11.5

EVALUATION OF THE HOUSTON OZONE MODELING EMISSIONS INVENTORY VIA INVERSE MODELING WITH SENSITIVITY COEFFICIENTS FROM THE DECOUPLED DIRECT METHOD (DDM)

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1. BACKGROUND

Ground-level ozone concentrations in and around Houston, Texas frequently exceed health-based standard levels set by the U.S. Environmental Protection Agency. The Houston-Galveston Area (HGA) has been declared to be in non-attainment of the old (1-hour) and new (8-hour) ozone standards. Development of an effective air quality management plan for ozone in the 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) in developing the State Implementation Plan (SIP) for the HGA (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 Houston Ship Channel and Galveston Bay (TCEQ, 2003b). The ozone control plan developed for the HGA SIP may be less effective than expected if the photochemical models are missing substantial ozone production from industrial point source emissions.

An inverse modeling technique was used in this study 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). A description of the calculation and interpretation of DDM sensitivity coefficients is provided in the Appendix.

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 so-called "PT_O2N2" adjustment to the industrial VOC emissions improves ozone model performance, and determine whether further refinements to the "PT_O2N2" 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.

We briefly summarize here our analysis methods and results. More detailed information is available from Yarwood, Stoeckenius and Lau (2004).

2. DATA

2.1 *Modeling Databases*

CAMx modeling analyses were conducted for 25 – 31 August 2000 which includes several high ozone days in the Houston area for which detailed information are available from the TexAQS field study (Daum et al., 2002). The modeling databases were developed by the TCEQ as described in the mid-course review (MCR) modeling protocol (TCEQ, 2003a) and modeling results (TCEQ, 2003b). Meteorological input data for CAMx were prepared by Texas A&M University using the MM5 model. The

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CAMx modeling domain has 2-way nested 36, 12 and 4 km grids as shown in Figure 2-1. The meteorological and emissions input data are provided specifically for each of the 36, 12 and 4 grids. On the four modeling days with very high observed ozone (August 25th, 29th, 30th and 31st) an additional 1 km grid is introduced in the Houston area (Figure 2-2). The 1 km grid is also 2-way nested, but does not have explicit meteorology or surface emissions input files. Instead, the 1 km meteorology is interpolated from the 4 km grid and the 1 km surface emissions are assigned from the 4 km grid (interpolating emissions might not conserve emissions mass). The advantage of the 1 km grid is that point source emissions (which are geo-coded to precise coordinates) are injected into the correct 1 km grid cells and so plume dispersion and interaction is handled at the finer 1 km scale. This approach uses the CAMx flexi-nesting capability.

2.2 *Emissions*

Emission inventories used for this study were all for the year 2000 and were based on the TCEQ's "Base4a" inventory. This inventory includes the following data for the Houston area:

- On-road emissions from EPA's MOBILE6 model with day specific link-based emissions in the Houston area.
- Hourly utility point source emissions from EPA's acid rain database.
- Point source emissions from the TCEQ's 2000 point source database (PSDB) supplemented by version 4 of the special study inventory and with facility specific VOC speciation data.
- Off-road emissions from EPA's NONROAD model.
- Biogenic emissions from GloBEIS3 with satellite-based solar radiation data.
- Other area source emissions from TCEQ studies and data.

Under the PT_O2N2 emissions scenario defined by TCEQ, the olefin emissions for selected point sources (major chemical plants) in the Houston area were adjusted so that the total olefin emissions were equal to the NOx emissions on a molar basis. This adjustment was based on aircraft measurements for olefins and NOy from the TexAQS study. We made model runs with both the unadjusted ("Base4a") emission inventory and the adjusted ("PT_O2N2") emission inventory. Because olefins are highly reactive VOCs, the average reactivity of the point source emissions under the PT_O2N2 scenario is more than double that of the Base4a scenario.

2.3 *Ambient Data*

Two independent sets of ambient data were used in this study: aircraft and surface (fixed site) observations. Aircraft data for ozone, NOy and formaldehyde were used in the inverse modeling to derive emission inventory adjustments (Daum et al., 2002). The aircraft data were selected for this purpose because they provide an extensive set of collocated measurements for ozone and precursors downwind of both urban and industrial sources. The ozone, NOy and formaldehyde data were collected at high time resolution (seconds), which corresponds to high spatial resolution (~100 m). The NOy data reflect NOx emissions and are considered more useful than NOx data because the amount of chemical processing of emissions has less influence on NOy measurements than NOx measurements. The formaldehyde data are indicative of VOC emissions because formaldehyde is a ubiquitous reaction product of VOCs. Some VOC samples also were taken on the aircraft flights but the data were collected much less frequently than the formaldehyde data due to the analysis time required for VOC samples. Given the sparse nature of these data, the aircraft VOC samples were not used in the inverse modeling. The TexAQS data from NOAA aircraft (the NSF/NCAR Electra) and the BNL aircraft were obtained in a consolidated database prepared by Jeffries and McNally (2002).

Surface observations from more than 20 TCEQ routine monitoring sites plus the La Porte and Williams Tower special study sites were used to evaluate model performance under several different emission scenarios. These data were provided by the TCEQ and are the same data that the TCEQ used for model performance evaluation. The surface monitoring site locations in the 1 km grid are shown in Figure 2-3.

3. INVENTORY 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. A description of the DDM sensitivity coefficients is provided in the Appendix. DDM coefficients were computed 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 3-1)*.

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.

Using the DDM sensitivities together with the aircraft data described in Section 2, it is possible to compute adjustment factors to the emissions inventory that minimize model prediction errors for the three species considered (O_3, NOy and HCHO). Of course, the adjustments calculated in this way assume the predicted concentrations are a linear function of emissions from each of the above source categories and that the sensitivities are independent of one another. While the assumption of linearity only holds for sufficiently small adjustments from the base case condition, it is nevertheless instructive to determine the sign and relative magnitudes of the factors as this can provide important clues about *potential* errors in the inventory.† The assumption of independence between the sensitivities is discussed further below.

Adjustment factors were computed using a least squares fit:

$$X_o - X_p = \Sigma\, \beta_i\, S_i \qquad (1)$$

Where:

X_o Is the observed concentration of a species (either O_3, HCHO, or NOy)

X_p Is the predicted concentration of the species

β_i Are the unknown adjustment factors for emitted species (either VOC or NOx) and source category (see list above), and

S_i Are the corresponding DDM sensitivity coefficients (in units of ppb O_3 change per fractional change in emissions).

Using a standard linear regression algorithm, we solve for the adjustment factors such that the mean square difference between the model prediction error on the left hand side of Eq. 1 and the prediction adjustment on the right hand side is minimized. Minimization is performed simultaneously over all three predicted species. To avoid weighting one species more heavily than another in the least squares fit, all terms in Eq. 1 for each case corresponding to a given species were divided by the mean predicted concentration of that species.

4. RESULTS

4.1 *Source Category Sensitivities*

4.1.1 *Exploratory Results*

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

* The emission maps in Figure 3-1 also show a concentration of point and mobile source emissions in the Lake Charles, LA area but this is located too far east to be of interest in our analysis.

† It must be recognized that model prediction errors can arise from other sources such as errors in meteorological fields, errors in the temporal and spatial allocation of emissions, errors in the model's simulation of photochemical reactions, etc. but for the purposes of this discussion, we attempt to identify the largest possible fraction of the prediction error that can be eliminated under the noted assumptions of linearity and independence.

- 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. However, since the linear adjustments implied by the sensitivities are only valid locally, this finding does not rule out the possibility of achieving more significant improvements in model performance if just the right combination of relatively large adjustments were applied to the inventory and CAMx was rerun. There are several reasons for this:

- This sensitivity analysis considers adjustments to 10 emission "types" (VOC and NOx for five different source categories), but it may be that adjustments to very specific source categories (e.g., specific categories in specific geographic areas) are needed.
- The response of O_3 (and HCHO or NOy) to emissions changes may be non-linear.
- Interactions between emissions from different categories may be important and would be described by higher-order sensitivities not considered here.
- Some portion of the model error is due to factors other than emissions, for example, errors in meteorological fields.

4.1.2 *Emission Adjustment Scenarios*

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 (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 4-1. Scenario LPVOC represents an alternative to the PT_O2N2 scenario in which the point source VOC adjustment is restricted to the low level point sources with a magnitude derived from the regression analysis. Scenario BioVOC is designed to determine if correcting for the overestimation of biogenic VOC emissions suggested by the regression analysis results in any actual improvement in model performance. Scenario MABVOC represents a set of "optimal" VOC adjustments to the PT_O2N2 scenario suggested by the regression analysis. Scenario NOxMAP is designed to determine if NO_x reductions lead to any changes in model performance that differ from those under the MABVOC scenario. All adjustments were applied to emissions in the HGBPA 11-county area.

Model performance statistics under the five VOC emissions scenarios listed in Table 4-1 were computed against ozone data from the surface monitoring network. Results for the coarse (4 km) and fine (1 km) grid results in Table 4-2a and 4-2b, respectively. Shaded cells in these tables indicate those performance measures that exceed EPA's photochemical model performance guideline values (EPA, 1991). The guideline values are:

Accuracy of peak:	absolute value ≤ 20%
Normalized bias:	absolute value ≤ 15%
Normalized gross error:	value ≤ 35%

For the days with peak ozone concentrations in excess of the 1-hour standard level (i.e., all days except 8/27 – 8/28), the PT_O2N2 scenario has the fewest performance measures outside target ranges and this scenario represents a major performance improvement over the Base4a scenario. It is interesting to note, however, that performance for the two low ozone days (8/27 – 8/28) is better under the Base4a scenario than any of the other scenarios. Other major findings from the regression model and model performance under each VOC emissions scenario are as follows:

- 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. The LPVOC scenario in which the Base4a low-point VOC

emissions increased by a factor of 4 as suggested by the regression fit 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

4.1.3 *Convergence of the MABVOC Scenario*

A further examination of the MABVOC scenario was undertaken to determine the degree to which the emission adjustments under this scenario had converged to an "optimal" solution. CAMx DDM sensitivity coefficients were computed for this scenario and the least squares fitting procedure repeated. Results are summarized in Table 4-3.

Overall, these results show that no significant further adjustments to the VOC inventory beyond those incorporated into the VOCMAB scenario are indicated with the exception of about a 20% increase in mobile+area emissions. A reanalysis of the above results with HCHO removed from the fitting species showed that the coefficient for biogenic VOC is quite sensitive to HCHO errors whereas the mobile+area and point source coefficients are not. There is thus no clear cut evidence of a need for any further adjustments to the biogenic inventory.

4.1.4 *NOx Adjustment Scenarios*

Model performance was also evaluated for the NOxMAP scenario described in Table 4-1. Table 4-4 summarizes the ozone performance under this scenario on the 4 km and 1 km grids in comparison to the PT_O2N2 scenario. Performance under the NOxMAP scenario is slightly better on some days (e.g., 8/30) but slightly worse on others (e.g., 8/29). In terms of predicted O_3, the NOxMAP scenario generally produces performance on par with 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.

Table 4-1. Summary of emissions scenarios.

			Adjustment Factors (1 = no adjustment)				
	Scenario	**Description**[Φ]	**Relative to**	**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 [§]	Varies [§]
	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

Φ See Section 3 for a full description.

§ Olefin emissions for apecific sources are set equal to NOx on a molar basis.

Table 4-2a. Summary of model performance statistics for emission scenarios described in the text. Shading indicates performance outside acceptable range as defined in text: a) predicted values on 4 km modeling grid, b) predicted values on 1 km modeling grid.

Base 4a

	Date							
	24	25	26	27	28	29	30	31
Peak Observation (ppb)	120.1	194.0	140.0	87.0	112.0	146.0	200.5	175.5
Peak Predication (ppb)	96.2	118.2	118.5	107.6	113.9	117.9	149.3	144.9
Accuracy of Peak (%)	-19.9	-39.1	-15.3	23.7	1.7	-19.2	-25.6	-17.4
Normalized Bias (%)	-27.5	-38.2	-19.7	12.0	10.7	-15.8	-16.1	-1.0
Normalized Gross Error (%)	29.7	40.7	24.7	14.3	18.3	22.5	25.7	13.1

PT_O2N2

	Date							
	24	25	26	27	28	29	30	31
Peak Observation (ppb)	120.1	194.0	140.0	87.0	112.0	146.0	200.5	175.5
Peak Predication (ppb)	107.4	198.0	142.0	123.7	127.7	156.4	151.3	160.7
Accuracy of Peak (%)	-10.5	2.0	1.5	42.1	14.1	7.1	-24.5	-8.4
Normalized Bias (%)	-15.0	-12.9	-2.0	25.3	24.6	2.2	-10.2	1.9
Normalized Gross Error (%)	21.6	32.1	17.5	25.3	27.6	21.0	21.8	13.6

LPVOC

	Date							
	24	25	26	27	28	29	30	31
Peak Observation (ppb)	120.1	194.0	140.0	87.0	112.0	146.0	200.5	175.5
Peak Predication (ppb)	98.1	153.1	129.4	114.2	120.0	126.1	150.0	149.8
Accuracy of Peak (%)	-18.3	-21.1	-7.5	31.3	7.2	-13.6	-25.2	-14.7
Normalized Bias (%)	-22.5	-26.7	-12.6	17.8	16.9	-9.0	-13.2	0.1
Normalized Gross Error (%)	26.3	32.4	20.0	17.9	22.2	19.9	23.9	13.0

Bio VOC

	Date							
	24	25	26	27	28	29	30	31
Peak Observation (ppb)	120.1	194.0	140.0	87.0	112.0	146.0	200.5	175.5
Peak Predication (ppb)	98.0	188.4	133.2	117.7	119.9	146.6	148.0	152.6
Accuracy of Peak (%)	-18.4	-2.9	-4.9	35.3	7.1	0.4	-26.2	-13.1
Normalized Bias (%)	-21.9	-18.1	-7.4	18.5	15.6	-7.9	-18.5	-3.2
Normalized Gross Error (%)	25.2	33.4	16.9	19.0	20.5	20.9	24.1	12.5

MABVOC

	Date							
	24	25	26	27	28	29	30	31
Peak Observation (ppb)	120.1	194.0	140.0	87.0	112.0	146.0	200.5	175.5
Peak Predication (ppb)	129.6	243.1	148.2	120.4	134.4	160.4	188.4	162.3
Accuracy of Peak (%)	7.9	25.3	5.9	38.4	20.0	9.9	-6.0	-7.5
Normalized Bias (%)	-15.3	1.9	1.8	23.1	31.6	19.1	0.5	1.5
Normalized Gross Error (%)	25.5	29.3	18.9	23.7	34.1	28.1	20.3	12.7

Table 4-2b. Summary of model performance statistics for emission scenarios described in the text. Shading indicates performance outside acceptable range as defined in text: a) predicted values on 4 km modeling grid, b) predicted values on 1 km modeling grid.

Base 4a

	Date			
	25	29	30	31
Peak Observation (ppb)	194.0	146.0	200.5	175.5
Peak Predication (ppb)	113.3	120.6	131.3	145.4
Accuracy of Peak (%)	-41.6	-17.4	-34.5	-17.2
Normalised Bias (%)	-44.1	-18.0	-17.0	-0.2
Normalised Gross Error (%)	45.0	25.9	28.4	13.8

PT_O2N2

	Date			
	25	29	30	31
Peak Observation (ppb)	194.0	146.0	200.5	175.5
Peak Predication (ppb)	214.2	160.1	161.1	172.5
Accuracy of Peak (%)	10.4	9.7	-19.7	-1.7
Normalised Bias (%)	-16.0	3.5	-10.7	2.7
Normalised Gross Error (%)	34.7	21.8	23.8	14.0

LPVOC

	Date			
	25	29	30	31
Peak Observation (ppb)	194.0	146.0	200.5	175.5
Peak Predication (ppb)	156.4	131.1	136.8	151.8
Accuracy of Peak (%)	-19.4	-10.2	-31.8	-13.5
Normalised Bias (%)	-31.6	-10.1	-13.8	0.9
Normalised Gross Error (%)	35.1	21.9	26.2	13.8

BioVOC

	Date			
	25	29	30	31
Peak Observation (ppb)	194.0	146.0	200.5	175.5
Peak Predication (ppb)	214.2	149.9	150.7	164.7
Accuracy of Peak (%)	10.4	2.7	-24.8	-6.2
Normalised Bias (%)	-21.0	-7.4	-19.6	-2.8
Normalised Gross Error (%)	36.1	21.5	26.3	13.0

MABVOC

	Date			
	25	29	30	31
Peak Observation (ppb)	194.0	146.0	200.5	175.5
Peak Predication (ppb)	251.5	166.3	197.1	170.0
Accuracy of Peak (%)	29.6	13.9	-1.7	-3.1
Normalised Bias (%)	0.6	23.6	2.0	2.9
Normalised Gross Error (%)	31.8	29.6	21.5	13.0

Table 4-3. Regression coefficients from least squares fits to combinations of VOC emission categories under the MABVOC emissions scenario.

	Source Category	Coefficient	Std. Error	Stat. Significant?[1]
Three-term model	(Mobile+Area)	0.18	0.07	Yes
	Biogenic	0.10	0.14	No
	Low+Elev Points	0.04	0.06	No
Single-term model	Mobile+Area	0.23	0.05	Yes
Single-term model	Biogenic	0.38	0.12	Yes

Table 4-4. Summary of ozone model performance statistics for the NOxMAP emission scenario relative to the PT_O2N2 scenario (scenarios are defined in Table 4-1); cells with red borders indicate performance does not meet EPA guideline values (see discussion of Table 4-2 above); cells under NOxMAP scenario with light (dark) shading indicate performance is better (worse) than under PT_O2N2 scenario at least two percentage points.

a) Results for 4 km grid

PT_O2N2	**Date**							
	0824	**0825**	**0826**	**0827**	**0828**	**0829**	**0830**	**0831**
Peak Observed	120.1	194.0	140.0	87.0	112.0	146.0	200.5	175.5
Peak Predicted	112.0	197.0	144.0	121.6	128.8	157.1	155.3	162.1
Unpaired Peak Prediction Accuracy	-6.7	1.6	2.8	39.8	15.0	7.6	-22.6	-7.6
Bias (normalized)	-20.3	-12.5	-1.3	23.9	24.7	2.7	-10.2	4.4
Error (normalized)	26.7	32.4	17.7	23.9	27.5	21.4	22.1	14.1
NOxMAP	**Date**							
	0824	**0825**	**0826**	**0827**	**0828**	**0829**	**0830**	**0831**
Peak Observed	120.1	194.0	140.0	87.0	112.0	146.0	200.5	175.5
Peak Predicted	121.8	217.3	142.2	118.6	123.7	155.8	169.8	154.9
Unpaired Peak Prediction Accuracy	1.4	12.0	1.6	36.3	10.5	6.7	-15.3	-11.7
Bias (normalized)	-16.0	-4.9	-1.7	17.7	23.0	10.9	-6.2	-2.8
Error (normalized)	27.6	28.9	18.6	19.0	27.3	23.0	19.0	13.0

b) Results for 1 km grid

	Date			
PT_O2N2	**0825**	**0829**	**0830**	**0831**
Peak Observed	194.0	146.0	200.5	175.5
Peak Predicted	226.9	160.8	160.3	175.9
Unpaired Peak Prediction Accuracy	16.9	10.1	-20.0	0.2
Bias (normalized)	-15.7	3.8	-11.1	4.8
Error (normalized)	34.8	22.4	24.5	14.5
	Date			
NOxMAP	**0825**	**0829**	**0830**	**0831**
Peak Observed	194.0	146.0	200.5	175.5
Peak Predicted	226.2	164.4	180.6	170.6
Unpaired Peak Prediction Accuracy	16.6	12.6	-9.9	-2.8
Bias (normalized)	-6.1	15.0	-6.0	-2.1
Error (normalized)	31.2	23.4	20.3	12.9

Time series of ozone at surface observing sites along with corresponding predicted values under the PT_O2N2 and NOxMAP scenarios were also examined but are not shown here due to space limitations; complete details are provided by Yarwood, Stoeckenius and Lau (2004). In some cases, prediction of daily maximum $O_3$is improved under the NOxMAP scenario while in others it is worse. During most hours at most sites, there is little difference between O_3 predicted under these two scenarios. In particular, there are cases in which observed O_3 is severely under predicted and the model predictions are unaffected by the NOx reductions

under the NOxMAP scenario, leading to the conclusion that these under predictions are either due to the influence of sources that do not appear in the inventory, errors in the VOC inventory, inaccuracies in the meteorological modeling, or some combination of the above.

4.2 Emission Sub-Region Sensitivities

As described in Section 3, DDM coefficients were computed representing sensitivity of predicted ozone to emissions within six sub-regions within the modeling domain. The six sub-regions (and dominant source categories in each) were (see Figure 3-1):

1. Freeport (point sources)
2. Texas City (point sources)
3. Houston metro (near and inside the beltway) (area/mobile)
4. Houston Ship Channel – West (point sources)
5. La Porte/Baytown Industrial region (point sources)
6. Beaumont - Port Arthur (point and area/mobile)

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.

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.

4.3 VOC Reactivity

The top-down inventory evaluation discussed above considered potential errors in the total emission rates for VOC emissions from several source categories. However, ozone model results are also sensitive to the mix of VOCs assumed to represent VOC emissions (the VOC speciation). 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 ozone forming potential of VOCs can be compared simply using the Maximum Incremental Reactivity (MIR) factors developed by Carter (1999). These factors express the potential moles of ozone formed per mole of VOC emitted under a standard chemical condition. A common concern with these MIR factors is that they are developed using box model scenarios that may not represent the atmospheric conditions for all situations. A recent study for the NARSTO Reactivity Research Working Group (RRWG) demonstrated how to calculate relative VOC reactivities using CAMx and the DDM (Carter, Tonnesen and Yarwood, 2003). The methods developed for the RRWG were applied for the Houston TexAQS CAMx simulation to calculate point source VOC relative reactivities under the specific conditions of the PT_O2N2 emissions scenario for the TexAQS 25-31 August 2000 episode. Details of the reactivity calculation methodology are provided by Yarwood, Stoeckenius and Lau (2004). A series of Houston-specific VOC reactivities were calculated and evaluated relative to ethylene, as reported in Table 4-5. These results show that the Houston specific relative reactivities are consistent with existing maximum incremental reactivity (MIR) factors developed by Carter

(1999) 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.

Table 4-5. Reactivities for CB4-VOCs relative to ethylene for the Houston points source emissions and the EKMA box model MIR scenario.

Species Name	Description	Houston Specific Relative Reactivity	EKMA Box Model MIR	
			Relative Reactivity	Reactivity (moles O_3 per mole C)
ETH	Ethylene	1.00	1.00	2.64
PAR	Paraffins, e.g. butane	0.16	0.15	0.40
OLE	Olefins, e.g. propylene	1.96	2.08	5.50
TOL	Toluene and monoalkylbenzenes	0.17	0.22	0.57
XYL	Xylene and di/tri-alkybenzenes	0.91	1.02	2.68
FORM	Formaldehyde	2.77	2.45	6.47
ALD2	Acetaldehyde and higher aldehydes	1.03	1.31	3.45
MEOH	Methanol	0.20	0.18	0.47
ETOH	Ethanol	0.23	0.29	0.76
ISOP	Isoprene	1.14	1.88	4.95
Point VOC	PT_O2N2 point source emissions	0.93	N/A	N/A

Notes:

The relative reactivity of ethylene is 1 by definition.
The EKMA box model MIRs are from Carter, Tonnesen and Yarwood (2003).

5. CONCLUSIONS AND RECOMMENDATIONS

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 described above (see Yarwood, Stoeckenius and Lau, 2004 for additional supporting information):

- 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 used in this study. 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 Houston) 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 the simulation of meteorological parameters (winds, mixing heights).

- Calculation of Houston-specific VOC reactivities using the DDM results showed that the 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

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. The analysis should 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.

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APPENDIX: Calculation of DDM Sensitivity Coefficients

The inverse modeling approach uses sensitivity coefficients to relate model outputs (concentrations) to inputs (emissions) calculated via the DDM (Dunker, 1980, 1981). DDM sensitivity coefficients are calculated explicitly by specialized algorithms implemented in the host model (in this case, CAMx). The CAMx DDM permits the evaluation of sensitivity coefficients with respect to parameters related to emissions, boundary or initial conditions (BCs or Ics). The sensitivity to be evaluated may bear a simple relationship to the regular model input, such as scaling the ozone boundary concentration by a factor ($BC_{new} = \lambda \times BC_0$). To allow complete flexibility, the perturbations are specified by providing additional IC, BC, and/or emission input files with the same format as the regular model input files.

In mathematical terms, a regular model input file, for example the BC input file, represents some set of functions of space and time $f_i(\underline{x},t)$, where each chemical species can be defined by a unique function. An additional input file provided for the DDM represents another set of functions of space, time, and chemical species $g_i(\underline{x},t)$ that can be different from the regular input file. The scalar parameter λ_i is then defined by:

$$F_i(\underline{x},t) = f_i(\underline{x},t) + \lambda_i \times g_i(\underline{x},t) \quad . \tag{1}$$

Here, $\lambda_i \times g_i(\underline{x},t)$ is the perturbation, and the user desires information on how the model would respond if the input $f_i(\underline{x},t)$ is replaced by the input $F_i(\underline{x},t)$. The DDM calculates the sensitivity $s_i(\underline{x},t)$ with respect to the scalar parameter λ_i. The Taylor series to first order then gives the estimate:

$$c_l(\underline{x},t;\lambda_i) = c_l(\underline{x},t;\lambda_i=0) + \lambda_i \times s_i(\underline{x},t) \tag{2}$$

where $c_l(\underline{x},t;\ i)$ is the estimated model result for species l when $F_i(\underline{x},t)$ is used as input, and $c_l(\underline{x},t;\ i=0)$ is the base case model result when $f_i(\underline{x},t)$ is used as input.

For example, to calculate the sensitivity of the predicted ozone concentration to scaling boundary ozone by a factor, CAMx would be provided with a DDM BC file that has the same ozone values as the regular model BC file. The sensitivity coefficient fields output by CAMx could then be used to estimate the resulting ozone concentration if the ozone BCs were increased by 20%, as follows:

$$c_{\lambda=0.2} = c_{\lambda=0} + (0.2 \times s) \quad (3)$$

In this study, sensitivity coefficients were calculated between modeled concentrations and specific emissions inputs. These sensitivity coefficients were used to estimate how the emissions inputs should be changed to improve the agreement between the predicted concentrations and observed concentrations. Sensitivity coefficients were calculated for emissions from the 11 counties in the Houston/Galveston and Beaumont/Port Arthur (HGBPA) nonattainment areas.

Two different emission source groupings were used in the sensitivity calculations: grouping by source category and grouping by geographic region. For grouping by source categories, sensitivity coefficients were calculated with respect to VOC and NOx emissions from on-road mobile, area (which include off-road mobile), biogenic, low-level point and elevated point sources. The difference between low-level and elevated point sources is the effective release height of the emissions, which is equal to the stack height plus the plume rise. Point sources that will always be released into the surface layer of the model are called low-level point sources. Other point sources are classified as elevated and the plume rise for each source is calculated hour-by-hour in CAMx according to the stack parameters and the local meteorology. Elevated points tend to be combustion sources (e.g., utilities, boilers, flares, large engines) whereas low-level points tend to be vents and fugitives.

For grouping by geographic regions, sensitivity coefficients were calculated with respect to VOC and NOx emissions from low-level and elevated sources in each of several sub-regions within the modeling domain. Low-level sources include all on-road mobile, off-road mobile and area, biogenic, and low-level point sources as defined above; elevated sources included just the elevated point sources. Emission subregions were defined so as to differentiate between key source areas contributing to ozone formation in Houston. These regions and the process by which they were selected are described in Section 3.