

# Source Apportionment of High Reactive Volatile Organic Compounds in a Region with the Massive Hydrocarbon Processing Industries

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## Abstract

In the Persian Gulf region, conditions are highly favorable for ozone air pollution and the region is a hot spot of photochemical smog. The elevated concentrations of reactive hydrocarbons co-emitted with nitrogen oxides from Hydrocarbon Processing Industries (HPIs), highly centralized in this region lead to the substantial photochemical ozone formation. The South Pars Zone (SPZ) in Iran encompasses large gas plants and petrochemical complexes and elevated concentrations of ozone were recorded by air quality monitoring stations in the SPZ. The first step to dealing with ozone air pollution is to quantify Volatile Organic Compounds (VOCs) emission and identify main emission sources. In this research, a reactivity-based VOCs emission inventory established to provide necessary input data for Air quality models and determine which compounds deserve relatively more attention in control strategy. To do this, first, a fully- speciated VOCs emission inventory was prepared. Then, VOCs were weighted by Maximum Incremental Reactivity scale. Results show that alkenes have the biggest role in mass emission (41%) and ozone creation (78%). Propylene, ethylene, isobutylene, and formaldehyde have the most important roles in ozone formation. In addition, the major sources of their emissions are the leakage of equipment in the olefin processes and polymer production plants. The contribution of VOCs in the emission inventory and reactivity-based emission inventory of the SPZ is pretty different from the inventory composition of typical urban areas and areas with gas production industries, but it has similarities with areas with petrochemical industries.

**Keywords:** Reactivity-based emission inventory, Speciation, HRVOCs, Reactivity scale

## Introduction

Photochemical ozone formation is an important air pollution problem in many areas. Although for human health, high peak values of ozone are of particular importance, permanent exposure to lower levels is also problematic (Bell, 2006; Pires, 2018). Furthermore, the concentration of about 0.04 ppm for extended periods of several months can cause crop loss and damage to natural ecosystems (Emberson, 2003). The gas-phase reactions of emitted Volatile Organic Compounds (VOCs) with oxides of nitrogen (NO<sub>x</sub>) in the presence of

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sunlight form ground-level ozone. Differences in atmospheric reaction rates, the way in which reactions affect ozone and atmospheric abundance of Individual VOCs can significantly affect ozone formation (Carter, 1987). For example, ozone formation can be completely different in typical urban areas from areas where industrial sources such as refineries, chemical plants, oil and gas production facilities are concentrated (Daum, 2003).

The Middle East region has almost more than half of the world's oil and gas reserves. The vast activities in processing oil and gas and their derivatives will be associated with remarkable VOCs and NO<sub>x</sub> emission. Therefore, this region is expected to face elevated ozone concentration and to affect vast areas. Satellite measurements confirm that average tropospheric column levels of ozone precursors are highest over oil ports and refineries in the Middle East (Barkley et al, 2017). A survey of the vertical distribution of ozone observed by Troposphere Emission Spectrometer over the Middle East indicates a High abundance of ozone of approximately 100 parts per billion (ppbv) in the middle troposphere in summer (Worden et al. 2009). This value is notable in comparison with 75 ppbv which is the ambient air quality standard of ozone in many countries. Other studies have shown that highly favorable conditions for ozone air pollution exist, especially in the Persian Gulf region, and severe ozone pollution events frequently take place over it (Lelieveld, 20015, 2009; Smoydzin, 2012; Zanis, 20014). Model calculations indicate that this is mostly because of local emissions and highly favorable weather conditions for ozone formation and long-distance transported air pollution fosters it (Lelieveld, 2009; Fountoukis, 2018).

The scale of the most studies which have done to investigate the ozone concentration in the Middle East was large, and they didn't take into account VOCs emissions from local sources, especially Hydrocarbon Processing Industries (HPIs), perhaps because of data shortage. Thereby, one of the main issues remained is to identify the role played by industrial sources of hydrocarbons in the Middle East ozone problem.

An intensive study was conducted in Houston and eastern Texas to provide a better understanding of the sources and atmospheric processes responsible for the formation of high concentrations of ozone observed in this area. Results showed Reactive alkenes from petrochemical industries in the vicinity of this city play an important role in the formation of ozone in Houston, Texas. (Czader, 2008; Allen, 2017; Ge,2018; Pan,2017). Assessments of the influence of emissions associated with Oil & Natural gas activity on regional O<sub>3</sub> production in several regions of the United States of America show that Oil & Natural gas VOCs have a great contribution (Field et al., 2015; McDuffie, 2016, Ahmadov., 2015; Brantley ,2015; Edwards et al., 2014; Gilman, 2013)

The South Pars Zone (SPZ) is located along the Persian Gulf coast. Huge gas processing plants and petrochemical complexes have been constructed in this zone to take advantage of the South Pars gas field, the largest independent gas reserve in the world. Plumes HPIs routinely are characterized by simultaneous strongly elevated concentrations of NO<sub>x</sub> and reactive VOCs. It is predicted that these conditions lead to the fastest rate of O<sub>3</sub> formation and highest yields per NO<sub>x</sub> molecule emitted (Ryerson, 2003). Intensive natural sunlight and moisture, and a rich source of anthropogenic NO<sub>x</sub>, and VOC emissions lead to high O<sub>3</sub> concentration in the SPZ and air quality monitoring stations in the zone also have recorded elevated ozone concentration.

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 Air-quality models (AQMs) need good speciation for accurate input data in order to make valid predictions. Furthermore, having speciated VOC emission inventory can help in selecting appropriate chemical mechanism for AQMs. Chemical mechanisms are used to describe complex processes relevant to the O<sub>3</sub> formation in AQMs. In these mechanisms, the chemistry of the organics is

treated by grouping or “lumping” together with a number of reactions and/or chemical species. One approach for determining kinetics and products of a group of organics is to weight the rate constants by the relative number of moles of the individual compounds in this class (Finlayson-Pitts, 1999). Thus, the atmospheric abundance of VOCs species affected directly by emission sources in each area, play a significant role in preparing a proper chemical mechanism for that area. Knowing atmospheric composition and Reactivity-based Emission Inventory (RBEI) can be useful for deciding which available chemical mechanism is appropriate for a region and which modification is needed to adjust it with the condition. In this survey, a fully speciated VOC Emission Inventory (EI) has been prepared for the SPZ. Atmospheric abundance and reactivity have been used in ranking compounds. Relative ground-level ozone impacts of emitted VOCs were quantified using the Maximum Incremental Reactivity (MIR) scale, which is widely used for this purpose (Carter, 2013). This EI and RBEI then have been compared to other regions. With this reactivity-based volatile organic compounds emission inventory, deciding which compounds need more attention than other compounds in regard to developing appropriate chemical mechanisms for this kind of regions would be possible. Also, it is useful for defining realistic and robust pollution control strategies which focus on those organic compounds which contribute most to ozone formation in SPZ.

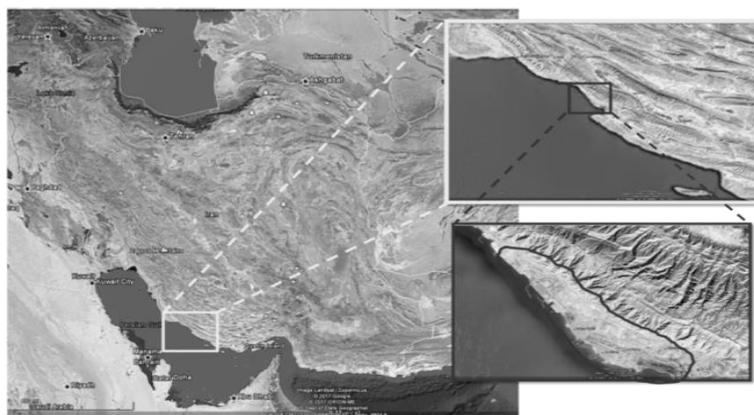
## Materials and methods

### *Domain of the study*

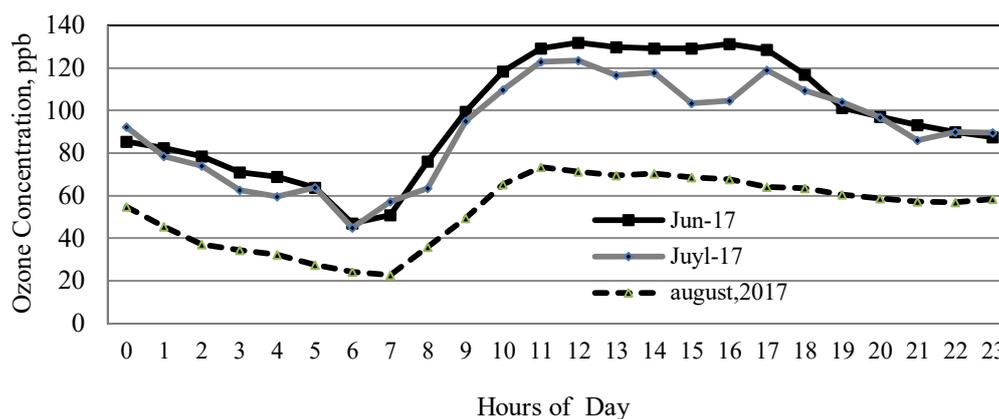
the SPZ South Pars Zone with 140 km<sup>2</sup> is located in the Persian Gulf coast in latitude and longitude 27.626 N and 53.05 E respectively, and approximately 100 km away from the South Pars Gas Field, the largest independent gas reserve in the world (Figure 1). Ten gas processing plants with production capacity of 80,000 million cubic meters of gas and 148 million barrels of condensate annually and sixteen huge petrochemical companies with the nominal capacity of 32 million tons per year have been constructed in this zone by 2016.

Ethylene, poly-ethylene, Propylene, Methanol, Ammonia, Granular Urea, Paraxylene, Benzene, O-Xylene, LPG are some of the main petrochemical products in the SPZ.

Hot, sunny climate, massive refining/petrochemical industry and complex coastal meteorology, all work together to create high ground-level ozone concentrations in the SPZ. The ozone concentration often exceeds the national ambient air quality standard of ozone (75 ppb) in this zone. Hourly ozone concentration for June, July and August (favorable time for photochemical formation of ozone) of 2017, recorded by an air quality station in the SPZ are shown in Figure 2.



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



**Figure 2.** Hourly average of ozone concentration (ppb) for 3 months of 2017 in the SPZ.

### *Approach for developing Emission Inventory for South Pars*

The inventory of the SPZ domain is comprised of data from the 16 petrochemical companies and 10 gas refinery trains. This emission inventory is a bottom-up emission inventory combining activity data, emission factors, modeling, and Engineering calculations. The emission inventory database which is prepared by Research Institute of Petroleum Industry of Iran was used for gas plants. There is another zone in Iran, where petrochemical companies are concentrated, called the Petrochemical Special Economic Zone. Since there are similarities between the petrochemical process in two zones, the EI of this zone prepared in 2016 (Ashrafi, unpublished results) has been used for some comparison and filling missed data. The approach followed to develop EI is described below:

1. To identify all emission sources, the process description and process flow diagram of each plant were reviewed.
2. The best methods for estimating the emissions were determined based on the preferred and alternative methods for estimating air emissions of EPA (Environmental Protection Agency of US) and Emission Estimation Protocol for Petroleum Refineries-version 2.1.1 (RTI International, 2011), hereinafter called "Protocol." These methods for each emission source category are listed in Table 2.
3. For selecting the most appropriate emission estimation methods and obtaining the most accurate data, we interacted with each company representative.
4. The data elements required to estimate emissions for each emission source category were specified, and Questionnaires were developed for obtaining data efficiently. Activity data for 2013, 2014 and 2015 were provided by companies through questionnaires.
5. The data were collated.

### *Speciation of VOCs*

There are no VOC emission measurements in the region, and the most methods used to quantify the mass emission rate, usually report only total non-methane VOCs (NMVOCs) so a subdivision into VOCs species was required. Speciation of VOCs is the top-down process of breaking the prepared EI of total VOCs into its constituents. In this study, Speciated VOCs are generally provided by choosing an appropriate VOCs profile for emission sources and then applying it for calculating total VOCs emissions. SPECIATE version 4.4 (EPA, 2014) was used for this purpose. Also, engineering calculations, site-specific emission factors and modeling are used whenever possible and applicable to provide the desired speciation. Due to desert nature of the area and its insignificant vegetation, only anthropogenic emissions are addressed.

### *SPZ's Reactivity- Based VOCs Emission Inventory*

The amount of HRVOCs being emitted have profound influence on Ozone formation. We can define reactivity as the potential of a given compound to make ozone. The reactivity and subsequent ozone formation potentials can be quantified by several metrics such as  $K_{OH}$ , MIR, MOIR and EBIR (Carter 2013).

The formation of ozone occurs through a sequence of reactions having the OH radical as driving Force during the day. Each organic compound reacts with hydroxyl (OH) radicals at a different rate, so this rate coefficient,  $K_{OH}$ , can be used to define a reactivity scale. However, organic compounds also react with ozone, nitrate radicals ( $NO_3$ ), or are photolyzed, so ozone productivity is not just a question of kinetic reactivity and also depend on the environment where the VOC is emitted.

MIR, MOIR, and EBIR are in the incremental reactivity scales family. Incremental Reactivity (IR) of an individual VOC is defined as changes in the amount of ozone produced (grams) due to the addition of small amount to the emission of that VOC(grams). When incremental reactivity is calculated in a rich  $-NO_x$  condition and thus the formation of ozone is the most sensitive to VOC emissions, the calculated IR is defined as the Maximum Incremental Reactivity (MIR). In lower  $NO_x$  conditions that result in the highest ozone concentrations, the calculated IR is defined as The Maximum Ozone Incremental Reactivity (MOIR) scale and when  $NO_x$  control and VOC control are equally effective in reducing ozone formation, Equal Benefit Incremental Reactivity (EBIR) scale is define.

MIR is used widely in VOC reactivity Evaluation because the MIR scale represents conditions where VOCs have the most effect on ozone formation (Liang, 2017; Ou, 2015). Accordingly, The MIR is the basis for several reactivity-based regulations. In the SPZ, MIR is a proper metric, due to a large amount of  $NO_x$  emitted in this area in comparison with VOCs. In this study, Combination of emission inventories, speciation profiles, and MIR was used in ranking the relative importance of different compounds in ozone creation in the SPZ according to equation (1) and developing a Reactivity-Based Emission Inventory (RBEI) in the SPZ.

$$\text{Rank of VOC}_i \text{ in Reactivity - based EI} = \frac{E_i \times MIR_i}{\sum_1^n E_i \times MIR_i} \quad (1)$$

Where  $E_i$  (ton/year) is annually emitted mass of the  $i^{\text{th}}$  compound in the SPZ,  $MIR_i$ (ratio) is maximum reactivity scales of  $i^{\text{th}}$  compound (Carter, 2013) and  $n$  is the total number of volatile organic compounds in EI.

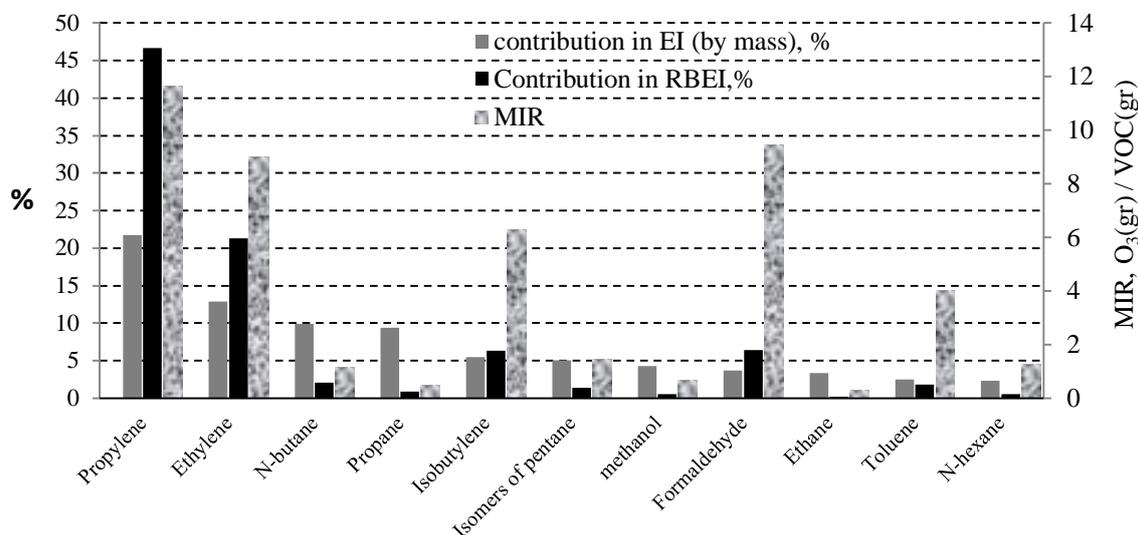
## **Results and discussion**

The VOCs emission inventory of 177 species was developed for the SPZ for 2015. The resulting VOCs emissions are available as an electronic supplementary table in this article. The Figure 3 represents the emitted mass and share of the individual VOC in total emission. The Results show 79.7 % of VOCs emissions in the SPZ are from petrochemical companies, and 20.2% are emitted from gas refineries. 99 % of the emitted mass is due to 48 compounds, so we limited the analysis to these compounds. Our results show the top 11 species contribute 80 % of the total emission (grey column in Figure 3). The most abundant species are propylene (21.7%), followed by ethylene (12.8%), n-butane (9.8%) and propane (9.3%).

When Emissions were weighted by MIR according to equation 1, as shown in Figure 3 by black column, the orders of substances differ significantly from those in mass emission inventory. Amounts of MIR for each compound are shown in the dotted columns in Figure 3. In RBEI, just four notable species remain, including propylene, ethylene, isobutylene and

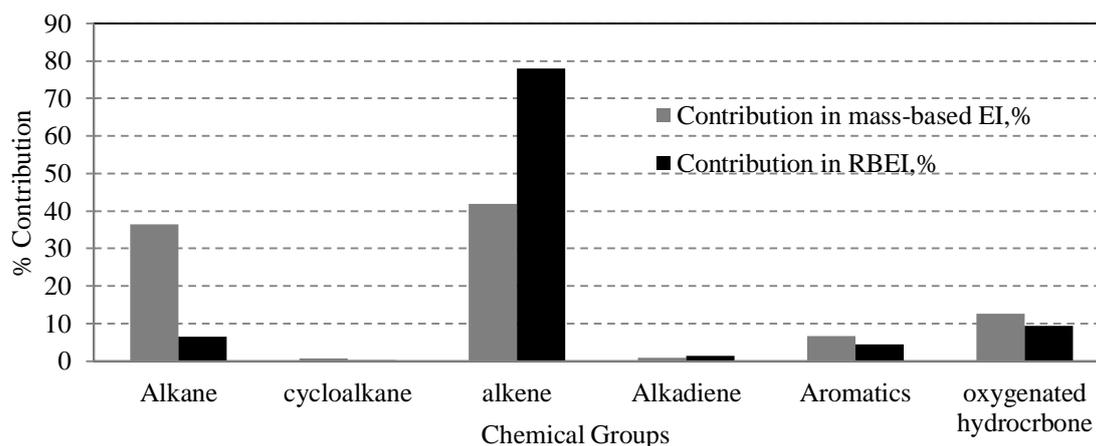
Formaldehyde with contributing 46.7%, 21.3%, 6.3% and 6.4% respectively. These four compounds, together, contribute more than 80% of the total RBEI while accounting for 43.7% of the total emission by mass. Since it sounds that these four compounds have the most important role in ozone creation in the SPZ, hereinafter called High Reactive VOCs (HRVOCs).

In this study, VOCs species divided into seven categories. Figure 4 shows emission contributions of these seven categories (grey column).



**Figure 3.** Comparison of the contribution of VOCs in Emission Inventory (by mass%, right axis, red column), Reactivity-Based Emission Inventory (% , right axis, blue column) and MIR (gr O<sub>3</sub>/gr VOC, left axis, yellow column)

The contribution of Chemical groups in RBEI is quite different from those in the mass-based inventory. As shown in Figure 4, alkenes contribute 78% in the RBEI while their corresponding mass-based emissions are 42%. In contrast, Alkanes account for 36.4% in mass-based emission, but just 6.5% in RBEI.



**Figure 4.** The contribution of chemical groups in EI and RBEI (%)

Emission sources were classified into the five categories shown in **Table 1**. Since most of the plants located in the SPZ, processing VOC-containing streams in high pressure and temperature, Equipment leaks, storage and process vents are the most important sources in the zone.

**Table 1.** Source apportionment of VOCs for five sources categories in the SPZ

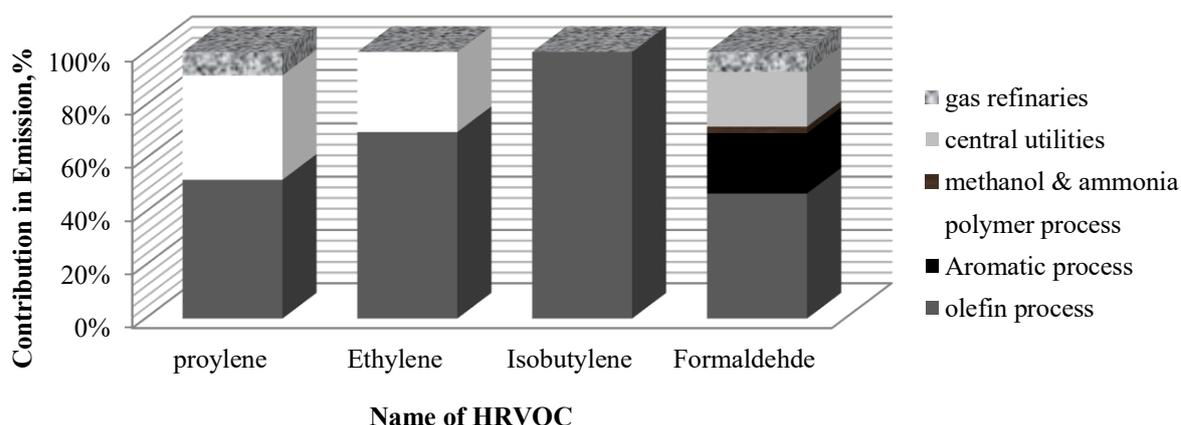
Source category	Petrochemicals, %	Refineries, %	Total, %
flares	10.80	2.97	9.35
Equipment leaks, storage, and process vents	63.67	83.45	66.82
Combustion	4.42	13.58	6.02
Loading	0.88	0.00	0.72
Cooling tower	20.92	0.00	17.09
Total	100	100.00	100.00

To rank industrial groups according to HRVOCs emission's amounts, industrial process apportionment has been done for six main industrial processes located in the zone. As Figure 5 shows, olefin processes with 62%, have the most important contribution in emissions of all the four HRVOCs. The second one is the polymer process with the 28.8% contribution.

The fact that the EI composition of the SPZ is much different from the typical urban area has great implications for choosing or developing appropriate chemical mechanisms for air quality applications. Some comparisons were done to identify these differences and similarities. This survey can be promising in choosing the proper chemical mechanism to have a more accurate modeling and more reliable prediction. Typical urban area, an Industrial City with refinery/petrochemical industry, and an industrial city with natural gas production industry were chosen for comparison.

#### *Typical urban area*

United States EPA for assessing how various reactive organic gas and NO<sub>x</sub> control strategies would affect ozone non attainment in various areas throughout the country developed a set of scenarios (Carter, 1987). Briefly, 39 urban areas in the United States were selected based on the geographical representativeness of ozone nonattainment areas and data availability, and a

**Figure 5.** Process types' contribution in HRVOCs Emission in the SPZ, %

Representative high ozone episode was selected for each. Then an "averaged conditions" scenario was derived from the averages of the relevant inputs of the 39 base case scenarios. The speciation for this mixture was derived by Croes (Croes, 1991; Croes, 1994; Lurmann, 1992) based on an analysis of the EPA database of the hydrocarbons and the 1987 Southern California Air Quality Study (SCAQMS) database for the oxygenates. This "averaged conditions" was used as Base ROG Mixture for developing MIR and species lumping in

SAPRC mechanism (Carter, 2010). Table 2 shows the composition of these averaged conditions (by carbon) and species contribution in mass-based EI of the SPZ based on same hydrocarbon groups. Since large amounts of emissions take place in a small area in the SPZ, it is assumed that ambient and EI composition is the same.

The main difference is between the contribution of alkanes, alkenes, and aromatics. Alkanes are the most abundant species in the typical urban ambient air, but in the SPZ, alkenes are the most. On the other side, aromatics contribution in the typical urban area is more than the SPZ.

**Table 2.** The Relative amount of hydrocarbon groups in the base ROG mixture used to represent emissions from all sources in averaged conditions of 39 American urban used to prepare MIR and SAPRC mechanism and contribution of hydrocarbon groups in mass-based EI of the SPZ (by carbon %).

NO.	Compound name	39 American cities	SPZ (present study)
1	alkanes	52	38.10
2	alkenes	15	45.65
3	Aromatics	27	7.74
4	Formaldehyde	1	1.87
5	higher aldehydes	2	0.38
6	Ketones	1	0.19
7	acetylene	2	0.28
8	others	0	5.79

Alkanes, alkenes, and aromatics are the three main chemical groups participating in EI of these two type areas. Reactivity of hydrocarbon groups decreases as aromatics>alkenes>alkanes, (Carter, 2013) but according to corresponding MIR, the difference between reactivity of aromatics and alkenes is much less than the difference between reactivity of alkanes and alkenes, therefore, the SPZ has more reactive species in its atmosphere because emission of aromatics + alkenes in the SPZ is greater than emission of aromatics + alkenes in typical urban area and accordingly, ozone formation potential should be higher in the SPZ in comparison with typical urban area.

#### *Industrial city whit refining/petrochemical industry*

Houston-Galveston-Brazoria (HGB) has a large urban population and a massive refining/petrochemical industry. The 2000 Texas Air Quality Study (TexAQS I) and The 2006 Texas Air Quality Study (TexAQS II) were conducted in eastern Texas to discover the role played by VOC species in the rapid, intense formation of ozone in this ozone nonattainment area (Daum, 2003; Parrish, 2009). The analysis concluded that, while some compounds (e.g., alkanes) occasionally caused high reactivity, those frequently responsible for high reactivity days have been propylene, ethylene, butenes (1-butene, cis-2-butene, trans-2-butene), and 1,3-butadiene. Substantial emission reductions of these compounds were hypothesized to make a large impact on elevated ozone, rapid ozone formation, and transient high ozone observed in the Houston area.

The Table 3 shows the results of the fully-speciated EI of the HGB and corresponding values in EI of the SPZ. There is more similarity between compositions of these two EI due to the similarity of sources, but as the Table 3 shows the most important species such as Ethylene and Propylene have more contributions in EI of the SPZ than the HGB.

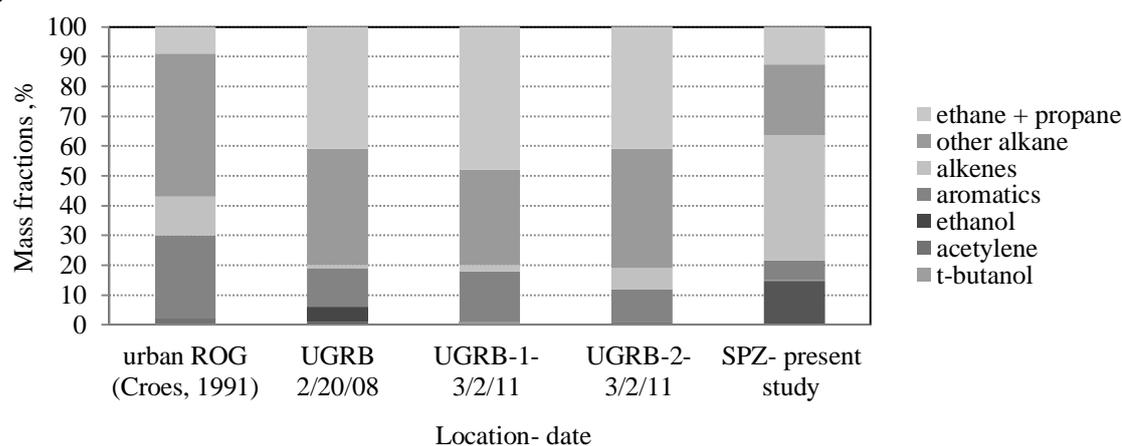
**Table 3.** Contribution of VOCs in EI of HGB and EI of the SPZ by mass

NO.	Compound Name	HGB, %	SPZ, %
1	Propane	7.00	9.38
2	N-butane	7.00	9.87
3	Ethylene	6.00	12.86
4	Propylene	6.00	21.76
5	methanol	5.00	4.28
6	Isobutane	4.00	2.01
7	Isomers of pentane	4.00	5.03
8	hexane	4.00	2.34
9	Benzene	3.00	2.07
10	pentane	3.00	2.03

### Industrial City Whit natural gas production Industry

William P.L. Carter and John H. Seinfeld studied the 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 (Carter, 2012). They assumed that gas production operations are the sole emission sources in UGRB. Accordance with this paper, total production in 2008 was approximately 24 million cubic meters of gas and 7 million barrels of condensate. These values for the SPZ are 80,000 million cubic meters of gas and 148 million barrels of condensate annually. Although the volume ratio of condensate to natural gas in UGRB seems very high and incorrect, UGRB's gas production capacity is very low in comparison with the SPZ. Anyway, it could be useful to compare EI of UGRB with the SPZ due to the similarity with the emission source type.

The conditions of two ozone episodes in 2011 and 2008 winter seasons resulted in additional high O<sub>3</sub> concentration for the UGRB were modeled as part of this study. The conditions of two ozone episodes in three locations of UGRB were represented in Figure 6 and compared with the composition of EI of the SPZ and ROG mixture used to represent emissions from all sources in averaged conditions of 39 American urban (Carter, 1994; Carter, 2010).



**Figure 6.** Mass fractions of various types of VOCs in ambient mixtures used in the UGRB simulations for the conditions of two ozone episodes and EI of the SPZ. The urban ROG mixture used in the MIR and other Carter reactivity scale is shown for comparison. The mixtures are grouped by similarity. the picture is reproduced from (Carter, 2012)

Figure 6 depicts a big difference between the SPZ profile and UGRB. In UGRB, alkanes play the main role, but in the SPZ, alkenes are the main. This leads to two results: first, the reactivity of the ambient mixture in SPZ is much higher than UGRB and second confirming the results of the previous section; ozone formation in the SPZ is more affected by petrochemical sources.

Therefore, chemical mechanisms that were developed or modified for regions with petrochemical industries such as HGB can be useful for the SPZ.

Heo et al. Modeled alkaline chemistry for conditions relevant to southeast Texas-USA analyses showed adding just one additional species to explicitly represent propene (the most important species on our list) in SAPRC condensed chemical mechanism. Using the reactions of this explicit model species resulted in ozone predictions that were more robust to changes of the propene concentration (Heo, 2010; Heo, 2012).

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 which just propylene, ethylene, isobutene and Formaldehyde are presented explicitly can be proper.

## Conclusions

The plumes from HPIs routinely are characterized by simultaneous strongly elevated concentrations of NO<sub>x</sub> and reactive VOCs, and these conditions lead to the fastest rate of O<sub>3</sub> formation and highest yields per NO<sub>x</sub> molecule emitted. Satellite measurements and model calculations 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. The previous studies that investigated this issue in the Middle East didn't pay attention to the amount and composition of emitted VOCs from many HPIs located in this region. The composition of emitted VOCs from HPIs is markedly different from other anthropogenic sources and contains more Highly-Reactive VOCs (HRVOCs). In this study, we tried to characterize VOC emission from a zone with highly centralized HPIs in the Middle East and specify Highly-Reactive VOCs, which play the main role in ozone formation in this region. Air quality in the SPZ is heavily influenced by HPIs concentrated in this zone. Additionally, Hot and sunny climate and complex coastal meteorology intensify the ozone formation in the SPZ.

Preparation of Reactivity-Based Emission Inventory of VOCs is the first step in formulating proper and cost-effective control strategies to reduce O<sub>3</sub> Levels. The RBEI can be useful in two ways: first, preparing appropriate chemical mechanism used in AQMs to obtain a valid prediction. Second, by knowing the relative importance of compounds emitted from large industrial hydrocarbon sources located in this region, Control strategies can be effectively defined.

The results of this study show alkenes have the most contribution to mass emission (41%) and ozone creation (78%). Propylene, ethylene, isobutylene, and formaldehyde probably have the most important role in the ozone formation in the SPZ, and the major sources of their emissions are the leakage of equipment in the olefin process and then polymer production plants, but Air Quality modeling is needed to confirm these results. The petrochemical plants have more influence on ozone formation than gas production plants because the most HRVOCs are emitted by them. These results are in good agreement with the Texas Air Quality Studies (TexAQS I, TexAQS II) and the first and second substances in the prioritized list of both regions are the same (e.i. Propylene, ethylene), but as expected, there were significant differences with the urban areas because of differences between emission sources. There were differences with the city with natural gas production industry too because the gas

production plants play a much lower role in the emission of HRVOCs rather than the petrochemical units.

The underlying database can be used as input data for AQMs and the results can be used to select and modify chemical mechanisms, which are more proper to atmospheric composition in the SPZ. The SAPRC mechanism in which there are more possibilities to represent more important species explicitly is recommended. The toxic version of SAPRC-07, SAPRC-07T can be proper for use in air quality modeling of the SPZ.

In preparation of EI, some assumptions and simplifications have been entered that modification can result in more accurate estimations. For example, Leakage of equipment that shows the most important role in HRVOC emission was estimated based on default emission factors. Of course, it is needed to make a better estimation based on more accurate methods. The profiles, especially those for flares and leakages have large uncertainties. There is an enormous need for measurements to achieve an improved species resolution. Additionally, it is needed to evaluate this emission inventory against ambient measurements to confirm the results of HRVOCs of the SPZ.

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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

