2013

Long term trend and source apportionment of ambient VOCs in Windsor

Zhi Li
University of Windsor

Recommended Citation

Li, Zhi, "Long term trend and source apportionment of ambient VOCs in Windsor" (2013). *Electronic Theses and Dissertations*. 4984.
https://scholar.uwindsor.ca/etd/4984

Long term trend and source apportionment of ambient VOCs in Windsor

By

Zhi Li

A Thesis
Submitted to the Faculty of Graduate Studies
through Civil and Environmental Engineering
in Partial Fulfillment of the Requirements for
the Degree of Master of Applied Science
at the University of Windsor

Windsor, Ontario, Canada

2012

Long term trend and source apportionment of ambient VOCs in Windsor

by

Zhi Li

APPROVED BY:

Dr. David Ting
Department of Mechanical, Automotive & Material Engineering

Dr. Jerald Lalman
Department of Civil and Environmental Engineering

Dr. Xiaohong (Iris) Xu, Advisor
Department of Civil and Environmental Engineering

Dr. Faouzi Ghrib, Chair of Defense
Department of Civil and Environmental Engineering

December 18th, 2012

DECLARATION OF ORIGINALITY

I hereby certify that I am the sole author of this thesis and that no part of this thesis has been published or submitted for publication.

I certify that, to the best of my knowledge, my thesis does not infringe upon anyone's copyright nor violate any proprietary rights and that any ideas, techniques, quotations, or any other material from the work of other people included in my thesis, published or otherwise, are fully acknowledged in accordance with the standard referencing practices. Furthermore, to the extent that I have included copyrighted material that surpasses the bounds of fair dealing within the meaning of the Canada Copyright Act, I certify that I have obtained a written permission from the copyright owner(s) to include such material(s) in my thesis and have included copies of such copyright clearances to my appendix.

I declare that this is a true copy of my thesis, including any final revisions, as approved by my thesis committee and the Graduate Studies office, and that this thesis has not been submitted for a higher degree to any other University or Institution.

ABSTRACT

Ambient VOC concentrations measured at Windsor West Station from 2001 to 2009 were used for a VOC source apportionment study using Chemical Mass Balance model. The ranking of source contribution estimates was: “Vehicle Emission”, “Commercial Natural Gas”, “Industrial Refinery”, “Liquefied Petroleum”, “Coke Oven”, “Architectural Coating”, and “Biogenic Emission”.

From 2003 to 2009, PAMS measurements in Windsor decreased by approximately 37%. Source contribution reduction of “Vehicle Emission” accounted for 57.6% of total source contribution reduction. Source contribution reduction percentages of “Vehicle Emission”, “Architectural Coating”, and “Biogenic Emission” were above PAMS reduction percentage; however, source contribution reduction percentages of “Commercial Natural Gas”, “Industrial Refinery”, “Coke Oven”, and “Liquefied Petroleum” were below it.

From 2001 to 2009, a seasonal pattern of PAMS measurements with low level in winter and spring but high in summer and fall was observed in some years. A similar seasonal pattern of “Vehicle Emission” source contributions was also obeserved in most years.

DEDICATION

To my wife Jie Long.

ACKNOWLEDGEMENTS

I would like to acknowledge and thank many people who helped me in my study in University of Windsor. Particularly, I am deeply grateful to my advisor, Dr. Xiaohong Xu, for her support and guidance. I would also want to express my gratitude to my committee members, Dr. Jerald Lalman and Dr. David Ting, for their valuable suggestions and comments. Especially, I would like to thank Dr. Ghrib for his patience and kindness. With his help, it is impossible for me to finish my study.

I sincerely like to thank my wife, without her support I could not finish the project. I would also like to thank Hassan Mohseni Nameghi for his help and encouragement. In addition, I am thankful to the National Air Pollution Surveillance Network (NAPS) for making the VOC data used in this study available. Funding of this research was provided by NSERC Discovery Program.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS/SYMBOLS

AAQC – ambient air quality criteria

BDL – below detection limit

BTEX – benzene, toluene, ethylbenzene, and xylene

CMB – Chemical Mass Balance Model

CO – carbon monoxide

DL – detection limit

H_2O – dihydrogen monoxide

LPG – liquefied petroleum gas

MKT – Mann-Kendall test

MPIN – modified pseudo inverse matrix

NAPS – National Air Pollution Surveillance

NMHC – non-methane hydrocarbon

NO_2 – nitrogen dioxide

NO_x – nitrogen oxide

O_3 – ozone

OH – hydroxyl

PAC – principle component analysis

PAMS – Photochemical Assessment Monitoring Sites

PMF – positive matrix factorization

$PM_{2.5}$ – air pollutants with a diameter of 2.5 micrometers or less

SCE – source contribution estimate

SD – standard deviation

SOA – secondary organic aerosol

SO_2 – sulphur dioxide

Std Err – standard error

Tstat – t-statics

U.S.EPA – United States Environmental Protection Agency

VOCs – volatile organic compounds

CHAPTER 1

INTRODUCTION

“Volatile organic compounds (VOCs) are organic chemical compounds whose composition makes it possible for them to evaporate under normal indoor atmospheric conditions of temperature and pressure (EPA, 2012a)”. VOCs are major contributors to ground-level ozone (O_3) and secondary organic aerosol (SOA). These pollutants pose a threat to public health, agricultural production, and the ecosystem (Liu et al., 2008; Kroll et al., 2006). Some VOC species are directly classified as toxic, such as 1, 3-butadiene, acrolein, benzene, styrene, and other aromatics (Blanchard et al., 2010). There are a host of sources emitting VOCs into atmosphere, including natural sources and synthetical sources, such as: coal-burning category, vegetative burning and cooking, diesel exhaust, gasoline exhaust, gasoline evaporative emissions, fugitive dust, solvents and coatings, metals, aggregate handling, commercial natural gas, liquefied petroleum, and biogenic emission (Watson, 2004; Fujita, 1998). The actual VOC sources depend on the actual condition and should be determined case-by-case.

Various VOC sources are distributed in Windsor area, which increases the difficulty for VOCs sources investigation. As an industrial city in Canada, Windsor has a prosperous automobile industry, including many automobile assembly plants and part plants, as well as some other local industries, such as beer plant and chemical plant. All of these factories produce different kinds of industrial pollutants into the airshed. Furthermore, there is a cross-border bridge in Windsor - the Ambassador Bridge, a link between Windsor and Detroit, which is known to be the busiest transportation junction in North America. In 2010, approximately, 262 million trucks and 342 million cars passed it

(Transport Canada, 2011). The Windsor-Detroit tunnel is also a busy passage which is used mostly by cars and buses. In 2010, about 3.4 million cars and buses moved through this tunnel (Transport Canada, 2011). As a result, vehicle emission is a heavy air pollution source of VOCs (Wheeler et al., 2008).

The population of Windsor in 2011 was 210,891 (Statistics Canada, 2012). Due to the high populaition, there is a lot of contributions to air pollution from the resident daily activities, including the vehicle emission from local transportaiton, the commecrial natural gas emission from the building heating, and the liquefied petroleum gas emssion from the propane for cooking. Besides, Windsor also suffers from cross-border pollution originating from Detroit. Referred to as the automobile capital of the world, Detroit is well known for its automobile industry as well as heavy industrial pollution. Windsor, which is only separated from Detroit by a narrow river, has to withstand the industrial pollution produced in Detroit which is transferred by the predominantly westerly winds (Wheeler et al., 2008). As mentioned above, multiple pollution sources are contributing to the VOCs in Windsor airshed, including local industrial and municipal sources, commercial and residential sources, vehicle exhaust sources, and trans-border pollution sources throughout the Windsor area. As a result, the diversity and the complicated spatial pattern of these sources make the VOC sources scrutinization a challenging problem in Windsor.

Windsor area has higher incidences of poor quality air than any other part in Ontario province on average (Ontario Ministry of the Environment, 2008) and its air quality has become a concern for both authorities and researchers. Some studies on air pollution of VOCs have been carried out in Windsor and nearby areas. Templer (2007) carried out a VOCs source apportionment in Windsor using the data measured in the summer and winter at 52 sampling points in 2005. In her research, the main VOC sources were identified and quantified, which included diesel exhaust, gasoline exhaust, liquid gasoline, gasoline vapor, commercial natural gas, liquefied petroleum gas, industrial refinery, coke oven, biogenic emissions, and architectural coatings. Furthermore, the spatial patterns of high and low source contributions were also studied. However, for policy making and the policy and technology evaluating, the inter-annual and seasonal pollution trend study based on multi-year study might be more convincing. Bellack et al. (2008) carried out a study on air pollution based on sampling data of each season between 2005 and 2006 in Windsor. They found that the VOCs concentration peak appeared in the summer and there were little changes of the VOC concentrations by the geographical variables. Miller et al. (2009) studied the spatial variability of VOC concentrations in Sarnia, Ontario, Canada. The results indicated that the VOC concentrations distribution pattern was strongly influenced by the pollutant releasing facilities location and this pattern represented the chronic exposure in Sarnia. Another interesting thing found in their research was that these VOCs might have a common source. Mukerjee et al. (2009) carried out a spatial analysis and land use regression of VOCs in Detroit/Dearborn, USA. They found that VOCs varied little by geographic sections or distance to major roads and furthermore, the mobile and point sources may be major sources for ambient VOCs. Miller (2012) carried out a study of the concentrations and correlations among the benzene, toluene, ethylbenzene, and xylene (BTEX) group of VOCs in Windsor in the period from 2004 to 2006. The results showed that there was a significant temporal and spatial variation and the existence of a major common source of BTEX. However, further research is needed to determine the detailed information of sources and the impacts of influential factors on source contributions. In addition, the understanding of the influences of wind speed and wind direction on VOC source contributions would be helpful for locating the possible sites of major sources and explaining the source contribution variation (Lau et al., 2010; Roukos et al., 2009; Cetin et al., 2003). Therefore, some efforts should be made in this field.

In summary, a research on the inter-annual and seasonal tendency and the source apportionment of atmospheric VOCs in Windsor is needed. It will be helpful for pollution control strategies evaluation and policy making. The overall objective of this project is to identify the long term trend of ambient VOCs and their source contributions in Windsor.

The specific objectives include:

1) To identify ambient VOC sources and quantify the their contributions;

2) To detect the seasonal and year-to-year trends of ambient VOCs and VOC source contributions;

CHAPTER 2

LITERATURE REVIEW

2.1 Air Pollution Models

Air pollution models are tools to identify air pollution sources and quantify the air pollution source contributions. There are two categories of models for air pollution simulation: dispersion models and receptor models.

Many source dispersion models have been developed in past decades. Based on source emission and meteorology, source dispersion models describe the chemical and physic processes of dispersion to estimate the pollutant concentrations on receptor in a specific period of time (El-Harbawi et al., 2008). There are four common types of air pollution dispersion models: Box model, Gaussian model, Lagrangian model and Computational fluid dynamic model (El-Harbawi et al., 2008; Holmes and Morawska, 2006).There is a significant advantage in this kind of models: they can predict the concentrations on receptor according to the emission. Thus they can be used for scenario studies to evaluate the emission control policy according to the pollutant concentration variations before and after the policy execution. However, they require detailed emission information which is not always available or accurate enough (Viana et al., 2008). Moreover, it is difficult for them to track the source information from pollution. Therefore, they can’t be used for source apportionment.

Contrary to the dispersion models, the receptor models use the measured pollutant concentrations on receptor to quantify source contributions. They don’t describe the complicated dispersion process but use algorithm to compute the contributions from different sources (Watson et al., 2002). Therefore this kind of models can be used for source apportionment. They are introduced briefly in the next section.

2.2 Receptor Models

The fundamental principle of receptor models is the mass balance equation shown as Equation (1) (Watson et al., 2008).

$$C_{ij} = \sum_{k=1}^{m} a_{jk} S_{ik} + e_{ij} \quad i = 1, \dots N; j = 1, \dots n \tag{1}$$

where:

C_{ij} = the concentration of the j-th species in the i-th sample

a_{jk} = the mass fraction of species j in source k

S_{jk} = the total mass of material from source k to sample i, which indicates the source contribution

e_{ij} = the error between the measurements and calculated results.

According to the pre-requirements to solve the Equation (1), receptor models can be further classified into two categories: receptor models with prespecified source profiles, such as chemical mass balance model, and source-receptor models (Larsen and Baker, 2003). In the CMB model, ambient data and their source profiles are needed as input files to solve equation (1). While in source-receptor models, only the ambient data are required (Larsen and Baker, 2003). The potential sources profiles and source contributions will be derived from the model calculation. There are three widely applied source-receptor models: Principle Component Analysis (PCA), Positive Matrix Factorization (PMF), and UNMIX. The characteristics of these four models are shown in Table 2.1.

Table 2.1: Characteristics of CMB, PMF, PCA, and UNMIX

Model	**Strength**	**Weakness**	**Application**
CMB	Provides uncertainties on SCEs based on input concentrations, measurement uncertainties, and collinearity of source profiles (Watson et al., 2008); Doesn't need a large number of samples, and can be applied to each measurement (Watson et al., 2008; Miller et al., 2002)	Can't predict the pollution on receptor (. Watson et al., 2008); Need comprehensive knowledge of potential sources and source profiles (Watson et al., 2008); The samples are assumed to be "fresh" (. Watson et al., 2008); Can't apportion the secondary pollutants (Watson et al., 2008); SCEs might have no physical meaning (Watson et al., 2008)	If the potential sources and source profiles are known, CMB can be used as an "ideal" source apportionment tool (Mijić et al., 2010).
PMF	No need of potential sources and source profiles; Derive source profiles, source contributions through modeling simultaneously; Can handle missing or below-detection-limit data; Can prevent disproportional effects because of outlier data. (Watson et al., 2008)	Difficulty in explaining the calculated source profiles ; Unable to distinguish the covariant sources clearly (Viana et al., 2008) ; Need a large number of sample data (>100) (Shi et al., 2009); Assume that all sources have been identified (Shi et al., 2009); Need to determine the factor numbers subjectively (Watson et al., 2008);	If the potential sources and source profiles are unknown, the PMF can be applied to source apportionment.
PCA	No need to know the potential sources and source profiles (Thurston and Spengler, 1985); Identify sources and estimate the elemental composition and contributions of the indentified sources (Thurston and Spengler, 1985); Most useful if a small number of factors responsible for most variances of the measured data (Miller et al., 2002).	Unavailability of some tracers. The fact that one tracer may be marker for more than one source will cause misinterpretation for the results (Viana et al., 2008); Unable to separate the covariant sources (Viana et al., 2008); The calculated source profiles or source contributions may has no physical meaning.(Viana et al., 2008); Assume all sources have been identified (Shi et al., 2009)	If the potential sources and source profiles are unavailable, and a small number of factors responsible for the most part of the ambient data variances (Miller et al., 2002).

Table 2.1- continued

UNMIX	No need to know the number of sources or source profiles; Can output the source profiles, and source contributions; No need of the knowledge or assumption of errors; Can automatically correct source profiles due to the chemical reactions. (Henry, 2000)	There should be some ambient data with no or very low impact from each source; Source composition was assumed approximately constant.(Henry, 2000)	UNMIX can be applied to the situation when the data are a convex combination of underlying factors, and the potential sources, source number, and source profiles are unknown.(Henry, 2003)

Comparisons between these models have been carried out by researchers. Rizzo and Scheff (2007) had a comparison study between CMB and PMF. In their study, it was found that both models produced the similar major sources and source profiles; however, in PMF's results, there is one general source profile containing some small sources and there are some overlapped species between the source profiles. Bullock et al, (2008) also made a comparison between CMB and PMF. They found that only CMB could distinguish strongly correlated sources; species selection was crucial for the accuracy to both models. Viana et al. (2008) carried out an inter-comparison of PMF, PCA, and CMB in a case study in an industrial area. They found a good agreement of the major source identification between all three models. However, large variations were found in the quantification of some source contributions due to the correlation between the sources.

A comprehensive comparison study of four models, namely CMB, PMF, PCA, and UNMIX, was conducted by Miller et al. (2002). In this study, these four models were used to apportion the VOCs concentrations which were calculated out by Monte Carlo Simulation using actual source profiles and source contributions. These simulated VOCs concentrations were composed of 829 samples and represented 7 source profiles: environmental tobacco smoke, paint emissions, cleaning and /or pesticide products, pumping gasoline, gasoline vapors, automobile exhaust, and wastewater treatment plant emissions. The source profile used for the gasoline vapor concentrations calculation was almost as same as the one for pumping gasoline except that decane was excluded from the latter. The collinearity between them might distort the CMB results. Therefore, only the gasoline vapor source profile was included into the input source files instead of both of them. The modeling results from CMB, PCA, PMF, and UNMIX are shown in Table 2.2 together with the actual source profiles (Miller et al., 2002).

Table 2.2: Case study of the comparison among CMB, PMF, UNMIX, and PCA (Miller et al., 2002)

Major compounds(5)	**Actual situation**		**CMB**		**PMF**		**UNMIX**		**PCA**	
	Profile	SCE(1)	Profile	SCE	Profile	SCE	Profile	SCE	Profile	SCE
TET,TCA,CFM	Cleaning/ pesticides	21±33	Cleaning/ pesticides	23±34	P1: Cleaning/ pesticides	23±33	U1: Cleaning/ pesticides	21±35	PA1: Cleaning/ pesticides	29±42
BNZ,EBZ,MPX, OXY,STR,TOL	Auto exhaust	27±8	Auto exhaust	30±26	P2: aromatics-dominated(2)	59±30				
	environmental tobacco smoke	29±3	environmental tobacco smoke	26±31						
TCA,BNZ,CFM, EBZ,MPX,OXY, TOL							U2(3)	54±30	PA2(4)	71±42
TCA,BNZ,TET, CFM,EBZ,TCE	Wastewater plant	16±7	Wastewater plant	12±16	P3: Wastewater plant	18±13				
TOL							U3	25±20		
BNZ,EBZ,MPX, DEC,OXY,TOL	Pumping gasoline	2±8	Pumping gasoline	6±11						
	Gasoline vapor	2±1	Gasoline vapor							
EBZ,MPX,DEC, UND,OXY,TOL	Paint	3±10	Paint	3±8						

(1) SCE: estimated source contribution (%).

(2) Aromatic-dominated profile consists of auto exhaust, gasoline vapor, and environmental tobacco smoke.

(3) Combination of auto exhaust, gasoline vapor, and wastewater

(4) Combination of auto exhaust, gasoline vapor, and wastewater

(5) TCA-1,1,1-Trichoroethane; BNZ-Benzene; TET-Carbon Tetrachloride; CFM-Chloroform; EBZ-Ethylbenzene; MPX-*m, p*-Xylene; DEC-n-Decane; UND-*n*-Undecane; OXY-*o*-Xylene; PDB-*p*-Dichlorobenzene; STR-Styrene; TCE-Trichloroethylene; TOL-Toluene.

As shown in Table 2.2, SCEs from CMB agreed with the actual concentrations best among all four models. Nevertheless, in 90% of CMB modeling results, the negative SCEs appeared in at least one of the three aromatics-dominated sources: auto exhaust, gasoline vapor, and environmental tobacco smoke. These negative values had no physical meaning. Additionally, 25 of the 100 randomly chosen input samples couldn’t successfully produce converged results through CMB modeling.

Among the three source-receptor models (PMF, NUMIX, and PCA), PMF produced the best source profiles (Miller et al., 2002). However, the P2 profile extracted by PMF was an aromatics-dominated profile consisting of auto exhaust, gasoline vapor, and environmental tobacco smoke. It means that PMF could not distinguish these correlated sources. Furthermore, PMF failed to extract the two small sources: pumping gasoline and paint. Both PCA and UNMIX extracted an outdoor source consisting of auto exhaust, gasoline vapor, and wastewater plant, which indicates that none of them could separate these three sources. In addition, both of them failed to extract the sources of environmental tobacco smoke, pumping gasoline, and paint. In summary, none of these three source-receptor models could distinguish all these correlated sources successfully (Miller et al., 2002).

To overcome the disadvantages of these receptor models, Shi et al. (2009) used a combination of PMF, PAC, and CMB for the apportionment of a synthesis dataset and an ambient dataset. In their study, the combination of models produced reasonable results. However, one case study is not convincing enough for the application of this method. Furthermore, more theoretical study is needed to understand the mechanisms behind this method.

From what mentioned above, CMB might be the best choice, if the appropriate source profiles are available. However, the problems of negative SCE and divergent calculation result originated from CMB modeling (Miller et al., 2002) should be paid attention to.

2.3 CMB Model Description

2.3.1 History and Application of CMB

Since 1970s, the CMB receptor model has been widely used for air pollution source apportionment. The first interactive, user-oriented software for CMB was programmed in 1978. The latest version, CMB8.2, was subjected to the researchers by EPA in 2004 with the development spanning two decades (Coulter, 2004). The CMB8.2 model is applicable to multi-species data sets, the most common of which are chemically particulate matter (PM) and VOC. Its calculation principle is relatively simple to understand, and its user-friendly interface is easy to manage.

In recent years, many CMB VOCs source apportionment studies have been conducted and some are summarized in Table 2.3. From Table 2.3, it is concluded that CMB could produce a satisfying VOC sources apportionment in location with complicated sources and source locations distribution.

Table 2.3: Summary of VOCs source apportionment studies using CMB in recent years

Reference	**Sampling location and time**	**Findings**
Using a source-receptor approach to characterise VOC behaviour in a French urban area influenced by industrial emissions: Part II: Source contribution assessment using the Chemical Mass Balance (CMB) model (Badol et al., 2008)	A French industrial city: Dunkerque Samples from September 2002 to August 2003	Seasonal evolution of source contributions Evolution of source contributions with wind direction
Source apportionment of ambient volatile organic compounds in the Pearl River Delta, China: Part II (Liu et al., 2008)	A industrial area in China: Pearl River Delta Samples from seven sampling sites located in the Pearl River Delta were collected in the fall of 2004	Ambient organic compounds source apportionment The source contribution differences between sites were influenced by transportation patterns, the consumed fuel types, and the primary industries.
Comparison of receptor models for source apportionment of volatile organic compounds in Beijing, China (Song et al., 2008)	Beijing VOCs data were simulated based on 7 known sources in 2005	CMB performed best in source contribution estimation The discrepancy among results of 4 models may be attributable to their inherent weaknesses of models.
Levels and source apportionment of volatile organic compounds in southwestern area of Mexico City (Sosa et al., 2009).	Three sampling sites in Mexico City: university campus, gasoline refuelling station, a high-rise condominium area At all these sites, samples were collected at the same time every six days during July 2000 and February 2001	The source contributions at three sites In residential area, the liquid petroleum service contribution was on and off during 12-h cycles, which was caused by the operation in the liquid petroleum gas station.

Table 2.3-continued

Source apportionment of particulate matter in the ambient air of Hyderabad city, India (Gummeneni et al., 2011)	From June 2004 to May 2005 Sampling site was located in a city near busy street	Five major sources were identified including suspended dust, vehicles, industrial emissions, combustion, and refuse burning.
Sources of high PM2.5 concentrations in Milan, Northern Italy: Molecular marker data and CMB modelling (Perrone et al., 2012)	Over a three-year sampling campaign, from 2006 to 2009 Three sampling sites were in North Italy: an urban site, a rural site, and a remote site	The major contributors to ambient particulate matter, which include traffic, secondary inorganic and organic aerosol, and biomass burning. The latter two. major sources showed distinct seasonal variance

2.3.2 Basic Principles of CMB

The CMB consists of a group of least-squares solutions corresponding to a set of chemical mass-balance equations that describe each chemical species concentration on the receptors as a linear sum of products of source profiles and source contributions (Watson et al., 2000).

The principle of CMB can be expressed as shown in Equation (2) (Watson, 2004).

$$C_i = \sum_{j=1}^{J} F_{ij} \cdot S_j \qquad i = 1,2,\dots I \qquad (2)$$

where:

C_i = the concentration of element i on receptor

S_j = the contribution from source j

F_{ij} = the fraction of source contribution S_j composed of element i

To solve this equation, the ambient data (C_i) and the mass fraction of each species in a source (F_i), which is also named source profile, are needed as input. Then the contribution estimate from each source (S_j) could be computed by solving Equation (2).

The mass fraction of species in a certain source constructs a profile which can describe the characteristics of this specific source and distinguish it from other sources. This profile is named as source profile and will be explained later in detail. From equation (2), it can be seen that the essential mechanism of CMB is to estimate the source contributions (S_j) by fitting the measured data into the source profiles with acceptable uncertainty. Then, by multiplying the estimated contributions from a source by its source profile, the contributions of this source to each species concentrations on the receptor are calculated.

2.3.3 Boundary of CMB

CMB model assumes that the species mass ratio does not change when emission transfer from the source to the receptor. But when the species life time is shorter than the transmission time, the species will be consumed and the ratio will change. Most ambient NMHCs are oxidized in the lowest 2 km of the troposphere with tropospheric lifetimes ranging from hours to several months (Fujita and Lu, 1998). Therefore, the pollutants moved from long distance cannot be represented by the CMB modeling.

Emissions can dissipate without adverse impacts on sensitive land uses if adequate buffer distance is kept between emission and the land (EPA, 1990). Some recommended buffer distances are listed in Table 2.4.

Table 2.4: Buffer distance from industry for sensitive land use (EPA, 1990)

Source	**Buffer distance (meters)**	**Corresponding source profile**
Petroleum Refinery	2000	Industrial Refinery
Iron and steel production	1000	Coke-oven
Extraction of natural gas	1000	Commercial Natural Gas
Petroleum product	500	Liquefied Petroleum Gas
Printing and coating works with heated curing ovens	500	Building Coating

Taking into consideration of both facts that only pollutants which can reach receptor in several hours can be represented by CMB and the pollutants 2000 meters away will have little effects on receptor, it can be determined that the boundary of CMB is several kilometers away from the receptor. As a result, only local major source contributions can be figured out by CMB modeling. This is the limitation of this model.

The pollutants from London, Sarnia, and Ohio are not considered because they might have decayed during the dispersion or might in small concentrations and they could not be the major sources. As a result, these inputs at boundary are not considered.

2.3.4 Some Terminologies Used in CMB

Non-methane Hydrocarbon (NMHC)

Non-methane hydrocarbons are hydrocarbons except methane, generally including C_2 to C_{12}. These light hydrocarbons can react with hydroxyl radicals, ozone, and nitrate to influence the atmosphere oxidizing capacity. They are deemed ozone precursors.

PAMS

Photochemical Assessment Monitoring Sites (PAMS) are a series of species, whose concentrations sum is recommended as the common standard for the source profile normalization by the CMB8.2 protocol.

Detection Limit

“The "detection limit" (DL) is the smallest amount of a substance that an analytical method can reliably distinguish from zero. More formally, it is the minimum concentration or amount of a target analyte that produces a signal the tester can distinguish, at a specified confidence level, from the signal produced by a blank (EPA, 2012b).” Testers sometimes mistakenly use the term "limit of quantification" when they mean "limit of detection." The limit of quantification is the minimum concentration or amount of an analyte that a method can measure with a specified degree of precision. Each laboratory should report its limit of detection, identify its procedure for measuring the limit of detection, and label results below the detection limit as "below detection limit (BDL)" (EPA, 2012b). First, the limit of bank should be determined. Limit of bank equals the average concentration of the blanks plus 1.645 times the standard deviation of the blanks. Then, the detection limit can be calculated out. DL equals the limit of blank plus 1.645 times the standard deviation sample containing low concentration (Armbruster D.A., and T. Pry, 2008.)

If a concentration is below detection limit (BDL), its real value is a number between zero and the detection limit. Before running the CMB model, the BDL data in PAMS should be treated. The BDL data excluded from PAMS could be left untouched (Templer, 2007).

2.3.5 Ambient Measurements Processing

The measured data should be processed before using them to compile the input data file. There are several points worthy of attention in the measure data processing, which were explained as follows in this section.

Screening out Outliers

Potential outliers are measurements that are suspected of misrepresenting the population from which they were collected (EPA, 2006). Outliers can be checked out by the histogram and skewness of population (Templer, 2007). Special attention should be given to species with large skewness value which indicates potentially heavy influence on the mean by of a few large members. Then the histogram of this suspicious species should be drawn to find out the potential outliers (Templer, 2007).

Potential outliers may result from man-made errors or measurement system problems or may describe true extreme values. This means that they may represent true extreme values of a distribution and indicate more variability in the population than was expected. Therefore, scientific reasoning needs to be carried out to separate the outliers and true extreme values (EPA, 2006).

Ambient Measurements Completeness

Ambient data for CMB modeling are supposed to represent the general pollution conditions on the receptor. Not all the data sets are complete for analysis. Curren et al. (2006) offered the following criteria for the complete data set at a given sampling site for a year: a valid month of data was defined as consisting of a minimum of one sample per month; a valid quarter consisted of two valid months per quarter, and a valid year consisted of four valid quarters per year. Each complete year of data at a site therefore consists of a minimum of eight measurements.

Bellow Detection Limit Percentage Criteria

If the percentage of BDL data in measured data of a species is over a certain criterion, this species should be excluded from further calculation (Heo et al., 2009). Different criteria have been used in different studies. Table 2.5 summarizes some criteria used in air pollution source apportionment studies.

Table 2.5: The BDL data percentage criteria in some references

Reference	**Percentage**
Source apportionment of PM2. 5 in Seoul, Korea (Heo et al., 2009)	80
Source identification of fine particles in Washing, DC, by expanded factor analysis modeling (Begum et al., 2005)	80
Apportionment of sources of fine and coarse particles in four major Australian cities by positive matrix factorization (Chan et al., 2008)	50
Great Tit (Parus major) Nestlings as Biomonitors of Organochlorine Pollution (Dauwe et al., 2003)	50
The response of Chironomidae to sediment pollution and other environmental characteristics in urban wetlands (Carew, et a., 2007)	40
Comparison application of multiple receptor methods to identify aerosol sources in North Vermont (Poirot et al., 2001)	33

From Table 2.5, it is shown that the BDL data percentage criteria for invalid sample varied from 33% to 80%. It is logical that more data could be collected if the 80% would be used as the BDL data percentage criterion.

BDL Data Treatment

There are three methods to treat the BDL data: substitute BDL data with DL, 1/2 DL, and zero. There is no general guidance of method selection. The user should decide how to handle this according to the practical situation (EPA, 2012b) and choose the method which will not affect the decisions based on the data derived from this method.

If the data are used to make a risk analysis for emissions from a particular facility, the DL could be substituted for BDL data. Because the data treated by this method will describe the worst case, the risk analysis based on these data will protect the public health at the maximum. If the data are sued to develop an emission factor, 1/2 DL should be substituted for BDL data due to the reason that 1/2 DL can represent the general situation of the emission better than zero or DL. If the data are used to test the compliance of the emission with the limit, sometimes zero could be substitute for BDL data. Because the BDL data is not a reliable value, it can't be used as a strong proof. As a result, zero is preferable under this situation (EPA, 2012b).

In source apportionment studies, both DL and 1/2 DL have been adopted by researchers. Some application cases are listed in Table 2.6.

Table 2.6: BDL data treatment examples

References	**Replacement**
Source apportionment study of PM2.5 in Santiago, Chile. (Jorquera and Barraze, 2012)	1/2 DL
PM2.5 source apportionment study at four locations near the World Trade Center in New York. (Olson and Norris, 2008)	1/2 DL
Source apportionment of 3-year PM2.5 data at four sites in USA. (Lee et al., 2008)	1/2 DL
VOC source apportionment in Izmir, Turkey. (Elbir et al., 2007)	1/2 DL
VOC source apportionment in Windor, Ontario, Canada. (Templer, 2007)	DL
Determination of trace elements in ambient aerosol samples (Pekney and Davidson, 2005)	DL

2.3.6 Input Files

There are two input files needed for CMB modeling. In addition, the fitting species should be selected by user. The user can select the fitting species through an interface offered by the CMB software or input a fitting species selection file to complete the selection process.

Ambient Data File

Observed VOC concentrations must be processed into the specific format required by CMB. The detailed ambient data file processing procedure is shown in Appendix A.

Source Profile

In CMB modeling, a pollution source is expressed by a series of species. A source profile is a set of values which consist of the mass ratios of each species to the total mass. A source profile is designed to represent a kind of pollution source rather a specific emission (Watson, 2004). Compiling proper source profiles is the key step for a successful CMB modeling.

The samples to create a source profile are taken from the emission source and subjected to chemical and physical tests to determine the properties of emission sources. Each species concentration must be normalized to a same standard to form a set of ratios. This set of ratios will not only represent the unique characteristics of the specific source where these species originated from but also help to distinguish this source from other sources. This set of ratios is named as source profile. According to the recommendation of CBM 8.2 protocol, the total concentration of PAMS should be used as this common standard for normalization. There are two ways to compile proper source profiles. One is to directly measure the samples collected at the source site, normalize the measured data, and then set up a source profile representing this source. This way is relatively accurate but costly and time-consuming (Fujita and Lu, 1998). The second way is to collect the source profiles constructed in similar situations. This method is convenient and economical, and has been used by some scholars (Song et al., 2008; Templer, 2007; Fujita et al., 1994).

Nevertheless, there are some problems worthy of attention in the second method. The source profiles representing the same source type may vary greatly due to the composition variances in different regions and times. For example, gasoline compositions vary with location and time of year (Watson, 2004). The modelers should be careful in selecting proper source profiles for their projects.

Another problem is the "collinearity" among profiles. If a group of similar source profiles are put into CMB modeling together, the collinearity may appear among them in solving the chemical mass balance equations, and then this collinearity might prevent the CMB from identifying these sources. Consequently, non-convergent results or meaningless answers (e.g., negative source contribution estimate) could be produced by CMB modeling, or the standard errors in SCEs might be so high that the accuracy of modeling results will be jeopardized. These correlated source profiles should be combined into a generalized source profile to represent a general source type. For example, the pollution source in a place might include emissions from coal-fired power generation, industrial and institutional coal combustion. Since these combustion processes in these sources are similar in a given place, a strong collinearity might exist among them. Therefore, they had better be integrated into a wide "coal-burning category". The actual combining procedure depends on the profiles which are available and are likely to be acquired for a CMB study (Watson, 2004). A sensitivity test can be used to select the proper source profiles with no or acceptable collinearity between them.

Templer (2007) carried out a VOC source apportionment in Windsor in 2007. In Templer's study, local emission inventories and source apportionment references from nearby or similar areas were examined in order to find the emission sources contributing to the VOCs in Windsor airshed and the proper VOC source profiles for the CMB modeling. The most published and reviewed profiles from these references were compiled for evaluation and 25 source profiles were selected as candidates. Then an evaluating method developed by Fujita and Lu (Fujita and Lu, 1998), which involves interactive applications of the CMB model with evaluation of the diagnostic measures, was used to screen out the proper profiles. Then the model was applied to the ambient data with various subsets of source types and source profiles and the model outputs were examined in order to determine which subset is most suitable for the ambient data. This profile evaluation method also included a sensitivity test of the ambient data using different source profiles. Finally, a set of VOC source profiles were chosen for the CMB modeling in Windsor based on their sensitivity to ambient data and CMB results performance. The majority of this set of VOC source profiles consists of 55 PAMS species and only these species will be used in CMB calculation.

Fitting Species

Fitting species will be used in the CMB modeling and must be selected by modeler. There are two criteria for selecting fitting species: it should be major or unique component of the sources; it must be consistently identified and measured above its detection limits (Coulter, 2004; Fujita and Lu, 1998). Species not included in this calculation are named floating species (Watson, 2004).

An assumption for CMB is that the species mass proportion change in emission could not be considered from the source to the receptor. However, most ambient non-methane hydrocarbons are oxidized in the lowest 2 km of the troposphere with lifetime ranging from hours to several months. This oxidization will change the species mass proportion in emission during its way from source to receptor. As a result, only these species with atmospheric lifetimes greater than that of toluene (9 hours during the summer) will be used as fitting species so as to reduce the influence from the oxidization process. An exception to this is isoprene. Although its high reactivity, isoprene is still used as a fitting species because it serves as the only marker for biogenic emissions (Fujita and Lu, 1998).

Measurement Uncertainty

The uncertainties of ambient concentrations are needed data for CMB. In the weighted least squares solution employed in CMB, the estimates of the uncertainty of the SCEs are based on the uncertainty of ambient data and greater influences will be given to the species with lower concentration uncertainties. If the uncertainties of field data are accessible, they should be used as the uncertainties of measured data. But if they are not available, it is recommended by the CMB8.2 protocol that 15% should be used as the uncertainty of the measured concentrations (Watson, 2004).

2.3.7 Output Files

There are three output files from CMB: “Source Contribution Estimates”, “Species-Source Contribution”, and “Modified Psuedo Inverse Matrix (MPIN)”. These three output files are described as follows and a detailed explanation is listed in “Appendix B”.

“Source Contribution Estimate” file is the major output file. It includes three parts: “Fitting Statistics”, “Source Contribution Estimates Calculation”, and “Species Concentrations”. “Fitting Statistics” part includes “R Square”, “Chi Square”, “Mass %”, and “Degree of Freedom”. These parameters describe the calculation performance and determine if the calculation process is acceptable. “Source Contribution Estimates Calculation” part consists of “Source Contribution Estimates (SCE)”, “Standard Error (Std Err)”, and “t-statics (Tstat)” and is the most important output of CMB modeling. SCE is the calculated source contribution from the modeling; Std Err and Tstat offer the information about the accuracy of SCE. “Species Concentrations” part includes the measured species concentrations, calculated species concentrations, the ratio of calculated to measured species, and the ratio of residual to uncertainty. This part can not only offer the calculated concentrations of species but also tell the user how well the model can account for the measured species concentrations and offer useful information of the reasons. In summary, this output file can offer the most needed information for apportionment: statics of the calculation process performance, source contribution estimates, calculated species concentrations, the parameters to decide if the calculation results are acceptable, and some clues for the abnormal calculation results.

“Species-Source Contribution (Contribution by Species)” file lists the ratios of the calculated contributions from sources to each species to the measured concentration of each species. Therefore, this table can reveal the major contributors to a specific species and quantify their contributions.

“Modified Psuedo Inverse Matrix (MPIN)” file is a matrix composed of the values indicating of the influences from species on SCEs. The values of these indicators range from -1 to 1 and their absolute values can reflect the impacts of each species on SCEs. The higher the absolute value is, the stronger the influence is. From this file, modeler can identify the major and minor influential species on a specific source estimates.

The “Fitting Statistics” parameters can be used to decide whether accept or reject the modeling results. Tstat can be used to determine the extreme Std Err.

2.4 Handling of Negative Source Contribution Estimate

In respect of mathematics, the mechanism of CMB is to solve a group of linear equations. Therefore, the algorithm of CMB will try to produce a series of SCEs to balance these equations. Consequently, if the input source profiles have collinearity among them or if the real source contribution is close to zero, some negative SCEs might be produced to keep the equations in equilibrium. These negative values are only the results from mathematics and have no physical meaning.

If the negative SCE is caused by the source profiles collinearity, replacing this set of source profiles with a new set of source profiles might solve the problem. For example, Liu et al. (2008) found that if the source profile of "vehicle exhaust" was used to replace the "light-duty gasoline vehicle" and "heavy-duty diesel vehicles" in CMB, the negative SCEs of "gasoline vapors" appeared. The reason was that the "vehicle exhaust" source profile also contained gasoline vapors. Therefore "vehicle exhaust" source profile was collinear with the source profile of "gasoline vapors".

If the negative SCEs are caused by the fact that the real source contributions are close to zero, the problem could be solved by just replacing negative values by zero. Sometime, when the real source contribution is close to zero, the mathematic algorithm might produce some negative values to replace the real values to balance the equations. As a result, using zero as the source contribution instead of negative values would fit this situation better and the deviation of source contribution estimate caused by this would be acceptable in engineering (Watson, 2004; Watson et al., 1990; Lowenthal et al., 1987). Li et al. (2003) used this method in their study of source apportionment of sediment PAHs in Lake Calumet, Chicago, US.

2.5 Annual Trend of VOCs and Source Contributions

To properly evaluate the impacts of emission control strategies and the emission sources, the year-to-year trend should be analyzed. Many researchers carried out studies on annual trends of VOCs in Canada. Geddes et al. (2009) had a study of NO_2 and VOCs in Toronto and surrounding areas in summer time from 2000 to 2007. They found a decreasing trend of VOCs during this period of time by up to 40%, which was likely due to the improving of vehicle technology, regulatory initiatives, and incentive programs to control emissions. However, the biogenic VOCs showed little variation. Curren et al. (2006) carried out a study on 1, 3-butadiene concentrations trend in Canada using the data from 1995 to 2004. At most urban sites, the 1, 3-butadiene concentrations decreased from 1995 to 2004, including Windsor. This phenomenon might be contributed by the automotive emission control technologies and fuel emission reduction initiatives. Dann and Wang (1995) carried out a long term study of the ambient benzene concentrations at over 30 urban and rural sites in Canada from 1989 to 1993. From their study, it was found that the annual median benzene concentrations decreased by 20% in urban and suburban sites and by 33% in sites near industries. The strong correlationship between CO and benzene indicated that benzene was mainly due to vehicle exhaust.

2.5.1 Influential Factors

Many scholars have studied the influential factors to annual trends of VOCs, which are summarized in Table 2.7. From Table 2.7, it can be concluded that change of mobile source pollution might be the major reason for the annual trend, which might resulted from the change of vehicle quantity, introduction of new technology, implementation of emission control measures, and change of contents in gasoline. In addition, the change of economy, regional emission control measures, and new pollution sources might also affect the annual trend.

Table 2.7: Annual trend analysis in references

Author	**Sampling**	**Tendency**	**Explanation**
Characterization of volatile organic compounds in the urban area of Beijing from 2000 to 2007 (Wang et al., 2012)	VOCs measured in urban are of Beijing from 2000 to 2007	From 2000 to 2003, increasing; from 2003 to 2007, decreasing	Increase in the quantity of vehicles. The implementation of air pollution control policies.
Global comparison of VOC and CO observations in urban areas (Schneidemesser et al., 2010)	VOCs and CO measured in urban area of London from 1998 to 2008	Decreasing	Reduction of emission from vehicles due to the mobile source emission reduction measures implemented from 2000.
Long term measurement and source apportionment of non-methane hydrocarbons in three French rural areas (Sauvage et al., 2009)	46 NMHC species measured in three French rural areas between 1997 and 2006.	Significant reducing	Emission control measures in Europe.
Resolving the Long-Term Trends of Polycyclic Aromatic Hydrocarbons in the Canadian Arctic Atmosphere (Becker et al., 2006)	Polycyclic aromatic hydrocarbon (PAH) measured at Canadian High Arctic station from 1992 to 2000	A marked reduction in first few years followed by a leveling off trend from the mid-1990s onward	The reduction in early 1990s was attributed to the decline in heavy industry in the former Soviet Union at this time. From mid-1990s, other sources of PAHs, such as fuel combustion from heating and transportation, might result in the ongoing concentration of PAHs.
Ambient air 1,3-butadiene concentrations in Canada (1995–2003): seasonal, day of week variations, trends, and source influences (Curren et al., 2006)	1, 3-butadiene measured from 38 sites throughout Canada during 1995 and 2003.	Declining	Vehicle emission rate reduction due to fleet turnover, increase of low emission vehicles, implementation of new heavy-duty vehicle standard, and the reduction of sulphur and benzene content in gasoline

2.5.2 Annual Trend Detection Methods

For the monotonic increasing or decreasing trend detection, there are three statistical methods: linear regression method, Mann-Kendall test, and Sen's slope estimator (Sicard et al., 2011)". In environmental engineering, the target of annual trend analysis is to determine the general increasing or decreasing trend. Therefore, these three methods are widely applied in the annual trend analysis.

Linear regression method assumes that a linear relationship might exist between a pair of observations (X_i, Y_i) and try to obtain the slope and intercept of a line that best fits the data. The magnitude of the trend could be estimated by a regression calculation and the strength of the trend could be measured by the slope of the line (EPA, 2006). Linear regression method is easy to apply. Many researchers used this method in their studies. Geddes et al. (2009) used the linear regression analysis to determine the annual trends in VOCs and nitrogen oxides in Toronto from 2000 to 2007. It was also used in the report from Environment Canada (Environment of Canada, 2004) to determine the trend of pollutants from 1990 to 2001. However, there are some limitations in it. First, it is sensitive to outliers and BDL data, which are almost unavoidable in air pollution monitoring. Second, there are two crucial assumptions in it: normally distributed errors, and constant variances. These assumptions are difficult or exhausting to verify in practice (EPA, 2006).

"The Mann-Kendall test (MKT) is a non-parameter statistical test to detect the presence of a monotonic increasing or decreasing trend within a time series in absence of any seasonal variation or other cycles (Sicard et al., 2010)." Non-parameter statistics is a kind of techniques which does not assume that data belong to any known probability distribution. The MKT doesn’t require the data to be normally distributed and it is not sensitive to the outliers and BDL data (Tabari et al., 2011). Therefore, it is a robust tool for annual trend detection. Sicard et al. (2011) used Mann-Kendall test to determine the annual trends of ambient ozone concentrations in Mercantour National Park in France during 2000 to 2008. Sauvage et al. (2009) used Mann-Kendall test to detect the temporal trend of non-methane hydrocarbons in three areas from 1997 to 2006. However, MKT can’t describe the magnitude of the data. In other word, MKT can’t distinguish the “huge change” and “small change” in the data.MKT only expresses the significance of the trend but not the real slope of the change. Additionally, MKT is limited to annual data to be free from the seasonal variation (Sicard et al., 2010).

Sen’s slope estimator method is a consistent non-parameteric procedure to estimate the true slope for a linear trend in a time series (Sicard et a., 2010; Sen, 1968). First, this non-parameter method doesn’t require that the data should be normally distributed. Second, it is little affected by errors in the data and insensitive to the extreme and missing values (Sicard et al., 2010). In addition, it evaluates the magnitude of the data and interprets the real slope of the data by the Sen’s coefficient. Compared with MKT, the Sen’s slope test estimates the percent change in the concentration level while MKT describes the significant level of the trend (Berg, 2008). Sicard et al. (2010) used the Sen’s slope estimator to detect the trend of many air pollutants from 1990 to 2005 in France. Sauvage et al. (2009) found a significant decreasing trend of NMHC concentrations by using Sen's slope estimator to compute the trend of data which were measured in three sites in France from 1997 to 2006.

2.6 Seasonal Variation of VOCs and Source Contributions

2.6.1 Influential Factors

After being released from the sources, the VOCs will disperse in the atmosphere, which depends on the meteorological phenomena and topography. At the same time some VOCs are unstable and will be removed by chemical reactions. Most of these reactions involve reaction of VOCs with NO_3, OH radical, or O_2 and the products involve H_2O, CO_2, NO_2, O_3, and intermediates. The reaction with OH radical radicals is the major role. In summary, seasonal variation of ambient VOCs might be affected by three factors: emission, meteorological conditions (primarily wind speed, temperature, and mixing depth), and removal rate of VOCs from the airshed (such as the abundance of the OH radical) (Na and Kim, 2001; Dann and Wang, 1995). During the atmospheric dispersion process of the VOCs, the major influences come from two factors: meteorology, and chemical reaction. In winter, the calm weather condition and stable atmosphere will hinder the pollutant from dispersing. In addition, low mixing height caused by temperature inversion will also hamper the dilution of pollutants. On the contrary, in summer, the higher mixing height and unstable conditions will accelerate the dispersion of the pollutants and lead to lower concentrations. Therefore, the VOCs generally have a higher concentration in winter than in summer (Hoque et al., 2008). Besides, the inter-seasonal changes of chemical reaction also have great influences on VOC concentrations in atmosphere. The oxidation of VOCs is dominated by the OH radical concentration since VOCs oxidation rate has exponential relationship with the OH radical concentration (Zalel et al., 2008). The strong insolation in summer will increase the formation of OH radical due to the photolysis reaction of species, such as ozone and aldehyde, in the atmosphere (Hoque et al., 2008). There is a long-term measurement indicating that OH radical concentration in atmosphere is linear with solar ultraviolet radiation (Rohrer and Berresheim, 2006). The study from Hewitt (1985) suggests that the OH radical concentration in summer is probably 3 to 4 times higher than in winter. As a result, the oxidation of VOCs will be enhanced greatly in summer, which will increase the removal of VOCs from atmosphere (Hoque et al., 2008). Increase of temperature will also promote the reaction coefficient, but this kind of influence is relatively small compared with the influences of meteorology and OH radical. Therefore, meteorology and OH radical concentration are essential in understanding the seasonal VOCs variation.

Curren et al. (2006) carried out a study on 1, 3-butadiene concentrations trend in Canada using the data from 1995 to 2004. Most sites showed a seasonal pattern of high in winter and low in summer. Sarnia didn’t show this pattern and the reason might be due to its proximity to significant local industrial point sources.

Additionally, there are some other facts might be helpful in seasonal VOC concentration trend explanation. They are summarized in Table 2.8.

Table 2.8: Some influences on seasonal VOC source contribution variability

Reference	**Affected source**	**Effect**
Spatial and temporal variation of BTEX in the urban atmosphere of Delhi, India (Hoque et al., 2008)	Diesel exhaust, Gasoline exhaust, Liquid gasoline	Cold start of engine in winter will increase the vehicle emission and boost the source contribution
Long term measurement and source apportionment of non-methane hydrocarbons in three French rural areas (Sauvage et al., 2009)	Evaporation source	Lower OH radical concentration, lower rate constants and weaker UV radiation increase the chemical lifetime; lower mixing height in winter hinders the pollutant dispersion.
Seasonal characteristics of ambient volatile organic compounds in Seoul, Korea (Na and Kim, 2001)	Commercial natural gas	The influence caused by more consumption of natural gas in winter than in summer might overcome the influence of leakage increased in summer, which leads to higher contribution in winter.
Characteristics of atmospheric non-methane hydrocarbons in Foshan City, China (Tan et al., 2011)	Liquefied petroleum gas	Propane, which is the major species in “liquefied petroleum gas” profile with the mass percent of 90.6%, mainly comes from the leakage. Therefore, the contribution of liquefied petroleum gas might increase in summer due to the increase of evaporation with higher temperature.
Regional assessment of ambient volatile organic compounds in an industrial harbor area, Shizuoka, Japan (Ohura et al., 2006)	Industrial refinery	The industrial refinery pollutants can be carried to downwind place by wind.
Ambient volatile organic compound (VOC) concentrations around a petrochemical complex and a petroleum refinery (Cetin et al., 2003).	Industrial refinery	They increase with temperature due to the evaporation increase with temperature.
Determination of Benzene, Toluene and Xylene in Ambient Air Inside Three Major Steel Plant Airsheds and Surrounding Residential Areas (Chattopadhyay et al., 1996)	Coke Oven	There is no significant seasonal variation in pollutant concentrations in steel plant.

Table 2.8-continued

Reference	**Affected Source**	**Effect**
Seasonal variations of isoprene emissions from deciduous trees (Zhang et al., 2000)	Biogenic emission	Light and temperature are the main influencing factors for isoprene emission from plant. This emission rate increases with the light and temperature. Especially, this emission rate increases exponentially with the temperature.
Weather effects on isoprene emission capacity and applications in emission s algorithms (Sharkey et al., 1999)	Biogenic emission	The contribution from "biogenic emission" is always high in summer and low in winter.
Characteristics of atmospheric non-methane hydrocarbons in Foshan City, China (Tan et al., 2011)	Architectural coatings	"Architectural coatings" contribution increases with the temperature due to the solvent evaporation increased by the temperature.

2.6.2 Seasonal Trend Detection Methods

There are three statistic methods can be used for seasonal trends detection. They are linear regression analysis, Sen's slope estimator test, and seasonal Kendall test.

If the season cycle has been determined, the linear regression analysis could be used for seasonal trend analysis. Tabari et al. (2011) used linear regression test to detect the seasonal trends of reference evapotranspiration in Iran from 1996 to 2005. However, as describe in 2.5.2, the linear regression needs to satisfy the assumption of normally distributed errors and constant variance; it is sensitive to extreme data and BDL data. This hinders the application of linear regression in a practical project, including the seasonal trend determination.

If the seasonality could be determined, the Sen's slope estimator test can also used for seasonal trend quantification. Tabari et al. (2011) used the Sen's slope estimator test to detect the seasonal trends of reference evapotranspiration in Iran during 1996 to 2005. Berg et al. (2008) used the Sen's slope estimator to estimate the seasonal trend slope of trace metal concentrations in Southern Norway from 1980 to 2005. As mentioned in 2.5.2, it is a satisfying candidate method for seasonal trend determination.

The seasonal Kendall test (Hirsch and Slack, 1984) determine the seasonality by computing the MKT on each season separately and then combine the results together to form an overall result over the time. For example, data in winter data are compared only with those data in winter. No comparisons between seasons are made. Then, the Kendall's statistics for every season are summed to form the overall statistic for the whole year. In order to detect the seasonal trend, the seasonality would better be determined before the quantification of slope. However, it should be pointed out that the Seasonal Kendall test can only express the significance of trend.

Salvador et al. (2012) used the Seasonal Kendall test to detect the seasonal trends of SO_2, NO_x, CO, and $PM_{2.5}$ in Madrid from 1999 to 2008. Sicard et al. (2011) also used the Seasonal Kendall test to determine the seasonal tendencies of ozone in Mercantour National Park in France over the 2000 to 2008 period.

Some Influential Factors in Seasonal VOC Concentration Trend Analysis

(1) In winter, cold start of engine will increase the vehicle emission. This

phenomenon might boost the contributions from “vehicle exhaust”, including “diesel exhaust”, “gasoline exhaust”, and “liquid gasoline” (Hoque et al., 2008).

(2) Evaporation is directly correlated with temperature, which might make the contribution from “gasoline vapour” increase with temperature (Kourtidis et al., 1999).

(3) More natural gas will be burnt in winter to heat building and generate hot water than in summer (Sauvage et al., 2009). However, natural gas leakage increases in summertime with high temperature. Nevertheless, the contribution from consumption related to combustion might be more important than from leakage, which leads to the higher contribution of “commercial natural gas” in winter and lower in summer (Na and Kim, 2001).

(4) Propane, which is the major species in “liquefied petroleum gas” (LPG) profile with the mass percent of 90.6%. This species mainly comes from the LPG leakage (Tan et al., 2011). Therefore the contribution of LPG should increase in summer due to the increase of evaporation with higher temperature.

(5) The industrial refinery pollutants can be carried to downwind place by wind (Ohura et al., 2006). They increase with temperature due to the evaporation increase with temperature (Cetin et al., 2003).

(6) Source profile of “Coke Oven” represents the type of air pollution source from the steel (Lin et al., 2007). There is no significant seasonal variation in pollutant concentrations in steel plant (Chattopadhyay et al., 1996); therefore the Coke Oven emission should have no significant inter-seasonal changes.

(7) Light and temperature are the main influencing factors for isoprene emission from plant. This emission rate increases with the light and temperature. Especially, this emission rate increases exponentially with the temperature (Zhang et al., 2000). As a result, the contribution from "biogenic emission" is always high in summer and low in winter (Sharkey et al., 1999).

(8) Source contribution of "Architectural coatings" increases with the temperature due to the solvent evaporation increased by the temperature (Tan et al., 2011).

Mann-Kendall Test and the Sen's Slope Estimator

Mann-Kendall test:

There is a sequence of samples based on time series X_1, X_2, X_3, …, and X_n. People want to test the following hypothesis: H_0, the observations X_i have no trend; or the alternative hypothesis, H_1, there is an increasing or decreasing monotonic trend. When the samples number is less than 10, the S test is used, or the normal approximation Z is used when the samples number is more than 10 (Sicard et al., 2010).

(1) Number of values < 10

The statistical S test is defined as follows:

$$S = \sum_{k=1}^{n-1} \sum_{j=k+1}^{n} sign(x_j - x_k) \qquad (3)$$

$$sign(x_j - x_k) = \begin{cases} +1 \ if \ (x_j - x_k) > 0 \\ 0 \quad if \ (x_j - x_k) = 0 \\ -1 \ if \ (x_j - x_k) < 0 \end{cases}$$

where:

x_j = the values at time j (j>k) and exception values E(S) = 0

x_j = the values at time k (j>k) and exception values E(S) = 0

n = the number of data.

If S is more than 0, an increasing monotonic trend is noted. If S is less than 0, a decreasing trend is determined.

(2) Number of values ≥ 10

When the number of data is no less than 10, the normal approximation Z test is used. In addition, several equal values exist in the time series, the quality of MKT result will be damaged. The S variance can be written in the following equation:

$$Var(S) = \frac{n(n-1)(2n+5) - \sum_{p=1}^{q} tp(tp-1)(2tp+5)}{18} \tag{4}$$

where:

q = the number of tied groups

t_p = the number of data values in the pth group.

If there is no tied value in the series, then the S variance can be calculated in the following equation:

$$Var(S) = \frac{n(n-1)(2n+5)}{18} \tag{5}$$

The value of S and Var(S) are used to determine the Z test statistic and is expressed in the following equation.

$$Z = \begin{cases} \frac{S-1}{\sqrt{Var(S)}} & if\ S > 0 \\ 0 & if\ S = 0 \\ \frac{S+1}{\sqrt{Var(S)}} & if\ S < 0 \end{cases} \tag{6}$$

If Z is larger than 0, an increasing monotonic trend can be determined. If Z is less than 0, then a decreasing monotonic trend can be noted. Var(S) is the variance of the statistical S test. The “critical area” of the MKT at significance level α is given by “$S < Z_{\alpha}\sqrt{Var(S)}$” or “$S > Z_{1-\alpha/2}\sqrt{Var(S)}$”, where $Z_{\alpha/2}$ and $Z_{1-\alpha/2}$ respectively. The α/2 and (1- α/2) are quantiles of normal distribution. If an absolute value of Z is greater than $Z_{1-\alpha/2}$, the H_0 hypothesis is rejected, which means there is a trend in the time series values. The smaller of value of α, the more confidence there is that there is a trend in the data.

The p values will be used to measure the statistical significance. The p value or the observed significance level of a statistical test is the smallest value of α for which H_0 hypothesis can be rejected. The p value describes the strength of evidence against H_0. If p value is less than or equal to the pre-determined significance level α, then H_0 should be rejected. In this project, this situation means a strong trend exists in the observed data. The common used sliding scale for the p values is listed below (Mendenhall et al., 2009).

1) If the p value is less than 0.01, H_0 is rejected. The trend is highly significant.

2) If the p value is between 0.01 and 0.05, H_0 is rejected. The trend is statistically significant.

3) If the p value is between 0.05 and 0.1, H_0 is usually not rejected. The trend is inclined to statistical significance.

4) If the p values is larger than 0.1, H_0 is rejected. The trend is not statistically

significant.

The Sen's slope estimator:

Sen's slope estimator test is a non-parameter procedure to estimate the coefficient of a linear regression. The time series is assumed as the following equation (Tabari et al., 2011):

$$f(t_i) = Qt + B \tag{7}$$

where:

Q = the slope and B is a constant.

If there are n pairs of data, the slopes of N pairs of data are first defined as follows:

$$Q_i = \frac{x_j - x_k}{j-k} \quad for\ i = 1, \ldots., N \tag{8}$$

where:

x_j = data values at times j

x_k = data values at times k (j > k)

The median value of Q_i is the Sen's estimator of slope and is computed as follows:

$$Q = \begin{cases} A_{\frac{n+1}{2}} & \text{if n is odd} \\ \frac{1}{2}\left(A_{\frac{n}{2}} + A_{\frac{n+2}{2}}\right) & \text{if n is even} \end{cases} \tag{9}$$

The p values about the slope estimate are calculated by the non-parameter test based on a normal distribution. The common used sliding scale for the p values is as same as for MKT which is listed before.

An Application Case:

Tabari (2011) used the MKT to study the temporal trend of precipitation from 1996 to 2005. The partial results of MKT results of the annual trend were shown in the Table 2.9.

Table 2.9: Values of statistics Z of the Mann-Kendall test for annual precipitation (1966-2005)

Station	**Z**	**p**
Bushehr	2.12	0.055
Kemanshah	-2.62	0.012
Gorgan	-3.32	0.003

From the Table 2.9, it can be seen that at station "Bushehr", the Z statistics is positive, which means the trend is increasing. The p value is 0.055, which means the possibility to reject the hypothesis H_0, which is that there is no trend, is 0.945, less than 0.95. As a result, the H_0 can't be rejected and the trend can't be accepted.

At the station "Kemanshah", the p value is 0.012 and the Z is -2.62. Therefore, a significant monotonic decreasing trend from 1966 to 2005 was accepted.

At the station "Gorgan", the p value is less than 0.01, therefore, the monotonic trend is strong. The Z statistics is negative, indicating the trend is decreasing. As a result, there was a highly significant decreasing trend of the precipitation trend from 1966 to 2005.

2.7 Wind Speed Directional Dependence

Wind speed and wind direction are two influential factors which should be taken into consideration in VOC source apportionment study. Many scholars have used the wind direction in their studies of source apportionment. Dann and Wang (1995) constructed concentration roses to study the relationship between benzene concentrations and wind direction at the sites of Saint John, Montreal, Hamilton, and Sarnia in Canada during 1989 to 1993. The concentration roses showed the clear impact of nearby industries at these sites. Curren et al. (2005) used the wind roses and concentration roses to examine the origin of 1, 3-butadiene at Sarnia and Mentreal-Saint-Jeen-Bapiste in Canada with the measurements between 1995 and 2003. It was found that the industries located at south of Sarnia accounted for a significant fraction of 1, 3-butadiene measurements in Sarnia. However, the 1, 3-butadiene sources locations at Montreal-Saint-Jean-Baptiste were not clear, which might be due to the fact that 1, 3-butadiene sources distributed at different directions of this site. Cai et al. (2010) used the prevailing wind map in different seasons to study the characteristics and source apportionment of VOCs in Shanghai, China. This study shows that, due to the seasonal wind direction pattern, chemical factories located in the west, southwest, and south of the sampling site had the strongest effects on VOCs in summer and winter but less in fall and spring. In light of the above mentioned, it is shown that wind direction was a crucial factor in determining the influences of VOC sources on a sampling place.

Wind speed also played an important role in determining the transport time of pollutant from source to receptor. If the transport time was shorter than its chemical lifetime, that pollutant might not be able to reach the sampling site. In addition, short transport time also means dispersion of VOCs is weak. This means the VOC concentrations remain relatively high when the emission reaches the receptor. Nevertheless, some researchers claimed that no clear influence from wind speed on the VOCs concentration distribution could be identified and just excluded the wind speed from their study (Roukos et al., 2009). Lau et al. (2010) used the wind direction in their study but ignored the wind speed.

However, some researchers used both wind direction and wind speed in their studies. Miller, et al., (2009) used both wind speed and wind direction to study the influence from weather conditions on VOC spatial variability in Sarnia, Ontario, Canada. Clougherty, et al. (2008) used the mean wind speed and direction of daytime hours in sampling time to investigate the influence of traffic on air quality and showed that pollutant spatial patterns were different due to different pollutants and meteorology.

2.8 Ambient Concentration, Air Source Emission, and Model Output

Ambient concentration describes the quantity of pollutants in unit space in atmosphere. Usually, its unit is $\mu g/m^3$. The ambient concentration is influenced by the air source emission, meteorology, or distance from the emission source to receptor.

Air source emission is the release of pollutants into the atmosphere from a source during a period of time. Air source emission describes how mach pollutants come into atmosphere during a period of time, i.e. the ability of the source to release the pollutants. Usually, its unit is ton/hour. After the pollutants are emitted from the source, they will experience a dispersion process before they reach receptor. Therefore, the change of ambient concentration is not definitely caused by the variance of air source emission but possibly caused by it.

Model output is the source contribution estimate (SCE). SCE describes the contribution from a source to ambient pollutant concentration. Usually, its unit is $\mu g/m^3$. High SCE means the contribution to the ambient pollutant concentration from a source is high. However, due to the fact that pollutant will disperse from its source to receptor, the high contribution from a source doesn't mean that the air emission of this source is high. For example, high contribution from a source might be caused the accumulation of its emission under stable weather condition and low mixing height during a period of time. In this scenario, low air source emission can also caused high SCE.

In addition, SCE and ambient concentration are two different concepts. High SCE just means that the contribution from a source is high. It does not indicate if the ambient concentration is high or low.

CHAPTER 3

Methodology

3.1 Software Selection

The Chemical Mass Balance Model 8.2 (CMB 8.2), which is one of widely applied receptor models, was selected for this project. CMB 8.2 is free software which is available from the website of U.S.EPA (EPA, 2010)). In 2007, Templer (2007) used it in her study on VOC sources apportionment in Windsor and got satisfying results, which proved the feasibility of this software. In this study, the CMB8.2 was selected as the modeling software in this project.

3.2 Ambient Data

3.2.1 Ambient Measurements Collection

NAPS (National Air Pollution Surveillance) was established in 1969 to monitor and assess the quality of ambient (outdoor) air in the populated regions of Canada. The goal of the NAPS program is to provide accurate and long-term air quality data with a uniform standard across Canada. Now there are 286 sites in 203 communities located in every province and territory (Environment Canada, 2011; Environment Canada, 2008). One monitoring station of the NAPS in Windsor - Windsor West Station can offer these data for this project. As shown in Figure 3.1, the Windsor West Station of NAPS is located in the urban of Windsor, where the air quality can reflect the general air quality in the city. At this station, one 24-hour sample was taken every 6 days. These samples were analyzed for 177 species including the 118 hydrocarbon species which are needed to compile VOC ambient data profiles for CMB.

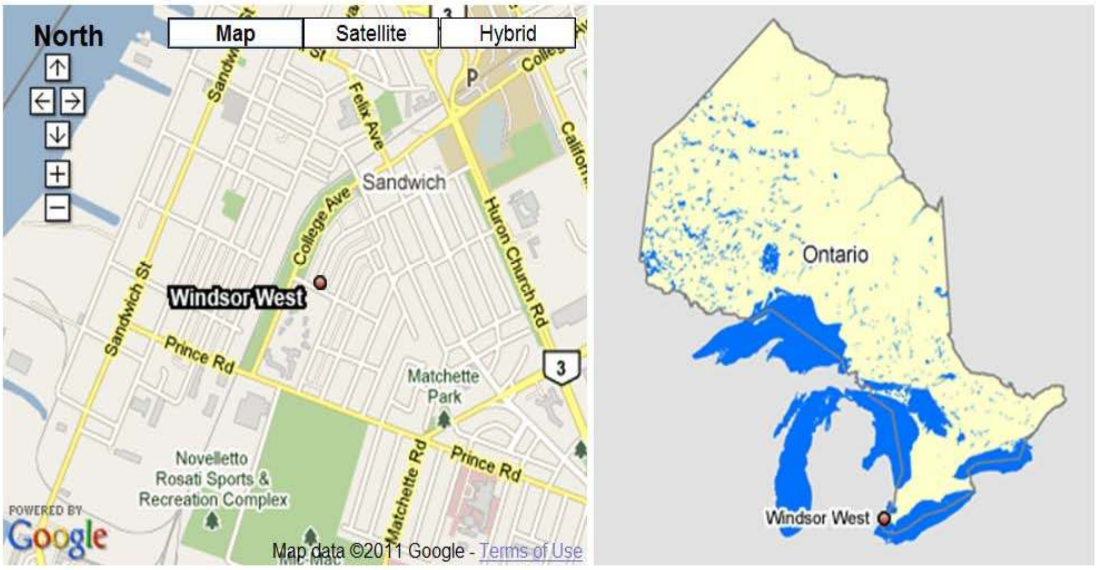


Figure 3.1: Location of Windsor West Station (source: Ontario Ministry of Environment, Canada. http://www.airqualityontario.com/history/station.php?stationid=12016)

In this project, the VOCs measurements from the Windsor West Station of NAPS from 2001 to 2009 were used as ambient data. In the 177 measured species, 118 hydrocarbon species were used to compile the ambient data profile.

3.2.2 Season Division

As mentioned in section 2.6.1, the OH radical concentration and light intensity play crucial roles in VOCs oxidation rate (Zalel et al., 2008); the temperature also influences the chemical reaction coefficient. Spivakovsky et al. (2000) calculated the global OH radical concentrations in January, April, July, and October using observed distributions of O_3, H_2O, NO_x, CO, hydrocarbons, temperature, and cloud optical depth. The results of the area at 42° N were shown in Table 3.1. The lowest OH radical concentration appeared in January and highest in July. Hakola et al. (2003) calculated the monthly OH radical concentrations in central Finland in 2000 using an observationally constrained photochemical box model. As shown in Table 3.2, in the central Finland area, the minimum OH radical concentration was in December and the maximum in June.

Table 3.1: The OH radical concentrations in area of 42° N with the atmosphere pressure of 1000 hPa (Spivakovsky et al., 2000)

	January	**April**	**July**	**October**
OH radical (10^5 molecules cm-3)	0.95	7.5	12.95	4.9

Table 3.2: The monthly OH radical concentrations in central Finland in 2000 (Spivakovsky et al., 2000)

	January	**February**	**March**	**April**	**May**	**June**
OH radical (ppt)	0.002	0.004	0.013	0.030	0.058	0.063
	July	**August**	**September**	**October**	**November**	**December**
OH radical (ppt)	0.058	0.035	0.029	0.006	0.002	0.001

The longitude of Windsor is 42° N, while the longitude of central Finland is 62° N. The difference of the longitude in these two areas is about 20° and they are in the north hemisphere. As a result, it is acceptable to estimate that the low OH radical concentration in Windsor might be between December and January, while the peak between June and July.

Summer solstice is the day with the longest daytime in a year, while the winter solstice is the day with the shortest daytime in a year. The summer solstice in northern hemisphere is June 20 or 21, and the winter solstice is December 21 or 22 (Encyclopedia Britannica Online, 2009).

The monthly temperatures in Windsor from 2001 to 2009 (Environment Canada, 2012) were listed in Table 3.3. It could be seen that the lowest monthly temperature was in February and the highest was in July.

Table 3.3: The average monthly temperature of Windsor from 2001 to 2009 (Environment Canada, 2012)

Month	January	February	March	April	May	June
Temperature (C°)	-2.8	-3.2	2.2	9.8	14.9	21.4
Month	July	August	September	October	November	December
Temperature (C°)	23.2	22.8	19.0	11.8	5.8	-1.0

As a result, it is logical to assume that the peak OH radical concentration appears near the summer solstice and the bottom OH radical concentration arose near the winter solstice in Windsor area. From 2001 to 2009, the highest monthly temperature was close to summer solstice while the lowest monthly temperature was about two months away from the winter solstice. Therefore, the winter and summer solstices are selected as the criteria for season division (Zalel et al., 2008; Lau et al., 2010). Accordingly, winter is classified as from November to January; spring is from February to April; summer is from May to July; autumn is from August to October.

3.2.3 Ambient Data Checking

Ambient measurements were check in order to get some general information of the VOCs, which might be helpful for the further analysis. The checking list included missing data, BDL, and the incomplete data sets.

Checking Key Species

If there are only a few species in a source profile belong to fitting species, these species will have strong influences on the modeling results of this source. Therefore, these species can be deemed as key species in CMB modeling. The results are in Table 3.4.

Table 3.4: Key species in source profiles

Species	**Source**	**Reason**
I_PREN (isoprene)	Biogenic Emission	Only marker
IPENTA (isopentane)	Gasoline Vapour	With mass ratio of 0.285
N_BUTA (butane)	Gasoline Vapour	With mass ratio of 0.238
N_BUTA	Industrial Refinery	With mass ratio of 0.229
ETHANE (ethane)	Commercial Natural Gas	With mass ratio of 0.689
N_PROP (propane)	Commercial Natural Gas	With mass ratio of 0.211
N_PROP	Liquefied Petroleum	With mass ratio of 0.906
TOLUE (toluene)	Architectural Coating	With mass ratio of 0.259

Screening out PAMS Outliers

The skewness values of PAMS from 2001 to 2009 were calculated. The results were listed in Table 3.5.

Table 3.5: Skewness of PAMS, 2001 to 2009

Year	2001	2002	2003	2004	2005	2006	2007	2008	2009
Skewness	1.84	4.26	2.12	2.43	1.54	1.99	3.77	4	2.06

Table 3.5 shows that the skewness values in every year were all above 1.5. If the distance between a sample's measurements to the mean value of samples in a year was more than 2 times of corresponding standard deviation, this sample was determined as sample outlier. According to The histogram of the PAMS was drawn year by year from 2001 to 2009 shown in Figure 3.2, 9 sample outliers were screened out and the results were listed in Table 3.6.

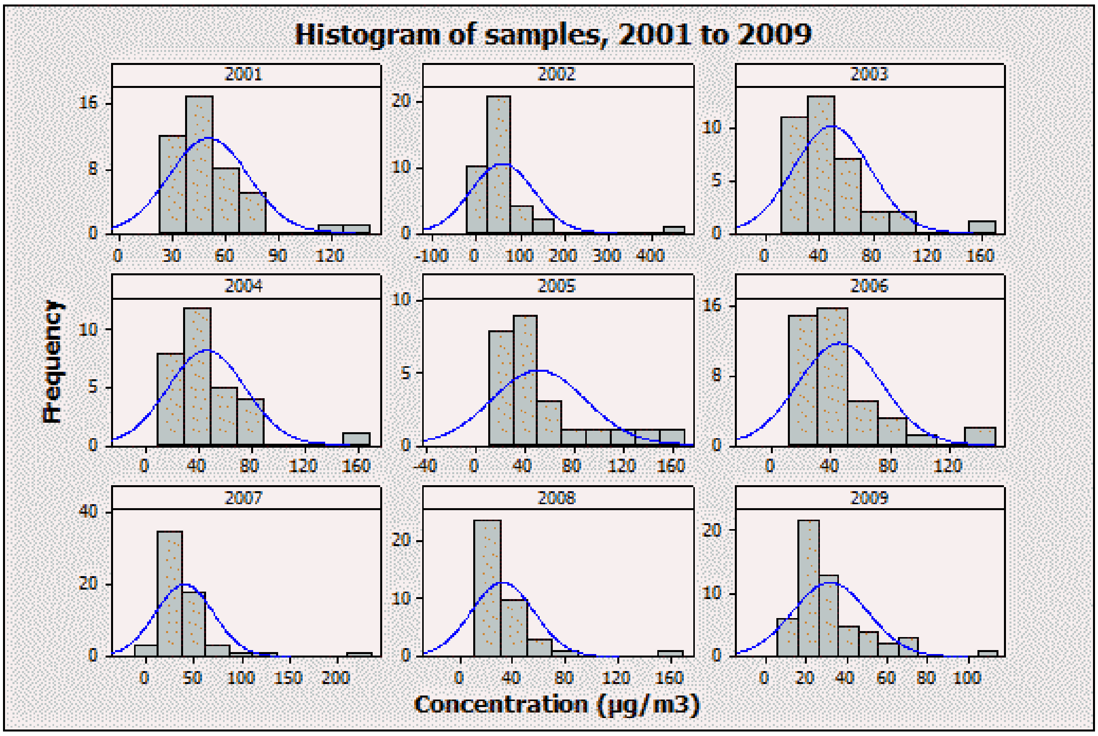


Figure 3.2: Histogram of samples in each year, 2001 to 2009

Table 3.6: Sample outliers

Sample	2001/9/16	2001/10/22	2002/1/14	2003/10/6	2004/9/30	2005/2/27	2005/3/5
Concentration ($\mu g/m^3$)	116.1	134.1	434.5	162.9	164.5	136.2	156.9
Sample	2006/8/9	2006/10/8	2007/3/19	2007/11/2	2008/10/15	2009/9/4	
Concentration ($\mu g/m^3$)	145.1	134.5	116.4	221.3	156.7	112.6	

Potential species outlier detection:

After sample outliers were deleted, the skewness of each PAMS species in each year during 2001 to 2009 were calculated. Table 3.7 shows that there were 13 PAMS species with skewness value more than 4, which accounted for approximately 3% of total species. If the distance between a species' measurements to its mean value in a year was more than 5 times of corresponding standard deviation, this species was determined as sample outlier. According to the histogram shown in Figure 3.3 to Figure 3.5, 13 species outliers were screened out and listed in Table 3.8.

Table 3.7: Species with potential outliers

Year	**Species outliers**			
2002	Toluene			
2003	2-Methylheptane	1-Pentene	Propylene	Ethylene
2006	Heptane,	3-Methylhexane,	2-Methylhexane,	2,3-Dimethylpent
2007	iso-Propylbenzen	Toluene		
2008	Methylcyclohexan			
2009	Isoprene			

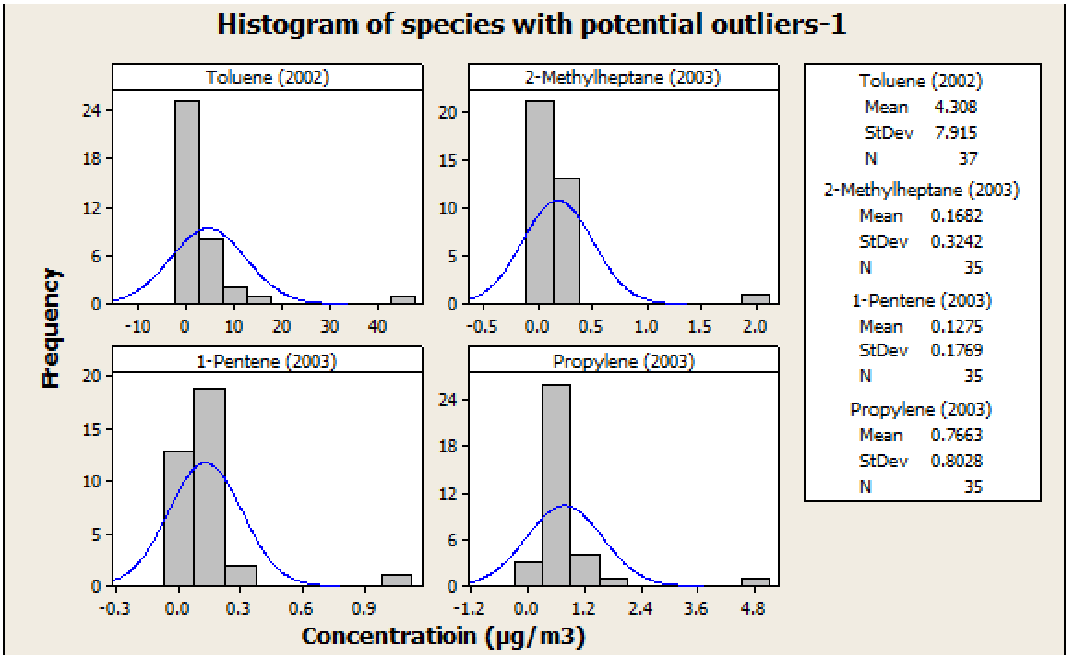


Figure 3.3: Histogram of species with potential outliers-1

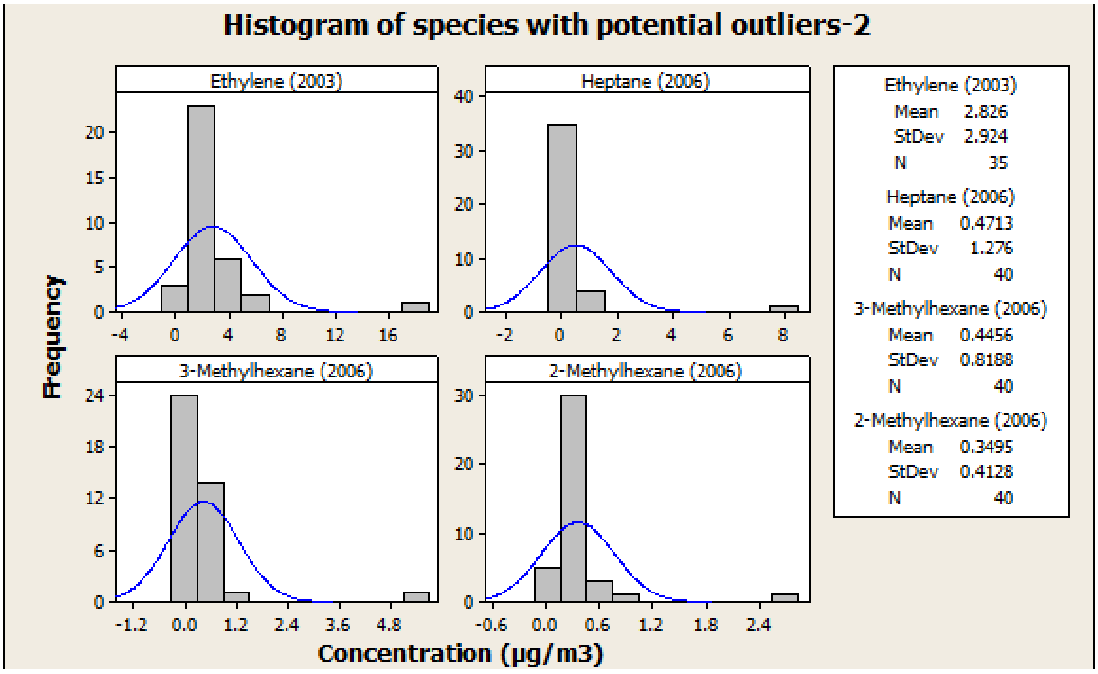


Figure 3.4: Histogram of species with potential outliers-2

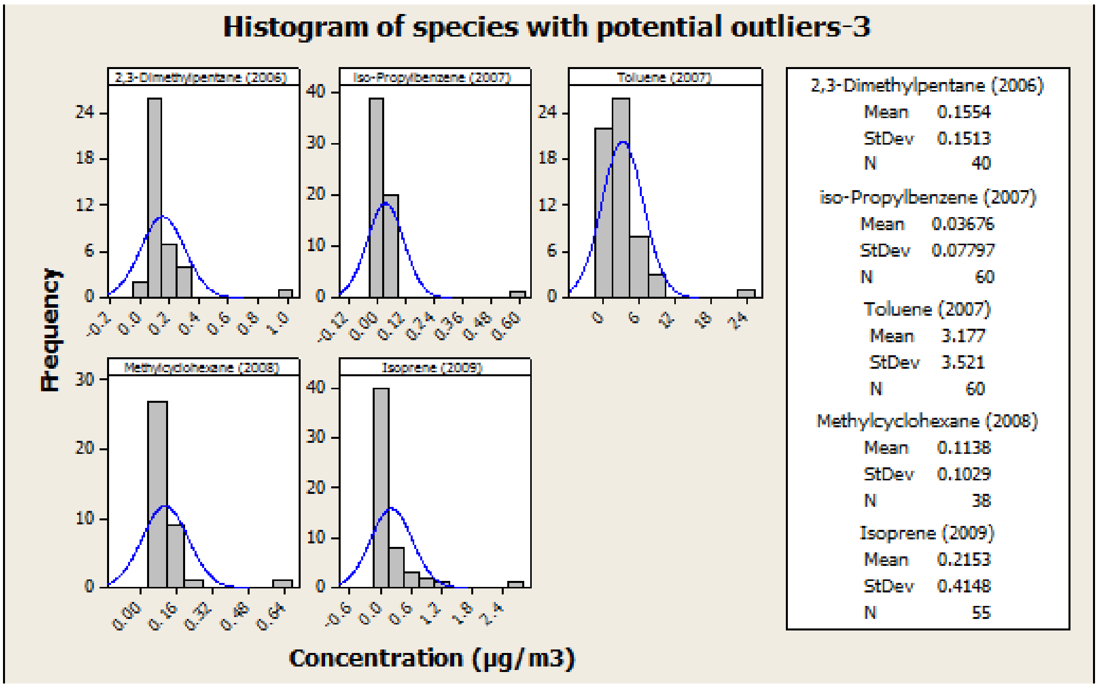


Figure 3.5: Histogram of species with potential outliers-3

Table 3.8: Potential species outliers

Sample	Potential species outliers			
2002/9/17	toluene			
2003/3/28	2-methylheptane	1-pentene	propylene	ethylene
2006/3/30	heptane	3-methylhexane	2-methylhexane	2,3-dimethylpentane
2007/9/15	iso-propylbenzene	toluene		
2008/8/16	methylcyclohexane			
2009/6/24	isoprene			

Potential species outlier analysis:

A source can be expressed as the mass ratios or concentration ratios between the species composing this source. Therefore, people can identify sources by calculating the ratios of concentration or mass between species. It is logic that key species should be included in this ratio. If there is no key species in a source, the important species, which takes a relatively large part of mass in the source, should be included in the ratio at least. This kind of ratio is defined as reference ratio here. If the potential species outlier is the real reflection of the contribution from a source, the reference ratio's practical value should not differ a lot from its theoretic. Here, the practical reference ratio value is defined as the concentration ratio between the potential species outlier and the key species/important species in the sample; the theoretic reference ratio value is defined as the ratio of these species' values in source profile. Therefore, by comparing these two values, the species outlier will be identified. This comparison can be carried out by calculating the ratio between these two values. Here, this ratio is defined as indicating ratio.

There are two scenarios. When the potential species outlier itself is key species or important species, the potential species outlier reflects the real extreme contribution from a source. In this situation, the indicating ratio will be 1. When the potential species outlier is neither key species nor important species, the situation will be complicated: if the potential species outlier reflects the real source contribution, the indicating ratio should be in the range from 0.5 to 2; otherwise, the indicating ratio will be outside of the range from 0.5 to 2 and the potential species is outlier and should be treated. As a result, examining the indicating ratio value will help people to separate the species outliers and true extreme value. The examining results of all potential species outliers are listed in Table 3.9.

Table 3.9: Potential species outliers checking

Sample	**Potential species outlier**	**Possible source**	**Reference Ratio**	**Practical value**	**Theoretic value**	**Indicating ratio**
2002/9/17	toluene	Architectural Coating	toluene / (m and p-xylene)	7.02	9.59	0.73
2003/3/28	ethylene	Gasoline Exhaust	ethylene/ ethylene	1	1	1
	propylene		propylene /ethylene	0.281	0.462	0.610
	1-penten		1-penten/ ethylene	0.061	0.046	1.327
	2-methylheptane		2-methylheptane/ ethylene	0.111	0.077	1.447
2006/3/30	2,3-dimethylpentane	Gasoline Exhaust	ethylene/2,3-dimethylpentane	2.060	7.222	3.505
2006/3/30	2-methylhexane	Industrial Refinery	2-methylhexane/butane	0.006	0.004	1.449
	3-methylhexane		3-methylhexane/butane	0.006	0.022	0.268
	heptane		heptane/butane	0.004	0.031	0.127

Table 3.9-continued

Sample	**Potential species outlier**	**Possible source**	**Reference Ratio**	**Practical value**	**Theoretic value**	**Indicating ratio**
2008/8/16	methylcyclohexane	Gasoline Exhaust	methylcyclohexane/ 1,4-diethylbenzene	1.924	1.500	1.283
2009/6/24	isoprene	Biogenic Emission	isoprene/ isoprene	1	1	1
2007/9/15	toluene	Architectural Coating	toluene/ toluene	1	1	1
	iso-propylbenzene	Coke Oven	iso-propylbenzene/ benzene	0.7450	0.0857	8.6922

Table 3.9 shows that the indicating ratios of almost all potential species outliers are in the acceptable range with the exception of 2,3-dimethylpentane in sample “2006/3/30” and iso-propylbenzene in sample “2007/9/15”. Therefore, these two species were determined as species outliers.

None of these two species outliers belonged to key species or important species. Their concentrations were low (2, 3-dimethylpentane 0.98 $\mu g/m^3$, iso-propylbenzene 0.62 0.98 $\mu g/m^3$) and took only 1.41 % and 1.03 % of PAMS in their samples, respectively. This means they will not have strong influences on the CMB modeling. Therefore, they were replaced by the average concentrations of the corresponding year in CMB modeling.

Checking Mass Percentage of PAMS in 118 NMHC

Generally, PAMS compounds should take about 80% of ambient hydrocarbon (Watson, 2004). If the percentage of PAMS in ambient hydrocarbon is too low, the variations between the CMB modeling results and the reality might be too huge to make the modeling results unusable. The mass percentages of the PAMS species in total NMHC species in each sample during 2001 to 2009 were checked. The results showed that this index in every sample was above 80% and its average value was 95%. As a result, there was no sample excluded from modeling due to the low mass percentage of PAMS in NMHC.

Checking Missing Species in Each Sample

If the percentage of missing species in a sample is too high, the accuracy of sample will be damaged and this sample should be dropped. As a result, each sample was cheked fro missing species in this study. Due to the fact the average mass percentage of PAMS in NMHC in this study was 95%, only PAMS species were checked for missing species. The results showed that the highest percentage of missing species in PAMS species was 5%. Therefore, no sample was excluded due to this reason.

Checking Missing Species in Fitting Species and Key Species of Each Source Profile

In CMB8.2, the missing species will be flagged and removed from calculation automatically (Coulter, 2004). If there were too many missing fitting-species in a source profile, the accuracy of its SCE would be damaged. Every sample was checked for the missing fitting-species. The results showed that the highest number of missing fitting-species in a sample was only two. Therefore, no sample was excluded for this reason.

In addition, if the key species were missing, the precision of the modeling would also be undermined. Especially, if the missing key-species was the only marker for a source, the model would not be able to estimate the contribution of this source. As a result, the key species should be examined for the missing measurements. However, the results showed that there was no missing key-species

Checking BDL Data in Key Species and Fitting Species in Each Sample

BDL data are not accurate data, but estimates of the real value. As a result, BDL data in the fitting species would affect the accuracy of the modeling results. This kind of influences could be estimated from two aspects: the key species with BDL data; the percentage of the fitting species with BDL data in each source. The fitting species with BDL data were checked and the results were included in Table 3.10 and Table 3.11.

Table 3.10: Samples containing key species with BDL data

Sample	**Species**	**Source Profiles**
2003/1/9	isoprene	Biogenic Emission
2007/10/21	isoprene	Biogenic Emission
2008/3/31	isoprene	Biogenic Emission
2008/12/14	isoprene	Biogenic Emission

Table 3.11: The samples containing fitting species with BDL data

Sample	2007/6/22	2007/10/21	2008/3/31	2008/12/14	2009/4/13	2009/9/16
BDL	2,2-Dimethyl butane	Isoprene	Isoprene	Isoprene	2,3,4-Trimethylpentane	2,2-Dimethylbutane

Table 3.10 shows that only there was one key species with BDL data in samples: isoprene. Isoprene was the only marker for “Biogenic Emissions”. The samples containing this key species with BDL data were also listed in Table 3.10.

From Table 3.11, it was shown that each sample contained as most one fitting species with BDL data. In each source, there was only one fitting species contained BDL data at same sampling time. Therefore, if the influence from the key species was excluded, on source was strongly affected by the fitting species with BDL data.

Incomplete data set checking

The criterion mentioned in 2.3.5 was used to filter out the incomplete data sets. The seasons were divided according to the way mentioned in 3.2.2. The results are listed in Table 3.12. Table 3.12 shows that there were some incomplete data sets, including the spring of 2002, summer of 2005, and fall of 2005.

Table 3.12: Incomplete data sets, 2001 to 2009

Year	2002	2005	2005
Season	Spring	Spring	Summer

3.2.4 BDL Data Treatment Method Selection

BDL Treatment Method Selection

The influence of species with BDL data on CMB modeling can be estimated by the sum of their percentages in the source profiles. The larger is this sum, the stronger is the influence. According to this criterion, after checking all the samples, it was found that the sample collected on December 14, 2008, was the one with the strongest influence. Therefore, this sample was used to test the influences of these two different BDL measurements treatment methods. Two different input ambient data files were constructed by replacing the BDL measurements in this sample with DL or (1/2) DL, respectively. The results are shown in Table 3.14 and Table 3.14.

Table 3.13: CMB modeling results from two different BDL treatment methods

		Replacing BDL by DL			**Replacing BDL by 1/2 DL**		
Fitting Statistics	R Square	0.84			0.84		
	Chi Square	3.16			3.16		
	Mass	97.70			97.70		
	Freedom	22.00			22.00		
SCE		SCE ($\mu g/m^3$)	Std Err	Tstat	SCE ($\mu g/m^3$)	Std Err	Tstat
	Diesel Exhaust	0.76	0.28	2.70	0.76	0.28	2.70
	Gasoline Exhaust	3.26	1.17	2.78	3.26	1.17	2.78
	Liquid Gasoline	-0.98	0.91	-1.08	-0.98	0.91	-1.08
	Gasoline Vapour	2.50	0.68	3.66	2.50	0.68	3.66
	Commercial Natural Gas	5.21	1.27	4.11	5.21	1.27	4.11
	Liquefied Petroleum Gas	7.72	1.81	4.27	7.72	1.81	4.27
	Industrial Refinery	3.73	0.94	3.97	3.73	0.94	3.97
	Coke Oven	0.95	0.33	2.86	0.95	0.33	2.86
	Architectural Coatings	0.07	0.54	0.13	0.07	0.54	0.13
	Biogenic Emissions	0.00	0.01	0.29	0.00	0.01	0.29
	Total	23.23			23.23		

Table 3.14: Paired T-test of the CMB modeling results from two BDL treatment methods

	N	Mean	Std Dev	SE Mean
Replacing BDL by DL	35	5.78365	16.84997	2.84817
Replacing BDL by 1/2 DL	35	5.78547	16.78564	2.83729
Difference	35	-0.001818	0.09381	0.015857
T-test of mean difference= 0 (vs. not = 0): T-Value = -0.11; P-Value = 0.909				

Table 3.14 shows that the p value with confidence of 0.95 was 0.909. This indicated that there was no significant difference between the results. Therefore, using DL or (1/2) DL to replace BDL measurements will not have significant different influences on CMB modeling results. In this research, the (1/2) DL was chosen as the

substitution of BDL data.

3.2.5 Ambient Data File Compiling

There were totally 177 measured species from the data collected from the Windsor West Station of NAPS. In these measured data, 117 were NMHC which were used to compile the ambient data file. In these 117 NMHC, 55 PAMS species were used to construct the ambient data file, while those excluded from 55 PAMS were grouped into a category named "others" which took about 5% of the total hydrocarbon mass. These species in "others" were not involved into the calculation of solving the chemical mass balance equations (Fujita and Lu, 1998). Among these 55 PAM species, only 32 species were fitting species which were used to solve the chemical mass balance equations to figure out the SCEs. The concentration estimates of those floating species were computed by multiplying their ratios in source profiles to the SCEs of corresponding sources. The specific process to compile the ambient data file was included in Appendix A.

The measured data were compiled to form an ambient input data file. In this project, the 80% was employed as the BDL percentage criteria to filter out those species which could not be used. The BDL data were replaced with 1/2 DL.

3.3 Fitting Species

According to the lifetime criterion mentioned in 0.0.0, among the 55 PAMS target species, 31 hydrocarbons can satisfy the lifetime criterion and are selected as fitting species candidates. Including isoprene, the total number of fitting species is 32, which are shown in Table 3.15 (Templer, 2007). These fitting species were selected for the modeling in this project.

Table 3.15: 55 PAMS species and CMB fitting species (Templer, 2007)

PAMS Species	CMB Fit	PAMS Species	CMB Fit
acetylene	*	methylcyclopentane	*
benzene	*	2-methylhexane	*
n-butane	*	3-methylhexane	*
1-butene		2-methylheptane	*
c-2-butene		3-methylheptane	*
t-2-butene		2-methylpentane	*
cyclohexane	*	3-methylpentane	*
cyclopentane	*	2-methyl-1-pentene	
n-decane	*	n-nonane	*
1,3-dimethylbenzene		n-octane	*
1,4-diethylbenzene		n-pentane	*
2,2-dimethylbutane	*	1-pentene	
2,3-dimethylpentane	*	c-2-pentene	
2,3-dimethylbutane	*	t-2-pentene	
2,4-dimethylpentane	*	n-propane	*
ethane	*	propene	
ethene		n-propylbenzene	
ethylbenzene		styrene	
2-ethyltoluene		1,2,3-trimethylbenzene	
3-ethyltoluene		1,2,4-trimethylbenzene	
4-ethyltoluene		1,3,5-trimethylbenzene	
n-heptane	*	2,2,4-trimethylpentane	*
n-hexane	*	2,3,4-trimethylpentane	*
isobutane	*	toluene	*
isopentane	*	n-undecane	*
isoprene	*	m,p-xylene	
iso-propylbenzene		o-xylene	
methylcyclohexane	*		

3.4 Source Profiles Preparation

3.4.1 Source Profiles Compiling

Templer (2007) set up a set of source profiles suitable for VOC sources apportionment in Windsor by CMB. This set of source profiles, which were listed in Table 3.16, were used in this project. Their source profiles are listed in Appendix C.

Table 3.16: Source Profiles Used for VOC Sources Apportionment in Templer's thesis (Templer, 2007)

	Mnemonics	**Type**
1	Tu_MchHD	Diesel Exhaust
2	Exh_Lin1	Gasoline Exhaust
3	WA_Liq	Liquid Gasoline
4	WA_Vap	Gasoline Vapour
5	CNG	Commercial Natural Gas
6	LPG	Liquefied Petroleum Gas
7	Ind_Ref	Industrial Refinery
8	Coke_Ovn	Coke Oven
9	Biogenic	Biogenic Emissions
10	Arc_Coat	Architectural Coatings

3.4.2 Source Profiles Collinearity and Key Species Checking

The mass percentages of 32 fitting species in the selected source profiles were listed in Table 3.17. From it, the following information about source collinearity could be extract.

(1) “Biogenic Emissions” has no collinearity with any other source.

(2) “Architectural Coatings” only has overlap with “Commercial Natural Gas” and “Liquefied Petroleum Gas”.

The following information about the key species in source profiles could be inferred from Table 3.17. The less fitting species means the calculation results will be less reliable.

(1) “I_PREN (Isoprene)” is only included in “Biogenic Emissions” and it is also the only fitting species in “Biogenic Emissions”.

(2) “Liquefied Petroleum Gas” includes three fitting species: “ETHANE (ethane)”, “N_PROP (propane)”, and “I_BUTA (isobutene)”.

(3) “Architectural Coatings” contains three fitting species: “PEN24M (2, 4-dimethylpentane)”, BENZE (benzene), and “TOLUE (toluene)”.

Table 3.17: The fitting species percentages in source profiles

Sources	**ETHANE**	**ACETYL**	**N_PROP**	**I_BUTA**	**N_BUTA**	**IPENTA**	**N_PENT**	**I_PREN**
Diesel Exhaust	0.011	0.023	0.02	0.002	0.006	0.012	0.014	0
Gasoline Exhaust	0.017	0.037	0	0.005	0.022	0.069	0.026	0
Liquid Gasoline	0	0	0	0.003	0.028	0.094	0.063	0
Gasoline Vapour	0	0	0	0.027	0.238	0.285	0.122	0
Commercial Natural Gas	0.689	0	0.211	0.021	0.031	0.007	0.007	0
Liquefied Petroleum Gas	0.041	0	0.906	0.002	0	0	0	0
Industrial Refinery	0.005	0	0.037	0.096	0.229	0.013	0.066	0
Coke Oven	0	0	0	0.003	0.02	0.007	0.005	0
Biogenic Emissions	0	0	0	0	0	0	0	1
Architectural Coatings	0	0	0	0	0	0	0	0
Sources	**BU22DM**	**CPENTA**	**BU23DM**	**PENA2M**	**PENA3M**	**N_HEX**	**MCYPNA**	**PEN24M**
Diesel Exhaust	0.024	0.003	0.003	0.018	0.008	0.009	0.006	0.003
Gasoline Exhaust	0.007	0.003	0.009	0.028	0.018	0.017	0.012	0.007
Liquid Gasoline	0.003	0	0.02	0.043	0.026	0.036	0	0.012
Gasoline Vapour	0.004	0.008	0.012	0.036	0.02	0.022	0	0.005
Commercial Natural Gas	0	0	0	0.003	0.001	0.004	0.01	0
Liquefied Petroleum Gas	0	0	0	0	0	0	0	0
Industrial Refinery	0.007	0.005	0	0.002	0.016	0.029	0.013	0.004
Coke Oven	0.002	0	0	0.004	0.004	0.005	0	0.002
Biogenic Emissions	0	0	0	0	0	0	0	0
Architectural Coatings	0	0	0	0	0	0	0	0.011

Table 3.17- continued

Sources	**BENZE**	**CYHEXA**	**HEXA2M**	**PEN23M**	**HEXA3M**	**PA224M**	**N_HEPT**	**MECYHX**
Diesel Exhaust	0.029	0.002	0	0.008	0.021	0.013	0.005	0.004
Gasoline Exhaust	0.033	0.002	0.013	0.009	0.012	0.035	0.008	0.006
Liquid Gasoline	0.03	0.005	0.016	0.023	0.018	0.036	0.015	0.003
Gasoline Vapour	0.014	0.003	0.005	0.008	0.006	0.009	0.005	0.001
Commercial Natural Gas	0	0	0	0	0.002	0.003	0.002	0.001
Liquefied Petroleum Gas	0	0	0	0	0	0	0	0
Industrial Refinery	0.016	0.003	0.001	0	0.005	0.002	0.007	0.002
Coke Oven	0.105	0	0	0.035	0.009	0.013	0.01	0.007
Biogenic Emissions	0	0	0	0	0	0	0	0
Architectural Coatings	0.001	0	0	0	0	0	0	0
Sources	**PA234M**	**TOLUE**	**HEP2ME**	**HEP3ME**	**N_OCT**	**N_NON**	**N_DEC**	**N_UNDE**
Diesel Exhaust	0.003	0.041	0	0.004	0.003	0.01	0.024	0.048
Gasoline Exhaust	0.012	0.077	0.005	0.005	0.004	0.001	0.001	0
Liquid Gasoline	0.016	0.149	0.006	0.007	0.006	0.003	0	0.001
Gasoline Vapour	0.003	0.044	0.001	0.002	0.001	0	0	0
Commercial Natural Gas	0	0	0.004	0	0	0	0	0
Liquefied Petroleum Gas	0	0	0	0	0	0	0	0
Industrial Refinery	0.001	0.019	0	0.001	0.001	0	0	0
Coke Oven	0.001	0.02	0	0.001	0.002	0.031	0.013	0
Biogenic Emissions	0	0	0	0	0	0	0	0
Architectural Coatings	0	0.259	0	0	0	0	0	0

3.5 Output and Post Data Processing

The ambient data file and the selected source profiles were inputted into the CMB 8.2. Then, for each sample, the suitable fitting species were chosen and the model was run.

3.5.1 Consistently Negative Source Contribution Estimates Checking

At first, the all 10 source profiles from Templer's thesis (Templer, 2007) were used for CMB modeling. The results of the negative SCEs are showed in Table 3.18.

Table 3.18: Consistently negative SCEs checking

CMB Modeling with 10 source profiles	Source with negative SCE	Coke Oven	Architectural Coating	Liquid Gasoline	Gasoline Vapour
	Negative SCEs Percentage (%)	1.4	9.8	66.0	0.6
	Percentage in total SCE (%)	4.6	4.4	3.9	13.2
CMB Modeling with 9 source profiles	Source with negative SCE	Coke Oven	Architectural Coating		
	Negative SCEs Percentage (%)	1.1	13.7		
	Percentage in total SCE (%)	4.5	4.2		

Table 3.18 shows that in the CMB modeling with 10 source profiles, negative SCEs existed in the results of four sources, including "Coke Oven", "Architectural Coating", "Liquid Gasoline", and "Gasoline Vapour". Consistently negative SCEs existed in the modeling results of "Liquid Gasoline", which was indicated by the fact that 66% of the SCEs of "Liquid Gasoline" were negative. This means that this source profile might be not accurate enough and have some collinearity between other source profiles (Liu et al., 2008). Besides, the SCEs of "Liquid Gasoline" only took

3.9% of the total SCE. Therefore, “Liquid Gasoline” should be excluded from modeling (Li et al., 2003).

After excluding “Liquid Gasoline”, the CMB modeling was carried out using the left 9 source profiles. The results are also listed in Table 3.18. Table 3.18 shows that only two sources contained negative SCEs and the highest percentage of negative SCEs was merely 14%. Therefore, after the “Liquid Gasoline” was excluded, there were no consistently negative SCEs. In addition, the negative SCEs percentages were also small (4.5% and 4.2%). This proved that the “Liquid Gasoline” should be deleted from the source profiles. As a result, this source was excluded from the CMB modeling in this study and only the left 9 source profiles were used.

3.5.2 Model Output Performance Checking

The performance of the modeling was examined by its statistics. These statistics and their corresponding criteria were listed in Table 3.19(Coulter, 2004). Their detailed explanations were in Appendix B. The checking results were summarized in Table 3.20.

Table 3.19: Calculation performance statistics checking, 2001 to 2009

Number of calculation performance statistics which are outside of target	1	2	3	4
Number of samples	164	44	6	0
Percentage of samples (%)	45.9	12.3	1.7	0.0

Table 3.20: Modeling performance statistics (Coulter, 2004)

Parameter	**Target range**
R Square	0.8 ~ 1
Chi Square	1 ~ 4
MASS %	80 ~ 120
Degree of Freedom	More than 5

3.5.3 Extreme Std Err Checking

The standard error is the standard deviation of the sampling distribution. It describes the variability of the sampling. In CMB modeling, the uncertainty of the ambient data, the source profile, and the amount of collinearity among the different profiles is reflected by the standard error (Std Err) (Watson, 2004).

Standard deviation (Std Dev) shows how much variation differs from the average. It describes the variability of the population. In CMB modeling, the source contribution estimate (SCE) is assumed as the real reflection of the source contribution. Therefore, the uncertainty of the SCE is expressed as one standard deviation of the most probable SCE (Watson, 2004).

The relationship between Std Err and Std Dev can be expressed by the Equation (10).

$$\text{Standard error} = \text{Standard deviation} / \text{sqrt}(\text{n}) \tag{10}$$

Where:

n = the number of observations of the sample.

In CMB modeling, the extreme Std Err is examined by “Std Err/SCE” which is included in the output report. The target of this parameter was far less than 1. Outliers of “Std Err/SCE” implies that there is something wrong with this SCE and it might not be accepted.

Using the skewness and histogram of “Std Err/SCE”, the outliers of “Std Err/SCE” can be screened out. The results are listed in Table 3.21.

Table 3.21: Skewness in Std Err of SCEs

Sources	Diesel Exhaust	Gasoline Exhaust	Gasoline Vapor	Commercial Natural Gas	Liquefied Petroleum
Skewness	1.39	1.28	1.55	1.6	2.36
Sources	Industrial Refinery	Ocke Oven	Architectural Coating	Biogenic Emission	
Skewness	1.2	1.2	1.77	3.47	

Table 3.21 shows that the skewness values of Std Err in SCEs of “Liquefied Petroleum” and “Biogenic Emission” were above 2. The Std Err outliers in these two SCEs were screened out by the histogram which are shown in Figure 3.6.

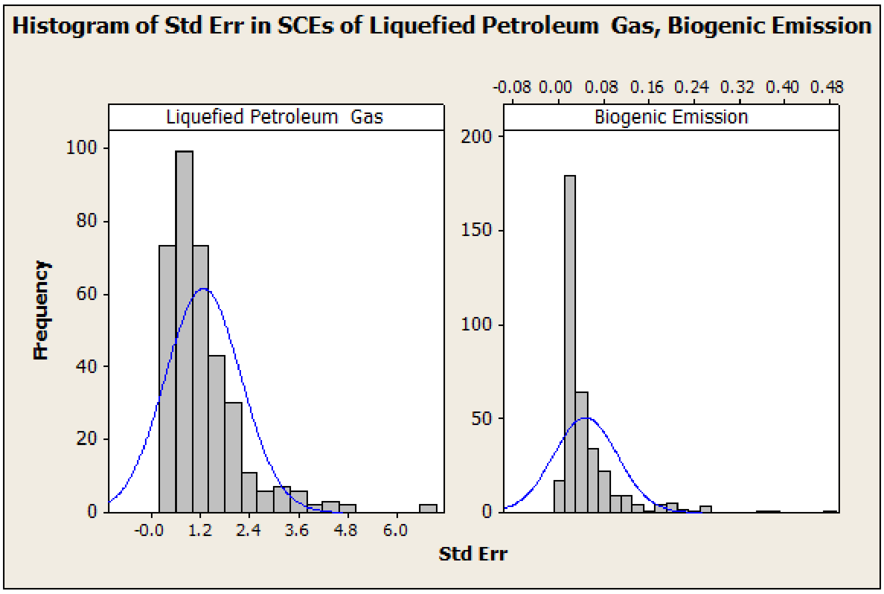


Figure 3.6: Histograms of Std Err in SCEs of “Liquefied Petroleum Gas” and “Biogenic Emission”

According to Figure 3.6, the outliers of Std Err in SCEs of "Liquefied Petroleum Gas" and "Biogenic Emission" were checked out. The results were summarized in Table 3.22.

Table 3.22: Extreme Std Err of "Liquefied Petroleum Gas" and "Biogenic Emission"

Source	Liquefied Petroleum Gas	Biogenic Emission
Number of Std Err outliers	9	19
Percentage of Std Err outliers (%)	2.5	5.3

There were two ways to solve this problem. The first way was to abandon this source profile and run the model again. However, if there was one fitting species which only existed in this source profile, abandoning this source profile would cause the problem: which source should this species belong to? Under this situation, it was logically to assume that this fitting species came from this abandoned source; therefore, the contribution from this source could be estimated by dividing the concentration of this species by its mass percentage in this source profile. The SCEs from other sources were estimated by CMB modeling without this source profile. This calculation might add additional mass to the total results; therefore, the total calculated mass would not be as 100% of the measured mass. Therefore, a normalization process was carried out, which was explained later in detail.

If there was no such species in this source profile, this source profile could be abandoned and the contribution from this source was deemed as zero. The other source contribution estimates could be calculated out by CMB modeling with left source profiles.

The second way was to just abandon the SCE of this source profile without doing the modeling again. However, abandoning the SCE of this source would reduce the total calculated mass of the modeling. Too many reduced mass would damage the accuracy of the modeling results. As a result, the percentage of the abandoned mass should not exceed 5% of the total calculated mass. Or this method couldn't be used. Consequently, a normalization process was also carried out due to fact that the some mass was removed from the calculation results.

Screening out Result Outliers

The calculation performance statistics which is outside of target and the extreme Std Err all indicated possible result outliers and were used as result outlier indicators. All the SCEs during 2001 to 2009 were checked for result outlier by using these indicators. The results were summarized in Table 3.23.

Table 3.23: Results outlier indicators checking, 2001 to 2009

Number of indicators	1	2	3	4	5
Number of corresponding samples	162	54	8	1	0
Percentage of samples (%)	45.4	15.1	2.2	0.3	0.0

(Indicators: extreme Std Err; R Square outside of target; Chi Square outside of target; Mass Percent outside of target; Freedom Degree outside of target)

In this study, any result containing no less three result outlier indicators was screened out as result outlier and deleted. The 9 result outliers were listed in Table 3.24.

Table 3.24: CMB result outliers

	Result outlier				
Sampling date	2003/3/28	2007/6/18	2007/8/22	2008/1/19	2009/4/7
Sampling date	2009/6/24	2009/6/30	2009/7/30	2009/8/17	

3.5.4 Negative Source Contribution Estimates Treatment

If the negative SCEs just appeared occasionally, some measures would be adopted for negative SCEs treatments. Because the source profiles have been optimized and tested by Templer (2007) in her thesis, replacing the source profiles or compiling several of source profiles into a comprehensive source profile was not an option to address of the problem of negative SCEs in this project. Therefore, the negative SCEs were replaced with zero.

When the negative SCE was replaced with zero, there was a scaling calculation of SCE percentage. Here the CMB result for the sample of “01/01/2009” was used as an example to show how to carry out this calculation. As shown in Table 3.25, the calculated SCE for “liquid gasoline” was -0.86 and other SCEs were positive. Therefore, this negative value was replaced by zero while other positive values remained the same, which was named as “converted values” and listed in the third column-“SCE (converted)”. Then each converted value was scaled to the total converted value and timed by 100 to get the SCE percent which indicated the contribution percentage of each source to the total pollution.

There are some concepts in Table 3.25 which need to be clarified. The total calculated value is the sum of all the SCEs calculated from CMB modeling. These calculated SCEs are just the mathematically calculated SCEs including meaningless negative SCEs. The converted SCEs are the data converted from the CMB calculation results and are supposed to represent the real source contributions.

Table 3.25: Process for negative SCEs conversion and their percent calculation

Source	**SCE (calculated) (μg/m^3)**	**SCE (converted) (μg/m^3)**	**Percentage (%)**
Diesel Exhaust	0.54	0.54	1.92
Gasoline Exhaust	4.97	4.97	17.69
Liquid Gasoline	*-0.86*	*0*	*0.00*
Gasoline Vapour	3.35	3.35	11.93
Commercial Natural Gas	7.84	7.84	27.91
Liquefied Petroleum Gas	3.59	3.59	12.78
Industrial Refinery	6.32	6.32	22.50
Coke Oven	1.04	1.04	3.70
Biogenic Emissions	0.03	0.03	0.11
Architectural Coatings	0.41	0.41	1.46
Total	*27.23*	28.09	100

3.5.5 Source Contribution Estimates Normalization

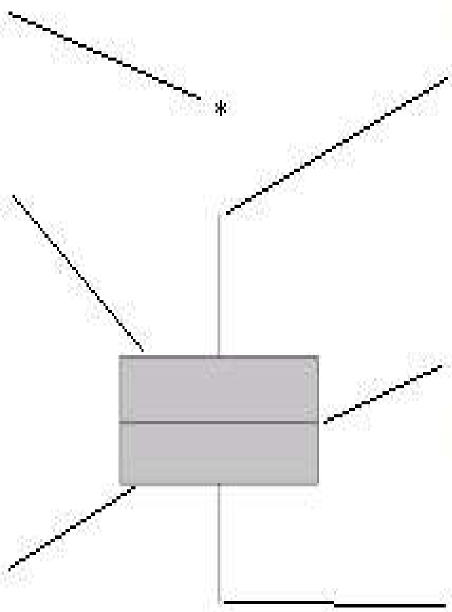
If the sum of SCE percentages was not 100%, the SCEs would be normalized to 100%. The normalized SCE was the product of its percentage in total SCEs and total measured data. For example, if the sum of SCEs percentage is 120%, then the normalized SCE of “building coating” will be computed by the following equation:

$$SCE = \frac{\text{"building coating" } SCE}{Total\ SCE} \times (total\ measured\ data) \tag{11}$$

3.6 Annual Trend Detection and Seasonal Variance Analysis

In the annual trend detection, the linear regression method was used as the annual trend detection method. The Minitab 14 was used for the linear regression analysis.

In the seasonal variance analysis, the data of same season in different years were compared in terms of statistics. The function of “box plot” in Minitab 14 was used for analysis. The meaning of each symbol of box plot is shown in Figure 3.1.



Outlier □ an unusually large or small observation. Values beyond the whiskers are outliers.

Q3: By default, the top of the box is the third quartile. □ 75% of the data values are less than or equal to this value.

Q1: By default, the bottom of the box is the first quartile. □ 25% of the data values are less than or equal to this value.

Upper limit: By default, the upper whisker extends to this adjacent value □ the highest data value within the upper limit. Upper limit = Q3 + 1.5 (Q3 □ Q1)

Median: The middle of the data. Half of the observations are less than or equal to it.

Lower limit: By default, the lower whisker extends to this adjacent value □ the lowest value within the lower limit. Lower limit = Q1□ 1.5 (Q3 □ Q1)

Figure 3.7: Symbols of the Box Plot

CHAPTER 4

RESULTS AND DISCUSSION

4.1 PAMS Analysis

4.1.1 Analysis on PAMS during 2001 to 2009 by Season

The total concentrations of 55 PAMS species were used to investigate the ambient VOCs (Nguyen et al., 2009; Brown et al., 2007; Watson et al., 1998). The 9-year PAMS measurements were analyzed by seasons and the results are shown in Figure 4.1. The sample numbers in each season and the ratios of the sample number in each season to the average sample number of each season during 2001 to 2009 are listed in Table 4.1 year by year.

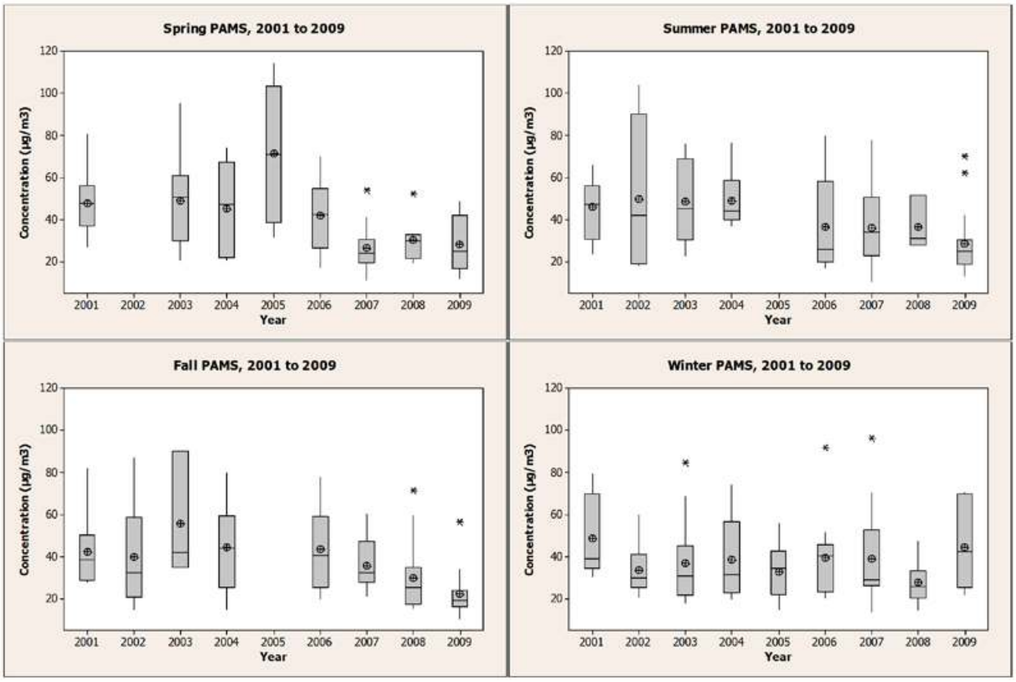


Figure 4.1: PAMS measurements analysis by seasons, 2001 to 2009

Table 4.1: Sample number in each season and the ratio of sample number in each season to the average sample number of each season during 2001 to 2009

	Spring		**Summer**		**Fall**		**Winter**	
	Sample number	Ratio	Sample number	Ratio	Sample number	Ratio	Sample number	Ratio
2001	18.00	1.73	7.00	0.77	11.00	1.04	9.00	0.74
2002			9.00	0.99	12.00	1.13	12.00	0.98
2003	12.00	1.16	5.00	0.55	3.00	0.28	13.00	1.06
2004	5.00	0.48	6.00	0.66	8.00	0.75	12.00	0.98
2005	6.00	0.58					15.00	1.23
2006	8.00	0.77	5.00	0.55	12.00	1.13	15.00	1.23
2007	13.00	1.25	23.00	2.52	11.00	1.04	14.00	1.15
2008	8.00	0.77	3.00	0.33	14.00	1.32	13.00	1.06
2009	13.00	1.25	15.00	1.64	14.00	1.32	7.00	0.57
Average	10.38		9.13		10.63	1.00	12.22	1.00

(Ratio= sample number in each season/average sample number of corresponding season during 2001 to 2009)

Figure 4.1 shows that in 2005, the mean concentration of spring PAMS was extremely high, which was approximately 1.9 times of the average spring PAMS level of all the other years. This means the PAMS level in spring of 2005 was an extreme value from the opinion of long-term trend. Table 4.1 shows that ratio in the spring of 2005 is 0.58. It is the forth lowest ratio in all the ratios. The small sample number of a data set might bring extreme and unrealistic value and damage its reliability. Furthermore, the annual data set in 2005 was not complete due to the fact that only measurements in spring and winter are available. Therefore, considering the small sample number and extreme high seasonal PAMS level in spring of 2005 and the fact that data set of 2005 is incomplete, the data set of 2005 was excluded from the analysis.

In addition, Figure 4.1 also shows that there were declining trends in PAMS measurements in the spring, summer, and fall from 2001 to 2009. However, the PAMS level changed little in winter from 2001 to 2009.

4.1.2 Annual PAMS Analysis

The annual VOC source contributions and corresponding percentages during 2001 to 2009 were calculated. The results are shown in Figure 4.2. Figure 4.2 shows a declining trend of PAMS by approximately 33% from 2001 to 2009. This is consistent with the observations in other studies on long-term VOC trends in Canada. Geddes et al. (2009) found a decreasing trend of VOCs in summer from 2000 to 2007 in Toronto. They attributed the decreasing trend to the improving vehicle technology, regulatory initiatives, and incentive programs to control emissions. Curren et al. (2006) observed a decreasing trend of 1, 3-butadiene concentrations during 1995 to 2004 in Canada. This might be due to the automotive emission control technologies and the fuel emission reduction initiatives.

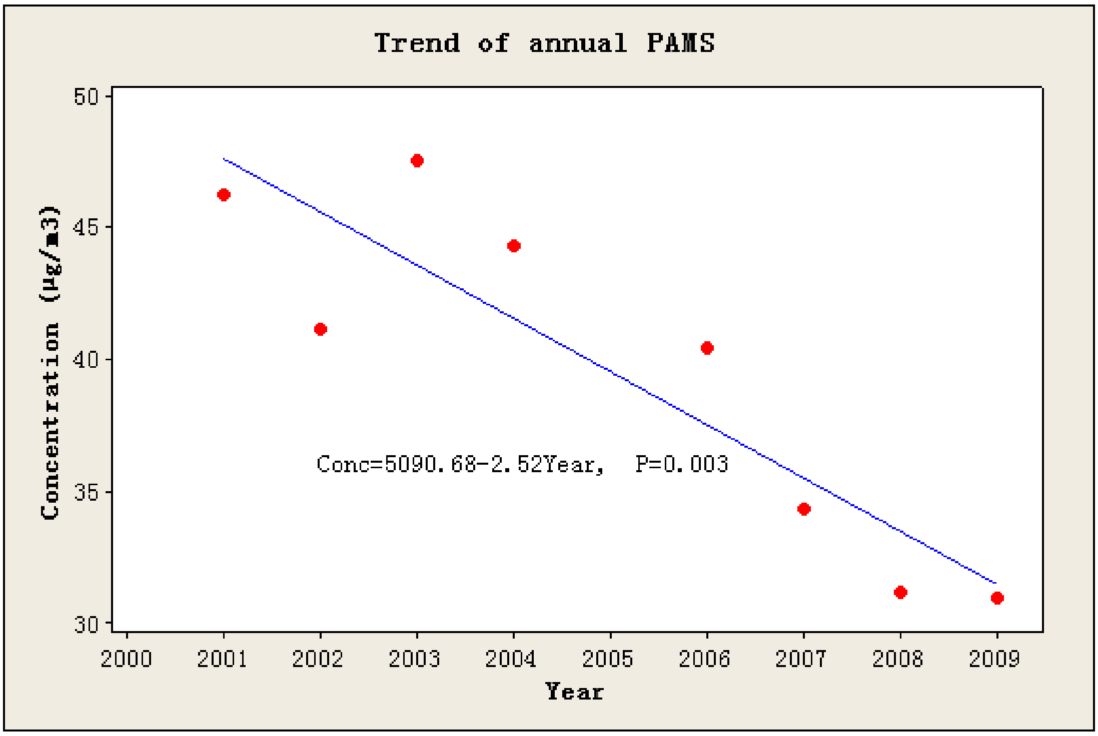


Figure 4.2: Annual VOC measurements, 2001 to 2009

4.2 Annual Source Contribution Analysis

The VOC source contributions and contribution percentages from 2001 to 2009 are shown in Figure 4.3 and Figure 4.4. “Vehicle Emission” was composed by “Diesel Exhaust”, “Gasoline Exhaust”, and “Gasoline Vapour”. From Figure 4.3 and Figure 4.4, the source contribution ranking during 2001 to 2009 could be found: “Vehicle Emission” (source contribution 17.5 µg/m^3; source contribution percentage 44%), “Industrial Refinery” (source contribution 7.3 µg/m^3; source contribution percentage 19%), “Commercial Natural Gas” (source contribution 6.9 µg/m^3; source contribution percentage 18.4%), “Liquefied Petroleum” (source contribution 3.7 µg/m^3; source contribution percentage 9.3%), “Coke Oven” (source contribution 1.7

μg/m^3; source contribution percentage 4.5%), "Architectural Coating" (source contribution 1.9 μg/m^3; source contribution percentage 4.2%), and "Biogenic Emission" (source contribution 0.2 μg/m^3; source contribution percentage 0.4 %).

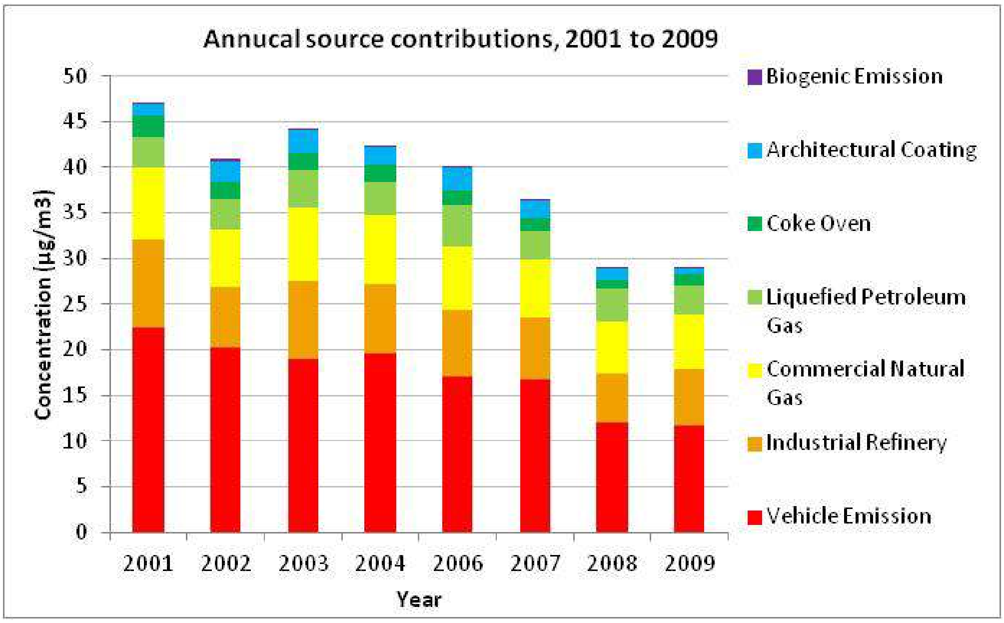


Figure 4.3: Annual source contributions, 2001 to 2009

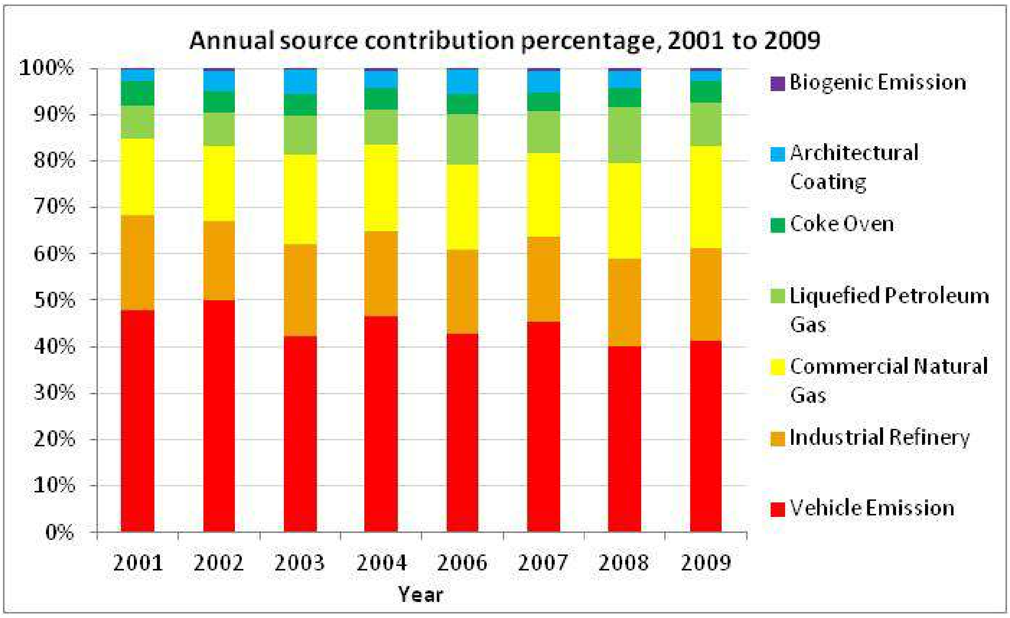
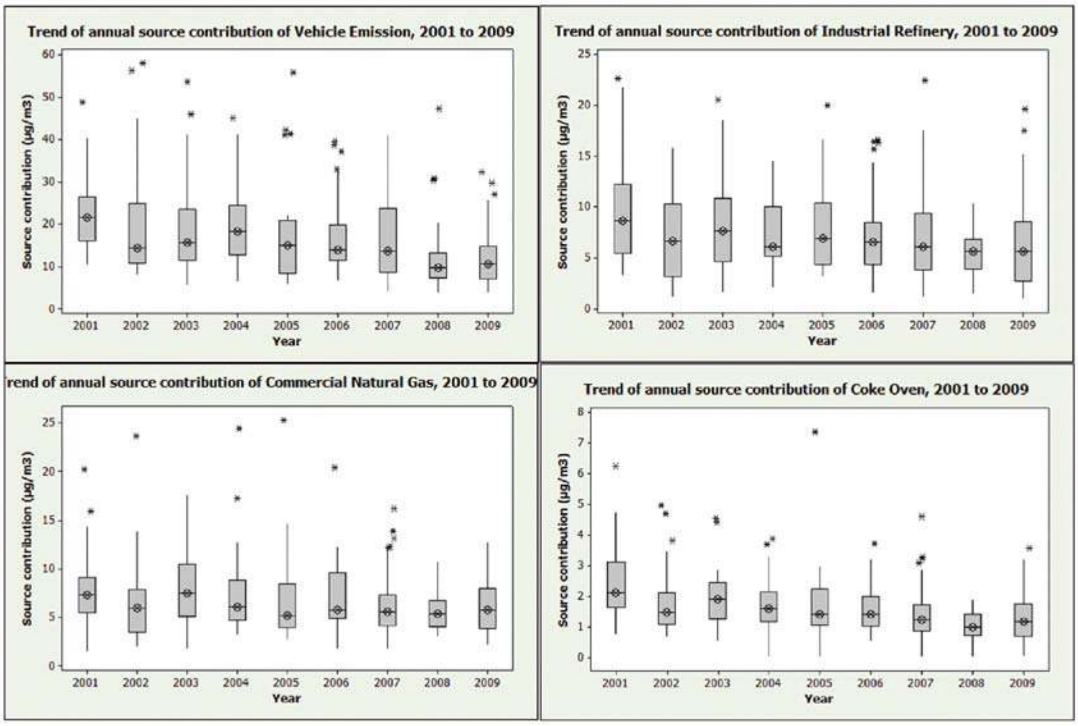


Figure 4.4: Annual source contribution percentages, 2001 to 2009

4.3 Trend of Annual Source Contribution of Each Source

The annual source contributions of each source during 2001 to 2009 were analyzed. The results are shown in Figure 4.5 and Figure 4.6. Figure 4.5 shows declining trends in source contribution of “Vehicle Emission”, “Industrial Refinery”, “Commercial Natural Gas”, and “Coke Oven” during 2001 to 2009. This is consistent with other studies (Geddes et al., 2009; Curren et al., 2006). The reason could be due to the improving of vehicle technology, regulatory initiatives, and incentive programs to control emissions. However, Figure 4.6 shows that during 2001 to 2009, the annual source contributions of “Liquefied Petroleum Gas”, “Architectural Coating”, and “Biogenic Emission” changed little.



Trend of annual source contribution of Vehicle Emission, 2001 to 2009

Trend of annual source contribution of Industrial Refinery, 2001 to 2009

rend of annual source contribution of Commercial Natural Gas, 2001 to 2009

Trend of annual source contribution of Coke Oven, 2001 to 2009

Figure 4.5: Trends of annual source contributions of “Vehicle Emission”, “Industrial Refinery”, “Commercial Natural Gas”, and “Coke Oven”, 2001 to 2009

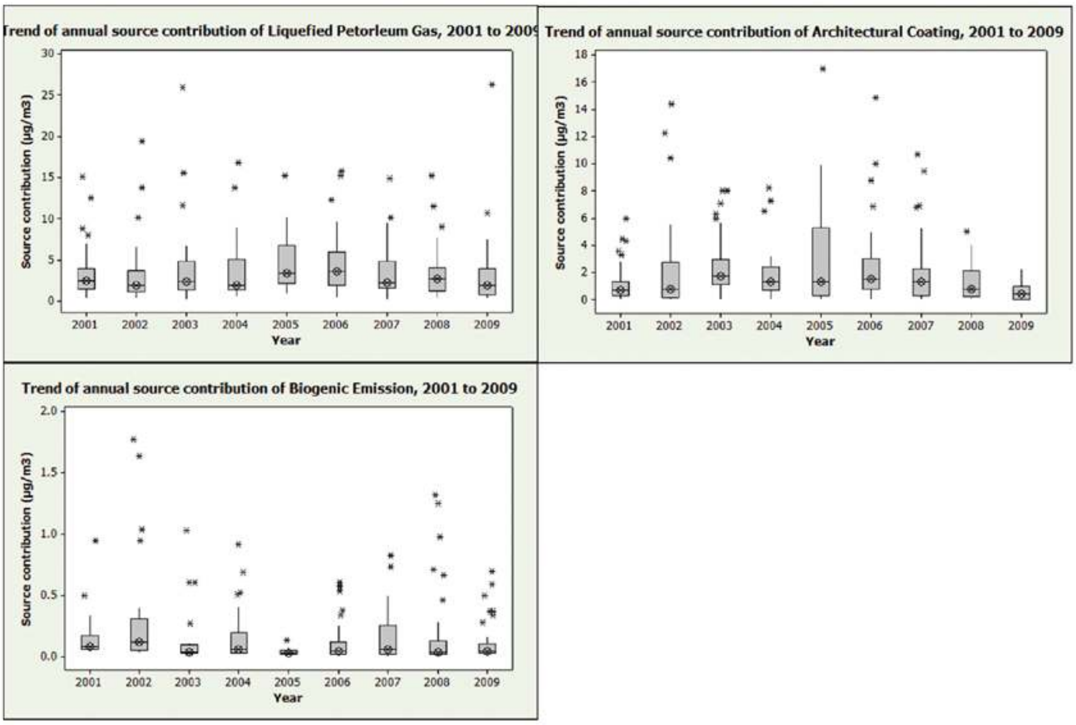


Figure 4.6: Trends of annual source contributions of "Liquefied Petroleum Gas", "Architectural Coating", and "Biogenic Emission", 2001 to 2009

4.4 Source Contribution Reduction Analysis

4.4.1 Total Source Contribution Reduction Analysis

The total source contribution reduction during 2001 to 2009 was analyzed. The results are shown in Figure 4.7. Figure 4.7 shows that the major contribution to the total source contribution reduction was the source contribution reduction of "Vehicle Emission", which was reduced by 10.8 µg/m^3 and accounted for 59.7% of total source contribution reduction, followed by "Industrial Refinery" (source contribution reduction 3.59 µg/m^3, percentage in total source contribution reduction 19.9%), "Commercial Natural Gas" (source contribution reduction 1.73 µg/m^3, percentage in total source contribution reduction 9.5%), "Coke Oven" (source contribution reduction 1.11 µg/m^3, percentage in total source contribution reduction 6.2%), "Architectural Coating" (source contribution reduction 0.56 µg/m^3, percentage in total source contribution reduction 3.1%), "Liquefied Petroleum Gas" (source contribution reduction 0.28 µg/m^3, percentage in total source contribution reduction 1.5%), and "Biogenic Emission" (source contribution reduction 0.03 µg/m^3, percentage in total source contribution reduction 0.2%).

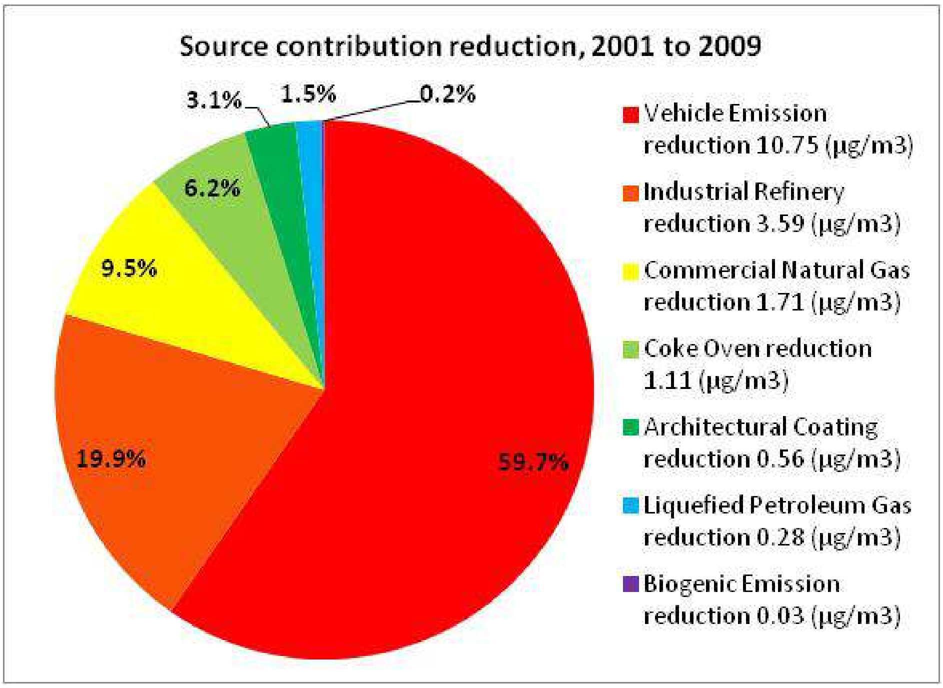


Figure 4.7: Source contribution reduction, 2001 to 2009

4.4.2 Vehicle Emission Reduction Analysis

The "Vehicle Emission" was composed of three sources: "Diesel Exhaust", "Gasoline Exhaust", and "Gasoline Vapour". Their annual source reductions during 2001 to 2009 are shown in Figure 4.8. Figure 4.8 shows that source contribution of

“Vehicle Emission” was reduced by 48% during 2001 to 2009. Source contributions of its three components (“Diesel Exhaust”, “Gasoline Exhaust”, and “Gasoline Vapour”) all decreased during 2001 to 2009. Among them, “Gasoline Exhaust” was the major contributor to the total source contribution reduction of “Vehicle Emission”, which accounted for 62% of total reduction, followed by “Diesel Exhaust” (22% of total source contribution reduction) and “Gasoline Vapour” (16% of total source contribution reduction).

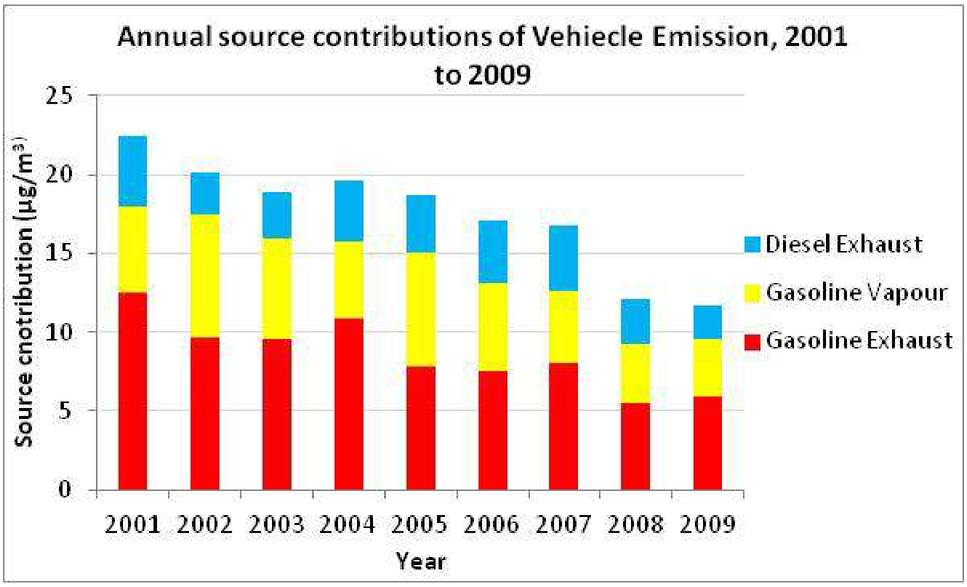
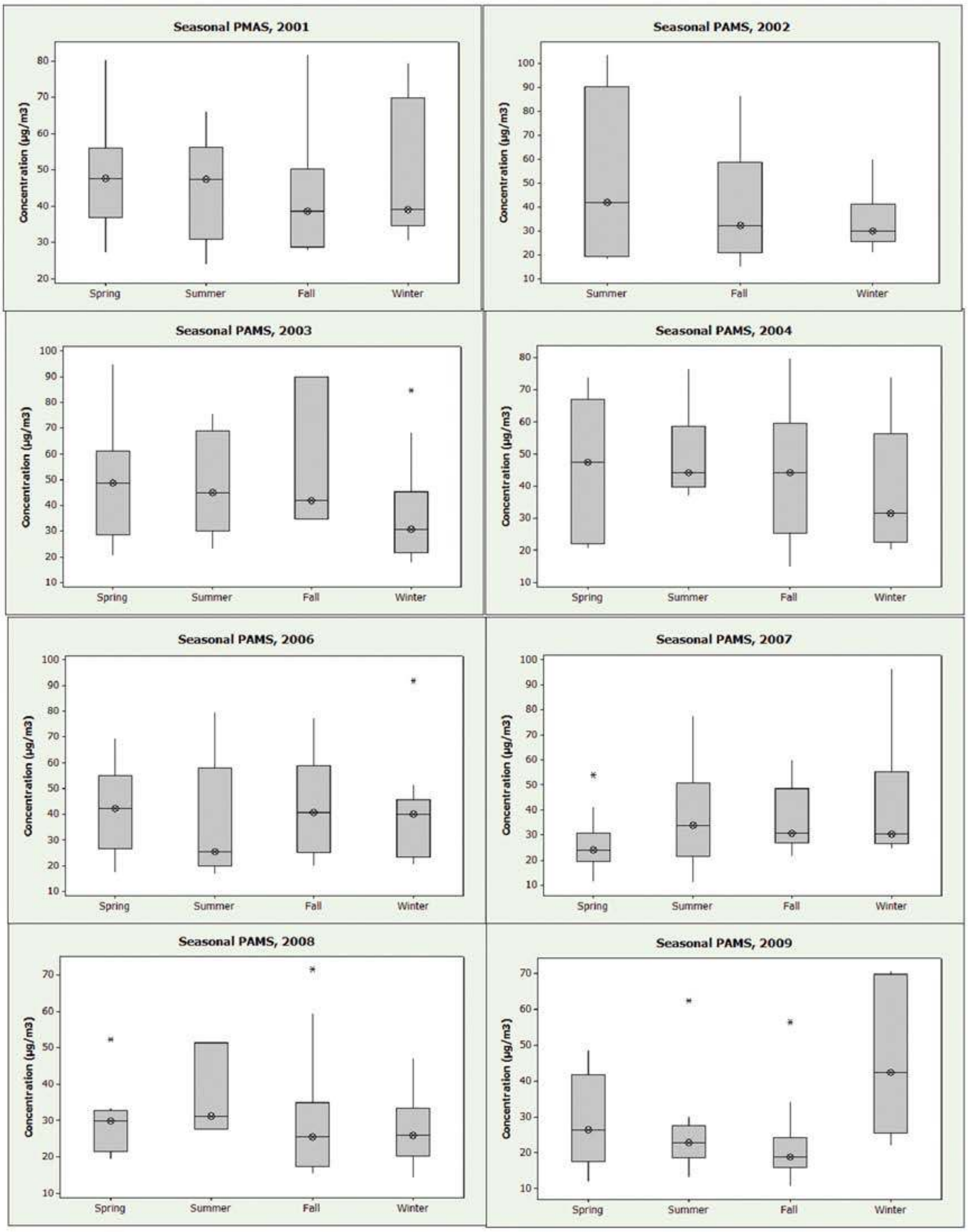


Figure 4.8: Annual source contribution of Vehicle Emission

4.5 Seasonal Pattern of VOCs

4.5.1 Seasonal PAMS Analysis

The seasonal variabilities of 55 PAMS species from 2001 to 2009 are analyzed. The results are shown in Figure 4.9. Figure 4.9 shows that seasonal PAMS levels were approximately the same in each year during 2001 to 2008. In 2009, the source contribution level in winter was higher than in other seasons. Therefore, in general, a special relatively flat pattern of seasonal PAMS was observed during 2001 to 2009. This contradicts the results of other studies (Sauvage et al., 2009; Hoque et al., 2008; Na and Kim, 2001). They observed a seasonal VOCs pattern of high level in spring and winter but low in summer and fall in their studies. Given that the vehicle emission was the major contributor to total source emission, the reduction of vehicle emission contribution caused by low traffic counts in winter and spring in Windsor might be the reason for this special even pattern of seasonal PAMS.


Seasonal PMAS, 2001

Seasonal PAMS, 2002

Seasonal PAMS, 2003

Seasonal PAMS, 2004

Seasonal PAMS, 2006

Seasonal PAMS, 2007

Seasonal PAMS, 2008

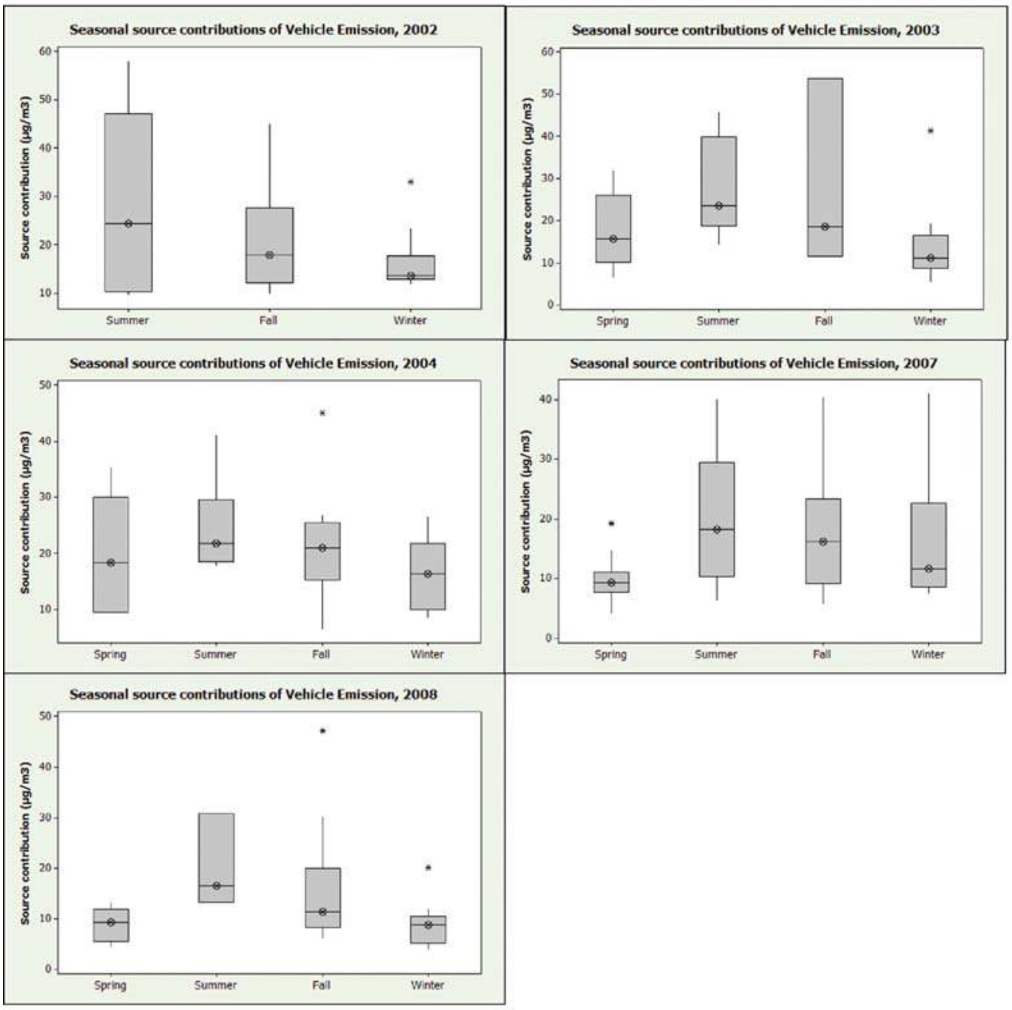
Seasonal PAMS, 2009

Figure 4.9: Seasonal PAMS, 2001 to 2009

4.5.2 Analysis on seasonal source contributions of each source

Seasonal Source Contributions of "Vehicle Emission"

The seasonal source contributions of "Vehicle Emission" were analyzed. The results were shown in Figure 4.10 and Figure 4.11. Figure 4.10 shows a pattern of high level in summer and fall but low in spring and winter was observed in the seasonal source contributions of “Vehicle Emission” in most of years during 2001 to 2009, including 2002, 2003, 2004, 2007, and 2008. Figure 4.11 shows that in 2001, 2006, and 2009, the seasonal source contributions of “Vehicle Emission” were almost the same. Overall, a pattern of high level in summer and fall but low in spring and winter could be observed in the seasonal source contributions of “Vehicle Emission” during 2001 to 2009. This contradicts the findings from other reserachers (Sauvage et al., 2009; Hoque et al., 2008). They found that vehicle emission was high in winter and low in summer and attributed it to two facts: “cold start” of engine in winter will boost the pollutants from vehicle emission; weather condition in winter will also increase the VOC concentrations in atmosphere. However, Windsor is a city in northern part of North America. In winter, its traffic counts might be reduced; while, in summer, the situation might be the opposite (SENES Consultants Limited, 2008). The reduced traffic counts might lead to less vehicle emission in winter than in summer. This might be the reason for this interesting observation in this study.


Seasonal source contributions of Vehicle Emission, 2002

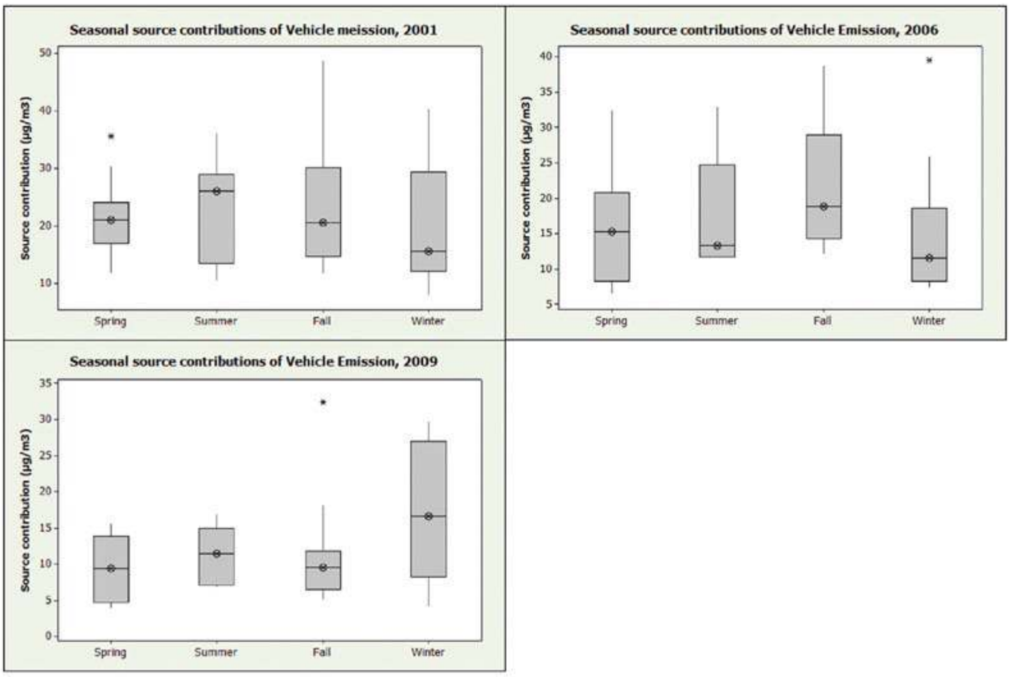
Seasonal source contributions of Vehicle Emission, 2003

Seasonal source contributions of Vehicle Emission, 2004

Seasonal source contributions of Vehicle Emission, 2007

Seasonal source contributions of Vehicle Emission, 2008

Figure 4.10: Seasonal source contribution of "Vehicle Emission" -1


Seasonal source contributions of Vehicle meission, 2001

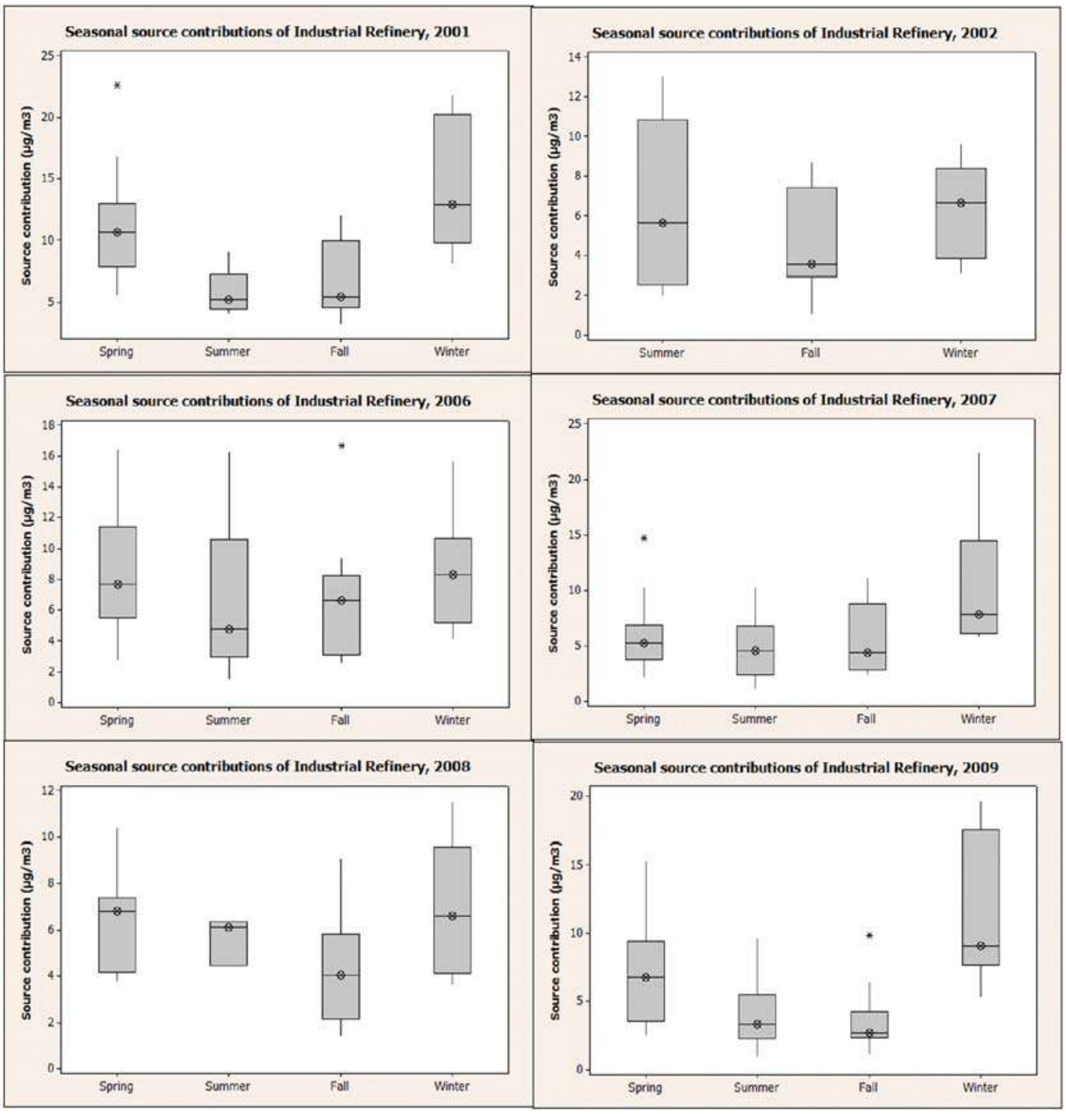
Seasonal source contributions of Vehicle Emission, 2006

Seasonal source contributions of Vehicle Emission, 2009

Figure 4.11: Seasonal source contribution of "Vehicle Emission" -2

Seasonal Source Contributions of "Industrial Refinery"

The seasonal source contributions of "Industrial Refinery" were analyzed. The results were shown in Figure 4.12 and Figure 4.13. Figure 4.12 shows a pattern of high level in spring and winter but low in summer and fall could in the seasonal source contributions of "Industrial Refinery" in most of the years during 2001 to 2009, including 2001, 2002, 2006, 2007, 2008, and 2009. Figure 4.13 shows that in 2003 and 2004, no clear pattern can be found. Generally, a pattern of high level in spring and winter but low in summer and fall could be found in the seasonal source contributions of "Industrial Refinery" during 2001 to 2009. Cetin et al. (2003b) found that in summer, the high temperature increases the evaporation and thus incrase the source contribution from industrial refinery. However, in winter, lower OH radical concentration, lower temperature, and weaker UV radiation will increase the chemical lifetime; meanwhile, lower mixing height in winter will lead to less dispersion (Sauvage et al., 2009). The combined impacts of all the factors mentioned above might cause the seasonal pattern of "Industrial Refinery" source contributions observed in this study.



Seasonal source contributions of Industrial Refinery, 2001

Seasonal source contributions of Industrial Refinery, 2002

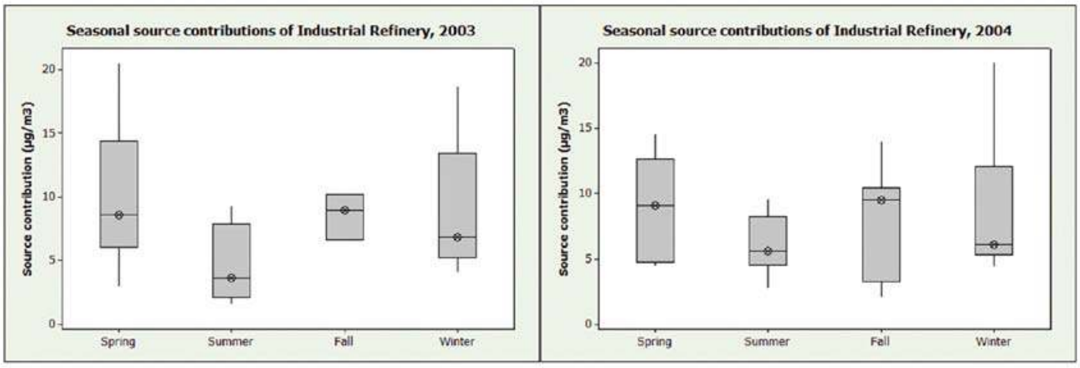
Seasonal source contributions of Industrial Refinery, 2006

Seasonal source contributions of Industrial Refinery, 2007

Seasonal source contributions of Industrial Refinery, 2008

Seasonal source contributions of Industrial Refinery, 2009

Figure 4.12: Seasonal source contributions of “Industrial Refinery” -1



Seasonal source contributions of Industrial Refinery, 2003

Seasonal source contributions of Industrial Refinery, 2004

Figure 4.13: Seasonal source contributions of “Industrial Refinery” -2

Seasonal Source Contributions of "Commercial Natural Gas"

The seasonal source contributions of "Commercial Natural Gas" were analyzed. The results were shown in Figure 4.14 and Figure 4.15. Figure 4.14 shows a pattern of high level in spring and winter but low in summer and fall in the seasonal source contributions of "Commercial Natural Gas" in most of the years during 2001 to 2009, including 2001, 2002, 2006, 2008, and 2009. Figure 4.15 shows that in 2003, 2004, and 2007, the seasonal source contributions of "Commercial Natural Gas" were the same. Generally, a pattern of high level in spring and winter but low in summer and fall could be observed in the seasonal source contributions of "Commercial Natural Gas" during 2001 to 2009. This is consistent with the observation in the study from Na and Kim (2001). The reason could be that the influences caused by more consumption of commercial natural gas in winter and spring than in summer and fall might overcome the influence of leakage increased with the increase of temperature in summer and fall (Na and Kim, 2001).

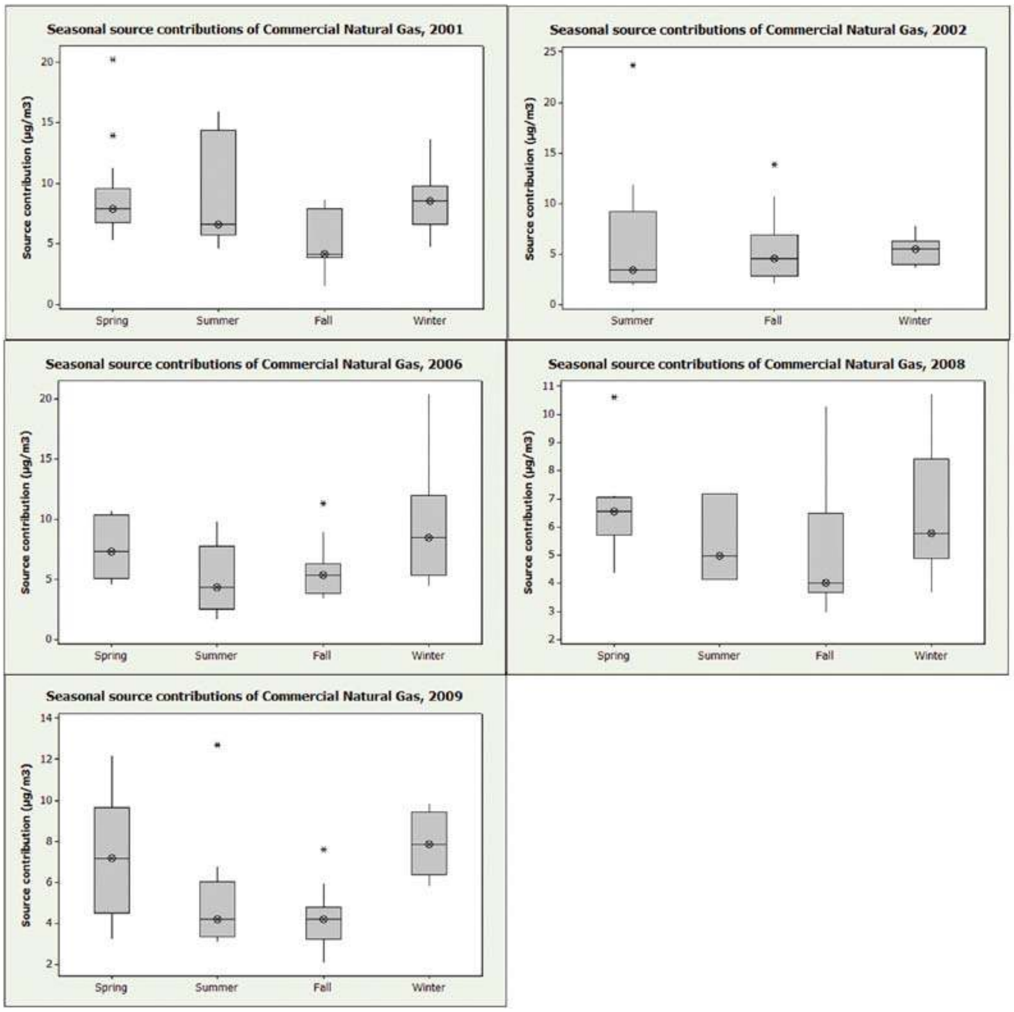


Figure 4.14: Seasonal source contributions of “Commercial Natural Gas” -1

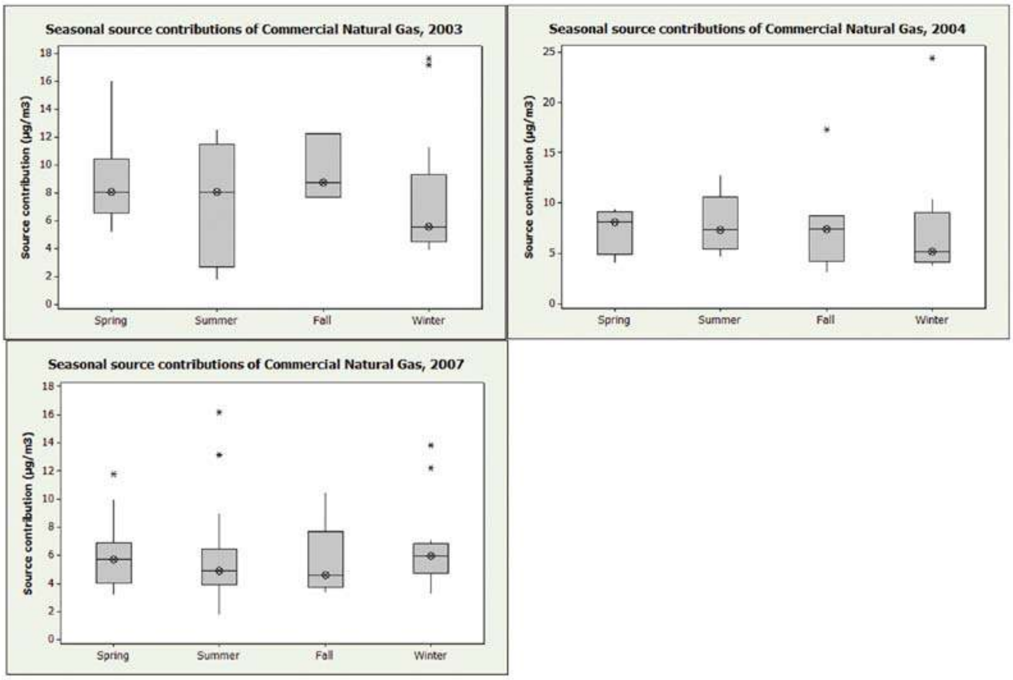


Figure 4.15: Seasonal source contributions of “Commercial Natural Gas” -2

Seasonal Source Contributions of "Architectural Coating"

The seasonal source contributions of "Architectural Coating" were analyzed. The results were shown in Figure 4.16 and Figure 4.17. Figure 4.16 shows a pattern of high level in summer and fall but low in spring and winter in the seasonal source contributions of "Architectural Coating" in half of the years during 2001 to 2009, including 2001, 2002, 2003, and 2007. However, Figure 4.17 shows that no clear pattern could be observed in in the seasonal source contributions of "Architectural Coating" in 2004, 2006, 2008, and 2009. On the whole, a pattern of high level in summer and fall but low in spring and winter could be observed in the seasonal source contributions of "Architectural Coating" during 2001 to 2009. This is consistent with the observation from Tan et al. (2011). The reason could be that solvent evaporation increases by the temperature (Tan et al., 2011).

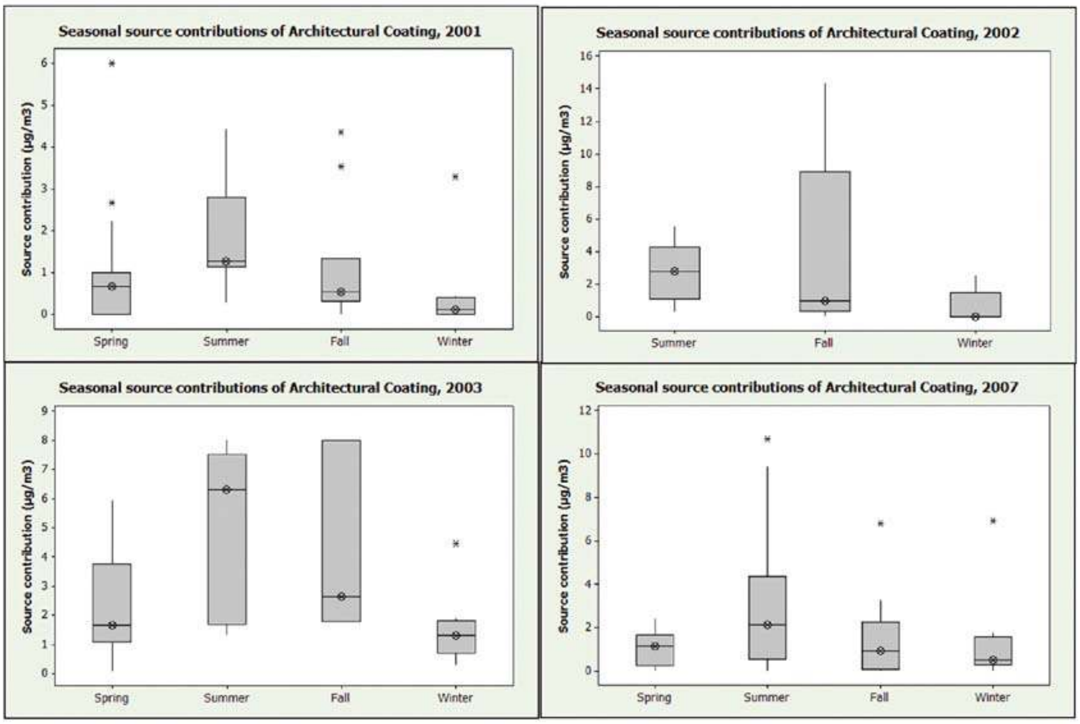


Figure 4.16: Seasonal source contributions of "Architectural Coating" -1

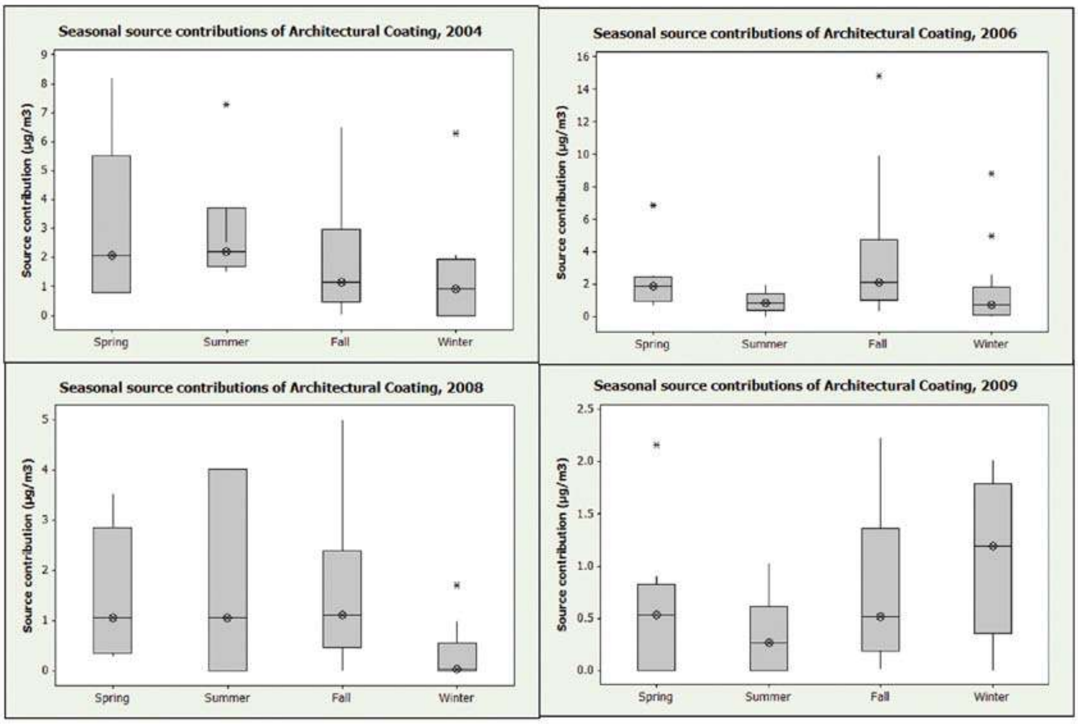
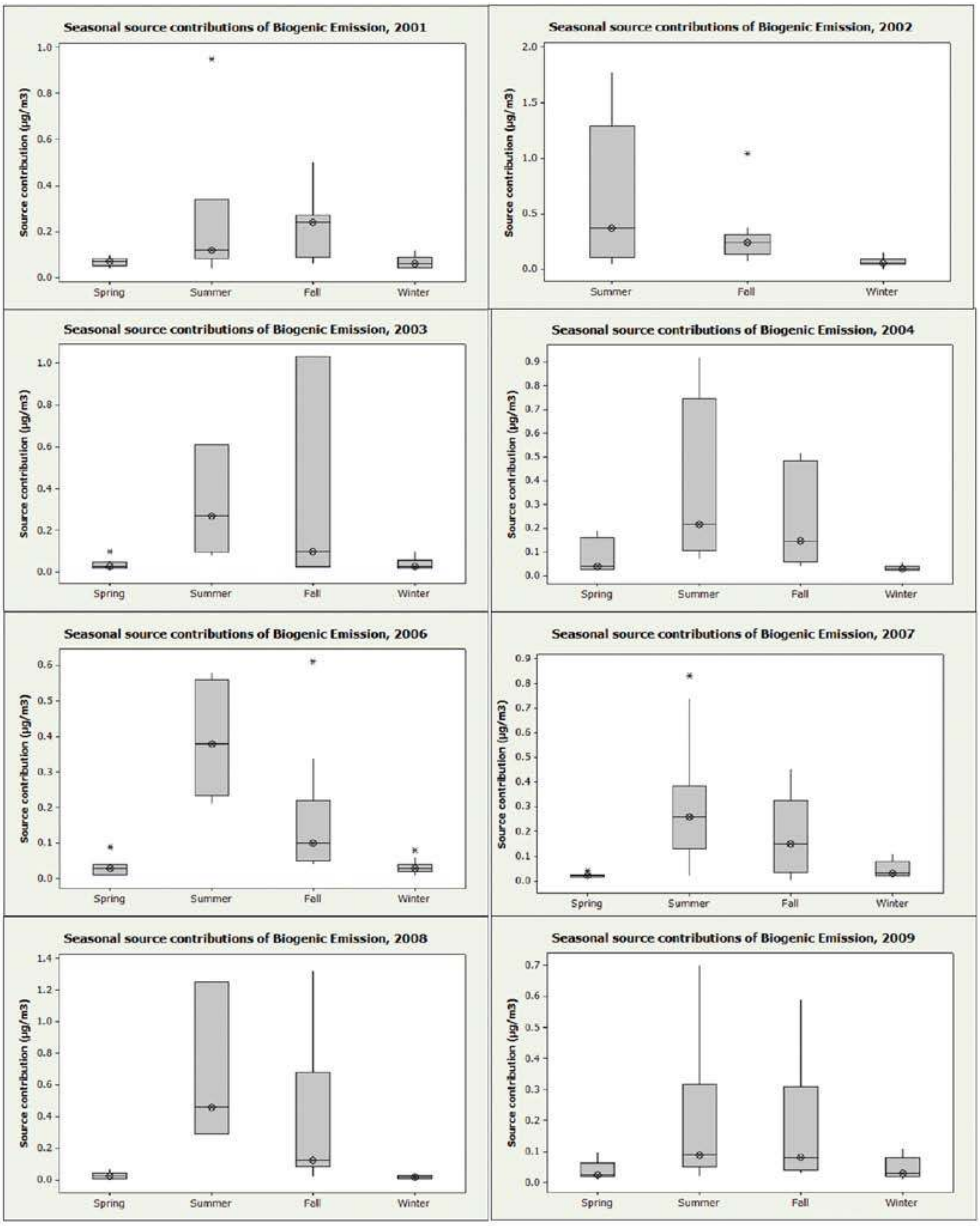


Figure 4.17: Seasonal source contributions of “Architectural Coating” -2

Seasonal Source Contributions of “Biogenic Emission”

The seasonal source contributions of “Biogenic Emission” were analyzed. The results were shown in Figure 4.18. Figure 4.18 shows a general pattern of high level in summer and fall but low in spring and winter in the seasonal source contributions of “Biogenic Emission” during 2001 to 2009. This is consistent with the results of other studies (Sharkey et al., 1999; Zhang et al., 2000). Isoprene is the only marker of “Biogenic Emission” and comes from the emissions of many plants (i.e. aspen and oak). It is influenced by light and temperature and will increase with the increase of light and temperature (Zhang et al., 2000). This could be the reason for this pattern.


Seasonal source contributions of Biogenic Emission, 2001

Seasonal source contributions of Biogenic Emission, 2002

Seasonal source contributions of Biogenic Emission, 2003

Seasonal source contributions of Biogenic Emission, 2004

Seasonal source contributions of Biogenic Emission, 2006

Seasonal source contributions of Biogenic Emission, 2007

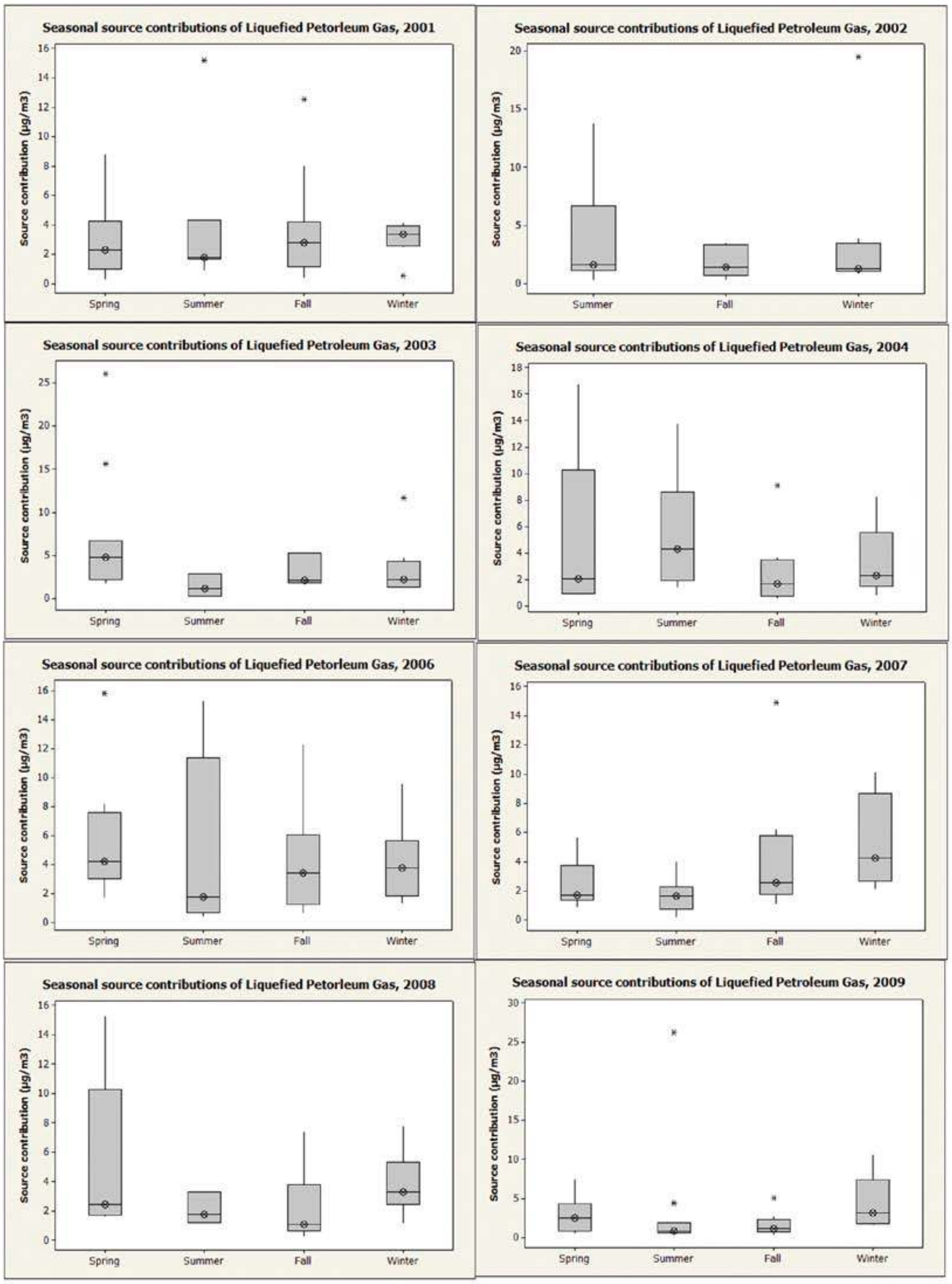
Seasonal source contributions of Biogenic Emission, 2008

Seasonal source contributions of Biogenic Emission, 2009

Figure 4.18: Seasonal source contributions of “Biogenic Emission”, 2001 to 2009

Seasonal Source Contributions of “Liquefied Petroleum Gas”

The seasonal source contributions of “Liquefied Petroleum Gas” were analyzed. The results were shown in Figure 4.19. Figure 4.19 shows that the seasonal source contributions of “Liquefied Petroleum” were approximately same during 2001 to 2009. Some researchers found that its emission was high in summer and low in winter (Tan et al., 2011). This is because that the propane, which accounts for 90.6% of total mass of this source, mainly comes from leakage of water pipes. Therefore, the evaporation increased by temperature in summer improves the emission of this source (Tan et al., 2011). However, Sauvage (2009) reported that evaporation source contribution was high in winter and low in summer due to the effects of low OH radical concentratining, weak UV radiation and low mixingin spring. The combination of different effects might have cuased the unclear pattern of seasonal contributions from “Liquefied Petroleum”.


Seasonal source contributions of Liquefied Petorleum Gas, 2001

Seasonal source contributions of Liquefied Petroleum Gas, 2002

Seasonal source contributions of Liquefied Petroleum Gas, 2003

Seasonal source contributions of Liquefied Petroleum Gas, 2004

Seasonal source contributions of Liquefied Petorleum Gas, 2006

Seasonal source contributions of Liquefied Petorleum Gas, 2007

Seasonal source contributions of Liquefied Petorleum Gas, 2008

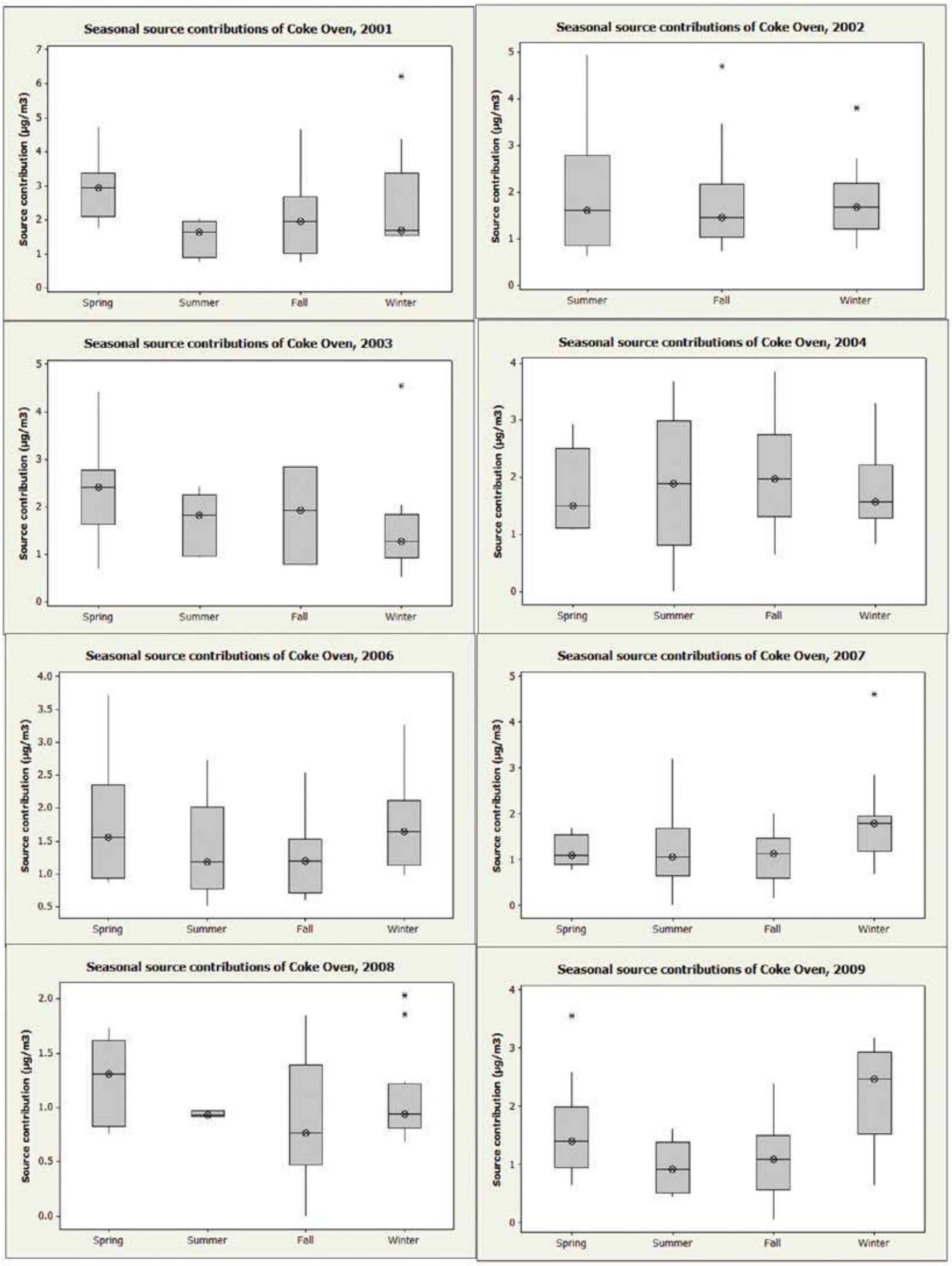
Seasonal source contributions of Liquefied Petroleum Gas, 2009

Figure 4.19: Seasonal source contributions of “Liquefied Petroleum Gas”, 2001 to 2009

Seasonal Source Contributions of “Coke Oven”

The seasonal source contributions of “Coke Oven” were analyzed. The results were shown in Figure 4.20. Figure 4.20 shows the seasonal source contributions of

"Coke Oven" were approximately same during 2001 to 2009. This is consistent with the observation of other study (Chattopadhaya et al., 1996).



Seasonal source contributions of Coke Oven, 2001

Seasonal source contributions of Coke Oven, 2002

Seasonal source contributions of Coke Oven, 2003

Seasonal source contributions of Coke Oven, 2004

Seasonal source contributions of Coke Oven, 2006

Seasonal source contributions of Coke Oven, 2007

Seasonal source contributions of Coke Oven, 2008

Seasonal source contributions of Coke Oven, 2009

Figure 4.20: Seasonal source contributions of "Coke Oven", 2001 to 2009

4.6 Significant Changes after the Outliers Were Deleted

After the sample outliers and species outliers were deleted, some significant changes happened in the seasonal patterns of source contributions of “Commercial Natural Gas”. The comparison before and after the deleting of outliers are shown in Figure 4.21.

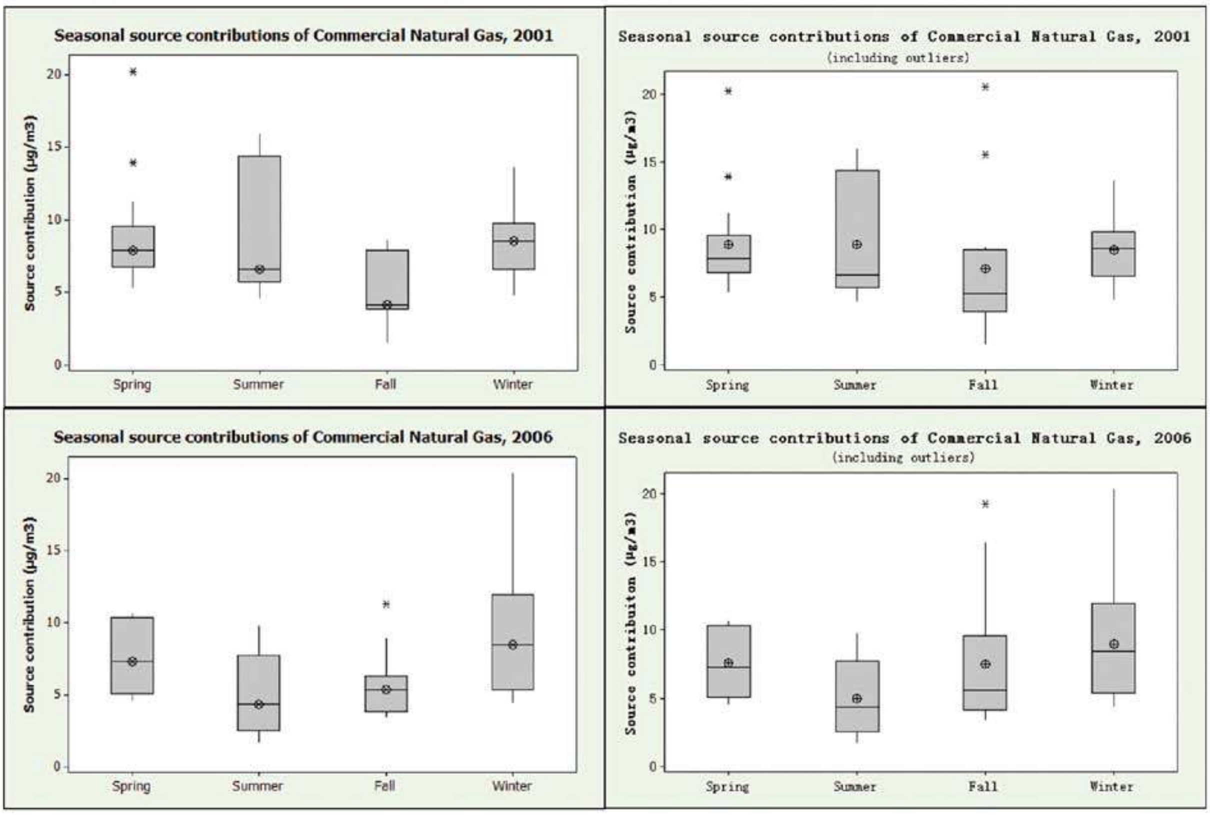


Figure 4.21: Significant changes on seasonal source contributions of Commercial Natural Gas after the outliers were deleted

After the outliers were excluded, a general pattern of high level in spring and winter but low in summer and fall in the seasonal source contributions of “Commercial Natural Gas” in most of the years during 2001 to 2009, including 2001, 2002, 2006, 2008, and 2009 (4.5.2). However, Figure 4.21shows that if these outliers were kept, this pattern would not exist in 2001 and 2006, which means this pattern only existed in three years during 2001 to 2009. A pattern existing in three years out of nine years would not be strong enough to justify that it is a general pattern. In other words, if the outlier were kept, the real general pattern of “Commercial Natural Gas” would be hidden. Therefore, it is necessary to exclude the outliers before the CMB modeling and analysis. The calculation and analysis results before the outliers were deleted are enclosed in Appendix D.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusions

VOC measurements from the Windsor West Station of NAPS from 2001 to 2009 were used for CMB modeling. Source profiles were from the thesis of Templer (2007), which had been tested for CMB modeling of VOCs in Windsor. The estimated source contributions of “Liquid Gasoline” showed consistently negative source contribution estimates from the CMB modeling. It indicated that that this source profile might be not accurate enough and have some collinearity between other source profiles (Liu et al., 2008). After deleting this source profile, there was no consistently negative source contribution estimated anymore and the negative SCEs in results were also reduced to only a few with small percentages in total SCE. Therefore, the “Liquid Gasoline” was excluded from CMB modeling and the left 9 source profiles were used as input source profiles.

The Std Err outliers and the calculation performance statistics which were outside of target were used as result outlier indicators to screen out the modeling result outliers. Any result with no less than three result outlier indicators was screened out as result outliers. Finally, 9 reuslts were screened out.

The ranking of sources according to their source contributions and percentages from 2001 to 2009 was: “Vehicle Emission” (source contribution 17.5 $\mu g/m^3$; source contribution percentage 44.7%), “Commercial Natural Gas” (source contribution 7.3

µg/m^3; source contribution percentage 18.8%), "Industrial Refinery" (source contribution 6.9 µg/m^3; source contribution percentage 17.6%), "Liquefied Petroleum" (source contribution 3.7 µg/m^3; source contribution percentage 9.4%), "Architectural Coating" (source contribution 1.9 µg/m^3; source contribution percentage 4.5%), "Coke Oven" (source contribution 1.7 µg/m^3; source contribution percentage 4.3%), and "Biogenic Emission" (source contribution 0.2 µg/m^3; source contribution percentage 0.4%).

From 2001 to 2009, total source contributions in Windsor decreased by 38% (from 47 µg/m^3 to 29 µg/m^3). This was mainly because the source contribution reduction of "Vehicle Emission" which was reduced by 10.8 µg/m^3 and accounted for 59.7% of total source contribution reduction, followed by "Industrial Refinery" (source contribution reduction 3.59 µg/m^3, percentage in total source contribution reduction 19.9%), "Commercial Natural Gas" (source contribution reduction 1.73 µg/m^3, percentage in total source contribution reduction 9.5%), "Coke Oven" (source contribution reduction 1.11 µg/m^3, percentage in total source contribution reduction 6.2%), "Architectural Coating" (source contribution reduction 0.56 µg/m^3, percentage in total source contribution reduction 3.1%), "Liquefied Petroleum Gas" (source contribution reduction 0.28 µg/m^3, percentage in total source contribution reduction 1.5%), and "Biogenic Emission" (source contribution reduction 0.03 µg/m^3, percentage in total source contribution reduction 0.2%).

The source contribution of "Vehicle Emission" was reduced by 48% during

2001 to 2009. The source contributions of its three components, including "Gasoline Exhaust", "Diesel Exhaust", and "Gasoline Vapour", all decreased during 2001 to 2009. Among them, the major contributor to the source contribution reduction of "Vehicle Emission" was "Gasoline Exhaust" which accounted for 62% of total source contribution reduction, followed by "Diesel Exhaust" (22% of total source contribution reduction) and "Gasoline Vapour" (16% of total source contribution reduction).

The declining trends could be observed in the annual source contributions of "Vehicle Emission", "Industrial Refinery", "Commercial Natural Gas", and "Coke Oven" during 2001 to 2009. However, the annual source contributions of "Liquefied Petroleum Gas", "Architectural Coating", and "Biogenic Emission" changed little during 2001 to 2009.

Overall, a pattern of high level in summer and fall but low in spring and winter could be observed in the seasonal source contributions of "Vehicle Emission" during 2001 to 2009. This contradicts the findings from other reserachers (Sauvage et al., 2009; Hoque et al., 2008). The reason could be due to the fact that traffic accounts are low in winter and spring in Windosr.

In general, a special relatively flat pattern of seasonal PAMS was observed during 2001 to 2009. This contradicts the results of other studies (Sauvage et al., 2009; Hoque et al., 2008; Na and Kim, 2001). Given that the vehicle emission was the major contributor to total source emission, the reduction of vehicle emission contribution caused by low traffic counts in winter and spring might be the reason for this even seasonal pattern of seasonal PAMS.

The outliers might distort the real seasonal source contributions of some sources. It is necessary to excluded the outliers before calculation and analysis.

This study is the first long-term VOC source apportionment study in Windsor. Its results demonstrated the effective control of ambient VOCs pollution in Windsor from 2001 to 2009, especially the control of vehicle emission. However, more effective measures should be made to reduce the pollution from "Liquefied Petroleum" and "Architectural Coating". The results can be helpful for the ambient air pollution control stategies evaluating and policy making.

5.1 Recommendations

Pollution Control:

- Although effective strategies were performed to reduce vehicle emission during 2001 -2009, it is still recommended that more and continuous efforts might be carried out.
- More efforts should be carried out on pollution control of "Commercial Natural Gas", "Industrial Refinery" and "Coke Oven".
- Immediate measures should be made on emissioin control of "Liquefied Petroleum" and "Architectural Coating".

Future studies:

- Longer inter-year study on VOCs and VOC source contributions could be made to confirm the annual trend.
- Continuous and accurate measurments of ambient VOCs in Windsor might be made to offer more and reliable measurements.
- Carrying out another study on the relationship between traffic accounts and VOC concentrations in Windsor might offer detailed information about the reasons for seasonal VOC concentrations pattern.

REFERENCES

Armbruster D.A., and T. Pry, 2008. Limit of blank, limit of detection and limit of quantitation. http://www.ncbi.nlm.nih.gov/pmc/articles/PMC2556583/ (assessed January 25th, 2013)

Badol, C., N. Locoge, and J.C. Galloo. 2008. Using a source-receptor approach to characterise VOC behaviour in a French urban area influenced by industrial emissions: Part II: Source contribution assessment using the Chemical Mass Balance (CMB) model. *Science of The Total Environment*. 389 (2-3):429-440. doi: 10.1016/j.scitotenv.2007.09.002.

Becker, S., C.J. Halsall, W. Tych, H. Hung, S. Attewell, P. Blanchard, H. Li, P. Fellin, G. Stern, B. Billeck, and S. Friesen. 2006. Resolving the long-term trends of polycyclic aromatic hydrocarbons in the Canadian arctic atmosphere. *Environmental Science & Technology*. 40 (10):3217-3222. doi: 10.1021/es052346l.

Begum, B.A., P.K. Hopke, and W. Zhao. 2005. Source identification of fine particles in Washington, DC, by expanded factor analysis modeling. *Environmental Science & Technology*. 39 (4):1129-1137. doi: 10.1021/es049804v.

Bellack, N., A. Wheeler, A. Anastassopoulos, R. Kulka, K. van Ryswyk, D. van Rijswijk, H. You, J. Brook, I.X. Xu, P. Rasmussen, and A. Grgicak-Mannion. 2008. Factors influencing the spatial associations between nitrogen dioxide and other ambient airborne pollutants across four seasons in Windsor, Ontario. *Epidemiology*. 19 (6):S13-S379. doi: 10.1097/01.ede.0000339804.14584.59.

Berg, T., W. Aas, J. Pacyna, H.T. Uggerud, and M. Vadset. 2008. Atmospheric trace metal concentrations at Norwegian background sites during 25 years and its relation to European emissions. *Atmospheric Environment*. 42 (32):7494-7501. doi: 10.1016/j.atmosenv.2008.05.020.

Blanchard, C.L., G.M. Hidy, S. Tanenbaum, R. Rasmussen, R. Watkins, and E. Edgerton. 2010. NMOC, ozone, and organic aerosol in the southeastern United States, 1999-2007: 1. Spatial and temporal variations of NMOC concentrations and composition in Atlanta, Georgia. *Atmospheric Environment*. 44 (38):4827-4839. doi: DOI: 10.1016/j.atmosenv.2010.08.036.

Border air quality study-an ambient air quality overview for Southwestern Ontario. Ontario Ministry of the Environment, 2008.

http://www.ene.gov.on.ca/environment/en/resources/STD01_076513.html (accessed January 12th, 2012)

Bullock, K.R., R.M. Duvall, G.A. Norris, S.R. McDow, and M.D. Hays. 2008. Evaluation of the CMB and PMF models using organic molecular markers in fine particulate matter collected during the Pittsburgh Air Quality Study. *Atmospheric Environment*. 42 (29):6897-6904. doi: 10.1016/j.atmosenv.2008.05.011.

Cai, C., F. Geng, X. Tie, Q. Yu, and J. An. 2010. Characteristics and source apportionment of VOCs measured in Shanghai, China. *Atmospheric Environment*. 44 (38):5005-5014. doi: 10.1016/j.atmosenv.2010.07.059.

Carew, M.E., V. Pettigrove, R.L. Cox, and A.A. Hoffmann. 2007. The response of Chironomidae to sediment pollution and other environmental characteristics in urban wetlands. *Freshwater Biology*. 52 (12):2444-2462. doi: 10.1111/j.1365-2427.2007.01840.x.

Cetin, E., M. Odabasi, and R. Seyfioglu. 2003a. Ambient volatile organic compound (VOC) concentrations around a petrochemical complex and a petroleum refinery. *Science of The Total Environment*. 312 (1-3):103-112. doi: 10.1016/s0048-9697(03)00197-9.

Chan, Y.-C., D.D. Cohen, O. Hawas, E. Stelcer, R. Simpson, L. Denison, N. Wong, M. Hodge, E. Comino, and S. Carswell. 2008. Apportionment of sources of fine and coarse particles in four major Australian cities by positive matrix factorisation. *Atmospheric Environment*. 42 (2):374-389. doi: 10.1016/j.atmosenv.2007.09.030.

Chattopadhyay, G., S. Chatterjee, and D. Chakraborti. 1996. Determination of benzene, toluene and xylene in ambient air inside three major steel plant airsheds and surrounding residential areas. *Environmental Technology*. 17 (5):477-488. doi: 10.1080/09593331708616409.

Clougherty, J., R. Wright, L. Baxter, and J. Levy. 2008. Land use regression modeling of intra-urban residential variability in multiple traffic-related air pollutants. *Environmental Health.* no. 7 (1):17. doi: 10.1186/1476-069X-7-17.

Coulter, C.T. 2004. EPA-CMB8.2 users manual. EPA. http://www.epa.gov/scram001/models/receptor/EPA-CMB82Manual.pdf

Curren, K.C., T.F. Dann, and D.K. Wang. 2006. Ambient air 1,3-butadiene concentrations in Canada (1995–2003): seasonal, day of week variations, trends, and source influences. *Atmospheric Environment*. 40 (1):170-181. doi: 10.1016/j.atmosenv.2005.09.025.

Dann, T.F., and D.K. Wang. 1995. Ambient air benzene concentrations in Canada (1989-1993): seasonal and day of week variations, trends, and source influences. *Journal of the Air & Waste Management Association*. 45 (9):695-702. doi: org/10.1016/j.atmosenv.2005.09.025.

Dauwe, T., S.G. Chu, A. Covaci, P. Schepens, and M. Eens. 2003. Great tit (Parus major) nestlings as biomonitors of organochlorine pollution. *Archives of Environmental Contamination and Toxicology*. 44 (1):0089-0096. doi: 10.1007/s00244-002-1243-y.

SENES Consultants Limited. 2008. Detroit river international crossing final air quality monitoring report October 1st, 2006 – October 31st, 2007. http://www.partnershipborderstudy.com/pdf/33900-7%2010APR08%20Quarterly%20Report%204%20-%20FINAL.pdf

El-Harbawi, M., Sa'ari Mustapha, and Z.A. Rashid. 2008. Air pollution modelling, simulation and computational methods: a review. Paper presented at the meeting of ICERT 2008: International Conference on Environmental Research and Technology, Penang, Malaysia, May 28–30, 2008.

Elbir, T., B. Cetin, E. Cetin, A. Bayram, and M. Odabasi. 2007. Characterization of volatile organic compounds (VOCs) and their sources in the air of Izmir, Turkey. Environmental Monitoring and Assessment. 133 (1):149-160. doi: 10.1007/s10661-006-9568-z.

Encyclopædia Britannica Online, 2009.Solstice http://www.britannica.com/EBchecked/topic/553654/solstice (accessed Juen 22th, 2012)

Environment Canada, 2004. National Air Pollution Surveillance (NAPS) network- air quality in canada:2001 summary and 1990-2001 trend analyses. http://www.ec.gc.ca/Publications/default.asp?lang=En&xml=937329E2-A70A-47D1-AB2F-11B9AE7C40A0 (accessed January 12th, 2011)

Environment Canada, 2008. National Air Pollution Surveillance (NAPS) network: annual data summary for 2005 and 2006. http://www.ec.gc.ca/Publications/default.asp?lang=En&xml=8928E8A8-0C6F-4B1B-8597-AB3E0F31F4A5 (accessed January 10th, 2012)

Environment Canada, 2011. National Air Pollution Surveillance Program (NAPS). http://www.ec.gc.ca/rnspa-naps/default.asp?lang=En&n=5C0D33CF-1 (accessed September 20th, 2011)

Environment Canada, 2012. Climate Data Online http://www.climate.weatheroffice.gc.ca/climateData/monthlydata_e.html?timeframe=3&Prov=ONT&StationID=4716&mlyRange=1940-01-01|2011-12-01&Year=2009&Month=01&Day=01 (accessed September 20th, 2012)

EPA, 2006, Data quality assessment: statistical methods for parctitionaers (EPA QA/G-9S). http://www.epa.gov/quality/qs-docs/g9s-final.pdf (accessed August 15th, 2012)

EPA,2010. Chemical Mass Balance (CMB) Model. http://www.epa.gov/scram001/receptor_cmb.htm

EPA, 2012a. Volatile Organic Compounds (VOCs). http://www.epa.gov/iaq/voc2.html#definition (accessed September 7th, 2012)

EPA, 2012b. Technology Transfer Network Emission Measurement Center. http://www.epa.gov/ttn/emc/facts.html (accessed August 15th, 2012).

EPA,EPA, 1990. Recommended buffer distances for industrial residual air emissions. http://epanote2.epa.vic.gov.au/EPA%5Cpublications.nsf/PubDocsLU/AQ2-86?OpenDocument (accessed November 11, 2012)

Fujita, E.M., and Z.Q. Lu Desert Research Institute, 1998. Analysis data from the 1995 NARSTO-northeast study. Volume-III: chemical mass balance receptor modeling. Perpared for Coordinating Research Council, Atlanta, GA, by Desert Institute, Reno, NV.

Fujita, E.M., J.G. Watson, J.C. Chow, and Z. Lu. 1994. Validation of the chemical mass balance receptor model applied to hydrocarbon source apportionment in the southern California air quality study. *Environ Sci Technol.* 28 (9):1633-1694. doi: 10.1021/es00058a016.

Geddes, J.A., J.G. Murphy, and D.K. Wang. 2009. Long term changes in nitrogen oxides and volatile organic compounds in Toronto and the challenges facing local ozone control. *Atmospheric Environment* no. 43 (21):3407-3415. doi: 10.1016/j.atmosenv.2009.03.053.

Gummeneni, S., Y.B. Yusup, M. Chavali, and S.Z. Samadi. 2011. Source apportionment of particulate matter in the ambient air of Hyderabad city, India. *Atmospheric Research* no. 101 (3):752-764. doi: 10.1016/j.atmosres.2011.05.002.

Henry, R.C.,United States Environment Protection Agency, 2000. Final report of workshop on UNMIX and PMF as applied to PM2.5. http://www.epa.gov/ttnamti1/files/ambient/pm25/workshop/report.pdf

Henry, R.C. 2003. Multivariate receptor modeling by N-dimensional edge detection. *Chemometrics and Intelligent Laboratory Systems* no. 65 (2):179-189. doi: 10.1016/s0169-7439(02)00108-9.

Heo, J.B., P.K. Hopke, and S.M. Yi. 2009. Source apportionment of PM2. 5 in Seoul, Korea. *Atmospheric Chemistry and Physics*. 9:4957-4971. doi: 10.5194/acp-9-4957-2009

Hewitt, C.N., and R.M. Harrison. 1985. Tropospheric concentrations of the hydroxyl radical—a review. *Atmospheric Environment.* 19 (4):545-554. doi: 10.1016/0004-6981(85)90033-2.

Hirsch, R.M., and J.R. Slack. 1984. A nonparametric trend test for seasonal data with serial dependence. *Water Resour*. 20 (6):727-732. doi: 10.1029/WR020i006p00727.

Hole, L.R., J.H. Christensen, T. Ruoho-Airola, K. Tørseth, V. Ginzburg, and P. Glowacki. 2009. Past and future trends in concentrations of sulphur and nitrogen compounds in the Arctic. *Atmospheric Environment*. 43 (4):928-939. doi: 10.1016/j.atmosenv.2008.10.043.

Holmes, N.S., and L. Morawska. 2006. A review of dispersion modelling and its application to the dispersion of particles: An overview of different dispersion models available. *Atmospheric Environment*. 40 (30):5902-5928. doi: DOI: 10.1016/j.atmosenv.2006.06.003.

Hoque, R.R., P.S. Khillare, T. Agarwal, V. Shridhar, and S. Balachandran. 2008. Spatial and temporal variation of BTEX in the urban atmosphere of Delhi, India. *Science of The Total Environment*. 392 (1):30-40. doi: 10.1016/j.scitotenv.2007.08.036.

Jorquera, H., and F. Barraza. 2012. Source apportionment of ambient PM2.5 in Santiago, Chile: 1999 and 2004 results. *Science of The Total Environment*. 435–436 (0):418-429. doi: 10.1016/j.scitotenv.2012.07.049.

Karner, A.A., D.S. Eisinger, and D.A. Niemeier. 2010. Near-roadway air quality: synthesizing the findings from Real-World data. Environmental Science & Technology no. 44 (14):5334-5344. doi: 10.1021/es100008x.

Kesselmeier, J., and M. Staudt. 1999. Biogenic volatile organic compounds (VOC): an overview on emission, physiology and Ecology. *Journal of Atmospheric Chemistry*. 33 (1):23-88. doi: 10.1023/a:1006127516791.

Kourtidis, K.A., I.C. Ziomas, B. Rappenglueck, A. Proyou, and D. Balis. 1999. Evaporative traffic hydrocarbon emissions, traffic CO and speciated HC traffic emissions from the city of Athens. *Atmospheric Environment*. 33 (23):3831-3842. doi: 10.1016/s1352-2310(98)00395-1.

Kroll, J.H., N.L. Ng, S.M. Murphy, R.C. Flagan, and J.H. Seinfeld. 2006. Secondary organic aerosol formation from isoprene photooxidation. *Environmental Science & Technology*. 40 (6):1869-1877. doi: 10.1021/es0524301.

Larsen, R.K., and J.E. Baker. 2003. Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: a comparison of three methods. *Environmental Science & Technology*. 37 (9):1873-1881. doi: 10.1021/es0206184.

Lathière, J., D.A. Hauglustaine, A.D. Friend, N.D. Noblet-Ducoudré, N. Viovy, and G.A. Folberth. 2006. Impact of climate variability and land use changes on global biogenic volatile organic compound emissions. *Atmospheric Chemistry and Physics*. 6 (8):2129-2146. doi: 10.5194/acp-6-2129-2006

Lau, A.K.H., Z. Yuan, J.Z. Yu, and P.K.K. Louie. 2010. Source apportionment of ambient volatile organic compounds in Hong Kong. *Science of The Total Environment*. 408 (19):4138-4149. doi: 10.1016/j.scitotenv.2010.05.025.

Lee, S., W. Liu, Y. Wang, A.G. Russell, and E.S. Edgerton. 2008. Source apportionment of PM2.5: comparing PMF and CMB results for four ambient monitoring sites in the southeastern United States. *Atmospheric Environment*. 42 (18):4126-4137. doi: 10.1016/j.atmosenv.2008.01.025.

Li, A., J.-K. Jang, and P.A. Scheff. 2003. Application of EPA CMB8.2 model for source apportionment of sediment PAHs in Lake Calumet, Chicago. *Environmental Science & Technology*. 37 (13):2958-2965. doi: 10.1021/es026309v.

Liao, C.-H., and M.D. Gurol. 1995. Chemical oxidation by photolytic decomposition of hydrogen peroxide. *Environmental Science & Technology*. 29 (12):3007-3014. doi: 10.1021/es00012a018.

Lin, C., N. Liou, P.E. Chang, J.C. Yang, and E. Sun. 2007. Fugitive coke oven gas emission profile by continuous line averaged open-path fourier transform infrared monitoring. *Journal of the Air & Waste Management Association*. 57 (4):472-479. doi: 10.3155/1047-3289.57.4.472.

Liu, Y., M. Shao, W.C. Kuster, P.D. Goldan, X. Li, S. Lu, and J.A.d. Gouw. 2008. Source identification of reactive hydrocarbons and oxygenated VOCs in the summertime in Beijing. *Environmental Science & Technology*. 43 (1):75-81. doi: 10.1021/es801716n.

Liu, Y., M. Shao, S. Lu, C.-C. Chang, J.-L. Wang, and L. Fu. 2008. Source apportionment of ambient volatile organic compounds in the Pearl River Delta, China: Part II. *Atmospheric Environment*. 42 (25):6261-6274. doi: 10.1016/j.atmosenv.2008.02.027.

Lowenthal, D.H., R.C. Hanumara, K.A. Rahn, and L.A. Currie. 1987. Effects of systematic error, estimates and uncertainties in chemical mass balance apportionments: Quail Roost II revisited. *Atmospheric Environment*. 21 (3):501-510. doi: 10.1016/0004-6981(87)90033-3.

Luginaah, I., K.Y. Fung, K.M. Gorey, and S. Khan. 2006. The impact of 9/11 on the association of ambient air pollution with daily respiratory hospital admissions in a Canada-US border city, Windsor, Ontario. *International Journal of Environmental Studies*. 63 (4):501–514. doi: 10.1080/00207230600802148

Luginaah, I., X. Xu, K.Y. Fung, A. Grgicak - Mannion, J. Wintermute, A. Wheeler, and J. Brook. 2006. Establishing the spatial variability of ambient nitrogen dioxide in Windsor, Ontario. *International Journal of Environmental Studies*. 63 (4):487-500. doi: 10.1080/00207230600802122.

Maykut, N.N., J. Lewtas, E. Kim, and T.V. Larson. 2003. Source apportionment of PM2.5 at an urban IMPROVE site in Seattle, Washington. *Environmental Science & Technology*. 37 (22):5135-5142. doi: 10.1021/es030370y.

Mendenhall, W., B.J. Beaver, B.M. Beaver, and S.E. Ahmed. 2009. Introduction to probability and statistics (12th ed). Toronto: Nelson Education Ltd.

Mijić, Z., S. Rajšić, A. Žekić, M. Perišić, A. Stojić, and M. Tasić. 2010. Characteristics and application of receptor models to the atmospheric aerosols research. *Air Quality*, edited by Ashok Kumar. Toledo: www.sciyo.com (accessed June 4th, 2011)

Miller, L., X.Xu, and I.Luginaah. 2009. Spatial Variability of Volatile Organic Compound Concentrations in Sarnia, Ontario, Canada. *Journal of Toxicology and Environmental Health, Part A*. 72 (9):610-624. doi: 10.1080/15287390802706413.

Miller, S.L., M.J. Anderson, E.P. Daly, and J.B. Milford. 2002. Source apportionment of exposures to volatile organic compounds. I. Evaluation of receptor models using simulated exposure data. *Atmospheric Environment*. 36 (22):3629-3641. doi: 10.1016/s1352-2310(02)00279-0.

Mukerjee, S., L.A. Smith, M.M. Johnson, L.M. Neas, and C.A. Stallings. 2009. Spatial analysis and land use regression of VOCs and NO_2 from school-based urban air monitoring in Detroit/Dearborn, USA. *Science of The Total Environment*. 407 (16):4642-4651. doi: 10.1016/j.scitotenv.2009.04.030.

Na, K., and Y.P. Kim. 2001. Seasonal characteristics of ambient volatile organic compounds in Seoul, Korea. *Atmospheric Environment*. 35 (15):2603-2614. doi: 10.1016/s1352-2310(00)00464-7.

Ohura, T., T. Amagai, and M. Fusaya. 2006. Regional assessment of ambient volatile organic compounds in an industrial harbor area, Shizuoka, Japan. *Atmospheric Environment*. 40 (2):238-248. doi: 10.1016/j.atmosenv.2005.09.064.

Olson, D.A., and G.A. Norris. 2008. Chemical characterization of ambient particulate matter near the World Trade Center: source apportionment using organic and inorganic source markers. *Atmospheric Environment*. 42 (31):7310-7315. doi: 10.1016/j.atmosenv.2008.07.007.

Pekney, N.J., and C.I. Davidson. 2005. Determination of trace elements in ambient aerosol samples. *Analytica Chimica Acta* no. 540 (2):269-277. doi: 10.1016/j.aca.2005.03.065.

Perrone, M.G., B.R. Larsen, L. Ferrero, G. Sangiorgi, G. De Gennaro, R. Udisti, R. Zangrando, A. Gambaro, and E. Bolzacchini. 2012. Sources of high PM2.5 concentrations in Milan, northern Italy: molecular marker data and CMB modelling. *Science of The Total Environment*. 414 (0):343-355. doi: 10.1016/j.scitotenv.2011.11.026.

Poirot, R.L., P.R. Wishinski, P.K. Hopke, and A.V. Polissar. 2001. Comparative application of multiple receptor methods to ddentify aerosol sources in northern Vermont. *Environmental Science & Technology*. 35 (23):4622-4636. doi: 10.1021/es010588p.

Rizzo, M.J., and P.A. Scheff. 2007. Fine particulate source apportionment using data from the USEPA speciation trends network in Chicago, Illinois: comparison of two source apportionment models. *Atmospheric Environment*. 41 (29):6276-6288. doi: 10.1016/j.atmosenv.2007.03.055.

Rohrer, F., and H. Berresheim. 2006. Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation. *Nature* no. 442 (7099):184-187. doi: 10.1038/nature04924

Roukos, J., V. Riffault, N. Locoge, and H. Plaisance. 2009. VOC in an urban and industrial harbor on the French North Sea coast during two contrasted meteorological situations. *Environmental Pollution*. 157 (11):3001-3009. doi: 10.1016/j.envpol.2009.05.059.

Salvador, P., B. Artíñano, M. Viana, A. Alastuey, and X. Querol. 2012. Evaluation of the changes in the Madrid metropolitan area influencing air quality: analysis of 1999–2008 temporal trend of particulate matter. *Atmospheric Environment*. 57 (0):175-185. doi: 10.1016/j.atmosenv.2012.04.026.

Sauvage, S., H. Plaisance, N. Locoge, A. Wroblewski, P. Coddeville, and J.C. Galloo. 2009. Long term measurement and source apportionment of non-methane hydrocarbons in three French rural areas. *Atmospheric Environment*. 43 (15):2430-2441. doi: DOI: 10.1016/j.atmosenv.2009.02.001.

Schneidemesser, E.v., P.S. Monks, and C. Plass-Duelmer. 2010. Global comparison of VOC and CO observations in urban areas. *Atmospheric Environment*. 44 (39):5053-5064. doi: 10.1016/j.atmosenv.2010.09.010.

Sen, P.K. 1968. Estimates of the regression coefficient based on Kendall's Tau. *Journal of the American Statistical Association*. 63 (324):1379-1389. doi: 10.1080/01621459.1968.10480934

Sharkey, T.D., E.L. Singsass, M.T. Lerdau, and C.D. Geron. 1999. Weather effects on isoprene emission capacity and applicaitons in emission s algorithms. *Ecological Applications*. 9 (4):1132-1137.

Shi, G.L., X. Li, Y.C. Feng, Y.Q. Wang, J.H. Wu, J. Li, and T. Zhu. 2009. Combined source apportionment, using positive matrix factorization-chemical mass balance and principal component analysis/multiple linear regression-chemical mass balance models. *Atmospheric Environment*. 43 (18):2929-2937. doi: 10.1016/j.atmosenv.2009.02.054.

Sicard, P., L. Dalstein-Richier, and N. Vas. 2011. Annual and seasonal trends of ambient ozone concentration and its impact on forest vegetation in Mercantour National Park (South-eastern France) over the 2000–2008 period. *Environmental Pollution*. 159 (2):351-362. doi: 10.1016/j.envpol.2010.10.027.

Sicard, P., A. Mangin, P. Hebel, and P. Malléa. 2010. Detection and estimation trends linked to air quality and mortality on French Riviera over the 1990–2005 period. *Science of The Total Environment*. 408 (8):1943-1950. doi: 10.1016/j.scitotenv.2010.01.024.

Song, Y., W. Dai, M. Shao, Y. Liu, S. Lu, W. Kuster, and P. Goldan. 2008. Comparison of receptor models for source apportionment of volatile organic compounds in Beijing, China. *Environmental Pollution*. 156 (1):174-183. doi: 10.1016/j.envpol.2007.12.014.

Song, Y., M. Shao, Y. Liu, S. Lu, W. Kuster, P. Goldan, and S. Xie. 2007. Source apportionment of ambient volatile organic compounds in Beijing. *Environ Sci Technol*. 41 (12):4348-4354. doi: 10.1021/es0625982.

Sosa, E.R., A.H. Bravo, A.V. Mugica, A.P. Sanchez, L.E. Bueno, and S. Krupa. 2009. Levels and source apportionment of volatile organic compounds in southwestern area of Mexico City. *Environmental Pollution*. 157 (3):1038-1044. doi: DOI: 10.1016/j.envpol.2008.09.051.

Statistics Canada, 2012. http://www12.statcan.gc.ca/census-recensement/2011/dp-pd/prof/details/page.cfm?Lang=E&Geo1=CSD&Code1=3537039&Geo2=CD&Code2=3537&Data=Count&SearchText=windsor&SearchType=Begins&SearchPR=01&B1=All&Custom=&TABID=1 (accessed June 6th, 2012)

Suwattiga, P., and W. Limpaseni. 2005. Seasonal source apportionment of volatile organic compounds in Bangkok ambient air. *Science Asia*. 31:395-401. doi: 10.2306/scienceasia1513-1874.2005.31.395.

Symeonidis, P., I. Ziomas, and A. Proyou. 2003. Emissions of air pollutants from the road transport sector in Greece: year to year variation and present situation. *Environmental Technology*. 24 (6):719-726. doi: 10.1080/09593330309385608.

Tabari, H., S. Marofi, A. Aeini, P.H. Talaee, and K. Mohammadi. 2011. Trend analysis of reference evapotranspiration in the western half of Iran. *Agricultural and Forest Meteorology*. 151 (2):128-136. doi: 10.1016/j.agrformet.2010.09.009.

Tan, J., S. Guo, Y. Ma, K. He, F. Yang, Y. Yu, and J. Wang. 2011. Characteristics of atmospheric non-methane hydrocarbons in Foshan City, China. *Environmental Monitoring and Assessment*. 183 (1):297-305. doi: 10.1007/s10661-011-1922-0.

Templer, J. 2007. *VOC Source Apportionment in Windsor*, Environmental Engineering, Windsor University, Windsor.

Thurston, G.D., and J.D. Spengler. 1985. A quantitative assessment of source contributions to inhalable particulate matter pollution in metropolitan Boston. *Atmospheric Environment*. 19 (1):9-25. doi: 10.1016/0004-6981(85)90132-5.

Transport Canada, 2011. Transportation in Canada 2010-Addendum Tables and Figures. http://www.tc.gc.ca/eng/policy/report-aca-anre2010-index-2700.htm (accessed June 13th, 2012)

Vecchi, R., M. Chiari, A. D'Alessandro, P. Fermo, F. Lucarelli, F. Mazzei, S. Nava, A. Piazzalunga, P. Prati, F. Silvani, and G. Valli. 2008. A mass closure and PMF source apportionment study on the sub-micron sized aerosol fraction at urban sites in Italy. *Atmospheric Environment*. 42 (9):2240-2253. doi: 10.1016/j.atmosenv.2007.11.039.

Viana, M., T.A.J. Kuhlbusch, X. Querol, A. Alastuey, R.M. Harrison, P.K. Hopke, W. Winiwarter, M. Vallius, S. Szidat, A.S.H. Prévôt, C. Hueglin, H. Bloemen, P. Wåhlin, R. Vecchi, A.I. Miranda, A. Kasper-Giebl, W. Maenhaut, and R. Hitzenberger. 2008. Source apportionment of particulate matter in Europe: a review of methods and results. *Journal of Aerosol Science*. 39 (10):827-849. doi: 10.1016/j.jaerosci.2008.05.007.

Viana, M., M. Pandolfi, M.C. Minguillón, X. Querol, A. Alastuey, E. Monfort, and I. Celades. 2008. Inter-comparison of receptor models for PM source apportionment: case study in an industrial area. *Atmospheric Environment*. 42 (16):3820-3832. doi: 10.1016/j.atmosenv.2007.12.056.

Wang, Y., X. Ren, D. Ji, J. Zhang, J. Sun, and F. Wu. 2012. Characterization of volatile organic compounds in the urban area of Beijing from 2000 to 2007. *Journal of Environmental Sciences*. 24 (1):95-101. doi: 10.1016/s1001-0742(11)60732-8.

Watson, J.G.,US. EPA, 2004. Protocol for Applying and Validating the CMB Model for PM2.5 and VOC.

Watson, J.G., L.W.A. Chen, J.C. Chow, P. Doraiswamy, and D.H. Lowenthal. 2008. Source apportionment: findings from the U.S. supersites program. *Journal of the Air and Waste Management Association*. 58 (2):265-288. doi: 10.3155/1047-3289.58.2.265

Watson, J.G., J.C. Chow, and E.M. Fujita. 2000. Review of volatile organic compound source apportionment by chemical mass balance. *Atmospheric Environment*. 35 (9):1567-1584. doi: org/10.1016/S1352-2310(00)00461-1

Watson, J.G., N.F. Robinson, J.C. Chow, R.C. Henry, B.M. Kim, T.G. Pace, E.L. Meyer, and Q. Nguyen. 1990. The USEPA/DRI chemical mass balance receptor model, CMB 7.0. *Environmental Software*. 5 (1):38-49. doi: 10.1016/0266-9838(90)90015-x.

Watson, J.G., T. Zhu, J.C. Chow, J. Engelbrecht, E.M. Fujita, and W.E. Wilson. 2002. Receptor modeling application framework for particle source apportionment. *Chemosphere*. 49 (9):1093-1136. doi: 10.1016/s0045-6535(02)00243-6.

Wheeler, A.J., M. Smith-Doiron, X. Xu, N.L. Gilbert, and J.R. Brook. 2008. Intra-urban variability of air pollution in Windsor, Ontario—Measurement and modeling for human exposure assessment. *Environmental Research*. 106 (1):7-16. doi: 10.1016/j.envres.2007.09.004.

Zalel, A., Yuval, and D.M. Broday. 2008. Revealing source signatures in ambient BTEX concentrations. *Environmental Pollution*. 156 (2):553-562. doi: 10.1016/j.envpol.2008.01.016.

Zhang, X.S., Y.J. Mu, W.Z. Song, and Y.H. Zhuang. 2000. Seasonal variations of isoprene emissions from deciduous trees. *Atmospheric Environment*. 34 (18):3027-3032. doi: 10.1016/s1352-2310(99)00311-8.

APPENDICES

Appendix A:

Ambient Data Processing Steps

1. Copy the “Mnemonics” of species to the header of the measured data table and brush the cells in pink and words in red.

2. Copy the 118 NMHC to the header of the measured data table and brush the cells in light blue.

3. Copy the 55 PAMS to the header of the measured data table and brush the cells in yellow.

4. Copy the detection limit of the 55 PAMS to the header of measured data table and brush the cells in orange.

5. Delete all the useless data including those excluded from 118 NMHC.

6. Put all 55 PAMS species at the left side and others on the right side. Brush the species with all missing data into green in the name row.

7. Delete the species with all the missing data in non-PAMS. Put all these deleted species in a table.

8. If there is any missing data in PAMS, brush it into green. And if there is any PAMS species with all-missing data, summarize it into the table.

9. Use “min” function in the Excel to find the minimum data in each PAMS species and put them in a row after the measured data.

10. Copy the “DL” to the row after the “minimum data” row.

11. Minus the “DL” by “minimum data” and put the result in the row of “Min-

DL" after the "DL" row and change the format of this row to show the negative number in red. Therefore, if the result is negative, the number will be in red.

12. Find out all the data less than DL and brush the cell into red, except the missing data.

13. Put the "(1/2) DL" in the row after the "Min-DL" row.

14. Copy the row of "(1/2) DL". Use "Paste Special" function and copy it to the same place by choosing only "values". So the numbers in this row will only be numbers and have no connection with function. Brush this row with sky-blue.

15. And put the "(5/6) DL" in the row after "(1/2) DL".

16. Copy the row of "(5/6) DL" and use the function of "Paste Special" by choosing only value. Then brush the cells into light purple.

17. Replace all the BDL data with "(1/2) DL". Check the row of "Min-DL" until all the data in this row are positive or negative "(1/2) DL".

18. Add a row of BDL Percent after the row of "(1/2) DL". Using the function of "COUNTIF" to count the numbers of "(1/2) DL" and calculate the BDL Percent. If 80% of data in a species are BDL, this species could not be used as fitting species and should not exists in the PR, which means this species in PR should be deleted in PR.

19. Copy and "Paste Special" the BDL Percent by choosing the values.

20. Insert a column named "TMAC" in front of the PAMS, and sum the data of PAMS together into the "TMAC".

21. Copy the data of "TMAC" and "Paste Special" to the same place choosing only value.

22. Insert a column named “OTHER” behind PAMS. Sum the non-PMAS data into “OTHER”.

23. Copy the data of “OTHER” and “Paste Special” to the same place choosing only value.

24. Delete the non PAMS species after the “OTHER”. 25. Insert a column after each species and copy the row of “Mnemonics with uncertainty” from the sample to the header of this sheet. Check the names in the header and make sure there is no mistake.

26. Time the data with 0.15 and put the result in the column of “**U”, which means the uncertainty is 15%.

27. Replace the uncertainty of DBL with “(5/6) DL”. Pay attention to the color, the purple should match the purple.

28. Copy all the data and then use the function of “Paste Special” by choosing “value”.

29. Replace all the missing data as “-99” and fill their uncertainty also as “-99”.

30. Change the format of the data into “4 decimal” number and red for negative number.

31. Delete all the useless rows, such as detective limitation and so on.

32. Insert 5 columns in front of the TMAC, name them as “ID”, “DATE”, “DUR”, “STHOUR”, and “SIZE” and fill these columns with proper contents. The format of “ID” should be as “WI200*-*”, the format of “DATE” should be as

“14/03/01”, and the format of “DUR” and “STHOUR” should be 0 decimal

33. Delete the first column of “Mnemonics”.

34. Save this excel as “CSV” format, and change the name as “AD_***”.

Appendix B:

CMB Performance Parameters

Using the source profiles and the ambient data with the sampling date of “01/01/2009”, a CMB calculation was made. Taking its output files as an example, these three output files of CMB were introduced as follows.

B.1 Fitting Statistics

Table B.1 shows the part of “Fitting Statistics”. This part illustrates the statistics measurements which can reveal if the calculation is acceptable and how well the calculation is.

Table B.1: Fitting Statistics

Parameter	**Value**
R Square (1)	0.85
Chi Square(2)	3.36
MASS %(3)	105.10
Degree of Freedom(4)	22

(1) The R-square (R^2) is the differences between measured and calculated concentrations explained by the calculated species concentrations. It is determined by a linear regression of the measured versus calculated values for the fitting species. R^2 ranges from 0 to 1. The closer the value is to 1, the better the calculated concentrations can describe the measured concentrations (Watson, 2004). When R-square is less than 0.8, the modeled results do not explain the measured concentrations very well through the fitting source profiles and/or species. The target

range of R-square is from 0.8 to 1 (Watson, 2004).

(2) Chi-square (χ^2) is the weighted sum of squares of the differences between calculated and measured fitting species concentrations (Watson, 2004). The weighting is inversely proportional to the squares of the precision in the source profiles and ambient data for each species. It is similar to R^2 but the differences are explained by the uncertainties of measured concentrations and calculated concentrations. The better the calculated data can describe the ambient data, the smaller the Chi-square is. Ideally it should equal zero if the calculated concentrations could precisely describe the measured concentrations. A Chi-square value less than 1 indicates a very good fit to the data, and value between 1 and 2 is also acceptable. Chi-square value greater than 4 indicates that one or more species concentrations are not well explained by the SCEs. Target of Chi-square is from 0 to 4 (Watson, 2004).

(3) Percent Mass (Mass %) represents the total calculated data versus the total measured data used in the CMB calculation (Watson, 2004). In my thesis, it is the total calculated concentrations versus the total measured concentrations of 55 PAMS. A value approaching 100% which means the calculated data is explaining the ambient data very well in the total quantity is desire. But sometimes a poor fit can also produce a satisfying Mass % which would be misleading. So the Percent Mass should always be used in combination with other performance parameters. The target of this value is 100%±20% (Watson, 2004).

(4) Degree of Freedom (DF) is the number of fitting species minus the number

of sources in calculation. Equation sets with larger DF are typically more stable and robust than those with small DF. The target of DF is more than 5 (Watson, 2004).

B.2 Source Contribution Estimates

The "Source Contribution Estimates" are shown in Table B.2. This part is the most important output for CMB. In this part, the SCEs and uncertainty of SCEs are illustrated, and the information that if the SCEs are acceptable will be indicated.

Table B.2: Source Contribution Estimates

Source	**SCE (μg/m^3) (5)**	**Std Err (μg/m^3)(6)**	**Tstat (μg/m^3)(7)**
Tu_MchHD	0.54	0.32	1.68
Exh_Lin1	4.97	1.70	2.93
WA_LiqGs	-0.86	1.31	-0.66
WA_Vap	3.35	0.99	3.39
CNG	7.84	1.64	4.78
LPG	3.59	1.13	3.18
Ind_Ref	6.32	1.35	4.68
Coke_Ovn	1.04	0.36	2.88
Biogenic	0.03	0.01	2.32
Arc_Coat	0.41	0.80	0.51
Total Cal	27.23		
Total Mea	25.90		
Total Mean Uncertainty	3.90		

(5) SCEs are the calculated contributions of expected sources which are expressed in concentrations (Watson, 2004). Ideally, there should be no negative SCEs. But if a source profile is collinear with another profile or if the source contribution is close to zero, the negative SCEs might appear which have no physically meaning (for example, the SCE of "WA_LiqGs" in Table B.2). The sum of all SCEs should be equal to the total measured concentrations, which is explained by

M % in output file (Watson, 2004).

(6) Standard error (Std Err) is the uncertainty of the SCE, expressed as one standard deviation of the most probable SCE. It indicates the precision of each SCE and should be reported with every SCE (Watson, 2004). Standard error is a function of the uncertainties in the input data and the amount of collinearity among source profiles. There is about 66% probability that the true source contribution lies within one standard error from the SCE and 95% probability that the true contribution lies within two standard errors. Target is Std Err << SCE (Watson, 2004).

(7) The t-statics (Tstat) is the ratio of the SCE to the standard error. A Tstat value less than 2.0 indicates that the SCE is at or below the detective limit. Collinearity among several source profiles may cause their Tstat values low (Watson, 2004). A high Tstat value indicates the SCE is not zero. The target value of Tstat is more than 2.0 (Watson, 2004).

B.3 Species Concentrations

The part of “Species Concentrations” is shown inTable B.3. This part displays how much and how well the individual species concentrations are produced by the modeling. ”Species concentrations” part can offer clues about which source might be missing and which source should not be included into calculation (Watson, 2004).

Table B.3: Species Concentrations

	Fitting(8)	**Measured**	**Uncertainty**	**Calculated**	**Uncertainty**	**Calculated/Measured(9)**	**Uncertainty**	**Residual/Uncertainty(10)**
TMAC(11)		25.91	3.89	27.23	1.85	1.05	0.17	0.3
ETHANE	*	7.2	1.08	5.67	0.81	0.79	0.16	-1.1
ACETYL	*	1.2	0.18	0.2	0.02	0.16	0.03	-5.5
N_PROP	*	5.11	0.77	5.15	0.57	1.01	0.19	0
I_BUTA	*	1.13	0.17	0.9	0.15	0.8	0.18	-1
N_BUTA	*	2.32	0.35	2.6	0.55	1.12	0.29	0.4
IPENTA	*	1.26	0.19	1.37	0.24	1.08	0.25	0.3
N_PENT	*	0.84	0.13	0.97	0.15	1.15	0.25	0.6
I_PREN	*	0.03	0	0.03	0.01	1	0.43	0
BU22DM	*	0.06	0.01	0.1	0.02	1.81	0.47	2
CPENTA	*	0.07	0.01	0.07	0.01	1.02	0.26	0.1
BU23DM	*	0.07	0.01	0.07	0.03	0.98	0.4	0
PENA2M	*	0.37	0.06	0.27	0.05	0.74	0.18	-1.3
PENA3M	*	0.26	0.04	0.25	0.04	0.95	0.21	-0.2
N_HEX	*	0.43	0.06	0.35	0.09	0.82	0.25	-0.7

(8) Fitting species are marked with an asterisk in this column (Watson, 2004).

(9) The Ratio of Calculated to Measured Species ($\frac{\text{CALCULATED}}{\text{MEASURED}}$) and its uncertainty are used to demonstrate how well the model can explain the measured concentrations (Watson, 2004). Ideally the ratios should be near 1.0, which means the model can accurately explain the measured concentrations. If rations deviated from 1.0 by more than two uncertainty intervals, it means an incorrect set of source profiles is used by the model. Its target is from 0.5 to 2 (Watson, 2004).

(10) Ratio of Residual to Uncertainty (R/U or $\frac{\text{RESIDUAL}}{\text{UNCERTAINTY}}$) is the ratio of the signed difference between the calculated and measured concentrations (residual = calculated – measured) divide by the uncertainty (standard error) of that residual (i.e., square root of the sum of the squares of the uncertainty in the calculated and measured concentrations). It describes the difference between the calculated and measured concentrations explained by the uncertainty interval of this difference (Watson, 2004). It can identify if a species is over-or-under-accounted for by the model and offer some clues concerning the reasons for this inaccuracy. When the absolute value of the ration R/U exceeds 2, the residual is significant. If it is positive, it means one or more profiles are contributing too much to that species. If it is negative, then there is an insufficient contribution to that species and one or more sources may be missing. The target of R/U is from -2.0 to 2.0. The sum of the squared ratio R/U for fitting species divided by the degrees of freedom yields the Chi-square. The higher ratio R/U values for fitting species is the cause of a high Chi-square value

(Watson, 2004).

(11) TMAC is the sum of all 55 PAMS concentration, and TMAU is its uncertainty which is 15% of TMAC. TMAC is not a species, but it is required by the model to construct the input file (Watson, 2004).

B.4 Species-Source Contribution

As shown in Table B.4, Species-Source Contribution (Contribution by Species) shows the contribution of each source to each species (Watson, 2004). The first two columns are the calculated and measured concentrations of each species. The other values are the ratios of the calculated species concentrations contributed from each source or source category to each measured species concentration. Multiplying the ratio of a species in a source by the measured concentration of that species indicates the contribution from this source to this species (Watson, 2004). Summing all the products of this species from all sources will equal the calculated mass of this species. In theory, the values except the first two columns should be no more than 1.0. But if the contribution from a particular source to a species is over-estimated, it can be > 1.0. “Species-Source Contribution” file can be used to identify the sources which are major contributors to particular species (Watson, 2004).

Table B.4: Species-Source Contribution (µg/m3)

Species	**Calculated**	**Measured**	**Tu_Mch**	**Exh_Li**	**WA_Liq**	**WA_Vap**	**CNG**	**LPG**	**Ind_Re**	**Coke_O**	**Biogen**	**Arc_Co**
TMAC	27.23	25.91	0.02	0.19	-0.03	0.13	0.3	0.14	0.24	0.04	0	0.02
ETHANE	5.67	7.2	0	0.01	0	0	0.75	0.02	0	0	0	0
ACETYL	0.2	1.2	0.01	0.15	0	0	0	0	0	0	0	0
N_PROP	5.15	5.11	0	0	0	0	0.32	0.64	0.05	0	0	0
I_BUTA	0.9	1.13	0	0.02	0	0.08	0.15	0.01	0.54	0	0	0
N_BUTA	2.6	2.32	0	0.05	-0.01	0.34	0.11	0	0.62	0.01	0	0
IPENTA	1.37	1.26	0.01	0.27	-0.06	0.76	0.04	0	0.07	0.01	0	0
N_PENT	0.97	0.84	0.01	0.15	-0.06	0.49	0.07	0	0.5	0.01	0	0
I_PREN	0.03	0.03	0	0	0	0	0	0	0	0	1	0
BU22DM	0.1	0.06	0.22	0.6	-0.04	0.23	0	0	0.76	0.04	0	0
CPENTA	0.07	0.07	0.02	0.2	0	0.37	0	0	0.43	0	0	0
BU23DM	0.07	0.07	0.02	0.64	-0.24	0.57	0	0	0	0	0	0
PENA2M	0.27	0.37	0.03	0.38	-0.1	0.33	0.06	0	0.03	0.01	0	0
PENA3M	0.25	0.26	0.02	0.34	-0.09	0.25	0.03	0	0.38	0.02	0	0
N_HEX	0.35	0.43	0.01	0.2	-0.07	0.17	0.07	0	0.43	0.01	0	0

B.5 Modified Psuedo Inverse Matrix

Modified Psuedo Inverse Matrix (MPIN) is shown in Table B.5. This file indicates the influences of species to SCEs (Watson, 2004). The value of MPIN is normalized with range from -1 to 1 so that user can judge the influence of a species to a SCE by its absolute MPIN value: absolute value from 0.5 to 1.0 means the species is influential to this source's SCE; absolute values between 0.3 to 0.5 means this species is ambiguous and should generally be considered as non-influential; absolute values less than 0.3 shows this species is non-influential (Watson, 2004).

Table B.5: MPIN Matrix

	Tu_Mch	**Exh_Li**	**WA_Liq**	**WA_Vap**	**CNG**	**LPG**	**Ind_Re**	**Coke_O**	**Biogen**	**Arc_Co**
ETHAN	0.05	-0.48	0.26	0.1	1	-	-0.34	0.02	0	0.05
ACETY	0	0.94	-0.95	0.07	-0.1	0.0	-0.23	0.02	0	0.08
N_PRO	0	0.02	-0.01	0	-	1	0	0	0	0
I_BUT	-0.05	-0.49	0.38	-0.2	0.05	-	1	-0.01	0	-0.05
N_BUT	-0.04	-0.28	-0.01	0.16	0.01	-	0.58	0.04	0	0
IPENT	0	0.43	-0.96	1	0.08	0	-0.84	0.09	0	0.09
N_PEN	-0.02	-0.54	0.32	0.32	0.03	-	0.38	-0.01	0	-0.06
I_PREN	0	0	0	0	0	0	0	0	1	0
BU22D	0.26	0.62	-0.69	-0.01	-	0.0	0.36	-0.08	0	0.02
CPENT	0	0.61	-1	0.37	-	0.0	0.13	0.06	0	0.09
BU23D	0.02	-0.53	0.91	0.14	0.03	0	-0.24	-0.13	0	-0.18
	Tu_Mch	**Exh_Li**	**WA_Liq**	**WA_Vap**	**CNG**	**LPG**	**Ind_Re**	**Coke_O**	**Biogen**	**Arc_Co**
PENA2	0.04	0.08	0.06	0.31	0.06	-	-0.41	-0.06	0	-0.08
PENA3	-0.03	-0.14	0.31	-0.01	-	0.0	0.42	-0.05	0	-0.11
N_HEX	-0.02	-0.55	0.71	-0.14	0	-	0.58	-0.06	0	-0.12
MCYP	-0.04	0.84	-0.94	-0.14	0.28	-0.1	0.46	0.03	0	0.09
PEN24	-0.02	-0.09	0.21	-0.05	-	0.0	0.22	-0.03	0	0.27
BENZE	-0.11	0.51	-0.49	0.01	-	0.0	0.1	0.35	0	0.02
CYHEX	0.02	-0.54	0.71	-0.11	-	0	0.44	-0.09	0	-0.12
HEXA2	-0.06	0.39	0.03	-0.05	-0.1	0.0	-0.13	-0.07	0	-0.09
PEN23	-0.06	-0.56	0.83	-0.02	0.03	-	-0.04	0.22	0	-0.14

Table B.5-Continuted

	Tu_Mch	**Exh_Li**	**WA_Liq**	**WA_Vap**	**CNG**	**LPG**	**Ind_Re**	**Coke_O**	**Biogen**	**Arc_Co**
HEXA3M	0.14	-0.2	0.56	-0.14	0.04	-0.0	0.19	-0.07	0	-0.14
PA224	-0.05	1	-0.45	-0.05	-	0.0	-0.34	-0.01	0	-0.08
N_HEP	-0.04	-0.53	0.83	-0.21	0.05	-	0.49	0.01	0	-0.15
MECY	-0.05	0.95	-0.9	0.01	-	0.0	-0.05	0.16	0	0.05
PA234	-0.04	0.31	0.39	-0.21	-	0.0	-0.06	-0.14	0	-0.18
TOLUE	0.01	0.03	-0.07	0.02	0.02	0	-0.07	0.01	0	1
HEP2M	-0.03	0.07	0.23	-0.04	0.51	-	-0.34	-0.06	0	-0.06
HEP3M	0.04	0.08	0.34	-0.12	-	0.0	0.03	-0.1	0	-0.13

Appendix C: Source Profiles

Table C.1: Source Profiles Used in This Study

PROFILE	ETHANE	ETHANEU	ETHENE	ETHENEU	ACETYL	ACETYLU
Tu_MchHD	0.011	0.006	0.089	0.025	0.023	0.016
Exh_Lin1	0.017	0.001	0.065	0.002	0.037	0.003
WA_LIQ	0	0.002	0	0.002	0	0.002
WA_VAP	0	0.002	0	0.002	0	0.002
CNG	0.689	0.103	0	0.001	0	0.001
LPG	0.041	0.006	0	0.001	0	0.001
Ind_Ref	0.005	0.004	0	0.001	0	0.001
Coke_Ovn	0	0.002	0	0.002	0	0.002
Arc_Coat	0	0.002	0	0.002	0	0.002
Biogenic	0	0.001	0	0.001	0	0.001
PROFILE	LBUT1E	LBUT1EU	PROPE	PROPEU	N_PROP	N_PROPU
Tu_MchHD	0.027	0.007	0.036	0.008	0.02	0.009
Exh_Lin1	0.004	0.001	0.03	0.001	0	0
WA_LIQ	0	0.002	0	0.002	0	0.002
WA_VAP	0	0.002	0	0.002	0	0.002
CNG	0	0.001	0	0.001	0.211	0.032
LPG	0	0.001	0.051	0.008	0.906	0.136
Ind_Ref	0	0.002	0.013	0.041	0.037	0.024
Coke_Ovn	0	0.002	0	0.002	0	0.002
Arc_Coat	0	0.002	0	0.002	0	0.002
Biogenic	0	0.001	0	0.001	0	0.001
PROFILE	I_BUTA	I_BUTAU	N_BUTA	N_BUTAU	T2BUTE	T2BUTEU
Tu_MchHD	0.002	0.003	0.006	0.014	0.002	0.004
Exh_Lin1	0.005	0.001	0.022	0.001	0.005	0
WA_LIQ	0.003	0.001	0.028	0.012	0.001	0
WA_VAP	0.027	0.013	0.238	0.119	0.004	0.004
CNG	0.021	0.003	0.031	0.005	0	0.001
LPG	0.002	0.001	0	0.001	0	0.001
Ind_Ref	0.096	0.022	0.229	0.059	0.008	0.002
Coke_Ovn	0.003	0	0.02	0.003	0	0.002
Arc_Coat	0	0.002	0	0.002	0	0.002
Biogenic	0	0.001	0	0.001	0	0.001

Table C.1-continued 1

PROFILE	C2BUTE	C2BUTEU	IPENTA	IPENTAU	PENTE1	PENTE1U
Tu_MchHD	0.003	0.001	0.012	0.031	0.008	0.002
Exh_Lin1	0.004	0	0.069	0.009	0.003	0
WA_LIQ	0.001	0	0.094	0.02	0.003	0.001
WA_VAP	0.005	0.004	0.285	0.046	0.007	0.002
CNG	0	0.001	0.007	0.002	0	0.001
LPG	0	0.001	0	0.001	0	0.001
Ind_Ref	0.006	0.001	0.013	0.029	0.006	0.002
Coke_Ovn	0	0.002	0.007	0.001	0	0
Arc_Coat	0	0.002	0	0.002	0	0.002
Biogenic	0	0.001	0	0.001	0	0.001
PROFILE	N_PENT	N_PENTU	I_PREN	I_PRENU	T2PENE	T2PENEU
Tu_MchHD	0.014	0.012	0	0.003	0.003	0.003
Exh_Lin1	0.026	0.002	0	0.001	0.007	0
WA_LIQ	0.063	0.025	0	0	0.005	0.003
WA_VAP	0.122	0.041	0	0	0.01	0.006
CNG	0.007	0.002	0	0.001	0	0.001
LPG	0	0.001	0	0.001	0	0.001
Ind_Ref	0.066	0.01	0	0.001	0.009	0.002
Coke_Ovn	0.005	0.001	0	0.002	0	0.002
Arc_Coat	0	0.002	0	0.002	0	0.002
Biogenic	0	0.001	1	0.1	0	0.001
PROFILE	C2PENE	C2PENEU	BU22DM	BU22DMU	CPENTA	CPENTAU
Tu_MchHD	0.003	0.002	0.024	0.009	0.003	0.002
Exh_Lin1	0.004	0	0.007	0.001	0.003	0
WA_LIQ	0.003	0.002	0.003	0.001	0	0.002
WA_VAP	0.005	0.003	0.004	0.001	0.008	0.003
CNG	0	0.001	0	0.001	0	0.001
LPG	0	0.001	0	0.001	0	0.001
Ind_Ref	0.004	0.001	0.007	0.003	0.005	0.001
Coke_Ovn	0	0.002	0.002	0	0	0.002
Arc_Coat	0	0.002	0	0.002	0	0.002
Biogenic	0	0.001	0	0.001	0	0.001

Table C.1-continued 2

PROFILE	BU23DM	BU23DMU	PENA2M	PENA2MU	PENA3M	PENA3MU
Tu_MchHD	0.003	0.006	0.018	0.01	0.008	0.006
Exh_Lin1	0.009	0	0.028	0	0.018	0
WA_LIQ	0.02	0.004	0.043	0.014	0.026	0.008
WA_VAP	0.012	0.007	0.036	0.012	0.02	0.007
CNG	0	0.001	0.003	0.001	0.001	0.001
LPG	0	0.001	0	0.001	0	0.001
Ind_Ref	0	0.001	0.002	0.005	0.016	0.005
Coke_Ovn	0	0.002	0.004	0.001	0.004	0.001
Arc_Coat	0	0.002	0	0.002	0	0.002
Biogenic	0	0.001	0	0.001	0	0.001
PROFILE	P1E2ME	P1E2MEU	N_HEX	N_HEXU	MCYPNA	MCYPNAU
Tu_MchHD	0.002	0.002	0.009	0.005	0.006	0.004
Exh_Lin1	0.002	0	0.017	0.001	0.012	0
WA_LIQ	0.002	0.001	0.036	0.014	0	0.002
WA_VAP	0.001	0.001	0.022	0.011	0	0
CNG	0	0.001	0.004	0.001	0.01	0.002
LPG	0	0.001	0	0.001	0	0.001
Ind_Ref	0	0	0.029	0.013	0.013	0.003
Coke_Ovn	0	0.002	0.005	0.001	0	0.002
Arc_Coat	0	0.002	0	0.002	0	0.002
Biogenic	0	0.001	0	0.001	0	0.001
PROFILE	PEN24M	PEN24MU	BENZE	BENZEU	CYHEXA	CYHEXAU
Tu_MchHD	0.003	0.002	0.029	0.014	0.002	0.001
Exh_Lin1	0.007	0	0.033	0.001	0.002	0
WA_LIQ	0.012	0.01	0.03	0.005	0.005	0.003
WA_VAP	0.005	0.006	0.014	0.006	0.003	0.002
CNG	0	0.001	0	0.001	0	0.001
LPG	0	0.001	0	0.001	0	0.001
Ind_Ref	0.004	0.001	0.016	0.005	0.003	0.001
Coke_Ovn	0.002	0	0.105	0.016	0	0
Arc_Coat	0.011	0.002	0.001	0	0	0.002
Biogenic	0	0.001	0	0.001	0	0.001

Table C.1-continued 3

PROFILE	HEXA2M	HEXA2MU	PEN23M	PEN23MU	HEXA3M	HEXA3MU
Tu_MchHD	0	0.001	0.008	0.003	0.021	0.012
Exh_Lin1	0.013	0	0.009	0	0.012	0
WA_LIQ	0.016	0.002	0.023	0.023	0.018	0.001
WA_VAP	0.005	0.004	0.008	0.01	0.006	0.004
CNG	0	0.001	0	0.001	0.002	0.001
LPG	0	0.001	0	0.001	0	0.001
Ind_Ref	0.001	0.003	0	0.001	0.005	0.002
Coke_Ovn	0	0.002	0.035	0.005	0.009	0.001
Arc_Coat	0	0.002	0	0.002	0	0.002
Biogenic	0	0.001	0	0.001	0	0.001
PROFILE	PA224M	PA224MU	N_HEPT	N_HEPTU	MECYHX	MECYHXU
Tu_MchHD	0.013	0.011	0.005	0.003	0.004	0.002
Exh_Lin1	0.035	0.001	0.008	0	0.006	0.001
WA_LIQ	0.036	0.034	0.015	0.002	0.003	0.002
WA_VAP	0.009	0.011	0.005	0.003	0.001	0.001
CNG	0.003	0.001	0.002	0.001	0.001	0.001
LPG	0	0.001	0	0.001	0	0.001
Ind_Ref	0.002	0.001	0.007	0.003	0.002	0.001
Coke_Ovn	0.013	0.002	0.01	0.001	0.007	0.001
Arc_Coat	0	0.002	0	0.002	0	0.002
Biogenic	0	0.001	0	0.001	0	0.001
PROFILE	PA234M	PA234MU	TOLUE	TOLUEU	HEP2ME	HEP2MEU
Tu_MchHD	0.003	0.004	0.041	0.033	0	0.002
Exh_Lin1	0.012	0.001	0.077	0.004	0.005	0
WA_LIQ	0.016	0.013	0.149	0.029	0.006	0.001
WA_VAP	0.003	0.004	0.044	0.032	0.001	0.001
CNG	0	0.001	0	0.001	0.004	0.001
LPG	0	0.001	0	0.001	0	0.001
Ind_Ref	0.001	0	0.019	0.017	0	0.001
Coke_Ovn	0.001	0	0.02	0.003	0	0.002
Arc_Coat	0	0.002	0.259	0.039	0	0.002
Biogenic	0	0.001	0	0.001	0	0.001

Table C.1-continued 4

PROFILE	HEP3ME	HEP3MEU	N_OCT	N_OCTU	ETBZ	ETBZU
Tu_MchHD	0.004	0.002	0.003	0.002	0.026	0.018
Exh_Lin1	0.005	0	0.004	0	0.011	0
WA_LIQ	0.007	0.001	0.006	0.001	0.026	0.006
WA_VAP	0.002	0.001	0.001	0.001	0.007	0.007
CNG	0	0.001	0	0.001	0	0.001
LPG	0	0.001	0	0.001	0	0.001
Ind_Ref	0.001	0.001	0.001	0.001	0.002	0.003
Coke_Ovn	0.001	0	0.002	0	0.009	0.001
Arc_Coat	0	0.002	0	0.002	0.005	0.001
Biogenic	0	0.001	0	0.001	0	0.001
PROFILE	MP_XYL	MP_XYLU	STYR	STYRU	O_XYL	O_XYLU
Tu_MchHD	0.1	0.062	0.017	0.007	0.034	0.021
Exh_Lin1	0.041	0	0.001	0	0.015	0
WA_LIQ	0.098	0.021	0	0.002	0.037	0.008
WA_VAP	0.024	0.026	0	0.002	0.009	0.01
CNG	0	0.001	0	0.001	0	0.001
LPG	0	0.001	0	0.001	0	0.001
Ind_Ref	0	0.001	0	0.001	0.003	0.005
Coke_Ovn	0.012	0.002	0	0.002	0.014	0.002
Arc_Coat	0.027	0.004	0	0.002	0.029	0.004
Biogenic	0	0.001	0	0.001	0	0.001
PROFILE	N_NON	N_NONU	IPRBZ	IPRBZU	N_PRBZ	N_PRBZU
Tu_MchHD	0.01	0.003	0.003	0.002	0.01	0.006
Exh_Lin1	0.001	0	0	0	0.003	0
WA_LIQ	0.003	0.001	0.002	0	0.008	0.001
WA_VAP	0	0	0	0	0.001	0.001
CNG	0	0.001	0	0.001	0	0.001
LPG	0	0.001	0	0.001	0	0.001
Ind_Ref	0	0	0.001	0.003	0	0
Coke_Ovn	0.031	0.005	0.009	0.001	0.007	0.001
Arc_Coat	0	0.002	0	0.002	0	0.002
Biogenic	0	0.001	0	0.001	0	0.001

Table C.1-continued 5

PROFILE	M_ETOL	M_ETOLU	P_ETOL	P_ETOLU	BZ135M	BZ135MU
Tu_MchHD	0.038	0.026	0.013	0.007	0.019	0.01
Exh_Lin1	0.013	0.001	0.006	0	0.007	0
WA_LIQ	0.024	0.003	0.01	0.001	0.012	0.003
WA_VAP	0.004	0.004	0.002	0.002	0.002	0.002
CNG	0	0.001	0	0.001	0	0.001
LPG	0	0.001	0	0.001	0	0.001
Ind_Ref	0	0.002	0	0.002	0	0.001
Coke_Ovn	0.006	0.002	0.004	0.002	0.004	0.001
Arc_Coat	0	0.002	0	0.002	0	0.002
Biogenic	0	0.001	0	0.001	0	0.001
PROFILE	O_ETOL	O_ETOLU	BZ124M	BZ124MU	N_DEC	N_DECU
Tu_MchHD	0.018	0.01	0.068	0.042	0.024	0.006
Exh_Lin1	0.004	0	0.02	0.002	0.001	0
WA_LIQ	0.008	0.001	0.039	0.011	0	0
WA_VAP	0.002	0.002	0.006	0.006	0	0
CNG	0	0.001	0	0.001	0	0.001
LPG	0	0.001	0	0.001	0	0.001
Ind_Ref	0	0.002	0.003	0.005	0	0.002
Coke_Ovn	0.003	0.002	0.001	0	0.013	0.002
Arc_Coat	0	0.002	0	0.002	0	0.002
Biogenic	0	0.001	0	0.001	0	0.001
PROFILE	BZ123M	BZ123MU	DETBZ1	DETBZ1U	DETBZ2	DETBZ2U
Tu_MchHD	0.015	0.009	0	0.001	0	0.001
Exh_Lin1	0.005	0	0.001	0	0.004	0
WA_LIQ	0.009	0.001	0.003	0.001	0	0
WA_VAP	0.001	0.001	0	0	0	0
CNG	0	0.001	0	0.001	0	0.001
LPG	0	0.001	0	0.001	0	0.001
Ind_Ref	0	0.002	0	0.002	0	0.002
Coke_Ovn	0.041	0.002	0	0.002	0	0.002
Arc_Coat	0	0.002	0	0.002	0	0.002
Biogenic	0	0.001	0	0.001	0	0.001

Table C.1-continued 6

PROFILE	N_UNDE	N_UNDEU	OTHER	OTHERU
Tu_MchHD	0.048	0.009	0.092	0.02
Exh_Lin1	0	0.001	0.246	0.019
WA_LIQ	0.001	0	0.046	0.02
WA_VAP	0	0	0.024	0.015
CNG	0	0.001	0.005	0.153
LPG	0	0.001	0	0.193
Ind_Ref	0	0.002	0.363	0.147
Coke_Ovn	0	0.002	0.593	0.084
Arc_Coat	0	0.002	0.669	0.1
Biogenic	0	0.001	0	0.142

Appendix D:

RESULTS AND DISCUSSION

D.1 Annual Monitored PAMS

PAMS species were a set of VOC species used by many researchers to reflect the ambient VOCs (Nguyen et al., 2009; Brown et al., 2007; Watson et al., 1998). In thie project, the total concentrations of 55 PAMS species were used to study the ambient VOCs. The annual VOC source contributions and corresponding percentages from 2001 to 2009 were shown in Figure D.1

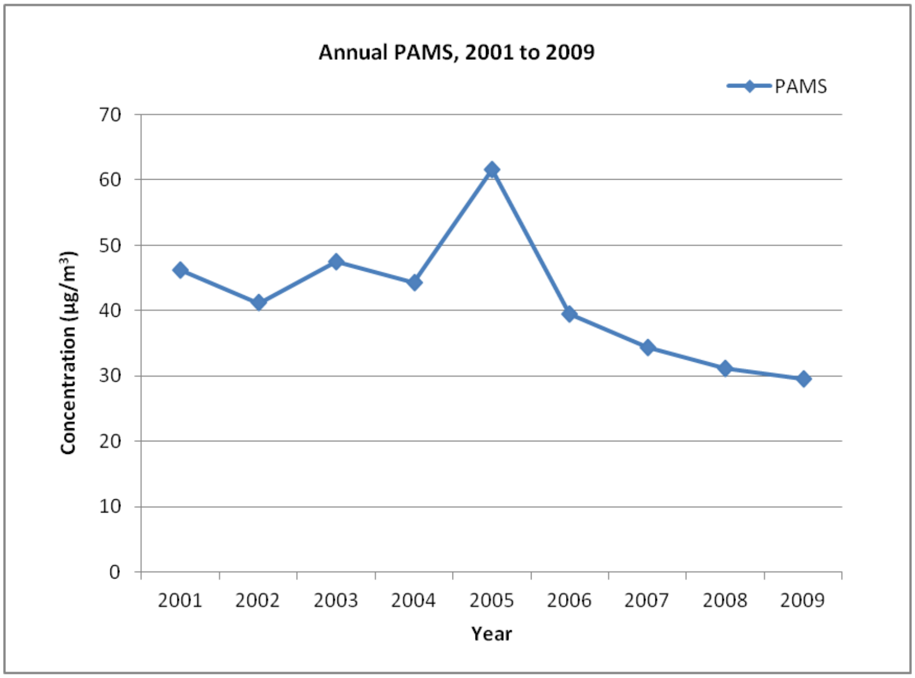


Figure D.1: Annual VOC measurements, 2001 to 2009

As shown in Figure D.1, there was a sudden peak of annual VOC measurements in 2005. This could be due to the fact that in 2005, VOC measurements were only available during winter and spring and VOC concentrations are usually high in these two seasons. Therefore, the annual VOC measurements calculated using the measurements in these two seasons might be higher than its real level. If the peak of VOC measurement in 2005 was not considered, a declining trend of approximately 36% was found from 2001 to 2009. The decreasing trend is consistent with the phenomenon observed in other studies on long-term VOCs trend in Canada. Geddes et al. (2009) found a decreasing trend of VOCs in summer from 2000 to 2007 in Toronto. They attributed the decreasing trend to the improving vehicle technology, regulatory initiatives, and incentive programs to control emissions. Curren et al. (2006) also found a decreasing trend of 1, 3-butadiene concentrations during 1995 to 2004 in Canada. This could be due to automotive emission control technologies and fuel emission reduction initiatives.

D.2 Annual Source Contribution Composition

The VOC source contributions and contribution percentages from 2001 to 2009 are shown in Figure D.2 and Figure D.3. "Diesel Exhaust", "Gasoline Exhaust", and "Gasoline Vapour" all belong to "Vehicle Emission".

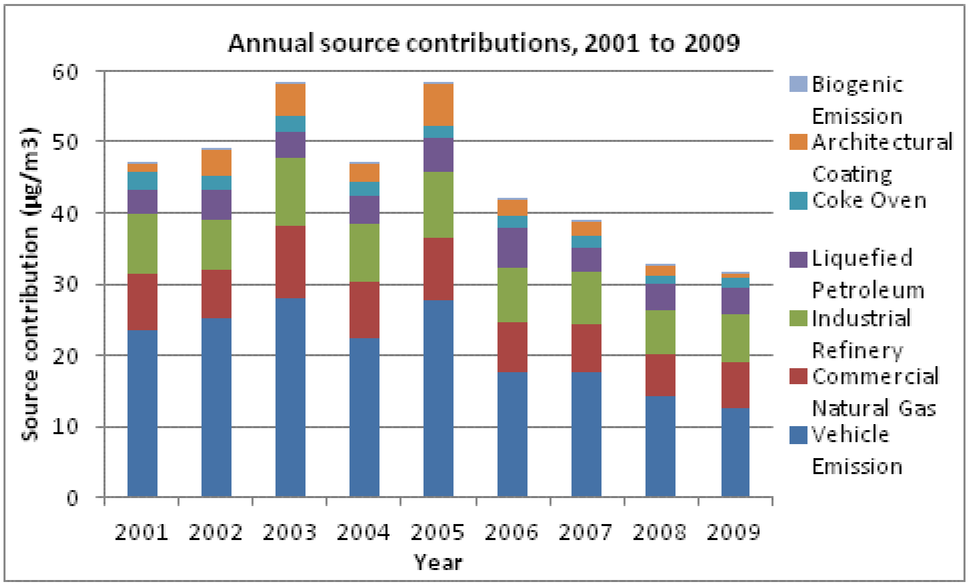


Figure D.2: Annual source contributions, 2001 to 2009

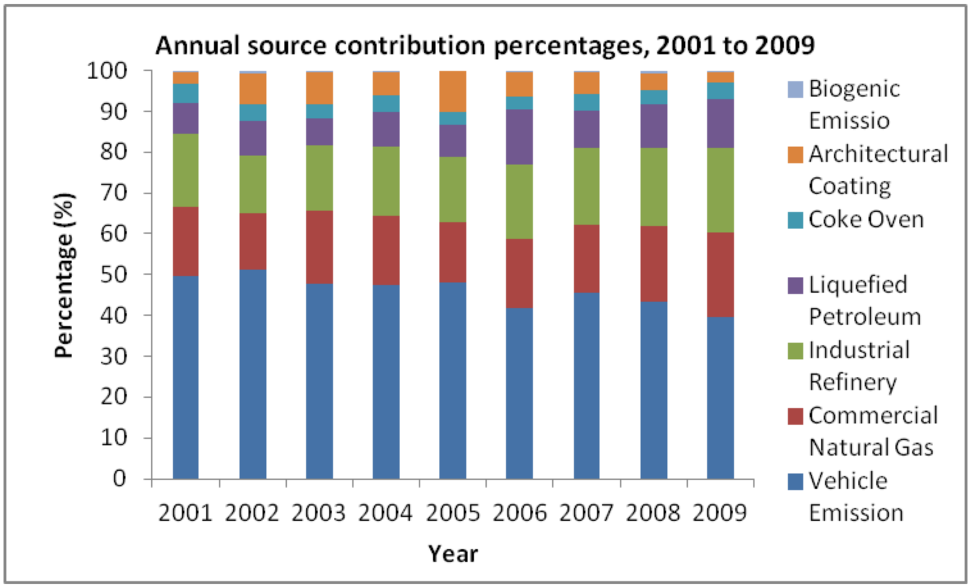


Figure D.3: Annual source contribution percentages, 2001 to 2009

From Figure D.2 and Figure D.3, it was found that the ranking of sources according to their estimated source contributions and percentages from 2001 to 2009 was: “Vehicle Emission” (source contribution 12.5 µg/m^3; source contribution percentage 39.6%), “Commercial Natural Gas” (source contribution 6.6 µg/m^3; source contribution percentage 20.8%), “Industrial Refinery” (source contribution 6.6 µg/m^3; source contribution percentage 20.7%), “Liquefied Petroleum” (source contribution 3.7 µg/m^3; source contribution percentage 11.7%), “Coke Oven” (source contribution 1.3 µg/m^3; source contribution percentage 4.2%), “Architectural Coating” (source contribution 0.8 µg/m^3; source contribution percentage 2.6%), and “Biogenic Emission” (source contribution 0.1µg/m^3; source contribution percentage 0.3%).

From Figure D.2, it was also found that source contribution percentage of “Vehicle Emission” decreased from 50% in 2001 to 40% in 2009, and it was consistently the largest component of total contribution. Among the three sources of “Vehicle Emission”, the “Gasoline Exhaust” accounted for 64% of the total source contribution reduction, followed by “Diesel Exhaust” (20%) and “Gasoline Vapour” (15%).

There were three sources which experienced an increase in percentage, including “Commercial Natural Gas”, “Liquefied Petroleum”, and “Industrial Refinery”. “Liquefied Petroleum” increased the most from 7% to 12% , followed by “Commercial Natural Gas” (from 17% to 21%) and “Industrial Refinery” (from 18% to 21%).

The percentages of the other three sources changed little, including “Coke Oven”, “Architectural Coating”, and “Biogenic Emission”. They accounted for 7% of total source contribution.

D.3 Annual Variability of Source Contributions

The annual variability of source contributions and corresponding percentages of all sources from 2001 to 2009 are shown from Figure D.4 to Figure D.12. The relationship between source contribution and source contribution percentage can be helpful to reveal the reason for the source contribution composition changes.

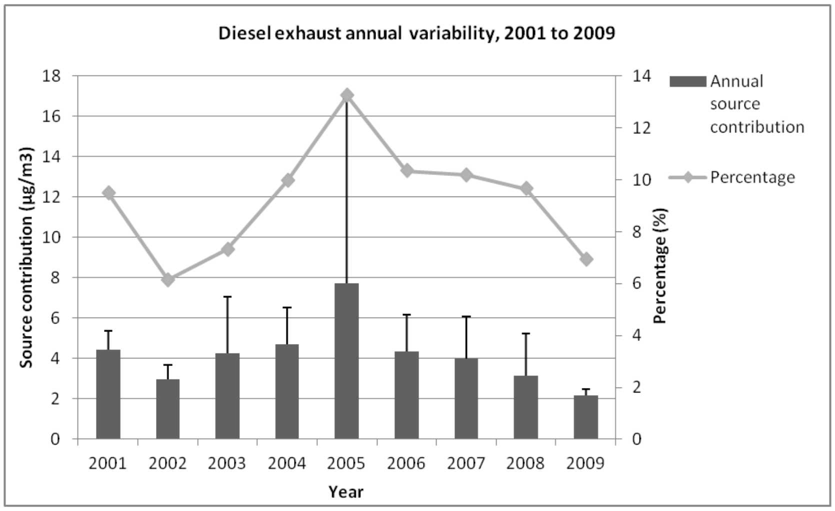


Figure D.4: Diesel exhaust seasonal variability, 2001 to 2009

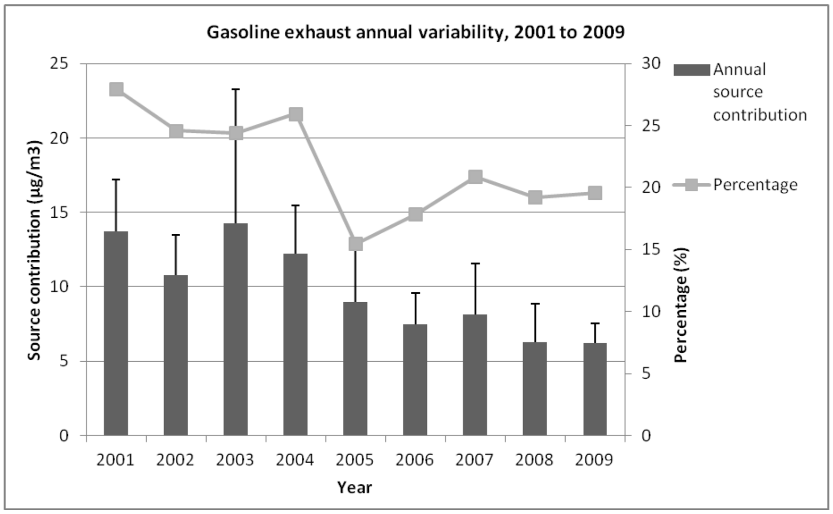


Figure D.5: Gasoline exhaust annual variability, 2001 to 2009

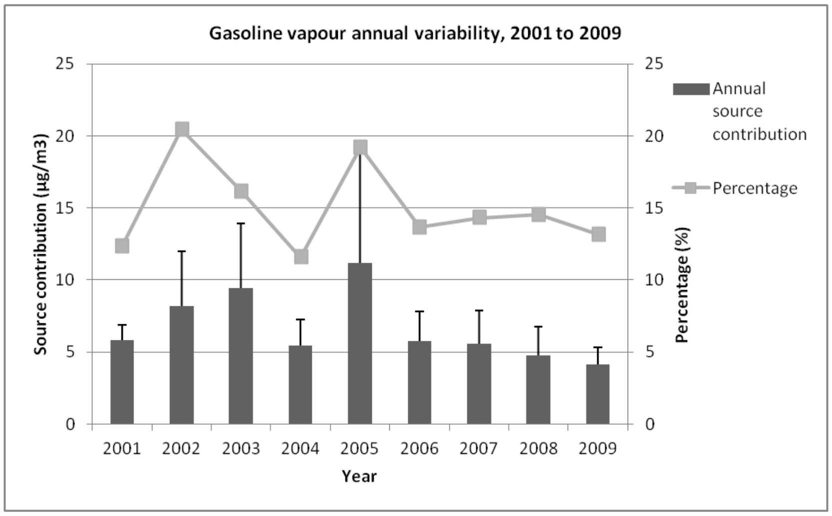


Figure D.6: Gasoline vapour annual variability, 2001 to 2009

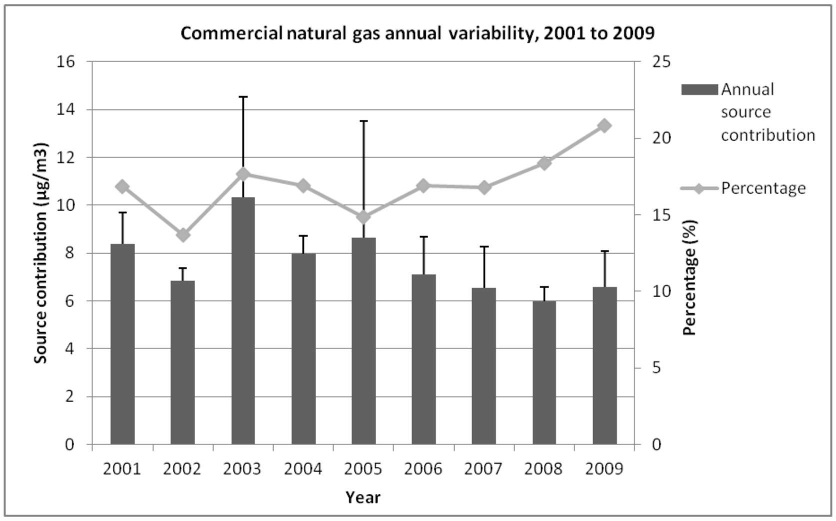


Figure D.7: Commercial natural gas annual variability, 2001 to 2009

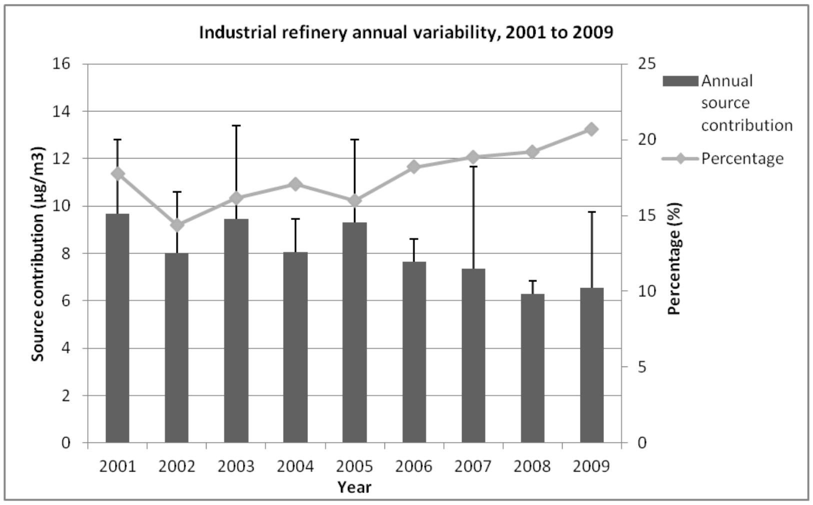


Figure D.8: Industrial refinery annual variability, 2001 to 2009

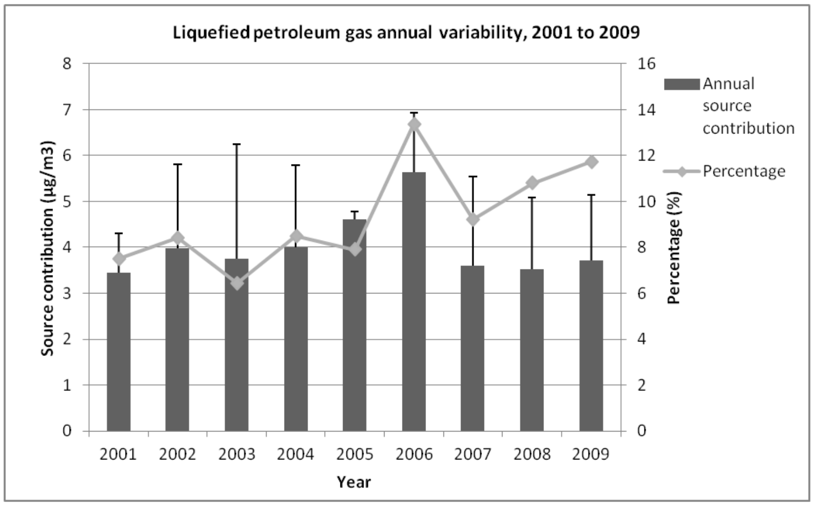


Figure D.9: Liquefied petroleum annual variability, 2001 to 2009

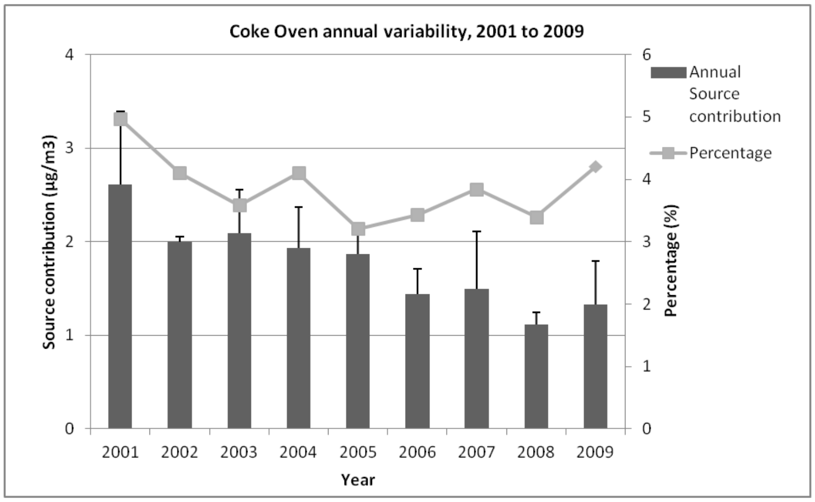


Figure D.10: Coke Oven annual variability, 2001 to 2009

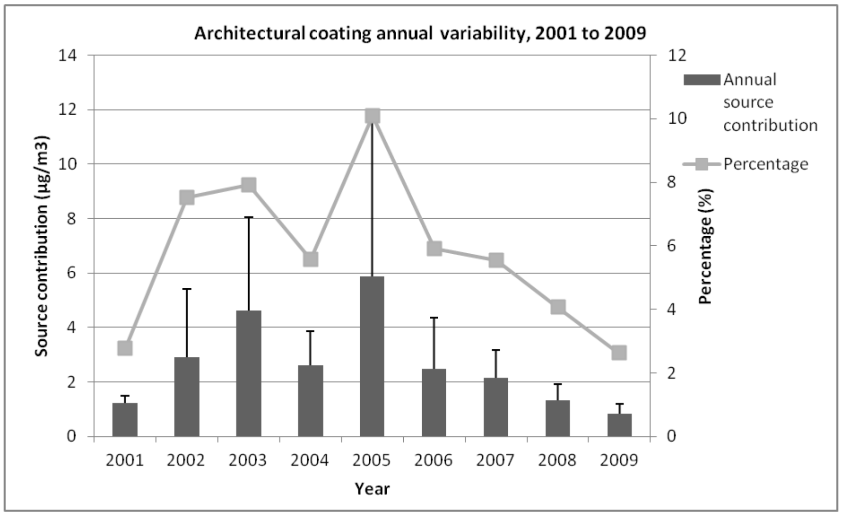


Figure D.11: Architectural coating annual variability, 2001 to 2009

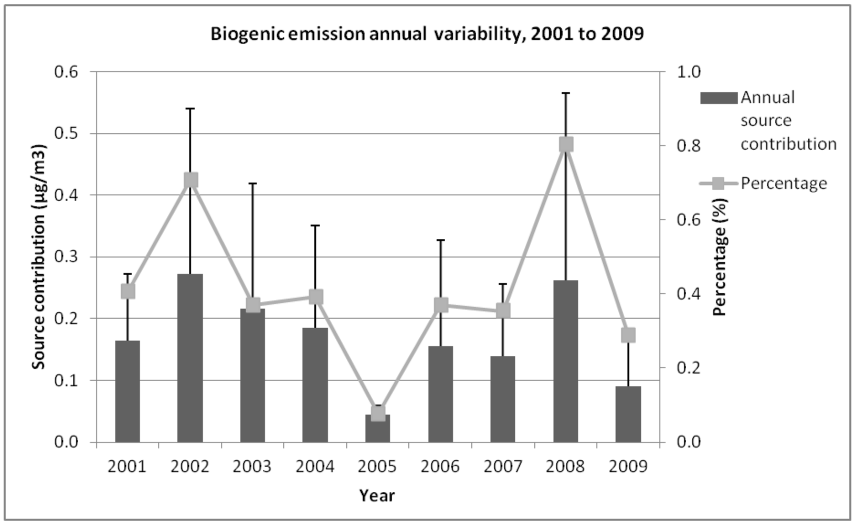


Figure D.12: Biogenic emission annual variability, 2001 to 2009

From Figure D.4 to Figure D.12, it is found that “Diesel Exhaust”, “Gasoline Vapour”, “Commercial Natural Gas”, “Industrial Refinery”, and “Architectural Coating” all experienced a peak of source contribution in 2005. This might be due to the fact that there were only complete data sets in the winter and spring of 2005. In winter and spring, the pollutant concentrations usually are higher than summer and fall. If the measurements in 2005 were not considered, a declining trend of source contribution from 2001 to 2009 could be found in most sources, including “Diesel Exhaust”, “Gasoline Exhaust”, "Gasoline Vapour", "Commercial Natural Gas", "Industrial Refinery", "Coke Oven", "Architectural Coating", and "Biogenic Emission". However, "Liquefied Petroleum" emission increased from 3.5μg/m^3 to 3.7μg/m^3 from 2001 to 2009.

However, the trend of source contribution percentage was not consistent with the trend of source contribution from 2001 to 2009. Percentage of "Biogenic Emission", "Architectural Coating", and "Diesel Exhaust" remained the same. Percentages of "Gasoline Exhaust", and "Gasoline Vapour" decreased. However, the percentages of "Commercial Natural Gas", "Industrial Refinery", "Coke Oven", and "Liquefied Petroleum" increased.

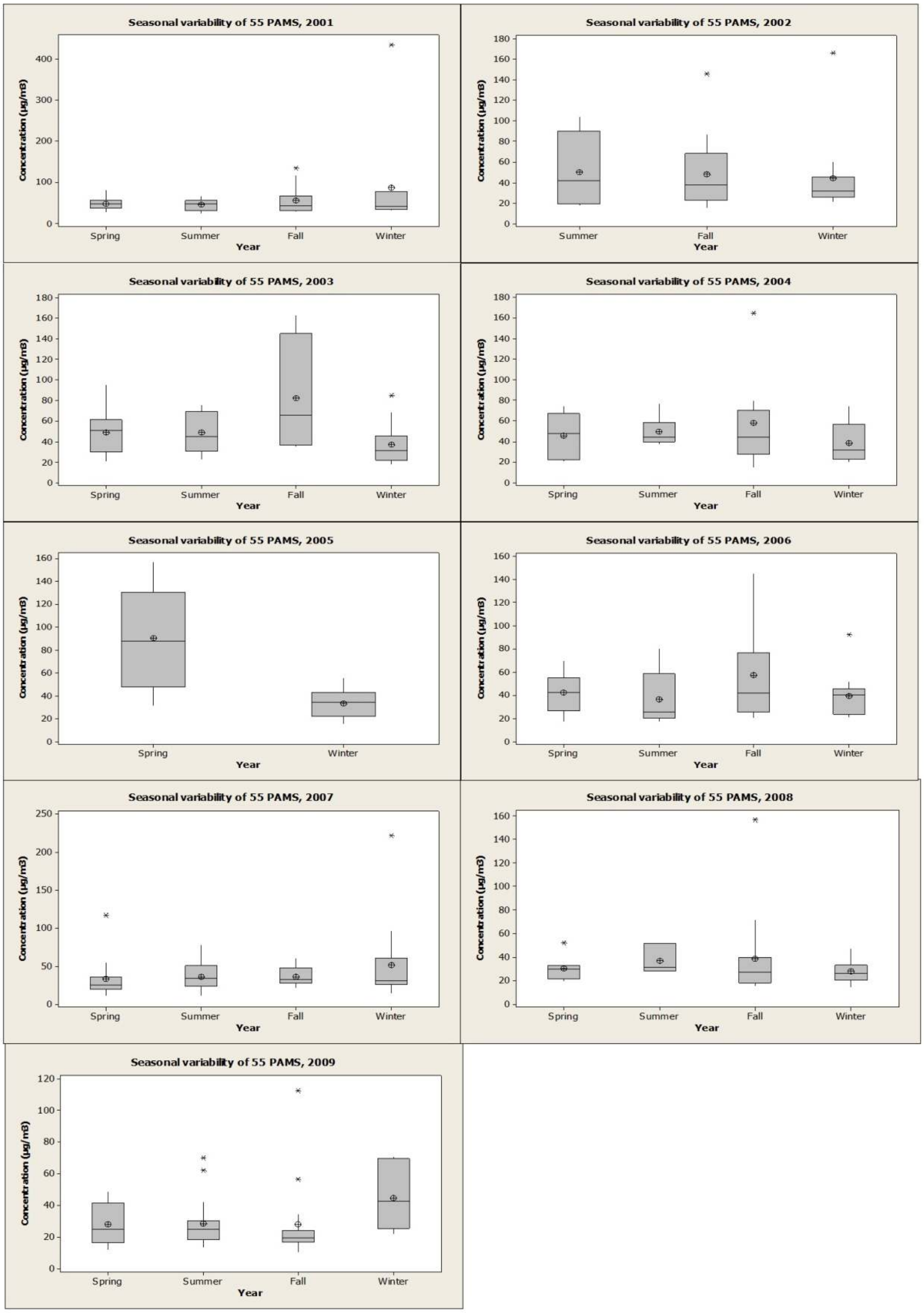
Compared with the trend of source contributions, it was found that change of percentages was caused by the different decreasing rates of source contributions. Some source decreased faster than other sources; therefore, their source contribution percentages would decline. Other sources were just the opposite. Their source contribution percentages would increase.

Overall, emission from most sources decreased during 2001 to 2009. However, more efforts should be put on the pollution reduction from "Commercial Natural Gas", "Industrial Refinery", and "Liquefied Petroleum" due to their increased source contribution percentages

.

D.4 Seasonal Pattern of VOCs

The seasonal variabilities of 55 PAMS species from 2001 to 2009 are shown in Figure D.13. The seasonal variability of source contributions from 2001 to 2009 are shown from Figure D.14 to Figure D.22.



Seasonal variability of 55 PAMS, 2001

Seasonal variability of 55 PAMS, 2002

Seasonal variability of 55 PAMS, 2003

Seasonal variability of 55 PAMS, 2004

Seasonal variability of 55 PAMS, 2005

Seasonal variability of 55 PAMS, 2006

Seasonal variability of 55 PAMS, 2007

Seasonal variability of 55 PAMS, 2008

Seasonal variability of 55 PAMS, 2009

Figure D.13: Seasonal patterns of total PAMS concentrations, 2001 to 2009

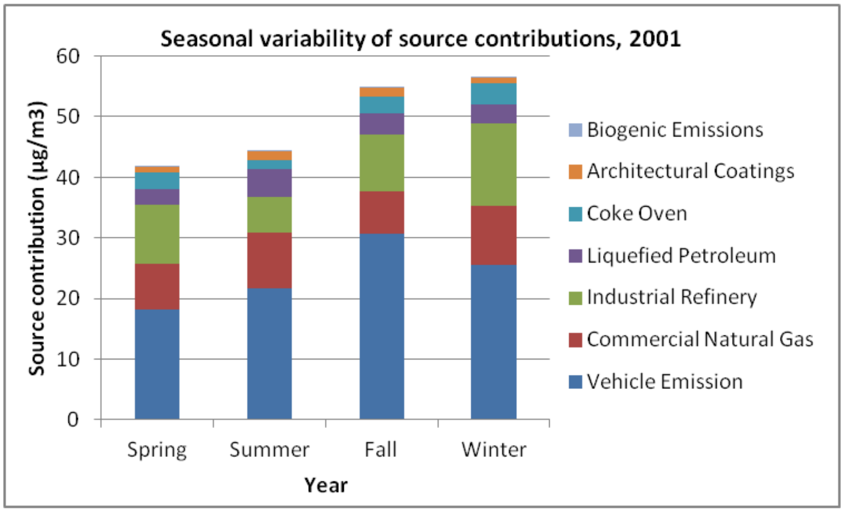


Figure D.14: Seasonal variability of source contributi0ns, 2001

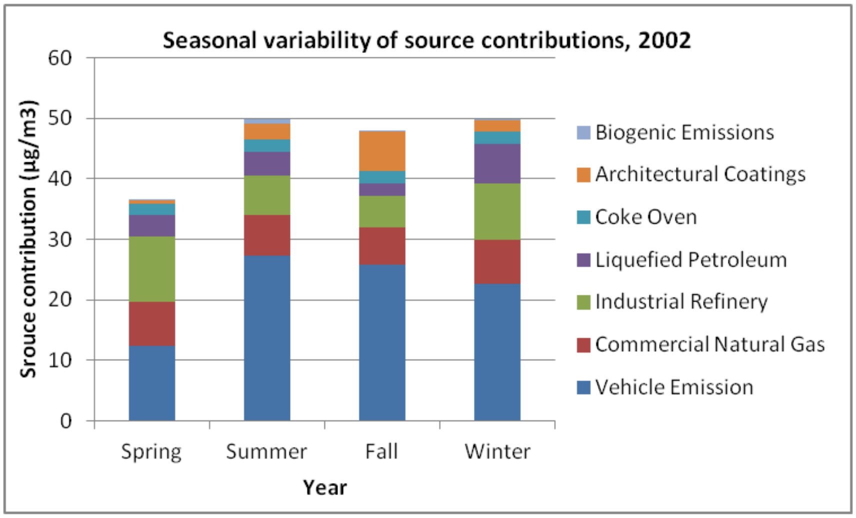


Figure D.15: Seasonal variability of source contributi0ns, 2002

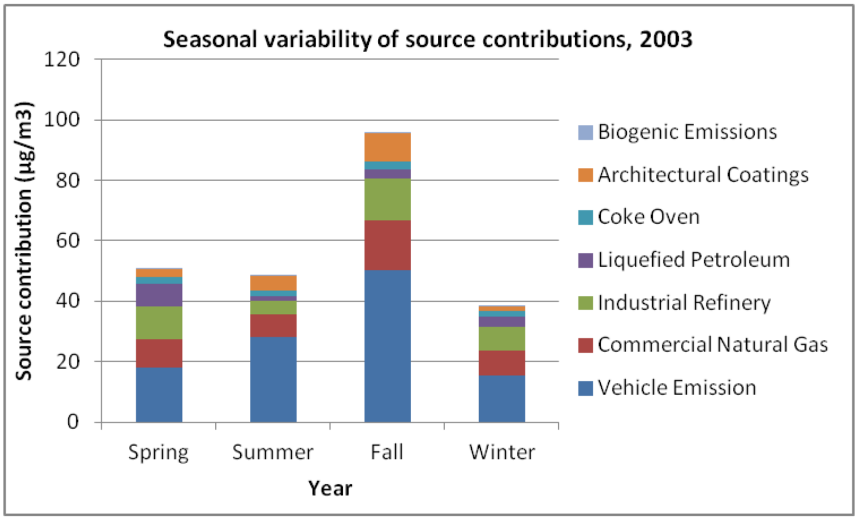


Figure D.16: Seasonal variability of source contributi0ns, 2003

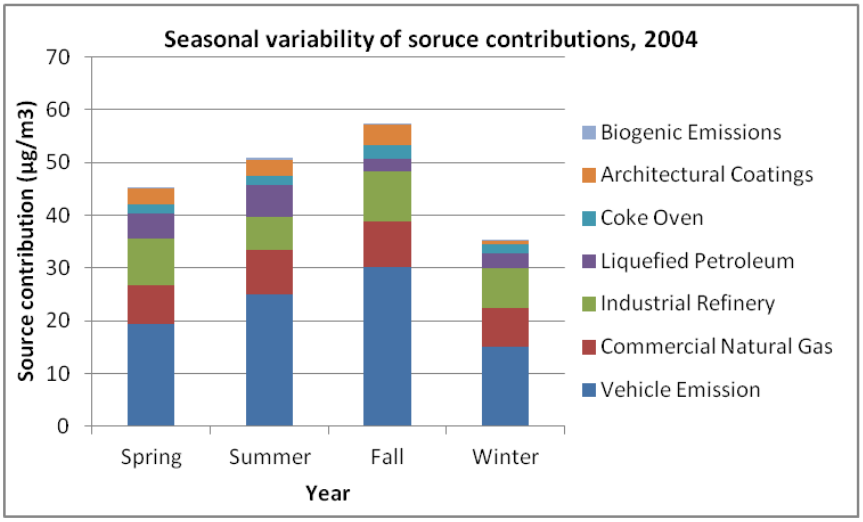


Figure D.17: Seasonal variability of source contributi0ns, 2004

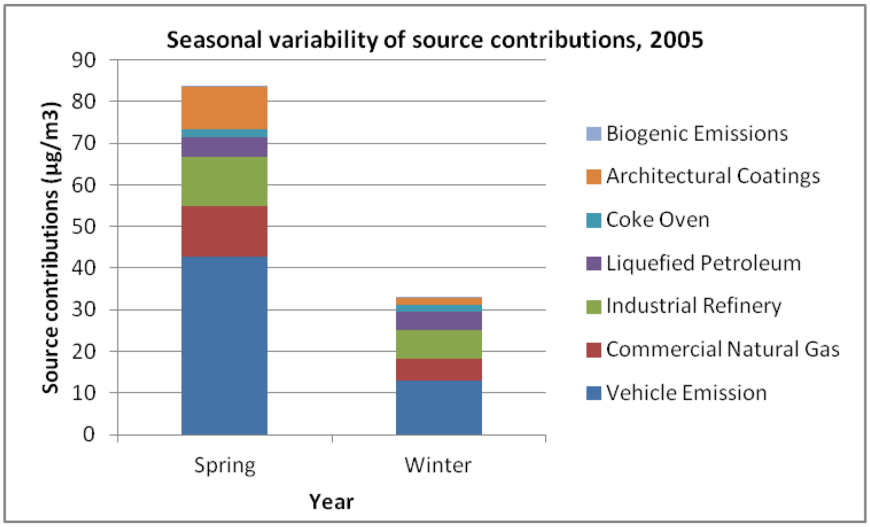


Figure D.18: Seasonal variability of source contributi0ns, 2005

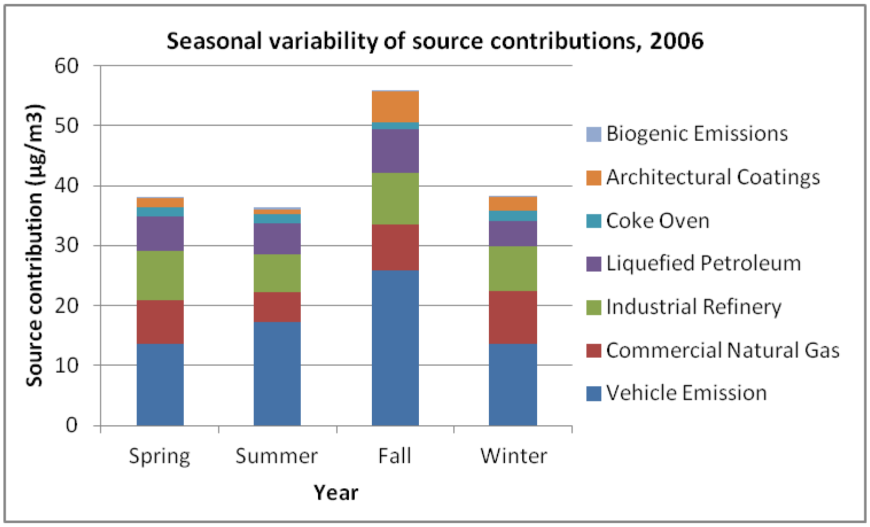


Figure D.19: Seasonal variability of source contributi0ns, 2006

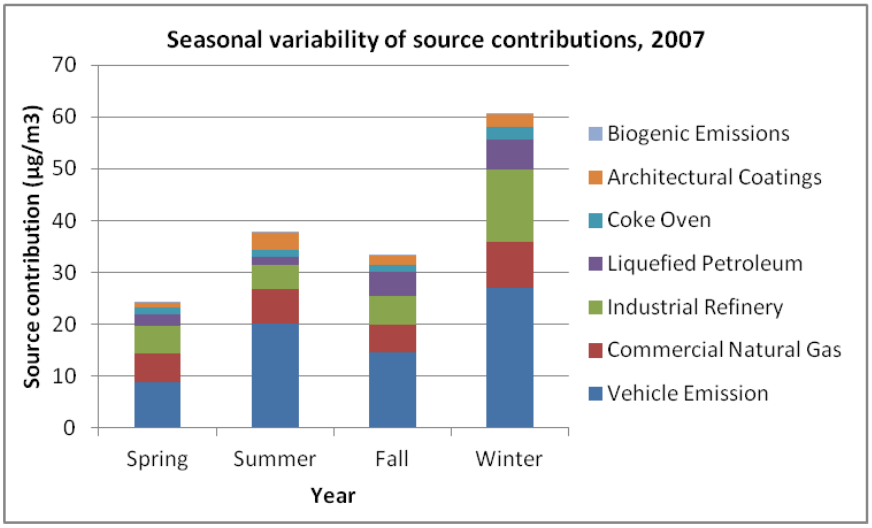


Figure D.20: Seasonal variability of source contributi0ns, 2007

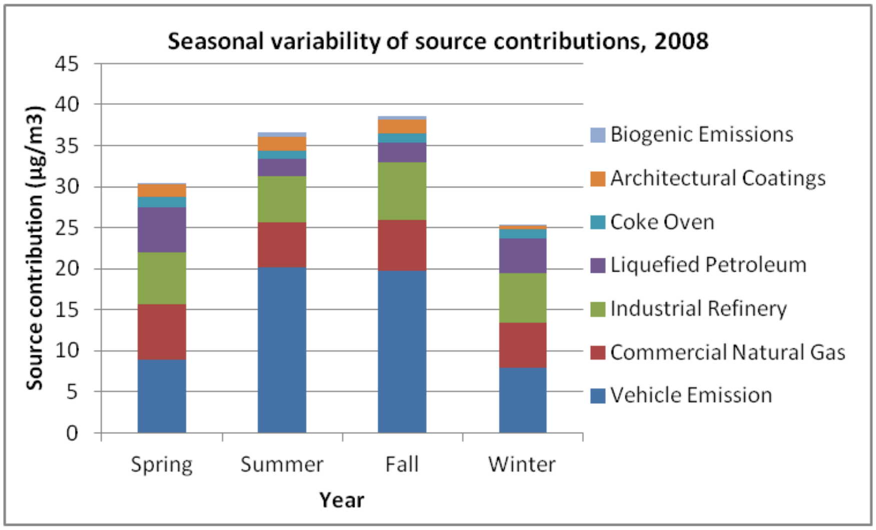


Figure D.21: Seasonal variability of source contributi0ns, 2008

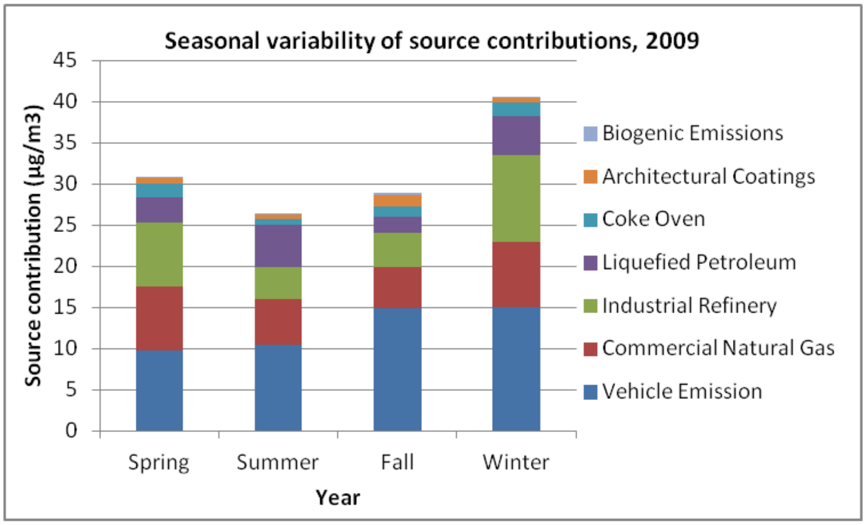


Figure D.22: Seasonal variability of source contributi0ns, 2009

Figure D.13 shows that PAMS measurements were relatively high in winter and spring and low in summer and fall in 2001, 2006, and 2009. Similar patterns were observed in some other studies (Sauvage et al., 2009; Hoque et al., 2008; Na and Kim, 2001). The higher concentrations in winter and spring than summer and fall could be due to the low mixing, low temperature, and low insolation. Low mixing leads to less dispersion of ambient VOCs, and low temperature and low insolation lowers the VOCs consumption rate in the atmosphere. However, the pattern of total PAMS concentrations were high in summer and fall and low in winter and spring in 2002, 2003, 2004, 2007, and 2008. This was because the low traffic accounts in winter and spring, which is explained lanter. In 2005, there were only complete measurements for winter and spring. Therefore, no pattern could be observed in this year.

From FIgure 4.13 to Figure 4.22, it was observed that "Commercial Natural Gas", "Industrial Refinery", and "Coke Oven" usually showed a pattern of high source contributions in winter and low in summer. This phenomenon is consistent with the results from other studies (Sauvage et al., 2009; Cetin et al, 2003; Na and Kim, 2001; Chattopadhyay et al., 1996).

Na and Kim (2001) found that in winter, more commercial natural gas would be consumed than in summer which caused the high contribution from this source in winter than in summer. Chattopadhaya et al. (1996) found that there was no significant seasonal changes of "Coke Oven" source emission. Cetin et al. (2003b) found that in summer, the high temperature increases the evaporation and thus incrase the source contribution from industrial refinery. However, in winter, lower OH radical concentration, lower temperature, and weaker UV radiation will increase the chemical lifetime; lower mixing height in winter will lead to less dispersion (Sauvage et al., 2009). All these factors increases the atmospheric VOC concentraions in winter. As a result, the contributions from these three sources were high in winter and low in summer (Sauvage et al., 2009; Cetin et al, 2003; Na and Kim, 2001; Chattopadhyay et al., 1996).

“Architectural Coating” showed a seasonal variability of high contributions in summer and low in winter from 2001 to 2009. It is consistent with the observation by Tan (2011). The reason could be due to the enhanced evaporation by high temperature in summer (Tan et al., 2011).

“Biogenic Emission” was high in summer and almost zero in winter from 2001 to 2009. This result is consistent with the results from other studies (Zhang et al., 2000; Sharkey et al., 1999). Isoprene is the only marker of “Biogenic Emission”. This species comes from the emissions of many plants (i.e. aspen and oak). It is influenced by light and temperature and will increase with the increase of light and temperature (Zhang et al., 2000).

“Liquefied Petroleum” did not show a steady pattern. It was high in summer and fall all but low in winter and spring in 2001, 2004, 2006, and 2009; while it was low in summer and high in winter in the figures? of 2002, 2003, 2007, and 2008. Other researchers found that its emission was high in summer and low in winter (Tan et al., 2011). This is because that the propane, which accounts for 90.6% of total mass of this source, mainly comes from leakage of water pipes. Therefore, the evaporation increased by temperature in summer improves the emission of this source (Tan et al., 2011). However, Sauvage (2009) reported that evaporation source contribution was high in winter and low in summer due to the effects of low OH radical concentratining, weak UV radiation and low mixingin spring. The combination of different effects might have cuased the pattern of “Liquefied Petroleum” contributions.

One interesting observation is the seasnoal variability of vehicle emission. It showed a high in summer and low in winter in most years including 2001, 2002, 2003, 2004, 2006, and 2008. This contradicts the findings from other reserachers (Sauvage et al., 2009; Hoque et al., 2008). They found that vehicle emission was high in winter and low in summer and attributed it to two facts. The “cold start” of engine in winter will boost the pollutants from vehicle emission; the weather condition in winter will also increase the VOC concentrations in atmosphere. However, Windsor is a city in northern part of North America. In winter, its traffic counts will be reduced; while, in summer, the situation is the opposite. Therefore, the reduced traffic counts will lead to less vehicle emission in winter than in summer. This might be the reason for this interesting observation in this project.

Vehicle emission was the largest VOC source from 2001 to 2009, i.e. 40% of total source contribution. Vehicle emission was low in winter and spring; consequently, the total ambient VOC concentrations could also be dragged down. This might also be the reason for observing a different seasonal VOC pattern in this study compared to those in other studies (Sauvage et al., 2009; Hoque et al., 2008; Na and Kim, 2001).

VITA AUCTORIS

NAME:	Zhi Li
PLACE OF BIRTH:	Changsha, Hunan Province, China
YEAR OF BIRTH:	1978
EDUCATION:	Hunan University, MASc., Changsha, Hunan Province, China, 1999-2002 University of Windsor, MASc., Windsor, ON, 2010-2012