Atmospheric Pollution Research

Modeling analysis of the impact of anthropogenic emission sources on ozone concentration over selected urban areas in Texas

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ABSTRACT

Due to several regional–scale high ozone episodes that impacted the urban areas in south and central Texas over the past decade, the Texas Commission on Environmental Quality (TCEQ) has designated several urban regions as near non–attainment areas. A regional photochemical modeling experiment was set up to simulate a high ozone episode of September 11–14, 2002 in order to evaluate the impact of various anthropogenic emissions sources on ozone concentrations. The base case simulation showed reasonable model performance by capturing the peaks and the diurnal variability of observed ozone concentrations within the modeling domain. A comprehensive impact assessment of anthropogenic emissions from various source categories to the 8–hour ozone concentration was evaluated for each of the urban areas within the study region. Through a source apportionment analysis of emissions influencing the 8–hour ozone concentrations, NO_x and VOC limited areas were identified. The model results showed that the net effect of all anthropogenic emissions was approximately 8.4 ppb in Victoria, 8.8 ppb in Corpus Christi, and 31.2 and 34.1 ppb in Austin and San Antonio, respectively. Impact of major emissions source categories differed regionally with ozone concentrations in Austin and San Antonio mainly influenced by mobile sources, while Corpus Christi and Victoria were largely impacted by long–range transport of ozone. On a local scale, Corpus Christi was also impacted by non–road sources, while Victoria was influenced by point sources. Ozone sensitivity analysis showed higher sensitivity towards VOC within the urban cores of Austin, San Antonio, and Corpus Christi, while the overall modeling regions showed higher NO_x sensitivity. This would indicate that both NO_x and VOC emissions reduction plans need to be developed and implemented for the mitigation of regional and urban ozone. The results also revealed that biogenic emissions played an important role in the urban regions of south and central Texas.

Keywords: Photochemical modeling, anthropogenic emissions, urban air quality, ozone concentration

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1. Introduction

A large number of scientific studies indicate that major urban regions in the United States and across the world continue to be affected by elevated ground level ozone concentrations (Krzyscin et al., 2007; Kulkarni et al., 2011). Ozone is a secondary pollutant and it is formed by the oxides of nitrogen (NO_x) and volatile organic compounds (VOC) through complex non–linear photochemical reactions under conducive meteorological conditions (Sillman, 1999). In addition, regional ozone concentrations are influenced by long–range transport of pollutants (OTAG, 2010; Ohara, 2011) and by the various meteorological regimes (Rao et al., 1997). Further a multifaceted interaction of anthropogenic and biogenic sources influence ozone formation under high temperatures and photolytic conditions (Wang et al., 2008). Thus, it becomes rather difficult to design effective local and regional emission reduction strategies to alleviate the regional–scale ozone problem.

The ozone standards are becoming more stringent worldwide based on strict health criteria (U.S.EPA, 2008; European Communities, 2008). The US EPA has set the 8–hour ozone standard to 0.075 ppm, based on stricter health based criteria. The 3–year average of the fourth highest daily maximum 8–hour average ozone concentration measured within an area over each year must not exceed the prescribed value (U.S. EPA, 2008). In the United States, the regions that violate the federally mandated National Ambient Air Quality Standards (NAAQS) are designated as ozone non–attainment areas. These areas must develop effective emissions control strategies and demonstrate attainment of the 8–hour ozone NAAQS as specified in the individual State Implementation Plans (SIP). The efficacy of any ozone control measure must consider the complexity of processes that affect its formation which can only be simulated by sophisticated three–dimensional Eulerian models (European Communities, 2002). It is recognized globally that numerical air quality models play an essential role in air quality management are an indispensable part of air quality management and planning activities (Hakami, et al., 2003) and they are also used for evaluating the atmospheric response to different emission control measures . Non–attainment areas in USA and Europe have to demonstrate ozone attainment status using computer based air quality modeling to test efficient emission control strategies.

Air quality planning procedures involve usage of air quality models for demonstration of effectiveness of emission control strategies. Ozone attainment demonstration is usually accomplished through the use of grid–based photochemical models such as CAMx (ENVIRON, 2011), CMAQ (Byun and Schere, 2006) and others. These are designed to simulate the complex physical, chemical, and meteorological processes associated with the production of ozone. Several studies in the past have illustrated the importance of photochemical models in making regulatory decisions (Biswas and Rao, 2001; Hogrefe et al., 2001; Sistla et al., 2001; Roth et al., 2005). Modeling simulations have

been successfully applied in assessing ozone abatement strategies in terms of their effectiveness on the regional and urban scales (Moussiopoulos et al., 2000; Peng et al., 2011). Typically, this is accomplished by modeling high ozone episodes, usually spanning over three to ten days. Since photochemical modeling development is both costly and resource intensive process, it is important to select a representative set of episodes and not attempt to model all days that may exceed the 8–hour ozone standard.

Due to several regional–scale high ozone episodes that impacted the urban areas in south and central Texas over the past few years, the Texas Commission on Environmental Quality (TCEQ) has designated four urban areas in this region as near non–attainment areas (NNAs). These include Austin, Corpus Christi, San Antonio, and Victoria. This term defines a geographic area that meets the national ambient air quality standards by a slim margin. These urban areas also need to design appropriate planning processes to continue to remain in attainment without any mandatory controls in place, and this poses a huge challenge for rapidly growing urban areas that are currently in compliance with the current ozone NAAQS.

In order to characterize and describe the ozone air quality within the Texas NNAs, a comprehensive photochemical modeling experimental setup was designed for a high ozone episode that affected all NNA regions in south and central Texas. To select representative ozone episode, conceptual modeling based on EPA guidelines (U.S. EPA, 2005) was undertaken using surface observed air quality and meteorological data to identify high ozone days for air quality modeling. The high ozone days of September 11–14, 2002, were considered to be the best representative ozone episode affecting all the urban areas within the study region. To best determine the impacts of various local and regional control strategies on the ozone air quality within the NNA regions, a single consistent modeling experimental framework was designed to support this study.

Identification of sources is a primary consideration towards the development of effective emission reduction strategies for an urban area. The aim of this study was to identify the source regions, source categories, and pollutant affecting ozone formation at designated receptor location(s) within the NNA domain. Different methods (zeroing out emissions, ozone source apportionment technology and decoupled direct method) were applied in this study to minimize uncertainties related to classification of sources to obtain a consistent approach for emissions control strategies in the near non attainment urban areas. While developing emissions control strategies it is also essential to classify regions based on NO_x and VOC sensitivities. While under NO_x sensitive conditions, NO_x emissions govern ozone formation and it has negligible influence from VOC, and while under VOC sensitive condition, ozone formation is directly influenced by VOC emissions (Im et al., 2011). This study inter-compared relative emission distribution patterns in the four near non–attainment areas located in south and central Texas and their subsequent impact on surface 8–hour ozone levels by "zeroing" out anthropogenic emissions from various emission source categories. The sensitivity of ozone formation was determined by quantifying an index of improvements based on sequential emission reductions and using tools such as first and higher order Decoupled Direct Method (DDM) (Hakami, et al., 2003). The influence of long–range transport, local emissions, source regions, and categories to ozone formation were determined by using the Ozone Source Apportionment Technology (OSAT) tool in CAMx photochemical model.

The aim of this study was to identify the source regions, source categories, and pollutant affecting ozone formation at designated receptor location(s) within the NNA domain. This study also attempted to inter–compare relative emission distribution patterns in the four near non–attainment areas located in south

and central Texas and their subsequent impact on surface 8–hour ozone levels by "zeroing" out anthropogenic emissions from various emission source categories. Another objective included evaluation of atmospheric responses to NO_x and VOC emissions from anthropogenic sources and the determination of ozone formation sensitivity. The sensitivity of ozone formation due to NO_x and VOC emissions from sources was also determined using DDM analysis tool built in CAMx model. These types of analysis not only help in identifying key emission sources affecting the ozone levels but they also provide initial direction of prospective emission control strategies for the study region in light of the current and possibly future ozone standards.
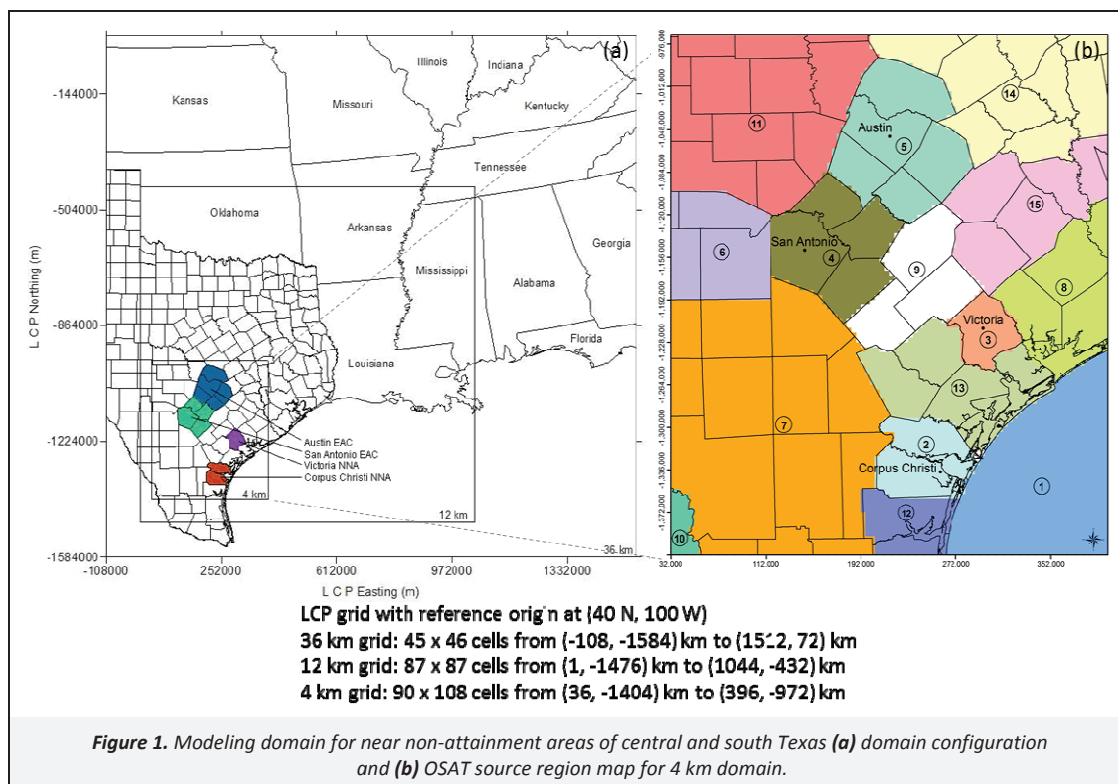
2. Model Setup

2.1. Study area

The study area consists of the four NNAs in south and central Texas as shown in Figure 1. Austin, the capital of Texas has a total population of approximately 1.25 million and an area of 10 940 km^2. The Austin urban airshed comprises of five counties. San Antonio consists of four counties and has the highest population density amongst the four NNAs with approximately 1.6 million individuals within 8 614 km^2 of area. This is the third largest metropolitan area in Texas and is home to several large corporations and firms. There are several power plants on the outskirts of these two urban areas. Corpus Christi is located within the semi–arid coastal region of south Texas, approximately 241 km north of the US–Mexico border and 354 km southwest of Houston, Texas, along the Gulf of Mexico. The population of Corpus Christi is approximately 380 000 and the urban airshed is comprised of two counties spread over 3 955 km^2. The dominant sectors of economy in Corpus Christi include petroleum refineries, chemical process industries, defense bases, port operations and tourism. Victoria in south Texas is located 129 km northeast of Corpus Christi and is home to several petrochemical industries and a major coal–fired power plant.

2.2. CAMx–MM5 model

The photochemical model used in the study was Comprehensive Air quality Model with extensions (CAMx) version 5.40 with the Carbon Bond Mechanism version 5 (CB05) (ENVIRON, 2011). The projection of the photochemical model grid system was Lambert Conformal (LCP) centered at (–100˚, 40˚) with standard parallel latitudes at 30° and 60°, respectively. CAMx was applied in the nested–grid mode as shown in Figure 1 with the outermost coarse grid of 36 km grid resolution. The next inner grid also known as the regional emissions grid of 12 km included the regions of Houston–Galveston, Beaumont–Port Arthur, Dallas–Fort Worth area and all of eastern Texas. The innermost fine grid at 4 km horizontal grid cell dimensions encompassed the urban areas of central and south Texas including Austin, San Antonio, Victoria and Corpus Christi. The CAMx model consisted of 12 vertical layers extending from the surface up to 4 km. Vertical layer configuration of CAMx and MM5 is shown in Table S1 of the Supporting Material (SM). These meteorological inputs such as layer interface height, winds, temperature, pressure, vertical diffusivity, water vapor, cloud cover, and precipitation were generated from the meteorological modeling simulations of the Fifth Generation Pennsylvania State University/National Center of Atmospheric Research (PSU/NCAR) Meteorological Model (MM5) (Grell et al., 1995). Nested grids in MM5 were used to resolve the wind patterns and thermodynamic fields over USA and over south and central Texas. The meteorological modeling domain is shown in Figure S1 of the SM. The four–dimensional data assimilation (FDDA) technique was applied to the MM5 simulations. In addition, sea surface temperatures were used as model inputs to better resolve the coastal meteorological effects.

Figure 1. Modeling domain for near non-attainment areas of central and south Texas **(a)** domain configuration and **(b)** OSAT source region map for 4 km domain.

Statistical evaluation of the CAMx and MM5 model, as shown in Table S2 and S3 (see the SM), was conducted at all available surface observation stations across San Antonio, Austin region, Corpus Christi, and Victoria urban areas. The base case modeling simulations were evaluated according to EPA's recommended statistical metrics (U.S. EPA, 2005). The base case evaluation was done only for high ozone days of September 11–14, 2002 and not for spin–up days. The model captured the diurnal variability of observed ozone concentrations in the coastal region of Corpus Christi and in the inland regions of San Antonio and Austin. Overall, the model performed reasonably well for each of the urban area and was within the U.S. EPA prescribed acceptable norms for performance. The time series plots of 8–hour ozone comparing model predicted and surface observed 8–hour ozone at continuous air monitoring site (CAMS) in San Antonio, Corpus Christi, Victoria, and Austin are shown in Figure S2 (see the SM) for the entire simulation period.

2.3. Emissions

The biogenic emissions inventory was derived using Global Biosphere Emissions Interactions System (GloBEIS3), version 3 (Yarwood et al., 2007). Emission Processing System (EPS) version 3 (ENVIRON, 2010) was utilized to process emissions temporally and spatially to generate CAMx ready gridded emissions input files. The emission inventories used in this study were EPA's National Emissions Inventory 2002 (NEI 2002) (U.S. EPA, 2012) for the regional emissions. Point source emissions provided by TCEQ (Yarwood et al., 2004) were used for the State of Texas. In addition the non–road and marine emissions within the Corpus Christi urban airshed were further refined and incorporated. The emissions were processed in LCP in congruence with the photochemical modeling grid system.

2.4. Methodology

Emission control scenarios. The following scenarios with uniform anthropogenic emission reductions at all grid cells over the 4 km NNA domain were also simulated:

- NO$_x$ emission reduction by 25% and VOC emission reduction by 50% (*n25v50*)
- NO$_x$ emission reduction by 50% and VOC emission reduction by 25% (*n50v25*)

The index of improvement (IOI) was determined and it is the percentage of difference between the base and the control case in relation to the base case. The IOI for modeled ozone concentrations was computed for the *n25v50* and *n50v25* control runs relative to the base case *n00v00* run in the following manner:

$$IOI = \frac{Max\left(O_{3,8-hour,base}\right) - Max\left(O_{3,8-hour,control}\right)}{Max\left(O_{3,8-hour,base}\right)} \times 100 \quad (1)$$

where, $O_{3,8-hour,base}$ is the 8–hour ozone in the base case and $O_{3,8-hour,control}$ is the 8–hour ozone in the emissions control case.

Zero–out emissions. Emission impact assessment was performed in order to find the impact of particular source category of emissions within and around the urban airsheds by conducting "zero–out runs" in which emissions from particular source category (area, on–road mobile, non–road mobile, point, anthropogenic, and biogenic) within each urban airshed was completely removed from the processed input emissions to the photochemical model. The influence of various emission source categories on peak ozone levels was calculated by subtracting the peak episodic ozone concentrations for each particular zero–out run from the maximum episode ozone concentrations of the base case as shown below:

$$\begin{array}{l} Impact\ of \\ emissions \end{array} = Max(O_{3,8-hour,base}) - Max(O_{3,8-hour,control}) \quad (2)$$

The use of episode maximum ozone concentration correctly interprets the actual reduction in peak ozone concentrations and the location of the highest impact in the each of the urban area.

OSAT analysis. The ozone source apportionment technology (OSAT) analysis tool built in CAMx was used in this study for identifying the sources and regions contributing towards the ozone

in the four urban areas of the 4 km grid of NNA domain. The 4 km modeling domain was divided in to 15 source regions as shown in Figure 1b, and the emissions in each source region were classified into five emissions categories: biogenic, area, non–road, mobile, and point. The boundary conditions (BC) were also tracked separately for quantifying their contribution towards the ozone concentrations.

DDM ozone formation analysis. The first order ozone formation sensitivity was obtained using the DDM probing tool in CAMx. DDM is a stable and computationally efficient tool which integrates the sensitivity equations, decoupled from the model equations (Hakami, et al., 2003). Due to its efficiency, DDM is widely used as a local emissions sensitivity analysis technique in three–dimensional air quality models to determine response of ozone to emissions (Cohan et al., 2005).

3. Results and Discussions

3.1. Emission distribution

The relationship between ozone and its precursors is considered to be a major source of uncertainty, which is further enhanced by the uncertainty in the emission inventory. Prior studies have indicated that emissions are often underestimated (Sistla et al., 2001). It therefore becomes very important to identify the emission sources and estimate emissions as accurately as possible. Thus a comprehensive study of allocation and under-standing of the distribution of emissions was the first step towards the eventual development of successful emission reduction strat-egies. Emissions in tons/day from different source categories for the four NNAs sub–regions are shown in Table 1 for both the weekdays and weekend days. The variability in emissions on the weekdays and weekend days are primarily due to variations in day specific activities and to a lesser extent due to meteorological variations.

Austin. As depicted in Table 1, on–road mobile sources had a major influence on the total NO_x emissions contributing ~50% (101 tons/day) on a typical weekday and over 46% (84 tons/day) on weekend days in Austin. The NO_x emissions from on–road mobile sources exceeded VOC emissions indicating the greater influence of heavy–duty diesel vehicles in comparison to lighter gasoline powered vehicles. It was found that biogenic emissions accounted for 72% (386 tons/day) of the total VOC emissions in this region. There were no noticeable differences in weekday–weekend emissions for any of the other source categories and the magnitude of emissions from these sources were considerably lower in comparison to mobile NO_x and biogenic VOC emissions. The total VOC emissions in Austin significantly surpassed the total NO_x emissions in this region indicating the dominance of biogenic VOC emissions in this region.

***Table 1.** Distribution of emissions in tons/day for September 11-14, 2002*

	11-Sep-02 Weekday		12-Sep-02 Weekday		13-Sep-02 Weekday		14-Sep-02 Weekend	
	NO_x	VOC	NO_x	VOC	NO_x	VOC	NO_x	VOC
Austin, tons/day								
Elevated Point	21.9	1.2	21.9	1.2	21.9	1.2	20.7	1.2
Low Level Point	12.6	1.6	12.6	1.6	12.6	1.6	11.6	1.6
Area	10.0	61.4	10.0	61.4	10.0	61.4	9.3	61.4
Non-road	26.8	15.4	26.8	15.4	26.8	15.4	25.4	12.7
On-road	100.5	68.9	100.5	68.9	100.5	68.9	84.0	56.8
Biogenic	30.0	393.0	29.0	386.8	30.9	417.4	30.6	413.5
Total	**201.8**	**541.6**	**200.8**	**535.4**	**202.7**	**566.0**	**181.6**	**547.1**
San Antonio, tons/day								
Elevated Point	74.3	2.7	74.3	2.7	74.3	2.7	70.7	2.6
Low Level Point	45.2	4.3	45.2	4.3	45.2	4.3	41.7	4.3
Area	18.3	97.8	18.3	97.8	18.3	97.8	17.8	97.8
Non-road	21.3	15.2	21.3	15.2	21.3	15.2	19.9	12.0
On-road	118.3	81.0	118.3	81.0	118.3	81.0	97.4	66.0
Biogenic	25.4	282.2	25.9	283.7	25.8	291.5	24.9	270.4
Total	**302.8**	**483.0**	**303.4**	**484.6**	**303.2**	**492.4**	**272.4**	**453.1**
Corpus Christi, tons/day								
Elevated Point	46.7	2.5	46.7	2.5	46.7	2.5	45.6	2.5
Low Level Point	13.3	22.9	13.3	22.9	13.3	22.9	12.5	22.9
Area	10.2	50.9	10.2	50.9	10.2	50.9	30.9	50.9
Non-road	49.0	23.4	49.0	23.4	49.0	23.4	46.0	20.8
On-road	31.0	22.3	31.0	22.3	31.0	22.3	25.6	18.2
Biogenic	42.9	42.2	44.5	46.5	45.7	48.6	44.1	45.0
Total	**193.0**	**164.2**	**194.7**	**168.6**	**195.9**	**170.7**	**204.7**	**160.2**
Victoria, tons/day								
Elevated Point	14.6	1.1	14.6	1.1	14.6	1.1	14.5	1.1
Low Level Point	1.3	1.6	1.3	1.6	1.3	1.6	1.2	1.6
Area	2.9	6.7	2.9	6.7	2.9	6.7	2.9	6.7
Non-road	1.9	1.1	1.9	1.1	1.9	1.1	1.6	0.8
On-road	5.8	3.8	5.8	3.8	5.8	3.8	5.0	3.3
Biogenic	10.1	30.8	10.3	31.8	9.9	31.8	9.5	27.5
Total	**36.6**	**45.1**	**36.7**	**46.0**	**36.4**	**46.1**	**34.8**	**40.9**

San Antonio. Table 1 reveals that on–road mobile sources contributed the maximum of about 40% (118 tons/day) of NO_x followed by point source emissions which was about ~25% (74 tons/day) on weekdays and weekend in San Antonio. Biogenic emissions were once again a major source of VOC emissions in this urban airshed with relative contributions above 60% (270 tons/day) of the total VOC. The total VOC emissions exceeded the total NO_x emissions by more than 180 tons on all of the modeling episode days. San Antonio NNA has shown point source as another significant source of emissions compared to Austin NNA. This region has also shown higher NO_x to VOC ratio of 0.63 compared to ratio of 0.38 in Austin NNA region. The difference in ratio was due to lower (of about 110 tons/day) biogenic VOC emissions in San Antonio region.

Corpus Christi. As seen from Table 1, the emission distribution pattern in the Corpus Christi area is very much different when compared to the other urban areas in the study region. For instance, non–road emissions contributed the most followed closely by elevated point sources and biogenic sources for NO_x emissions in the urban airshed. On the whole considering both NO_x and VOC emissions, non–road emissions were noted to be the dominant source category in NO_x emissions and area source was dominant in VOC emissions. Since Corpus Christi is a port area and a coastal tourist destination, the emissions from non–road marine sources contribute significantly towards the total anthropogenic NO_x emissions. Biogenic emissions contributed 22% (43 tons/day) of NO_x and 25% (42 tons/day) of VOC in the area. The total magnitude of biogenic NO_x and VOC emissions are nearly the same on most episode days in this region. The NO_x to VOC ratio in the

region was approximately 1.15 indicating nearly equal contribution of NO_x and VOC emissions.

Victoria. Elevated point sources had a significant contribution to the overall NO_x emissions. About 40% (~15 tons/day) NO_x was due to elevated point sources followed by on–road mobile of about ~16% (~6 tons/day) in anthropogenic emissions. In anthropogenic emissions, area source contributed maximum of 15% (7 tons/day) to VOC emissions. Biogenic emissions contributed 68% (31 tons/day) of the total VOC of the urban airshed. The magnitude of total VOC emissions exceeded NO_x emissions by (6–10) tons over the episode days. The comparable magnitude of total NO_x emissions and total VOC emissions indicate the equal importance of anthropogenic and biogenic emissions in this region.

3.2. Source apportionment analysis

The aim of this analysis was not only to help in identifying the source groups having a maximum impact on the predicted ozone concentrations, but also to help identifying source groups having a minimum impact on ozone concentrations in the NNA domain. This analysis provides an initial step towards developing effective emissions control strategies for a region. The assessment of emissions source categories, source regions, and pollutants on the modeled ozone concentrations at CAMS 03 (Austin), CAMS 23 (San Antonio), CAMS 04 (Corpus Christi), and CAMS 87 (Victoria) within the NNA domain. Furthermore, this analysis also provided useful information on the influence of transport on ozone concentrations on the NNA regions.
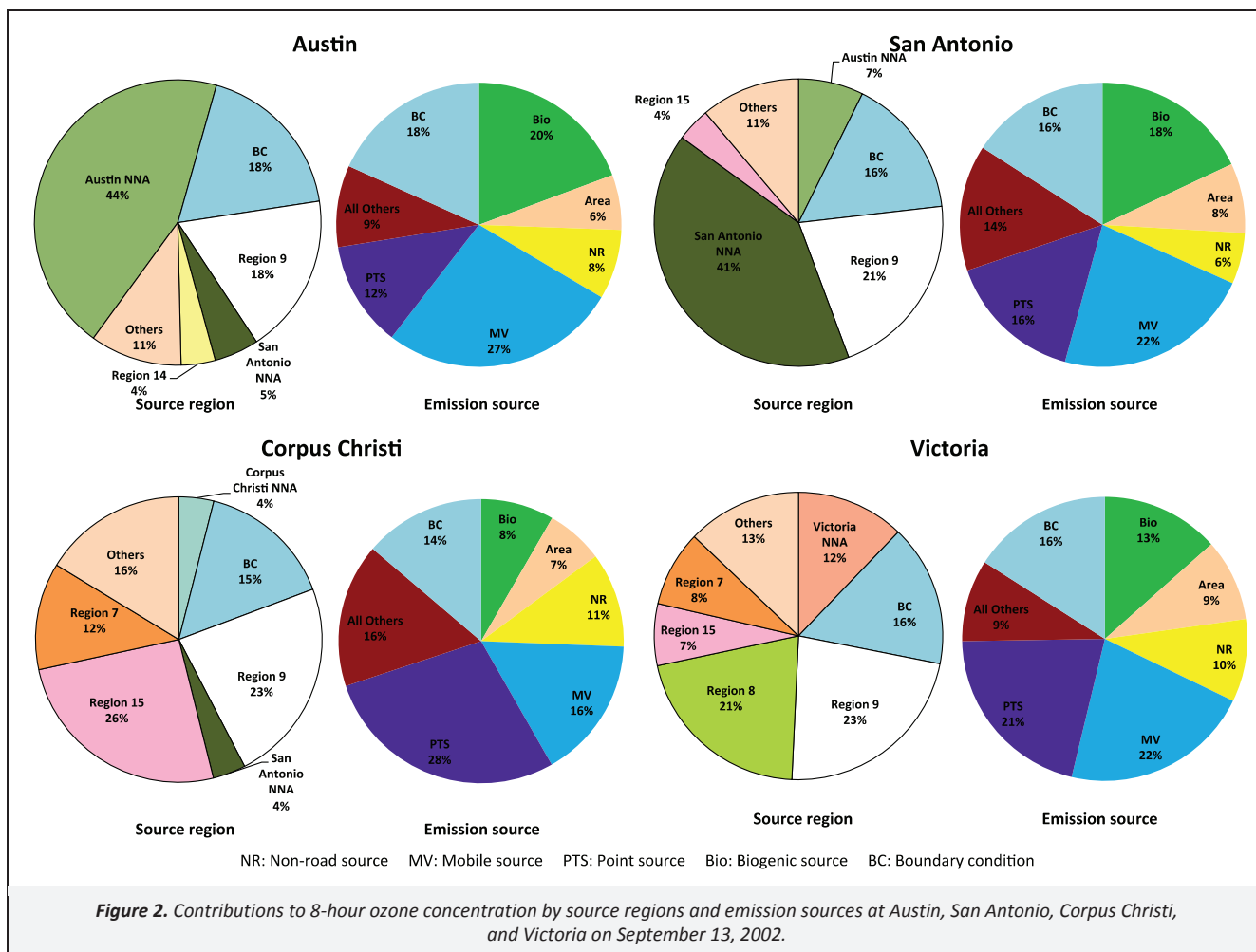
Figure 2. Contributions to 8-hour ozone concentration by source regions and emission sources at Austin, San Antonio, Corpus Christi, and Victoria on September 13, 2002.

Table 2. Contribution from emission groups and precursors to the 8-hour ozone on September 13, 2002

Ozone due to		NOx	VOC	Total	NOx	VOC	Total	NOx	VOC	Total	NOx	VOC	Total
8-h Ozone	Min	46.3	16.3	62.6	51.7	28.0	79.7	63.4	13.7	77.2	63.4	10.4	73.8
	Max	55.7	28.0	83.7	60.7	38.7	99.3	76.7	15.1	91.8	71.3	12.0	83.4
	Mean	51.8	24.3	76.0	56.5	34.6	91.1	71.6	14.7	86.3	67.5	10.9	78.3
Point (ppb)	Min	8.2	0.1	8.3	12.3	0.2	12.5	18.4	0.1	18.4	15.7	0.0	15.8
	Max	10.0	0.1	10.1	15.2	0.2	15.4	25.7	0.1	25.9	19.4	0.1	19.5
	Mean	9.3	0.1	9.4	14.0	0.2	14.2	23.2	0.1	23.3	17.6	0.1	17.6
Mobile (ppb)	Min	15.6	1.6	17.2	16.0	2.3	18.3	10.6	0.3	11.0	13.0	0.2	13.2
	Max	19.1	3.4	22.5	18.8	3.5	22.3	15.1	0.4	15.5	17.5	0.3	17.8
	Mean	17.7	2.8	20.6	17.5	3.1	20.7	13.5	0.3	13.9	15.7	0.2	15.9
Non-road (ppb)	Min	5.0	0.4	5.4	4.4	0.5	4.8	7.4	0.2	7.6	6.9	0.1	6.9
	Max	5.9	0.7	6.6	5.1	0.7	5.8	9.9	0.2	10.1	7.8	0.1	7.9
	Mean	5.5	0.6	6.1	4.8	0.6	5.4	9.0	0.2	9.2	7.4	0.1	7.5
Area (ppb)	Min	3.1	0.8	3.8	4.9	1.5	6.3	3.3	0.3	3.6	5.0	0.2	5.2
	Max	3.8	1.5	5.3	5.7	2.2	7.9	6.1	0.4	6.5	8.1	0.3	8.4
	Mean	3.5	1.3	4.8	5.3	1.9	7.2	5.2	0.3	5.5	6.6	0.2	6.7
Biogenic (ppb)	Min	3.6	5.4	9.1	3.2	10.0	13.2	1.9	1.5	4.3	7.6	1.3	9.0
	Max	6.1	10.6	16.7	4.0	14.0	18.0	6.8	2.6	9.4	9.8	1.5	11.3
	Mean	5.3	8.9	14.3	3.7	12.4	16.1	5.0	2.0	7.0	8.9	1.4	10.3
BC (ppb)	Min	6.0	5.1	11.1	6.7	6.0	12.7	7.0	5.3	12.3	6.4	4.9	11.3
	Max	8.2	7.2	15.4	8.2	7.5	15.8	7.7	5.9	13.5	7.5	5.7	13.2
	Mean	7.4	6.4	13.9	7.7	7.0	14.7	7.3	5.5	12.8	7.0	5.4	12.4
Others (ppb)	Min	2.5	3.0	5.5	2.8	7.6	10.4	4.0	4.6	8.6	3.4	2.9	6.3
	Max	3.2	4.6	7.8	3.8	10.5	14.3	11.9	7.0	18.9	5.1	5.2	10.3
	Mean	2.9	4.0	7.0	3.4	9.4	12.8	8.4	6.1	14.5	4.3	3.6	7.8

(City columns left to right: **Austin**, **San Antonio**, **Corpus Christi**, **Victoria**)

Austin. The analysis identified that local emissions within Austin NNA contributed to a maximum of 39 ppb (44%) to the 8–hour ozone concentration as shown in Figure 2 followed by region 9 (East of San Antonio) and boundary conditions contributed the same amount about 15 ppb (18%) each. Among the anthropogenic emissions, OSAT analysis has shown that on–road mobile and point source contribute to 21 ppb (27%) and 9 ppb (12%) to the 8–hour ozone concentrations as shown in Figure 2. Although, OSAT identified biogenic emissions as one of the major contributors towards ozone, however from an air quality management perspective the biogenic emissions are uncontrollable. Therefore, for effective air quality management it was critical to control the anthropogenic emissions from mobile, point, and non–road sources within Austin airshed. Table 2 presents the hourly minimum, maximum, and mean contribution of NO_x and VOC emissions from emissions groups to the modeled 8–hour ozone concentration greater than 75 ppb. Since the majority of local ozone was mainly formed under NO_x–limited conditions as OSAT analysis has shown 46 to ~56 ppb contribution to 8–hour ozone concentration as shown in Table 2. NO_x emissions from mobile and point sources contribute maximum of 19 and 10 ppb to the 8–hour ozone. Therefore, controlling anthropogenic NO_x emissions from mobile and point emissions sources could be an effective control strategy for reducing ozone concentration in the Austin region.

San Antonio. The results showed a pattern similar to that noted for the Austin NNA. Local emissions contributed to about 40 ppb (41%) of the 8–hour ozone concentrations as shown in Figure 2 followed by region 9 (East of San Antonio) as the second largest region impacting the ozone at CAMS 23. This region contributed about 21 ppb (21%) indicating transported ozone affecting CAMS 23. This analysis also identified mobile, biogenic, and point sources contributing 22 ppb (22%), 18 ppb (18%), and 16 ppb (16%) respectively to 8–hour ozone in the San Antonio urban airshed as shown in Figure 2. Since majority of local ozone is formed under

NO_x–limited conditions with a range between ~52 and ~61 ppb as shown in Table 2 indicated that controlling anthropogenic NO_x emissions from mobile and point emissions source could be an effective control strategy for reducing ozone concentration in San Antonio NNA region.

Corpus Christi. Corpus Christi airshed had been affected by long–range transportation by region 15 (North of Victoria) and region 9 (East of San Antonio) of about 26% and 23% of 8–hour ozone was contributed by these two regions, respectively which are to the North and North–East direction. Besides, influence of long–range transport, the contribution of the local emissions to the 8–hour ozone concentrations in Corpus Christi airshed was about 3.5 ppb (4%) with local emissions as the main contributors as shown in Figure 2. The analysis showed a significant influence of long–range transport of ozone and its precursors and very little from local emissions to the urban ozone concentrations. Therefore, any local emission control strategies alone will not be effective in controlling the urban ozone in this area. The results indicated that the majority of ozone was formed under NO_x–limited conditions with contribution between 63 and 77 ppb as shown in Table 2. Point, mobile, and non–road NOx emissions contributed maximum to the 8–hour ozone concentration with maximum of ~26%, 15%, and ~10% respectively. Therefore, controlling anthropogenic NO_x emissions from local emissions sources from point, mobile, and non–road could be helpful in reducing ozone concentration in the Corpus Christi region.

Victoria. The primary source of NO_x emissions were elevated point sources. The elevated point sources contributed about 40% of the total NO_x emissions in this area. The main source of VOC emissions was biogenic emissions with 68% of the total VOC emissions. The OSAT analysis at CAMS 87 showed that about total of 35.8 ppb (44%) of the total 8–hour average ozone concentration was transported into the urban area from region 8 (East of Victoria)

and 9 (East of San Antonio). The local emissions contributed to about 10 ppb (12%) toward the 8–hour average ozone concentration. Locally, between 63 and 71 ppb of ozone was formed under NO_x–limited conditions as shown in Table 2. Therefore, controlling anthropogenic NO_x emissions from point and mobile emissions source could be an effective control strategy for reducing ozone concentration in Victoria region.

3.3. Efficacy of emissions reductions

Ozone exhibits a complex dependence on its precursors NO_x and VOC with ozone formation being sometimes associated with NO_x sensitive chemistry and at other times with VOC sensitive chemistry (Sillman, 1999), and these NO_x or VOC sensitive regimes determine the response of the photochemical modeling systems to various emission control strategies. Since photochemical models are traditionally used in a regulatory setting, it is imperative to evaluate the variability in the response to differing ozone precursor control strategies. It has been established that elevated ozone levels in urban and rural areas were decreased by applying an appropriate set of NO_x controls along with VOC controls (Kumar and Russell, 1996).

The index of improvement for the anthropogenic *n50v25* and *n25v50* control runs was computed relative to the base run *n00v00* over the entire 4 km NNA sub–domain. The results indicate a greater ozone benefit from NO_x emission reductions than from VOC emission reductions over the entire modeling domain as shown in Figure 3. As shown in Figure 3a, the *n50v25* scenario shows a decrease in the 8–hour ozone peak by 12% and 14% in San Antonio and Austin urban areas, respectively. Victoria observed a smallest reduction ranging from 2–3% in the peak 8–hour ozone concentrations in a small pocket while rest of the urban area showed a negative impact. Corpus Christi showed the reductions in ozone concentrations ranging from 1–4.5% within the urban airshed. However, the urban cores of San Antonio and Corpus Christi did not show a decrease in the 8–hour ozone concentrations, indicating ineffectiveness of NO_x reductions in the area. Similar patterns were noted for small areas southeast from the Austin urban core. A 50% reduction in VOC emissions resulted in a decrease in the 8–hour ozone concentration ranging from 2–6% for San Antonio, 3–7.5% in Austin areas and 1–3% for Corpus Christi and Victoria areas as shown in Figure 3b. Corpus Christi exhibited a comparable ozone benefit from both NO_x and VOC emission reductions, while Austin and San Antonio clearly displayed a greater ozone benefit from NO_x emission reductions alone, and Victoria was more sensitive to VOC reduction overall except for a small region impacted by a NO_x–rich plume downwind of a major coal–fired power plant. The San Antonio urban core also showed a negative impact of 50% VOC reductions similar to 50% NO_x reduction, demonstrating that these areas require both NO_x and VOC control strategies for better air quality management.

3.4. Spatial impact assessment

The potential control strategies for a region can be resolved only after the influence from various emission source categories can be ascertained. This can be accomplished by zeroing out the emissions from different source categories and determining the net reduction in the ozone concentrations. This study consisted of a number of emission sensitivity runs performed by zeroing out emissions from area, elevated point, on–road mobile, non–road, anthropogenic, and biogenic emissions for the four NNA regions. The influence of a particular emissions–reduction run in a region can be gauged by analyzing the reduction in the peak 8–hour ozone concentration during the episode. The positive differences reveal ozone benefit and negative differences show ozone dis-benefit as a result of the reduction of emissions from each of the specific emissions source category. The results for each of the urban area are shown below:

Austin. Spatial impacts of anthropogenic and biogenic sources of emissions for Austin are shown in Figure 4. Within Austin, on–road mobile source emissions have the greatest impact, 26 ppb of peak 8–hour ozone levels followed by point sources affecting peak ozone reductions of up to 6 ppb. Area and non–road sources have relatively lesser impact of 4 ppb each on the 8–hour peak ozone concentrations. Impact of area sources in all near non–attainment areas was up to 2 ppb. With regard to the anthropogenic emissions in Austin, it was noted that on–road mobile sources were the major contributors of NO_x emissions followed by point sources. Removal of all biogenic emissions resulted in a net decrease of 16 ppb in the peak 8–hour ozone concentrations, suggesting a significant influence of this category. As noted earlier, Austin is a NO_x sensitive region than a VOC–sensitive region. Anthropogenic emissions in Austin are dictated by NO_x emissions and consequently the removal of NO_x emissions resulted in a greater decrease of 33 ppb from the peak ozone levels.

San Antonio. This urban area was strongly influenced by on–road mobile source emissions as shown in Figure 4a. Zero–out on–road mobile runs showed a reduction of 24 ppb in the 8–hour ozone maxima. Zeroing out point and non–road emission sources resulted in the reduction of peak ozone concentrations by 8 ppb and 3 ppb, respectively. San Antonio was not significantly impacted by area sources. Overall elimination of total anthropogenic emissions would result in a net decrease of 39 ppb of peak 8–hour value. Biogenic emissions contributed up to 12 ppb of the 8–hour ozone episode maxima and this reveals that biogenic VOC also plays a crucial role in the observed ozone levels in San Antonio.

Corpus Christi. This urban area was most affected by non–road mobile emissions followed by point source emissions as shown in Figure 4b. The removal of non–road mobile and point source emissions caused a decrease of 3–6 ppb of peak 8–hour ozone concentrations, respectively. The other emission sources such as on–road mobile and area resulted in a smaller impact of up to 2 ppb reduction in the maximum 8–hour ozone concentrations, respectively. Overall, the anthropogenic emissions influenced around 9 ppb of the peak 8–hour ozone levels. From the emissions distribution in the urban airshed, it was noted that non–road source categories were significant contributors to both NO_x and VOC emissions and subsequently had a stronger impact on the predicted peak ozone concentrations. Since the levels of biogenic emissions were smaller, they had negligible impact on the maximum 8–hour ozone levels.
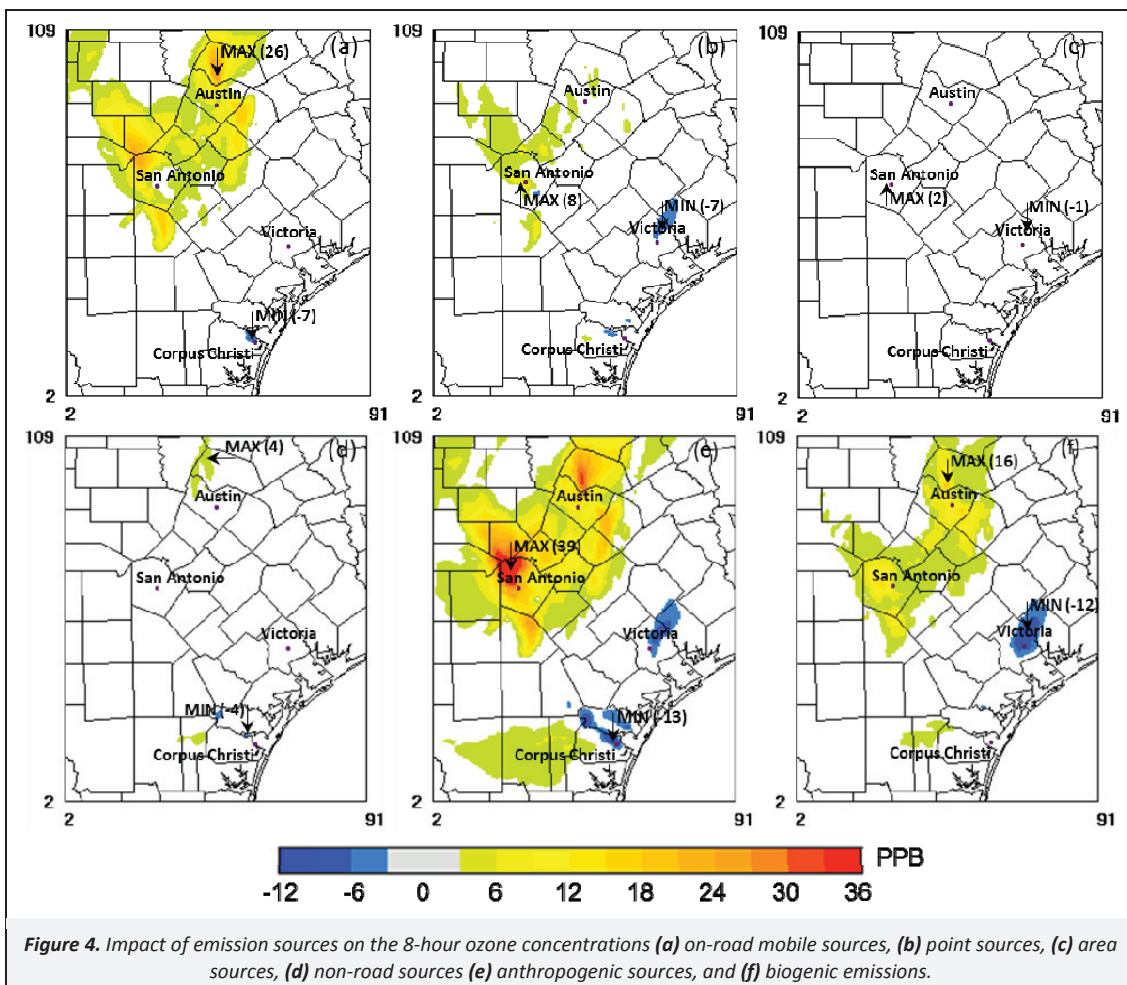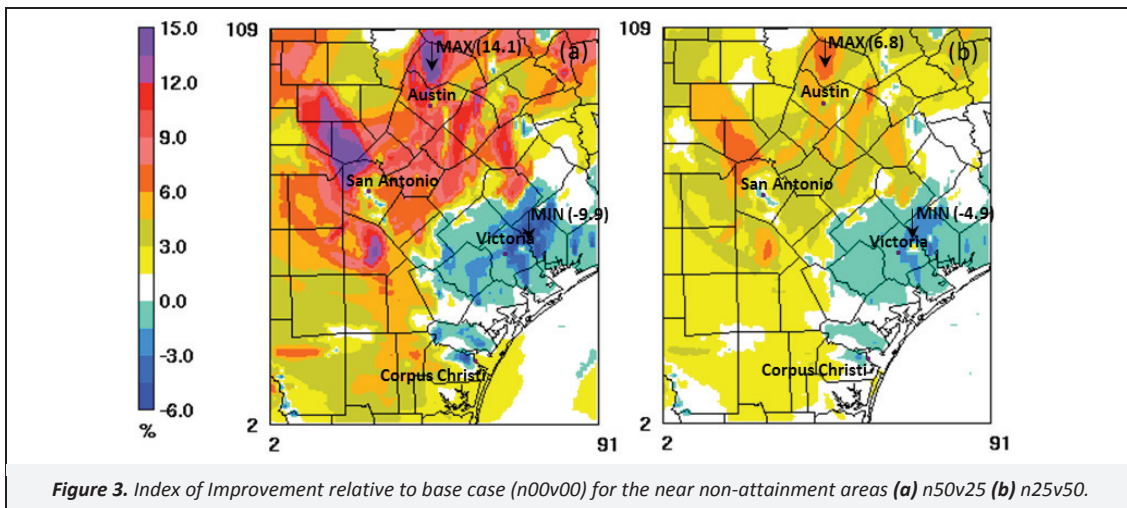
Victoria. This urban area was predominantly impacted by elevated point source emissions and the elimination of which resulted in an overall reduction of less than 3 ppb in the peak 8–hour ozone levels as shown in Figure 4b. The negative impact indicated the titration of ozone due to NO_x emissions from elevated point sources. Area and non–road sources impacted less than 1 ppb each in the predicted 8–hour ozone concentrations. On–road mobile emissions showed an impact of less than 3 ppb to the 8–hour ozone levels in the urban area. Overall, the anthropogenic emissions impacted less than 3 ppb on the peak 8–hour ozone concentrations. Biogenic emissions were a significant component of the urban VOC emissions and it was also the second highest contributor of urban NO_x emissions. These emissions impacted up to 12 ppb in the southern portion of the Victoria. Both anthropogenic and biogenic emissions equally affect the region but an effective control of elevated sources of point emissions will benefit Victoria in reducing the 8–hour ozone concentrations.

3.5. Ozone sensitivity coefficients

The sensitivity of ozone formation was determined by implementing the Decoupled Direct Method (DDM) technique. In this analysis, the sensitivity of ozone to anthropogenic emissions from four source categories was determined. First order ozone sensitivity coefficients due to NO_x and VOC emissions from four

source categories are shown in Figure 5. The DDM analysis has shown higher ozone sensitivity coefficients to NO_x emissions than VOC emissions. On–road mobile sources have the highest sensitivity coefficient of 4–23 ppb from NO_x emissions in the Austin and San Antonio regions, about up to 6 ppb in Victoria and Corpus Christi area as shown in Figure 5. However, San Antonio urban area showed a negative coefficient of up to 8 ppb, and in Corpus Christi urban area of up less than ppb. This indicates that the urban core of San Antonio and Corpus Christi are not sensitive to on–road NO_x emissions. Ozone sensitivity coefficients analysis of point source emissions shows predominantly more NO_x sensitivity coefficients in all NNAs. Contrary to this, within the urban core of San Antonio the

VOC sensitive coefficient for on–road emissions showed an impact of up to 8 ppb as shown in Figure 5. Higher ozone sensitivity due to on–road NO_x and VOC emissions indicated combined NO_x and VOC emissions control strategies will be a more effective strategy for air quality management in these areas. Ozone sensitivity coefficients analysis of point source emissions shows predominantly more NO_x sensitivity coefficients in all NNAs. Area and non–road mobile has shown maximum NO_x sensitive coefficient of up to 4 ppb, while in Corpus Christi NNA one small patch of negative region has been observed. VOC emissions from non–road sources showed a maximum sensitivity of 2 ppb.
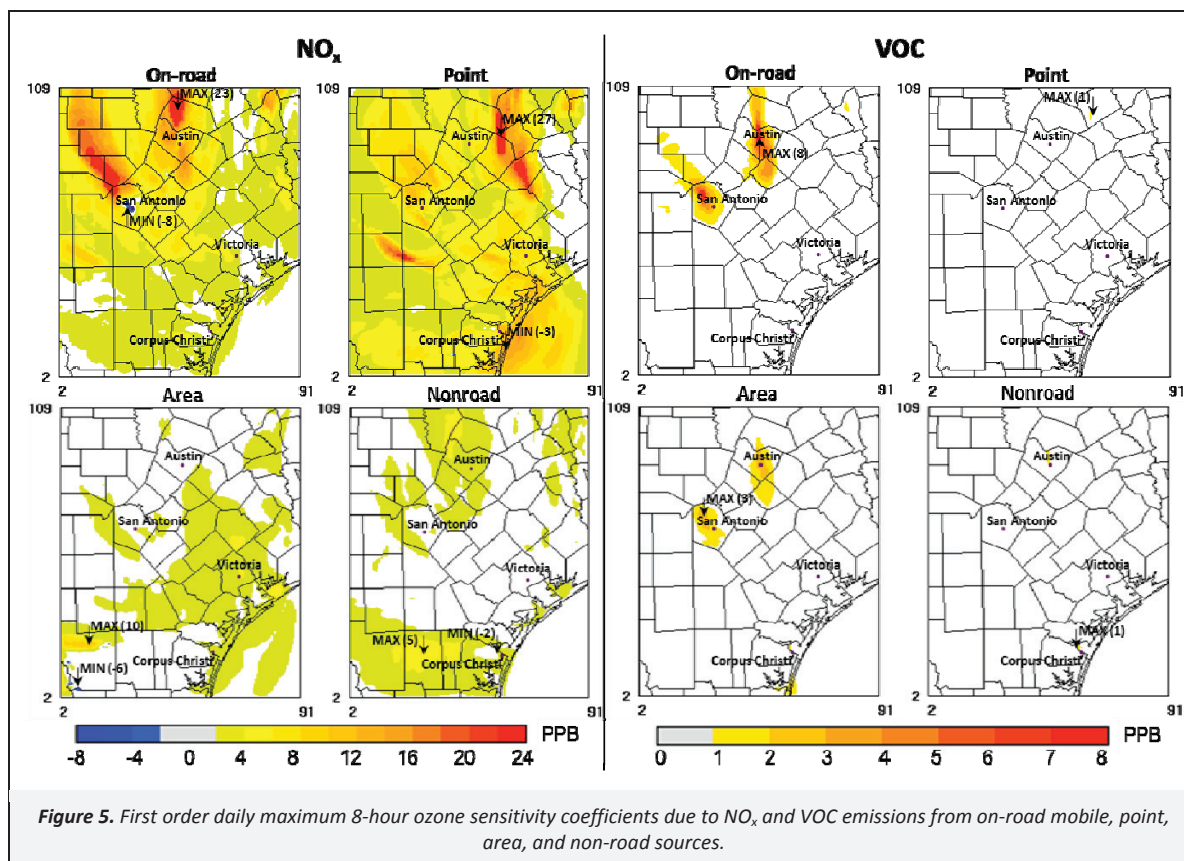

Figure 3. *Index of Improvement relative to base case (n00v00) for the near non-attainment areas (a) n50v25 (b) n25v50.*

Figure 4. *Impact of emission sources on the 8-hour ozone concentrations (a) on-road mobile sources, (b) point sources, (c) area sources, (d) non-road sources (e) anthropogenic sources, and (f) biogenic emissions.*

Figure 5. First order daily maximum 8-hour ozone sensitivity coefficients due to NOₓ and VOC emissions from on-road mobile, point, area, and non-road sources.

Overall, the DDM analysis indicated that in order to develop effective emission control strategies for San Antonio and Corpus Christi both NOₓ and VOC controls should be implemented. For the Victoria region, NOₓ control strategies for point and mobile sources will benefit the urban area. For the Austin, control of NOₓ emissions from mobile and point source will benefit the region. Thus, the ozone sensitivity analysis using the DDM technique reinforces the findings from the efficacy of emission reduction analysis conducted in the previous section.

4. Conclusions

A photochemical modeling framework using CAMx for the high ozone episode of September 8–16, 2002 was developed for the four NNA regions in south and central Texas. The photochemical model performance was evaluated as per EPA's recommended statistical methods and the models performed within the limits set by EPA. An assortment of ozone sensitivity runs was undertaken for varying emissions reductions over the urban regions in south and central Texas using the designed high ozone episode. The four techniques (index of improvement, zero–out emissions reduction model simulations, OSAT, and DDM) applied in this study for appraisal of potential emission control runs presented a consistent representation of efficiency of emission reductions over the four near non–attainment regions of south and central Texas. The methodology presented herein can be applied effectively in case of other ozone modeling studies as well. The results conclusively indicated that emission distribution patterns strongly influenced the choice of effective emission controls. A majority of these urban areas revealed a greater ozone benefit from NOₓ reductions than from VOC reductions. Only the urban cores areas in San Antonio and Corpus Christi demonstrated a higher sensitivity towards VOC emissions, suggesting thereby that the implementation of a combined NOₓ and VOC control strategy will benefit these areas. There was considerable variability in the impact of different emission source categories with their resulting impacts on peak 8–hour ozone levels. The ozone

concentrations in San Antonio and Austin were influenced mostly by emissions from on–road vehicles. The peak ozone concentrations over Corpus Christi were mostly affected by long–range transport from the Northern and Northeastern regions of Houston and local non–road emissions. Victoria was significantly impacted by elevated point source emissions. The DDM ozone sensitivity studies corroborated the findings presented earlier that most of the regions were NOₓ–limited with specific pockets of urbanized areas in San Antonio and Corpus Christi more sensitive to VOC emissions. The results prove that a regional NOₓ control strategy coupled with source specific VOC strategies will be beneficial for these urban areas. Therefore effective air quality management will require judicious combination of NOₓ and VOC control strategies with NOₓ emissions reductions on regional scale and VOC emissions reductions on a local scale over specific urban areas of San Antonio and Corpus Christi.

Despite the uncertainties inherent with emission reduction approaches, the results presented here depict an initial preliminary guidance of the type of emission reductions needed in the urban areas of south and central Texas. These investigations clearly reveal that policy makers need to develop an effective blueprint to mitigate ozone concentrations over local and regional levels to sustain the air quality under the present and any future ozone standards. These strategies need to be reexamined under tighter standard setting processes which if and when implemented will bring these regions into the non–attainment category.

Acknowledgement

Supporting Material Available

Figure S1 shows MM5 modeling domain described in the manuscript and Figure S2 shows time–series of observed as well as model predicted continuous running 8 hours average values of 1–hour ozone concentrations at four sites in the study area. Table S1 shows vertical grid structure of MM5 meteorological model and CAMx photochemical model. MM5 model has total 28 vertical layers while CAMx has 12 layers related to MM5 layers. It also shows height, thickness, pressure levels of MM5 and CAMx models. Tables S2 and S3 show statistical model performance evaluation (with set limits) of MM5 and CAMx model for September 11–14, 2002. This information is available free of charge via the Internet at http://www.atmospolres.com.

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