

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

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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 NO_x 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 NO_x 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 NO_x 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 NO_x 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 NO_x emission rates. Such co-emissions of NO_x and reactive VOCs lead to rapid nonlinear gas-phase chemistry, which produces large amounts of ozone and other secondary products (e.g., NO_z, 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 NO_x 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), NO_x 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 NO_x emissions from downwind sources may provide the NO_x 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 $u < 3$ 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 NO_z (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 NO_x 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 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 NO_x 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-NO_x 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.

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1. INTRODUCTION

A major intensive 3-D field measurement program was conducted in the Houston-Galveston area of Texas in the Summer of 2000 (the Texas 2000 Air Quality Study, or TexAQS). An important preliminary finding of an accelerated science evaluation of ozone formation in the area, based on comparison of field observations (aircraft and ground-based) and simplified diagnostic Lagrangian reactive plume modeling (LRPM) using the latest available point-source emissions inventory (EI), was that emissions estimates of certain reactive VOCs from large industrial point-sources may be grossly under-estimated in the EI (TNRCC, 2002). In particular, the new finding suggested that emissions of the low molecular weight reactive alkenes, especially ethene and propene, from such sources, which are particularly concentrated in the Ship Channel area to the northwest of Galveston Bay, may be 1 to 2 orders of magnitude higher than in the EI, and comparable to the co-emissions of NO_x, and that these emissions, together, may be largely responsible for the observed very rapid and efficient formation of ozone in the corresponding plumes (Trainer, 2001). This finding, if true, has serious implications for the new SIP which is under development, particularly in terms of development of an optimum ozone control strategy based on *combined* VOC and NO_x control. It would also explain why air quality grid models based on the EI have failed to simulate the observed rapid and high ozone events in H-G. An urgent need existed to test this important finding more rigorously, based on a top-down (observation-based) emissions verification (TD_EV), using the state-of-the-art ambient measurements of TexAQS. The above finding was based mainly on somewhat idealized analyses, and even those, for the isolated emissions from the Sweeny and Freeport sources. There is need for a rigorous diagnostic study of the transport and chemistry of not only these emissions, but also of emissions from the ship channel complex (SCC).

This report presents findings of such a rigorous diagnostic modeling study targeted at the various clusters of industrial point sources in the Houston-Galveston area, including the SCC. It is based on use of the TexAQS data and two diverse models --- the single- and multi- plume versions of a state-of-the-art LRPM (the UAH-LRPM), and an LES (Large Eddy Simulation) model with detailed chemistry added into it by us (UAH-LESchem). As much as possible, the TD_EV was to be targetted at individual large point sources. In the case of most cities, the largest emissions uncertainties are generally associated with reactive VOC emissions from *area and mobile* sources. The H-G area, however, is different from most other cities in that a relatively limited number of large industrial *point*-sources contribute an unusually large component of the reactive VOC emissions here, and their emission inventories are now suspect, hence the focus on such sources.

The present work is a follow on to a previous study (Gillani and Wu, 2003; henceforth, GW03), in which the focus was on LRPM upgrade and application to the 28 August 2000 case study. In that study, the existing single-plume version of UAH-LRPM was upgraded to a multi-plume version capable of simulating multiple interacting plumes from a many-source complex such as the SCC. In the present study, we have performed similar LRPM diagnostic analyses of the plumes from the same sources for the 27 August 2000 case study also, and we compare the results from the two case studies to seek corroboration. Here, we have also performed a pioneering LESchem study of the plume from an isolated source cluster (Sweeny), to test the feasibility of realistic LES simulations of point-source plumes, and if feasible, then an assessment of the contribution to the chemical reaction rates from turbulent concentration fluctuations of the reactants (generally neglected in operational air quality models, OAQMs).

Unfortunately, we could not extend such LESchem study to the ship channel complex, because of computational constraints resulting from limitations of the current LESchem computer code (elaboration later).

2. RELEVANT PRIOR FINDINGS OF TexAQS --- BACKGROUND

The Houston-Galveston (H-G) and the Dallas-Ft. Worth (DFW) areas have about the same population (~ 4 million), as well as area-source and mobile-source emissions (based on current EIs) of both the ozone precursors, VOC and NO_x. Yet, H-G has far more annual exceedances of the 1-h ozone NAAQS (129 v 28), a much higher ozone design value (199 ppb v 131 ppb), and a significantly longer ozone season, peaking in late August/early September (Breitenbach, 2002). The main reason appears to be that H-G has much higher emissions (an order of magnitude, or more) of both VOC and NO_x from major *point* sources, particularly, industrial point sources which co-emit both VOC and NO_x in large quantities. There is a particularly dense concentration of such sources in the Ship Channel Complex (SCC) of petrochemical industry to the northwest of Galveston Bay and east of the Houston urban core (see Fig. 1). The highest monitored ozone concentrations occur most frequently close to the SCC, east of the urban core (TNRCC, 2001a). Co-emissions of large quantities of reactive VOC and NO_x from such industrial point sources may react very quickly, resulting in very rapid and efficient ozone production, much more so than in plumes of typical urban core emissions (Houston and most other cities) and of large power plant emissions (Trainer, 2001; Ryerson et al., 2001). Such industrial source plumes of high ozone are also rather compact and dynamic, with the ozone peak advecting sequentially over particular downwind surface monitoring sites, registering distinct transient high ozone events (*THOEs*) at the impacted sites (TNRCC, 2001a). The ozone rise rates of these *THOEs*, and related ozone production rates, frequently exceed 40 ppb/h, and as much as 200 ppb/h, as measured at surface sites and in aircraft (TNRCC, 2001a; Daum, 2002). These are much higher than those observed in most other cities. Lidar measurements of vertical profiles of ozone and aerosol backscatter reveal complex cross-sectional structure in such plumes (Senff et al., 2001).

Another important reason for the distinct spatial-temporal distribution of ozone in H-G appears to be that meteorology related to the fairly frequent land/sea breeze recirculations, occurring on about 37% of the days in August-September (Breitenbach, 2002), is also more conducive to high ozone formation and buildup (TNRCC, 2001b). On such days, a conceptually distinct local flow pattern prevails: light nocturnal flow, turning from W at midnight to NW by 6 a.m., promotes accumulation of urban precursor emissions in a shallow mixing layer, and their slow drift toward Galveston Bay; by noon, the winds have rotated to the E, and then strengthen from the SE as the sea breeze comes in during the afternoon; in the meanwhile, under the daytime sunlight and heat, these precursors convert to ozone and related smog, being reinforced by the rapidly reacting embedded emissions from the elevated industrial point sources into the rising morning mixing layer and the deep afternoon mixing layer. The resulting soup in the afternoon consists of a fairly broad area of high ozone, with embedded, relatively compact, peaks of rapidly-formed ozone in industrial source plumes.

The existence of the moving *THOEs* downwind of the industrial source complexes was suspected even before TexAQS, but there was much speculation about the mechanism(s) of the rapid chemistry causing them. The following possible chemical mechanisms had been

hypothesized as the likely cause(s) (TNRCC, 2001a): (a) high co-emissions of reactive VOCs and NO_x from industrial sources, including possible upset emissions; (b) chemical pathways for ozone formation other than those in current photochemical models, such as atomic chlorine reactions in the presence of alkanes (based on detection of products of such chemistry), and possible heterogeneous reactions on aerosol surfaces; and, (c) enhanced (observed) nocturnal radical production and accumulation (from ozone-alkene or other pathways), possibly contributing to accelerated daytime ozone production. More recently, a fourth potential cause of speeded up chemistry (d) has been hypothesized (Herwehe et al., 2002; Gillani and Wu, 2003) --- that relates to possible enhancement of reaction rates (of the VOC-NO_x chemistry) due to highly correlated turbulent fluctuations in the concentrations of co-emitted species (VOC, NO_x), or directly related other reactants, particularly oxidants (ozone, odd-H radicals). Such turbulent chemistry effect is not currently included in the grid models used for SIP calculations or the LRPMS used in diagnostic studies. To include such effects, model simulations must explicitly resolve large turbulent eddies (Large Eddy Simulations, LES), and include detailed chemistry in such simulations, particularly in industrial plume modeling close to the source. Herwehe et al.'s preliminary application of LES-with-chem to an isolated point source plume with large NO_x and ethene co-emission has resulted in simulations with excessive levels of ozone in the plume (as much as 400 ppb!) attributed to the very low wind speed and enhancement of the chemistry by turbulent effects. If such enhancement is true, the high inferred estimates of ethene and propene emissions from the industrial sources in the preliminary findings of the accelerated science evaluation could themselves be in significant error, and may be considered to be upper-bound estimates. There is a need to evaluate the findings of Herwehe et al., and to explore (quantitatively) the significance of both --- low wind speed and turbulent chemistry.

Aircraft observations and diagnostic reactive plume modeling under TexAQS (Trainer, 2001; Ryerson et al., 2001) appear to suggest strongly that item (a) above may be the most likely and dominant cause, even under conditions of routine (rather than upset) emissions. Emissions of NO_x from the industrial plumes appear to be more-or-less consistent with the latest TNRCC emission inventories (EIs), but emissions of low-molecular-weight reactive alkenes (particularly ethene, propene and 1,3-butadiene) appear to be MUCH higher than in the EIs (up to two orders of magnitude for ethene and at least one order of magnitude for propene), making these VOC emissions comparable with (or even higher than) the corresponding NO_x emissions. Such high co-emissions of these reactive VOCs and NO_x can give the observed rapid and efficient production of not only ozone, but also of correlated secondary species such as aldehydes and PANs, based on standard chemical mechanisms currently used in photochemical models (e.g., CB-IV and SAPRC). It may, therefore, not be necessary to invoke substantial participation of the other hypothesized mechanisms (e.g., chlorine-alkane, heterogeneous chemistry, or nocturnal radical production). The limited role of chlorine chemistry has also been confirmed by Tanaka et al (2000; 2001), using chlorine-related data of Riemer et al (2001) and photochemical modeling including appropriate chlorine chemistry. Aircraft observations of only small quantities of products of isoprene chemistry (e.g., MPAN) also indicate a relatively minor role of isoprene in the rapid and efficient formation of ozone in the industrial plumes, especially during southerly flow. Lack of significant correlation between observed ozone and Beryllium-7 (a tracer of stratospheric origin) at the LaPorte surface monitoring site also ruled out significant contribution of stratospheric ozone to the *THOEs* (Wood, 2002). However, the excessive ozone production in the Herwehe et al. (2002) LESchem study remains an enigma, and needs to be checked out.

In the present project, the focus was dual, first on mechanism (a), i.e., high co-emissions of reactive VOCs and NO_x from industrial sources, and second, on mechanism (d), i.e., the turbulent chemistry. The approach used in our study is that of diagnostic applications of UAH-LRPM and UAH-LESchem (distinct from Herwehe et al's), in conjunction with TexAQS data.

3. UAH-LRPM: Single-plume Version and Multi-plume Upgrade

3.1 Single-plume Version

The model applied here is the current version of the UAH-LRPM (University of Alabama in Huntsville --- Lagrangian Reactive Plume Model). It originated as the Gillani-LRPM (Gillani 1986), and further evolved as UAH-LRPM, first during its upgrade for use as the building block of the Plume-in-Grid (PinG) module (Gillani et al., 1998; Gillani and Godowitch, 1999) of EPA's urban-regional modeling system, Models-3/CMAQ (EPA 1999), and more later (Gillani et al., 2002). Conceptually, the model simulates the time-dependent, two-dimensional concentration evolution within a semi-infinite lagrangian vertical slab moving with the average transport wind, which may vary with time (in speed and direction) along the slab trajectory. It does not allow for wind shear effects; hence, its application is best suited in the convective summer boundary layer during the daytime, and particularly when wind shear effects are not very significant. Such was indeed the condition in its application to the simulations of the case studies presented here (27, 28 August 2000). The slab framework of our LRPM permits arbitrary spatial resolution (externally specified) in both the crosswind (y) and the vertical (z) directions. The model is designed to simulate the change in concentration of all modeled chemical species in each slab cell, in response to emissions, their subsequent lateral and vertical dilution and diffusion, gas-phase chemistry, dry deposition at the surface (for selected species), and an optional linear volumetric removal process (proportional to the local species concentration), which may be applied for selected species, if deemed necessary. The model is quite suitable for plume(s) with inhomogeneous (including asymmetric) spatial concentration distributions in the plume(s). Emissions may be from an elevated point source at a given time, as well as continuously from the surface in a spatially-temporally variable gridded areal distribution. The chemistry can be based on any externally specified chemical mechanism; the CB-IV mechanism, with the condensed Carter isoprene scheme (Carter, 1996), is used in all simulation results presented here.

Horizontal diffusion is based on horizontally homogeneous eddy diffusion (K_y), but different options are available for vertical diffusion (details in Gillani and Wu, 2003a), including height-dependent eddy diffusion (K_z), asymmetric convective mixing (ACM, Pleim and Chang 1992) in the convective boundary layer (CBL), and a combination of eddy diffusion (in the lowest 15% of the CBL) and ACM (higher up in the CBL). This last combination best simulates the observed profiles of species emitted at the surface, which have significant gradients in the lowest part of the CBL, but a more well-mixed profile higher up. This hybrid option is exercised in all simulations included in this report. The vertical domain of the model must extend to at least the peak mixing height of the day, in order to allow for realistic fumigation or entrainment of mass from above the mixing layer into the mixing layer as this layer grows during the morning hours. A constant small value of K_z is used for vertical diffusion in the aloft layers outside the CBL.

Every model run of a point source plume actually involves two parallel slab simulations, one with the point-source emission into a dynamic and kinetic background (the “plume” run), and another without such emission (the “background” run). Both runs include crosswind and vertical spatial resolution, the same distribution of surface emissions, and the same physical-chemical processes. From the difference between the two parallel simulations, we can determine plume excess concentrations above the background in a very local sense. The spatial resolution of the background is fixed in time: the background slab has a constant crosswind width (chosen to be significantly wider than the widest simulated plume width) and a constant horizontal spatial resolution (typically, 1.5 km); the vertical domain is chosen to significantly exceed the peak mixing height during the full simulation period, and is resolved into 32 layers of varying thicknesses, the lowest five typically chosen to be 10m thick each, and the coarsest ones above the mixing layer to be 100 m. The spatial resolution of the plume slab is variable in time. Horizontally, the expanding plume width, $W_p(t)$, can be divided into an arbitrary number of plume pillars of arbitrary widths. Our common practice in the simulation of isolated single plumes is to divide $W_p(t)$ into 20 side-by-side pillars of equal width. Thus, plume horizontal resolution is very fine in the very fresh plume (typically, $\sim 20\text{m}$), and gradually relaxes to approach the background pillar resolution (1.5 km) in the aged plume (plume width $\sim 30\text{ km}$). Vertically, plume core (= initial plume thickness at the end of the plume rise stage) is divided into a selected fixed number of thin layers (typically about 20m in thickness each), and as the plume expands, it does so sequentially into the adjacent layers of the plume slab.

In a typical simulation, the background (in the mixing layer and aloft) is initialized at 0600, and is subsequently evolved dynamically (physics) and kinetically (emissions, chemistry and removal). The background slab simulation is arranged to pass the point-source plume release location at the desired plume release time. The plume slab is then initialized 15 minutes after plume release time at the appropriate downwind location. At such initialization, the plume cross-section is centered at the effective stack height of the emission, and has finite width and height (externally specified, based on the Plume Rise Module of our Plume Dynamics Model, PDM, which is described in Gillani and Godowitch, 1999). The plume emission mass of each species is injected into this finite plume area (on top of the underlying background concentration field) in an assumed initial 2-D Gaussian distribution, calculated using input values of the species emission rate and the current local wind speed. The NO_x emission is assumed to be as NO. The distributions then evolve as the plume is advected along its pre-calculated trajectory (from the PDM run), under the influence of the various physical-chemical processes identified above. The model requires several inputs related to these processes: e.g., point-source and surface emissions; the dynamic mixing height [$z_i(t)$] and plume width and height [$W_p(t)$, $H_p(t)$]; diffusion parameters; the j -values of the photolytic species; the deposition velocities (v_d) of the depositing species; meteorological variables, p , T , RH ; etc. These inputs may be empirical or semi-empirical (calculated based on parameterizations available in PDM), or some of them may be derived from larger-scale grid model results (e.g., p , T , RH , Z_i , J , etc.). More specific information about particular model inputs for the case study are given in the following sections.

3.2 Multi-plume Version

Large coal-fired power plants operated by large utilities in the US typically emit between 10K and 100K tons of NO_x (as NO_2) per year, or about 25 to 250 kmol(NO)/h. By comparison, the largest sources of NO_x in the H-G ship channel complex (SCC) emit about 25-

50 kmol(NO)/h. Some of them are power plants (negligible VOC emissions), but most co-emit both NO_x and VOC. There are a large number of major industrial point sources (IPSs) in the SCC. Within a fairly short distance downwind of the SCC, the plumes of these sources begin to merge; some of these plumes are totally embedded in larger plumes emitted upwind. The treatment of such multiple interacting plumes is a complex challenge, particularly in the context of a *plume* model such as UAH-LRPM, with a rather fine spatial resolution (say, 200 m or finer horizontally) in the near-source downwind stretch where the plume merging is occurring. As shown in Fig. 1, most of the IPSs are concentrated in five clusters or local complexes --- three relatively small and more or less isolated ones, viz., Sweeney, Freeport and Chocolate Bayou in the south of the H-G area, and two (Texas City and the SCC), which are larger and tend to interact with each other. SCC is by far the largest complex with more than 100 individual IPSs of significant size. In GW03, we modified the single plume version of UAH-LRPM specifically for the TD_EV studies in the H-G area, to create a new multi-plume version (M-LRPM).

Conceptually, our approach in multiplume modeling is to initialize the plume slab just downwind of the most upwind source in the complex, then simulate its processes during downwind transport past the next source downwind until the new source has reached a certain minimum width (we have chosen that as 2 km). At that point, if there is physical interaction between the two plumes (based on overlap of their widths), then the plume slab is reinitialized, with the two plumes merged into a new single inhomogeneous plume with two (or more) concentration modes of the primary emission species. The merged plume has a new geometry, pillar configuration, spatial resolution, and rate of growth, as well as a new merged concentration distribution of the transported species (free radical species adjust rapidly to a new equilibrium with the new distribution of the transported species). The new plume is then transported and evolved downwind until it interacts with the next downwind plume which is at least 2 km wide. If so, then these interacting plumes are merged and the simulation is re-initialized and resumed. This process is continued (i.e., reinitialization of the master plume at each new interaction) until all plumes in the complex have been accommodated in the master plume simulation. Thereafter, the simulation of the combined (master) plume is continued to the end of the prescribed simulation time and location.

In practice, a new plume physics preprocessor to M-LRPM was developed and implemented, which uses PDM to perform the dynamics of each individual plume in the complex independently, determines when plume interactions occur and the criteria for merging are met. It sets up flags to indicate when particular identified plumes are ready to be merged. M-LRPM thus receives its multi-plume dynamics and merging information from the preprocessor outputs. When a plumes-merge is flagged, M-LRPM picks up the plume dynamics and merge information, rechecks the merge criteria, and if satisfied, performs the actual merge (re-initialization of the merged plume), and then proceeds forward with the simulation of the merged plume.

One important practical issue to contend with in such multi-plume simulation is that when two plumes of different ages and stages of development interact and are flagged as ready for merge, they will have different spatial resolutions. Our approach is to limit maximum plume cell size (horizontally) to 200 m during the merge phase; at merge time, the new resolution of the merged plume is set at the coarser of the two individual plume resolutions, or 200m, whichever

is smaller (remember that the newer of the two plumes will have a resolution of at least 100m before merge, because of the merge criterion that each member plume to be merged must be at least 2 km wide, and because each isolated plume has 20 pillars before it is merged). One problem in this process is that fairly fresh plumes (of width comparable to, or less than, the turbulent eddy scale) have a lateral diffusion rate which is different from that of a more aged plume in which turbulent eddies are significantly smaller than plume dimension, and merely perform internal plume diffusion. When two such diverse plumes are merged, the model limitation of a single lateral diffusivity for the whole plume (that of the larger member) leads to somewhat excessive post-merging diffusion of the younger member plume. This is one of the limitations of our approach. This is the reason that we require each merging plume member to be at least 2 km wide, so that it has already spread to a width which is larger than the turbulent eddy scale. Thus, if the smaller plume is embedded within the larger plume at its emission, then it will be simulated as an isolated plume until it is 2 km wide. While this will introduce some error, we do not think that such error will be too large in the total scheme of things. Two better approaches for simulation of plume-plume interactions, both requiring MUCH more computation, are the LES approach (Eulerian) and the *puff* modeling approach (Lagrangian) with fine spatial resolution (e.g., with the requirement that puffs are split up when they reach some critical size, e.g., 200 m). Both of these approaches also have the advantage that they can naturally and explicitly simulate wind shear effects. However, using either of those approaches is much more computation-intensive, and remains a future project for application to the H-G area plumes.

4. SELECTION OF THE CASE STUDIES --- 27, 28 August 2000

Our goal was to perform top-down emissions verification (TD_EV) of ozone precursor emissions (VOC and NO_x) by diagnostic Lagrangian modeling using 3-D field observations, principally those made during the NCAR Electra aircraft traverses in the plumes of the target industrial point sources (IPSS, particularly those concentrated in the five clusters identified as Sweeny, Freeport, Chocolate Bayou, Texas City and SCC --- see Fig. 1) for selected case study days, for which ambient meteorological and chemical conditions were most favorable for our purpose. Such a Lagrangian study of TD_EV is most suitable under relatively uniform and steady meteorological conditions, as when relatively steady winds are sustained in the same direction for a few hours, thus, fairly steady in time and fairly uniform in space. The main requirement is that the quantity and identity of the emission mass remain as close to the emission condition as possible (except for dispersion), and that it be measured as fully as possible. Thus, downwind measurements of the target precursors closest to the target source(s) are the most desirable (minimal chemistry and removal, and mixing with extraneous matter). Such near-source downwind concentrations of NO_x and VOC emissions would be quite non-uniform spatially. However, the aircraft VOC data are sparse (discrete) point measurements only, and rather inadequate for such purpose. We must, therefore, also exploit other continuous and semi-continuous data which are sensitive to the VOC emissions. Such data include ozone and PAN (continuous), and HCHO (semi-continuous). These variables, however, represent secondary species formed from the plume VOC-NO_x chemistry, and their concentrations become most pronounced and chemically stable at intermediate distances from the sources. Appropriate diagnostic modeling can provide source-oriented 3-D estimates of both the precursors (for near-source analysis) and the measured secondary species (for intermediate-range analyses).

We selected August 27 and 28, 2000 as near-ideal case studies for our analyses. On each of those days, the winds were consistently from a southerly direction, with the NCAR Electra making crosswind (E-W) traverses across the H-G area at nine sections, four upwind (south) of the ship channel, and five downwind (north) of it (the closest-in of these being about 10 km downwind). Figure 2 presents the Electra flight maps of 27 and 28 August, with measured ozone distribution along the flight path. It shows the more “isolated” plumes from Sweeny, Freeport A/B, Chocolate Bayou and Texas City being sampled in the southernmost traverses, and the SCC plumes in the five northernmost traverses, these latter at downwind distances (from the ship channel) ranging from about 10 to 75 km on 8/27 and about 10 to 100 km on 8/28. Apart from the relatively simple/steady/uniform meteorology of these days, these were also days with limited chemistry (also desirable in a study with particular focus on the primary emissions), with the highest surface level concentrations of ozone measured in the area (north of the SCC) being only 87 ppb (8/27) and 112 ppb (8/28). The data base for the diagnostic study is also rich for these days, including the excellent coverage of the Electra (*in situ* chemical), UV-DIAL lidar aircraft of NOAA-ETL (8/28 only, remote-sensing vertical profiles of ozone and aerosol backscatter), considerable amount of surface chemical sampling and upper air meteorological soundings, GOES-8 satellite data of the local cloud fields, plus, availability of Eulerian sub-regional simulations of gridded emissions/meteorology/chemistry at fairly fine spatial-temporal resolution, to provide some of the input information needed to drive the local-scale modeling (LRPM and LES).

5. SELECTION OF INDUSTRIAL POINT SOURCES FOR SIMULATION

The H-G area has a rather large number of industrial point sources. Even the high-resolution aircraft data cannot resolve all of their plumes. Figure 3 shows maps of the location and emission size of the largest (by emission) 200 point sources of NO_x (Fig. 3a) and of OLE (Fig. 3b), where OLE is the aggregated class of olefins simulated as a group in the CB4 chemical mechanism, which we have used in all our simulations. It includes all alkenes other than ethene, which is treated separately and explicitly in CB4. Nearly 80% of the OLE emissions in the industrial point sources in the H-G area are, typically, as propene. Effectively, OLE represents the propene-equivalent concentration of all alkenes other than ethene, and is heavily dominated in the Houston IPSs by propene. For modeling and top-down emissions verification, we need to aggregate the sources to a manageable number. We went through a process of performing such aggregation of all major point sources (MPSs) in the five VOC emission clusters shown in Fig. 1, using the emissions inventory information supplied by the Texas Commission for Environmental Quality (TCEQ). The most important criterion in such aggregation, of course, was the proximity of the sources. We first aggregated all sources within 1 km of each other, and then did further aggregation by a manual examination process, finally resulting in a total of 35 composited (aggregated) sources: the sources at Sweeny were combined into a single aggregate point source; those at Freeport into three (Freeport A, B and a source in between them = M); those at Chocolate Bayou into two (for the wind directions of both selected case studies, these two plumes merged quickly, and are essentially treated as one), and those in the Texas City and Ship Channel complexes into 29. These 35 sources are shown in Figure 4 (Fig. 4a shows the locations of the sources and a measure of their NO_x emissions, and Fig. 4b shows the same for a measure of the OLE emissions, as in the EI). Figure 5 shows the 29 aggregated sources of the Texas City-SCC group in a more detailed plot, showing the sources numbered individually. Our

diagnostic model-data analyses aimed to resolve each of these 35 sources individually, and to come up with diagnostic estimates of NO_x and VOC emissions from each of these aggregated sources.

6. THE METEOROLOGICAL SCENARIOS FOR 27 and 28 Aug 2000

The meteorological scenarios for the two selected case study days (27 and 28 Aug 2000) were quite similar. Figure 6 shows, for the 8/28 scenario, the five IPS clusters, the NCAR Electra flight path (~1200 – 1800 CST), the measured ozone concentration distribution (mostly in the boundary layer) along the flight path (hence also the plume locations), and the approximate plume trajectories from the emission sources. The figure shows graphically that the winds were sustained throughout the daytime from the S-SE direction. Figure 7 shows the map of the H-G area and the aircraft flight paths for both days, 8/27 (7a) and 8/28 (7b), along with locations of met monitoring sites. Along the aircraft flight paths, aircraft locations are shown at half-hour intervals, the nine separate traverses are delineated as T1 – T9, and segments where the aircraft was either ascending or descending (usually where the aircraft was making a turn) are highlighted (in color). The data from these segments have been used to infer continuous vertical soundings or distributions of the measured variables. There were five met monitoring sites with 915 MHz wind profilers (Houston SW [Hsw], Ellington Field [Ell], LaMarque [LaM], Wharton [Wha] and Liberty [Lib]), three sites with radiosondes (Wharton [Wha], Downtown [Dntn] and LaMarque [LaM]), and two sites with met towers (Downtown [Dntn] and LaPorte [LaP]). These various datasets collectively provided vital meteorological information related to transport winds and mixing heights. In addition, very useful information about continuous spatial distribution of mixed layer height was also deduced from the remote-sensing UV-DIAL data (vertical profiles of ozone and aerosol backscatter, available for 8/28 only) from the NOAA-ETL lidar aircraft. Also, very vital information related to actual plume transport trajectories of the sampled and simulated plumes could be inferred from the *in situ* aircraft chemistry data (e.g., the ozone data shown in Fig. 6). Finally, information about cloud fields and solar insolation (for use, especially, in the calculation of photolysis rates) was derived from the GOES-8 geostationary satellite data.

On both days, the flow was onshore all day (8/28 case illustrated in Figure 8). The winds were generally southerly onshore in the morning, turning to a SE direction later on this day. The trajectory shown is based on the profiler data. A sampling of the hourly profiler data (vertical wind profiles) at Ellington and Liberty for 8/27 are presented in Figure 9 (similar data for 8/28 at Ellington, Wharton and Liberty are given in GW03). The profiler wind data shown were available to us during the periods of our analyses, and provided the wind speed information, in particular, which was of critical importance in plume dynamics calculations and in the initialization of plume concentrations of the primary emission species. We adjusted the profiler wind directions a little, as necessary, to ensure that the target plumes arrived at the correct aircraft sampling locations as inferred from the aircraft data (e.g., Fig. 6).

Mixed layer height is a critical parameter in air quality modeling. Particularly during onshore flow, the Houston area is characterized by a considerable spatial variability of mixed layer depth due to its coastal location and due to variations in land use (Senff et al., 2002). The

gradients are particularly sharp near the land-sea interface, as shown in Figure 10, based on continuous aircraft lidar data of aerosol backscatter. The aircraft lidar data are particularly useful in providing such snapshot information about the spatial variability of mixed layer depth (Z_i). Figures 11, 12 and 13 collectively show such data in segments, which together make up the whole flight of the NOAA-ETL lidar aircraft, lasting about the same time period (~1200 – 1800 CST) as that of the flight of the NCAR Electra (8/28). These figures depict in detail the spatial distribution of Z_i over the study area for the 8/28 case study timeframe. Whereas the lidar aircraft data provide excellent snapshots of the *spatial* distribution of Z_i , the profiler data at specific sites provide good local information about its *temporal* variation. Figure 14 provides such temporal variation of Z_i based on the profiler data at the Houston Southwest inland site. For 8/28, it clearly shows the growth of the mixing layer from 0800 to 1400 CST (Fig. 14b), reaching a peak height of about 2000m AGL at 1400 CST, and its subsequent fall-off after 1600 CST (2200 UT). Figure 15 shows the temporal variations of Z_i at all five profiler sites for 8/28. Figure 16 shows results of vertical soundings on 8/27 (similar data for 8/28 are shown in GW03) of ambient temperature (T), dew point temperature (T_d), relative humidity (RH) and specific humidity (q) for the radiosondes at the LaMarque site (Fig. 16a, b), as well as results of vertical soundings of T and RH, NO_y and O_3 , for aircraft soundings (Fig. 16c, d) at locations V1 and V2, respectively (see Figs. 7a for these locations). There was a good degree of agreement in these variety of mixing height data, which were used in determining the corresponding model inputs.

Senff et al. (2002) performed an analysis of the mixing height data of both the lidar aircraft and of the profilers for the 8/28 case study day. The following description is based on their analysis and depictions in Figs. 10-15. Due to the persistent onshore flow all day, the evolution of mixing height was strongly influenced by advection of marine air from the Gulf of Mexico and Galveston Bay. The data show a significant SE-to-NW gradient in mixing height, which increased with distance from the shore. The peak mixing height at LaMarque (near shore) was significantly lower than that at Ellington (somewhat inland) which, in turn, was lower than that at Houston SW (farther inland, Fig. 15). The lidar measurements from the first portion of the flight (12:06 – 13:15 CST, Figure 11) clearly support this assessment. Low mixing depths of 400 to 800 m were found over the Gulf of Mexico and the northern end of Galveston Bay, while mixing depths of around 2000 m were measured west and northwest of downtown Houston. The lidar measurements from the second part of the flight (13:15 – 15:11 CST, figure 12) confirm the existence of strong spatial gradients in mixing depth in the vicinity of Galveston Bay. Over a distance of about 40 km to the west and northwest of the Baytown and La Porte areas the mixing depth increased by up to 1500 m. North of the Houston urban area, the lidar data show a localized enhancement of the boundary layer depth with peak values reaching, and even exceeding, 2500 m (Fig. 13). This appears to indicate that a deeper boundary layer developed over the Houston urban area and was transported to the north by the large-scale onshore flow. During the remainder of the flight (15:15 – 18:00 CST, figure 13), the airborne lidar mapped out the Houston urban and Ship Channel pollution plume that had been transported to the vicinity of Conroe. It appears that the influence of the marine air advected by the onshore flow did not reach that far north, allowing the mixed layer there to grow to depths of up to 2800 m. In our diagnostic modeling, we have tried to incorporate such observed variabilities in mixing depths as accurately as possible.

7. MEASURED AND MODELED PHOTOLYSIS RATES

Figure 17 shows maps of cloudiness in the study area at midday on August 27, 28, based on GOES-8 satellite data related to surface insolation. There were light scattered clouds in the area on both days, with 8/27 being somewhat more cloudy, particularly in the southern part of the study area. We have used such satellite-based cloud and insolation information in the calculation of species photolysis rates used in the chemical modeling. Vertical profiles of the aircraft-measured values of the photolysis rate of NO_2 (J_{NO_2}) at locations J_i ($i = 1-2$ on 8/27 and 1-4 on 8/28) are also used in this study to check those calculated in the regional models CAMx and CMAQ. Figure 18 shows a comparison of the measured (in the Electra) photolysis rates of NO_2 (J_{NO_2}) at aircraft locations J_i , $i = 1,2$ (shown in Figs. 7a and 17a) and the corresponding *clear-sky* values calculated in the models CAMx and Models3-CMAQ (similar data for 8/28 are shown in GW03). The measured data show decreased values related to attenuation by clouds. The data-model comparisons indicate that the CAMx clear-sky values compare very well with the measured clear-sky values; the calculated CMAQ clear-sky values are somewhat lower, with the error increasing with height, and approaching 10% at 3 km. For our model input of J-values for all photolytic species, we started with the CAMx-calculated tabulations of the clear-sky values (available at 4 km horizontal grid resolution and the CAMx vertical resolution), and then attenuated these locally using GOES-8 observed surface insolation data (available at 1 km horizontal resolution).

8. RESULTS OF DIAGNOSTIC DATA ANALYSES BASED ON APPLICATIONS OF LRPM

8.1 LRPM Study of the Isolated Southern Complexes: Sweeny, Freeport and Chocolate Bayou

Figure 19 (left panels) shows the southern part of the study domain, the corresponding largest sources of NO_x , OLE and ETH (top to bottom, respectively), the southernmost and earliest three traverses (T1, T2, T3) of the NCAR Electra on 8/28 and, in the center panel, the approximate trajectories of the sampled plumes from the Sweeny, Freeport, Chocolate Bayou and Texas City complexes which were encountered in these traverses. We performed a diagnostic analysis (model-data comparisons) of each of these sampled plumes in each traverse. GW03 presented four selections out of these analyses (the four selected sampled plume locations are shown in Fig. 19 as solid blue round symbols along the traverses in the left center panel), viz., the Sweeny plume sampled along T2 and T3, the Freeport plume along T2, and the Bayou plume along T3. The right panels in Figure 19 show the Electra continuous data traces for NO_y and ozone along traverses T1, T2 and T3 (respectively, from bottom to top) of 8/28, along with identification of the four selected plumes (solid blue round symbols). As can be seen, each of these plumes is isolated from the others. In our analyses, the Sweeny industrial point sources were combined into a single composite source, the Freeport sources were combined into three composited sources (Freeport A, Freeport B, and a composite source in the middle, which we will call Freeport M), and the Bayou sources were effectively aggregated into a single composite source.

The correct simulation of plume dynamics is of critical importance in the simulation of

nonlinear plume chemistry. GW03 illustrated in detail, for the 8/28 case study, the procedure followed in observation-based plume dynamics simulation using the Plume Dynamics Model of UAH (PDM-UAH) in conjunction with the met monitoring data and the Electra chemistry data, such that the simulated plume *dynamics* were quite true to the same for the observed plumes. GW03 also demonstrated the iterative application of LRPM-UAH, using the simulated plume dynamics, to simulate the corresponding observed chemistry as closely as possible for each of the four selected plumes of 8/28. We performed similar analyses for selected plume traverses of 8/27. Figure 20 shows, for the 8/27 Electra flight, relevant portions of traverses T1, T2 and T3 south of the SCC, and traverses T5, T7 and T8 north of the SCC, for which we have performed the data-model diagnostic analyses. We shall present here, for 8/27, our simulations for the Sweeny plume in T2 and T3, for the Freeport plumes in T1 and T2, and for the Chocolate Bayou plume in T3. Following that, we shall aggregate, for comparison, the corresponding inferred best-fit NO_x, ethene and olefin emissions from these sources for both the 8/27 and 8/28 analyses.

Diagnostic Analysis of the Sweeny Plume in T2 and T3 of 8/27

Figure 21 shows a comparison of measured (in the Electra) crosswind plume concentration profiles of a number of selected species in the Sweeny plume sampled in T2 on 8/27 with the corresponding LRPM-simulated profiles using EI values of the emissions of NO_x, ethene and olefins [$Q_{\text{NO}_x}(\text{EI}) = 13.8 \text{ kmol/h}$, $Q_{\text{ETH}}(\text{EI}) = 0.74 \text{ kmol/h}$ and $Q_{\text{OLE}}(\text{EI}) = 0.79 \text{ kmol/h}$]. Observe that the EI values for ETH and OLE are about twenty times smaller than the EI value for NO_x. The last panel in the plot (bottom right) also shows the simulated profile of OH, for which no measurements were made in the Electra. Observe that continuous measurements are available for ozone and all the plotted NO_y species (NO_y, NO and NO₂, which were individually measured, and the derived species NO_x = NO + NO₂, NO_z = NO_y – NO_x, HNO₃ ~ NO_y – NO_y* [NO_y* was measured using an NO_y monitor with a denuder to remove HNO₃ and particulate nitrate], and NO_z – HNO₃ [measure of organic nitrates]); semi-continuous measurements were made of formaldehyde (FORM), but were not available for the plume portion of this particular traverse; and finally, very discrete canister samples were collected of whole air, later analyzed for VOC species, including ethene, propene and other olefins. For the traverse in question, T2 (Sweeny), there was only one such point measurement of ethene and propene, somewhere within the plume. Clearly, the VOC information for this traverse is very scanty. The data-model comparisons show that, for almost all the species, there is a substantial discrepancy, due largely to inaccurate EI values of the emissions. We next ran the model with the emissions we had inferred for NO_x, ethene and propene for Sweeny from the previous 8/28 analyses. That made a big improvement in the comparison (not shown), but to get the best fit for this 8/27 scenario, we had to increase the emissions of these species somewhat more. The results of the best-fit comparison are shown in Figure 22, in which the simulations correspond to the following choices of emissions: $Q_{\text{NO}_x} = 1.8 Q_{\text{NO}_x}(\text{EI})$, $Q_{\text{ETH}} = 3.6 Q_{\text{NO}_x}$ and $Q_{\text{OLE}} = 2.0 Q_{\text{NO}_x}$ (compared to coefficients of 1.66, 3.6 and 2.0 in the 8/28 best-fit simulation of Sweeny in the rather similar T2 of that day). The best fits are excellent for all the measured species shown, but of course, for ethene and propene, this was for single points only. The conclusion based on the diagnostic analyses of Sweeny T2 of both 8/27 and 8/28 is that the results of the two days are quite consistent, and indicate that the NO_x-EI for Sweeny is within a factor of two, while the EI of both ethene and OLE are gross under-estimates by 1-2 orders of magnitude, being comparable to the NO_x emissions. The Sweeny T2 was about 25 km downwind for 8/27 and about 23 km

for 8/28, and within this short transport distance (and transport time of under 2 h), the initial deficits of both ozone and OH had been recovered, and for ozone, an excess of more than 20 ppb had been generated over a background of about 38 ppb. Similarly, quite efficient production of NO_z also took place, with somewhat greater production of organic NO_z than of HNO₃.

Figures 23 and 24 show a similar analysis for the Sweeny plume sampled in T3 of 8/27. Figure 23 shows a comparison of measured and simulated crosswind plume concentration profiles of the same selected species, corresponding to EI values of the emissions of NO_x, ethene and olefins, and Figure 24 shows the same with simulations based on the following set of emissions, which gave the best fit: $Q_{NO_x} = 1.8 Q_{NO_x}(EI)$, $Q_{ETH} = 2.0 Q_{NO_x}$ and $Q_{OLE} = 2.0 Q_{NO_x}$ (compared to corresponding coefficients of 1.25, 3.6 and 2.0 in the 8/28 best-fit simulation of Sweeny in the rather similar T3 of that day). In this case, there were no ethene and OLE measurements at all in the plume, but the FORM measurements were much more complete. In the best-fit case, the data-model comparisons are excellent for NO_y, as well as for the secondary species ozone, FORM and NO_z, at this downwind distance of about 50 km and plume age of about 3 h. Once again, the new analysis for 8/27 corroborates the essential conclusion that the NO_x-EI is within a factor of 2, but that the ETH and OLE EIs are off by orders of magnitude, and the emissions of these species are comparable to those of NO_x.

Diagnostic Analysis of the Freeport Plumes in T1 and T2 of 8/27

Figures 25 and 26 show a similar analysis for the rather fresh Freeport plumes sampled in T1 of 8/27 (only about 6 km downwind of Freeport B and about 12 km downwind of Freeport A). Figure 25 shows a comparison of measured and simulated crosswind plume concentration profiles of the same selected species, corresponding to EI values of the emissions of NO_x, ethene and olefins (the EI values are as follows:

Freeport A --- $Q_{NO_x}(EI) = 6.6$ kmol/h, $Q_{ETH}(EI) = 0.02$ kmol/h and $Q_{OLE}(EI) = 0.08$ kmol/h ;
 Freeport M --- $Q_{NO_x}(EI) = 3.7$ kmol/h, $Q_{ETH}(EI) = 0.21$ kmol/h and $Q_{OLE}(EI) = 0.20$ kmol/h;
 Freeport B --- $Q_{NO_x}(EI) = 28.3$ kmol/h, $Q_{ETH}(EI) = 1.67$ kmol/h and $Q_{OLE}(EI) = 0.48$ kmol/h).

In such fresh plumes, the measured information related to the secondary species ozone, FORM and NO_z is not particularly useful in inferring primary emissions of the precursor species, while the relevance of the measured information about the precursors themselves is of paramount value. The continuous data of NO_y are invaluable in inferring the true emissions of NO_x, while the discrete data of ETH and OLE, while very useful, leave much to be desired, underscoring the importance of, and need for, continuous measurements of the VOC species, particularly in the near-source regime. Figure 26 shows the data-model comparisons with simulations based on the following set of emissions, which gave the best fits based on a number of iterative trials:

Freeport A --- $Q_{NO_x} = 2.0 Q_{NO_x}(EI)$, $Q_{ETH} = 0.2 Q_{NO_x}$ and $Q_{OLE} = 0.2 Q_{NO_x}$;
 Freeport M --- $Q_{NO_x} = 2.5 Q_{NO_x}(EI)$, $Q_{ETH} = 0.4 Q_{NO_x}$ and $Q_{OLE} = 0.2 Q_{NO_x}$; and
 Freeport B --- $Q_{NO_x} = 1.25 Q_{NO_x}(EI)$, $Q_{ETH} = 0.4 Q_{NO_x}$ and $Q_{OLE} = 0.4 Q_{NO_x}$.

No analysis was performed for any plumes sampled during T1 on 8/28.

Figures 27 and 28 show a similar analysis for the Freeport plumes sampled in T2 of 8/27 (about 36 km downwind of Freeport B and about 42 km downwind of Freeport A). Figure 27 shows a comparison of measured and simulated crosswind plume concentration profiles of the same selected species, corresponding to EI values of the emissions of NO_x, ethene and olefins.

Figure 28 shows the data-model comparisons with simulations based on the following set of emissions, which gave the best fits based on a number of iterative trials:

Freeport A --- $Q_{\text{NO}_x} = Q_{\text{NO}_x}(\text{EI})$, $Q_{\text{ETH}} = Q_{\text{NO}_x}$ and $Q_{\text{OLE}} = 0.2 Q_{\text{NO}_x}$;

Freeport M --- $Q_{\text{NO}_x} = Q_{\text{NO}_x}(\text{EI})$, $Q_{\text{ETH}} = Q_{\text{NO}_x}$ and $Q_{\text{OLE}} = 0.2 Q_{\text{NO}_x}$; and

Freeport B --- $Q_{\text{NO}_x} = 1.25 Q_{\text{NO}_x}(\text{EI})$, $Q_{\text{ETH}} = Q_{\text{NO}_x}$ and $Q_{\text{OLE}} = 0.33 Q_{\text{NO}_x}$.

The corresponding results for 8/28 are shown in Table 1. Once again, we wish to note that, in such information for a plume which is several hours old, the value of the discrete data of the precursor VOCs becomes less valuable, and that of the secondary species sensitive to VOC emissions, such as ozone, FORM and NO_z, become more important. Continuous measurements of the precursor VOCs, however, could possibly have much useful value.

Diagnostic Analysis of the Chocolate Bayou Plume in T3 of 8/27

Finally, we present the results for the Bayou plume sampled in T3, at a downwind distance of about 32 km, and for plume age of about 1.75h. Figure 29 shows the data-model comparisons for emissions of NO_x, ETH and OLE at the EI values ($Q_{\text{NO}_x}(\text{EI}) = 7.9$ kmol/h, $Q_{\text{ETH}}(\text{EI}) = 0.08$ kmol/h and $Q_{\text{OLE}}(\text{EI}) = 0.13$ kmol/h). There were no VOC data of ethene, olefins and FORM in this Bayou sampled plume. Figure 30 shows our best-fit comparison, corresponding to the following emissions: $Q_{\text{NO}_x} = 3 Q_{\text{NO}_x}(\text{EI})$, $Q_{\text{ETH}} = Q_{\text{NO}_x}$ and $Q_{\text{OLE}} = Q_{\text{NO}_x}$ (compared to corresponding coefficients of 4.5, 4 and 2 in the 8/28 best-fit simulation of Bayou in the rather similar T3 of that day --- the measured dataset was more complete on 8/28).

The results of inferred emission rates of the precursors for both 8/27 and 8/28 are summarized in Table 1, along with the EI emission rates. The following points are consistent and important in all the results presented above for the relatively isolated southern sources :

- (1) the results of 8/27 are essentially corroborative of the results of the similar analyses for 8/28 in the earlier study;
- (2) the EI emission rates of NO_x are underestimates within a factor of 2 for Sweeny and Freeport A,B, upto a factor of 2.5 for Freeport M, and by 3 – 4.5 times for Bayou; and
- (3) the EI emission rates of ETH and OLE are most probably grossly underestimated by 1- 2 orders of magnitude, and that the real emission rates of these species appear to be of the same order of magnitude as Q_{NO_x} . It is also clear that when you combine such high rates of emission of the reactive species ETH and OLE with the type of NO_x emissions from these sources, the standard gas-phase chemical mechanisms such as CB4 do indeed provide a reasonable explanation for the observed high and rapid formation of ozone (and of aldehydes and PAN) that are observed in these industrial point source plumes, and that UAH-LRPM does simulate the observed compact spatial-temporal scales of the plumes. However, the simulated emission rates of these VOC species must be considered as tentative, since we have neglected (in LRPM) the effects of the chemistry related to the turbulent fluctuations in the concentrations (more on this subject in the next chapter).

In the above analyses, particularly for plumes which are several hours old, we have used information about VOC-sensitive secondary species (e.g., ozone, FORM, NO_z) to infer emissions of the precursor VOCs, which are variable by up to a factor of 5 between the results of 8/27 and 8/28. An important question then is: how sensitive is such nonlinear chemistry to the

VOC emissions? Figure 31 presents results of such a sensitivity analysis. It presents, for the Sweeny T3 scenario of 8/28, the simulated concentration evolutions of the primary emission variables NO_x, the propene-equivalent ETH+OLE, the ratio of the last two variables, and of the secondary variables OH, O₃, FORM, HNO₃ and “PAN”~ NO_z – HNO₃ (the values are crosswind-profile average species concentrations at the height of the aircraft traverse, about 600 m), to three sets of VOC emission rates, as follows: the red traces, marked EI, correspond to the EI values of the emission rates of ETH and OLE; the blue traces, marked EI+, correspond to ETH and OLE emission rates which are the same as the NO_x emission rates; and, the black traces, marked EI++, are for $Q_{ETH} = 3.6 Q_{NOx}$ and $Q_{OLE} = 2.0 Q_{NOx}$. Thus, the EI+ case involves VOC emissions which are about 2 orders of magnitude greater than the EI case, and the EI++ case involves a further increase in the VOC emissions by about a factor of 2-4. It is most instructive to interpret the sensitivities to the ratio VOC/NO_x. We observe clearly that the formation of ozone, PAN and FORM is positively sensitive to the ratio VOC/NO_x, and that the increased sensitivity to an increase in the ratio by a factor of 2-4 between the cases EI+ and EI++ is comparable to the increased sensitivity to an increase in the ratio by more than an order of magnitude between the cases EI and EI+. Thus, on an absolute basis, the sensitivity is greater in the range EI+ to EI++, than it is in the range EI to EI+. The uncertainty in our inferred emission rates of ETH and OLE (e.g., the difference between the 8/27 and 8/28 results) is in the former range, and therefore, quite important. The conclusion is that there is a need for additional studies to reduce the uncertainty in the results presented. Perhaps, the best way to reduce this uncertainty would be by making reliable *continuous* measurements of the VOC species.

By contrast to the behavior of ozone, PAN and FORM, the behavior of OH and HNO₃ is the opposite, except during near-field transport. The chemistry of these variables appears to be more NO_x-limited in the mature plume, and more VOC-limited in the near field. This near-field regime is about 1-2 hours in duration (~ the time to recover the initial sharp depletion of OH by reaction with the high initial concentrations of both NO_x and VOC), with this duration being correlated inversely with the VOC/NO_x ratio.

8.2 LRPM Study of the Multi-plume Complex: Texas City and the Ship Channel

As shown in Figure 5, this complex of sources was aggregated into 29 composite sources, three in the Texas City area (the sources numbered 1, 2, 3, source #3 being a power plant), three more in the Ellington Field-LaPorte area (sources numbered 4, 5, 6) south of the Ship Channel Complex (SCC), 16 in the SCC (the sources numbered 7 through 22, source #21 being a power plant to the east of the SCC), and the remaining 7 sources (#23 – 29) situated to the north of the SCC. The emissions from all of these sources were sampled by the Electra during its traverses T5 – T9 on both 27 and 28 August 2000. In GW03, we presented results of our diagnostic analyses (model-data comparisons) of what was sampled by the Electra during the eastern legs of its traverses T5, T6, T7 and T8 on 8/28, being respectively, about 10, 25, 50 and 75 km downwind of the Ship Channel. For each traverse, GW03 showed the poor model-data comparison when EI-values of the emission rates of NO_x, ethene and olefins were used, as well as the much improved comparisons when inferred best-fit values of these emissions were used (the same for all four traverse analyses). These inferred best-fit emission rates are summarized for all 29 sources individually in Table 2 (taken from GW03). As a sample of the analyses for 8/28, we present here the plots from GW03 for traverse T7 (about 50 km downwind of the Ship

Channel). Figure 32 shows the model-data comparison based on use of EI-values of the precursor emission rates. There were only two point measurements of the precursor VOC in this traverse, and only one of them was in the SCC plume; hence, the diagnosis in this fairly aged plume complex had to rely substantially on data-model comparisons of the secondary species sensitive to VOC, viz., ozone, FORM and NO_z-HNO₃. Such comparison for precursor and secondary species is shown in Figure 33 using the inferred “best-fit” emission rates of NO_x, ethene and olefins. Except for NO_z, the comparison is excellent, even for ethene and olefins. Our focus here will be on similar diagnostic analyses for the following three Electra traverses of 8/27 downwind of SCC --- T5 (<10 km downwind of the ship channel), T7 (~ 44 km downwind of the ship channel) and T8 (~56 km downwind of the ship channel).

Figure 34 shows the data-model comparison for T5, with the simulation of the interacting multi-plumes from Texas City and SCC being based on EI-values of the emission rates of NO_x, ethene and olefins. As has been stated before, in such a fresh plume scenario, the utility of the secondary species measurements is limited, and there was only a single point measurement of VOC, and even that (at y ~ -8km) was at the eastern edge of the SCC plume complex, and hence of little useful information content. Figure 35 shows the data-model comparison based on use of the inferred emissions from the 8/28 study (Table 2). The best improvement can be judged from the data of FORM, but even there, where the model showed the simulated peaks, the measured data were missing. One cannot, thus, get much confidence from this particular comparison. However, there is an important lesson: the best way to check the precursor emissions is to do so in a fresh plume while most of the emitted precursors are still mostly present in the plumes, but invariably in such a fresh set of plumes, the spatial variability of the precursor concentrations is considerable and can only be captured if the measurements are continuous (e.g., NO_y) or nearly so. It is critical that continuous or near-continuous aircraft measurements be made also for the VOC precursors in such a traverse. This is why the continuous VOC measurements in 2001 in the Baylor Twin Otter need to be examined carefully in such a near-source TD_EV test.

Figures 36 and 37 present similar data-model comparisons based on the data of traverse T7 (40-50 km downwind of the SCC) and two alternate simulation scenarios: one based on EI-values of emissions of NO_x, ethene and olefins (Fig. 36), and the other (fig. 37) based on the inferred emission rates from the 8/28 study (Table 2). The improvement in the model-data fit from Fig. 36 to 37 is obvious, especially for ozone in the west half of the plume complex (where the most adjustment was also needed for NO_x emissions) and particularly dramatically for FORM throughout the plume complex. There is also a strong improvement in the fit for ethene and olefins (four plume point measurements and one on the eastern edge). We conclude that the analysis of 8/27 corroborates the inferred adjustments of the NO_x, ethene and olefins emissions for the Texas City-SCC sources. The model performance is less impressive for NO_z.

Figures 38 and 39 present a similar model-data comparison for traverse T8 (~ 50-60 km downwind of SCC). The comparison in Fig. 38 (simulation based on emissions as in the EI) is generally poor, most strikingly for ETH, OLE and FORM. By contrast, the comparison is much improved in Fig. 39, based on simulations using the inferred emission rates of 8/28 (Table 2). Here (Fig. 39), the model-data fit is still slightly off even for FORM, but it is considerably better than in Fig. 38. We conclude that the analysis for 8/27 substantially, though not perfectly, corroborates the findings from the 8/28 LRPM study. Evidently, there is indication of some day-to-day variability in the emissions, especially of the precursor VOC species.

Table 2 summarizes the EI values of the emissions, as well as the “corrections” applied to NO_x, ETH and OLE EI emission rates for each of the 29 sources included in the simulations presented by GW03 in their diagnostic study of the Texas City-SCC emissions on 8/28/00. Information related to the EI emission rates (columns 2-6) is for NO_x, ETH and OLE, as well as for ETH/NO_x and OLE/NO_x. For both of these ratios, the values are typically between 0.01 and 0.1. The next five columns show the same information after “correction”. For most sources, no correction was made to the NO_x emission rate. Upward corrections had to be applied to the NO_x emission rates for sources # 8, 9, 10, 13, 15, 17, 19, 27 and 29 (see third column from the end); in particular, for sources # 9, 10, 13 and 17 (all in the left half of the SCC), the NO_x emission rate had to be increased by at least a factor of 3. For most sources also, the *corrected* ETH/NO_x and OLE/NO_x ratios have the value 1 (columns 10,11), i.e., ETH and OLE corrected emission rates are taken to be similar to the corresponding NO_x emission rates. Thus, the essential conclusion is same for these industrial point sources as for those in the isolated complexes (Sweeny, Freeport and Bayou): the NO_x emission rates in the EI appear to be verified within a factor of 2 for most sources, but they appear to be underestimated by a factor of up to 5 for Bayou and a few SCC sources; and typically, the ETH and OLE emission rates appear to be underestimated in the EI by one to two orders of magnitude (last two columns in Table 2), and are rather comparable to the co-emitted NO_x emission rates (columns 10, 11).

In all of the model-data comparisons in this section, there has been an implicit assumption --- that the effect of turbulent chemistry is negligible. We now proceed to test that assumption based on our pioneering LESchem study of the Sweeny plume.

9. RESULTS OF DIAGNOSTIC DATA ANALYSES BASED ON APPLICATION OF LESchem

9.1 UAH-LESchem and Its Present Exploratory Application

LES involves Eulerian grid modeling at very high spatial-temporal resolution capable of resolving individual large energy-containing turbulent flow eddies. Subgrid-scale information is parameterized. Most applications of LES have been for the convective boundary layer (CBL), and without chemistry, and even then, mainly to small domains (<10 km to a side horizontally and <4 km vertically). In the past (pre-2000), LES application with chemistry to a point-source plume appears to have been limited to just one study by Sykes et al. (1992), in which they included just the three-reaction photostationary chemistry of NO, NO₂ and ozone. More recently, a limited number of studies, such as that of Herwehe (2000), have explored the inclusion of detailed organic photochemistry (Trainer chemistry, in their case) into existing LES models (henceforth, LESchem), for application to small CBL domains. Very recently, Herwehe et al. (2002) even applied their LESchem (modified to implement the CB4 chemistry) to plumes from industrial point sources co-emitting VOC and NO_x, and Gillani and Wu (2003a) performed a fairly detailed study of UAH-LESchem application to power plant plumes. Thus, any application of LES, with detailed gas-phase chemistry, to point-source plumes, with or without co-emissions of NO_x and VOC, is still of a pioneering nature at this time.

When we started looking into a candidate LESchem for our use, about two years ago, we had

two potential options, the RAMS-LESchem of Herwehe and the NCAR-LESchem. RAMS (Regional Atmospheric Modeling System) is a well-established, well-evaluated, and widely-used, mesoscale-regional meteorological model (Pielke et al., 1992) which, for some years now, has included an LES option (Hadfield, 1989; Hadfield et al. 1991a,b; Walko et al., 1992; Avissar et al. 1999). For LES, RAMS is run in the non-hydrostatic configuration, solving the prognostic equations for the three velocity components (u , v , w), potential temperature (θ), perturbation Exner function (π), and subgrid-scale turbulent kinetic energy (ε). Subgrid (smaller turbulent eddies than the resolved scale of large eddies) diffusion is parameterized in terms of ε , as in Deardorff (1980). Hadfield (1991) reported that RAMS-LES simulates a field of updrafts and downdrafts with the right dimensions, characteristic velocities, and the crucial property that ε is transported upwards. Herwehe (2000) added (hard-wired) the Trainer chemistry with simplified isoprene mechanism (Trainer et al., 1987; 1991) into the then current version of RAMS (v. 3.2b, limited to single-processor implementation only, in the LES option), and applied the model to the CBL. At first, it was our plan to use that version of LES, but the single-processor limitation seemed too confining. We, therefore, also explored the possible use of the NCAR-LESchem, which was developed for, and implemented on, the CRAY, and included the massively parallel computing option. We were also granted the use of up to 250 hours of CRAY time on the NCAR CRAY for such application for our project, at no cost. We, therefore, decided to try out that option.

The NCAR-LES was developed by Moeng (1984; 1986), and has been applied by Moeng and Wyngaard (1988; 1989), Moeng and Rotunno (1990), Moeng et al. (1996) and Bretherton et al. (1999). In essence, it is similar to RAMS-LES, except for one important difference in the numerical integration technique for the spatial coordinates: whereas RAMS-LES applies finite differencing in all three spatial directions, NCAR-LES utilizes a pseudospectral representation in the horizontal directions (x and y), and finite differencing in the vertical. Also, NCAR-LES is more hard-coded in terms of input specifications. Later, Moeng added detailed chemistry to the NCAR-LES (hard-wired). All testing and applications of the NCAR-LES were for the CBL. We devoted considerable effort to become familiar with this NCAR LESchem. We started with CBL applications, and it performed very well. Unfortunately, when we began exploring its application to point-source plumes (without chemistry), we ran into a ringing problem (systematic spurious periodic ringing effect of mass along both horizontal axes through the point source of emissions). We suspect the source of this problem is related to the pseudospectral treatment in the model. We tried to smear the source over multiple grid cells, without success. It was a serious enough problem that needed substantial code modifications to correct, which we were not in a position to perform. Finally, we abandoned use of the NCAR-LESchem, and returned our attention to RAMS-LES. By then, however, there was a new version of RAMS (v 4.2), which did include the parallel processing facility in the LES option. Our tests with point-source emission of a tracer in this RAMS-LES showed no ringing effect. We, therefore, undertook the task of adding generalized (not hard-wired) detailed chemistry into this current version of RAMS, and developed it into a state-of-the-art RAMS-LESchem (UAH-LESchem). All applications of LESchem presented here have used the full CB4 chemistry with the one-product isoprene mechanism of Carter (1996).

Our new chemistry module is coded in FORTRAN 90 and is platform-independent, but unfortunately, it is not yet parallelized. Hence, the LESchem option can only be run on a single

processor which, in our case, is the Linux-based Pentium PC. This limitation has made it impossible to apply the model to the relatively large domain (~60 km x 30 km x 4 km) necessary for simulation of the ship channel plumes complex. Thus, our application of LESchem here is limited to the isolated plume of Sweeny (the 8/28 scenario corresponding to T2) over a maximum domain size of 32km x 20km x 4km, and is of an exploratory nature. The spatial resolution (grid size) is 125m horizontally, and is staggered vertically from 40m near the surface, in 15% incremental steps, to 125m (reached at the 10th cell), and held constant above, to a domain height of 4000m. Thus, the full gridded domain contains 260 x 160 x 40 grid cells. Each hour of real-time run in such a Sweeny application takes about 72 h of CPU time on a 2.4 GHz Pentium-4 processor in a dual-processor node with available memory of about 2 GB. The simulation is started at 0900, and the first 8500s are devoted to model spin-up --- 7000s of spin up with just CBL physics and a further 1500s with CBL chemistry also (based on initial conditions and spatially-averaged surface emissions of chemical species derived from the appropriate operational model inputs or simulations, such as CAMx and UAH-LRPM). Thereafter, the Sweeny emission is initiated (at about 1120), with the elevated emissions being injected into a single grid cell at an effective stack height of about 150m. Such full run with CBL physics, steady point-source emission, and chemistry, is maintained for about 4h (~1120 – 1530), during which time, the mixing height is simulated in its dynamic mode (see Figure 40), through input of spatially-uniform, but temporally variable, surface heat flux. The Electra sampling of the Sweeny plume during T2 on 8/28 was around 1315, and estimated to be of the release at about 1150. In order to have enough runtime for meaningful averaging of information in each grid cell (16000s after local plume impact), we run two realizations (on separate processors) with the Sweeny emissions offset slightly in space. Thus, it takes nearly 20 days of CPU time on each of two separate single processors for each 4h application of the Sweeny plume simulation (total run from ~0900 to 1530). And in each case, we use most of the available memory. This is why we need to upgrade our chemistry code for multi-processing so that we can run ship channel applications requiring much more CPU time and memory.

9.2 Results of the LESchem Application to the Sweeny Plume Sampled in T2 on 8/28

We made LESchem runs for the conditions of the Sweeny plume sampled in T2 on 8/28, with $Q_{NOx} = 1.66 Q_{NOx}(EI)$ as inferred to be the best fit to the observations based on the LRPM diagnostic simulation, and two alternate sets of stack VOC emissions, as follows:

- (a) a low-VOC emissions case (or EI case) with $Q_{ETH} = Q_{ETH}(EI)$ and $Q_{OLE} = Q_{OLE}(EI)$; and,
- (b) a high-VOC emissions case (or “best-fit” case) with $Q_{ETH} = 3.6 Q_{NOx}$ and $Q_{OLE} = 2.0 Q_{NOx}$.

In order to interpret the turbulent chemistry results in an ensemble-average way, we must identify an appropriate statistic to quantify and study. Such a statistic is the so-called “segregation coefficient”, which we now define. Chemical reactants are brought into contact by the combined action of the mean flow field, large coherent eddies, a non-linear cascade of finer eddies, and ultimately by molecular diffusion. If the rate of a given reaction itself is fast compared to the rate of turbulent mixing, the reactants cannot be brought together fast enough by the turbulent cascade process, and the overall reaction rate could be controlled by the scale of turbulence (diffusion-limited). In the chemical modules of applied air quality models (AQMs), perfect (instantaneous) mixing of the reactants is assumed within the grid-cell volume whose horizontal dimensions are typically one to two orders of magnitude (or more) larger than the

scale of turbulence. More accurately, the reaction rate, R , of the bimolecular reaction $A + B \rightarrow$ products may be expressed as :

$$R = k C_A \cdot C_B = k (\overline{C_A} \cdot \overline{C_B} + \overline{C_A' C_B'}), \quad (1)$$

where C_A and C_B represent the local instantaneous concentrations (mean + fluctuation), k is the reaction rate coefficient, the overbar denotes the spatial or temporal ensemble average, and the prime denotes fluctuations from the average. The last two terms on the right side denote, respectively, the contributions to the reaction rate of the mean (explicitly resolved, gridcell-average) and the fluctuating (subgrid scale) concentrations. The covariance term (second term on the right side) is neglected in operational models (including the LRPM) in spite of the fact that it can possibly cause significant retardation or acceleration of many atmospheric reactions (Donaldson and Hilst, 1972; Schumann, 1989; Sykes et al., 1992; 1994). Its importance depends on the so-called segregation coefficient (Sykes et al., 1992),

$$s \equiv \overline{C_A' C_B'} / \overline{C_A} \cdot \overline{C_B} \quad (2)$$

which, in the range -1 to 0 (anti-correlation of the fluctuating concentration components of A and B) corresponds to states of inhomogeneous mixing of non-coemitted reactants (-1 = total segregation and no chemistry; 0 = perfect mixing and no hinderance to chemistry by diffusion-limitation). “s” is thus a measure of the diffusion limitation of the reaction. In terms of s,

$$R = k (1+s) \overline{C_A} \cdot \overline{C_B} = k' \overline{C_A} \cdot \overline{C_B}, \quad (3)$$

where $k' = (1 + s) k = f k$ is an enhanced reaction rate, and $f = 1+s$ is the enhancement factor. In operational models, s is assumed to be always and everywhere equal to 0. For segregated reactants, $-1 < s < 0$, and $k' < k$; for co-emitted reactants, the covariance may be positive, increasing the net reaction rate, with $s > 0$ (with no strict upper limit) and $k' > k$. The cases of A = plume or updraft species and B = background or downdraft species represent such states of inhomogeneous mixing in which the negative co-variance term ($s < 0$) can cause a significant slowing down of the chemistry (Sykes et al. 1992, 1994; Schumann, 1989; Gillani and Wu, 2003a, etc.). For co-emitted reactants, their positive correlation ($s > 0$) can also lead to enhancement of the reaction rate over the mean component. The magnitude of s depends on the Damkohler #, $N_D \equiv \tau_d / \tau_c$, the dimensionless ratio of the time-scales of diffusion and chemistry, respectively (Schumann, 1989). The magnitude of N_D has an important influence on the nature of the chemistry : $N_D \gg 1$ ($s \approx -1$) corresponds to diffusion-limited fast chemistry which is confined to thin interfacial regions between segregated regimes (of A and B); $N_D \ll 1$ ($s \approx 0$) corresponds to slow chemistry which permits enough time for diffusion to mix the reactants; and, $N_D \sim 1$ ($-1 < s < 0$) corresponds to intermediate chemistry involving a complex interplay between chemistry and diffusion. τ_d ($\sim z_i / w^*$, where z_i is the CBL height and w^* is the convective velocity scale) depends mainly on the large eddy structure; $\tau_{c,A}$ ($\sim 1/kC_B$) and $\tau_{c,B}$ ($\sim 1/kC_A$) depend on local species concentrations which, even for a given reaction, are likely to be quite variable in space and time. Only with explicit resolution of the large eddies, as in models with large eddy simulation (LES = grid model with spatial resolution of 20-200 m), can the diffusion limitation (covariance term) be justifiably neglected for all reactions. Even then, there will still be some error, of magnitude related to grid size, but this error is believed to be small (Schumann, 1989). An appropriate comparison between the chemistry results of an LES solution and of a corresponding operational model solution can provide insights about the

magnitude of the neglected turbulent effect error in the operational model. The use of LES can also provide a basis for developing parameterizations of the covariance term for use in operational models. The quantity $1+s$ ($= f$) may be called the reaction enhancement factor, and it is a focus of our study.

Figure 41 shows a comparisons of LRPM, LESchem and measured crosswind concentration profiles of NO_y, O₃, OLE and FORM for the Sweeny T2 scenario of 8/28 (about 23 km downwind of the emission source, with plume age of about 1.7h), for the two VOC emission scenarios. The LESchem results shown represent temporal averaging in each grid cell over a period of 16000s. The NO_y plot for both cases shows that the simulated plume width in LESchem was somewhat narrower than that simulated by LRPM. Actually, in LRPM, this width is an externally specified input, and was specified to match the observed width. In LESchem, however, this width is a result of the intensity of the simulated turbulence in the CBL (our specified initial and boundary conditions of the mean wind field were idealized and spatially uniform, hence perhaps curtailing some plume spread by shear in the mean wind field). The CBL turbulence is controlled mainly by the input surface sensible heat flux, which also controls the mixing height. In our LESchem run, we had tailored this surface heat flux to obtain the observed mixing height variation (as shown in Fig. 40). The simulated plume width was a result of the corresponding CBL turbulence which, evidently, turned out to be a little inadequate to provide the correct plume spread. Unfortunately, this discrepancy in the simulated plume spreads in LRPM and LESchem results in a significant difference in the peak values of the simulated concentrations of primary emission species, with the LES peak being higher for NO_y.

Focus first on the results of the low-VOC case (ethene and olefins emissions as per the EI) in the left panels of Fig. 41. We notice first that the simulated concentrations of OLE, ozone and FORM in both LRPM and LESchem fall far short of the observed values, indicating inadequate VOC reactivity. When the emissions of ethene and olefins are increased to those inferred by LRPM (the high-VOC scenario, right panels), the LRPM results match the observed profiles well, as expected, and the LESchem profiles of these species all peak a little higher than the LRPM counterparts, in about the same proportions as for NO_y, implying that the discrepancy between the LRPM and LESchem profiles are mainly due to the unequal plume widths. Within the bounds of this error, the LESchem simulations also match the observed profiles closely and, evidently, the inclusion of the turbulent chemistry in LESchem did NOT make very much difference. For example, the peak ozone for the high-VOC case is about 70 ppb, only a few ppb more than the observed peak. This result is in sharp contrast to the main LESchem result of Herwehe et al. (2002) for the same co-emission of ethene as in our case, but they emitted no propene as we did. Thus, their emission mix was, if anything, somewhat *less* reactive. Still, after two hours of transport, the peak ozone in the plume, even after averaging to a 4-km x 4-km box, was about 300 ppb. Furthermore, in our simulation, as the plume transported further downwind and aged another two hours, the peak ozone *subsided* significantly, because even at 1.7 h, plume NO_x concentration had declined to less than 2 ppb only, leaving little fuel for further ozone production. In the Herwehe et al. simulation, by contrast, the plume ozone continued to *increase*, reaching 400 ppb (!!!) after 4 hours of plume transport. Clearly, our result that LESchem did NOT make much difference to the Sweeny plume chemistry for the high-VOC case is quite plausible (close to observation), while that of Herwehe et al. appears to be very unrealistic, with as much as 400 ppb ozone production. Why? Perhaps the reason has more to do

with the fact they used a very low transport wind speed ($\bar{u} = 1$ m/s) while we used one closer to measured (3.2 m/s), than with the role of turbulent chemistry, *per se*.

Herwehe et al. attributed at least part of their greatly enhanced chemistry in the high-VOC case to positive values of s (hence $f > 1$) attained for some reactions. Let us examine the behavior of s (or equivalently of f) in our LESchem simulations for the two VOC-emissions cases. Remember that f is a reaction enhancement factor, i.e., values of $f > 1$ ($s > 0$) indicate enhancement of the chemistry by the turbulent effects, and $f < 1$ ($s < 0$) implies that the turbulent effects cause slowing down of the chemistry by subgrid scale diffusion limitation.

Figure 42 presents crosswind-averaged values of f (at plume release height --- actually, the plume became quite well-mixed vertically very quickly) as a function of downwind distance x from the source. The crosswind average involves averaging of individual cell values along the traverse, but the value of s ($= \overline{C_A' C_B'} / \overline{C_A} \overline{C_B}$) in each cell is based on temporal averaging over 16000s after first plume arrival to this traverse location (~ 1300). To achieve such sample size, we had to simulate two separate plume realizations, with their emissions slightly dislocated. We present such results of $f(x)$ separately for the following important reactions in the smog chemistry: NO+HO₂ and NO+O₃ (NO-to-NO₂ oxidation step); NO₂+OH and NO₂+C₂O₃ (NO_x termination step, or NO₂-to-nitrate oxidation step producing, respectively, HNO₃ and PAN); and OLE+OH and ETH+OH (VOC breakdown step, producing HO₂). We find that, in general, the pattern of behavior of f is qualitatively rather similar in both the VOC emission scenarios: by and large, in both cases, $f < 1$, meaning that the turbulent effects caused, if anything, a *slowing down* of the chemistry, even for the high-VOC case (!). In both cases, there is an initial sharp drop in f below 1 in the first 1-2 km downwind (and of similar magnitudes), and thereafter, there is recovery in f , back toward 1. This recovery is significantly faster in the high-VOC case. For example, for the NO+HO₂ reaction, the recovery is nearly complete in the low-VOC case only at about 25 km downwind, while the recovery is complete in the high-VOC case by about 7-8 km, and thereafter, f even exceeds 1 very slightly, and somewhat more so after 17 km. The recovery of the NO+O₃ reaction is complete in only 3-4 km in the high-VOC case, but takes until more than 15 km in the low-VOC case. The overall observation is that, (a) in the high-VOC case, the turbulence effect in the Sweeny plume was mostly decelerative in the first 5-10 km, and made little difference thereafter; in the low-VOC case, such decelerative effect lasted longer, being variable from reaction to reaction; and, (b) the difference between LRPM and LESchem is not very dramatic for oxidant production in the Sweeny plume. Let us now examine the details, including crosswind details, to understand and explain these observations.

Figure 43 shows, for both VOC-emission cases, crosswind detail in f of the above reactions, as well as in the profiles of the relevant species concentrations, at 2 km, when the crosswind-average value of f was at nearly its lowest value for all the reactions. The species plotted are either precursors (NO, ETH and OLE), or products (HNO₃ and PAN), or oxidants (O₃, OH, HO₂, C₂O₃). NO₂ is the exception, being each of these in different respects. As expected, in such a fresh plume, the precursors (being primary emissions) have crosswind concentration profiles which are sharply above background values (observe that for ETH and OLE, the full scales, given above the plots, are quite different for the low-VOC and high-VOC cases); the product HNO₃ has a slight excess in the plume, and PAN is at almost background level in the plume; all the oxidants have deficits in the plume. The oxidants are very rapidly depleted by

reaction with the relatively high concentrations of the precursors (notice that the radical concentrations are in ppt while the others are in ppb). The reactants in each of the six key reactions considered are a precursor and an oxidant; the former are in excess in the plume, while the latter are in deficit. There is thus anti-correlation of the reactants in all six reactions. It is thus not surprising that $s < 0$ ($f < 1$) at this stage, and f is even close to zero (no chemistry) in some cases (the negative contribution to the reaction rate by turbulent effects almost cancelling the positive contribution of the mean chemistry). At this stage of plume chemical evolution, therefore, the turbulence effect tends to retard the chemistry, even in the high-VOC case, and significantly so.

Figure 44 shows similar plots at $x = 6$ km, where the crosswind-averaged f was well in recovery mode for all reactions. The concentrations of the precursors have decreased considerably (NO peak down from about 40 ppb to about 2 ppb in the high-VOC case, and ETH from more than 200 ppb to less than 35 ppb). The peroxy radicals still have deficit in the plume (less so in the high-VOC case), hence are still anti-correlated with NO₂ and cause negative s for their reactions with NO₂ (less so in the high-VOC case). Ozone is still slightly in deficit in the low-VOC case, but has already formed an excess in the high-VOC case. Consequently, there is still anti-correlation between NO and O₃ in the low-VOC case (hence, $f < 1$ for the NO+O₃ reaction), but a positive correlation in the high-VOC case, and hence f slightly exceeding 1. Crosswind-averaged OH is nearly 0, hence its reactions with NO₂, ETH and OLE have $s \sim 0$ and $f \sim 1$. Overall, in this stage of plume chemical evolution, the turbulence effect still tends to slow down the chemistry a little, but significantly less than in the case of the low-VOC case.

Figure 45 shows similar plots at 10 km, where the crosswind averaged f has recovered to close to 1 for most reactions in the high-VOC case. In this case, the OH profile is almost flat, and so is the f -profile for the reactions NO₂+OH, ETH + OH and OLE + OH. Ozone still has a small deficit in the low-VOC case (hence a slight deficit in the f -profile for NO+O₃), but it has developed a nearly 8 ppb peak excess in the plume in the high-VOC case, but NO has fallen to a peak well below 1 ppb, resulting in just a slightly enhanced f above 1. The peroxy radicals have also developed some excesses (in the ppt levels), but the reactant partners (NO and NO₂) are rather depleted. Consequently, in this stage of plume chemical evolution, the turbulence effect still tends to slow down the chemistry somewhat in the low-VOC case, but it has very little effect on the rate of chemistry, either way, in the high-VOC case.

Finally, we present the results at $x = 20$ km (close to the location of T2 at 23 km) in Figure 46. Here, in the high-VOC case, O₃, HO₂ and C₂O₃ have developed significant excesses, but their partner reactants, NO (pretty flat) and NO₂ (down to a peak of less than 2 ppb above background) are pretty flat, and the corresponding f -values are pretty flat. Similarly, OH is pretty flat, hence f is pretty flat for the OH reactions with NO₂, ETH and OLE. In this stage of plume chemical evolution, thus, the turbulence effect has relatively little effect on the rate of plume chemistry in either the low-VOC or the high-VOC case.

We see that the result that, even for the high-VOC case, there is no accelerational effect of the chemistry, and that there is even a decelerative effect initially, is quite explainable. Evidently, the emission rates from Sweeny are such that, by the time the oxidants have recovered and built some excess in the plume, NO_x is mostly spent. Also, we never get a significant excess of OH to

cause any acceleration in the VOC+OH reactions. Thus, the high-VOC emissions shorten the phase when the turbulence effects decelerate the chemistry, but the conditions in the Sweeny plume never develop to combinations of precursor and oxidant concentrations for which the turbulence effects significantly accelerate the chemistry. Perhaps a different mix of VOC and NO_x, or a situation which is dynamic in terms of availability of VOC and NO_x, as in the case of the SCC, may lead to the turbulent effects accelerating the chemistry. For this to happen significantly, we must get significant excesses of both the precursors and the oxidants in the plume simultaneously, for which the likelihood is probably maximum in the SCC mega-plume.

10. CONCLUSIONS AND RECOMMENDATIONS

10.1 Conclusions

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 NO_x 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 NO_x 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 NO_x 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 NO_x 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 NO_x emission rates. Such co-emissions of NO_x and reactive VOCs lead to rapid nonlinear gas-phase chemistry, which produces large amounts of ozone and other secondary products (e.g., NO_z, 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 NO_x 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), NO_x 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 NO_x emissions from downwind sources may provide the NO_x 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., $u = 3.2$ 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 $u < 3$ 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 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 NO_z (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 NO_x 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.

10.2 Recommendations

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 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 then 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 directly into the OAQMs (LRPM or CAMx, etc.). LESchem is a good 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 NO_z 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-NO_x 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.

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Table 1. Summary of Inferred Emissions of VOC and NOx from Isolated Industrial Point-source Complexes in the H-G Area

SOURCE	TRAVERSE	DIAGNOSTICALLY INFERRED								
		EMISSION INVENTORY			27 AUGUST 2000			28 AUGUST 2000		
		$\frac{Q_{NOx}}{(Kmol/h)}$	$\frac{Q_{ETH}}{Q_{NOx}}$	$\frac{Q_{OLE}}{Q_{NOx}}$	$\frac{Q_{NOx}}{Q_{NOx}(EI)}$	$\frac{Q_{ETH}}{Q_{NOx}}$	$\frac{Q_{OLE}}{Q_{NOx}}$	$\frac{Q_{NOx}}{Q_{NOx}(EI)}$	$\frac{Q_{ETH}}{Q_{NOx}}$	$\frac{Q_{OLE}}{Q_{NOx}}$
Sweeny	T2	13.8	0.054	0.057	1.80	3.60	2.00	1.66	3.60	2.00
	T3				1.80	2.00	2.00	1.25	3.60	2.00
Freeport – A	T1	6.6	0.003	0.013	2.00	0.20	0.20	-	-	-
	T2				1.00	1.00	0.20	2.00	1.00	0.20
– M	T1	3.7	0.055	0.053	2.50	0.40	0.20	-	-	-
	T2				1.00	1.00	0.20	2.00	1.00	0.20
– B	T1	28.3	0.059	0.017	1.25	0.40	0.40	-	-	-
	T2				1.25	1.00	0.33	1.50	1.50	1.00
Choc. Bayou	T3	7.9	0.080	0.130	3.00	1.00	1.00	4.50	4.00	2.00

TABLE 2. Data of EI and "Corrected" Emission Rates for the Industrial Point Sources in the Texas City and Ship Channel Complexes

Source #	EI Emission Rates, Q_{ei} (Kmol/h)					"Corrected" Emission Rates, Q_c (Kmol/h)					Correction Ratios(Q_c/Q_{ei})		
	NOx	ETH	OLE	ETH/NOx	OLE/NOx	NOx	ETH	OLE	ETH/NOx	OLE/NOx	NOx	ETH	OLE
1	20.05	0.57	1.51	0.0285	0.0758	20.05	6.66	6.66	0.33	0.33	1	11.69	4.4
2	17.60	0.78	1.45	0.0442	0.0822	17.6	5.87	5.87	0.33	0.33	1	7.54	4.06
3	32.36	~	~	~	~	32.36	~	~	1	1	1	~	~
4	10.19	0.13	0.44	0.0127	0.0431	10.19	10.19	20.41	1	2	1	78.9	46.41
5	7.63	0.28	0.10	0.036	0.0125	7.63	7.63	7.63	1	1	1	27.72	79.76
6	4.64	0.14	0.08	0.0293	0.0158	4.64	4.64	15.3	1	1	1	34.21	200.81
7	~	~	~	~	~	~	~	~	1	1	1	~	~
8	8.35	1.36	0.44	0.1626	0.0532	16.7	16.7	33.41	1	2	2	12.3	75.15
9	15.52	1.14	0.70	0.0732	0.0451	46.55	46.55	46.55	1	1	3	41.01	66.46
10	12.87	0.38	0.79	0.0367	0.0611	51.48	51.48	64.33	1	1.25	4	136.08	81.88
11	~	~	~	~	~	~	~	~	1	1	1	~	~
12	~	~	~	~	~	~	~	~	1	1	1	~	~
13	10.55	0.48	1.23	0.0453	0.1165	31.64	31.64	31.64	1	1	3	66.25	25.75
14	~	~	~	~	~	~	~	~	1	1	1	~	~
15	7.99	0.31	0.73	0.3819	0.0911	15.98	15.98	15.98	1	1	2	52.37	21.95
16	1.54	~	0.78	0.0251	0.506	1.54	~	0.78	0.0251	0.506	1	1	1
17	6.91	0.13	0.16	0.0181	0.0354	34.56	34.56	34.56	1	1	5	275.51	211.61
18	~	~	~	~	~	~	~	~	1	1	1	~	~
19	5.42	0.07	0.20	0.0132	0.0368	10.84	10.84	10.84	1	1	2	151.2	54.33
20	1.46	~	~	0.0429	0.184	1.46	~	~	0.0429	0.184	1	1	1
21	15.95	~	~	~	~	15.95	~	~	1	1	1	~	~
22	15.23	0.33	0.65	0.0217	0.0425	15.23	15.23	15.23	1	1	1	46.15	23.5
23	~	~	~	~	~	~	~	~	1	1	1	~	~
24	4.39	0.25	0.04	0.0571	0.0101	4.39	44.06	17.64	10	4	1	175.28	395.16
25	7.74	~	~	~	~	7.74	~	~	1	1	1	~	~
26	~	0.13	0.00	~	~	~	72.72	22.03	~	~	~	546.15	7802.5
27	21.15	1.07	2.59	0.0504	0.1223	31.72	31.72	31.72	1	1	1.5	29.75	12.27
28	~	0.38	~	16.7	0.869	~	0.38	~	16.7	0.869	1	1	1
29	2.79	0.28	0.22	0.0183	0.001	5.58	27.94	22.36	5	4	2	100	100

~ = small