SOURCE APPORTIONMENT ANALYSIS OF MEASURED VOLATILE ORGANIC COMPOUNDS IN CORPUS CHRISTI, TEXAS

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Corpus Christi among of the largest industrialized coastal urban areas in Texas. The strategic location of the city along the Gulf of Mexico allows for many important industries and an international business to be located. The cluster of industries and businesses in the region contribute to the air pollution from emissions that are harmful to the environment and to the people living in and visiting the area. Volatile organic compounds (VOC) constitute an important class of pollutants measured in the area.

The automated gas chromatography (Auto GC) data was collected from Texas Commission of Environmental Quality (TCEQ) and source apportionment analysis was conducted on this data to identify key sources of VOC affecting this study region. EPA PMF 3.0 was employed in this sources apportionment study of measured VOC concentration during 2005 - 2012 in Corpus Christi, Texas. The study identified nine optimal factors (Source) that could explain the concentration of VOC at two urbane monitoring sites in the study region.

Natural gas was found to be the largest contributor of VOC in the area, followed by gasoline and vehicular exhaust. Diesel was the third highest contributor with emissions from manufacturing and combustion processes. Refineries gases and evaporative fugitive emissions were other major contributors in the area; Flaring operations, solvents, and petrochemicals also impacted the measured VOC in the urban area. It was noted that he measured VOC concentrations were significantly influenced by the economic downturn in the region and this was highlighted in the annual trends of the apportioned VOC.
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ACKNOWLEDGMENT

I was privileged to have the help and support of many wonderful people in my life who have helped, taught, and enlightened my vision to continue my education and the path of knowledge.

The rich experience and the wise input I have learned from my thesis supervisor and advisor Dr. Kuruvilla John made the journey of writing this thesis wonderful, rich, smooth, and a joyful destination. Without his support and believing in my abilities, this work would not be written and documented, and I will always be indebted for him; thank you.

My family and friends thank you for all the times you helped me; you taught me many valuable lessons in all the aspects of my life; I would not be the man I am today without your help and support.

Here at the University of North Texas I have learned a lot, gained knowledge and wisdom at your classes. You have opened my eyes in many ways to be a better person. Thank you; it was a wonderful experience.
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CHAPTER 1
INTRODUCTION

Volatile organic compounds (VOC) are a major class of primary pollutant that are harmful to the environment and human health. VOC are also suspected of causing cancer and other serious deleterious health effects (Bhawan et al., 2008). Toxic volatile organic compounds along with other VOC form more than 80% of the compounds in the federal hazardous air pollutant list (Anderson et al., 2002) as per the Clean Air Act of 1990 (EPA, 1990). Because of large emissions that are readily vaporized at low temperatures, some of the photochemically reactive hydrocarbons could potentially form ground-level ozone (Sarkhosh, 2010). Depending on their chemical structure and reactivity, the VOC are important in the oxidation process that produces ground-level ozone which happens by the reaction of NOx and VOC under the influence of sunlight (Cheremisinoff, 2002). Corpus Christi urban airshed is currently in attainment with the national ambient air quality standards however this area is close to violation standard for ozone (Karnae et al., 2013) so it is important to study precursor chemical such as VOC as potential sources contributing to ozone formation. VOC are typically emitted from different sources including combustion processes, solvents operations, industrial operations, household, chemicals, commercial products, gasoline, kerosene, and other fuel types (Sanchez et al., 2008).

Receptor models like chemical mass balance (CMB), positive matrix factorization (PMF), and principal component analysis/absolute principal component analysis (PCA/APCA) are models that can be used to quantify the contributions of a particular source at a receptor site. CMB is used as single- sample receptor model. While PMF is a multivariate technique used to simulate a number of VOC factors as well as their chemical composition (EPA, 2008). Both
CMB and PMF have the same aim but they have different mechanisms. With CMB the user must provide a source profile which the model uses to apportion mass. In a comparison study between CMB and PMF it was found that major factors correlated in a good manner and had a similar magnitude, but PMF can identify additional factors that are not found in CMB even though good correlations were found between factors (EPA, 2008).

Numerous studies have been conducted around the world to evaluate the number and the sources emitting VOC in various regions. Different model receptors were used and different numbers of sampling were collected for varying number of VOC. In Clinton Drive site in Houston, a study was conducted in 1998-2001 using 40 measured VOC that employed PMF and UNMIX and 15 sources were resolved (Brown et al., 2003). In Melbourne, Sydney, and Brisbane, in Australia, where a study was conducted in 2003-2004 using 14 measured VOC and PMF was used to resolve 5 sources responsible for these VOC in each of the urban area (Chan et al., 2008). In Azusa Los Angeles model produced 6 sources was identified using PMF on 32 measured VOC 32 concentration data between 2001 and 2003 (Brown et al., 2005). In Houston another study used PMF at 2001 for three sites and resulted in 7 sources (Chan et al., 2008). Other studies employed CMB and resolved 8 sources in Mumbai with VOC measurement at 12 site (Srivastava, 2004)

EPA PMF 3.0 is a multi factor analysis tool which speciates matrix samples data into two matrices: one is the factor contributions and the other is the factor profile. The non negativity of the resulting matrices makes the data easier to inspect and analyze, since the profiles are not easily discernible in the first place. (Hopke, 2000).

The influence of wind (directional component) could be assessed using conditional probability function (CPF) as tool. As wind direction is important to locate where the highest
concentrations of the samples are coming from, it can reveal the frequency of wind orientation for each modeled source factor during the highest contributions. CPF uses wind direction rather than wind trajectory to determine the likely direction of the source (Brown et al., 2003).

In the present study, EPA PMF 3.0 along with CPF was employed to study the measured VOC concentrations in Corpus Christi, Texas for a comprehensive source apportionment analysis.

1.1 The Study Area

Corpus Christi is a coastal city located along the Gulf of Mexico. The city is home to one of the largest ports in the nation (and the deepest along the Gulf of Mexico), six oil refineries, over 1500 oil wells, chemicals, fabrication sites, metals, and many other products being produced near the bay and this has made it an important hub for many industries. With a population of almost 450,000 in the metropolitan area, it is the 8th highest populated city in Texas. The port of Corpus Christi is the fifth largest port in the USA. The city has a humid subtropical climate (Sanchez et al., 2008).

The semi-arid region of Corpus Christi is equipped with many air quality monitoring stations; some of them are operated by the University of North Texas in collaboration with Texas A&M University-Kingsville. The two sites chosen for this study are operating by the University of Texas and they collect samples monitoring data that is made publicly available by Texas Commission of Environmental Quality (TCEQ).

Only three monitoring sites in Corpus Christi uses the automated gas chromatography (Auto GC) for measuring VOC and they are located at Oak Park in Nueces county, Palm in Nueces county, and Solar Estate also in Nueces county. For this study only two sites were chosen
(Oak Park and Solar Estate) because of the amount of the available sample data over a long period of time. All of these sites are adjacent to major urban and industrial activities.

Details of the Oak Park site at the Nueces County location (data taken from GeoTAM viewer from TECQ website) are shown below:

- Figures 1.1 and 1.2 show TCEQ monitoring site Oak Park C634 EPA site number: 48-355-0035
- State: Texas
- County: Nueces
- City: Corpus Christi
- Address: 842 Erwin St.
- Site coordinates:
  - Latitude: 27° 47' 56.00" North (+27.798889°)
  - Longitude: 97° 26' 2.00" West (-97.433889°)
  - Elevation: 10 m (33 ft)

Maintained by: ORSAT & TMSI for the UT CEER COCP Project (TCEQ, GeoTAM Viewer, 2013)

Figure 1.1 . Location of the monitoring site 842 Erwin St. C 634.
Details of the Solar Estate site in Nueces county (data taken from GeoTAM viewer from TECQ website) are shown below:

- Figures 1.3 and 1.4 show TCEQ monitoring site Solar Estate C633
- EPA site number: 48-355-0041
- State: Texas
- County: Nueces
- City: Corpus Christi
- Address: 9122 Leopard St
- Site Coordinates:
  - Latitude: 27° 49' 45" North (27.8291667°)
  - Longitude: -97°32' 37" West(-97.543611°)
  - Elevation: 12.0 m

Owned By: UTCEER (TCEQ, GeoTAM Viewer, 2013)
1.2 Goals and Objectives

• Identify key VOC sources in Corpus Christi, Texas, by finding the number of factors that explain the emission characteristics affecting this region.

• Quantify the species by concentrations for each factor to identify the factor by profile and species concentrations.

• Explain the unique signature of each factor (for example, which industry contributes) to the ambient VOC measured in the area.

• Analyze the contribution of each factor, to obtain temporal results that explain the highest VOC polluted periods.

• Show that the strong relation between these pollutants, the relevant industry, and the economy can be simulated by data and reveal a realistic picture of pollution trends.

• Understand the differences and similarities between the number of factors, factor concentration percentages, modeling methods, chemical compositions and species
concentrations; this study compares the results from different locations within the city as well as with similar studies for different regions.

1.3 VOC Measurement

The automated gas chromatography sampler (Auto GCs) located in Corpus Christi area are used to measure VOC concentration through one 40-minute sample and it is analyzed on the site automatically and data is collected hourly (Texas Commission on Environmental Quality, 2013).

The data are measured in ppbC units only for the non methane hydrocarbons. The available data include 46 VOC species. The data from Auto GCs operating in Solar Estate (CAM 633) and Oak Park (CAM 634) (Texas Commission on Environmental Quality, 2013) was employed at this study.

1.4 Data

VOC data were collected from the TCEQ public data website and used in the modeling analysis for the two operating locations. For both Oak Park and Solar Estate sites, data was collected from 2005 to 2012. The collected data was formatted and the uncertainty matrix was created with the same dimensions as the concentration data sample matrix according to the EPA PMF 3.0 user guide (EPA, 2008). Some sample data were missing and some data values were below detection limit. About 20% of the total sample data for Oak Park and about 21% of total sample data for Solar Estate were either missing or below detection limit.

One of the important features of EPA PMF 3.0 when compared to other source apportionment tools is that PMF 3.0 can individually weight each sample of data and adjust the influence on the weight. This along with the modified uncertainty for such samples reduce the
influence on the solution. Thus the missing data or data below detection limit will have less
influence on the solution matrix (EPA, 2008).

Samples were collected for Oak Park between 2005 and 2012 and the total samples for
all species were 3,226,992 hourly samples (46 Species). All hourly concentrations of species
were averaged on a daily basis. Furthermore the analysis was conducted on 134,458 daily
average concentrations for all species at Oak Park 2005-2012. Solar Estate sample data
collected had exactly the same matrix dimensions of data as well.

1.5 Volatile Organic Compounds Group Classification

Only the non methane hydrocarbons were measured at the Auto GC sites (CAM 634,
and CAM 633) in Corpus Christi. Table 1.1 below specifies which species were used in this
study, the measured sampled compounds, the air quality system (AQS) code, and their main
groups of hydrocarbons (46 VOC species) are listed.

Table 1.1 Species name, AQS code and main group of hydrocarbon

<table>
<thead>
<tr>
<th>AQS Code</th>
<th>Species Group</th>
<th>AQS Code</th>
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<th>AQS Code</th>
<th>Species Group</th>
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<td>1,2,3-trimethyl benzene</td>
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<td>45201</td>
<td>Benzene</td>
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<td>45208</td>
<td>1,2,4-trimethyl benzene</td>
<td>Aromatic</td>
<td>43217</td>
<td>C-2-butene</td>
<td>Olefin</td>
</tr>
<tr>
<td>43218</td>
<td>1,3-butadiene</td>
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CHAPTER 2

METHODOLOGY

2.1 Positive Matrix Factorization Version 3.0 (EPA PMF 3.0)

United States Environmental Protection Agency Positive Matrix Factorization (PMF) version 3.0 is a multivariate factor analysis tool that conceptualizes mass conservation and mass balance as the methodology used in the program (EPA, 2008). All the receptor modeling employed in air pollution studies are based on the factor analysis technique (EPA, 2008; Hopke, 2000). PMF is a multivariate receptor model that utilizes the least square technique (Paatero, 1997).

The measured data sample concentrations matrix is decomposed into two matrices: one is the factor contributions and the other matrix is the factor profile. The data sample can be viewed as a matrix $X$ of dimensions $i$ by $j$, where $i$ is the number of samples representing the dates they were taken at, and $j$ represents the number of the chemical species measured as shown below in equation 1 below.

$$X_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \quad \text{......(1)}$$

where $X_{ij}$ represents the concentration of measured species $j$ in sample $i$, $P$ is the number of factors that the analyst will estimate, $f$ the species profile of each factor, $g_{ik}$ the amount of mass contributed by each factor, and $e_{ij}$ residual for the model fit of each sample species (Brown et al., 2003).

The aim of the program is to minimize the object function $Q$ (the sum of squares) based upon the uncertainties as shown below in equation 2 below.

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[ \frac{e_{ij}}{u_{ij}} \right]^2 = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[ \frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{u_{ij}} \right]^2 \quad \text{(2)}$$

where $u_{ij}$ is the known matrix of error estimations, $n$ is the elements, and $m$ is the samples.
This equation represents the least square problem in which \( \psi_{ij} \), the residual, is minimized and therefore \( Q \) is minimized. The optimization is done to get the best fit when the residual reaches minimum difference between the observed and fitted data (EPA, 2008; Hopke, 2000). Using EPA PMF 3.0 no source should have negative concentration or negative contribution according to fundamental and natural physical constraints. Also the original data must be reproduced by the model.

The program allows for each sample data point to be individually weighted, with the flexibility to downweight and reduce the influence of the uncertainty and below-detection limits using a modified uncertainty matrix and, therefore, downweighting a species can be achieved (EPA, 2008; Hopke, 2000).

For part of the analysis the user must indicate how much confidence he/she has in the data by supplying an uncertainty file; the uncertainties are not always reported and must be estimated by the using equations 3 and 4 below.

Concentration > minimum detection limit (MDL)

\[
Unc = \frac{5}{6} \text{MDL} \quad \ldots \ldots \text{(3)}
\]

Concentration < minimum detection limit (MDL)

\[
Unc = \sqrt{(Error \ Fraction \times Concentration)^2 + (MDL)^2} \quad \ldots \ldots \text{(4)}
\]

where \( MDL \) is minimum detection limit, \( Error \ Fraction \) is experimental value depend on the confidence in data and the region, and \( Concentration \) is the original measured concentration for each data sample (EPA, 2008).

Signal to noise ratio (S/N) can specify if the variability in the data is really present or if it is within the noise of the measurements and it is calculated by equation 5 below.

\[
\left( \frac{S}{N} \right)_j = \sqrt{\frac{\sum_{i=1}^{n}(s_{ij} - \bar{s}_{ij})^2}{\sum_{i=1}^{n}s_{ij}^2}}
\]

where \( s_{ij} = \psi_{ij} \) is the heuristic error estimates.
Classification of the species can be done using the S/N ratio. Species can be classified as follows: if the ratio is less than 0.2, the species is categorized as bad, between 0.2 and 2, categorized as weak, and above 2, categorized as strong. The data have to be categorized by the user as strong, as the default, or as bad or weak (Figure 2.1). The data categorized as bad will not contribute to the factor and will instead only contribute to the noise in the results, because the default is strong. When modified the species categorized as bad will not contribute to the rest of the analysis, and classifying species as weak will triple the uncertainty in the analysis.

![Figure 2.1. Example signal to noise ratio (S/N) program interface (EPA, 2008)](image)

The residual analysis histogram (Figure 2.2) can be used to judge how well each species fits by the model, and when species have a large residual or non-normal curve, it is an indication of poor simulation for the species (EPA, 2008).
2.2 Determination of the Number of Factors

One approach is using multi linear regression test for total mass concentration of the resultant matrix compared to the measured mass concentration. It is a good indication of the correct number of factors since there should be no negative mass emitted and produced by the simulation of factors (all coefficients of the factors should be positive) and if it appears (negative) then the model was forced to the wrong number of factors (Brown et al., 2003).
Another good indication of number of factors is the optimization of the theoretical Q values (Figure 2.4). In factor analysis rotation ambiguity is inherent. A unique solution may not be found even with the global minimum squares. PMF 3.0 applies the non-negative constraint which can reduce the rotational freedom; this along with using F peak values to manage the rotation, F peak is zero by default, and when forcing the F peak values to be non zero values, the Q values also change and slightly positive values give more interruptible results, and the best meaningful results will occur before the noticeable raise in Q value (EPA, 2008; Brown et al., 2003).

![Figure 2.4. Example Q value against F peak graph (Brown et al., 2003)](image)

Another technique to determine the correct number of factors is also by examining the residuals to see if they are well fitted and normally distributed in the plotted residual distributions. If they are not symmetrical and have a wide spread in the residual, then the number of the factor should be changed (EPA, 2008; Brown et al., 2003).
The observed verses predicted values (Figure 2.5) can be a good indication of how well the model regenerated the sample data when the data were not fitted to each other and the values are far apart, and then the species could be downweighted form further analysis (EPA, 2008; Puthenparampil, 2012).

![Figure 2.5. Example Observed vs predicted values (well modeled left, and poorly modeled right) (EPA, 2008)](image)

2.3 The Conditional Probability Function (CPF)

Wind direction and geographical location are key indications for the location of VOC emissions affecting the measured concentrations in certain sites. CPF can be used to identify the location of the high concentrations (Figure 2.6) and point to the source. It is a useful technique for verifying the direction of the highest concentrations for individual sources. The function could identify the possible source location origin, as seen in equation 6

$$CPF = \frac{m_{\theta}}{n_{\theta}}$$  \hspace{1cm} \ldots \ldots \hspace{1cm} (6)$$

in which $m_{\theta}$ is the number of simulated data points that exceeds the 75th percentile of all data concentrations in the wind direction of $\theta$ while $n_{\theta}$ is the number of all data in the same direction of $\theta$. Missing wind direction was excluded from the study, wind sectors are divided into 30° segments to simulate the best accuracy of the wind’s highest concentrations per direction (Brown et al., 2003).
The results of PMF 3 are used to execute the CPF analysis as well as wind directions (also collected from the TCEQ website). By using CPF to plot polar coordinates that show the directions based on the magnitude and the angle of the wind direction. This would locate where the fraction of sample are coming from (Puthenparampil, 2012).

Data need to be adjusted in order to be used in the CPF analysis. Wind directions need to be arranged and fitted with its days in conjunction with the highest concentrations within the same dated days with no wind directions being eliminated and also negative and zero concentrations should be removed to get accurate results.

Figure 2.6. Sample CPF plot
CHAPTER 3
RESULTS AND DISCUSSION

Multiple runs and detailed analysis were done using PMF 3.0 and CPF to find the correct number of factors representing the sources of VOC affecting the study region. More than one technique was used to identify the correct number of factors. The various techniques used include the multi linear regression test, optimizing the Q value against the F-peak, residual analysis curve orientation, and observed/predicted concentration evaluation. Signal to Noise S/N ratio was classified for each species and adjusted from the standard value (strong by default) to its appropriate categorization according to the S/N values for a robust solution. Several numbers of factors were tested (between 7 and 11 for both Oak Park and Solar Estate) robust results were established at 9 factors, which showed positive values for all the coefficients of the factors. Strong r² values (the coefficient of determination for how well the data points fit the statistical model) of 0.98 for Oak Park and 0.96 for Solar Estate were calculated. The conditional probability function analysis strengthened the results by showing where these VOC were coming from.

3.1 Oak Park
3.1.1 PMF Results

In this study 9 factors were found to be optimal in describing the source contribution of VOC concentration in the area; the Q values did not rise sharply with the F-peak change. All the coefficients for the multi linear regression test showed positive values; no residual value had a large residual or non-normal curve.
Some species were downweighted in the analysis of data from Oak Park. 1, 3 butadiene and isoprene were downweighted because these two species showed a poor fit of predicted to simulated concentration results. And, the $r^2$ values were low for those two species. Results from this analysis are highlighted in Appendix A.

3.1.2 Analysis of Apportioned Factors

The overall results obtained for Oak Park are highlighted in figure 3.1, where the percentage contributions by source (factors) types are displayed on a pie chart.

![Figure 3.1. Percentage contributions by source factors at Oak Park](image-url)
3.1.3 Factor 1 (Natural Gas)

Natural gas has the highest percentage contribution among the sources identified at Oak Park. At 26.62% of the overall VOC contribution at the site, natural gas components from multiple sources are a significant contributor to the overall VOC concentrations observed at Oak Park. The species profile of this factor concentrations and percentages are shown figure 3.2 which indicate clear signature of natural gas with ethane ranked the highest within the factor along with significant amount of, propane, isobutane, n-butane and some ethylene.

The shale gas revolution in the last decade increased the amount of natural gas produced, processed, handled, transmitted, storaged and exported. The petroleum industry in Corpus Christi uses large amount of natural gas as feedstock. All these operations and facilities have burning and leaking of natural gas which contributes to the total VOC emissions in the area.

The site location is adjacent to major refineries and to Nueces Bay. The CPF plot confirmed the direction where the VOC in this factor were coming from and showed that the highest contributions were coming from the northeast, northwest and south, the first two directions pointed to the nearby petroleum refinery facilities as the primary source as shown in figure 3.3.
3.1.4 Factor 2 (Refinery Gases)

Refinery gases has the fifth highest contribution at this site with 10.01% of the overall contributions. The factor is composed of paraffins or alkanes, olefins or alkenes, and aromatics and is typical of VOC from refinery gases see (figure 3.4). The refinery process gases can be produced from separation, conversion or treatment of the crude oil and natural gas, using equipment such as furnaces or cracking units, among many other equipment that could potentially be the emissions source. Fuel gas is produced as a supplementary product of refining in the furnace and also used as a fuel for the furnaces. Residual cracking units are another
possible source for the refinery gases that break the long chained hydrocarbons into smaller shorter chains of hydrocarbons (USA RTI, 2011).

Oak Park is adjacent to major refineries, and their VOC emissions are significant contributors to the air pollution in the area. The CPF plot showed that the VOC came from the north and pointed to the nearby refinery facilities as primary sources as shown in figure 3.5.

Figure 3.5. CPF plot factor 2 (refinery gases) Oak Park

3.1.5 Factor 3 (Solvents)

Factor 3 with a percentage contribution of 5.78% was the seventh highest source affecting this site. The species profile with concentrations and percentages of key species is
shown in figure 3.6. Toluene was the dominant species in this factor. Other species within this factor that have modestly high concentrations include benzene, styrene, o-xylene, cyclopentane, isopentane, and n-pentane. Thus this factor could be named as solvents with a strong signature of aromatics such as benzene, toluene and xylene.

Solvents can evaporate easily at room temperature and release their emissions; they are widely used for cleaning and degreasing, dissolving, thinning, dispersing, coating and painting. They are widely used in petroleum refineries. Another source of solvents includes domestic and commercial business usage.

The location and the surrounding industries play a great role in contributing to this factor, the CPF plot showed the sources came from the surrounding area with industries and residential all around the site as shown in figure 3.7.

Figure 3.7. CPF plot Factor 3 (solvents) Oak Park
3.1.6 Factor 4 (Evaporative Fugitive Emissions)

Evaporative fugitive emissions was classified as factor 4 with the second highest percentage contributions of 17.22%. The percentages and concentration of individual species are shown in figure 3.8. High concentrations of n-alkanes, n-alkenes, cycloalkenes, benzene and some toluene suggest a clear signature of evaporative fugitive emissions.

Leaks from pressurized equipment and tanks are responsible for these kinds of emissions. Most of these leaks are from industrial facilities with old infrastructure, poorly maintained and with unrepaired equipment. The monitoring at refineries report these leaks only if they presents over 2% escapage, and some are as easy to fix as to tighten the valves with a wrench and some require intensive repairing or replacing the equipment, thus leaks contributes evaporative fugitive emissions as major source category (Congressional Report, 1999).

Most of the evaporative fugitive emissions come from oil and gas processing and storage units. While refineries contribute to significant amount of VOC in the atmosphere, gas stations and other storage facilities also contribute to these emissions.

The CPF plot as shown in figure 3.9 highlights the directions from where the VOC emissions were coming as coming from northeast and northwest of the monitoring site.
3.1.7 Factor 5 (Gasoline and Vehicle Exhaust)

Factor 5 was classified as gasoline and vehicular exhaust with the third highest contribution of 14.95% affecting Oak Park. The factor species profile as shown in figure 3.10 primarily consist of ethane, tri-methylated species, di-methylated species, methyl alkanes, alkenes, and some cyclo compounds (paraffins, olefins, and aromatics). The highest concentrations of ethylene, acetylene, and the second highest concentration of benzene within
this factor strongly indicate the influence of gasoline and vehicle exhaust emissions. An abundance of VOC species was found in this factor.

Traffic emissions from the nearby highways and streets were directly responsible for this factor, this included traffic on interstate highway 37 and Leopard Street as shown in the CPF plot in figure 3.11. The highest concentrations came from the north and south and pointed to these major arteries.

The factor also indicates the potential influence of other source such as refinery processes involved in the manufacturing of gasoline.

![Factor 5 Gasoline and Vehichale Exhaust](image1)

Figure 3.11. CPF plot factor 5 (gasoline and vehicle exhaust) Oak Park

3.1.8 Factor 6 (Petrochemicals)

![Factor Profile](image2)

Figure 3.12. Factor 6 profile (petrochemicals) Oak Park
Factor 6 profile was classified as petrochemicals. This factor was influenced by high concentrations of benzene, ethane, propane, propylene, isopropyl benzene (cumene), and ethylene as shown in figure 3.12. The overall contribution of this source was about 4.72% of the total VOC measured at Oak Park.

Petrochemical VOC typically comes from vents, transfer processes, storage emissions, control, and disposal. Petrochemical manufacturing equipments produce intermediate or final products that are processed through several stages including pre-treatment of raw material, synthetics, and reduction (separation, refinement, and co-product recovery). In addition, fugitive emissions from leakage, wastewater, and cooling also contribute to this source type (Bhawan et al., 2008).

The CPF plot predominantly pointed to the north and northwest indicating the influence of major petrochemicals source nearby as shown in figure 3.13.
3.1.9 Factor 7 (Flare)

Flaring operation is a common practice in refinery, natural gas processing, and chemical plants. The process is used to destroy excess organic compounds, purged products, or waste gases. Factor 7 provided a strong signature of flaring operations due to the presence of propane, propylene, 1-butene, c-2-butene, and ethylene. This factor contributed 6.93% of the total VOC observed at Oak Park (see figure 3.14). The CPF plot as shown in figure 3.15 points to the north and southwest, indicating the influence of the flaring operations in the nearby refineries.
3.1.10 Factor 8 (Refinery 2)

Figure 3.16. Factor 8 profile (refinery 2) Oak Park

A second refinery factor was identified with a profile similar to an asphalt blowing unit factor 8 contributed to 3.12% of the total concentrations observed at this site. The profile of this factor is primarily represented by butanes, pentanes, propane, ethane, and some cycloparaffins as shown in figure 3.16.

An air blowing might be conducted at the petroleum refinery by bubbling air through the liquid asphalt and the emissions from this process include gases and hydrocarbons—those among other species. These gases are combusted by thermal oxidizer which gives a VOC profile similar to combusted flare gas (RTI, 2011). The CPF plot as shown in figure 3.17 shows that the emissions were primarily coming from the northeast and southwest of the site, again pointing major refineries along these two directions.

Figure 3.17. CPF plot factor 8 (refinery 2) Oak Park
3.1.11 Factor 9 (Diesel)

Factor nine represents the fourth highest source affecting Oak Park. This factor with 10.64% of the overall contributions was named as a diesel source. The profile of this factor as shown in figure 3.18 has high n-alkane, cycloalkanes, styrene and the BTX compounds (benzene, toluene and xylenes) primarily coming from diesel emissions.

Diesel can come from two different sources, diesel engine exhaust from combustion and leaks from handling and storage of diesel fuel. Both sources were counted as part of this factor. The CPF plot as shown in figure 3.19 highlights the influence of two major arteries Interstate Highway 37 and Leopard Street. Also, wind carrying emissions came from the nearby where the refineries’ facilities clustered together, indicating mobile sources in the facilities as well as the production and storage tanks with large diesel storage located along the that direction.
3.1.12 Temporal Contributions of the VOC Sources at Oak Park

EPA PMF 3.0 apportioned results were studied to detect inter-annual variability in the contribution of each factor detected. Results were plotted for 2005 through 2012 as shown in the figure 3.20. VOC contributions were dominant between 2005 and 2007. A sharp reduction in the VOC was noticed in 2008. This coincided with the economy down term affecting the region. Contributions of refinery and petrochemicals showed significant reduction post 2007. Since 2011 there has been a small uptick in the VOC represent improvement in the economy suggesting a moderate recovery in the overall economy.

Figure 3.20. Overall yearly contributions Oak Park

3.2 Solar Estate:

3.2.1 PMF Results

In Solar Estate also 9 factors were found to be optimal in describing the source contribution of VOC concentration in the area; the Q values did not rise sharply with the F-peak
change. All the coefficients for the multi linear regression test showed positive values; no residual value had a large residual or non-normal curve.

Only isoprene was downweighted in the analysis of data from Solar Estate. Because this species showed continuous poor fit of predicted to simulated concentration results and had low $r^2$ value.

3.2.2 Analysis of Apportioned Factors

The overall results for Oak Park are highlighted in figure 3.21, where the percentage contributions by source (Factors) type are displayed on a pie chart.

![Pie chart showing percentage contributions by source factors at Solar Estate](chart.png)

Figure 3.21. Percentage contributions by source factors at Solar Estate
3.2.3 Factor 1 (Evaporative Fugitive Emissions)

Figure 3.22. Factor 1 profile (evaporative fugitive emissions) Solar Estate

Factor 1 was classified as evaporative fugitive emissions an estimated percentage contribution of 8.05%. The percentages and concentrations of the species in this factor are shown in figure 3.22. High concentrations of propane, n-butane, isopentane, ethane, p-xylene-m-xylene, toluene, benzene, and n-pentane were noted in this factor. The n-alkanes, n-alkenes and cycloalkenes presented in this factor indicated the influence of evaporative fugitive emissions as dominant VOC source.

The CPF plot as shown in figure 3.23 highlights the directions from where the VOC emissions were coming as coming from, particularly from the northeast and northwest of the monitoring site.
3.2.4 Factor 2 (Diesel Manufacture)

Factor 2 represents the fifth highest source affecting Solar Estate. This factor with 8.20% of the overall contribution was named as a diesel manufacturing source. Species profile of this factor is shown in figure 3.24. Highest concentrations include n-alkane, cyclo alkanes, styrene and the BTX compounds (benzene, toluene, and xylenes) primarily coming from diesel manufacturing source.

Manufacturing and storage were counted in this factor because of the presence of the heavier fraction of the diesel composition n, iso, cycloparaffines. Additionally, the aromatic compounds like alkyl benzene indicated the influence of a diesel fuel manufacturing units as this factor.

The CPF plot as shown in figure 3.25 highlights the influence of wind carrying emissions from the nearby refineries facilities that manufacture and store diesel compounds.

Figure 3.25. CPF plot factor 2 (diesel manufacture) Solar Estate
3.2.5 Factor 3 (Natural Gas)

Figure 3.26. Factor 3 profile (natural gas) Solar Estate

Natural gas has the highest percentage contribution among the sources identified at Solar Estate with 31.86% of the overall VOC contribution at this site. Species profile with the highest concentrations is shown in figure 3.26 and indicates a clear signature of natural gas with ethane ranking the highest in all concentrations, and followed by propane, n-butane, n-pentane, and isopentane (paraffins and some olefins).

Natural gas processing, handling, transmission and storage are all sources contributions to this factor emissions. When processing and distributing to large customers such as power plants or chemicals manufacturers all these operations and facilities experience escape and leaking of natural gas.

The CPF radar plot (figure 3.27) pointed to the northeast indicating the nearby refinery facilities as the primary source of natural gas.
3.2.6 Factor 4 (Gasoline and Vehicle Exhaust)

Figure 3.28. Factor 4 profile (gasoline and vehicle exhaust) Solar Estate

Factor 4 has the second highest contribution of the measured VOC in Solar Estate and it was estimated to be 14.11%. The factor species profile as shown in figure 3.28 consists of high concentration of propylene, acetylene, benzene, propane, and 1,3-butadiene. The factor profile could indicate a very compelling signature of gasoline and vehicular exhaust emissions. Ethane and propane were the second highest concentrations that could be due to the influence from other factors such as natural gas or refinery or petrochemicals suggesting possible co-mingling of sources.

The location of the monitoring site between Interstate Highway 37 and Leopard Street, and also the neighboring streets, is clearly shown in figure 3.29. The CPF plot for the highest concentration pointed northeast and southwest, where these arteries are located.

Figure 3.29. CPF plot factor 4 (gasoline and vehicle exhaust) Solar Estate
3.2.7 Factor 5 (Commercial Solvents)

Figure 3.30. Factor 5 profile (commercial solvents) Solar Estate

Factor 5 with a percentage of 3.84% was named as commercial solvents affecting the site of Solar Estate. The species profile with concentrations and percentage are shown in figure 3.30. Solvents are widely used for cleaning and degreasing, dissolving and thinning, dispersing coating and painting, and are used in petroleum refinery, as well as by domestic and commercial businesses surrounding the area.

With the highest concentrations of ethane, styrene, methylated benzene compounds, 1,3-butadiene, n-propyl benzene, ethylene, and toluene, factor 5 could be named as commercial solvents.

The location and the surrounding industries play a great role in contributing to this factor. The CPF plot showed the directions the VOC in this factor were coming from and showed that the highest concentrations were coming from the southwest, a residential and commercial area as shown in figure 3.31.

Figure 3.31. CPF plot factor 5 (commercial solvents) Solar Estate
3.2.8 Factor 6 (Flare)

Factor 6 has high concentrations of 1-butene, c-2-butene, benzene, isopropyl benzene (cumene), 1-pentane, n-butane, isopentane, and some toluene as shown in figure 3.32. The species in the profile is the flare emissions. The factor has 5.83% contribution of the total VOC measured at Solar Estate.

Flaring is a common process in refineries and natural gas processing. Flaring processes in refineries are conducted to destroy excess organic compounds of fuel gases, waste gas, or purged products.

The CPF plot as shown in figure 3.33 pointed to the northeast and southwest, and was little influenced from the northwest, while the north influence could be due to the refineries clustered at the north of the site. Southwest indicated the influence of major petrochemical complex located further away from this site.
3.2.9 Factor 7 (Petrochemicals)

Factor 7 with 9.99% of the total VOC contribution at this site was the fourth highest source percentage contribution among the sources identified at Solar Estate. This factor was influenced by high concentrations of propane, isobutene, ethane, benzene, n-butane, and toluene as shown figure 3.34. The factor could be named as petrochemicals because concentrations are results of petrochemical industrial emissions in the area, Isobutene could be used in the petrochemical industry for alkylation to create high-octane gasoline blendstock, and it is also used in manufacturing hair spray and cooking spray (Termeer, 2013).

The direction of the highest concentration as shown in the CPF plot in figure 3.35 pointed mostly northeast and pointed the nearby refineries facilities and to the southwest.
3.2.10 Factor 8 (Refinery)

Refinery has the third highest contribution with 10.57% at Solar Estate. Refinery processes have a wide range of emissions. The species profile of factor 8 as shown in figure 3.36 had high concentrations and percentages of paraffins, olefins and aromatics.

The location of the site adjacent to major refineries facilities and their VOC emissions are significant contributor to the air pollution in the area. The CPF plot as shown in figure 3.37 pointed to the nearby refineries facilities and showed that highest concentrations were coming from the northeast.
3.2.11 Factor 9 (Diesel Combustion 2)

Factor 9 has a contribution percentage of 7.55% of the overall VOC contribution affecting the site and ranked the seventh highest contributor in Solar Estate. The species concentrations and percentages profile as shown in figure 3.38 and was named as diesel combustion 2.

The profile concentrations indicate diesel combustion with high concentrations of n-alkane, ethane, propane, cycloalkanes, xylenes, and toluene. The profile could be named as diesel emissions; again ethane and propane should not be presented in the factor, even though their percentages are low in the factor comparing to their percentages in other factors.

Diesel can come from two different sources: diesel engines exhaust and from diesel handling and storage tank leaks. The handling, manufacturing and storage were counted as factor 2, because this factor has more of the heavier compounds fraction of the diesel while this factor contained more concentration percentages of the lighter fractions of the diesel combustion emissions.

The CPF plot as shown in figure 3.39 highlights the influence of two major streets Interstate Highway 37 and Leopard Street. Also, wind carrying emissions came from the nearby where the refineries’ facilities clustered together, indicating mobile sources within the facilities also can influence this site.
3.2.12 Temporal Contributions of VOC Sources at Solar Estate

EPA PMF 3.0 apportioned results were studied to detect inter-annual variability in the contribution of each factor detected. Results were plotted for 2005 through 2012 as shown in the figure 3.40. In this site like Oak park site VOC contributions were dominant between 2005 and 2007. Again a sharp reduction in the VOC was noticed in 2008. Contributions of refinery and petrochemicals showed significant reduction post 2007 due to the economic downturn. Since 2011 there have been a small uptick in the VOC suggestion improvement in the economy.
3.3 Discussion

PMF 0.3 apportioned nine factors in both Oak Park and Solar Estate were explained in detail in the sections above. Table 3.1 highlights a summary of all factors (sources) affecting these two sites. Both sites had similar set of nine factors (sources) affected the measured VOC concentration. While Oak Park was influenced by two distinct refinery sources, Solar Estate showed the influence of two diesel sources.

<table>
<thead>
<tr>
<th>Site Name (Oak Park)</th>
<th>(Solar Estate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Years Sampled</td>
<td>(2005-2012)</td>
</tr>
<tr>
<td>Number of Factors</td>
<td>9</td>
</tr>
<tr>
<td>Factor</td>
<td>%</td>
</tr>
<tr>
<td>Natural gas</td>
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<td>Evaporative fugitive emissions</td>
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<td>Gasoline and vehicle exhaust</td>
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<tr>
<td>Petrochemicals</td>
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</tr>
<tr>
<td>Flare</td>
<td>6.926</td>
</tr>
<tr>
<td>Refinery gases</td>
<td>10.01</td>
</tr>
<tr>
<td>Refinery 2</td>
<td>3.12</td>
</tr>
<tr>
<td>Diesel</td>
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<tr>
<td>Solvent</td>
<td>5.781</td>
</tr>
<tr>
<td>Factor</td>
<td>%</td>
</tr>
<tr>
<td>Natural gas</td>
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<tr>
<td>Evaporative fugitive emissions</td>
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<tr>
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<td>Refinery</td>
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<td>Diesel Combustion</td>
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<td>Diesel Manufacturing</td>
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</tr>
<tr>
<td>Commercial Solvent</td>
<td>3.84</td>
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</table>

The results from this study was also compared and contrasted to other studies in the and in other locations around the world. In comparison to other studies this study evaluated more
sample measured VOC from 2005 to 2012 for two sites while most of the other studies analyzed far less data samples. Table 3.2 provides a comprehensive overview of the results from the literature and compare it to the current study.

All source apportionment analysis provides an understanding about VOC and their affect to the monitoring site. While the exact VOC chemical composition combination of each source was not specified but a very possible VOC emissions profile from the source could be developed. Also comparing other receptor models VOC studies helped identify that PMF to be the most suitable model to optimize the VOC in Corpus Christi.
Table 3.2 Comparison to other studies average results by site

<table>
<thead>
<tr>
<th>Area</th>
<th>Site</th>
<th>Method for Modeling</th>
<th>Number of VOC species measured</th>
<th>Dates</th>
<th>Number of Sources</th>
<th>Sources</th>
<th>Reference</th>
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</thead>
<tbody>
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<td>Oak Park</td>
<td>PMF</td>
<td>46</td>
<td>Jan/1/ 2005-Dec/31/ 2012</td>
<td>9</td>
<td>Natural Gas, Evaporative Fugitive Emissions, Gasoline and Vehicle Exhaust, Petrochemicals, Flare, Refinery 2, Diesel, and Solvents.</td>
<td>Present Study</td>
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<td>USA/Corpus Christie</td>
<td>Solar Estate</td>
<td>PCA/APC S</td>
<td>46</td>
<td>2005-2006</td>
<td>5</td>
<td>Natural Gas, Flare Emissions, Fugitive Gasoline Emissions, Refineries Operation, Vehicles Exhaust.</td>
<td>(Sanchez et al., 2008)</td>
</tr>
<tr>
<td>USA/Corpus Christie</td>
<td>Oak Park</td>
<td>PCA/APC S</td>
<td>46</td>
<td>2005-2006</td>
<td>6</td>
<td>Natural Gas, Refineries Operations, Flare Emissions, Vehicles Exhaust, Secondary Industrial Process, and Fugitive Gasoline Emissions</td>
<td>(Sanchez et al., 2008)</td>
</tr>
<tr>
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<td>Clinton Drive</td>
<td>PMF, UNMIX</td>
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<td>1998-2001</td>
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<td>(Brown et al., 2003)</td>
</tr>
<tr>
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<tr>
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<td>Beijing /PKU</td>
<td>PMF</td>
<td>45</td>
<td>August 1 – August 27, 2005</td>
<td>8</td>
<td>Natural Gas, Biogenic, Paint, Petrochemical, LPG, Diesel Exhaust, Liquid/Evaporated/Exhaust gasoline, gasoline Exhaust.</td>
<td>(Song et al., 2008)</td>
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<tr>
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<td>City</td>
<td>Method</td>
<td>Method</td>
<td>Start - End</td>
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<td></td>
</tr>
<tr>
<td>USA/Los Angeles</td>
<td>Azusa</td>
<td>PCA</td>
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<td>2001-2003</td>
<td>Motor Vehicle Exhaust, Coating/Industrial, Industrial 2, Evaporative Emissions, Coating Industrial 2, Evaporative 2, and Biological Source.</td>
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<td>(Brown et al., 2005)</td>
<td></td>
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<td>Chile</td>
<td>Santiago</td>
<td>UNMIX</td>
<td>47</td>
<td>Nov-Dec 1996</td>
<td>Biogenic, Diesel Exhaust, Fuel Evaporation, and Gasoline exhaust.</td>
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<td>Fall 2007</td>
<td>16</td>
<td>Paint and Varnish, Biomass Burning, Household solvent Use, Gasoline Vehicular Emissions, and Diesel Vehicular Emissions.</td>
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<td>48 days at, July, Sep, Oct, Dec 2011</td>
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<td>Heavy-Duty Gasoline Engine/ Air Craft Exhaust), (Diesel Engine Vehicle Exhaust), Light Duty Gasoline Engine.</td>
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CHAPTER 4
SUMMARY FINDING AND RECOMMENDATIONS

The source apportionment study employing PMF 3.0 has identified the source factor affecting the measured VOC concentration in the industrialized urban area. One result from this study can assist policy planners with a tool to identify major VOC sources that can be controlled in the event of a major air pollution event.

EPA PMF 3.0 was employed in this source apportionment study of measured VOC concentration during 2005-2012 in Corpus Christi, Texas. The study identified nine optimal factors (sources) that could explain the concentration of VOC at two urban monitoring sites within the study region.

Natural gas was found to be the major contributor of the VOC concentrations in the area. It explained about 31.86% of the VOC concentration at Solar Estate and 26.62% at Oak Park. Gasoline and vehicular exhaust emission contributed to the measured VOC concentration in the area with overall contribution of 14.11%, at Solar Estate and 14.95% at Oak Park. Diesel another major contributor in this urban area, primarily from manufacturing and from combustion contributed to 15.7% at Solar Estate and 10.64% at Oak Park. Evaporative fugitive emissions was also identified as contributor to the measured VOC concentrations in the area, with apportioned amount of 8.05% at Solar Estate and 17.22% at Oak Park. Refinery gases that included the contributions from the refineries and asphalt blowing unit contributed to the measured concentrations in the area, with percentages of 10.57% at Solar Estate and 13.013% at Oak Park. Contribution from emissions from petrochemicals in the area amounted to , 9.99% at Solar Estate and 4.71% at Oak Park.
Flaring operation is another contributor to the VOC in the area with contribution of about 5.83% at Solar Estate and 6.92% at Oak Park. A minor contribution from solvents with about 3.84% at Solar Estate and 5.78% at Oak Park was also found in this study.

The emission concentrations were at an overall high in 2005, 2006, and 2007. The levels began to decrease in 2008 until it reached its lowest level in 2011. Then the level slightly increased in 2012. These levels were observed at both Oak Park and Solar Estate monitoring site. The lower levels observed during 2008 – 2011 have been attributed to the economic down turn in the area. To further refine this study, similar source apportionment analysis should be conducted using additional monitoring sites that are in the urban area and away from the industrial cluster. In addition, the data could be used in multiple source apportionment modeling techniques including Chemical Mass Balance (CMB) model and other source apportionment methodologies. These techniques can be coupled with photochemical models to evaluate the efficacy of emissions control strategies on local temporal ozone levels with Maximum Incremental Reactivity (MIR) scale for evaluating the formation of ozone by reactive VOC.
APPENDIX A

GRAPHS AND TABLES USED IN THE ANALYSIS OF OAK PARK
Figure A-1: Q Values as function of F-peak (9 Factors) Oak Park

Observed/Predicted Concentration

Figure A-2: (1, 3-butadiene) Observed/Predicted concentration Oak Park

Figure A-3: Oak Park (isoprene) Observed/Predicted concentration Oak Park
Figure A-4: O/P scatter plots shows $r^2$ values 9 Factors Oak Park
<table>
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<tr>
<th>VOC species</th>
<th>Factor 1 Natural Gas</th>
<th>Factor 2 Refinery gases</th>
<th>Factor 3 Solvent</th>
<th>Factor 4 Evaporative Fugitive Emissions</th>
<th>Factor 5 Gasoline and Vehicle Exhaust</th>
<th>Factor 6 Petrochemicals</th>
<th>Factor 7 Flare</th>
<th>Factor 8 Refinery 2</th>
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Yearly, Seasonal, and Weekly and Weekend’s Concentrations Distributions

Figure A-5: Yearly concentrations distribution Factor 1 (natural gas) Oak Park

Figure A-6: Seasonal concentrations distribution Factor 1 (natural gas) Oak Park

Figure A-7: Weekly and weekend’s concentrations distribution Factor 1 (natural gas) Oak Park

Figure A-8: Yearly concentrations distribution Factor 2 (refinery gases) Oak Park

Figure A-9: Seasonal concentrations distribution Factor 2 (refinery gases) Oak Park

Figure A-10: Weekly and weekend’s concentrations distribution Factor 2 (refinery gases) Oak Park
Figure A-11: yearly concentrations distribution Factor 3 (solvents) Oak Park

Figure A-12: seasonal concentrations distribution Factor 3 (solvents) Oak Park

Figure A-13: weekly and weekends concentrations distribution Factor 3 (solvents) Oak Park

Figure A-14: yearly concentrations distribution Factor 4 (evaporative fugitive emissions) Oak Park

Figure A-15: seasonal concentrations distribution Factor 4 (evaporative fugitive emissions) Oak Park

Figure A-16: weekly and weekends concentrations distribution Factor 4 (evaporative fugitive emissions) Oak Park
Figure A-17: yearly concentrations distribution Factor 5 (gasoline and vehicle exhaust) Oak Park

Figure A-18: seasonal concentrations distribution Factor 5 (gasoline and vehicle exhaust) Oak Park

Figure A-19: weekly and weekends concentrations distribution Factor 5 (gasoline and vehicle exhaust) Oak Park

Figure A-20: yearly concentrations distribution Factor 6 (gasoline and vehicle exhaust) Oak Park

Figure A-21: seasonal concentrations distribution Factor 6 (gasoline and vehicle exhaust) Oak Park

Figure A-22: weekly and weekends concentrations distribution Factor 6 (gasoline and vehicle exhaust) Oak Park
Figure A-23: yearly concentrations distribution Factor 7 (flare) Oak Park

Figure A-24: seasonal concentrations distribution Factor 7 (flare) Oak Park

Figure A-25: weekly and weekends concentrations distribution Factor 7 (flare) Oak Park

Figure A-26: yearly concentrations distribution Factor 8 (refinery 2) Oak Park

Figure A-27: seasonal concentrations distribution Factor 8 (refinery 2) Oak Park

Figure A-28: weekly and weekends concentrations distribution Factor 8 (refinery 2) Oak Park

Figure A-29: yearly concentrations distribution Factor 9 (diesel) Oak Park
Figure A-30: seasonal concentrations distribution Factor 8 (diesel) Oak Park

Figure A-31: weekly and weekends concentrations distribution Factor 8 (diesel) Oak Park
Monthly and Seasonal Contributions results:

Figure A-32: all Factors monthly contributions summed Oak Park
Overall Individual Factors Concentrations

Figure A-34: Factor 1 (natural gas) Oak Park

Figure A-35: Factor 2 (refinery gases) Oak Park
APPENDIX B

GRAPHS AND TABLES USED IN THE ANALYSIS SOLAR ESTATE
Figure B-1: Q values as function of F-peak (9 Factors) Solar Estate

Observed/Predicted Concentration

Figure B-2: (isoprene) Observed/Predicted concentration Solar Estate
Figure B-3: O/P scatter plots shows r² values 9 Factors Solar Estate
Table B-1 species concentrations by Factor Solar Estate

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Isoprene 0.0000 0.0000 0.0000 0.0000 0.4710 0.1856 0.0000 0.0000 0.0056
IsopropylBenzene (cumene) 0.0673 0.0224 0.0000 0.0000 0.0000 0.0032 0.0000 0.0000 0.0011
Methylocyclohexane 0.0000 0.5775 2.2813 0.0262 0.0610 0.070 0.0195 0.5664 0.0599
Methylocyclopentane 0.0299 0.1511 0.2142 0.0424 0.0112 0.070 0.0097 0.3616 0.0399
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Toluene 0.3136 0.2858 0.0696 0.3055 0.1339 0.0000 0.0475 0.5111 0.0443

Yearly, Seasonal, and Weekly and Weekend’s Concentrations Distributions

Figure B-4: yearly concentrations distribution Factor 1 (evaporative fugitive emissions) Solar Estate

66
Figure B-5 seasonal concentrations distribution Factor 1 (evaporative fugitive emissions) Solar Estate

Figure B-6: weekly and weekends concentrations distribution Factor 1 (evaporative fugitive emissions) Solar Estate

Figure B-7: yearly concentrations distribution Factor 2 (diesel manufacture) Solar Estate

Figure B-8: seasonal concentrations distribution Factor 2 (diesel manufacture) Solar Estate

Figure B-9: weekly and weekends concentrations distribution Factor 2 (diesel manufacture) Solar Estate

Figure B-10: yearly concentrations distribution Factor 3 (natural gas) Solar Estate

Figure B-11: seasonal concentrations distribution Factor 3 (natural gas) Solar Estate
Figure B-12: weekly and weekends concentrations distribution Factor 3 (natural gas) Solar Estate

Figure B-13: yearly concentrations distribution Factor 4 (gasoline and vehicle exhaust) Solar Estate

Figure B-14: seasonal concentrations distribution Factor 4 (gasoline and vehicle exhaust) Solar Estate

Figure B-15: weekly and weekends concentrations distribution Factor 4 (gasoline and vehicle exhaust) Solar Estate

Figure B-16: yearly concentrations distribution Factor 5 (commercial solvents) Solar Estate

Figure B-17: seasonal concentrations distribution Factor 5 (commercial solvents) Solar Estate

Figure B-18: weekly and weekends concentrations distribution Factor 5 (commercial solvents) Solar Estate
Figure B-19: yearly concentrations distribution Factor 6 (flare) Solar Estate

Figure B-20: seasonal concentrations distribution Factor 6 (flare) Solar Estate

Figure B-21: weekly and weekends concentrations distribution Factor 6 (flare) Solar Estate

Figure B-22: yearly concentrations distribution Factor 7 (petrochemicals) Solar Estate

Figure B-23: seasonal concentrations distribution Factor 7 (petrochemicals) Solar Estate

Figure B-24: weekly and weekends concentrations distribution Factor 7 (petrochemicals) Solar Estate

Figure B-25: yearly concentrations distribution Factor 8 (refinery) Solar Estate
Figure B-26: seasonal concentrations distribution Factor 8 (refinery) Solar Estate

Figure B-27: weekly and weekends concentrations distribution Factor 8 (refinery) Solar Estate

Figure B-28: yearly concentrations distribution Factor 9 (diesel combustion 2) Solar Estate

Figure B-29: seasonal concentrations distribution Factor 8 (diesel combustion 2) Solar Estate

Figure B-30: week and weekends concentrations distribution Factor 8 (diesel combustion 2) Solar Estate
Monthly and Seasonal Contributions Results:

Figure B-31: all Factors monthly contributions summed Solar Estate
Figure B-32: all Factors seasonal contributions summed Solar Estate

Overall Individual Factors Concentrations

Figure B-33: Factor 1 (evaporative fugitive emissions) Solar Estate
Figure B-34: Factor 2 (diesel manufacturing) Solar Estate

Figure B-35: Factor 3 (natural gas) Solar Estate

Figure B-36: Factor 4 (gasoline and vehicles exhausts) Solar Estate

Figure B-37: Factor 5 (commercial solvents) Solar Estate

Figure B-38: Factor 6 (flare) Solar Estate

Figure B-39: Factor 7 (petrochemicals) Solar Estate

Figure B-40: Factor 8 (refinery) Solar Estate

Figure B-41: Factor 9 (diesel combustion 2) Solar Estate
REFERENCES


