Dispersion Modeling of Benzene and 1,3-Butadiene in Corpus Christi, Texas

Prepared for
The Honorable Janis Graham Jack
U.S. District Court, Southern District of Texas
Corpus Christi, Texas

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EXECUTIVE SUMMARY

Background and Objectives

Toxic air pollutants, also known as hazardous air pollutants or air toxics, are pollutants that are classified by the U.S. Environmental Protection Agency as known or suspected human carcinogens or as having other adverse environmental or human health impacts, including reproductive, developmental, neurological, and respiratory effects. Air toxics have the potential to be emitted from numerous anthropogenic sources with different spatial, temporal, chemical and physical release profiles. Ambient concentrations of urban air toxics are highly influenced by local emissions sources and strong spatial gradients have been found to exist in urban areas. Characterization of these gradients is necessary for accurate assessments of human health risks.

In human exposure assessments, atmospheric concentrations of air toxics are frequently determined using both ambient measurements and air quality modeling. Ambient measurement networks for air toxics are not as spatially dense as for criteria pollutants, (e.g., ozone) in most regions of the US. Consequently, air quality modeling can be an important supplement for air toxics exposure assessments. Modeling can provide estimates of ambient concentrations in areas where monitors are not located and can indicate potential "hotspots", or areas with elevated concentrations, for future investigation.

This study examines dispersion model predictions of benzene and 1,3-butadiene concentrations from stationary industrial and other anthropogenic emissions sources in Corpus Christi, Texas. These air toxics are national or regional drivers of carcinogenic risk in the United States. Corpus Christi, with a population of nearly 400,000 in the encompassing counties of Nueces and San Patricio, has the 6th largest port in the United States with significant petroleum refining and chemical manufacturing industries. The close proximity of residential to these emissions sources has raised concerns about exposure to air toxics. Since mid-2005, The University of Texas at Austin has operated a seven site ambient monitoring network that includes measurements of hydrogen sulfide (total reduced sulfur), sulfur dioxide, total non-methane hydrocarbons, and meteorological data. In addition, hourly measurements of approximately 55 speciated volatile organic compounds (VOCs) are collected continuously at two sites, Oak Park and Solar Estates, using automated gas chromatographs (auto-GCs) with flame ionization detection. The network design provides the flexibility to trigger the collection of 20-minute integrated VOC samples collected in canisters at sites that do not have auto-GCs.

Dispersion models have historically been used in the air permitting process to estimate the concentration of a pollutant at ground-level receptors surrounding an emissions source. This work applies two air dispersion modeling systems, AERMOD and CALPUFF, which represent the state-of-the-practice for dispersion modeling in the United States. This study had the following objectives:

- To apply the AERMOD and CALPUFF modeling systems to predict benzene and 1,3-butadiene concentrations in the Corpus Christi area using three years of

meteorological data (2006-2008). Modeling was conducted with stationary point source emissions alone and in combination with area and mobile source emissions. These inventories were obtained from the Texas Commission on Environmental Quality (TCEQ).

- To evaluate AERMOD and CALPUFF predictions under different meteorological conditions, to identify factors that influence model predictions, and to compare model predictions against ambient measurements from the Corpus Christi Air Quality Program auto-GC sites.

- To map the spatial distributions of predicted benzene and 1,3-butadiene concentrations.

Emission Inventory Evaluation

A key element in performing air quality modeling is the selection or development of an emissions inventory. Thirteen existing emission inventories for stationary point sources in Nueces and San Patricio counties were evaluated and compared, including data from the National Emissions Inventory, the Toxics Release Inventory Program, the State of Texas Air Reporting System, and the Texas Commission on Environmental Quality emissions inventories used for photochemical modeling to support State Implementation Plan Development. Pronounced differences were evident between inventories, and the differences in annual emissions between inventories can be more than a factor of two. The 2005 TCEQ Photochemical Modeling Emissions Inventory was selected for the dispersion modeling analyses presented here. Although this inventory has the same level of spatial resolution of emissions sources as the National Emissions Inventory, it was processed by the TCEQ's air quality modeling group to account for rule effectiveness and, importantly, to further speciate emissions that are otherwise reported as VOC with unspecified composition. Accounting for rule effectiveness primarily affected VOC emissions from flares, equipment leak fugitives, external floating roof tanks, internal floating roof tanks, and, to a lesser extent, vertical fixed tanks. These are among the largest sources of benzene emissions in the region, primarily associated with petroleum refining.

According to the 2005 TCEQ Photochemical Modeling Inventory, stationary point sources have the largest contribution to benzene emissions in Nueces and San Patricio counties with 256 tpy, followed by area and mobile sources with approximately 160 tpy each, and non-road mobile sources with 34 tpy. On-road mobile sources have the largest contribution to 1,3-butadiene emissions in the 2005 TCEQ Photochemical Modeling Inventory for the region with 17 tpy, followed by point and non-road sources with 7 tpy each, and area sources with 0.15 tpy. Reported point source emissions of benzene primarily originate from floating and fixed roof tanks along with fugitive sources. Point source emissions of 1,3-butadiene originate from chemical manufacturing fuel fired equipment and fugitive emissions from petroleum refining and chemical manufacturing.

Modeling Methodology
The modeling system configurations are described in detail in the report. The AERMOD system was used with surface meteorological data collected at the Solar Estates and Oak Park monitors, and surface and upper data from the National Weather Service Surface Station at the Corpus Christi International Airport during 2006-2008.

The CALPUFF system incorporated 2006-2008 meteorological data from 18 surface stations, 1 upper air site at the Corpus Christi International Airport, 5 precipitation sites, and 1 buoy. Data from the U. S. Geological Survey were used to determine the fractional land use for each of the 38 land use categories in CALMET. Surface roughness length, albedo, Bowen ratio, soil heat flux parameter, anthropogenic heat flux, and leaf area index were computed from the default values for each land use category in CALMET weighted by the fractional land use in each grid cell. Use of high resolution coastline data and terrain kinematics, reducing the terrain radius of influence to 1 km, and increasing the number of smoothing passes for wind fields aloft were all found to improve the performance of CALMET.

Comparisons of AERMOD and CALPUFF predictions with ambient data focused on 2006, which was approximately the time period of the 2005 TCEQ Photochemical Modeling Inventory and for which the first complete year of ambient data were available from the Oak Park and Solar Estates auto-GC sites.

Key Findings

Table E.1 provides a summary of mean, maximum, 75th, 95th, and 99th percentile observed and AERMOD and CALPUFF predicted benzene concentrations during 2006. Predicted concentrations are presented for modeling with stationary point source benzene emissions only and with all anthropogenic benzene emissions (i.e., point, area, and mobile), respectively, from the 2005 TCEQ Photochemical Modeling Inventory. Table E.2 provides similar results for observed and AERMOD and CALPUFF predicted 1,3-butadiene concentrations. Key findings from the dispersion modeling of each pollutant are summarized below. In addition, the sensitivities of AERMOD predictions to assumptions about the calm wind speed threshold and land cover in the region are discussed.

Benzene:
(a) Model Performance at Oak Park during 2006. AERMOD and CALPUFF replicated observed seasonal and locational differences in benzene concentrations, with increases in fall/winter relative to spring/summer and higher concentrations at Oak Park versus Solar Estates. Important industrial emissions sources for benzene are located to the northeast and northwest of Oak Park, and higher observed concentrations during the fall/winter than spring/summer at Oak Park were associated with more frequent northwesterly clockwise through northeasterly winds. AERMOD and CALPUFF predictions were similar, but not identical, with respect to their agreement with observations at both sites.

Table E.1. Summary of mean, maximum, 75th, 95th, and 99th percentile observed (OBS) and predicted benzene concentrations from AERMOD (AER) and CALPUFF (CAL) during two seasonal periods at Oak Park and Solar Estates in 2006. Predicted concentrations are presented for modeling with stationary point source emissions only and with all anthropogenic emissions from the 2005 TCEQ Photochemical Modeling Inventory. Ratios of predicted to observed concentrations are shown in parentheses.

Site	Mean (ppbC)			75th Percentile (ppbC)			95th Percentile (ppbC)			99th Percentile (ppbC)			Maximum (ppbC)		
	OBS	AER	CAL	OBS	AER	CAL	OBS.	AER	CAL	OBS	AER	CAL	OBS	AER	CAL
Oak Park															
Spring/Summer															
Point Sources		2.03 (1.1)	1.16 (0.6)		1.00 (1.2)	0.01 (0.01)		8.36 (1.3)	3.78 (0.6)		34.56 (1.1)	27.08 (0.9)		169.83 (1.0)	155.00 (0.9)
All Anthropogenic	1.91	3.12 (1.6)	2.23 (1.2)	0.84	1.67 (2.0)	1.28 (1.5)	6.51	13.90 (2.1)	6.14 (0.9)	31.01	47.61 (1.5)	33.75 (1.1)	168.03	184.62 (1.1)	164.50 (1.0)
Fall/Winter															
Point Sources		4.30 (0.7)	4.47 (0.7)		3.54 (0.6)	2.88 (0.5)		20.15 (0.7)	20.57 (0.8)		55.47 (0.7)	84.52 (1.1)		198.71 (0.6)	162.10 (0.5)
All Anthropogenic	6.52	6.10 (0.9)	6.20 (1.0)	5.48	4.90 (0.9)	4.45 (0.8)	27.11	27.53 (1.0)	25.09 (0.9)	74.69	69.87 (0.9)	93.49 (1.3)	306.90	214.41 (0.7)	188.70 (0.6)
Solar Estates															
Spring/Summer															
Point Sources		0.59 (0.4)	0.67 (0.5)		0.30 (0.2)	0.44 (0.3)		2.46 (0.5)	2.60 (0.5)		10.31 (0.9)	10.70 (0.9)		49.89 (1.0)	94.22 (1.8)
All Anthropogenic	1.32	0.92 (0.7)	1.37 (1.0)	1.44	0.57 (0.4)	1.33 (0.9)	4.96	3.68 (0.7)	4.09 (0.8)	12.01	14.98 (1.2)	13.41 (1.1)	52.26	61.71 (1.2)	103.30 (2.0)
Fall/Winter															
Point Sources		1.18 (0.4)	1.77 (0.6)		0.74 (0.2)	1.28 (0.4)		4.23 (0.4)	6.68 (0.7)		18.36 (1.0)	28.76 (1.5)		229.53 (3.3)	136.70 (2.0)
All Anthropogenic	2.84	1.63 (0.6)	2.72 (1.0)	3.24	1.12 (0.3)	2.35 (0.7)	9.64	6.09 (0.6)	9.23 (1.0)	19.14	22.19 (1.2)	33.14 (1.7)	69.96	259.66 (3.7)	148.40 (2.1)

When only point source emissions were modeled, AERMOD and CALPUFF generally under-predicted observed concentrations during the fall/winter of 2006 at Oak Park; ratios of predicted to observed concentrations (mean, maximum, 75th, 95th, and 99th percentiles) ranged from 0.5 to 1.1. Surrounding Oak Park are industrial emissions sources located to the northeast and northwest, respectively, and the Corpus Christi urban area to the south. Lower observed and predicted benzene concentrations were associated with southerly winds, and both models, but to a greater extent AERMOD, over-predicted observed concentrations during low wind speeds from this sector. AERMOD predicted concentrations are an interpolation between two concentration limits: a coherent plume, which assumes that the wind direction is distributed about a well-defined mean direction, and a random plume, which assumes an equal probability of any wind direction. The contribution from the random plume to the predicted AERMOD concentration often grows larger as the wind speed decreases (dependent on the atmospheric stability), resulting in a "bulls-eye" of concentric concentration rings that decrease with distance around each emissions source. During periods of light wind speeds, concentrations predicted by AERMOD upwind of emission sources were frequently larger than expected, most notably during periods with southerly winds when only the Corpus Christi urban area was in the upwind region. The relatively high concentrations that were predicted to the south of Oak Park were associated with the contributions from the random plume, and resulted in a greater over-prediction of observed concentrations.

Agreement between observed and AERMOD or CALPUFF predicted benzene concentrations at Oak Park was better for the northwest than for the northeast industrial sector when only point source emissions were modeled. Observed and AERMOD and CALPUFF predicted concentrations for the northwest sector tended to increase as wind speed decreased. For the northeast sector, the highest observed concentrations occurred at moderate wind speeds, but AERMOD and CALPUFF predicted the highest concentrations at low wind speeds and under-predicted observed concentrations during moderate wind speeds. At this time, the environmental factor(s) contributing to the observed difference in concentration/wind speed relationships between the northwest and northeast sectors is unknown. Working hypotheses include uncertainties in the emission rates for important nearby sources, emission rates that change as a function of wind speed (e.g., increasing emissions with increasing wind speed from external floating roof tanks), and/or differences in mechanical and/or thermally-driven atmospheric turbulence that impact the dispersion of emissions in the downwind regions.

When all anthropogenic emissions were modeled, agreement between AERMOD and CALPUFF predicted concentrations and observed concentrations during the fall/winter of 2006 at Oak Park generally improved relative to modeling with only point source emissions; ratios of predicted to observed concentrations (mean, maximum, 75th, 95th, and 99th percentiles) ranged from 0.6 to 1.3. Both models under-predicted the observed maximum concentration, which may be associated with non-routine emissions that are not captured by the 2005 TCEQ Photochemical Modeling Inventory. Both models primarily over-predicted observed concentrations during the spring/summer of 2006, but CALPUFF predictions were generally in closer agreement with observations.

(b) Model Performance at Solar Estates during 2006. When only point source emissions were modeled at Solar Estates, CALPUFF and AERMOD under-predicted mean, 75th, and 95th percentile observed benzene concentrations, were in relatively closer agreement with 99th percentile observed concentrations, and over-predicted the maximum observed concentration during the fall/winter of 2006, as shown in Table E.1. The AERMOD predicted maximum concentration at Solar Estates was comparable to that predicted at Oak Park which was not consistent with observations. However, the frequency of occurrence of relatively higher predicted concentrations (above a 50 ppbC threshold) was greater at Oak Park than Solar Estates. Similar to the results for Oak Park, the inclusion of all anthropogenic emissions in the modeling generally improved performance at Solar Estates with respect to the agreement with observed mean, 75th percentile, and 95th percentile benzene concentrations. For example, from Table E.1, ratios of mean, 75th, or 95th percentile AERMOD or CALPUFF predicted concentrations to observed concentrations with the inclusion of all anthropogenic emissions ranged from 0.3 to 1.0, in contrast to 0.2 to 0.7 when only industrial point sources were included. The addition of area and mobile sources in the models exacerbated the models over-prediction of observed maximum concentrations. At this time, the reason(s) for the models over-prediction of higher observed benzene concentrations at Solar Estates is unknown.

(c) Annual Variability in Model Performance between 2006 and 2008. For modeling conducted with point source benzene emissions only and with all anthropogenic benzene emissions and assuming that benzene emissions remained constant from 2006-2008, neither CALPUFF nor AERMOD were able to consistently replicate the decreases in observed benzene concentrations that occurred at Oak Park and Solar Estates between 2006 and 2008. Predicted and observed annual mean benzene concentrations at Oak Park and Solar Estates during 2006 through 2008 are shown in Figures E.1 and E.2, respectively; all anthropogenic emissions were included in the dispersion models in these figures.

These results suggest that decreases in observed benzene concentrations may be associated with decreases in benzene emissions since 2006, a finding which would be consistent with the declines in annual benzene emissions reported in the TRI. It is recommended that the reported annual TRI emissions inventories continue to be tracked in conjunction with trends in the ambient measurements from the CCAQP network. Emissions inventories with the spatial resolution in emission points and full chemical speciation of VOCs, such as the 2005 TCEQ Photochemical Modeling Inventory, are not routinely developed on an annual basis, which creates disparities in evaluating trends in regions with rapidly changing inventories. If a more recent or future year emissions inventory with the same spatial resolution in emission points and full chemical speciation of VOCs as the 2005 TCEQ Photochemical Modeling EI is developed by the State of Texas, it should be utilized for dispersion modeling in the region.

Figure E.1. Predicted and observed annual mean benzene concentrations at Oak Park during 2006 – 2008 with all anthropogenic emissions sources included in the dispersion models. Note that predictions assume emissions remain constant from 2006-2008.

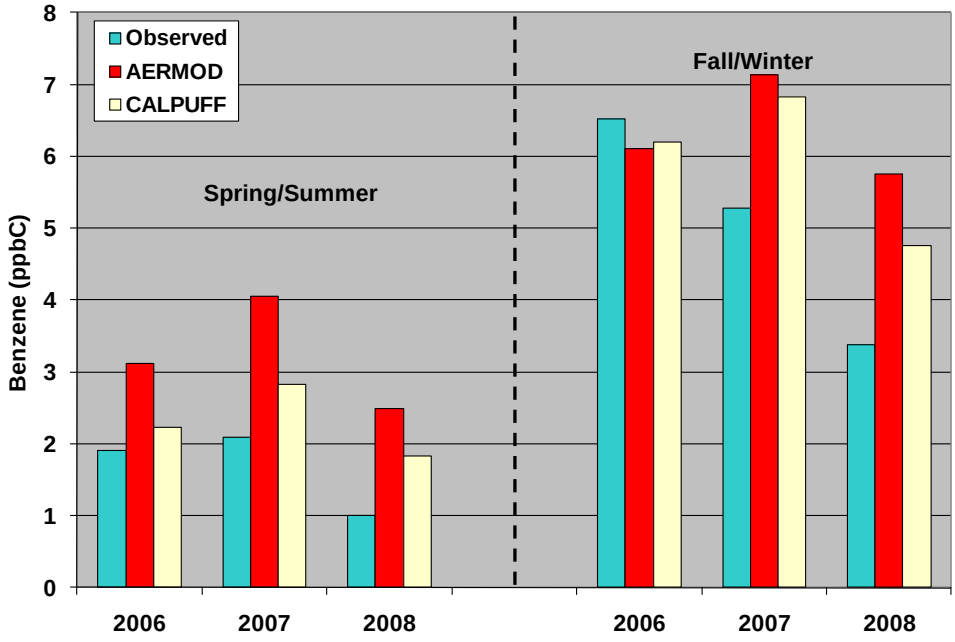
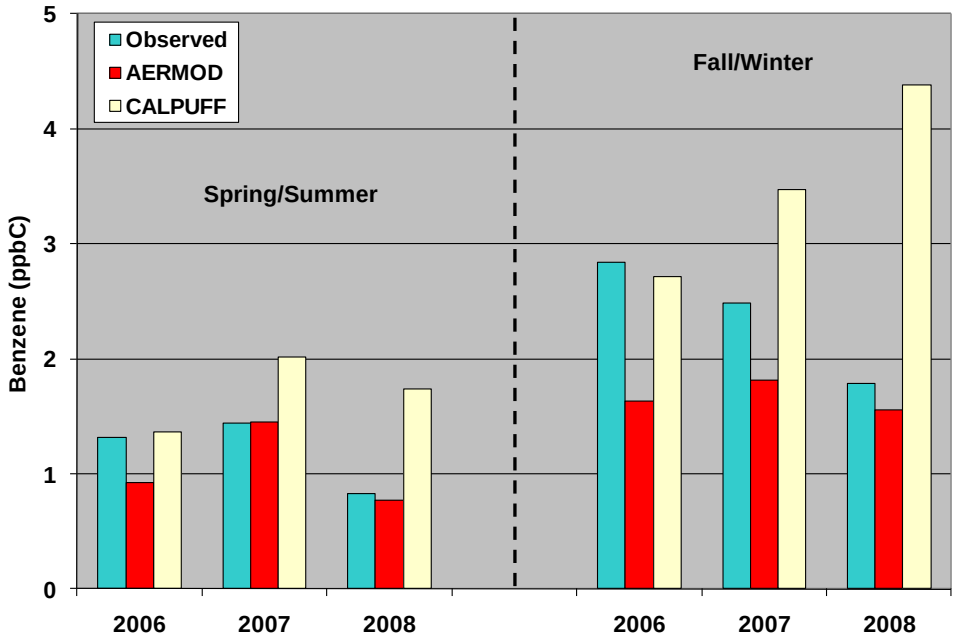


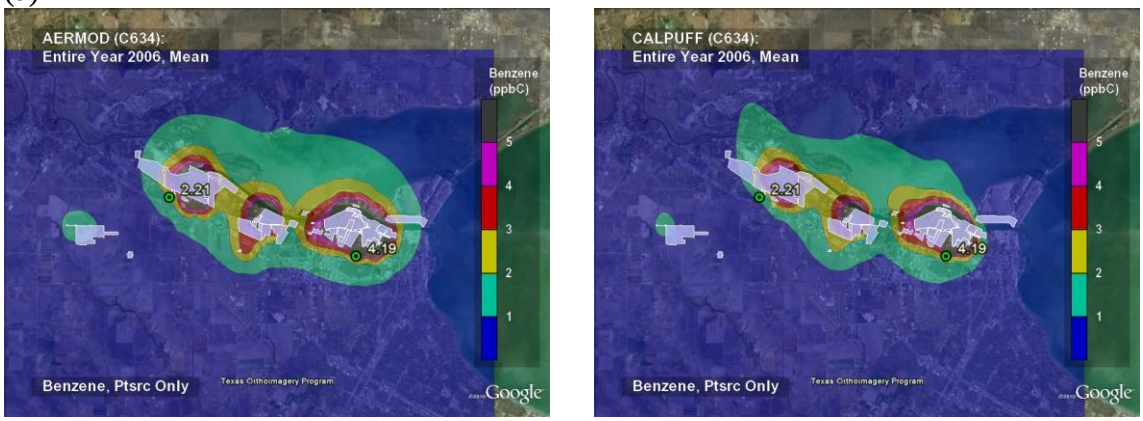
Figure E.2. Predicted and observed annual mean benzene concentrations at Solar Estates during 2006 – 2008 with all anthropogenic emissions sources included in the dispersion models. Note that predictions assume emissions remain constant from 2006-2008.



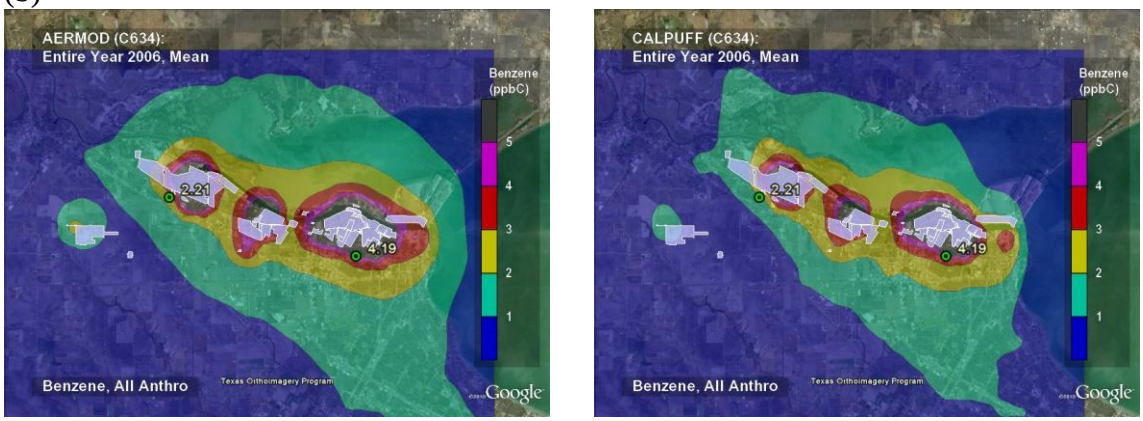
(d) Spatial Maps of Predicted Concentrations during 2006. Spatial maps of predicted concentrations during 2006 were similar for both models, with the exception of annual maximum concentrations that were strongly affected by AERMOD's restriction of on-site meteorological data from a single site. As an example, Figure E.3 shows annual mean benzene concentrations from AERMOD and CALPUFF with point source emissions only and with all anthropogenic emissions using on-site meteorological data from the Oak Park (C634) monitor for AERMOD. The Oak Park and Solar Estates monitors are located within two areas of influence at either end of the Ship Channel. However, neither monitor is positioned to capture benzene concentrations within the Dona Park area more centrally located in the Ship Channel industrial complex or near the Equistar facility located to the southwest of Solar Estates. Although total non-methane hydrocarbon measurements are made at Dona Park, chemically speciated measurements, such as those made with an

Figure E.3. Predicted annual mean benzene concentrations in the receptor grid (colored area) from AERMOD (left) and CALPUFF (right) for 2006 using on-site meteorological data from the Oak Park (C634) monitor for AERMOD and (a) point source emissions only and (b) all anthropogenic emissions. Property boundaries of the stationary point sources are shown in gray.

(a)



(b)



auto-GC, are not routinely determined. Spatial maps of benzene concentrations indicated broader areas of influence when all anthropogenic emissions were included in the modeling than when only point sources were included. These results were consistent with the contributions of area and/or mobile sources to the inventories for this pollutant.

1,3-Butadiene:

(a) Model Performance at Oak Park during 2006. Unlike benzene, the highest observed concentrations of 1,3-butadiene occurred at Solar Estates rather than Oak Park. Table E.2 illustrates that AERMOD and CALPUFF replicated observed seasonal differences in 1,3-butadiene concentrations, with increases in fall/winter relative to spring/summer. Mean and maximum observed concentrations were higher at Solar Estates than Oak Park, but were not well replicated by either model. AERMOD and CALPUFF predictions were similar, but not identical, with respect to their agreement with observations at both sites.

Comparison of results from modeling with point source emissions only and with all anthropogenic emissions, respectively, to observations at Oak Park during 2006 demonstrated an under-prediction bias by both models. For example, ratios of mean, 75th, or 95th percentile AERMOD or CALPUFF predicted concentrations to observed concentrations during fall/winter when all anthropogenic emissions sources were included in the modeling simulations ranged from 0.4 to 0.9. Both models substantially underestimated the observed maximum concentration; the ratios of maximum AERMOD and CALPUFF predicted concentrations to the observed concentration were 0.2 and 0.1, respectively, with all anthropogenic sources included in the modeling. The potential for missing industrial emissions information should be investigated. Observed concentrations may also be associated with non-routine emissions that are not captured by the 2005 TCEQ Photochemical Modeling Inventory.

(b) Model Performance at Solar Estates during 2006. Higher observed 1,3-butadiene concentrations at Solar Estates were associated with southwesterly, west-southwesterly, or westerly winds. These latter wind directions are rare throughout the year, but are more frequent during fall/winter than spring/summer. Observed and predicted spring/summer concentrations at Solar Estates during 2006 were similar to fall/winter concentrations suggesting a weaker seasonal pattern than at Oak Park.

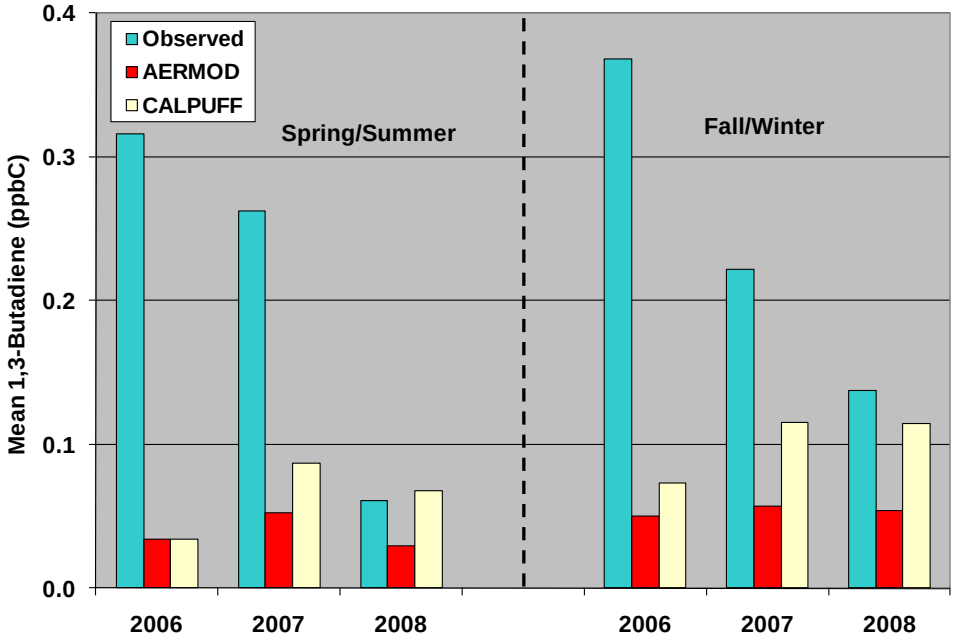
Comparison of results from modeling with point source emissions only and with all anthropogenic emissions, respectively, to observations at Solar Estates during 2006 indicated a strong under-prediction bias by both models. For example, ratios of mean, 75th percentile, 95th percentile, 99th percentile, and maximum AERMOD or CALPUFF predicted to observed concentrations during the fall/winter of 2006, shown in Table E.2, ranged from 0.02 to 0.5 when all anthropogenic emissions sources were modeled. Collectively, the modeling results for Oak Park and Solar Estates suggested the need for future studies aimed at improving the understanding the 1,3-butadiene emissions inventory for Corpus Christi.

Table E.2. Summary of mean, maximum, 75th, 95th, and 99th percentile observed (OBS) and predicted 1,3-butadiene concentrations from AERMOD (AER) and CALPUFF (CAL) during two seasonal periods at Oak Park and Solar Estates in 2006. Predicted concentrations are presented for modeling with stationary point source emissions only and with all anthropogenic emissions from the 2005 TCEQ Photochemical Modeling Inventory. Ratios of predicted to observed concentrations are shown in parentheses.

Site	Mean (ppbC)			75th Percentile (ppbC)			95th Percentile (ppbC)			99th Percentile (ppbC)			Maximum (ppbC)		
	OBS	AER	CAL	OBS	AER	CAL	OBS.	AER	CAL	OBS	AER	CAL	OBS	AER	CAL
Oak Park															
Spring/Summer															
Point Sources		0.04 (0.4)	0.02 (0.2)		0.02 (0.2)	0.00 (0.00)		0.16 (0.6)	0.05 (0.2)		0.63 (1.0)	0.24 (0.4)		3.00 (0.1)	3.44 (0.1)
All Anthropogenic	0.11	0.10 (0.9)	0.05 (0.5)	0.11	0.06 (0.5)	0.04 (0.4)	0.29	0.43 (1.5)	0.17 (0.6)	0.63	1.25 (2.0)	0.58 (0.9)	28.41	3.87 (0.1)	3.64 (0.1)
Fall/Winter															
Point Sources		0.07 (0.2)	0.07 (0.2)		0.06 (0.2)	0.03 (0.1)		0.28 (0.4)	0.26 (0.3)		0.88 (0.5)	1.52 (0.9)		3.12 (0.1)	3.99 (0.1)
All Anthropogenic	0.29	0.17 (0.6)	0.15 (0.5)	0.30	0.14 (0.5)	0.12 (0.4)	0.80	0.73 (0.9)	0.56 (0.7)	1.65	1.99 (1.2)	1.83 (1.1)	34.65	5.30 (0.2)	4.93 (0.1)
Solar Estates															
Spring/Summer															
Point Sources		0.01 (0.03)	0.01 (0.03)		0.00 (0.0)	0.00 (0.0)		0.02 (0.1)	0.03 (0.1)		0.12 (0.04)	0.20 (0.1)		0.84 (0.01)	0.59 (0.01)
All Anthropogenic	0.32	0.03 (0.09)	0.03 (0.09)	0.18	0.03 (0.2)	0.03 (0.2)	0.33	0.11 (0.3)	0.11 (0.3)	3.21	0.50 (0.2)	0.40 (0.1)	99.08	1.81 (0.02)	0.73 (0.01)
Fall/Winter															
Point Sources		0.01 (0.03)	0.02 (0.1)		0.00 (0.0)	0.01 (0.04)		0.05 (0.1)	0.09 (0.2)		0.22 (0.1)	0.27 (0.1)		0.90 (0.01)	0.70 (0.01)
All Anthropogenic	0.37	0.05 (0.1)	0.07 (0.1)	0.24	0.04 (0.2)	0.08 (0.3)	0.57	0.20 (0.4)	0.30 (0.5)	3.08	0.54 (0.18)	0.58 (0.2)	79.55	2.04 (0.03)	1.71 (0.02)

(c) Annual Variability in Model Performance between 2006 and 2008. Annual observed 1,3-butadiene concentrations were generally lower in 2008 than in 2006 at both sites, with marked decreases in both the mean and maximum observed values at Solar Estates. Consequently, the agreement between predicted and observed concentrations also improved between 2006 and 2008 (i.e., reduction in the under-prediction bias of the models). As an example, Figure E.4 shows predicted and observed annual mean concentrations of 1,3-butadiene during this time period. Reported annual air emissions of 1,3-butadiene in 2006, 2007, and 2008 TRI data were 14, 7, and 9 tpy, respectively, indicating lower emissions in 2008 than in 2006. The modeling assumes constant emissions between 2006 through 2008.

Figure E.4. Predicted and observed annual mean 1,3-butadiene concentrations at Solar Estates during 2006 through 2008 with all anthropogenic emissions sources included in the dispersion models. Note that predictions assume emissions remain constant from 2006-2008.



It is recommended that the reported annual TRI emissions inventories for 1,3-butadiene continue to be tracked in conjunction with trends in the ambient measurements from the CCAQP network. In addition, if a more recent or future year emissions inventory with the same spatial resolution in emission points and full chemical speciation of VOCs as the 2005 TCEQ Photochemical Modeling EI is developed by the State of Texas, it should be utilized for dispersion modeling in the region. The potential for missing industrial emissions information also should be investigated, especially near Solar Estates; observed concentrations may often be associated with non-routine emissions that are not captured by the existing emissions inventories.

(d) Spatial Maps of Predicted Concentrations during 2006. Spatial maps of predicted 1,3-butadiene concentrations during 2006 were similar for both models, with the exception of annual maximum concentrations that were strongly affected by AERMOD's restriction of on-site

meteorological data from a single site. As an example, Figure E.5 shows annual mean 1,3-butadiene concentrations from AERMOD and CALPUFF with point source emissions only and with all anthropogenic emissions using on-site meteorological data from the Solar Estates (C634) monitor for AERMOD.

Spatial maps of predicted 1,3-butadiene concentrations and surface wind back trajectories indicate that Equistar is an important emissions source, but neither of the current auto-GC sites are well positioned to characterize concentrations close to this source. The maps also indicate that neither monitor is positioned to capture 1,3-butadiene concentrations within the Dona Park area more centrally located in the Ship Channel industrial complex. Although total non-methane hydrocarbon measurements are made at Dona Park, chemically speciated measurements, such as those made with an auto-GC, are not routinely determined. Spatial maps of 1,3-butadiene concentrations indicated broader areas of influence when all anthropogenic emissions were included in the modeling than when only point sources were included. These results were consistent with the contributions of area and/or mobile sources to the inventories for this pollutant. A mobile monitoring effort may provide insights on the magnitude and spatial gradients of 1,3-butadiene concentrations in the region.

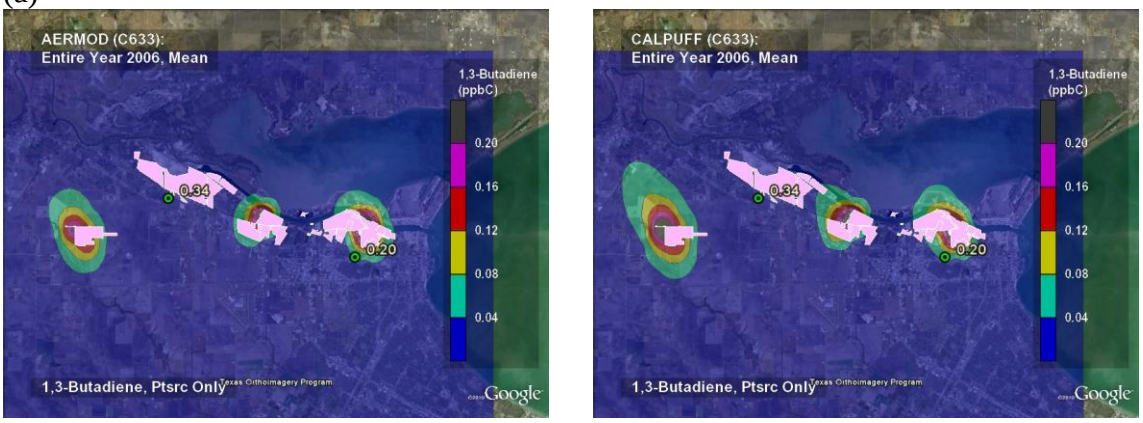
Sensitivity of AERMOD Predictions to the Calm Wind Speed Threshold:
CALPUFF can be used to predict concentrations during calm conditions; however, AERMOD requires a calm wind speed threshold below which the model does not provide predictions. The AERMOD calm threshold was set at 0.22 mps for this study, which is set to the starting wind speed for the wind speed sensor used at the CCAQP monitoring sites. It is recommended that this value continue to be used. However, the AERMOD calms threshold influences model predictions and interpretation of model performance. Stakeholders should continue to track emerging studies in the literature or guidance by the TCEQ and the EPA.

Sensitivity of AERMOD Predictions to Land Cover Characterization:
The AERMOD modeling system requires the specification of land surface characteristics including albedo (the fraction of total incident solar radiation reflected by the surface back to space without absorption), Bowen ratio (the ratio of sensible heat flux to latent heat flux), and surface roughness (the characteristic length related to the height of obstacles to the wind flow or the height at which the mean horizontal wind speed is zero based on a logarithmic profile). In this study, the albedo and Bowen ratio used for AERMOD were based on TCEQ guidance for Nueces County. The roughness lengths of 0.5 and 1.0 meters were used for Solar Estates and Oak Park, respectively, following TCEQ guidance based on a general categorization of land cover in the immediate vicinity of the sites. Predicted surface concentrations were found to be most sensitive to surface roughness length, but were relatively insensitive to albedo and Bowen ratio.

Although not used for this project, the US EPA has developed an AERSURFACE tool that uses USGS 1992 National Land Cover Data to determine land cover types and surface parameters for a user-specified location. Given the vintage of the USGS data currently available in AERSURFACE, use of the roughness lengths of 0.5 meters and 1.0 meters for Solar Estates and Oak Park, respectively, following TCEQ guidance is recommended. Application of

Figure E.5. Predicted annual mean 1,3-butadiene concentrations in the receptor grid (colored area) from AERMOD (left) and CALPUFF (right) for 2006 using on-site meteorological data from the Solar Estates (C633) monitor for AERMOD and (a) point source emissions only and (b) all anthropogenic emissions. Property boundaries of the stationary point sources are shown in pink.

(a)



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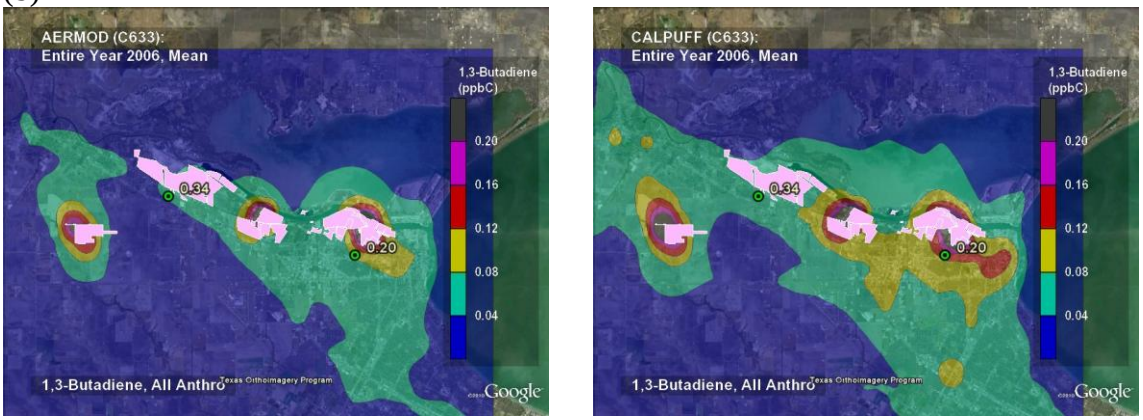

contemporaneous land use/land cover data from satellite instrumentation in AERSURFACE and field validation are recommended for future investigation.

Recommendations

This study resulted in several key recommendations for the region:

- Reported annual TRI emissions inventories for benzene and 1,3-butadiene should continue to be tracked in conjunction with trends in the ambient measurements from the CCAQP network.

- If a more recent or future year emissions inventory with the same spatial resolution in emission points and full chemical speciation of VOCs as the 2005 TCEQ Photochemical

Modeling Inventory is developed by the State of Texas, it should be utilized for dispersion modeling in the region.

- Dona Park and areas to the southwest of the Ship Channel (near the Equistar facility) should be considered for future auto-GC and/or VOC canister sampling efforts.

- Mobile monitoring studies should be considered to compare with predicted spatial gradients of benzene and 1,3-butadiene concentrations. Such studies would be valuable if repeated annually or semi-annually over an extended period of time to examine long-term trends in measured concentrations.

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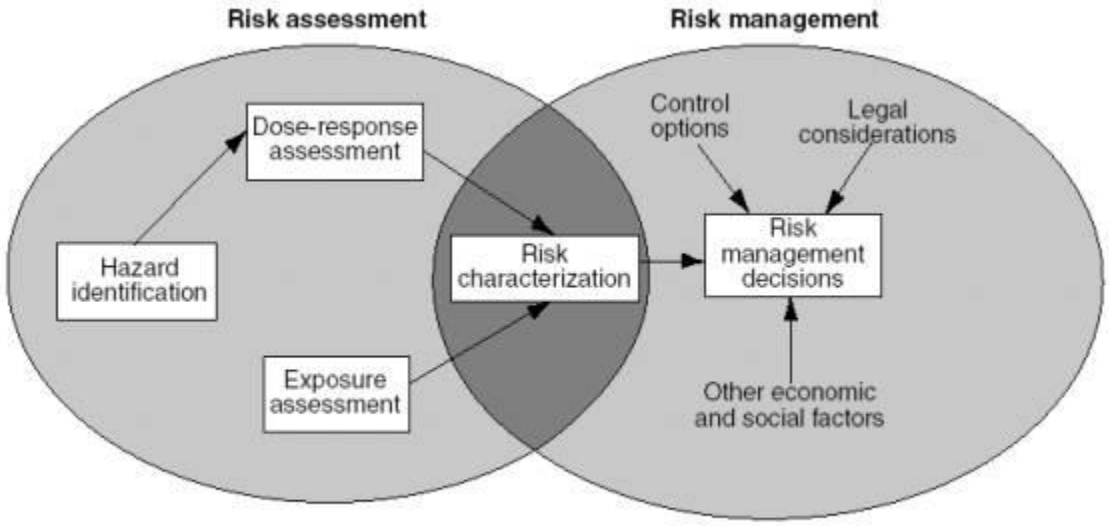
1. Introduction

Toxic air pollutants, also known as hazardous air pollutants (HAPs) or air toxics, are pollutants that are classified by the U.S. Environmental Protection Agency (EPA) as known or suspected human carcinogens or as having other adverse environmental or human health impacts, including reproductive, developmental, neurological, and respiratory effects (Rosenbaum et al., 1999; http://www.epa.gov/airtoxics/brochure.html). Section 112 of the Clean Air Amendments of 1990 identified 189 toxic air pollutants (ref. Appendix A) that are subject to regulatory control. Since then, caprolactam and methyl ethyl ketone were delisted, resulting in a current list of 187 air toxics (http://www.epa.gov/ttn/atw/pollutants/atwsmod.html).

Toxic substances differ in their sources, pathways for human exposure, and pharmacokinetic effects. The EPA's human health risk assessment under the air toxics program is reflective of the National Academy of Sciences (National Research Council; NRC) risk assessment/risk management paradigm shown in Figure 1 (http://www.epa.gov/ttn/atw/toxsource/paradigm.html; Furtraw, 2001). The risk assessment paradigm is comprised of four components: hazard identification, exposure assessment, dose-response assessment, and risk characterization.



Source: EPA Office of Research and Development.

Figure 1. The National Research Council human health risk assessment/risk management paradigm from http://www.epa.gov/ttn/atw/toxsource/paradigm.html.

Risk assessment begins with hazard identification. The EPA utilizes a weight-of-evidence approach, based on epidemiological, toxicological, and ecological data, to determine the likelihood that a substance causes an adverse effect in humans. Exposure assessment follows a substance's release to the environment, transport and transformation, and contact with humans through one or more pathways. A dose can occur through different portals of entry into the human body, most frequently through inhalation, ingestion, and dermal contact. Once in the body, the dose may lead to a toxicological response or an adverse health effect. Dose-response relationships can be established by examining responses to variations in dose levels using similar

data sources as for hazard identification. Exposure assessment and dose-response assessment are coupled for an overall characterization of risk.

Air toxics have the potential to be emitted from numerous anthropogenic sources with different spatial, temporal, chemical and physical release profiles. On a national scale, emissions of air toxics are tracked through the Toxics Release Inventory (TRI) Program, which compiles annual reported emissions from industrial point sources that meet threshold emissions levels, and through the National Emissions Inventory (NEI) for HAPs, which compiles emissions from anthropogenic source sectors, including some not included in the TRI, across the US on a three-year cycle.

Ambient concentrations of urban air toxics are highly influenced by local emissions sources and strong spatial gradients have been found to exist in urban areas throughout the United States (Wang et al, 2009; Marshall et al., 2008; Isakov et al., 2007; Rosenbaum et al, 1999). In addition, human location, activity patterns, behavioral, and sociological factors influence personal exposures, which have been found to vary markedly across communities (Linder et al., 2008; Sexton et al., 2004; Gibbs and Melvin, 2008; Brooks and Sethi, 1997; Morello-Frosch et al, 2002). Characterizations of the magnitudes and spatial gradients of air toxics concentrations are necessary for accurate assessments of human health risks and environmental equity.

In human exposure assessments, atmospheric concentrations of air toxics are frequently determined using both ambient measurements and air quality modeling. Ambient measurement networks for air toxics are not as spatially dense as for criteria pollutants, (e.g., ozone) in most regions of the US (Rosenbaum, 1999; Isakov et al., 2007). Consequently, air quality modeling can be an important supplement for air toxics exposure assessments. Modeling can provide estimates of ambient concentrations in areas where monitors are not located and can indicate potential “hotspots” or areas with elevated concentrations for future investigation. Models can be used with ambient monitoring data to examine air quality trends, to assess the impacts of new or expanding emissions sources, and to evaluate the potential effectiveness of emissions controls.

Two general forms of air quality models are used in the United States; dispersion models and photochemical grid models (US EPA, 2010). Dispersion models have historically been used in the air permitting process to estimate the concentration of a pollutant at ground-level receptors surrounding an emissions source. Dispersion models are limited in their representation of atmospheric chemical and physical processes, but require less computational burden than photochemical grid models. Photochemical grid models simulate the emissions, transport, chemical transformation and physical removal of pollutants in the atmosphere in the framework of a three-dimensional grid or nested grids over larger spatial scales than dispersion models. These models have been used extensively in regulatory assessments of criteria air pollutants, such as State Implementation Plan development in Texas and other states.

The EPA’s National Air Toxics Assessment (NATA) is developed to identify air toxics, emissions source types, and locations which are of greatest concern for chronic cancer and non-cancer health risks in the United States. The NATA is not intended to provide comprehensive risk assessments for local areas or “hotspots” or for regulatory action, but rather to prioritize substances, sources, and regions for further study and potential community efforts. It is

illustrative of the integration of atmospheric modeling within the risk assessment process. NATAs have been conducted for 1996, 1999, and, most recently, for 2002, the results of which were released in June 2009.

The NATA process is comprised of four elements: (1) compilation of a national emissions inventory of air toxics emissions from outdoor sources; (2) estimation of ambient air toxics concentrations using dispersion models; (3) estimation of population exposures using the Hazardous Air Pollutant Exposure Model (HAPEM); and (4) characterization of the potential public health risks, including both cancer and non-cancer effects, due to inhalation of air toxics. The NATA process is described in detail at http://www.epa.gov/ttn/atw/natamain/. The dispersion modeling (2) provides necessary input data for HAPEM (3), which combines predicted ambient air toxics concentrations with data characterizing demographic, locational, and human activity patterns to determine inhalation exposure concentrations for groups of individuals.

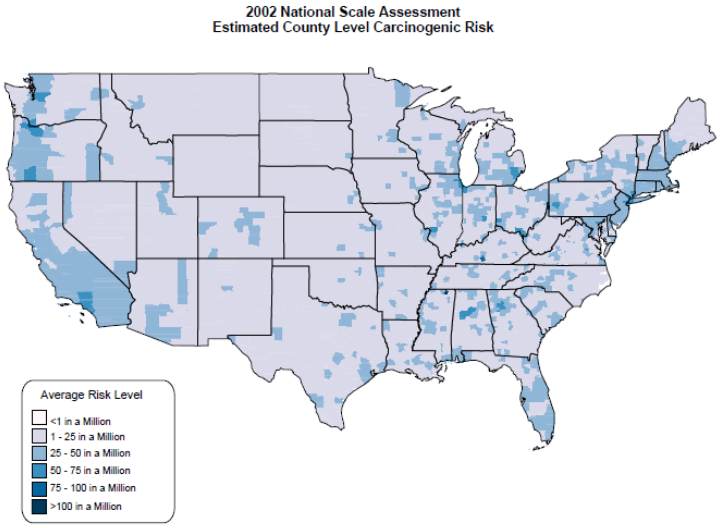
Modeling of 180 air toxics in addition to diesel particulate matter (DPM) was conducted for the 2002 NATA. Cancer and non-cancer risks from chronic inhalation exposure were determined for 124 species. Cancer risks were represented as lifetime risks or the risk of developing cancer as a result of exposure to each air toxic over a normal lifetime of 70 years. Non-cancer risks were represented as a hazard quotient or ratio between the exposure and a reference concentration (see Appendix B). National and regional drivers and contributors to cancer and non-cancer health risks are summarized in Table 1 http://www.epa.gov/ttn/atw/nata2002/risksum.html. Maps from the 2002 NATA showing the estimated county level carcinogenic risk and estimated county level non-cancer (respiratory) risk are presented in Figure 2.

Table 1. Criteria for classification of air toxics in the 2002 NATA, and risk characterization results. Note that the Hazard Index (HI) is the sum of hazard quotients for substances that affect the same target organ or organ system for non-cancer drivers.
Source: http://www.epa.gov/ttn/atw/nata2002/risksum.html.

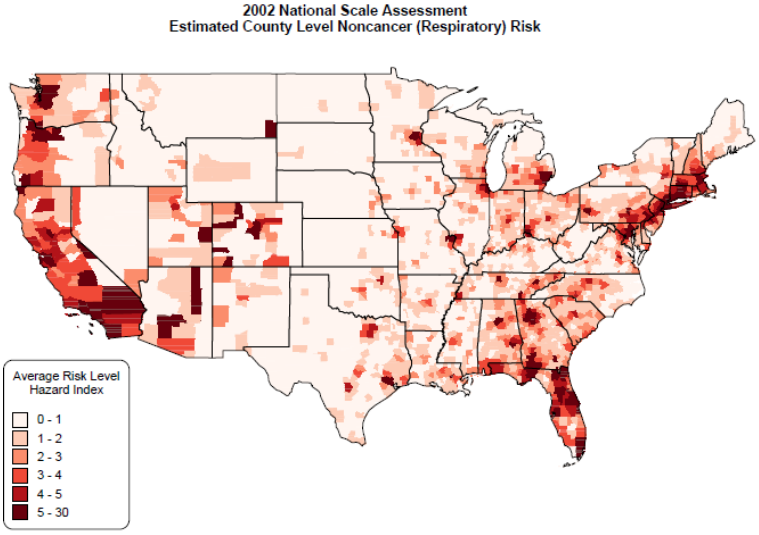
Risk Characterization Category	Risk Exceeds (in a million)	HI > 1.0	Number of People or Greater Exposed (in millions)	Results of the 2002 NATA
National Cancer Driver	10		25	• Benzene "Carcinogenic to humans"
Regional Cancer Driver	10		1	• 1,3-butadiene, arsenic compounds, chromium 6, coke oven emissions: "Carcinogenic to humans". • Hydrazine, tetrachloroethylene, PAHs: "likely carcinogenic to humans" (The Weight of evidence for the 8 PAH groups range from "likely" to "not likely carcinogenic to humans"). • Naphthalene: "Suggestive evidence of carcinogenicity".
Regional Cancer Driver	100		0.01	
National Cancer Contributor	1		25	• 1,4-dichlorobenzene, acetaldehyde, acryonitrile, carbon tetrachloride, ethylene oxide : "Likely carcinogenic to humans".
Regional Cancer Contributor	1		1	• Nickel compounds: "Carcinogenic to humans" • 1,3-dichloropropene, beryllium compounds, cadmium compounds, methylene chloride: "Likely carcinogenic to humans" • 1,1,2,2-tetrachloroethane: "Suggestive evidence of human carcinogencicity" • N-nitrosomorpholine, methyl tert-butyl ether: No EPA weight of evidence classifications.
National Non-cancer Driver		1.0	25	• Acrolein
Regional Non-cancer Driver		1.0	0.01	• 2,4-toluene diisocyanate, chlorine, chromium compounds, diesel engine emissions, formaldehyde, hexamethylene diisocyanate, hydrochloric acid, manganese compounds, nickel compounds.

Figure 2. Maps from the 2002 NATA showing the (a) estimated county level carcinogenic risk, (b) estimated county level non-cancer (respiratory) risk.

(a)



(b)



2. Case Study Area and Objectives

This study examines dispersion model predictions of benzene and 1,3-butadiene concentrations from stationary point and other anthropogenic emissions sources in Corpus Christi, Texas. These air toxics are national or regional drivers of carcinogenic risk in the United States and are associated with industrial activities that occur in the region. Corpus Christi, with a population of nearly 400,000 in the encompassing counties of Nueces and San Patricio (http://quickfacts.census.gov/qfd/states/48/48355.html; http://quickfacts.census.gov/qfd/states/48/48409.html), has the 6th largest port in the United States with significant petroleum refining and chemical manufacturing industries (http://www.iwr.usace.army.mil/ndc/wcsc/portton01.htm). In the 2008 TRI, the most recent available at the time of writing this report, the Valero Corpus Christi West Plant ranked 7th in the United States for total on-site and off-site disposal and other releases (via air, land, and water) of toxic compounds under the North American Industrial Classification System (NAICS) code 324 for petroleum refining. The Flint Hills Resources West Plant ranked 15th on this list; the Valero Corpus Christi East Plant and Flint Hills Resources East Plant were both ranked within the top 50 refineries (http://www.epa.gov/tri/tridata/tri08/national_analysis/pdr/2008%20TRI%20Workbook%20Section%20C.pdf). Fugitive and point source air emissions reported in Nueces County from petroleum refining and chemical manufacturing were 908 tons per year (tpy) and 205 tpy, representing 80% and 18%, respectively, of total air emissions in the 2008 TRI.
The close proximity of residential to industrial areas has raised concerns about exposure to air toxics. Nueces County contained a sub-region on the Texas Commission on Environmental Quality's Air Pollutant Watch List (APWL) for benzene emissions that was recently de-listed in January 2010.

Since mid-2005, The University of Texas at Austin (UT) has operated a seven-site ambient monitoring network as part of the Corpus Christi Air Monitoring and Surveillance Camera Installation and Operation Project (referred to as the CCAQP). Analysis of the temporal variability of measured total non-methane hydrocarbons (TNMHC), benzene, and 1,3-butadiene concentrations has been described by McGaughey et al. (2009, 2010) and McDonald-Buller et al. (2009a). The UT network includes measurements of hydrogen sulfide (total reduced sulfur), sulfur dioxide (SO_2), TNMHC, and meteorological data (e.g., temperature, wind speed, wind direction, and relative humidity). In addition, hourly measurements of approximately 55 VOCs are collected continuously at two sites, Oak Park and Solar Estates shown in Figure 3, using automated gas chromatographs (auto-GCs) with flame ionization detection. The network design provides the flexibility to trigger the collection of 20-minute integrated air samples stored in stainless steel canisters during high TNMHC events (using a TECO 55C with 90-second observations, high TNMHC events are defined as 10 consecutive values or 900 seconds at or above 2000 ppbC TNMHC) at the five sites that do not have auto-GCs.

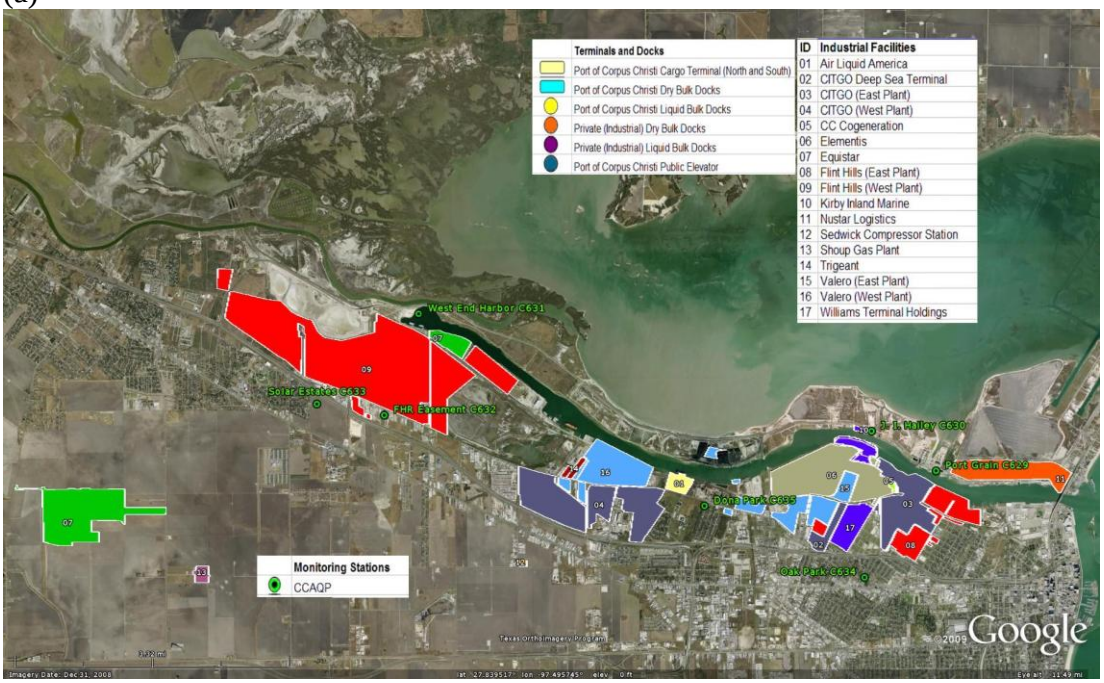
Analysis of measured benzene concentrations during 2006-2009 at the Solar Estates and Oak Park auto-GC sites indicated that highest benzene concentrations occur in the fall and winter during 0400 - 0900 CST, which includes the morning rush hour. Mean, 75th, 95th, and 99th percentile observed benzene concentrations are shown in Figure 4. Consistent with the decreases in ambient concentrations over time, the TRI data for Nueces County also show a decrease in

reported benzene emissions: 105 tpy (2005), 84 tpy (2006), 79 tpy (2007), and 76 tpy (2008). In the 2008 TRI, fugitive and point source air emissions account for 56% and 44% of the total 76 tpy of reported benzene emissions. Point sources of benzene emissions included in the 2005 TCEQ Photochemical Modeling Inventory used for this study are shown in Figure 3a. Consistent upwind geographic source regions have been identified during high observed benzene concentration events (defined as 30 ppbC or greater; reference McGaughey et al., 2009) at Oak Park and Solar Estates. For hours with higher benzene concentrations, Oak Park is dominated by flow from either the north-northwest or north-northeast; while at Solar Estates, winds are generally from the northeast or east (McGaughey et al, 2009; McDonald-Buller et al., 2009a).

A similar analysis of measured 1,3-butadiene concentrations is shown in Figure 5. The highest observed 1,3-butadiene concentrations occur during the fall/winter; however, relatively high concentrations at Solar Estates also occur during the summer. High 1,3-butadiene concentrations (defined as 5 ppbC or greater; reference McGaughey et al., 2010) are most frequently measured during the early morning, including rush hour, but show no consistent difference between weekday and weekend days. These results suggest that other emissions sources, besides mobile sources, may be important during time periods with the highest 1,3-butadiene concentrations. Concentrations decreased between 2006 and 2009. Unlike benzene, the TRI annual release data for 1,3-butadiene emissions show greater variability: 6 tpy (2005), 14 tpy (2006), 7 tpy (2007), 9 tpy (2008). Fugitive and point source air emissions account for 93% and 7% of the total 9 tpy of TRI reported 1,3-butadiene emissions in 2008. Consistent upwind geographic source regions during high 1,3-butadiene events at Oak Park and Solar Estates were identified. Solar Estates is dominated by flow from the southwest and west-southwest, while Oak Park is dominated by flow from the west-southwest and west. A majority of the Solar Estates and Oak Park back-trajectories during periods with measured 1,3-butadiene concentrations of 5 ppbC or greater pass over or nearby the Equistar facility, which is located approximately 5 km west-southwest of Solar Estates (McGaughey et al., 2010).

Figure 3. Maps showing (a) CCAQP monitoring locations, (b) industrial facilities that are sources of benzene emissions, and (c) industrial facilities that are sources of 1,3-butadiene emissions. All maps include the Corpus Christi Ship Channel and the locations of docks and terminals that may be used for ship loading/unloading operations.

(a)



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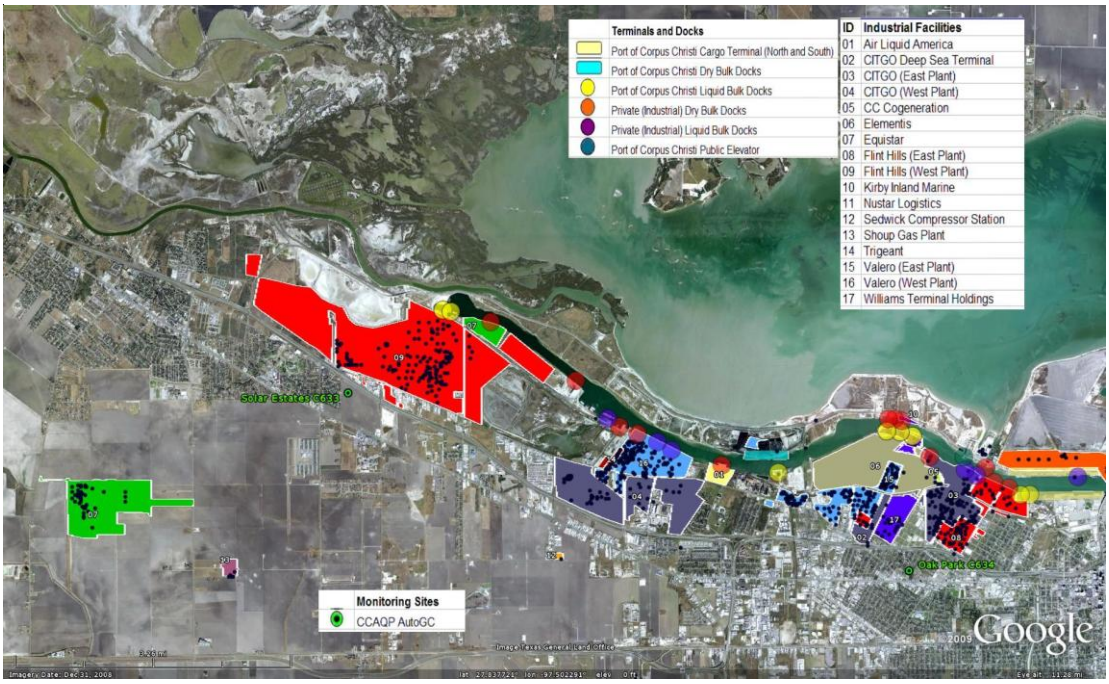


(c)

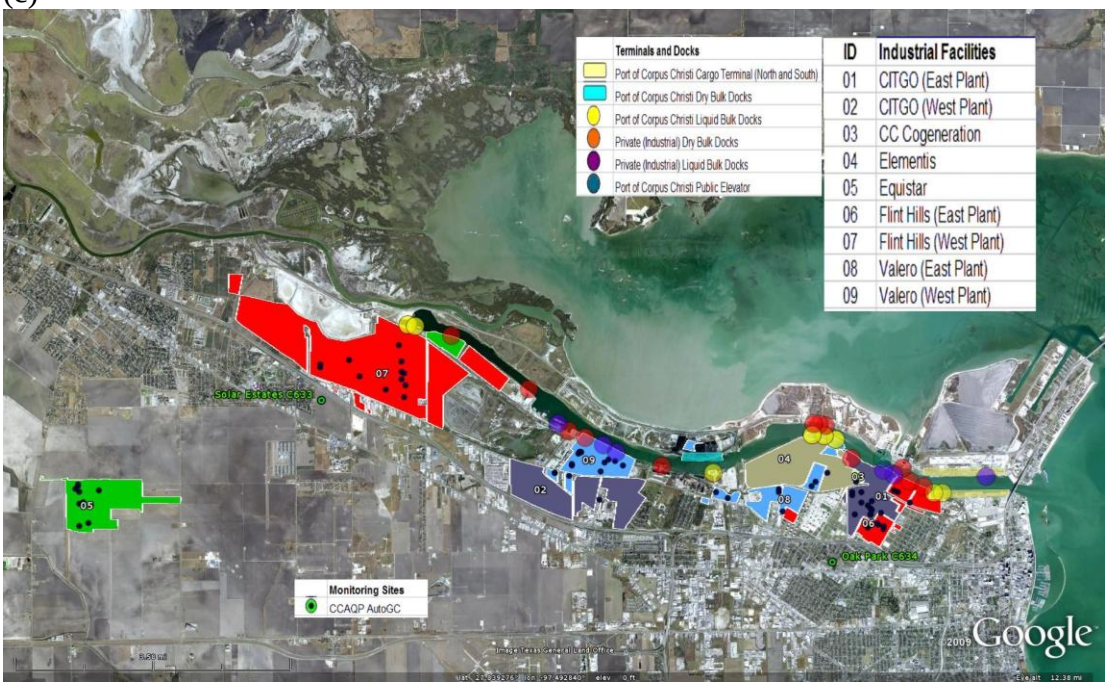
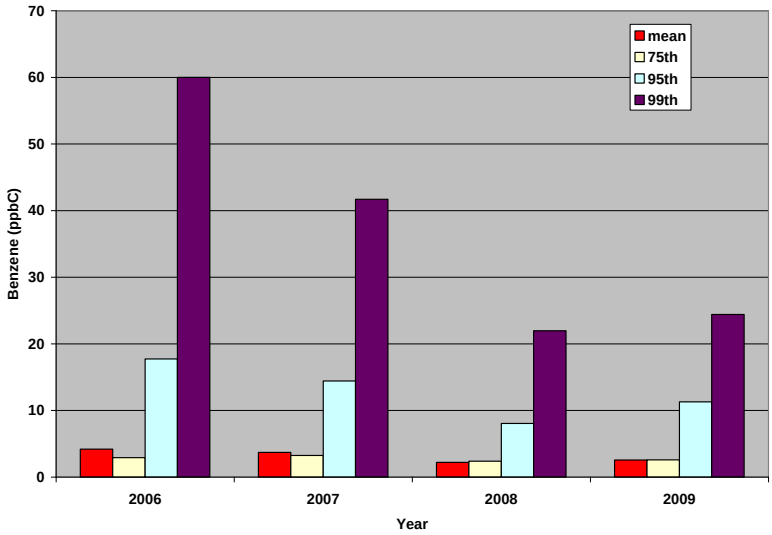

Terminals and Docks
Port of Corpus Christi Cargo Terminal (North and South)
Port of Corpus Christi Dry Bulk Docks
Port of Corpus Christi Liquid Bulk Docks
Private (Industrial) Dry Bulk Docks
Private (Industrial) Liquid Bulk Docks
Port of Corpus Christi Public Elevator
ID Industrial Facilities
01 CITGO (East Plant)
02 CITGO (West Plant)
03 CC Cogeneration
04 Elementis
05 Equistar
06 Flint Hills (East Plant)
07 Flint Hills (West Plant)
08 Valero (East Plant)
09 Valero (West Plant)
Monitoring Sites
CCAQP AutoGC
Solar Estates C633
Oak Park C634
Google

Figure 4. Observed mean, 75th, 95th, and 99th percentile concentrations of benzene at (a) Oak Park and (b) Solar Estates during 2006-2009 (Note differences in scales between the plots).

(a)



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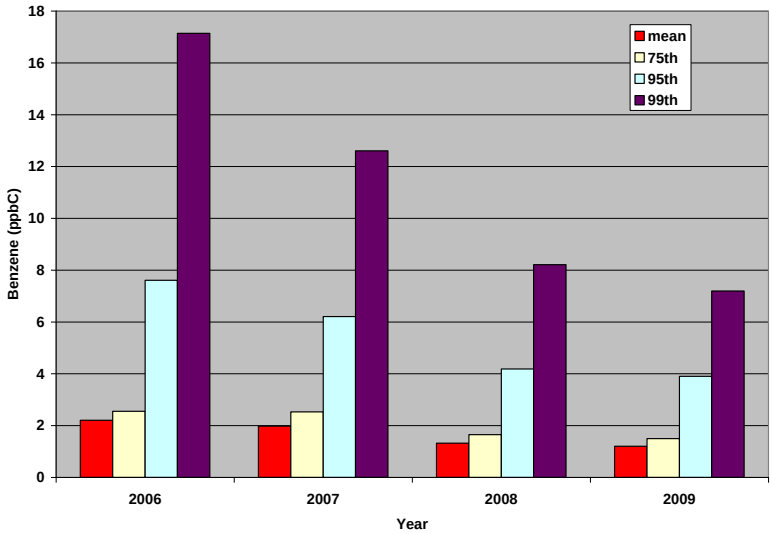
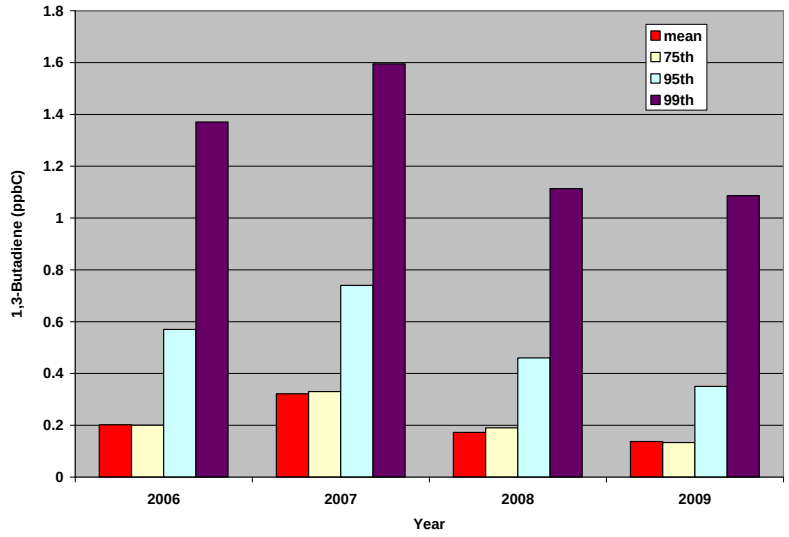


Figure 5. Measured mean, 75th, 95th, and 99th percentile concentrations of 1,-3-butadiene at (a) Oak Park and (b) Solar Estates during 2006-2009 (Note differences in scales between the plots).

(a)



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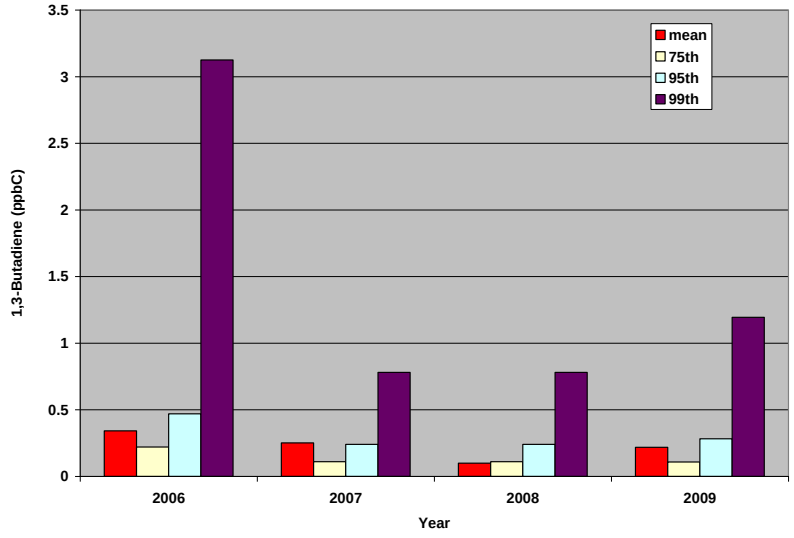


This work applies two air dispersion modeling systems, AERMOD and CALPUFF, to predict benzene and 1,3-butadiene concentrations from stationary point and other anthropogenic emissions sources in the Corpus Christi area. AERMOD and CALPUFF represent the state-of-the-practice for dispersion modeling in the United States (US EPA, 2010). AERMOD is a steady-state dispersion model designed for short-range (≤ 50 kilometers) dispersion of emissions from stationary industrial sources (US EPA, 2010; Cimorelli et al., 2005). CALPUFF is a Gaussian puff modeling system that is recommended by the U.S. EPA for assessing long range transport of pollutants and on a case-by-case basis for near-field applications with complex meteorological conditions (US EPA, 2010; Brode and Anderson, 2008). Both models have undergone evaluations of their performance against field datasets and their responses to uncertainties in model inputs (Perry et al., 2005; Kumar et al., 2006; Hanna et al., 2007; US EPA, 2003; Oshan et al., 2005; MacIntosh et al., 2010). This work is being conducted under the Corpus Christi Neighborhood Air Toxics (CCNAT) Project.

This study has the following objectives:

- To apply the AERMOD and CALPUFF modeling systems to predict benzene and 1,3-butadiene concentrations in the Corpus Christi area using three years of meteorological data (2006-2008). Modeling was conducted with stationary point source emissions alone and in combination with area and mobile source emissions with an inventory obtained from the TCEQ.

- To evaluate AERMOD and CALPUFF predictions under different meteorological conditions, to identify factors that influence model predictions, and to compare model predictions against ambient measurements from the CCAQP auto-GC sites.

- To map the spatial distributions of predicted benzene and 1,3-butadiene concentrations.

The next chapter of the report discusses the input data requirements and configurations of the modeling systems.

3. Modeling Methodology

This chapter describes the point, area, and mobile source emissions inventories for benzene and 1,3-butadiene selected for the dispersion modeling and the model input data and configurations for the Corpus Christi area.

3.1 Point Source Emissions of Benzene and 1,3-Butadiene

Air toxics have numerous anthropogenic emissions sources with different spatial, temporal, chemical and physical release profiles. Previous studies have indicated that the variability in volatile organic compound (VOC) emission estimates between inventories can be significant (McDonald-Buller et al., 2009b; Pavlovic et al., 2009a, 2009b). McDonald-Buller et al. (2009b) compared eleven stationary point source inventories for benzene and 1,3-butadiene in Nueces and San Patricio Counties:

1. 2002 TRI
2. 2003 TRI
3. 2004 TRI
4. 2005 TRI
5. 2006 TRI
6. TCEQ Submittal to the EPA 2002 HAP NEI
7. 2002 EPA HAP NEI
8. TCEQ Submittal to the EPA 2005 HAP NEI
9. 2000 TCEQ Photochemical Modeling Emissions Inventory
10. 2005 TCEQ Photochemical Modeling Emissions Inventory
11. 2008 update to the City of Corpus Christi Emissions Inventory prepared by Air Consulting and Engineering Solutions, Ltd. (ACES)

Since that time, TRI inventories for 2007 and 2008 have become publicly available. Annual benzene and 1,3-butadiene emissions are summarized in Table 2 for eleven inventories. The 2008 ACES inventory for major point sources matched the TCEQ submittal to the 2005 HAP NEI and is not included in Table 2. The TCEQ submittal to the 2002 NEI submittal was identical to the 2002 HAP NEI for most facilities, with several exceptions related to quality assurance, and is also not included (McDonald-Buller et al., 2009b).

Pronounced differences were evident between inventories. For example, benzene emissions from point sources in Nueces County were 167 tpy in the 2002 HAP NEI versus 109 tpy in the 2002 TRI. Benzene emissions from point sources in Nueces County were 105 tpy in the 2005 TRI, 95 tpy in the TCEQ submittal to the 2005 NEI, and 259 tpy in the 2005 TCEQ Photochemical Modeling Inventory.

Table 2. Annual point source emissions of benzene and 1,3-butadiene (tpy) in eleven inventories for Nueces and San Patricio Counties. The 2005 TCEQ Photochemical Modeling Emissions Inventory, which was used in the dispersion modeling, is highlighted.

County	Species	2000 TCEQ Photochemical Modeling EI	2002 HAP NEI	2005 TCEQ Photochemical Modeling EI	2005 HAP NEI Submittal	TRI						
						2002	2003	2004	2005	2006	2007	2008
Nueces	Benzene	248.2	166.8	259.3	93.5	109.0	123.8	120.4	104.9	84.4	78.7	76.5
	1,3-Butadiene	0.0	0.99	7.0	4.9	1.4	2.9	5.4	5.6	13.5	6.7	9.4
San Patricio	Benzene	30.3	2.1	5.8	1.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	1,3-Butadiene	0.0	0.01	0.10	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

In some cases, differences between inventories reflect temporal trends; TRI point source emissions decrease between 2005 and 2008, consistent with decreases in measured ambient benzene concentrations. For other cases, differences between inventories reflect differences in data processing or perhaps even quality assurance/quality control analyses. The TRI is useful for analyzing annual trends but reports emissions broadly by facility. The TCEQ photochemical modeling inventories and the NEIs have greater spatial resolution of emission points than the TRI and originate from a common source, the State of Texas Air Reporting System (STARS). However, the TCEQ conducts additional processing of reported emissions data to account for rule effectiveness and to further chemically speciate emissions that are otherwise reported as VOC with unspecified composition to generate an inventory for photochemical modeling. Accounting for rule effectiveness primarily affected VOC emissions from flares, equipment leak fugitives, external floating roof tanks, internal floating roof tanks, and, to a lesser extent, vertical fixed tanks in the Corpus Christi area. As described below, these are among the largest sources of benzene emissions in the region, primarily associated with petroleum refining.

Table 2 demonstrates that it is important to recognize that emissions inventories can have different origins, objectives, and spatial resolutions that can lead to pronounced differences in the inputs used for air quality modeling studies. The 2005 TCEQ Photochemical Modeling Emissions Inventory, which was developed to support the technical analyses for the State Implementation Plan (SIP), was selected for the dispersion modeling studies presented in this report. Use of an inventory that has full chemical speciation of VOC emissions has been critical for the Houston-Galveston-Brazoria area because of regulations that target emissions of highly reactive VOCs (HRVOCs; ethylene, propylene, 1,3-butadiene, and butenes). Emission points for benzene and 1,3-butadiene included in this inventory and the locations of the Oak Park and Solar Estates auto-GC sites are shown in Figure 6. A total of 1032 and 85 emission points for benzene and 1,3-butadiene, respectively, were included in the simulations.

The most significant point sources of benzene and 1,3-butadiene emissions in Nueces County by EPA Source Classification Code (SCC) are shown in Table 3. Exhibits 1 and 2 below show portions of the AERMOD input runstream file specifying the location, and stack parameters and emission rates of the point sources, respectively. Exhibit 3 shows similar information for CALPUFF. Point source emissions of benzene in the 2005 TCEQ Photochemical Modeling Inventory for Nueces County primarily originated from floating and fixed roof tanks along with fugitive sources. Emissions of 1,3-butadiene originated from chemical manufacturing fuel fired equipment, and fugitive emissions from petroleum refining and chemical manufacturing.

Exhibit 1. Segment of an AERMOD input file specifying point source locations. The last three columns of numbers on the right for the "SO LOCATION" records specify the point source horizontal coordinates in the UTM projection (zone 14) and elevation above sea level. Alphanumerical tags, such as FWS04, uniquely identify the point sources being modeled.

```
** AERMAP - VERSION 06341
**  Using 30m NAD27 DEM Data Files
**  With NAD83-Equivalent Anchor Point
** A total of     48  7.5-minute DEM files were used
** A total of   1066  sources were processed
** DOMAINXY  608111.681 3043175.821 14  683500.681 3115675.821 14
** ANCHORXY  615111.681 3043675.821    615111.681 3043675.821  14  4
** Terrain heights were extracted by default

SO ELEVUNIT METERS
SO LOCATION  FWF04     POINT        645231.11    3079520.52         14.67
SO LOCATION  VETK202   POINT        653953.74    3077873.96          7.62
SO LOCATION  SCTK01    POINT        647654.20    3076040.90         13.72
SO LOCATION  FWFB144   POINT        645139.05    3080350.48         13.36
```

Exhibit 2. Segment of an AERMOD input file specifying point source emission rates and stack parameters. Each source parameter record includes five values representing: (1) the emission rate of the species in grams per seconds, (2) the stack height above ground level in meters (3) the stack gas exit temperature in Kelvin (K), (4) the stack gas exit velocity in meters/sec, and (5) the stack inside diameter in meters.

```
** converted by calpuff_aermod_reformat.v1.4
** data: STARS_2005_unique_EPN.v2.proj.csv
SO SRCPARAM  FWF04    0.2807484775  0.91 294.00 0.01000 0.01000
SO SRCPARAM  VETK202  0.1989553048 12.20 295.22 0.00305 0.91463
SO SRCPARAM  SCTK01   0.1286731516  4.57 294.72 0.00305 0.91463
SO SRCPARAM  FWFB144  0.1186035374 12.20 301.02 0.00305 0.91463
```

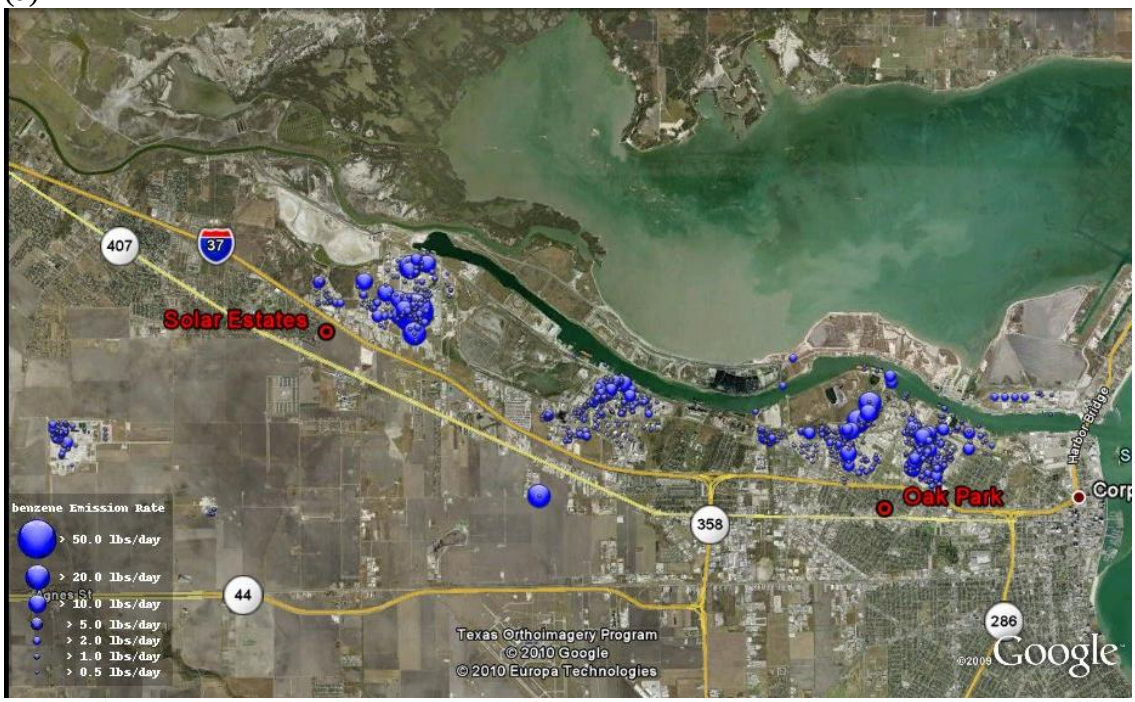
Exhibit 3. Segment of a CALPUFF input file specifying point source emission parameters. The token SRCNAM identifies each point source, as in AERMOD. Emission rates are in gram per seconds.

```
---------------
Subgroup (13b)
---------------
                                      a
          POINT SOURCE: CONSTANT DATA
          ----------------------------
                                                                                  b          c
  Source       X         Y       Stack    Base     Stack    Exit  Exit    Bldg.  Emission
   No.     Coordinate Coordinate Height Elevation Diameter  Vel.  Temp.   Dwash   Rates
              (km)      (km)       (m)      (m)       (m)  (m/s) (deg. K)
  ------   ---------- ---------- ------  ------   -------- ----- -------- ----- --------

FWF04    !SRCNAM  = FWF04   !
FWF04    !X =   245.717,  -1331.092,  0.91463, 15.00,  0.01000,  0.01000,  294.00000,  0.0,  0.2807485579!
FWF04    !SIGYZI = 0.,0.!
FWF04    !FMFAC = 1.! !END!
VETK202  !SRCNAM  = VETK202 !
VETK202  !X =   254.543,  -1332.592,  12.19512, 7.73,  0.91463,  0.00305,  295.22222,  0.0,  0.1989553618!
VETK202  !SIGYZI = 0.,0.!
VETK202  !FMFAC = 1.! !END!
SCTK01   !SRCNAM  = SCTK01  !
SCTK01   !X =   248.228,  -1334.572,  4.57317, 13.00,  0.91463,  0.00305,  294.72222,  0.0,  0.1286731884!
SCTK01   !SIGYZI = 0.,0.!
SCTK01   !FMFAC = 1.! !END!
FWFB144  !SRCNAM  = FWFB144 !
FWFB144  !X =   245.610,  -1330.253,  12.19512, 9.61,  0.91463,  0.00305,  301.02222,  0.0,  0.1186035714!
FWFB144  !SIGYZI = 0.,0.!
FWFB144  !FMFAC = 1.! !END!
```

Figure 6. Point source emissions of (a) benzene and (b) 1,3-butadiene in the 2005 TCEQ Photochemical Modeling Inventory near the Solar Estates and Oak Park auto-GC sites.

(a)



(b)

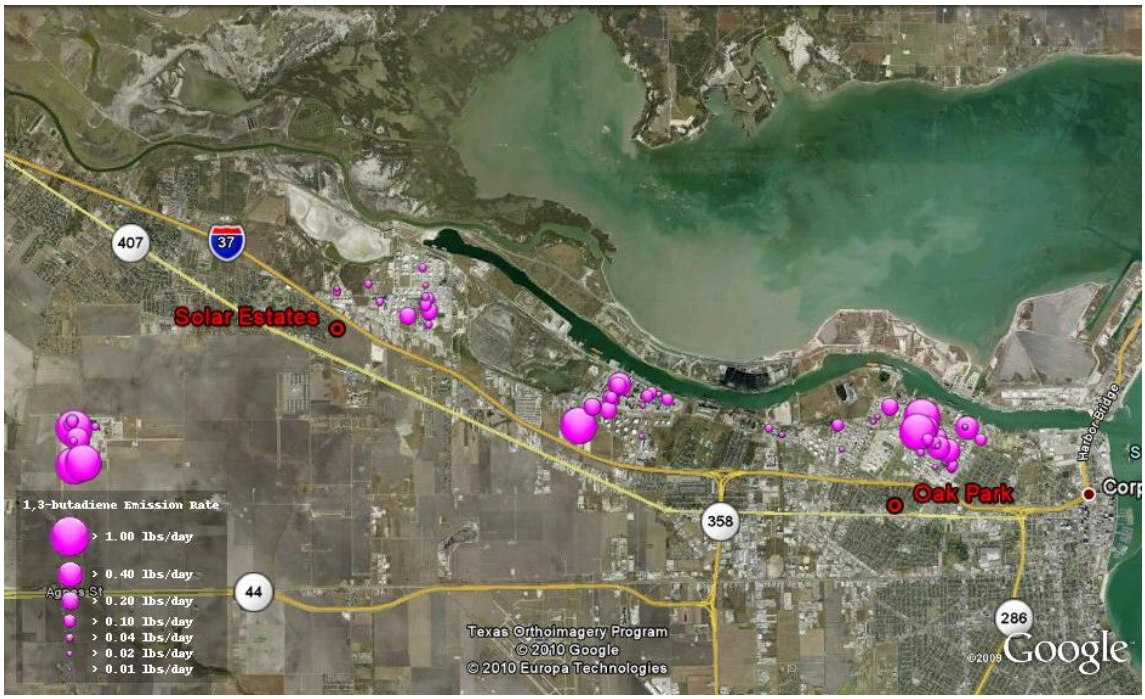


Table 3. Most significant point sources of benzene and 1,3-butadiene emissions in Nueces County by U.S. EPA Source Classification Code (SCC) from the 2005 TCEQ Photochemical Modeling Inventory.

Species	SCC	Emissions (tpd)	Emissions (tpy)	Stack Height (m) (5th percentile/ mean / 95th percentile: weighted by emissions)	Exit Gas Temperature (°C) (5th percentile/ mean / 95th percentile: weighted by emissions)	Description
Benzene	40301197	0.1594	58.2	6.1 / 11.9 / 14.3	16.5 / 29.0 / 33.1	Petroleum Product Storage at Refineries; Floating Roof Tanks (Varying Sizes)
	30688801	0.1061	38.7	0.9 / 5.5 / 30.5	21.0 / 48.7 /315.6	Petroleum Industry; Fugitive Emissions
	40301099	0.0512	18.7	4.9 / 12.0 / 14.6	21.7 / 29.9 / 32.2	Petroleum Product Storage at Refineries; Fixed Roof Tanks (Varying Sizes)
	40301150	0.0459	16.8	6.1 / 11.9 / 17.1	22.2 / 23.1 / 25.6	Petroleum Product Storage at Refineries; Floating Roof Tanks (Varying Sizes)
	30600104	0.0213	7.8	15.5 / 40.3 / 61.0	37.8 / 202.8 / 332.2	Petroleum Industry; Process Heaters
1,3-Butadiene	30190099	0.0063	2.3	36.6 / 36.6 / 36.6	537.8 / 537.8 / 537.8	Industrial Processes, Chemical Manufacturing; Fuel Fired Equipment
	30688801	0.0032	1.2	0.9 / 2.0 / 6.1	21.0 / 21.0 / 21.0	Industrial Processes, Petroleum Industry; Fugitive Emissions
	30188801	0.0023	0.8	3.0 / 3.0 / 3.0	21.0 / 21.0 / 21.0	Industrial Processes, Chemical Manufacturing; Fugitive Emissions
	28888802	0.0016	0.6	0.9 / 0.9 / 0.9	21.0 / 21.0 / 21.0	Internal Combustion Engines, Fugitive Emissions
	20200101	0.0012	0.4	3.0 / 9.4 / 12.2	315.6 / 325.7 / 371.1	Internal Combustion Engines, Industrial; Distillate Oil (Diesel)

3.2 Area and Mobile Source Emissions of Benzene and 1,3-Butadiene

According to the 2005 TCEQ Photochemical Modeling Inventory, stationary point sources had the largest contribution to benzene emissions in Nueces and San Patricio counties with 256 tpy, followed by area and mobile sources with approximately 160 tpy each, and non-road mobile sources with 34 tpy. On-road mobile sources had the largest contribution to 1,3-butadiene emissions in the inventory for the region with 17 tpy, followed by point and non-road sources with 7 tpy each, and area sources with 0.15 tpy. Thus, analysis of the 2005 TCEQ Photochemical Modeling Inventory indicated that other anthropogenic emissions sources in addition to point sources could be important for replicating observed concentrations at Oak Park and Solar Estates and for providing estimates of concentrations in areas without monitoring sites. AERMOD and CALPUFF modeling was conducted with stationary point source benzene emissions only and with all anthropogenic benzene emissions (i.e., point, area, and mobile), respectively, from the 2005 TCEQ Photochemical Modeling Inventory.

Emissions for area and mobile sources in the 2005 TCEQ Photochemical Modeling Inventory were processed by ENVIRON at a 200 m horizontal resolution for the 72 km x 72 km modeling domain. Tables 4 through 6 present the most significant subcategories within the area, non-road mobile, and on-road mobile source sectors, respectively.

Emissions from these three categories were first merged into a single file, and then, in order to maintain a reasonable computational time for the model simulations, grid cells that were remote from the receptor grid and/or had relatively small emission rates were aggregated to 1 km, 2 km or 4 km horizontal resolution. This was accomplished by first dividing the modeling region into three zones identified as the receptor zone, transient zone and remote zone. The receptor zone approximately matched the 35 km by 30 km rectangular region shown in Section 3.2 and described in Table 7. The transient region was the area within 8 km of the receptor zone, and the remainder of the modeling domain was designated as the remote zone. The zones are shown in Figure C.1 of Appendix C.

Emissions in the remote and transient zones were grouped into 4 km x 4 km grid cells (e.g., 400 of the 200 m cells were grouped within a single 4 km x 4 km grid cell). Emissions in the receptor zone were grouped into 1 km x 1 km resolution grid cells (25 of the 200 m cells were grouped within a single 1 km x 1 km grid cell). In the next step, emissions in each 200 m grid cell of the modeling domain were ranked by their daily emission rate of the modeled species in descending order. If the cell resided within the receptor zone, the centroid of the 200 m cell was added as an emission point and modeled independently from its assigned 1 km cell. If the cell fell within the transient zone, emissions from the 4 km cell were divided into a 1 km x 1 km cell and 2 km x 1 km cell, such that the point with the largest emission rate was released within a 1 km x 1 km cell. This process was continued until (1) 2000 cells were selected from the receptor zone as 200 m resolution emission points, and (2) 80% of the total emissions were emitted with a resolution of at least as fine as 1 km. The ability of this aggregation scheme to produce reasonable results was evaluated against a simulation that used a 1 km resolution for all emissions in both the remote and transient zones and 200 m resolution for the receptor zone. The maximum difference in predicted benzene concentrations between the two

simulations was 0.6 ppbC, which was regarded as an acceptable level of agreement. Figure C.1 in Appendix C shows the locations of non-point source releases, color coded with the spatial area that each emission point represents. A total of 3,439 grid cells of varying spatial resolution were used to represent the non-point source emissions in the modeling domain.

The emissions were introduced into each dispersion model as volume sources, which required estimation of initial values for the lateral and vertical standard deviations of the plume (for AERMOD) or puff (for CALPUFF). The initial value of the lateral standard deviation of the puff (σ_y) was set to the horizontal resolution of the particular emission point divided by 2.5, in accordance with EPA (1995) guidance for modeling of volume sources using the Industrial Source Complex v. 3 (ISC3) model. The effective height of the emissions (H) was set to 10 m. The EPA (1995) recommended the vertical dimension of the emission source to be an estimate of the effective height. In order to represent the range of source categories reflected in Tables 4 through 6, the effective height was set at 10 m rather than at ground level. The initial vertical standard deviation of the puff (σ_z) was set at H/2.15 = 4.65 m.

Table 4. Most significant area sources of benzene and 1,3-butadiene emissions in Nueces County by U.S. EPA Source Classification Code (SCC) from the 2005 TCEQ Photochemical Modeling Inventory.

Species	SCC	Emissions (tpd)	Emissions (tpy)	Description
Benzene	2460800000	0.1074	39.2	Solvent Utilization; Miscellaneous Non-industrial: Consumer and Commercial; All FIFRA Related Products; Total: All Solvent Types
	2310001000	0.0884	32.3	Industrial Processes; Oil and Gas Production: SIC 13;All Processes : On-shore; Total: All Processes
	2505020000	0.0430	15.7	Storage and Transport; Petroleum and Petroleum Product Transport; Marine Vessel; Total: All Products
	2630020000	0.0183	6.7	Waste Disposal, Treatment, and Recovery; Wastewater Treatment; Public Owned; Total Processed
	2501995120	0.0120	4.4	Storage and Transport; Petroleum and Petroleum Product Storage; All Storage Types: Working Loss; Gasoline
1,3-Butadiene	2801500000	0.00008	0.03	Miscellaneous Area Sources; Agriculture Production - Crops; Agricultural Field Burning - whole field set on fire; Total, all crop types
	2810030000	0.00005	0.02	Miscellaneous Area Sources; Other Combustion; Structure Fires
	2810050000	0.00002	0.01	Miscellaneous Area Sources; Other Combustion; Motor Vehicle Fires
	2810020000	0.00005	0.02	Miscellaneous Area Sources; Other Combustion; Prescribed Burning of Rangeland

Table 5. Most significant non-road sources of benzene and 1,3-butadiene emissions in Nueces County by U.S. EPA Source Classification Code (SCC) from the 2005 TCEQ Photochemical Modeling Inventory.

Species	SCC	Emissions (tpd)	Emissions (tpy)	Description
Benzene	2282005010	0.0076	2.8	Mobile Sources; Pleasure Craft; Gasoline 2-Stroke;Outboard
	2265004055	0.0073	2.7	Mobile Sources; Off-highway Vehicle Gasoline, 4-Stroke;Lawn and Garden Equipment; Lawn and Garden Tractors (Residential)
	2265006005	0.0067	2.4	Mobile Sources;Off-highway Vehicle Gasoline, 4-Stroke;Commercial Equipment; Generator Sets
	2265004010	0.0052	1.9	Mobile Sources; Off-highway Vehicle Gasoline, 4-Stroke;Lawn and Garden Equipment; Lawn Mowers (Residential)
	2260001030	0.0049	1.8	Mobile Sources; Off-highway Vehicle Gasoline, 2-Stroke;Recreational Equipment; All Terrain Vehicles
1,3-Butadiene	2265004055	0.00200	0.73	Mobile Sources; Off-highway Vehicle Gasoline, 4-Stroke;Lawn and Garden Equipment; Lawn and Garden Tractors (Residential)
	2265006005	0.00190	0.69	Mobile Sources; Off-highway Vehicle Gasoline, 4-Stroke;Commercial Equipment; Generator Sets
	2265004010	0.00150	0.55	Mobile Sources; Off-highway Vehicle Gasoline, 4-Stroke;Lawn and Garden Equipment; Lawn Mowers (Residential)
	2265001030	0.00100	0.37	Mobile Sources; Off-highway Vehicle Gasoline, 4-Stroke;Recreational Equipment; All Terrain Vehicles
	2282010005	0.00100	0.37	Mobile Sources; Pleasure Craft; Gasoline 4-Stroke; Inboard/Sterndrive

Table 6. Most significant on-road sources of benzene and 1,3-butadiene emissions in Nueces County by U.S. EPA Source Classification Code (SCC) from the 2005 TCEQ Photochemical Modeling Inventory.

Species	SCC	Emissions (tpd)	Emissions (tpy)	Description
Benzene	MV01270EXH	0.0512	18.7	Mobile Sources; Highway Vehicles - Gasoline; Light Duty Gasoline Vehicles (LDGV); Urban Other Principal Arterial: Total
	MV01250EXH	0.0369	13.5	Mobile Sources; Highway Vehicles - Gasoline; Light Duty Gasoline Vehicles (LDGV); Urban Other Freeways and Expressways: Total
	MV03270EXH	0.0249	9.1	Mobile Sources; Highway Vehicles - Gasoline; Light Duty Gasoline Trucks 3 & 4 (M6) = LDGT2 (M5); Urban Other Principal Arterial: Total
	MV01330EXH	0.0244	8.9	Mobile Sources; Highway Vehicles - Gasoline; Light Duty Gasoline Vehicles (LDGV); Urban Local: Total
	MV03250EXH	0.0172	6.3	Mobile Sources;Highway Vehicles - Gasoline; Light Duty Gasoline Trucks 3 & 4 (M6) = LDGT2 (M5); Urban Other Freeways and Expressways: Total
1,3-Butadiene	MV01270EXH	0.00630	2.30	Mobile Sources; Highway Vehicles - Gasoline; Light Duty Gasoline Vehicles (LDGV); Urban Other Principal Arterial: Total
	MV01250EXH	0.00460	1.68	Mobile Sources; Highway Vehicles - Gasoline; Light Duty Gasoline Vehicles (LDGV); Urban Other Freeways and Expressways: Total
	MV03270EXH	0.00310	1.13	Mobile Sources; Highway Vehicles - Gasoline; Light Duty Gasoline Trucks 3 & 4 (M6) = LDGT2 (M5); Urban Other Principal Arterial: Total
	MV01330EXH	0.00300	1.10	Mobile Sources; Highway Vehicles - Gasoline; Light Duty Gasoline Vehicles (LDGV);Urban Local: Total
	MV03250EXH	0.00210	0.77	Mobile Sources; Highway Vehicles - Gasoline; Light Duty Gasoline Trucks 3 & 4 (M6) = LDGT2 (M5);Urban Other Freeways and Expressways: Total

3.3 AERMOD Configuration

The AERMOD modeling system configuration originally developed by Tai et al (2009) is briefly reviewed here, along with modifications made since this original study. Modeling was conducted with three complete years of meteorological data (2006 through 2008). The 2005 TCEQ Photochemical Modeling Inventory remained constant with each year of meteorological data because alternative inventories with full VOC chemical speciation were not available for 2006 through 2008. Comparisons of AERMOD and CALPUFF predictions with ambient data focused on 2006, which was approximately the time period of the 2005 TCEQ Photochemical Modeling Inventory and for which the first complete year of ambient data were available from the Oak Park and Solar Estates auto-GC sites.

The CALPUFF modeling domain was defined using Lambert Conformal Projected coordinates with the projection parameters shown in Table 7. A subset of grid cells in the CALPUFF modeling domain was selected, and their centroids were specified as receptors for the AERMOD and CALPUFF simulations. The domain shown in Figure 7 was designed to include all UT CCAQP and TCEQ monitors, industrial sources adjacent to or near the Corpus Christi Ship Channel, residential areas in close proximity to the Ship Channel, and populated regions according to recent U.S. Census data.

Figure 7. Corpus Christi regional modeling domain used for CALPUFF (exterior box) and receptor grids used for both the CALPUFF and AERMOD simulations (interior box).

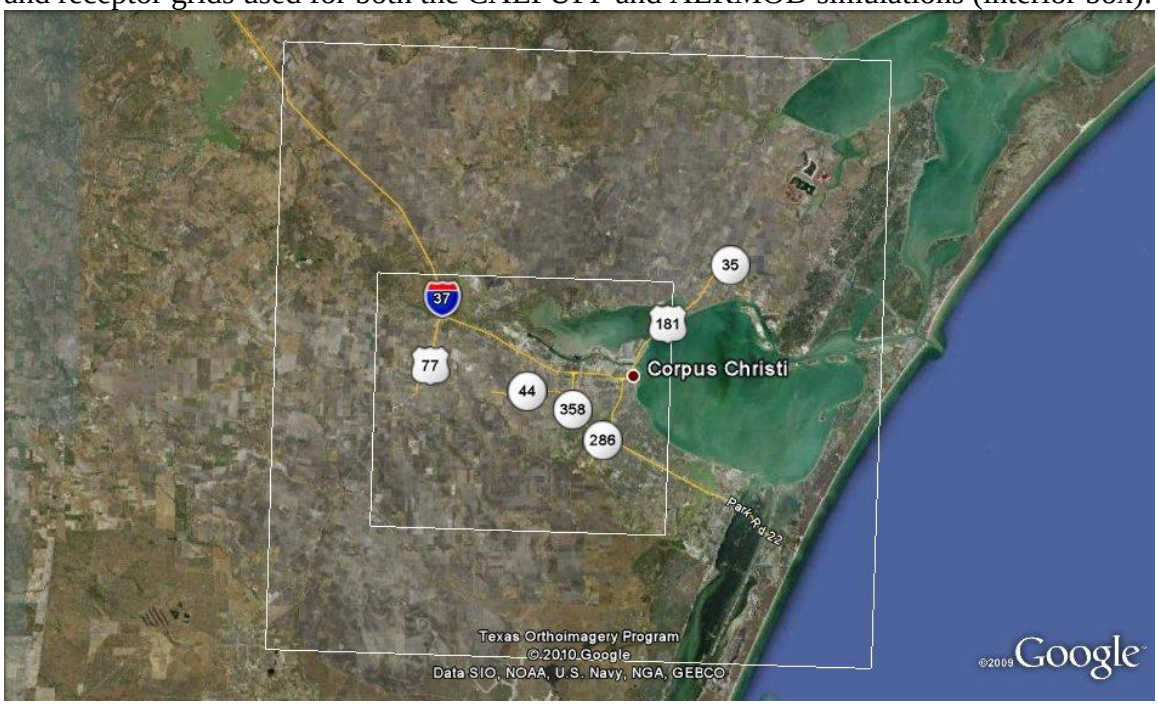


Table 7. Map projection, modeling domain for CALPUFF simulations, and receptor grid specifications for the AERMOD and CALPUFF simulations.

Projection:

Reference spheroid	Perfect sphere, diameter=6370 km
Two standard parallels	30° N and 60° N
Latitude of Origin	40° N
Central meridian	100° W

CALPUFF Modeling Grid:

Origin (South/West Corner)	Easting 216km, Northing -1368 km
Grid Resolution	1km x 1km
Number of columns/rows	72 columns, 72 rows

(The CALPUFF modeling domain covers approximately from 97° 49' 30" W to 97° 06' 29" W and 27° 30' 06" N to 28° 08' 33" N)

Receptor Grid:

Origin (South/West Corner)	Easting 228km, Northing -1353 km
Grid Resolution	1km x 1km
Number of columns/rows	35 columns, 30 rows

(The receptor grid covers approximately from 97° 42' 20" W to 97° 21' 13" W and 27° 38' 15" N to 28° 54' 16" N. Centroids of the grid cells were specified as receptors)

The AERMOD system consisted of one main program (AERMOD) and three pre-processors, AERSURFACE, AERMAP and AERMET.

AERMAP is the terrain preprocessor that determines the elevation for each source and the elevation and terrain height scale (h_c) for each receptor. AERMOD uses the hill height scale (h_c) determined by AERMAP to calculate the critical dividing streamline height (H_c), which is used to distinguish a two-layer flow structure in complex terrain. This work used the regulatory version of AERMAP (Version 06341), available at the time from the U.S. EPA http://www.epa.gov/scram001/dispersion_related.htm. AERMAP requires digital terrain data for the modeling domain and an input runstream file. As described by Tai et al. (2009), 46 digital elevation model (DEM) files in the 7.5-minute North American Datum of 1927 (NAD27) format with 30 meter resolution were obtained for the domain from http://www.mapmart.com or http://www.webgis.com. In the runstream file, the ANCHORXY keyword is used to relate the origin of the user-specified coordinate system for the receptors and sources to the UTM coordinate system. For this work, the anchor coordinates were defined at the southwest corner of the modeling domain. The NADA parameter specifies the horizontal datum that was used to establish the coordinates of the anchor point, and was set to 4, representing datum NAD83.

AERSURFACE can be used to determine the land surface characteristics including albedo (the fraction of total incident solar radiation reflected by the surface back to space without absorption), Bowen ratio (the ratio of sensible heat flux to latent heat flux), and surface roughness (the characteristic length related to the height of obstacles to the

wind flow or the height at which the mean horizontal wind speed is zero based on a logarithmic profile) for use in the AERMET meteorological preprocessor. AERSURFACE was not used for the AERMOD modeling for Corpus Christi. Instead, TCEQ recommended values for albedo (0.18) and Bowen ratio (1.5) for Nueces County were used. The surface roughness value was set to 1.0 meters, which is indicative of typical urban/industrial areas, for simulations using on-site meteorological observations from Oak Park. For simulations using on-site meteorological data from Solar Estates, a surface roughness of 0.5 meters was chosen to account for greater diversity in land use and land cover in the surrounding area, which included flat open grassy and agricultural areas.

AERMET processes meteorological data and estimates planetary boundary layer (PBL) parameters for use in AERMOD. The AERMET processing used the regulatory version of AERMET (Version 06341) (http://www.epa.gov/scram001/dispersion_related.htm). AERMET requires an input runstream file (see Tai et al., 2009) that directs the actions of AERMET, and meteorological observations. Surface, upper air and on-site meteorological data were obtained from the following:

- Surface: Corpus Christi International Airport (12924) TD-3505 format
- Upper Air : Corpus Christi International Airport (12924) FSL format
- On-Site: Solar Estates (C633) and Oak Park (C634) meteorological monitors

Because only one set of on-site monitoring data can be used by AERMET, meteorological data for the two on-site monitors were processed individually for each AERMET run, resulting in two sets of AERMET output files to be used by AERMOD, one corresponding to Solar Estates and the other to Oak Park.

AERMOD uses a Gaussian distribution in the horizontal and vertical directions in the stable boundary layer (SBL). In the convective boundary layer (CBL), AERMOD uses a Gaussian distribution in the horizontal direction, but a bi-Gaussian probability distribution function (pdf) in the vertical direction. The regulatory version of AERMOD at the time of the study (Version 07026) was obtained from the EPA http://www.epa.gov/scram001/dispersion_prefrec.htm#aermod. AERMOD was run twice, using AERMET files generated with Solar Estates and Oak Park on-site data, respectively. AERMOD requires an input runstream file, which directs the actions of AERMOD. The following is a summary of the AERMOD input runstream file options:

- Terrain: Elevated (from AERMAP processing)
- Pollutant: Benzene
- Averaging Periods: 1-hour and 8-hour
- Dispersion Options: Concentration
Deposition (Dry, Wet and Total)

The TOXICS keyword was specified in order to model deposition. The following season definition values were specified through the GDSEASON keyword:

- Seasonal Category 1 (Midsummer with lush vegetation): June, July, August
- Seasonal Category 2 (Autumn with unharvested cropland): September, October, November
- Seasonal Category 3 (Late autumn after frost and harvest, or winter with no snow): December, January, February
- Seasonal Category 5 (Transitional spring): March, April, May

Land use categories were defined by wind direction through the GDLANUSE keyword. A land use category of 5 (suburban areas, grassy) was assigned to each of the 36 wind direction sectors (every 10 degrees) for all receptors.

As described above, emissions source characteristics were obtained from the 2005 TCEQ Photochemical Modeling Inventory. The INCLUDE keyword was used to include location (UTM coordinates) and elevation information for the sources from the AERMAP processing. Parameters for the gaseous deposition of benzene and 1,3-butadiene are listed in Table 8[*].

Table 8. Gaseous deposition parameters for benzene and 1,3-butadiene used in AERMOD.[*]

Parameter	Benzene	1,3-Butadiene
Diffusivity in air (D_a):	0.08962 cm^2/s	0.1013 cm_2/s
Diffusivity in water (D_w):	104,000 cm^2/s	114,600 cm^2/s
Cuticular resistance (r_{cl}	25,100 s/cm	11,400 s/cm
Henry's Law Constant:	557 Pa-m^3/mol	7450 Pa-m^3/mol

The DEPOUNIT keyword was applied to convert the default output units (g/m^2) to microgram per square meter ($\mu g/m^2$).

AERMOD created an output file in the format of a tabulated text file, with each line corresponding to hourly average concentrations at a particular receptor, in units of $\mu g/m^3$, along with a log file indicating errors in processing, if any.

3.4 CALPUFF Configuration

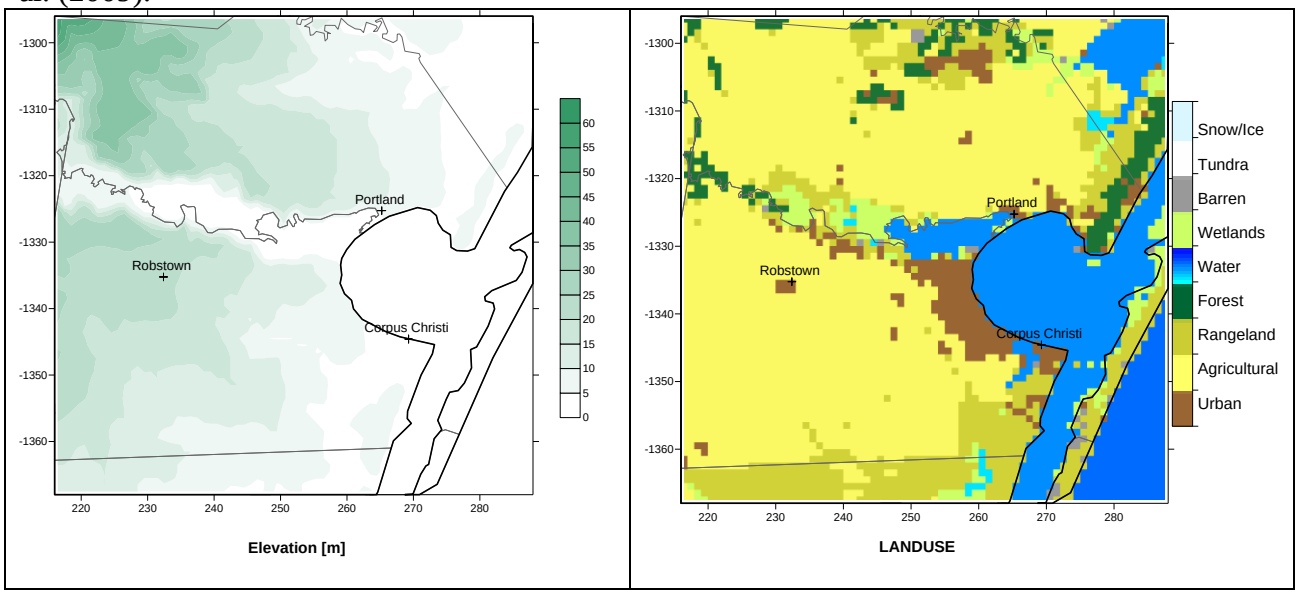
The CALPUFF system configuration is described by Tai et al. (2009) and briefly reviewed here.

CALMET, which is part of the CALPUFF modeling system, is a diagnostic meteorological model that uses terrain, landuse, and meteorological observations to produce gridded wind and temperature fields, and other surface parameters. CALMET Version 5.8, which was the latest version approved by the EPA at the time of the study, was used. CALMET uses terrain following coordinates. The vertical structure in the final

[*] Argonne National Laboratory. 2002. *Deposition Parameterizations for the Industrial Source Complex (ISC3) Model*. Argonne, IL.

configuration selected for the CALPUFF performance evaluation was 14 layers up to 3 km to provide reasonable coordination with the TCEQ CAMx vertical layer structure. Tai et al. (2009) processed USGS 1-degree terrain data (~90 m resolution; http://edcftp.cr.usgs.gov/pub/data/DEM/250/) for output at 1 km resolution for the Corpus Christi domain in the NWS-84 spherical datum. USGS landuse/land cover data files in the Composite Theme Grid (CTG) format (http://edcftp.cr.usgs.gov/pub/data/LULC/250K/) were processed to determine the fractional land use for each of 38 CALMET land use categories in each grid cell. Figure 8 shows the spatial plots of terrain and the dominant land use category. Tai et al. (2009) used a preprocessor known as MAKEGEO to list the terrain and the dominant land use category for each grid cell, as well as the roughness length, albedo, Bowen ratio, soil heat flux parameter, anthropogenic heat flux, and leaf area index of each cell. These parameters were computed from the default values of each property that were assigned to each land use category in CALMET, weighted by the fractional land use in each grid cell.

Figure 8. Gridded fields of terrain (left) and dominant land use type (right) from Tai et al. (2009).



CALMET incorporated data from 18 surface stations, including 8 local monitors near the Port of Corpus Christi and 10 land-based National Weather Service (NWS) stations. The CALMET-formatted surface meteorology file contained surface wind speed and direction, temperature, relative humidity, pressure, cloud cover, and ceiling height. For each hour, CALPUFF requires the temperature, relative humidity, cloud cover and ceiling height for at least one surface site. When temperature data were unavailable, the average temperature at all sites was first calculated for the hour immediately before and after the missing period, and then linearly interpolated to fill values for missing hours. When relative humidity, cloud cover and ceiling height were unavailable for all of the sites, the default values of 80% humidity, 50% cloud cover and "unlimited ceiling height" were assumed. Upper air data were obtained from the Corpus Christi International Airport upper air station (http://raob.fsl.noaa.gov/) and processed to obtain multi-level pressure,

height, temperature, and wind speed and direction data from the surface to 500 mb every 12 hours. CALMET requires data at least once every 12 hours for at least six mandatory pressure levels, which are surface and 1000, 925, 850, 700, and 500 mb. Missing data were filled by two methods. If a missing sounding was an isolated event, such that the gap in the observation was equal to or less than 24 hours, the preceding and succeeding observations were used to fill the gap. From 850 mb to 500mb, all data were linearly interpolated using records from 12 hours before and after the missing period. Below 850 mb, height and temperature data were interpolated using records from ±24 hours to account for diurnal impacts; winds were interpolated using records from ±12 hours. When the gap in the soundings was greater than 24 hours, the sounding at Brownsville was used as a substitute.

Hourly buoy data for Buoy 42020, located 50 nautical miles southeast of Corpus Christi, were obtained from the National Data Buoy Center. Data were processed to obtain hourly air temperature, relative humidity, wind speed and direction, and the difference in air and sea surface temperature. If the consecutive number of hours of missing observations was equal to or less than five, observations from the preceding and succeeding hours were used for linear interpolation. If the period of missing observations was longer, observations from Buoy 42019, located 60 nautical miles south of Freeport, were used as a surrogate. Data for five precipitation monitoring stations were obtained in the National Climate Data Center TD-3240 format and processed to extract and then merge individual monitoring stations near Corpus Christi. No processing was conducted to address missing observations from precipitation stations.

CALMET sensitivity tests were subjectively evaluated by Tai et al. (2009) to determine the optimal model configuration for the region. Use of high resolution coastline data and terrain kinematics, reducing the terrain radius of influence to 1 km, and increasing the number of smoothing passes for wind fields aloft were all found to improve the performance of CALMET in the Corpus Christi area.

The model configuration options selected for the CALPUFF run are summarized in Table 9.

Table 9. Summary of CALPUFF technical options.

Description	Variable	Option Selected
Vertical distribution in near field	MGAUSS	1 = Gaussian
Terrain adjustment method	MCTADJ	3 = partial plume path adjustment
Subgrid scale complex terrain	MCTSG	0 = not modeled
Near-field puffs modeled as elongated slugs	MSLUG	0 = no
Transitional plume rise modeled	MTRANS	1 = yes
Stack tip downwash	MTIP	1 = yes
Method for building downwash	MBDW	2 = ISC method
Vertical wind shear modeled above stack top	MSHEAR	0 = no
Allow puff splitting	MSPLIT	0 = no

Description	Variable	Option Selected
Chemical mechanism flag	MCHEM	0 = no chemistry (not default)
Wet removal modeled	MWET	1 = yes
Dry deposition modeled	MDRY	1 = yes
Gravitational settling	MTILT	0 = no
Method to compute dispersion coefficients	MDISP	2=dispersion coefficients from internally calculated sigma v, sigma w using micrometeorological variables (not default)
Method used to compute turbulence sigma-v and sigma-w using micrometeorological variables	MCTURB	1 = Standard CALPUFF subroutines
PG sigma-y,z adjustments for roughness	MROUGH	0 = no
Partial plume penetration of elevated inversion	MPARTL	1 = yes
Strength of temperature inversion from PROFILE.DAT	MTINV	0 = no (computed from measured/default gradients)
PDF for dispersion when convective	MPDF	0 = no

Gaseous dry deposition parameters used for the CALPUFF simulations are shown in Table 10. The diffusivity and Henry's law constant were the same as those used for the AERMOD simulations. The solubility enhancement factor is unity as the modeled compounds do not dissociate, and the reactivity was assumed to be zero (Wesely, 1989). The mesophilic resistance was estimated according to the approach of Wesely (1989 ref eq. 6; $R_m = (H/3000 + 100 \cdot f)^{-1}$ where H is the Henry's law constant in M/atm, f is the reactivity factor, which was assumed to be zero for the modeled species.

As an alternative to using empirical formulas based on Pasquill-Gifford stability class and downwind distance, micrometeorological variables were used to compute the dispersion coefficients (σ_y and σ_z) in CALPUFF. Micrometeorological variables, such as friction velocity, convective velocity scale, and Monin-Obukhov length, were derived from meteorological observations and surface characteristics from CALMET.

Table 10. Deposition properties for benzene and 1,3-butadiene used in CALPUFF.

Property	Benzene	1,3-Butadiene
Diffusivity	0.0896 cm^2/s	0.1013 cm^2/s
Solubility enhancement factor	1.0	1.0
Reactivity	0	0
Mesophyll resistance	163.82 s/cm	2140 s/cm
Henry's Law coefficient (dimensionless, i.e. c_g/c_w)	0.2287	3.0

CALPUFF creates an output file in a Fortran binary format of hourly average concentration of modeled species at the centroid of each grid cell with the unit of g/m^3. The data was converted into a comma separated text format for further analysis.

4. Model Predictions and Evaluation

This chapter presents the dispersion modeling predictions and comparisons with observations at the Oak Park and Solar Estates auto-GC sites. Predicted concentrations are presented for modeling with stationary point source benzene emissions only and with all anthropogenic benzene emissions (i.e., point, area, and mobile) from the 2005 TCEQ Photochemical Modeling Inventory. The impacts of the variability in meteorological conditions on model performance are examined. In addition, the sensitivities of AERMOD predictions to assumptions about the calm wind speed threshold and land cover in the region are discussed.

NOTE: In order to provide for a consistent comparison across the observed and predicted datasets, the results presented here are based on those hours with (1) a valid observation, (2) valid AERMOD and CALPUFF predictions, and (3) an hourly wind speed greater than or equal to the instrument detection limit of 0.22 mps. The number of hours for each combination of pollutant, site, year, and season are provided in Appendix D.

4.1 Benzene

(a) Model Performance at Oak Park during 2006. Table 11 provides a summary of mean, maximum, 75th, 95th, and 99th percentile observed and AERMOD and CALPUFF predicted benzene concentrations during 2006 at Oak Park and Solar Estates. Predicted concentrations are presented for modeling with stationary point source benzene emissions only and with all anthropogenic benzene emissions (i.e., point, area, and mobile), respectively, from the 2005 TCEQ Photochemical Modeling Inventory. Scatter plots of predicted versus observed benzene concentrations by season during 2006 at Oak Park are shown in Figures 9 and 10 for modeling with stationary point source emissions only and with all anthropogenic emissions, respectively.

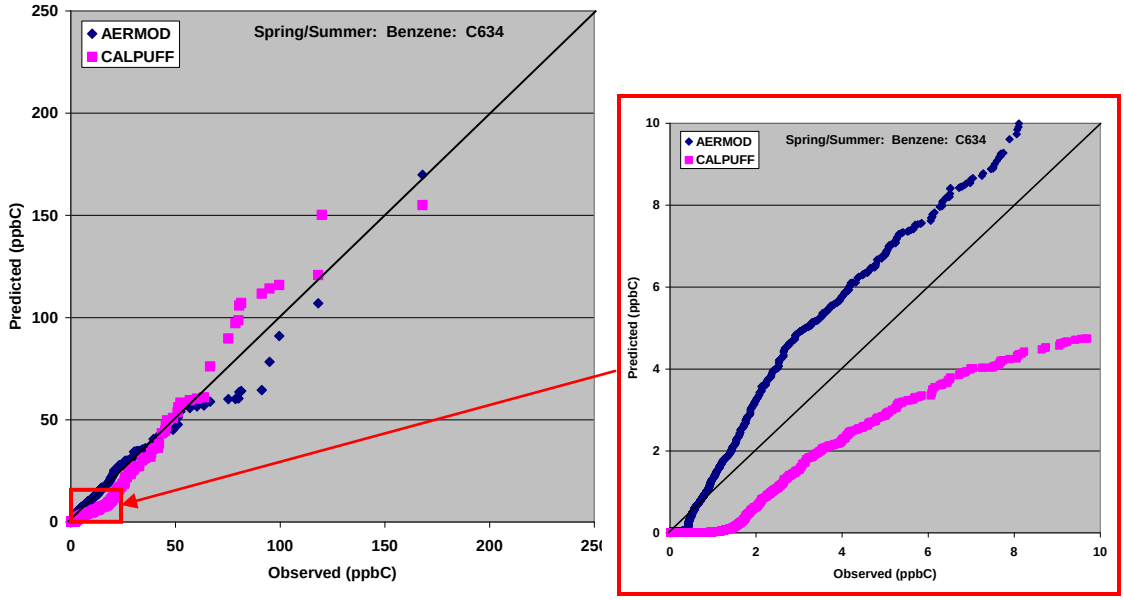
The ratio of observed fall/winter to spring/summer mean benzene concentrations at Oak Park during 2006 was 3.4. This seasonal pattern was consistent with national-scale analyses by Touma et al. (2006) and McCarthy et al. (2007) that found that concentrations of benzene, 1,3-butadiene, and most hydrocarbon air toxics were typically greatest during the cool season when meteorological conditions more often favor the accumulation of pollutants near the surface and removal rates by atmospheric oxidants were lower. These national-scale analyses found, on average, a factor-of-two difference in concentrations by season for pollutants with the highest seasonal variability. As shown in Table 11, AERMOD and CALPUFF replicated observed seasonal and locational differences in benzene concentrations, with increases in fall/winter relative to spring/summer and higher concentrations at Oak Park versus Solar Estates. AERMOD and CALPUFF predictions were similar, but not identical, with respect to their agreement with observations at both sites.

Table 11. Summary of mean, maximum, 75th, 95th, and 99th percentile observed (OBS) and predicted benzene concentrations from AERMOD (AER) and CALPUFF (CAL) during two seasonal periods at Oak Park and Solar Estates in 2006. Predicted concentrations are presented for modeling with stationary point source emissions only and with all anthropogenic emissions from the 2005 TCEQ Photochemical Modeling Inventory. Ratios of predicted to observed concentrations are shown in parentheses.

Site	Mean (ppbC)			75th Percentile (ppbC)			95th Percentile (ppbC)			99th Percentile (ppbC)			Maximum (ppbC)		
	OBS	AER	CAL	OBS	AER	CAL	OBS.	AER	CAL	OBS	AER	CAL	OBS	AER	CAL
Oak Park															
Spring/Summer															
Point Sources		2.03 (1.1)	1.16 (0.6)		1.00 (1.2)	0.01 (0.01)		8.36 (1.3)	3.78 (0.6)		34.56 (1.1)	27.08 (0.9)		169.83 (1.0)	155.00 (0.9)
All Anthropogenic	1.91	3.12 (1.6)	2.23 (1.2)	0.84	1.67 (2.0)	1.28 (1.5)	6.51	13.90 (2.1)	6.14 (0.9)	31.01	47.61 (1.5)	33.75 (1.1)	168.03	184.62 (1.1)	164.50 (1.0)
Fall/Winter															
Point Sources		4.30 (0.7)	4.47 (0.7)		3.54 (0.6)	2.88 (0.5)		20.15 (0.7)	20.57 (0.8)		55.47 (0.7)	84.52 (1.1)		198.71 (0.6)	162.10 (0.5)
All Anthropogenic	6.52	6.10 (0.9)	6.20 (1.0)	5.48	4.90 (0.9)	4.45 (0.8)	27.11	27.53 (1.0)	25.09 (0.9)	74.69	69.87 (0.9)	93.49 (1.3)	306.90	214.41 (0.7)	188.70 (0.6)
Solar Estates															
Spring/Summer															
Point Sources		0.59 (0.4)	0.67 (0.5)		0.30 (0.2)	0.44 (0.3)		2.46 (0.5)	2.60 (0.5)		10.31 (0.9)	10.70 (0.9)		49.89 (1.0)	94.22 (1.8)
All Anthropogenic	1.32	0.92 (0.7)	1.37 (1.0)	1.44	0.57 (0.4)	1.33 (0.9)	4.96	3.68 (0.7)	4.09 (0.8)	12.01	14.98 (1.2)	13.41 (1.1)	52.26	61.71 (1.2)	103.30 (2.0)
Fall/Winter															
Point Sources		1.18 (0.4)	1.77 (0.6)		0.74 (0.2)	1.28 (0.4)		4.23 (0.4)	6.68 (0.7)		18.36 (1.0)	28.76 (1.5)		229.53 (3.3)	136.70 (2.0)
All Anthropogenic	2.84	1.63 (0.6)	2.72 (1.0)	3.24	1.12 (0.3)	2.35 (0.7)	9.64	6.09 (0.6)	9.23 (1.0)	19.14	22.19 (1.2)	33.14 (1.7)	69.96	259.66 (3.7)	148.40 (2.1)

Figure 9. Scatter plots of predicted versus observed benzene concentrations at Oak Park during the (a) spring/summer and (b) fall/winter of 2006. Only point source emissions are included in the dispersion models.

(a)



(b)

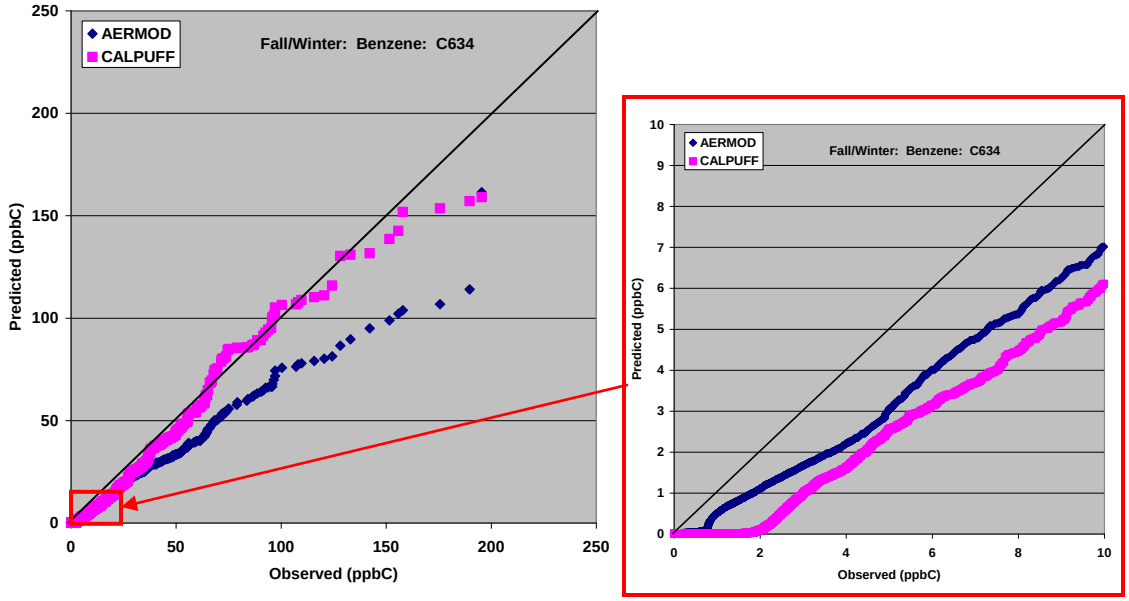
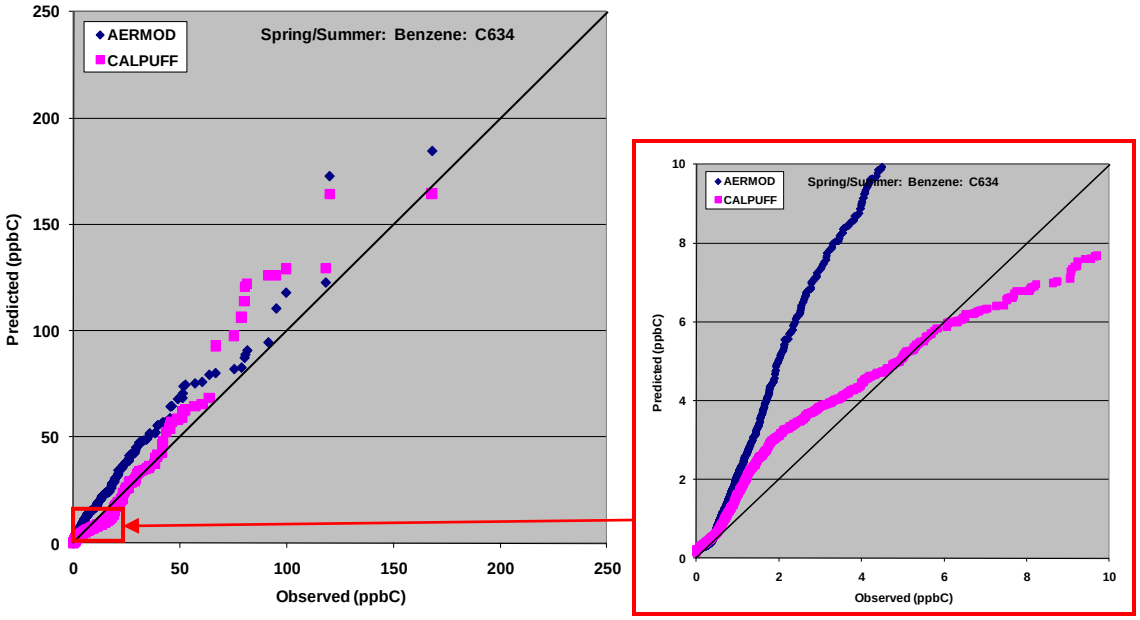
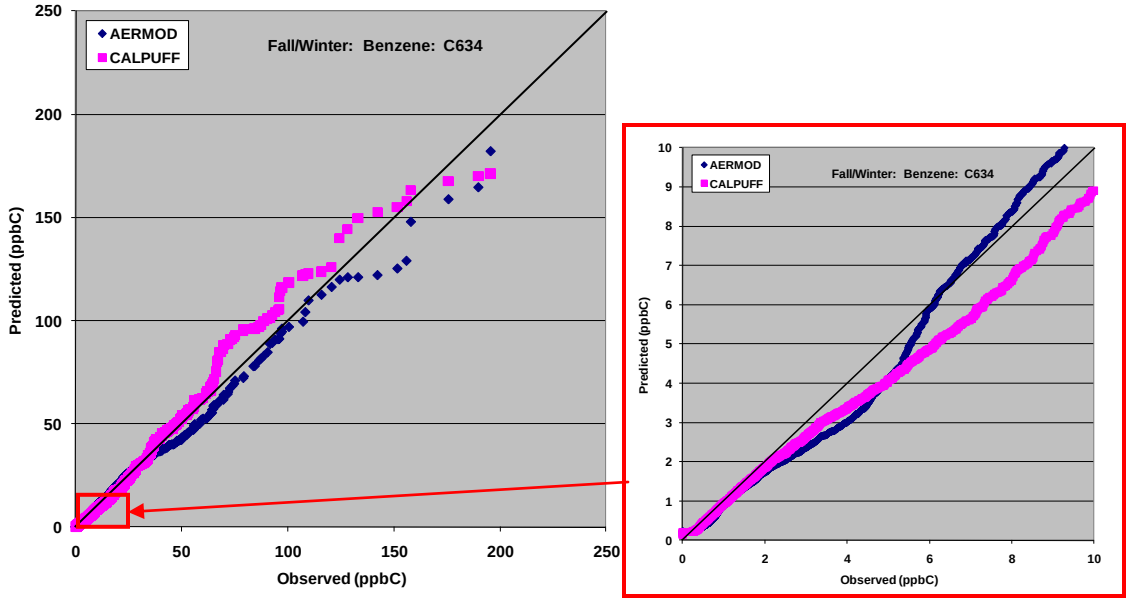


Figure 10. Scatter plots of predicted versus observed benzene concentrations at Oak Park during the (a) spring/summer and (b) fall/winter of 2006 with all anthropogenic emissions sources included in the dispersion models.

(a)



(b)



When only point source emissions were modeled, AERMOD and CALPUFF generally under-predicted observed concentrations during the fall/winter of 2006 at Oak Park; ratios of predicted to observed concentrations (mean, maximum, 75th, 95th, and 99th percentiles) ranged from 0.5 to 1.1 (reference Table 11). Surrounding Oak Park are industrial emissions sources located to the northeast and northwest, respectively, and the Corpus Christi urban area to the south. Prevailing near-surface winds determine if emission plumes from Ship Channel industrial facilities are transported towards nearby monitors. Figure 11 presents observed 95th percentile benzene concentrations for 2006 through 2008 categorized by wind direction and the wind direction frequency during spring/summer and fall/winter at Oak Park. The 95th percentile concentrations vary from 1.9 ppbC during southeasterly winds to 67.3 ppbC during north-northeasterly winds. Figure 11 illustrates that higher observed benzene concentrations during the fall/winter than spring/summer are associated with more frequent northwesterly clockwise through northeasterly winds. McGaughey et al. (2009, 2010) generated one-hour surface back-trajectories for high concentration hours to identify potential emissions source regions that may impact concentrations at Oak Park shown in Figure 12. Figure 12 indicates that important industrial emission sources for benzene are located to the north-northwest and especially north-northeast of Oak Park. In this study, the geographic areas surrounding Oak Park were divided into three broad sectors illustrated in Figure 13, and measured Oak Park hourly wind directions were classified into appropriate sectors. The performance of the models, with only point source emissions included, was evaluated for each of these sectors and found to vary as a function of wind direction at Oak Park.

Figure 14 presents observed and predicted mean and 95th percentile concentrations during 2006 by sector. Lower observed and predicted benzene concentrations were associated with southerly winds. Observed and predicted concentration and wind speed relationships for the southern sector are shown in Figure 15. Both models, but to a greater extent AERMOD, over-predicted observed concentrations during the lowest wind speeds from this sector. Given the lack of industrial sources to the south of Oak Park and the fact that urban area and mobile sources were not included in these modeling simulations, one would expect the models to under-predict observed concentrations. However, AERMOD over-predicted observed concentrations at wind speeds less than 2 m/s. According to the EPA in a report entitled "AERMOD: Description of Model Formulation"[1], AERMOD predicted concentrations are an interpolation between two concentration limits: a coherent plume, which assumes that the wind direction is distributed about a well-defined mean direction, and a random plume, which assumes an equal probability of any wind direction. The contribution from the random plume to the predicted AERMOD concentration often grows larger as the wind speed decreases (dependent on the atmospheric stability), resulting in a "bulls-eye" of concentric concentration rings that decrease with distance around each emissions source. Figure 16 shows the spatial variation in modeled concentrations for an example hour with light southerly winds. The spatial extent of relatively high concentrations is primarily located to the north or in the immediate vicinity of the Ship Channel industrial facilities, which is consistent with the transport of industrial source plumes northward by nearly calm to light southerly winds.

[1] Cimorelli et al. AERMOD: Description of Model Formulation, EPA-454/R-03-004, 2004, accessible at http://www.epa.gov/scram001/7thconf/aermod/aermod_mfd.pdf

Figure 11. Oak Park observed 95th percentile benzene concentrations, number of fall/winter hours, and number of spring/summer hours grouped by wind direction during 2006 – 2008 (McGaughey et al., 2009; 2010).

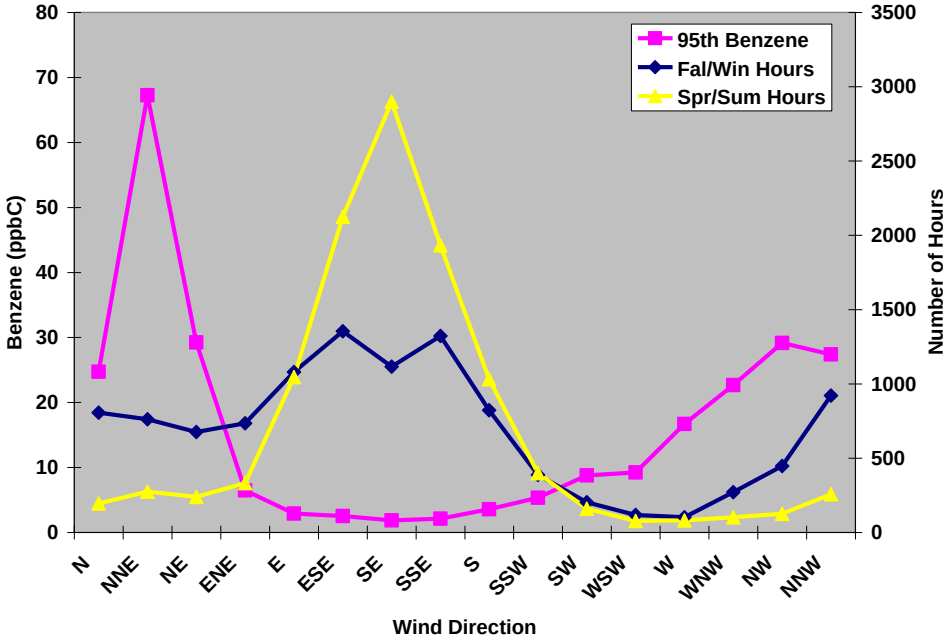


Figure 12. Surface back-trajectories as generated by the Corpus Christi Trajectory Analysis Tool for all hours characterized by an observed benzene concentration of 30 ppb or greater at Oak Park during June 2005 - May 2008 (McGaughey et al., 2009; 2010).

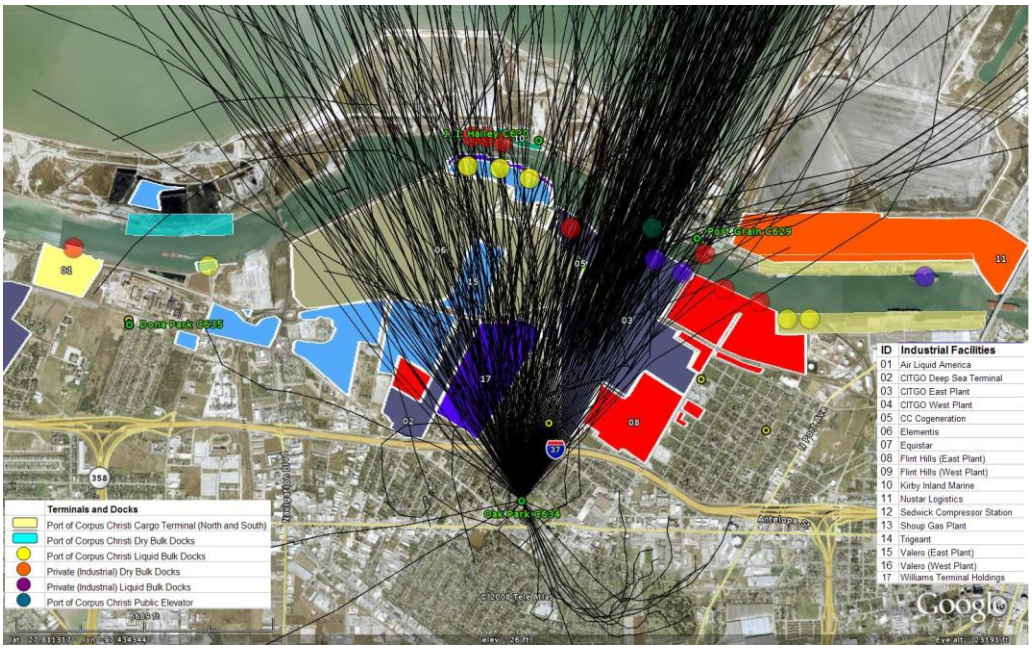


Figure 13. Emissions source sectors for Oak Park.

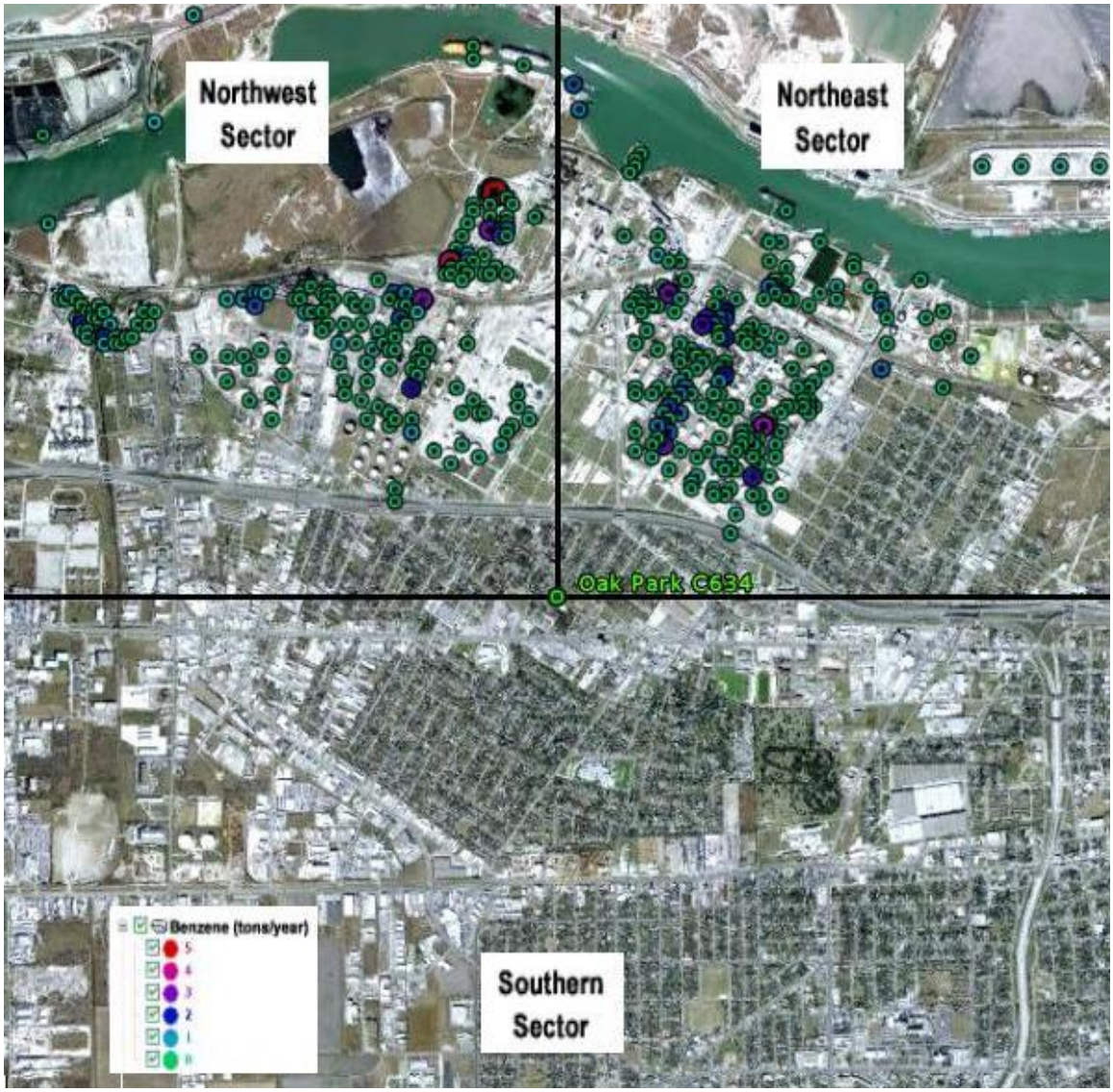
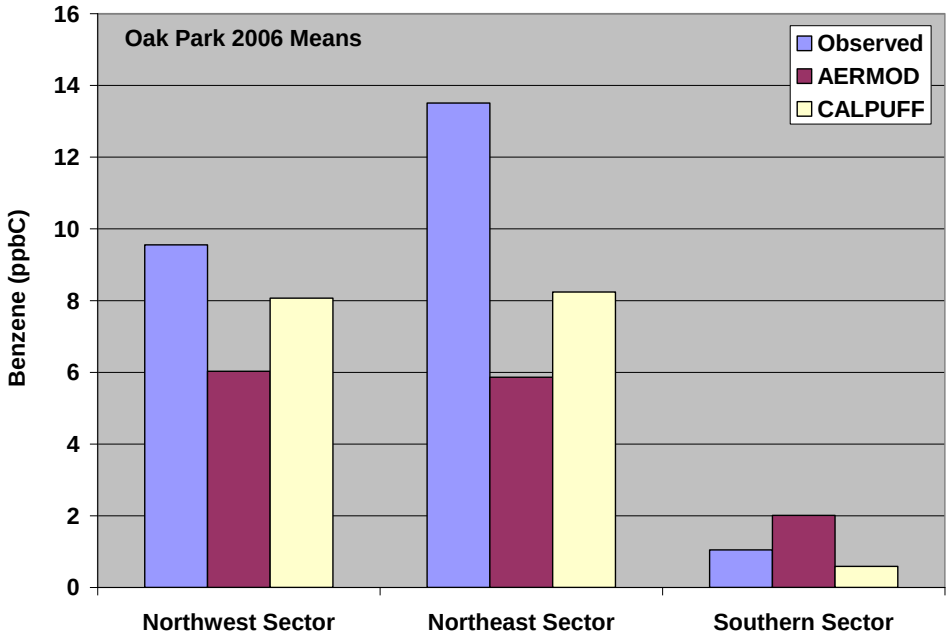


Figure 14. Predicted and observed (a) mean and (b) 95th percentile benzene concentrations by upwind emission sector at Oak Park during 2006. Only point source emissions are included in the dispersion models.

(a)



(b)

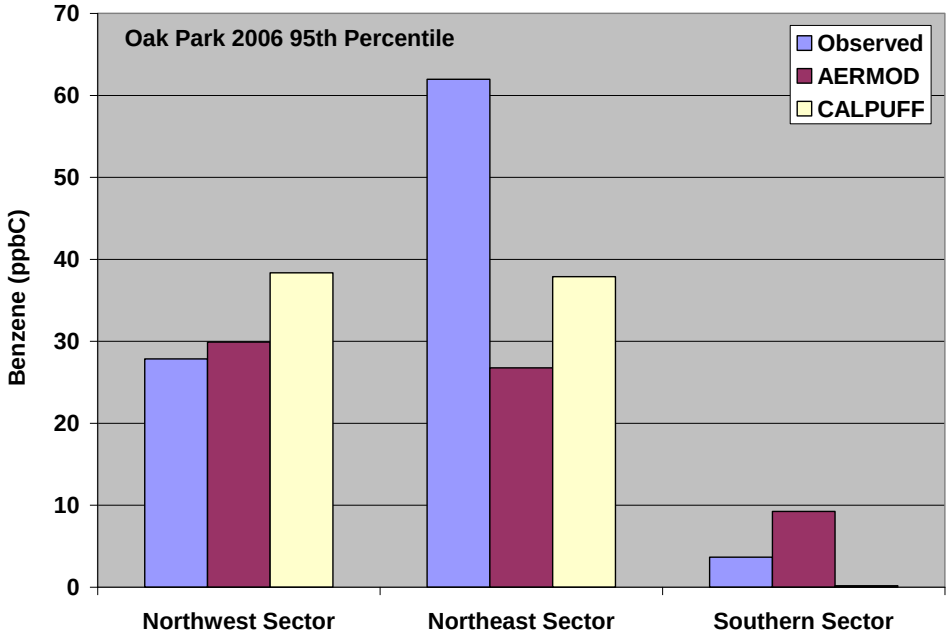


Figure 15. Oak Park hourly wind speed versus observed and predicted benzene concentrations during 2006 for the southern sector. Only point source emissions are included in the dispersion models.

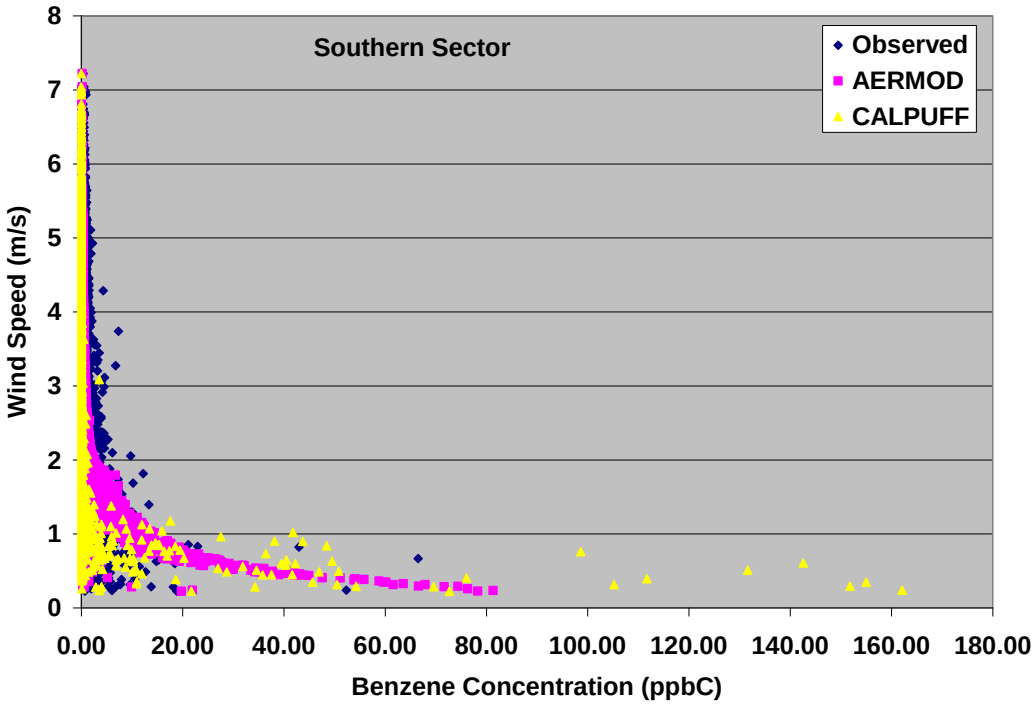
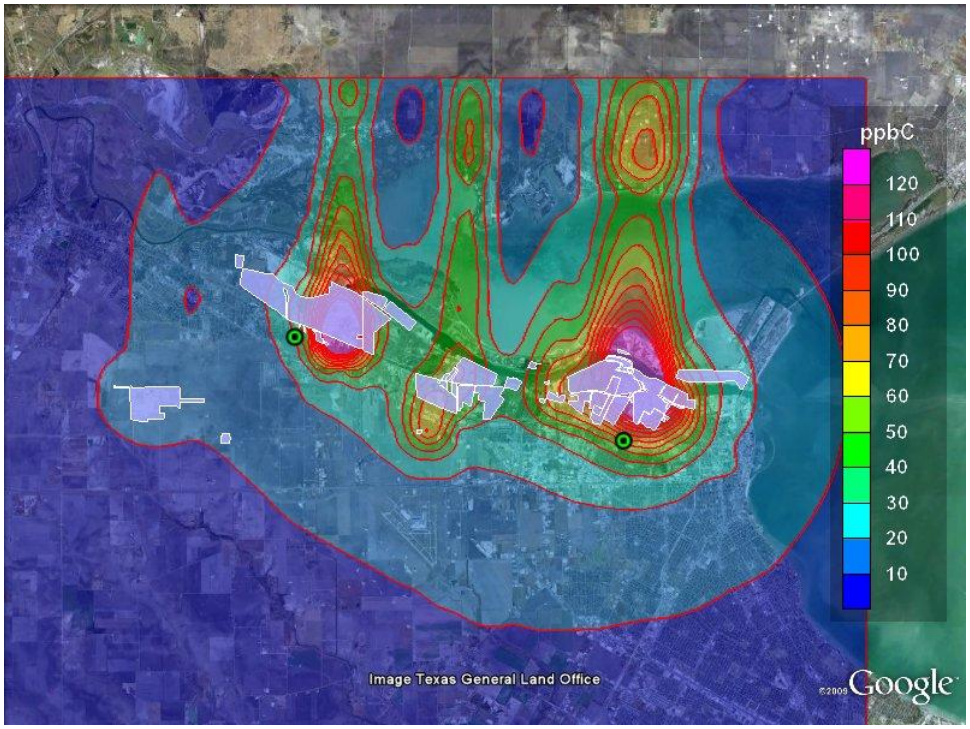
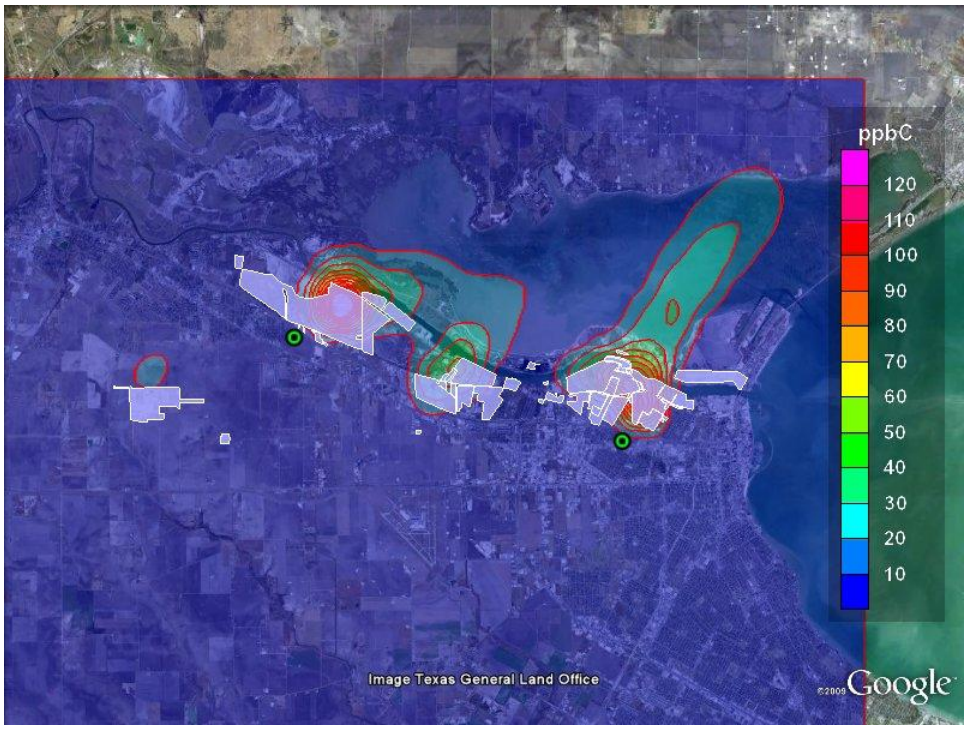


Figure 16. Predicted (a) AERMOD and (b) CALPUFF benzene concentrations for 0300 CST on July 23, 2006. Only point source emissions are included in the dispersion models.

(a)



(b)



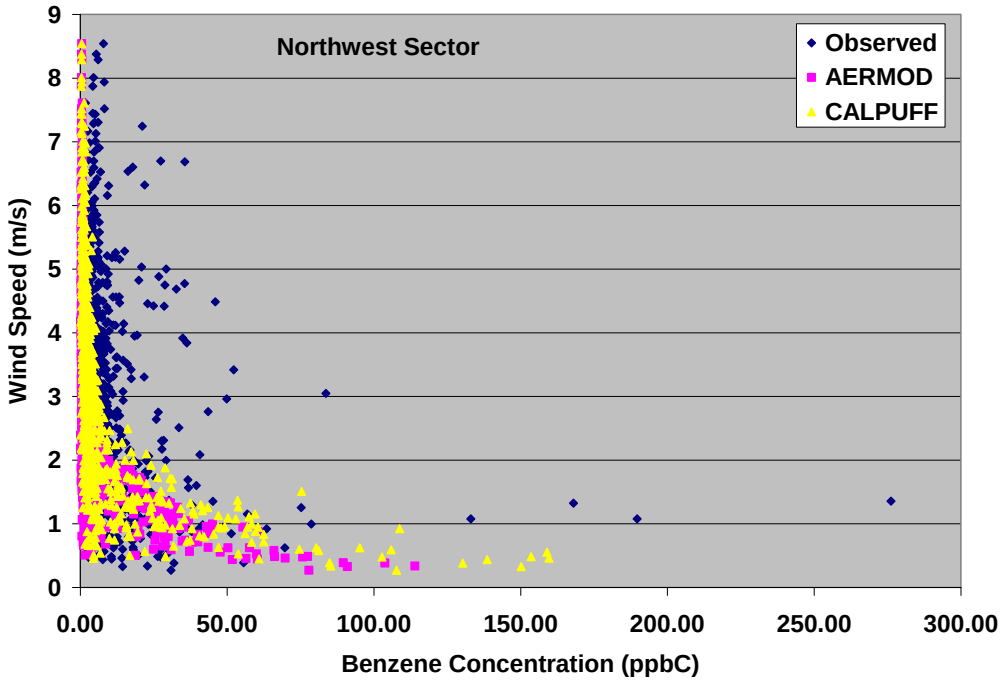
The concentration footprints vary substantially between the two models. Relatively high CALPUFF concentrations are located in the immediate vicinity of the industrial facilities and quickly fall to zero in the upwind area, while relatively high AERMOD concentrations extend farther downwind and upwind of the industrial region. The relatively high concentrations that were predicted to the south of Oak Park were associated with the contributions from the random plume, and resulted in a greater over-prediction of observed concentrations.

Figure 14 indicates that the agreement between observed and AERMOD or CALPUFF predicted benzene concentrations at Oak Park was better for the northwest than for the northeast industrial sector when only point source emissions were modeled. For both the northwest and northeast sectors, CALPUFF predicted higher concentrations relative to AERMOD. Hourly observed and predicted data are plotted against hourly wind speed at Oak Park for the northeast and northwest sectors in Figure 17. Observed and predicted 95th percentile hourly concentrations during 2006 for the northwest and northeast sectors are shown in Figure 18. AERMOD and CALPUFF predictions showed a strong wind speed dependence that was characterized by an increase in predicted concentrations as wind speed decreased. Model predictions for the northwest sector were similar to observations, with generally the best agreement during the morning hours.

For the northeast sector, the highest observed benzene concentrations occurred during the early morning (0400– 1000 CST) and evening (1900– 2300 CST), with the lowest concentrations during the afternoon (1100 – 1800 CST). In contrast to the northwest sector, the highest observed concentrations occurred at moderate wind speeds for the northeast sector. Both models predicted the highest concentrations at low wind speeds and were unable to replicate the relatively higher observed concentrations during moderate wind speeds. Figure 18 indicates that the models generally captured the early morning observed peak, but their predictions declined too rapidly during the mid-morning hours relative to observations which exacerbated the under-prediction of observed concentrations during the daytime. Observed daytime wind speeds were typically higher than nighttime wind speeds (not shown), and this difference contributed to model underperformance at moderate wind speeds for the northeast sector. At this time, the environmental factor(s) contributing to the observed difference in concentration/wind speed relationships between the northwest and northeast sectors is unknown. Working hypotheses include uncertainties in the emission rates for important nearby sources, emission rates that change as a function of wind speed (e.g., increasing emissions with increasing wind speed from external floating roof tanks), and/or differences in mechanical and/or thermally-driven atmospheric turbulence that impact the dispersion of emissions in the downwind regions. An additional contributing factor may be that the modeled vertical and/or horizontal mixing is overly vigorous such that the models predict that individual plumes are dispersed into the surrounding atmosphere too rapidly.

Figure 17. Oak Park hourly wind speed versus observed and predicted benzene concentrations during 2006 for the (a) northwest and (b) northeast sectors. Only point source emissions are included in the dispersion models.

(a)



(b)

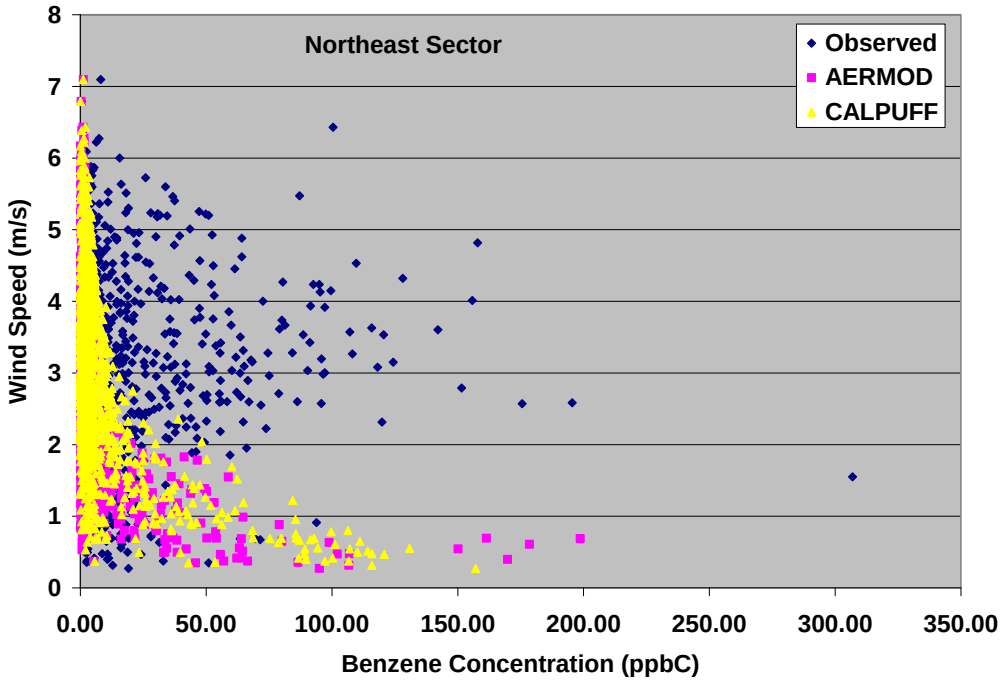
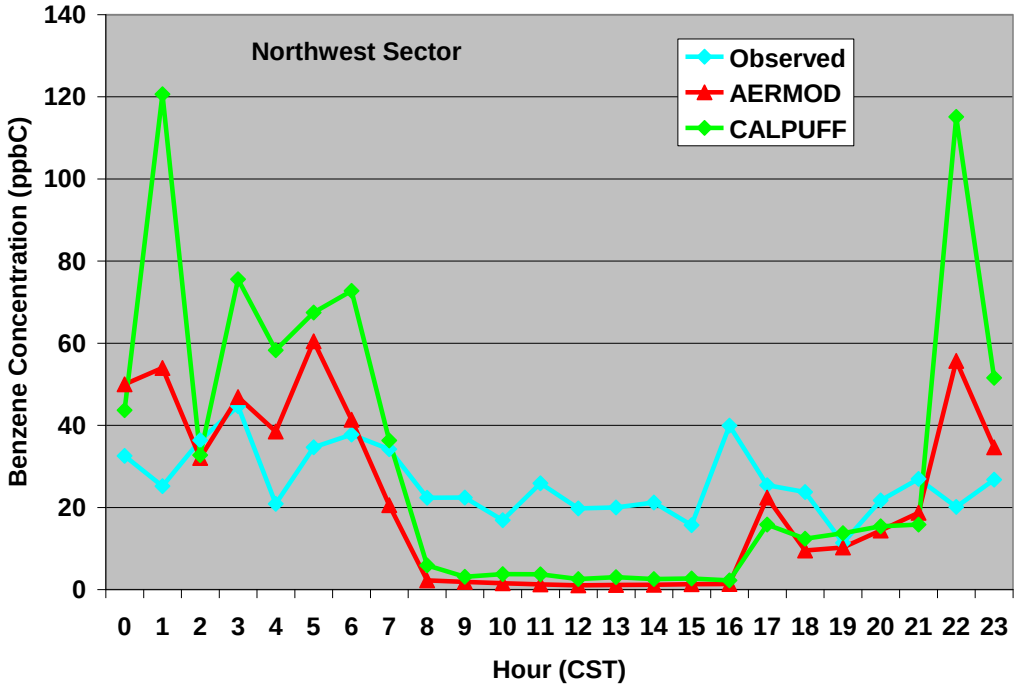
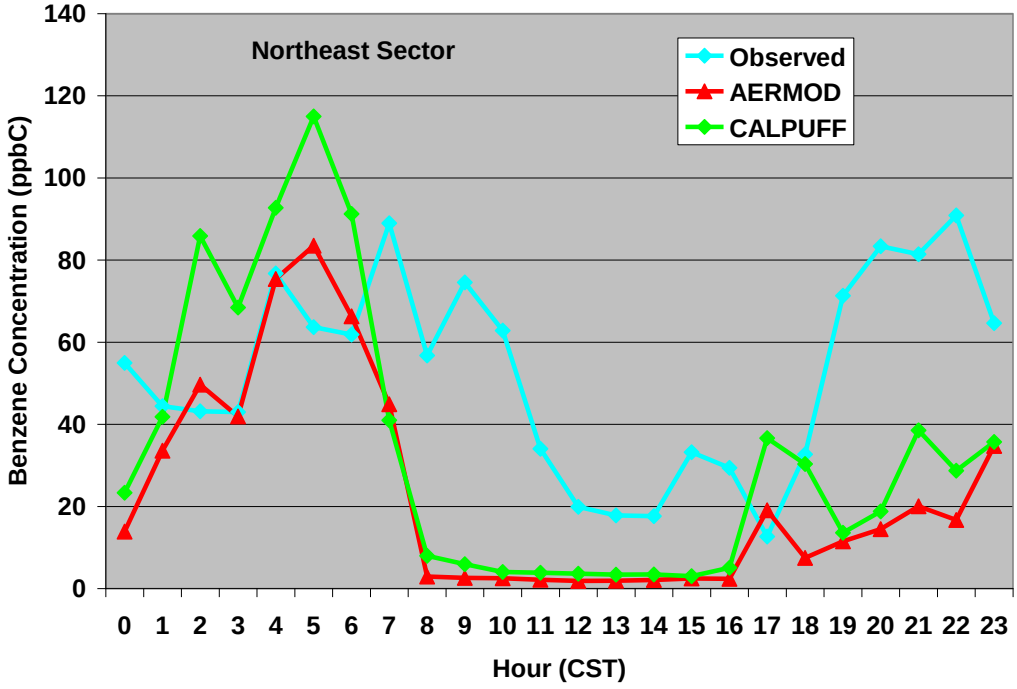


Figure 18. Oak Park predicted and observed hourly 95th percentile benzene concentrations for the (a) northwest and (b) northeast sectors during 2006.

(a)



(b)



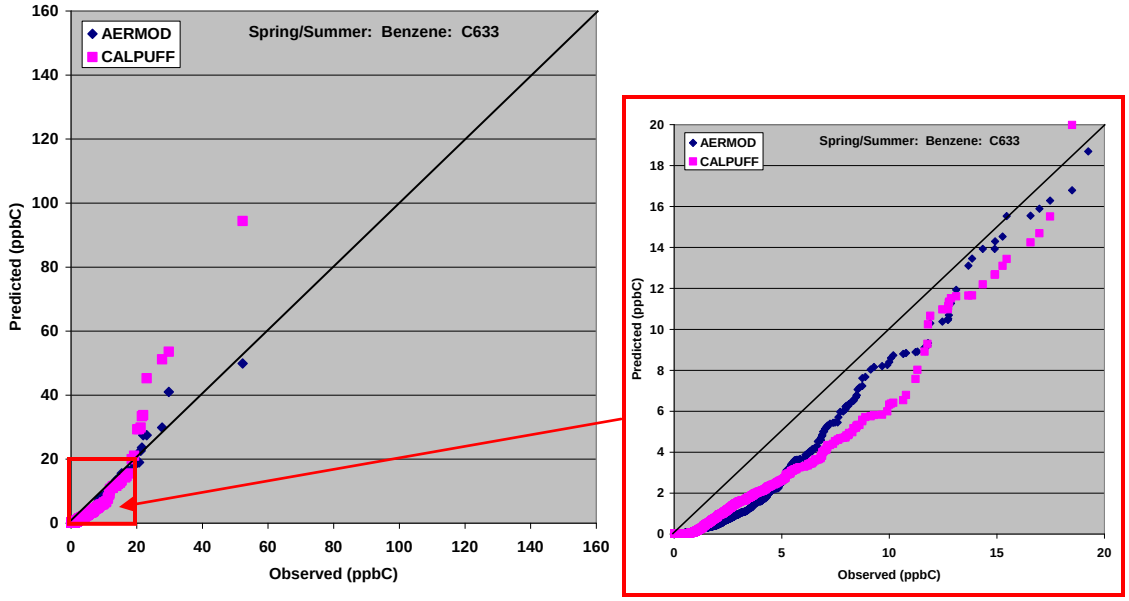
The tendency of the models to under-predict observed concentrations when only point source emissions were included in the dispersion modeling suggested that adding mobile and area source emissions may improve model performance. When all anthropogenic emissions were modeled, agreement between AERMOD and CALPUFF predicted concentrations and observed concentrations during the fall/winter of 2006 at Oak Park generally improved relative to modeling with only point source emissions; ratios of predicted to observed concentrations (mean, maximum, 75th, 95th, and 99th percentiles) ranged from 0.6 to 1.3 (reference Table 11 and Figure 10). Both models under-predicted the observed maximum concentration, which may be associated with non-routine emissions that are not captured by the 2005 TCEQ Photochemical Modeling Inventory. Both models over-predicted observed concentrations during the spring/summer of 2006, regardless of the metric, but CALPUFF predictions were generally in closer agreement with observations.

(b) Model Performance at Solar Estates during 2006. The fall/winter to spring/summer ratio of observed mean benzene concentrations was 2.2 at Solar Estates. AERMOD and CALPUFF replicated the observed seasonal pattern at Solar Estates with relatively higher concentrations during the fall/winter than spring/summer (reference Table 11). Scatter plots of predicted versus observed benzene concentrations by season during 2006 at Oak Park are shown in Figures 19 and 20 for modeling with stationary point source emissions only and with all anthropogenic emissions, respectively.

When only point source emissions were modeled at Solar Estates, CALPUFF and AERMOD under-predicted mean, 75th, and 95th percentile observed benzene concentrations, were in relatively closer agreement with 99th percentile observed concentrations, and over-predicted the maximum observed concentration during the fall/winter of 2006, as shown in Table 11. The AERMOD predicted maximum concentration at Solar Estates was comparable to that predicted at Oak Park which was not consistent with observations. However, the frequency of occurrence of relatively higher predicted concentrations (above a 50 ppbC threshold) was greater at Oak Park than Solar Estates. Similar to the results for Oak Park, the inclusion of all anthropogenic emissions in the modeling generally improved performance at Solar Estates with respect to the agreement with observed mean, 75th percentile, and 95th percentile benzene concentrations. For example, from Table 11, ratios of mean, 75th, or 95th percentile AERMOD or CALPUFF predicted concentrations to observed concentrations with the inclusion of all anthropogenic emissions ranged from 0.3 to 1.0, in contrast to 0.2 to 0.7 when only industrial point sources were included. The addition of area and mobile sources in the models exacerbated the models over-prediction of observed maximum concentrations. At this time, the reason(s) for the models over-prediction of higher observed benzene concentrations at Solar Estates is unknown.

Figure 19. Scatter plots of predicted versus observed benzene concentrations at Solar Estates during the (a) spring/summer and (b) fall/winter of 2006. Only point sources emissions are included in the dispersion models.

(a)



(b)

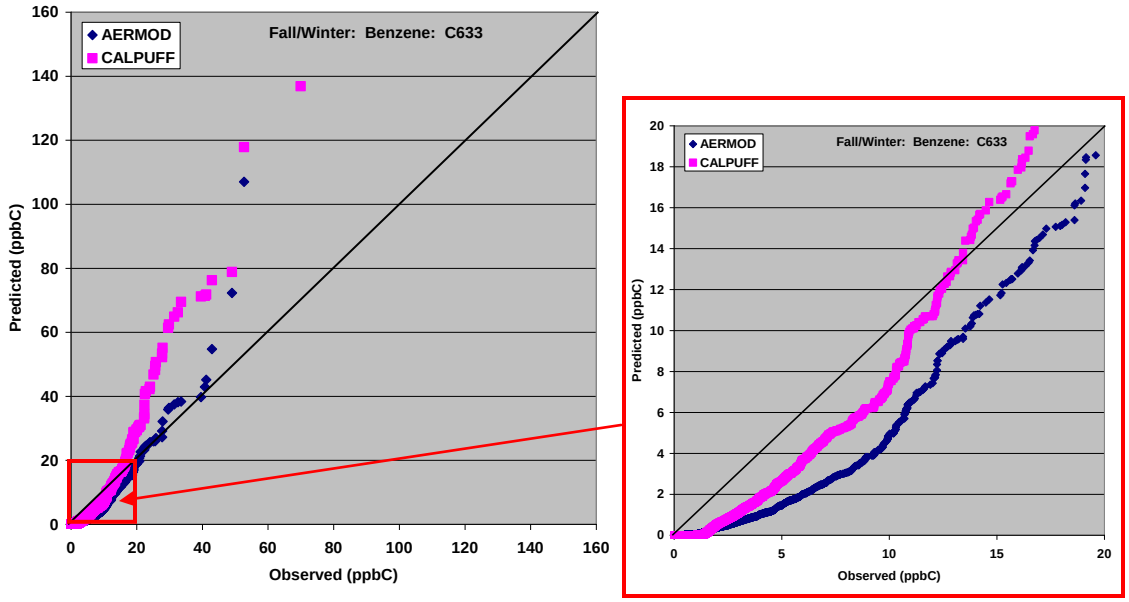
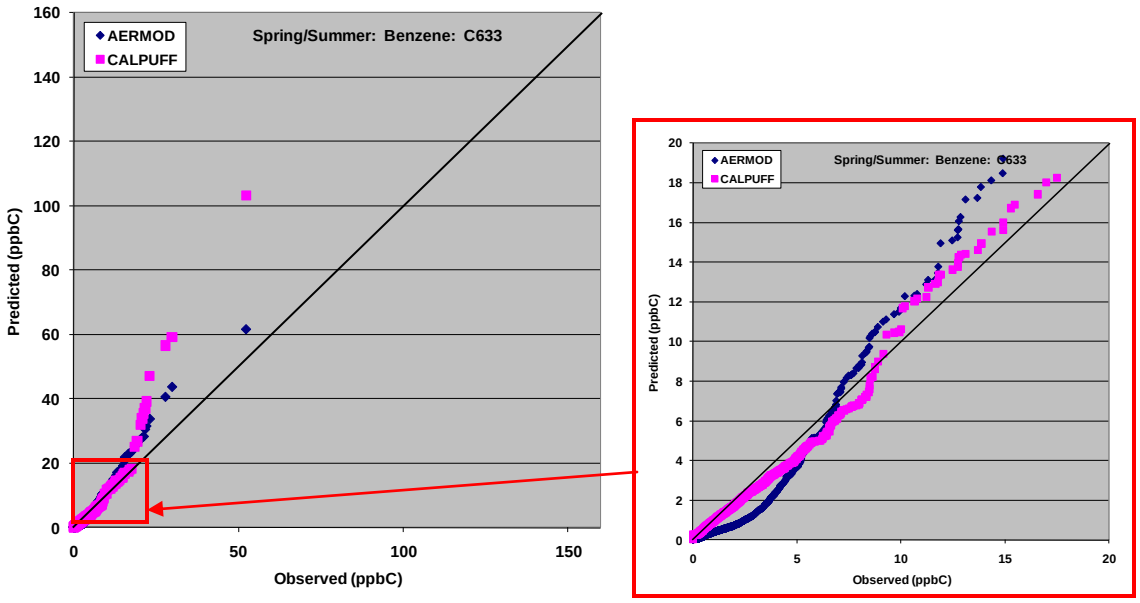
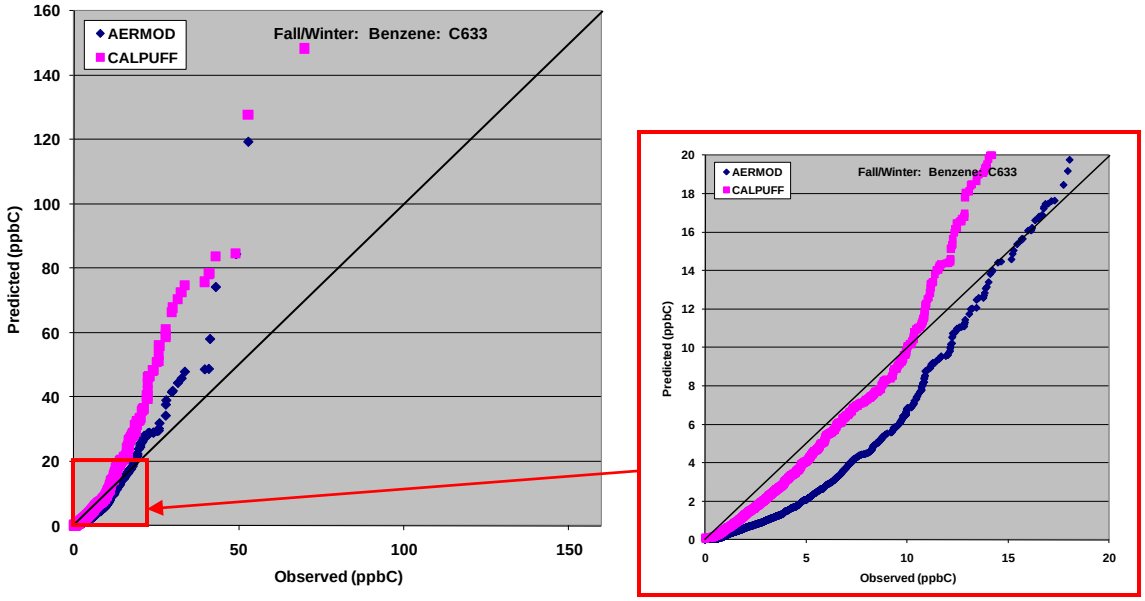


Figure 20. Scatter plots of predicted versus observed benzene concentrations at Solar Estates during the (a) spring/summer and (b) fall/winter of 2006 with all anthropogenic emissions sources included in the dispersion models.

(a)



(b)



(c) Annual Variability in Model Performance between 2006 and 2008. Tables 12 and 13 provide summaries of mean, maximum, 75th, 95th, and 99th percentile observed and AERMOD and CALPUFF predicted benzene concentrations during 2007 and 2008, respectively, at Oak Park and Solar Estates. Predicted concentrations are presented for modeling with stationary point source benzene emissions only and with all anthropogenic benzene emissions (i.e., point, area, and mobile), respectively, from the 2005 TCEQ Photochemical Modeling Inventory.

Mean observed benzene concentrations at Oak Park during the spring/summer 2008 (1.0 ppbC) and fall/winter 2008 (3.4 ppbC) were approximately 50% of the 2006 values. Mean observed benzene concentrations at Solar Estates during spring/summer 2008 (0.8 ppbC) and fall/winter 2008 (1.8 ppbC) were approximately 60% of the 2006 values. For modeling conducted with point source benzene emissions only and with all anthropogenic benzene emissions, neither CALPUFF nor AERMOD were able to consistently replicate the decreases in observed benzene concentrations that occurred at Oak Park and Solar Estates between 2006 and 2008 assuming that emissions remain constant. As an example, predicted and observed annual mean benzene concentrations at Oak Park during 2006 through 2008 are shown in Figure 21; all anthropogenic emissions were included in the dispersion models in Figure 21. Similar results are shown in Figure 22 for Solar Estates. At Oak Park, changes in predicted annual mean concentrations were similar between AERMOD and CALPUFF and did not show consistent decreases over time, although mean predicted concentrations were the lowest in 2008 similar to observations. AERMOD and CALPUFF maximum concentrations (reference Tables 12 and 13) varied little from year-to-year. At Solar Estates, AERMOD showed little variation in mean concentrations between 2006 and 2008, while CALPUFF predicted the highest mean concentrations during 2008. Both models over-predicted observed maximum concentrations for 2007 and 2008 (reference Tables 12 and 13), similar to the results for 2006 discussed above.

Annual variability in meteorological conditions may contribute to differences in observed and modeled concentrations. However, these results suggested that decreases in observed benzene concentrations may be associated with decreases in benzene emissions since 2006, a finding which would be consistent with the declines in annual benzene emissions reported in the TRI. It is recommended that the reported annual TRI emissions inventories continue to be tracked in conjunction with trends in the ambient measurements from the CCAQP network. Emissions inventories with the spatial resolution in emission points and full chemical speciation of VOCs, such as the 2005 TCEQ Photochemical Modeling Inventory, are not routinely developed on an annual basis, which creates disparities in evaluating trends in regions with rapidly changing inventories. If a more recent or future year emissions inventory with the same spatial resolution in emission points and full chemical speciation of VOCs as the 2005 TCEQ Photochemical Modeling EI is developed by the State of Texas, it should be utilized for dispersion modeling in the region.

Table 12. Summary of mean, maximum, 75th, 95th, and 99th percentile observed (OBS) and predicted benzene concentrations from AERMOD (AER) and CALPUFF (CAL) during two seasonal periods at Oak Park and Solar Estates in 2007. Predicted concentrations are presented for modeling with stationary point source emissions only and with all anthropogenic emissions from the 2005 TCEQ Photochemical Modeling Inventory. Ratios of predicted to observed concentrations are shown in parentheses.

Site	Mean (ppbC)			75th Percentile (ppbC)			95th Percentile (ppbC)			99th Percentile (ppbC)			Maximum (ppbC)		
	OBS	AER	CAL	OBS	AER	CAL	OBS.	AER	CAL	OBS	AER	CAL	OBS	AER	CAL
Oak Park															
Spring/Summer															
Point Sources		2.64 (1.3)	1.61 (0.8)		1.37 (1.1)	0.02 (0.02)		12.55 (1.5)	6.27 (0.7)		44.09 (1.7)	37.67 (1.5)		168.45 (1.1)	126.90 (0.8)
All Anthropogenic	2.09	4.05 (1.9)	2.82 (1.3)	1.25	2.14 (1.7)	1.84 (1.5)	8.39	19.62 (2.3)	9.46 (1.1)	25.85	56.69 (2.2)	43.45 (1.7)	158.22	183.36 (1.2)	147.90 (0.9)
Fall/Winter															
Point Sources		5.02 (1.0)	4.98 (0.9)		3.18 (0.6)	3.22 (0.6)		22.47 (1.2)	23.72 (1.2)		74.83 (1.4)	86.25 (1.6)		193.69 (0.3)	196.50 (0.3)
All Anthropogenic	5.28	7.13 (1.4)	6.82 (1.3)	5.01	4.35 (0.9)	4.86 (1.0)	19.11	33.24 (1.7)	27.75 (1.5)	52.88	99.45 (1.9)	104.02 (2.0)	720.95	216.67 (0.3)	212.40 (0.3)
Solar Estates															
Spring/Summer															
Point Sources		0.97 (0.7)	1.14 (0.8)		0.41 (0.2)	0.50 (0.3)		3.58 (0.7)	4.09 (0.8)		15.84 (1.6)	20.85 (2.2)		75.07 (1.7)	95.41 (2.1)
All Anthropogenic	1.45	1.45 (1.0)	2.02 (1.4)	1.71	0.81 (0.5)	1.63 (1.0)	5.13	5.60 (1.1)	6.40 (1.2)	9.64	20.25 (2.1)	28.36 (2.9)	44.47	90.57 (2.0)	103.00 (2.3)
Fall/Winter															
Point Sources		1.30 (0.5)	2.38 (1.0)		0.78 (0.3)	1.75 (0.6)		5.64 (0.8)	10.20 (1.5)		18.68 (1.3)	35.30 (2.5)		87.25 (2.3)	121.10 (3.2)
All Anthropogenic	2.48	1.81 (0.7)	3.47 (1.4)	3.05	1.16 (0.4)	3.10 (1.0)	6.87	7.68 (1.1)	13.88 (2.0)	14.16	23.70 (1.7)	38.93 (2.7)	37.74	94.83 (2.5)	127.80 (3.4)

Table 13. Summary of mean, maximum, 75th, 95th, and 99th percentile observed (OBS) and predicted benzene concentrations from AERMOD (AER) and CALPUFF (CAL) during two seasonal periods at Oak Park and Solar Estates in 2008. Predicted concentrations are presented for modeling with stationary point source emissions only and with all anthropogenic emissions from the 2005 TCEQ Photochemical Modeling Inventory. Ratios of predicted to observed concentrations are shown in parentheses.

Site	Mean (ppbC)			75th Percentile (ppbC)			95th Percentile (ppbC)			99th Percentile (ppbC)			Maximum (ppbC)		
	OBS	AER	CAL	OBS	AER	CAL	OBS.	AER	CAL	OBS	AER	CAL	OBS	AER	CAL
Oak Park															
Spring/Summer															
Point Sources		1.57 (1.6)	0.97 (1.0)		1.02 (1.2)	0.01 (0.01)		7.06 (1.6)	3.64 (0.8)		19.23 (1.9)	19.68 (1.9)		117.33 (0.9)	101.60 (0.8)
All Anthropogenic	1.00	2.50 (2.5)	1.83 (1.8)	0.85	1.67 (2.0)	1.00 (1.2)	4.29	11.36 (2.6)	5.88 (1.4)	10.24	28.85 (2.8)	24.62 (2.4)	125.59	141.96 (1.1)	116.10 (0.9)
Fall/Winter															
Point Sources		4.00 (1.2)	3.22 (1.0)		3.28 (0.8)	2.16 (0.5)		18.22 (1.6)	13.29 (1.2)		49.57 (1.8)	61.80 (2.2)		242.92 (2.5)	157.70 (1.6)
All Anthropogenic	3.38	5.76 (1.7)	4.77 (1.4)	4.10	4.33 (1.1)	3.37 (0.8)	11.30	26.84 (2.4)	19.82 (1.8)	27.58	68.53 (2.5)	71.97 (2.6)	97.85	265.13 (2.7)	171.50 (1.8)
Solar Estates															
Spring/Summer															
Point Sources		0.48 (0.6)	1.01 (1.2)		0.27 (0.3)	0.28 (0.3)		1.65 (0.6)	3.12 (1.1)		7.96 (1.5)	20.51 (4.0)		45.84 (1.4)	125.30 (3.9)
All Anthropogenic	0.83	0.77 (0.9)	1.74 (2.1)	1.08	0.53 (0.5)	1.11 (1.0)	2.74	2.45 (0.9)	4.72 (1.7)	5.16	11.91 (2.3)	27.00 (5.2)	31.85	56.30 (1.8)	136.10 (4.3)
Fall/Winter															
Point Sources		1.04 (0.6)	3.26 (1.8)		0.73 (0.3)	1.71 (0.8)		3.40 (0.6)	14.80 (2.7)		16.27 (1.8)	60.99 (6.7)		80.27 (2.9)	135.60 (4.8)
All Anthropogenic	1.79	1.56 (0.9)	4.39 (2.5)	2.15	1.18 (0.5)	2.82 (1.3)	5.44	5.12 (0.9)	18.30 (3.4)	9.13	21.44 (2.3)	70.35 (7.7)	28.15	98.77 (3.5)	142.00 (5.0)

Figure 21. Predicted and observed annual mean benzene concentrations at Oak Park during 2006 – 2008 with all anthropogenic emissions sources included in the dispersion models. Note that predictions assume emissions remain constant from 2006-2008.

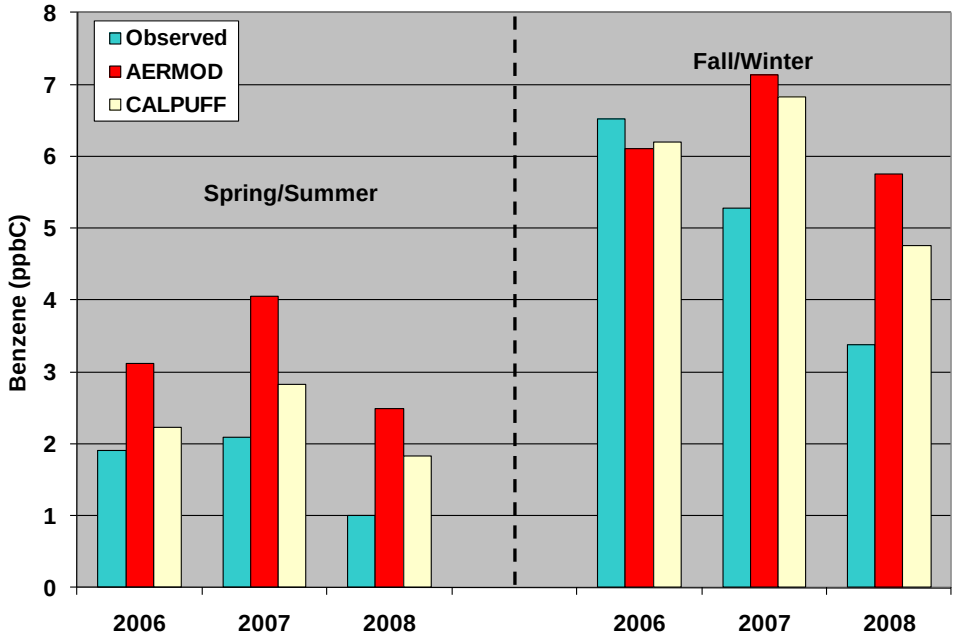
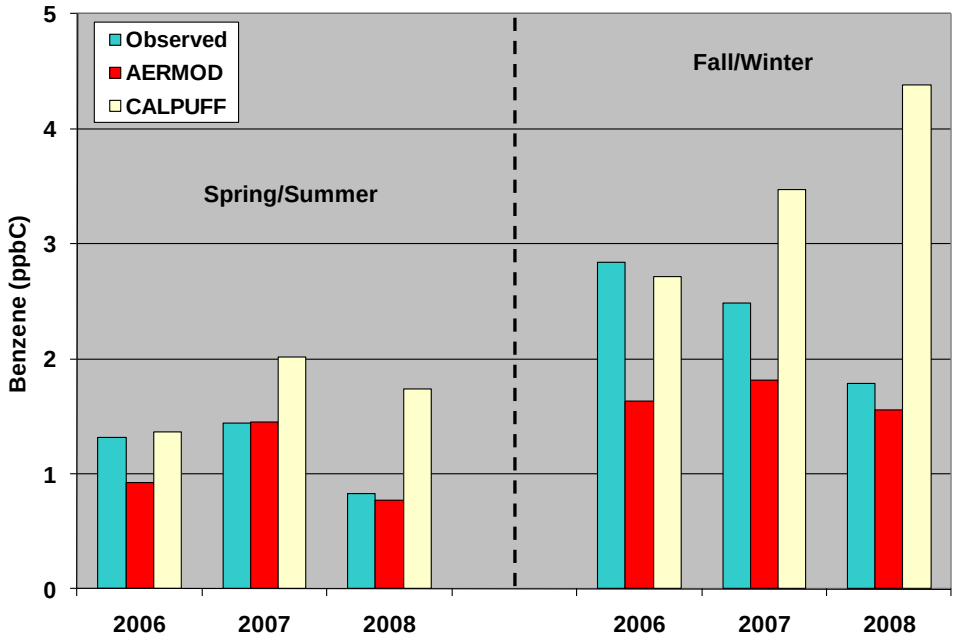


Figure 22. Predicted and observed annual mean benzene concentrations at Solar Estates during 2006 – 2008 with all anthropogenic emissions sources included in the dispersion models. Note that predictions assume emissions remain constant from 2006-2008.

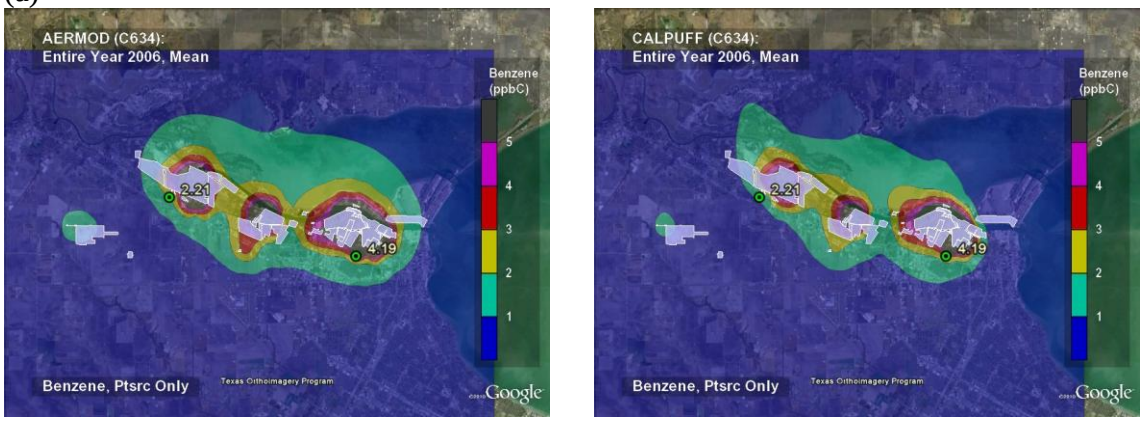


(d) Spatial Maps of Predicted Concentrations during 2006. Spatial maps of predicted concentrations allow air toxics concentrations to be estimated in areas without monitoring sites and provide necessary information for assessing human exposure and health risks. They also allow identification of other potential "hotspots" in the area that could be targeted for future measurement efforts. As an example, Figure 23 shows annual mean predicted benzene concentrations in the receptor grid (reference Figure 7) from AERMOD and CALPUFF with point source emissions only and with all anthropogenic emissions using on-site meteorological data from the Oak Park (C634) monitor for AERMOD. Industrial facility property boundaries are shown in each map, along with observed concentrations at the locations of the monitors. Figure 24 shows annual mean concentrations from AERMOD and CALPUFF with point source emissions only and with all anthropogenic emissions using on-site meteorological data from the Solar Estates (C633) monitor for AERMOD. Unlike AERMOD, CALPUFF is not restricted to use of on-site meteorological data from a single site. Figures 25, 27, and 29 show annual 75th percentile, 95th percentile, and maximum predicted benzene concentrations, respectively, with point source emissions only and with all anthropogenic emissions using on-site meteorological data from the Oak Park monitor for AERMOD. Figures 26, 28, and 30 show annual 75th percentile, 95th percentile, and maximum predicted benzene concentrations, respectively, with point source emissions only and with all anthropogenic emissions using on-site meteorological data from the Solar Estates monitor for AERMOD.

Spatial maps of predicted concentrations during 2006 were similar for both models, with the exception of annual maximum concentrations. Wind patterns in AERMOD reflect constant hourly trajectories associated with the restriction of on-site meteorological data from a single site, which lead to the "fingerlike" appearance of predicted maximum concentrations. In contrast, CALPUFF represents the spatial variability in wind patterns by incorporating data from multiple sites. The Oak Park and Solar Estates monitors are located within two areas of influence at either end of the Ship Channel. However, neither monitor is positioned to capture benzene concentrations within the Dona Park area more centrally located in the Ship Channel industrial complex or near the Equistar facility located to the southwest of Solar Estates. Although total non-methane hydrocarbon measurements are made at Dona Park, chemically speciated measurements, such as those made with an auto-GC, are not routinely determined. Spatial maps of benzene concentrations indicated broader areas of influence when all anthropogenic emissions were included in the modeling than when only point sources were included. These results were consistent with the contributions of area and/or mobile sources to the inventories for this pollutant.

Figure 23. Predicted annual mean benzene concentrations in the receptor grid (colored area) from AERMOD (left) and CALPUFF (right) for 2006 using on-site meteorological data from the Oak Park (C634) monitor for AERMOD and (a) point source emissions only and (b) all anthropogenic emissions. Property boundaries of the stationary point sources are shown in gray.

(a)



(b)

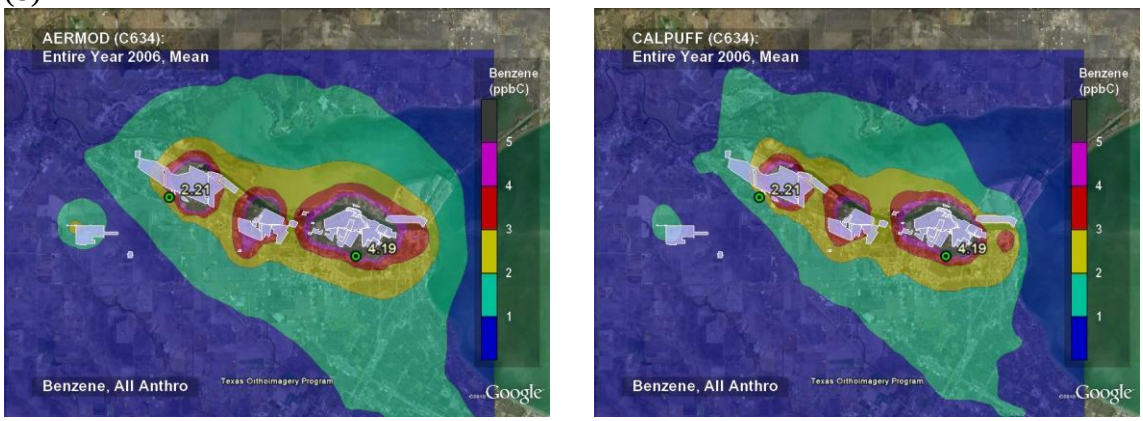
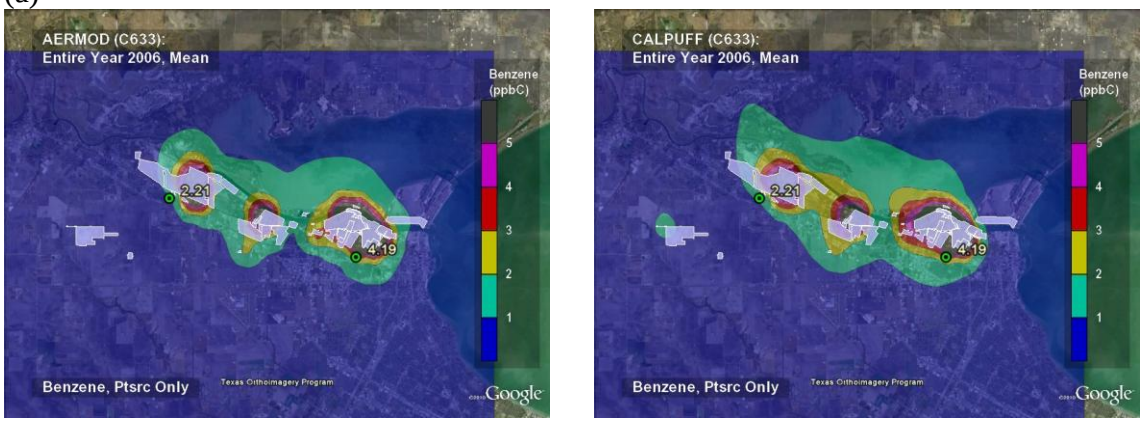


Figure 24. Predicted annual mean benzene concentrations in the receptor grid (colored area) from AERMOD (left) and CALPUFF (right) for 2006 using on-site meteorological data from the Solar Estates (C633) monitor for AERMOD and (a) point source emissions only and (b) all anthropogenic emissions. Property boundaries of the stationary point sources are shown in gray.

(a)



(b)

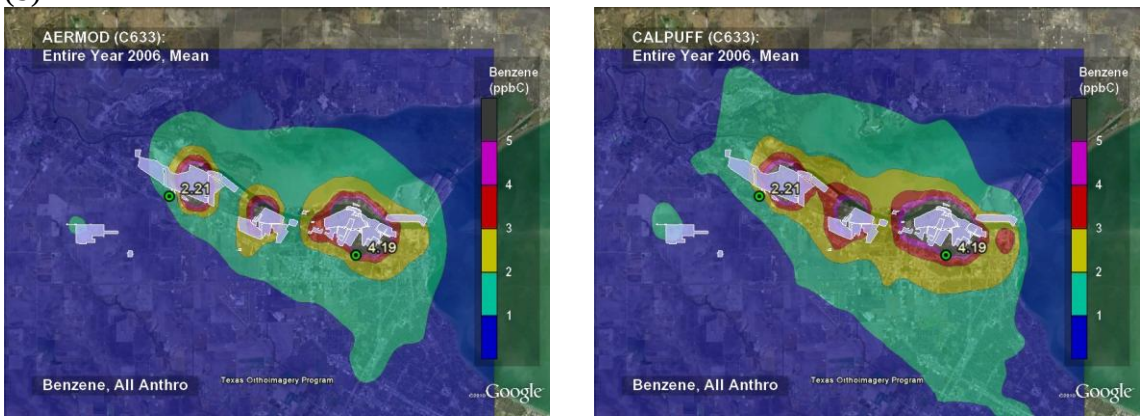
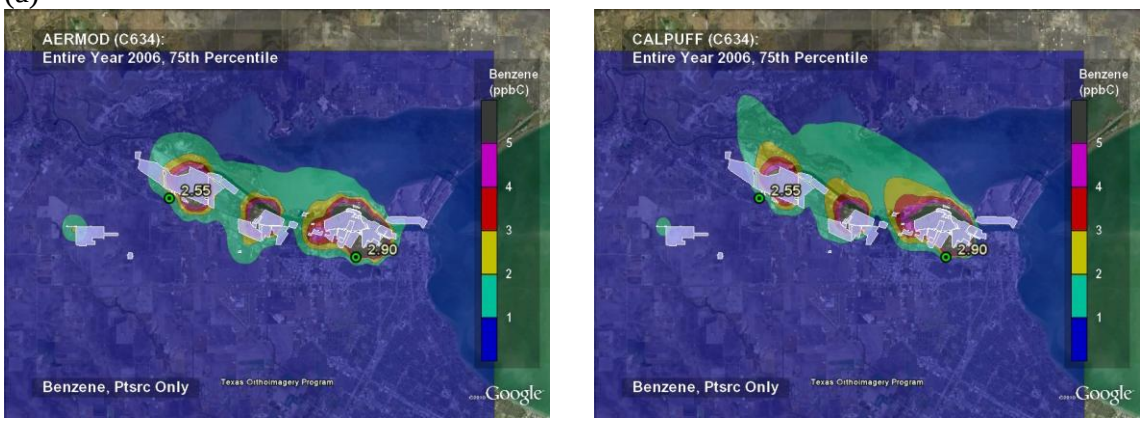


Figure 25. Predicted annual 75th percentile benzene concentrations in the receptor grid (colored area) from AERMOD (left) and CALPUFF (right) for 2006 using on-site meteorological data from the Oak Park (C634) monitor for AERMOD and (a) point source emissions only and (b) all anthropogenic emissions. Property boundaries of the stationary point sources are shown in gray.

(a)



(b)

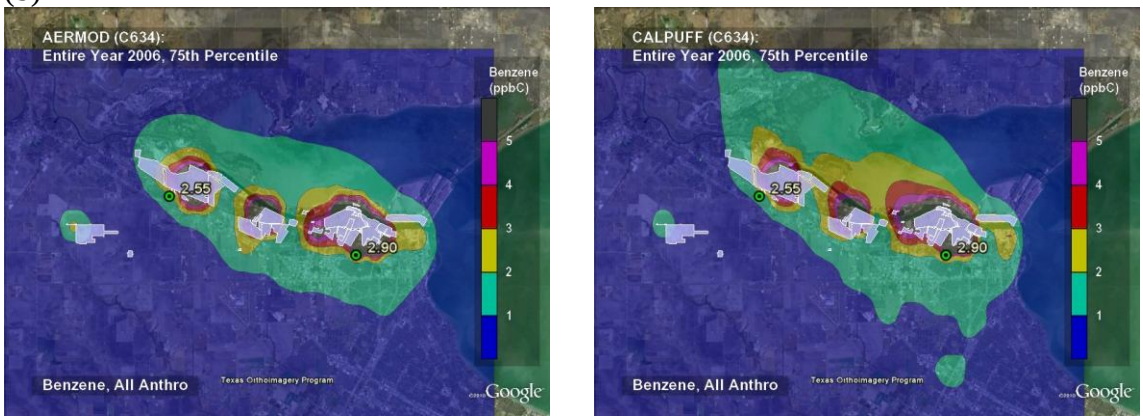
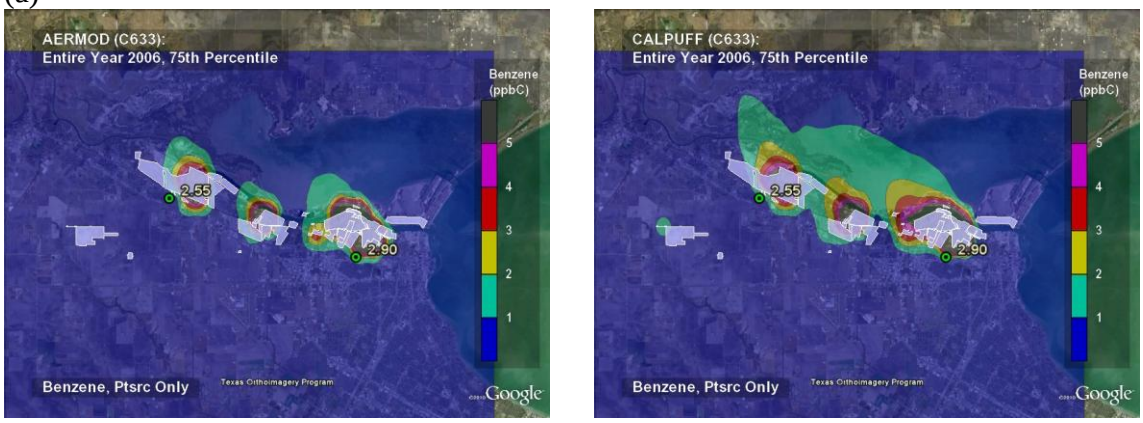


Figure 26. Predicted annual 75th percentile benzene concentrations in the receptor grid (colored area) from AERMOD (left) and CALPUFF (right) for 2006 using on-site meteorological data from the Solar Estates (C633) monitor for AERMOD and (a) point source emissions only and (b) all anthropogenic emissions. Property boundaries of the stationary point sources are shown in gray.

(a)



(b)

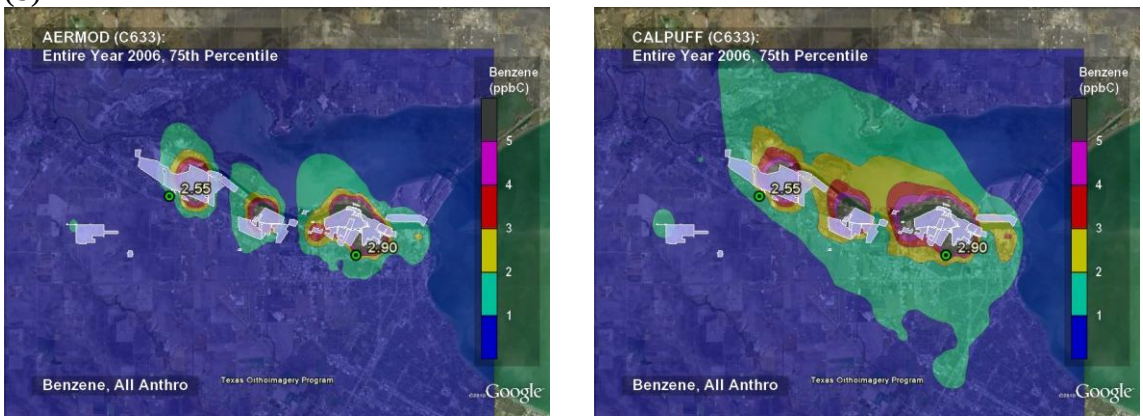
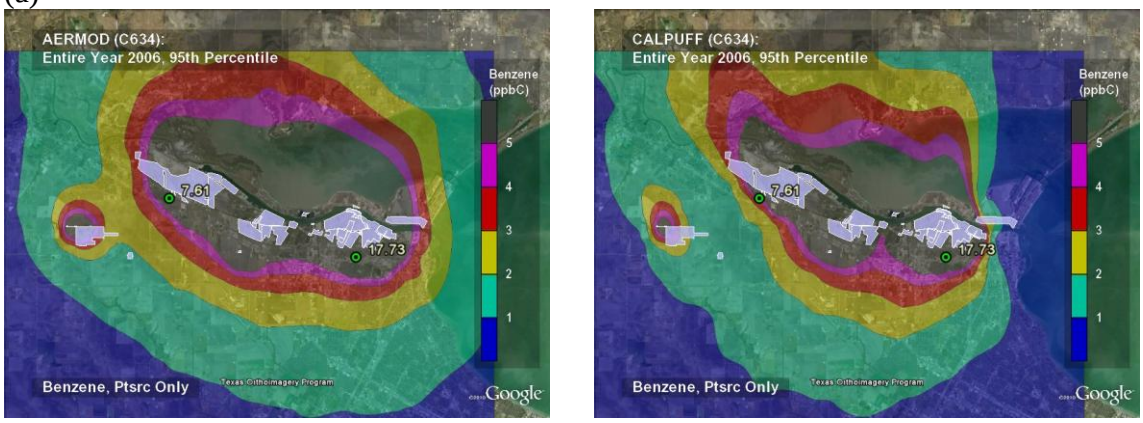


Figure 27. Predicted annual 95th percentile benzene concentrations in the receptor grid (colored area) from AERMOD (left) and CALPUFF (right) for 2006 using on-site meteorological data from the Oak Park (C634) monitor for AERMOD and (a) point source emissions only and (b) all anthropogenic emissions. Property boundaries of the stationary point sources are shown in gray.

(a)



(b)

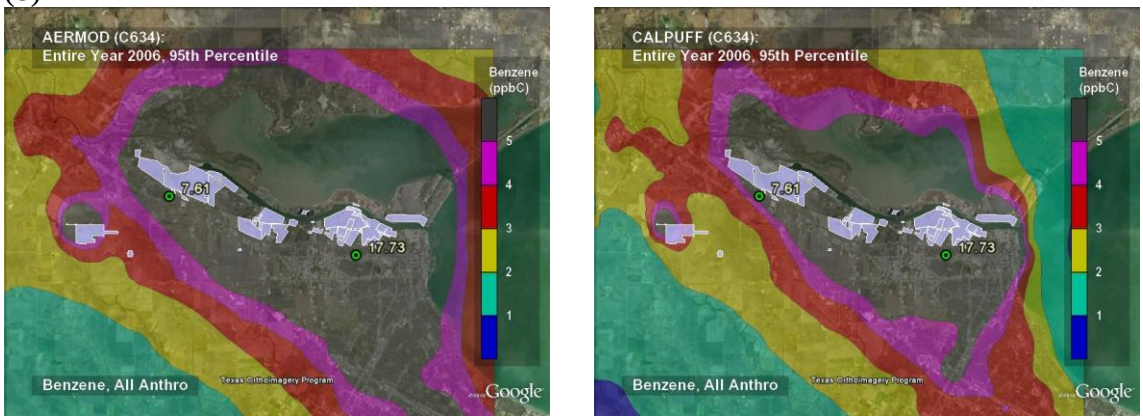
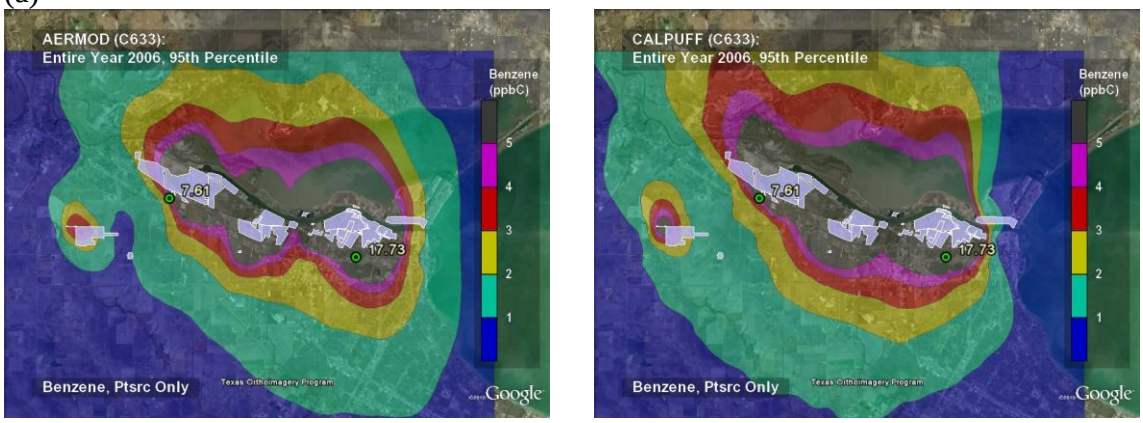


Figure 28. Predicted annual 95th percentile benzene concentrations in the receptor grid (colored area) from AERMOD (left) and CALPUFF (right) for 2006 using on-site meteorological data from the Solar Estates (C633) monitor for AERMOD and (a) point source emissions only and (b) all anthropogenic emissions. Property boundaries of the stationary point sources are shown in gray.

(a)



(b)

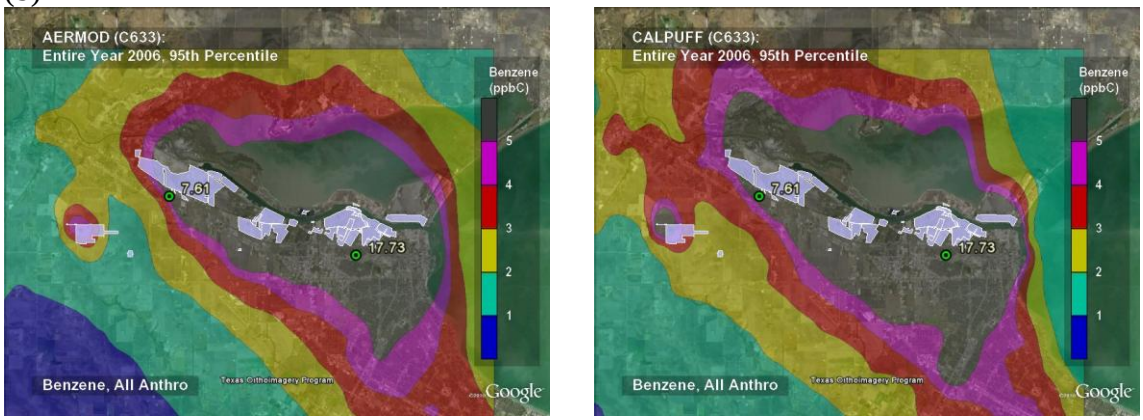
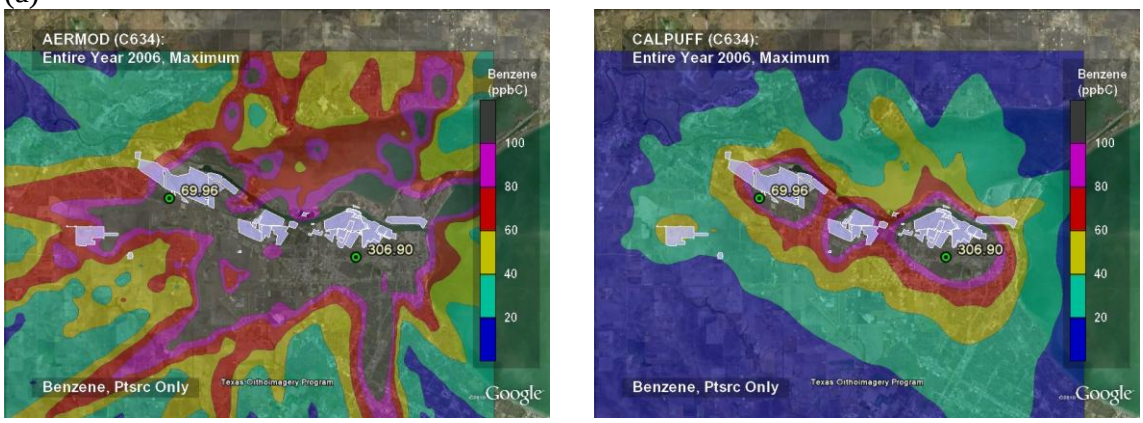


Figure 29. Predicted annual maximum benzene concentrations in the receptor grid (colored area) from AERMOD (left) and CALPUFF (right) for 2006 using on-site meteorological data from the Oak Park (C634) monitor for AERMOD and (a) point source emissions only and (b) all anthropogenic emissions. Property boundaries of the stationary point sources are shown in gray.

(a)



(b)

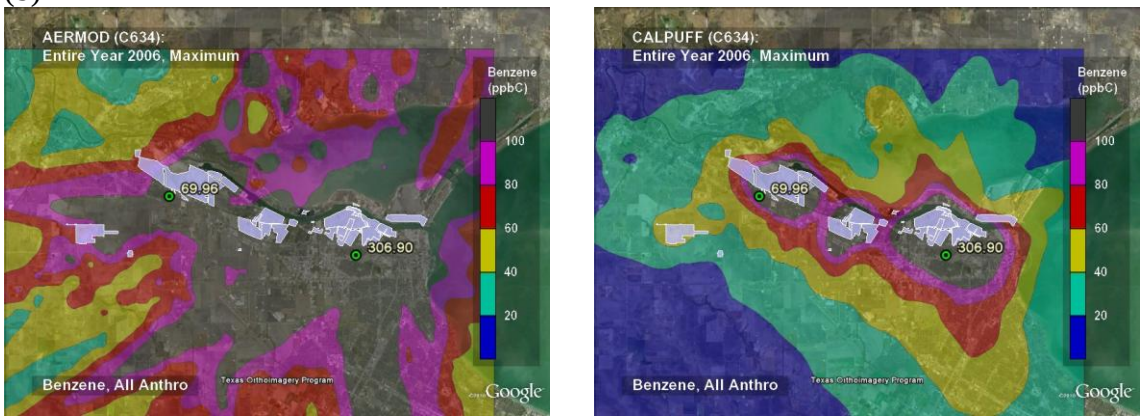
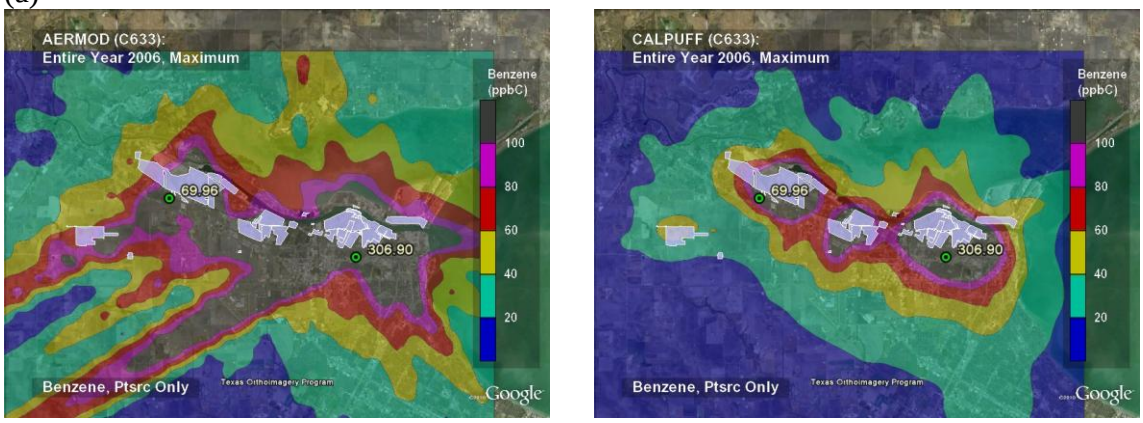
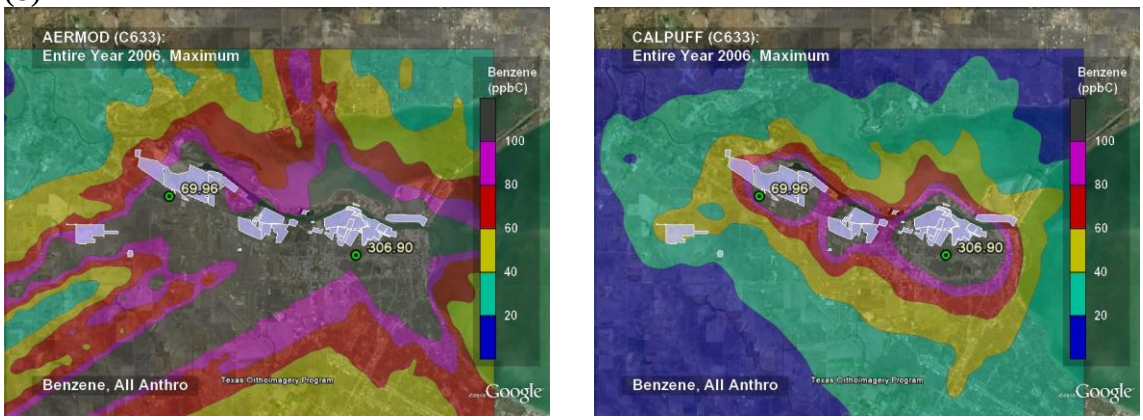


Figure 30. Predicted annual maximum benzene concentrations in the receptor grid (colored area) from AERMOD (left) and CALPUFF (right) for 2006 using on-site meteorological data from the Solar Estates (C633) monitor for AERMOD and (a) point source emissions only and (b) all anthropogenic emissions. Property boundaries of the stationary point sources are shown in gray.

(a)



(b)



4.2 1,3-Butadiene

(a) Model Performance at Oak Park during 2006. Table 14 provides a summary of mean, maximum, 75th, 95th, and 99th percentile observed and AERMOD and CALPUFF predicted 1,3-butadiene concentrations during 2006 at Oak Park and Solar Estates. Predicted concentrations are presented for modeling with stationary point source 1,3-butadiene emissions only and with all anthropogenic 1,3-butadiene emissions (i.e., point, area, and mobile), respectively, from the 2005 TCEQ Photochemical Modeling Inventory. Scatter plots of predicted versus observed 1,3-butadiene concentrations by season during 2006 at Oak Park are shown in Figures 31 and 32 for modeling with stationary point source emissions only and with all anthropogenic emissions, respectively.

The fall/winter to spring/summer ratio of mean observed 1,3-butadiene concentrations at Oak Park during 2006 was 2.6. In contrast to benzene, the highest observed concentrations of 1,3-butadiene occurred at Solar Estates not Oak Park. AERMOD and CALPUFF replicated the observed seasonal difference in observed 1,3-butadiene concentrations at Oak Park with relatively higher concentrations during the fall/winter than spring/summer.

Comparison of results from modeling with point source emissions only and with all anthropogenic emissions, respectively, to observations at Oak Park during 2006 demonstrated an under-prediction bias by both models. At Oak Park, the under-prediction bias of both models was reduced but not resolved by modeling area and mobile sources in addition to point sources. For example, ratios of mean, 75th, or 95th percentile AERMOD or CALPUFF predicted concentrations to observed concentrations during fall/winter ranged from 0.1 to 0.4 when only point sources were modeled. Ratios of mean, 75th, or 95th percentile AERMOD or CALPUFF predicted concentrations to observed concentrations when all anthropogenic emissions sources were included in the modeling simulations ranged from 0.4 to 0.9. Both models substantially underestimated the observed maximum concentration; the ratios of maximum AERMOD and CALPUFF predicted concentrations to the observed concentration were 0.2 and 0.1, respectively, with all anthropogenic sources include in the modeling, and 0.1 when only point sources were included in the modeling.

(b) Model Performance at Solar Estates during 2006. Scatter plots of predicted versus observed 1,3-butadiene concentrations by season during 2006 at Oak Park are shown in Figures 33 and 34 for modeling with stationary point source emissions only and with all anthropogenic emissions, respectively. As described above, Table 14 provides a summary of observed and predicted 1,3-butadiene concentration metrics.

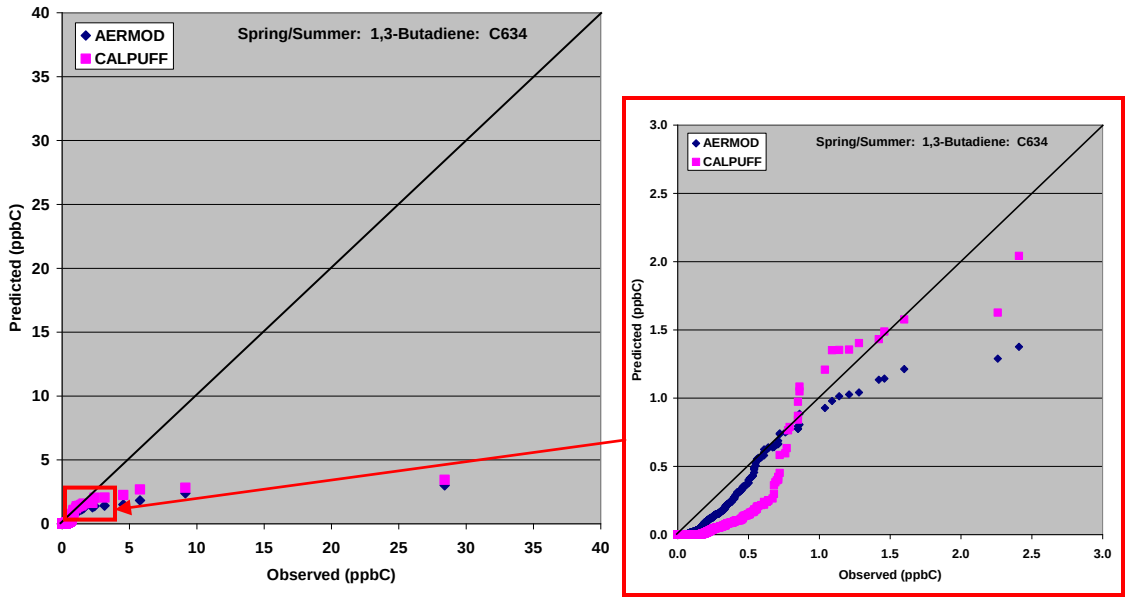
The fall/winter to spring/summer ratio of mean observed 1,3-butadiene concentrations at Solar Estates during 2006 was 1.2, indicating a weaker seasonal pattern than at Oak Park. AWRMOD and CALPUFF predicted spring/summer concentrations were also more similar to fall/winter concentrations during 2006 at Solar Estates than at Oak Park. The highest observed 1,3-butadiene concentrations are associated with southwesterly, west-southwesterly, or westerly winds, as shown in Figure 35. These latter wind directions are rare throughout the year, but are more frequent during the fall/winter than spring/summer.

Table 14. Summary of mean, maximum, 75th, 95th, and 99th percentile observed (OBS) and predicted 1,3-butadiene concentrations from AERMOD (AER) and CALPUFF (CAL) during two seasonal periods at Oak Park and Solar Estates in 2006. Predicted concentrations are presented for modeling with stationary point source emissions only and with all anthropogenic emissions from the 2005 TCEQ Photochemical Modeling Inventory. Ratios of predicted to observed concentrations are shown in parentheses.

Site	Mean (ppbC)			75th Percentile (ppbC)			95th Percentile (ppbC)			99th Percentile (ppbC)			Maximum (ppbC)		
	OBS	AER	CAL	OBS	AER	CAL	OBS.	AER	CAL	OBS	AER	CAL	OBS	AER	CAL
Oak Park															
Spring/Summer															
Point Sources		0.04 (0.4)	0.02 (0.2)		0.02 (0.2)	0.00 (0.00)		0.16 (0.6)	0.05 (0.2)		0.63 (1.0)	0.24 (0.4)		3.00 (0.1)	3.44 (0.1)
All Anthropogenic	0.11	0.10 (0.9)	0.05 (0.5)	0.11	0.06 (0.5)	0.04 (0.4)	0.29	0.43 (1.5)	0.17 (0.6)	0.63	1.25 (2.0)	0.58 (0.9)	28.41	3.87 (0.1)	3.64 (0.1)
Fall/Winter															
Point Sources		0.07 (0.2)	0.07 (0.2)		0.06 (0.2)	0.03 (0.1)		0.28 (0.4)	0.26 (0.3)		0.88 (0.5)	1.52 (0.9)		3.12 (0.1)	3.99 (0.1)
All Anthropogenic	0.29	0.17 (0.6)	0.15 (0.5)	0.30	0.14 (0.5)	0.12 (0.4)	0.80	0.73 (0.9)	0.56 (0.7)	1.65	1.99 (1.2)	1.83 (1.1)	34.65	5.30 (0.2)	4.93 (0.1)
Solar Estates															
Spring/Summer															
Point Sources		0.01 (0.03)	0.01 (0.03)		0.00 (0.0)	0.00 (0.0)		0.02 (0.1)	0.03 (0.1)		0.12 (0.04)	0.20 (0.1)		0.84 (0.01)	0.59 (0.01)
All Anthropogenic	0.32	0.03 (0.09)	0.03 (0.09)	0.18	0.03 (0.2)	0.03 (0.2)	0.33	0.11 (0.3)	0.11 (0.3)	3.21	0.50 (0.2)	0.40 (0.1)	99.08	1.81 (0.02)	0.73 (0.01)
Fall/Winter															
Point Sources		0.01 (0.03)	0.02 (0.1)		0.00 (0.0)	0.01 (0.04)		0.05 (0.1)	0.09 (0.2)		0.22 (0.1)	0.27 (0.1)		0.90 (0.01)	0.70 (0.01)
All Anthropogenic	0.37	0.05 (0.1)	0.07 (0.1)	0.24	0.04 (0.2)	0.08 (0.3)	0.57	0.20 (0.4)	0.30 (0.5)	3.08	0.54 (0.18)	0.58 (0.2)	79.55	2.04 (0.03)	1.71 (0.02)

Figure 31. Scatter plots of predicted versus observed 1,3-butadiene concentrations at Oak Park during the (a) spring/summer and (b) fall/winter of 2006. Only point source emissions are included in the dispersion models.

(a)



(b)

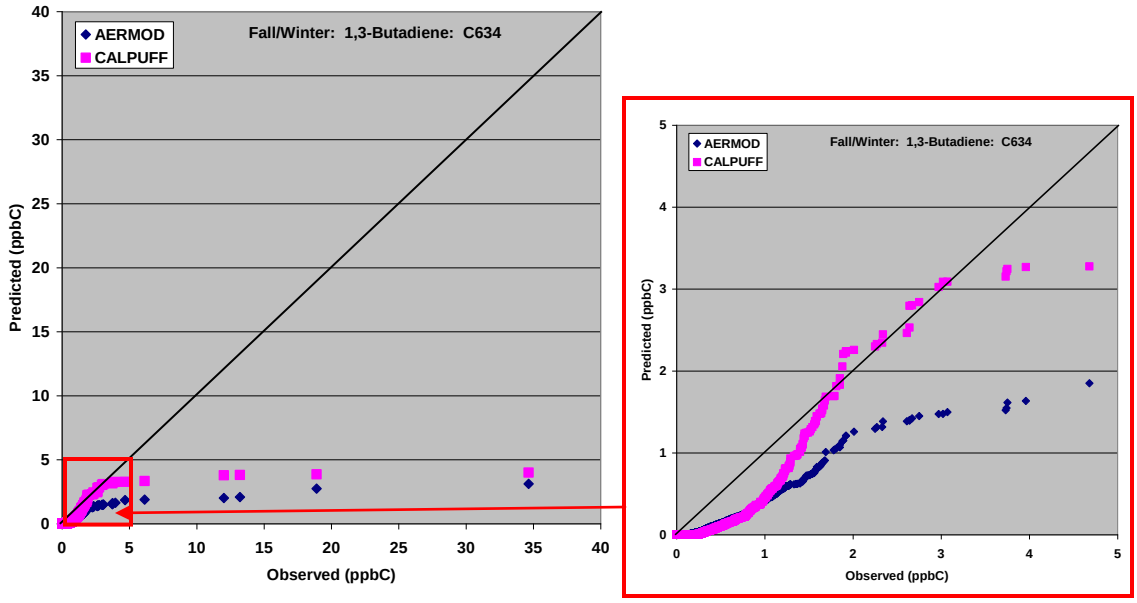
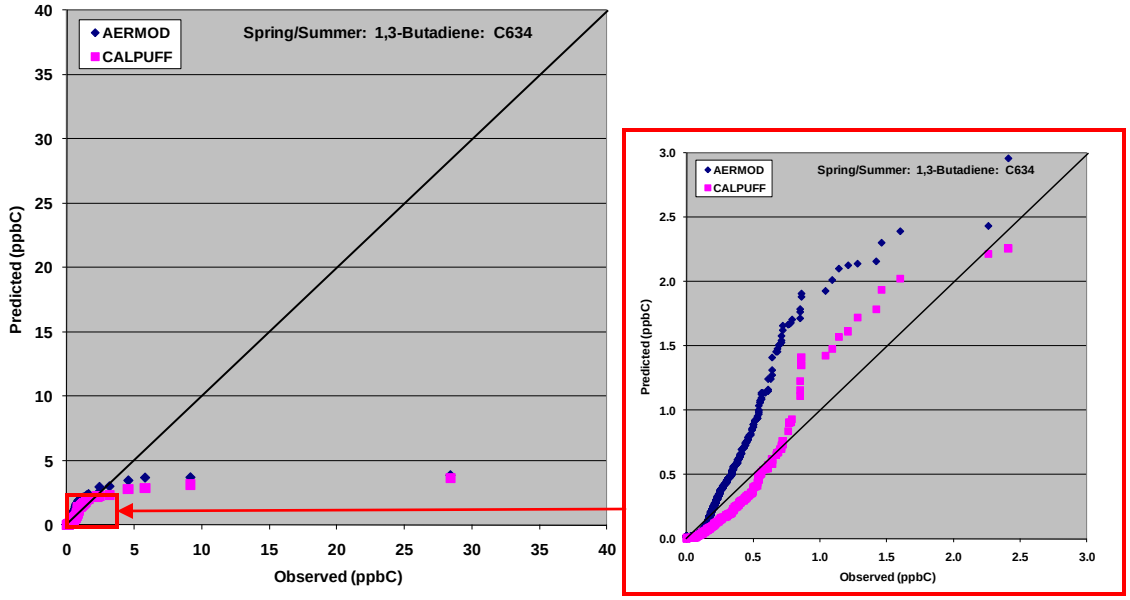


Figure 32. Scatter plots of predicted versus observed 1,3-butadiene concentrations at Oak Park during the (a) spring/summer and (b) fall/winter of 2006 with all anthropogenic emissions sources included in the dispersion models.

(a)



(b)

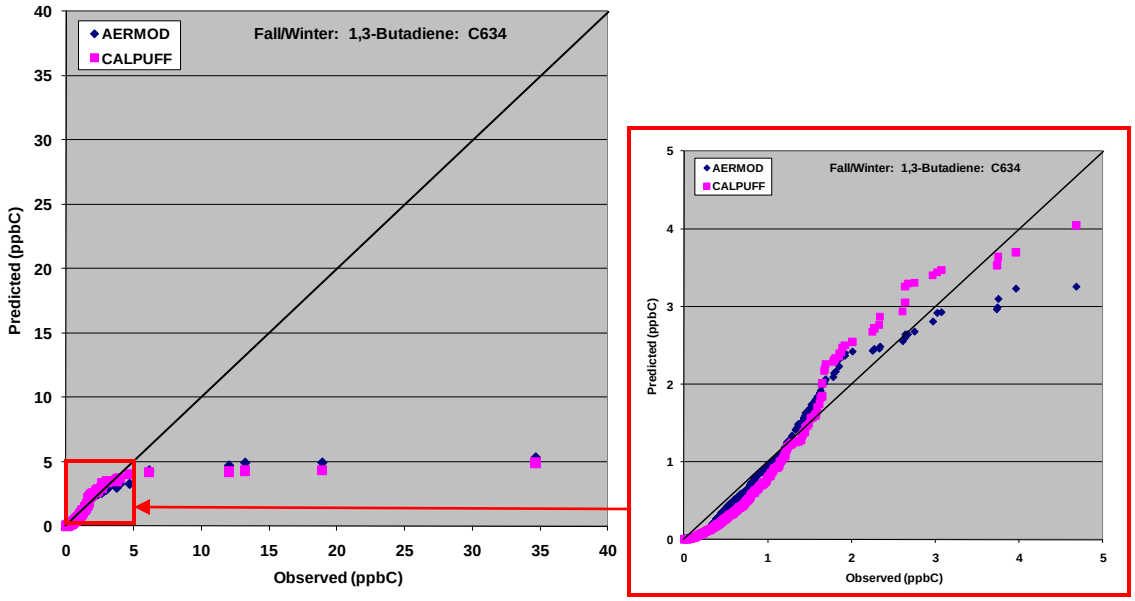
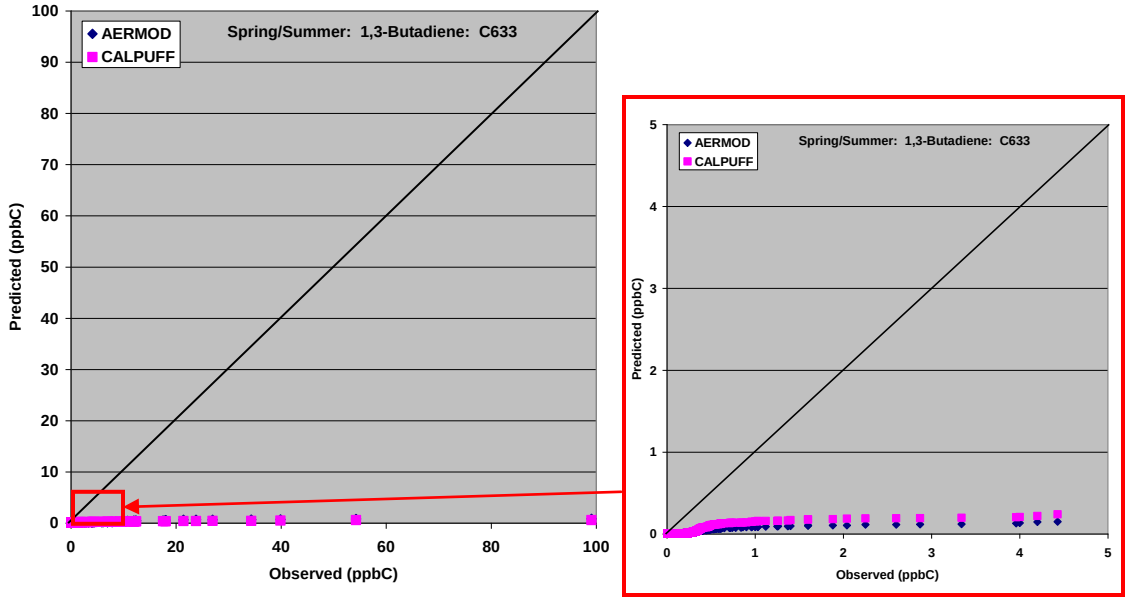


Figure 33. Scatter plots of predicted versus observed 1,3-butadiene concentrations at Solar Estates during the (a) spring/summer and (b) fall/winter of 2006. Only point source emissions were included in the dispersion models.

(a)



(b)

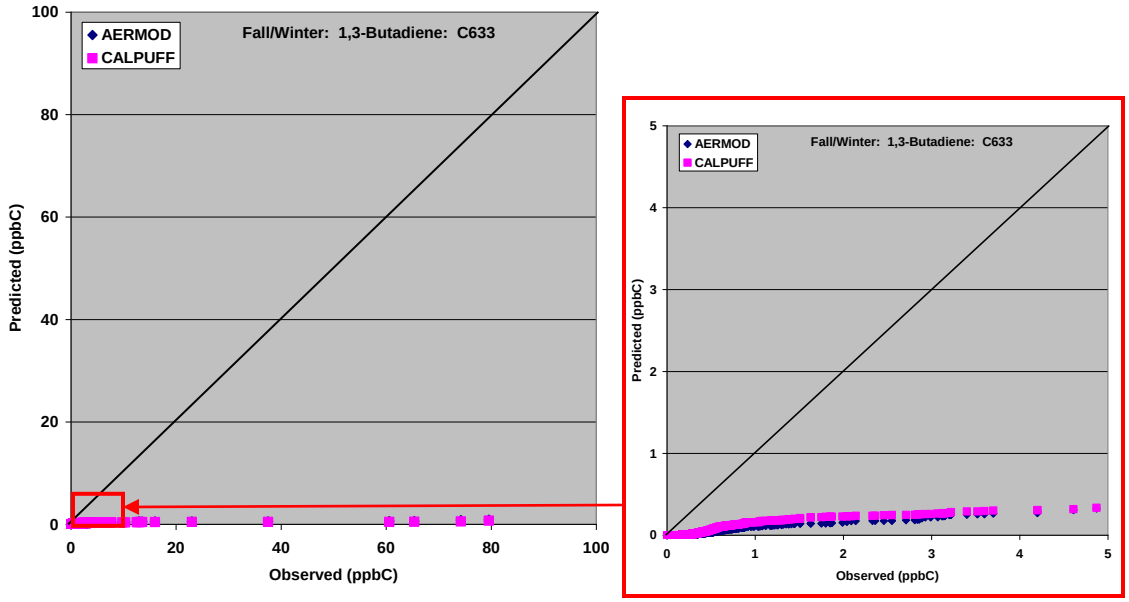
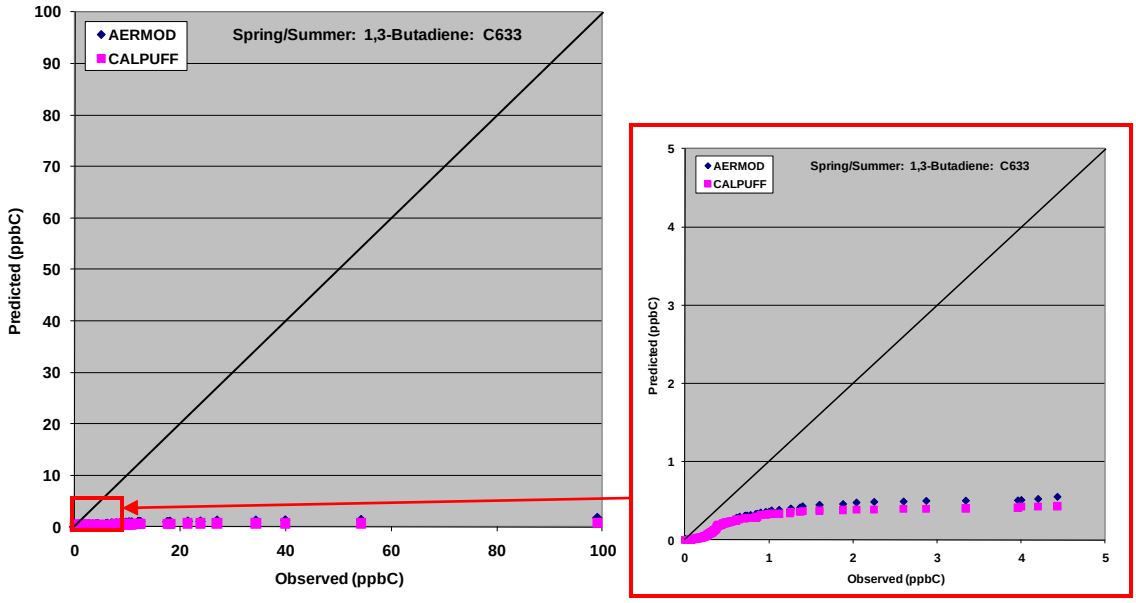


Figure 34. Scatter plots of predicted versus observed 1,3-butadiene concentrations at Solar Estates during the (a) spring/summer and (b) fall/winter of 2006 with all anthropogenic emissions sources included in the dispersion models.

(a)



(b)

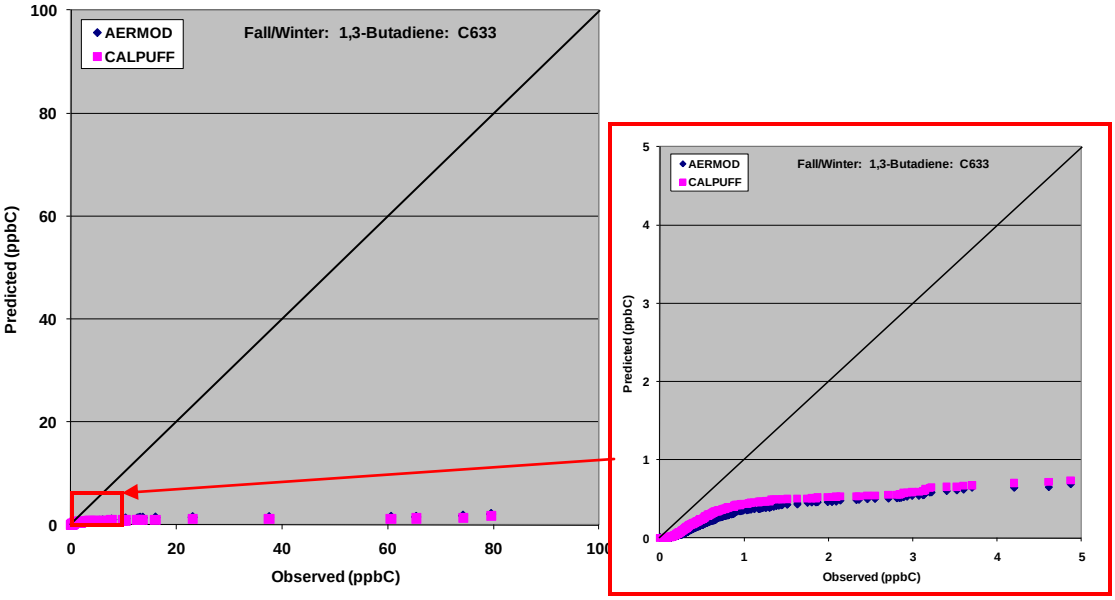
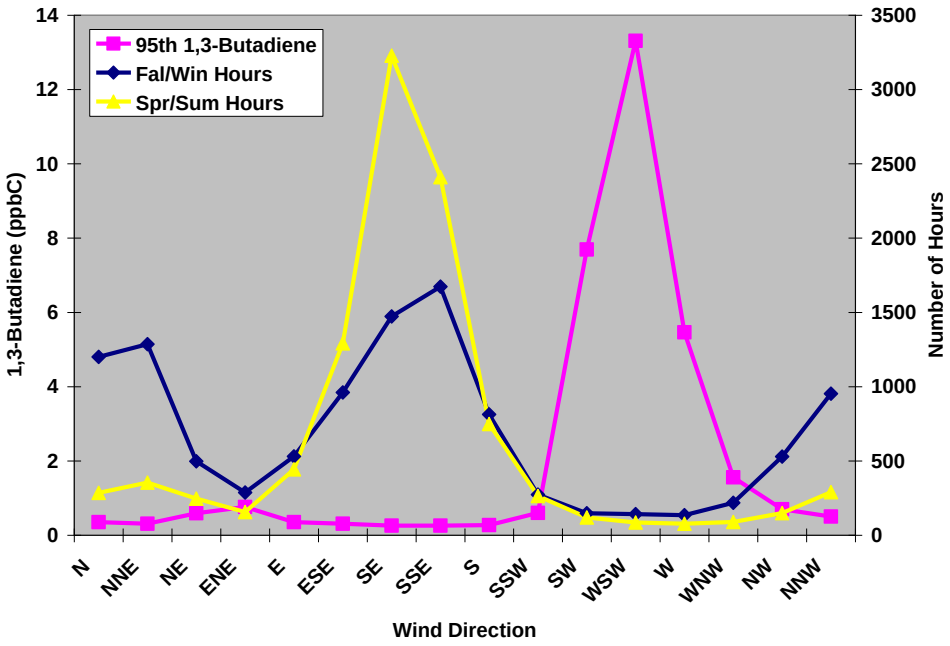


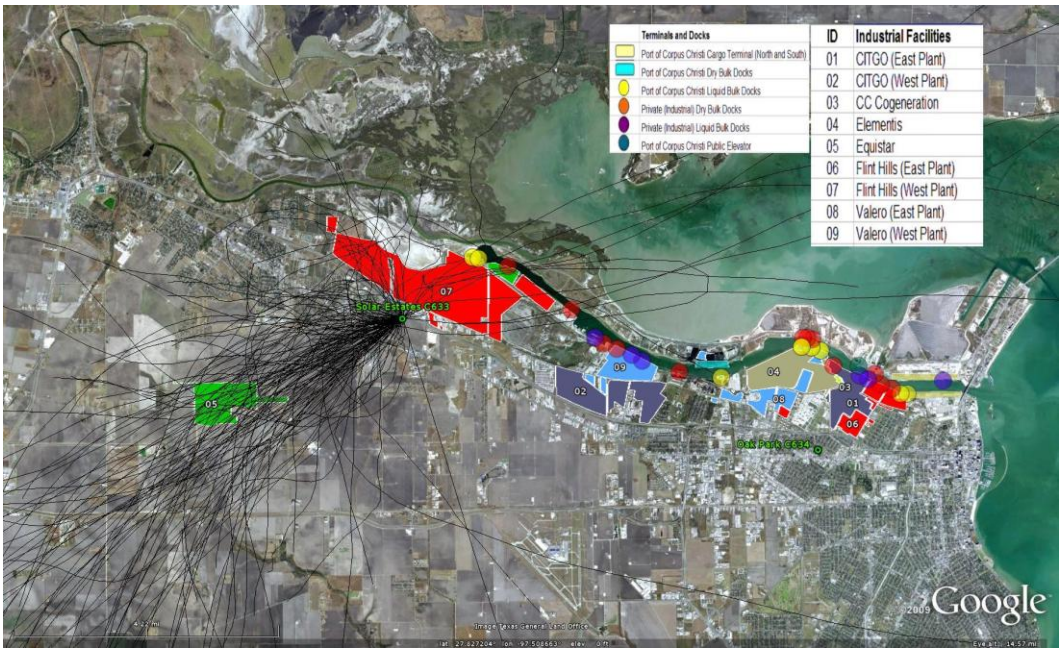
Figure 35. Solar Estates observed 95th percentile 1,3-butadiene concentrations, number of fall/winter hours, and number of spring/summer hours grouped by wind direction during 2006 – 2008.



McGaughey et al. (2009, 2010) generated one-hour back-trajectories during high concentration hours to identify potential emissions source regions that may impact concentrations at Solar Estates. Figure 36 demonstrates that a majority of back-trajectories pass over or to the southeast of the Equistar facility. These results indicated that seasonal variations in the frequency of occurrence of wind directions associated with the transport of industrial emission plumes likely influences observed concentrations at the monitor.

AERMOD and CALPUFF predictions were similar, but not identical, with respect to their agreement with observations at both sites. Comparison of results from modeling with point source emissions only and with all anthropogenic emissions, respectively, to observations at Solar Estates during 2006 indicated a strong under-prediction bias by both models. Inclusion of emissions from area and mobile sources in addition to point sources reduced but did not resolve the under-prediction bias. For example, ratios of mean, 75th percentile, 95th percentile, 99th percentile, and maximum AERMOD or CALPUFF predicted to observed concentrations during the fall/winter of 2006, shown in Table 14, ranged from 0.02 to 0.5 when all anthropogenic emissions sources were modeled, and from 0 to 0.2 when only point source emissions were included. Similar to the results for Oak Park, both models substantially underestimated the observed maximum concentration, which occurred during the spring/summer; the ratios of maximum AERMOD and CALPUFF predicted concentrations to the observed concentration were 0.02 and 0.01, respectively, with all anthropogenic sources include in the modeling, and 0.01 when only point sources were included in the modeling.

Figure 36. Surface back-trajectories as generated by the Corpus Christi Trajectory Analysis Tool for all hours characterized by a 1,3-butadiene concentration greater than or equal to 5 ppbC at Solar Estates during 2006 - 2009.



Collectively, the modeling results suggest the need for future studies aimed at improving the understanding the 1,3-butadiene emissions inventory for Corpus Christi. It is recommended that the reported annual TRI emissions inventories continue to be tracked in conjunction with trends in the ambient measurements from the CCAQAP network. In addition, if a more recent or future year emissions inventory with the same spatial resolution in emission points and full chemical speciation of VOCs as the 2005 TCEQ Photochemical Modeling EI is developed by the State of Texas, it should be utilized for dispersion modeling in the region. The potential for missing industrial emissions information also should be investigated, especially near Solar Estates; observed concentrations may often be associated with non-routine emissions that are not captured by the existing emissions inventories.

(c) Annual Variability in Model Performance between 2006 and 2008. Tables 15 and 16 provide summaries of mean, maximum, 75th, 95th, and 99th percentile observed and AERMOD and CALPUFF predicted 1,3-butadiene concentrations during 2007 and 2008, respectively, at Oak Park and Solar Estates. Predicted concentrations are presented for modeling with stationary point source 1,3-butadiene emissions only and with all anthropogenic 1,3-butadiene emissions (i.e., point, area, and mobile), respectively, from the 2005 TCEQ Photochemical Modeling Inventory.

Annual observed 1,3-butadiene concentrations were generally lower in 2008 than in 2006 at both sites, with marked decreases in both the mean and maximum observed values at Solar Estates. For example, the highest Solar Estates spring/summer 2008 (14.0 ppbC) and fall/winter 2008 (9.8 ppbC) concentrations were 12-14% of the 2006 values. Both models under-predicted observed concentrations throughout the three-year period, assuming constant emissions. However, the agreement between predicted and observed concentrations also improved between 2006 and 2008 (i.e., reduction in the under-prediction bias of the models) as observed concentrations declined. As an example, Figures 37 and 38 shows predicted and observed annual mean concentrations of 1,3-butadiene during this time period at Oak Park and Solar Estates, respectively, with all anthropogenic emissions sources included in the dispersion models. Reported annual air emissions of 1,3-butadiene in 2006, 2007, and 2008 TRI data were 14, 7, and 9 tpy, respectively, indicating lower emissions in 2008 than in 2006.

Table 15. Summary of mean, maximum, 75th, 95th, and 99th percentile observed (OBS) and predicted 1,3-butadiene concentrations from AERMOD (AER) and CALPUFF (CAL) during two seasonal periods at Oak Park and Solar Estates in 2007. Predicted concentrations are presented for modeling with stationary point source emissions only and with all anthropogenic emissions from the 2005 TCEQ Photochemical Modeling Inventory. Ratios of predicted to observed concentrations are shown in parentheses.

Site	Mean (ppbC)			75th Percentile (ppbC)			95th Percentile (ppbC)			99th Percentile (ppbC)			Maximum (ppbC)		
	OBS	AER	CAL	OBS	AER	CAL	OBS.	AER	CAL	OBS	AER	CAL	OBS	AER	CAL
Oak Park															
Spring/Summer															
Point Sources		0.04 (0.2)	0.02 (0.1)		0.02 (0.1)	0.00 (0.00)		0.23 (0.4)	0.08 (0.1)		0.65 (0.6)	0.39 (0.3)		1.67 (0.2)	2.40 (0.4)
All Anthropogenic	0.25	0.13 (0.5)	0.10 (0.4)	0.27	0.07 (0.3)	0.08 (0.3)	0.60	0.54 (0.9)	0.32 (0.5)	1.13	1.58 (1.4)	0.90 (0.8)	6.70	5.01 (0.7)	3.04 (0.5)
Fall/Winter															
Point Sources		0.08 (0.2)	0.08 (0.2)		0.05 (0.1)	0.04 (0.1)		0.36 (0.4)	0.33 (0.4)		1.23 (0.7)	1.90 (1.1)		5.62 (0.1)	4.23 (0.1)
All Anthropogenic	0.38	0.20 (0.5)	0.19 (0.5)	0.40	0.12 (0.3)	0.15 (0.4)	0.82	0.88 (1.1)	0.68 (0.8)	1.71	2.60 (1.5)	2.46 (1.4)	44.62	7.42 (0.2)	4.96 (0.1)
Solar Estates															
Spring/Summer															
Point Sources		0.01 (0.1)	0.01 (0.1)		0.00 (0.0)	0.01 (0.1)		0.04 (0.1)	0.06 (0.2)		0.30 (0.1)	0.24 (0.1)		1.08 (0.01)	0.60 (0.01)
All Anthropogenic	0.26	0.05 (0.2)	0.09 (0.4)	0.14	0.04 (0.3)	0.09 (0.6)	0.35	0.19 (0.5)	0.26 (0.7)	2.83	0.66 (0.2)	0.59 (0.2)	101.13	3.37 (0.03)	1.21 (0.01)
Fall/Winter															
Point Sources		0.01 (0.1)	0.02 (0.1)		0.00 (0.0)	0.01 (0.1)		0.05 (0.1)	0.11 (0.2)		0.23 (0.1)	0.28 (0.2)		1.03 (0.03)	0.50 (0.02)
All Anthropogenic	0.22	0.06 (0.3)	0.12 (0.6)	0.19	0.04 (0.2)	0.12 (0.6)	0.49	0.23 (0.5)	0.45 (0.9)	1.69	0.79 (0.5)	0.86 (0.5)	29.43	2.14 (0.1)	1.80 (0.1)

Table 16. Summary of mean, maximum, 75th, 95th, and 99th percentile observed (OBS) and predicted 1,3-butadiene concentrations from AERMOD (AER) and CALPUFF (CAL) during two seasonal periods at Oak Park and Solar Estates in 2008. Predicted concentrations are presented for modeling with stationary point source emissions only and with all anthropogenic emissions from the 2005 TCEQ Photochemical Modeling Inventory. Ratios of predicted to observed concentrations are shown in parentheses.

Site	Mean (ppbC)			75th Percentile (ppbC)			95th Percentile (ppbC)			99th Percentile (ppbC)			Maximum (ppbC)		
	OBS	AER	CAL	OBS	AER	CAL	OBS.	AER	CAL	OBS	AER	CAL	OBS	AER	CAL
Oak Park															
Spring/Summer															
Point Sources		0.03	0.01		0.02	0.00		0.14	0.06		0.34	0.28		1.80	2.42
		(0.2)	(0.1)		(0.1)	(0.0)		(0.5)	(0.2)		(0.5)	(0.4)		(0.2)	(0.2)
All Anthropogenic	0.13	0.08	0.07	0.14	0.06	0.06	0.29	0.36	0.20	0.70	0.89	0.71	10.01	2.99	2.66
		(0.6)	(0.5)		(0.4)	(0.4)		(1.2)	(0.7)		(1.3)	(1.0)		(0.3)	(0.3)
Fall/Winter															
Point Sources		0.06	0.06		0.05	0.04		0.27	0.21		0.75	1.20		2.71	3.66
		(0.3)	(0.3)		(0.2)	(0.2)		(0.5)	(0.4)		(0.6)	(0.9)		(0.5)	(0.7)
All Anthropogenic	0.21	0.16	0.15	0.25	0.12	0.11	0.60	0.70	0.53	1.33	1.81	1.83	5.62	4.72	4.01
		(0.8)	(0.7)		(0.5)	(0.4)		(1.2)	(0.9)		(1.4)	(1.4)		(0.8)	(0.7)
Solar Estates															
Spring/Summer															
Point Sources		0.01	0.01		0.00	0.00		0.02	0.04		0.10	0.21		1.22	0.54
		(0.1)	(0.1)		(0.0)	(0.0)		(0.1)	(0.2)		(0.2)	(0.3)		(0.1)	(0.04)
All Anthropogenic	0.06	0.03	0.07	0.07	0.02	0.07	0.17	0.09	0.21	0.62	0.40	0.61	13.97	1.64	1.18
		(0.5)	(1.2)		(0.3)	(1.0)		(0.5)	(1.2)		(0.7)	(1.0)		(0.1)	(0.1)
Fall/Winter															
Point Sources		0.01	0.02		0.01	0.01		0.04	0.14		0.18	0.35		0.96	0.58
		(0.1)	(0.1)		(0.1)	(0.1)		(0.1)	(0.4)		(0.2)	(0.4)		(0.1)	(0.1)
All Anthropogenic	0.14	0.05	0.11	0.14	0.05	0.11	0.32	0.19	0.47	0.95	0.62	0.95	9.75	5.62	2.01
		(0.4)	(0.8)		(0.4)	(0.8)		(0.6)	(1.5)		(0.7)	(1.0)		(0.6)	(0.2)

Figure 37. Predicted and observed annual mean 1,3-butadiene concentrations at Oak Park during 2006 through 2008 with all anthropogenic emissions sources included in the dispersion models. Note that predictions assume emissions remain constant from 2006-2008.

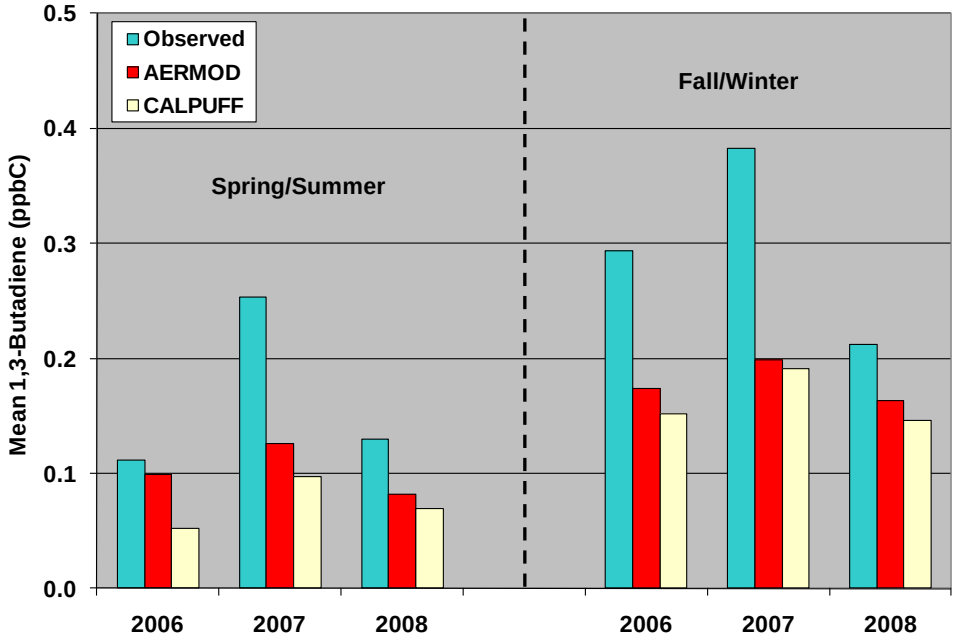
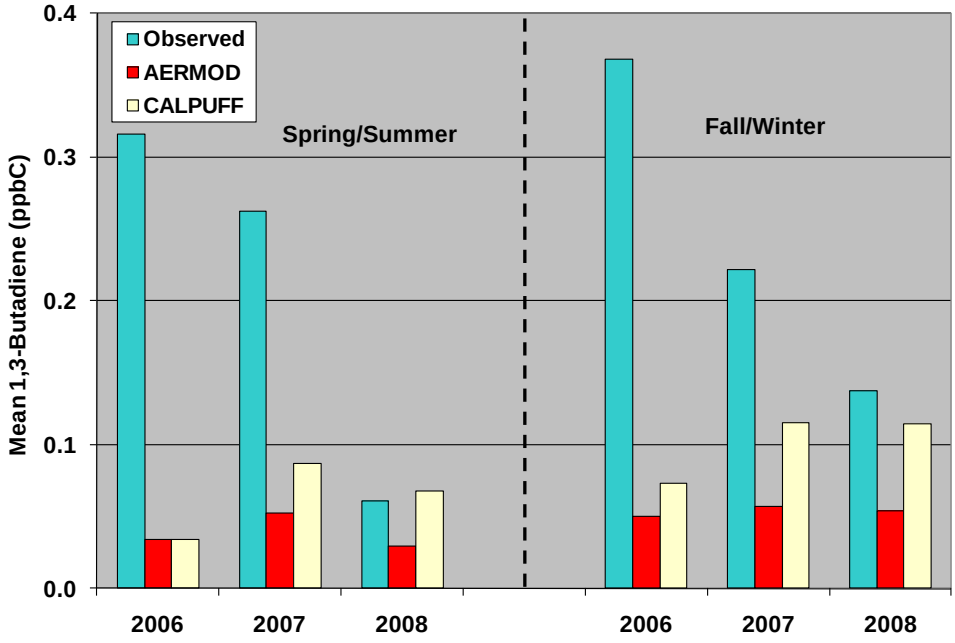


Figure 38. Predicted and observed annual mean 1,3-butadiene concentrations at Solar Estates during 2006 through 2008 with all anthropogenic emissions sources included in the dispersion models. Note that predictions assume emissions remain constant from 2006-2008.

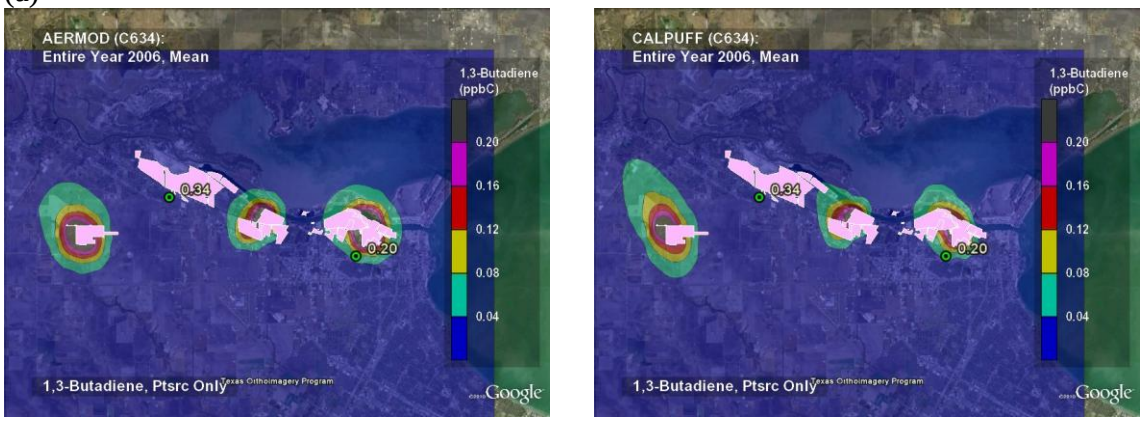


(d) Spatial Maps of Predicted Concentrations during 2006. Figures 39, 41, 43, and 45 show annual mean, 75th percentile, 95th percentile, and maximum predicted 1,3-butadiene concentrations, respectively, with point source emissions only and with all anthropogenic emissions using on-site meteorological data from the Oak Park monitor for AERMOD. Figures 40, 42, 44, and 46 show annual mean 75th percentile, 95th percentile, and maximum predicted 1,3-butadiene concentrations, respectively, with point source emissions only and with all anthropogenic emissions using on-site meteorological data from the Solar Estates monitor for AERMOD.

Spatial maps of predicted 1,3-butadiene concentrations during 2006 were similar for both models, with the exception of annual maximum concentrations that were affected by AERMOD's restriction of on-site meteorological data from a single site. The maps and surface wind back trajectories (reference Figure 36) indicate that Equistar is an important emissions source, but neither of the current auto-GC sites are well positioned to characterize concentrations close to this source. The maps also indicate that neither monitor is positioned to capture 1,3-butadiene concentrations within the Dona Park area more centrally located in the Ship Channel industrial complex. Although total non-methane hydrocarbon measurements are made at Dona Park, chemically speciated measurements, such as those made with an auto-GC, are not routinely determined. Spatial maps of 1,3-butadiene concentrations indicated broader areas of influence when all anthropogenic emissions were included in the modeling than when only point sources were included, consistent with the contributions of area and/or mobile sources to the inventories for this pollutant. A mobile monitoring effort may provide insights on the magnitude and spatial gradients of 1,3-butadiene concentrations in the region.

Figure 39. Predicted annual mean 1,3-butadiene concentrations in the receptor grid (colored area) from AERMOD (left) and CALPUFF (right) for 2006 using on-site meteorological data from the Oak Park (C634) monitor for AERMOD and (a) point source emissions only and (b) all anthropogenic emissions. Property boundaries of the stationary point sources are shown in pink.

(a)



(b)

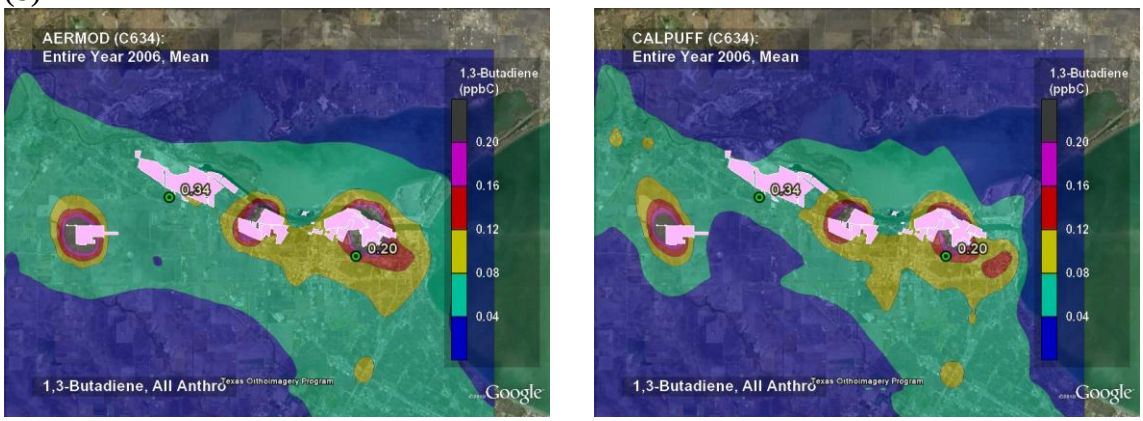
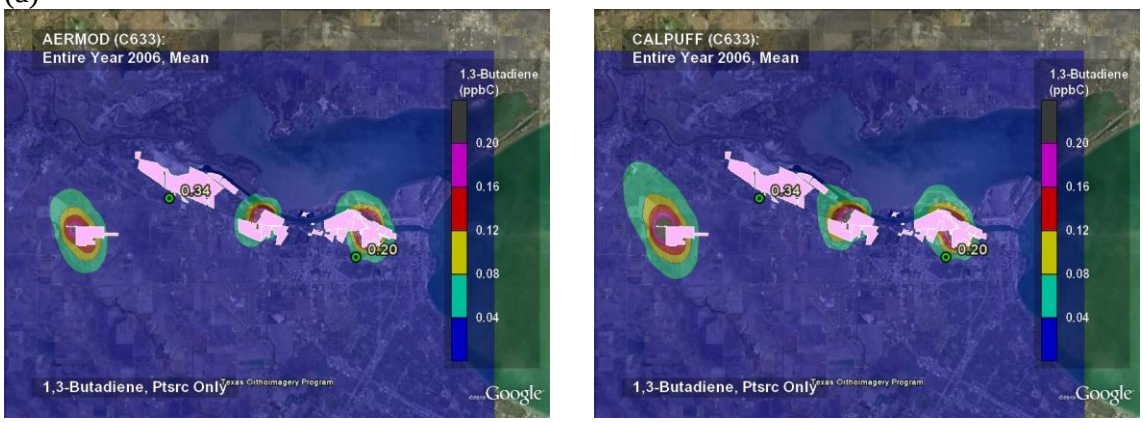


Figure 40. Predicted annual mean 1,3-butadiene concentrations in the receptor grid (colored area) from AERMOD (left) and CALPUFF (right) for 2006 using on-site meteorological data from the Solar Estates (C633) monitor for AERMOD and (a) point source emissions only and (b) all anthropogenic emissions. Property boundaries of the stationary point sources are shown in pink.

(a)



(b)

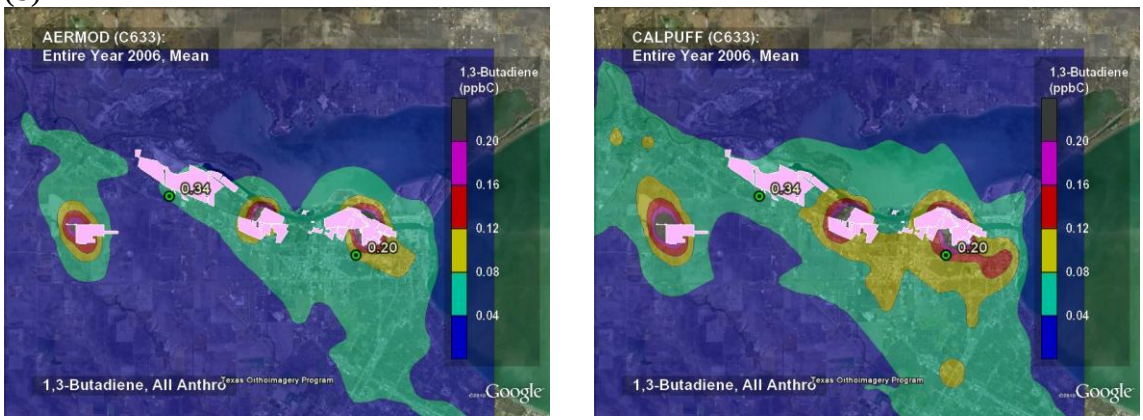
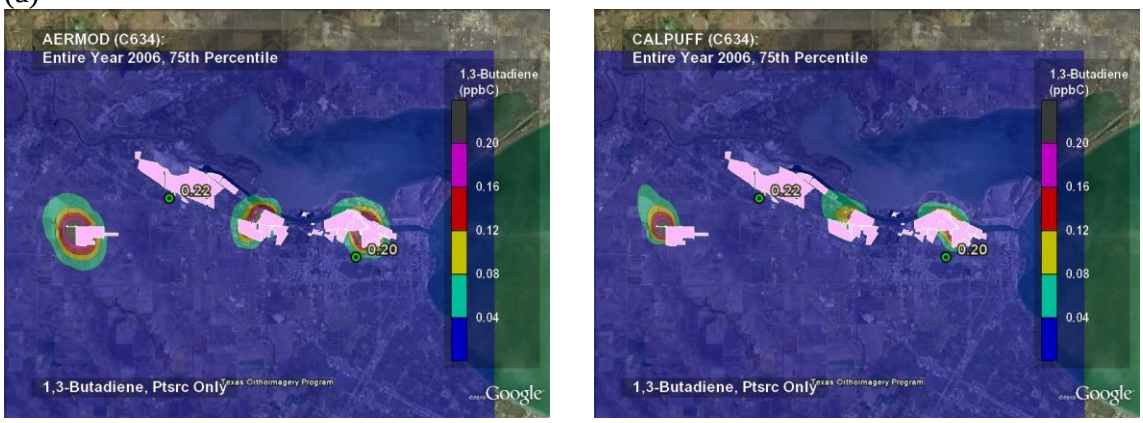


Figure 41. Predicted annual 75th percentile 1,3-butadiene concentrations in the receptor grid (colored area) from AERMOD (left) and CALPUFF (right) for 2006 using on-site meteorological data from the Oak Park (C634) monitor for AERMOD and (a) point source emissions only and (b) all anthropogenic emissions. Property boundaries of the stationary point sources are shown in pink.

(a)



(b)

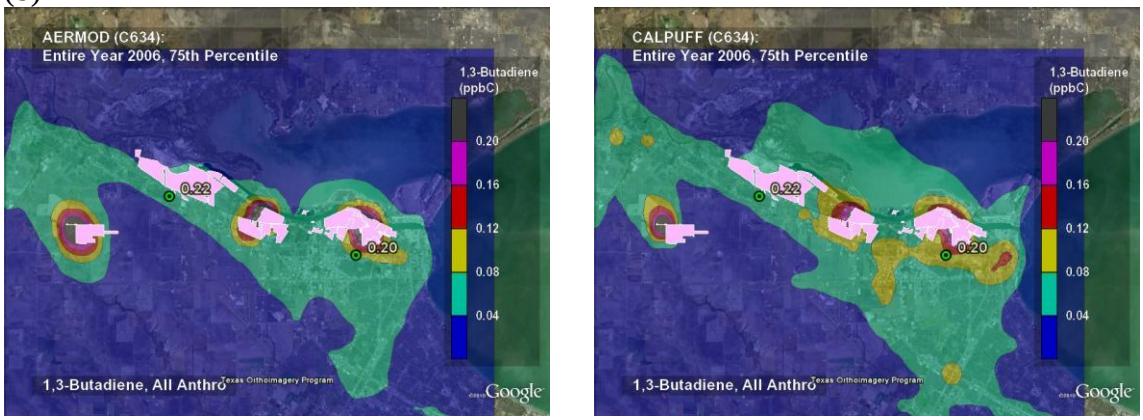
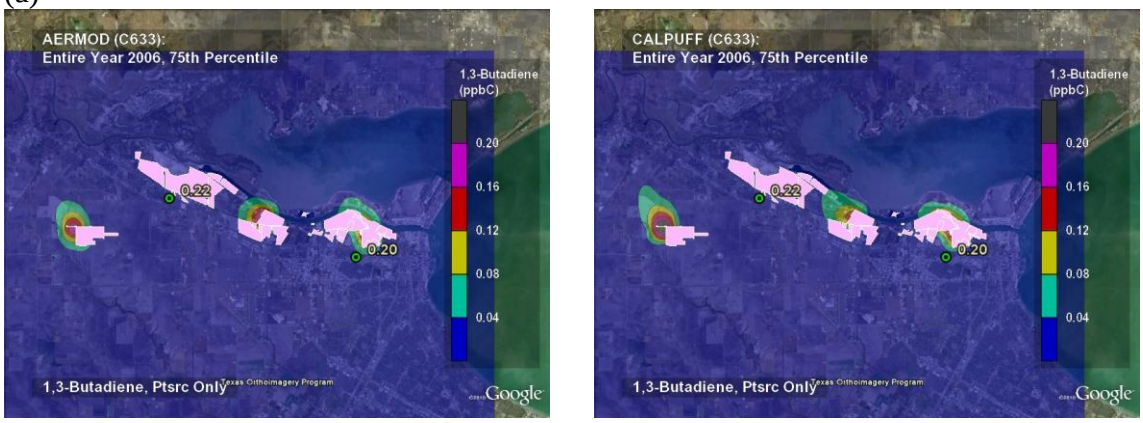


Figure 42. Predicted annual 75th percentile 1,3-butadiene concentrations in the receptor grid (colored area) from AERMOD (left) and CALPUFF (right) for 2006 using on-site meteorological data from the Solar Estates (C633) monitor for AERMOD and (a) point source emissions only and (b) all anthropogenic emissions. Property boundaries of the stationary point sources are shown in pink.

(a)



(b)

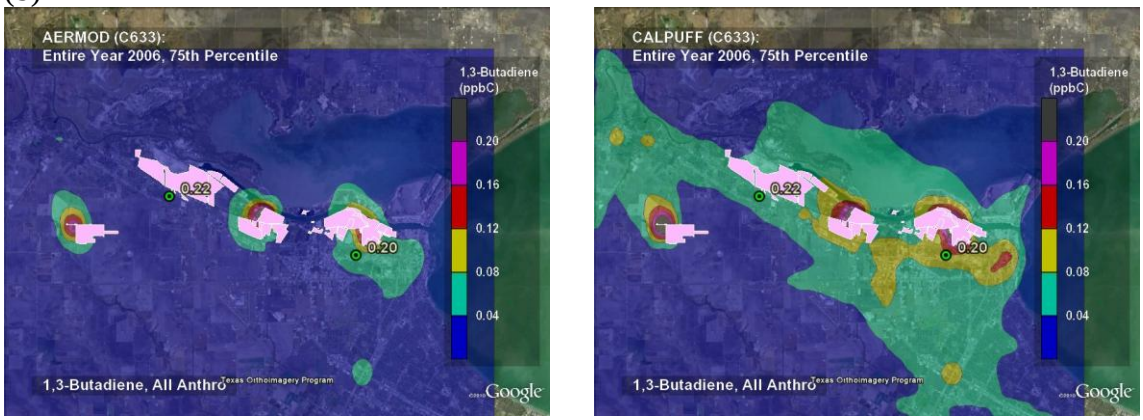
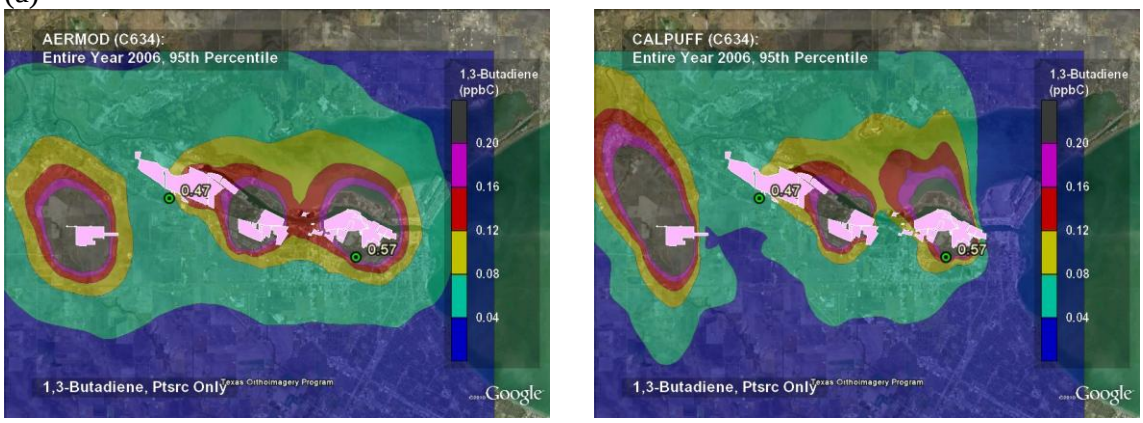


Figure 43. Predicted annual 95th percentile 1,3-butadiene concentrations in the receptor grid (colored area) from AERMOD (left) and CALPUFF (right) for 2006 using on-site meteorological data from the Oak Park (C634) monitor for AERMOD and (a) point source emissions only and (b) all anthropogenic emissions. Property boundaries of the stationary point sources are shown in pink.

(a)



(b)

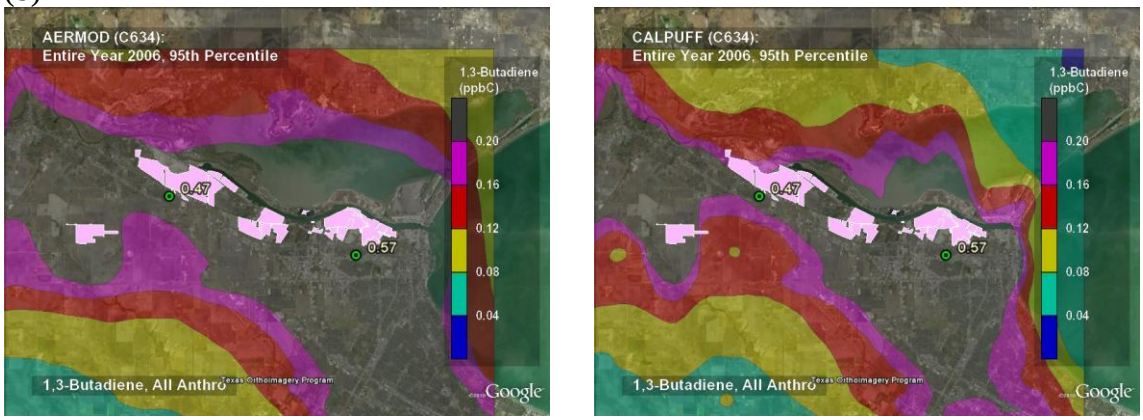
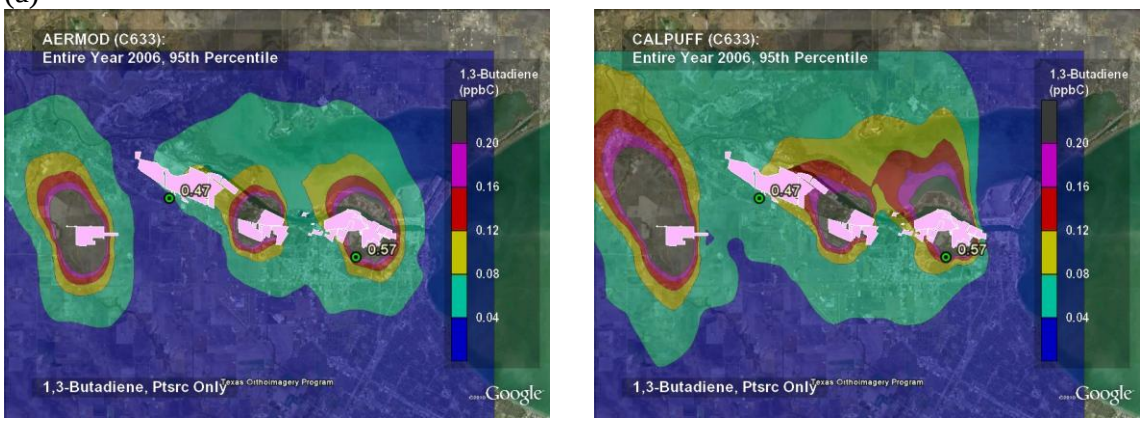


Figure 44. Predicted annual 95th percentile 1,3-butadiene concentrations in the receptor grid (colored area) from AERMOD (left) and CALPUFF (right) for 2006 using on-site meteorological data from the Solar Estates (C633) monitor for AERMOD and (a) point source emissions only and (b) all anthropogenic emissions. Property boundaries of the stationary point sources are shown in pink.

(a)



(b)

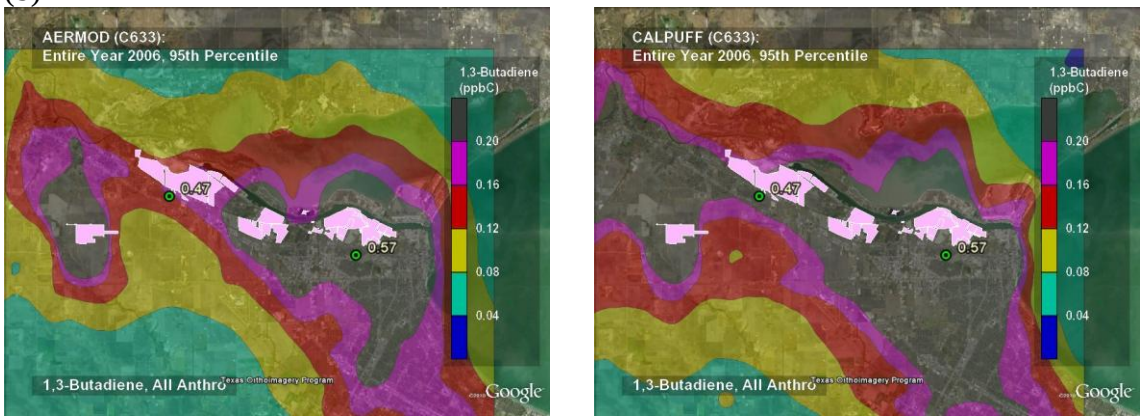
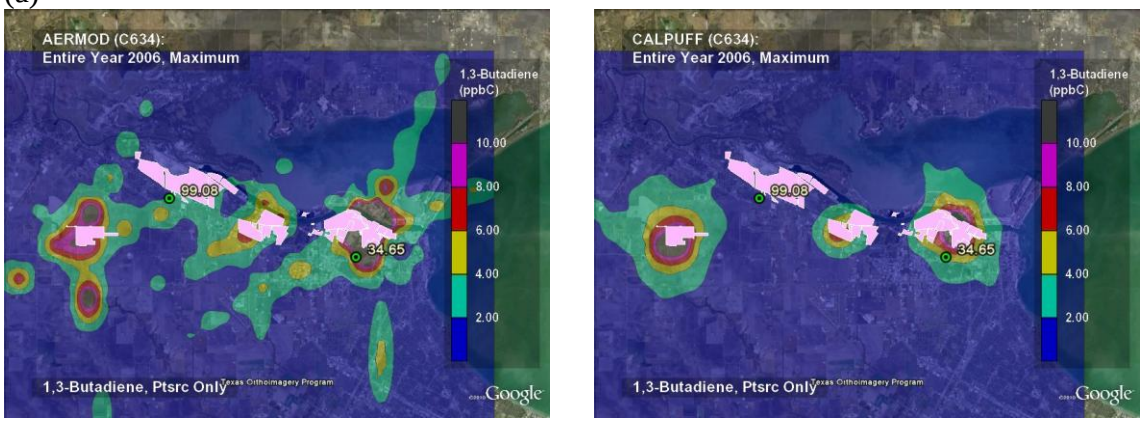


Figure 45. Predicted annual maximum1,3-butadiene concentrations in the receptor grid (colored area) from AERMOD (left) and CALPUFF (right) for 2006 using on-site meteorological data from the Oak Park (C634) monitor for AERMOD and (a) point source emissions only and (b) all anthropogenic emissions. Property boundaries of the stationary point sources are shown in pink.

(a)



(b)

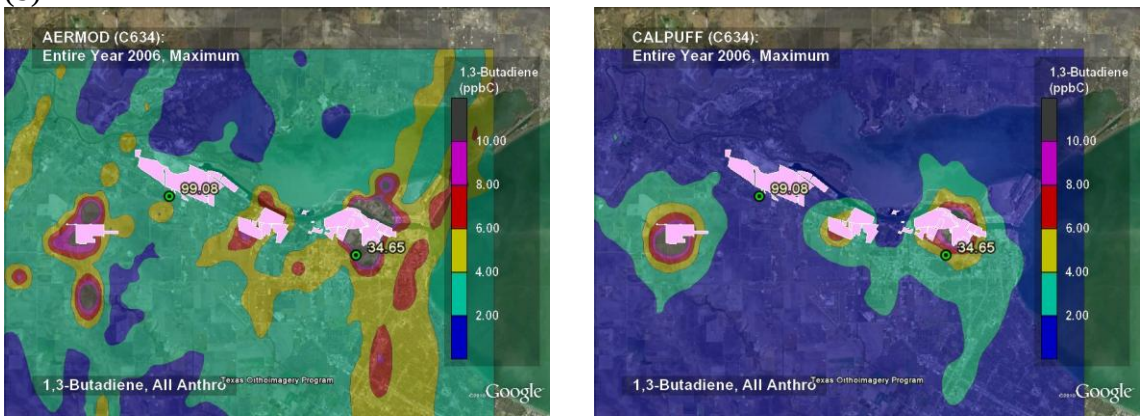
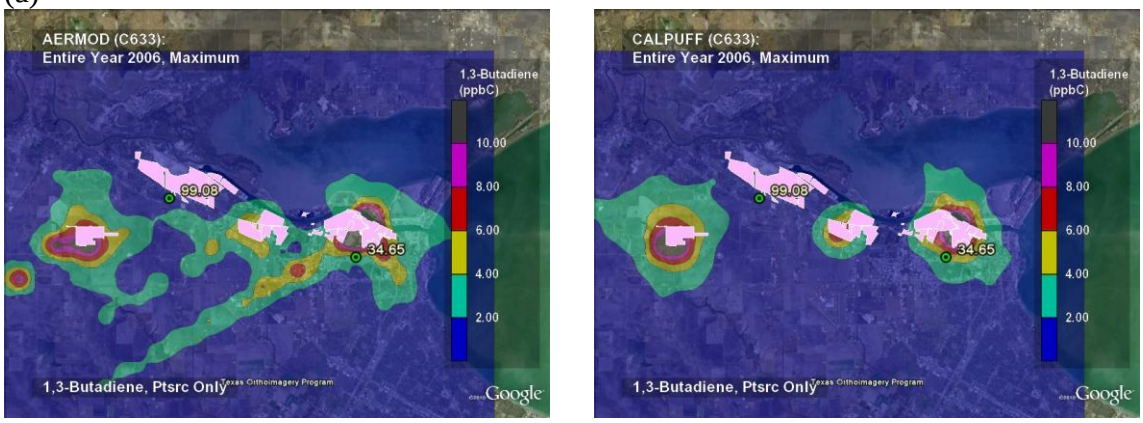
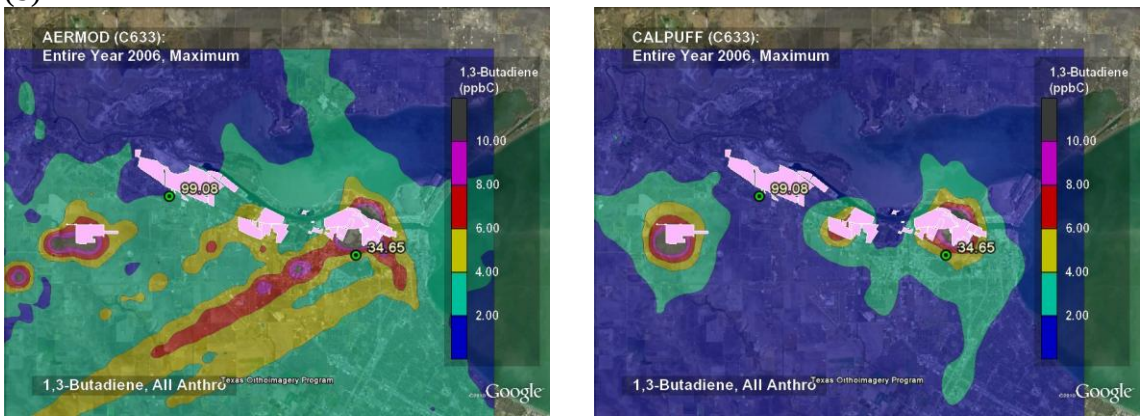


Figure 46. Predicted annual maximum 1,3-butadiene concentrations in the receptor grid (colored area) from AERMOD (left) and CALPUFF (right) for 2006 using on-site meteorological data from the Solar Estates (C633) monitor for AERMOD and (a) point source emissions only and (b) all anthropogenic emissions. Property boundaries of the stationary point sources are shown in pink.

(a)



(b)



4.3 Sensitivity of AERMOD Predictions to the Calm Wind Speed Threshold

CALPUFF can be used to predict concentrations during calm conditions; however, AERMOD requires a calm wind speed threshold below which the model does not provide predictions. For the analyses presented in Sections 4.1 and 4.2, the AERMOD calm threshold was set at 0.22 mps, which was the starting wind speed for wind speed sensor used at the CCAQP monitoring sites. The validity of AERMOD predictions at wind speeds as low as 0.22 mps is uncertain. This uncertainty is primarily related to the applicability of the Gaussian assumption at relatively low wind speeds. Barclay (2008) noted that calm conditions (wind speeds < 2 mps) historically have not been an area of focus and highlighted the need for sub-hourly meteorological measurements to capture the variability during low wind speeds.

A sensitivity study was conducted to investigate benzene model performance associated with an increase of the AERMOD calm wind speed threshold from 0.22 mps to 1.0 mps. Only point source emissions were included in these simulations. In order to provide consistent comparisons between observed and predicted concentrations, analyses were conducted using only those hours with valid observed, CALPUFF, and AERMOD concentrations. It is important to note that only the AERMOD configuration was altered according to the selected calms threshold. However, because only hours with valid observed, CALPUFF, and AERMOD concentrations were compared, measured and CALPUFFF predicted concentrations reported in this sensitivity study had the potential to change as well.

Mean and maximum observed and predicted benzene concentrations at Oak Park using calm wind speed thresholds of 0.22 mps and 1.0 mps are presented in Figure 47. Figure 48 presents analogous results for Solar Estates. Observed concentrations show little change compared to larger reductions in predicted concentrations. In contrast, AERMOD and CALPUFF mean and maximum concentrations decrease when the calm wind speed threshold is increased to 1.0 mps. As described in Sections 4.1 and 4.2, AERMOD and CALPUFF tended to under-predict observed benzene concentrations at high wind speeds and over-predict concentrations at low wind speeds when the AERMOD calm wind speed threshold was set to 0.22 mps. The removal of hours with low wind speeds associated with an increase in the calm wind speed threshold reduces the number of hours with an over-prediction bias, resulting in a larger under-prediction of modeled concentrations relative to observations. Spatial maps of predicted 2006 annual mean concentrations for AERMOD using Oak Park meteorology, AERMOD using Solar Estates meteorology, and CALPUFF are shown in Figure 49. Although the area with predicted concentrations greater than 1 ppbC contracts for the 1.0 mps threshold relative to the 0.22 mps threshold, the overall spatial patterns are similar.

At this time, it is recommended that the analyses for Corpus Christi continue to apply the 0.22 mps threshold for AERMOD because it is consistent with the starting wind speed of the CCAQP network wind speed sensors. It is important to recognize that assumptions about the AERMOD calms threshold will influence model predictions and interpretation of performance. Stakeholders should continue to track emerging studies in the literature or specific guidance by the TCEQ and the EPA.

Figure 47. Observed, AERMOD, and CALPUFF mean benzene concentrations for 2006 at Oak Park and Solar Estates using calm wind speed thresholds of 0.22 mps and 1.0 mps. Only point source emissions are included in the dispersion models.

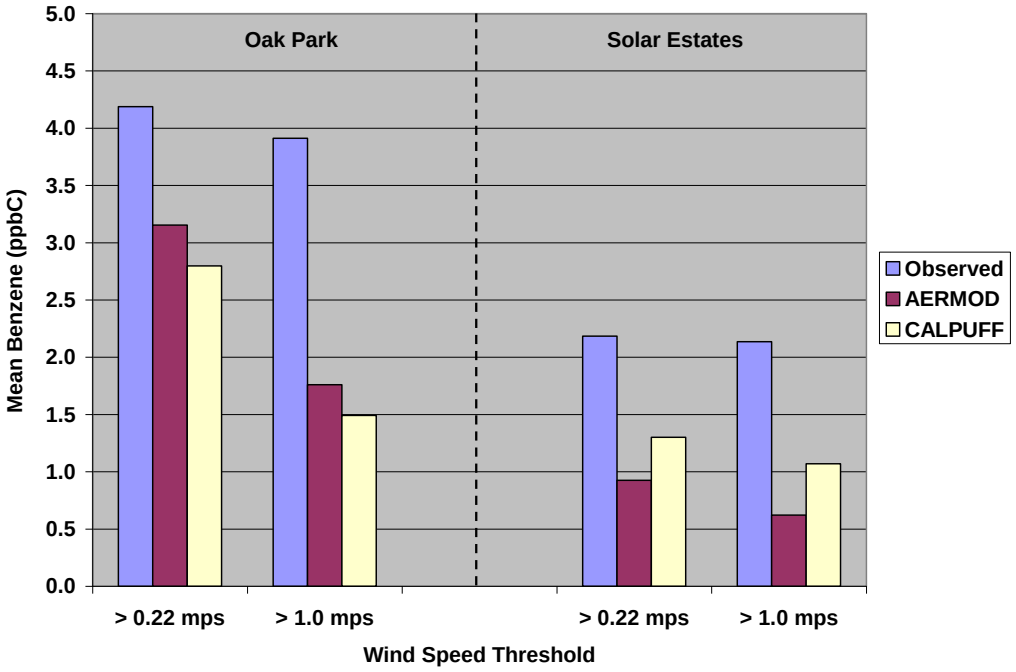


Figure 48. Observed, AERMOD, and CALPUFF maximum benzene concentrations for 2006 at Oak Park and Solar Estates using calm wind speed thresholds of 0.22 mps and 1.0 mps. Only point source emissions are included in the dispersion models.

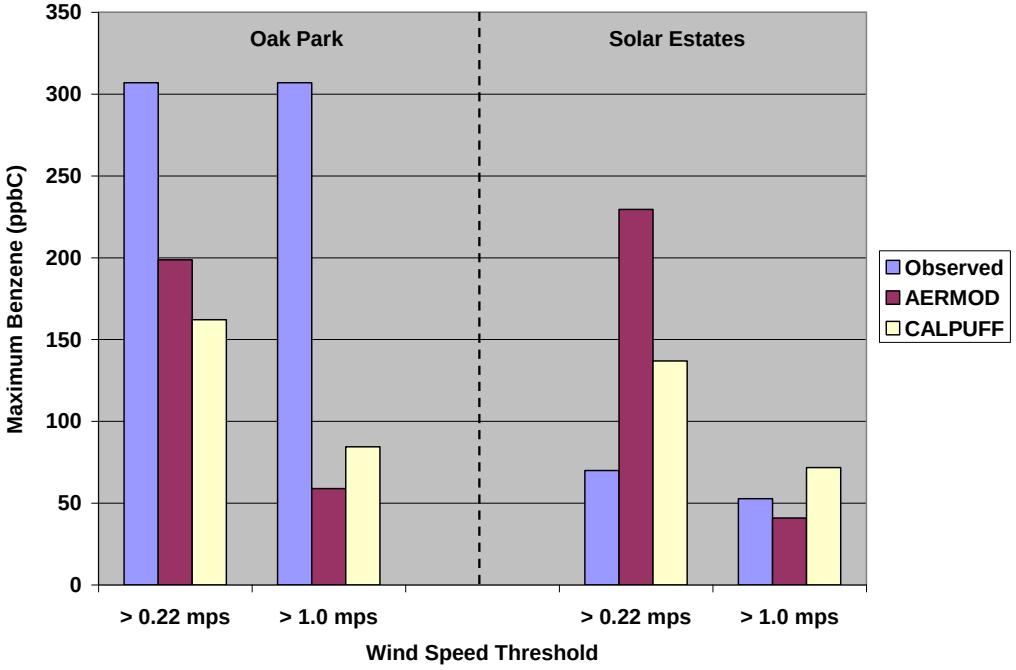
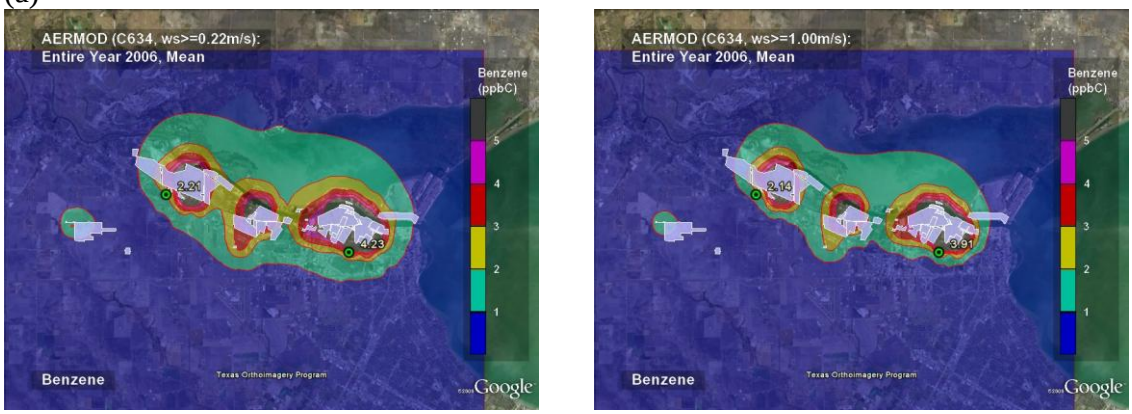
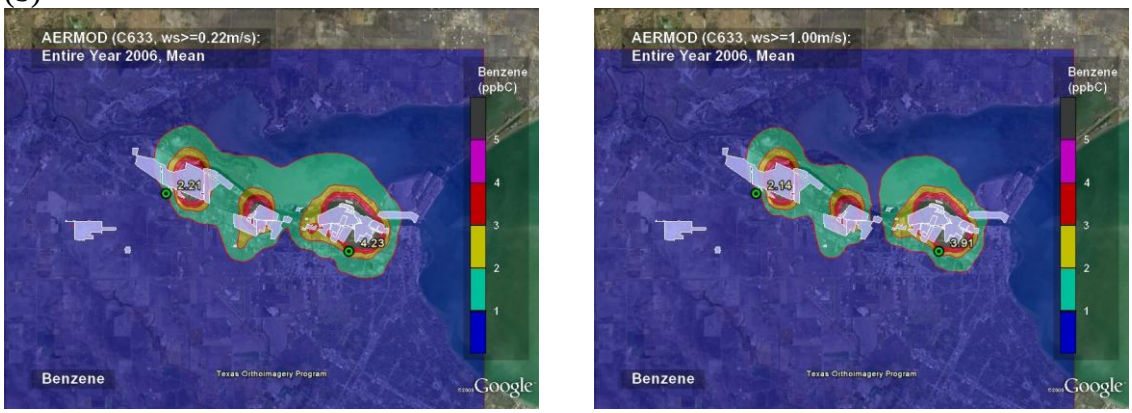


Figure 49. Predicted annual mean benzene concentrations in the receptor grid (colored area) for 2006 for (a) AERMOD (using Oak Park meteorology), (b) AERMOD (using Solar Estates meteorology), and (c) CALPUFF based on two calm wind speed thresholds of 0.22 mps (left) and 1.0 mps (right). Only point source emissions are included in the dispersion models. Property boundaries of the stationary point sources are shown in gray.

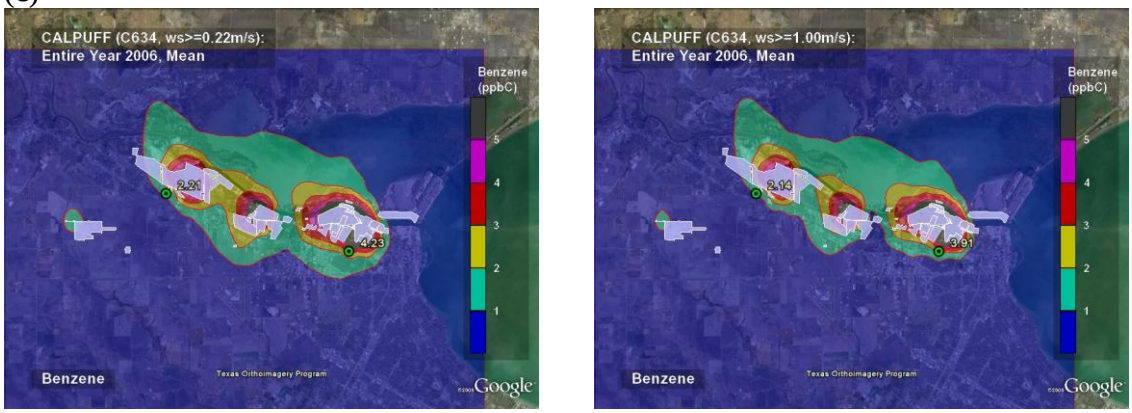
(a)



(b)



(c)



4.4 Sensitivity of AERMOD Predictions to Land Cover Characterization

Atmospheric dispersion parameters that vary by land cover can impact predicted surface concentrations. The AERMOD modeling system requires the specification of land surface characteristics including albedo (the fraction of total incident solar radiation reflected by the surface back to space without absorption), Bowen ratio (the ratio of sensible heat flux to latent heat flux), and surface roughness (the characteristic length related to the height of obstacles to the wind flow or the height at which the mean horizontal wind speed is zero based on a logarithmic profile).

Albedo and Bowen ratios used for this study were obtained from the TCEQ (ftp://ftp.tceq.state.tx.us/pub/OPRR/APD/AERMET/AERMETv06341/BackgroundInformation/counties.xls) for Nueces County. The roughness lengths of 0.5 meters and 1.0 meters for Solar Estates and Oak Park, respectively, were chosen following TCEQ guidance (http://www.tceq.com/permitting/air/modeling/aermet.html) that provided a generalized categorization of land cover in the immediate vicinity of the monitors.

Although not used for this project, the EPA's AERSURFACE tool, which is distributed with the AERMOD system, uses USGS National Land Cover Data for 1992 to determine land cover types for a user-specified location. A look-up table of surface characteristics that vary by season and land cover provides the values necessary to calculate roughness length, albedo, and Bowen ratio. AERSURFACE calculates surface roughness by sector for a default upwind distance of one kilometer surrounding the monitoring site. Bowen ratio and albedo are calculated based on land cover data within a 10 km x 10 km region centered on the monitoring site. Table 17 presents the AERSURFACE results for Oak Park and Solar Estates. Figure 50 presents the 1992 USGS land cover for the 10 km x 10 km regions surrounding the Solar Estates and Oak Park monitors. The land cover varies substantially throughout the 10 km x 10 km domains. This highlights a challenge of using the AERMOD model, which assumes that both the meteorological and land cover conditions are similar throughout the entire 30 km x 30 km modeling domain used in this project. In order to determine the sensitivity of AERMOD predictions to land cover characteristics, predicted benzene concentrations using the TCEQ and AERSURFACE datasets were compared. Only point source emissions were included in the dispersion modeling. The results of these limited AERMOD sensitivity simulations (not shown here) indicated that predicted surface concentrations were most sensitive to surface roughness length but were relatively insensitive to albedo and Bowen ratio.

Comparison of predicted hourly benzene concentrations at Oak Park during 2006 for the TCEQ and AERSURFACE datasets indicated relatively small differences except at higher concentrations, as shown in Figure 51; mean benzene concentrations using the TCEQ and AERSURFACE data were 3.15 ppbC and 3.41 ppbC, respectively. At Solar Estates, AERMOD predictions using AERSURFACE were relatively greater than those using the TCEQ data. Predicted annual mean benzene concentrations at Solar Estates using the TCEQ and AERSURFACE data were 0.89 ppbC and 1.25 ppbC, respectively. Maps of predicted annual mean concentrations during 2006 using the two land cover datasets are shown in Figure 52. AERMOD predictions using Solar Estates

Table 17. Monthly land surface characteristics calculated by AERSURFACE for (a) Solar Estates and (b) Oak Park. The TCEQ-derived land surface characteristics are provided beneath each table.

(a) Solar Estates

		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Albedo		0.16	0.16	0.14	0.14	0.14	0.17	0.17	0.17	0.17	0.17	0.17	0.16
Bowen ratio		0.47	0.47	0.31	0.31	0.31	0.37	0.37	0.37	0.47	0.47	0.47	0.47
Surface Roughness	1	0.245	0.245	0.29	0.29	0.29	0.443	0.443	0.443	0.443	0.443	0.443	0.245
Surface Roughness	2	0.083	0.083	0.125	0.125	0.125	0.229	0.229	0.229	0.229	0.229	0.229	0.083
Surface Roughness	3	0.083	0.083	0.112	0.112	0.112	0.254	0.254	0.254	0.254	0.254	0.254	0.083
Surface Roughness	4	0.072	0.072	0.098	0.098	0.098	0.304	0.304	0.304	0.304	0.304	0.304	0.072
Surface Roughness	5	0.021	0.021	0.031	0.031	0.031	0.196	0.196	0.196	0.196	0.196	0.196	0.021
Surface Roughness	6	0.029	0.029	0.042	0.042	0.042	0.223	0.223	0.223	0.223	0.223	0.223	0.029
Surface Roughness	7	0.031	0.031	0.048	0.048	0.048	0.21	0.21	0.21	0.21	0.21	0.21	0.031
Surface Roughness	8	0.055	0.055	0.081	0.081	0.081	0.263	0.263	0.263	0.263	0.263	0.263	0.055
Surface Roughness	9	0.282	0.282	0.333	0.333	0.333	0.532	0.532	0.532	0.532	0.532	0.532	0.282
Surface Roughness	10	0.318	0.318	0.371	0.371	0.371	0.557	0.557	0.557	0.556	0.556	0.556	0.318
Surface Roughness	11	0.224	0.224	0.275	0.275	0.275	0.437	0.437	0.437	0.437	0.437	0.437	0.224
Surface Roughness	12	0.171	0.171	0.209	0.209	0.209	0.359	0.359	0.359	0.359	0.359	0.359	0.171

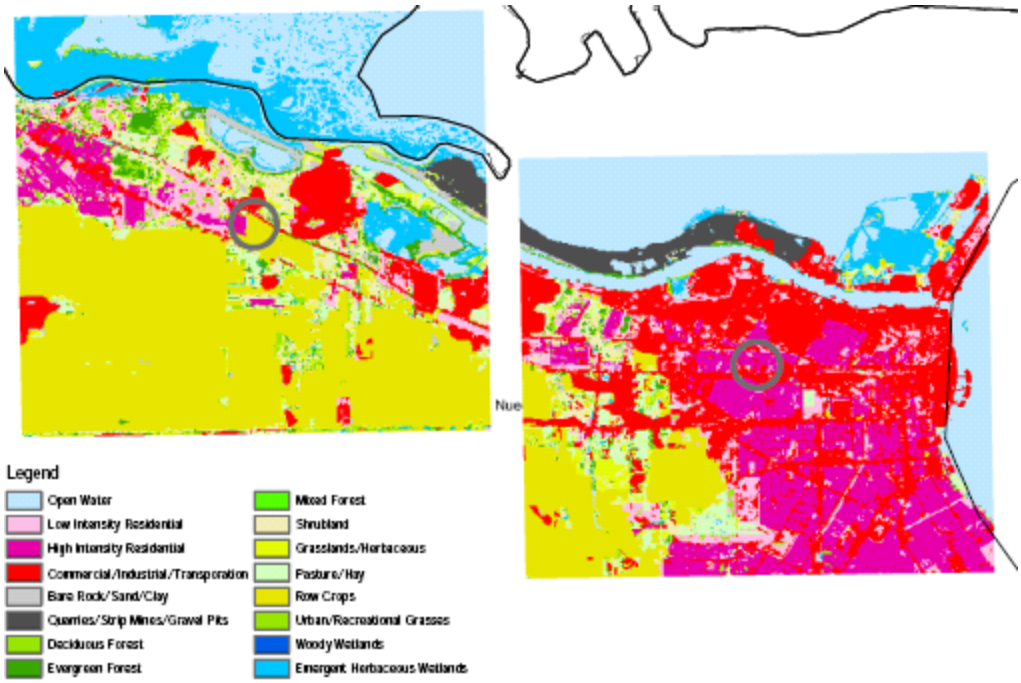
Solar Estates TCEQ-derived values: Albedo (0.18), Bowen ratio (1.5), Surface Roughness (0.5)

(b) Oak Park

		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Albedo		0.16	0.16	0.15	0.15	0.15	0.16	0.16	0.16	0.16	0.16	0.16	0.16
Bowen ratio		0.6	0.6	0.51	0.51	0.51	0.55	0.55	0.55	0.6	0.6	0.6	0.6
Surface Roughness	1	0.883	0.883	0.886	0.886	0.886	0.889	0.889	0.889	0.889	0.889	0.889	0.883
Surface Roughness	2	0.818	0.818	0.823	0.823	0.823	0.827	0.827	0.827	0.827	0.827	0.827	0.818
Surface Roughness	3	0.896	0.896	0.899	0.899	0.899	0.902	0.902	0.902	0.902	0.902	0.902	0.896
Surface Roughness	4	0.873	0.873	0.876	0.876	0.876	0.879	0.879	0.879	0.878	0.878	0.878	0.873
Surface Roughness	5	0.856	0.856	0.858	0.858	0.858	0.859	0.859	0.859	0.859	0.859	0.859	0.856
Surface Roughness	6	0.893	0.893	0.895	0.895	0.895	0.901	0.901	0.901	0.901	0.901	0.901	0.893
Surface Roughness	7	0.922	0.922	0.923	0.923	0.923	0.924	0.924	0.924	0.924	0.924	0.924	0.922
Surface Roughness	8	0.772	0.772	0.785	0.785	0.785	0.795	0.795	0.795	0.786	0.786	0.786	0.772
Surface Roughness	9	0.835	0.835	0.84	0.84	0.84	0.845	0.845	0.845	0.844	0.844	0.844	0.835
Surface Roughness	10	0.912	0.912	0.915	0.915	0.915	0.921	0.921	0.921	0.921	0.921	0.921	0.912
Surface Roughness	11	0.84	0.84	0.845	0.845	0.845	0.85	0.85	0.85	0.849	0.849	0.849	0.84
Surface Roughness	12	0.837	0.837	0.841	0.841	0.841	0.844	0.844	0.844	0.844	0.844	0.844	0.837

Oak Park TCEQ-derived values: Albedo (0.18), Bowen ratio (1.5), Surface Roughness (1.0)

Figure 50. USGS land cover types used in the calculation of surface characteristics by AERSURFACE at Solar Estates (left) and Oak Park (right) within a 10 km x 10 km area centered on each monitor. The circles are approximately 1 km in diameter centered on each monitor.

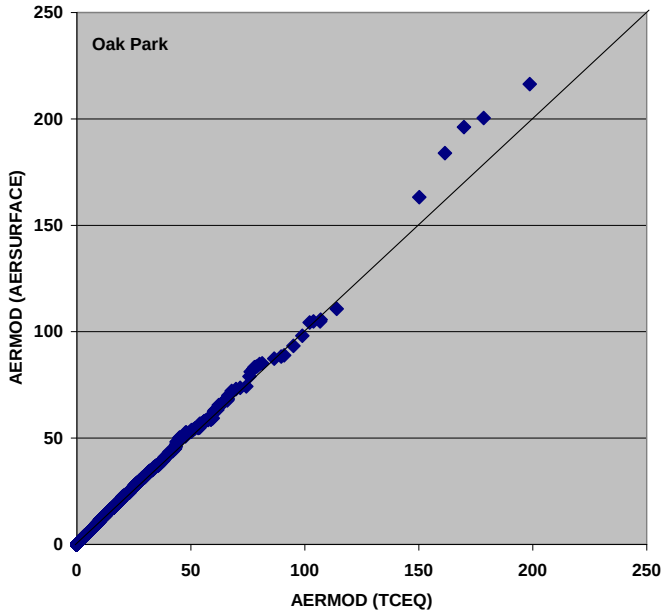


meteorological data were substantially different between the two land cover datasets, and more significant than the differences between the land cover datasets at Oak Park.

Given the vintage of the USGS data currently available in AERSURFACE (i.e., nearly 20 years old), the CCNAT project work will continue using roughness lengths of 0.5 meters and 1.0 meters for Solar Estates and Oak Park, respectively based on TCEQ guidance. However, contemporaneous land use/land cover data sources, for example from satellite remote sensing instrumentation, and their application in AERSURFACE should be a considered for future investigation. Field validation of land use/land cover characterization in the region is also recommended.

Figure 51. Predicted benzene concentrations for 2006 using TCEQ-derived and AERSURFACE land surface characteristics for (a) Oak Park and (b) Solar Estates. Only point source emissions are included in the dispersion models. The predicted concentrations are matched in space but not in time. Note differences in scales between the plots.

(a)



(b)

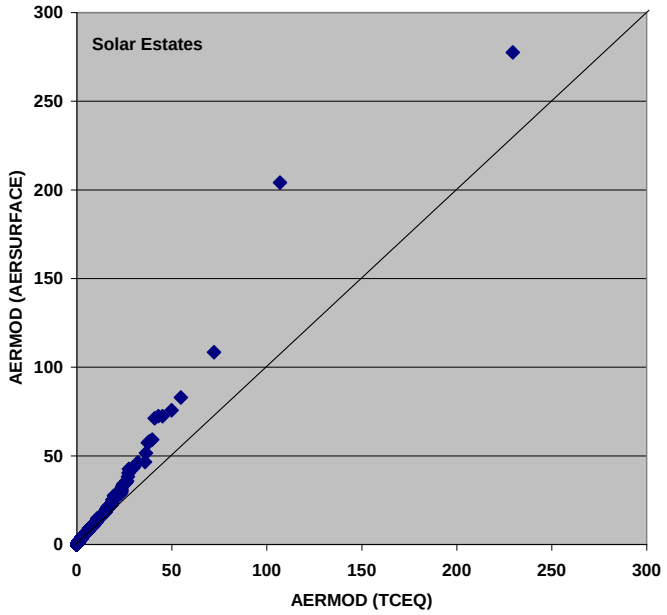
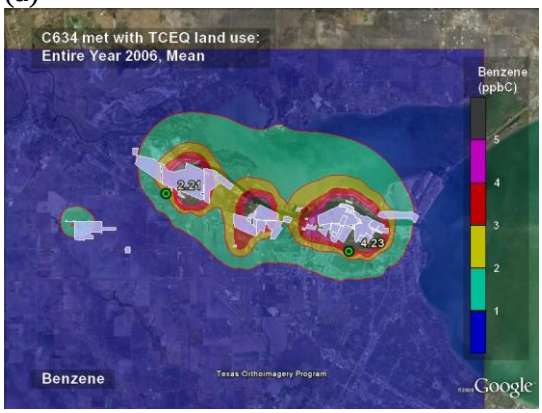
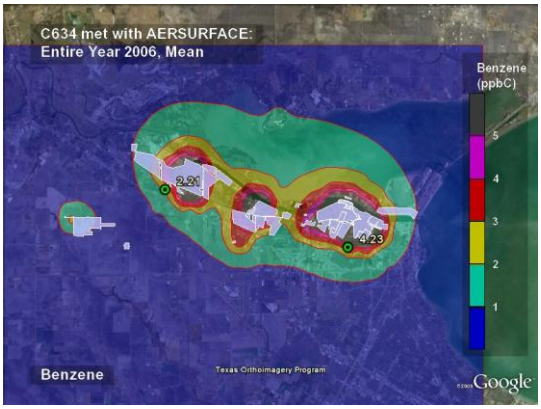


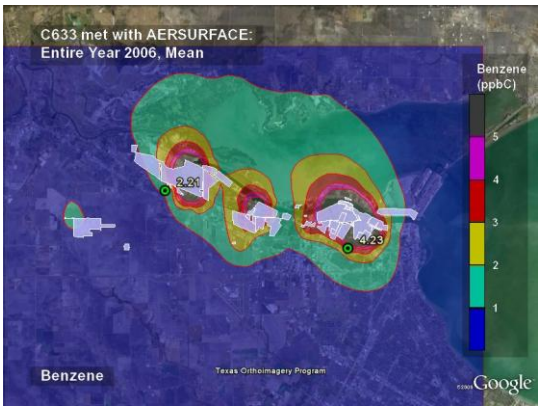
Figure 52. Contoured spatial maps of predicted benzene concentrations in the receptor grid (colored area) for 2006 using TCEQ-derived and AERSURFACE land surface characteristics for (a) Oak Park and (b) Solar Estates. Only point source emissions are included in the dispersion models. Property boundaries of the stationary point sources are shown in gray.

(a)





(b)



5. Summary and Recommendations

This study examined dispersion model predictions of benzene and 1,3-butadiene concentrations from stationary industrial and other anthropogenic emissions sources in Corpus Christi, Texas. Corpus Christi, with a population of nearly 400,000 in the encompassing counties of Nueces and San Patricio, has the 6th largest port in the United States with significant petroleum refining and chemical manufacturing industries. The close proximity of residential areas to these emissions sources has raised concerns about exposure to air toxics. Since mid-2005, The University of Texas at Austin has operated a seven site ambient monitoring network that includes measurements of hydrogen sulfide (total reduced sulfur), sulfur dioxide, total non-methane hydrocarbons, and meteorological data. In addition, hourly measurements of approximately 55 speciated VOCs are collected continuously at two sites, Oak Park and Solar Estates, using auto-GCs with flame ionization detection. This work applied two air dispersion modeling systems, AERMOD and CALPUFF, which represent the state-of-the-practice for dispersion modeling in the United States.

Thirteen existing emission inventories for stationary point sources in Nueces and San Patricio counties were evaluated and compared, including data from the National Emissions Inventory, the Toxics Release Inventory Program, the State of Texas Air Reporting System, and the Texas Commission on Environmental Quality emissions inventories used for photochemical modeling to support State Implementation Plan Development. Pronounced differences were evident between inventories. The differences in annual emissions between inventories can be more than a factor of two.

The 2005 TCEQ Photochemical Modeling Emissions Inventory was selected for the dispersion modeling presented here. Although this inventory had the same level of spatial resolution of emissions sources as the National Emissions Inventory, it was processed by the TCEQ's air quality modeling group to account for rule effectiveness and, importantly, to further speciate emissions that are otherwise reported as VOC with unspecified composition. According to the 2005 TCEQ Photochemical Modeling Inventory, stationary point sources have the largest contribution to benzene emissions in Nueces and San Patricio counties with 256 tpy, followed by area and mobile sources with approximately 160 tpy each, and non-road mobile sources with 34 tpy. On-road mobile sources have the largest contribution to 1,3-butadiene emissions in the 2005 TCEQ Photochemical Modeling inventory for the region with 17 tpy, followed by point and non-road sources with 7 tpy each, and area sources with 0.15 tpy. Dispersion modeling of point source benzene and 1,3-butadiene emissions, respectively, with AERMOD and CALPUFF was conducted using three years of meteorological data for 2006 through 2008.

Key Findings
AERMOD and CALPUFF predicted mean, maximum, 75th, 95th, and 99th percentile benzene and 1,3-butadiene concentrations, respectively, were compared with observed concentrations at Oak Park and Solar Estates during 2006 through 2008. Predicted concentrations were evaluated for modeling with stationary point source emissions only and with all anthropogenic emissions (i.e., point, area, and mobile) from the 2005 TCEQ Photochemical Modeling Inventory. Key findings from the dispersion modeling of each pollutant are summarized below. In addition, the sensitivities of AERMOD predictions to assumptions about the calm wind speed threshold and land cover in the region are discussed.

Benzene:
(a) Model Performance at Oak Park during 2006. AERMOD and CALPUFF replicated observed seasonal and locational differences in benzene concentrations, with increases in fall/winter relative to spring/summer and higher concentrations at Oak Park versus Solar Estates. Important industrial emissions sources for benzene are located to the northeast and northwest of Oak Park, and higher observed concentrations during the fall/winter than spring/summer at Oak Park were associated with more frequent northwesterly clockwise through northeasterly winds. AERMOD and CALPUFF predictions were similar, but not identical, with respect to their agreement with observations at both sites.

When only point source emissions were modeled, AERMOD and CALPUFF generally under-predicted observed concentrations during the fall/winter of 2006 at Oak Park; ratios of predicted to observed concentrations (mean, maximum, 75th, 95th, and 99th percentiles) ranged from 0.5 to 1.1 (reference Table 11). Surrounding Oak Park are industrial emissions sources located to the northeast and northwest, respectively, and the Corpus Christi urban area to the south. Lower observed and predicted benzene concentrations were associated with southerly winds, and both models, but to a greater extent AERMOD, over-predicted observed concentrations during low wind speeds from this sector. AERMOD predicted concentrations are an interpolation between two concentration limits: a coherent plume, which assumes that the wind direction is distributed about a well-defined mean direction, and a random plume, which assumes an equal probability of any wind direction. The contribution from the random plume to the predicted AERMOD concentration often grows larger as the wind speed decreases (dependent on the atmospheric stability), resulting in a “bulls-eye” of concentric concentration rings that decrease with distance around each emissions source. During periods of light wind speeds, concentrations predicted by AERMOD upwind of emission sources were frequently larger than expected, most notably during periods with southerly winds when only the Corpus Christi urban area was in the upwind region. The relatively high concentrations that were predicted to the south of Oak Park were associated with the contributions from the random plume, and resulted in a greater over-prediction of observed concentrations.

Agreement between observed and AERMOD or CALPUFF predicted benzene concentrations at Oak Park was better for the northwest than for the northeast industrial

sector when only point source emissions were modeled. Observed and AERMOD and CALPUFF predicted concentrations for the northwest sector tended to increase as wind speed decreased. For the northeast sector, the highest observed concentrations occurred at moderate wind speeds, but AERMOD and CALPUFF predicted the highest concentrations at low wind speeds and under-predicted observed concentrations during moderate wind speeds. At this time, the environmental factor(s) contributing to the observed difference in concentration/wind speed relationships between the northwest and northeast sectors is unknown. Working hypotheses include uncertainties in the emission rates for important nearby sources, emission rates that change as a function of wind speed (e.g., increasing emissions with increasing wind speed from external floating roof tanks), and/or differences in mechanical and/or thermally-driven atmospheric turbulence that impact the dispersion of emissions in the downwind regions.

When all anthropogenic emissions were modeled, agreement between AERMOD and CALPUFF predicted concentrations and observed concentrations during the fall/winter of 2006 at Oak Park generally improved relative to modeling with only point source emissions; ratios of predicted to observed concentrations (mean, maximum, 75th, 95th, and 99th percentiles) ranged from 0.6 to 1.3. Both models under-predicted the observed maximum concentration, which may be associated with non-routine emissions that are not captured by the 2005 TCEQ Photochemical Modeling Inventory. Both models primarily over-predicted observed concentrations during the spring/summer of 2006, but CALPUFF predictions were generally in closer agreement with observations.

(b) Model Performance at Solar Estates during 2006. When only point source emissions were modeled at Solar Estates, CALPUFF and AERMOD under-predicted mean, 75th, and 95th percentile observed benzene concentrations, were in relatively closer agreement with 99th percentile observed concentrations, and over-predicted the maximum observed concentration during the fall/winter of 2006, as shown in Table 11. The AERMOD predicted maximum concentration at Solar Estates was comparable to that predicted at Oak Park which was not consistent with observations. However, the frequency of occurrence of relatively higher predicted concentrations (above a 50 ppbC threshold) was greater at Oak Park than Solar Estates. Similar to the results for Oak Park, the inclusion of all anthropogenic emissions in the modeling generally improved performance at Solar Estates with respect to the agreement with observed mean, 75th percentile, and 95th percentile benzene concentrations. For example, from Table 11, ratios of mean, 75th, or 95th percentile AERMOD or CALPUFF predicted concentrations to observed concentrations with the inclusion of all anthropogenic emissions ranged from 0.3 to 1.0, in contrast to 0.2 to 0.7 when only industrial point sources were included. The addition of area and mobile sources in the models exacerbated the models over-prediction of observed maximum concentrations. At this time, the reason(s) for the models over-prediction of higher observed benzene concentrations at Solar Estates is unknown.

(c) Annual Variability in Model Performance between 2006 and 2008. For modeling conducted with point source benzene emissions only and with all anthropogenic benzene emissions and assuming that benzene emissions remained constant from 2006 through 2008, neither CALPUFF nor AERMOD were able to consistently replicate the decreases

in observed benzene concentrations that occurred at Oak Park and Solar Estates between 2006 and 2008 (reference Tables 12 and 13). These results suggested that decreases in observed benzene concentrations may be associated with decreases in benzene emissions since 2006, a finding which would be consistent with the declines in annual benzene emissions reported in the TRI. It is recommended that the reported annual TRI emissions inventories continue to be tracked in conjunction with trends in the ambient measurements from the CCAQP network. Emissions inventories with the spatial resolution in emission points and full chemical speciation of VOCs, such as the 2005 TCEQ Photochemical Modeling Inventory, are not routinely developed on an annual basis, which creates disparities in evaluating trends in regions with rapidly changing inventories. If a more recent or future year emissions inventory with the same spatial resolution in emission points and full chemical speciation of VOCs as the 2005 TCEQ Photochemical Modeling EI is developed by the State of Texas, it should be utilized for dispersion modeling in the region.

(d) Spatial Maps of Predicted Concentrations during 2006. Spatial maps of predicted concentrations during 2006 were similar for both models, with the exception of annual maximum concentrations that were strongly affected by AERMOD's restriction of on-site meteorological data from a single site (reference Figures 23-30). The Oak Park and Solar Estates monitors are located within two areas of influence at either end of the Ship Channel. However, neither monitor is positioned to capture benzene concentrations within the Dona Park area more centrally located in the Ship Channel industrial complex or near the Equistar facility located to the southwest of Solar Estates. Although total non-methane hydrocarbon measurements are made at Dona Park, chemically speciated measurements, such as those made with an auto-GC, are not routinely determined. Spatial maps of benzene concentrations indicated broader areas of influence when all anthropogenic emissions were included in the modeling than when only point sources were included. These results were consistent with the contributions of area and/or mobile sources to the inventories for this pollutant.

1,3-Butadiene:

(a) Model Performance at Oak Park during 2006. Unlike benzene, the highest observed concentrations of 1,3-butadiene occurred at Solar Estates rather than Oak Park. AERMOD and CALPUFF replicated observed seasonal and locational differences in 1,3-butadiene concentrations, with increases in fall/winter relative to spring/summer (reference Table 14). Mean and maximum observed concentrations were higher at Solar Estates than Oak ark, but were not well replicated by either model. AERMOD and CALPUFF predictions were similar, but not identical, with respect to their agreement with observations at both sites.

Comparison of results from modeling with point source emissions only and with all anthropogenic emissions, respectively, to observations at Oak Park during 2006 demonstrated an under-prediction bias by both models. For example, ratios of mean, 75th, or 95th percentile AERMOD or CALPUFF predicted concentrations to observed concentrations during fall/winter when all anthropogenic emissions sources were included in the modeling simulations ranged from 0.4 to 0.9 (reference Table 14). Both

models substantially underestimated the observed maximum concentration; the ratios of maximum AERMOD and CALPUFF predicted concentrations to the observed concentration were 0.2 and 0.1, respectively, with all anthropogenic sources included in the modeling (reference Table 14). The potential for missing industrial emissions information should be investigated. Observed concentrations may also be associated with non-routine emissions that are not captured by the 2005 TCEQ Photochemical Modeling Inventory.

(b) Model Performance at Solar Estates during 2006. Higher observed 1,3-butadiene concentrations at Solar Estates were associated with southwesterly, west-southwesterly, or westerly winds. These latter wind directions are rare throughout the year, but are more frequent during fall/winter than spring/summer. Observed and predicted spring/summer concentrations at Solar Estates during 2006 were similar to fall/winter concentrations suggesting a weaker seasonal pattern than at Oak Park.

Comparison of results from modeling with point source emissions only and with all anthropogenic emissions, respectively, to observations at Solar Estates during 2006 indicated a strong under-prediction bias by both models. For example, ratios of mean, 75th percentile, 95th percentile, 99th percentile, and maximum AERMOD or CALPUFF predicted to observed concentrations during the fall/winter of 2006, shown in Table 14, ranged from 0.02 to 0.5 when all anthropogenic emissions sources were modeled. Collectively, the modeling results for Oak Park and Solar Estates suggested the need for future studies aimed at improving the understanding the 1,3-butadiene emissions inventory for Corpus Christi.

(c) Annual Variability in Model Performance between 2006 and 2008. Annual observed 1,3-butadiene concentrations were generally lower in 2008 than in 2006 at both sites, with marked decreases in both the mean and maximum observed values at Solar Estates. Consequently, the agreement between predicted and observed concentrations also improved between 2006 and 2008 (i.e., reduction in the under-prediction bias of the models; reference Tables 15 and 16). Reported annual air emissions of 1,3-butadiene in 2006, 2007, and 2008 TRI data were 14, 7, and 9 tpy, respectively, indicating lower emissions in 2008 than in 2006. The modeling assumes constant emissions between 2006 through 2008.

It is recommended that the reported annual TRI emissions inventories for 1,3-butadiene continue to be tracked in conjunction with trends in the ambient measurements from the CCAQAP network. In addition, if a more recent or future year emissions inventory with the same spatial resolution in emission points and full chemical speciation of VOCs as the 2005 TCEQ Photochemical Modeling EI is developed by the State of Texas, it should be utilized for dispersion modeling in the region. The potential for missing industrial emissions information also should be investigated, especially near Solar Estates; observed concentrations may often be associated with non-routine emissions that are not captured by the existing emissions inventories.

(d) Spatial Maps of Predicted Concentrations during 2006. Spatial maps of predicted 1,3-butadiene concentrations during 2006 were similar for both models, with the exception of annual maximum concentrations that were strongly affected by AERMOD's restriction of on-site meteorological data from a single site (reference Figures 39-46). Spatial maps of predicted 1,3-butadiene concentrations and surface wind back trajectories indicated that Equistar is an important emissions source, but neither of the current auto-GC sites are well positioned to characterize concentrations close to this source. The maps also indicated that neither monitor is positioned to capture 1,3-butadiene concentrations within the Dona Park area more centrally located in the Ship Channel industrial complex. Although total non-methane hydrocarbon measurements are made at Dona Park, chemically speciated measurements, such as those made with an auto-GC, are not routinely determined. Spatial maps of 1,3-butadiene concentrations indicated broader areas of influence when all anthropogenic emissions were included in the modeling than when only point sources were included. These results were consistent with the contributions of area and/or mobile sources to the inventories for this pollutant. A mobile monitoring effort may provide insights on the magnitude and spatial gradients of 1,3-butadiene concentrations in the region.

Sensitivity of AERMOD Predictions to the Calm Wind Speed Threshold:
CALPUFF can be used to predict concentrations during calm conditions; however, AERMOD requires a calm wind speed threshold below which the model does not provide predictions. The AERMOD calm threshold was set at 0.22 mps for this study, which is set to the starting wind speed for the wind speed sensor used at the CCAQP monitoring sites. It is recommended that this value continue to be used. However, the AERMOD calms threshold influences model predictions and interpretation of model performance. Stakeholders should continue to track emerging studies in the literature or guidance by the TCEQ and the EPA.

Sensitivity of AERMOD Predictions to Land Cover Characterization:
The AERMOD modeling system requires the specification of land surface characteristics including albedo (the fraction of total incident solar radiation reflected by the surface back to space without absorption), Bowen ratio (the ratio of sensible heat flux to latent heat flux), and surface roughness (the characteristic length related to the height of obstacles to the wind flow or the height at which the mean horizontal wind speed is zero based on a logarithmic profile). In this study, the albedo and Bowen ratio used for AERMOD were based on TCEQ guidance for Nueces County. The roughness lengths of 0.5 and 1.0 meters were used for Solar Estates and Oak Park, respectively, following TCEQ guidance based on a general categorization of land cover in the immediate vicinity of the sites. Predicted surface concentrations were found to be most sensitive to surface roughness length, but were relatively insensitive to albedo and Bowen ratio.

Although not used for this project, the US EPA has developed an AERSURFACE tool that uses USGS 1992 National Land Cover Data to determine land cover types and surface parameters for a user-specified location. Given the vintage of the USGS data currently available in AERSURFACE, use of the roughness lengths of 0.5 meters and 1.0 meters for Solar Estates and Oak Park, respectively, following TCEQ guidance is

recommended. Application of contemporaneous land use/land cover data from satellite instrumentation in AERSURFACE and field validation are recommended for future investigation.

Recommendations

This study resulted in several key recommendations for the region:

- Reported annual TRI emissions inventories for benzene and 1,3-butadiene should continue to be tracked in conjunction with trends in the ambient measurements from the CCAQP network.

- If a more recent or future year emissions inventory with the same spatial resolution in emission points and full chemical speciation of VOCs as the 2005 TCEQ Photochemical Modeling Inventory is developed by the State of Texas, it should be utilized for dispersion modeling in the region.

- Dona Park and areas to the southwest of the Ship Channel (near the Equistar facility) should be considered for future auto-GC and/or VOC canister sampling efforts.

- Mobile monitoring studies should be considered to compare with predicted spatial gradients of benzene and 1,3-butadiene concentrations. Such studies would be valuable if repeated annually or semi-annually over an extended period of time to examine long-term trends in measured concentrations.

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Appendix A: Hazardous Air Pollutants

Table A.1. Chemical or trade name of hazardous air pollutants (189) identified by Section 112 (b) 1 of the 1990 Clean Air Act. Note that caprolactam and methyl ethyl ketone (bolded) were successfully delisted (Source: Cornell University Law School Legal Information Institute, U.S. Code Collection; http://www.law.cornell.edu/uscode/html/uscode42/usc_sec_42_00007412----000-.html).

Acetaldehyde	Acetamide	Acetonitrile	Acetophenone
2-Acetylaminofluorene	Acrolein	Acrylamide	Acrylic acid
Acrylonitrile	Allyl Chloride	4-Aminobiphenyl	Aniline
o-Anisidine	Antimony compounds	Arsenic compounds	Asbestos
Benzene	Benzedrine	Benzotrichloride	Benzyl chloride
Beryllium compounds	Biphenyl	Bromoform	1,3-Butadiene
Cadmium compounds	Calcium cyanamide	**Caprolactam**	Captan
Carbaryl	Carbon disulfide	Carbon tetrachloride	Carbonyl sulfide
Catechol	Chloramben	Chlordane	Chlorine
Chloroacetic acid	2-Chloroacetophenone	Chlorobenzene	Chlorobenzilate
Chloroform	Chloromethyl methyl ether	Coke oven emissions	Chloroprene
Chromium compounds	Cobalt compounds	2,4-D salts and esters	Cresols /Cresylic acid
Cumene	Cyanide compounds	1,2-Dibromo-3-chloropropane	DDE
Diazomethane	Dibenzofurans	Dichloroethyl ether	Dibutyl phthalate
1,4-Dichlorobenzene (p)	3,3-Dichlorobenzidine	Diethyl sulfate	1,3-Dichloropropene
Dichlorvos	Diethanolamine	4-Dimethylaminoazobenzene	3,3-Dimethoxybenzidine
Dimethyl phthalate	Dimethyl sulfate	*N*,*N*-Dimethylformamide	*N*,*N*-Dimethylaniline
3,3-Dimethylbenzidine	Dimethyl carbomoyl chloride	2,4-Dinitrotoluene	1,1-Dimethylhydrazine
4,6-Dinitro-*o*-cresol , and salts	2,4-Dinitrophenol	1,2-Epoxybutane	1,4-Dioxane
1,2-Diphenylhydrazine	Epichlorohydrin	Ethylbenzene	Ethyl acrylate
Ethyl carbamate	Ethyl chloride	Ethylene oxide	Ethylene dibromide
Ethylene dichloride	Ethylene glycol	*bis*(2-ethylhexyl)phthalate	Ethylene thiourea
Ethylene imine	Ethylidine dichloride	Heptachlor	Fine Mineral Fibers
Formaldehyde	Glycol ethers	Hexachloroethane	Hexachlorobenzene
Hexachlorobutadiene	Hexachlorocyclopentadiene	Hydrazine	Hexamethylene-1-6- diisocyanate
Hexamethylphosphoramide	Hexane	Isophorone	Hydrochloric acid
Hydrogen fluoride	Hydroquinone	Manganese compounds	Lead compounds
Lindane	Maleic anhydride	Methyl bromide	Mercury compounds
Methanol	Methoxychlor	**Methyl ethyl ketone**	Methyl chloride
Methyl chloroform	Methyl *tert*-butyl ether	Methyl methacrylate	Methyl iodide
Methyl isobutyl ketone	Methyl isocyanate	4,4-Methylenediphenyl diisocyanate	Methylene chloride
4,4-Methylene bis (2-chloroaniline)	4,4-Methylenedianiline	Nitrobenzene	Methylhydrazine
Naphthalene	Nickel compounds	*N*-Nitroso-*N*-methylurea	4-Nitrobiphenyl

4-Nitrophenol	2-Nitropropane	Pentachloronitrobenzene	*N*-Nitrosodimethylamine
N-Nitrosomorpholine	Parathion	Phosgene	Pentachlorophenol
Phenol	*p*-Phenylendiamine	Polychlorinated biphenyls	Phosphine
Phosphorus	Phthalic anhydride	Propionaldehyde	Polycyclic organic matter
1,3-Propane sultone	ß-Propiolactone	1,2-Propyleneimine	Propoxur
Propylene dichloride	Propylene oxide	Selenium compounds	Quinoline
Quinone	Radionuclides (inc. radon)	1,1,2,2-Tetrachloroethane	Styrene
Styrene oxide	2,3,7,8-Tetrachlorodibenzo-p-dioxin	Toluene-2,4-diamine	Tetrachloroethylene
Titanium tetrachloride	Toluene	1,2,4-Trichlorobenzene	2,4-Toluene diisocyanate
o-Toluidine	Toxaphene	2,4,6-Trichlorophenol	1,1,2-Trichloroethane
Trichloroethylene	2,4,5-Trichlorophenol	Vinyl acetate	Triethylamine
Trifluralin	2,2,4-Trimethylpentane	Xylenes (isomers and mixture)	Vinyl bromide
Vinyl chloride	Vinylidene chloride	o-Cresol	*bis*(chloromethyl)ether
o-Xylenes	p-Xylenes	p-Cresol	
m-Xylenes		m-Cresol	

APPENDIX B: Chronic Dose-Response Assessments

EPA chronic dose-response assessments for air toxics typically specify health effects reference concentrations for protection from non-cancer effects (e.g. respiratory or neurological) and/or unit risks estimates of the probability of contracting cancer. The EPA has established databases of these values, as well as resources that describe the weight-of-evidence that exposures to specific air toxics lead to cancer. These sources include the Air Toxics Health Effects Database (ATHED; http://www.epa.gov/ttn/atw/toxsource/summary.html) that provides reference values for chronic inhalation and oral exposures including cancer, as well as acute inhalation exposures (Woodall and Smith, 2008), and the Health Effects Notebook for Hazardous Air Pollutants (http://www.epa.gov/ttn/atw/hlthef/hapindex.html) that provides chemical-specific fact sheets that describe routes of environmental, occupational and personal exposures and chronic and acute health effects.

Chronic dose-response values originate from a variety of sources including the EPA, the US Agency for Toxic Substances and Disease Registry (ATSDR), the California Environmental Protection Agency (CalEPA) Office of Environmental Health Hazard Assessment, and the International Agency for Research on Cancer (IARC) http://www.epa.gov/ttn/atw/toxsource/chronicsources.html. The EPA uses a priority system for establishing chronic dose-response values in the ATHED (http://www.epa.gov/ttn/atw/toxsource/chronicpriority.html;):

1. Draft Reference Concentrations (RfCs)[2], Reference Doses (RfDs)[3], and Unit Risk Estimates (UREs)[4] under development for the EPA Integrated Risk Information System (IRIS) that have already undergone external peer review and subsequent revision
2. Current IRIS information

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[2] The EPA Reference Concentration (RfC; (http://www.epa.gov/ttn/atw/nata/gloss.html#rfc) derived from human or animal data, is "an estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure to the human population (including sensitive subgroups which include children, asthmatics and the elderly) that is likely to be without an appreciable risk of deleterious effects during a lifetime."

[3] The EPA Reference Dose (RfD; http://www.epa.gov/iris/help_ques.htm#whatiris) is expressed in units of mg of substance/kg body weight-day and is defined "as an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime. An RfD can be derived from a no-observed-adverse-effect level (NOAEL), lowest-observed-adverse-effect level (LOAEL), or benchmark dose, with uncertainty factors generally applied to reflect limitations of the data used."

[4] The EPA Unit Risk Estimate (URE; http://www.epa.gov/ttn/atw/nata/gloss.html#rfc) is the "upper-bound excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of 1 $\mu g/m^3$ in air. The interpretation of the Unit Risk Estimate would be as follows: if the Unit Risk Estimate = 1.5 x 10-6 per $\mu g/m^3$, 1.5 excess tumors are expected to develop per 1,000,000 people if exposed daily for a lifetime to 1 µg of the chemical in 1 cubic meter of air. Unit Risk Estimates are considered upper bound estimates, meaning they represent a plausible upper limit to the true value". The EPA derives inhalation UREs for some carcinogenic substances lacking data, such as the insecticide diclorvos, from oral carcinogenic potency estimates.

3. US Agency for Toxic Substances and Disease Registry (ATSDR) chronic Minimum Risk Levels (MRLs) for non-cancer effects[5]
4. The California Environmental Protection Agency (CalEPA) non-cancer chronic inhalation and oral reference exposure levels (RELs) and UREs for carcinogenicity by inhalation exposure[6]
5. Health Effects Assessment Summary Tables (HEAST) assessments[7].

The International Agency for Research on Cancer (IARC) of the World Health Organization develops "degrees of evidence", but not quantitative categories, indicating carcinogencity in humans for chemicals or mixtures: Group 1 (carcinogenic in humans), Group 2A (probably carcinogenic), Group 2B (possibly carcinogenic), Group 3 (not classifiable), and Group 4 (probably not carcinogenic). These classifications are also included in the ATHED. Figure B.1 shows a segment of chronic inhalation and oral reference values from the ATHED database as an example.

[5] The ATSDR Miminim Risk Level (MRL; http://www.epa.gov/ttn/atw/toxsource/chronicsources.html) is defined as "an estimate of daily human exposure to a substance that is likely to be without an appreciable risk of adverse effects (other than cancer) over a specified duration of exposure. It is important to note that MRLs are intended to identify substances for further evaluation and not to establish a threshold for a threat to human health."

[6] The California Environmental Protection Agency (CalEPA) Office of Environmental Health Hazard Assessment develops non-cancer chronic inhalation and oral reference exposure levels (RELs) "as a concentration level at (or below) which no health effects are anticipated (http://www.epa.gov/ttn/atw/toxsource/chronicsources.html", and, similar to the EPA, an URE for carcinogenicity by inhalation exposure.

[7] Dose-response assessments are disseminated based on the level of peer review, with those that achieve full independent consensus, with external peer review, incorporated into the Integrated Risk Information System (IRIS), and those that do not have established EPA consensus into the Health Effects Assessment Summary Tables (HEAST).

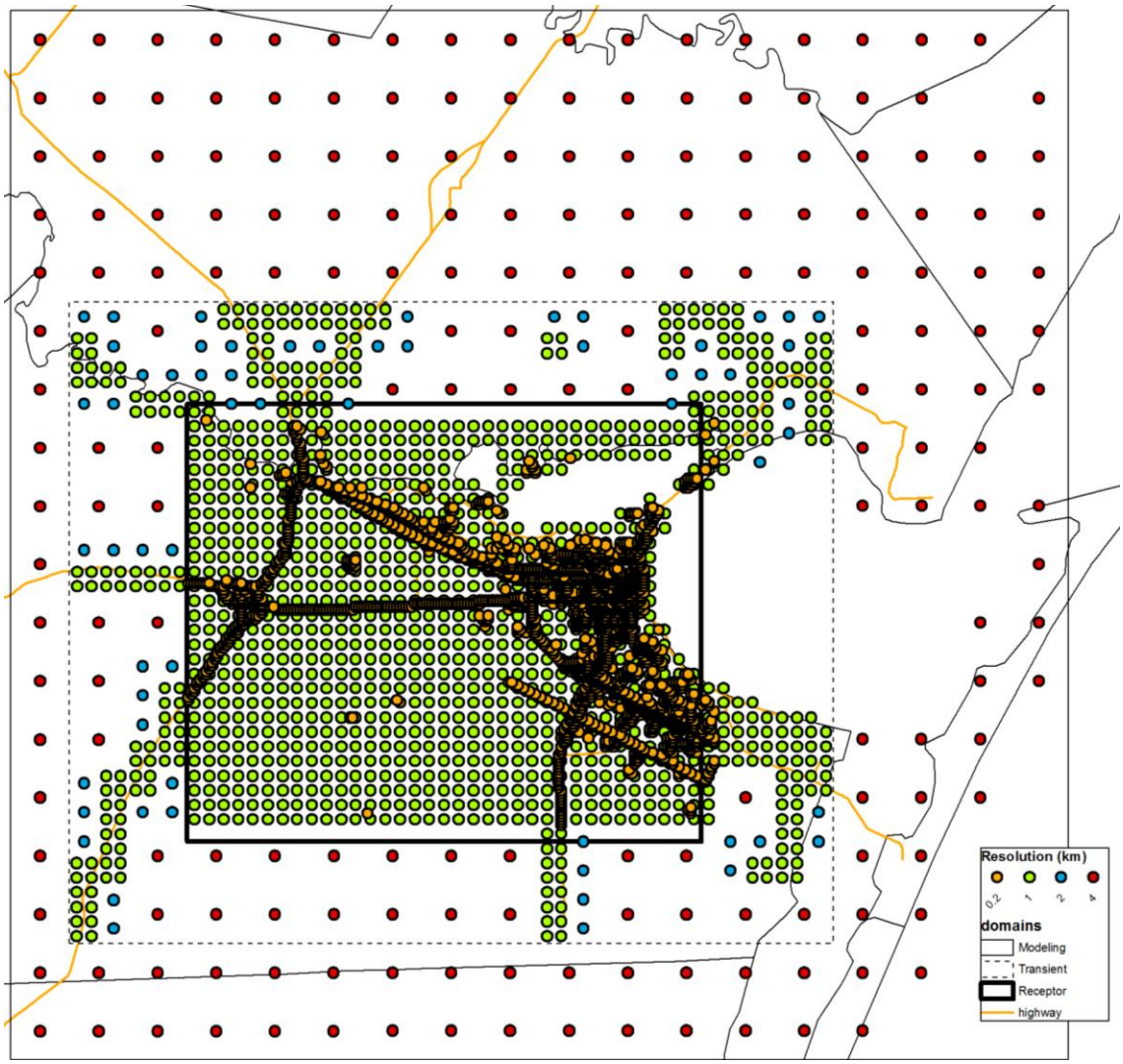
Figure B.1. Example of chronic inhalation and oral reference values for substances in the the US EPA's ATHED database.
Source:http://www.epa.gov/ttn/atw/toxsource/table1.pdf .

Table 1. Prioritized Chronic Dose-Response Values (6/12/2007). CAS NO. = Chemical Abstracts Services number for the compound. HAP NO. = Position of the compound on the HAP list in the Clean Air Act (112(b)(2)). "999" denotes substances under consideration for listing. IARC WOE = weight-of-evidence for carcinogenicity in humans (1 - carcinogenic; 2A - probably carcinogenic; 2B - possibly carcinogenic; 3 - not classifiable; 4 - probably not carcinogenic). EPA WOE = weight-of-evidence for carcinogenicity under the 1986 EPA cancer guidelines, as superseded for specific compounds by the 1999 interim guidelines (1986 guidelines: A - human carcinogen; B1 - probable carcinogen, limited human evidence; B2 - probable carcinogen, sufficient evidence in animals; C - possible human carcinogen; D - not classifiable E - evidence of noncarcinogenicity. 1999 guidelines: CH - carcinogenic to humans; LH - likely to be carcinogenic; SE - suggestive evidence for carcinogenicity; Inl - inadequate information to determine carcinogenicity; NH - not likely to be carcinogenic). Revisions since 2/28/05 are shown

Table 1. Prioritized Chronic Dose-Response Values for Screening Risk Assessments (6/12/2007)				CHRONIC INHALATION					CHRONIC ORAL				
				NONCANCER		CANCER			NONCANCER		CANCER		
CHEMICAL NAME	CAS NO.	HAP NO.	IARC WOE	mg/m3	SOURCE	EPA WOE	1/(µg/m3)	SOURCE	mg/kg/d	SOURCE	EPA WOE	1/(mg/kg/d)	SOURCE
Acetaldehyde	75-07-0	1	2B	0.009	IRIS	B2	0.0000022	IRIS					
Acetamide	60-35-5	2	2B				0.00002	CAL					
Acetonitrile	75-05-8	3		0.06	IRIS	Inl							
Acetophenone	98-86-2	4				D							
Acrolein	107-02-8	6	3	0.00002	IRIS	Inl							
Acrylamide	79-06-1	7	2A	0.0007	P-CAL	B2	0.0013	IRIS					
Acrylic acid	79-10-7	8		0.001	IRIS								
Acrylonitrile	107-13-1	9	2A	0.002	IRIS	B1	0.000068	IRIS					
Allyl chloride	107-05-1	10	3	0.001	IRIS	C	0.000006	CAL					
Aniline	62-53-3	12	3	0.001	IRIS	B2	0.0000016	CAL					
Antimony compounds	7440-36-0	173											
Antimony pentoxide	1314-60-9	173											
Antimony potassium tartrate	304-61-0	173											
Antimony tetroxide	1332-81-6	173											
Antimony trioxide	1309-64-4	173	2B	0.0002	IRIS								
Arsenic compounds	7440-38-2	174	1	0.00003	CAL	A	0.0043	IRIS					
Arsenic pentoxide	*1303-28-2*	*174*		*0.00003*	*CAL*								
Arsine	7784-42-1	174		0.00005	IRIS								
Benzene	71-43-2	15	1	0.03	IRIS	CH	0.0000078	IRIS					
Benzidine	92-87-5	16		0.01	P-CAL	A	0.067	IRIS					
Benzotrichloride	98-07-7	17	2B			B2	0.0037	Conv. Oral					
Benzyl chloride	100-44-7	18	2B			B2	0.000049	CAL					
Beryllium compounds	7440-41-7	175	1	0.00002	IRIS	LH	0.0024	IRIS					
Beryllium oxide	*1304-56-9*	*175*		*0.000007*	*CAL*								
Biphenyl	92-52-4	19				D							
Bis(2-ethylhexyl)phthalate	117-81-7	20	2B	0.01	P-CAL	B2	0.0000024	CAL					
Bis(chloromethyl)ether	542-88-1	21	1			A	0.062	IRIS					
Bromoform	75-25-2	22	3			B2	0.0000011	IRIS					
1,3-Butadiene	106-99-0	23	2A	0.002	IRIS	CH	0.00003	IRIS					
Cadmium compounds	7440-43-9	176	1	0.00002	CAL	B1	0.0018	IRIS	0.0005	IRIS	B1		
Captan	133-06-2	26	3			B2	0.000001	Conv. Oral					
Carbaryl	63-25-2	27											
Carbon disulfide	75-15-0	28		0.7	IRIS								

Appendix C: Mobile and Area Source Emissions

Figure C.1 Spatial distributions of non-point emissions source locations within the dispersion modeling domain.



Appendix D: Number of Hours with Valid Observations, Valid AERMOD and CALPUFF Predictions, and Observed Hourly Wind Speeds >= 0.22 mps.

Table D.1 Number of hours with (1) valid observation, (2) valid AERMOD and CALPUFF predictions, and (3) observed hourly wind speed >= 0.22 mps.

Pollutant	Site Name (CAMS)	Year	Season	Hours
Benzene	Solar Estates (C633)	2006	Fal/Win	3688
			Spr/Sum	2784
		2007	Fal/Win	3290
			Spr/Sum	3157
		2008	Fal/Win	3715
			Spr/Sum	3733
	Oak Park (C634)	2006	Fal/Win	3581
			Spr/Sum	3668
		2007	Fal/Win	3609
			Spr/Sum	3714
		2008	Fal/Win	3621
			Spr/Sum	3679
1,3-Butadiene	Solar Estates (C633)	2006	Fal/Win	3690
			Spr/Sum	3128
		2007	Fal/Win	3461
			Spr/Sum	3205
		2008	Fal/Win	3723
			Spr/Sum	3733
	Oak Park (C634)	2006	Fal/Win	3582
			Spr/Sum	3670
		2007	Fal/Win	3609
			Spr/Sum	3714
		2008	Fal/Win	3646
			Spr/Sum	3680