MONITORING AND MODELLING OF NON METHANE HYDROCARBONS (NMHCs) IN VARIOUS AREAS IN PULAU PINANG, MALAYSIA

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By

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TABLE OF COTENTS

	Page No.
ACKNOWLEDGMENT	ii
TABLE OF CONTENT	iii
LIST OF TABLES	vi
LIST OF FIGURES	vii
LIST OF PLATES	x
LIST OF MAPS	x
ABBREVIATIONS	xi
ABSTRAK	xiii
ABSTRACT	xiv
CHAPTER 1. INTRODUCTION	1
1.1. Background	1
1.2. Traffic in Pinang	5
1.3. Problem Statements	7
1.4. Objectives	8
1.5. Hypotheses	8
1.6. Scope of Study	9
1.7. Thesis Organization	9
CHAPTER 2.LITERATURE REVIEW	10
2.1. Introduction	10
2.2. Health Impacts	12
2.3. Non Methane Hydrocarbon	13
2.4. NMHC Trends Worldwide	14
2.5. BTEX Trends Globally	16
2.6. Atmospheric Chemistry of VOC's	28
2.7. Atmospheric Chemistry of BTEX	30
2.8. NMHC and BTEX Standards	32
CHAPTER 3. STUDY METHODOLOGY	34
3.1. Introduction	34
3.2. Overview of Pulau Pinang	34
3.2.1. Study Locations	35
3.3. Monitoring Methods	37
3.3.1. Monitoring of NMHC	37
3.3.2. Monitoring of BTEX	39
3.3.2.1. Sampling	39
3.3.2.2. Analytical Method	39
3.3.3. Monitoring of Benzene	41
3.4. Meteorological Factors	42
3.5. Traffic Count	42
3.6. Data Analysis and Modeling	44
3.6.1. Descriptive Statistics	44
3.6.2. Statistical Distribution of NMHC	44
3.6.3. Seasonal Variations	46
3.6.4. Correlation Analysis	47

3.6.5. Multiple Linear Regression (MLR) 47
3.6.6. Factor Analysis 48
3.6.7. Site Layout Effect 49
CHAPTER 4. RESULTS AND DISCUSSION 50
4.1 Introduction 50
4.2. Temporal Distribution of NMHC 50
4.2.1. Island Station 50
4.2.2 Prai Station 58
4.3. Correlation Between NMHC and Carbon Monoxide (CO) 65
4.4. Weather Parameter Contribution to NMHC 65
4.5. BTEX Concentrations and Trends 67
4.5.1.BTEX Chromatograms 67
4.5.2.Nibong Tebal Area 68
4.5.2.1.Sungai Kecil “SK” (Roadside) 68
4.5.2.2.Kampung Nanas “KN” (Rural) 70
4.5.2.3.Taman Cowin “TC” (Sub Urban) 71
4.5.2.4.Taman Nibong Tebal Jaya “TNTJ” (Urban) 71
4.5.2.5.Pekan Nibong Tebal “PNT” (Town Area) 72
4.5.2.6.Comparison among the Nibong Tebal Area sites 72
4.5.3. Jalan Pinang (Urban) 78
4.5.3.1. Chowrasta Market “CM” 78
4.5.3.2. Mydin Intersection “MI”- Urban 87
4.5.4. Komtar Area (Urban) 90
4.5.4.1. Jalan Dr. Lim Chwee Leong “JDL” 91
4.5.4.2. Gamma Intersection “GI” 94
4.5.4.3. Jalan Dato Keramat “JDK” 95
4.5.5. Jelutong Area (Urban) 99
4.5.5.1. Chevrolet Intersection “CI” 99
4.5.5.2. Jalan Jelutong “JJ” 100
4.5.6. Bayan Lepas Area (Industrial) 103
4.5.6.1. C.C. School Intersection “CCI” 103
4.5.6.2. Jalan Dato Ismail Hashim “JDIH” 104
4.5.6.3. Jalan Sultan Azlan Shah “JSAS” 107
4.5.6.4. Bayan Permai Intersection “BPI” 109
4.5.7. Gelugor Area (Sub Urban) 111
4.5.7.1. Pensonic Intersection “PI” 112
4.5.7.2. Persiaran Sungai Gelugor 2 “PSG” 113
4.5.8. Pinang Bridge Exit “PBE” (Roadside) 116
4.5.9. Juru Autocity “JA” (Industrial) 119
4.5.10. Bertam Area (Sub Urban) 122
4.5.11. Overall Comparison 125
4.5.11.1. Correlation Between Benzene and CO 125
4.5.11.2. Correlation among BTEX members 126
4.5.11.3. Multiple Linear Regression Model for Benzene 127
4.5.11.4. Traffic Composition 128
4.5.11.5. Comparison of Benzene in Different Sites 129
4.5.11.6. Comparison of Benzene Concentrations During Sunny 129

and Rainy days
4.5.11.7. Weather Parameter Contribution 132
4.5.11.8. Statistical Distribution for Benzene 133
CHAPTER 5. CONCLUSIONS AND FUTURE RESEARCH 134
5.1. Conclusions 134
5.1.1. NMHC 134
5.1.2. BTEX 136
5.2. Recommendations 138
5.3. Future Research 139
REFERENCES 140
PUBLICATIONS 153
APPENDIX 154
Appendix A- Maps 155
Appendix B- Statistical Analysis 162

LIST OF TABLES

		Page No
Table 2.1	BTEX Studies Worldwide	26
Table 3.1	Study locations	36
Table 3.2	Equations to convert traffic to PCU	42
Table 4.1	Mean and standard deviation (SD) of NMHC levels	50
Table 4.2	Statistical Distribution for NMHC (Island)	51
Table 4.3	The probability of the NMHC to exceed certain limits (Island)	57
Table 4.4	Statistical distribution for NMHC (Prai)	59
Table 4.5	The probability of the NMHC to exceed certain limits (Prai)	64
Table 4.6	The Correlation between NMHC concentrations and CO Emissions	65
Table 4.7	Contribution of the weather parameters to the NMHC Variance	66
Table 4.8	Average and standard deviation (SD) of Benzene concentrations, and traffic volume	69
Table 4.9	Traffic composition during morning rush hour (%)-Nibong Tebal	72
Table 4.10	Traffic composition during afternoon peak (%)-Nibong Tebal	75
Table 4.11	Average and standard deviation (SD) of Benzene concentrations, temperature and traffic volume at Jalan Pinang Sites	89
Table 4.12	Contribution of the weather parameters to the benzene variance	90
Table 4.13	Average, standard deviation (SD) of Benzene concentrations, temperature and traffic volume at Komtar Area Sites	98
Table 4.14	Influence of the weather parameters on the benzene variance Komtar Area Sites	99
Table 4.15	Average and standard deviation (SD) of benzene concentrations, temperature and traffic volume at Bayan Lepas Area Sites	111
Table 4.16	Contribution of the weather parameters to the benzene variance at Bayan Lepas Area Sites	111
Table 4.17	Average of benzene concentrations, temperature and traffic volume at Gelugor Area Sites	116
Table 4.18	Contribution of the weather parameters to the benzene variance Gelugor Area Sites	116
Table 4.19	The correlation between benzene concentrations and CO emissions	125
Table 4.20	The correlation between benzene concentrations and CO emissions	126
Table 4.21	Traffic composition during rush hours (%)-Overall Comparison	128
Table 4.22	Contribution of the weather parameters to the benzene variance	133

LIST OF FIGURES

Page No.

Figure 1.1	Benzene Rate in Gasoline in Malaysia	3
Figure 1.2	Growth Rate of Motor Vehicles in Pinang	5
Figure 1.3	Air Quality Status in Pinang	6
Figure 3.1	Research Flow Chart	38
Figure 3.2	Research Methodology	43
Figure 3.3	Data Analysis	45
Figure 4.1	Diurnal Variation of NMHC at the Island Site	51
Figure 4.2	Diurnal Variations of NMHC and Temperature during South West Monsoon in 2005 (Island)	53
Figure 4.3	Diurnal Variations of NMHC and Temperature during South-West Monsoon in 2006 (Island)	54
Figure 4.4	Diurnal Variations of NMHC and Temperature during North-East Monsoon in 2005-2006 (Island)	55
Figure 4.5	cdf Plot for NMHC (2005)-Island	56
Figure 4.6	cdf Plot for NMHC (2006)-Island	56
Figure 4.7	Diurnal Variation of NMHC at Prai Site (Mainland)	58
Figure 4.8	Diurnal Variations of NMHC and Temperature during South West Monsoon in 2005 (Prai)	60
Figure 4.9	Diurnal Variations of NMHC and Temperature during South West Monsoon in 2006 (Prai)	61
Figure 4.10	Diurnal Variations of NMHC and Temperature during North East Monsoon in 2005-2006 (Prai)	62
Figure 4.11	cdf Plot for NMHC (2005)-Prai	63
Figure 4.12	cdf Plot for NMHC (2006)-Prai	63
Figure 4.13	Chromatogram of BTEX Standard (25ppm)	67
Figure 4.14	Chromatogram of BTEX Concentrations (Real sample from Site)	67
Figure 4.15	Average Traffic Flow at the Study Sites in the Morning Peak	68
Figure 4.16	Average Traffic Flow at the Study Sites in the Afternoon Peak	69
Figure 4.17	Average traffic volume, benzene concentrations and temperature in the Study Sites at the Morning Peak	70
Figure 4.18	Average traffic volume, benzene concentration and temperature in the study sites at the afternoon peak	70
Figure 4.19	Benzene behavior with the change in temperature trends at SK Site	76
Figure 4.20	Benzene trends with the change in temperature at PNT	76
Figure 4.21	Behavior of Benzene with the temperature changing at TNTJ	77
Figure 4.22	Benzene levels influenced by the temperature changing at TC site	77
Figure 4.23	Correlation between benzene concentrations and temperature at KN Site	78
Figure 4.24	Traffic cycle trends at CM Site	79
Figure 4.25	BTEX trends at CM Site	79
Figure 4.26	Traffic trends during the three peaks at CM site	81
Figure 4.27	BTEX Concentrations during the three peaks at CM Site (30/3)	82
Figure 4.28	Relatioship between benzene and temperature change at CM Site (22/3)	83

Figure 4.29 Benzene levels and temperature trends at CM Site Peak (24/3) 83
Figure 4.30 Benzene behavior with temperature change at CM Site (25/3) 84
Figure 4.31 Levels of benzene and temperature trends at CM Site (29/3) 85
Figure 4.32 Trends of benzene with the temperature change at CM Site (30/3) 86
Figure 4.33 Traffic Trends during morning peaks at MI 87
Figure 4.34 BTEX Concentrations during morning peaks at MI 88
Figure 4.35 Benzene patterns with the temprature trends MI Site (22/3 & 14/4) 88
Figure 4.36 Traffic Trends during the three peaks at JDL 91
Figure 4.37 BTEX concentrations at JDL (31/3) 92
Figure 4.38 Benzene levels with the temperature trends at JDL Site (31/3) 92
Figure 4.39 Benzene behavior with the temperature changes at JDL Site (1/4) 93
Figure 4.40 Benzene patterns with the temperature changes at JDL Site (2/4) 94
Figure 4.41 Traffic trends during the morning peak at GI 94
Figure 4.42 BTEX concentrations during the morning peak at GI 95
Figure 4.43 Traffic trends during the morning peak at JDK 96
Figure 4.44 BTEX concentrations during the morning peak at JDK 96
Figure 4.45 Benzene behavior with the temperature trends JDK Site (15/4) 97
Figure 4.46 Traffic trends during the morning peak at CI 99
Figure 4.47 BTEX concentrations during the morning peak at CI 100
Figure 4.48 Traffic trends during the morning peak at JJ 100
Figure 4.49 BTEX concentrations during the morning peak at JJ 101
Figure 4.50 Trends of benzene with the temperature patterns at JJ Site (16/4) 101
Figure 4.51 Traffic trends during the morning peak at CCI 103
Figure 4.52 BTEX concentrations during the morning peak at CCI 104
Figure 4.53 Correlation between benzene levels and temperature rends at CCI Site (19/4) 104
Figure 4.54 Traffic trends during the morning peak at JDIH 105
Figure 4.55 BTEX concentrations during the morning peak at JDIH 105
Figure 4.56 Trends of benzene with the temperature changes at JDIH Site (19/4) 106
Figure 4.57 Traffic trends during the morning peak at JSAS 107
Figure 4.58 BTEX concentrations during the morning peak at JSAS 108
Figure 4.59 Benzene behavior with the temperature trends at JSAS Site (20/4) 108
Figure 4.60 Traffic trends during the morning peak at BPI 109
Figure 4.61 BTEX concentrations during the morning peak at BPI 109
Figure 4.62 Benzene trends with the temperature changes at BPI Site (20/4) 110
Figure 4.63 Traffic trends during the morning peak at PI 112
Figure 4.64 BTEX concentrations during the morning peak at PI 113
Figure 4.65 Benzene level with the temperature trends at PI Site (21/4) 113
Figure 4.66 Traffic trends during the morning peak at PSG 114
Figure 4.67 BTEX concentrations during the morning peak at PSG 114
Figure 4.68 behavior of benzene and temperature trends at PSG site (21/4) 115
Figure 4.69 Traffic trends during the morning peak at PBE 117
Figure 4.70 BTEX concentrations during the morning peak at PBE 117
Figure 4.71 Trends of Benzene with the temperature changes at PBE Site 118
Figure 4.72 Traffic trends during the morning peak at JA 120
Figure 4.73 BTEX concentrations during the morning peak at JA 120
Figure 4.74 Benzene concentrations and temperature levels 121

at JA (Near McDonald's)
Figure 4.75 Traffic trends during the morning peak at JKM Site 122
Figure 4.76 BTEX concentrations during the morning peak at JKM site 123
Figure 4.77 Benzene behavior and temperature trends at JKM site (Near TM Point) 124
Figure 4.78 Comparison of benzene concentrations 129

LIST OF PLATES

Page No.

Plate 1 Pump Calibration	40
Plate 2 Solvent Used	40
Plate 3 Transfer sample to vial	40
Plate 4 Final samples ready for analysis	40
Plate 5 Auto sampler and vials	41
Plate 6 Gas Chromatography used to analyze samples	41

LIST OF MAPS

Page No.

Map 4.1	Average benzene concentrations monitored at Nibong Tebal Area	73
Map 4.2	Average benzene concentrations recorded at SK and KN sites	74
Map 4.3	Average benzene concentrations at Jalan Pinang	89
Map 4.4	Average benzene concentrations at Komtar Area	98
Map 4.5	Average benzene concentrations at Jelutong Area	102
Map 4.6	Average benzene concentrations at CCI and JDIH Sites	106
Map 4.7	Average benzene concentrations at JSAS and BPI Sites	110
Map 4.8	Average benzene concentrations at Gelugor area sites	115
Map 4.9	Average benzene concentrations at PBE Site	119
Map 4.10	Average benzene concentrations at JA Sites	122
Map 4.11	Average benzene concentrations at JKM sites	124
Map 4.12	Average ambient benzene concentrations during sunny days	130
Map 4.13	Average ambient benzene concentrations during rainy days	130

LIST OF ABBREVIATIONS

AML	Acute Myeloid Leukemia
ASMA	Alam Sekitar Malaysia
BPI	Bayan Permai Intersection
BTEX	Benzene, Toluene, Ethylbenzene and Xylene
CCI	C.C. School Intersection
CI	Chevrolet Intersection
CM	Chowrasta Market
DNA	Deoxyribonucleic Acid
GC/FID	Gas Chromatography/Flame Ionization Detector
GC-MS	Gas Chromatography-Mass Spectrometry
GC-MSD	Gas Chromatography/Mass Selective Detector
GC-PID	Gas Chromatography with Photoionization Detector
GI	Gamma Intersection
HDV	Heavy Duty Vehicle
ID	Internal Diameter
JA	Juru Autocity
JDIH	Jalan Dato Ismail Hashim
JDK	Jalan Dato Keramat
JDL	Jalan Dr. Lim Chwee Leong
JJ	Jalan Jelutong
JKM	Jalan Kubang Menderung
JSAS	Jalan Sultan Azlan Shah
KN	Kampung Nanas
LDV	Light Duty Vehicle
MI	Mydin Intersection
MLR	Multiple Linear Regression
MV	Motor Vehicle
NIOSH	National Institute for Occupational Safety and Health
NMHC	Non Methane Hydrocarbon
OSHA	Occupational Safety and Health Administration
PBE	Pinang Bridge Exit
PCU	Passenger Car Unit
PI	Pensonic Intersection
PNT	Pekan Nibong Tebal
ppb	part per billion
ppm	part per million
ppbv %	part per billion by volume %
pptv	part per trillion by volume
PSG	Persiaran Sungai Gelugor 2
SD	Standard Deviation
SEK	Swedish krona
SK	Sungai Kecil
TC	Taman Cowin
TLV	Threshold Limit Value

TNTJ	Taman Nibong Tebal Jaya
TV	Total Vehicle
TWA	Time-Weighted Average
VOC	Volatile Organic Compounds
USEPA	United States Environment Protection Agency
WHO	World Health Organization
€	Euro
$	USD
L	Liter
$\mu g/m^3$	Micro gram per meter cube

PEMONITORAN DAN PEMODELAN HIDROKARBON BUKAN METANA (NMHCs) DI PELBAGAI KAWASAN DI PULAU PINANG, MALAYSIA

ABSTRAK

Hidrokarbon bukan metana (NMHC) memainkan peranan penting dalam proses pembentukan ozon dalam persekitaran bandar, di mana pembebasan dari asap kenderaan adalah dominan. Ozon dikenali kerana kesan negatif terhadap kesihatan manusia dan persekitaran. Tujuan kajian ini dijalankan adalah untuk mengkaji; statistik taburan kepekatan NMHC di dua lokasi di Pulau Pinang (satu di tanah besar dan satu di pulau); untuk menghasilkan sistem permodelan peramalan kepekatan NMHC; untuk memantau kepekatan NMHC di beberapa tempat dengan status pembangunan yang berbeza; untuk mengkaji hubungan di antara kepekatan NMHC dan faktor meteorologi (suhu, kelembapan, kelajuan angin dan arah angin); untuk mengkaji sumber pembebasan NMHC; dan mencadangkan tindakan yang sesuai yang harus diambil untuk mengurangkan kadar kepekatan NMHC di Pulau Pinang. Keputusan kajian menunjukkan bahawa kepekatan NMHC di sekitar stesen di pulau adalah diwakili oleh taburan Weibulll pada tahun 2005 dan taburan lognormal pada tahun 2006 dengan ketepatan masing-masing ialah 99.6% dan 99.4%. Sementara itu, kepekatan NMHC di sekitar stesen di tanah besar (Prai), diwakili oleh taburan log-normal pada 2005 dan 2006 dengan ketepatan masing-masing, 99.4% dan 96.6%. Jumlah hari yang diramalkan melebihi piawaian AS untuk NMHC (0.24ppm) untuk stesen di sebelah pulau ialah 78 pada tahun 2006, berbanding stesen di tanah besar, iaitu 285 pada tahun 2005. Untuk kedua-dua kawasan kajian di pulau dan tanah besar, analisis korelasi Pearson menunjukkan pekali hubungan saling yang kuat (purata $r > 0.85$) di antara kepekatan NMHC dan pembebasan CO. Ini menunjukkan bahawa mereka mungkin berasal dari sumber yang sama (pembebasan dari asap kenderaan). Keputusan analisis faktor menunjukkan bahawa suhu dan kelembapan mempunyai pengaruh terbesar (28-29%) kepada variasi kepekatan NMHC di kedua-dua kawasan kajian di pulau dan Prai. Benzena, toluena, Etilbenzena dan Xylena (BTEX) membentuk kelompok penting Sebatian Organik Mudah Meruap (VOC) aromatik, yang dilepaskan terutama dari kenderaan bermotor. Kepekatan BTEX (karsinogenik) telah dicerap di pinggir jalan beberapa buah daerah (Nibong Tebal, Jalan Pinang, Komtar, Jelutung, Gelugor dan Bayan Lepas) di Pulau Pinang. Jumlah kenderaan dicatatkan secara serentak. Sampel diambil pada tiga waktu puncak (pagi, tengahari dan petang) dan analisis dilakukan dengan menggunakan kromatografi gas yang dilengkapi dengan pengesan pengionan nyala (GC / FID). Keputusan menunjukkan bahawa kepekatan BTEX jauh melampaui piawaian antarabangsa sedia ada (5 ppb). Pemantauan benzena dilakukan dengan menggunakan pengesan foto pengionan (PID). Purata kepekatan Benzena berada dalam julat 20.6 ppb waktu puncak (pagi) di kawasan Bertam (separa bandar) kepada 284.5 ppb pada waktu puncak (pagi) di kawasan Komtar (bandar). Analisis regresi linear berganda menunjukkan kepekatan benzena berkorelasi positif dengan jumlah lalu lintas, suhu, dan kelembaban sebagai faktor ramalan; r^2 adalah 0.91. Korelasi negatif diperolehi di antara kepekatan benzena dan suhu, sebaliknya korelasi positif dengan kelembapan. Hasilnya kajian mencadangkan keperluan segera mengetatkan peraturan pembebasan BTEX dari kenderaan bermotor kerana ia berpotensi menimbulkan kesan negatif kepada kesihatan orang awam.

MONITORING AND MODELLING OF NON METHANE HYDROCARBONS (NMHCs) IN VARIOUS AREAS IN PULAU PINANG, MALAYSIA

ABSTRACT

Non Methane Hydrocarbons (NMHC) plays a vital role in the formation process of ozone in urban environment, where vehicle emissions are dominant. Ozone is known for its negative impacts on human health and environment. The objectives of this research were to study; the statistical distribution of NMHC concentrations at two sites in Pinang (one on the Mainland and one on the island); to develop modeling system of NMHC concentrations prediction; to monitor NMHCs concentrations in several places with different development status; to investigate the relationship between NMHC concentrations and meteorological factors (temperature, humidity, wind speed and wind direction); to verify the NMHC emission sources; and to propose suitable actions to reduce the NMHC levels in Pulau Pinang. The results show that the NMHC concentrations surrounding the island station were represented by Weibulll distribution (2005) and lognormal distribution (2006) with accuracies of 99.6% and 99.4%, respectively. Conversely, NMHC concentration surrounding the station on the mainland (Prai), was better represented by the log-normal distribution in both 2005 and 2006 with 99.4% and 96.6% accuracy, respectively. The predicted number of days exceeded the US standard for NMHC (0.24ppm) for the island station, were 78 in 2006, and 285 in 2005 for the mainland station. For both island and Prai sites, the Pearson's correlation analysis suggests strong mutual correlation (average $r > 0.85$) between NMHC concentrations and CO emissions which indicates that they might originate from the similar sources (vehicular emissions). The factor analysis results show that temperature and humidity mainly influenced (28-29%) the variations of NMHC concentrations in both island and Prai areas. Benzene, Toluene, Ethylbenzene and Xylene (BTEX) are aromatic Volatile Organic Compounds (VOCs), emitted mainly from motorized vehicles. BTEX (a known carcinogenic) concentrations were monitored at roadsides of several areas (Nibong Tebal, Jalan Pinang, Komtar, Jelutong, Gelugor and Bayan Lepas) in Pulau Pinang. Traffic volume was recorded simultaneously. Samples were collected during the three mean peaks (morning, afternoon and evening) and the analysis were done using Gas chromatography equipped with flame ionization detector (GC/FID). The results show that the concentrations of BTEX concentrations were far beyond the international standards (5 ppb). The monitoring of benzene using the Photo Ionization Detector (PID shows that the mean concentrations of Benzene ranged from 20.6 ppb (morning peak) Bertam area (sub-urban) to 284.5 ppb (the morning peak) at the Komtar area (urban). Multiple linear regression analysis suggested that the benzene concentrations were influenced by traffic volume, temperature, and humidity (as predictors); R^2 was 0.91. Negative correlation was found between benzene concentration and temperature, while positive correlation with humidity. These results indicate the need for regulating the BTEX emission from motor due to their potential negative health impacts posed to the public.

CHAPTER 1

INTRODUCTION

1.1. Background

Air pollution is defined as the presence of one or more contaminants or combinations in the outdoor and /or indoor atmosphere thereof in such quantities and of such duration as may be or may tend to be injurious to human, plant, or animal life (Wark et al. 1998).

The rapid growth of the Malaysian economy over the past 27 years, due to the development of industrial estates, free trade zones, thermal power plants and petroleum industries, could result in the deterioration of the environment if due care is not taken. The severity of the environmental problems associated with air quality degradation may result from vehicles emissions and industries, particulate matters from stacks and exhaust, dust from quarrying activities, construction projects and open burning (Hassan et al. 2000).

In several large cities, air pollution has been increasing with time and at times exceeds the levels prescribed by national ambient air quality guidelines. This is shown from monitoring and studies on ambient air quality such as that of Md Yusof et al. (2010). Mobile sources account for 82% of air pollution in Malaysia (Norela et al. 2010).

The importance of non-methane hydrocarbons (NMHCs) as a group of Volatile Organic Compounds (VOCs) in the urban areas because of their reaction with the hydroxyl radical (OH), which plays a critical role in atmospheric photochemical reactions and the potential health effects associated with prolonged exposure to such compound as benzene (Baker et al. 2008; O'Donoghue et al. 2007; Tang et al. 2007).

Benzene, toluene, ethylbenzene and xylene (BTEX) are elements of an important VOC group. They are emitted from many sources notably from vehicles. BTEX play a vital role in the troposphere chemistry and poses health risk to human (Khoder, 2007). Benzene is known as a carcinogenic compound, which is emitted mainly from petrol-fuelled cars and thus it is found in all urban areas (Skov et al. 2001).

The relative contributions of light-duty vehicles (LDVs) and heavy duty vehicles (HDVs) to the total emissions indicated that aldehydes, BTEX (benzene, toluene, ethylbenzene, xylenes), and alkanes are mainly produced by LDV, while HDV dominated emissions of CO, NO_x, SO_2, and PM_{10} (Schmid et al. 2001).

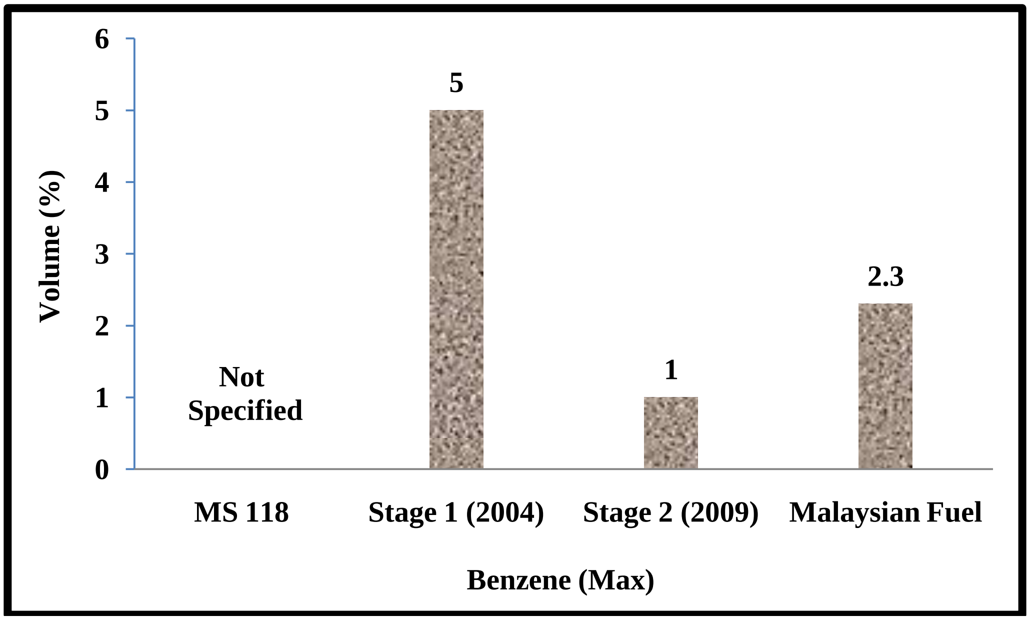

Figure 1.1 Benzene Rate in Gasoline in Malaysia
Adopted from Idris (2004)

In Malaysia reduction of lead content started in July 1985 from the initial of 0.84 g/l to 0.5 g/l and further reduced to 0.15 g/l in January 1990. Benzene levels is limited to 5% by volume (Euro 2) by year 2004 and will be further reduced to 1% (Euro 4) by year 2009, as shown in Figure 1.1 (Firdaus and Muthiah, 2006).

Statistics on transport-related pollution death for Pulau Pinang and Malaysia is yet to be available for reference purposes. However, figures in London shows that each year, Londoners lose about 34,000 years of life from transport related pollution and this high figure is very much related to the average traffic speed in central London of 16 kmph due to the ever worsening congestion. In addition, soot from diesel pollution also leads to 27,000 non-fatal heart attacks and more than 400,000 emergency room visits in the US annually (SERI, 2005).

World Health Organization (WHO) has estimated that a lifetime exposure of 0.17 $\mu g/m^3$ of VOC gives rise to an excess risk of developing leukemia of 1 per 1,000,000 inhabitants based on toxic-kinetic models (Skov et al. 2001). In Sweden, relationship between acute myeloid leukemia (AML) and car density was found; the incidence of AML was 5.5 in regions that have more than 20 cars / km^2 (Rommelt et al. 1999).

Exposure to benzene and treatment with chemotherapeutic agents are leading to AML. It is thought to be caused by damage to specific regions of Deoxyribonucleic Acid (DNA) (Bono et al. 2010; Mondal et al. 2010), which is resulting in chromosome rearrangements or its loss (Escobar et al. 2007; Marcon et al. 1999).

Although benzene concentrations found to be low in the ambient air, it is likely to be dangerous when an excess risk of leukemia is associated with cumulative benzene exposures and benzene exposure intensities (Glass et al. 2003). Other studies (Savitz and Feingold, 1989 and Wolff, 1994) have also found an association between traffic density and incidence of leukemia in children (Rommelt et al. 1999).

In the economically developed countries, cancer is the second leading cause of death (following heart diseases) and in the developing countries; it is the third leading cause of death (following heart diseases and diarrheal diseases). In 2007, the estimated total cancer deaths are 7.6 million (about 20,000 cancer deaths a day), 2.9 million in economically developed countries and 4.7 million in economically developing countries. Global statistics show that in 2007, number of leukemia cases leading to death were 245,871 (Badakhshan et al. 2009).

Few studies reported that in Netherland, the lifetime cost per patient of AML $104,000 (in 1995$ rate) (2001 € rate, 151,827); SEK819,000 (in 1992 SEK rate) and SEK335,000 (1980) in Sweden and $42,000 (in 1998) (2001€ rate, 55,828) among Medicare beneficiaries in the US (predominantly patients aged 65 years and older) (Redaelli et al. 2004).

1.2. Traffic in Pulau Pinang

In Pulau Pinang, there are 2,013,154 registered motor vehicles (MV) averaging to 1.25 cars per person for a population that totals 1,609,900 (SERI Website, 2010a). The MV registration rate is increasing at an average of 9.5 percent per annum–higher than the country's rate of 7.2 percent and the fact that in 2001, Asian Demographics placed Malaysia second only to Japan in the number of households owning cars, which indicates that the level of car ownership in Pinang is comparatively high (SERI, 2005). The trend of the growth rate of motor vehicle in Pulau Pinang is shown in Figure 1.2.

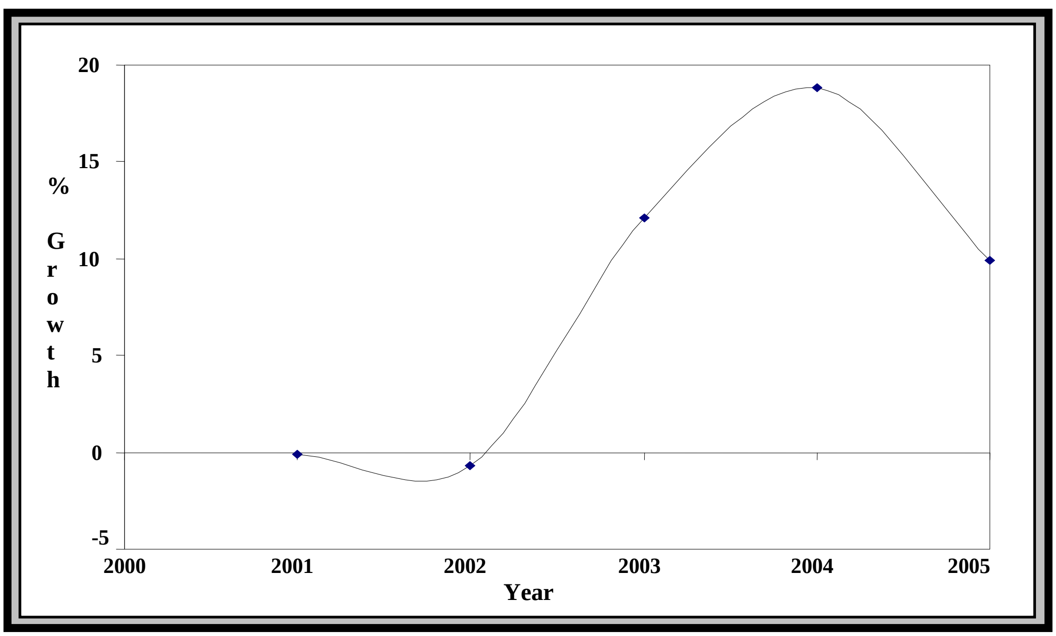

Figure 1.2 Growth Rate of Motor Vehicles in Pulau Pinang
Adopted from (Pinang State Government Website, 2008a)

The negative growth (2001-2002) is due to the economic recession at that time (Athukorala, 2002).

Figure 1.3 shows the air quality trends in Pinang (2005-2009), which shows that the highest good status was during 2009 (310 days) and the lowest was during 2005 (135 days). In terms of moderate status, the year 2006 holds the second highest place with 159 days and the year 2008 ranked at third place with 126 days.

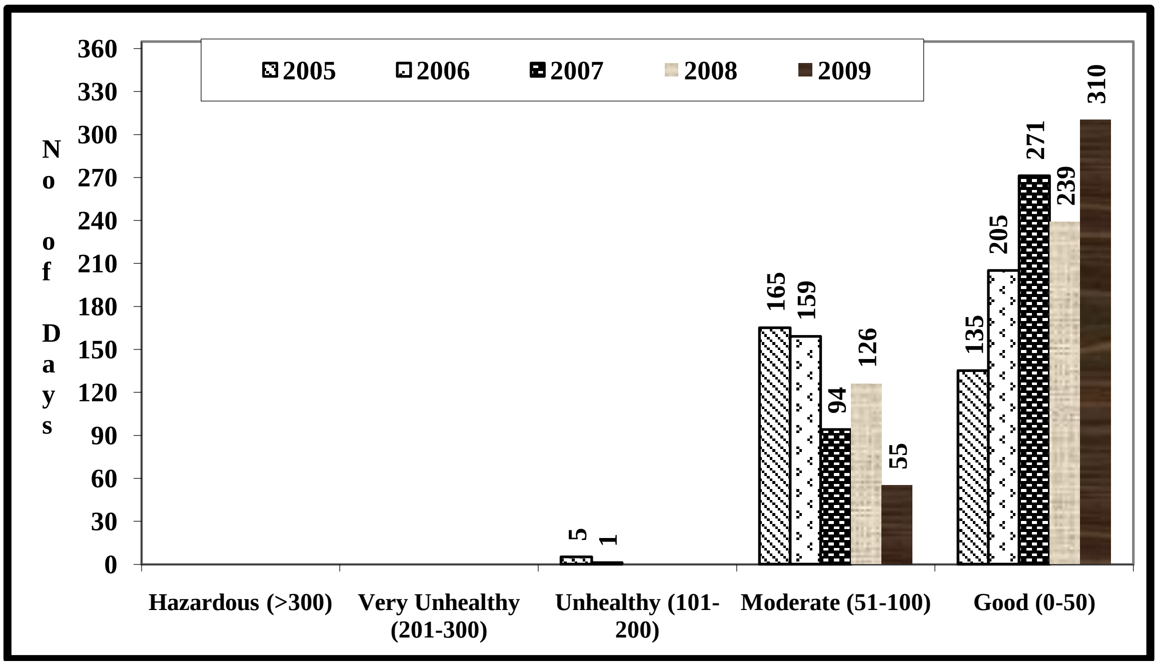

Figure 1.3 Air Quality Status in Pulau Pinang
Adopted from (Pinang State Website, 2010b)

A survey conducted by Japan International Cooperation Agency (JICA) identified the main transportation problems in Pinang Island, particularly in Georgetown, as congestion combined with rapid increases in car ownership, high rates of accidents mainly due to lack of traffic safety policies, lack of auto education, inadequate space for pedestrians and a shortage of parking spaces (Tjandradewi et al. 2006**).**

1.3. Problem Statement

In urban areas the air quality deteriorated drastically due to industrial activities and heavy traffic volume. Ambient total concentration of airborne VOCs (155 species) in urban and suburban areas have been reported to be in the range of 16.2–1033 $\mu g/m^3$. Some VOCs have toxic health effects depending on duration and levels of exposure, even at low $\mu g/m^3$ concentrations (e.g., exposure to BTEX at high levels can cause respiratory, neurological. genetic and excretory system damage) (Badjagbo et al. 2007).

Non Methane Hydrocarbon (NMHC) is a subset of the VOCs (Petrea et al. 2005), traffic is the main source of the NMHC emissions (Dommen et al. 2001), and benzene is the most recognized hydrocarbon member that has a strong positive exposure–response relationship with leukemia (Belson et al. 2007; Lamm et al. 2009).

There has been marked increase in motor vehicles ownership in Malaysia. In 2007, there were 16,813,943 registered vehicles (2,013,154 of them are in Pulau Pinang state) running on the roads (Kulanthayan et al. 2010). Some studies found a link between benzene emitted from traffic and the occurrence of cancer cases in the surrounding community and particularly children (Jarvholm and Forsberg 2000; Nordlinder and Jarvholm 1997; Steffen et al. 2004). In Malaysia, cancer is one of the major health problems where the estimated annual incidence of cancer is 30,000 (3,600 cases out of them are leukemia) (Lim, 2001).

Pulau Pinang is one of the developing states with the highest population density (1,500 people per km^2) (OECD web, 2010), and it has different development status (urban, sub-urban, industrial. rural and roadside). There are lack of reported studies that been carried out on NMHC levels and trends in Malaysia; therefore this study is urgently needed to understand the behaviour of NMHCs in Pulau Pinang and to determine the extent of their risks, which can serve as an alert system for the decision makers to take the actions for saving the public health.

1.4. Objectives

The objectives of this research are:

i. To develop modeling system of NMHC concentration prediction by studying the statistical distribution of NMHC concentration at 2 sites in Pulau Pinang.
ii. To model the relationship between NMHC concentration and meteorological factors by monitoring NMHC concentration in several places with different development status.
iii. To verify the NMHC emission sources and proposing suitable actions that should be taken to reduce the NMHC levels in Pulau Pinang.

1.5. Hypothesis

This study maneuvers on the hypothesis that NMHC concentrations in the study areas are expected to be high in the busy places where the traffic volume is high, the behavior of NMHCs trends will follow the traffic flow patterns and the meteorological factors (temperature, humidity, wind speed and wind direction) will contribute to the NMHCs concentration variances.

1.6. Scope of the study

During this study, monitoring of NMHC was carried out in several places with different development status as background locations. Later on, the collected data were modeled to check the current NMHC trends and to develop a prediction model for NMHC concentrations.

Hence, at the end of this research, the behaviours and levels of NMHCs were established which will make it easier to decision makers to take suitable actions to reduce the NMHC levels up to the international standards to save the community health from the expected risks.

1.7. Thesis Organization

The thesis contains 5 chapters. Chapter 1 gives a general introduction to this thesis and general background of air pollution and NMHC. These include explanation on the problem statements and the study objectives. Chapter 2 reviews the relevant literature on air pollution and NMHC; furthermore the NMHC chemistry and health impacts are discussed. Chapter 3 discusses the methodology of NMHC monitoring and modelling carried out for this study and the statistical tools that were used. Chapter 4 presents the results and discussion on the NMHC monitoring results, modelling process and statistical analysis outcomes. Finally Chapter 5 concludes the research outputs and draws suggestions for future research.

CHAPTER 2

LITERATURE REVIEW

2.1. Introduction

A dramatic impact on air quality world-wide was created by the rapid urbanization and industrialization over the past decades. Risks on human health are posed by the ambient air pollutants such as suspended particulate matters and volatile organic compounds that originate from automobile exhaust, combustion exhaust, industry processes and domestic activities (Wong et al. 2002). Urban air quality is controlled by pollutant emissions, meteorological and geographical conditions, solar radiation, deposition and dispersion parameters (Martins et al. 2007).

In the urban areas volatile organic compounds may cause adverse human health effects, such as adverse effects on reproductive systems or birth defects, even at parts per billion (ppb) levels. A study carried in United States of America (USA) has discovered that ambient VOCs contribute to the outdoor air cancer risk in the USA by 35–55% (Liu et al. 2008).

Perturbations in the chemical composition of the atmosphere are caused by the volatile organic compounds (VOCs), that results in increased temperatures and other changes to climate (Nolasco et al. 2005). Globally, the estimated average emissions of VOCs are about 1,809 million tones /year (Badjagbo et al. 2007).

In Canada, it was estimated that industrial sources contributed only 6% of total benzene emissions in 1991, while light-duty vehicles were the major source of benzene pollution (67% of 22,000 tonnes) (Burstyn et al. 2007).

In order to maintain low ozone levels in urban areas where its formation is under a VOC-limited regime, better management of ambient concentrations of VOCs is essentially needed. In urban areas in many developed countries, the significant decrease in traffic-induced VOC emissions has resulted in relatively comparable shares of traffic and non-traffic VOC emissions (Zalel et al. 2008).

NMHC is an important sub-group of VOCs, which affect human health, ecology and climate (Srivastava and Majumdar, 2010) and BTEX is a typical surrogate for anthropogenic NMHC (Rappengliick et al. 1999). The major sources of BTEX are automotive exhausts and evaporative emissions from plastics production, paints, glues, solvents, etc. In indoor environments, a major part of BTEX emissions is directly related to indoor activities such as cooking, heating, smoking and cleaning, and also include emissions from building materials, varnishes, paints and solvents (Allou et al. 2008; Schneider et al. 1999).

Industrial sources of BTEX are printing and laminating facilities, foundries, electronics and paint manufacturing units; moreover, they also occur at hazardous waste sites (Hsieh et al. 2005). The International Agency for Research on Cancer (IARC); classified benzene as a carcinogenic compound, where it is emitted mainly from petrol-fuelled cars and thus it is found in all urban areas (Burstyn et al. 2007; Kerbachi et al. 2006; Khoder, 2007; Skov et al. 2001). Reports indicated that mobile sources account for 75–85% of the benzene emissions of which 70% is from exhaust, near heavy road traffic and high emissions and are related to the use of gasoline in non-catalytic cars (Kerbachia et al. 2006).

2.2. Health Impacts

Interest in determining the ambient concentrations of volatile organic compounds (VOCs) due to their significant adverse effects on human health has increased in the past few years (Pilidisa et al. 2005).

On average, an adult breathes 11,000 L/day containing a multitude of components, which may cause a variety of adverse health effects. BTEX (benzene, toluene, ethylbenzene, xylenes) are among these pollutants which are particularly abundant in indoor and ambient environments (Cardinal et al. 2005).

BTEX are harmful volatile organic compounds (VOCs) which have negative effects on human health such as headache, eyes irritation, chest tightness, etc. Vehicular emissions are main sources of BTEX as well as other sources such as building and furnishing materials emissions, etc. (Hsieh et al. 2005; Lu et al. 2006).

In the non-smoking population of Chinese women, exposure to toluene emitted from Chinese-style cooking is observed to be highly correlated with risk of lung cancer (Thanacharoenchanaphas et al. 2007).

In Malaysia, cancer is one of the major health problems where the estimated annual incidence of cancer is 30000 (Lim, 2001). WHO has estimated that a lifetime exposure of 1 $\mu g/m^3$ of benzene gives rise to an excess risk of developing leukemia of 6 per 1,000,000 inhabitants (Skov et al. 2001; Wang et al. 2002).

In Sweden, relationship between acute myeloid leukemia (AML) and car density was found; the incidence of AML was 5.5 in regions having more than 20 cars / km^2. Low benzene concentrations in ambient air are likely to be dangerous; other studies have also found an association between traffic density and incidence of leukemia in children (Rommelt et al. 1999).

2.3. Non Methane Hydrocarbon

Automobiles and various commercial and industrial sources are the main sources of the VOCs (Ghazali et al. 2010). Non-methane hydrocarbons (NMHCs) are an important group of VOCs in the urban areas because of their reaction with the hydroxyl radical (OH). This plays a critical role in atmospheric photochemical reactions and the potential health effects associated with prolonged exposure to compounds i.e., benzene (Baker et al. 2008; O'Donoghue et al. 2007; Tang et al. 2007). In addition, NMHC can also act as precursor for secondary pollutants formation such as O_3 (Ghazali et al. 2010).

NMHCs are emitted from both anthropogenic and biogenic sources (vegetation and seawater). Major anthropogenic sources are related to fossil fuel combustion (vehicle exhaust, heat generation and industrial processes), storage and distribution of fuels (evaporation) and solvent use (Liakakou et al. 2009; Saito et al. 2000; Sauvage et al. 2009).

Vehicular exhaust emissions are the most significant sources of NMHCs in urban areas (Guo et al. 2004). There are few non-negligible minor municipal sources (e.g., leakage from liquefied petroleum gases (LPG), natural gas (NG), dry cleaning, incinerator, etc.) (Chang et al. 2006).

2.4. NMHC Trends Worldwide

Globally, several studies were carried out to monitor NMHC emitted from different sources at different locations such as the study of So and Wang (2004), that examined the NMHC spatial distribution and seasonal variation for different areas in Hong Kong. The results of the study show that the highest levels of NMHCs were found at roadsides and the lowest levels were observed at rural sites. In term of seasonal variations, rural sites showed the lowest NMHCs levels in summer while roadside sites have the highest NMHCs levels in summer; this is due to the strong evaporation of alkanes in the hot season.

Forty-eight species of NMHC were measured during the study of Saito et al. (2009) in Nagoya, Japan. The samples were analyzed using Gas chromatography equipped with flame ionization detector (GC-FID); the results showed that the total normal concentration of NMHC was high from November to February (winter) and low from June to August (summer). The pattern of the seasonal variation was influenced mainly by that of alkanes.

NMHC concentrations in a suburban region in south-central China were investigated by Zhang et al. (2009) where samples were collected weekly and analyzed using Gas chromatography-mass spectrometry (GC-MS). The results showed that there was a seasonal variation in the NMHC measurement, which is a higher level in winter than in summer. Furthermore, the analysis identified that vehicular emission is the dominant source for NMHC species.

Spatial concentrations of NMHC in the atmosphere of Taipei metropolitan were monitored by Ding and Wang (1998). 20 species were identified and quantified in 50 samples which were analyzed using GC/FID. The results showed that gasoline-fueled car and motorcycle emissions are the two major sources of NMHC in Taipei, when compared to the NMHC concentration profiles of other cities where high correlation coefficients were found.

In twenty-eight USA states, sampling campaign to monitor non-methane hydrocarbon (NHMC) was carried out (1999-2005). The air samples were collected by canisters and analyzed by GC-FID. The results showed that the mean mixing ratios for BTEX concentration in Los Angeles were 480, 1380, 210, 200 parts per trillion by volume (pptv), respectively (Baker et al. 2008).

Chang et al. (2006) investigated non methane hydrocarbon (NMHC) in three roadways in Taiwan. The samples were collected using stainless steel canisters and analyzed by

GC-FID. The results showed that BTEX concentrations were 2.37, 7.74, 1.45 and 3.28 part per billion by volume % (ppbv%), respectively.

Rappengluck et al. (1998) measured non methane hydrocarbon (NMHC) in two sites (city center and suburban) in Athens. The samples were analyzed by GC-FID. The results revealed that the mean BTEX concentrations in the center of Athens were 11.7, 21.2, 4, and 7.8 ppbv, respectively.

Rappengluck and Fabian (1999) monitored NMHC in several locations in Munich by using online gas chromatography methods. Low NMHC values compared to other cities worldwide were revealed from the study. The data suggests that fuel evaporation and solvent releases can be added to traffic emissions as sources of summertime NMHC inventories. Furthermore, BTEX are considered being important ozone precursors in the Munich area.

2.5. BTEX Trends Worldwide

In a study by Rommelt et al. (1999), BTX concentrations were measured between 1993 and 1997 in buses and trams in Munich city center and along main roads during regular rides. The sampling time was between 07.00 and 00.00 hr and the samples were analyzed by GC-FID. The results showed that the mean concentrations for benzene, toluene and xylenes over the monitoring period are 15 $\mu g/m^3$, 42.1 $\mu g/m^3$ and 37.3 $\mu g/m^3$, respectively.

Six monitoring campaigns were carried out (over one year) in the Municipality of Copenhagen, Denmark, as part of the project monitoring of atmospheric concentrations of benzene in European towns and homes. In each campaign, measurement of the personal exposure to benzene of 50 volunteers (non-smokers living with non-smoking families) living and working in Copenhagen was done. Simultaneously, benzene in their homes and in an urban network distributed over the municipality was measured. The Radiello diffusive sampler was used to sample 5 day averages of benzene and other hydrocarbons and the samples were analyzed by GC-FID (Skov et al. 2001).

The annual averages of the geometrical mean values were 5.22, 4.30 and 2.90 $\mu g/m^3$ for personal exposure, home concentrations and urban concentrations, respectively. The general level of benzene is controlled by two main parameters in Copenhagen: the emission from traffic and dispersion due to wind speed (Skov et al. 2001).

Real-world emissions of a traffic fleet on a transit route in Austria were determined in the Tauerntunnel experiment in October 1997. Individual hydrocarbons were sampled by an automated mobile Airmotec GC type HC 1010. Separation and analysis of the BTEX components (BTEX) were done by GC-FID. The results showed that BTEX concentrations were 4.5, 9.4, 2, 6.7 $\mu g/m^3$, respectively (Schmid et al. 2001).

Benzene in gasoline samples and petroleum fractions in Bulgaria was determined by GC–FID methods using two different capillary columns. Five calibration solutions of benzene in isooctane, with and without internal standard, were prepared. The approximate concentrations of benzene were 0.1, 0.5, 1.0, 1.5, and 2.0 % (v/v) (Pavlova and Ivanova, 2003).

Lu et al. (2006) measured BTEX in four hospitals of Guangzhou from 2nd January to 20th March 2004. Collections of samples were carried out in five consecutive daytimes for each hospital. Commercial stainless steel canister was used for collection of BTEX samples and analysis was done using GC-MSD. Results show that Toluene was the most abundant BTEX.

During the study of Martins et al. (2007), a 12-month comprehensive monitoring campaign to assess aldehydes and BTEX concentrations was carried out in Tijuca district (Rio de Janeiro), where it is an area of commercial activities and a high density of vehicles. BTEX were sampled by drawing air through activated coconut shell charcoal tubes 7 cm long and 4 mm ID, which were used for sampling of BTEX and analysis was carried out by GC-MS . Results show that the mean concentrations for benzene, toluene, ethylbenzene, m,p-xylene and o-xylene, were 1.1, 4.8, 3.6, 10.4 and 3.0 $\mu g/m^3$, respectively (Martins et al. 2007).

Hsieh et al. (2005) measured the BTEX concentrations at four representative night markets and one background location in southern Taiwan. Sampling was done once monthly (non-rainy days) for a period of 14 months and the samples were analyzed using GC-FID. Results show that BTEX concentrations during night market activities obtained from this study were still lower than the current TLVs-TWA.

Wong et al. (2002) measured BTEX concentration inside and outside car parks in Hong Kong. The samples were collected in 6-litre fused silica-coated stainless steel canisters equipped with passive air sampling restrictors, and were then analyzed using GC-FID. The results show that the BTEX concentrations were 29.4, 36.8, 597 and 87μg/m^3, respectively.

Pilidisa et al. (2005) carried out monitoring campaign for BTX in Ioannina, a medium-sized Greek city. The samples were collected using passive sampling tubes which were placed at different points of the city and analyzed using GC-FID. Measurements were repeated in an exact manner over the four seasons and the results show that benzene levels, at all sampling points, exceed the limits of the EU Directive 2000/69. A strong correlation ($r > 0.9$) between Benzene levels and traffic density was found, while BTX ratios present a seasonal variation linked to meteorological conditions.

In Strasbourg (East of France), Allou et al. (2008) measured BTEX concentrations in twenty university libraries using Radiello passive sampling systems containing activated charcoal. samples were quantified by GC-PID. The results show that the mean BTEX concentrations were 0.2, 3.8, 0.8, 1.9 μg/m^3.

Zalel et al. (2008) studied the urban roadside BTEX in Haifa; the data were collected from two monitoring stations. Results show that a large portion of the ambient BTEX concentrations in Haifa currently are below the monitoring instruments' reliable measurement level (<0.5 μg/m^3), due to better traffic exhaust control measures.

Liu et al. (2008) investigated volatile organic compounds (VOC) at two sites in the largest industrial area Kaohsiung, southern Taiwan, designated for traffic and industry. The samples were collected during rush and non rush hours in summer and autumn seasons, at the two sites simultaneously. VOC groups were found to have the same pattern at both sites: aromatics were most abundant (78–95%) followed by alkanes (2–16%) and alkenes (0–6%). The measured BTEX concentration at the two sites ranged from 69 to 301 ppb.

Halek et al. (2004) conducted a BTEX monitoring campaign in Tehran; the measurements were carried out under different conditions in the indoor environment. Samples were collected by drawing air through charcoal-filled tubes with a portable pump and they were analyzed using GC-FID. The results show high level of BTEX concentrations especially the concentration of benzene was 2–4 times greater than the maximum levels (0.1ppm) recommended by OSHA.

In Romania, Culea et al. (2005) investigated the BTEX emitted from different materials, adhesives, combustion sources or tobacco smoke. The samples were collected by drawing air through active charcoal cartridges and analyzed using GC-MS. The results show that BTEX concentrations were 60.15, 157.86, 1.5, 2.5 ppm respectively.

Nolasco et al. (2005) monitored VOCs emission from road traffic inside a 1 km long tunnel located at the exit of the Tenerife's biggest town, Santa Cruz de Tenerife. Samples were taken by grab-sampling in 400 cm^3 stainless-steel canister, and were analyzed using the GC-tandem MS (GC/MS/MS). The preliminary results show that BTEX are the dominant pollutants of the traffic vehicles in the tunnel. Moreover, 8.3 kg per kilometer was an estimate for the BTEX concentrations due to the traffic movement.

BTEX concentration were measured in three typical cities (Guangzhou, Macau and Nanhai), China by Wang et al. (2002). Multi-bed adsorbent tubes were used for air sampling at typical ground level microenvironments. The thermal desorption–gas chromatography–mass selective detector (TD–GC–MSD) technique was used to analyze the BTEX concentrations. The results show that the mean concentrations of BTEX in Guangzhou were 51.5, 77.3, 17.8 and 81.6 $\mu g/m^3$, respectively; 34.9, 85.9, 24.1 and 95.6 $\mu g/ m^3$ in Macau; and 20.0, 39.1, 3.0 and 14.2 $\mu g/m^3$ in Nanhai (Wang et al. 2002).

Schneider et al. (1999) carried out a pilot study to examine BTEX concentrations in 20 homes in Erfurt, Germany. The samples were collected using passive sampling device and were analyzed using GC-FID. The results show that mean BTEX concentrations at 1.2m level in the twenty homes were 3.86, 50.13, 3.59, 2.84 $\mu g/m^3$, respectively.

According to the study of Kerbachia et al. (2006), which was carried out in three representative sites with high traffic volume in Algiers, results show that BTEX were the dominant pollutants. The mean concentrations of benzene and toluene were 27 and 39 μg/m^3, respectively.

Khoder (2007) monitored VOCs in two urban areas (Ramsis and Haram) in Cairo and one rural area (Kafr El Akram) in Manoufiah in Egypt. The samples were collected using activated coconut charcoal tubes and analyzed by GC-FID. The results show that the BTEX ratios were (2.01:4.94:1:4.95), (2.03:4.91:1:4.87) and (2.31:2.98:1:2.59) in Ramsis, Haram and Kafr El-Akram, respectively.

O'Donoghue et al. (2007) studied the difference in pollution exposure between bus and cycling commuters on a route that was compared in Dublin; the samples were collected using a SKC Vac-U-Chamber™ and analyzed by GC-FID. The mean bicycle and bus benzene concentrations are 1.62 and 2.21 ppb, respectively.

BTEX emissions were monitored at roadsides by Truce and Oanh. (2007) in Hanoi, Vietnam. The samples were collected by SKC charcoal tubes and analyzed by GC-FID. The results show that the geometric mean of hourly BTEX concentrations in a street with high traffic volume, were 65, 62, 15, 43 μg/m^3, respectively.

Rappengluck et al. (2005) monitored volatile organic compounds (VOCs) in three locations in the metropolitan area of Santiago de Chile. The sampling was carried out using air canisters and the samples were analyzed by GC-FID. The results show that the