

A Reactivity Based Emission Inventory for the South Pars and Its Implication for Ozone Pollution Control

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ABSTRACT: *The South Pars zone in Iran encompasses the largest gas refineries and petrochemical complexes in the world. In the South Pars zone, elevated concentrations of reactive hydrocarbons co-emitted with nitrogen oxides from industrial facilities lead to substantial ozone production downwind. To understand the role of these emissions on the ozone formation and, to formulate appropriate control strategies in this zone, emissions of precursors of ozone were quantified, and compounds that deserve relatively more attention were determined. To do this, first, a fully-speciated ozone precursors emission inventory was prepared to provide necessary input data for air quality simulation models. Then, the emission inventory was weighted by emitted mass and incremental reactivity scales to determine which compounds deserve relatively more detailed representation in the modeling. Afterward, a photochemical model was applied to determine the ozone sensitivity to its precursors. Finally, source apportionment was done for the most important compounds. Additionally, the reactivity-based inventory was compared with other regions. Results show that nitrogen oxides - sensitive chemistry is dominant in the zone thus the most effective control strategy is the mitigation of the nitrogen oxides emissions. Gas refinery plants have a larger share than petrochemical plants in the nitrogen oxides emission and, the gas turbines are the main sources of nitrogen oxides emission in this region. Emitted volatile organic compounds contain more highly reactive species in comparison with the ambient air composition of typical urban areas and areas with gas production industries. Propylene and ethylene have the most contribution to the ozone formation in comparison with other volatile organic compounds. The major sources of their emissions are the olefin processes and polymer production plants.*

KEYWORDS: *Reactivity-based emission inventory; Speciation; Highly-reactive VOCs; Photochemical model; Reactivity scale.*

INTRODUCTION

Photochemical ozone formation is an important air pollution problem in many areas. The gas-phase reactions of emitted Volatile Organic Compounds (VOCs) with Oxides of Nitrogen (NO_x) in the presence of sunlight form

ground-level ozone [1]. NO_x is one of the criteria pollutants and most VOCs are considered as hazardous air pollutants that many efforts have been made to prevent their emission [2]. Differences in atmospheric reaction

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rates, the way in which reactions affect ozone and atmospheric abundance of individual VOCs can significantly affect ozone formation [3]. For example, ozone formation can be completely different in typical urban areas with areas where industrial sources such as refineries, chemical plants, and oil and gas production facilities are concentrated [4].

Plumes from hydrocarbon industrial facilities routinely are characterized by simultaneous strongly elevated concentrations of NO_x and reactive VOCs. It is predicted that these conditions lead to the fastest rate of O₃ formation and highest yields per NO_x molecule emitted [5-8]. An assessment about local air quality changes over the Middle East for 2005–2014 showed that average tropospheric column levels of formaldehyde (HCHO), and glyoxal (CHOCHO) are highest over oil ports and refineries[8]. Satellite measurements confirm the high mixing ratios of tropospheric NO₂ [10, 11] and high concentrations of ozone in the Middle East, especially in the Persian Gulf [12-16]. Model calculations indicate that this is mostly because of local emissions and highly favorable weather conditions for ozone formation in the Middle East and long-distance transported air pollution fosters it [12, 17].

An intensive study to identify the role played by petrochemical plants in ozone formation in Houston and eastern Texas showed reactive alkenes from petrochemical industries near of this city played an important role in ozone formation [20-23]. Assessments of the influence of emissions associated with oil and natural gas activity on regional O₃ production in several regions of the United States of America show that oil and natural gas VOCs have a significant contribution [24-28].

The studies, which have assessed the ozone concentration in the Middle East to date, are mainly based on analyzing satellite and in situ measurement data [13, 16, 18] or using global models [12,13]. The most of previous studies focused on the middle and upper troposphere [13, 19]. There are just a few studies investigated the lower troposphere [12, 17]. None of them considered speciated VOCs emissions from local sources, especially hydrocarbon industries that might be due to the lack of data. Thus, developing a speciated emissions inventory, determining how the emissions of accumulated hydrocarbon industries can affect ozone formation and suggesting appropriate control strategies based on Reactivity-Based Emissions Inventory (RBEI) are the aim of this study.

For formulating proper and cost-effective control strategies to reduce O₃ levels in areas where this is a problem, it is needed to relate emissions of these species to ambient levels of O₃ by reliable and scientifically valid methods. Air Quality Simulation Models (AQSMs) can be used for this purpose. Chemical mechanisms are used to describe complex processes relevant to the O₃ formation in AQSMs. It is necessary to prepare a fully speciated VOC emission inventory for the SPZ in the best possible way for two reasons. First, ozone production is very sensitive to the amount of Highly-Reactive VOCs (HRVOCs) being emitted and second, the models need good speciation for accurate input data to make valid predictions. Additionally, having the Reactivity Based Emission Inventory (RBEI) can be useful for deciding which species require more attention and should represent separately in the mechanism and model.

The South Pars Zone (SPZ) is located along the Persian Gulf coast within Iranian territory. The South Pars gas field is the largest independent gas reserve in the world. The field contains more than 51 trillion cubic meters of natural gas. Large gas processing plants and petrochemical complexes have been constructed in this zone to take advantage of this gas field. Intensive natural sunlight and moisture, and a rich source of anthropogenic NO_x and VOC emissions lead to high-elevated O₃ concentration in the SPZ. In this work, for defining realistic and robust ozone pollution control strategies which focus on those ozone precursors which contribute most to ozone formation in the SPZ, a fully speciated VOC and NO_x Emission Inventory (EI) has been prepared and ozone production sensitivity was represented. Analyses of NO_x-VOC chemistry for the SPZ were made for June to August of 2017 by a photochemical trajectory model, OZIPR (a Research oriented version of Ozone Isopleths Plotting package), coupled with SAPRC (Statewide Air Pollution Research Center) chemical mechanism.

The OZIPR is a simple photochemical model, previously developed [29] and has been used to simulate photochemical pollution in many studies [30-32]. The SAPRC-07 photochemical mechanism has been greatly studied and validated and has been used in numerous studies around the world [33]. The relative impacts of ozone precursors on ground-level ozone concentration were quantified by using the atmospheric abundance and some reactivity metrics for VOCs. Finally, source apportionment was done for the most important species.

METHODOLOGY

A fully- speciated ozone precursors Emission Inventory (EI) was prepared for the SPZ by a bottom-up method. Since each VOC can significantly influence differently on the ozone formation due to the differences in atmospheric abundance, atmospheric reaction rates and the way in which reactions affect ozone, it was necessary to determine which compounds warrant relatively more detailed representation in modeling. A combination of speciated emission inventory and Maximum Incremental Reactivity (MIR) were used in ranking the relative importance of different compounds in ozone formation. Then, these HRVOCs were introduced explicitly to the model for the more accurate prediction. After determining the chemistry regime by model calculation, it was made possible to decide how to set the control strategies for ozone pollution control in the SPZ and downwind. The details are described in the following sections.

Approach of developing emission inventory for the South Pars

The SPZ with 140 km² was established in 1998 for the utilization of South Pars oil and gas resources and encouraging commercial activities in the field of oil, gas and petrochemical industries (Fig. 1). This zone is located in the Persian Gulf coast in latitude and longitude 27.626 N and 53.05 E respectively and approximately 100 km away from the South Pars Gas Field. South Pars gas field is the largest independent gas reserve in the world. According to the latest figures, the field contains more than 51 trillion cubic meters of natural gas. The field has already been developed in different phases; 10 gas processing plants and fourteen large petrochemical plants have been constructed by 2014. The characteristics of the industries in the region are given in Table 1.

To prepare the required emission data for NO_x, CO and VOCs, we needed to collect the measurement and activity data from industries located in the SPZ. The emission inventory database prepared by the Research Institute of Petroleum Industry of Iran was used for the gas plants. A bottom-up emission inventory combining activity data, emission factors, modeling and engineering calculations was prepared for petrochemical companies in collaboration with the Iranian National Petrochemical Company according to the "Emission Estimation Protocol for Petroleum Refineries-version 2.1.1" [34] hereafter

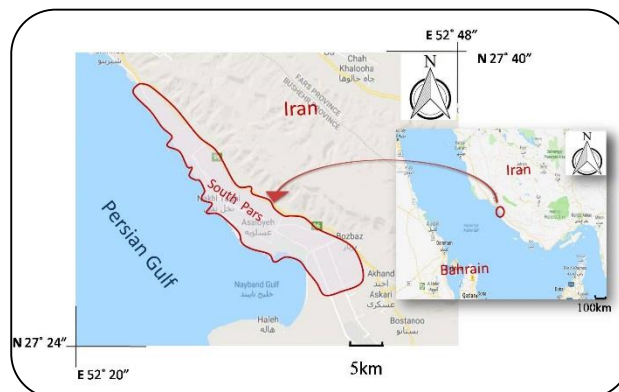


Fig. 1: South Pars Zone on the map- the area with the red line is the area of study.

called "protocol" and "EPA's emission inventory improvement program" [35]. In the protocol, the emission measurement or estimation methods are ranked in order of preference. The highest ranked method (with methodology rank 1 being the highest) for which data are available were used for emission estimation. Table 3 shows the selected methods and their rank for each group of emission sources.

The activity data for 2013, 2014 and 2015 were provided through questionnaires by the plants. In addition, the measurement data for emissions were gathered if there were any during these years. There were no measurements for rate or composition of emissions through this work and, all the estimations are based on data provided by the plants. Emission factors recommended by the AP-42 document were used whenever we needed to use emission factors.

For quality control and elimination of distracted and false data, the reasonableness of emission values was checked by several methods. For example, when the emission rate was determined based on measurement data, other less accurate methods that need different activity data were also used or emission values were compared to those calculated for the same category in the petrochemical special economic zone (the similar zone in Iran) to ensure that the emission values are within a specific range that is considered reasonable.

Speciation of VOCs

Since the most methods for quantifying the amount of emission rate report only total VOCs, it is needed to subdivide total VOCs into VOCs species by an appropriate method. Speciation of VOCs is the top-down process of breaking the prepared EI of total VOCs into its constituents.

Table 1: Characteristics of the industries in the SPZ.

Industry group	NAME	Industry type	Main Products	Capacity based on main product (1000ton/year)
gas refineries	south Pars complex, phases 1 to 10	Gas refinery	Natural gas, Condensate, Sulphur, LPG, Ethan	25MMSCM of natural gas/ each phase per day
Petrochemical companies	Aryasasol	Olefin	Ethylene , poly-ethylene,	Ethylene:1000
	Jam	Olefin	Ethylene ,Propylene	Ethylene: 1300
	Kaviyan	Olefin	Ethylene,C3+	Ethylene: 1000
	Morvarid	Olefin	Ethylene,C3+	Ethylene: 500
	Zagros	Methanol	Methanol	Methanol: 3200
	Pardis	Urea and Ammonia	Ammonia ,Granular Urea	Ammonia: 1360
	Pars	Ethane recovery, polymers	Ethane,Propane,Butan Ethylbenzne,Styrene Monomer	Ethane: 1600
	Noori	Aromatics	xylene, ,Benzene	Paraxylene 750
	Mobin	Central Utility	Electerricity, steam,...	Electricity 986 MW
	MEHR	Polymer	HDPE	HDPE: 300
	Jam Ehtemam	Formaldehyde	Formaldehyde,UFC	Formaldehyde: 40
	Farsashimi	MonoEthylene Glycol (MEG)	MEG,DEG,TEG	MEG: 400
	Jam Propylene	Propylene	Propylene	Propylene:300
Petrochemical Port	Storage and Ship loading port			

In this work, Speciated VOCs are generally provided by choosing an appropriate VOCs profile for emission sources and then applying it for calculated total VOCs emissions. SPECIATE version 4.4 [36] was used for this purpose. Table 2 lists the profile number (P_NUMBER), type of emission source and quality level of the profiles in SPECIATE version 4.4 which were used in this study to map total VOCs emissions or total organic gases emissions into specific. Also, in some cases, engineering calculations (for flares and for guessing the composition of process streams), site-specific emission factors (for process vents) and modeling (for *storage tanks*) are used whenever were possible and applicable to provide the desired speciation.

The emission sources of VOCs were classified in 7 groups including equipment leaks, storage tanks, stationary combustion sources, flares, cooling towers, wastewater collection, treatment systems and, loading operations. The details for estimating methods for total VOCs and their speciation have been summarized in Table 3. Due to the desert nature of the area and its insignificant vegetation, only anthropogenic emissions are addressed. The following sections outline the methods and profiles were used in this regard.

Reactivity- Based VOCs Emission Inventory of the SPZ

Ozone production is very sensitive to the amount of HRVOCs being emitted. Knowing these compounds can be useful for deciding which species require more attention and should represent separately in the chemical mechanism or model to have predictions that are more accurate.

The reactivity can be defined as the potential of a given compound to form ozone. There are several reactivity scales in use today. Incremental reactivity scales such as the Maximum Incremental Reactivity (MIR), the Maximum Ozone Incremental Reactivity (MOIR) and the Equal Benefit Incremental Reactivity (EBIR), can be used for quantifying the reactivity [36]. These reactivity scales are applicable for a certain chemical regime including rich-NO_x condition (MIR), lower NO_x conditions that lead to the highest ozone concentrations (MOIR) and conditions that NO_x control and VOC control have an equal effect on reducing ozone formation.

The MIR is a measure of the maximum amount of ozone (grams) that can be formed by adding an incremental amount of a particular VOC (grams) to a mixture of NO_x-rich air. MOIR is the corresponding value for lower NO_x conditions that lead to the highest ozone

Table 2: Profiles of SPECIATE 4.4 [35] used to speciate VOCs in this study.

P_NUMBER	Type of emission source	QUALITY*
001	External Combustion Boiler - Residual Oil	4
003	External Combustion Boiler - Natural Gas	4
007	Natural Gas Turbine	3
0079	Chemical Manufacturing - Flares:	2
0051	Flares - Natural Gas	2
8949	Natural Gas Production	D
8861	Olefins manufacturing (ethylene and propylene	D
0068	Polypropylene	3
2547	Polyethylene Plant:	N/A

*5 = highest quality, 1= lowest quality for Legacy profiles originating from SPECIATE 3.2 and A=highest quality to "E"=lowest quality to each non-legacy profile.

Table 3: Used methods for estimating and speciating VOCs in this study.

Source name	Estimation method for total VOC	Methodology Ranks *	speciation
Equipment Leaks	Counting or estimating of numbers of equipment components and emission factors.	4 and 5	1-According to the composition of the process stream in contact with the equipment. 2- for unknown composition, the 8861 code of SPECIATE4.4
Storage Tanks	TANKS v4.09D; U.S. EPA, 2006 software. Missed data were filled by similar plants data	2	TANKS v4.09D Missed data were filled by similar plants data
Stationary Combustion Sources	1-AP-42 emission factors or 2- Source-specific stack testing.	3B,4	003 code of SPECIATE 4.4.
Flares	Engineering calculations to assess certain release events	4	0051 and 0079 codes of SPECIATE 4.4
Cooling Towers	emission factors from AP-42; Sections 5.1 and 13.4	5	Depending on the process, the profiles of SPECIATE4.4 as described in Table
Wastewater Collection and Treatment Systems	WATER9 (in most cases the activity data were not available)	2	WATER9
Loading Operations	AP-42 emission factor and loading rates	4	According to the composition of the product

*According to Emission Estimation Protocol for Petroleum Refineries-version 2.1.1

concentrations and, EBIR is the value for conditions that NO_x control and VOC control have an equal effect on reducing ozone formation [38].

The MIR has been widely used to describe the relative reactivity effects of VOCs on ozone formation [39-41] because the MIR scale represents conditions where VOCs have the most effect on ozone formation and, has been the basis for several reactivity-based regulations (for example: section 112 of the clean air act amendments of U.S.A federal regulations). Therefore, the VOCs were prioritized by the MIR, because we wanted to introduce the HRVOCs to the model separately to have a better prediction of

the chemical regime of the zone. Thus, a combination of speciated emission inventory and MIR were used in ranking the relative importance of different compounds in ozone formation and develop a reactivity-based emission inventory (RBEI) in the SPZ according to the Equation (1).

the rank of VOC_i in Reactivity – based EI = (1)

$$\frac{E_i \times \text{MIR}_i}{\sum_1^n E_i \times \text{MIR}_i}$$

Where E_i (ton/year) is annually emitted mass of the i th compound in the SPZ, MIR_i (ratio) is maximum reactivity

scales of i^{th} compound [42] and, n is the total number of volatile organic compounds in the EI. This procedure was repeated with MOIR and EBIR for comparison.

Model preparation

To simulate the conditions, the OZIPR (research-oriented version of ozone isopleths plotting package), a trajectory model based on a well-mixed column of air that moves with the wind, was used. The height of the column is variable with the mixed layer but cannot expand horizontally. Various complex chemical mechanisms can be coupled with the OZIPR. Air from above the column is mixed in when the boundary layer increases and emissions from the surface enter the column when the column passes over different emission sources [29]. Statewide Air Pollution Research Center chemical mechanism, version 07 (SAPRC07) was chosen to represent chemical processes [43]. The SAPRC photochemical mechanism family is used widely for regulatory and research applications [21, 38]. This mechanism is not as condensed as Carbon Bound [44, 45] and is not as detailed as the Master Chemical Mechanism [46] and it is possible to define some of the more effective species in this mechanism explicitly.

To determine whether the model can simulate the region's conditions well six days were selected for modeling including August 2 and 12, July 6 and 26 and June 11 and 15 of 2017. These days had the valid monitoring data recorded by the Continuous Air Quality Monitoring Stations (CAQMS) located in the SPZ and had a quite good distribution over the summer of the SPZ. Trajectories and required meteorological data along the trajectories were computed by the NOAA HYSPLIT (Hybrid single particle Lagrangian integrated trajectory) model. Since it was needed to compare model results with measurement data in CAQMS, back trajectories were determined from CAQMS at each hour of the day (8:00 to 18:00) to the place that air mass had been at 6:00. Therefore, 11 back trajectories were computed per day, which each of them illustrates the movement path of a mass of air before reaching CAQMS at the specified time. These trajectories were generated from Global Data Assimilation (GDAS) meteorological data (0.5°) and for 02/08/2017 were depicted in Fig. 2.

The concentrations of gases in the volume of air being modeled and the aloft concentrations must be specified



Fig.2: Back trajectories from continuous air quality monitoring station, starting at each hour of 02/8/2017 (from 8:00 to 18:00) to the place that air mass had been at 6:00.

for the model as the initial conditions. In the present set of runs, four species including CO, ozone, VOC, and NO_x are initialized aloft. Inside the box, six species are specified: the four aloft species and the two HRVOCs in the SPZ including propylene and ethylene which are treated explicitly in the model. The initial concentrations of the HRVOCs were set to fixed fractions of the total VOCs. For backward trajectories which the airbox movement started over the Persian Gulf in the early morning, because of the lack of measurement data and emission sources, surface and aloft values were set to the O₃, CO, and NO_x values reported by Lelieveld et al. (2009) as follows: O₃= 80 ppbv, NO_x=1.4ppbv, CO=180 ppbv. These values are calculated for the region of 25–30°N and 45–55° E [12]. Since there were no measured or calculated VOCs concentration for the region, the VOC = 100 ppbv was considered according to the value assigned to Houston in the study done by U.S. EPA (1999) because of the similarities between emission sources. On the other hand, sensitivity analysis in the next step showed that the model is sensitive to the aloft concentration of NO_x and surface and aloft concentration of VOC have a negligible effect on the results. Having boundary conditions, trajectories and meteorological data along with them, just compiling of EI in terms of the selected chemical mechanism species (SAPRC07) was needed. A chemical speciation database managed by Carter was used for mapping chemical compounds into model species [47]. Since propylene and ethylene had been identified as the HRVOCs in the region, emission data for these compounds were given explicitly to the model.

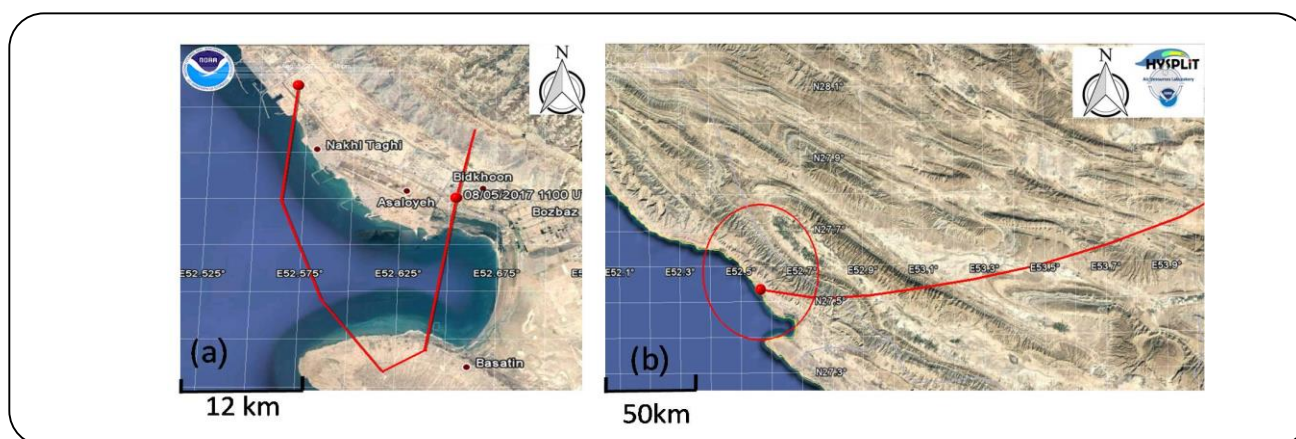


Fig. 3: The trajectories which start from the SPZ at 8:00 forwardly and end at 20:00. (a) The trajectory of 5 August 2017
(b) The trajectory for 1 June 2017

Evaluation of the ozone formation sensitivity to its precursors

For identifying the features of ozone-NO_x-VOC chemistry, The response to reduced emissions is derived by repeating the model base case with reduced NO_x or VOC emission. A specified set of simulations were performed (121 simulations) to calculate ozone levels at fixed intervals for a selected day of summer 2017. This made it possible to plot the fixed ozone concentration lines (isolines) as a function of initial precursors. The fifth of August was selected because the airbox moved from the upwind on the morning of this day, remained most of the day in the SPZ (Fig. 3-a). The same calculations were repeated for some other days. The trajectories of these days were set to start from the SPZ at 8 am forwardly and were tracked until 20:00. The model calculations for these trajectories illustrate the changes in VOC and NO_x concentrations calculated for the air parcels started from the SPZ and allowed to react chemically for eight hours. Almost all the trajectories for other days in the summer of 2017 traveled up to 300 kilometers away from the SPZ at the end of modeling period and are to the north-east and south-east of the region. Fig.3-b show one of these trajectories for the first of June.

RESULTS AND DISCUSSION

The composition of emitted VOCs

The results show 80% of VOCs and 30% of NO_x emissions in the SPZ are from petrochemical companies, and the rest belongs to gas refineries. The VOCs emission inventory of 177 species was developed for the SPZ

for 2015. According to our results, 99 % of the emitted mass is due to 48 compounds, so we limited the analysis to these compounds. The emissions of these 48 compounds, corresponding reactivity values in MIR, MOIR, and EBIR and the share of the each in the EI and in the RBEI are available in the supplementary table. Our results show the top 10 species contribute 80 % of the total emission (red column in Fig. 4). The most abundant species were propylene (3170 ton/year, 21.7%), followed by ethylene (1873 ton/year, 12.8%), n-butane (1437 ton/year, 9.8%) and propane (1366 ton/year, 9.3%). When emissions were weighted by MIR, MOIR, and EBIR according to Eq. 1, as shown in Fig. 4 by blue and yellow and green columns respectively, the orders of substances differ significantly from those in mass emission inventory. In all the weighted inventories, just two notable species remain, including propylene and ethylene. The top two species are the same although, the differences between values of MIR, MOIR, and EBIR for each species are notable. These two compounds, together, contribute about 68% of the total RBEIs while accounting for 34.6 % of the total emission by mass.

In this study, VOCs species divided into seven categories based on their chemical characteristics. Although the contribution of chemical groups in MIR-RBEI and MOIR-RBEI and EBIR-RBEI is quite different from those in the mass-based inventory, there are small differences between themselves. As shown in Fig. 5, alkenes contribute more than 75% in the RBEIs while their corresponding mass-based emissions are 42%. In contrast, Alkanes account for 36.4 % in mass-based emission

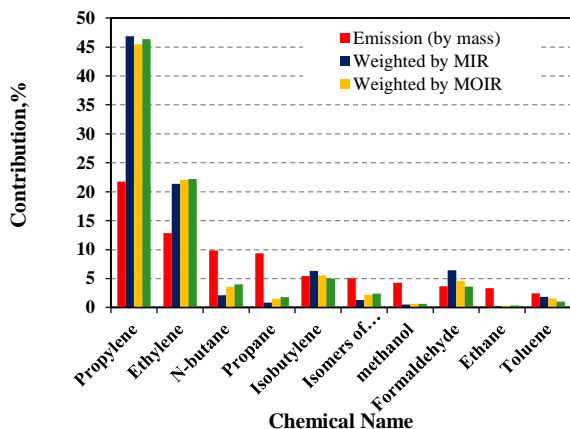


Fig.1: Comparison of the contribution of VOCs in emission inventory by mass (percentage, red column), Emission Inventory weighted by MIR (percentage, blue column) and weighted by MIOR (percentage, yellow column)

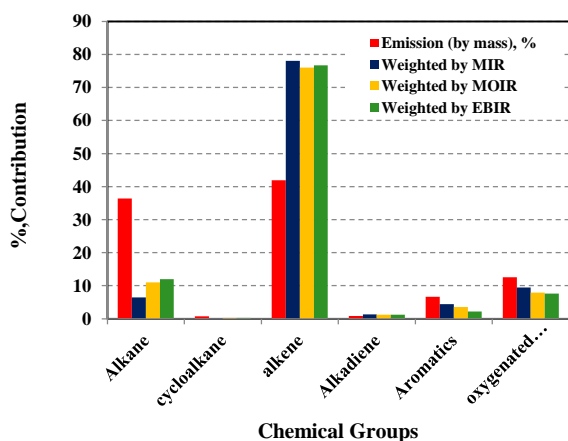


Fig. 5: Share of chemical groups in EI and RBEIs (%).

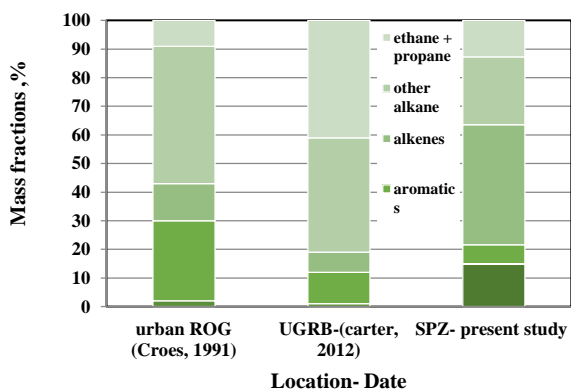


Fig. 6: The mass fractions of various types of VOCs in ROG mixture used in MIR and other Carter reactivity scales, ambient mixtures used in the UGRB simulations and EI of SPZ. The mixtures are grouped based on similarity. The UGRB column is reproduced from [49].

but just 6.5%, 11%, and 12% in the MIR-RBEI and MOIR-RBEI and EBIR-RBEI respectively.

Comparison with other regions

Some comparisons were made to determine how much the EI composition of the SPZ is different from the other regions. Typical urban area, an industrial city with natural gas production industries and an industrial city with refining/petrochemical industries were selected for comparison. The first column at Fig. 6 shows "ROG mixture" that is averaged conditions of 39 urban areas [38, 48-49], used as a base mixture for developing MIR and species lumping in SAPRC mechanism [37, 43].

William P.L. Carter and John H. Seinfeld studied winter ozone formation and, VOC incremental reactivities in the Upper Green River Basin (UGRB) of Wyoming, one of the largest areas of natural gas production in the United States [50]. The second column of Fig. 6 represented the conditions of UGRB. The third column in this figure is the composition of EI of the SPZ.

As this figure shows, alkanes, alkenes, and aromatics are three main chemical groups participating in EI of these areas (four upper parts in each column) but, alkanes are the most abundant species in the typical urban ambient air and UGRB while alkenes are the most in the EI of the SPZ. Reactivity of hydrocarbon groups is in the order of aromatics > alkenes > alkanes but, according to the corresponding MIR, the difference between the reactivity of aromatics (with average of 16 for MIR) and alkenes (with average of 12.3 for MIR) is much less than the difference between the reactivity of alkanes (with average of 3.6 for MIR) and alkenes [37]. Therefore, the SPZ has more reactive species in its atmosphere because emission amounts of aromatics + alkenes in the SPZ are more than the emission of aromatics + alkenes in two other areas.

Massive refining/petrochemical industries adjacent to Houston-Galveston-Brazoria (HGB) lead to the rapid and intense formation of ozone. The results of the analysis that were conducted in HGB to discover the role played by VOC species in the ozone formation concluded that propylene, ethylene, butenes (1-butene, cis-2-butene, trans-2-butene), and 1,3-butadiene are responsible for high reactivity days in HGB [4, 51]. These VOCs mostly emit from petrochemical facilities. The first and second substances in the priority list of the SPZ and HGB are the same (e.i. propylene, ethylene).

Evaluation of model performance

The model was run for 6 (day) \times 11 (trajectory per day) times. Each trajectory specified the path of air mass from 6 a.m. until it reached to CAQMS. So the last hourly value reported by OZIPR in each run was comparable with measured value at CAQMS. RMSD (Root mean square deviation) and R^2 (square of the coefficient of correlation) of OZIPR outputs were calculated against the observations for O_3 at CAQMS to evaluate the model's results. The overall RMSD for 66 hours modeling is 0.023 ppm and, the R^2 is 0.76. Fig. 7 shows the results of a total of 66 hours modeling in comparison with observation data for O_3 concentration at CAQMS. Results show although OZIPR is a box model with some simplifications, with the customization that has done to adjust it with the condition of the region, it can simulate O_3 formation in the SPZ with appropriate precision for our goals.

Evaluation of ozone formation sensitivity to precursors

Fig. 8 depicts the plotting of fixed ozone concentration lines (isolines) as a function of initial precursors concentration for the base case of the fifth of August 2017. Unfortunately, there is no measured data for VOCs concentrations in the ambient but data for NO_x are available. The maximum and minimum of measured data of the NO_x concentration are shown in Fig. 8. It is clear that NO_x -sensitive chemistry is dominant at the SPZ. The measured data for ozone in this day ranged from 37 to 85 ppb that is consistent with these results. Fig. 9 shows the lower part of Fig. 8 with a better resolution. The results for the other days that the air box traveled out of the region indicate NO_x -sensitive chemistry along the entire path. The Fig. 10 shows the isopleths for June 1. The red line shows the NO_x and VOC concentrations along the trajectory calculated by OZIPR. It should be noted that the trajectory of 2017/08/05 remained in the SPZ during the day (Fig. 3.a). The concentration of ozone in the SPZ is often lower than downwind because of a process referred to as NO_x titration that leads to reduced O_3 in the vicinity of large emission point sources of NO . This is the main reason for the difference between ozone concentration levels in at Figs. 9 & 10.

Typically, a polluted air mass within an urban area is characterized by the VOC-sensitive chemistry when it is close to its emission sources and evolves towards the NO_x -sensitive chemistry as the air mass ages. However,

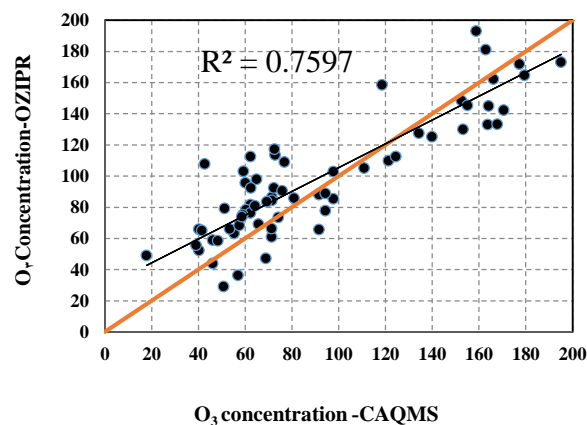


Fig. 7: Simulated O_3 concentration against observed values at the CAQMS for 66 hours during from summer 2017, (ppb).

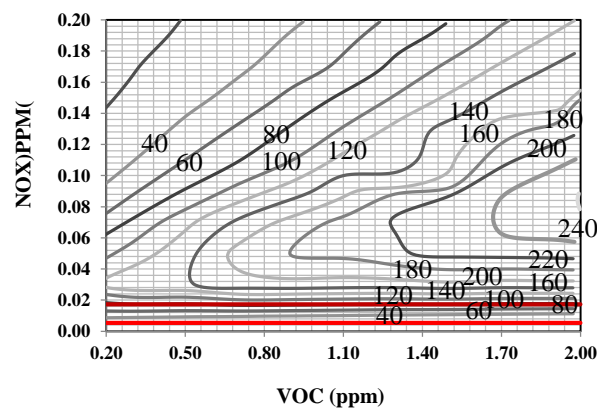


Fig. 8: The peak ozone isopleths for the base case 2017/08/05.

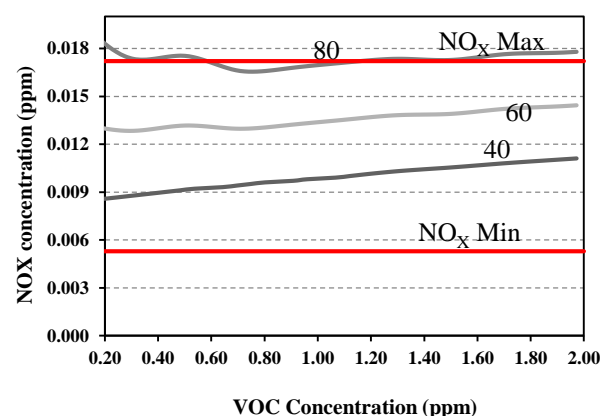
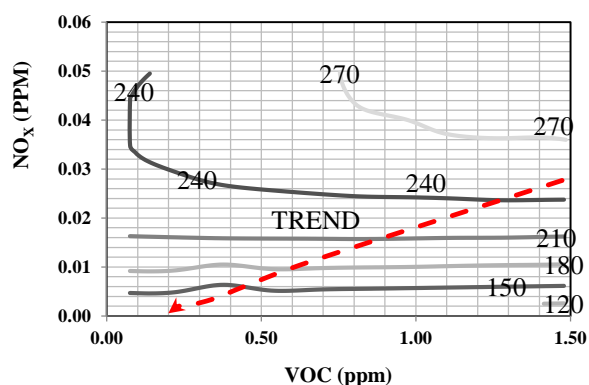


Fig. 9: The peak ozone isopleths for the base case 2017/08/05 with better resolution for low NO_x concentrations.

Table 4: Source apportionment for NO_x in the SPZ.

Sources of NO _x Emission	Emission (ton/year)	%
Boilers, Furnaces, Heaters, ...	19355	28.61
Flares	316	0.47
Gas turbines	47957	70.90
Incinerators	15	0.02
total	67643	100

**Fig. 10: The peak Ozone isopleths for 2017-06-01 Hours: 8:00 to 20:00.**

the environment and types of emitted VOCs would modify this pattern. When there are more HRVOCs in the air mass, it is more likely to have NO_x-sensitive chemistry compared to those with similar total VOC but lower reactivity. The SPZ has more reactive species in its atmosphere than a typical urban area, thus having NO_x-sensitive chemistry is reasonable.

Source apportionment of precursors

The results of EI analysis show 80% of VOCs and 30% of NO_x emissions in the SPZ are from petrochemical companies and the rest emitted from gas refineries. When there is a NO_x-sensitivity regime, the NO_x emission sources must get more attention. Table 4 shows the source apportionment of NO_x emission in the SPZ.

Considering that 70% of NO_x emits from refinery plants and the data represented in Table 4, NO_x mitigation methods for gas turbine could be an effective strategy for Surface ozone reduction in the SPZ and downwind.

Although the results of this study indicated the NO_x sensitivity regime in the SPZ and downwind areas, most

of HRVOCs are in the list of hazardous air pollution and, their emission must be controlled. In addition, their emission reduction is likely to moderate or change the chemical regime in the SPZ. Table 5 depicts the contributions of different industrial processes in HRVOCs emissions in the zone. As Table 5 shows, the olefin processes have the largest share in the emissions of both HRVOCs. The second one is the polymer process.

CONCLUSIONS

The plumes from oil, gas and petrochemical plants routinely are characterized by simultaneous strongly elevated concentrations of NO_x and reactive VOCs and, these conditions lead to the fastest rate of O₃ formation and highest yields per NO_x molecule emitted. Previous studies confirm that concentrations of ozone precursors are highest over oil ports and refineries in the Middle East, and the region is a hot spot of photochemical smog. Air quality in the SPZ is heavily influenced by gas and, petrochemical plants concentrated in this zone. Additionally, hot and sunny climate and complex coastal meteorology and area topography intensify the ozone formation in the SPZ. For formulating proper and cost-effective control strategies to reduce O₃ levels, the emission of O₃ precursors must be quantified and, ozone production sensitivity to its precursors must be represented well.

The model calculations show that NO_x-sensitive chemistry is dominant in the SPZ thus the most effective control strategy can be mitigation of the NO_x emission. The gas refinery plants have the larger share than the petrochemical plants in NO_x emission and, the gas turbines are the principal source of NO_x emission in this region.

The composition of emitted VOCs from petrochemical plants is markedly different from other anthropogenic sources and contains more HRVOCs and, it is more likely to have NO_x-sensitive chemistry. As a result, controlling

Table 5: Process type share in HRVOCs emission in the SPZ, %.

process type	HRVOCs type	
	proylene	Ethylene
olefin process	52.12	70.01
Aromatic process	0.00	0.00
polymer process	39.1	29.99
methanol & ammonia	0.00	0.00
central utilities	0	0
gas refineries	8.78	0.00
total	100.00	100.00

the emission of HRVOCs is likely to change the region's chemical regime. In the SPZ, the main emission sources of HRVOCs are located in the olefin processes and then polymer production plants.

This fact that the EI composition of the SPZ is much different from the typical urban area has considerable implications for choosing or developing appropriate chemical mechanisms for air quality applications. For this study, we used OZIPR with SAPRC but, with the results of this survey, modification of the mechanism for better adjustment with the conditions of the region will be possible.

For the SPZ, using a mechanism in which there are more possibilities to represent more important species explicitly, is recommended. For example, developing a new version of the SAPRC that propylene and ethylene are presented explicitly can be proper.

It is needed to apply a better estimation method for quantifying the HRVOCs emission from its principal sources such as leakage of equipment in olefin processes. Additionally, the VOC profiles, especially those used for flares have high uncertainties. Some measurements are needed to achieve an improved species resolution.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article (resulting VOCs emissions) are available as an electronic supplementary table to this article.

ABBREVIATIONS

CAQMS	Continuous Air Quality Monitoring Stations
EBIR	Equal Benefit Incremental Reactivity
EI	Emission Inventory
GDAS	Global Data Assimilation
HGB	Houston-Galveston-Brazoria
HRVOCs	Highly Reactive Volatile Organic Compounds
IR	Incremental Reactivity
MIR	Maximum Incremental Reactivity
MOIR	Maximum Ozone Incremental Reactivity
NOx	Nitrogen Oxide
OZIPR	Research-oriented version of Ozone Isopleths Plotting package
R ²	Square of coefficient of correlation
RMSD	Root Mean Square Deviation
ROG	Reactive Organic Gas
SAPRC	Statewide Air Pollution Research Center chemical mechanism
SPZ	South Pars Zone
UGRB	Upper Green River Basin
VOCs	Volatile Organic Compounds

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