Evaluation of Urban Ozone Formationby Photochemical Ozone Creation Potential Indices and Generalized Additive Model

Sirithorn Saengsai[1] and Wanida Jinsart[2]

***Abstract*—**Ozone formation potential (OFP) of 43 VOCs species were analyzed usingthe ambient concentrations data from 2008 to 2013 and the Photochemical ozone creation potential indices, the indicator of a VOCs' capacity to contribute to the photochemical ozone formation).The ozone production potential contribution (OPC) can then be calculated as the percentage of individual OFP to the summation of all VOCs' OFPs. The predicted ozone formation potential species were verified by Generalized Additive Model (GAM). The impacts of the photochemical ozone creation potential to surface ozone level were analyzed. Halogenated hydrocarbons were found to be the main group that affected to the ozone production 40.2% with the overall mean of response and r^2 changes (9.4%). Althoughfrom the calculation, the OFP level of Hydrocarbons (59.5%) and oxygenated hydrocarbons (39.4%) were high but from GAM results, their effects to ozone production (6.0% and 1.6%) were lower than those of halogenated hydrocarbons.

***Keywords*—**generalized additive model, ozone formation potential, photochemical ozone creation potential, volatile organic compound

I. Introduction

BANGKOK'Sair quality was affected by rapid urbanization, economic development, and increases in number of transport vehicles. On-road vehicles and industrial sources are typically the major sources of common urban air pollutants e.g. ozone and VOCs, [1]. The trace gas ozone and halogenated VOCs in the troposphere are interchange media for air pollution and climate change [2]. In Thailand, the surface levels of 1-hour and 8-hour average of ozone recording 1996-2013 have been exceeded the standard (100 ppb) over many areas, especially in Bangkok and its vicinity [3]. Furthermorefrom other reports, Zhang and Kim Oanh[4],[5] revealed that the ratios of NO_x to Non-methane Hydrocarbons(NMHCs) toward tropospheric ozone formation were VOC-sensitive reactions occurred in inner Bangkok, whereas outer Bangkok sites were NO_xsensitive condition with higher concentrations, at downwind. On the other hand, the increasing of oxygenated hydrocarbons could be resulted from the National promotion program for phasing out of methyl tertiary butyl ether (MTBE) in gasoline and phasing in of ethanol-gasoline blended since 2004. These have possibly been the additional emission sources for urban ozone precursors because the levels of oxygenated hydrocarbons emitted from gasohol are higher than gasoline fuels [6].

The objective of this research is to quantify the extent in which regional photochemical creation potential of volatile organic compounds, as ozone precursors, respond to atmospheric ozone in Bangkok and vicinity, Thailand. This was achieved by the application of generalized additive model (GAM) to estimate the response of ozone (O_3) affected from VOCs' reactivity associated with other ozone precursors, namely nitrogen oxides (NO_x), carbon monoxide (CO) and local meteorological variables.

II. Method

A. Study Area

The study sites for evaluating the potential of surface ozone formation were consisted of three inner districts and one outer district of Bangkok comparable to its suburban area in PathumThani province, located at the north-east of Bangkok, showed in Figure 1. The monitoring stations, with roughly 50 kilometer-long, were selected based on a year-round wind direction at upwind and downwind, which mainly impacted by SW and NE monsoon of the center of Bangkok.

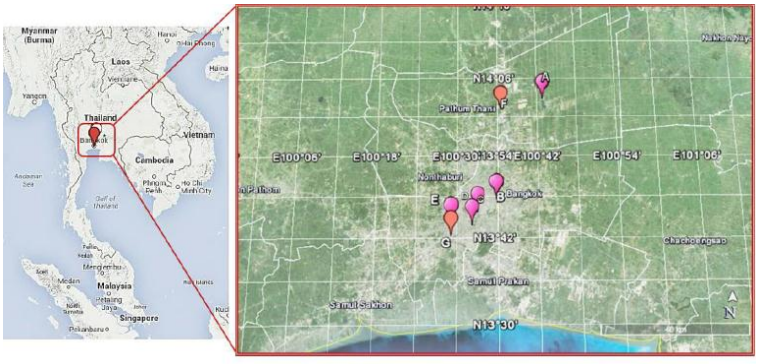

Fig. 1 Map of Bangkok with the monitoring sites in this study

B. Data Information

All monitoring data, including43VOCs, O_3, NO_x and CO, together with surface meteorological parameters during 2008 to 2013, were obtained from Pollution Control Department, Thailand. VOCs samples were quantified by the standard operating procedures equivalent to US EPA method TO-11A and TO-15A. In addition, NO_x and O_3 were determined by continuous chemiluminescence detections along with CO that analyzed by online non-dispersive infrared analyzers equivalent to U.S EPA ambient standard methods [7]-[9]. All

The funding research for this work was supported by National Research Council of Thailand 2013 GRB_APS_20572304.

Sirithorn Saengsai[1] was with Interdisciplinary Program in Environmental and Hazardous Waste Management (International Program), Graduate School, Chulalongkorn University, Bangkok, Thailand e-mail: ssaengsai@gmail.com

Wanida Jinsart[2] is with the Department of Environmental Science, Faculty of Science, Chulalongkorn University, Bangkok 10330 Thailand (corresponding author's phone:66-81-8375127 ; e-mail: jwanida2013@gmail.com or jwanida@chula.ac.th).

data were extracted correspondingly to monthly VOCs samples data. The input data were air pollutants concentrations ($\mu g.m^{-3}$), temperature (K), pressure (mmHg), relative humidity(%), wind speed ($m.s^{-1}$), wind direction (^{o}) and global radiation ($W.m^{-2}$) respectively.

C. Ozone formation potential (OFP)

VOCs have been concerned as the reactive species in photochemical oxidations of O_3. Individual VOC participates in the complex reactions of ozone formation differently because of its reactivity, its mechanism and the ratio of VOC to other precursors and meteorological parameters [10]-[12]. Several methods were used to study the competency of ozone formation throughout VOCs' reactivity such as the maximum increment reactivity (MIR) scale, which is relevant to the change of ozone creation to unit amount of added chemical in the system [12] and the photochemical ozone creation potential (POCP) scale that quantified the formation of ozone relatively to the capacity of ethylene using photochemical trajectory model allowing for long range transport, as expressed in (1) and (2) indicated the calculation for the VOCs' OFP using POCP indices [13].

$$POCP_i = \frac{O_{3i} - O_{3basecase}}{O_{3ethylene} - O_{3basecase}} \times 100 \quad (1)$$

$$OFP_i\ [\mu g \cdot m^{-3}] = C_{VOC_i}\left(\mu g \cdot m^{-3}\right) \times POCP_i \quad (2)$$

where $O_{3basecase}$ refers to the ozone mixing ratio along the trajectory in the base case, O_{3i} with an additional of the i^{th} VOC species, $O_{3ethylene}$ refers to that with the same mass of ethylene, OFP_i ,C_{VOCi} and $POCP_i$ are the ozone formation potential, the concentration and the photochemical ozone creation potential coefficient of i^{th} VOC respectively. The ozone production potential contribution (OPC) can then be calculated as the percentage of individual OFP to the summation of all VOCs' OFPs.

D. Statistical model

Generalized Additive Model (GAM): As an alternative model of non-parametric regression, GAM has become a prevalent tool for prediction of air pollution levels because it can be applied with various flexible frameworks and input data [14]. GAM illustrates non-linear relationships by estimating non-parametric functions of covariate variables using loess or splines smoother performed with respect to the partial residuals [15]. 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 $g(\mu)$ 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 (3).

$$\log(y_i) = \beta_0 + \sum_{j=1}^{n} S_{ij}(x_{ij}) + \varepsilon_i \quad (3)$$

where y_i is the i^{th} ozone concentration, $\beta_0$is the overall mean of the response or an intercept of the scatter plot and $S_j(x_{ij})$ is the smooth function of i^{th} value of covariate j (ie. temperature, pressure,..., global radiation, NO_x, CO, VOC_1, VOC_2,...,VOC_{38}, excluding VOCs with POCP indices equal to zero) and n is the total number of covariates, and ε_i is the i^tresidual.

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 NO_x 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, (b) 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. 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 [16] along with the root mean square error (RMSE), where X_{obs} was observed values and X_{model} was from the model values at time/place i, expressed in (4).

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n}(X_{obs,i} - X_{model,i})^2}{n}} \quad (4)$$

III. Results And Discussion

A. Ozone formation potential

Toluene, as a backbone hydrocarbon in urban atmosphere, which emitted from vehicular petroleum combustion and coke oven industry [17], the average OFP level of toluene were the highest rank, about 916.39 $\mu g.m^{-3}$, found in Bangkok. The OFPs of aromatic hydrocarbons, benzene, xylene and ethylbenzene were ranged from 22.40 to225.52 $\mu g.m^{-3}$. In the cases of oxygenated hydrocarbons with high POCP indices [13], formaldehyde and acetaldehyde, their OFPs were 487.69 and 299.37 $\mu g.m^{-3}$ which were higherthan the OFPs of aromatic HCs. These compounds were the principal species released from biomass and bio-fuels oxidation which found from automobile exhaust pipes[18],[19]. The OFP levels of halogenated HCs, which normally come from industrial sector [20] were lower than other VOCs groups. The two compounds with lowest average OFPs were 1,2-dichloroethane and 1,1,1-

trichloroethane, data summarized in Figure 2. In addition, the OFP trends, after excluding halogenated HCs, toluene was the most was most abundant VOCs species. This finding is similar to a report by Tsai *et al.*, 2007 in the central Taiwan [21]. However, the ratio of toluene OFP to benzene OFP of these two countries was different which implied that the amounts of VOCs in the two areas were not in the same scale. The emission sources and locally meteorological conditions in both countries were different. Whereas, VOCs with the highmaximum increment reactivity, another scale of ozone formation, created in Shanghai, China werecis& trans-2-butene, propene and isoprene [22]. These emphasized that emission sources and local meteorology were significant to ozone formation [23].

The ozone production contributions of all VOCs were similarly to the OFPs' trend depended on their molecular weights and POCP indices [24] 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%, respectively.

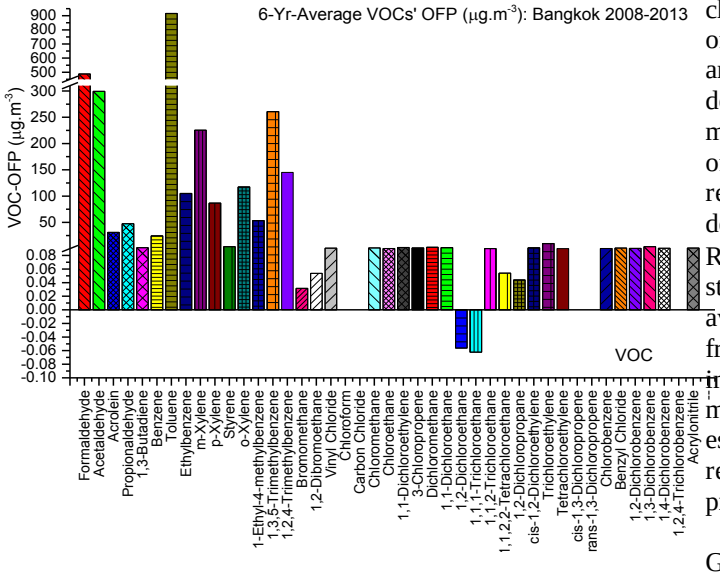

Fig. 2 Six years average of Ozone Formation Production for each VOC in Bangkok ambient air.

B. Generalized Additive Model (GAM)

The impacts of locally meteorological parameters, inorganic ozone precursors and the OFPs of each VOC group on surface ozone levels were analyzed by the different r^2 of the model (a) to (f). Following GAM analysis in (3), data inTable 1 specified that meteorological predictors played a major role, with 60.75%, in the ozone formation, whereas halogenated HCs were 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 the response 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 [25], [26].

TABLE I
GAM STATISTICAL ANALYSIS FOR MODEL (A) TO (F) AT SCALE ESTIMATE 1 AND NUMBER OF OBSERVATION 360

Model	Final deviance (D_m)	Residual df	D_m/df	μ	μ change (%)	r^2 *100 %	r^2 change (%)
a	780.35	319.94	2.44	38.00	0.00	60.75	0.00
b	726.83	311.98	2.33	38.06	0.16	63.44	2.69
c	695.64	295.93	2.35	37.29	-2.02	65.01	1.57
d	679.13	291.91	2.33	36.91	-1.02	65.84	0.83
e	559.59	247.90	2.26	35.94	-2.63	71.85	6.01
f*	373.01	159.94	2.33	50.39	40.21	81.24	9.39

* Data in Figure 2

However, acrylonitrile, as other HCs affected to r^2 change 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). The final scatter plot coupled with spline lines of selected predictors, imaged in Figure 3a-c, 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 5.13μg.m^{-3} (=10.26 ppb). In comparison to a previous studied by Davis and Speckaman (1999), predicted 8-hr-average ozone, r^2ranged from 66% to 73% and RMSE ranged from 13.2 to 16.3 ppb [27], our results indicated the improvement of the predicted values.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 [28].

The quantile (Q-Q) plot accomplished by auto-regression GAM at 95% confident level was illustrated in Fig. 3a. The examples of Poisson regression model using smoothing spline smoother were shown in Figure 3b and 3c. Two VOCs, formaldehyde and m-xylene were chosen as their different outcomes. Fig. 4 displayed the plots of ozone response against OFP levels of formaldehyde and global radiation, over time which displayed the lift of OFP levels and ozone in recent years straightly coupled with association of global radiation. 3D plot clearly illustrated the association between formaldehyde OFP and Ozone formation. In Fig. 5, the predicted and response ozone levels by GAM of 360 monthly samples from 5 monitoring sites between January 2008 and December 2013duration. The predicted and observed values were found significantly correlation in the same trend.

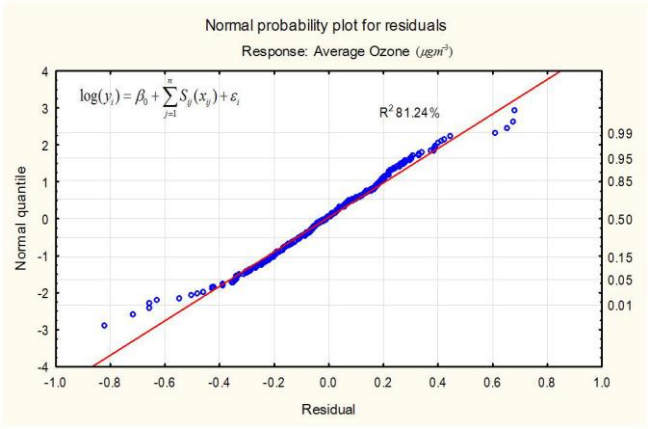

Fig. 3(a) Q-Q plot of residual and regression ozone

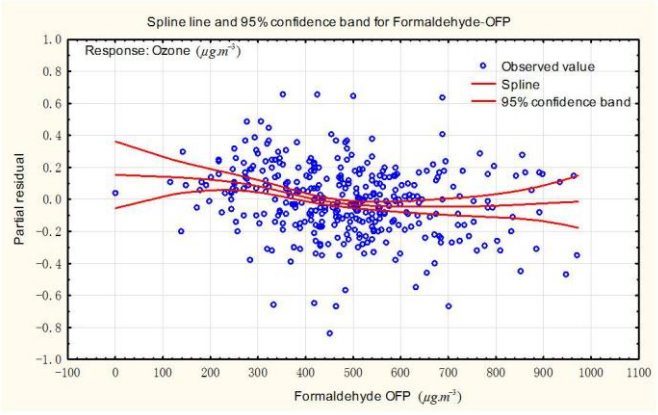

Fig. 3(b) Spline lines and 95% CI of formaldehyde OFP

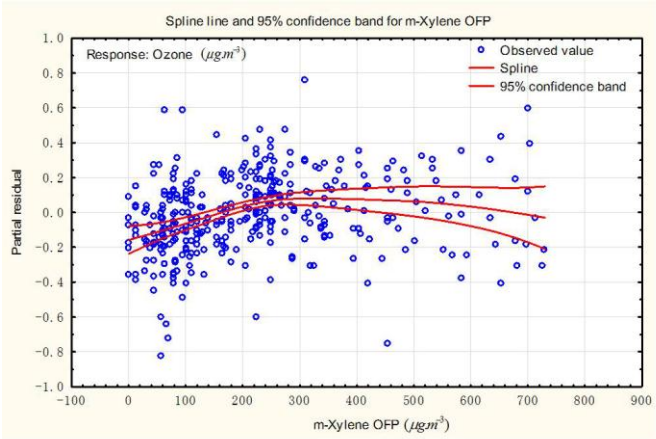

Fig. 3(c) Spline lines and 95% CI of m-xylene OFP

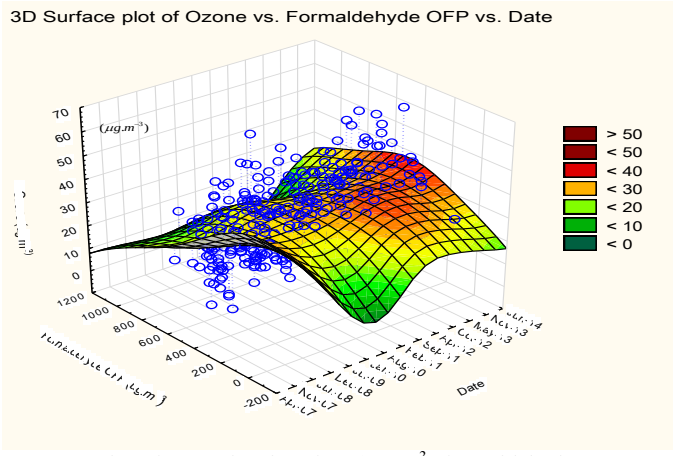

Fig. 4 3D plot of ozone level against (μg.m^{-3}) formaldehyde OFP (μg.m^{-3}) and date

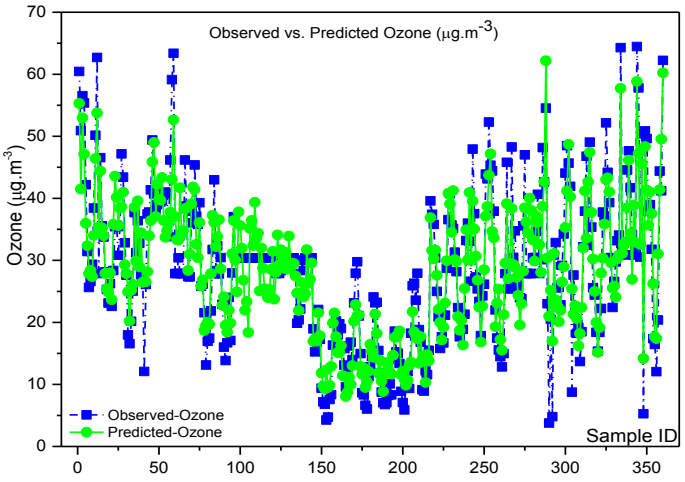

Fig. 5 Comparison plots of observed and predicted ozone concentration by GAM analysis

IV. Conclusion

The cumulative impacts of VOCs through ozone formation in Bangkok, Thailand was the highest level, directly impacted by halogenated HCs indicated by the overall mean of response (40.21%) and r^2 change 9.39% of GAM. Even though their ozone production contribution was lower than other HCs found in Bangkok. Meanwhile HCs, as the group with greatest OPC (59.51%), had a moderate effect (6.01%) to ozone production with dropped the change of R^2, which suggested the VOCs limiting conditions of Bangkok area. Similarly, in the cases of oxygenated HCs and others HCs. Toluene was the key specie that had the highest OFP level and contribution to ozone (607.28 μg.m^{-3}, 0.30%); however it did not significantly impact to ozone formation validated from GAM analysis ($p<0.05$). Additionally, these results can be employed to provide a frame for modeling the impacts of VOCs to ozone production and selecting the appropriate tool to control VOCs species which significantly incline ozone levels in urban atmosphere and affect to environmental air quality.

ACKNOWLEDGMENT

The authors are deeply appreciated the valuable suggestion from Assisstant Professor Dr. SarawutThepanondh, Department of Sanitary Engineering, Faculty of Public Health, Mahidol University, Bangkok Thailand. The authors would sincerely thank to Thailand Pollution Control Department for providing the air quality and meteorological data.

REFERENCES

[1] N.A. Amin, "Reducing Emissions from Private Cars: *Incentive Measures for Behavioural Change*,."Prepared for economics and trade branch, division of technology, industry and economics, UNEP, 2009

[2] S.D. Stevenson, Science *Report:" Influence of emissions, climate and the stratosphere on tropospheric ozone*," The Environment Agency, Bisrol, UK., 2006

[3] Pollution Control Department [PCD]. *Thailand State of Pollution Report 2011-2013*.

[4] N.B. Zhang and N.T. Kim Oanh,"Photochemical smog pollution in the Bangkok Metropolitan Region of Thailand in relation to ozone precursor concentrations and meteorological conditions,"*Atmospheric Environment*,vol. 36, no. 26, pp. 4211-4222, 2002.

[5] N.T. Kim Oanh and N.B. Zhang, "Photochemical smog modeling for assessment of potential impacts of different management strategies on air quality of the Bangkok metropolitan region, Thailand," *Air &Waste***,**vol. 44, no. 54, pp.1321–1338, 2004

[6] N.A. Shah, G. Yun-Shan and Zhao H. "Aldehyde and BTX emissions from a light duty vehicle fueled on gasoline and ethanol-gasoline blend, operating with a three-way catalytic converter," *Jordan Journal of Mechanical and Industrial Engineering*,vol. 4, pp. 340-345, 2010

[7] The Royal Thai Government Gazette [GG].*The Royal Government Gazette No.126 Part 114, Notification of National Environmental Board No.33, B.E 2552 (2009) under the Enhancement and Conservation of National Environmental Quality Act, B.E.2535 (1992).*

[8] U.S. EPA *Compendium Method TO-15, Determination of Volatile Organic Compounds (VOCs) in Air Collected In Specially-Prepared Canisters and Analyzed by Gas Chromatography. Mass Spectrometry (GC/MS) U.S EPA. Report nr EPA/625/R-96/010b*. (1999a).

[9] U.S. EPA. *Compendium Method TO-11, Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC) [Active Sampling Methodology] EPA/625/R-96/010b*. (1999b).

[10] R.Ooka, M. Khiem, H. Hayami, H. Yoshikado, H. Huang andY. Kawamoto,"Influence of meteorological conditions on summer ozone levels in the central Kanto area of Japan," *Procedia Environmental Sciences*, vol.4, pp.138-150, 2011

[11] C. Dueñas, C.M.Fernández, S. Cañete, J. Carretero andE. Liger,"Assessment of ozone variations and meteorological effects in an urban area in the Mediterranean Coast,"*Science of the Total Environment*vol.299, no.1, pp. 97-113, 2002

[12] P.W. Carter,"Development of ozone reactivity scales for volatile organic compounds,"*Air &Waste*, vol.44, no.7, pp. 881-899, 1994

[13] G.R. Derwent, E.M. Jenkin, R.N. Passantc and J.M. Pilling,"Reactivity-based strategies for photochemical ozone control in Europe,"*Environmental Science & Policy***,**vol. 10, pp.445–453, 2007

[14] M. Aldrin andH.I. Haff, "Generalised additive modelling of air pollution, traffic volume and meteorology,"*Atmospheric Environment*, vol.39, no.11, pp.2145-2155, 2005

[15] J.T. Hastie andJ.R. Tibshirani,*Generalized Additive Models*,vol.43, CRC Press. 1990

[16] A. Agresti, *An Introduction to Categorical Data Analysis***,** vol.135, Wiley. 1996

[17] World Health Organization,*Air Quality Guidelines for Europe*, WHO Regional Office for Europe, 2000

[18] W. Wei,S. Wang, S. Chatani, Z. Klimont, J. Cofala andJ. Hao,"Emission and speciation of non-methane volatile organic compounds from anthropogenic sources in China,"*Atmospheric Environment*,vol.42, no.20, pp. 4976-4988, 2008

[19] N.T. Kim Oanh, M. Martel, P. Pongkiatkul andR. Berkowicz,"Determination of fleet hourly emission and on-road vehicle emission factor using integrated monitoring and modeling approach,"*Atmospheric Environment***,** vol.89, pp. 223–232, 2008

[20] J. Suthawaree, Y. Tajima, A. Khunchornyakong, S. Kato, A. Sharp andY. Kajii,"Identification of volatile organic compounds in suburban Bangkok, Thailand and their potential for ozone formation,"*Atmospheric Research***,**vol.104, pp. 245-254, 2012

[21] W.Tsai, "Environmental risk of new generation fluorocarbons in replacement of potent greenhouse gases," *Int.J. Global Warming*, vol.5, no.1, pp 84-95, 2013

[22] C. Cai, F. Geng, X. Tie, Q.Yu andJ. An, "Characteristics and source apportionment of VOCs measured in Shanghai, China,"*Atmospheric Environment***,**vol.44, no.38,pp. 5005-5014, 2010.

[23] US. EPA. "*Regulatory Impact Analysis of the Proposed Revisions to the National Ambient Air Quality Standards" 2007 Report nr EPA-452/R-07-008*

[24] J.H. Shin, C.J. Kim, J.S. Lee andP.Y. Kim,"Evaluation of the optimum volatile organic compounds control strategy considering the formation of ozone and secondary organic aerosol in Seoul, Korea,"*Environmental Science and Pollution Research***,**vol.20, no.3, pp. 1468-1481, 2013

[25] T.M. Latif, S. L. Huey and L. Juneng, "Variations of surface ozone concentration across the Klang Valley, Malaysia,"*Atmospheric Environment***,**vol.61, pp.434-445, 2012

[26] K.L. Sahu, S. Lal, V. Thouret andG.H. Smit,"Climatology of tropospheric ozone and water vapour over Chennai: a study based on MOZAIC measurements over India,"*International Journal of Climatology*,vol.31, no.6, pp.920-936, 2011

[27] M.J. Davis and P.Speckman,"A model for predicting maximum and 8h average ozone in Houston,"*Atmospheric Environment*,vol.33, no.16,pp.2487-2500, 1999

[28] K.H. Preisler, J.M. Arbaugh, A. Bytnerowicz andL.S. Schilling "Development of a statistical model for estimating spatial and temporal ambient ozone patterns in the Sierra Nevada, California,"*The Scientific World Journal***,**vol.2, pp.141-154, 2002