4.0 Emissions Inventory Assessment and Dispersion Modeling of Benzene and 1,3-Butadiene

4.1 Introduction

Ambient concentrations of urban air toxics, such as benzene and 1,3-butadiene, 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 (EPA, 2010). Dispersion models are used to estimate concentrations of a pollutant at ground-level receptors surrounding an emissions source. 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. The models differ in their capabilities and applications. Dispersion models have historically been used in the air permitting process. Such models are limited in their representation of atmospheric chemical and physical processes, but require less computational burden than photochemical grid models. Photochemical grid models have been used extensively in regulatory assessments of criteria air pollutants, such as for the development of State Implementation Plans (SIPs) for ozone in Texas and other states.

4.2 Objectives and Motivation

This overall objective of this work, which was completed in 2010, was to apply 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. Benzene and 1,3-butadiene are air toxics that are national or regional drivers of carcinogenic risk in the United States, and their emissions are associated with industrial activities that occur in the Corpus Christi region. At the time of this work, Corpus Christi had a population of nearly 400,000 in the encompassing counties of Nueces and San Patricio and the 6th largest port in the United States with significant petroleum refining and chemical manufacturing industries. Nueces County included a sub-region on the Texas Commission on Environmental

Quality's (TCEQ's) Air Pollutant Watch List (APWL) for benzene emissions that was de-listed in January 2010.

The motivations for the air dispersion modeling efforts were to compare model predictions with measured concentrations at Oak Park and Solar Estates, to estimate concentrations of these pollutants in areas where ambient monitoring sites were not present, and to provide guidance for potential locations for additional sites should the monitoring network be expanded in the future. In 2011, after completion of the modeling efforts, the Agency for Toxic Substances and Disease Registry (ATSDR), an agency of the U.S. Department of Health and Human Services, also requested the results for their investigations in the region. The specific objectives of the air dispersion modeling tasks were to:

- Identify and compare existing emissions inventories for air toxics in the Corpus Christi area and select an appropriate emissions inventory for air dispersion modeling.

- 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.

- 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 auto-GC sites.

- Map the spatial distributions of predicted benzene and 1,3-butadiene concentrations in Corpus Christi communities.

AERMOD and CALPUFF represent the state-of-the-practice for dispersion modeling in the United States (EPA, 2010). AERMOD is a steady-state dispersion model designed for short-range ($\leq$ 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 EPA for assessing long-range transport of pollutants and on a case-by-case basis for near-field applications with complex meteorological conditions (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; EPA, 2003; Oshan et al., 2005; MacIntosh et al., 2010).

4.3 Emissions Inventory Assessment

Emissions inventories characterize the total emissions of a pollutant across source sectors in a particular region over a period of time and are a crucial requirement for air quality modeling studies. Existing emissions inventories for air toxics in the Corpus Christi area were identified and compared, with a primary focus on stationary industrial sources. The rationale for the selection of specific emissions inventories for air dispersion modeling of benzene and 1,3-butadiene is described in this section.

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

Thirteen stationary point source inventories for benzene and 1,3-butadiene in Nueces and San Patricio Counties were obtained and evaluated in this work, including: (1-7) the TRIs from 2002-2008, (8) TCEQ submittal to the EPA 2002 Hazardous Air Pollutant National Emission Inventory (HAP NEI), (9) 2002 EPA HAP NEI, (10) TCEQ submittal to the EPA 2005 HAP NEI, (11) 2000 TCEQ Photochemical Modeling Emissions Inventory, (12) 2005 TCEQ Photochemical Modeling Emissions Inventory, and (13) 2008 update to the City of Corpus Christi Emissions Inventory prepared by Air Consulting and Engineering Solutions, Ltd. (ACES). Annual benzene and 1,3-butadiene emissions are summarized in Table 4-1, page 4-4, for eleven inventories. The 2008 ACES inventory for major point sources matched the TCEQ submittal to the 2005 HAP NEI and was not included. 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 was also not included.

Pronounced differences were evident between inventories, indicating that emissions inventories may have different origins, objectives, and spatial resolutions that can lead to variability in the inputs used for air quality modeling studies. In some cases, differences between inventories were consistent with the temporal trends in measured ambient concentrations; TRI point source emissions decreased between 2005 and 2008, consistent with decreases in measured ambient benzene concentrations. For other cases, differences between inventories reflected differences in data processing or perhaps even quality assurance/quality control analyses. The TRI was useful

Table 4-1. Annual point source emissions of benzene and 1,3-butadiene (tpy) in eleven available inventories for Nueces and San Patricio Counties. The 2005 TCEQ Photochemical Modeling Emissions Inventory, which was used in the air dispersion modeling, is highlighted.

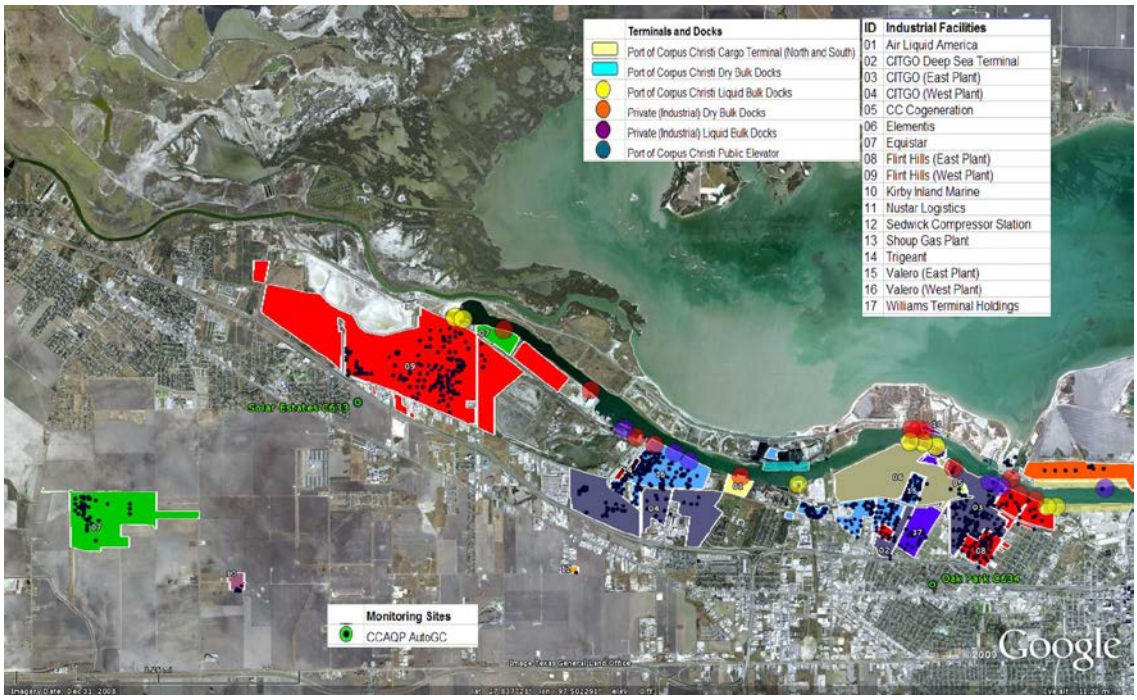
County	Species	2000 TCEQ Photochemical Modeling EI	2002 HAP NEI	2005 TCEQ Photochemical Modeling EI	2005 HAP NEI Submittal	TRI						
						2002	2003	2004	2005	2006	2007	2008
Nueces	Benzene	248.2	166.8	259.3	93.5	109.0	123.8	120.4	104.9	84.4	78.7	76.5
	1,3-Butadiene	0.0	0.99	7.0	4.9	1.4	2.9	5.4	5.6	13.5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

for analyzing annual trends but reported emissions broadly by facility. The TCEQ photochemical modeling inventories and the NEIs had greater spatial resolution of emission points than the TRI and originated from a common source, the State of Texas Air Reporting System (STARS). However, the TCEQ conducted additional processing of reported emissions data to account for rule effectiveness and to further chemically speciate emissions that were 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. 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 in this work. Use of an inventory that had full chemical speciation of VOC emissions was critical because of regulations that targeted emissions of highly reactive VOCs (HRVOCs; ethylene, propylene, 1,3-butadiene, and butenes). Industrial facilities that are sources of benzene and 1,3-butadiene emissions are shown in Figure 4-1, page 4-6. Emission points for benzene and 1,3-butadiene included in the 2005 TCEQ Photochemical Modeling Inventory and the locations of the Oak Park and Solar Estates auto-GC sites are shown in Figure 4-2, page 4-7. 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 4-2, page 4-8. The AERMOD and CALPUFF input runstream files specify the locations, stack parameters (i.e., height above ground level, inside diameter, stack gas temperature and exit velocity), and emission rates of the point sources. 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.

Figure 4-1. Industrial facilities that are sources of (a) benzene and (b) 1,3-butadiene emissions. Maps include the Corpus Christi Ship Channel and the locations of docks and terminals that may be used for ship loading/unloading operations.

(a)



(b)

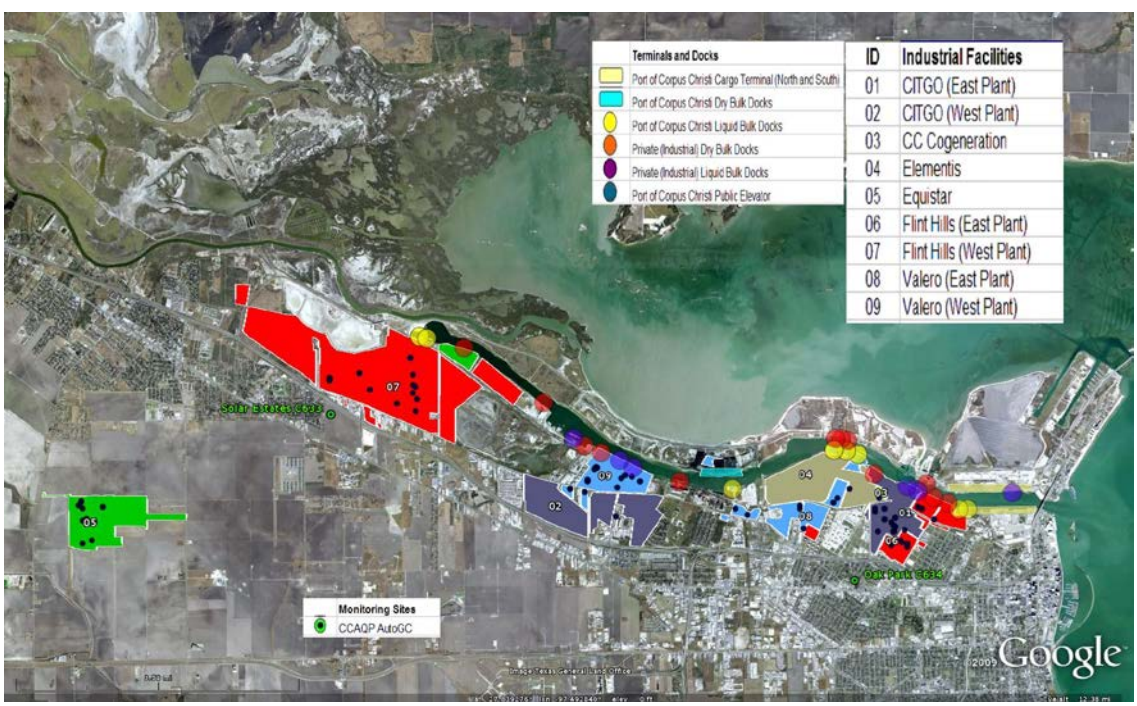
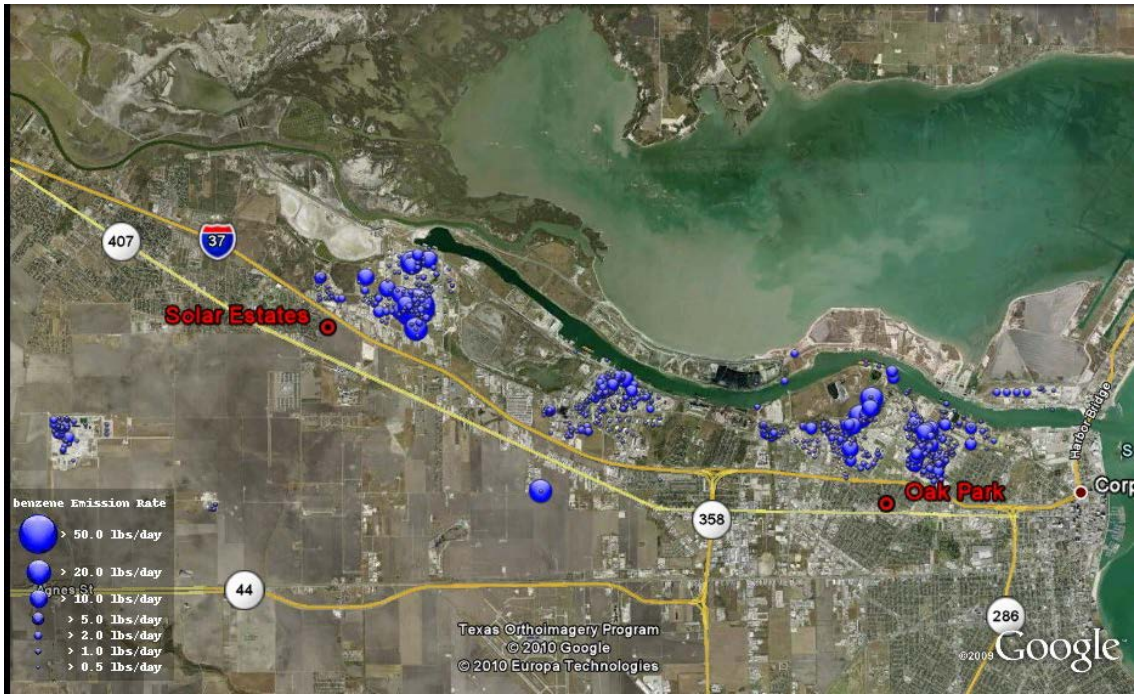


Figure 4-2. Point source emissions of (a) benzene and (b) 1,3-butadiene in the 2005 TCEQ Photochemical Modeling Inventory near the Solar Estates and Oak Park auto-GC sites.

(a)



(b)

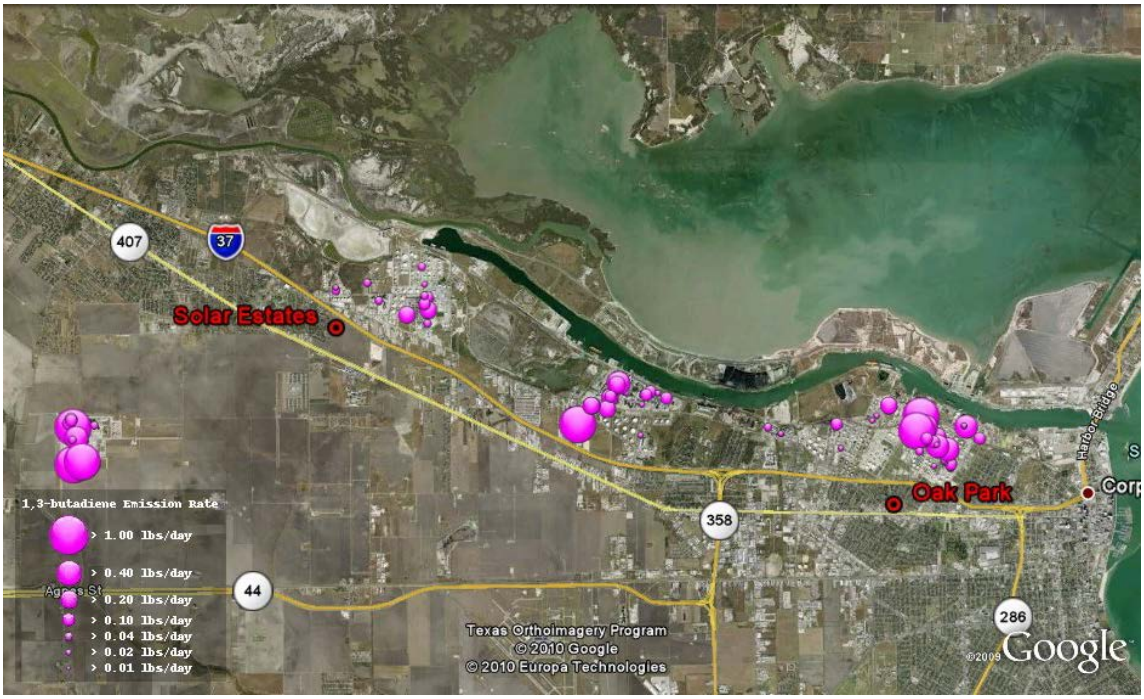


Table 4-2. Most significant point sources of benzene and 1,3-butadiene emissions in Nueces County by U.S. EPA Source Classification Code (SCC) from the 2005 TCEQ Photochemical Modeling Inventory.

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)

4.3.2 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 Ramboll Environ (formerly ENVIRON International Corporation) at a 200 m horizontal resolution for the 72 km x 72 km modeling domain. Tables 4-3 through 4-5, pages 4-11 to 4-13, 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 Figure 4-3, page 4-14, and described in Table 4-6, page 4-15. 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 A.1 (Appendix A).

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 A.1 (Appendix A) 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 4-3 through 4-5, 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 4-3. 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 4-4. 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 4-5. 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

4.4 Air Dispersion Modeling Methodology

Air dispersion modeling was conducted with three complete years of meteorological data (2006 through 2008). The 2005 TCEQ Photochemical Modeling Inventory was used with each year of meteorological data because alternative year-specific inventories with full VOC chemical speciation were not available for 2006 through 2008. A conceptual model of meteorological conditions and associated temporal trends in total non-methane hydrocarbon and benzene concentrations in the Corpus Christi area was developed and is provided in Appendix B.

4.4.1 Modeling Domain and Receptor Grids

The CALPUFF modeling domain was defined using Lambert Conformal Projected coordinates with the projection parameters shown in Table 6. 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 4-3 was designed to include all UT Corpus Christi Air Quality Project (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 4-3. Corpus Christi regional modeling domain used for CALPUFF (exterior box) and receptor grids used for both the CALPUFF and AERMOD simulations (interior box).

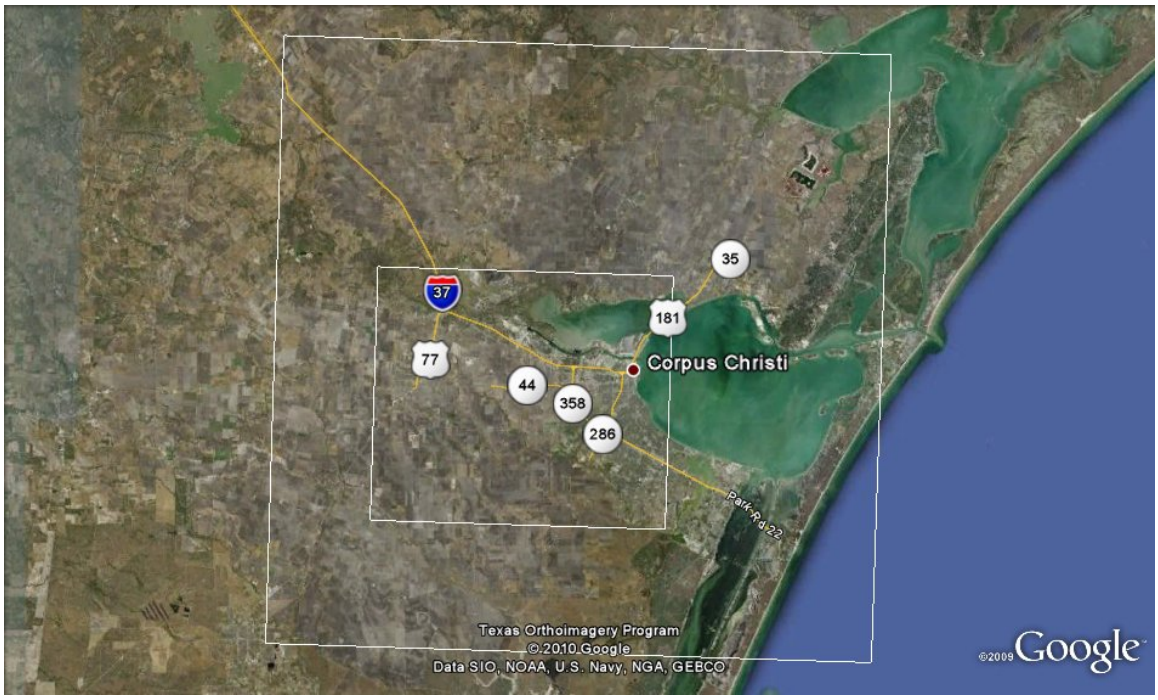


Table 4-6. Map projection, modeling domain for CALPUFF simulations, and receptor grid specifications for the AERMOD and CALPUFF simulations.

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)

4.4.2 AERMOD Configuration

The original development of the AERMOD modeling system configuration is described in detail in Appendix C (Tai et al., 2009). It is summarized here, along with modifications that were made during the course of the work. 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 EPA http://www.epa.gov/scram001/dispersion_related.htm. AERMAP required digital terrain data for the modeling domain and an input runstream file. As described by Tai et al. (2009) in Appendix C, 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 (Appendix C: 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.

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 this work, the AERMOD calm threshold was set at 0.22 mps, which was the starting wind speed for wind speed sensor used at the Project monitoring sites. Uncertainty in AERMOD predictions at wind speeds as low as 0.22 mps is 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. Sensitivity studies in this work highlighted that that assumptions about the AERMOD calms threshold have the potential to influence model predictions and interpretation of performance. The TCEQ and EPA have not established specific guidance.

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.

Emissions source characteristics were obtained from the 2005 TCEQ Photochemical Modeling Inventory as described above. 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 4-7*, below.

Table 4-7. 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 ($\mu g/m^2$).

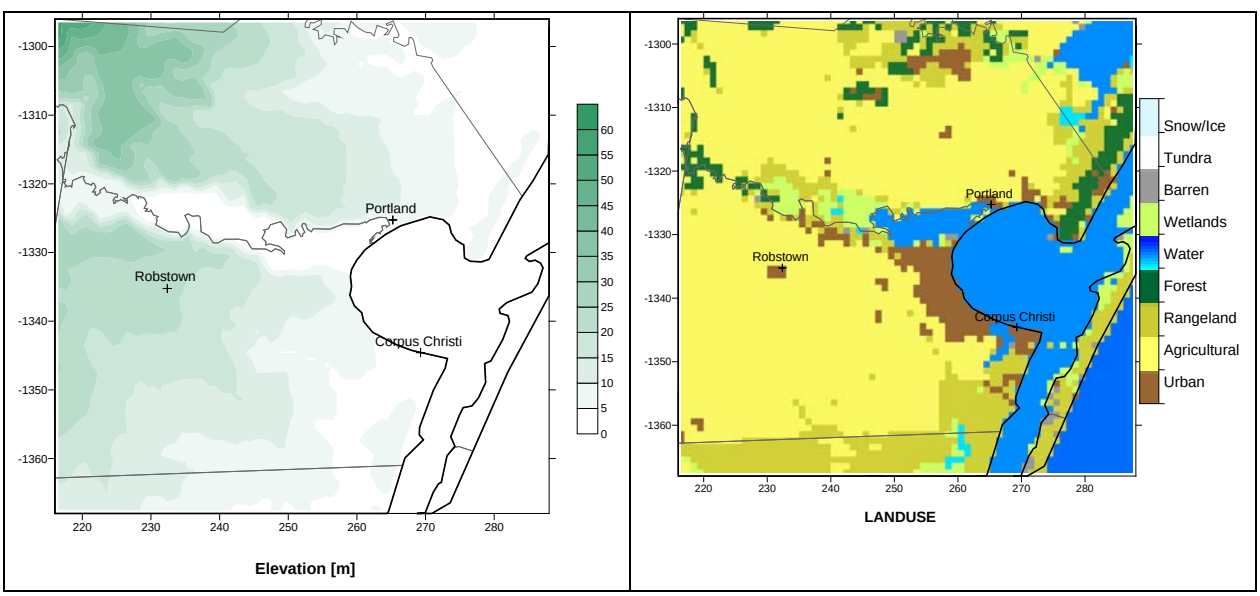
* Argonne National Laboratory. 2002. *Deposition Parameterizations for the Industrial Source Complex (ISC3) Model*. Argonne, IL.

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 µg/m^3, along with a log file indicating errors in processing, if any.

4.4.3 CALPUFF Configuration

The CALPUFF system configuration is described in detail in Appendix C (Tai et al., 2009) and summarized 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 configuration selected for the CALPUFF performance evaluation was 14 layers up to 3 km to provide reasonable coordination with the TCEQ photochemical grid model vertical layer structure. USGS 1-degree terrain data (~90 m resolution; http://edcftp.cr.usgs.gov/pub/data/DEM/250/) were processed for output at 1 km resolution for the Corpus Christi domain in the NWS-84 spherical datum. USGS land use/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 4-4, below, shows the spatial plots of terrain and the dominant land use category. A preprocessor known as MAKEGEO was used 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 4-4. Gridded fields of terrain (left) and dominant land use type (right).



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 (ref. Appendix C, 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 4-8, page 4-20.

Table 4-8. 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
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 4-9, page 4-21. 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 4-9. 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.

4.5 Comparisons of Predicted and Observed Concentrations in 2006

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. Results presented here focus on modeling that included all anthropogenic benzene emissions (i.e., point, area, and on-road and non-road mobile) from the 2005 TCEQ Photochemical Modeling Inventory. 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.

4.5.1 Benzene

Table 4-10, page 4-23, 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. Scatter plots of predicted versus observed benzene concentrations by season during 2006 at Oak Park are shown in Figure 4-5, page 4-24, and at Solar Estates in Figure 4-6, page 4-25.

The ratio of observed fall/winter to spring/summer mean benzene concentrations at Oak Park during 2006 was 3.4 and at Solar Estates was 2.2. 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. 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.

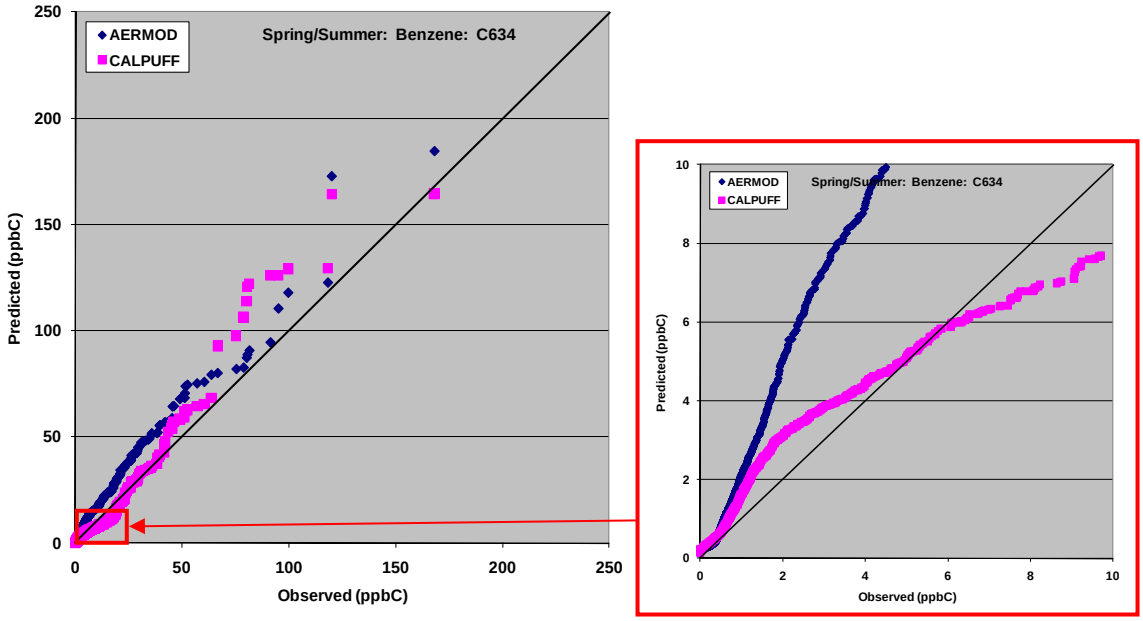
The frequency of occurrence of relatively higher predicted concentrations (above a 50 ppbC threshold) was greater at Oak Park than Solar Estates. Prevailing near-surface winds determine if emission plumes from Ship Channel industrial facilities are transported towards nearby monitors. Figure 4-7, page 4-26, 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, at. The 95th percentile concentrations vary from 1.9 ppbC during southeasterly winds to 67.3 ppbC during north-northeasterly winds. Figure 4-7 illustrates that higher observed benzene concentrations during the fall/winter than spring/summer are associated with more frequent northwesterly clockwise through northeasterly winds. One-hour surface back-trajectories for high concentration hours in Figure 4-8, page 4-26, indicate that important industrial emissions sources for benzene are located to the north-northwest and especially north-northeast of Oak Park.

Table 4-10. 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. 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	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	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	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	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 4-5. Scatter plots of predicted versus observed benzene concentrations at Oak Park during the (a) spring/summer and (b) fall/winter of 2006.

(a)



(b)

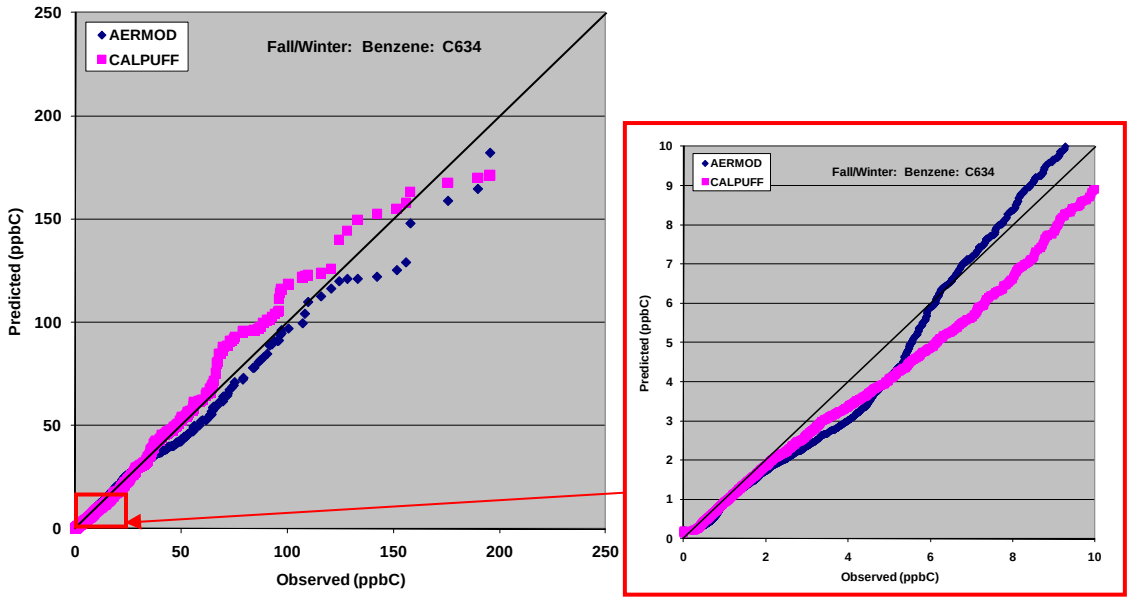
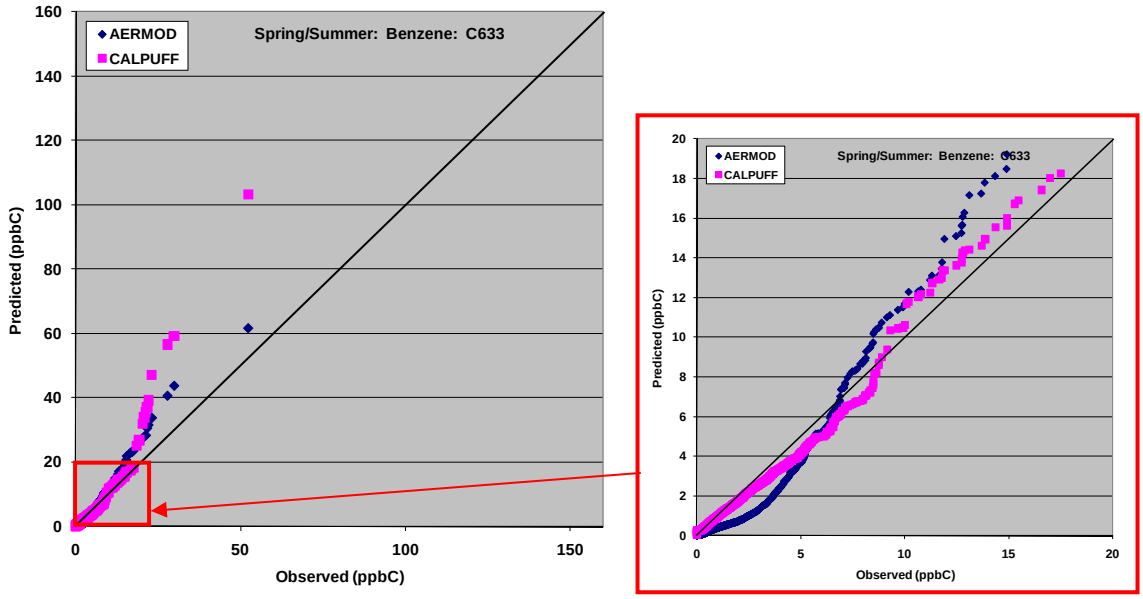


Figure 4-6. Scatter plots of predicted versus observed benzene concentrations at Solar Estates during the (a) spring/summer and (b) fall/winter of 2006 with all anthropogenic emissions sources included in the dispersion models.

(a)



(b)

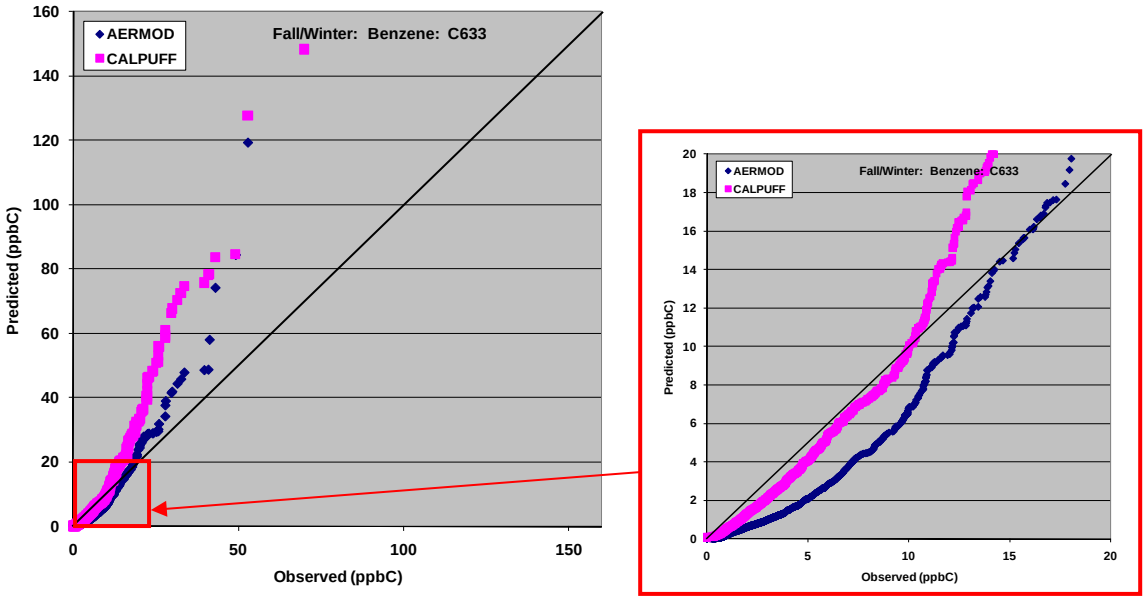


Figure 4-7. Oak Park observed 95th percentile benzene concentrations, number of fall/winter hours, and number of spring/summer hours grouped by wind direction during 2006 – 2008 (Appendix B: McGaughey et al., 2009).

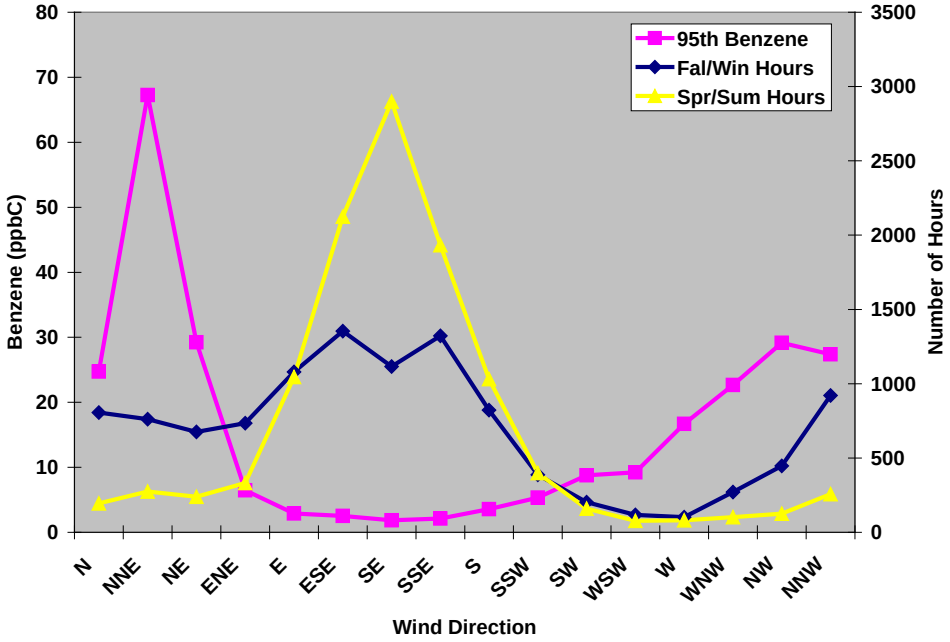
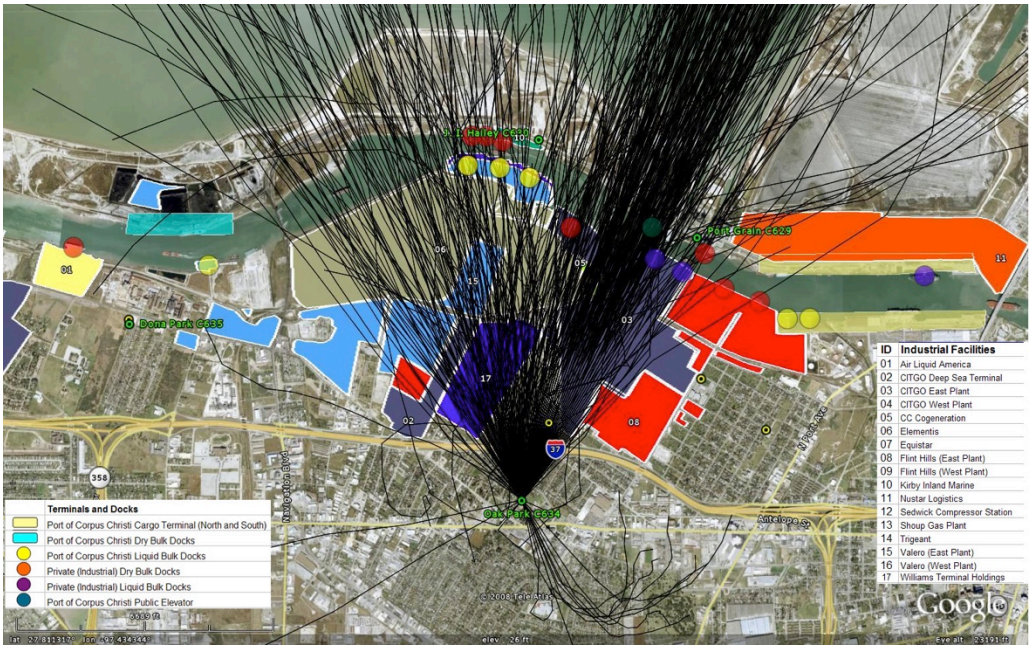


Figure 4-8. Surface back-trajectories as generated by the Corpus Christi Trajectory Analysis Tool for all hours characterized by an observed benzene concentration of 30 ppb or greater at Oak Park during June 2005 - May 2008 (Appendix B: McGaughey et al., 2009).



AERMOD and CALPUFF predictions were similar, but not identical, with respect to their agreement with observations at both sites. Ratios of predicted to observed concentrations for all metrics (mean, maximum, 75th, 95th, and 99th percentiles) at Oak Park were within a factor of two or less (Table 4-10). Both models under-predicted the observed maximum concentration at Oak Park, 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. Ratios of mean, 75th, or 95th percentile AERMOD or CALPUFF predicted concentrations to observed concentrations ranged from 0.3 to 1.0 at Solar Estates. Both models over-predicted the highest (99th percentile and maximum concentrations) observed benzene concentrations at Solar Estates.

4.5.2 1,3-Butadiene

Table 4-11, page 4-29, 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. Scatter plots of predicted versus observed 1,3-butadiene concentrations by season during 2006 at Oak Park are shown in Figure 4-9, page 4-30, and at Solar Estates in Figure 4-10, page 4-31.

In contrast to benzene, the highest observed concentrations of 1,3-butadiene occurred at Solar Estates not Oak Park. The fall/winter to spring/summer ratio of mean observed 1,3-butadiene concentrations at Oak Park during 2006 was 2.6. 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. 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. AERMOD 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 at Solar Estates were associated with southwesterly, west-southwesterly, or westerly winds, as shown in Figure 4-11, page 4-32. These latter wind directions are rare throughout the year, but are more frequent during the fall/winter than spring/summer. One-hour back-trajectories during high concentration hours were generated to identify potential emissions source regions that may impact concentrations at Solar Estates. Figure 4-12, page 4-32, 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 influenced observed concentrations at the monitor.

Comparisons of modeled to observed concentrations at Oak Park and Solar Estates during 2006 indicated a strong under-prediction bias by both models. At Oak Park, ratios of mean, 75th, or 95th percentile AERMOD or CALPUFF predicted concentrations to observed concentrations ranged from 0.4 to 0.9 with a single exception (i.e., the 95th percentile ratio for AERMOD). Both models substantially underestimated the observed fall/winter maximum concentration at Oak Park and Solar Estates. The ratios of maximum AERMOD and CALPUFF predicted concentrations to the observed concentration were 0.2 and 0.1, respectively. Ratios of mean, 75th

percentile, 95th percentile, 99th percentile, and maximum AERMOD or CALPUFF predicted to observed concentrations during the fall/winter of 2006 at Solar Estates ranged from 0.02 to 0.5.

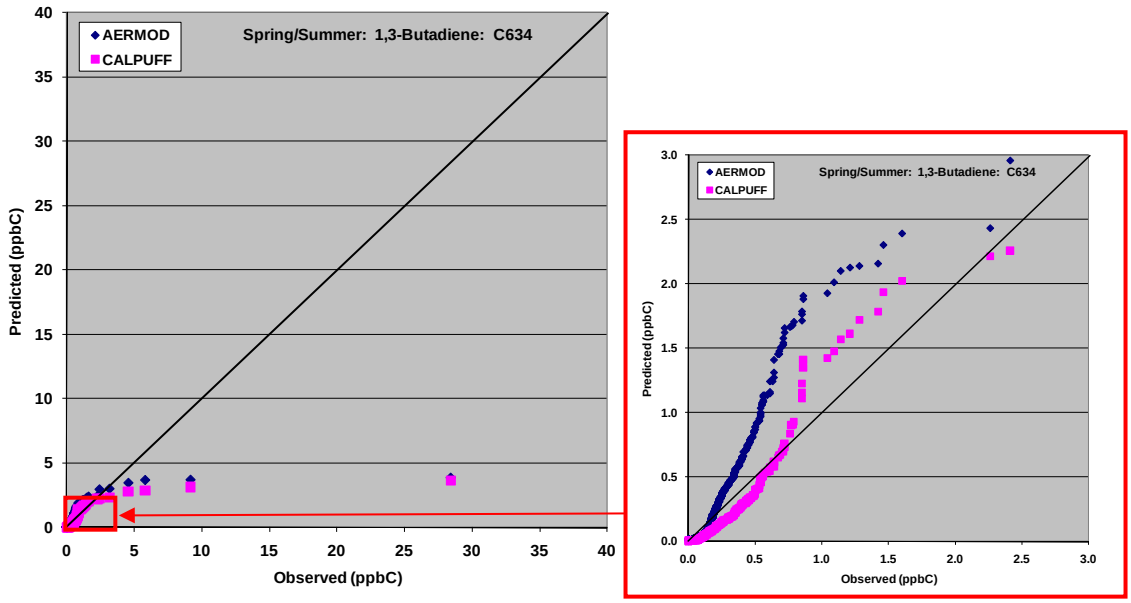
Application of AERMOD and CALPUFF for 1,3-butadiene in Corpus Christi provided valuable insights regarding emissions reporting at the time. The strong under-prediction biases in the modeling results for 1,3-butadiene at Oak Park and Solar Estates suggested that the 2005 TCEQ Photochemical Modeling Inventory, which was generated from emissions reported to the State of Texas Air Reporting System (STARS) by affected facilities, was not fully representative of actual emissions sources in Corpus Christi. The potential for missing industrial emissions information was also indicated, especially near Solar Estates, as observed concentrations may often be associated with non-routine emissions that are not captured by the existing emissions inventories.

Table 4-11. 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. 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	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	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	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	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 4-9. Scatter plots of predicted versus observed 1,3-butadiene concentrations at Oak Park during the (a) spring/summer and (b) fall/winter of 2006.

(a)



(b)

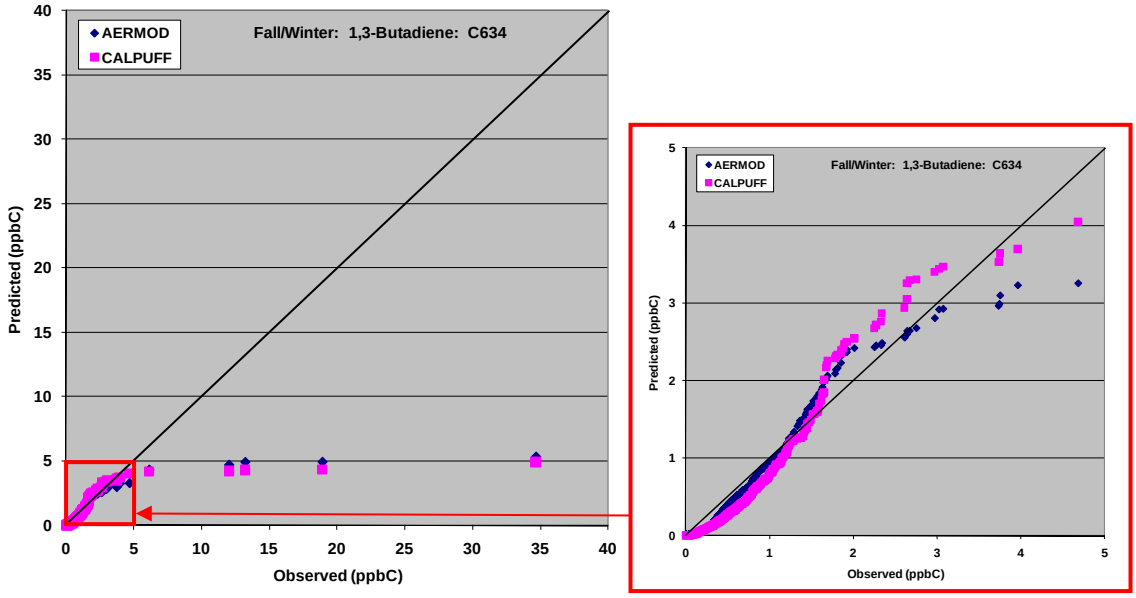
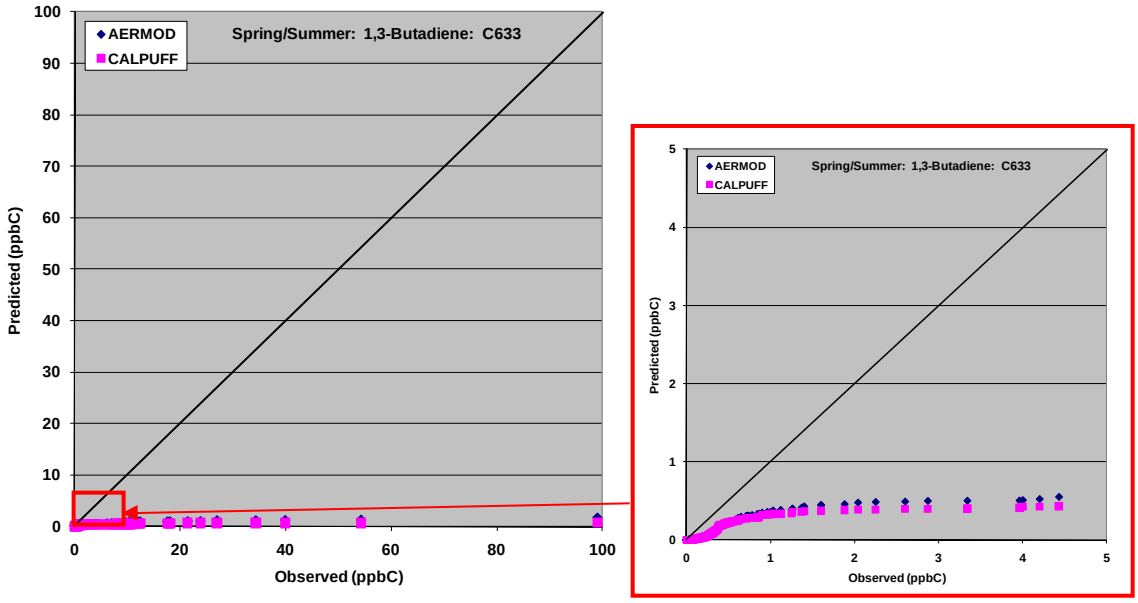


Figure 4-10. Scatter plots of predicted versus observed 1,3-butadiene concentrations at Solar Estates during the (a) spring/summer and (b) fall/winter of 2006.

(a)



(b)

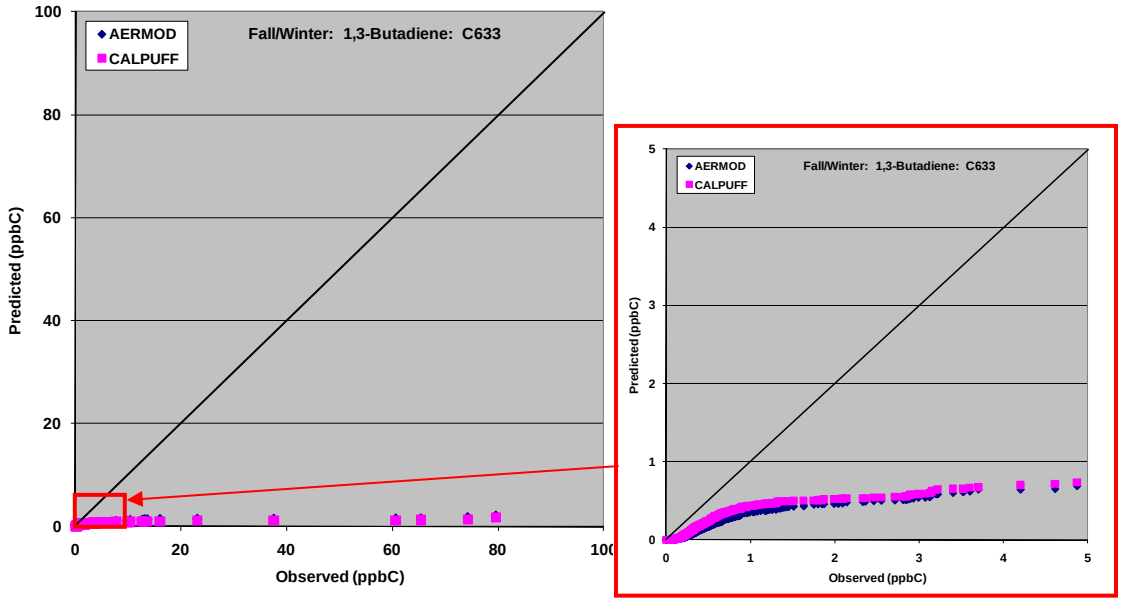


Figure 4-11. Solar Estates observed 95th percentile 1,3-butadiene concentrations, number of fall/winter hours, and number of spring/summer hours grouped by wind direction during 2006 – 2008.

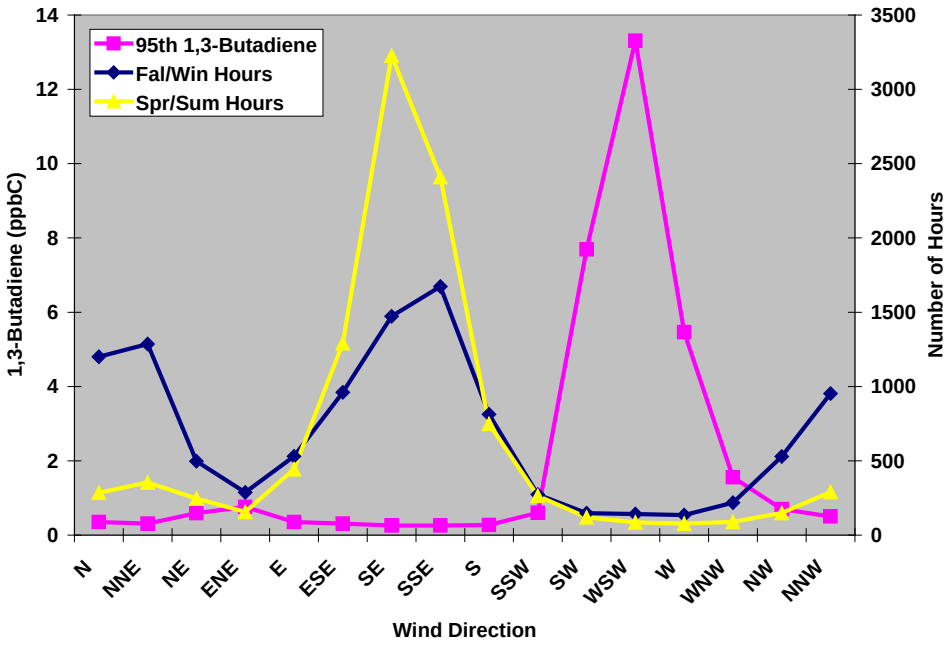
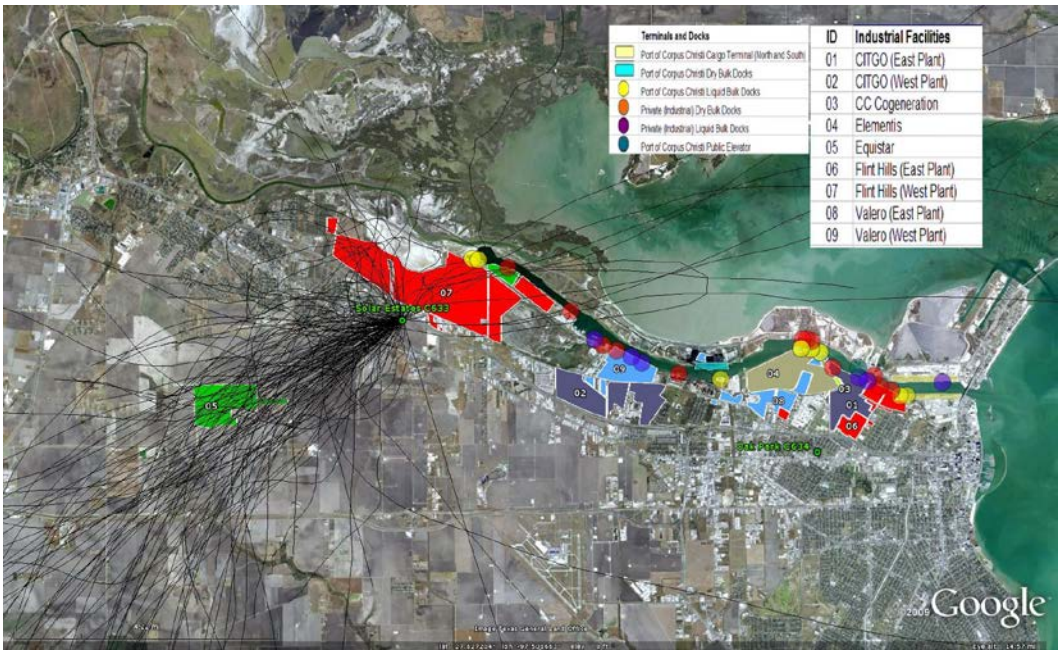


Figure 4-12. Surface back-trajectories as generated by the Corpus Christi Trajectory Analysis Tool for all hours characterized by a 1,3-butadiene concentration greater than or equal to 5 ppbC at Solar Estates during 2006 - 2009.



4.6 Annual Trends in Predicted and Observed Concentrations

The previous section described air dispersion modeling conducted with the 2005 TCEQ Photochemical Modeling Inventory and 2006 meteorological data for comparisons with observations during 2006. 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. This has the potential to create disparities in evaluating trends in regions with rapidly changing inventories. Although it is ideal to utilize year-specific emissions inventories for modeling, inventories with the same level of detail as the 2005 TCEQ Photochemical Modeling Inventory for Corpus Christi were not available for more recent years at the time of this work. Nonetheless, additional air dispersion modeling was also conducted using the 2005 TCEQ Photochemical Modeling Inventory with meteorological data for 2007 and 2008. Comparisons with observations at Oak Park and Solar Estates provided insights on the influences inter-annual meteorological variability and emission trends on model performance.

Mean observed benzene concentrations at Oak Park (Figure 4-13, page 4-34) and Solar Estates (Figure 4-14, page 4-34) during the spring/summer and fall/winter of 2007 and 2008 were approximately 50% and 60%, respectively, of 2006 values. With the assumption that emissions remained constant annually, neither CALPUFF nor AERMOD were able to consistently replicate decreases in observed benzene concentrations that occurred at Oak Park and Solar Estates between 2006 and 2008. At Oak Park, changes in predicted annual mean concentrations were similar between AERMOD and CALPUFF and did not show consistent decreases over time, although predicted mean concentrations were the lowest in 2008 similar to observations. At Solar Estates, AERMOD showed little variation in mean concentrations between 2006 and 2008, while CALPUFF predicted the highest mean concentrations during 2008. Although, annual variability in meteorological conditions likely contributed to differences in observed and modeled concentrations, these results suggested that decreases in observed benzene concentrations were also 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 (Table 4-1).

Annual observed 1,3-butadiene concentrations were generally lower in 2008 than in 2006 at both sites, Oak Park (Figure 4-15, page 4-35) and Solar Estates (Figure 4-16, page 4-35), with marked decreases at Solar Estates. Although both models under-predicted observed concentrations throughout the three-year period, the agreement between predicted and observed concentrations improved between 2006 and 2008 as observed concentrations declined. TRI emissions inventories lack the specificity necessary for air dispersion modeling but because they are reported on an annual basis, they serve as a useful resource in conjunction with trends in the ambient measurements from the CCAQAP network for assessing overall changes in emission sources, Reported annual air emissions of 1,3-butadiene in 2006, 2007, and 2008 TRI data were 14, 7, and 9 tpy (Table 4-1), respectively, indicating lower emissions in 2008 than in 2006. Equistar's decision to idle operations of its butadiene extraction units as part of its transition to feedstock of nearly all natural gas liquids (NGL) was announced in 2009 (https://www.lyondellbasell.com/en/news-events/products--technology-news/equistar-to-add-feedstock-flexibility-at-corpus-christi/). It is possible but could not be confirmed that this transition contributed to declines in emissions and observed concentrations of 1,3-butadiene.

Figure 4-13. Predicted and observed annual mean benzene concentrations at Oak Park during 2006 - 2008. Predictions are based on air dispersion modeling conducted with the 2005 TCEQ Photochemical Modeling Inventory for all years.

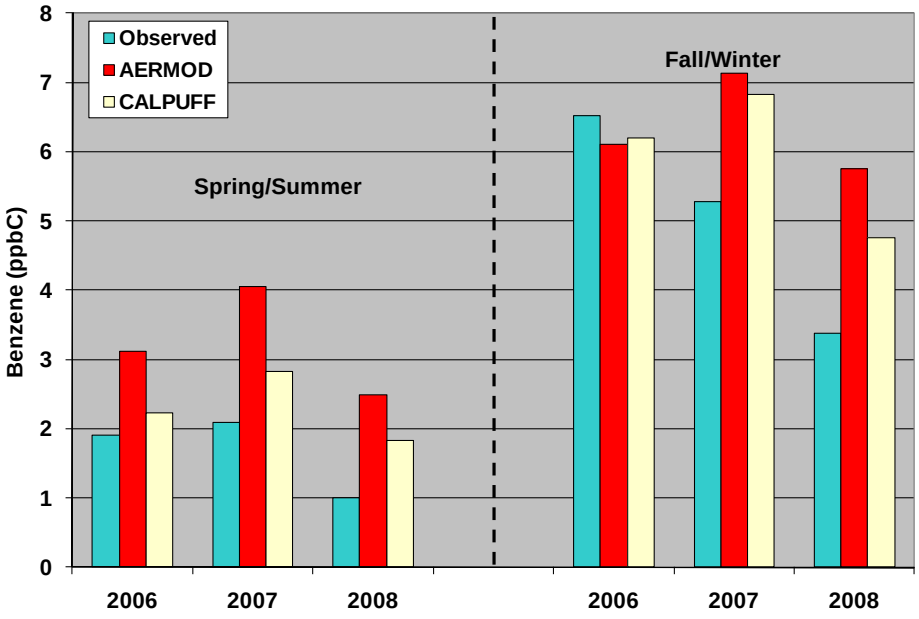


Figure 4-14. Predicted and observed annual mean benzene concentrations at Solar Estates during 2006 - 2008. Predictions are based on air dispersion modeling conducted with the 2005 TCEQ Photochemical Modeling Inventory for all years.

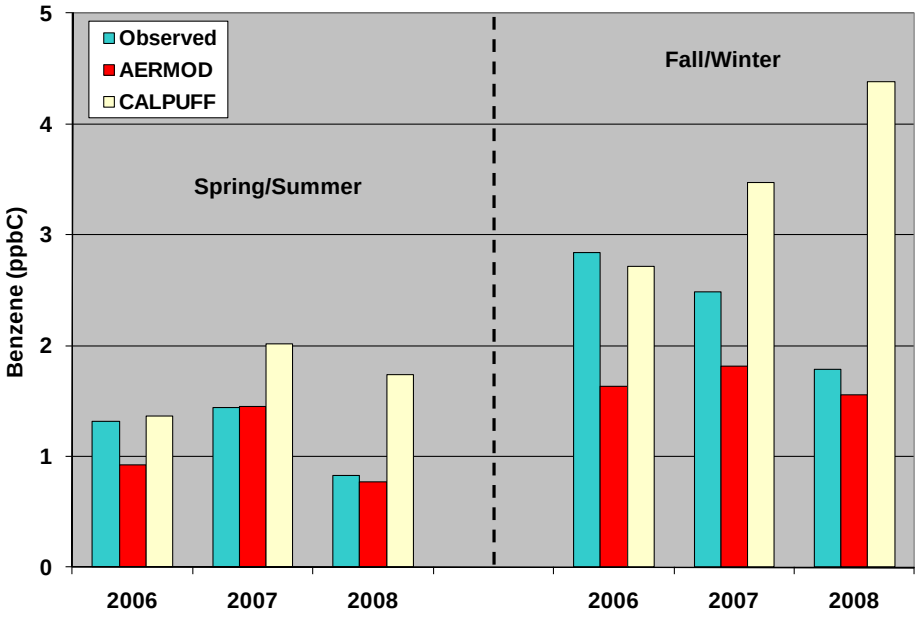


Figure 4-15. Predicted and observed annual mean 1,3-butadiene concentrations at Oak Park during 2006 - 2008. Predictions are based on air dispersion modeling conducted with the 2005 TCEQ Photochemical Modeling Inventory for all years

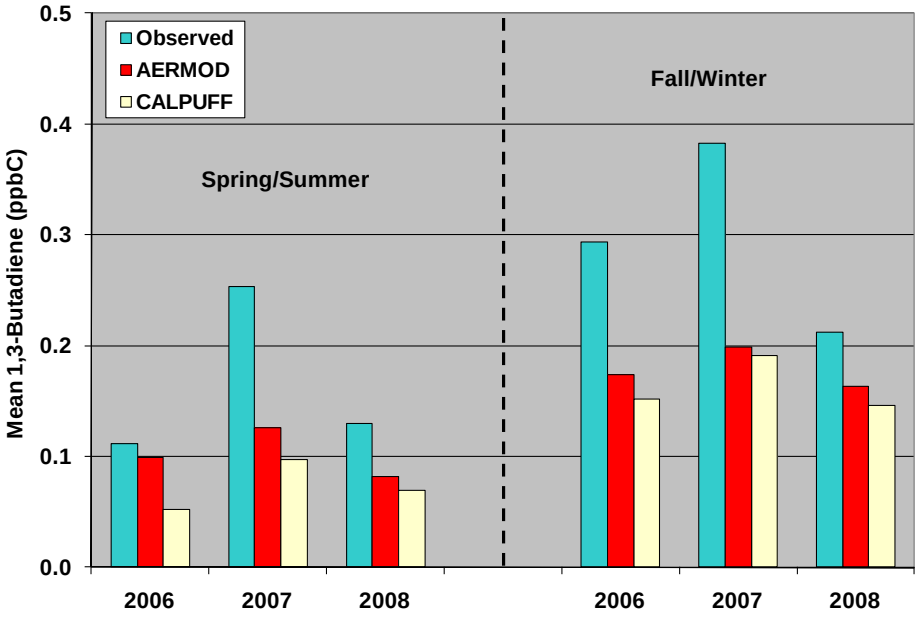
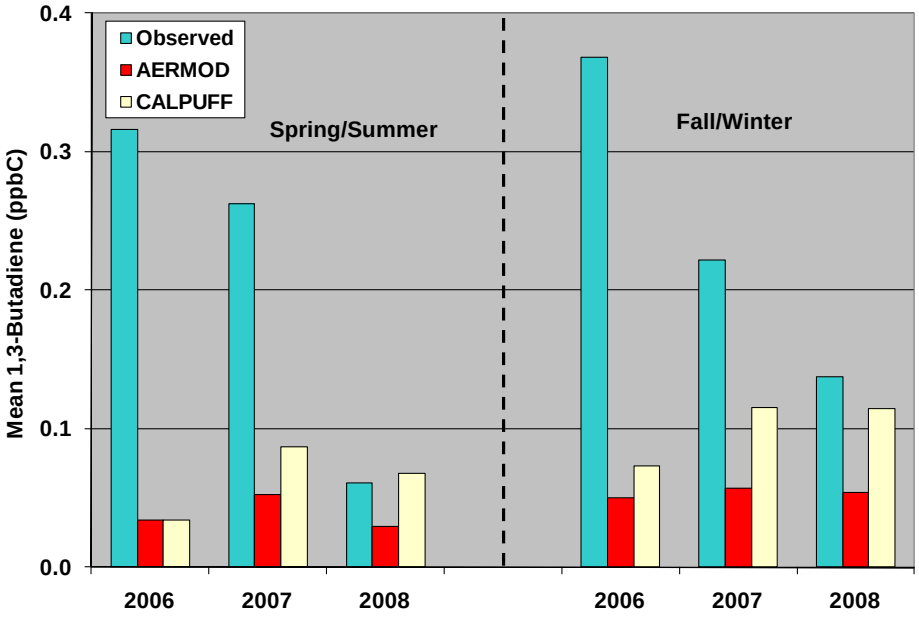


Figure 4-16. Predicted and observed annual mean 1,3-butadiene concentrations at Solar Estates during 2006 - 2008. Predictions are based on air dispersion modeling conducted with the 2005 TCEQ Photochemical Modeling Inventory for all years



4.7 Spatial Maps of Predicted Concentrations

Spatial maps of predicted concentrations allow air toxics concentrations to be estimated in areas without monitoring sites, providing necessary information for assessing human exposure and health risks. They also allow identification of locations with relatively higher concentrations in the area that could be targeted for future measurement efforts.

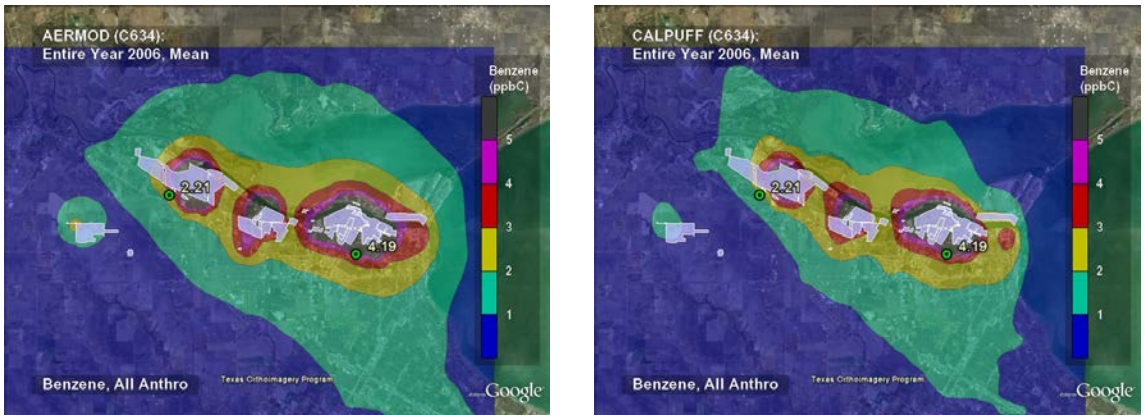
Figure 4-17, pages 4-37 and 4-38, shows annual mean, 75th percentile, 95th percentile, and maximum predicted benzene concentrations in the receptor grid (refer to Figure 3) from AERMOD and CALPUFF for Oak Park (C634). Similar maps are shown for the Solar Estates (C633) monitor in Figure 4-18, pages 4-39 and 4-40. On-site meteorological data from the Oak Park monitor or Solar Estates monitor were used for the respective AERMOD simulations. Note that unlike AERMOD, CALPUFF is not restricted to use of on-site meteorological data from a single site. Industrial facility property boundaries are shown in each map, along with observed concentrations at the locations of the monitors.

Maps of predicted benzene concentrations during 2006 were similar for both models, with the exception of annual maximum concentrations. Wind patterns in AERMOD reflected constant hourly trajectories associated with the restriction of on-site meteorological data from a single site, which led to the “fingerlike” appearance of predicted maximum concentrations. In contrast, CALPUFF represented the spatial variability in wind patterns by incorporating data from multiple sites. The Oak Park and Solar Estates monitors were located within two areas of influence at either end of the Ship Channel. However, neither monitor was 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 were made at Dona Park, chemically speciated measurements, such as those made with an auto-GC, were not routinely determined during the time period of this work.

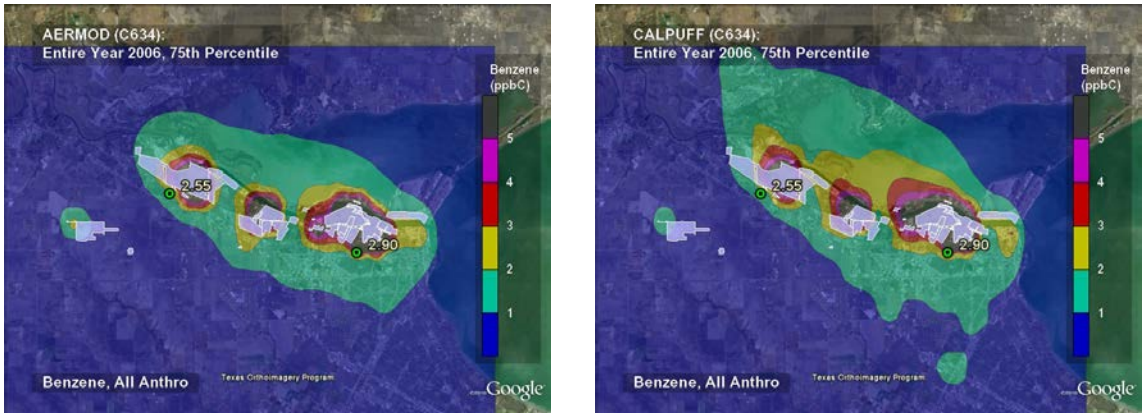
Annual mean, 75th percentile, 95th percentile, and maximum predicted 1,3-butadiene concentrations from AERMOD and CALPUFF are shown for Oak Park in Figure 4-19, pages 4-41 and 4-42, and Solar Estates in Figure 4-20, pages 4-43 and 4-44. Spatial maps of predicted 1,3-butadiene concentrations during 2006 were similar for both models, with the exception of annual maximum concentrations that, similar to the results for benzene, were affected by AERMOD’s restriction of on-site meteorological data from a single site. The maps and surface wind back trajectories indicated that Equistar was an important emissions source, but neither of the current auto-GC sites were well positioned to characterize concentrations close to this source. The maps also indicated that neither monitor was positioned to capture 1,3-butadiene concentrations within the Dona Park area.

Figure 4-17. Predicted annual (a) mean, (b) 75th percentile, (c) 95th percentile, and (d) 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. Property boundaries of the stationary point sources are shown in gray.

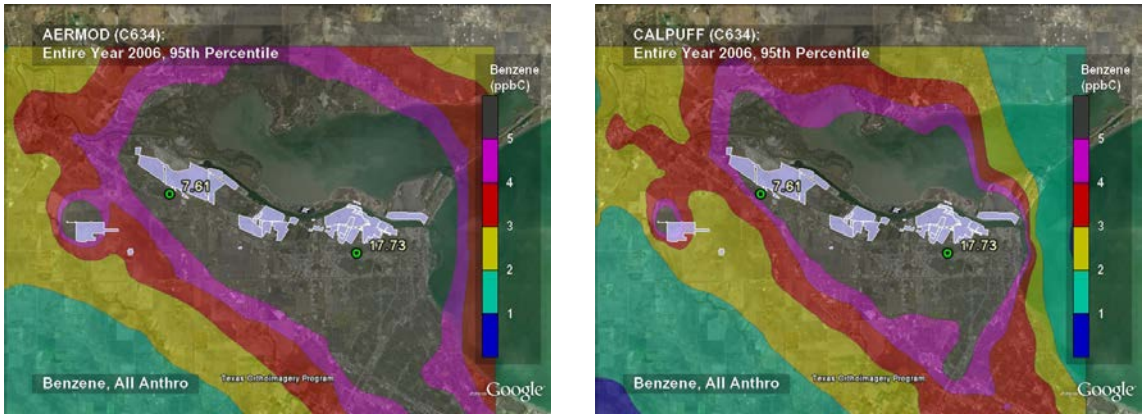
(a)



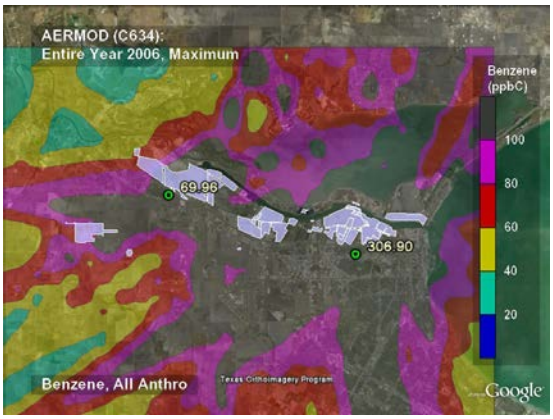
(b)



(c)



(d)


AERMOD (C634):
Entire Year 2006, Maximum
Benzene (ppbC)
100
80
60
40
20
69.96
306.90
Benzene, All Anthro
Google

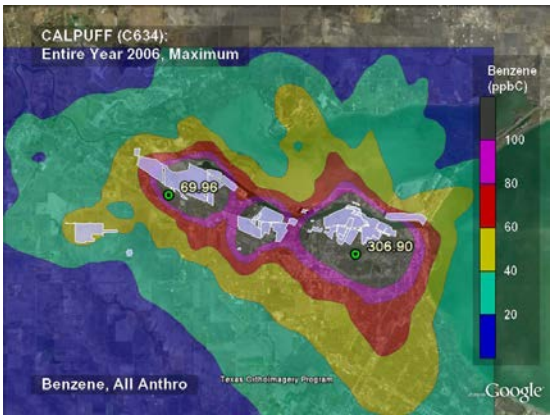
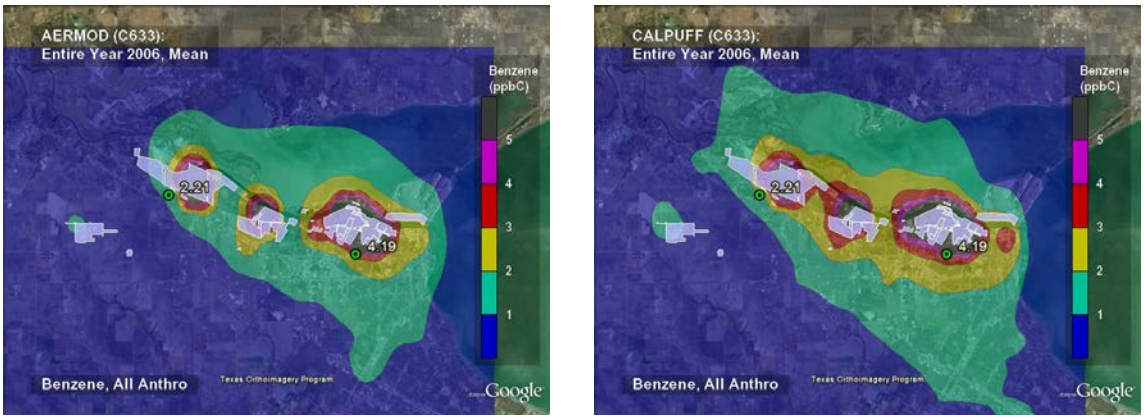
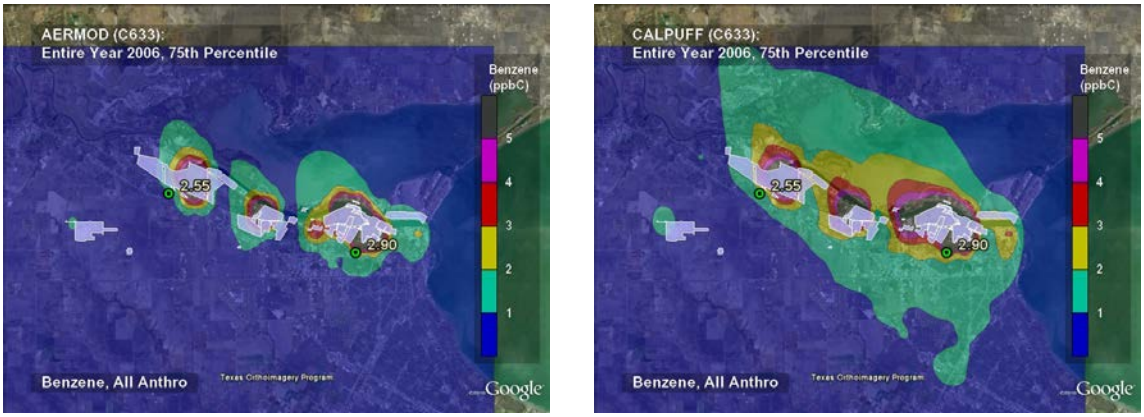

CALPUFF (C634):
Entire Year 2006, Maximum
Benzene (ppbC)
100
80
60
40
20
69.96
306.90
Benzene, All Anthro
Google

Figure 4-18. Predicted annual (a) mean, (b) 75th percentile, (c) 95th percentile, and (d) 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. Property boundaries of the stationary point sources are shown in gray.

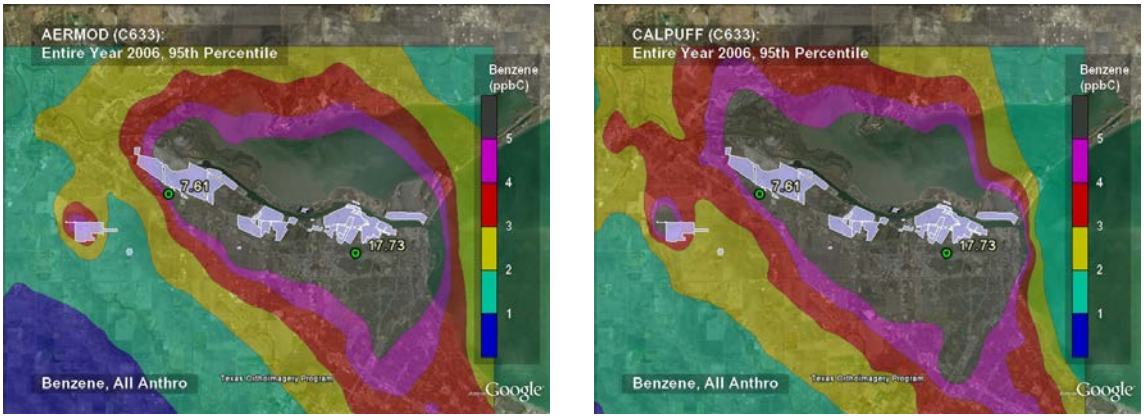
(a)



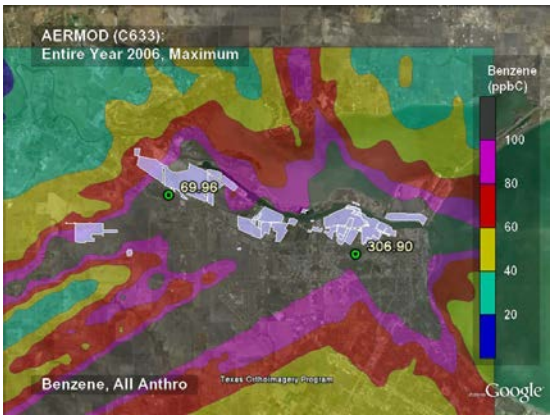
(b)



(c)



(d)


AERMOD (C633):
Entire Year 2006, Maximum
Benzene (ppbC)
100
80
60
40
20
69.96
306.90
Benzene, All Anthro
Google

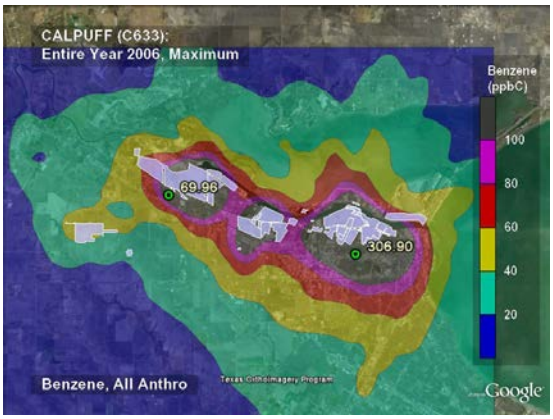
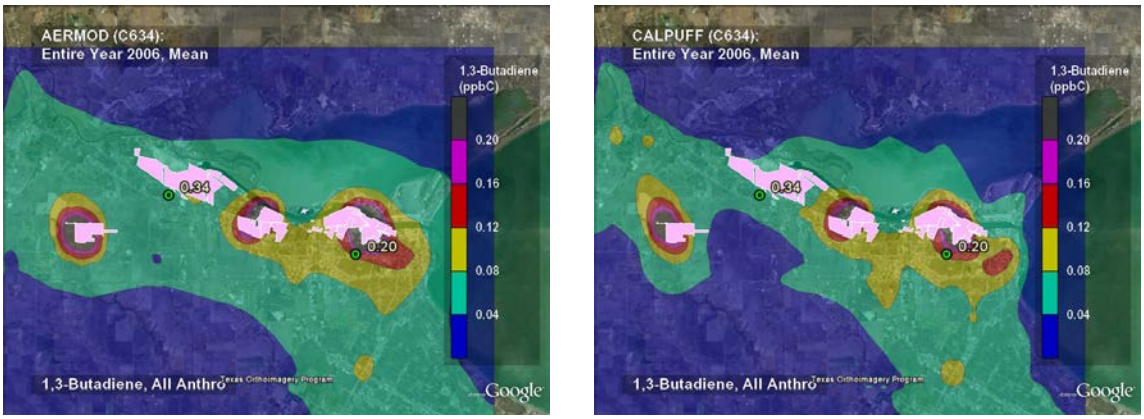
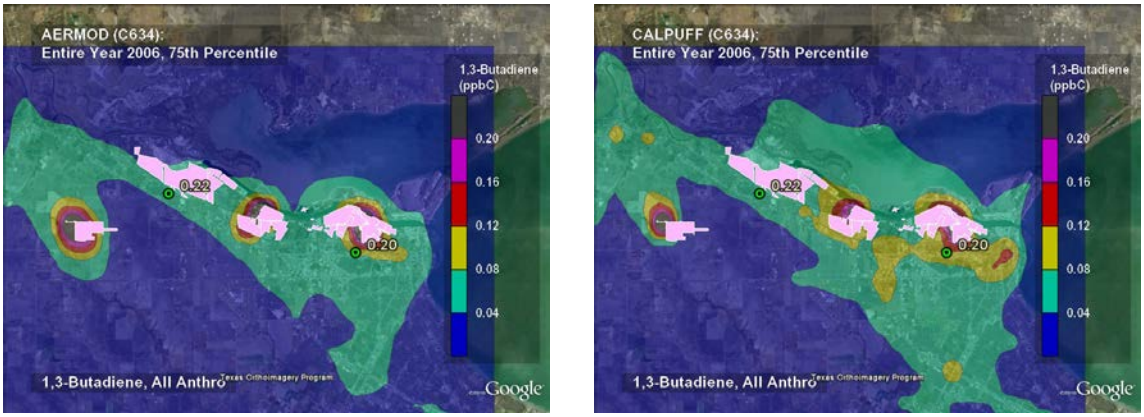

CALPUFF (C633):
Entire Year 2006, Maximum
Benzene (ppbC)
100
80
60
40
20
69.96
306.90
Benzene, All Anthro
Google

Figure 4-19. Predicted annual (a) mean, (b) 75th percentile, (c) 95th percentile, and (d) 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 Oak Park (C634) monitor for AERMOD. Property boundaries of the stationary point sources are shown in pink.

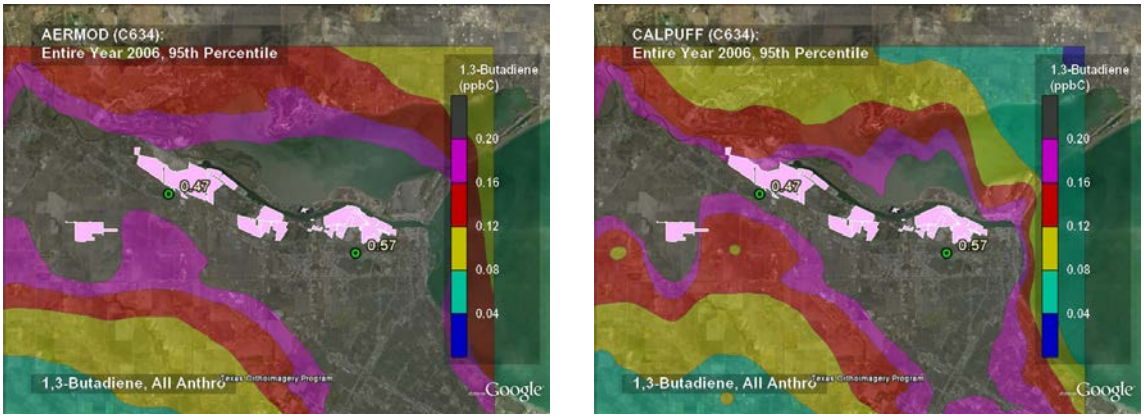
(a)



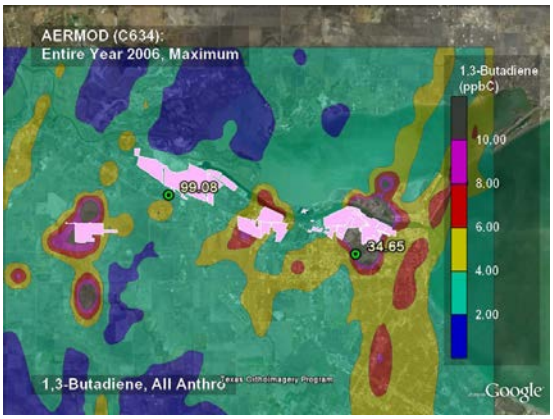
(b)



(c)



(d)


AERMOD (C634):
Entire Year 2006, Maximum
1,3-Butadiene (ppbC)
10.00
8.00
6.00
4.00
2.00
99108
34165
1,3-Butadiene, All Anthro
Google

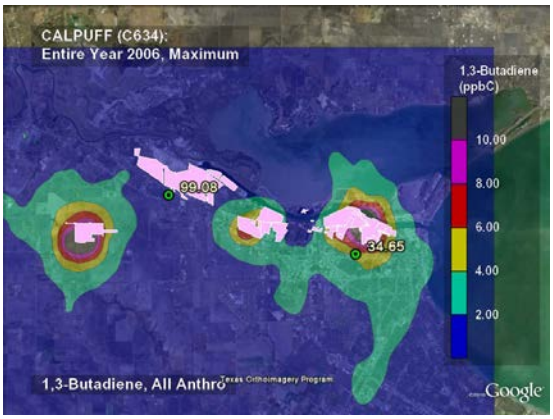
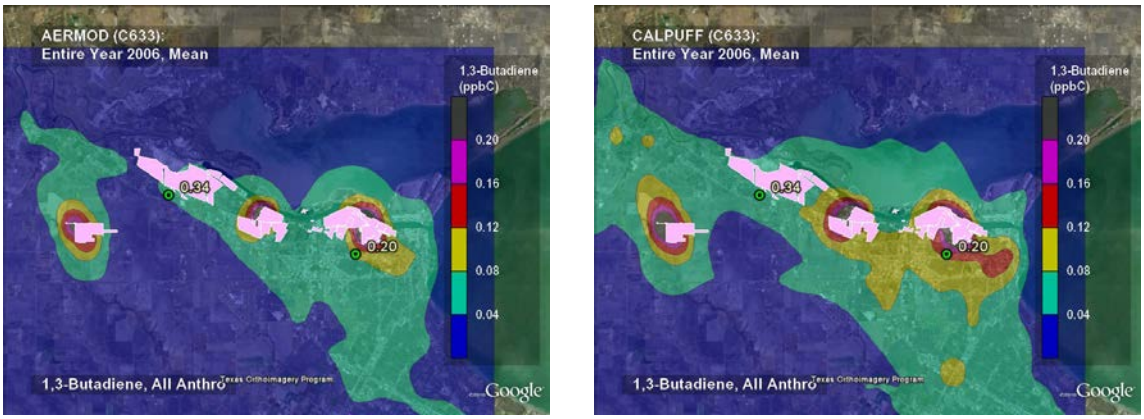
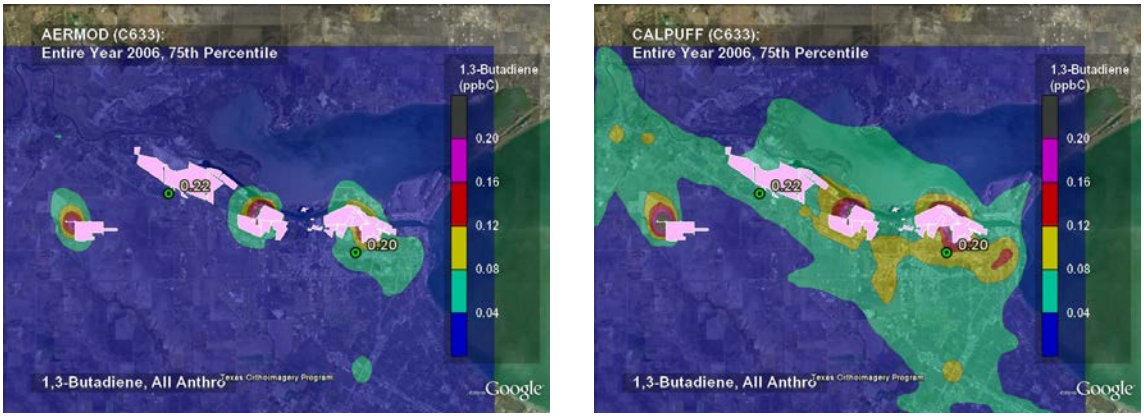

CALPUFF (C634):
Entire Year 2006, Maximum
1,3-Butadiene (ppbC)
10.00
8.00
6.00
4.00
2.00
99108
34165
1,3-Butadiene, All Anthro
Google

Figure 4-20. Predicted annual (a) mean, (b) 75th percentile, (c) 95th percentile, and (d) 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. Property boundaries of the stationary point sources are shown in pink.

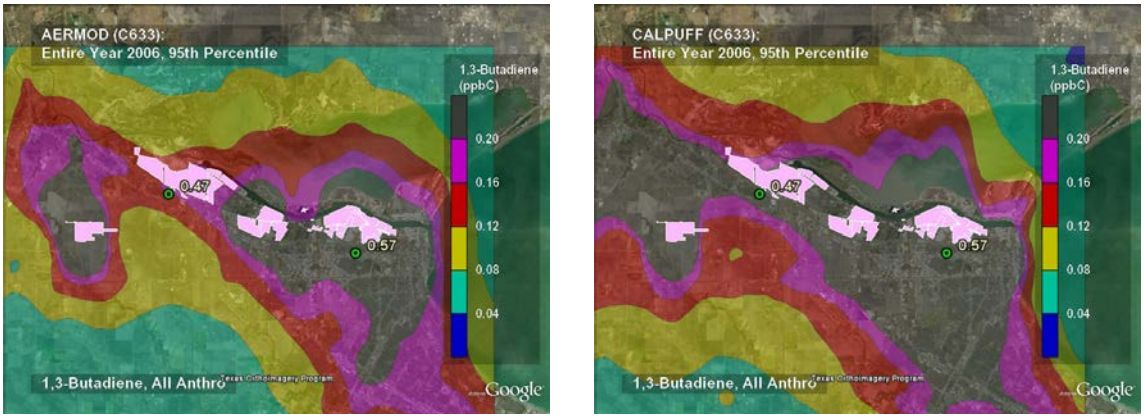
(a)



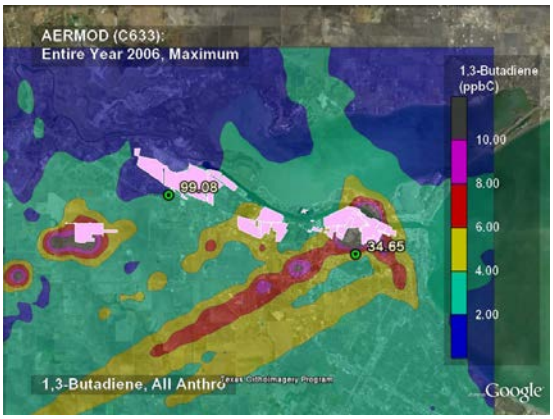
(b)

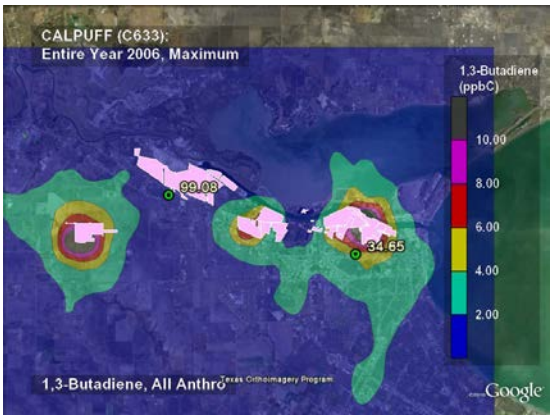


(c)



(d)


AERMOD (C633):
Entire Year 2006, Maximum
1,3-Butadiene (ppbC)
10.00
8.00
6.00
4.00
2.00
99.08
34.65
1,3-Butadiene, All Anthro
Google


CALPUFF (C633):
Entire Year 2006, Maximum
1,3-Butadiene (ppbC)
10.00
8.00
6.00
4.00
2.00
99.08
34.65
1,3-Butadiene, All Anthro
Google

4.8 Air Dispersion Modeling Conclusions

This work examined predictions of benzene and 1,3-butadiene concentrations from stationary industrial and other anthropogenic emissions sources in Corpus Christi, Texas using AERMOD and CALPUFF, which represent the state-of-the-practice for air dispersion modeling in the United States. Dispersion models require meteorological, emissions, and geographic information as input. Modeling was conducted using three years of meteorological data for 2006 through 2008. Thirteen existing emission inventories developed between 2000 and 2008 for stationary point sources in Nueces and San Patricio counties were obtained and compared; these included 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. Differences in annual emissions between some inventories were found to be more than a factor of two.

The 2005 TCEQ Photochemical Modeling Emissions Inventory was selected for the dispersion modeling. This inventory had the same level of spatial resolution of emissions sources as the National Emissions Inventory. However, 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 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 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.

The objectives for the air dispersion modeling efforts were to compare model predictions with measured concentrations at Oak Park and Solar Estates, to estimate concentrations of these pollutants in areas where ambient monitoring sites were not present, and to provide guidance for potential locations for additional sites should the monitoring network be expanded in the future.

Key findings from the air dispersion modeling are described below:

- AERMOD and CALPUFF replicated observed seasonal and locational differences in benzene concentrations, with increases in fall/winter relative to spring/summer at the residential monitoring sites (Solar Estates and Oak Park). Higher observed concentrations during the fall/winter than spring/summer were associated with more frequent northwesterly clockwise through northeasterly winds.

- Observed maximum benzene concentration at Oak Park were under-predicted by both models. This result may be associated with non-routine emissions not necessarily represented in the emission inventory.

- Observed benzene concentrations declined at Oak Park and Solar Estates between 2006 and 2008. These trends are consistent with declines in annual benzene emissions reported in the Toxics Release Inventory (TRI).

- Comparisons of modeled to observed 1,3-butadiene concentrations at Oak Park and Solar Estates during 2006 indicated a strong under-prediction bias by both models. This finding suggested that emissions of 1,3-butadiene could be missing from or under-reported in the emission inventories evaluated in this project. The potential for missing industrial emissions information was particularly pronounced near Solar Estates.

- Spatial maps of predicted mean, percentile, and maximum concentrations of benzene (e.g., Figure 4-21, below) and 1,3-butadiene (e.g., Figure 4-22, below) were developed to allow air toxics concentrations to be estimated in areas without monitoring sites. Maps of predicted benzene concentrations during 2006 were generally similar for both models. The locations of the Oak Park and Solar Estates monitors (shown as green dots in the Figures) were in regions with high-predicted concentrations of benzene and 1,3-butadiene.

Figure 4-21. Predicted annual mean benzene concentrations in the receptor grid (colored area) from AERMOD (left) and CALPUFF (right) for 2006. Property boundaries of the stationary point sources are shown in gray.

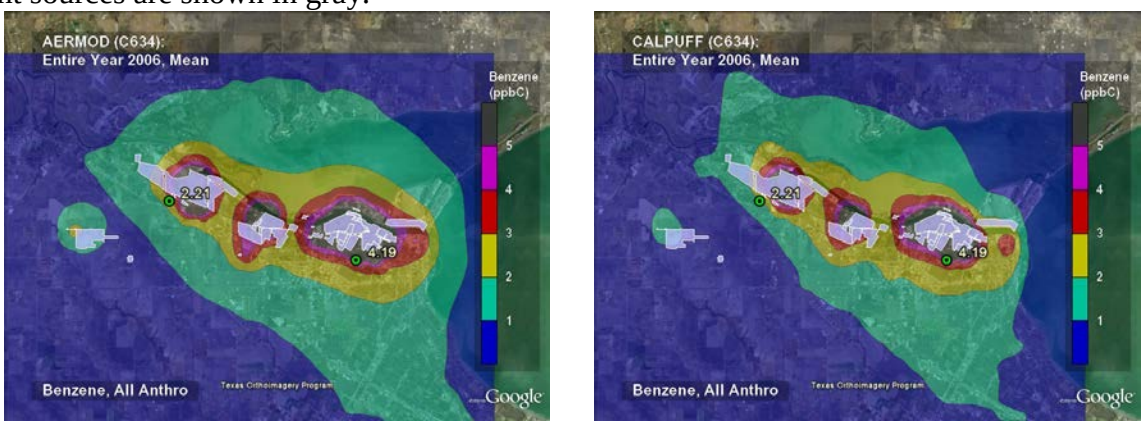
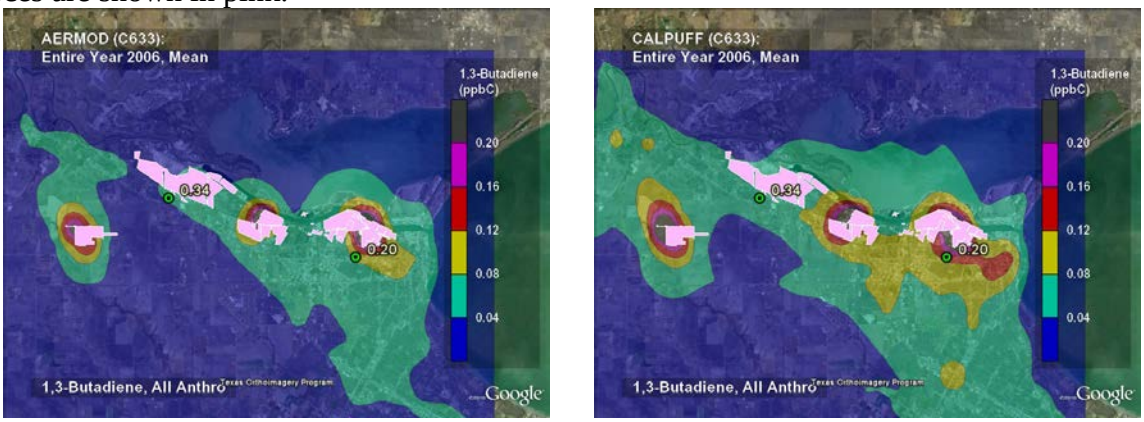


Figure 4-22. Predicted annual mean 1,3-butadiene concentrations in the receptor grid (colored area) from AERMOD (left) and CALPUFF (right) for 2006 using on-site meteorological data from the Solar Estates (C633) monitor for AERMOD. Property boundaries of the stationary point sources are shown in pink.



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