Air-quality Conscious Coordination for Multiple Olefin Plant Startup and Shutdown Operations

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Abstract

The ground-level ozone is a pervasive air pollutant, which can be potentially elevated by flaring emissions during chemical plant turnaround operations (i.e., startup and shutdown). Especially in chemical plant concentrated regions, the regional air-quality (i.e., the ozone concentration) may be aggravated by simultaneous turnaround emissions from multiple chemical plants. Thus, under viable manufacturing permissions it is environmentally and cost-effectively important for coordinating multi-plant turnaround operations to minimize the adverse air-quality impact. In this paper, a systematic methodology on air-quality conscious coordination for multi-plant turnaround operations has been developed. Through case studies, it demonstrates that multi-plant turnaround without any coordination could cause the worst air-quality impact (i.e., 11.4 ppb of maximum 8 h ozone increment); however, the optimal coordination plan with several-hour difference tuning on their turnaround starting time would significantly reduce such impact (only 1.4 ppb of maximum 8 h ozone increment). The study couples process dynamic simulation for flare emissions with regional air-quality modeling together; and explores cost-effective and environmentally benign air-quality control strategies. It may provide valuable quantitative supports for relevant stakeholders, including environmental agencies, regional plants, and local communities.

Keywords

Olefin Plant startup and shutdown; Coordination; Air quality; Ozone pollution; Multi-scale modeling

Introduction

Ozone is predominantly produced from the photochemical reactions of NO_x and volatile organic compounds (VOCs) in the presence of sunlight rather than being emitted directly. The ground-level ozone is detrimental to people's health and many other organisms (Schlink et al., 2006). It is one of six criteria air pollutants regulated by the U.S. Environmental Protection Agency (U.S. EPA) by according to its authority under the Clean Air Act. The EPA currently sets National Ambient Air Quality Standards (NAAQS) for ozone criteria 70 ppb (8 h averaging ozone concentration, the fourth highest daily maximum averaged over 3 years) to protect human health and welfare (EPA, 2016).

Olefin plants produce the most important olefin products like ethylene, propylene, and butadiene. These products are most important and widely distributed chemical plants in the world. Meanwhile, olefin plants are the largest emission producers in chemical and petrochemical industries. Flare emissions can be largely generated during olefin plant turnaround operations including plant startup and shutdown, which are the major emission format of olefin plant emissions and harmful to the regional air quality. Those flare emission mainly includes nitrogen oxides (NO_x), volatile organic compounds (VOCs), carbon dioxide (CO_2), carbon monoxide (CO). VOCs are generated from the incomplete combustion of vent gases. These emissions may cause highly localized and transient air pollution events and negative societal impacts (Xu et al., 2009a; Xu et al., 2009b; Yang et al., 2010; Liu et al., 2010; Wang et al., 2014; Wang et al. 2016; Ge et al., 2016). Note that the amount of incomplete combustion of vent gases will depend on the value of destruction and removal efficiency (DRE) regulated by Texas Commission on Environmental Quality (TCEQ). NO_x are not directly generated by the vent gases but formed by the reaction between nitrogen and oxygen from the ambient air under the high temperature due to the combustion of vent gases.

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In chemical plant concentrated industrial regions, the regional air quality (e.g., the ground-level ozone concentration) could not only be impacted by emission events from single chemical plant, but could also be aggravated by accumulative adverse effects from simultaneous emission events of multiple plants that are geographically close to each other. For this purpose, scholars have employed dynamic simulation method to obtain dynamic vent gases profiles including chemical species and quantity during olefin plant startup and shutdown (Liu et al., 2010; Wang et al., 2014). Those dynamic simulations can provide valuable hourly emission information to enrich emission inventories that could be employed for air-quality study.

In this paper, a systematic methodology on air-quality conscious coordination for multi-plant turnaround operations has been developed. It couples dynamic startup and shutdown flare emission profiles from multiple chemical plants and regional air-quality modeling together to examine regional air-quality impacts (i.e., ozone concentration increment) due to olefin plant turnaround operations. Based on such simulations, cost-effective air-quality control strategies will be investigated. This strategy explains how to mitigate the ozone impact by coordinating the starting time of multi-plant turnaround operations. Through case studies, the paper demonstrates that simultaneous startup and shutdown of two olefin plants without any coordination could cause a significant air-quality impact (11.4 ppb of the maximum 8 h ozone increment in the case study). However, an optimal coordination plan with several-hour tuning on the starting time of their turnaround operations would greatly reduce such adverse air-quality impact (only 1.4 ppb of the maximum 8 h ozone increment). The study helps identify possible solutions for cost-effective industrial emission controls in the future, and also provides valuable and quantitative supports for all relevant stakeholders, including environmental agencies, regional chemical plants, and local communities.

Problem Statement

This study firstly employs the dynamic profiles of flare emissions from olefin plant startup and shutdown operations to quantify the ozone precursors that can be incorporated into the air-quality model for ozone impact simulation. Secondly, the case study start to evaluate original coordination plan for two given chemical plants located in a concentrated industrial region. Finally, the optimal coordination plan for cost-effective turnaround emissions control can be obtained. For clarification, the assumption, given information and information to be determined are listed as follows.

Assumption: (1) starting time of olefin plant startup and shutdown operations can be changed within a time window (between at 07:00 and at 12:00 in our case studies), which is supposedly subject to plant allowance; (2) the startup and shutdown operations of studied olefin plant occur during the ozone episode in Southeast Texas; and (3) case studies on ozone increment due to olefin plant startup and shutdown have all of the same modeling inputs as the base case, except the addition of the point source from the startup and shutdown flare emissions of the studied plants.

Given information: (1) spatial locations of two virtual olefin plants; (2) stack parameters of each plant including stack height and outlet temperature; (3) geological domain information of the employed episode region; (4) ozone episode during May 31 and June 15, 2006 is served as the base case of air-quality modeling provided from TCEQ; (5) the completed input meteorological data and emission inventory; and (6) initial and boundary conditions of the employed ozone episode.

Information to be determined: (1) dynamic ozone concentration distribution in the studied region (southern east of Texas) under different coordination plans of olefin plant turnaround operations; (2) air-quality impacts (ozone concentration increment) under different coordination plans; and (3) the optimal coordination plan for plant turnaround operations with the minimum ozone impact.

General Methodology

This developed general methodology framework is shown in Figure 1. The vent gases profiles from plant startup and shutdown are obtained by Aspen dynamic simulation. After that, the speciation and quantification of flare emissions, which are released to the atmospheric environment due to the incomplete combustion of vent gases, are estimated by the DRE value and flare speciation method regulated by TCEQ (TCEQ, 2015). These ozone precursor data are inserted into the air-quality model to simulate the regional ozone increment under various scenarios. Comprehensive Air-quality Model with Extensions (CAMx) model is selected to study the ozone increment impacted from various coordination plans. The completed meteorological data, geological data and emission inventories for running CAMx model are obtained from TCEQ website (TCEQ, 2014). Note that this methodology framework is based on the previous research work (Ge et al., 2016) and is extended to study on the regional air-quality impacted from plant turnaround operations.

Three scenarios will be employed to study the regional air-quality impact from the olefin plant startup and shutdown operations. In scenario I, two olefin plants simultaneously start their turnaround operations without any coordination. Next, scenario II is that only one plant can tune its starting time within the allowable time window. Scenario III investigates the ozone increment impacted from all coordination plans (i.e., all two plants can tune the starting time of their turnaround operation within the time window). The study of these three scenarios aim to demonstrate that multi-plant turnaround operation without any coordination could cause the significant adverse air-quality impact; meanwhile, an optimal coordination plan with several-hour adjustment of their starting time would greatly reduce such an adverse air-quality impact.

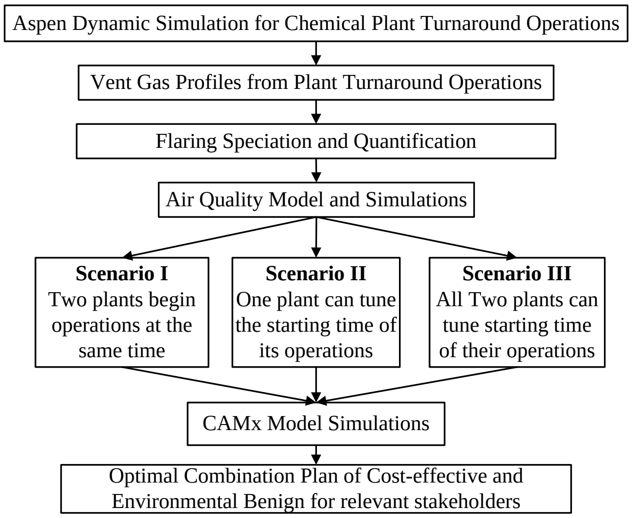

Figure 1. Methodology framework

Dynamic profiles of vent gases from chemical plant turnaround operations

To investigate the turnaround operations of olefin plant impact on the regional air-quality, this study references the typical vent gas profiles of plant A (shutdown) and plant B (startup), which have been achieved by the dynamic simulation and shown in Figure 2 (Liu et al., 2010; Wang et al, 2014). Plant A completes its shutdown process in 28 hours. Note that the amount of flare emissions from plant A is very little after the 11th hour (less than 1 kmol/hr) and gradually approaches zero. Plant B takes 17 hours to complete its startup process. The amount of flare emissions from plant B gradually increases and reaches the peak value at 12th hour. Also, the peak value of flare emissions from plant B sustains four hours.

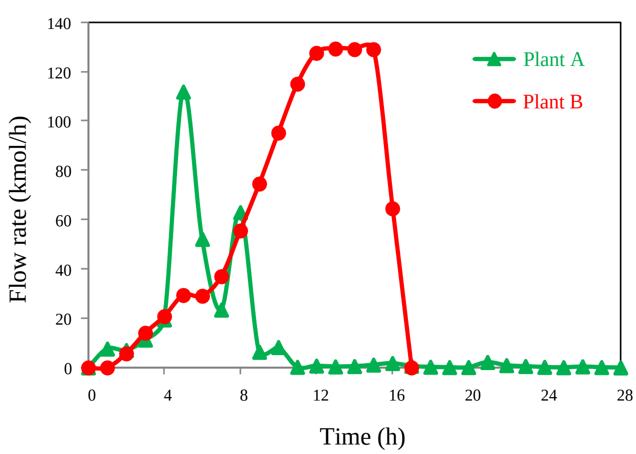

Figure 2. Dynamic vent gas profiles during two olefin plant turnaround operations: plant A and plant B

Flare speciation and quantification

Note that exact flare emissions need to be determined by the combustion of vent gases. The amount of VOCs and NO_x are calculated based on both the flow rate and chemical species of the vent gases and the appropriate DRE value. The DRE value proposed by TCEQ is employed to obtain the amount of flare emissions (TCEQ, 2014) through Scenario I to Scenario III. The 99% DRE will be only applied for vent gas compounds containing three or less carbons; the 98% DRE will be applied for vent gas compounds containing more than three carbons. Thus, 98% or 99% of vent gases will be converted into CO_2, CO, and H_2O; while the 1% or 2% of vent gases will be converted to various VOCs as the ozone precursors.

Note that the flare emissions out of the stack need to be discerned by the air-quality model. This study employs carbon bond 05 of photochemical reaction mechanism of ozone formation to convert the flare emissions into the model specie (Environ, 2005). NO_x and CO emissions generated from the plant turnaround operations can be estimated based on the combustion heating values. Thus, the amount of NO_x and CO emissions can be estimated by the following equations.

$$MS_{p}^{i}(\tau) = \phi^{i} \sum_{s} Q_{p}(\tau, s)\, \eta_{j}\, \Delta H_{c,s} \quad (1)$$

$$MS_{p}^{NO_2}(\tau) = \alpha\, MS_{p}^{NOx}(\tau) \quad (2)$$

$$MS_{p}^{NO}(\tau) = \beta\, MS_{p}^{NOx}(\tau) \quad (3)$$

$$\alpha + \beta = 1 \quad (4)$$

where $\Delta H_{c,s}$ is the lower heating value of vent gas specie *s*; *i* represents the NO_x and VOC, respectively; ϕ^{i} is respective emission factors of NO_x and CO from flare combustions. Based on the TCEQ recommendations (TCEQ, 2015), ϕ^{NOx} = 0.0485 and ϕ^{CO} = 0.3503 are employed in this study as heating values of all vent gas species are greater than 1,000 Btu/scf. $MS_{p}^{CO}(\tau)$, $EM_{p}^{NOx}(\tau)$, $MS_{p}^{NO}(\tau)$ and $MS_{p}^{NO_2}(\tau)$ are molar flow rates of CO, NO_x, NO, and NO_2, respectively. NO_x consist of NO and NO_2 according to splitting factors of α and β (Olaguer, 2012).

Air-quality modeling and simulation

In this study, the CAMx version 4.53 with the Carbon Bond 05 photochemical mechanism of ozone formation was employed to obtain the spatial and temporal distribution of ozone concentration (TCEQ, 2014). The episode of the completed meteorological and emission inventories data from May 31, 2006 to June 15, 2006 established by TCEQ was selected as the base case for model simulation. All the CAMx simulations were run on a computer with four 3.6GHz CPUs and 8GB memories. The 2 km $\times$ 2 km domain is selected for CAMx simulation. The geological information of two hypothetic olefin plants A and B are shown in Figure 3. The air-quality equations (Eqs. (5) through (8)) are borrowed from the previous study of Ge et al. (2016).

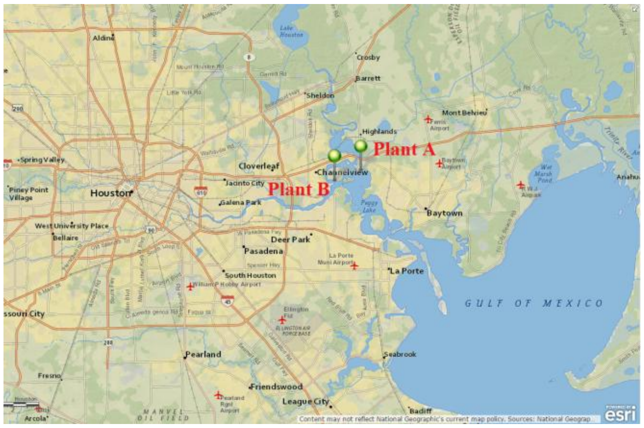

Figure 3. Hypothetic location of two olefin plants in Houston ship channel area of Texas

CAMx model simulations provide the hourly ozone concentration at each spatial domain grid. To clearly study the impact of plant turnaround effect on the regional air-quality, the amount of ozone difference between turnaround simulation case and base case will be illustrated by the Eq.(5).

$$\Delta C_n^{O_3}(d,h,\mathbf{x}) = C_n^{O_3}(d,h,\mathbf{x}) - C_0^{O_3}(d,h,\mathbf{x}) \tag{5}$$

where $C_0^{O_3}(d,h,\mathbf{x})$ represents the background ozone concentration of the base case at hour h on day d without the flare emissions of plant turnaround emissions in grid **x**; $C_n^{O_3}(d,h,\mathbf{x})$ represents the hourly (the h-th hour in a day) ozone concentration of the *n*-th coordination plan in the domain grid **x**; $\Delta C_n^{O_3}(d,h,\mathbf{x})$ represents the hourly ozone increment at hour h on day d in grid **x**, ppb; $h = 0, 1, \ldots,$ 23. The current ozone standard value (70 ppb) is based on the backward 8 h average. Thus, the 8 h ozone increment will be calculated by the following equations:

$$\overline{\Delta C_n^{O_3}}(d,h,\mathbf{x}) = \begin{cases} \frac{1}{8}\sum_{k=0}^{7}\Delta C_n^{O_3}(d,h+k,\mathbf{x}), & \text{if } 0 \le h \le 16 \\ \frac{1}{8}\left(\sum_{k=0}^{23-h}\Delta C_n^{O_3}(d,h+k,\mathbf{x}) + \sum_{k=0}^{h-16}\Delta C_n^{O_3}(d+1,h+k,\mathbf{x})\right), & \text{if } 17 \le h \le 23 \end{cases} \tag{6}$$

$$\Re\overline{\Delta C_n^{O_3}}(d,h) = \max_{\mathbf{x}} \overline{\Delta C_n^{O_3}}(d,h,\mathbf{x}) \tag{7}$$

$$\Pi\overline{\Delta C_n^{O_3}} = \max_{d,h}\left(\Re\overline{\Delta C_n^{O_3}}(d,h)\right) \tag{8}$$

where $\overline{\Delta C_n^{O_3}}(d,h,\mathbf{x})$ represents the 8 h ozone concentration increment of the *n*-th simulation case study at hour h on day d in grid **x**. Because some hourly ozone value may come from day $d+1$ to calculate a $\overline{\Delta C_n^{O_3}}(d,h,\mathbf{x})$, Eq. (6) gives a general formula to identify $\overline{\Delta C_n^{O_3}}(d,h,\mathbf{x})$. Equation (7) is to calculate the maximum value of 8 h ozone increment at hour h on day d in the entire domain, $\Re\overline{\Delta C_n^{O_3}}(d,h)$. Based on $\Re\overline{\Delta C_n^{O_3}}(d,h)$, Equation (8) is to calculate the maximum value of 8 h ozone increment of the *n*-th simulation case, which is designated as $\Pi\overline{\Delta C_n^{O_3}}$.

Case studies

Note that the flare and stack parameters of two olefin plants are given in Table 2 for all simulation cases. The plant A and B are set up in the process of startup and shutdown, respectively. The two olefin plants have the same stack height (58 m) and temperature out of stack (413 K). They are hypothetically located in Houston Ship Channel area of Texas and the geographical coordinate of their location are also given in Table 2. The two ethylene plants have the different times to reach their peak emission rates and different peak emission rates. The flare emission profiles of plant turnaround operations have been illustrated by Figure 3.

Table 2. Descriptions of Two Olefin Plants

plant	Duration time(h)	Location	Product (tons/yr)
A	28	(29.780, -95.060)	790,000
B	17	(29.757, -95.084)	1,000,000

Scenario I: Two plants begin their turnaround operations at the same time

The air-quality has been firstly analyzed to examine the original coordination plan, which assumed the starting time of two olefin plants at the same time (i.e. 07: 00 on June 4, 2006). The maximum $\Delta C_1^{O_3}(d,h,\mathbf{x})$ on June 4, 2006 was 28.9 ppb occurring at 13:00 pm. Note that the maximum $\Delta C_1^{O_3}(d,h,\mathbf{x})$ did not occur at the peak time of flare emission. $\Pi\overline{\Delta C_1^{O_3}}$ is 11.4 ppb occurring at 11:00 am in the vicinity of plants' location. To cost-effectively mitigate the ozone impact due to such plant turnaround operations, the starting time of plants' operations should be coordinated.

Scenario II: One plant can tune its starting time of turnaround operation

In this scenario, plant B keep its startup operations at 07:00 on June 4, 2006; while plant A is assumed to delay two hours of its starting time of shutdown operations(i.e. at 09:00). The maximum $\Delta C_2^{O_3}(d,h,\mathbf{x})$ is 17.0 ppb occurring at 14:00 on June 4, which is much less than the maximum $\Delta C_1^{O_3}(d,h,\mathbf{x})$ of 28.9 ppb. $\Pi\overline{\Delta C_2^{O_3}}$ is 7.0 ppb at 11:00 am on June 4, which is also much less than $\Pi\overline{\Delta C_1^{O_3}}$ of 11.4 ppb. So, it is inspiring that the regional air-quality has been remarkably improved due to only delay the starting time of plant A shutdown operations into 2 hours.

Scenario III: Two plants can tune their starting times of turnaround operations

In this scenario, both plants can tune their operation starting times within their plant allowanced time window to identify an optimal case n, which has the minimum $\Pi\overline{\Delta C_n^{O_3}}$, which is shown in Figure 4. It is a four dimension figure containing four parameters (h_A , h_B , h, and $\Re\overline{\Delta C_n^{O_3}}(d,h)$) to specify a coordination plan, where h_A, h_B, and h represent the starting time of plant A, plant B, and the h-th hour on June 4, 2006, respectively. Because the emission input of the studied ozone episode should be prepared hourly, h_p for each plant will be discretized as integer hours from 07:00 and 12:00. The color represents the domain maximum 8 h ozone increment (i.e., $\Re\overline{\Delta C_n^{O_3}}(d,h)$). For instance, the point (7, 8, 9, 10.3) represents the 8 h ozone increment is 10.3 ppb at 09:00 when the starting time of plants A and B are at 07:00 and 08:00, respectively. It can be also observed that most of the maximum 8 h ozone increments occur around 10:00.

The value of $\Re\overline{\Delta C_n^{O_3}}(d,h)$, which are changed with various coordination plans under the different starting time of plant turnaround operations, are presented in Figure 5. It is a three dimension figure containing three parameters (h_A , h_B , and $\Pi\overline{\Delta C_n^{O_3}}$) to specify a coordination plan, where h_A and h_B represent the starting time of plants A and B, respectively. The color represents the domain maximum 8 h ozone increment (i.e., $\Pi\overline{\Delta C_n^{O_3}}$). The results shown in Figure 5 indicate that the minimum air-quality impact can be obtained when the starting time of plant A at 11:00 and the starting time of plant B at 12:00. It has only 1.4 ppb ozone increment. Thus, the optimal coordination plan is obtained by only delaying the starting time of both plants just several hours (4 hours for plant A and 5 hours for plant B). The ozone increment has been observably decreased about 10.0 ppb comparing to the initial coordination plan in scenario I.

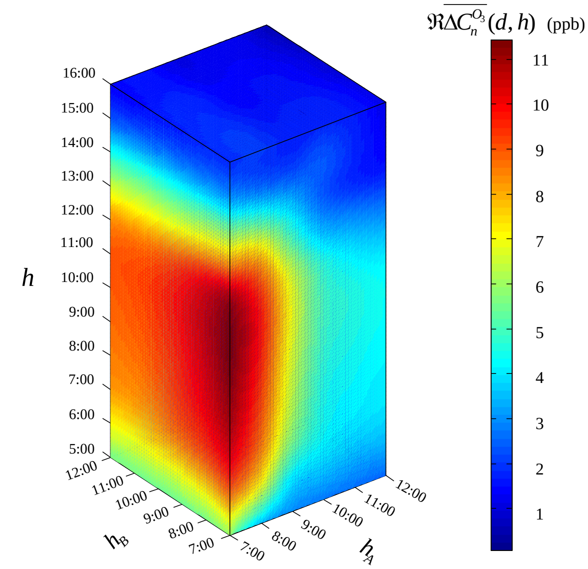

Figure 4. Comprehensive view of $\Re\overline{\Delta C_n^{O_3}}(d,h)$ under various combinations of plant turnaround

By fixing the starting time of plant A at 07:00 am, the sensitivity of the emission impact from the starting time of plant B on air-quality can be observed in Figure 5. Similarly, the sensitivity of plant A impact on air-quality can also be observed. Note that the ozone increment can be decreased much more by delaying the starting time of plant B instead of the starting time of plant A. Thus, plant B's impact on air-quality has more sensitive than that of plant A. Thus, the starting time of plant B should be delayed as much as possible to achieve the minimum ozone impact. Note that the maximum allowable delay bound is 5 hours due to the assumed time span. It demonstrates that the capability of each plant to the air-quality control is different, which should be well understood and utilized.

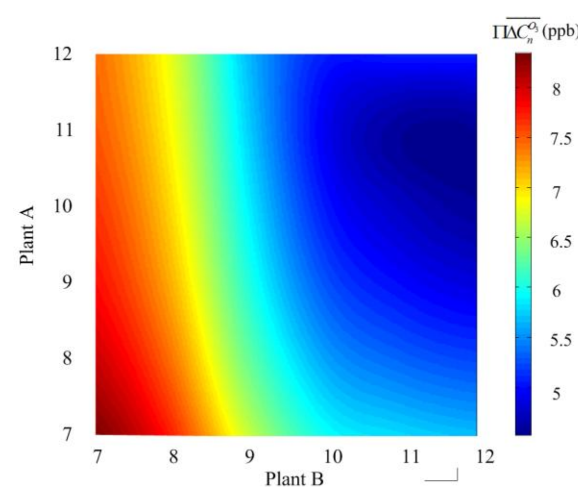

Figure 5. Comprehensive view of $\Pi\overline{\Delta C_n^{O_3}}$ under various combinations of plant turnaround

Conclusions

In this paper, a systematic methodology on air-quality conscious coordination for multiple olefin plant startup and shutdown operations has been developed. The methodology couples process dynamic simulations for industrial flare emissions with regional air-quality modeling together to investigate the regional ozone increment due to flare emission from multiple olefin plants' turnaround operations. The results indicated that the worst ozone increment 11.4 ppb and the best ozone increment 1.4 ppb during the startup and shutdown operations can be obtained at time pint (7, 7) and (12, 11), respectively. The ozone increment can be totally minimized 10.0 ppb by delaying the starting time of plant turnaround operation. The study helps identify possible solutions on cost-effective industrial emission controls in the future, and also provides valuable and quantitative supports for all relevant stakeholders, including environmental agencies, regional plants, and local communities.

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