The Influence of Air Toxics Emission Inventory Selection on Air Quality Model Predictions in Corpus Christi, Texas

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ABSTRACT

Ambient monitoring, emission inventory development, and air quality modeling of air toxics are critical elements of human exposure and health risk assessments. The Port of Corpus Christi, Texas is among the largest in the United States with significant petroleum refining and chemical manufacturing industries. The close proximity to residential areas has raised concerns about exposure to air toxics. Since mid-2005, The University of Texas at Austin has operated a seven-site network that measures total non methane hydrocarbon and meteorological data as well as threshold triggered canister samples. Automated gas chromatographs are operated at two of the seven sites. Numerous inventories of air toxics emissions from industrial sources have been compared for the Corpus Christi region. Predicted concentrations of historically important air toxics in the region using the AERMOD and CALPUFF dispersion modeling systems are also under development. This study reports the findings of the emission inventory comparisons for benzene and 1,3-butadiene, respectively, and examines the implications of point source emissions inventory variability on dispersion model predictions of benzene concentrations using CALPUFF. An underlying difference between the emission inventories is related to the chemical speciation of emissions that are otherwise reported as VOC with unspecified composition and the accounting for rule effectiveness.

INTRODUCTION

Corpus Christi, Texas, 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 (http://www.iwr.usace.army.mil/ndc/wcsc/portton01.htm) with significant petroleum refining and chemical manufacturing industries. The area is currently in attainment with the National Ambient Air Quality Standards for both ozone and fine particulate matter. However, the close proximity of residential to industrial areas has raised concerns about exposure to air toxics.

Since mid-2005, The University of Texas at Austin (UT) has operated a seven site ambient monitoring network that includes measurements of hydrogen sulfide (total reduced sulfur), sulfur dioxide (SO_2), TNMHC, and meteorological (e.g., temperature, wind speed, wind direction, and relative humidity) 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 auto-GCs with flame ionization detection. The network design provides the flexibility to trigger the collection of

20-minute integrated VOC canister samples 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. The air toxics monitoring network and an analysis of the temporal variability of measured total non-methane hydrocarbons (TNMHC) and benzene concentrations in the Corpus Christi area are described by McGaughey et al.[1] and McDonald-Buller et al.[2]

Predicted concentrations of historically important air toxics in the region using the AERMOD and CALPUFF dispersion modeling systems are also under development. In preparation for the modeling, numerous inventories of air toxics emissions from industrial sources were evaluated and compared for the Corpus Christi region. This study reports the findings of the emission inventory comparison, focusing on benzene and 1,3-butadiene, and examines the implications of point source emissions inventory variability on dispersion model predictions using AERMOD.

EMISSION INVENTORY SELECTION AND EVALUATION

Air toxics have the potential to be emitted from numerous anthropogenic emission sectors with disparate spatial, temporal, chemical and physical release profiles. A key element in performing air quality modeling is the development of an emissions inventory, preferably with a high degree of spatial and temporal resolution. Multiple emission inventories for Nueces and San Patricio counties were obtained and evaluated, including data from the National Emission Inventory (NEI), the Toxics Release Inventory (TRI) Program, the State of Texas Air Reporting System (STARS), and the Texas Commission on Environmental Quality (TCEQ) emission inventories used for photochemical modeling to support State Implementation Plan development. These inventories were used to examine annual trends in point source emissions of toxic air pollutants, to identify differences between reported emissions and emissions used in state or national-level air quality modeling efforts, and to select emissions input data for dispersion and photochemical modeling for the region.

The Toxics Release Inventory Program history and data are available from the U.S. EPA on an annual reporting cycle.[3] Air emissions are segregated as stack and fugitive emissions in the TRI database. Facilities are identified in the TRI by name, TRI facility ID, NAICS code, latitude and longitude, and facility-wide total stack and fugitive emissions are provided by chemical. The TRI database does not provide any greater source resolution than the facility-wide summaries and does not include detailed stack parameters in contrast to other inventories evaluated for the region. Although the lack of source resolution limits its use in air quality modeling efforts that necessitate a high degree of spatial resolution, the TRI nonetheless provides a temporally continuous source of reported emissions that is useful in assessing annual trends.

As its title implies, the NEI is a national-scale inventory of criteria air pollutants (CAPs) and hazardous air pollutants (HAPs) that was developed to support the mandates of the 1990 Clean Air Act Amendments (CAAA). Application of the NEI is broad, including use in State Implementation Plan (SIP) development, compliance demonstrations, photochemical modeling studies for evaluation of air pollutant concentrations and for use in the National Air Toxics Assessment (NATA) and risk assessments. Texas submits data on both CAPs and HAPs for the NEI. The TCEQ does not have a reporting threshold for inclusion in their NEI submittal; thus, all data that is reported through the State of Texas Air Reporting System (STARS) database, described below, is included in the State’s submittal to the NEI.[4] According to the U.S. EPA, data from the Texas submittals undergo quality assurance/quality control assessments, but are not otherwise altered before public release of the NEI.[5] The NEI has greater source resolution than the TRI. Among the data elements that are requested by the U.S. EPA are facility name and address, NAICS code, latitude and longitude, emission unit descriptions, emission process descriptions, source classification codes (SCC), actual throughputs, emission process activities, pollutant codes, emission estimates, stack parameters, and control equipment device types and efficiencies.

Annual point source emissions are reported by facilities to the State of Texas using the STARS electronic reporting system. In addition to NEI submittals, the State of Texas also generates point source emission inventories suitable for photochemical modeling using the STARS database. Consequently, the photochemical modeling inventories have the same level of source resolution as the U.S. EPA NEI and the State of Texas submittals to the NEI. However, TCEQ's air quality modeling group does additional processing of the STARS data to account for rule effectiveness (RE) as well as to further speciate emissions that are otherwise reported as VOC with unspecified composition. Thomas et al.[6] provides a detailed description of the speciation process, in a study presented at the 17th Annual International Emission Inventory Conference in June 2008. Using a fully speciated inventory for the Houston-Galveston-Brazoria area has been critical for assessing the effectiveness of control strategies because of regulations that target highly reactive VOCs in the region. RE attempts to account for actual in-use control efficiency, which is less than the assumed maximum destruction efficiency in the reported emissions. RE factors for VOC emissions generally applied by the TCEQ at the SCC/SIC level according to geographic regions in Texas[7.] Analysis of the 2005 TCEQ Photochemical Modeling Inventory indicated that accounting for RE primarily affects VOC emissions from flares, equipment leak fugitives, external floating roof tanks, internal floating roof tanks, and, to a lesser extent, vertical fixed tanks. These sources are among the largest in Nueces and San Patricio Counties and account for almost 70% of the total VOC after RE emissions with most associated with petroleum refining. Overall VOC emissions increase from approximately 6600 tpy to 8500 tpy (28.6%) after accounting for RE in the two counties.

In addition to differences in source resolution between the inventories, there were also found to be differences between the number and type of species included in each. While many air toxics such as benzene and 1,3-butadiene appeared in all of the inventories, the photochemical modeling inventories had the most comprehensive level of VOC speciation relative to the other inventories. Finally, we note that caution should be used when summing emissions by species name. Small differences such as the presence of spaces or hyphens in names such as 1,3-butadiene can cause these emissions to be sorted and summed separately. This is resolved by careful quality assurance during data processing.

Table 1 summarizes annual emissions of benzene and 1,3-butadiene for Nueces and San Patricio Counties in eleven point source inventories emissions. Pronounced differences were evident between inventories, and the variability in annual emissions between inventories can be more than a factor of two. For example, point source benzene emissions in Nueces County in the 2002 HAP NEI were 167 tpy versus 109 tpy in the 2002 TRI. Reported Nueces County benzene emissions in 2005 TRI database were 105 tpy, whereas emissions in the 2005 NEI submittal and the TCEQ 2005 Photochemical Modeling EI were 94 tpy and 260 tpy, respectively. Emissions of 1,3-butadiene in the 2005 NIE submittal and the TCEQ 2005 Photochemical Modeling EI were 5 tpy and 7 tpy, respectively. The TRI indicates that annual emissions of benzene in Nueces County have decreased over time, while reported emissions of 1,3-butadiene show greater annual variability.

In some cases, differences between inventories reflect changes in temporal trends; TRI point source emissions decrease between 2005 and 2008 along with measured ambient benzene concentrations. For other cases, differences between inventories reflect differences in data processing or perhaps even quality assurance/quality control analyses. It is important to recognize that emission inventories can have different origins, objectives, and spatial resolutions that can lead to pronounced differences in the inputs used for air quality modeling. The 2005 TCEQ Photochemical Modeling Emissions Inventory, which was developed to support the technical analyses for the State Implementation Plan and has the greatest level of VOC chemical speciation, is being used for the dispersion modeling studies.

Table 1. Annual emissions of benzene and 1,3-butadiene (tpy) in eleven stationary point source inventories for Nueces and San Patricio Counties.

County	Species	2000 TCEQ Modeling EI	2002 HAP NEI	2005 TCEQ 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

DISPERSION MODEL CONFIGURATION

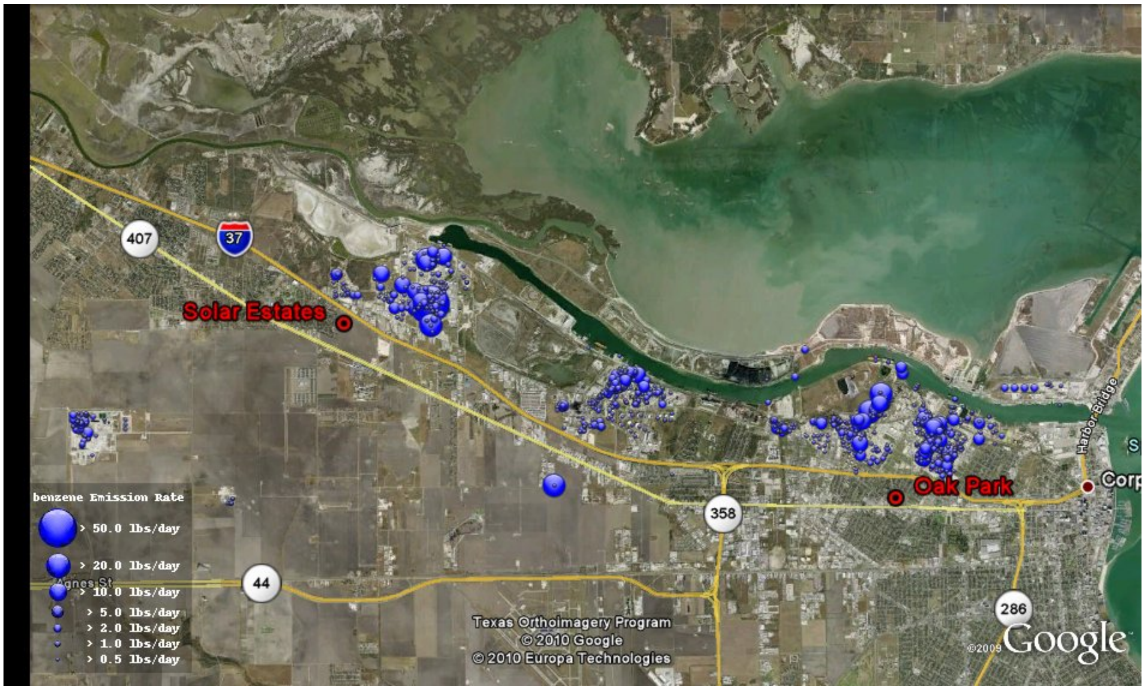
According to the 2005 TCEQ Photochemical Modeling Inventory, stationary point sources have the largest contribution to benzene emissions in Nueces and San Patricio counties with 256 tpy, followed by area and mobile sources with approximately 160 tpy each, and non-road mobile sources with 34 tpy. On-road mobile sources have the largest contribution to 1,3-butadiene emissions in the region with 17 tpy, followed by point and non-road sources with 7 tpy each, and area sources with 0.15 tpy. Reported industrial point source emissions of benzene primarily originate from floating and fixed roof tanks along with fugitive sources. Emissions of 1,3-butadiene originate from chemical manufacturing fuel fired equipment, and fugitive emissions from petroleum refining and chemical manufacturing. As described below, the simulations presented here focus specifically on model predictions of benzene concentrations resulting from industrial point source emissions.

AERMOD and CALPUFF represent the state-of-the-practice for dispersion modeling in the United States.[8] AERMOD is a steady-state dispersion model designed for short-range ($\leq$ 50 kilometers) dispersion of emissions from stationary industrial sources.[8,9] 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.[8,10] Both models have undergone evaluations of their performance against field datasets and of their responses to uncertainties in model inputs.[11,12,13,14,15,16] The CALMET/CALPUFF modeling system was used for the simulations presented here because of its capability to incorporate on-site meteorological data from multiple sites.

The modeling system configurations used for this study are described in detail by Tai et al.[17] The CALPUFF system incorporated data from 18 surface stations, 1 upper air site at the Corpus Christi International Airport, 5 precipitation sites, and 1 buoy.[17] Data from the U. S. Geological Survey were used to determine the fractional land use for each of the 38 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.[17] Micrometeorological variables were used to compute the dispersion coefficients in CALPUFF. The modeling presented here focus on predicted benzene concentrations during 2006, which is approximately the time period of the point source emission inventory and for which the first complete year of ambient data were available from the UT auto-GC sites.

In order to examine the impacts of emission inventory variability on dispersion model predictions, two simulations were conducted with CALPUFF. Both used 2006 meteorological data and identical modeling configurations, but had different point source benzene emission inventories. One used the existing 2005 TCEQ Photochemical Modeling Inventory for industrial point source benzene emissions described above, while the second reduced all point source benzene emissions in the TCEQ Photochemical Modeling Inventory by 50%, which approximately encompasses the difference between the Modeling Inventory and others shown in Table 1. Emission points for benzene and 1,3-butadiene included in the 2005 TCEQ Photochemical Modeling Inventory relative to the locations of the Oak Park and Solar Estates auto-GC sites are shown in Figure 1. A total of 1032 industrial source emission points were included in the simulations.

Figure 1. Industrial emission points in the 2005 TCEQ Photochemical Modeling Inventory for (a) benzene near the Solar Estates and Oak Park auto-GC sites.



MODELED BENZENE CONCENTRATIONS

A summary of mean, 95th percentile, and maximum observed and CALLPUFF predicted benzene concentrations for both emission scenarios during the spring/summer and fall/winter of 2006 at Oak Park and Solar Estates is shown in Figure 2. CALPUFF replicates the observed seasonal and locational differences in benzene concentrations at both sites, with increases in fall/winter relative to spring/summer and relatively higher concentrations at Oak Park versus Solar Estates. Based on observed seasonal concentrations, the fall/winter to spring/summer ratios are 3.4 at Oak Park and 2.2 at Solar Estates. These seasonal patterns are consistent with national-scale analyses by Touma et al.[18] and McCarthy et al. [19], which 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 are lower. These national-scale analyses found, on average, a factor-of-two difference in concentrations by season for pollutants with the highest seasonal variability.

Using the existing 2005 TCEQ Photochemical Modeling Inventory, CALPUFF over-predicted the maximum observed seasonal benzene concentrations at Solar Estates, but under-predicted mean and 95th percentile concentrations at both sites and maximum seasonal benzene concentrations at Oak Park. Under-prediction of mean and 95th percentile observed concentrations at Oak Park and Solar Estates with the inclusion of only industrial point sources suggests that addition of mobile and area sources may be important for improving agreement. Incorporation of emissions from area and mobile sources is on-going, with expected contributions of 0.5 - 1.3 ppbC based on preliminary analyses. At Oak Park, the maximum observed concentrations may be associated with non-routine emissions that are not captured by the 2005 TCEQ Photochemical Modeling EI. However, this hypothesis is not consistent with the over-prediction of the highest benzene concentrations at Solar Estates. Without consideration of chemical processes, the predicted concentration in CALPUFF is proportional to the emission rate. In this case, decreasing benzene emission rates generally exacerbated the model under-prediction bias.

Figure 3 shows the CALPUFF spatial distributions of predicted annual benzene concentrations statistics (mean, 75th percentile, 95th percentile and maximum) for the two emission scenarios. Industrial facility property boundaries are shown in each plot, along with the observed concentrations at the locations of the monitors. These spatial predictions allow air toxics concentrations to be estimated in areas without monitoring sites, which provides 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.

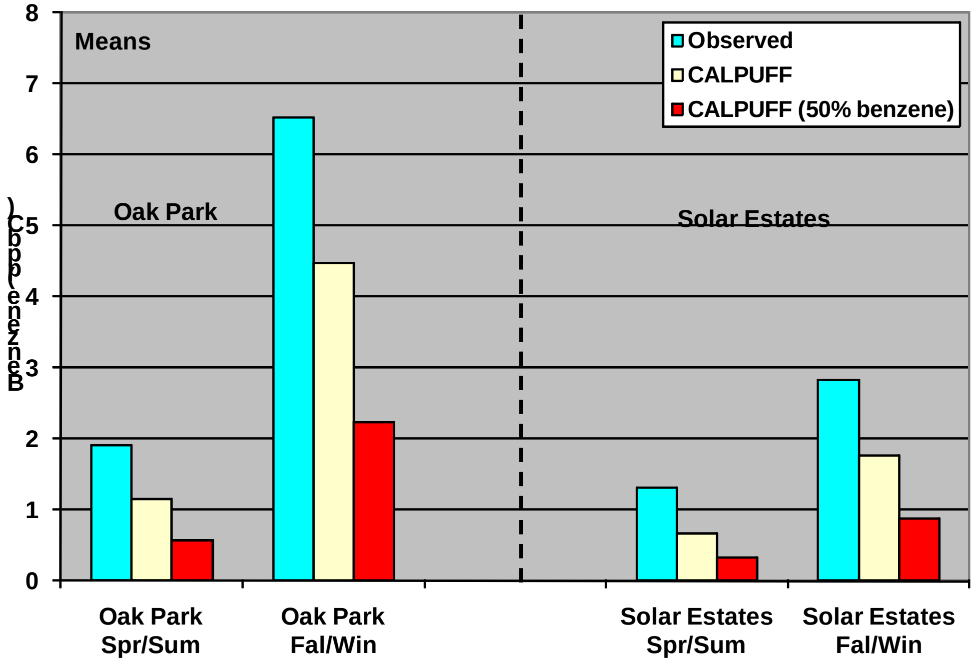
Mean, 75th percentile, and 95th percentile spatial predictions of benzene concentrations are similar between the two scenarios, with the highest concentrations predicted closest to the industrial facilities and decreasing radially. However, the area of influence decreased with the emission rates. Both figures indicate that the Oak Park and Solar Estates monitors are located within two predicted spheres of influence at either end of the Ship Channel; 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 industrial facility located to the southwest of Solar Estates.

CONCLUSIONS

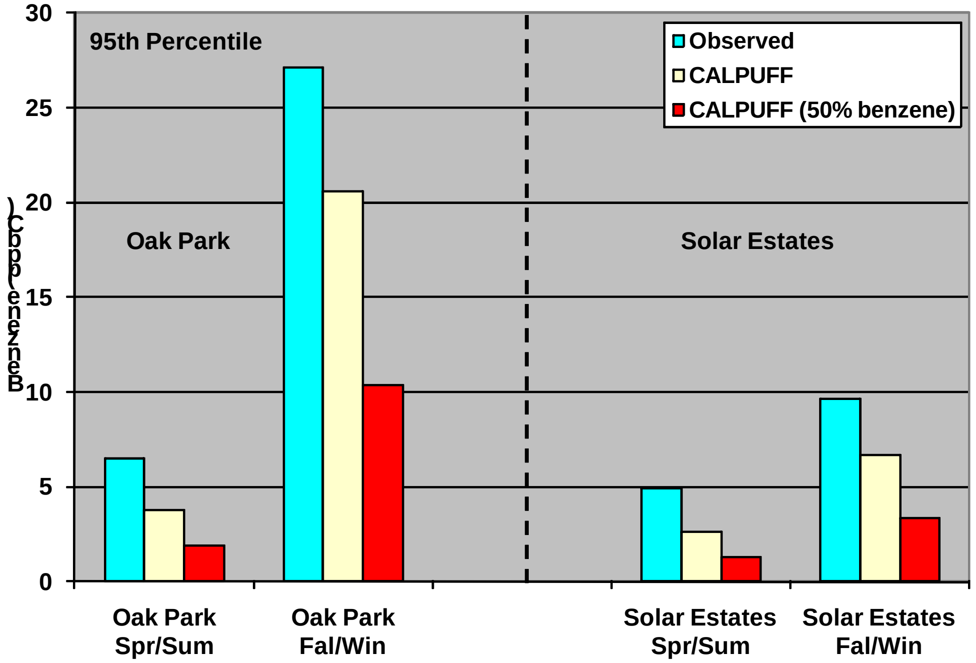
Emission inventories can have different origins, objectives, and spatial resolutions that can lead to pronounced differences in the inputs used for air quality modeling and evaluation of model performance. In this study, underlying differences between emissions inventories investigated for the Corpus Christi area were primarily related to the chemical speciation of emissions that are otherwise reported as VOC with unspecified composition and the accounting for rule effectiveness.

Figure 2. (a) Average, (b) 95th percentile, and (c) maximum predicted and observed benzene concentrations at Oak Park and Solar Estates for spring/summer and fall/winter of 2006

(a)



(b)



(c)

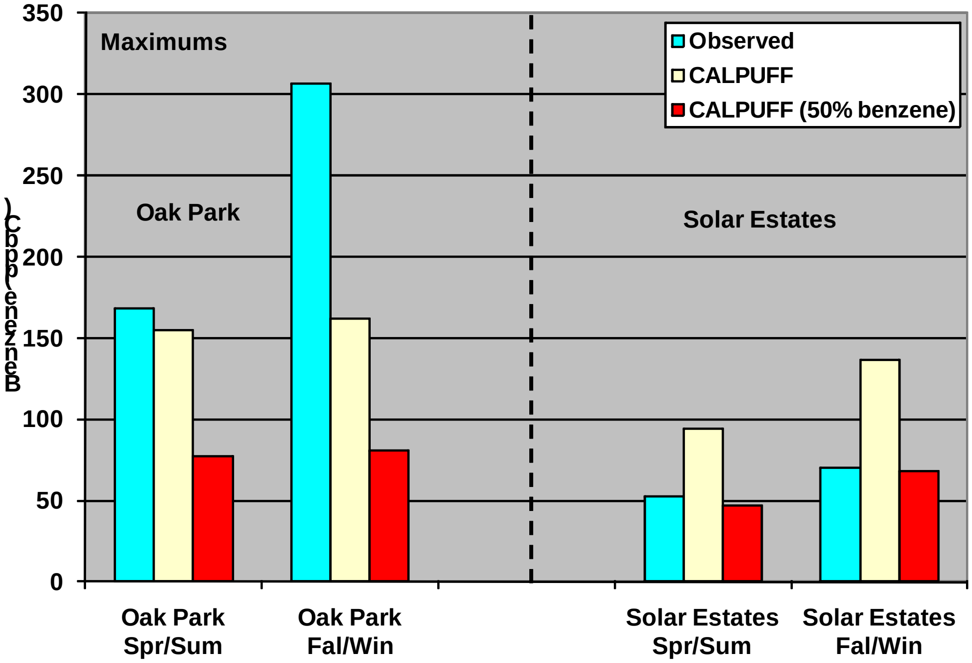
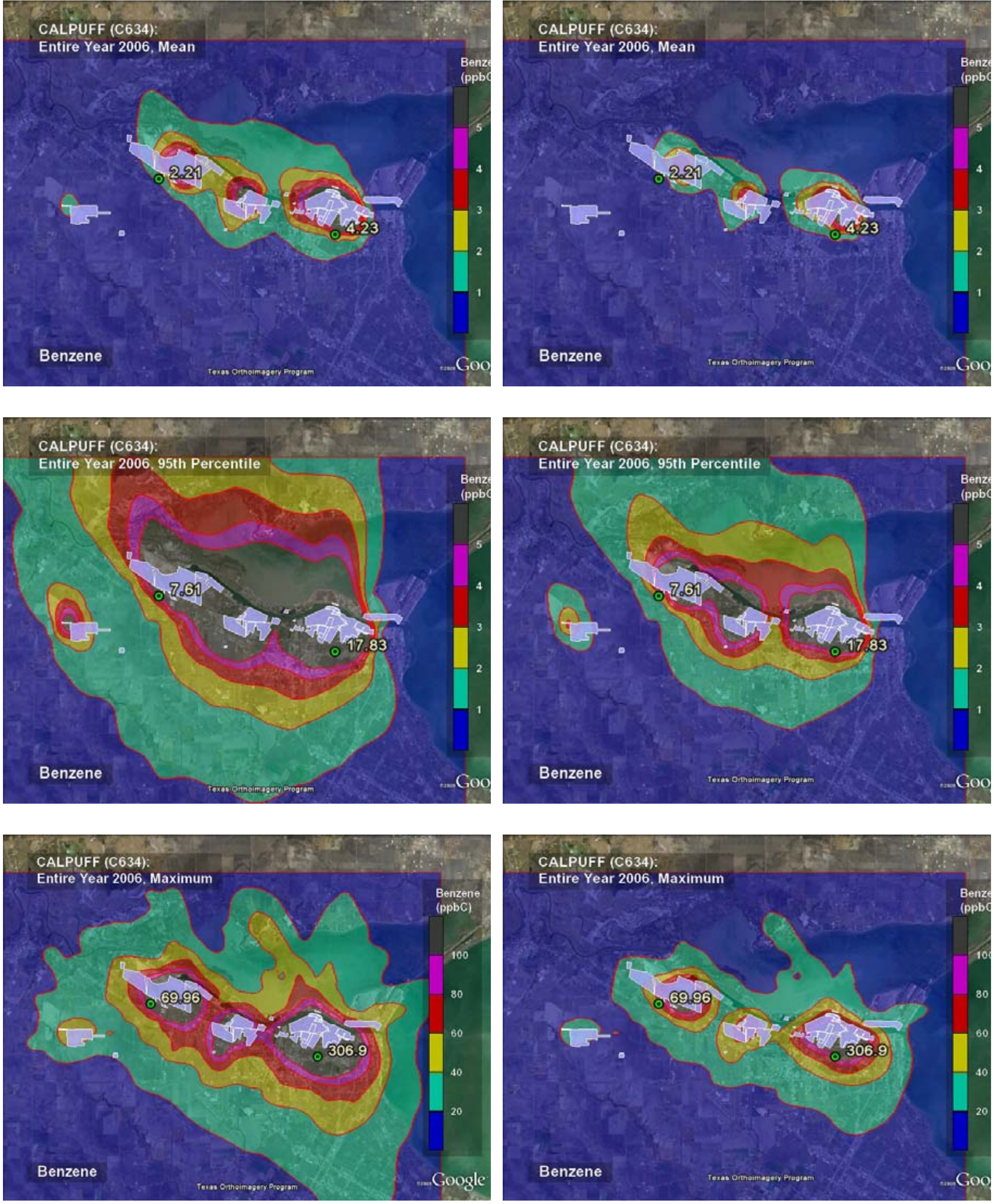

Benzene (ppbC)
350
300
250
200
150
100
50
0
Maximums
Oak Park
Solar Estates
Observed
CALPUFF
CALPUFF (50% benzene)
Oak Park Spr/Sum
Oak Park Fal/Win
Solar Estates Spr/Sum
Solar Estates Fal/Win

Figure 3. CALPUFF predicted annual benzene concentrations statistics: (a) mean, (b) 95th percentile and (c) maximum) from two benzene emission scenarios: TCEQ Photochemical Modeling EI for industrial point sources (left) and a 50% reduction in the TCEQ Photochemical Modeling EI for industrial point sources (right).



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