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Impacts of flare emissions from an ethylene plant shutdown to regional air quality

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HIGHLIGHTS

- Dynamic plant shutdown emissions are provided for accurate air-quality modeling.
- Multi-scale modeling quantitatively studies O_3 impacts from CPI operations.
- O_3 impacts from plant shutdown emissions vary by spatial and temporal factors.
- Cost-effective emission and air-quality controls have been identified.

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ABSTRACT

Critical operations of chemical process industry (CPI) plants such as ethylene plant shutdowns could emit a huge amount of VOCs and NOx, which may result in localized and transient ozone pollution events. In this paper, a general methodology for studying dynamic ozone impacts associated with flare emissions from ethylene plant shutdowns has been developed. This multi-scale simulation study integrates process knowledge of plant shutdown emissions in terms of flow rate and speciation together with regional air-quality modeling to quantitatively investigate the sensitivity of ground-level ozone change due to an ethylene plant shutdown. The study shows the maximum hourly ozone increments can vary significantly by different plant locations and temporal factors including background ozone data and solar radiation intensity. It helps provide a cost-effective air-quality control strategy for industries by choosing the optimal starting time of plant shutdown operations in terms of minimizing the induced ozone impact (reduced from 34.1 ppb to 1.2 ppb in the performed case studies). This study provides valuable technical supports for both CPI and environmental policy makers on cost-effective air-quality controls in the future.

1. Introduction

Industrial regions with high concentrations of chemical process industry (CPI) plants sometimes experience highly localized and transient air pollution events, such as elevated ozone concentrations that violate the National Ambient Air Quality Standards (NAAQS) (U.S. EPA, 2015a). The identified major emission sources associated with such high ozone events include nitrogen oxides (NO_X), volatile organic compounds (VOCs), and highly reactive volatile organic compounds (HRVOCs). HRVOC defined in Texas air quality regulation includes ethylene, propylene, isomers of butene and 1, 3-butadiene (TCEQ, 2015a). The 2000 Texas Air Quality Study (Kleinman et al., 2003; Ryerson et al., 2003) collected observational data for studying the formation of ozone. It indicates that rapid and efficient ozone formation is associated almost exclusively with abundant HRVOCs from petrochemical facilities.

According to Texas Administrative Code (TAC) Title 30, Chapter 115, subchapter H, industrial flaring has been identified as the largest source for producing HRVOCs (TAC, 2002). In June 2007, ENVIRON (2009) representing TCEQ conducted a special emissions inventory, requesting HRVOC emissions data from those sources in Houston, Texas, that are subject to HRVOC emissions cap-and-trade (HECT) program requirements. The reporting period for this special inventory was February 1, 2006, through January 31, 2007. The results show that flaring accounts for approximately 61% of the total industrial HRVOC emissions of Houston-Galveston-Brazoria

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(HGB) area. Olefins manufacturing reported the biggest amount of HRVOC emissions from maintenance, startup, shutdown and events among five investigated industry sectors including chemical manufacturing (non-olefin, non-polymer), olefins (ethylene) manufacturing, polymer manufacturing, petroleum refining, and independent storage terminals.

The shutdown operation of ethylene plants is considered as one of the most intensive industrial emission events, which could generate dozens or even hundreds of tons of emissions per hour. The U.S. Clean Air Act lists six common air pollutants, among which at least three (ozone, carbon monoxide, and nitrogen oxides) are related to ethylene plant shutdown flaring emissions (U.S. EPA, 2015b). Therefore, the study of air-quality impacts from plant shutdown emissions is essential for both environmental regulators and CPI plants.

Previous studies have reported the great air-quality impacts from industrial emission events. According to Texas Administrative Code (TAC) Title 30, Chapter 101, subchapter F, the emission regulated entity must report their emissions event information to Texas Commission on Environmental Quality (TCEQ). Based on the data extracted from TCEQ air emissions event reports, Murphy and Allen (2005) analyzed the emission magnitude and frequency of those emission events and showed that ozone concentrations detected at monitor can be increased by as much as 100 ppb for large HRVOC emission events.

Hitherto, most air-quality modeling works for industrial emission events assume that the emissions were emitted at a constant, average flow rate. They cannot well explain localized and transient air-pollution events. Nam et al. (2006) conducted the study using a sub-domain air-quality model, and suggested that 1.5% of emission events would produce an additional 10 ppb of ozone, and 0.5% of events would produce more than 70 ppb of additional ozone. TCEQ (2004) examined the air-quality impacts of various emission events through air-quality modeling. Due to the lack of dynamic emission data, averaged emission profiles were utilized for investigating the impacts of the emission events such as startup. The result suggested that there were no significant changes in ozone generation from those emission events. Unfortunately, due to the absence of process operating information and real-time dynamic monitoring data, the above-mentioned studies cannot address detailed industrial emission inventory (EI) in terms of flaring speciation and quantification for emission events; and thus the air-quality impact for a specified emission event is difficult to get the accurate prediction.

Pavlovic et al. (2012) analyzed flare emissions based on the 2006 special inventory data from TCEQ. Stochastic models of the flare emissions were developed to generate hourly emissions inventories for flares. This approach provides some information for flare emissions inventories when hourly data is not available. However, the study is not suitable for evaluating plant shutdown emissions because shutdown flare emissions are strongly related to process equipment, plant capacities, and operating procedures.

Plant-wide dynamic simulations (Dinh et al., 2014; Fu and Xu, 2013; Liu and Xu, 2010; Wang et al., 2014; Wei et al., 2014; Xu et al., 2009a, 2009b; Yang et al., 2009) have been demonstrated to be a powerful tool for developing flare minimization strategies and characterizing flare emission sources (FES). Specifically, Liu and Xu (2010) utilized plant-wide dynamic simulation to obtain dynamic emission source profiles including chemical species and quantity for proactive flare minimization during ethylene plant start-ups. Wang et al. (2014) employed dynamic model to simulate an ethylene plant shutdown and characterized its flare emission sources. Such plant-wide dynamic simulation results actually provide valuable dynamic emission information to enrich emission inventories that can be used for accurate air-quality modeling. The approach using dynamic simulations to calculate flare emissions fully considers root causes from process facilities and operation procedures for various emission events. It is an important technical support for CPI plants to evaluate different flare minimization strategies. It can also help update industrial flare EIs to study associated air-quality impacts.

The air-quality study in this paper focuses on tropospheric ozone, which is mainly formed when ozone precursors such as NO_X and VOCs/HRVOCs react in the atmospheric environment at the presence of sunlight. When people experience long-time exposure to a high-ozone concentration environment, it will have irreparable consequences for people's health, such as irritation of the respiratory system, aggravation of asthma, and lung function reduction. Thus, U.S. Environmental Protection Agency (EPA) has issued a stringent standard of 70 ppb for 8-h average ozone concentration on the ground level (U.S. EPA, 2015c), and requires ozone non-attainment states to develop their state implementation plan (SIP) to demonstrate their control policy effectiveness to attain and maintain the 8-h standard by the prescribed attainment date. Obviously, industrial flare emission control is an important part of SIP. To demonstrate the effectiveness of SIP, extensive air-quality modeling and simulations have to be conducted.

Regional air-quality impacts associated with industrial flare emissions can be studied by a computational tool named Comprehensive Air Quality Models with Extensions (CAMx). CAMx (ENVIRON, 2008) is an Eulerian photochemical dispersion model based on well-established treatments of advection, diffusion, deposition, and chemistry. CAMx is approved by U.S. EPA and has been used to demonstrate attainment of the federal standards for ozone by some states like Texas. For evaluating air-quality control plans for southeast Texas, TCEQ has conducted meteorological and photochemical modeling to support development of the SIP in the ozone nonattainment area. The SIP revision includes the base case modeling of representative ozone exceedance episodes that occurred during 2005 and 2006. The model used in the revised SIP was a nested regional-to-urban scale with grid resolutions of 36×36 km, 12×12 km, 4×4 km, and 2×2 km shown in Fig. 1. The outputs from Emissions Processing System Version 3 (EPS3), Global Biosphere Emissions and Interactions System (GloBEIS), and the fifth generation Meteorological Model (MM5) serve as the CAMx inputs for emission rates and meteorological parameters, respectively. Additional CAMx inputs include initial and boundary conditions, spatially resolved surface characteristic parameters, spatially resolved opacity, and photolysis rates. Detailed documentation concerning the generation of EIs, and meteorological inputs for the SIP model can be found at the TCEQ website (TCEQ, 2013).

In order for the photochemical model to properly simulate pollutant formation in the attainment demonstration, it is important that the meteorological conditions are realistically modeled and the quality of episode-specific emissions is ensured. The meteorological model generates the prediction for wind flow, temperature, humidity, vertical air mixing, and other parameters in time and space (TCEQ, 2015b). During the modeling and simulation, predicted parameters are blended with observations through a process called Four-Dimensional Data Assimilation (FDDA) or nudging. The emission inventory data including point emissions, mobile emissions, area emissions and biogenic emissions are collected and processed for photochemical modeling. To demonstrate that the photochemical model is capable of replicating historical episodes for which high daily 8-hr ozone was measured, operational (e.g., statistical and graphical evaluations) and diagnostic (e.g., sensitivity and diagnostic evaluations) are recommended in the EPA guidance (U.S. EPA, 2007) for evaluating the model performance.