Assessment of air quality model predictions of ozone concentrations characterized by large hourly changes in Houston, Texas.

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A thesis submitted to the faculty of the University of North Carolina at Chapel Hill in partial fulfillment of the requirements for the degree of Master of Science in the Department of Environmental Science and Engineering.

Chapel Hill
2011

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ABSTRACT

ADEOLA O. OLATOSI: Assessment of air quality model predictions of ozone concentrations characterized by large hourly changes in Houston, Texas.
(Under the direction of William Vizuete.)

The Houston-Galveston-Brazoria (HGB) area has been shown to be affected by two types of ozone formation. The 'typical' ozone formation, common in most parts of Houston and other urban areas, depicted by a gradual rise in hourly ozone concentration. The other type of ozone formation is depicted by a rapid rise in ozone formation defined as either ≥ 40 ppb/hr or ≥ 60 ppb/2hr change in hourly ozone concentration. These rapid ozone formation or 'non-typical ozone formation' (NTOC) have been shown to affect attainment metric by as much as 10 ppb. We have evaluated the regulatory Air Quality Model's (AQM) ability to accurately simulate the observed rapid ozone formation peculiar to this region using the two major emission inventories and have compared it with observations from days that corresponded with the modeling period. Results show that the model lacks the ability to predict observed maximum one hour and two hour changes.

I dedicate this work to the Almighty God who has been a constant help in my life.

ACKNOWLEDGEMENTS

I owe my deepest gratitude to my darling husband, Dr Bankole Olatosi and our daughter Oluwashindara for their unflinching love, guidance, support and encouragement. I am also indebted to my wonderful research advisor Dr William Vizuete for giving me this wonderful opportunity at this prestigious institution and for his constant advise and mentoring.

Lastly, I would like to thank my committee members and my colleagues in the UNC Modeling Air Quality (MAQ) Lab who supported me during my thesis completion.

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LIST OF ABBREVIATION AND SYMBOLS

AQM	Air Quality Model
CAMx	Comprehensive Air Quality Model with Extensions
CB05	Carbon Bond V chemical mechanism
DV	Design value
EGU	Electric generating unit
EI	Emission Inventory
EPA	United States Environmental Protection Agency
ETH	Ethene
HGB	Houston-Galveston Brazoria area
HRVOC	Highly reactive volatile organic compound
IOLE	Internal olefin carbon bond
lb	pounds
LST	Local standard time
MM5	Fifth generation meteorological model
mol	moles
NAAQS	National Ambient Air Quality Standards
NOx	nitrogen oxides
NTOC	Non-typical ozone change
O_3	Ozone
OLE	Terminal olefin carbon bond
OSD	Ozone season daily
ppb	parts per billion

ppm	parts per million
SI	Special Inventory
SIP	State Implementation Plan
TCEQ	Texas Commission on Environmental Quality
VOC	volatile organic compound

CHAPTER 1

INTRODUCTION

The Houston-Galveston-Brazoria (HGB) area has been designated a severe non-attainment area due to non-compliance with the 1997 eight-hour national ambient air quality standards (NAAQS) for ozone set at 0.08 ppm. According to the United States Environmental Protection Agency (US EPA), to attain this standard, every regulatory monitor's design value (DV) should not exceed 0.08 ppm (EPA, 2011). When a DV exceeds the NAAQS, control strategies must be developed aimed at bringing the future DV into attainment. In the attainment demonstration, a regulatory air quality model (AQM) is used to create and justify control policies that ultimately must be approved by the EPA. To show attainment in HGB, the Texas Commission on Environmental Quality (TCEQ) has created an AQM episode to generate and justify control policies. These policies, and supporting observational and modeling data have been compiled in a document, called the State Implementation plan (SIP), which the TCEQ submitted to the EPA in April 2010. At the time of this study, the SIP approval by the EPA was still pending (TCEQ, 2010).

The SIP that was created by the TCEQ followed the EPA guidance in the development of the DV, and the use of modeling and observational data to show attainment (TCEQ, 2010b). This EPA attainment methodology, and the assumptions underlying it, has been the focus of several studies (Vizuete et al., 2011). For HGB, one study focused on the

method used to calculate the DV and its implications on attainment demonstration (Vizuete et al., 2011). The study showed that the DV calculation at certain monitors included observations that were characterized by a rapid increase in hourly ozone concentrations of greater than 40 ppb/hr. The authors showed that when these rapid increases occurred they were likely to lead to some of the highest 8-hr ozone exceedances. These occurred frequently enough that for monitors in the Houston Ship Channel, they significantly impacted the monitor's DV by as much as 10 ppb.

Using observational data from 2000-2009, Vizuete et al. (2011) noted that Houston's ozone violations appeared as either rapid 1-hr concentration increases, or more gradual increases that build to values above 85 ppb for a sustained time. Daily maximum 8-hr averages at a monitor may be exceeding the 8-hr NAAQS because of only 1 or 2 hours of high ozone concentration increase. Further, these rapid 1-hr concentration increases commonly appear at a limited number of monitors spanning a narrow geographic area. Due to the magnitude of the changes and the narrow spatial extent of the observations, this phenomenon is not the "typical" gradual increases to an ozone exceedance commonly seen in other cities. Therefore, understanding the cause of these "non-typical" 1-hr ozone values becomes critical to effective and defensible policy formulation in Houston. An open question, however, is the cause of these observed changes in hourly ozone concentrations, or non-typical ozone changes (NTOC).

There is considerable evidence that has linked NTOC behavior to emissions releases of what the TCEQ has labeled highly reactive volatile organic compounds (HRVOCs) (Nam et al., 2008; Murphy et al., 2005). HRVOCs are ethene, propene, 1,3-butadiene and isomers of butene and predominantly come from industrial sources located in the Houston Ship

Channel (Wert et al., 2003; Kleinman et al., 2002; Ryerson et al., 2003). In the Houston Ship channel, industrial sources release HRVOC emissions randomly, often lasting several hours (Murphy et al., 2005), and have emission rates of up to 10,000 - 50,000 lb/hr (Vizuete et al., 2008). When these emissions of HRVOCs are released in the morning, in an area of stagnant wind conditions, observational and modeling data have shown they can produce increases of up to 100 ppb in ozone concentration (Murphy et al., 2005). These resulting plumes of ozone have been characterized as narrow and impacting only a few monitors (Vizuete et al., 2011). What the data also supports is that for a HRVOC release to be effective, it must have sufficient magnitude, be released no later than the late morning, and coincide with the right meteorological conditions. These meteorological conditions include low wind speeds, and rotational wind directions common to high ozone days in Houston. Thus, releases of HRVOCs have the potential to produce NTOCs given the right circumstances.

The evidence linking HRVOC emission releases and high ozone was used by the TCEQ to justify, in their 2004 SIP, control strategies aimed at reducing this source (TCEQ, 2004). The HRVOC rule restricted routine industrial emissions to an annual cap and non-routine industrial emissions (emission events) to a 1,200lb/hr limit. As a result of these new rules, there has been a considerable decline in the observed annual averaged concentrations of HRVOC (TCEQ, 2010b).

Although data exists linking some NTOCs behavior with reported or observed HRVOC emissions, a vast majority of observed NTOCs lack any data that can provide a causal explanation. Thus, alternative causes for observed NTOC are still permissible. Further, DVs used in the current SIP include measurements with unexplained NTOCs that continue to impact DVs. The DV, however, is only part of the EPA attainment

demonstration. The EPA attainment demonstration also requires the use of modeling data to predict the reduction of the DV in a future attainment year. Since this phenomenon is observed in some of the DVs, this logically calls to question whether this phenomenon is adequately represented in the regulatory AQM.

The overall goals of this study are to use the regulatory AQM created for the HGB SIP to evaluate model performance for predicting observed NTOC behavior, and secondly, assess whether there is a link between predicted rapid hourly ozone changes and predicted HRVOC emission releases. The EPA recommends the use of a 'day-specific' emission inventory (EI) for model evaluation and this study focused on comparing measurements with predictions using the 'day-specific' EI. Days with rapid ozone formation were extracted from simulations using the two inventories used in attainment methodology and both ground layer hourly ozone concentrations and hourly ozone changes were compared with observations from ground monitors in the HGB region. Secondly, we compared hourly ozone concentrations of 'day-specific' simulations to hourly ozone concentrations of 'average' emissions for days with NTOCs to see the relevance of imputing HRVOC emissions variability in the AQM.

CHAPTER 2

METHODOLOGY

The TCEQ has developed an AQM system with emission inventories and meteorological data to support their SIP efforts. These efforts have followed EPA guidance (TCEQ, 2010) and all data are publically available (TCEQ, 2010). The following section describes the relevant modeling and observational data used in this analysis. The observed data set for this study was obtained from the TCEQ's website providing hourly data for parameters measured at all monitors (TCEQ, 2010c).

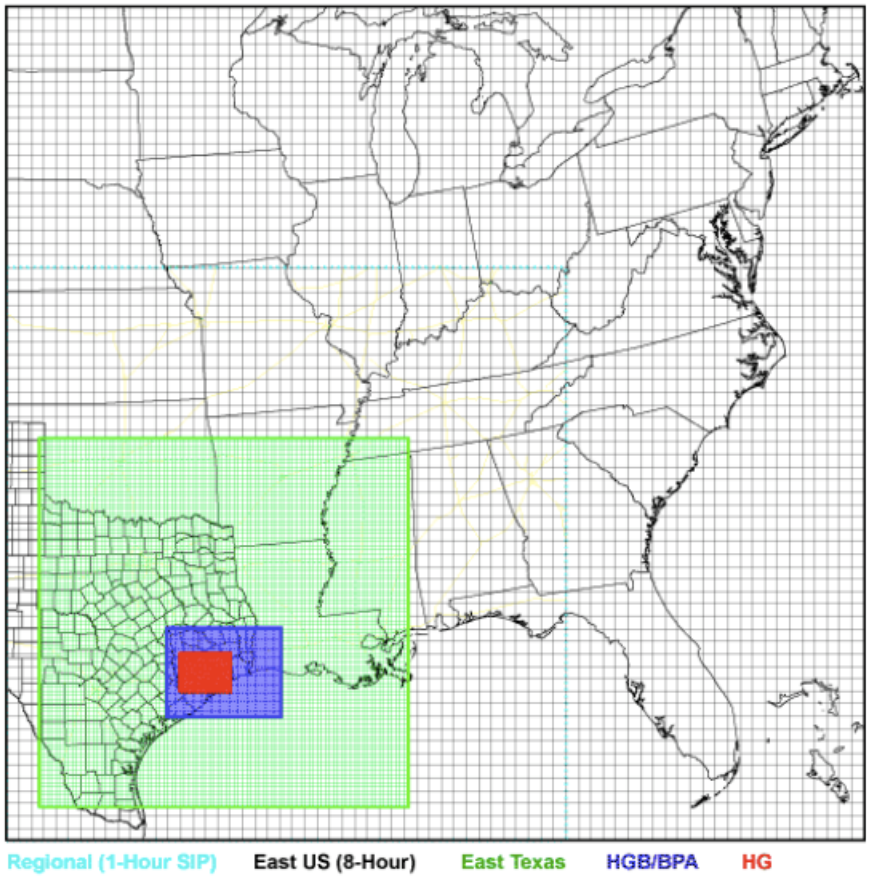
2.1 Air Quality Model Simulation

For the SIP, the TCEQ used the Comprehensive Air Quality Model with Extensions (CAMx) version 4.53 with carbon bond V (CB05) chemical mechanism (ENVIRON, 2009). In total, the TCEQ simulated 120 modeling days in 2005 and 2006 as shown in Table 2.1. The simulations used a horizontal modeling domain structure, which includes a 36 km coarse domain and three sequentially nested fine grid sub domains at 12 km, 4 km, and 2 km as shown in Figure 2.1. For meteorology, the TCEQ relied on the fifth generation meteorological model (MM5) version 3.7.3 to generate data for all simulation days (Grell et al., 1994). Although a single meteorological data file was used for all simulations, the TCEQ developed two different sets of emission inventories as prescribed by the EPA guidance.

Table 2.1:The six air quality modeling episodes created by the TCEQ in support of the 2010 8-hr O_3 SIP. Included are the simulation periods, and the naming conventions used by the TCEQ for their emissions inventories and meteorological data files.

Developer	Model Software	Simulation period	Emission Inventory				Met File Name	Chemical Mechanism
			Basecase	Baseline		Future		
			Name	Name	Year	Name		
TCEQ	CAMx v4.53	05/19 to 06/03/2005	reg 10	reg 3	2006	cs07	eta_dbemis_fdda_newuhsst_newutcsrlulc_grell.v45	CB05
		06/17 to 06/30/2005						
		07/26 to 08/08/2005						
		05/31 to 06/15/2006						
		08/13 to 09/15/2006	reg 10si					
		09/06 to 10/11/2006	reg 10					

TCEQ = Texas Commission on Environmental Quality
CB05 = Carbon Bond V Mechanism



Source: TCEQ, 2010b

Figure 2.1: Houston Galveston Brazoria (HGB) CAMx modeling domain.
The horizontal modeling domain structure consists of a coarse-grid East US domain (black) and nested fine-grid subdomains: East Texas subdomain (green), Houston-Galveston-Brazoria/Beaumont-Port Arthur (HGB/BPA) subdomain (blue), and the Houston-Galveston (HG) subdomain (red).

Emissions are treated either as gridded (low-level) emissions or point sources (elevated stack-specific) emissions in the CAMx modeling system (ENVIRON, 2009). Emissions that emit near the surface and are not buoyant to reach into the upper model layers are classified as gridded emissions. These include low-level point, mobile, residential, commercial, biogenic, natural and other non-point industrial sources. Point source emissions are classified as sources that emit from individual stacks with buoyant rise that may take emissions into the upper model layers. Examples of point sources are electric generators, smelters, refineries and large factories.

The EPA attainment method recommends the use of two types of emissions inventories in the AQM named basecase and baseline (EPA, 2007). The basecase emission inventory (EI) is used solely for model performance evaluation and not for the attainment demonstration. The basecase EI contains day specific information, and is the most accurate representation of a historical episode. Considerable resources were used by the TCEQ to increase accuracy in the representation of emission sources, especially with regards to industrial point sources. In an effort to reconcile emissions from point sources, specifically non-electric generating units (EGUs), the TCEQ requested additional volatile organic compounds (VOC) and nitrogen oxides (NOx) emission data from 141 facilities from August 15 to September 15, 2006. These reported emissions were collected and added to the basecase EI as part of what the TCEQ called the special inventory (SI). The basecase EI included hourly emissions data from reporting surveys and episode specific survey results of HGB floating roof tank landing losses. Further details on the basecase EI can be found in the 2010 8-hr SIP prepared by the TCEQ (TCEQ, 2010b). According to the EPA guidance, this

inventory is used solely for model performance evaluation ultimately allowing its use in the SIP.

The EPA guidance recommends the use of a different EI for the attainment demonstration. To reconcile the use of multi-year averaged observations in the calculation for the DV, the EPA recommended the use of average or "typical" emissions called the baseline EI. Unlike the basecase EI, the baseline EI lacks day-specific emissions and also has the SI removed. Point sources in the basecase EI are variable and are representative of real emissions whereas in the baseline EI, point sources are treated without variability. The baseline EI point source emissions are the average ozone season daily (OSD) emissions. The TCEQ used the same point source emissions for all the 120 modeling days in the baseline EI.

2.2 Simulations of high HRVOC emissions rates

Based on previous research (Wert et al., 2003; Kleinman et al., 2002; Ryerson et al., 2003), it has been noted that HRVOC emissions from industrial point sources can reproduce this observed phenomenom of rapid ozone formation. The AQM however, does not explicitly represent three of the four HRVOCs designated by the TCEQ. Since ethene is the only explicit HRVOC species in the CB05 mechanism, we defined an HRVOC in the model by summing predicted concentrations of ETH (ethene), OLE (terminal olefins) and IOLE (internal olefins). In the baseline EI, predicted HRVOC emission rates from industrial point sources had a maximum rate of 2,803 mol/hr, but the basecase EI had a maximum rate of 82,082 mol/hr on September 2, 2006 at 2000 LST. Considering the fact that observed rapid ozone formations have been linked to stochastic emission of HRVOCs that last hours, hourly changes of HRVOCs emission rates were calculated to have a knowledge of the magnitude of

change and how they affect predicted ozone concentrations. Our assumption of calculating the hourly difference was the closest representation of emissions variability but must not be mistaken as a true representation of an observed emission event. The six modeling episodes were classified as 2005_05 episode (05/19 to 06/03/2005), 2005_06 episode (06/17 to 06/30/2005), 2005_07 episode (07/26 to 08/08/2005), 2006_06 episode (05/31 to 06/15/2006), 2006_08 episode (08/13 to 09/15/2006) and the 2006_09 episode (09/06 to 10/11/2006). Figure 2.2 shows the distribution of hourly changes of point source emission rates for the baseline and basecase EIs. The basecase EI had larger differences than the baseline EI with the 2006_08 modeling episode having the largest differences in the basecase EI. The 2006_08 modeling episode values are indicated in the red circle of the boxplot. The maximum point source HRVOC hourly difference in the basecase EI is 78,818 mol/hr and it occurred on September 2, 2006 at 2000 LST, while the baseline EI had a maximum hourly difference of 158 mol/hr. As these data indicate, there is considerable difference in HRVOC emissions in these two inventories. These differences offer a natural sensitivity study of the impact of HRVOC emissions on predicted ozone concentration.

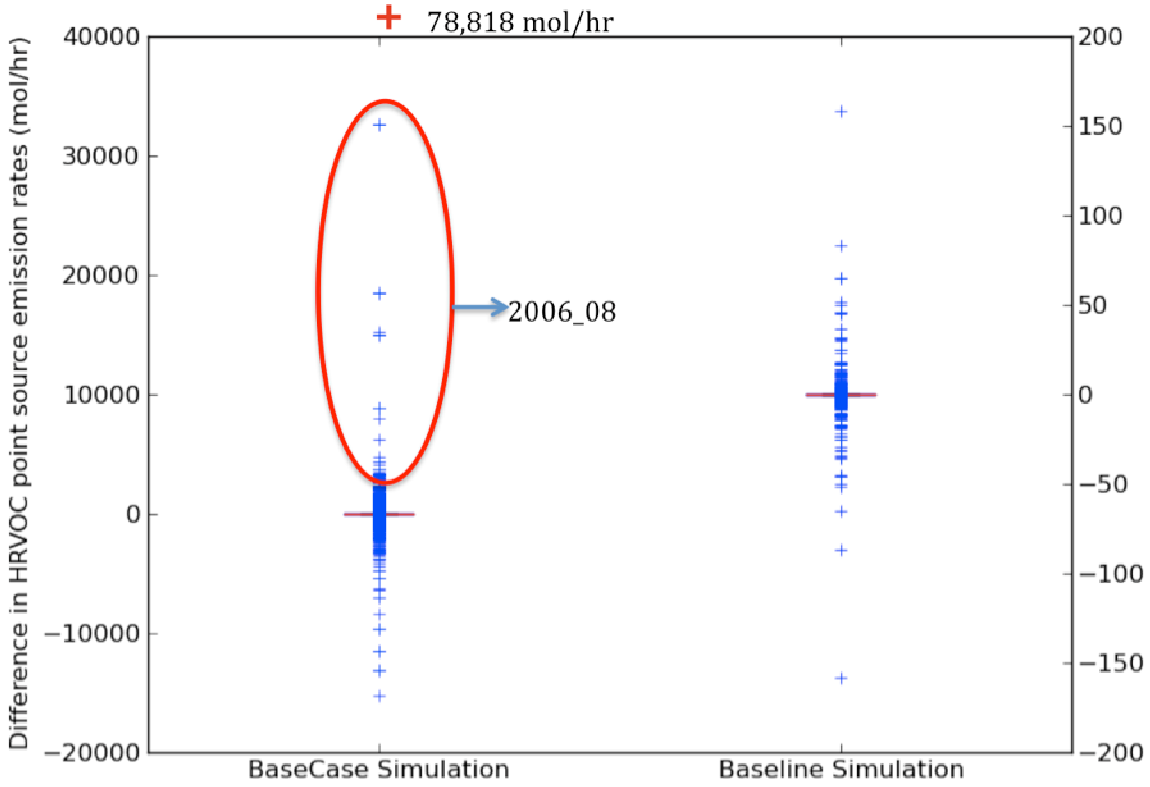


Figure 2.2: Distribution of hourly differences for the HRVOC emission rates of point sources in the baseline and basecase emission inventories for all modeling days. The are two scales in the plot. The left hand scale corresponds to the basecase simulation while the right hand scale corresponds to the baseline simulation. The red circle indicates the major differences which were found in the 2006_08 modeling episode.

CHAPTER 3

RESULTS

In this analysis we have defined a NTOC as either an hourly increase in ozone concentration equal to or greater than 40 ppb (≥40 ppb/hr), or any two-hour increase in ozone concentration equal to or greater than 60 ppb ((≥60 ppb/2hr). These criteria were first applied to modeling predictions using both the basecase and baseline emission inventories. Further, we applied these criteria to the observational data that coincided with the modeling period. Some NTOCs were both simulated and measured at late nights and very early mornings but it is important to note that this study focused on simulated and observed NTOCs between 0600 LST and 2000 LST.

3.1 Observed Non-Typical Ozone Changes

For the modeling period, we also calculated the number of measured NTOC using the 25 monitors shown in Figure 3.1, and described in Table 3.1. Based on these data there were 110 observed NTOCs of both criteria measured over the 34 days that coincided with the TCEQ model. The maximum observed 1-hr ozone change was 62 ppb/hr at the Texas City (TXCT) monitor at 1000 LST on June 9, 2006. The maximum observed 2-hr change was 95 ppb measured at the Houston Regional office (HROC) monitor on August 1, 2005 at 1100

LST. The average observed 1-hr change was 46 ppb while the average 2–hr change was 67 ppb.

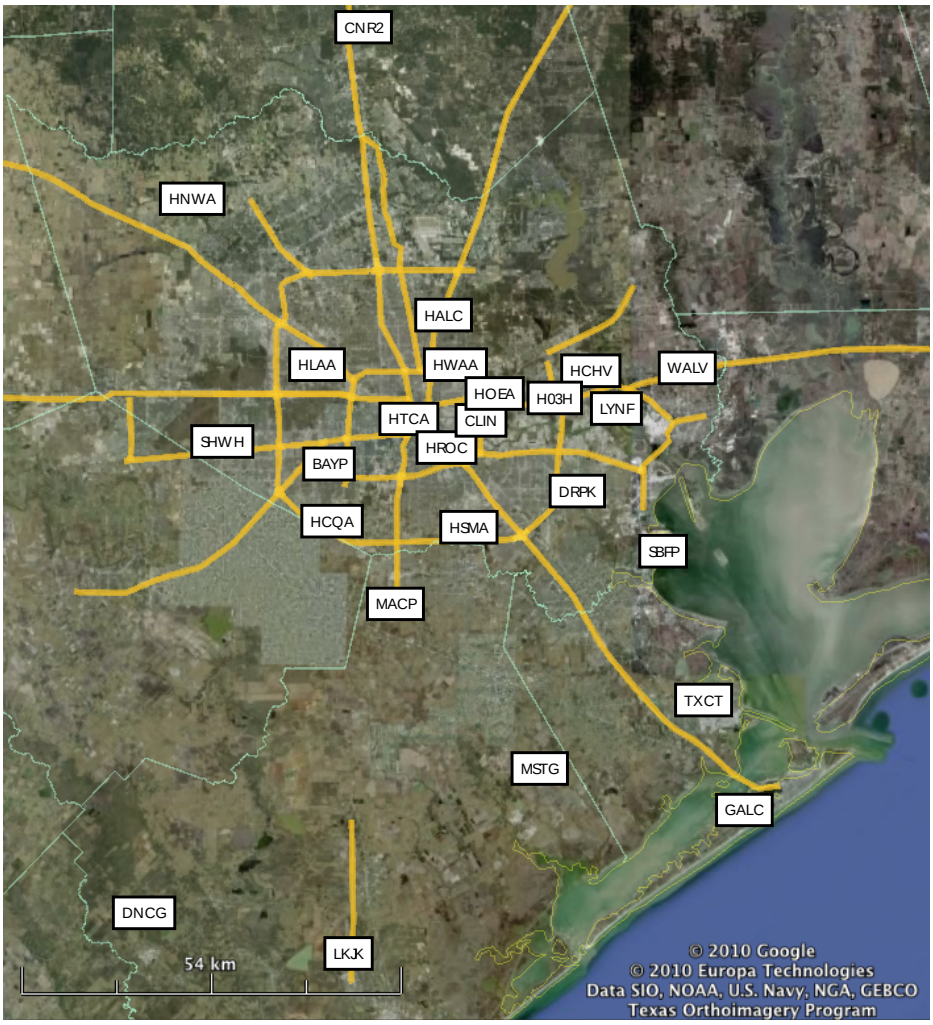


Figure 3.1: Map of the HGB area showing the surface monitors used in this study.

The observed days with NTOC, the corresponding surface monitors at which they occurred, and hours the NTOCs were measured are listed in Table 3.2. The highlighted days are the days common to the basecase simulation that had predicted NTOCs. Three monitors in the Houston Ship Channel region recorded the greatest number of NTOCs. Deer Park (DRPK) surface monitor recorded the most NTOCs with 19 occurrences of both NTOC criteria.

Wallisville (WALV) and Lynchburg Ferry (LYNF) monitors had 10 and 9 NTOC occurrences. From Table 3.2, we observe that the daily maximum number of monitors affected by NTOCs is 7 on August 1, 2006 occurring between 0900 LST to 1200 LST. About 74% of the days had measured NTOCs at three monitors or less and 89% of the days had measured NTOCs at four monitors or less. Most of the days with measured NTOCs at four monitors or less had monitors in close proximity to each other confirming previous studies by Vizuete et al. (2011), indicating that observed NTOCs occur over a small spatial scale.

Table 3.1: List of ground monitors and their 4 letter abbreviations

MONITOR NAME	**ABBREVIATION**
BAYLAND PARK	BAYP
CLINTON	CLIN
CONROE RELOCATED	CNR2
DANCIGER	DNCG
DEER PARK	DRPK
GALVESTON	GALC
HRM-3 HADEN ROAD	H03H
ALDINE	HALC
CHANNELVIEW	HCHV
CROQUET	HCQA
LANG	HLAA
NORTHWEST HARRIS COUNTY	HNWA
HOUSTON EAST	HOEA
HUSTON REGIONAL OFFICE	HROC
MONROE	HSMA
TEXAS AVENUE	HTCA
NORTH WAYSIDE	HWAA
LAKE JACKSON	LKJK
LYNCHBURG FERRY	LYNF
MANVEL CROIX PARK	MACP
MUSTANG BAYOU	MSTG
SEABROOK FRIENDSHIP PARK	SBFP
WESTHOLLOW	SHWH
TEXAS CITY	TXCT
WALLIVSVILLE	WALV

Table 3.2: Observed days with NTOC during modeling period, surface monitors at which they occurred and the hours in LST

Date	Monitor	Time (LST)	Date	Monitor	Time (LST)	Date	Monitor	Time (LST)
05/25/05	H03H	1200	07/31/05	HSMA	1100	**08/16/06**	HO3H	1200
	LYNF	1200	**08/01/05**	DRPK	0900		HCHV	1300
	HCHV	1300		HSMA	1000		LYNF	1500
	WALV	1300		HO3H	1000		WALV	1500
05/26/05	HCQA	1100		CLIN	1000	**08/17/06**	DRPK	1100
	MACP	1300		HROC	1100		LYNF	1300
05/27/05	BAYP	1200		LYNF	1100		HO3H	1400
06/02/05	DRPK	0700		BAYP	1200		HOEA	1400
	SBFP	0700	**08/02/05**	DRPK	0800		HSMA	1400
	HCQA	0800	**08/05/05**	DRPK	0800		CLIN	1500
	WALV	1000		WALV	1600	**08/18/06**	CNR2	0800
	HO3H	1000	08/06/05	DRPK	800		HNWA	0800
06/19/06	BAYP	1100		GALC	1000	08/31/06	CLIN	0900
06/21/05	DRPK	0800	**06/04/06**	LYNF	1000		HROC	1100
06/22/05	HCQA	0800		SBFP	1200	09/01/06	DRPK	1200
	CLIN	1100	06/05/06	WALV	1200		SBFP	1400
	DRPK	1100	06/08/06	DRPK	1200	09/03/06	MACP	0800
	HSMA	1200		LYNF	1400	09/07/06	BAYP	1200
06/23/05	DRPK	0800		WALV	1700		HCQA	1200
	CLIN	1100	06/09/06	TXCT	1000		MACP	1200
	HLAA	1100	06/10/06	LYNF	1200	09/08/06	HSMA	1100
07/27/05	SBFP	1500		WALV	1300	09/14/06	HTCA	1300
07/28/05	TXCT	1500	06/11/06	HOEA	0700		SHWH	1400
07/29/05	BAYP	1200	**06/12/06**	DRPK	1600	09/27/06	LYNF	0800
	HCQA	1200	06/15/06	DRPK	0700		HOEA	0900
	MACP	1300		HO3H	0800		WALV	0900
	HSMA	1300		HOEA	0800		HCHV	0900
	MSTG	1500		HCHV	1000			

Highlighted days are days common to the basecase simulation

3.2 Simulated Non-Typical Ozone Changes

In the model predictions, using the basecase EI, there were 670 grid cells with a simulated NTOC that satisfied either criteria spread across 22 simulation days. The baseline EI had 457 grid cells with simulated NTOC of either criteria spread across 17 simulated days. Both simulations had maximum predicted 1-hr ozone change of 54 ppb. The maximum predicted 2-hr change was 76 ppb for the basecase and 74 ppb for the baseline simulation. Both simulations predicted the same average 1-hr change and 2-hr change. The average predicted 1-hr change for both simulations was 42 ppb and 62 ppb for the average predicted 2-hr change. Table 3.3 lists all the basecase simulations days that predicted a NTOC with the maximum daily 1-hr and 2-hr changes in ozone concentrations. Also shown in Table 3.3 are the hourly ozone changes for the same grid cell and local standard time, but with the baseline EI. The basecase simulation predicted higher changes than the baseline with a maximum difference of 7 ppb at grid cells with predicted NTOCs and a maximum difference of 18 ppb at grid cells with no predicted NTOCs using the baseline EI (red entries). Overall, both predictions of hourly changes can be said to be quite similar despite the differences in the emission rates.

The basecase and baseline simulations had fewer days with predicted NTOCs when compared to observations. Although the basecase recorded 22 simulated days with NTOCs, there were only 9 days that matched observed days with NTOCs while the baseline simulation predicted 7 of the 34 observed days. The AQM was unable to reproduce most of the observed days with NTOCs. Simulations using either the baseline or basecase EI were unable to predict the magnitudes of the highest observed non-typical ozone change for either criterion.

Table 3.3: Simulation days with predicted non-typical ozone changes using the basecase EI and corresponding predictions using the baseline EI.

Date	Time (LST)	Max 1hr NTOC (ppb)		Time (LST)	Max 2hr NTOC (ppb)		Total number of grid cells with NTOCs	
		B.Case[a]	B.Line[b]		B.Case[a]	B.Line[b]	B.Case[a]	B.Line[b]
9/12/2006	1800	54	49	1100	66	60	60	43
8/1/2005	0900	51	47	1300	76	69	138	77
8/17/2006	1800	49	48	1200	72	74	117	115
10/9/2006	1200	49	50	1200	66	64	20	17
*8/21/2006	1300	48	44	1300	71	65	52	28
10/4/2006	1200	47	46	1200	64	65	60	45
8/5/2005	1900	46	28	1200	64	51	13	0
8/3/2005	1400	45	42	-	0	0	7	3
5/26/2005	1000	45	41	1000	71	70	110	44
6/4/2006	1100	44	42	1200	66	64	3	3
6/12/2006	1500	44	35	1300	65	50	9	0
8/8/2005	1200	44	30	-	0	0	2	0
6/3/2006	0600	43	44	-	0	0	3	3
5/22/2005	1400	43	37	1500	64	56	22	0
8/18/2006	0600	42	30	0900	64	63	10	11
*8/20/2006	1400	42	48	1400	49	61	6	21
8/07/2005	1700	42	41	1700	62	60	21	10
8/02/2005	1100	42	40	1100	61	57	4	1
5/28/2005	1300	42	41	-	0	0	3	2
6/25/2005	0800	41	39	0900	61	59	3	0
8/29/2006	1100	40	40	1200	60	60	2	2
8/16/2006	1400	40	37	1400	73	67	3	1

Entries in red are not classified as NTOCs

***Modeled HRVOC emission event confirmed upwind of predicted NTOC.**

[a] Basecase

[b] Baseline

On June 9, 2006, both simulations under predicted the observed maximum 1-hr change that occurred at the TXCT monitor by 47 ppb at 1000 LST and under predicted the hourly ozone concentration by 50 ppb. The basecase and baseline simulations over predicted the hourly ozone concentration at the HROC monitor on August 1, 2005 at 1300 LST by 11 ppb and 16 ppb and under predicted the observed maximum 2-hr ozone change at the monitor by 48 ppb and 52 ppb respectively.

3.3 Simulation of large HRVOC releases

In the regulatory model using the basecase EI, only two of the 22 days with predicted NTOCs had an upwind release of an industrial HRVOCs. On August 20, 2006 and August 21, 2006, there were increases in HRVOC emissions from 0500 to 0600 LST from the same industrial point source grid cell location. At 0600 LST there were increases of 32,643 mol/hr and 18,441 mol/hr occurring respectively on each day at grid cell location (column 60, row 60) depicted by the black X in Figure 3.2. It is important to note that this HRVOC emission release is absent in the baseline EI providing a natural sensitivity run. August 20, 2006 had the larger HRVOC release so model predicted ground layer ozone concentrations based on the basecase EI were subtracted from predictions based on the baseline EI as shown in Figure 3.2 for hours 0600 and 0800 LST. In the figure, a black X shows the area where the large hourly difference occurred. Two hours after the simulated large hourly point source difference, at 0800 LST, a maximum difference of 25 ppb (the area depicted by the red rectangular box in Figure 3.2b) occurred downwind of the HRVOC emission. The DRPK monitor depicted by a black diamond in Figure 3.2 was the closest monitor to the location (column 58, row 57) where the difference occurred. At 0800 LST, the monitor measured an

ozone concentration of 46 ppb compared to a basecase concentration of 51 ppb and baseline concentration of 26 ppb. The hourly ozone concentration time series for August 20, 2006 is shown in Figure 3.3.

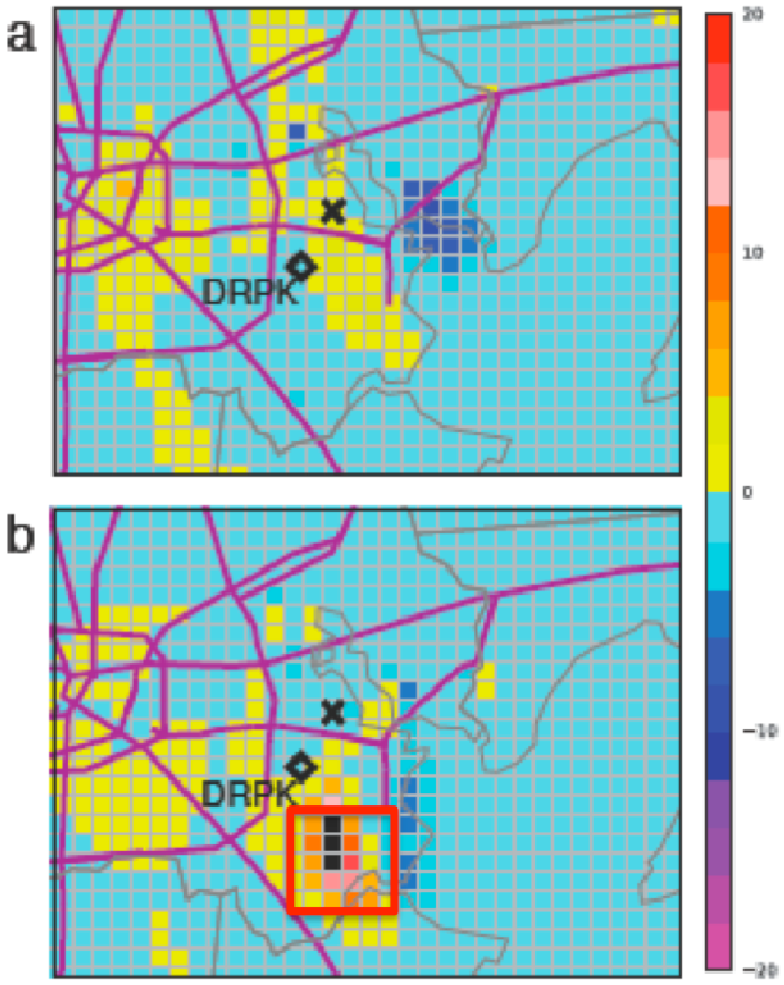


Figure 3.2(a): 1-hr ozone concentration difference spatial plots for August 20th 2006 at 0600 LST. The black X mark indicates the area the large hourly HRVOC emission rate difference occurred and the black diamond depicts the Deer Park (DRPK) monitor. Figure 3.2(b): 1-hr ozone concentration difference spatial plots for August 20th 2006 at 0800 LST. There was a maximum 1-hr ozone concentration difference of 25 ppb in the area depicted by the red rectangular box.

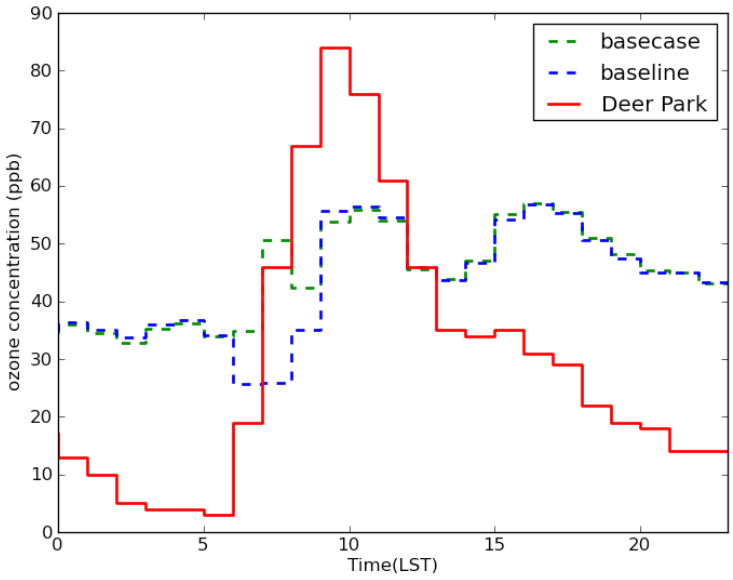


Figure 3.3: 24-hr time series plot for ozone concentrations for basecase and baseline simulations and the measured observed concentration at the deer park (DRPK) monitor. At 0800 LST, the ozone concentration using the basecase EI was 51 ppb, baseline EI, 26 ppb and at Deer Park 46 ppb.

The basecase and baseline simulations had similar ozone concentrations for all hours except from 0600 to 0900 LST after there was a large emission difference. The basecase ozone concentrations for 0800 LST is 6 ppb higher than the observed ozone concentration compared to a baseline ozone concentration which was 20 ppb lower than the observed ozone concentration.

Although there were several large releases of HRVOCs, not all HRVOCs resulted in an NTOC. The distribution shown in Figure 2.2 shows there were very few basecase-simulated differences of extreme magnitude that were predicted. Majority of the differences were below the 5000 mol/hr mark. Therefore, using 8000 mol/hr as a cutoff mark for hourly emission change, we extracted days with the large emission differences. The largest point

source HRVOC hourly differences for the basecase simulation are shown in Table 3.4 with the date, local standard time (LST) and grid location where the large differences occurred. From Table 3.4, we discover that four of the large hourly HRVOC differences occurred at the same grid location (around the Houston Ship Channel region) while two occurred at hours not conducive for ozone formation (2000 LST). The large hourly releases that both occurred at 2000 LST did not result in an NTOC likewise August 22, 2006 and September 14, 2006. This confirms previous studies that location and timing in addition to right ambient conditions conducive for ozone formation play important roles in rapid ozone formation (Allen et al, 2004).

Table 3.4: Days with large hourly point source HRVOC differences, emission rates, local standard time (LST) and the grid location where the difference occurred in the 2006_08 modeling episode.

Day	**Emission rate (mol/hr)**	**Time (LST)**	**Grid Location (column, row)**
08/20/2006	32643	0600	60,60
08/21/2006	18441	0600	60,60
08/22/2006	10327	1300	56,43
08/29/2006	8923	1200	60,60
09/02/2006	78818	2000	60,60
09/13/2006	17397	2000	47,57
09/14/2006	21804	1500	47,57

3.4 Simulation of Observed Non-Typical Ozone Changes

More interesting are those days with NTOC in the basecase episodes that were not downwind of a large HRVOC release. In the 2005 to 2006 modeling episodes, there are 20 days of non-HRVOC related NTOCs in the basecase episode. A majority of the NTOCs occurred between 0900 LST and 1800 LST. We examined the basecase simulation days that are common to the observed days with NTOCs.

On August 1, 2005 at 0900 LST, there was a measured NTOC at the DRPK monitor. Our study showed that the model however, did not simulate the right location of the observed NTOC at 0900 LST. Figure 3.4 shows predicted ozone concentrations for the grid 2km modeling domain for August 1, 2005 with predicted NTOCs in 10 grid cells at 0900 LST. The diamonds indicate the locations of ground monitors and the color of each diamond indicates the measured ozone concentration for that hour. A color mismatch between the grid cell and monitor indicates that the model has either over predicted or under predicted the measured ozone concentration. The red box at the bottom right region of the plot indicates the grid cells where the model predicted the NTOCs and the blue circle indicates the monitor (DRPK) where the observed NTOC was measured. From this figure, we discover that the model has not only predicted the wrong location for the NTOC, but has also under predicted both the hourly change and the measured ozone concentration. The DRPK monitor measured an ozone concentration of 96 ppb at 0900 LST while the model predicted an ozone concentration of 80 ppb. 24-hr time series for the basecase simulation and observed values on August 1, 2005 are shown in Figure 3.4b. There was a 1-hr change of 43 ppb measured at

DRPK at 0900 LST while the model predicted an hourly change of 22 ppb. The model under predicted the observed 1-hr change by 21 ppb.

(a) (b)

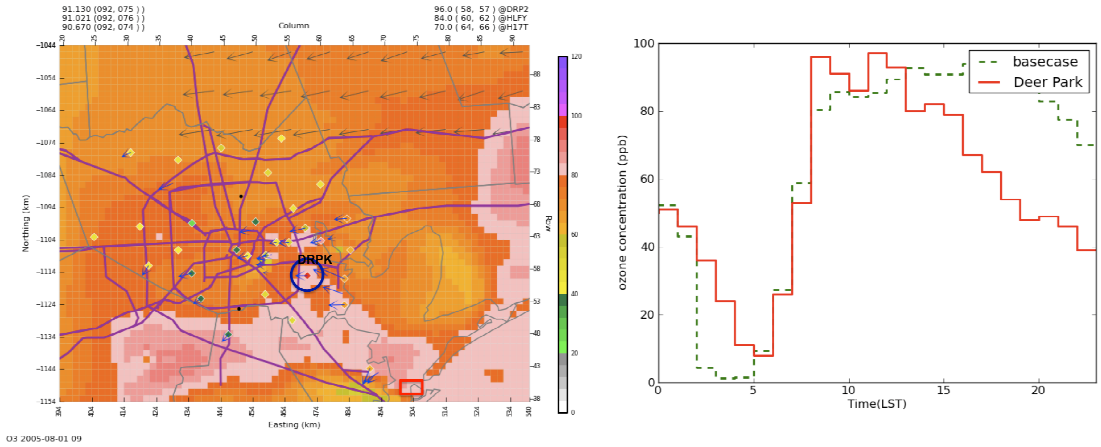


Figure 3.4(a): Basecase simulated spatial plots for 1-hr ozone concentrations for August 1, 2005 at 0900 LST. Diamond markers show the location of ground monitoring stations. The color of each diamond gives the measured 1-hr O_3 value at that site. Black arrows at each diamond show the measured 1-hr resultant wind vector at that site. Simulated 1-hr resultant wind vectors are also shown for select grid cells. The red box indicates the region of predicted NTOCs and the blue circle indicates the surface monitor with observed NTOC.
Figure 3.4(b): 24-hr ozone time series plot for basecase simulation and observed values at DRPK.

The model was also unable to predict the right ozone concentrations at several of the monitors as seen in the spatial plots. Most of the diamonds representing ground monitors as seen in Figure 3.4 show a color mismatch between them and the grid cell indicating either an under prediction or an over prediction. Figure 3.5 shows hourly concentrations of some ground monitors in the ozone plume at 0900 LST. The blue bars represent observations and the red bars, basecase predictions. The model over predicted most of the monitors with the exception of DRPK where there was an under prediction.

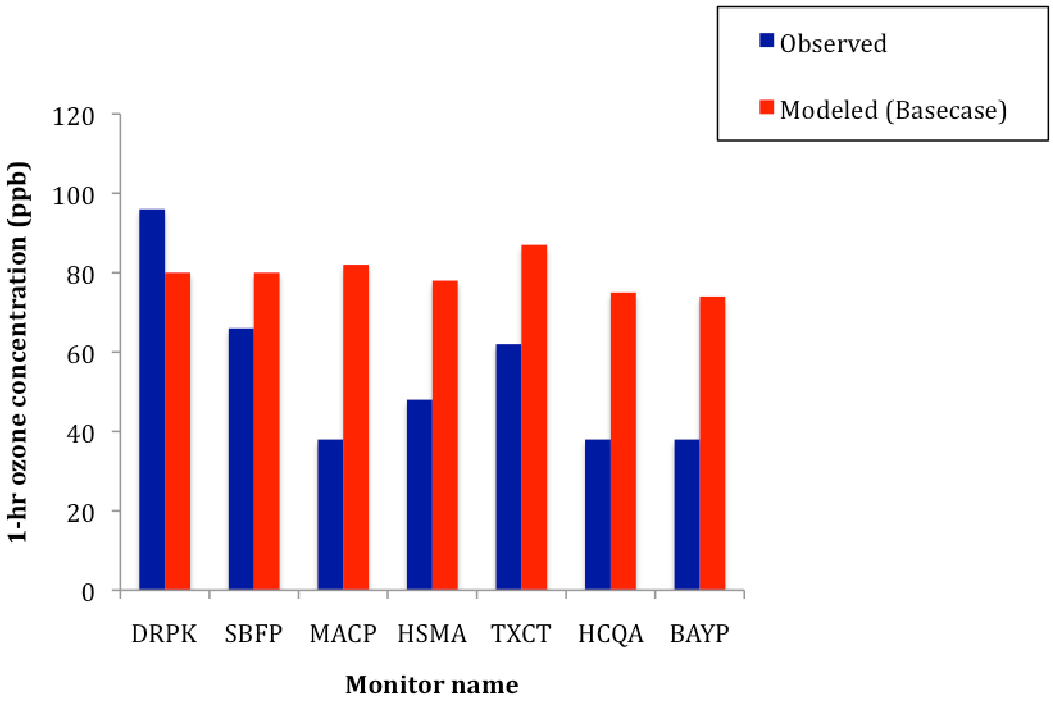


Figure 3.5. 1-hr ozone concentrations for modeled (red) and observations (blue) at some ground monitors on August 1 2005 at 0900 LST.

Another example of the lack of fine spatial resolution of predicted hourly ozone change is shown on August 1, 2005 at 1200 LST, which had both a measured and a predicted NTOC. Figure 3.6 shows the predicted ground level ozone concentration spatial plot for this day at 1200 LST. The model predicts large plumes of high ozone concentrations over much of the HGB region as seen in Figure 3.6. The yellow circle indicates the region where the model predicted the NTOCs using the basecase EI, and the BAYP monitor; the closest monitor to the region has also been highlighted. With the exception of the BAYP monitor, the model over predicts almost every monitor in the region as shown by the color mismatch between the diamonds and grid cells in Figure 3.6. The black ozone plume indicates that the

model predicted the ozone concentration to be greater than 120 ppb. At this hour, the model accurately matches the observed ozone concentration at BAYP monitor as shown with a corresponding black colored diamond at the BAYP monitor but over predicts the HCQA and the SHWH monitors which were both in close proximity to the BAYP monitor and other monitors in the ozone plume. Figure 3.6(b) shows both the modeled (red) and observed (blue) 1-hr ozone concentrations at the BAYP and six other monitors in the black ozone plume. The black line at 120 ppb indicates the black region of the ozone plume seen in the spatial plot. The model over predicted the HCQA and SHWH monitors by 37 ppb and 56 ppb.

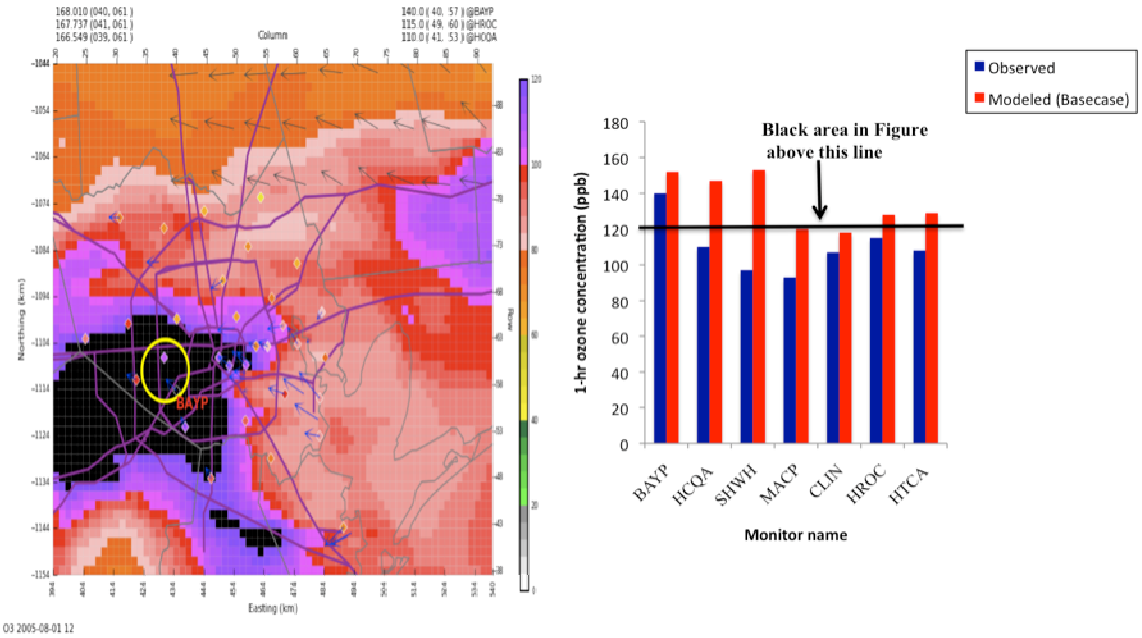


Figure 3.6(a): Basecase simulated spatial plots for 1-hr ozone concentrations for August 1st 2005 at 1200 LST. Diamond markers show the location of ground monitoring stations. The color of each diamond gives the measured 1-hr O_3 value at that site. Black arrows at each diamond show the measured 1-hour resultant wind vector at that site. Simulated 1-hr resultant wind vectors are also shown for select grid cells. The yellow circle indicates the grid cells where the model predicted NTOCs. Figure 3.6(b): 1-hr ozone concentrations for modeled (red) and observed (blue) values at the monitors in the black ozone plume. The black line at 120 ppb indicates the concentrations greater than 120 ppb as denoted by black in the spatial plot.

There was also an observed NTOC at the BAYP monitor for this hour with a 1-hr change of 56 ppb. The model was able to predict a high ozone concentration for this day but failed to reproduce the observed hourly change. The model predicted a maximum 1-hr ozone change of 46 ppb, which is 10 ppb less than the observed value within the predicted NTOC region as depicted by the yellow circle in the Figure 3.6 and at the exact monitor location (column 40 and row 57), the model under predicted the 1-hr ozone change by as much as 23 ppb.

Another limitation of the model is observed to have occurred on August 2, 2005 when the model predicted the right magnitude, but got the timing of the NTOC wrong. The DRPK monitor measured a 1–hr ozone change of 40 ppb at 0800 LST. Figure 3.7 shows the predicted 1-hr ozone concentrations for the 2 km-grid domain and from this plot we notice that the DRPK monitor was under predicted.

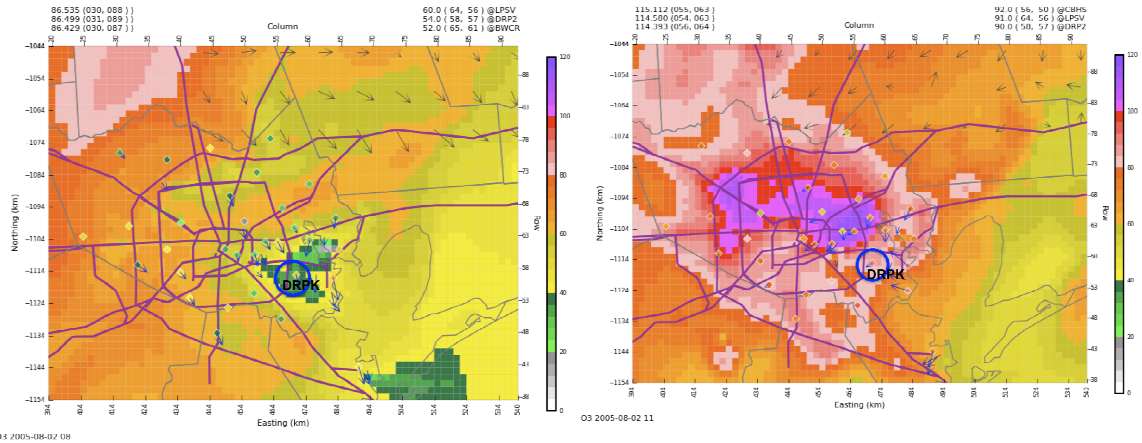


Figure 3.7: Basecase simulated spatial plots for 1-hr ozone concentrations for August 2, 2005 at 0900 LST and 1100 LST. Diamond markers show the location of ground monitoring stations. The color of each diamond gives the measured 1-hr O_3 value at that site. Black arrows at each diamond show the measured 1-hr resultant wind vector at that site. Simulated 1-hr resultant wind vectors are also shown for select grid cells. The blue circle indicates location of the ground monitor DRPK.

The DRPK monitor is highlighted in the spatial plot. The monitor measured an ozone concentration of 54 ppb compared to a predicted concentration of 30 ppb and a 1-hr ozone change of 40 ppb. The model however did not predict any NTOC at this hour but predicts an hourly change of 42ppb (which matched observed 1-hr ozone change near the DRPK monitor at 0800 LST) 3 hours later at 1100 LST. The model replicates the same trend of large ozone plumes as shown in Figure 3.7, which led to accurate prediction at the DRPK monitor but over predicts several other monitors in the ozone plume. Measured 1-hr concentration was 90 ppb while the model predicted an hourly ozone value of 85 ppb at 1100 LST.

CHAPTER 4

DISCUSSION

This study investigated the regulatory model's ability to predict the magnitude and location of observed NTOCs. From our study, we observe that the AQM is limited in its ability in predicting the observed rapid ozone formation noticed in HGB region. Model limitations could be due to some assumptions and uncertainties. Some of the uncertainties are discussed in the following section.

The TCEQ, in an attempt to reconcile emissions inventories, added the special inventory to the basecase EI but accuracy of the EI still poses a problem and remains one of the most important uncertainties. The SI was based on reports from a subset of plants in the HGB area and does not adequately represent the observed nature of the stochastic emission events. Cowling et al. (2007) found in the second Texas Air Quality Study II (Texas AQS II) that the latest EI still underestimates HRVOC emissions from industrial point sources by an order of magnitude. We are aware that the baseline EI lacks emission variability but often predicts similar rapid hourly ozone changes to the basecase simulation. Further, both inventories predicted similar spatial distributions of ozone concentrations and this brings to question how sensitive the model is to emission variability considering the fact that both simulations had the same meteorology.

The model's limitation in predicting the right location for rapid ozone formation could also be attributed to the complex nature of the meteorology observed in the HGB area. Wind patterns, wind directions, land/sea breeze, boundary layer height, temperature and stagnation have been known to favor rapid ozone formation. Errors in meteorology could affect the response of ozone to control strategies in the model.

Another possible explanation could be attributed to chemical mechanism and incorrect representations of HRVOC emissions. Due to the inexplicit nature of some of the HRVOCs, it is possible that model simulation of the HRVOCs using the carbon V mechanism might be inadequate. As mentioned, various studies have shown that HRVOCs have been linked to observed rapid hourly ozone formation but some other NTOCs are yet to be explained. Other contributing factors could be missing from the chemical simulations of the NTOCs. Radical sources and sinks and other sources of ozone precursors could also be responsible for high ozone formation.

Finally, previous studies have shown that grid resolution affects accurate prediction of rapid ozone formation and spatial resolution in the HGB region (Allen et al., 2004b; Henderson et al., 2010). The TCEQ used the 2 km-grid domain in the 2010 SIP, but these studies show that using a superfine grid resolution, like the 1 km horizontal grid cell size, improve model simulations of high ozone productions. The coarser the grid resolution, the more dilute the HRVOC concentrations tend to be in the model leading to lower ozone concentrations.

CHAPTER 5

CONCLUSIONS

This study has been able to show that the regulatory model used by the TCEQ is limited in its ability to reproduce observed large hourly ozone changes.

Observed NTOCs frequently affect only one or two monitors; the most observed NTOCS on single day was 7 on August 1, 2005. In contrast to this observed phenomena we noticed that model predictions of ozone plumes are very widespread and cover a large spatial extent. This large spatial area results in improved performance at the monitor with the observed NTOC, but over predictions at many monitors in close proximity. By magnitude, the model was unable to predict the wide range of observed maximum 1-hr and 2-hr changes in ozone concentrations. Both simulations could not predict greater than 54 ppb/hr and 76 ppb/2hr, which led to under predictions of some observed NTOCs.

The model was unable to predict most of the early morning (0600 LST to 0800 LST) NTOCs. The majority of the predicted NTOCs were between 0900 LST and 1800 LST. This study used NTOCs both measured and predicted between 0600 LST and 2000 LST but observations show that there were no measured NTOCs at 1800 LST. However, the model had several predictions of NTOCs to have occurred at 1800 LST.

Regulatory model predictions were based on both the basecase and baseline emission inventories. We found very similar ozone predictions and range of hourly ozone changes in

the two inventories. There were some higher predictions in the basecase and we found that given the right conditions, the inclusion of a large emission release of HRVOCs caused a 25 ppb increase in hourly ozone concentrations and improved performance at the DRPK monitor.

Understanding the implications of the regulatory air quality model's limitation to predict observed NTOCs could assist the HGB region in attaining future attainment. In showing future attainment, the EPA requires the use of both observations and model predictions and we observe that the model is not predicting these magnitude or spatial distribution of the observed phenomena. Inaccurate model predictions of both hourly changes and hourly ozone concentrations are likely to affect future predictions of ozone concentrations generated from simulated environmental response to proposed pollutant control strategies but further research is needed in this area. Inaccurate model predictions could be leading to ineffective control strategies.

Future work is needed on how the model simulates NTOCs and process analysis can be used to study the in-depth analysis of physical and chemical processes responsible for rapid ozone formation on simulated days. Secondly, a more detailed analysis into basecase and baseline EIs should be conducted to check model sensitivity to emissions events. Lastly, days having both observed NTOCs and emission events could be compared with corresponding days in the basecase simulation.

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