MODELING AND AMBIENT MONITORING OF AIR TOXICS IN CORPUS CHRISTI, TEXAS

Gary McGaughey, Elena McDonald-Buller, Yosuke Kimura, Hyun-Suk Kim, and David T. Allen*
Center for Energy and Environmental Resources, The University of Texas at Austin, Austin, TX

Greg Yarwood, Ed Tai and Chris Colville
ENVIRON International Corporation, Novato, CA

John Nielsen-Gammon and Wenfang Lei
Department of Atmospheric Sciences, Texas A&M University, College Station, TX

1. INTRODUCTION

Corpus Christi attains air quality standards for both ozone and fine particulate matter but the presence of a significant petrochemical industry has raised concerns about exposure to hazardous air pollutants (air toxics). Since 2005, The University of Texas at Austin has operated a dense ambient monitoring network that includes both hourly automated gas chromatographs (auto-GCs) as well as threshold triggered canister samples and meteorological data. The seven-site network, covering both industrial and residential areas in Corpus Christi, provides a unique opportunity to further the development and understanding of air quality modeling, in particular photochemical modeling, for toxic air pollutants at the neighborhood-scale. This paper describes the ambient monitoring network and on-going work in the application and evaluation of neighborhood-scale models for benzene in Corpus Christi. Models applied are the AERMOD Gaussian dispersion model, CALPUFF Lagrangian puff model and CAMx photochemical grid model. This paper presents results from the model applications for benzene.

2. EPISODE SELECTION

Previous analyses have described the seasonality, day-of-week, and diurnal variability of TNMHC and benzene concentrations measured in Corpus Christi. The seasonal analyses demonstrated that higher TNMHC and benzene concentrations commonly occurred during fall/winter, but were relatively rare during the spring. Higher TNMHC and benzene concentrations often occurred during the nighttime hours, with a maximum frequency of occurrence during the 0000 CST through 0900 CST period, which encompasses the morning rush hour. Day-of-week analyses revealed that most seasons were not characterized by weekday/weekend differences. These results are generally consistent with recent studies in other locations of the United States (McCarthy et al., 2006; Reiss, 2006; Touma et al., 2006). The October/November 2006 period, which had several occurrences of high monitored benzene concentrations, was selected for model development as representative of conditions associated with higher benzene concentrations in Corpus Christi.

3. AIR TOXICS MONITORING NETWORK

A map of the Corpus Christi area showing the locations of the seven UT monitoring stations maintained and operated by UT in support of the Corpus Christi Air Monitoring and Surveillance Camera Installation and Operation Project (CCAQP) is shown in Figure 1. Data collected at one or more monitoring stations include hydrogen sulfide (total reduced sulfur), sulfur dioxide (SO2), total non-methane hydrocarbons (TNMHC), and meteorological (e.g., temperature, wind speed, wind direction, and relative humidity) measurements. As shown in Table 1, hourly measurements of speciated volatile organic compounds (VOCs) are also collected continuously at the Oak Park and Solar Estates monitoring stations using auto GCs with flame ionization detection. Surveillance cameras are located at both of these sites for identification of visible plumes and event analysis. Data collection began in early 2005 and is expected to continue for at least several more years.

*Corresponding author: David T. Allen, Center for Energy and Environmental Resources, The University of Texas at Austin, 10100 Burnet Road, Bldg. 133, R7100, Austin, TX 78758; e-mail: allen@che.utexas.edu

Table 1. Identification and measurements made at the CCAQP monitoring stations.

Monitor Name	CAMS #	AIRS ID	Address	Measurements
Port Grain	629	48-355-0036	2001B East Navigation Blvd.	Sulfur Compounds, Met, TNMHC
J. I. Hailey	630	48-355-0037	2702B East Navigation Blvd.	Sulfur Compounds, Met, TNMHC
West End Harbor	631	48-355-0038	3149B Suntide Rd.	Sulfur Compounds, Met, TNMHC
FHR Easement	632	48-355-0039	8401B Up River Rd.	Sulfur Compounds, Met, TNMHC
Solar Estates	633	48-355-0041	9122 Leopard St.	AutoGC, Sulfur Compounds, Met, TNMHC, Camera
Oak Park	634	48-355-0035	842 Erwin St.	AutoGC, Sulfur Compounds, Met, TNMHC
Dona Park	635	48-355-0034	5707 Up River Rd.	Sulfur Compounds, Met, TNMHC, Camera

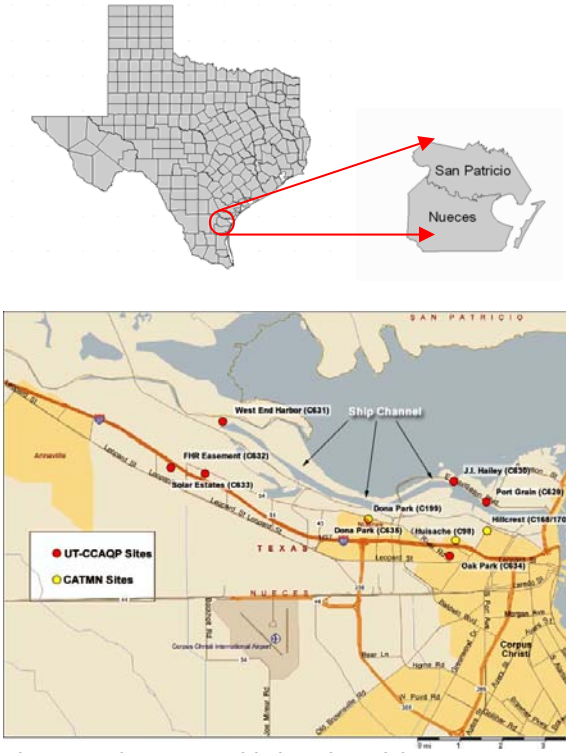


Figure 1. The geographic location of the seven CCAQP and three TCEQ CATMN monitoring stations.

In support of the Community Air Toxics Monitoring Network (CATMN), the Texas Commission on Environmental Quality (TCEQ) has collected samples at multiple monitoring stations within various Texas metropolitan areas since 1992. The samples are collected in evacuated stainless steel canisters over an integrated 24-hour period from midnight to midnight. Three CATMN sites are currently in operation in the Corpus Christi area as shown in Figure 1: Hillcrest (CAMS 170, AIRS ID 483550029), Huisache (CAMS 98, AIRS ID 483550032), and Dona Park (CAMS ID 199, AIRS ID 483550034). The CATMN samples have been collected at most locations on an every 6th day schedule. Following collection, CATMN samples are analyzed by the TCEQ for target compounds using gas chromatography and mass spectrometry detection in accordance with U.S. EPA methods.

The CCAQP network design provides the flexibility to trigger the collection of VOC canister samples during high TNMHC events. The Thermo Electron Co (TECO) Model 55C methane/total non-methane analyzer was selected to measure TNMHC concentrations because of its sensitivity at low concentration ranges and its rapid 90-second cycle time. Emissions from petroleum refineries are known to comprise a large number of hydrocarbon species (e.g., C2-C9 alkanes and alkenes, C6-C8 aromatics) and the TNMHC measurement provides a surrogate for a broad range of species. The TECO 55C was implemented to average 90-second observations to 5-minute averages for reporting purposes. However, the data-logger monitors the 90-second values, and if 10 consecutive values (900 seconds, or 15 minutes) are at or above 2000 ppbC, a 20-minute integrated canister sample is triggered. These event-triggered canister samples are analyzed for target compounds of interest in the region, including benzene, toluene, ethylbenzene, xylene (BTEX), and 1,3-butadiene. In addition to the TNMHC measurements, the Solar Estates and Oak Park monitoring stations are equipped with automated gas chromatographs (autoGCs) that

continuously analyze for approximately 55 VOCs.

4. METHODOLOGY

4.1 Point Source Emissions Inventory

The Port of Corpus Christi is surrounded by numerous refineries and chemical industries, which can emit air toxics such as benzene. Many of these facilities are located in close proximity to residential areas, as shown in Figure 2. Others sources of air toxic emissions beside industrial facilities, such as mobile sources and small stationary sources, were not included in this modeling but will be included in the next phase of the study. The concentrations of air toxics are strongly impacted by these nearby sources of emissions. For example, Figure 3 presents back-trajectories for hours characterized by benzene concentrations of 30 ppbC or greater at the Oak Park monitoring station. Upwind geographic regions during high benzene concentrations at Oak Park are most often located to the north-northwest or (especially) north-northeast of Oak Park, suggesting important industrial emissions sources in those areas.

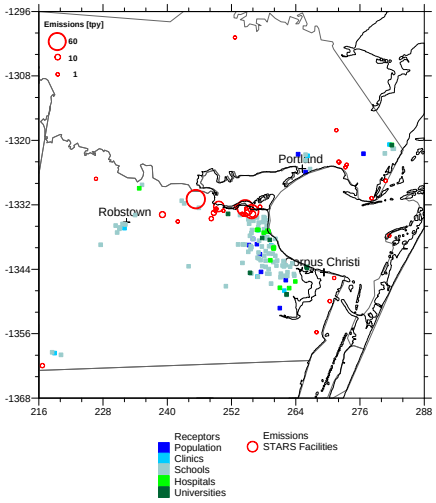


Figure 2. Map of the CALPUFF modeling domain with locations of the receptors and emission sources.

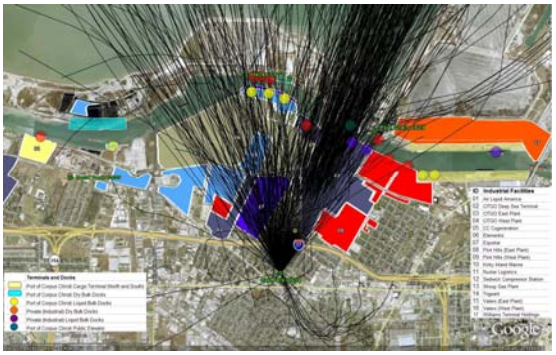


Figure 3. Surface back-trajectories for all hours characterized by a benzene concentration of 30 ppb or greater at the Oak Park monitoring station during June 2005 - May 2008.

The emissions inventory used for the modeling simulations is referred to as the 2005 Texas Commission on Environmental Quality (TCEQ) Photochemical Modeling EI. This photochemical modeling inventory has the same level of source resolution as the State of Texas submittals to the EPA's National Emission Inventory (NEI). However, TCEQ's air quality modeling group does additional processing to account for rule effectiveness (RE) as well as to further chemically speciate emissions that are otherwise reported as VOC with unspecified composition.

4.2 AERMOD and CALPUFF

CALPUFF and AERMOD were run from October 1 to November 30, 2006 to evaluate the impacts of benzene from individual and all chemical plants and refineries near Corpus Christi. The 2005 TCEQ Photochemical Modeling Inventory for stationary point sources was used for the simulations. Two AERMOD runs were evaluated to compare the impacts using different meteorology. One AERMOD run used meteorology from Solar Estates and a second run used meteorology from Oak Park. The meteorological preprocessor to CALPUFF is CALMET. CALMET sensitivity tests were performed to develop a model configuration that yielded the most acceptable wind fields in the Corpus Christi domain. Options that improved the wind fields included the use of high-resolution coastline data, the relocation of a buoy closer to the grid domain, terrain kinematics, and additional smoothing in higher layers. All evaluations were based on a subjective judgment since all the meteorological data was being nudged into the model, leaving no data for an independent evaluation.

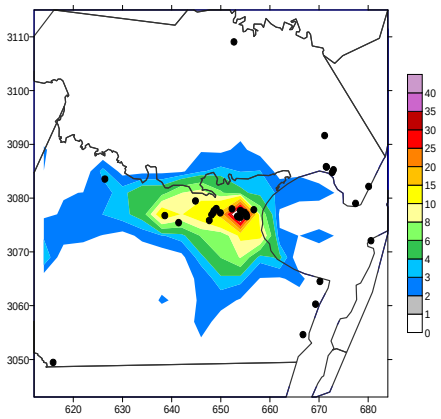
5. AERMOD RESULTS

The benzene concentrations predicted by AERMOD were sensitive to the choice of the on-site meteorological monitor used in the AERMET modeling. Contour plots of the episode maximum hourly benzene concentrations are shown in Figure 4 for AERMOD with Oak Park (top) and Solar Estates (bottom) meteorology. Black dots represent the locations of each emission source. The two stations are located only approximately 10km apart, yet the maximum benzene concentration using Oak Park meteorology is 44 ppb compared to 32 ppb when using Solar Estates meteorology. Oak Park also predicted higher concentrations further west. These results demonstrate that using only one on-site meteorological monitor in addition to one other monitor (Corpus Christi International Airport NWS station) to characterize the meteorological conditions within a 72 x 72km domain is a limitation that produces uncertainty in the results.

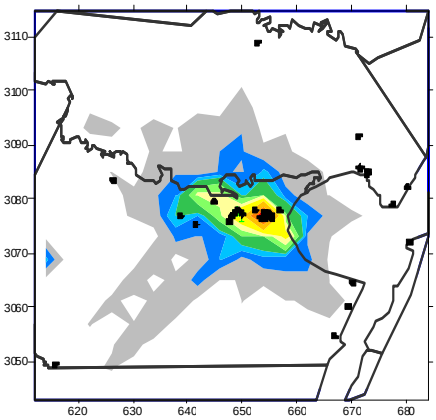
6. CALPUFF RESULTS

CALPUFF uses three-dimensional wind and temperature fields that incorporate meteorological data from multiple sites. Figure 5 shows spatial plots of the episode maximum benzene concentrations to gridded receptors when using CALPUFF. Compared to AERMOD with Oak Park meteorology (top of Figure 4), CALPUFF predicted higher benzene concentrations nearer to the emissions sources. AERMOD only simulated one peak that was lower than either peak in CALPUFF, possibly due to the coarser grid resolution in AERMOD. AERMOD tended to disperse benzene further downwind of emission sources than CALPUFF.

Among discrete receptors, which represent the locations of schools and hospitals, the highest hourly benzene concentration from all sources was comparable (34 ppb in CALPUFF and 33 ppb in AERMOD) but occurred at different receptors and dates.



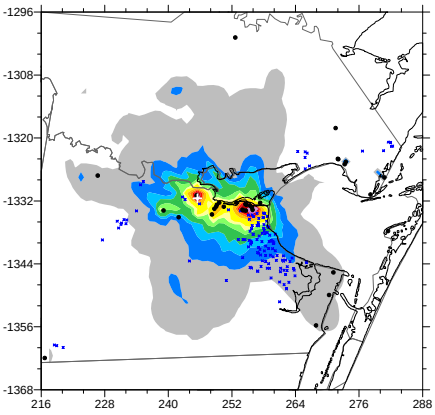
AERMOD with Oak Park Meteorology.
Max = 43.5 ppb



AERMOD with Solar Estates Meteorology.
Max = 31.8 ppb

Figure 4. Predicted episode maximum hourly benzene concentrations from two AERMOD runs using different surface meteorology.

The maximum contributions from each of the five largest sources of benzene at any discrete receptor are listed in Table 2 for the two AERMOD runs and for CALPUFF. Facility #1 emitted the most benzene, but Facility #2 produced the highest concentration at any discrete receptor in AERMOD, while Facility #3 produced the highest concentration among individual facilities in CALPUFF. The highest concentration to a discrete receptor in CALPUFF was always slightly higher or in between the two AERMOD runs, and always took place late at night or early in the morning. Dates and receptor locations of the highest benzene concentration between CALPUFF and AERMOD did not match.



CALPUFF. Max = 53.2 ppb, Second peak at 47.4. ppb

Figure 5. Predicted episode maximum hourly benzene concentrations from CALPUFF.

7. COMPARISON TO OBSERVATIONS

Figure 6 compares the maximum daily hourly observed benzene concentrations to those predicted by AERMOD (using Oak Park meteorology) and CALPUFF. Figure 7 presents the analogous results for Solar Estates. Although the modeled values capture the range of observed concentrations throughout the period, there is large variation on any given day. Analysis of model performance to support model evaluation and development is on-going.

8. PRELIMINARY WRF RESULTS

Recent work has included the development of a WRF simulation at 1km horizontal resolution. Figure 8 shows the CAMx and WRF 1km grid domains. In contrast to CALMET, WRF provides dynamically consistent meteorological output to drive the CAMx photochemical model. For example, the CALMET and (preliminary) WRF hourly surface wind results are shown in Figures 9 and 10, respectively.

Table 2. Maximum benzene concentrations at discrete receptors from individual facilities using AERMOD and CALPUFF.

Facility	AERMOD (Solar Estates Met)	Date	AERMOD (Oak Park Met)	Date	CALPUFF	Date
All	26.69	Nov 16	32.86	Nov 18	34.20	Oct 22
Facility #1	11.55	Nov 16	26.22	Nov 6	19.10	Nov 18
Facility #2	14.37	Nov 16	29.34	Nov 18	18.98	Nov 17
Facility #3	11.80	Oct 4	24.92	Nov 6	27.67	Oct 22
Facility #4	3.80	Oct 14	6.79	Nov 13	6.01	Oct 6
Facility #5	5.01	Nov 18	12.85	Nov 18	9.50	Nov 6

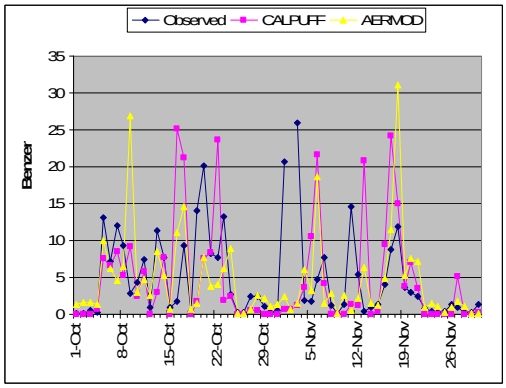


Figure 6. Daily maximum observed and modeled hourly benzene concentrations at Oak Park.

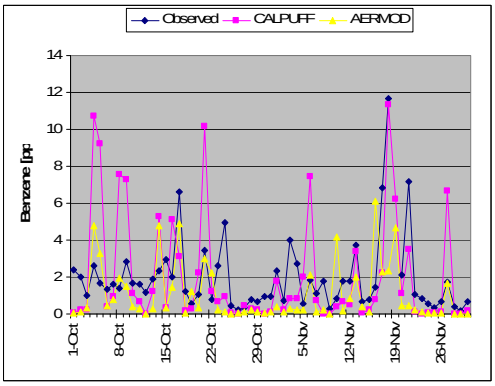


Figure 7. Daily maximum observed and modeled hourly benzene concentrations at Solar Estates.

The WRF wind field shows a clear distinction between winds over land and over water, while CALMET shows no differences at the land-water interface. In addition, the CALMET wind field is often characterized by localized "crop circles" associated with the locations of individual meteorological stations. On-going efforts during 2009 and 2010 will be focused on the development of CAMx simulations driven by WRF to predict benzene concentrations for comparison to the results of the AERMOD and CALPUFF models.

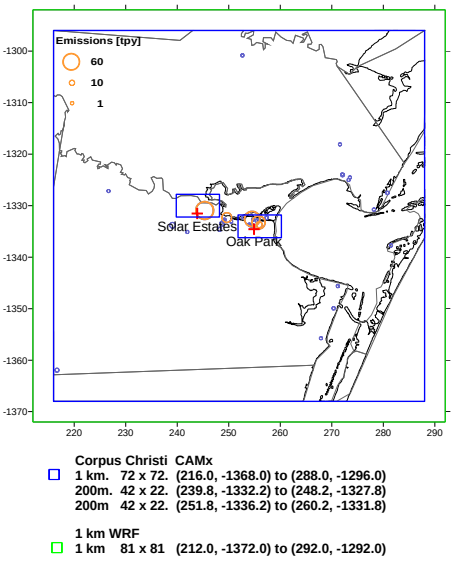


Figure 8. The 1km CAMx and WRF domains.

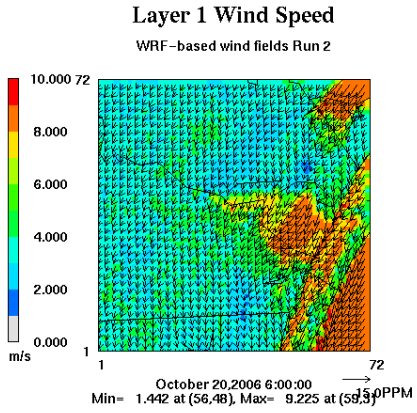


Figure 9. Hourly surface wind direction and wind speed from WRF for 0600 CST October 20.

9. SUMMARY

UT is currently operating an ambient monitoring network that includes both hourly auto GCs as well as threshold triggered canister samples and

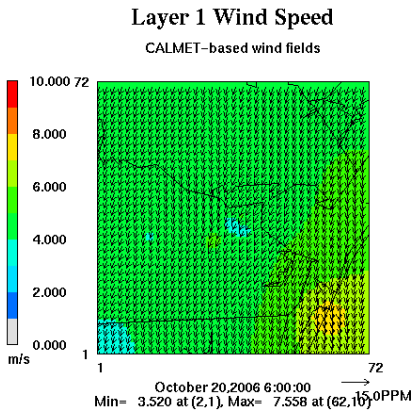


Figure 10. Hourly surface wind direction and wind speed from CALMET for 0600 CST October 20.

meteorological data in the Corpus Christi area. Together with dispersion and neighborhood-scale photochemical models under development, this dense seven site network and the CATMN sites operated by the TCEQ provide an extensive database over a prolonged time period to assess the spatial and temporal patterns and source attributes of air toxics concentrations in the region. A primary goal of our work is the development of a modeling system that predicts the three-dimensional concentrations of selected air toxics concentrations (e.g., benzene) at the neighborhood (< 1-km horizontal resolution) scale.

10. ACKNOWLEDGEMENTS

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11. REFERENCES

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