Final Report

Top-Down Evaluation of the Houston Emission Inventory using Inverse Modeling

Prepared for

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EXECUTIVE SUMMARY

BACKGROUND

Development of an effective air quality management plan for ozone in the Houston-Galveston Area (HGA) is critically dependent on photochemical modeling results. The Texas Commission on Environmental Quality (TCEQ) is using the Comprehensive Air Quality Model with extensions (CAMx; ENVIRON, 2002) for HGA SIP modeling (TCEQ, 2003a). Uncertainties in emission inventories represent a major source of uncertainty in any photochemical modeling study. Analyses of data collected in the TexAQS 2000 field study raised concerns that VOC emissions from very large industrial sources in the HGA are under-represented in the SIP emission inventories (Daum et al., 2002). This conclusion was based on the interpretation of extensive ambient measurements of ozone and precursors, and is consistent with tendencies for photochemical models to under-predict ozone levels in the areas close to and downwind of HGA industrial point source complexes, e.g., around the ship channel and Galveston Bay (TCEQ, 2003b). The ozone control plan developed for the HG SIP may be less effective than expected if the photochemical models are missing substantial ozone production from industrial point source emissions.

This study uses an inverse modeling technique to perform a top-down evaluation of the HGA SIP modeling emission inventory along with data from TexAQS 2000. Inverse modeling involves determining combinations of emission inventory adjustments that produce the best agreement between modeled and measured concentrations. The inverse modeling was carried out by calculating model sensitivity coefficients that relate model output concentrations to input emissions. First-order sensitivity coefficients were calculated using the Decoupled Direct Method (DDM) developed by Dunker (1980 and 1981) and implemented in CAMx as described in Dunker et al. (2002). Objectives of this study were to:

1. Evaluate whether industrial VOC emissions appear to be under-estimated in the TCEQ's base inventory for 2000 and, if they are, develop a quantitative and objective measure of the underestimation.
2. Evaluate whether TECQ's "PT_02N2" adjustment to the industrial VOC emissions improves ozone model performance, and determine whether further refinements to the "PT_02N2" adjustment are warranted.
3. Consider how uncertainties in other emission categories affect the existing conclusion that point source emissions are under-estimated.
4. Calculate relative reactivity factors for different VOC compounds emitted from industrial sources in the HGA for the purpose of evaluating VOC specific control strategies.

TOP-DOWN EVALUATION METHODOLOGY

A top-down evaluation of the Houston region emissions inventory was conducted using inverse modeling of the 25 – 31 August 2000 ozone episode. CAMx model runs with the Direct Decoupled Method (DDM) provided first-order sensitivities of ozone (O_3), total reactive nitrogen (NO_y) and formaldehyde (HCHO) to changes in VOC and NOx emissions under two different scenarios:

a) Source Category Sensitivities: Sensitivities calculated with respect to changes in emissions from five major source categories: on-road mobile, area (including off-road), biogenic, low-level point, and elevated point sources.
b) Emission Sub-Region Sensitivities: Sensitivities calculated with respect to changes in total emissions from six high emission density sub-regions within the modeling domain (sub-regions are shown in Figure ES-1).

DDM sensitivity coefficients calculated under (a) above represent the sensitivities of ozone, NO_y and HCHO mixing ratios to fractional across-the-board (domain-wide) changes in emissions for a given source category. DDM sensitivity coefficients calculated under (b) above represent the sensitivities of ozone, NO_y and HCHO mixing ratios to a unit (1 ton/day) increase in emissions within a sub-region. Thus, results from analysis (a) provide information on the effects of multiplicative emission changes applied to specific source categories (e.g., on-road mobile sources) whereas results from analysis (b) provide information on the effects of additive changes to total emissions within a specific sub-region.

Least-squares regression was used to calculate the set of emission adjustments which result in minimization of model prediction errors. An extensive database of aircraft observations of O_3, NOy, and HCHO concentrations collected on 27 – 31 August 2000 were used to develop the prediction errors required by the regression analysis. Exploratory analyses of the aircraft observations and corresponding CAMx predicted concentrations, the DDM sensitivity coefficients calculated by CAMx, and results of the regression fits were used to identify and quantify potential biases or errors in the emissions inventory. This information was then used to prepare several new CAMx simulations under various inventory adjustment (sensitivity) scenarios. The impact of the inventory adjustments on model performance was determined against an independent set of data from the surface monitoring network.

Several adjusted VOC scenarios were developed in this study (LPVOC, BioVOC and MABVOC) along with one adjusted NO_x scenario (NOxMAP) in addition to the scenarios provided by the TCEQ (Base4a and PT_O2N2). These scenarios are as defined in **Table ES-1**.

Table ES-1. Summary of emissions scenarios.

	Scenario	Description[1]	Relative to	Adjustment Factors (1 = no adjustment): On-Road Mobile + Area Sources	Biogenic	Low-Level Points	Elevated Points
VOC Scenarios	Base4a	Base case	--				
	PT_O2N2	Scale point source olefins to NOx	Base4a	1	1	Varies[2]	Varies[2]
	LPVOC	Increase Base4a low point VOCs	Base4a	1	1	4	1
	BioVOC	40% decrease in biogenics	PT_O2N2	1	0.6	1	1
	MABVOC	Increase mobile+area VOCs, decrease biogenics	PT_O2N2	3	0.3	1	1
NOx Scenario	NOxMAP	Decrease NOx from mobile+area and points	PT_O2N2	0.7	1	0.9	0.9

RESULTS

Comparisons of aircraft observations with model predictions under the Base4a emissions scenario showed a strong under prediction tendency when observed O_3 was greater than about 125 ppb although model performance was much better at lower ozone levels. Adjusting point source olefin emissions upwards by scaling to NOx emissions (the PT_O2N2 scenario) resulted in performance improvements but did not eliminate the under prediction errors. In addition, this adjustment resulted in larger ozone over predictions on the two days during the middle of the episode when observed peak ozone levels were relatively low.

Source Category Sensitivities

Analysis of the source category DDM sensitivity coefficients for the Base4a and PT_O2N2 scenarios showed that:

- Ozone sensitivities to VOC and NOx are strongly negatively correlated, making it impossible to distinguish between the impact of decreasing VOC emissions or increasing NOx emissions on the basis of ozone performance. Including prediction errors against aircraft NOy observations in the least squares fit provides an independent means of evaluating the NOx inventory. Given the model's NO_y over-prediction bias, one would expect improved model performance is generally consistent with NOx emission

[1] See Section 3 for a full description
[2] Olefin emissions for specific sources are set equal to NOx on a molar basis.

reductions. However, there is considerable scatter in the NO_y errors which minimizes the impact of NO_x emission adjustments on overall model performance.

- Predicted ozone values for times and locations with observed ozone greater than 125 ppb are particularly sensitive to point source VOC and NOx emissions in the modeling results.
- For VOCs and NOx, sensitivities to on-road mobile and area sources are strongly positively correlated, as are sensitivities to low points and elevated points. Thus the regression model could not distinguish between adjustments to on-road mobile vs. area or between low vs. elevated point source emissions.

Regression fits with different sets of VOC and/or NO_x sensitivity terms included showed that, while many of the fitted models were statistically significant and many of the regression coefficients were significantly different from zero (owing to the large number of observations contained within the aircraft database), the sum of squares error reductions achieved by the regression fits were quite modest in all cases.

Key results from the regression analysis and evaluation of the CAMx emissions sensitivity runs were:

- Regression results for the Base4a scenario suggested VOC emissions are too low in this scenario but there was no clear advantage to adjusting mobile/area in lieu of biogenic or point source emissions. A CAMx sensitivity run was performed using the Base4a scenario but with low-point VOC emissions increased by a factor of 4 as suggested by a single term regression fit (LPVOC scenario). In contrast to the PT_O2N2 scenario, this did not result in any significant overall improvement in model performance.

- Single term regression model results for the PT_O2N2 scenario showed that it is not possible to achieve a better least squares fit to the aircraft observations by making further across-the-board adjustments to the point source VOC emissions.

- Results from least squares fits including the biogenic emissions sensitivity coefficient suggested that biogenic VOCs may be too high whereas mobile+area emissions may be too low. Over estimation of biogenic VOCs is consistent with recent work indicating that drought conditions during the summer of 2000 resulted in biogenic VOC reductions not fully accounted for in the inventory. A CAMx sensitivity run based on the PT_O2N2 scenario with just biogenic VOCs reduced by 40% (the BioVOC scenario) resulted in somewhat worse model performance overall against the surface ozone data as compared to the PT_O2N2 scenario, indicating that any errors in the biogenic inventory may be offset by errors in other source categories.

- When mobile+area VOCs are increased and biogenics are simultaneously decreased (the MABVOC scenario), there was some improvement in model performance with respect to ozone at the surface sites relative to the PT_O2N2 scenario. Furthermore, a second least squares analysis using DDM coefficients computed under the MABVOC scenario indicated that this solution had effectively converged. In other words, no further improvement in model performance (at least within the linear predictions afforded by the DDM results) is achievable by emission adjustments beyond those contained in the MABVOC scenario.

- Reducing NO_x emissions (the NOxMAP scenario) produced mixed changes in model performance; overall performance statistics were on par with that achieved under the PT_O2N2 scenario. While the NO_x reductions did not produce any clear cut improvement or degradation in performance, overall performance is slightly better under the VOC reduction scenario (MABVOC) as compared to the NOxMAP scenario.

Emission Sub-Region Sensitivities

Examination of DDM sensitivity coefficients for six sub-regions of interest showed that predicted O_3, NO_y and HCHO over the locations and time periods covered by the aircraft data are not influenced by emissions from the Beaumont-Port Arthur area. Within the other five sub-regions, there was little distinction between sensitivities to low-level vs. elevated sources. Consistent with the emission category sensitivities discussed above, VOC and NO_x sensitivities were negatively correlated for the downtown Houston and Ship Channel sub-regions (sub-regions 3, 4 and 5) with negative NO_x sensitivity coefficients for O_3 (i.e., NO_x emission decreases produce ozone increases). These sub-regions also exhibited the largest sensitivities: model predictions were generally less sensitive to a unit emissions increase in sub-regions 1 (Freeport) and 2 (Texas City). Least squares minimization of model prediction errors based on the sub-region sensitivities showed that minor but statistically significant improvements in model performance could be achieved with:

- Decreasing VOC emissions in sub-region 1 by up to 10 tons/day (26%).
- Decreasing NO_x emissions in sub-region 1 by 2 – 3 tons/day (7% - 11%).
- Increasing VOC emissions in sub-regions 3, 4 and 5 by up to a few tons/day (generally less than 5%) and/or decreasing NO_x emissions in sub-regions 3, 4 and/or 5.

Model prediction errors are not very sensitive to changes in sub-region 2 emissions. Overall, these results are consistent with the source category sensitivity results presented in the previous section in that model prediction errors are reduced by a very small but statistically significant amount by increasing VOC emissions and/or decreasing NO_x emissions in the core urban area (where they most influence the prevailing ozone under prediction errors) and decreasing VOC and NO_x outside of this area.

VOC Reactivity

The top-down inventory evaluation considered potential errors in the total emission rates for VOC emissions from several source categories. However, ozone model results also are sensitive to the mix of VOCs assumed (VOC speciation) to represent VOC emissions. Highly reactive VOCs (HRVOCs, such as ethylene and propylene) have a greater tendency to form ozone than low reactivity VOCs (such as paraffins) on an equal emissions mass basis. Information on the relative reactivity of different VOC species emitted from Houston point-sources could be used to:

- Assess the importance of errors in point source VOC speciation.

- Develop and evaluate the effectiveness of rules to restrict emissions of HRVOCs and/or trade-off emissions of low reactivity VOCs against HRVOCs.

The DDM was used in CAMx to quantify the relative reactivity of different VOCs emitted from point sources with the TCEQ's PT_O2N2 emission inventory. The reactivity evaluation followed methods developed by Carter, Tonnesen and Yarwood (2003) to place the VOC reactivities on a consistent basis across all species. A series of Houston specific VOC reactivity were calculated and evaluated relative to ethylene, as reported in Table 3-6. This evaluation showed that the Houston specific relative reactivities were consistent with existing maximum incremental reactivity (MIR) factors developed by Carter (2000) and Carter, Tonnesen and Yarwood (2003). Therefore, the Carter MIR factors provide a reasonable basis for comparing the reactivity of different VOCs from Houston region point sources.

CONCLUSIONS

This study demonstrates that analysis of spatial patterns and correlations in DDM sensitivity coefficients and using such coefficients together with model prediction errors in a least squares regression analysis is a useful approach for diagnosing potential modeling issues and suggesting emission adjustments. It is important to keep in mind, however, that this approach can not discriminate between errors in emissions and other sources of error (e.g., meteorology or model formulation) and therefore one cannot state conclusively that model prediction errors are due solely to errors in emissions. Nevertheless, it is possible to draw several conclusions from the results summarized above:

- Based on results of both the source category and sub-regional analyses, it appears that the magnitudes of model prediction errors occurring when observed O_3 exceeds 125 ppb in the aircraft data are most sensitive to point source VOC and NOx emissions within the downtown Houston and Ship Channel areas as compared to sources in other locations and other anthropogenic source categories.

- Although reducing NO_x emissions does not result in a clear-cut improvement in model performance, the possibility that NOx emissions are overstated cannot be discounted since peak ozone predictions are inversely related to, and very sensitive to, NO_x emissions from the Ship Channel area and NO_y is over predicted on average.

- Assuming that modeling errors are due mostly to errors in emissions, scaling olefin to NOx emissions (as in the PT_O2N2 scenario) appears to be a good adjustment of point source VOCs as no further point source VOC adjustments were indicated by the inverse modeling.

- Results from this study indicate a possible overestimation of biogenic VOC emissions, consistent with the hypothesis that VOC reductions due to drought conditions in 2000 are not adequately reflected in the inventory. However, this result was found to be very sensitive to HCHO prediction errors and thus critically dependent on the accuracy of aircraft HCHO observations and the HCHO chemistry in the model, both of which require further study.

- Modest to moderate model performance improvements beyond that achieved by the PT_O2N2 scenario result from increasing the sum of mobile and area VOC emissions while simultaneously decreasing biogenic VOCs. These adjustments have the overall net effect of shifting some VOC emissions from biogenic rich regions (primarily north and northeast of downtown) into the downtown and Ship Channel areas. Similarly, the sub-regional analysis results point to potential performance improvements by increasing VOC emissions within the downtown and Ship Channel areas and decreasing them in (at least) one of the outlying areas (Freeport).

- Over prediction errors occurring at moderate ozone levels observed in Harris County generally along a line running due north from Freeport suggest the possibility that VOC and/or NO_x emissions in Freeport are over estimated. Our results cannot, however, rule out other possible contributing factors to these over predictions. In particular, we cannot rule out the possible contributing role of errors in source sub-regions outside of the six areas considered in this study or of errors in meteorological parameters (winds, mixing heights).

- Carter maximum incremental reactivity (MIR) factors were found to provide a reasonable basis for comparing the reactivity of different VOCs from Houston region point sources

RECOMMENDATIONS

This study shows how inverse modeling using CAMx and DDM can be used to diagnose potential biases in the Houston region SIP modeling inventory. However, further study is needed to address several remaining issues:

- Results from this analysis should be compared with results of a source attribution analysis to better identify the types and locations of sources contributing during periods of ozone over and under prediction.

- A key issue not addressed by this study is the extent to which prediction errors are related to errors in simulated meteorological fields. We therefore recommend that the analysis be repeated using an alternate set of meteorological fields (e.g., from RAMS simulations) to determine the sensitivity of the findings to the meteorological fields.

- Results presented above are consistent with a potential over estimate of NO_x emissions. Further inverse modeling should be conducted for the NOxMAB scenario in an iterative fashion to see how well converged this emissions adjustment scenario is.

- CAMx runs could be set up to compute DDM sensitivities of predicted concentrations to emission from more specific source categories (e.g., large chemical manufacturing plants, petroleum refineries) and additional emissions sub-regions to further refine the inverse modeling process.