example, the center-right panels in each 6-panel set shows that the local and instantaneous domain-wide peak ozone concentration in the

$U = 1$ m/s run (Figure 1.9) was about 207 ppb (about 5km downwind of the source), compared to corresponding concentrations of 146-150 ppb in the $U = 2$ m/s run (about 10 km downwind, Figure 1.10), and about 97 – 100 ppb in the 3.2 m/s run (about 17 km downwind, Figure 1.11). The corresponding value for $U = 3.8$ m/s and $t = 1.7$ h was around 70 ppb. Thus, the domainwide peak *local-instantaneous* concentration of ozone increases about 3-fold (from ~70 ppb to ~ 207 ppb) as the wind speed decreases about 4-fold, from about 3.8 m/s to about 1 m/s. Even on a local-instantaneous basis, it is limited to around 207 ppb at $t = 2$ h, for the $U = 1$ m/s case.

Figure 1.12 shows a comparison of results for the vertical distribution of ozone from H-02 (left set) and the $U = 1$ m/s run of our present study (the right set), based on horizontal spatial averaging at the 4km box level. For the 2h-results (1300 in H-02), the peak ozone occurs in the central box C2 in both cases: the peak values at ground level are ~250 ppb (H-02) and ~ 90 ppb (ours). Thus, the H-02 values are nearly 3 times higher, even though their VOC emission mix is about 3 times *less* reactive than ours! The spatially-averaged, domain-wide highest value in the H-02 results is nearly 400 ppb in box C3 at 4h (1500 LST), compared to our corresponding value of ~115 ppb. We believe that our results are more realistic.

Let us now return to Figures 1.9-1.11 of the instantaneous species concentration at $t = 2$ h. The species named $(OLE+ETH)_{eq}$ represents the propylene-equivalent concentration of ETH + OLE. In CB4, the OLE concentrations are in propylene equivalent units, but since the OH-reactivity of ETH is only about 0.28 of that of OLE, the ETH concentration gets reduced by nearly four-fold when cast in propylene equivalent units. The downwind extent of plume spread in two hours, of course, varies in proportion with the wind speed, to less than 10km for $U = 1$ m/s, around 15 km for $U = 2$ m/s, and over 25 km for $U = 3.2$ m/s. In all three figures, we see that the primary species dilute quickly, particularly in the lower part of the CBL, and even higher up, within the first 6 km from the source. The secondary species (O₃, HNO₃ and FORM) peak at around 5 km for $U = 1$ m/s (Fig. 1.9) and at around 10 km for $U = 2$ m/s (Fig. 1.10), but even at $U = 3.2$ m/s (Fig. 1.11), their peaks remain close to $x = 10$ km, with net dissipation thereafter; evidently, the fuel to generate the secondary products is spent and diluted. Instantaneous and localized values of FORM exceeding 100 ppb are evident in the $U = 1$ m/s run. The instantaneous peak value of HNO₃ appears to be limited to about 10 ppb, occurring in the $U = 1$ m/s run. The behavior of plume OH shows a very early spike close to the source ($x < 2$ km), then a plume deficit in the next 2 km or so, and then plume values close to the background level, with occasional excesses over the background level.

Figure 1.13 shows a direct comparison of vertical distributions of the species plume concentrations for all three cases of U (1, 2, 3.2 m/s) at a common plume age, $t = 2$ h: the 6-panel set to the left shows the result of crosswind averaging of the plume concentrations in each vertical layer, while the 6-panel set on the right shows the result along plume centerline, where the concentrations may be presumed to be peaked. What we are really showing here are the vertical concentration profiles, crosswind-averaged or along plume centerline, at $x = Ut$, or nominally, at $x = 7.2$, 14.4 and 23.0 km, out of the distributions shown in Figures 1.9-1.11. What we see for the primary species (NO_x and RVOC) is that, in a 2h-old plume, there is still fuel left in the crosswind-averaged plume in the $U = 1$ m/s case, but at higher speeds (both $U = 2$ and 3.2 m/s), the plumes are nearly exhausted of the fuel; near plume centerline, there is a similar

non-linear behavior, with still a fair amount of primary fuel left in the $U = 1$ m/s case, but it drops off fast, faster between the $U = 1$ and $U = 2$ m/s cases, than between the $U = 2$ and $U = 3.2$ m/s cases. The OH behavior seems to be insensitive to the wind speed at $t = 2$ h, with the plume concentration being close to background level in all cases. On the crosswind-average basis, we see a non-linear behavior in the secondary species (O₃, HNO₃ and FORM), which is somewhat like that of the primary species: there is increased production of each with decreasing wind speed, but such increase is greater between $U = 2$ and 1 m/s than between $U = 3.2$ and 2 m/s. We conclude that there is clearly increased production of the secondary products for decreasing wind speed in the first two hours of plume transport, and that such increase is non-linear, being more pronounced at lower values of U .

Another feature we observe in the Figure 1.13 plots along plume centerline is that there tends to be an accumulation of the RVOC near the top of the CBL in the $U = 1$ m/s case. Corresponding to this, we also see similar excesses of the secondary species (O₃, HNO₃ and FORM). As a result of this, there is a vertical variation in the pattern of non-linearity of secondary formations to wind speed. Figure 1.14 shows crosswind profiles of the species at $t = 2$ h and $z = 150$ m (effective point-source emission height). Here, the increase in secondary formations appears to be somewhat more pronounced between $U = 2$ and 3.2 m/s than between $U = 1$ and 2 m/s. Evidently, models which do not preserve the correct vertical behavior of pollutant distributions in the CBL are likely to result in errors related to the sensitivity of plume chemistry to U . The non-linear behavior shown in Figure 1.13 for the crosswind averaged plume is more representative of the behavior of the whole plume mass. We have seen that the behavior of OH is one of relative insensitivity to U and not very illuminating. Figure 1.15 is a plot similar to Figure 1.14, but for HO₂. It shows the sensitivity of HO₂ to variations in U . It is much more indicative of the sensitivity of plume secondary formations to U . Clearly, it is a much better sensitivity parameter than OH, for industrial plumes with high co-emissions of RVOC and NO_x. It must be noted here that in CB4, HO₂ includes all peroxy radicals, including the organic peroxy radicals.

We would like to point out here that the vertical and horizontal profiles shown in Figures 1.13-1.15 contain a great deal of *temporal* averaging. Since the stack emission is continuous (and for at least 4 hours), we have a plume at $t = 2$ h at every time step after the plume has reached the sampled location. The $t = 2$ h data shown are temporally averaged over thousands of such instantaneous profiles. Figure 1.16 illustrates this matter explicitly. It shows, for O₃ and NO₂, the same crosswind-average profiles (at $z = 150$ m) compared to two sets of instantaneous profiles about 10 minutes apart (the upper panels for t_1 and the lower panels for t_2). Observe that the two instantaneous profiles for each species (red) are quite different for both species. The temporally averaged profiles (black) represent the averaging of thousands of such instantaneous profiles.

Table 3 summarizes the variability of ozone production in response to changes in wind speed from 1 to 2 to 3.2 m/s. Our concluding statement on Task 1 is that, in an industrial plume such as that of the Sweeny complex, production of ozone up to 200-250 ppb in an instantaneous and local sense appears to be likely under light wind conditions ($U \sim 1$ m/s) on a summer day. However, our results do not support the formation of concentrations as high as 400 ppb averaged on a 4km spatial scale, as suggested by Herwehe et al. (2002). Also, our sensitivity analysis

shows that a 3-fold increase in ozone production in the Sweeny plant plume (from ~70 ppb to ~210 ppb, local-instantaneous) is indicated for a wind speed decrease from near 4 m/s down to about 1 m/s, with a somewhat more pronounced sensitivity between 1 and 2 m/s, than between 2 and 3 m/s. Light wind conditions are particularly conducive to high ozone production and deserve special attention.

Table 3. Summary of Sensitivity of Sweeny Plume Ozone to Wind Speed

Wind Speed U (m/s)	Peak plume ozone concentration (ppb) @ t = 2h after start of stack emission			
	Domainwide Local-instantaneous	Plume centerline time-averaged	Plume crosswind-average time-averaged	4km box average instantaneous
1	208	137	81	100
2	149	105	60	
3.2	100	73	54	

4. TASK 2: SENSITIVITY OF PLUME CHEMISTRY TO PRECURSOR EMISSIONS

The sensitivity analysis of Sweeny plume chemistry to plant emission rates of NO_x and the RVOCs ETH and OLE is performed based on variation of the these emission rates relative to the “standard” emission rates of NO_x and RVOC defined as follows: $Q_{\text{std}}(\text{NO}_x) = 24.6 \text{ kmol/h}$ (1.66 x EI value), $Q_{\text{std}}(\text{ETH}) = 3.6 Q_{\text{std}}(\text{NO}_x)$, and $Q_{\text{std}}(\text{OLE}) = 2.0 Q_{\text{std}}(\text{NO}_x)$. In the rest of this section, the quantity $Q(\text{RVOC})$ will denote $Q(\text{ETH})$ and $Q(\text{OLE})$ collectively. The “standard run” is defined as the run with $Q(\text{NO}_x) = Q_{\text{std}}(\text{NO}_x)$ and $Q(\text{RVOC}) = Q_{\text{std}}(\text{ETH})$ and $Q_{\text{std}}(\text{OLE})$. The sensitivity to $Q(\text{NO}_x)$ is considered for three values of $Q(\text{NO}_x)$ as follows: 0.5, 1.0 and 2.0 times $Q_{\text{std}}(\text{NO}_x)$, and constant $Q(\text{RVOC}) = Q_{\text{std}}(\text{RVOC})$; the sensitivity to $Q(\text{RVOC})$ is similarly considered for three values of $Q(\text{RVOC})$ as follows: 0, 0.5 and 1.0 times $Q_{\text{std}}(\text{RVOC})$, and constant $Q(\text{NO}_x) = Q_{\text{std}}(\text{NO}_x)$. We also tried to make a run for $Q(\text{RVOC}) = 2.0 Q_{\text{std}}(\text{RVOC})$, but it became numerically unstable and was excluded. Since, according to the EI, $Q(\text{RVOC}) \ll Q_{\text{std}}(\text{NO}_x)$, the case of $Q(\text{RVOC}) = 0 Q_{\text{std}}(\text{VOC})$ is close to the case with EI values of the precursors, in which the source is much like a power plant with high NO_x emission and small RVOC emission. All sensitivity runs for variable precursor emission rates are LESchem runs with $U = 3.2 \text{ m/s}$ and the CB4-CMAQ chemical mechanism. In each run, the Sweeny emissions were constant and continuous, starting at 1130 CDT, and all results in this sections are for $t = 2\text{h}$ (1330 CDT).

Figure 2.1 pertains to the sensitivity of plume chemistry to variations in $Q(\text{NO}_x)$. It shows three sets of 6-panel plots of instantaneous horizontal distributions over the simulation domain of the following six species at $t = 2\text{h}$ and $z = 150\text{m}$: NO_x, [ETH+OLE]_{eq}, HO₂, O₃, HNO₃, FORM; the three sets of 6-species plots are for the three cases of $Q(\text{NO}_x)$, in increasing order of $Q(\text{NO}_x)$ value. Figure 2.2 shows corresponding plots of the vertical distributions along plume centerline at $t = 2\text{h}$. Let us first focus on the ozone plots: for each case of $Q(\text{NO}_x)$, there is a small volume of plume air close to the source in which the ozone is depleted (white area) below the background level by titration with the large NO emission. The size of this volume correlates with the magnitude of the NO_x emission. Downwind of this space, there is a zone in which the ozone recovers to background value and then develops an excess over the background. The development of the excess occurs a little farther downwind with increasing $Q(\text{NO}_x)$, and the region of this excess also appears to be somewhat more intense for increasing NO_x. Still, the absolute value of the local excess in all three cases is not very different, being between 95 and 104 ppb (see local maximum values in each panel written above the plot). Figure 2.3 shows a comparison of the temporally-averaged crosswind (a) and vertical (b) profiles of the same six species at $t = 2\text{h}$ and 23 km (about the distance of the first cross-plume aircraft traverse) for all three inputs of $Q(\text{NO}_x)$; the vertical profiles are also crosswind-averaged. Examination of the ozone profiles shows that there is more or less a linear increase in peak plume ozone of 10-15 ppb in the CBL for each doubling of $Q(\text{NO}_x)$ from 0.5 to 1.0 to 2.0 times $Q_{\text{std}}(\text{NO}_x)$. Thus, even though there is not much difference in the domainwide peak ozone, there can be larger local differences. In Figure 2.3, we also observe that after 2h, there is about 1 ppb or less NO_x excess left in the plume for $Q(\text{NO}_x) \leq Q_{\text{std}}(\text{NO}_x)$, thus limiting much further ozone production (this was also the observation in the field measurements beyond 23 km downwind distance for $Q_{\text{std}}(\text{NO}_x)$). By contrast, for $Q(\text{NO}_x) = 2 Q_{\text{std}}(\text{NO}_x)$, there is still about 2.5 ppb of excess of both NO_x and RVOC (i.e., (ETH+OLE)_{eq}) left in the plume at 2h. The HO₂ levels in the plume at 2h are about the same for $Q_{\text{std}}(\text{NO}_x)$ and $2 Q_{\text{std}}(\text{NO}_x)$, and in both cases, there is still enough RVOC left to

continue to supply HO₂. Thus, whereas further ozone production is NO_x-limited beyond 2h for $Q(\text{NO}_x) \leq Q_{\text{std}}(\text{NO}_x)$, there is still some more fuel left for continued ozone production with $Q(\text{NO}_x) = 2Q_{\text{std}}(\text{NO}_x)$. In other words, had the Sweeny plant emitted more NO_x, there would be more ozone production too. With respect to HO₂ evolution, we observe a pattern somewhat similar to that of ozone initially: as $Q(\text{NO}_x)$ increases, there is initially a deficit in HO₂ relative to the background, and this deficit persists for significantly longer for HO₂ than for ozone, especially for $Q(\text{NO}_x) = 2Q_{\text{std}}(\text{NO}_x)$. Indeed, in this case, the recovery and excess production of HO₂ is significantly limited. Domainwide, there is much higher level of HO₂ production for $Q(\text{NO}_x) \leq Q_{\text{std}}(\text{NO}_x)$, as high as 109 ppt, compared to about 87 ppt for $Q(\text{NO}_x) = 2Q_{\text{std}}(\text{NO}_x)$.

We find that increasing NO_x emission from Sweeny would also result in somewhat greater production of FORM (and organic nitrates, not shown), but not as much as ozone. The largest sensitivity of secondary formation to $Q(\text{NO}_x)$ is for HNO₃, and particularly so for $Q(\text{NO}_x) > Q_{\text{std}}(\text{NO}_x)$. This means that additional NO_x emission from Sweeny would more effectively go into HNO₃ production than into ozone production. In other words, the ozone production efficiency (ozone production relative to NO_x production) is greatest for low $Q(\text{NO}_x)$, and diminishes as $Q(\text{NO}_x)$ increases.

Figures 2.4-2.6 are similar qualitatively to Figures 2.1-2.3, but they are for sensitivity of plume chemistry to $Q(\text{RVOC})$. Again, Figure 2.4 shows instantaneous horizontal distributions of the six species for three different rates of VOC emission from Sweeny (0, 0.5 and 1.0 times $Q_{\text{std}}(\text{RVOC})$), while Figure 2.5 shows the corresponding vertical profiles. Figure 2.6 shows the temporally-averaged crosswind and vertical (crosswind-averaged) profiles at $t = 2\text{h}$ and $x = 23\text{ km}$. As the RVOC emission rate increases, its downwind persistence increases ($[\text{ETH}+\text{OLE}]_{\text{eq}}$ plots). The corresponding persistence of NO_x is now similar for $Q(\text{RVOC}) = 0.5Q_{\text{std}}(\text{RVOC})$ and $Q_{\text{std}}(\text{RVOC})$, and somewhat greater for $Q(\text{RVOC}) = 0$. In other words, the chemistry is more vigorous in the presence of positive $Q(\text{RVOC})$ and results in faster depletion of NO_x. At 2h, HO₂ is still in deficit for $Q(\text{RVOC}) = 0$, and ozone has barely recovered and formed a slight excess. In other words, plume chemistry is quite slow for $Q(\text{RVOC}) = 0$ during the first 2h, and becomes progressively faster as $Q(\text{RVOC})$ increases. Excess HO₂ production over background is sensitive to $Q(\text{RVOC})$ and positively correlated with it; ozone production is a little less sensitive to $Q(\text{RVOC})$ than HO₂. The greatest positive sensitivity to $Q(\text{RVOC})$ is that of FORM (and also organic nitrates, not shown); FORM peaks domainwide at about 43 ppb (at $\sim 10\text{ km}$ at 2h) for standard emissions of both RVOC and NO_x (for standard emission of RVOC and 2 times standard emission of NO_x, it peaked at about 27 ppb, see Fig. 2.1). By contrast, HNO₃ production is anti-correlated with $Q(\text{RVOC})$, but this correlation is rather weak.

Table 4 summarizes the results of sensitivity of O₃, HNO₃, FORM and HO₂ to precursor emission rates based on the data in Figures 2.3 and 2.6 for the time-averaged plume centerline condition at a plume age of 2h ($x = 23\text{ km}$). To recapitulate, sensitivity to $Q(\text{NO}_x)$ is strongest for HNO₃ production, significantly weaker for ozone, and even weaker for HO₂, FORM and organic nitrates. By contrast, sensitivity to $Q(\text{RVOC})$ is strongest for FORM, organic nitrates and HO₂, somewhat weaker for ozone, and rather weakly inverse for HNO₃. Increasing $Q(\text{NO}_x)$ 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. Increasing $Q(\text{RVOC})$, instead, would be more productive particularly for aldehydes and organic nitrates, and less so for

ozone. The ozone production efficiency (OPE) varies inversely with $Q(\text{NO}_x)$ and positively with $Q(\text{RVOC})$, i.e., it is positively correlated with $Q(\text{RVOC})/Q(\text{NO}_x)$.

Table 4. Summary of Sensitivity of Sweeny Plume Chemistry to Precursor Emission Rates

Data below are for time-averaged plume centerline conditions at $z = 150\text{m}$ and plume age of 2h ($x = 23\text{km}$), and are taken from Figs. 2.3 and 2.6.

(a) Sensitivity to $Q(\text{NO}_x)$	$Q(\text{NO}_x)$	Plume Centerline Concentrations			
		O3	HNO3	FORM	HO2
$Q(\text{RVOC}) = \text{std.}$	0.5 Qstd	61	0.9	11.2	79
	1.0 Qstd	74	1.7	12.6	90
	2.0 Qstd	86	3.8	13.2	86
	Background --->	39	0.4	1.9	47

(a) Sensitivity to $Q(\text{RVOC})$	$Q(\text{RVOC})$	Plume Centerline Concentrations			
		O3	HNO3	FORM	HO2
$Q(\text{NO}_x) = \text{std.}$	0	45	2.5	2	29
	0.5 Qstd	66	2.2	7.9	74
	1.0 Qstd	74	1.7	12.4	90

We close this section with an examination of the sensitivity of fast eddy-scale chemistry (not resolved, i.e. ignored, in the operational models LRPM, CAMx, CMAQ, etc.), but explicitly included in LESchem. The practical effect of such chemistry due to turbulent concentration fluctuations is to modify the reaction constants (K) of the reactions between mean species concentrations. The modified reaction constant (say, K') may be expressed as $K' = f K = (1+s) K$, where f is a reaction enhancement factor. A measure of the enhancement of K'/K above 1 is the so-called segregation coefficient, s (for details, see Gillani and Wu, 2003a), which reflects the effect of segregation of reactants at the eddy scale which is masked by their instantaneous uniform mixing within the gridcells of operational models. Figure 2.7 shows plots of f as a function of downwind distance x , at $t = 2$ h, for four important reactions in photochemical modeling, viz. OLE+OH (VOC breakdown), NO+O₃ and NO+HO₂ (conversion of NO to NO₂, chain propagation), and NO₂+OH (chain termination). Collectively, the reactions cover the range of the major types of reactions involved in gas-phase atmospheric chemistry. Each panel in the plot also shows the sensitivity of $f(x)$ to $Q(\text{NO}_x)$ --- (upper panels), and $Q(\text{VOC})$ --- (lower panels). We observe that $f < 1$ in the near-field from the source, implying that the eddy effects tend to *slow down* the reaction rates in the fresh plume rather than to speed them up, and that such slowdown is general (for all reactions shown) and most pronounced close to the source. The intensity and downwind distance of this reactions deceleration effect is sensitive to the precursor emission rate, and limited to 5-10 km for all reactions shown except the reaction NO₂ + OH, for which the effect extends farther for high-NO_x and low-VOC emissions. Beyond the near-field, the value of f recovers, and in some cases, even becomes greater than 1 (implying speeding-up of the chemistry by the eddy effects). The recovery time varies from reaction to reaction, but in general, is sensitive to the precursor emission rates. In the case of $Q(\text{NO}_x)$, with $Q(\text{VOC}) = Q_{\text{std}}(\text{VOC})$, i.e., in the presence of a rather substantial rate of VOC emission, the recovery of f is fastest for lowest $Q(\text{NO}_x)$ and slowest for highest $Q(\text{NO}_x)$. In the case of $Q(\text{VOC})$, the opposite is true, i.e., the higher $Q(\text{VOC}) > 0$, the faster is the recovery of the slowed-down chemistry followed by speeding up, as a result of the eddy effects. The recovery is slowest for the case of $Q(\text{VOC}) = 0$ (power plant plume case). For the standard Sweeny emissions scenario of 8/28/2000, such recovery was completed within 5 to 10 km from the source for the four selected reactions, based on LESchem simulation.

5. TASK 3: SENSITIVITY OF PLUME CHEMISTRY TO CHEMICAL MECHANISM

5.1 The Target Chemical Mechanisms

Our original plan was to test the sensitivity of gas-phase photochemistry in the Sweeny plume to chemical mechanism based on three mechanisms, two versions of the Carbon-Bond mechanism (CB4-CMAQ and CB4-2003) and the latest version of the SAPRC mechanism, subject to availability of the related emissions inventories and photolysis rates. The emissions inventories were to be supplied by TCEQ. Unfortunately, TCEQ could not develop the emissions inventory for the SAPRC mechanism in time for this project. Hence, our sensitivity analysis is limited to the two versions of CB4. Chemical mechanisms used in operational air quality models are compacted and parameterized representations of the chemical species and their explicit reactions which occur in the atmosphere, and therefore, represent approximations of the actual chemistry, depending on the manner of compaction of the species and parameterization of the reactions. This is particularly the case for the VOC species, of which there are a very large number in the atmosphere, and for many of which the actual chemistry is very complex chain chemistry. The compaction of the species and reactions is achieved by one of two kinds of lumping: (a) lumping of species of like reactivities, with the reactions and reactivities of each lumped class being then represented by those of surrogate species (Lurmann et al., 1987), sometimes with some adjustments to account for the variations in the composition of the compounds being lumped (Carter, 1990; Stockwell et al., 1990); or, (b) the lumped structure technique, in which organic compounds are apportioned to one or more mechanism species on the basis of chemical bond type associated with individual carbon atoms (Whitten et al., 1980). The SAPRC mechanism is an example of the lumped surrogate species approach and the CB4 mechanism is an example of the lumped structure (carbon-bond) technique.

The CB4 mechanism (Gery et al., 1989) is the fourth in an evolving series of carbon-bond mechanisms. It was developed originally for urban applications, and is limited for applications to domains (and hence transport times) of limited size because of the nature of some of the particular assumptions in it. The domain size for our Sweeny applications meets this domain-size criterion, and the CB4 mechanism is, therefore, suitable for application in our case. CB4 is the most compact of the detailed mechanisms used in current operational photochemical air quality models, and therefore most economical to use. Its particular implementation in EPA's Models-3/CMAQ Eulerian modeling system is a fairly current version which is widely used. This is one of the mechanisms tested in the present study. We will identify it as CB4-CMAQ. It contains 36 species and 93 reactions (of which 11 are photolytic reactions). It uses 9 primary (emitted) organic species, three (ethylene, isoprene and formaldehyde: ETH, ISOP and FORM) being represented explicitly as themselves, and the other six being carbon-bond lumped species (5 for the reactive VOCs and one for the non-reactive species). Of the lumped primary reactive VOCs, the one of particular interest is that representing alkenes other than ethylene, or olefins (OLE). This is because the greatest uncertainty in the RVOC emissions from the petrochemical industrial sources is believed to be for ETH and OLE, both being among the more reactive of the primary VOCs.

CB4-CMAQ was recently upgraded significantly by the group of Professor Harvey Jeffries at the University of N. Carolina (UNC). This updated version was identified by them as CB4-2003

(Voicu, 2003), and it is our second choice of mechanism included in this study. The upgrade is particularly targeted at the inorganic chemistry, and is based on the latest inorganic chemistry kinetics and reaction pathways. 58 reaction rate constants are updated: 33 are inorganic, 18 are organic, and 7 describe the operator chemistry. Also, 6 inorganic reactions are added to the base mechanism (CB4-CMAQ); they involve mainly nitrogen-containing compounds. A new alkene chemistry representation is also included to encompass the chemistry of urban terminal alkenes, instead of only the chemistry of propene. Some organic reactions, such as aromatic compound reactions, are unchanged. Aromatic chemistry product identification uncertainties continue to be a problem, thus inhibiting its effective formulation. CB4-2003 was evaluated by its developers against data from approximately 100 experiments conducted in the UNC outdoor smog chamber. The “goodness-of-fit” measures included the time of NO-to-NO₂ crossover and the match between ozone data and ozone simulations, as well as accurate product prediction. The results of the evaluation indicated substantial improvement in the ability of the new version of the mechanism to simulate the chemistry of synthetic urban mixtures. In the tests based on such mixtures, CB4-2003 converted NO to NO₂ faster than CB4-CMAQ and also generated more ozone. It produced significantly less HNO₃.

5.2 Our Sensitivity Study: Results and Discussion

We have revised our code of UAH-LRPM to implement CB4-2003 also, and we have applied the revised LRPM in two recent nearly parallel studies to test the sensitivity of point-source plume chemistry to the two CB4 mechanisms. The first of these studies (for EPRI: Gillani and Wu, 2004) was focused on applications to the 12 July 1999 case study of a power plant plume (TVA’s Cumberland Steam Plant in NW Tennessee). The Cumberland Plant has a much higher NO_x emission rate than Sweeny (~266 kmol/h compared to ~24.6 kmol/h), and of course, negligible VOC emission. Our results for the Cumberland case study showed very considerable difference in large powerplant plume chemistry for these two versions of CB4, but the differences were not all as those found for an urban mixture by the developers of CB4-2003 (Voicu, 2003). We start by presenting some of these results for the powerplant plume first.

Figure 3.1 shows some Cumberland plume sensitivity analysis results taken from Gillani and Wu, 2004. Each of the three rows shows the results for a different Lagrangian model run (different plume release times) ending in the time of plume sampling by the NOAA-WP3 aircraft in a particular crosswind plume traverse. All three runs are for plume transport during a convective mid-summer day over mostly deciduous forested terrain with some of the highest isoprene emissions in the nation. The first row of results is for a 2.2h plume age at 21km downwind, the second is for a 6.3h plume age at 63 km, and the third is for a plume age of 9h at 80 km. Each row of results shows three panels, one for each of the three species NO_y, O₃ and HNO₃. Each panel contains three traces of crosswind plume concentration profiles: one is based on aircraft measurement, and the other two are based on LRPM simulations using CB4-CMAQ and CB4-2003. For NO_y, the two simulations are practically identical and very close to the observed for all three runs. For ozone, the three runs for increasing plume age depict the three well-known stages of plume chemical evolution (Gillani and Wilson, 1980; Gillani et al., 1981), from an early ozone deficit (Stage 1, top row) to an intermediate stage of ozone wings (Stage 2, middle row) to a case of the mature plume with excess ozone throughout the plume (Stage 3, bottom row). The ozone simulations based on CB4-2003 are closer to observation for all three runs, and there is significantly *less* ozone production in the mature plume for CB4-2003 than for CB4-

CMAQ (opposite of the result of Voicu, 2003 for an urban mix). For HNO₃ also, the simulations are closer to observed for CB4-2003, which produces considerably less HNO₃ (similar to the result of Voicu, 2003 for the urban mix). The conclusion for such high-NO_x emission powerplant plumes is that CB4-2003 gives improved simulation of plume chemistry for both ozone and HNO₃, and for both of these species, CB4-2003 is chemically substantially *less* productive, particularly for HNO₃.

Figures 3.2, 3.3 and 3.4 show, respectively for plume ages of 2, 6 and 8h, a comparison of similar results based on the two chemical mechanisms for 12 modeled species, for a single Lagrangian run of the Cumberland plume release of 1000 CDT on 12 July 1999. There is faster conversion of NO to NO₂ with CB4-2003 in this high-NO_x plume, but less production of the major secondary species (O₃, NO_z, HNO₃, NO_z-HNO₃ and FORM) as well as the intermediate radical HO₂. Also, in general, the gap in plume chemical evolution based on the two mechanisms grows with plume age. We now turn our attention to a similar sensitivity analysis for the Sweeny plume.

The Sweeny plume simulations are corresponding to the two crosswind plume traverses of the NCAR-Electra aircraft on 28 August 2000 (described in detail in Gillani and Wu, 2003b). These are identified here as T1 and T2. In T1, the aircraft traverse of the plume was at ~1310 CDT at a downwind distance from Sweeny of about 23 km, and from trajectory analysis, it was inferred that the plume here was about 1.7h old, corresponding to plume release from Sweeny at ~1130 CDT. T2 was at ~ 1355 CDT at a downwind distance of ~50 km, for plume age of ~3.75h (plume release ~ 1010 CDT). The simulations of the “standard run” (the run judged to be closest to observed reality) correspond to NO_x and RVOC emissions from Sweeny, for both runs (for T1 and T2), as follows: $Q(\text{NO}_x) = 24.6 \text{ kmol/h}$, $Q(\text{ETH}) = 3.6 Q(\text{NO}_x)$ and $Q(\text{OLE}) = 2.0 Q(\text{NO}_x)$. All other inputs are as described in Gillani and Wu, 2003b. All simulations are of UAH-LRPM.

Figure 3.5 shows the observed and simulated crosswind plume profiles in T1 for 12 modeled species. Each panel is for a different species and contains three traces: observed (red) and simulated (black), one for CB4-CMAQ (solid) and another for CB4-2003 (dotted). Both simulations show a somewhat more rapid depletion of NO_x than observed, and a corresponding overproduction of NO_z, mainly in the form of HNO₃. The simulation of the production of ozone, FORM and organic nitrates (NO_z – HNO₃) by both mechanisms is very close to observed. As for the difference between the two simulations, in terms of the difference between plume peak concentrations, it is less than 4% for NO_y and its component species, about 2% for ozone, and about 6% for HO₂ and FORM. The largest difference is that the consumption of ETH and OLE is considerably faster for CB4-2003 than for CB4-CMAQ. For this 1.7h old plume (with the NO_x mostly depleted) from a source with about one order of magnitude lower NO_x emission than Cumberland, and comparable RVOC and NO_x emissions, the sensitivity to the two CB4 mechanisms is considerably smaller than it was for the Cumberland plume. Evidently, the sensitivity to chemical mechanism appears to be strongly a function of the emission strength and composition. Whereas the sensitivity of ozone and HNO₃ production to the mechanism was strong for the very high-NO_x powerplant plume, it is relatively much smaller for the smaller Sweeny petrochemical plume.

Figure 3.6 shows the simulated crosswind plume profiles based on the two mechanisms for a somewhat more aged Sweeny plume of age 3h. In this even more spent plume (in terms of the

precursor fuels), other than a somewhat greater difference in the simulated peaks of the secondary nitrates, the results are qualitatively similar to the plume at T1.

Figure 3.7 is similar to Figure 3.5, but for T2. Here, the plume is more than twice as aged as in T1. Again the sensitivity of ozone and NO_z production to the mechanism is very small, but it is somewhat greater for HNO₃ and (~ 10% difference at plume peak) and the organic nitrates (~14%).

As stated before, it appears that the sensitivity of plume chemistry to the chemical mechanism is itself sensitive to NO_x emission rate and the ratio RVOC/NO_x of the emission. To check the sensitivity of the sensitivity to Q(RVOC)/Q(NO_x), we show a simulation of a Sweeny “powerplant” plume, i.e., with the RVOC emissions from Sweeny turned off. Figure 3.8 shows the corresponding results (the red trace is for the observed actual Sweeny plume). Here, the ozone production is about 21% less for CB4-2003 than for CB4-CMAQ. It appears that the sensitivity of ozone production to chemical mechanism is strong in proportion to NO_x emission rate, and inversely related to RVOC emission rate.

In the previous figures, we have examined the results in terms of species crosswind profiles at discrete downwind distances, e.g., T1, T2. Figure 3.9 shows simulation results for species concentrations at plume centerline continuously as a function of downwind distance up to 50km, for a Lagrangian simulation of the Sweeny “standard” release at 1000 for the conditions of 28 August 2000. The plot shows the traces corresponding to separate runs based on the two chemical mechanisms. For the primary oxides of nitrogen species, the sensitivity to the two mechanisms appears to be negligible; for the secondary nitrogen species HNO₃ and NO_z-HNO₃, the sensitivity remains fairly small throughout, but appears to grow slightly with plume age (or downwind distance); for ozone and FORM, the sensitivity peaks at a downwind distance of 10-20 km, where the plume concentrations of these species themselves peak. Figure 3.10 shows a similar plot for the Sweeny “powerplant” plume (Q(RVOC) = 0). In this case, the sensitivity to the mechanism is less pronounced generally, and we also observe that the peaking of the secondary products is considerably delayed (slowed down chemistry).

It is interesting to compare the conditions of the Sweeny and Cumberland plumes at a similar downwind distance of about 20 km and plume age near 2h. Let us do this with a focus on two species, NO_y and ozone. The Sweeny results are shown in Figure 3.5 and the Cumberland results in the top row of Figure 3.1. At such a comparable *physical* age of the plumes, there is more than 80 ppb of NO_y still left in the Cumberland plume, which is chemically still a quite fresh plume with a strong deficit of ozone (compared to background). By contrast, the smaller Sweeny plume is chemically quite aged and past its prime (having peaked chemically at 10-20 km), and is mostly spent of the fuel for the chemistry (peak NO_y < 4ppb). But we notice another significant difference in the two scenarios: the plume chemical *backgrounds* are considerably different in the two cases. For example, background ozone for the Sweeny plume of 8/28/2000 at around 1300 CDT was about 37 ppb, while the corresponding background for Cumberland at 1235 CDT was nearly 70 ppb. In the case of the powerplant plume (no RVOC in the plume emission), it is well known that background RVOC plays a critical role in plume chemistry (Gillani and Wilson, 1980; Gillani et al., 1981). The RVOC background is indeed very different NW of Nashville (Cumberland domain) and SW of Houston (Sweeny domain): the former is

much richer in biogenic RVOC (isoprene). The much higher ozone background (as well as the much higher NO_z background of 2.5 ppb v. 0.5 ppb) for Cumberland than for Sweeny is at least partly due to this difference in the chemical backgrounds of the two scenarios. Presumably, another possibly significant difference is also in the intensity of sunlight in the two cases, with the Cumberland scenario being near the summer peak (July 12), while the Sweeny scenario was near the end of the summer (28 August). How would the sensitivity of plume chemistry to chemical mechanism be itself sensitive to such differences related to such space-time differences? The discussion below examines this question.

Figure 3.11 shows a simulation of the Sweeny plume (i.e. Sweeny emissions) transposed to the Cumberland location in Tennessee, and at a plume age of 3h. This may be compared to the corresponding simulation of the Sweeny plume in Texas, also at 3h. The chemical backgrounds and solar radiation are different in the two simulations, but the plant emissions are exactly the same. We notice a significant difference in the sensitivity to chemical mechanism (separation between the solid and dotted traces) between the two cases. For comparison with these, we also present in Figure 3.12, the simulation results of the Sweeny “Tennessee” run with $Q(\text{RVOC}) = 0$, i.e., the results are for the Sweeny “powerplant” in Tennessee.

5.3 Conclusion

What we have done overall in this section is to examine the sensitivity of point-source plume chemistry to two variations of the CB4 chemical mechanism, and what we found rightaway was that the results did not duplicate the findings of the authors of the CB4-upgrade (CB4-2003), due to the main generalized reason that such sensitivity is itself sensitive to a number of other factors influencing plume chemistry. Such other factors include source NO_x emission strength, the RVOC/NO_x ratio of the source emission, and even the plume environmental (background) conditions. We found that the sensitivity of plume chemistry to the chemical mechanism becomes stronger as $Q(\text{NO}_x)$ increases, becomes weaker as the ratio $Q(\text{RVOC})/Q(\text{NO}_x)$ increases, and becomes stronger as the environmental factors favoring gas-phase chemistry (e.g., solar radiation, background reactivity) become more pronounced. For a large powerplant plume with high $Q(\text{NO}_x)$ and low $Q(\text{RVOC})/Q(\text{NO}_x)$, the chemical simulations are substantially different for the two CB4 mechanisms and significantly improved by CB4-2003; by contrast, for the Sweeny plume with relatively much lower $Q(\text{NO}_x)$ and much higher $Q(\text{RVOC})/Q(\text{NO}_x)$, the chemical simulations are not very different for the two CB4 mechanisms, and there is not much improvement by using CB4-2003.

6. CONCLUSION

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 $Q_{\text{NO}_x} = 24.6$ kmol/h, $Q_{\text{ETH}} = 3.6 Q_{\text{NO}_x}$ and $Q_{\text{OLE}} = 2.0 Q_{\text{NO}_x}$, 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). We have also presented results of such sensitivity for various different types of temporal and spatial averaging, and they all paint a similar picture.

Task 2 pertained to sensitivity of plume chemistry to source emission rates of NO_x and RVOC (ETH, OLE). The sensitivity analysis for $Q(\text{NO}_x)$ was performed for constant $Q_{\text{std}}(\text{RVOC})$ and the following three different values of $Q(\text{NO}_x)$: 0.5, 1.0 and 2.0 times $Q_{\text{std}}(\text{NO}_x)$. The sensitivity analysis for $Q(\text{RVOC})$ was performed for constant $Q_{\text{std}}(\text{NO}_x)$ and the following three different

values of $Q(\text{RVOC})$: 0, 0.5 and 1.0 times $Q_{\text{std}}(\text{RVOC})$. An attempt to make the run with 2 $Q_{\text{std}}(\text{RVOC})$ became numerically unstable. Sensitivity to $Q(\text{NO}_x)$ is strongest and positive for HNO_3 production, significantly weaker for ozone, and weakest for HO_2 , FORM and organic nitrates. By contrast, sensitivity to $Q(\text{RVOC})$ is strongest and positive for FORM, organic nitrates and HO_2 , somewhat weaker for ozone, and weakest and inverse for HNO_3 . Increasing $Q(\text{NO}_x)$ from Sweeny would produce much more HNO_3 , 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 $Q(\text{RVOC})$, instead, would be more productive particularly for aldehydes and organic nitrates, and less so for ozone. The ozone production efficiency (OPE) varies inversely with $Q(\text{NO}_x)$ and positively with $Q(\text{RVOC})$, i.e., it is positively correlated with $Q(\text{RVOC})/Q(\text{NO}_x)$. 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 $Q(\text{NO}_x)$ and $Q(\text{RVOC})$. 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 $Q(\text{NO}_x)$ and $Q(\text{RVOC})$: in general, such persistence increases with the magnitude of $Q(\text{NO}_x)$ and diminishes with the magnitude of $Q(\text{RVOC})$.

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 HNO_3 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 HNO_3 . 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 $Q_{\text{RVOC}} = 0$ (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 $Q(\text{RVOC})/Q(\text{NO}_x)$. 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.

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