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Modeling the uncertainty of several VOC and its impact on simulated VOC and ozone in Houston, Texas

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HIGHLIGHTS

- Estimating the uncertainty of VOC in Houston.
- Adjusting the VOC emissions using in-situ data.
- Investigating the impact of adjusted VOC on ozone.
- Validating the adjusted VOC emission using remote sensing.
- Finding the peaked ozone in the outflow region.

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ABSTRACT

A WRF-SMOKE-CMAQ modeling system was used to study Volatile Organic Compound (VOC) emissions and their impact on surface VOC and ozone concentrations in southeast Texas during September 2013. The model was evaluated against the ground-level Automated Gas Chromatograph (Auto-GC) measurement data from the Texas Commission on Environmental Quality (TCEQ). The comparisons indicated that the model over-predicted benzene, ethylene, toluene and xylene, while under-predicting isoprene and ethane. The mean biases between simulated and observed values of each VOC species showed clear daytime, nighttime, weekday and weekend variations. Adjusting the VOC emissions using simulated/observed ratios improved model performance of each VOC species, especially mitigating the mean bias substantially. Simulated monthly mean ozone showed a minor change: a 0.4 ppb or 1.2% increase; while a change of more than 5 ppb was seen in hourly ozone data on high ozone days, this change moved model predictions closer to observations. The CMAQ model run with the adjusted emissions better reproduced the variability in the National Aeronautics and Space Administration (NASA)'s Ozone Monitoring Instrument (OMI) formaldehyde (HCHO) columns. The adjusted model scenario also slightly better reproduced the aircraft HCHO concentrations from NASA's DISCOVER-AQ campaign conducted during the simulation episode period; Correlation, Mean Bias and RMSE improved from 0.34, 1.38 ppb and 2.15 ppb to 0.38, 1.33 ppb and 2.08 ppb respectively. A process analysis conducted for both industrial/urban and rural areas suggested that chemistry was the main process contributing to ozone production in both areas, while the impact of chemistry was smaller in rural areas than in industrial and urban areas. For both areas, the positive chemistry contribution increased in the sensitivity simulation largely due to the increase in emissions. Nudging VOC emissions to match the observed concentrations shifted the ozone hotspots outside the industrial/urban region and enhanced the peaked ozone in the outflow region with consistent southerly/southeasterly winds during the afternoon time (1–5 pm). This study helps in the understanding of these processes which are critical to constrain high peak ozone values in the outflow regions. The results indicate that formation of ozone in the outflow could complicate attainment status in neighboring counties.

1. Introduction

Volatile Organic Compounds (VOCs) can be a significant contributor to the criteria pollutant ground-level ozone in urban

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areas, where ozone concentrations are typically VOC-sensitive (e.g., Choi et al., 2012; Choi, 2014; Choi and Souri, 2015a, 2015b). Examples of VOCs include aromatics such as toluene and unsaturated hydrocarbons such as ethylene which have high ozone forming potential (Carter, 1994). Additionally, VOCs in urban regions often comprise of several air toxic species such as benzene and toluene which have a high potential to cause cancer. Ryerson et al. (2003) mentioned that the emissions of light molecular weight alkenes such as ethylene, propylene, 1,3-butadiene, and butenes are important to explain rapid ozone formation in the Houston area through the Texas Air Quality Study (TexAQS) 2000 aircraft campaign measurements. Vizuete et al. (2008) simulated a series of high industrial point source emissions for the VOC species, n-pentane, ethylene, propene and o-xylene by using the CAMx model and concluded that ozone concentrations showed the highest sensitivity to o-xylene.

The concentrations of the VOC species usually show significant temporal and spatial variations; hence the uncertainty of VOC emissions is one of the major contributions to simulated ozone bias in chemical transport models. Byun et al. (2007) showed ethylene concentrations exhibited significant variability over high ozone episode days as well as pronounced diurnal cycles. The authors indicated that these phenomena were representative of the dilution due to the increased mixing and chemistry. Nam et al. (2006) simulated a series of short-term (1–2-h) release of Highly Reactive Volatile Organic Compounds (HRVOCs) from industrial point sources and indicated that 11 out of 793 emission events produced more than 10 ppb of additional ozone and that 4 out of 793 events produced more than 70 ppb of additional ozone in the industrial area. Model simulations by Webster et al. (2007) using CAMx indicated that the changes in the industrial point source emissions had the potential to cause changes of 10–52 ppb (13–316%) or more in simulated ozone concentrations. Couzo et al. (2012, 2013) analyzed the long term (2000–2009 and 2000–2011, respectively) ground-level ozone measurements and found that in Houston, most non-typical ozone changes were measured at monitors near the ship channel, especially when monitors were downwind of petrochemical facilities.

The Houston metropolitan area is characterized by high population density and a large cluster of petrochemical industries. It is the fourth-largest metropolitan area in the United States (US Census Bureau, 2012) and is classified as a nonattainment area for ozone (U.S. EPA's Green Book, 2015). The presence of anthropogenic sources (Czader et al., 2008; Czader and Rappenglück, 2015) such as the petrochemical industry and transportation and biogenic sources (Li et al., 2007) such as vegetation makes the pollutant mix in this area unique in the region. Therefore it is important to understand and quantify the VOC emissions in this region so as to develop appropriate control policies for better air quality and correspondingly attainment status and human health. The modeling study by Kim et al. (2011) indicated that the uncertainties of VOC emissions in the industrial regions affected the surface ozone over Houston during the TexAQS 2006 aircraft campaign. Choi et al. (2012), Choi (2014) and Choi and Souri (2015b) indicated that the urban area of Houston is represented as an extreme NO_x-saturated or VOC-sensitive area in the model; one of the reasons for this is the uncertainties of the ozone precursors' emissions in the EPA National Emission Inventory of 2005 or 2011. These studies showed that the high ozone areas in the outflow regions were also influenced by the chemical characteristics of the urban core or industrial regions, where the concentrated ozone precursors may transport to rural areas under proper meteorology. Thus, understanding the chemical conditions of urban or industrial areas and outside of the urban cores in Houston is critical to constrain high ozone values both in source and outflow regions.

This study used a WRF-SMOKE-CMAQ modeling system to simulate VOC and surface ozone concentrations in southeast Texas for the month of September 2013, during which the NASA DISCOVER-AQ campaign took place in Houston providing an abundance of measurements which can be utilized for model evaluations. Rather than concentrating on the impact on ozone in the industrial area due to the uncertainty of the point source of the VOC emissions (Nam et al., 2006; Webster et al., 2007; Olaguer et al., 2009; Vizuete et al., 2008, 2011), this study focused on the impact on ozone both in the Houston industrial and its outflow regions by the uncertainties of the VOC emissions. The ambient concentrations of various VOCs from the routine surface measurement sites were used, and the model/measurement VOC concentration ratios were used to adjust the VOC emissions. In particular, in this study, the adjusted VOC emissions were indirectly evaluated by comparing model simulated formaldehyde (a proxy for ozone precursor, VOCs) with the NASA's OMI measurements (e.g., Shim et al., 2005; Choi et al., 2010, 2012; Choi, 2014; Duncan et al., 2014; Choi and Souri, 2015b). In TexAQS 2000 studies, TCEQ made its 'imputed' emissions by selectively increasing emissions of HRVOC, such as ethylene and propylene, from the regular Texas Emission Inventory (TEI) industrial point sources inside the Houston-Galveston-Brazoria eight counties with the assumption that point sources released the imputed alkene species into the atmosphere (Byun et al., 2007). The purpose of the adjustment of the VOC emissions in this study was to tune VOC concentrations in the model similar to the corresponding observed data and see how the adjustment of VOC emissions impacted the surface VOC and ozone concentrations both in the industrial areas and their outflow regions.

2. Methodology

Simulations were performed with the Community Multi-scale Air Quality (CMAQ) model (Byun and Schere, 2006) version 5.0.1 released by the U.S. Environmental Protection Agency (EPA). The model set-up follows Czader et al. (2015). The current analysis is based on the simulations performed with a 4 km grid for the domain covering southeast Texas, with 84 grid cells in the east-west direction, 66 in the north-south direction, and 27 vertical layers from surface to 100 hPa. Boundary conditions are obtained from the real-time Air Quality Forecasting system at University of Houston (AQF-UH) (http://spock.geosc.uh.edu/) employing a larger 12 km grid covering the United States, southern Canada and northern Mexico. Initial conditions are based on the 4 km AQF-UH predictions from nested southeast domain. Chemistry is simulated with the Carbon Bond 5 (CB-05) chemical mechanism (Yarwood et al., 2005). Emissions were modeled using the Sparse Matrix Operator Kernel Emissions (SMOKE) system (Houyoux et al., 2000) using the US EPA's 2008 National Emission Inventory (henceforth called NEI-2008). Meteorology was simulated with the Weather Research and Forecasting (WRF) model version 3.5 (Skamarock and Klemp, 2008). For this study, the inputs for WRF are National Centers for Environmental Prediction (NCEP) North American Regional Reanalysis (NARR) data provided by the NOAA/OAR/ESRL PSD (Mesinger et al., 2004). Conversion of the WRF output to CMAQ inputs are performed with the Meteorology–Chemistry Interface Processor (MCIP) (Byun and Schere, 2006).

Simulations were performed for the month of September 2013. The weather during the month was relatively dry with mostly southerly, easterly or southeasterly winds. From 09/05 to 09/19, there was lack of influence of strong synoptic weather systems. The wind pattern was light northeasterly in the early morning; gradually turning clockwise to southeasterly in the afternoon and evening hours. A cold front passed through in late of 09/20. Rain events