ASSESSMENT OF URBAN TROPOSPHERIC OZONE FORMATION POTENTIAL THROUGH VOLATILE ORGANIC COMPOUNDS

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Environmental Management
(Interdisciplinary Program)
Graduate School
Chulalongkorn University
Academic Year 2013

การประเมินค่าศักยภาพการเกิดโอโซนในบรรยากาศจากสารอินทรีย์ระเหย

นางสาวศิริธร แสงซ้าย

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาการจัดการสิ่งแวดล้อม (สหสาขาวิชา)
บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2556

Thesis Title	ASSESSMENT OF URBAN TROPOSPHERIC OZONE FORMATION POTENTIAL THROUGH VOLATILE ORGANIC COMPOUNDS
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Field of Study	Environmental Management
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ศิริธร แสงซ้าย : การประเมินค่าศักยภาพการเกิดโอโซนในบรรยากาศจากสารอินทรีย์ระเหย. (ASSESSMENT OF URBAN TROPOSPHERIC OZONE FORMATION POTENTIAL THROUGH VOLATILE ORGANIC COMPOUNDS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. วนิดา จีนศาสตร์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ผศ. ดร. สราวุธ เทพานนท์, 100 หน้า.

การประยุกต์ใช้ generalized additive model (GAM) ในการประเมินผลกระทบของศักยภาพการเกิดโอโซนโดยสารอินทรีย์ระเหย (Volatile Organic Compounds; VOCs) ต่อระดับความเข้มข้นของก๊าซโอโซนในบรรยากาศพื้นที่กรุงเทพมหานครและใกล้เคียง โดยพิจารณาจากค่า Photochemical Ozone Creation Potential (POCP) พบว่า hydrocarbons (HCs) เป็นกลุ่มสารอินทรีย์ระเหยที่มีส่วนร่วมใน ozone contribution production (OPC) มากที่สุด (59.51%) ในขณะที่ oxygenated HCs และ halogenated HCs มีส่วนร่วมใน OPC ระดับปานกลางและต่ำ (39.39% and 1.05%) ตามลำดับ ในทางตรงข้าม halogenated hydrocarbons เป็นกลุ่มที่มีผลกระทบต่อระดับความเข้มข้นของโอโซนมากที่สุด โดยพิจารณาจากเปลี่ยนแปลงของค่า coefficient of determination (9.39%) และค่า overall mean ของ response (40.21%) ซึ่งมีผลกระทบมากกว่าของ HCs (-2.63% และ 6.01%) และ oxygenated HCs (-2.02% and 1.57%) โดยปัจจัยที่มีนัยสำคัญ ($p < 0.05$, alpha = 0.05) ต่อการเกิดโอโซนในพื้นที่กรุงเทพมหานครและใกล้เคียง เรียงลำดับจากมาไปหาน้อย มีดังนี้ 1,3-บิวทาไดอีน, ทิศทางลม, โบรโมมีเธน, 1,2-ไดคลอโรโพรเพน, รังสีดวงอาทิตย์, คาร์บอนมอนอกไซด์, เมธา-ไซลีน, 1,1,1-ไตรคลอโรอีเธน, คลอโรมีเธน, ไตรคลอโรเอธิลีน, 1,3,5-ไตรเมธิลเบนซีน, ออร์โธ-ไซลีน, 1,2,4-ไตรเมธิลเบนซีน, คลอโรอีเธน, 1,2-ไดคลอโรเบนซีน, 1,1,2-ไตรคลอโรอีเธน, ออกไซด์ของไนโตรเจน, สไตรีน, ฟอร์มัลดีไฮด์, 1,4-ไดคลอโรเบนซีน, ความเร็วลม, คลอโรเบนซีน และความชื้นสัมพัทธ์ ซึ่งโมเดล GAM มีประสิทธิภาพเป็นอย่างดีทั้งในการใช้วิเคราะห์ผลกระทบของปัจจัยต่างๆต่อการเกิดโอโซนเฉลี่ย ($R^2 = 81.24\%$) ของ trained model และใช้ในการประมาณค่าโอโซนเฉลี่ย ($R^2 = 82.56\%$) ในบรรยากาศ โดยมีดัชนีบ่งชี้ประสิทธิภาพของโมเดล คือ root mean squared error (RMSE) 5.13 ไมโครกรัมต่อลูกบาศก์เมตร, normalized standard error (NSD) 0.87, normalized absolute error (NAE) 0.14, normalized root mean squared error (NRMSE) 0.08, degree of agreement (d) 0.95 และ normalized bias (NB) -7.49%.

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต

ปีการศึกษา 2556 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก

ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม

5587624920 : MAJOR ENVIRONMENTAL MANAGEMENT

KEYWORDS: PHOTOCHEMICAL OZONE CREATION POTENTIAL; POCP; VOCS; OZONE FORMATION POTENTIAL; GENERALIZED ADDITIVE MODEL

SIRITHORN SAENGSAI: ASSESSMENT OF URBAN TROPOSPHERIC OZONE FORMATION POTENTIAL THROUGH VOLATILE ORGANIC COMPOUNDS. ADVISOR: ASSOC. PROF. DR. WANIDA JINSART, CO-ADVISOR: ASST. PROF. DR. SARAWUT THEPANONDH, 100 pp.

A generalized additive model (GAM) was applied to investigate the potential impacts of VOCs towards ozone concentration levels in Bangkok and vicinity areas, based on the Indices of Photochemical Ozone Creation Potential (POCP). Hydrocarbons (HCs) were found to be the group with the highest contribution to ozone production (OPC; 59.51%), whereas oxygenated HCs and halogenated HCs yielded OPC at medium (39.39%) and low (1.05%) levels. However, according to the percent change for the coefficient of determination (R^2; 9.39%) and the overall mean of response (μ; 40.21%), halogenated HCs were the principal agents that affected the concentrations of urban ozone by comparison with HCs (-2.63% and 6.01%) and oxygenated HCs (-2.02% and 1.57%). In decreasing order, as validated by GAM ($p < 0.05$, alpha = 0.05), the model parameters that significantly increased the tropospheric ozone in Bangkok and surrounding area were 1,3-butadiene, wind direction, bromomethane, 1,2-dichloropropane, global radiation, carbon monoxide, m-xylene, 1,1,1-trichloroethane, chloromethane, trichloroethylene, 1,3,5-trimethylbenzene, o-xylene, 1,2,4-trimethylbenzene, chloroethane, 1,2-dichlorobenzene, 1,1,2-trichloroethane, oxides of nitrogen, styrene, formaldehyde, 1,4-dichlorobenzene, wind speed, 3-chloropropene, and relative humidity.

The obtained GAM regressions of the trained and estimating models were in accordance with each other with R^2 = 81.24% and 82.56% coupled with noticeable performance indicators in terms of root mean squared error (RMSE) of 5.13 $mg.m^{-3}$, normalized standard deviation (NSD) of 0.87, normalized absolute error (NAE) of 0.14 normalized root mean squared error (NRMSE) of 0.08, degree of agreement (d) 0.95 and normalized bias (NB) of -7.49%.

Field of Study:	Environmental Management	Student's Signature	
		Advisor's Signature	
Academic Year:	2013	Co-Advisor's Signature	

ACKNOWLEDGEMENTS

First, I would sincerely like to thank my adviser, Assoc. Prof. Dr. Wanida Jinsart and the academic program director of the National Center of Excellence for Environmental and Hazardous Waste Management (NCE-EHWM), Asst. Prof. Dr. Chantra Tongcumpou, who have encouraged and supported me for both educational and research issues. A greatly special thanks to Asst. Prof. Dr. Sarawut Thepanondh, my co-adviser, from Department of Sanitary Engineering, Mahidol University; this project could not be accomplished without his valuable comments and suggestions. I would like to express my appreciation to Assoc. Prof. Dr. Sirima Panyametheekul, the thesis examiner for spending her valued time towards my thesis and defense. I genuinely appreciate for all technical discussion to Dr. Natchanok Pala-En, the thesis external examiner from Pollution Control Department (PCD).

Additionally, I am deeply indebted to the Air Quality and Noise Management Bureau, PCD for providing the air quality and meteorological data. This study could neither start nor finish without those data. Equally, I appreciate for all supports from my PCD friends, namely Ms. Julalux Boonpak, Ms. Pitchaya Katenut, Ms. Noochjariya Aransri and Mr. Jiraphat Theamjun. I am grateful to all staffs of NCE-EHWM as well for their corporative contributions to my thesis research.

Finally, all worthily honor and gratitude, to my Dearest Father in Heaven who gave me my breath, inspiration and blessed me with the opportunity and direction to accomplish my goal.

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AU	Australia
B/T	Benzene-to-toluene concentration ratio
BMR	Bangkok Metropolitan Area
BP	Boiling point
BSD	Bansomdej Chaopraya Rajabhat University Station
BUR	Bangkok University at Rangsit Station
BVOCS	Biogenic volatile organic compounds
^{o}C	Degree Celsius
C	Concentration
CAI-Asia	The Clean Air Initiative Asia
CalEPA	California Environmental Protection Agency
CAS No.	Chemical Abstracts Service Registry Numbers
CC4	Chokchai Police Station
Cl	Chlorine
$ClNO_2$	Nitryl chloride
CO	Carbon monoxide
CO_2	Carbon dioxide
CUH	King Chulalongkorn Memorial Hospital Station
d	Degree of agreement
DD	DinDaeng National Housing Authority Station
DIN	Deutsches Institut für Normung (the German Institute for Standardization)
DoEB	Department of Energy Business
DV	Dependent variable
EC	European commission
EB/B	Ethylbenzene-to-benzene ratio
ECDF	Empirical distribution function
ERTC	The Environmental Research and Training Center Station
GAM	Generalized Additive Models

GC/MS	Gas Chromatography/Mass Spectrometry
HAPs	Hazardous air pollutants
HCs	Hydrocarbons
HK	Hong Kong
HPLC	High-performance liquid chromatography
IARC	International Agency for Research on Cancer
IBM	The International Business Machines Corporation
IPCC	Intergovernmental Panel on Climate Change
IV	Independent variable
IVL	The Swedish Environmental Research Institute
JICA	Japan International Cooperation Agency
K	Kelvin
LC	Liquid chromatography
LOD	Limit of detection
LOQ	Limit of quantification
LTO	Land Transportation Office
MAE	Mean absolute error
MCM	The Master Chemical Mechanism model
MGE	Mean Gross Error
MIR	Maximum incremental reactivity
mmHg	Millimeter of mercury
MoE	Ministry of Energy
MOIR	Maximum ozone incremental reactivity
MoNRE	Ministry of Natural Resources and Environment
MoSTE	Ministry of Science Technology and Environment
MW	Molecular weight
NAE	Normalized absolute error
NB	Normalized bias
ND	Non-detectable
NO_2	Nitrogen dioxide
NMAM	NIOSH Manual of Analytical Methods

NMB	Normalized Mean Bias
NSD	Normalized standard deviation
NRMSE	Normalized root mean squared error
NMHCs	Non-methane hydrocarbons
NMVOCs	Non-methane volatile organic compounds
NO_x	Oxides of Nitrogen
O_3	Ozone
OFP	Ozone formation potential
OH	Hydroxyl radical
OPC	Ozone production contribution
OTP	Office of Transport & Traffic Policy and Planning
PAN	Peroxy acetyl nitrate
PCD	Pollution Control Department
POCP	Photochemical ozone creation potential
POM	Particulate organic matter
ppbv	Parts per billion by volume
pptv	Parts per trillion by volume
QA/QC	Quality assurance/quality control
QRM	Quantile regression model
R^2	Coefficients of determination
R	Correlation coefficient
RMSE	Root Mean Square Error
S/N	Signal-to-noise ratio
SEA	South East Asia
SVOC	Semivolatile compounds
ThBri	The Metropolitan Power-Substation ThonBuri
TMD	The Thai Meteorological Department
TO	Compendium of Methods for the Determination of **T**oxic **O**rganic Compounds in Ambient Air
TVOCs	Total volatile organic compounds
UK	The United Kingdom

USEPA	The United States Environmental Protection Agency
UNECE	The United Nations Economic Commission for Europe
VOCs	Volatile organic compounds
VVOC	Very volatile compounds
VP	Vapor pressure
X/B	Xylene-to-benzene concentration ratio
WB	World Bank
WHO	The World Health Organization
λ	Wavelength

CHAPTER I

INTRODUCTION

1.1 Background and Motivation

Urban air pollution is one of the most important environmental problems for large cities (UNEP, 2013). As a consequence of extensive VOCs quantities are emitted into the atmosphere, many cities are currently facing with tropospheric ozone problems. VOCs are classified as hazardous air pollutants (HAPs) (USEPA, 2013), and renowned as surface ozone precursors according to their photochemical reactions with nitrogen oxides to form ground level ozone in the presence of sunlight (Atkinson, 2000). They not only can cause to environmental problems but also adversely affect to human health (Atkinson, 2000; Zhang et al., 2012). In addition, the trace gas ozone and halogenated VOCs in the troposphere are interchange media for air pollution and climate change (Liao et al., 1998; Stevenson, 2006).

Bangkok, is alike to other cities of the developing world, affected by rapid urbanization, economic development, and increases in number of transport vehicles which have caused detrimental effects on the air quality. On-road vehicles and industrial sources are typically the major sources of common urban air pollutants (e.g. ozone and VOCs) contribute to both local urban air quality and global environment (Faiz et al. 1996; IGES, 2007; CAI-Asia, 2010; WMO, 2010; Kurokawa et al., 2013). Additionally, Thailand VOCs emission was high, about 14% of all countries in South East Asia (SEA), added by road transport (Kurokawa et al., 2013), whereas 96.84% of greenhouse gases containing hydrocarbons (HCs) released by Thailand's transport sector was from road mode. (OTP, 2013).

Due to the traffic congestion and vehicles have been intensified, Bangkok and other large cities have challenged for critical air pollution. The concentrations of 1-hour and 8-hour average values of ozone have been fairly exceeded the standard in almost all areas around Bangkok Metropolitan Area (BMR) from 1996 to 2012. Furthermore, PCD revealed that the ambient concentrations of some VOCs emitted principally from automobiles; for examples, 1,3-Butadiene and Benzene were also over the standard values from 2008 to 2012, even though they slightly declined in 2012 (PCD, 2008 - 2012a).

In consideration of tropospheric ozone formation, the potential levels of ambient VOCs contribute to the photochemical ozone creation need to be determined and investigated. The investigation of VOCs contribution through ozone formation may provide the substantial information for the environmental mitigation in Thailand, the development of Thailand environmentally sustainable transport system (OTP, 2013) and the energy efficiency development plan toward the sustainable economics and communities of the country (MoE; 2010).

1.2 Objectives

The objectives of this study are to investigate the contribution of airborne Volatile Organic Compounds (VOCs) ozone precursors toward tropospheric ozone formation potential (OFP) and related factors as follows:

1.2.1 Ambient concentration levels for inorganic ozone precursors specifically oxides of Nitrogen (NO_x) and carbon monoxide (CO).

1.2.2 Meteorological factors (i.e. temperature, pressure, wind speed, wind direction, relative humidity, and solar radiation).

Additionally, the motivation for focusing on ozone and VOCs (rather than any other air pollutants) stems from the fact that O_3 is a secondary air pollutants occurred from complex photochemical reactions and mechanisms, which is not directly released from emission sources, and greatly dependent upon its precursors (e.g. VOCs, NO_x, CO) and meteorological circumstances.

1.3 Hypotheses

1.3.1 VOCs-ozone precursors perform a significant function on OFP and tropospheric ozone concentration levels.

1.3.2 Ambient NO_x and CO concentration levels considerably contribute to ozone formation.

1.3.3 Meteorological factors affect the OFP on VOCs' routes toward surface ozone creation.

1.4 Scope of the study

This investigation estimates the production of ground-level ozone formation throughout the photochemical reactions of volatile organic compounds in the six years period of 2008 to 2013 for forty three VOCs consisting of four carbonyl compounds and 39 compounds of HCs, halogenated HCs and Acrylonitrile associate with NO_x, CO and 6 meteorological variables . This study has covered 3240 samples collected from 5 monitoring sites of VOCs, NOx, CO and 6 meteorological factors in Bangkok and Thanyaburi District, Pathumthani. The study framework is demonstrated in Figure 1.1.

1.4.1 Preliminary study

The introductory study objects to do screening research for BMR's meteorological condition, the monitoring and analytical methodology (equivalent to USEPA Compendium Method TO-11A: Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography

(HPLC; Active Sampling Methodology), TO-14A and TO-15: Determination of VOCs In Ambient Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography Mass Spectrometry (GC/MS)) including the QA/QC process, summa/silco canister cleaning and database of ambient VOCs in BMR. The monitoring concentrations of 43 target VOCs, courteously devoted by PCD, involved in this study are listed below:

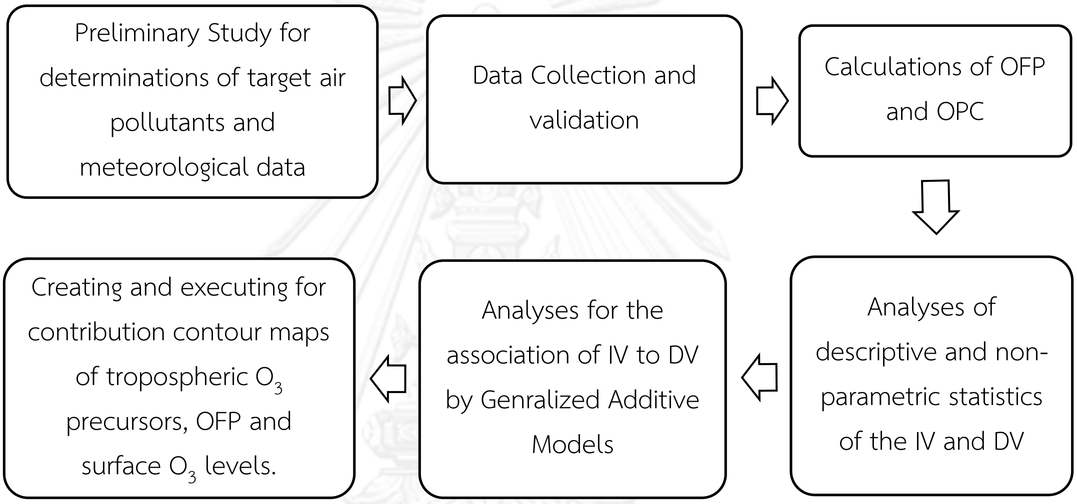


Figure 1.1 Flow Diagram for the Study Framework

- Formaldehyde
- Acetaldehyde
- Acrolein
- Propionaldehyde
- 1,3-Butadiene
- Benzene
- Toluene
- Ethyl benzene
- Bromomethane
- 1,2-Dibromoethane
- Vinyl chloride
- Chloroform
- Carbon tetrachloride
- Chloromethane
- Chloroethane
- 1,1-Dichloroethylene
- 1,2-Dichloropropane
- cis-1,2-Dichloroethylene
- Trichloroethylene
- Tetrachloroethylene
- cis-1,3-Dichloropropene
- trans-1,3-Dichloropropene
- Chlorobenzene
- Benzyl Chloride

- m-Xylene
- p-Xylene
- Styrene
- o-Xylene
- 1-Ethyl-4-methylbenzene
- 1,3,5-Trimethylbenzene
- 1,2,4-Trimethylbenzene
- 3-Chloropropene
- Dichloromethane
- 1,1-Dichloroethane
- 1,2-Dichloroethane
- 1,1,1-Trichloroethane
- 1,1,2-Trichloroethane
- 1,1,2,2-Tetrachloroethane
- 1,2-Dichlorobenzene
- 1,3-Dichlorobenzene
- 1,4-Dichlorobenzene
- 1,2,4-Trichlorobenzene
- Acrylonitrile

1.4.1.1 Data analysis and interpretation:

Data processing, statistical analysis and model development have been carried out by two commercial statistical softwares, which are Statistica V.10 (StatSoft Inc., 2010) and IBM SPSS Statistics V.22 (IBM, 2013).

The potential of tropospheric ozone formation and contribution of ozone production for individual VOC is determined throughout the photochemical ozone creation production (POCP) index as described in Eq. (1.1) – (1.2).

$$OFP_i\ [\mu g \cdot m^{-3}] \ = \ C_{VOC_i}\left(\mu g \cdot m^{-3}\right) \times POCP_i \qquad (1.1)$$

$$\text{Ozone production contribution} = \left[OFP_i \Big/ \sum OFP_i \right] x100 \qquad (1.2)$$

where *OFP* denotes the ozone formation potential, C_{VOC_i} refers to the concentration of i^{th} VOC and *POCP* is the photochemical ozone creation potential coefficient.

a. Test of descriptive statistics of both independent (OFP of each VOC) and dependent variables as follows: a) the Kolmogorov-Smirnov statistic is a tool for testing a normal distribution of a set of observations (Chakravart, et al., 1967, Aboelghar et al., 2010), which is based on the empirical distribution function (ECDF), The Kolmogorov–Smirnov test statistics is defined in Eq.(1.3).

$$ED = \max(F(Y_i - \frac{i-1}{N}, \frac{i}{N} - F(\mathrm{Y}_i)) \tag{1.3}$$

where ED denote the Kolmogorov–Smirnov test statistics and F is the theoretical cumulative distribution of the distribution being examined.

b. Grubbs test is employed to detect for ouliers, based on the difference of the mean of the sample and the most extreme data considering the standard deviation (Grubbs, 1950, 1969; DIN 32645; DIN 38402).

$$T_{\max} = \frac{\mathrm{X}_n - \overline{X}}{S} \qquad T_{\min} = \frac{\overline{X} - \mathrm{X}_1}{S} \tag{1.4}$$

where X_i or X_n is the (min or max) suspected single outlier, *S* denotes standard deviation of the whole data set $\overline{X}$ = mean

c. Correlation analysis: Pearson's correlation coefficients is used to evaluate the strength of the linear relationships between IV and DV individually as detailed in Eq. 1.5 - 1.8.

$$r = \frac{n(\sum x_i y_i) - (\sum x_i)(\sum y_i)}{\sqrt{\left[n\sum \mathrm{x}_i^2 - (\sum \mathrm{x}_i)^2\right]\left[n\sum \mathrm{y}_i^2 - (\sum \mathrm{y}_i)^2\right]}} \tag{1.8}$$

where $x_{i,}$ y_i is a sample of the i^{th} *pair*, *n* indicates the number of observations and *r* denotes the Pearson’s correlation coefficient.

1.4.2 Generalized Additive Models (GAM)

GAM is employed to investigate the interactive effects between atmospheric ozone level and its precursors, in terms of VOCs OFP levels and concentrations of NO_x and CO, associated with local meteorological conditions. The basic additive model is defined in Eq. 1.9 (Giannitrapani et al., 2005).

$$\log(y_i) = \beta_0 + \sum_{j=1}^{n} S_{ij}(x_{ij}) + \varepsilon_i \tag{1.9}$$

where y_i is the i^{th} ozone concentration, β_0 is the overall mean of the response or an intercept of the scatter plot, $S_j(x_{ij})$ is the smooth function of i^{th} value of covariate j (i.e. temperature, pressure,..., global radiation, NO_x, CO, VOC_1, VOC_2,..., VOC_{38}, excluding VOCs with POCP indices equal to zero), n is the total number of covariates and ε_i is the i^{th} residual.

1.5 Expected Outcome

1.5.1. Attained results for the contribution of airborne VOCs ozone precursors toward tropospheric ozone formation potential (OFP) during 2008-2013.

1.5.2. Achieved findings for influence of NO_x on the potential for ambient ozone creation through VOCs-ozone precursors.

1.5.3. Accomplished effects of meteorological factors on the potential for ambient ozone formation throughout VOCs-ozone precursors.

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Tropospheric Ozone

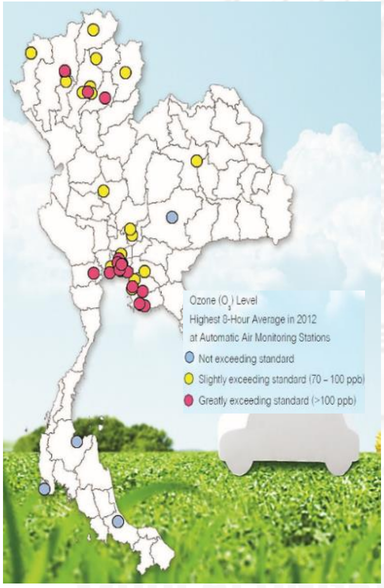
Tropospheric ozone (O_3), as a secondary pollutant, is not only a principal specie of photochemical smog but also is an important human health hazard, exclusively to the respiratory system (Lippmann, 1993; Jacob et al., 1993; Mudway & Kelly, 2000; Sillman, 2003; Xue et al., 2013). It is listed by the World Health Organization (WHO) and United States Environmental Protection Agency (EPA) as a criteria pollutant (Suh et al., 2000; Liao, et al., 2004; WHO, 2005). Volatile organic compounds (VOCs)/non-methane hydrocarbons (NMHCs) is the main group of compounds that play a significant role in photochemically atmospheric processes (Atkinson, 2000; Sahu, 2012). Their emission sources are a wide variety of sources and can exhibit a non-linear effect on local ozone production, while its accumulation is strongly influenced by meteorological processes. Many studies have defended that ambient ozone levels leaded to be increasing in urban areas in the past two decades (Sillman, 1999; Jenkin et al., 2002; Beaney & Gough, 2002; Jimenez et al., 2005; Debaje & Kadade, 2006).

In addition, ozone is recognized as a greenhouse gas which can absorb and emit radiation in the range of infrared radiation ($\lambda \sim$ 0.74 μm to 300 μm). This episode is thought to elevate of the average atmospheric temperature. Ozone plays as a key factor, both direct and indirect, to global warming. It, in a manner of a direct greenhouse gas, absorbs infrared radiation directly and is believed to have the impact about one third of all the direct greenhouse gases leaded on global warming. Moreover, ozone is a reactive gas which reacts to other atmospheric species (e.g.

VOCs, OH and NO_x) and modifies the lifetimes of other greenhouse gases. However, the tropospheric chemical processes are abundantly complex and not completely understood (IPCC, 2001; Bolin, 2007).

2.1.1 State of O_3 in Thailand

Ozone: the concentrations of 1-hour and 8-hour means of ozone have been impartially exceeded the standard over many areas in Thailand, especially in BMR from 1996 to 2012, showed in Figure 2.1 and 2.2. The results revealed that the highest 1-hour and 8-hour average values ranged from 64 – 166 ppb and 51 – 140 ppb in Muang District of Samut Prakan and Wang Thonglang District of Bangkok respectively.



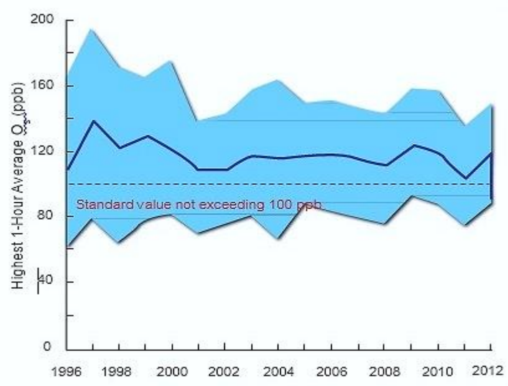


Figure 2.1 Maximum 1-Hour Average Ozone (O_3) from 1996 to 2012 Compared to Standard Value

Figure 2.2 Areas of Maximum 8-Hour Average Ozone (O_3) in 2012 at PCD Air Monitoring Stations (PCD, 2012)

In regional areas, ozone levels frequently and noticeably topped the standard affected from the neighborhoods of traffic transport/highways and industrial areas all the way through open burning and pollutants toward long-range transport, such as

Rayong, Chiang Mai, Lampang - Mae Moh District, and Saraburi provinces (PCD, 2011-2012).

2.1.2 Chemistry of Tropospheric Ozone Formation

Tropospheric O3 is formed generally through the reactions of either anthropogenic or biogenic (Préndez, et al., 2013) VOCs with NO_x emissions in the atmosphere with the presence of sunlight. The relationship of O3, VOCs and NO_x occurred in a complex conformation of non-linear photochemistry Sillman (1999). The amount of O3 production varies with respect to the relative concentrations ratios of VOCs and NOx. In NOx sensitive regime, a change in VOC emissions will simply cause a minimal modification in O_3 concentrations while a small change in NOx emissions will impact a major distinction in O_3 concentration levels. Alternatively, in the VOC sensitive conditions, an increase in NOx appears a reduction in O_3 levels, while increasing VOCs reveal in amplified actual O_3 concentrations. In the absence of VOC, NO_x undergoes a series of photochemical reactions that, both, create and eat ozone such that the net ozone accumulation is zero as shown in Figure 2.3.

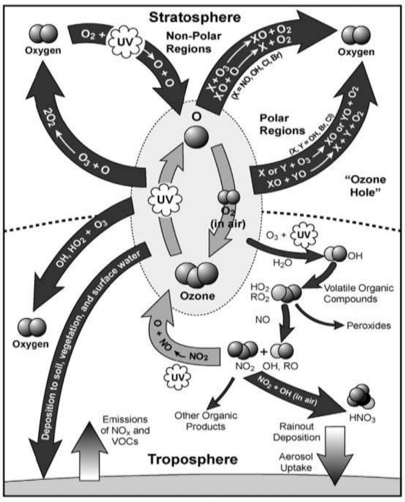


Figure 2.3 Diagram demonstration of atmospheric ozone chemistry and transformation (USEPA, 2006).

NO_2 is dissociated into nitric oxide and oxygen atom in the presence of sunlight. The oxygen atom then reacts with the oxygen molecule in the atmosphere to create ozone. Ozone, consecutively reacts rapidly with nitric oxide (NO) to form NO_2 and O_2. Then, VOCs are oxidized by the hydroxyl radical (OH) present in the atmosphere. The oxidized VOCs substitute ozone, hence reacting with NO to form NO_2 without consuming O_3. The other products of this reaction undergo further reactions, eventually forming more oxidants. The largest source of OH radicals in the atmosphere is the combination of excited oxygen atom with water vapor and the photolytic decomposition of O_3 is one source of excited oxygen atoms.

2.1.3 Factors of Contribution to Ozone Level

It is typically distinguished that vehicular emissions are the principle source of VOCs and NO_x However, contribution factors of ozone concentration are not limited to only automobiles and other emission sources (e.g indurtial sources, area sources). There are several variables affect to surface ozone concentrations; for example, temperature, soalr radiation, season, location/topography. (Schuck et al., 1965; Cleveland et al., 1974, Elkus & Wilson, 1977; Karl, 1978; Sillman, 1999; Marr & Harley, 2002; Jimenez et al., 2005; Debaje & Kadade, 2006).

2.1.4 Impacts of Ozone on Human Health

Irriatation and inflammation are the main responses of ozone exposure. (EEA, 2009; AQEG, 2009). Several epidemiology studies revealed that numbers of hospital admissions or emergency visits for respiratory conditions, mal-lung function, and other assorted health problems related to ozone exposure (Kinney, 1999; Koken et al., 2003). In addition, elevation of ground level ozone pollution over European Union countries causes approximately 21000 premature deaths and 14000 respiratory hospital admissions a year. Furthermore, long-term exposure to ozone is associated with inflammation, persistent structural airways and lung damage, while short-term exposure may cause to respiratory symptoms, lung inflammation, lung permeability, morbidity and mortality (USEPA, 2006; WHO, 2008).

2.2 Volatile Organic Ozone Precursors

2.2.1 State of Volatile Organic Compoundss in Thailand

In 2008, the monitoring of airborne VOCs in Thailand had firstly been processed; the target analytes were parted into two groups: (1) four compounds of oxygenated hydrocarbons including formaldehyde, acetaldehyde, acrolein and propionaldehyde (2) nine regulated VOCs under the 30th Announcement of the National Environment Board, B.E. 2550 (2007) comprising of 1,3-butadiene, benzene, vinyl chloride, 1,2-dichloroethane, trichloro-ethylene, dichloromethane, 1,2-dichloro-propane, tetrachloroethylene and chloroform. The monitoring has taken place in large cities around the country, which are Bangkok, Chiang Mai, Songkhla, Khon Kaen, and the industrialized area in Rayong province. It was found that the levels of carbonyl compounds in roadside areas were higher than general areas both in the large cities and Bangkok. The average values resulted in 2012 were trendily over than the monitoring data in 2009 – 2011.

During the period of 2008 – 2012, there were four VOCs which topped the standards pictured in Figure 2.4. Among all VOCs, benzene levels went beyond the standard at almost all monitoring sites. Due to strict VOCs control measures, 1,3-Butadiene levels exceeded the standard in Rayong since 2008 and went down in 2012.

2.2.2 Definitions and Classifications of VOCs

Definition of VOCs may be defined specifically depends on the aims and target of studies. However, in general, VOCs are termed for group of organic compounds that simply can vaporize at ambient temperatures. Some VOCs are greatly reactive and play a critical role in the formation of ground-level ozone. Other VOCs not only have chronic but also acute adverse health effects. In some circumstances, VOCs can be both highly reactive and potentially toxic. Sources of VOCs include vehicular exhaust, waste burning, gasoline business, industrial and consumer products, pesticides, industrial processes, degreasing operations, pharmaceutical manufacturing, and dry cleaning operations (CalEPA, 2014).

In addition, the European Union defines VOC as any organic compound having an initial boiling point less than or equal to 250° C measured at a standard atmospheric pressure of 101.3 kPa (1999/13/EC). Whereas WHO has defined VOCs as a group of organic compounds with boiling points from approximately 50^{o}C to 260^{o}C (WHO, 1989).

Moreover, USEPA has included photochemical reactivity and ability to produce ozone and photochemical smog of any VOCs in ambient air environment for controlling interest in VOCs definition: “Volatile organic compounds (VOC) means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions, except those designated by EPA as having negligible photochemical reactivity.” (USEPA, 2013).

Furthermore, United Nations Economic Commission for Europe (UNECE) even confines VOCs to those that are anthropogenic nature: “All organic compounds of anthropogenic nature, other than methane, those are capable of producing photochemical oxidants by reacting with nitrogen oxides in the presence of sunlight are VOCs." (UNECE, 2004).

Table 2.1 summarized the classifications of VOCs, which are elaborately grouped by WHO, namely very VOCs (VVOCs), VOCs, and semi VOCs (SVOCs), depending on their boiling points as in (WHO, 1989).

Table 2.1: Classification of organic pollutants (WHO, 1989)

Description	Abbreviation	Boiling point range (ºC)
Very volatile (gaseous)	VVOC	< 0 and 50-100
Volatile organic compounds	VOC	50-100 and 240-260
Semivolatile compounds	SVOC	240-260 and 380-400
Particulate organic matter	POM	> 380

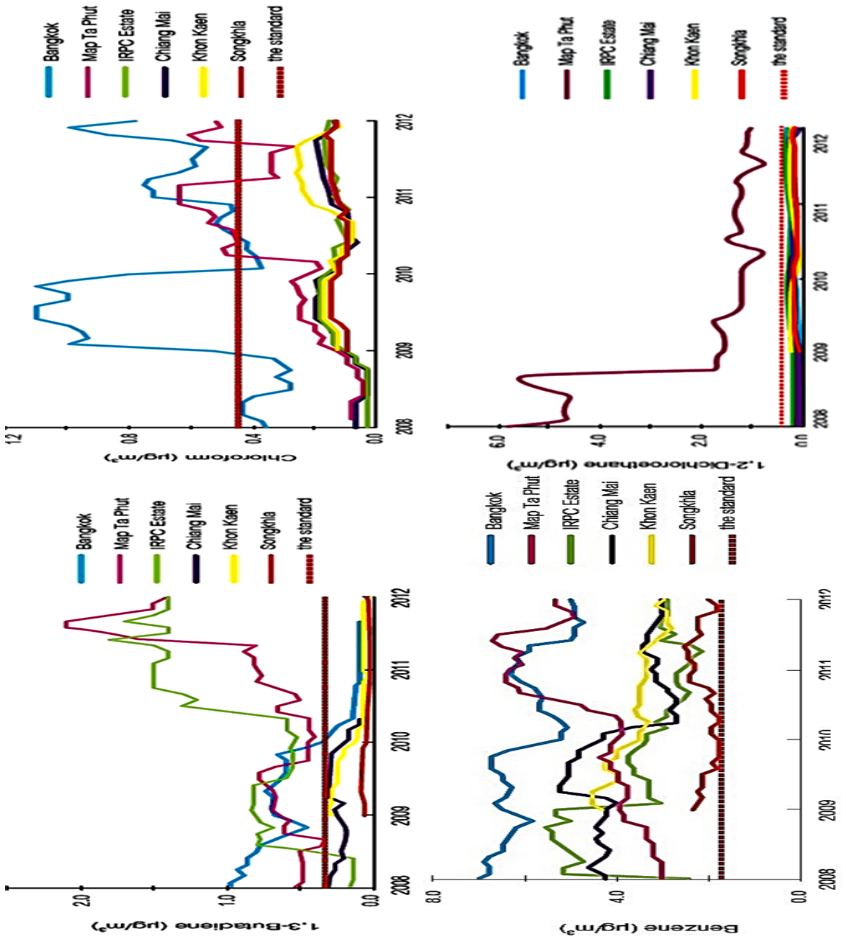


Figure 2.4. Maximum Annual (moving) Average of selected VOCs in the Atmosphere from 2008 to 2012

2.2.3 Physical and Chemical Properties of VOCs

Physical and Chemical Properties of target VOCs, selected from the Title III Clean Air Amendment, may vary depend on any compounds' characteristics, are summarized in Table 2.2.

Table 2.2. Physical and Chemical Properties of selected VOCs on the Title III Clean Air Amendment List[a]

Compound	CAS No.	BP (°C)	VP (mmHg)	MW
Formaldehyde	50-00-0	-19.5	2.7 x 10	30
Acetaldehyde (ethanal)	75-07-0	21.0	952	44
Propionaldehyde	123-38-6	49.0	235	58.1
Acrolein (2-propenal)	107-02-8	52.5	220	56
1,3-Butadiene	106-99-0	-4.5	2.0 x 10	54
Benzene	71-43-2	80.1	76.0	78.11
Toluene	108-88-3	111	22.0	92
Vinyl chloride	75-01-4	-14.0	3.2 x 10	62.5
Methyl bromide (bromomethane)	74-83-9	3.6	1.8 x 10	94.9
Chloroform	67-66-3	61.2	160	119.3
Carbon tetrachloride	56-23-5	76.7	90.0	64.51
Ethyl chloride (chloroethane)	75-00-3	12.5	1.0 x 10	64.5
Vinylidene chloride (1,1-dichloroethylene)	75-35-4	31.7	500	97
Methyl iodide (iodomethane)	74-88-4	42.4	400	141.9
Methylene chloride (Dichloromethane)	75-09-2	40.0	349	84.9
Allyl chloride (3-chloropropene)	107-05-1	44.5	340	76.5
Ethylidene dichloride (1,1-dichloroethane)	75-34-3	57.0	230	99
Chloroprene (2-chloro-1,3-butadiene)	126-99-8	59.4	226	88.5
Methyl chloride (chloromethane)	74-87-3	-23.7	3.8 x 10	50.5
Chloroprene (2-chloro-1,3-butadiene)	126-99-8	59.4	226	88.5
Chlorobenzene	108-90-7	132	8.8	112.6
Methyl chloroform (1,1,1-trichloroethane)	71-55-6	74.1	100	133.4
Ethylene dichloride (1,2-dichloroethane)	107-06-2	83.5	61.5	99
Propylene dichloride (1,2-dichloropropane)	78-87-5	97.0	42.0	113
2,2,4-Trimethyl pentane	540-84-l	99.2	40.6	114

Table 2.2. Physical and Chemical Properties of selected VOCs on the Title III Clean Air Amendment List[a] Cont'd

Compound	CAS No.	BP (°C)	VP (mmHg)	MW
1,3-Dichloropropene (cis)	542-75-6	112	27.8	111
Trichloroethylene	79-01-6	87.0	20.0	131.4
1,1,2-Trichloroethane	79-00-5	114	19.0	133.4
Ethylene dibromide (1,2-dibromoethane)	106-93-4	132	11.0	187.9

[a]USEPA TO-15, 1999.

2.2.1 Emission Regulations of VOCs

The first emission control guideline for VOCs was announced by US EPA in 1971. In order to both reduce the emissions of ozone precursors and to encourage the use alternative substances. The California Air Resources Board (CARB) began to research on the regulations for atmospheric VOCs' reactivity, which based on the VOCs composition and VOCs-NO_X ratios, and the reactivity scales were fused with the regulations in 1991 (USEPA, 1994; Atkinson et al., 2004).

In 2001, Thailand PCD firstly regulated the Emission Standard for Bulk Gasoline Terminals by limiting the total VOCs in gasoline emitted vapor. In 2006, the technical cooperation project between the Japan International Cooperation Agency (JICA) and PCD, for further development of the environmental and emission standards of VOCs in Thailand. By then, the national air quality standards of VOCs were issued in 2007, as summarized in Table 2.3 (Royal Government Gazette, 2001, 2007; Thepanondh, 2006).

2.2.5 Sources and Emissions of VOCs

VOCs can be released from not only natural sources but also man-made sources (Brasseur et al., 1999; Hewitt, 1999; Bates et al., 2000). In urban area, anthropogenic sources, such as transportation, solvent use, gasoline evaporation and industrial processes, are the dominants (Environment Canada; 2013).

Table 2.3. Thailand National VOCs in Ambient Air Standards[a]

Pollutants	Standard	Pollutants	Standard
Benzene	1.7 µg/m^3	1,2-Dichloropropane	4 µg/m^3
Vinyl Chloride	10 µg/m^3	Tetrachloroethylene	200 µg/m^3
1,2-Dichloroethane	0.4 µg/m^3	Chloroform	0.43 µg/m^3
Trichloroethylene	23 µg/m3	1,3 - Butadiene	0.33 µg/m3

[a] The annual-average VOCs ambient air standards were referred to the concentration at 25 °C at 1 atm or 760 mmHg

Natural Sources: Biogenic VOCs (BVOCs); for instance, isoprene, monoterpenes, play a significant role in tropospheric chemistry (Atkinson, 2000; Chetehouna et al., 2009; Shrestha et al., 2013), could enhance lifetime of methane (Pacifico et al., 2009) and rise up carbondioxide (CO_2) level (Peñuelas et al., 2010). Although there are other natural sources; for example, rural forested areas, oceans, marine phytoplanktons, soil-microbiota and geological hydrocarbon reservoirs, terrestrial vegetation is the key natural source of BVOCs (Guenther et al., 1995; Stavrakou et al., 2009; Van Langenhove, 2010; Sahu, 2012; Aleksandropoulou, et al., 2013).

Anthropogenic Sources: Transportation and industrial sectors (e.g. industrial solvent usage, production and storage processes and combustion processes) are the prime sources of anthropogenic VOCs. Vehicular emissions is regularly the main source of VOCs in urban areas (Barletta et al., 2005; Theloke et al., 2007; Van Langenhove, 2010; Huang et al., 2011;_Shrestha et al., 2013). Whereas open burning could also be the massive anthropogenic source of air VOCs (USEPA, 2002; Theloke and Friedrich, 2007; Van Langenhove, 2010). Urban emission sources can contribute to increase NOx level as well, which stimulates the creation of surface ozone even in small concentration of VOCs (Talapatra, 2011). Road transport related VOCs take account of alkanes, alkenes, alkynes and aromatic HCs, which mostly are 1,3 butadiene, benzene, toluene, ethyl benzene, and xylene isomers (BTEX), have public health significance and are in environmentally critical concern because of their virtual abundance (Han et al., 2006; Buczynska et al., 2009). VOCs from automotive emission depend on diverse factors including chemical composition in diesel and gasoline, and technology of the engine to control the emission. Decrease of aromatic HCs in vehicle exhaust was reported by shifting from Euro 1 to Euro 4 fuel standards (Department of Energy Business [DoEB], 2006; Caplain et al., 2006; PCD, 2012a, b; Simachaya, 2012; Delphi, 2013). For all vehicles fueled with methanol/gasoline blends, BTEX levels in exhaust were also informed to decline but incline in formaldehyde levels were also noted (Zhao et al., 2011; PCD, 2012c).

Indoor sources of VOCs: Building-furnishing materials, household products(e.g. products of cleaning, dry cleaning, paints, varnishes, waxes, solvents, glues, aerosol propellants, refrigerants, fungicides, germicides, cosmetics) and daily in-house activities (e.g. cooking, smoking and solid fuel combustion) can add up the concentrations of indoor VOCs (Weschler, 2009; Duricova et al., 2010; Sarigiannis et al., 2011; Talapatra, 2011).

2.2.6 Source Apportionment

Generally, the concentration ratio of two VOCs which have photochemically analogical characteristics (e.g. benzene to toluene ratio; B/T) can be used to follow the footprints to their emission sources (Perry and Gee, 1995; Brocco et al., 1997; Barletta et al., 2005; Khoder, 2007; Duan et al., 2008 Zhang et al., 2008). Formerly, the T/B ratios of the roadside samples in Shizuoka (JAP), Michigan (USA), Antwerpia (Belgium), Bari (Italy), Zabrze (Poland) were 6.81, 2.50, 3.80, 2.06 and 1.43 respectively (Ohura et al., 2006; Jia et al., 2008; Buczynska et al., 2009; Caselli et al., 2010; Pyta and Zajusz, 2010). These indicated that T/B ratio could be locally specific and greatly influenced by the source-nature. Alternatively, xylene-to-benzene ratio (X/B) (Barletta et al., 2005; Hoque et al., 2008; Buczynska et al., 2009) and xylene-to-ethylbenzene (X/EB) concentrations (Nelson and Quigley, 1983; Tiwari et al., 2010) have also been employed for source identification.

2.2.7 Photochemical Ozone Creation Potential (POCP)

According to the occurrences of VOCs and NO_x in ground level atmosphere, throughout fossil fuel combustion and oil/solvent evaporation, tropospheric ozone is formed, as showed in Eq. 2.1 (Atkinson, 2000). Other products in this reaction take in gaseous peroxyl acetyl nitrate (PAN), nitric acid and oxygenated hydrocarbons.

$$VOCs + NO_X + sunlight \rightarrow O_3 + other\ products \tag{2.1}$$

The reactions are reliant on the levels of VOCs and NO_x, where NO_x is the limiting reactant, VOCs is in higher concentrations, if otherwise VOCs are limiting reactants, as displayed in O3 isopleth plot (EKMA diagram) in Figure 2.5. It therefore is essential to keep the balance of VOCs and NO_x levels in low concentrations to keep ozone creation at low levels. Additionally, the concentrations of ozone are season dependence, hence VOCs concentration levels are effective to ozone creation over a year (Ismail et al, 2013).

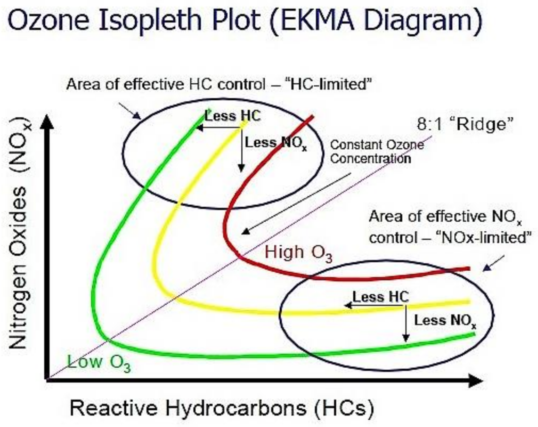


Figure 2.5 Ozone Isopleth Plot (EKMA) Diagram (modified from Fujita, et al., 2013)

POCP, is an indicator of a VOC's capability to contribute to photochemical ozone formation compared with ethylene (as a reference compound, scale of ethylene is valued = 100), indicated in Eq. 2 (Derwent et al., 1996). The valid reactivity scales of VOCs have been determined as regard to oblige the determination of the ozone sensitivity since ambient VOCs can undergo photochemical reactions leading to formation of surface ozone, which is the dominant interchange gas towards the upper atmosphere and cause to global warming, in the presence of sunlight (Grant et al., 2008; Mao et al., 2010; Cheng et al., 2013; Shin et al., 2013; Do et al., 2013).

$$POCP = \frac{Mean_{O3i} - Mean_{O3basecase}}{Mean_{O3ethylene} - Mean_{O3basecase}} \times 100 \qquad (2.2)$$

where mean $O_{3basecase}$ refers to the mean ozone mixing ratio along the 5-day trajectory in the base case, Mean O_{3i} with an additional 2.9% by mass of the i^{th} VOC species and mean $O_{3ethylene}$ refers to that with the same mass of ethylene.

The VOC reactivity and ranking are distinctly for different VOCs, depended on their contribution to ozone formation, which reflects the kinetic and mechanistic characteristics of the VOC oxidation process in the atmosphere. Presently, the reactivity scales applied to estimate hydrocarbon reactivity towards ozone formation consist of 2 types, which are the maximum incremental reactivity (Carter, 1994) and the POCP (Derwent et al., 1996; Derwent et al., 1998; Derwent et al., 2007; Hung-Lung et al., 2007; Elshorbany et al., 2009; Cheng et al., 2013; Shin et al., 2013). Both the quantitative data of VOCs occurrence and their reactivity headed for ozone formation are required for which the purpose of assess the extent of VOCs contribution to tropospheric ozone formation (Do et al., 2013; Shin et al., 2013). The POCP index and ozone production contribution for each VOC species, i, can be calculated using Eq. 2.3-2.4.

$$OFP_i\ [\mu g \cdot m^{-3}] \ = \ C_{VOC_i}\left(\mu g \cdot m^{-3}\right) \times POCP_i \tag{2.3}$$

$$\text{Ozone production contribution} = \left[{OFP_i}\big/{\sum OFP_i} \right] x100 \tag{2.4}$$

where *OFP* denotes the ozone formation potential, C_{VOC_i} refers to the concentration of i^{th} VOC and *POCP* is the photochemical ozone creation potential coefficient.

Practically, POCP is an incremental reactivity method developed by using a photochemical trajectory model, which firstly examines ozone formation under a more genuine Western European conditions over longer timescales. Then, POCP deliberates transport effects and spatial variations in NOx emissions by conveying ozone reactivity relative to some reference VOC species as mentioned above. However, there recently determined OFP by the photochemical trajectory model in other regions such as China, Hong Kong and Australia (Cheng et al., 2010; Cheng et al., 2013; Lam et al., 2013). The values of POCP are spatially and modally dependent as summarized in Table 2.4.

2.2.8 Impacts of VOCs on Climate Change

Most lifetimes of the VOCs are not long enough to reach the stratosphere layer; then they do not play a significant role in the stratospheric ozone. However some of the VOCs species such as methylchloroform and carbontetrachloride are reactants leading to ozone depletion (Sainfeld et al., 1998). Though there is virtually no direct effect of VOCs on climate change was observed, the significant effect on surface ozone formation and effect on water vapor affect the climate change in indirect ways. (Shea et al., 2008).

2.2.9 Impacts of VOCs on Human Health

VOCs can cause both acute and chronic effects as either non-carcinogenic or carcinogenic effects. They typically enter to the body toward respiratory system, eyes and skin by ingestion and/or digestion. (Demeestere et al., 2007; NMAM, 2007; Buczynska et al., 2009). The dominant target organs are blood, liver, kidneys and central nervous system (NMAM, 2007; Vichit-Vadakan et al., 2010 – 2011). Some of VOCs are classified to be human carcinogens (Group 1) with regard to their carcinogenic effects; for example, benzene, acetaldehyde (associated with consumption of alcoholic beverages), formaldehyde, 1,3-butadiene. Additionally, some of VOCs such as trichloroethylene, tetrachloroethylene and 1,2-dibromoethane are considered to be probable carcinogens for humans (Group 2A) (NMAM, 2007; IARC, 2011). The damage target organs may include lung, liver, kidney, blood and biliary tract cancer (WHO, 2000).

2.2.10 VOCs Sampling and Analysis

Anthropogenic VOCs concentrations in urban air are generally in range of part per billion by volume (ppbv). VOCs determination techniques must be proficient against the complex and fluctuations of VOCs' transport mechanism and their concentrations that change in time. By the accuracy, sensitivity, reproducibility and simplicity, diverse techniques for these purposes comes accessible considering. By either employ active or passive adsorptions, or whole air sampling (via sampling bags or Summa/Silco canisters), atmospheric VOCs can be sampled. Subsequently, the VOCs samples should be analyzed by suitable techniques, for example, GC/GC-MS, LC/HPLC (USEPA, 1999; Harper, 2000; NMAM, 2007).

Table 2.4 Comparison of POCP indices of selected VOCs by different studies

Group and Species	POCP / Region					
	UK[a]	UK[b]		Sweden[c]	AU[d]	HK[e]
		PARC-07	MCMv3.1			
Alkanes						
Ethane	8	2.5	3.0	14-36	1	25
Propane	14	4.5	9.0	39-71	6	37
Butane	31	10	18	53-92	10	65
i-Butane	28	12	1	47-69	21	49
Pentane	40	12	22	73-116	6	55
i-Pentane	34	13	21	25-65	17	64
Hexane	40	11	22	81-128	3	54
2-Methylpentane	41	2	26	73-108	10	72
Octane	34	7	13	74-122	-9	66
Decane	36	4.8	12.0	72-118	-4	70
p-Xylene	72	86	79	96-110	16	92
Ethylbenzene	46	32	36	74-90	2	72
Oxygenates						
Formaldehyde	46	119	78	18-55	74	100
Acetaldehyde	55	72	59	68-80	35	128
Methanol	13	7	8	13-21	7	12
Ethanol	34	14	17	44-63	9	38

Group and Species	UK[a]	POCP / Region				
		UK[b]		Sweden[c]	AU[d]	HK[e]
		PARC-07	MCMv3.1			
Acetone	6	3.8	4.0	35-53	-1	9
Halocarbons						
Methylene dichloride	3	0.4	1.0		-1	3
Ethyl chloride	11	2.6	12.0		1	8
Tetrachloroethylene	1	0.3	1.0	0.7-2.0	1	2
Trichloroethylene	29	6	14	5.6-15	11	25
Ethylidene dichloride	54	17	91		43	5
Methyl chloroform	-1				0	1
cis-dichloroethylene	0				19	40
trans-dichloroethylene	-1				17	37
Chloroform	0				-2	2

[a](Derwent *et al*., 2007), [b](Derwent *et al*., 2010), [c] (IVL, 1998), [d](Lama *et al*., 2013), [e] (Cheng *et al*., 2013)

2.2.11 Statistical Models for Ozone Prediction

Multiple linear regression (MLR), a regression model with two or more explanatory predictors, is the most notable statistical model applying for ozone estimation (Soja and Soja, 1999; Pont and Fanton, 2000; Tidblad et al. 2002; Sousa et al., 2007; Paschalidou et al.; 2008; Moustris et al., 2012). MLR model assumes that the variables have normal distributions. However, ozone, its precursors and meteorological parameters may not be fit for MLR because they lack normal distribution and may not suitable for evaluating ozone data (Gardner and Dorling, 1999; Baur et al. 2004). Robeson and Steyn (1990).

A comparison of a univariate model depending on a polynomial trend combined with first order autoregression, a univariate autoregressive integrated moving average

(ARIMA) model and a bivariate temperature and persistence-based regression model for ozone prediction was made by Robeson and Steyn (1990) and concluded that a decomposition of a time series into trend, cycle, and stochastic components was not suitable for forecasting ozone concentrations; probably because ozone concentrations are linked with many other factors (meteorological, traffic and other air pollutants), which are not considered by time series analysis. The same views were expressed by Schlink and Volta (2000). The main weakness of the Robeson and Steyn (1990) study is that it only compares time series and linear regression. Probably by then (1990) most of the latest advanced statistical and machine learning approaches (e.g., Boosted Regression Trees and Quantile regression Models) were not available or perhaps not applied to air quality related issues. Now much more wider choice of parametric and non-parametric models are available to the air quality scientists, which have resulted in much better understanding of the association between ozone and various controlling factors. These two approaches (time series and linear regression) are no more recommended for modelling ozone concentrations as these approaches are based on some assumptions which are not met by air quality data.

A critical review of several statistical techniques (regression, extreme value, and space-time methods) for the meteorological adjustment of ozone was performed by Thompson et al. (2001). They concluded that a number of approaches make useful contributions to the field of air quality, but that no one method is most appropriate for all purposes and all meteorological scenarios. Hence, the choice of methodology will depend on the purpose of the analysis and the meteorological complexity of ozone formation in a given region. Schlink et al. (2003) performed a model inter-comparison exercise in which 15 different statistical techniques for ozone forecasting were applied to ten data sets representing different meteorological and emission conditions throughout Europe. Their results favored neural networks and generalized additive models (GAMs) on the basis of their performance and ability to handle nonlinearities. Furthermore, GAMs have good learning and adaptability and can be easily transferred to work other data and threshold values. Davis and Speckman (1999) successfully predicted daily 8 hour average ozone concentration at Houston, Texas using a GAM where previous regression models had struggled due to the complex meteorological processes. Aldrin and Haff (2005) also applied GAM to model air pollutants concentrations in Oslo for quantifying the importance of meteorological and traffic-related parameters on the concentrations of particulate matter (PM_{10} and $PM_{2.5}$), NO_x and NO_2. More recently, Carslaw et al. (2007) developed a GAM model for assessing trends in traffic related emissions (NO_x, NO_2, CO, benzene and 1,3-butadiene) at Marylebone Road, London; and Westmoreland et al. (2007) applied GAM in a busy street canyon in Gillygate, York, comparing the outcomes of GAM with a dispersion model (ADMS-Urban). The predictions made with the GAM showed excellent agreement with measured concentrations of NO_x and NO_2 and out-performed ADMS-Urban. GAM not only performed better in reproducing both the magnitude of NO_x and NO2 concentrations but also demonstrated the wind speed and wind direction dependence of pollutant sources. However, the predictions made with ADMS-Urban underestimated the measured NO_x by 11% and NO_2 by 21% and there are clear differences in the bivariate polar plots.

However, previous work using Generalized Additive Mixed Models, which can account for the correlation structure of the data, showed that accounting for the autocorrelation only had a minor effect on the prediction uncertainties (Carslaw et al., 2007). Furthermore, model training and testing datasets used in this models and hence the predictions of the models were based on independent datasets.

Baur et al. (2004) and Sousa et al. (2008) suggested a quantile regression model (QRM) for ozone study; as this method could be used for both parametric and nonparametric regression methods and is capable of handling the non-linearities in the association of ozone and covariates (e.g., meteorology and traffic data). Both Baur et al. (2004) and Sousa et al. (2008) have assessed the model performance only by calculating coefficients of determination (R^2) and compared it with the global R1 of the QRM model. More recently, Carslaw (2011) and Derwent et al. (2010) have commented against the use of R^2 values for model performance and suggested using a combination of metrics, such as Root Mean Square Error (RMSE), Mean Bias (MB), Normalised Mean Bias (NMB), Mean Gross Error (MGE), Normalised and Mean Gross Error (NMGE) to obtain more robust measure of model performance.

On the basis of the fact that QRM and GAM can be applied to non-normal ozone distribution and can handle the potential non-linearities in the association of ozone and its predictors, and out-performed most of the other available statistical techniques (as mentioned above), this study intends to apply these two approaches for ozone modelling and extends the use of metrics for model performance as suggested above.

CHAPTER III

METHODOLOGY

3.1 Study sites

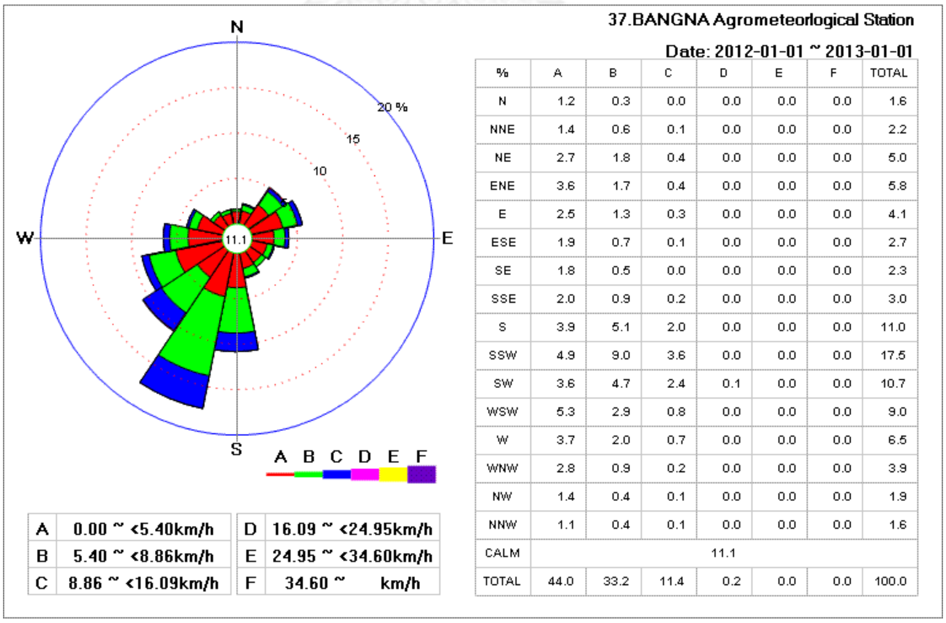
The study sites for evaluating the potential of ground level ozone formation were cautiously selected as the representative samples of the activities in the areas and independent from the air flow restrictions, security of the samplers and based on a year-round wind direction at upwind and downwind, which predominantly affected by SW and NE monsoon (Kim Oanh, 2008), displayed in Figure 3.1, of the center of Bangkok. The study sites were involved of three inner districts and one outer district of Bangkok comparable to its suburban area in Pathum Thani province located at the north-east of Bangkok, which was (a) the Environmental Research and Training Center Station (ERTC) and 4 districts of Bangkok which were (b) Chokchai Police Station (CC4), (c) DinDaeng National Housing Authority Station (DD), (d) King Chulalongkorn Memorial Hospital Station (CUH) and (e) Bansomdej Chaopraya Rajabhat University Station, (BSD). In addition, at CUH and ERTC monitoring stations did not have facilities for monitoring ambient ozone, NO_x, CO and meteorological parameters. Then the Metropolitan Power-Substation ThonBuri (ThBri) and Bangkok University at Rangsit Station (BUR) were employed as the alternative ozone and other ozone-precursors monitoring stations for CUH and ERTC stations respectively.

The characteristics and geographic locations of all monitoring stations were concluded in Table 3.1 and Figure 3.2.

Table 3.1. OFP monitoring sites for Bangkok and the adjacent area

Monitoring Station[a]	Geographic Location	Type of Site	Province
(A) Environmental Research &Training Center, ERTC	14°03' N 100°43' E	Residential / General	Pathum Thani
(B) Chokchai Police Station, CC	13°48' N 100°36' E	Urban	Bangkok
(C) DinDaeng National Housing Authority, DD	13°46' N 100°33' E	Urban	Bangkok
(D) King Chulalongkorn Memorial Hospital, CUH	13°44' N 100°32' E	Urban	Bangkok
(E) Bansomdej Chaopraya Rajabhat University, BSD	13°44' N 100°29' E	Residential /General	Bangkok

[a] The (F) & (G) stations in Bangkok University at Rangsit (BSU) and Thonburi Power Sub-Station (ThBri) were used as the specific alternations of (A) and (D) sites for air quality data other than VOCs data.



37.BANGNA Agrometeorlogical Station

Date: 2012-01-01 ~ 2013-01-01

%	A	B	C	D	E	F	TOTAL
N	1.2	0.3	0.0	0.0	0.0	0.0	1.6
NNE	1.4	0.6	0.1	0.0	0.0	0.0	2.2
NE	2.7	1.8	0.4	0.0	0.0	0.0	5.0
ENE	3.6	1.7	0.4	0.0	0.0	0.0	5.8
E	2.5	1.3	0.3	0.0	0.0	0.0	4.1
ESE	1.9	0.7	0.1	0.0	0.0	0.0	2.7
SE	1.8	0.5	0.0	0.0	0.0	0.0	2.3
SSE	2.0	0.9	0.2	0.0	0.0	0.0	3.0
S	3.9	5.1	2.0	0.0	0.0	0.0	11.0
SSW	4.9	9.0	3.6	0.0	0.0	0.0	17.5
SW	3.6	4.7	2.4	0.1	0.0	0.0	10.7
WSW	5.3	2.9	0.8	0.0	0.0	0.0	9.0
W	3.7	2.0	0.7	0.0	0.0	0.0	6.5
WNW	2.8	0.9	0.2	0.0	0.0	0.0	3.9
NW	1.4	0.4	0.1	0.0	0.0	0.0	1.9
NNW	1.1	0.4	0.1	0.0	0.0	0.0	1.6
CALM	11.1						
TOTAL	44.0	33.2	11.4	0.2	0.0	0.0	100.0

A	0.00 ~ <5.40km/h	D	16.09 ~ <24.95km/h
B	5.40 ~ <8.86km/h	E	24.95 ~ <34.60km/h
C	8.86 ~ <16.09km/h	F	34.60 ~ km/h

Figure 3.1: Wind Rose map showed the average BMR's wind direction in 2012 (TMD, 2013)

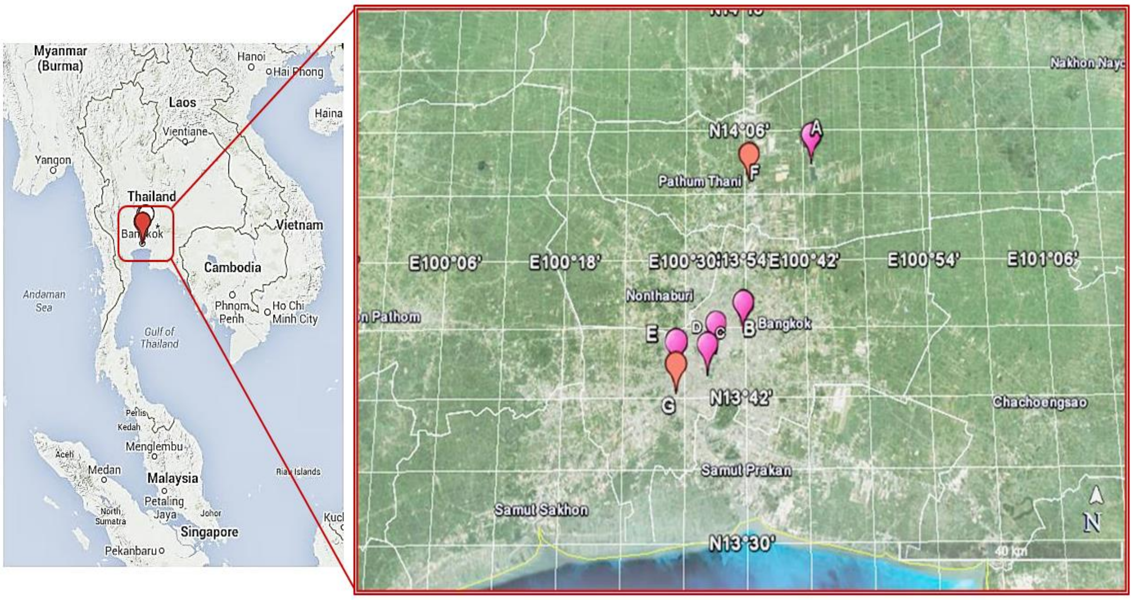


Figure 3.2. Map of OFP sites in Bangkok and the adjacent in 2008-2013, Main stations: (A) ERTC, (B) CC, (C) DD, (D) CUH, (E) BSD and alternative stations: (F) BSU (G) ThBri were employed as the alternations of (A) and (D) for air quality data other than VOCs

3.2 Evaluating OFP and OPC levels

The VOCs and oxygenated hydrocarbons sampling points were located on the PCD air quality monitoring stations where were 1.5-meter points from main traffic roads and sampler probe were around 3 to 6 meters above the ground for roadside stations, and distant from the focal street approximately 15 meters with sampling probe heights were above the ground roughly 3 to 6 meters or not exceeded 30 degrees for residential area sites, as imaged in Figure 3.3 (USEPA, 2013; PCD, 2007). VOCs including oxygenated HCs monthly samples were 24-hr whole air integrated samplings followed the USEPA compendium method TO-11A and TO-15A requirements, which were the accumulated sampling at low flow rate over 24 hours for each sample. The samples were then analyzed and quantified by gas chromatography/mass spectrometry (GC/MS) and High-performance liquid chromatography equipped with UV-Vis detector (HPLC/UV-Vis) for VOCs and carbonyl compounds respectively (USEPA, 1999; PCD, 2007).

Samples of ozone and NOx were quantified by online Chemiluminescence technique while CO samples were determined by non- dispersive infrared detection (MoSTE, 1995; MoNRE; 2007, 2009).

Table 3.2 summary of air pollutants sampling and analyses methods for this study

Pollutants	Sampling & Analysis Method
VOCs	TO-15: Canisters, GC/MS
Oxygenated HCs	TO-11, 2,4-Dinitrophenylhydrazine (DNPH) cartridge, HPLC equipped with UV dettector
NO & O_3	Chemiluminescence detection
CO	Non- dispersive infrared detection

Figure 3.3 Air pollutants sampling points over PCD Air Quality Monitoring Station at Bansomdej Chaopraya Rajabhat University Station

3.2.1. Determining OFP and OPC levels

The formulas in Eq. (3.1) – (3.2) were applied to evaluate the potential of surface ozone formation and contribution of ozone production towards individual VOC. The target pollutants and photochemical ozone creation production indices (POCP) were indicated in Table 3.3.

$$OFP_i\ [\mu g \cdot m^{-3}] \ = \ C_{VOC_i}\left(\mu g \cdot m^{-3}\right) \ \times \ POCP_i \qquad (3.1)$$

$$\text{Ozone production contribution} = \left[{OFP_i}\Big/{\sum OFP_i}\right] x100 \qquad (3.2)$$

where *OFP* denotes the ozone formation potential, C_{VOC_i} refers to the concentration of i^{th} VOC and *POCP* is the photochemical ozone creation potential coefficient.

Table 3.3 –Target VOCs and their POCPs

VOCs	POCP[a]	VOCs	POCP[a]
Hydrocarbons		Chloroform	0
1,3-Butadiene	89	Carbon Tetrachloride	0
Benzene	10	Chloromethane	1.0
Toluene	44	Chloroethane	11
o-Xylene	78	1,1-Dichloroethylene	52.60
m-Xylene	86	3-Chloropropene	46
p-Xylene	72	Dichloromethane	3.00
Styrene	5	1,1-Dichloroethane	54.00
Ethylbenzene	46	1,2-Dichloroethane	-1.00
1-Ethyl-4-methylbenzene	63	1,1,1-Trichloroethane	-1.00
1,2,4-Trimethylbenzene	110	1,1,2-Trichloroethane	3.40
1,3,5-Trimethylbenzene	107	1,1,2,2-Tetrachloroethane	1.00

Table 3.3 Target VOCs and their POCPs (Cont'd)

VOCs	POCP[a]	VOCs	POCP[a]
Oxygenated HCs		1,2-Dichloropropane	0.70
Formaldehyde	46	cis-1,2-Dichloroethylene	42.00
Acetaldehyde	55	Trichloroethylene	29.00
Acrolein	90.4	Tetrachloroethylene	1.00
Propionaldehyde	72	cis-1,3-Dichloropropene	0
Halogenated HCs		trans-1,3-Dichloropropene	0
Bromomethane	0.60	Chlorobenzene	9.90
Halogenated HCs		trans-1,3-Dichloropropene	0
Bromomethane	0.60	Chlorobenzene	9.90
1,2-Dibromoethane	-1.00	Benzyl Chloride	20.10
Vinyl chloride	36.10	1,2,4-Trichlorobenzene	0
1,2-Dichlorobenzene	12.00	**Other HCs**	
1,3-Dichlorobenzene	12.00	Acrylonitrile	25.00[b]
1,4-Dichlorobenzene	12.00		

[a]Derwent *et al.*, 2007. [b]Ontario Ministry of the Environment, 2000.

3.3 Investigating Impacts of Predictors on Ozone Levels

3.3.1. GAM, Model Development and Performance

The relationships between the response and explanatory variables in generalized additive model are described by $\eta = g(\mu)$, where η is the linear predictor and g(μ) denotes a link function. The fundamental of generalized linear model is expressed as: $y_{ij} = \mu+\tau_i+\varepsilon_{ij}$, where μ is an overall mean, τ_i denotes i^{th} treatment effects and ε_{ij} indicates the experimental residual. Then the simple additive model can be defined in Eq. (3.3).

$$\eta = \mathrm{g}(\mu) = \log(y_i) = \beta_0 + \sum_{j=1}^{n} S_{ij}(x_{ij}) + \varepsilon_i \qquad (3.3)$$

where yi is the ith ozone concentration, β_0 is the overall mean of the response or an intercept of the scatter plot and *Sj(xij)* is the smooth function of i^{th} value of covariate *j* (i.e. temperature, pressure,..., global radiation, NOx, CO, VOC1, VOC2,..., VOC38, excluding VOCs with POCP indices equal to zero) and n is the total number of covariates, and $\boldsymbol{\varepsilon}_i$ is the i^{th} residual.

$$\begin{aligned} \text{Log (Ozone)} &= \beta_0 + \Sigma\, S_{ij} * (X_{ij}) + \text{error}_i \\ &= \text{intercept} + \Sigma[S_{Metij} * (\text{Met}_{ij})] + [S_{NOx} * (C_{NOx})] \\ &\quad + [S_{CO} * (C_{CO})] + \Sigma[S_{OFPij} * (\text{OFP}_{ij})] \qquad (3.4) \end{aligned}$$

where S_{Metij} and Met_{ij} are the spline functions and levels of meteorological variables including global radiation, relative humidity, wind speed, wind direction, atmospheric pressure and temperature; S_{NOx} and C_{NOx} denote the spline function and ambient concentration of NOx; S_{CO} and C_{CO} are the spline function and surface concentration of CO and S_{OFPij} and OFP_{ij} define the spline function and OFP level of individual VOC.

The Poisson regression model using smoothing splines smoother, with the categorized predictors of the study sites and the sampling months, were used to investigate the interactive effects between atmospheric ozone level and its precursors, in terms of VOCs OFP levels and concentrations of NOx and CO, associated with local meteorological conditions. The quantile (Q-Q) plots were accomplished by auto-regression GAM at 95% confident level. The impacts of all predictors to ozone formation were tested from six distinct models as follows:

(a) Average ozone against meteorological predictors.

(b) Average ozone against meteorological predictors + inorganic ozone precursors.

(c) Average ozone against meteorological predictors + inorganic ozone precursors + oxygenated hydrocarbons.

(d) Average ozone against meteorological predictors + inorganic ozone precursors + oxygenated hydrocarbons + acrylonitrile.

(e) Average ozone against meteorological predictors + inorganic ozone precursors + oxygenated hydrocarbons + acrylonitrile + hydrocarbons.

(f) Average ozone against meteorological predictors + inorganic ozone precursors + oxygenated hydrocarbons + acrylonitrile + hydrocarbons + halogenated hydrocarbons.

(g) Halogenated hydrocarbons (run to confirm the impacts of halogenated hydrocarbons).

In addition, the goodness of fit was evaluated similarly to a generalized linear model, defined by Deviance (D) statistic: D = -2 * (*Lm - Ls*), where Lm represented the maximized log-likelihood value for the model of interest, and *Ls* is the log-likelihood for the saturated model (Agresti, 1996).

3.3.2. Impacts of Predictors

The impacts of predictors, which were the levels of meteorological parameters, NO_x, CO and OFPs of VOCs, were evaluated by their effects to a Poisson linear regression plot between the response of spline function of each predictor and log link function of ambient ozone concentrations. The performance of GAM was determined from normalized standard deviation (NSD), normalized absolute error (NAE), mean absolute error (MAE), normalized absolute error, root mean squared error (RMSE), normalized root mean squared error (NRMSE), degree of agreement (d), normalized bias (NB, %), correlation coefficient (R) and coefficient of determination (R^2) as formulated in Eq. (3.5) to (3.11)

$$NSD = \frac{SD_P}{SD_O} \tag{3.5}$$

$$MAE = \frac{1}{N}\sum_{i=1}^{n}\left|P_i - O_i\right| \tag{3.6}$$

$$RMSE = \sqrt{\frac{1}{N}(\sum_{i=1}^{n}(P_i - O_i)^{2}} \tag{3.7}$$

$$NAE = \frac{\sum_{i=1}^{n}\left[P_i - O_i\right]}{\sum_{i=1}^{n} O_i} \tag{3.8}$$

$$NB = \frac{1}{N}\sum_{i=1}^{n}\frac{O_i - P_i}{O_i} \tag{3.9}$$

$$d = 1 - \frac{\sum_{i=1}^{n}(P_i - O_i)^2}{\sum_{i=1}^{n}(|P_i - \overline{O}| + |O_i - \overline{O}|)^2} \tag{3.10}$$

where P_i denote the predicted value, O_i is the observed value, SD is the standard deviation.

CHAPTER IV

RESULTS AND DISCUSSION

4.1. Ozone Concentration Levels

During 2008 to 2013, the tropospheric ozone concentrations levels over five study sites of Bangkok and the adjacent area were vary from site to site. The monthly average and maximum ozone concentrations ranged from 14.37 to 35.87 and 112.78 to 158.25 $\mu g.m^{-3}$, illustrated in Figure 4.1 (a) and (b), consequently. The lowest peak and average ozone concentrations were found at Dindaeng site, the inner district of Bangkok and the highest levels by Bangkok University at Rangsit, the alternative site of ERTC for air quality monitoring, downwind site in Pathumthani Province. These might cause from the mechanisms of photochemical reactions that needed time to cook and produce ozone with long range transport at downwind suburb area, because the yearly average wind directions over the 5 stations were mainly from SSW, as imaged in Figure 4.2. These were correspondingly to the previous reports, revealing that the area of Bangkok and the adjacent provinces were impacted by SW and NE monsoon (Kim Oanh, 2008; Suwattiga and Limpaseni, 2005). However, the ozone levels of the other suburban sites, namely Bansomdej Chao Praya and also Thonburi Sub-power Station, which was employed as the alternative site of Chulalongkorn Memorial Hospital, were also higher than the ozone concentrations of inner districts of Bangkok. These might suggest that the two SW suburban sites of Bangkok, where were nearly to the gulf of Thailand, were associated by vehicle and industrial emission sources in Samut prakan and Samut Sakhon provinces with additional effects from sea breeze. Mixing of chlorine (Cl) in sea salt and urban NO_x could availably make crucial conditions to produce nitryl chloride ($ClNO_2$), which interacted in photolysis during the daytime yielded chlorine radicals, regenerated nitrogen dioxide (NO_2) and ozone production might incline from their reactions (Wagner, et al., 2012; Cohan, et al., 2008; Hov, 1985).

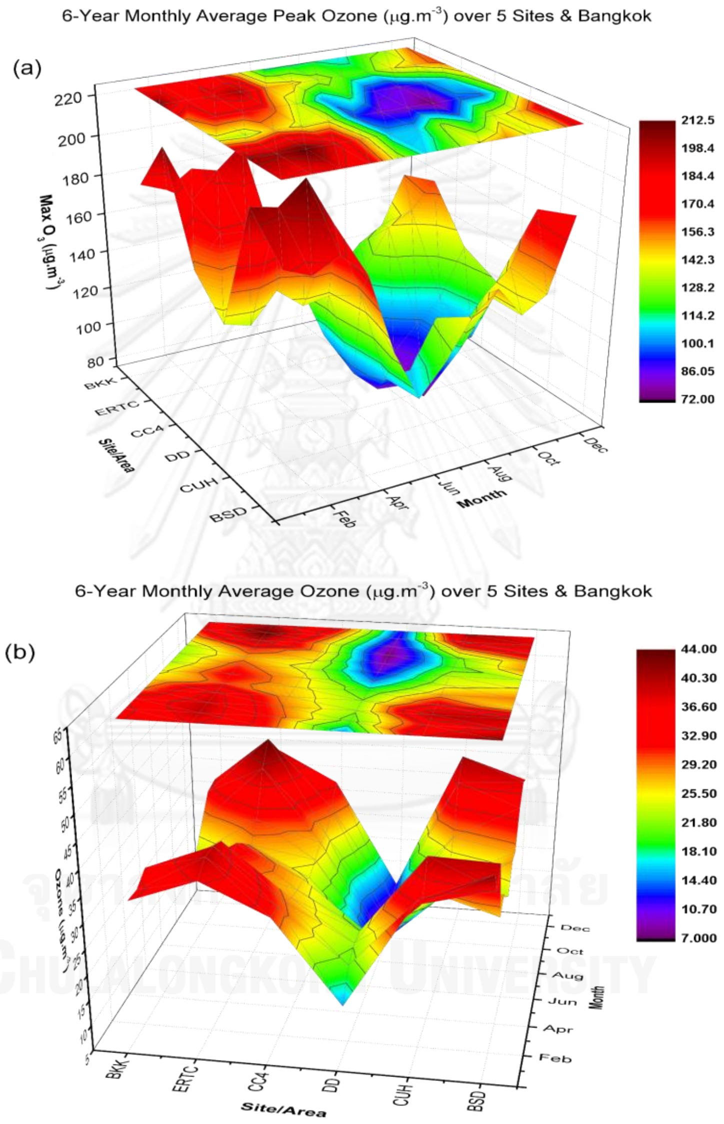
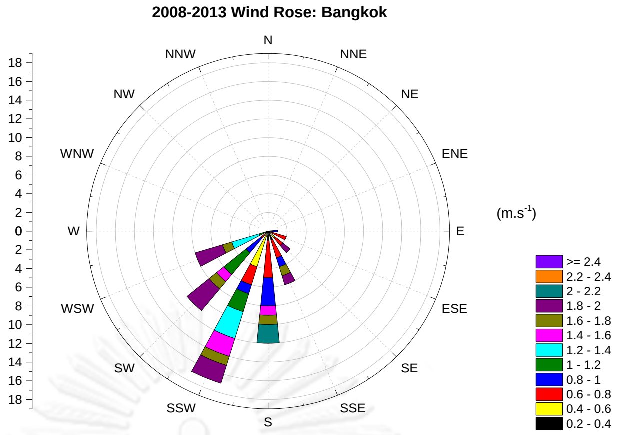


Figure 4.1. 3D Surface with projection plots of 6-year monthly averages of (a) maximum and (b) average ozone concentrations over 5 study sites and overall for Bangkok and vicinity area.



(a) ERTC (b) CC4 (c) DD (d) CUH (e) BSD

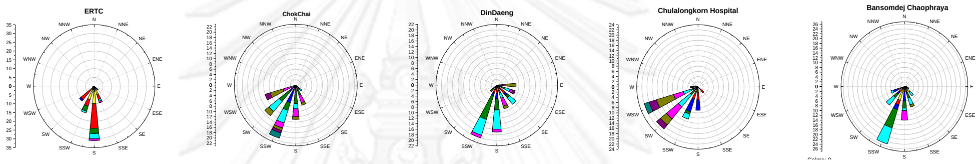


Figure 4.2. Average wind directions over Bangkok and vicinity area during 2008-2013

In addition, from 2008 to 2013, the means for monthly average and maximum of ambient ozone levels were seen to be 28.28 and 141.75 μg.m^{-3} separately. However, the highest level of monthly ozone concentration reached to 306 μg.m^{-3} which much exceeded the ozone air quality standard of Thailand at 200 μg.m^{-3} (100 ppb), as showed in Figure 4.3. In a year round, the levels of surface ozone were low between May through October and rise up from November to April. These episodes might be impacted by local meteorological conditions: the interval for late of May to October was high in percent relative humidity due to it was in rainy season with higher numbers of precipitation than the interval of November through April, which was in the condition of dry weather/low humidity (both in cool and dry seasons) with higher temperature and strength of solar radiation (in summer). Moreover, in dry weather and high temperature, volatilization of VOCs ozone precursors were in higher rates compared to wet season; they were then in reactive gaseous forms and incited to participate in photochemical reactions more than in wet season (Latif et al., 2012; Sahu et al., 2011; U.S EPA, 2007; Gold, 2005; Washington, 1996).

Table 4.1 summarized the data levels of surface ozone concentration together with VOCs' OFP, inorganic ozone precursors and meteorological predictors for Bangkok (and vicinity).

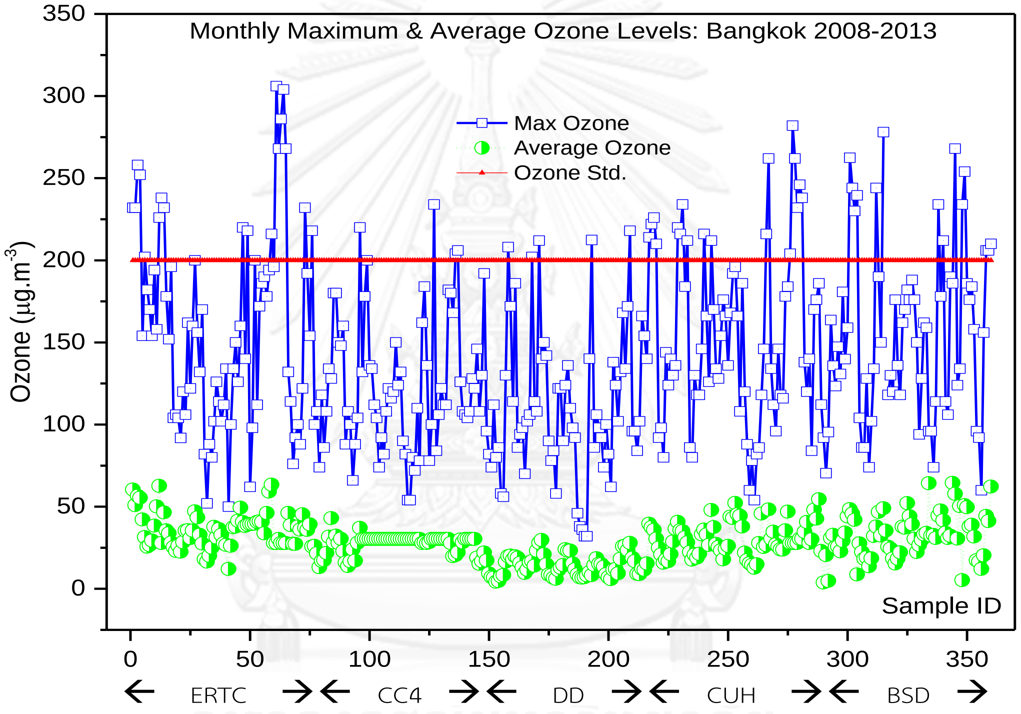


Figure 4.3. Variations of maximum and average of monthly ozone compare to the ozone standard, in Bangkok 2008-2013.

The concentration of surface ozone observed over the year 2008 to 2013 at all sites displayed in Figure 4.3 were found to be beyond the standard level for maximum ozone. However, at ERTC site located at downwind of Bangkok, the maximum ozone was higher than other sites at upwind. Whereas, CUH and BSD sites might get impacted by the emission sources from Samut Prakarn and Samut Sakhon province and also the effects from the reactions of halogenated hydrocarbons as stated previously.

4.2. Local Meteorological Conditions

The meteorological conditions in BMR have been predominantly by the tropical monsoon due to the geographic location of Thailand (Komatsu et al., 2003; Hashimoto et al., 2004). Hence the temperature in BMR throughout the years of 2008 to 2013 ranged between 25°C and 33°C. While the atmospheric pressures were approximately 751 to 762 mmHg (0.99 to 1.0 atmosphere) and relative humidity were fluctuate in the ranges from 48 to 89 percent. The wind directions were mainly from SSW as mentioned previously, whereas the wind speeds at ten-meter-height go between 0.19-2.28 ms^{-1}. The temperature over time from site to site during 2008 to 2013 were quite alike. Though the sites in urban area, DinDaeng and Chokchai stations, were seemly somewhat higher than the suburban sites liked ERTC and Bansomdej Chaopraya stations. There might be affected by “heat urban islands”. Additionally, the temperatures at the alternative site of Chulalongkorn Hospital site (Thonbuburi Sub-power Station) were a little lower than other urban sites due to its location was not in the center but suburban of Bangkok and nearly to the gulf of Thaialnd that caused more ventilation and dropped the surrounding temperature down. By the effects of heat urban islands, DinDaeng station located in the center of Bangkok, in contradiction to the temperature, pressure could be affected from rising of local warm air; while heat got advanced the particular atmospheric pressure descended (as the temperature rose up in the metropolitan area, it pulled in heat from the neighboring area and locally caused the area to be low pressure). In case of ERTC station in Pathumthani Province (EANET, 2000) the pressure was lower than the sites in Bangkok might be because of the height above sea level at ERTC was higher than the sites in Bangkok (BMA, 2009).

4.3. Trends of VOCs concentrations

Even though individual VOCs contributed to ozone production differently, the summation of VOCs concentration/total VOCs could roughly suggest the state of ozone formation. From 2008 to 2013, Figure 4.4, illustrated that monthly VOCs levels in Bangkok and vicinity have been in upward trends throughout the year correspondingly to ozone trends. Likewise, VOCs levels descended in the periods of May through September, which were in wet season, then initially ascended around October and went through April during cool and dry seasons.

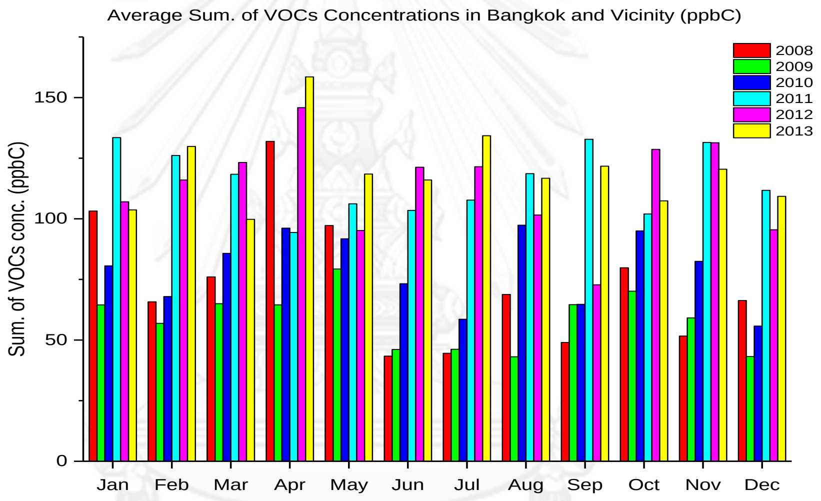


Figure 4.4. Trends of Monthly VOCs in a year round during 2008 to 2013.

All data were cleaned up, then did normality test. It was found that some of predictors; for example,

Table 4.1 Summary of data for overall area of Bangkok

Variable/ VOCs' OFP ($\mu g.m^{-3}$)	Mean	Median	Minimum	Maximum	Percentile		SD
					(10)	(90)	
Maximum O_3	141.75	132.00	32.00	306.00	80.00	219.00	54.76
Average O_3	28.28	28.26	3.77	64.46	12.07	44.49	12.24
Meteorological factors:							
Temperature (^oC)	29.46	29.43	25.55	33.29	27.9	31.3	1.30
Pressure (mmHg)	756.95	756.90	751.26	762.35	754.33	759.51	2.03
Relative Humidity (%)	68.52	68.20	48.24	88.68	60.19	77.57	7.03
Wind Speed ($m.s^{-1}$)	1.08	1.01	0.19	2.28	0.55	1.76	0.45
Wind Direction (°)	193.67	195.50	85.09	282.56	142.23	238.93	36.57
Global Radiation ($W.m^{-2}$)	149.56	150.33	23.74	282.86	87.35	209.29	50.08
Inorganic gases:							
CO	995.81	1019.91	145.49	2176.42	367.86	1543.29	447.06
NO_x	142.63	138.48	33.46	373.27	55.11	258.28	78.42
Oxygenated HCs:							
Formaldehyde	487.69	483.53	0.39	972.90	278.67	705.82	166.28
Acetaldehyde	299.37	305.69	0.39	631.55	165.99	445.70	115.02
Acrolein	31.08	30.90	1.18	90.40	3.98	57.40	19.87
Propionaldehyde	47.53	48.02	1.15	108.72	15.12	79.92	24.19
HCs:							
1,3-Butadiene	1.92	1.95	0.19	3.81	0.89	2.67	0.71
Benzene	24.40	19.82	0.22	74.00	7.10	49.93	16.86
Toluene	916.39	880.00	0.81	2728.00	206.80	1845.80	607.28
Ethyl benzene	105.10	101.20	0.39	303.60	21.62	207.00	69.24

*OFP index is zero.

Table 4.1 Summary of data for overall area of Bangkok (Cont'd)

Variable/ VOCs' OFP ($\mu g.m^{-3}$)	Mean	Median	Minimum	Maximum	Percentile (10)	Percentile (90)	SD
HCs:							
m-Xylene	225.52	206.40	0.97	730.41	47.00	478.53	169.99
p-Xylene	86.78	72.00	0.81	296.32	9.36	201.48	70.00
Styrene	3.81	3.73	0.05	10.00	0.80	7.00	2.34
o-Xylene	117.34	117.00	0.88	366.60	25.74	249.60	85.64
1-Ethyl-4-methylbenzene	53.52	50.40	0.89	170.10	7.56	113.40	39.07
1,3,5-Trimethylbenzene	260.85	139.10	2.27	1070.00	16.05	713.24	270.44
1,2,4-Trimethylbenzene	145.01	110.00	3.27	506.00	7.93	309.68	121.22
Halogenated HCs:							
Bromomethane	0.03	0.03	0.01	0.07	0.02	0.05	0.01
1,2-Dibromoethane	0.05	0.06	0.00	0.13	0.02	0.09	0.03
Vinyl chloride	0.90	0.72	0.17	2.35	0.36	1.81	0.51
Chloroform	0*	0*	0*	0*	0*	0*	0*
Carbon tetrachloride	0*	0*	0*	0*	0*	0*	0*
Chloromethane	1.33	1.30	0.01	3.10	0.52	2.15	0.64
Chloroethane	0.30	0.31	0.07	0.66	0.11	0.53	0.14
1,1-Dichloroethylene	2.31	1.58	0.39	5.07	1.05	3.68	1.05
3-Chloropropene	1.44	1.38	0.44	3.05	0.92	2.30	0.54
Dichloromethane	2.72	2.61	0.03	8.10	0.27	5.47	1.86
1,1-Dichloroethane	1.96	1.62	0.06	4.71	0.54	3.24	0.97
1,2-Dichloroethane	-0.06	-0.06	-0.15	-0.01	-0.10	-0.02	0.03
1,1,1-Trichloroethane	-0.06	-0.06	-0.17	0.00	-0.11	-0.02	0.04

*OFP index is zero.

Table 4.1 Summary of data for overall area of Bangkok (Cont'd)

Variable/ VOCs' OFP (μg.m^{-3})	Mean	Median	Minimum	Maximum	Percentile		SD
					(10)	(90)	
1,1,2-Trichloroethane	0.13	0.13	0.02	0.32	0.03	0.20	0.07
1,1,2,2-Tetrachloroethane	0.05	0.05	0.01	0.12	0.02	0.09	0.02
1,2-Dichloropropane	0.04	0.04	0.00	0.12	0.01	0.07	0.03
cis-1,2-Dichloroethylene	1.60	1.26	0.42	3.36	0.63	2.94	0.86
Trichloroethylene	9.92	7.54	0.01	34.80	0.87	22.91	8.72
Tetrachloroethylene	0.17	0.13	0.01	0.58	0.02	0.36	0.14
cis-1,3-Dichloropropene	0*	0*	0*	0*	0*	0*	0*
trans-1,3-Dichloropropene	0*	0*	0*	0*	0*	0*	0*
Chlorobenzene	0.29	0.30	0.10	0.55	0.13	0.40	0.11
Benzyl Chloride	1.17	1.41	0.06	2.71	0.43	1.61	0.54
1,2-Dichlorobenzene	0.59	0.61	0.17	1.27	0.24	0.96	0.25
1,3-Dichlorobenzene	3.82	1.89	0.02	16.80	0.48	11.64	4.33
1,4-Dichlorobenzene	0.72	0.72	0.34	1.39	0.42	0.96	0.23
1,2,4-Trichlorobenzene	0*	0*	0*	0*	0*	0*	0*
Other HCs:							
Acrylonitrile	1.24	1.16	0.20	3.00	0.50	2.00	0.61

*OFP index is zero.

4.4. Ozone formation potential and production contribution

Toluene as a backbone hydrocarbon in urban atmosphere, which released from the combustion form automobiles and coke oven industry (WHO, 2000) the average

OFP level of toluene were the highest rank, about 916.39 $\mu g.m^{-3}$, found in Bangkok area. The other aromatic hydrocarbons, benzene, o, m, p-xylene and ethylbenzne, their OFPs were found to be in moderate levels, ranged from 22.40 to 225.52 $\mu g.m^{-3}$. In the cases of oxygenated hydrocarbon: formaldehyde, acetaldehyde were 487.69 and 299.37 $\mu g.m^{-3}$, which were higher than the OFPs levels of aromatic HCs, with their high POCP indices of reactivity (Derwent et al., 2007) These compounds were the principal species released from biomass and biofuels oxidation which found from automobile exhaust pipes (Wei, 2008; Kim Oanh, 2008). The OFP levels of halogenated HCs, which generally caused from industrial sectors where were around suburb of Bangkok (Suthawaree, 2012; PCD, 2007), were initiated at low level compared to other groups of VOCs. The two lowest average OFPs were 1,2-dichloroethane and 1,1,1-trichloroethane about -0.06 $\mu g.m^{-3}$ equally, summarized in Table 4.2 and Figure 4.5. In addition, the OFP trends, excluding halogenated HCs, found in the central Taiwan (Tsai et al., 2007) and Bangkok were alike toluene was the most abundant specie compared to all other VOCs.

However, the ratio of toluene OFP/benzene OFP in the two countries were different; in other words, the amounts of ambient VOCs in the two areas were not in the same scale. It inferred that the emission sources and locally meteorological conditions in both countries were dissimilar. Whereas the greatest MIR, another scale of ozone formation, created in Shanghai, China were cis & trans-2-butene, propene and isoprene (Cai, et al., 2010). It emphasized that emission sources and local meteorology were significant to ozone formation (U.S EPA, 2007).

Table 4.2. OFP and OPC levels of VOCs and GAM results for Bangkok and vicinity

Variable	POCP Index^a	Level/ OFP (μg.m$^{-3)}$		OPC (%)	GAM		
		Mean	SD		Coefficient	Z-score	Sig.
Maximum ozone		141.75	54.83				
Average ozone		28.28	12.24				
Intercept					50.39		
Meteorological factors							
Temperature (^{O}C)		29.46	1.30		-4.56E-02	6.30	0.1574
Pressure (mmHg)		756.95	2.03		-4.29E-02	-3.41	0.8435
Relative Humidity (%)		68.52	7.03		-1.36E-02	-4.94	**0.0008**
Meteorological factors							
Wind Speed (m.s^{-1})		1.08	0.45		-1.94E-01	-5.10	**0.0084**
Wind Direction (^{O})		193.67	36.57		1.27E-03	-5.40	**0.0000**
Global Radiation (W.m^{-2})		149.56	50.08		7.23E-04	2.62	**0.0028**
Inorganic gases:							
CO		995.81	447.06		7.51E-05	1.85	**0.0412**
NO_x		142.63	78.42		-4.35E-04	-1.98	**0.0076**
Oxygenated HCs				**39.39**			
Formaldehyde	46	487.69	166.28	18.38	-2.84E-04	-3.10	**0.0161**
Acetaldehyde	55	299.37	115.02	11.36	3.39E-04	2.96	0.1972
Acrolein	90.4	31.08	19.87	1.23	-6.10E-04	-1.01	0.0585
Propionaldehyde	72	47.53	24.19	1.81	9.01E-04	1.59	0.6026
HCs				**59.51**			
1,3-Butadiene	89	1.92	0.71	0.07	-3.33E-02	-1.33	**0.0121**
Benzene	10	24.40	16.86	0.86	-2.12E-04	-0.21	0.2009
Toluene	44	916.39	607.28	32.30	1.48E-05	0.50	0.5942

Table 4.2. OFP and OPC levels of VOCs and GAM results for Bangkok and vicinity (Cont'd)

Variable	POCP Index[a]	Level/ OFP ($\mu g.m^{-3}$)		OPC (%)	GAM		
		Mean	SD		Coefficient	Z-score	Sig.
Ethyl benzene	46	105.10	69.24	3.70	-5.07E-04	-1.95	0.0775
m-Xylene	86	225.52	169.99	7.95	3.36E-04	2.47	**0.0000**
p-Xylene	72	86.78	70.00	3.06	5.66E-04	1.77	0.2506
Styrene	5	3.81	2.34	0.13	-1.67E-02	-3.03	**0.0092**
o-Xylene	78	117.34	85.64	4.14	-9.98E-05	-0.43	**0.0000**
1-Ethyl-4-methylbenzene	63	53.52	39.07	1.89	2.68E-04	0.56	0.6216
1,3,5-Trimethylbenzene	107	260.85	270.44	9.19	-5.32E-05	-0.82	**0.0006**
1,2,4-Trimethylbenzene	110	145.01	121.22	5.11	-1.71E-04	-1.30	**0.0000**
Halogenated HCs				**1.05**			
Bromomethane	0.03	0.01	0.03	<0.01	6.83E+00	5.91	**0.0377**
1,2-Dibromoethane	0.05	0.03	0.05	<0.01	3.92E+00	6.13	0.8634
Vinyl chloride	0.90	0.51	0.90	<0.01	-1.88E-01	-5.08	0.7088
1,1,2-Trichloroethane	3.4	0.13	0.07	<0.01	-7.55E-01	-2.41	**0.0386**
1,1,2,2-Tetrachloroethane	1	0.05	0.02	<0.01	2.40E+00	3.37	0.6643
1,2-Dichloropropane	0.7	0.04	0.03	<0.01	1.95E+00	3.62	**0.0000**
cis-1,2-Dichloroethylene	42	1.60	0.86	0.06	3.43E-02	1.06	0.7700
Trichloroethylene	29	9.92	8.72	0.34	1.44E-03	0.93	**0.0000**
Tetrachloroethylene	1	0.17	0.14	0.01	6.99E-02	0.64	0.5563
cis-1,3-Dichloropropene	0						
trans-1,3-Dichloropropene	0						
Chlorobenzene	9.9	0.29	0.11	0.01	-5.03E-01	-2.91	0.7806
Benzyl Chloride	20.1	1.17	0.54	0.05	6.17E-02	2.60	0.0687
1,2-Dichlorobenzene	12	0.59	0.25	0.02	-4.64E-02	-0.73	**0.0336**
1,3-Dichlorobenzene	12	3.82	4.33	0.12	-9.55E-03	-2.67	0.2023
1,4-Dichlorobenzene	12	0.72	0.23	0.03	-1.68E-01	-2.30	**0.0204**
1,2,4-Trichlorobenzene	0						
Other HCs				**0.05**			
Acrylonitrile	25[b]	1.24	0.61	0.05	9.29E-02	4.42	0.4669

[a]Derwent, 2007. [b]Ontario Ministry of Environment, 2000.

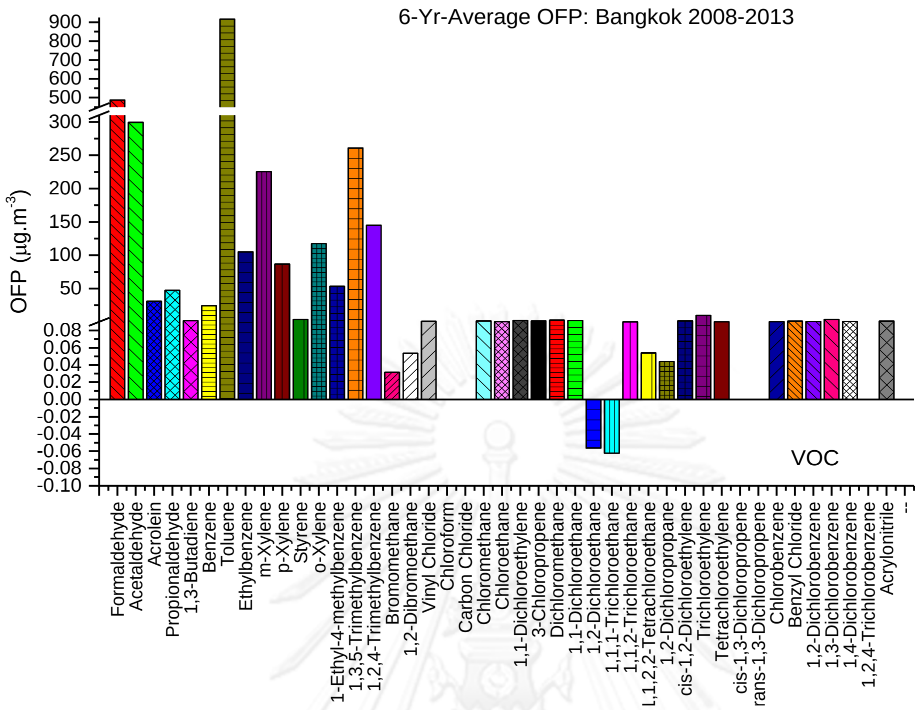


Figure 4.5. Six-year-average of ozone formation potential for each VOC in Bangkok 2008-2013 (a) Bangkok and surrounding areas (b) comparison sites

The ozone production contributions of all VOCs were similarly to the OFPs' trend depended on their molecular weights and POCP indices (Shin *et al.*, 2013; de Leeuw, 2002) and common HCs group was the largest significant group with 59.51% contribution, came after by oxygenated HCs, halogenated HCs and acrylonitrile with 39.39%, 1.05% and 0.05% independently, as appeared in Figure 4.6 and 4.7.

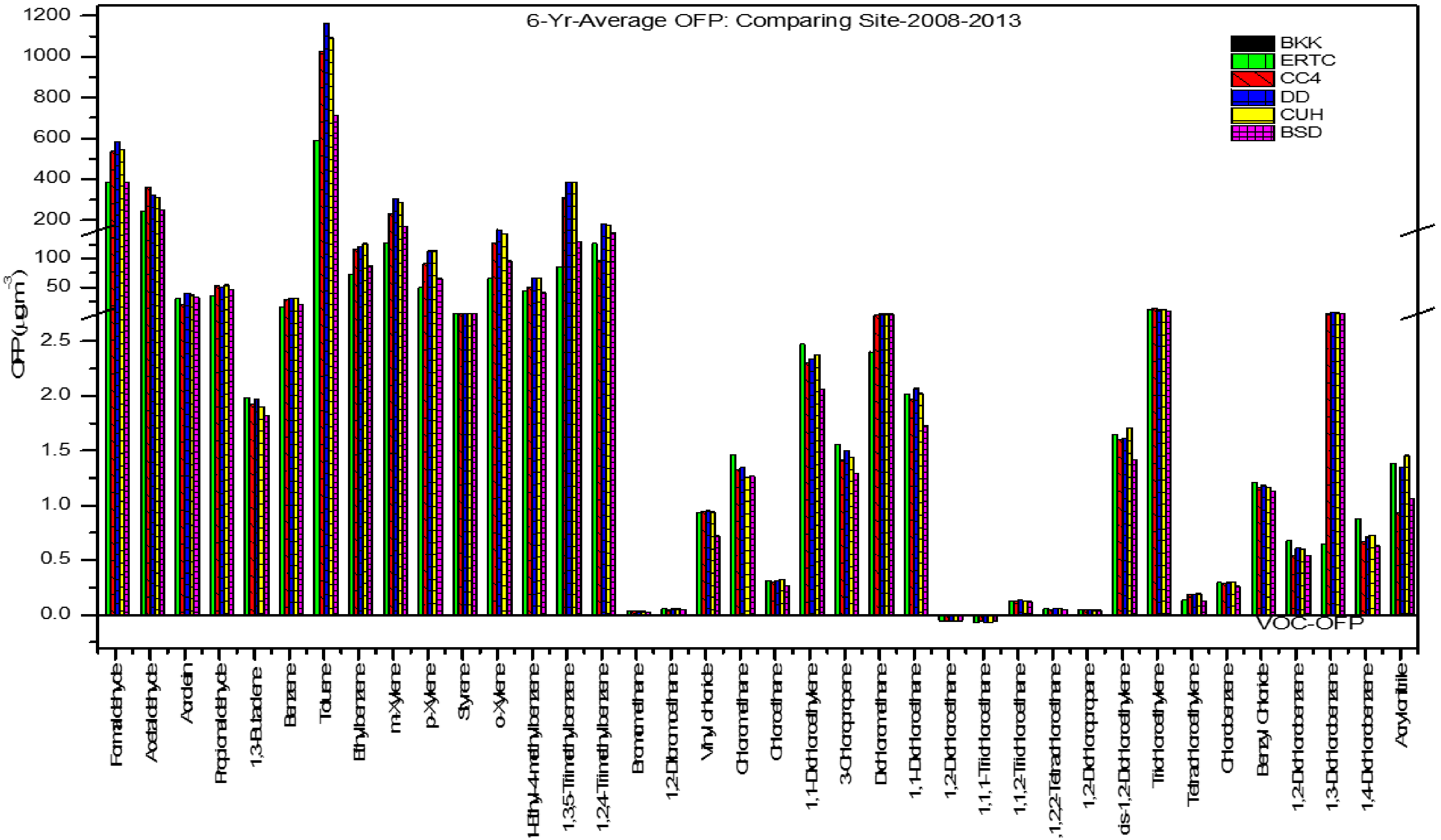


Figure 4.5b. Six-year-average of ozone formation production for each VOC in Bangkok 2008-2013: comparison sites

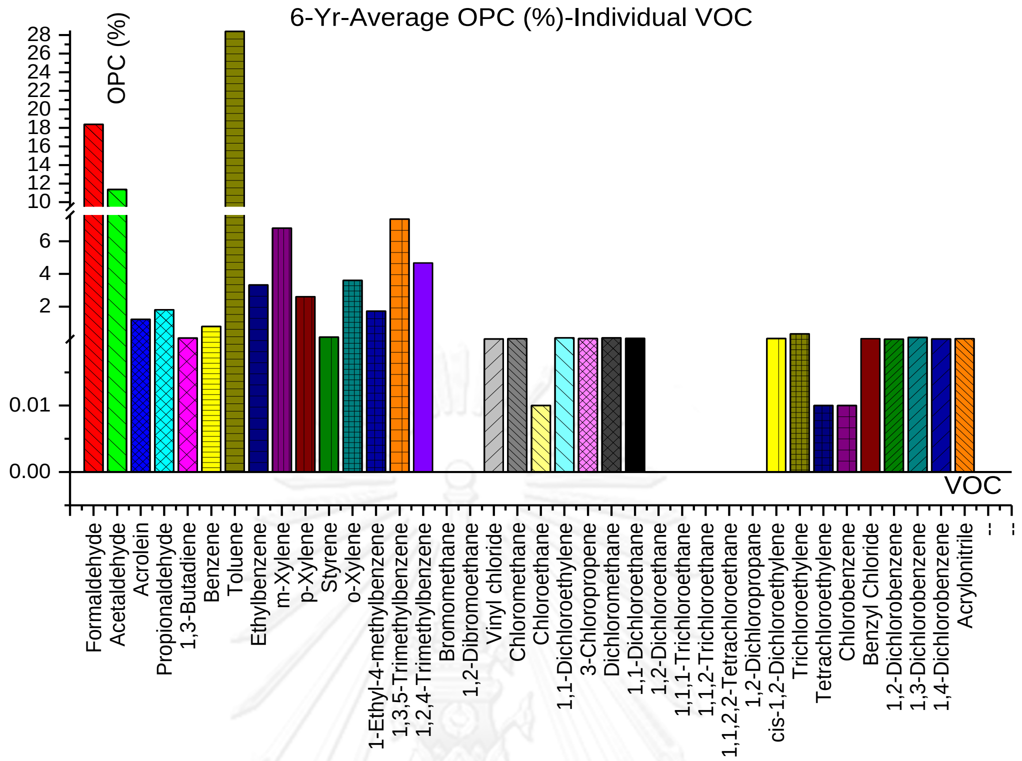


Figure 4.6. Six-year-average of ozone production contribution for individual of VOC in Bangkok 2008-2013

Even though the OPC levels of the four groups of hydrocarbons were insignificant over the five study sites, the individual OPC was diverse and significant for some VOCs. According to their emission source were dissimilar; the urban sites (e.g. DinDaeng, Chokchai) that had been impacted by transportation system and activities.

4.5. Generalized Additive Model (GAM)

The R^2 statistics, as the explanatory power of all studied models, indicated the impacts of locally meteorological parameters, inorganic ozone precursors and the OFPs of each VOC group on surface ozone levels by the difference in the R^2 of the model (a) to (f). Table 4.3 specified that meteorological predictors played a major role, with 60.75%, in the ozone formation, whereas halogenated HCs were

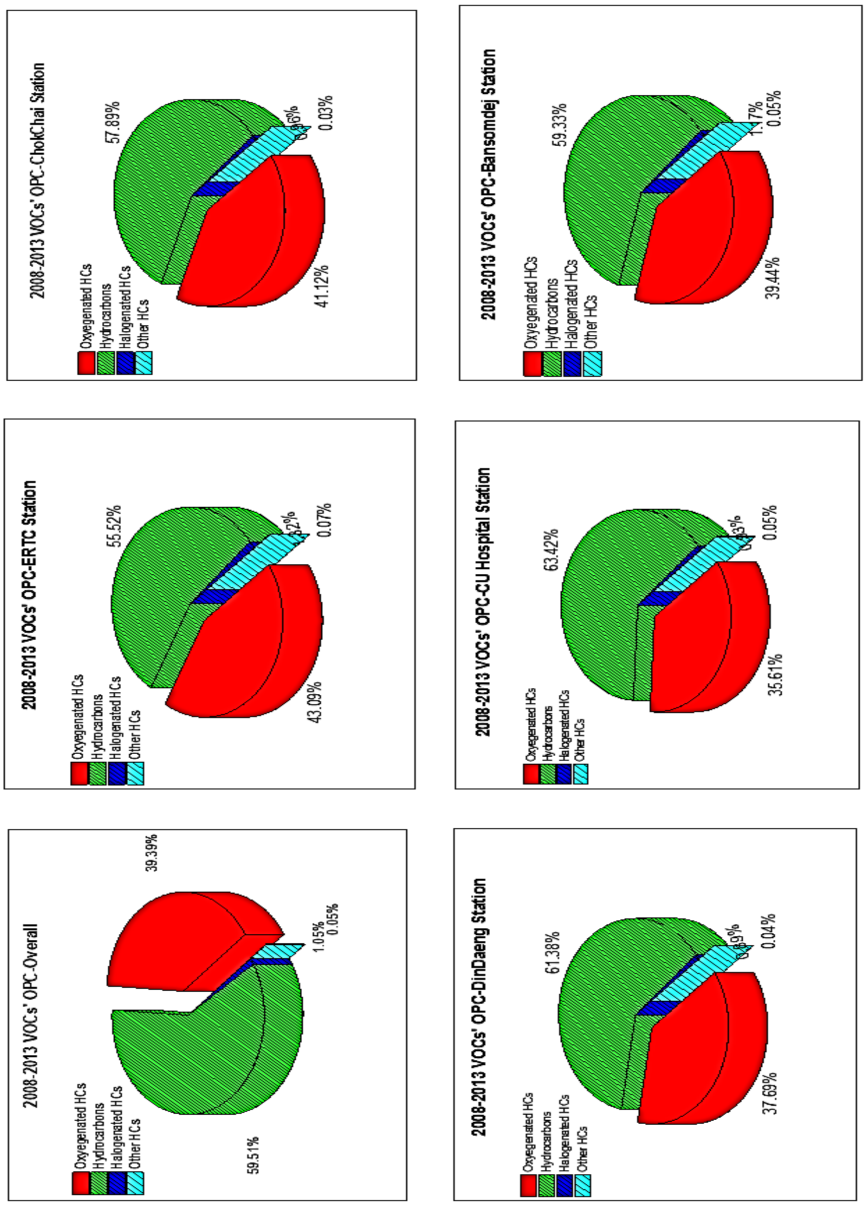


Figure 4.7a-f. Ozone production contribution of target VOCs in BMR from 2008 to 2013

participated in the process of ozone production over than typical HCs and oxygenated HCs, 9.39%, 6.01% and 1.57% consequently. In addition, the overall mean of theresponse was highly affected by halogenated HCs around 40.21% contradict to their contributions to ozone formation. This suggested that the association of the tropical climate with high temperature, humidity and solar radiation inclined the ozone production from halogenated HCs (Latif *et al.*, 2012; Sahu *et al.*, 2011; Hov, 1985).

However, acrylonitrile, as other HCs affected to R^2 about 0.83%. In addition, CO and NO_x, as inorganic ozone precursors, caused to R^2 change around 2.69%. In consideration of numbers of compounds in each group to % change of R^2, inorganic ozone precursors were rank at the top of all groups followed by acrylonitrile, HCs, halogenated HCs and oxygenated HCs orderly. While the ratio of deviance to degree of freedom for individual model was fairly steady from model (a) to (f) and model (g) was run to verify the impacts of halogenated HCs on ozone regression. The final scatter plot coupled with spline lines of selected predictors, imaged in Figure 4.8 a-d, of model (f) reached out the R^2 approximately 81.24% at 95%CI with deviance 373.01, residual degree of freedom 159.94 and RMSE 5.13 $\mu g.m^{-3}$ (=10.26 ppb). While the finding studied by Davis and Speckaman (1999), which employed GAM to forecast 8-hr-average of ozone, R^2 was ranging from 66% to 73% with RMSE ranged from 13.2 to 16.3 ppb, summarized in Table 4.4 and . Additionally, the fitted model carried out the overall R^2 around 58% through the estimation of spatial and temporal ambient ozone patterns related with elevation, maximum daily temperature and precipitation based on the log-likelihood (Preisler *et al.,* 2002).

Table 4.3. GAM statistical analysis for model (a) to (g) at scale estimate 1.0 and number of observation 360

Model conditions	Final deviance	Residual df	D_m/df	No. of smooths	Intercept (μ)	μchange (%)	R^2*100%	R^2 change (%)
a	780.35	319.94	2.44	39	38.00	0.00	60.75	0.00
b	726.83	311.98	2.33	43	38.06	0.16	63.44	2.69
c	695.64	295.93	2.35	45	37.29	-2.02	65.01	1.57
d	679.13	291.91	2.33	44	36.91	-1.02	65.84	0.83
e	559.59	247.90	2.26	52	35.94	-2.63	71.85	6.01
f*	373.01	159.94	2.33	68	50.39	40.21	81.24	9.39
g**	68522.33	255.98	267.68	52	3.57	NA	66.60	NA

*f detailed data in Table 4.2, **impacts of halogenated HCs only, detailed in Table 4.4.

Table 4.4 GAM detailed statistical analysis for model (g)

	GAM (coef.)	Sig.
Intercept	3.57E+00	
Bromomethane OFP	4.80E+00	**0.00**
1,2-Dibromoethane OFP	2.17E+00	**0.00**
Vinyl chloride OFP	-1.71E-01	**0.00**
Chloromethane OFP	-1.12E-02	**0.00**
Chloroethane OFP	-1.57E-01	**0.00**
1,1-Dichloroethylene OFP	5.92E-03	**0.00**
3-Chloropropene OFP	-1.42E-01	**0.00**
Dichloromethane OFP	8.71E-03	**0.00**
1,1-Dichloroethane OFP	-3.58E-02	**0.00**
1,2-Dichloroethane OFP	7.49E-01	**0.00**
1,1,1-Trichloroethane OFP	-1.16E+00	**0.00**
1,1,2-Trichloroethane OFP	-5.28E-01	**0.00**
1,1,2,2-Tetrachloroethane OFP	2.19E+00	**0.00**
1,2-Dichloropropane OFP	1.22E+00	**0.00**
cis-1,2-Dichloroethylene OFP	7.10E-02	**0.00**
Trichloroethylene OFP	-1.63E-03	**0.00**
Tetrachloroethylene OFP	2.13E-01	**0.00**
Chlorobenzene OFP	-2.85E-01	**0.00**
Benzyl Chloride OFP	9.42E-02	**0.00**
1,2-Dichlorobenzene OFP	-7.43E-02	**0.00**
1,3-Dichlorobenzene OFP	-7.04E-03	**0.00**
1,4-Dichlorobenzene OFP	1.08E-01	**0.00**

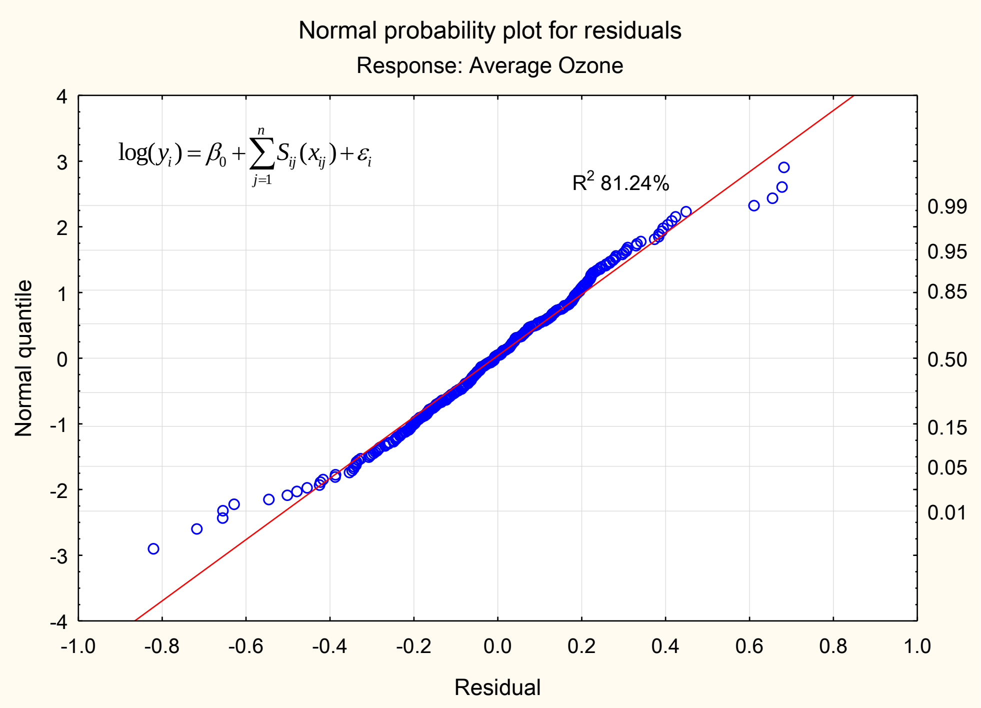


Figure 4.8a. Q-Q plot of residual and regressand ozone

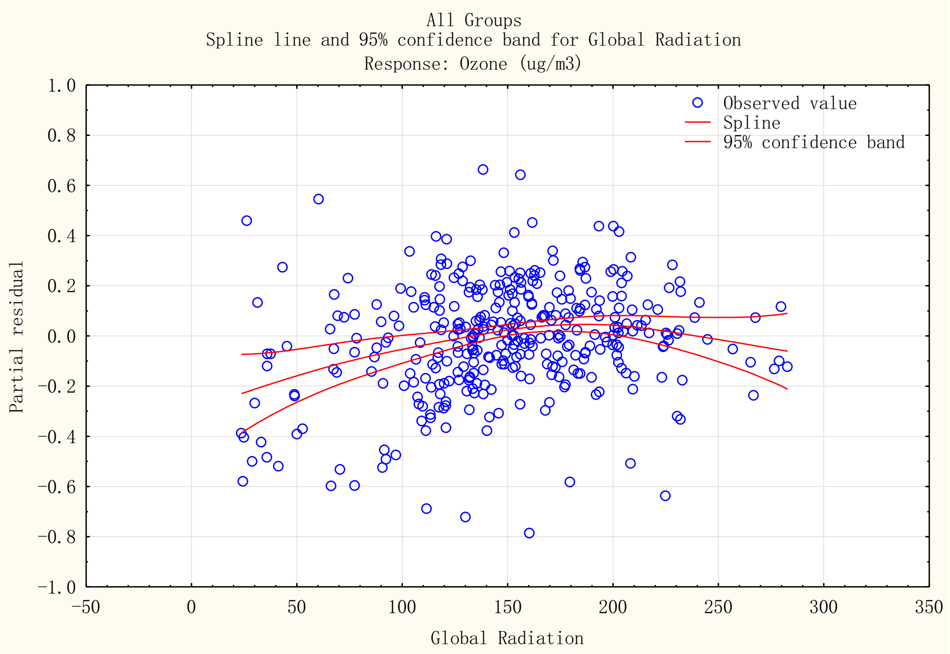


Figure 4.8b. Spline line of global radiation at 95%CI of cubic spline smoother

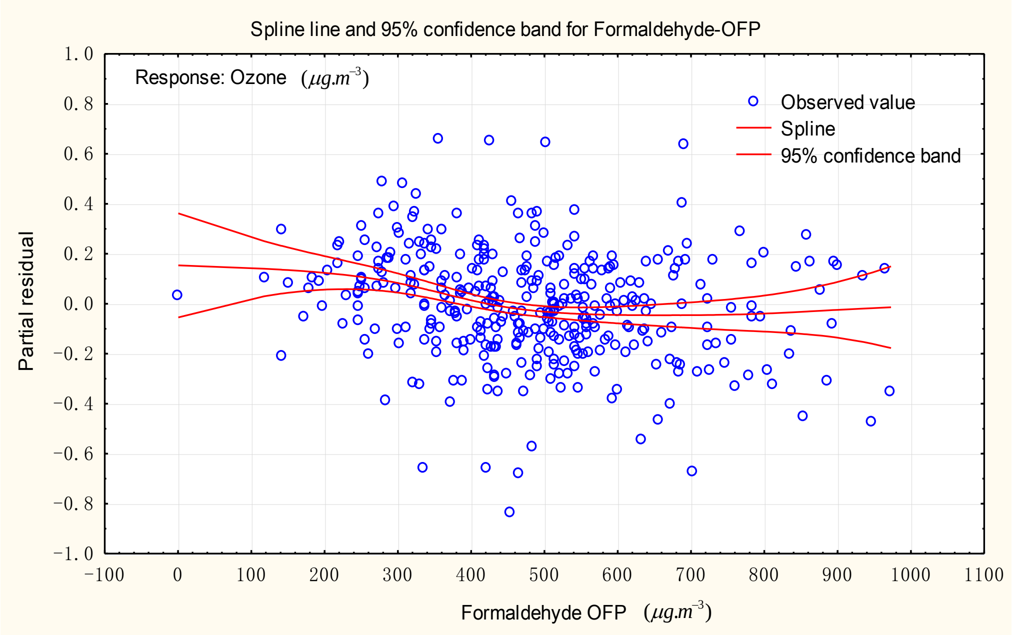


Figure 4.8c. Spline line of formaldehyde at 95%CI of cubic spline smoother

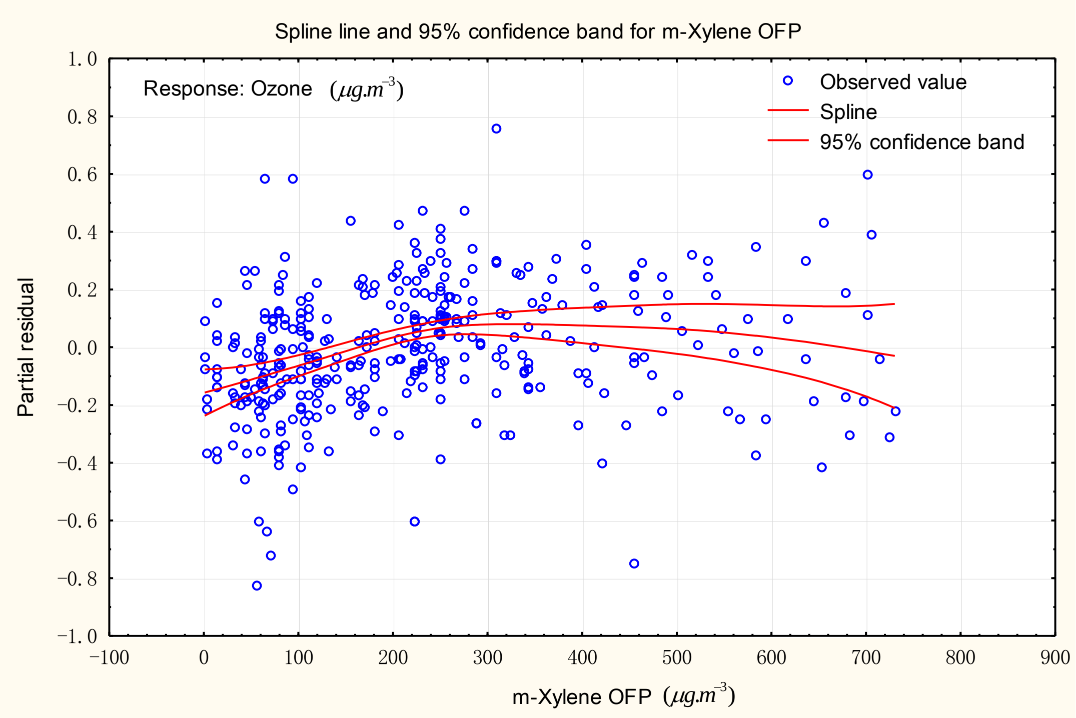


Figure 4.8d. Spline lines of m-xylene at 95%CI of cubic spline smoother

Figure 4.9a-c displayed the plots of ozone response against OFP levels of selected predictors, namely formaldehyde and o-xylene and global radiation, over time which displayed the lift of OFP levels and ozone in recent years straightly coupled with association of global radiation. Figure 5c exhibited the predicted and response ozone levels by GAM of 360 monthly samples for 5 sites from January 2008 to December 2013.

The performance of GAM were determined from statistical parameters listed in Table 4.4, which indicated that the prediction values were not much deviated from the observed values and could be applied to modelling tropospheric ozone, estimate the possible impacts and select the appropriate tool to control the levels of ozone in the future.

Table 4.4. Models error measurements, valid N=360

Performance Indicator	GAM		Ideal values
	Avg. O_3	Max.O_3	
Standard deviation (SD)	10.63	44.80	
Normalized standard deviation (NSD)	0.87	0.82	1.0
Mean absolute error (MAE)	4.05	21.48	0.0
Normalized absolute error (NAE)	0.14	0.15	0.0
Root mean squared error (RMSE)	5.13	27.57	0.0
Normalized root mean squared error (NRMSE)	0.08	0.10	0.0
Degree of agreement (d)	0.95	0.92	1.0
Normalized bias (NB, %)	-7.49	-5.52	±5–15%[c]
Correlation coefficient (R)	0.91	0.86	1.0
Coefficient of determination (R^2)	0.83	0.75	1.0

[c]EPA, 1996.

Figure 4.9, 4.10 and 4.11 illustrated the scatter, line and box plots of maximum and average ozone of predicted valued by GAM compare observed values derived for the results in Table 4.4.

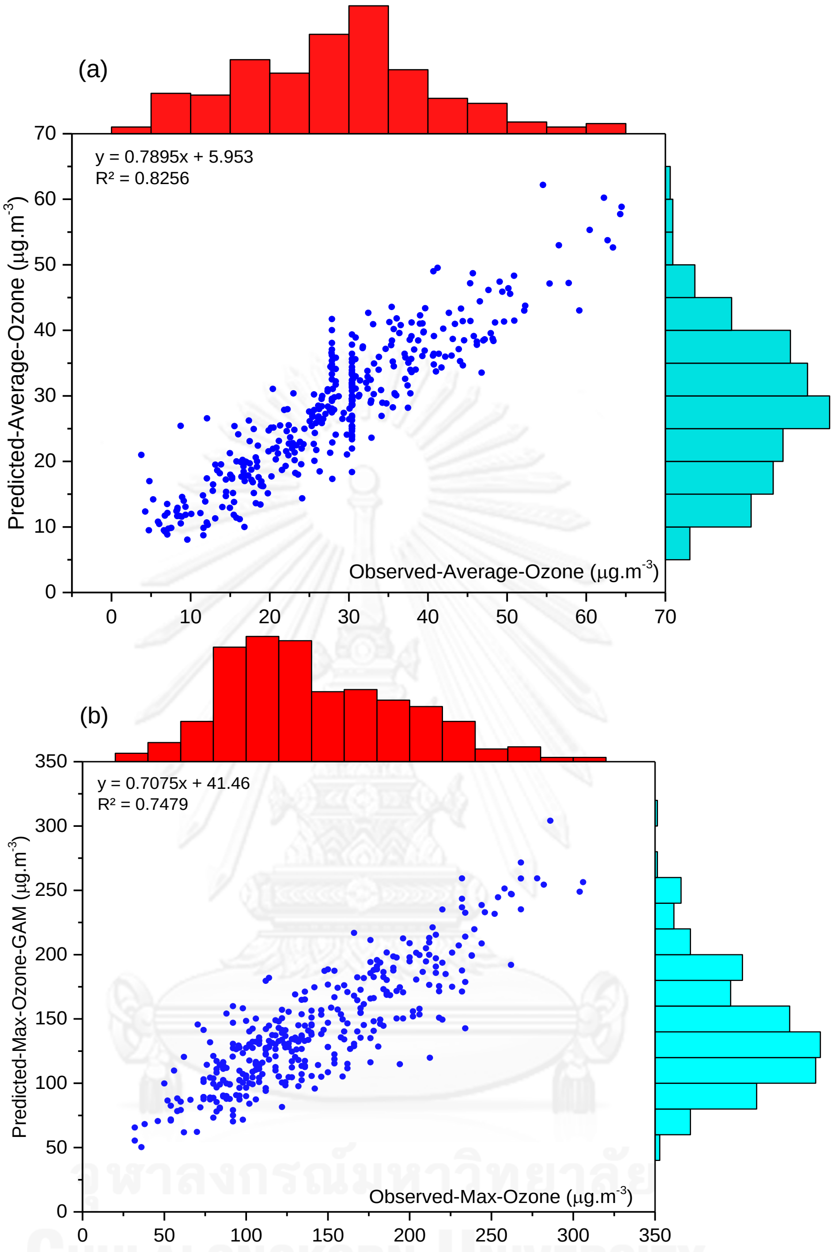


Figure 4.9. Scatter plots for the relationship of predicted against observed ozone values by GAM (a) average ozone (b) maximum ozone

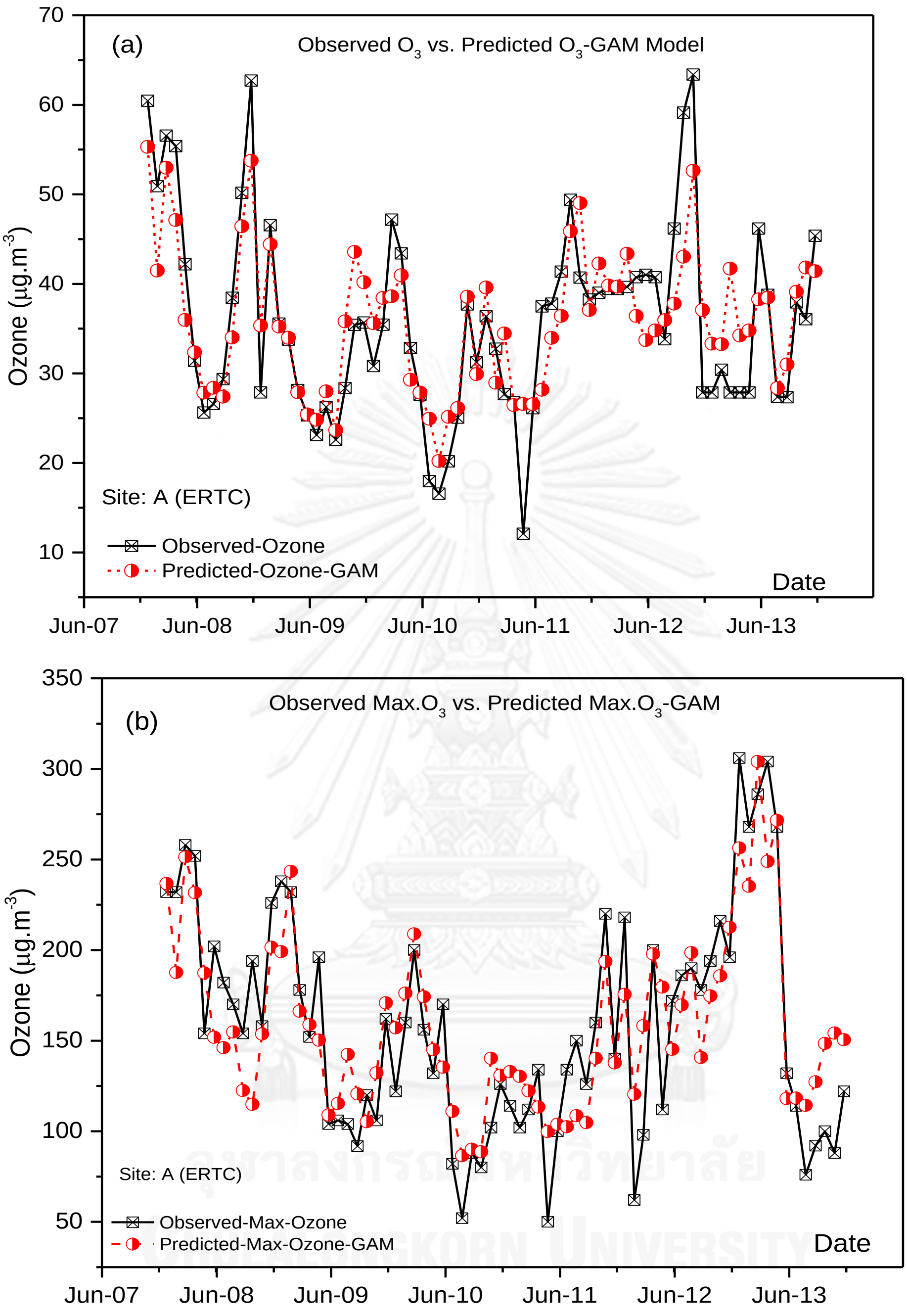


Figure 4.10. Comparing line plots of predicted and observed values forecasted by GAM (a) maximum ozone (b) average ozone

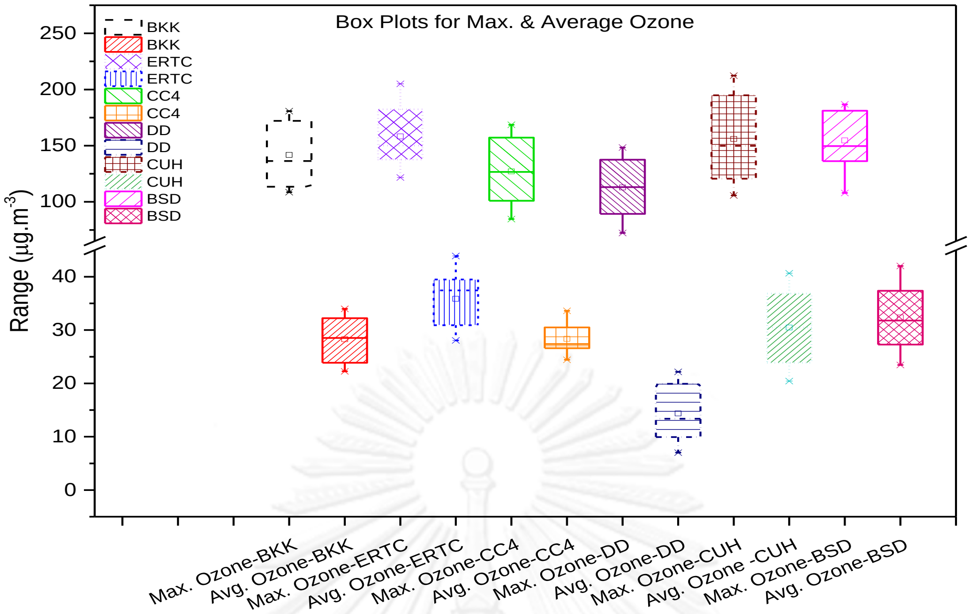


Figure 4.11. Comparing line box plots of maximum and average ozone over all sites

From the results of GAM, the levels of significant predictors, which were 1,3-butadiene, wind direction, bromomethane, 1,2-dichloropropane, global radiation, carbon monoxide, m-xylene, 1,1,1-trichloroethane, chloromethane, trichloroethylene, 1,3,5-trimethylbenzene, o-xylene, 1,2,4-trimethylbenzene, chloroethane, 1,2-dichlorobenzene, 1,1,2-trichloroethane, oxides of nitrogen, styrene, formaldehyde, 1,4-dichlorobenzene, wind speed, 3-chloropropene, and relative humidity, impacted to GAM regression of ambient ozone concentrations were compared as plotted in Figure 4.11. It was found that the levels of all significant parameters were increased after the compliance for gasohol application as the alternative fuel to gasoline.

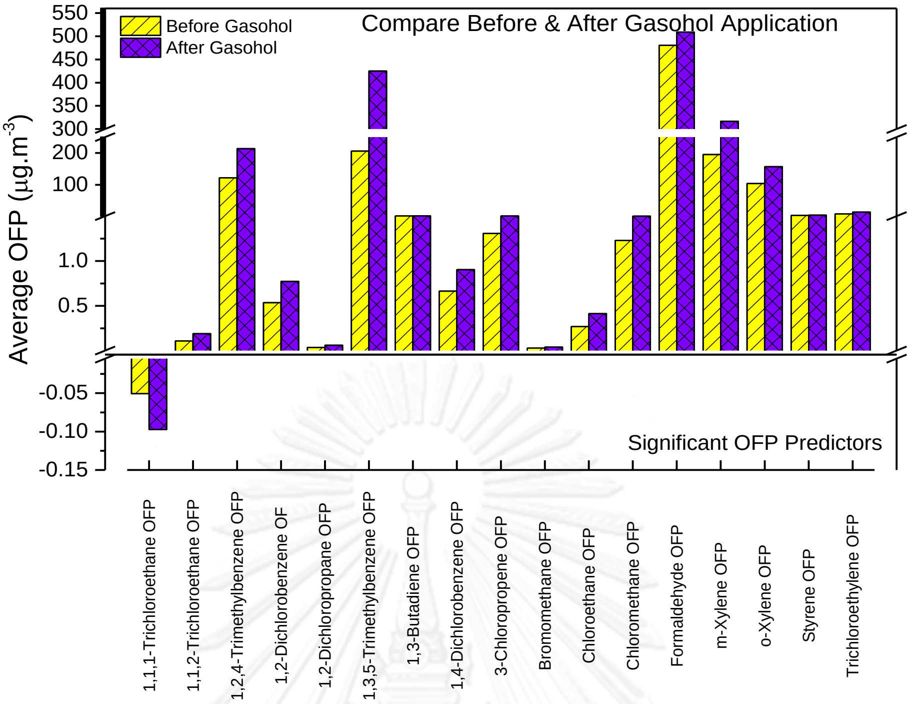


Figure 4.12. Comparing line OFP levels of significant factor on ozone concentration before and after gasohol compliance in Bangkok (July 2012).

CHAPTER V

CONCLUSIONS

The cumulative impacts of VOCs through surface ozone productions in Bangkok were performed by generalized additive model. The achieved R^2 of ozone and all independent variables was 81.24% with root mean squared error (RMSE) 5.13 $\mu g.m^{-3}$ and normalized root mean squared error (NRMSE) 0.08. Due to their contributions to the overall mean of response (μ, 40.21%) and R^2 changes (9.39%) topped the other groups of HCs, halogenated hydrocarbons were seen to be the key group of air pollutants to affect tropospheric ozone production. The ozone production contributions (OPC) of hydrocarbons (59.51%) and oxygenated hydrocarbons (39.39%) were much higher than the OPC of halogenated HCs (1.05%); however, their impacts to ozone production (6.01% and 1.57%) were poorer than those of halocarbons.

Individual significant predictors on ozone production, considering from inverse natural log for multiplication of GAM coefficient and ambient levels of the predictors, affected to tropospheric ozone over Bangkok and surrounding area were 1,3-butadiene, wind direction, bromomethane, 1,2-dichloropropane, global radiation, carbon monoxide, m-xylene, 1,1,1-trichloroethane, chloromethane, trichloroethylene, 1,3,5-trimethylbenzene, o-xylene, 1,2,4-trimethylbenzene, chloroethane, 1,2-dichlorobenzene, 1,1,2-trichloroethane, oxides of nitrogen, styrene, formaldehyde, 1,4-dichlorobenzene, wind speed, 3-chloropropene, and relative humidity by descending order. In addition, considering from the impacts to intercept (the overall mean of response) and coefficient of determination (R^2), a group of meteorological variables plays the most significant role on function log of zone concentration (%R^2= 60.75).

The performance indicators of GAM were resulted very well with normalized standard deviation (NSD; 0.82, 0.87), normalized absolute error (NAE; 0.15, 0.14), normalized root mean squared error (NRMSE; 0.10, 0.08), degree of agreement (d; 0.92, 0.95) and normalized bias (NB; -5.52%, -7.49%) for maximum and average ozone respectively.

However, the ranking for the levels of ozone formation potentials indexed through the POCP indices could be prioritized from high to low levels as summarized in Table 5.1.

Table 5.1 Descendent ranking of individual OFP level in Bangkok and vicinity from 2008 to 2013

No.	VOC's OFP	No.	VOC's OFP
1	Toluene	23	Chloromethane
2	Formaldehyde	24	Acrylonitrile
3	Acetaldehyde	25	Benzyl Chloride
4	1,3,5-Trimethylbenzene	26	Vinyl chloride
5	m-Xylene	27	1,4-Dichlorobenzene
6	1,2,4-Trimethylbenzene	28	1,2-Dichlorobenzene
7	o-Xylene	29	Chloroethane
8	Ethylbenzene	30	Chlorobenzene
9	p-Xylene	31	Tetrachloroethylene
10	1-Ethyl-4-methylbenzene	32	1,1,2-Trichloroethane
11	Propionaldehyde	33	1,1,2,2-Tetrachloroethane
12	Acrolein	34	1,2-Dibromoethane
13	Benzene	35	1,2-Dichloropropane
14	Trichloroethylene	36	Bromomethane
15	1,3-Dichlorobenzene	37	Chloroform OFP
16	Styrene	38	Carbon Tetrachloride
17	Dichloromethane	39	cis-1,3-Dichloropropene
18	1,1-Dichloroethylene	40	trans-1,3-Dichloropropene
19	1,1-Dichloroethane	41	1,2,4-Trichlorobenzene
20	1,3-Butadiene	42	1,2-Dichloroethane
21	cis-1,2-Dichloroethylene	43	1,1,1-Trichloroethane
22	3-Chloropropene		

The findings from GAM could extendedly be employed to predict to surface ozone concentrations towards the levels of VOCs' OFP associated with the ambient levels of NOx, CO and local meteorological predictors as formulated below:

$$\begin{aligned} \text{Log (Ozone)} &= \beta_0 + \Sigma\, S_{ij} * (X_{ij}) + \text{error}_i \\ &= 50.39 + \Sigma[S_{Metij} * (Met_{ij})] + [S_{NOx} * (C_{NOx})] + \\ &\quad [S_{CO} * (C_{CO})] + \Sigma[S_{OFPij} * (OFP_{ij})] \end{aligned}$$

where S_{Metij} and Met_{ij} are the spline functions and levels of meteorological variables including global radiation, relative humidity, wind speed, wind direction, atmospheric pressure and temperature; S_{NOx} and C_{NOx} denote the spline function and ambient concentration of NOx; S_{CO} and C_{CO} are the spline function and surface concentration of CO and S_{OFPij} and OFP_{ij} define the spline function and OFP level of individual VOC as follows: formaldehyde, acetaldehyde, acrolein, propionaldehyde, 1,3-butadiene, benzene, toluene, ethylbenzene, o-xylene, m-xylene, p-xylene, styrene, 1,3,5-trimethylbenzene, 1-ethyl-4-methylbenzene, bromomethane, vinylchloride, 1,2-dichloropropane, 1,2-dibromoethane, cis-1,2-dichloroethylene, trichloroethylene, tetrachloroethylene, chloromethane, chloroethane, chlorobenzene, 1,1-dichloroethylene, benzylchloride, 3-chloropropene, 1,2-dichlorobenzene, dichloromethane, 1,3-dichlorobenzene, 1,1-dichloroethane, 1,4-dichlorobenzene, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,2,4-trimethylbenzene, 1,1,2,2-tetra chloroethane and acrylonitrile.

Furthermore, these outcomes can be applied to provide a frame for modeling the effects of VOCs on the way to ozone production and selecting the appropriate tool to govern VOCs species which considerably increase levels of urban atmospheric ozone and affect to environmental air quality.

REFERENCES

APPENDICES

APPENDIX A

Input data preparation

The air quality and meteorological data, including VOCs concentrations of some compounds and samples were not suitable to put into the model, were treated as follows:

1. For the concentrations of VOCs labeled as “ND” (non-detectable), the input concentrations were computed from the MDL (method detection limit) by the formula in Eq. A-1

$$C_{ND} = \frac{C_{MDL}}{\sqrt{2}} \tag{A-1}$$

2. In case of the concentration of m+p-xylene, the concentrations were reported by PCD in mixed concentrations of the two isomers. However, POCP indices for m-xylene and p-xylene were not equal. Then, the m+p-xylene concentration was multiplied by percent natural abundant of the two isomers into the concentration of individual isomer.

3. Molar volume used in this study was 24.465 L at 25 °C, 760 mmHg.

4. O_3 1 ppbv = 2.0 μg.m-^{3}

5. NOx 1 ppb = 1 ppb NO + 1 ppb NO_2 = 1.23 $\mu g.m^{-3}$ NO + 1.88 $\mu g.m^{-3}$ NO_2

APPENDIX B

Table B-1 Method detection limit of selected VOCs

No.	Compounds	MDL, μg.m^{-3}
	Chloromethane	0.0073
	Vinyl chloride	0.008
	1,3-Butadiene	0.019
	Bromomethane	0.012
	Ethyl chloride	0.010
	1,1-Dichloroethene	0.010
	Propanal	0.041
	Dichloromethane	0.014
	1,1-Dichloroethane	0.0087
	cis-1,2-Dichloroethene	0.014
	Chloroform	0.0082
	1,1,1-Trichloroethane	0.0090
	Carbon tetrachloride	0.012

APPENDIX C

Descriptive Statistics of OFP levels over all study sites

Table C-1 Descriptive statistics of data for ERTC site

Variable/ VOCs' OFP ($\mu g.m^{-3}$)	Mean	Median	Minimum	Maximum	Percentile		SD
					(10.0)	(90.0)	
Max O_3	158.25	154.00	50.00	306.00	88.00	238.00	61.64
Ozone	35.87	35.50	12.08	63.37	25.32	50.17	10.86
Meteorological factors:							
Temperature (K)	302.13	302.06	298.70	305.62	300.61	303.67	1.30
Pressure (mmHg)	755.56	755.22	751.41	759.51	753.59	757.77	1.77
Relative Humidity (%)	73.92	73.73	61.48	88.68	66.04	84.24	7.17
Wind Speed (m/s)	0.91	0.83	0.50	1.69	0.66	1.35	0.28
Wind Direction (°)	188.27	186.61	129.63	238.12	157.49	222.13	24.33
Global Radiation	204.03	202.63	118.43	282.86	161.87	256.82	36.48
Inorg. O_3 precursors:							
CO	742.18	733.37	344.53	1425.75	484.45	1071.83	227.90
NOx	80.93	79.29	44.17	139.80	60.01	111.14	19.76
Oxygenated HCs:							
Formaldehyde	386.00	387.09	0.39	784.42	246.56	508.71	133.44
Acetaldehyde	245.87	232.19	0.39	509.25	157.30	347.02	93.92
Acrolein	29.38	31.19	1.21	80.33	5.21	54.77	17.69
Propionaldehyde	35.75	31.68	1.15	87.08	9.36	66.02	21.93
HCs:							
1,3-Butadiene	1.99	1.95	0.89	3.56	0.89	2.67	0.76
Benzene	14.69	13.00	0.22	37.00	5.50	28.06	8.60
Toluene	588.56	506.00	52.80	1496.00	206.80	1012.00	319.51
Ethylbenzene	72.86	65.12	0.46	187.86	23.00	138.00	43.99
m-Xylene	128.78	111.80	0.97	362.54	43.86	249.56	79.65
p-Xylene	49.54	41.76	2.16	115.20	14.40	94.38	30.00

Variable/ VOCs' OFP ($\mu g.m^{-3}$)	Mean	Median	Minimum	Maximum	Percentile (10.0)	Percentile (90.0)	SD
Styrene	3.66	3.68	0.05	9.00	0.80	6.53	2.18
o-Xylene	64.83	57.72	1.56	171.60	21.06	125.53	40.28
1-Ethyl-4-methylbenzene	44.41	39.38	1.89	113.40	10.71	84.48	29.23
1,3,5-Trimethylbenzene	86.74	52.43	2.27	376.04	12.84	317.90	101.49
1,2,4-Trimethylbenzene	127.00	110.00	3.27	341.00	38.50	242.00	81.53
Halogenated HCs:							
Bromomethane	0.03	0.03	0.01	0.06	0.02	0.05	0.01
1,2-Dibromoethane	0.06	0.06	0.01	0.11	0.02	0.10	0.03
Vinyl chloride	0.94	0.72	0.21	1.81	0.36	1.81	0.53
Chloroform	0	0	0	0	0	0	0
Carbon tetrachloride	0	0	0	0	0	0	0
Chloromethane	1.47	1.46	0.01	3.10	0.62	2.50	0.68
Chloroethane	0.31	0.33	0.07	0.66	0.11	0.55	0.15
1,1-Dichloroethylene	2.47	2.10	1.05	4.21	1.26	3.68	1.10
3-Chloropropene	1.56	1.38	0.46	2.76	0.92	2.30	0.56
Dichloromethane	2.40	2.15	0.03	7.50	0.24	4.80	1.74
1,1-Dichloroethane	2.02	1.62	0.54	3.24	0.54	3.24	0.98
1,2-Dichloroethane	-0.05	-0.06	-0.14	-0.01	-0.09	-0.02	0.03
1,1,1-Trichloroethane	-0.07	-0.06	-0.13	-0.01	-0.11	-0.03	0.04
1,1,2-Trichloroethane	0.13	0.12	0.03	0.29	0.03	0.20	0.07
1,1,2,2-Tetrachloroethane	0.06	0.05	0.01	0.10	0.02	0.09	0.02
1,2-Dichloropropane	0.04	0.04	0.01	0.12	0.01	0.07	0.03
cis-1,2-Dichloroethylene	1.65	1.26	0.42	3.36	0.42	2.94	0.91
Trichloroethylene	9.64	9.28	0.29	31.90	0.87	20.59	8.04
Tetrachloroethylene	0.13	0.11	0.01	0.47	0.02	0.35	0.12
cis-1,3-Dichloropropene	0	0	0	0	0	0	0
trans-1,3-Dichloropropene	0	0	0	0	0	0	0
Chlorobenzene	0.30	0.30	0.10	0.50	0.10	0.50	0.12

Variable/ VOCs' OFP ($\mu g.m^{-3}$)	Mean	Median	Minimum	Maximum	Percentile (10.0)	Percentile (90.0)	SD
Benzyl Chloride	1.21	1.41	0.16	2.30	0.43	1.61	0.50
1,2-Dichlorobenzene	0.68	0.61	0.17	0.96	0.48	0.96	0.20
1,3-Dichlorobenzene	0.65	0.65	0.24	1.36	0.24	0.96	0.27
1,4-Dichlorobenzene	0.88	0.85	0.34	1.32	0.48	1.20	0.26
1,2,4-Trichlorobenzene	0	0	0	0	0	0	0
Other HCs:							
Acrylonitrile	1.38	1.28	0.50	3.00	0.75	2.00	0.59

Table C-2 Descriptive statistics of data for Chokchai site

Variable/ VOCs' OFP ($\mu g.m^{-3}$)	Mean	Median	Minimum	Maximum	Percentile (10)	Percentile (90)	SD
Max O_3	127.11	117.00	54.00	234.00	78.00	192.00	43.82
Ozone	28.35	30.40	13.13	42.99	19.87	30.45	5.52
Meteorological factors:							
Temperature (K)	302.87	302.71	298.86	306.44	301.49	304.66	1.38
Pressure (mmHg)	758.62	758.40	755.23	762.35	756.70	761.07	1.71
Relative Humidity (%)	64.24	64.07	51.46	76.71	58.88	71.26	5.17
Wind Speed (m/s)	1.14	1.14	0.67	1.56	0.91	1.35	0.18
Wind Direction (°)	203.42	203.42	133.16	254.24	161.58	243.13	30.44
Global Radiation	136.65	138.49	67.56	202.52	90.07	177.63	31.02
Inorg. O_3 precursors:							
CO	1146.31	1166.87	253.73	1831.89	701.31	1524.45	352.31
NO_x	124.32	66.16	33.46	318.53	38.41	270.42	94.74
Oxygenated HCs:							
Formaldehyde	537.42	514.08	117.58	965.54	376.65	755.32	158.55
Acetaldehyde	359.84	345.68	0.39	631.55	293.57	525.80	127.53

Variable/ VOCs' OFP ($\mu g.m^{-3}$)	Mean	Median	Minimum	Maximum	Percentile		SD
					(10)	(90)	
Acrolein	18.50	14.42	1.18	70.42	1.18	44.93	17.69
Propionaldehyde	51.79	50.29	1.15	108.72	16.42	80.64	24.76
HCs:							
1,3-Butadiene	1.92	1.95	0.89	3.56	0.89	2.67	0.67
Benzene	28.07	24.00	4.20	73.10	8.80	54.00	18.04
Toluene	1024.39	994.79	0.81	2640.00	242.00	1794.98	604.18
Ethylbenzene	116.60	111.12	10.12	297.80	29.90	202.40	65.32
m-Xylene	232.55	232.37	2.58	584.80	61.06	413.15	144.47
p-Xylene	91.51	89.42	0.81	289.56	6.48	201.37	70.19
Styrene	3.92	3.75	0.05	9.89	0.80	7.60	2.52
o-Xylene	128.49	132.44	1.56	348.24	26.52	234.00	81.61
1-Ethyl-4-methylbenzene	50.21	50.09	0.89	157.46	7.56	94.50	37.86
1,3,5-Trimethylbenzene	311.57	251.45	2.27	1070.00	36.59	722.98	282.17
1,2,4-Trimethylbenzene	96.95	96.95	3.27	330.00	3.27	214.85	78.71
Halogenated HCs:							
Bromomethane	0.03	0.03	0.01	0.07	0.02	0.05	0.01
1,2-Dibromoethane	0.05	0.06	0.00	0.11	0.02	0.09	0.03
Vinyl chloride	0.94	0.72	0.21	2.35	0.36	1.81	0.54
Chloroform	0	0	0	0	0	0	0
Carbon tetrachloride	0	0	0	0	0	0	0
Chloromethane	1.33	1.37	0.01	2.70	0.62	2.15	0.62
Chloroethane	0.30	0.31	0.08	0.63	0.11	0.44	0.14
1,1-Dichloroethylene	2.30	1.58	0.73	5.07	1.05	3.68	1.08
3-Chloropropene	1.42	1.38	0.44	2.76	0.92	2.30	0.53
Dichloromethane	2.74	2.69	0.03	6.90	0.51	5.54	1.75
1,1-Dichloroethane	1.97	1.62	0.41	4.16	0.54	3.24	1.02
1,2-Dichloroethane	-0.06	-0.06	-0.15	-0.01	-0.10	-0.02	0.04

Variable/ VOCs' OFP ($\mu g.m^{-3}$)	Mean	Median	Minimum	Maximum	Percentile		SD
					(10)	(90)	
1,1,1-Trichloroethane	-0.06	-0.06	-0.13	-0.01	-0.11	-0.01	0.04
1,1,2-Trichloroethane	0.12	0.12	0.03	0.24	0.03	0.20	0.07
1,1,2,2-Tetrachloroethane	0.05	0.05	0.02	0.11	0.02	0.09	0.02
1,2-Dichloropropane	0.04	0.04	0.00	0.12	0.01	0.08	0.03
cis-1,2-Dichloroethylene	1.61	1.26	0.42	3.36	0.50	2.94	0.87
Trichloroethylene	11.62	10.40	0.27	34.80	0.58	24.94	9.79
Tetrachloroethylene	0.18	0.17	0.01	0.58	0.02	0.37	0.15
cis-1,3-Dichloropropene	0	0	0	0	0	0	0
trans-1,3-Dichloropropene	0	0	0	0	0	0	0
Chlorobenzene	0.29	0.30	0.10	0.54	0.13	0.40	0.11
Benzyl Chloride	1.16	1.20	0.06	2.71	0.40	1.61	0.60
1,2-Dichlorobenzene	0.54	0.61	0.24	1.13	0.24	0.72	0.21
1,3-Dichlorobenzene	4.30	2.30	0.02	15.60	0.48	11.88	4.41
1,4-Dichlorobenzene	0.67	0.72	0.34	0.96	0.36	0.85	0.18
1,2,4-Trichlorobenzene	0	0	0	0	0	0	0
Other HCs:							
Acrylonitrile	0.93	0.93	0.50	2.00	0.50	1.32	0.36

Table C-3 Descriptive statistics of data for DinDaeng site

Variable/ VOCs' OFP ($\mu g.m^{-3}$)	Mean	Median	Minimum	Maximum	Percentile		SD
					(10.0)	(90.0)	
Max O_3	112.78	104.00	32.00	218.00	58.00	172.00	44.52
Ozone	14.37	14.24	4.27	29.77	7.04	23.23	6.34
Meteorological factors:							
Temperature (K)	302.95	303.11	299.54	305.78	301.27	304.56	1.30
Pressure (mmHg)	755.77	755.79	751.26	759.52	753.17	758.22	1.87

Variable/ VOCs' OFP ($\mu g.m^{-3}$)	Mean	Median	Minimum	Maximum	Percentile		SD
					(10.0)	(90.0)	
Relative Humidity (%)	69.08	69.22	48.24	85.39	58.62	79.26	7.58
Wind Speed (m/s)	0.58	0.58	0.19	0.99	0.37	0.78	0.16
Wind Direction (Degree)	163.74	176.00	85.09	217.60	102.08	206.39	38.85
Global Radiation	90.09	98.95	23.74	161.68	33.05	144.07	39.41
Inorg. O_3 precursors:							
CO	1389.29	1393.18	741.50	2176.42	922.98	1859.59	349.79
NOx	207.95	160.22	139.44	373.27	142.63	332.78	73.47
Oxygenated HCs:							
Formaldehyde	584.29	554.85	141.22	972.90	371.50	854.68	182.68
Acetaldehyde	326.04	323.24	151.00	544.50	204.60	456.72	92.56
Acrolein	39.27	37.19	1.18	90.40	12.97	70.05	21.41
Propionaldehyde	50.64	54.29	6.91	90.43	23.04	75.60	20.52
HCs:							
1,3-Butadiene	1.97	1.95	0.89	3.81	0.89	2.67	0.75
Benzene	29.69	26.50	4.20	68.00	8.80	61.00	18.48
Toluene	1162.34	1022.99	52.80	2728.00	255.20	2200.00	707.30
Ethylbenzene	121.51	110.40	0.46	281.64	23.00	225.40	76.49
m-Xylene	307.23	249.56	0.97	725.51	57.62	654.51	220.42
p-Xylene	113.90	98.09	0.81	296.32	18.00	223.20	80.01
Styrene	4.19	3.97	0.56	10.00	1.10	8.00	2.41
o-Xylene	153.46	140.35	0.88	366.60	33.54	296.40	100.87
1-Ethyl-4-methylbenzene	65.54	57.99	0.89	163.80	8.19	132.30	45.38
1,3,5-Trimethylbenzene	388.04	310.27	3.21	995.10	49.22	834.60	287.93
1,2,4-Trimethylbenzene	181.37	146.26	3.27	506.00	19.80	418.33	146.13
Halogenated HCs:							
Bromomethane	0.03	0.03	0.01	0.07	0.02	0.04	0.01
1,2-Dibromoethane	0.05	0.06	0.01	0.11	0.03	0.08	0.03
Vinyl chloride	0.95	0.72	0.21	1.81	0.36	1.81	0.52

Variable/ VOCs' OFP ($\mu g.m^{-3}$)	Mean	Median	Minimum	Maximum	Percentile (10.0)	Percentile (90.0)	SD
Chloroform	0	0	0	0	0	0	0
Carbon tetrachloride	0	0	0	0	0	0	0
Chloromethane	1.35	1.20	0.01	3.10	0.49	2.15	0.69
Chloroethane	0.31	0.33	0.11	0.55	0.11	0.44	0.13
1,1-Dichloroethylene	2.34	1.58	1.05	4.21	1.55	3.68	1.04
3-Chloropropene	1.50	1.38	0.46	3.05	0.92	2.76	0.64
Dichloromethane	2.77	2.69	0.03	8.10	0.51	5.40	1.88
1,1-Dichloroethane	2.07	1.89	0.19	4.71	0.54	3.24	1.03
1,2-Dichloroethane	-0.06	-0.06	-0.15	-0.01	-0.10	-0.02	0.03
1,1,1-Trichloroethane	-0.06	-0.06	-0.13	-0.01	-0.11	-0.02	0.04
1,1,2-Trichloroethane	0.14	0.14	0.03	0.32	0.03	0.20	0.08
1,1,2,2-Tetrachloroethane	0.06	0.06	0.02	0.11	0.02	0.09	0.02
cis-1,3-Dichloropropene	0	0	0	0	0	0	0
trans-1,3-Dichloropropene	0	0	0	0	0	0	0
1,2-Dichloropropane	0.04	0.04	0.01	0.12	0.01	0.07	0.03
cis-1,2-Dichloroethylene	1.61	1.26	0.42	2.94	0.84	2.94	0.88
Trichloroethylene	9.68	6.82	0.27	31.90	0.87	20.88	8.88
Tetrachloroethylene	0.19	0.16	0.01	0.56	0.03	0.37	0.14
Chlorobenzene	0.30	0.30	0.10	0.50	0.13	0.50	0.11
Benzyl Chloride	1.18	1.41	0.20	2.31	0.60	1.61	0.48
1,2-Dichlorobenzene	0.61	0.61	0.24	0.96	0.24	0.96	0.27
1,3-Dichlorobenzene	5.82	4.08	0.09	16.80	1.08	15.60	5.27
1,4-Dichlorobenzene	0.71	0.72	0.34	1.39	0.48	0.96	0.23
1,2,4-Trichlorobenzene	0	0	0	0	0	0	0
Other HCs:							
Acrylonitrile	1.35	1.32	0.50	3.00	0.75	2.00	0.58

Table C-4 Descriptive statistics of data for Chulalongkorn Memorial Hospital site

Variable/ VOCs' OFP ($\mu g.m^{-3}$)	Mean	Median	Minimum	Maximum	Percentile		SD
					(10)	(90)	
Max O_3	156.00	146.00	54.00	282.00	86.00	226.00	54.01
Ozone	30.47	28.02	12.82	54.54	17.67	45.34	10.06
Meteorological factors:							
Temperature (K)	302.47	302.42	299.21	306.17	301.15	303.96	1.26
Pressure (mmHg)	757.82	757.90	755.40	761.17	756.04	759.76	1.55
Relative Humidity (%)	65.97	65.78	52.90	77.14	58.06	73.72	5.84
Wind Speed (m/s)	1.23	1.28	0.34	2.10	0.66	1.80	0.45
Wind Direction (°)	221.00	229.28	136.64	282.56	183.91	249.28	29.52
Global Radiation	147.19	140.56	104.36	202.99	121.28	174.89	22.22
Inorg. O_3 precursors:							
CO	1181.01	1120.73	729.02	1920.39	868.71	1523.42	268.94
NO_x	196.20	188.14	114.24	290.91	140.64	258.73	44.70
Oxygenated HCs:							
Formaldehyde	545.74	547.22	246.61	863.10	364.32	681.49	112.82
Acetaldehyde	313.46	308.69	100.27	605.11	206.14	431.20	103.19
Acrolein	36.23	34.59	1.18	89.92	12.85	66.26	21.23
Propionaldehyde	53.62	54.72	1.15	92.30	25.42	82.80	21.13
HCs:							
1,3-Butadiene	1.90	1.95	0.19	3.56	0.89	2.67	0.72
Benzene	29.73	27.85	3.10	74.00	8.60	61.00	19.20
Toluene	1093.30	994.79	52.80	2684.00	255.20	1936.00	647.37
Ethylbenzene	127.17	109.58	0.46	303.60	23.00	248.40	80.41
m-Xylene	288.43	249.56	2.58	730.41	55.11	561.18	194.95
p-Xylene	113.95	95.25	0.81	293.17	10.08	244.45	83.57
Styrene	4.05	3.82	0.05	9.18	0.80	7.00	2.27
o-Xylene	143.92	127.68	5.46	338.88	33.54	296.40	88.15

Variable/ VOCs' OFP ($\mu g.m^{-3}$)	Mean	Median	Minimum	Maximum	Percentile		SD
					(10)	(90)	
1-Ethyl-4-methylbenzene	66.86	62.81	0.89	170.10	9.45	120.70	42.39
1,3,5-Trimethylbenzene	387.64	310.27	2.27	1005.80	43.87	823.90	294.22
1,2,4-Trimethylbenzene	174.49	152.44	3.27	504.02	15.40	421.50	143.11
Halogenated HCs:							
Bromomethane	0.03	0.03	0.01	0.06	0.02	0.05	0.01
1,2-Dibromoethane	0.06	0.06	0.01	0.13	0.02	0.08	0.03
Vinyl chloride	0.94	0.72	0.21	2.23	0.36	1.81	0.51
Chloroform	0	0	0	0	0	0	0
Carbon tetrachloride	0	0	0	0	0	0	0
Chloromethane	1.26	1.20	0.01	3.00	0.63	2.10	0.60
Chloroethane	0.33	0.33	0.08	0.64	0.11	0.55	0.15
1,1-Dichloroethylene	2.37	1.58	0.92	4.21	1.33	4.06	1.10
3-Chloropropene	1.44	1.38	0.65	2.76	0.92	2.30	0.58
Dichloromethane	2.79	2.69	0.03	7.96	0.27	5.40	1.95
1,1-Dichloroethane	2.02	1.81	0.16	3.96	1.08	3.24	0.99
1,2-Dichloroethane	-0.06	-0.06	-0.15	-0.01	-0.10	-0.02	0.03
1,1,1-Trichloroethane	-0.07	-0.06	-0.15	0.00	-0.11	-0.03	0.04
1,1,2-Trichloroethane	0.13	0.14	0.02	0.25	0.03	0.20	0.08
1,1,2,2-Tetrachloroethane	0.06	0.06	0.02	0.12	0.03	0.09	0.02
1,2-Dichloropropane	0.04	0.04	0.01	0.12	0.01	0.07	0.03
cis-1,2-Dichloroethylene	1.71	1.26	0.42	3.36	0.84	2.94	0.92
Trichloroethylene	9.91	6.53	0.27	34.80	0.87	22.04	8.95
Tetrachloroethylene	0.19	0.17	0.01	0.57	0.03	0.36	0.15
cis-1,3-Dichloropropene	0	0	0	0	0	0	0
trans-1,3-Dichloropropene	0	0	0	0	0	0	0
Chlorobenzene	0.30	0.30	0.10	0.55	0.20	0.50	0.10
Benzyl Chloride	1.16	1.41	0.13	2.48	0.35	1.61	0.56
1,2-Dichlorobenzene	0.60	0.61	0.24	0.96	0.24	0.96	0.27

Variable/ VOCs’ OFP (μg.m^{-3})	Mean	Median	Minimum	Maximum	Percentile (10)	Percentile (90)	SD
1,3-Dichlorobenzene	5.13	3.05	0.25	16.80	0.96	13.20	5.04
1,4-Dichlorobenzene	0.73	0.73	0.36	0.96	0.48	0.96	0.20
1,2,4-Trichlorobenzene	0	0	0	0	0	0	0
Other HCs:							
Acrylonitrile	1.46	1.32	0.50	3.00	0.75	2.00	0.59

Table C-5 Descriptive statistics of data for Bansomdej Chao Phraya site

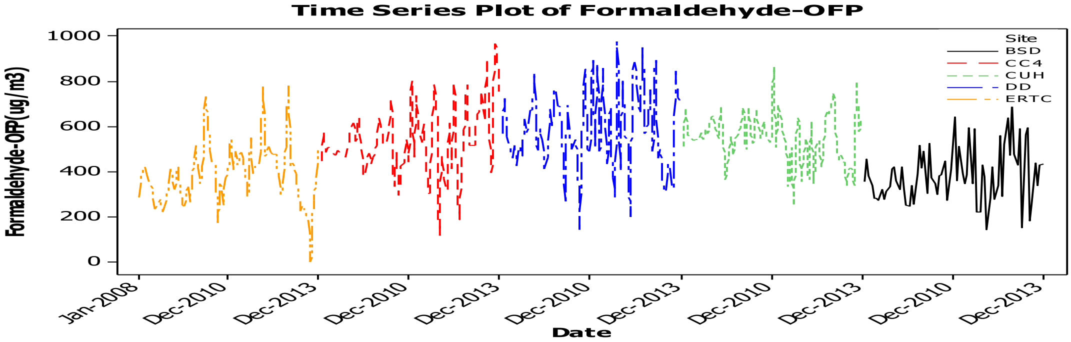
Variable/ VOCs’ OFP (μg.m^{-3})	Mean	Median	Minimum	Maximum	Percentile (10)	Percentile (90)	SD
Max O_3	154.63	150.00	60.00	278.00	92.00	234.00	53.13
Ozone	32.36	32.28	3.77	64.46	16.43	49.63	13.82
Meteorological factors:							
Temperature (K)	302.61	302.56	300.45	305.07	301.16	304.33	1.14
Pressure (mmHg)	520.26	395.41	145.49	1583.57	184.95	1121.03	361.26
Reative Humidity (%)	103.75	96.46	43.11	196.12	59.32	163.19	36.95
Wind Speed (m/s)	756.97	756.97	753.91	759.94	754.96	758.90	1.40
Wind Direction (Degree)	69.40	69.40	58.62	78.68	62.75	75.82	4.97
Global Radiation	1.55	1.64	0.87	2.28	1.08	1.96	0.38
Inorg. O_3 precursors:							
CO	191.95	195.14	99.26	253.41	141.93	231.26	32.67
NOx	169.85	169.34	85.49	232.02	130.00	216.57	34.00
Oxygenated HCs:							
Formaldehyde	385.02	375.59	141.86	701.87	255.76	560.69	119.11
Acetaldehyde	251.66	229.19	33.50	540.21	138.49	404.80	112.95
Acrolein	32.03	32.03	1.18	62.69	14.44	52.16	14.24
Propionaldehyde	45.83	45.24	1.15	106.70	7.20	81.22	28.06

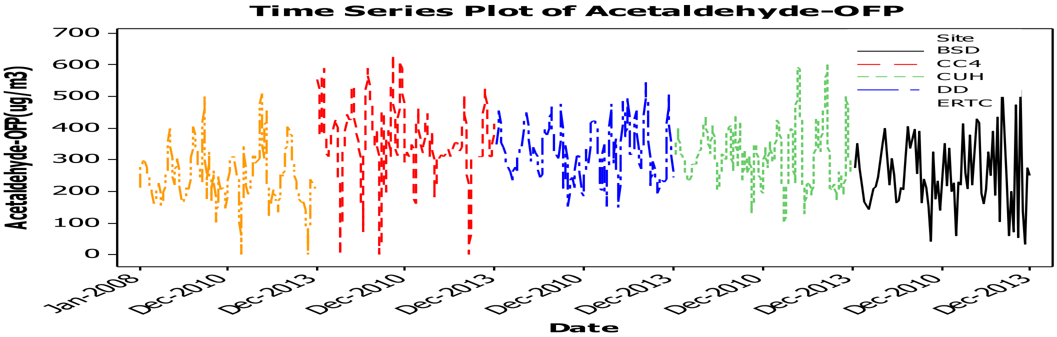
Variable/ VOCs' OFP ($\mu g.m^{-3}$)	Mean	Median	Minimum	Maximum	Percentile		SD
					(10)	(90)	
HCs:							
1,3-Butadiene	1.82	1.91	0.89	3.71	0.89	2.67	0.68
Benzene	19.82	19.39	0.22	47.00	6.50	36.00	11.80
Toluene	713.36	713.36	0.81	2010.54	101.64	1408.18	471.79
Ethylbenzene	87.36	75.90	0.39	243.80	13.80	170.20	58.71
m-Xylene	170.62	176.17	0.97	455.80	49.28	275.20	94.49
p-Xylene	65.00	65.62	0.81	185.75	6.48	134.25	46.44
Styrene	3.22	3.22	0.05	9.00	0.45	6.34	2.25
o-Xylene	96.00	89.70	0.88	283.13	5.46	223.60	73.69
1-Ethyl-4-methylbenzene	40.58	38.87	0.89	124.17	0.89	88.20	31.35
1,3,5-Trimethylbenzene	130.27	64.74	2.27	625.25	4.28	374.74	164.55
1,2,4-Trimethylbenzene	145.25	121.00	3.27	440.00	3.27	311.08	121.38
Halogenated HCs:							
Bromomethane	0.03	0.02	0.01	0.06	0.02	0.05	0.01
1,2-Dibromoethane	0.05	0.05	0.01	0.11	0.02	0.09	0.03
Vinyl chloride	0.72	0.72	0.17	1.84	0.21	1.44	0.40
Chloroform	0	0	0	0	0	0	0
Carbon tetrachloride	0	0	0	0	0	0	0
Chloromethane	1.27	1.25	0.01	2.50	0.32	2.10	0.60
Chloroethane	0.27	0.26	0.07	0.59	0.11	0.44	0.13
1,1-Dichloroethylene	2.06	1.58	0.39	3.68	1.05	3.61	0.90
3-Chloropropene	1.29	1.37	0.75	2.15	0.92	1.84	0.33
Dichloromethane	2.92	2.67	0.03	7.20	0.42	6.00	1.99
1,1-Dichloroethane	1.72	1.62	0.06	3.24	0.54	2.92	0.84
1,2-Dichloroethane	-0.05	-0.06	-0.14	-0.01	-0.10	-0.02	0.03
1,1,1-Trichloroethane	-0.06	-0.06	-0.17	-0.01	-0.11	-0.01	0.04
1,1,2-Trichloroethane	0.12	0.11	0.03	0.27	0.03	0.21	0.07

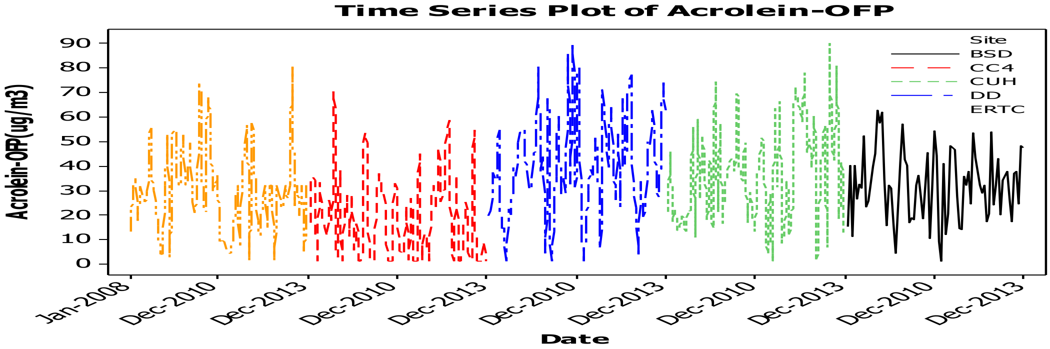
Variable/ VOCs' OFP ($\mu g.m^{-3}$)	Mean	Median	Minimum	Maximum	Percentile (10)	Percentile (90)	SD
1,1,2,2-Tetrachloroethane	0.05	0.04	0.01	0.10	0.02	0.08	0.02
1,2-Dichloropropane	0.04	0.04	0.01	0.12	0.01	0.09	0.03
cis-1,2-Dichloroethylene	1.42	1.26	0.42	3.01	0.75	2.88	0.70
Trichloroethylene	8.75	6.24	0.01	26.68	0.87	20.32	7.78
Tetrachloroethylene	0.13	0.11	0.01	0.38	0.02	0.32	0.11
cis-1,3-Dichloropropene	0	0	0	0	0	0	0
trans-1,3-Dichloropropene	0	0	0	0	0	0	0
Chlorobenzene	0.26	0.29	0.10	0.50	0.13	0.40	0.09
Benzyl Chloride	1.13	1.21	0.20	2.57	0.43	1.61	0.58
1,2-Dichlorobenzene	0.54	0.59	0.17	1.27	0.24	0.96	0.27
1,3-Dichlorobenzene	3.18	3.16	0.25	9.86	0.96	5.78	2.34
1,4-Dichlorobenzene	0.63	0.71	0.34	1.19	0.36	0.88	0.19
1,2,4-Trichlorobenzene	0	0	0	0	0	0	0
Other HCs:							
Acrylonitrile	1.06	0.75	0.20	3.00	0.50	2.00	0.71

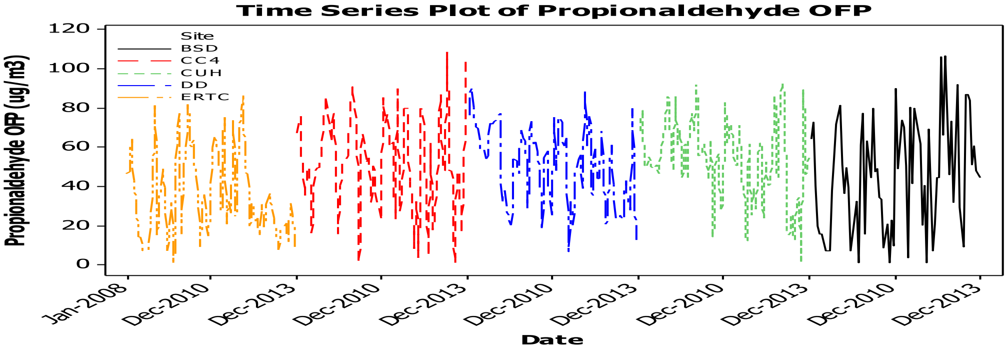
APPENDIX C

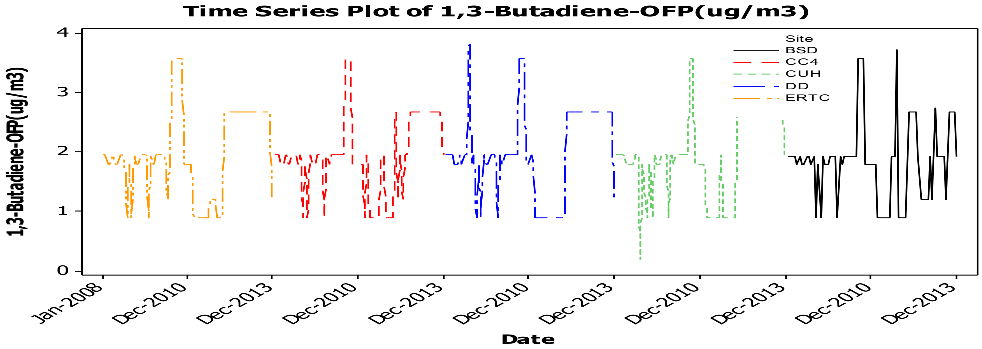
Figure C-1 Time series plots of selected VOCs' OFP

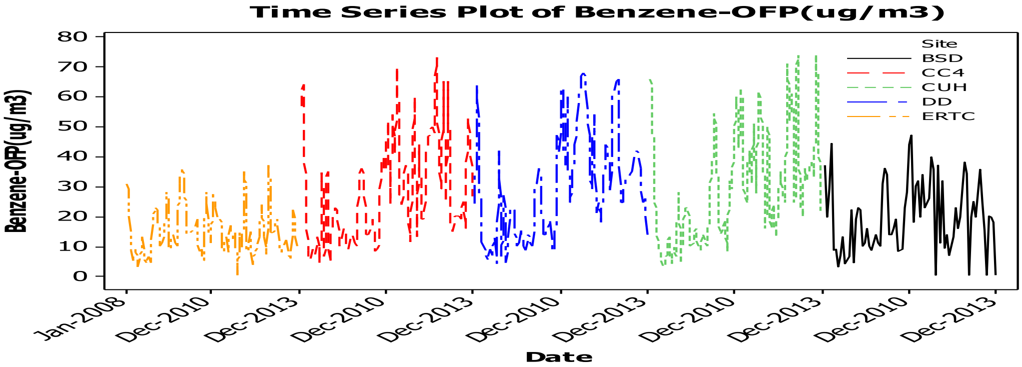


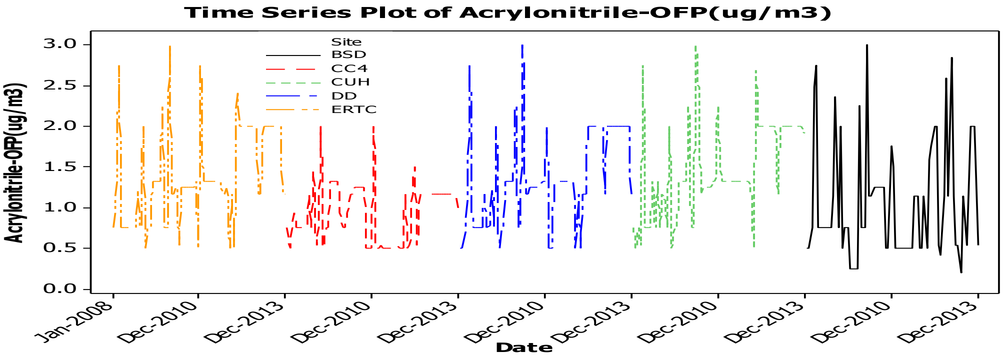







Time Series Plot of 1,3-Butadiene-OFP(ug/m3)
1,3-Butadiene-OFP(ug/m3)
0
1
2
3
4
Jan-2008
Dec-2010
Dec-2013
Dec-2010
Dec-2013
Dec-2010
Dec-2013
Dec-2010
Dec-2013
Dec-2010
Dec-2013
Date
Site
BSD
CC4
CUH
DD
ERTC


Time Series Plot of Benzene-OFP(ug/m3)
Benzene-OFP(ug/m3)
0
10
20
30
40
50
60
70
80
Jan-2008
Dec-2010
Dec-2013
Dec-2010
Dec-2013
Dec-2010
Dec-2013
Dec-2010
Dec-2013
Dec-2010
Dec-2013
Date
Site
BSD
CC4
CUH
DD
ERTC


Time Series Plot of Acrylonitrile-OFP(ug/m3)
Acrylonitrile-OFP(ug/m3)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Jan-2008
Dec-2010
Dec-2013
Dec-2010
Dec-2013
Dec-2010
Dec-2013
Dec-2010
Dec-2013
Dec-2010
Dec-2013
Date
Site
BSD
CC4
CUH
DD
ERTC

VITA

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