Diurnal Fluctuations of Ozone Concentrations and its Precursors and Prediction of Ozone Using Multiple Linear Regressions

NOR AZAM RAMLI, NURUL ADYANI GHAZALI & AHMAD SHUKRI YAHAYA

ABSTRACT

The chemical reaction of pollutants emitted into the atmosphere leads to a variety of oxidized products, which are commonly referred to as secondary pollutants. Ground level ozone is a known secondary photochemical pollutant of major importance possessing detrimental effects on health, agriculture, natural/urban ecosystems and materials. Ozone (O_3) can irritate lung airways and cause inflammation much like sunburn. Hourly and monthly variations of O_3 and their precursors – nitrogen oxides (NO_x) and meteorological parameters (temperature and wind speed) were presented using time series plots. Possibility of employing multiple linear regression models as a tool for prediction of O_3 concentration was also tested. Measurement was performed continuously in 2005 at two sampling stations located in the metropolitan area of Malaysia. Results indicated that the formation of O_3 in the study area was influenced by NO_x precursors and meteorological conditions. The hourly variation showed maximum O_3 concentrations were recorded between 1300 to 1400 hours, while NO_x and nitrogen dioxide (NO_2) exhibited two maxima, at 0800-1000 and 2000-2100 hours. The daily cycle of highest O_3 concentrations were revealed a lower night level and inverse relations between O_3 and NO_x. This is clear evidence of photochemical formation of O_3. Temperature has the highest influence to the high O_3 concentrations

Key words: Ground-level ozone, time series plot, multiple linear regression

ABSTRAK

Tindakbalas kimia ke atas bahan pencemar yang dilepaskan ke atmosfera menyumbang kepada pelbagai produk teroksida, yang umumnya dikenali sebagai bahan pencemar sekunder. Ozon aras permukaan yang juga dikenali sebagai bahan pencemar fotokimia sekunder yang sangat penting mempunyai kesan buruk pada kesihatan, pertanian, alam/ekosistem bandar dan bahan. Ozon (O_3) boleh merengsa saluran udara paru-paru dan menyebabkan radang yg menyerupai kesan terbakar akibat sinar matahari. Variasi kepekatan O_3 mengikut jam dan bulan dan prapenanda ozon - oksida nitrogen (NO_x) dan pembolehubah meteorologi (suhu dan kelajuan angin) digambarkan dengan menggunakan plot siri masa. Kebolehgunaan model regresi linear berganda sebagai alat untuk ramalan kepekatan O_3 juga diuji. Pengukuran dijalankan berterusan dari tahun 2005 di dua stesen pencerapan terletak di kawasan metropolitan Malaysia. Keputusan kajian menunjukkan bahawa pembentukan O_3 di kawasan kajian dipengaruhi oleh prapenanda NO_x dan keadaan meteorologi. Variasi kepekatan O_3 maksimum mengikut jam menunjukkan kepekatan O_3 maksimum berlaku antara jam 1300-1400 sementara kepekatan NO_x dan nitrogen dioksida (NO_2) menunjukkan dua maksima, pada jam 0800-1000 dan jam 2000-2100. Kitaran harian kepekatan tertinggi O_3 menunjukkan paras yang rendah pada sebelah malam dan hubungan berkadar songsang antara O_3 dan NO_x. Ini merupakan bukti jelas pembentukan O_3 melalui tindakbalas fotokimia. Suhu mempunyai pengaruh terbesar terhadap kepekatan O_3 maksimum.

Kata kunci: Ozon aras permukaan, plot siri masa, regresi linear berganda

INTRODUCTION

Ozone (O_3) is a gas composed of three atoms of oxygen and occurs both in the Earth's upper atmosphere and at ground level. This secondary pollutant, is generated in the presence of solar ultraviolet radiation through a complex series of photochemical reactions involving VOC combining with a group of air pollutants known as nitrogen oxides (NO_x), originating from both anthropogenic (e.g., industry and vehicle emissions) and biogenic sources (e.g., forest, and soil) (EPA 2007). There are no significant primary emissions of O_3 into the atmosphere and all the O_3 found has been formed by chemical reactions that occur in the air (WHO 2009). Ozone is mainly formed indirectly by the action of sunlight on nitrogen dioxide. As a result of the various reactions that take place in the atmosphere, O_3 tends to build up downwind of urban centers where most of the NO_x is emitted from vehicles (Andrew & Thomas 2003). Ozone, therefore, is a secondary photochemical pollutant that is not polluting in its own right. This is the main reason why the presence of O_3 is such a serious environmental problem that is difficult to control and predict (Abdul-Wahab et al. 2005).

Ozone is naturally present in relatively large concentrations in the stratosphere, an upper atmospheric layer. Stratospheric O_3 should not be considered a photochemical air pollutant; a phrase that's used which should be restricted to O_3 issues associated with the lower atmosphere or troposphere (Freedman 1995). It is known that ground level ozone is responsible for various adverse effects on human health, climate and vegetation. In addition, high O_3 levels not only play a role in causing damage to plant species, various natural materials and manufactured goods but also lead to the damage of lung tissues in humans (Abdul-Wahab et al. 2005). Therefore, understanding on the formation of ground level ozone is very important. It can be used as a basis for issuing advance warning to the public prior to O_3 reaching the peak concentration of a day (Ghazali et al. 2009).

CHARACTERISTICS AND TRANSFORMATION OF OZONE

The formation of O_3 in the upper atmosphere was explained as a chemical process involving radiant energy ($h\upsilon$) from the sun. Certain wavelengths in the ultraviolet range are able to break oxygen (O_2) into two low-energy oxygen atoms, O (^{3}P) (Ghazali et al. 2009).

Radiant energy was shown to break nitrogen dioxide (NO_2) into nitric oxide (NO) and O (^{3}P). When NO_2 is exposed to UV light ($\lambda<424$ nm), an oxygen atom and a NO molecule are generated via the NO_2 photolysis reaction (Lawrence 2003). As a result, O_3 is formed as the product of the reaction between O (^{3}P) and O_2. The O_3 that forms, however, can react quickly with NO to produce NO_2 and O_2.

The steady-state concentration of O_3 as is defined by Seinfeld and Pandis (2006) are:

$$[O_3] = \frac{J[NO_2]}{K''[NO]} \qquad (1)$$

The characteristics and transformation of ozone have been discussed in details in Ghazali et al. (2009).

STUDY AREA

Selangor is one of the most fascinating states in Malaysia, being the most developed in the country and among the best in infrastructure and telecommunication facilities in the region. The state covers about 125,000 km^2 and has an average temperature of 26° C. Selangor's geographical position in the centre of Peninsular Malaysia contributed to the state's rapid

development as Malaysia's transportation and industrial hub, which in turn attracts migrants from other country. The influx of illegal immigrants, particularly from Indonesia, has further contributed to Selangor's rapid population growth.

Shah Alam (Coordinates: 3°5′00″N 101°32′00″E) is a city in Malaysia, about 25 kilometers   west of the country's capital, Kuala Lumpur. Shah Alam is the state capital of Selangor (Figure 1). The total area for Shah Alam covers about 290.3 km² with a total population of 584,340 (July 2006). The monitoring station for Shah Alam was located at Sekolah Menengah Kebangsaan TTDI Jaya, Shah Alam, with coordinate N 03° 05' 19.819" and E 101° 34' 9.49". The station is surrounded by residential areas. However, it is not far from industrial zone (Ghazali 2009). The station of Shah Alam is located at latitude 3°06' 17" North of the equator and longitude 101° 33' 22" East of the prime meridian.
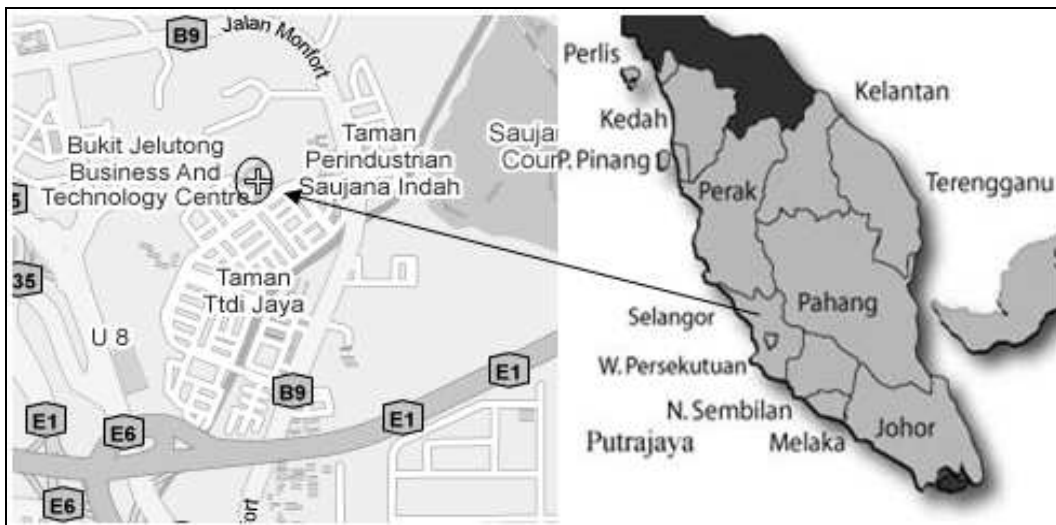

Figure 1. The location of monitoring station for Shah Alam

Figure 2. The location of monitoring station for Nilai

Nilai is a town located in Negeri Sembilan (Figure 2). It is geographically located at latitude 2°49' 00" North of the equator and longitude 101°48' 00" East of the prime meridian. Nilai covers an area of 738 km² from 6645 km² of the state of Negeri Sembilan. It is located in

the south part of Malaysia and is a heavily industrialized area. Climatically, Negeri Sembilan represents a typical tropical monsoon characterized by uniformly high temperatures between $27^{o}C – 30^{o}C$ in daytime and $22^{o}C – 24^{o}C$ in nighttime. Due to its proximity, and connection through the Malayan Railway Administration or known as 'Keretapi Tanah Melayu Berhad' to Kuala Lumpur, Putrajaya, and Kuala Lumpur International Airport (KLIA), it is a rapidly growing town.

Development projects can be seen as one drives around Nilai. The growth in industrial sectors have increased air pollution problem in Nilai. Apart from that, the growth in industrial activities is normally accompanied by the rapid increase in population and traffic density. The population distributions in Nilai had also growth every year due to the increase in vacancies offered by the industries. The total number of population estimated in Nilai for 2006 is about 458 300 from 1,004,807 total population of the state of Negeri Sembilan.

In addition to that, numbers of mobile sources that include passenger cars, taxis, buses, motorcycles, vans and lorries have also increased every year. The total number of mobile sources in 2005 is 640 322. In Nilai, the air quality was moderate for 84 percent of the time, 11 percent good and 5 percent unhealthy (DoE 2007). The station of Nilai is located at latitude 2°49' 18" North of the equator and longitude 101° 48' 41" East of the prime meridian.

RESEARCH METHOD

Multiple regression analysis is one of the most widely used methodologies for expressing the dependence of a response variable on several predictor variables (Abdul-Wahab et al. 2004; Ghazali et al. 2008; Ghazali et al. 2009). The application of multiple linear regression techniques allows formulation of explicit equations that are simple and can be used to better understand the processes involved in O_3 formation (Barrero et al. 2005). Our model is aimed at predicting hourly O_3 concentration maxima several hours in advance.

Data were collected in an urban area by continuous air monitoring stations in Shah Alam, Selangor and Nilai, Negeri Sembilan from January 2005 to December 2005. These facilities provided hourly concentrations of pollutants such as O_3, NO_2, NO, NO_x, non-methane hydrocarbons (NmHC) and total hydrocarbons (THC) as well as meteorological parameters such as temperature, wind speed, wind direction and humidity. Samples of O_3 concentrations were collected by using UV Absorption Ozone Analyzer Model 400A (EPA Approved EQOA 0992-087). The model 400A UV Absorption Ozone Analyzer is a microprocessor controlled analyzer that uses a system based on the Beer-Lambert law for measuring low ranges of ozone in ambient air. Samples of NO_x concentrations were collected using chemiluminescent $NO/NO_2/NO_X$ Analyzer Model 200A (EPA Approval RFNA 1194-099). The model 200A uses the proven chemiluminescence's detection principle, coupled with state of the art microprocessor technology to provide the sensitivity, stability and ease of use needed for ambient or dilution CEM monitoring requirement.

Time series plots of diurnal cycle for both O_3 and NO_2 concentrations were plotted using Microsoft Excel. The mathematical model was developed using multiple linear regression for variable introducing using SPSS Version 11.5. Coefficient of determination (R^2) and root mean squared error (RMSE) were used as performance indicators. R^2 measured the variability of the observed data explained by the model while RMSE indicated the difference between observed and predicted concentrations (Ghazali et al. 2009).

RESULTS AND DISCUSSIONS

Descriptive Statistics

Table 1 gives summaries of the descriptive statistics for each pollutant and meteorological parameters for Shah Alam and Nilai.

Table 1. Summary of descriptive statistics for Shah Alam and Nilai

Descriptive Statistics	O_3 (ppm)	NO_2 (ppm)	Temperature (°C)	Wind Speed (m/s)	Humidity (%)
SHAH ALAM					
Mean	0.022	0.017	27.8	4.51	78.1
Median	0.011	0.016	26.3	3.69	83.1
Std.Deviation	0.025	0.011	3.87	2.98	14.3
Maximum	**0.152**	**0.080**	**21.7**	**17.7**	**35.0**
NILAI					
Mean	0.019	0.012	27.1	6.98	75.9
Median	0.009	0.010	25.9	6.15	78.1
Std.Deviation	0.019	0.008	3.55	4.19	12.5
Maximum	**0.119**	**0.062**	**37.6**	**26.3**	**95.0**

The mean for both 2 pollutants are higher than the median, indicated that there were extreme event occurred. Mean O_3 concentration for Shah Alam and Nilai are 0.022 ppm and 0.019 ppm respectively and it is below the annual O_3 guideline value of 0.1 ppm (for 1 hour averaging time). However, the maximum hourly O_3 concentration recorded for the whole year is 0.152 ppm for Shah Alam and 0.119 ppm for Nilai. This value is higher than the Malaysia Ambient Air Quality Guidelines for 1-hour averaging time which is 0.1 ppm. This value also higher than other countries guideline such as USA with 0.12 ppm for 1-hour averaging time (US EPA 2009) and WHO guideline with 0.05 ppm for 8-hour averaging time (WHO 2009). The mean and maximum hourly NO_2 is also below the guideline which is 0.080 ppm (0.17 ppm for 1-hour averaging time).

Monthly Average Mean Concentrations

The monthly average mean concentrations for both O_3 and NO_2 from January to December 2005 are plotted using multiple line plots for Shah Alam and Nilai are shown in Figure 3.
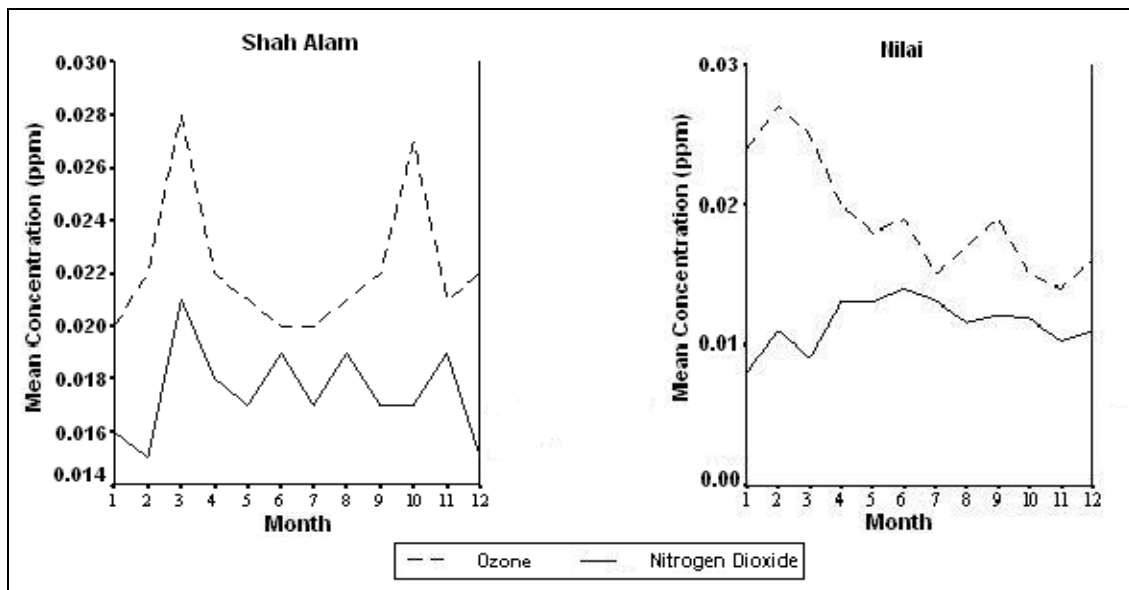
Figure 3. Plot of monthly average mean O_3 and NO_2 concentrations in Shah Alam and Nilai 2005

From the plot we can clearly shows that the highest monthly O_3 concentration recorded in 2005 for Shah Alam were found in March (0.028 ppm) while the lowest O_3 concentration are found in June and July (0.02 ppm). On the other hand, the highest monthly NO_2 concentrations are recorded in March (0.021 ppm) and the lowest monthly NO_2 concentrations are found in December (0.015 ppm). However, the highest monthly O_3 concentration for Nilai was recorded in February (0.0268 ppm) while the lowest monthly O_3 concentration is found in November (0.0139 ppm). Besides, the highest monthly NO_2 concentrations are recorded in June (0.0143 ppm) and the lowest monthly NO_2 concentrations are found in January (0.0084 ppm).

Roll-back Means

There are occasions where the magnitude of emission reductions needs to be quickly estimated. The 'roll-back' equation can be used to estimate a factor R which is by how much emissions should be reduced to achieve a given reduction in the annual mean concentration (it assumes the background concentration is constant) (Seinfeld & Pandis 2006).

$$R = \frac{mean - guidelines}{mean - background}$$

where mean is the current annual mean of the pollutant concentration, guidelines is the annual mean corresponding to the air quality standard and background concentration assumed to be constant. This approach may find application in assessing the control needed for sources influencing an air quality management area. The equation means that a measure of the reduction can be obtain without dispersion modeling. Table 2 presents the roll-back means for Shah Alam and Nilai.

Table 2. Roll-back means for Shah Alam and Nilai

Pollutants / Sites	Ozone	Nitrogen Dioxide
SHAH ALAM		
Mean	0.0220	0.0170
Guidelines	0.1000	0.1700
Background	0.0311	0.0026
Roll-back means	**8.5714**	**- 10.6250**
NILAI		
Mean	0.0190	0.0115
Guidelines	0.1000	0.1700
Background	0.0311	0.0026
Roll-back means	**6.6942**	**-17.8089**

Mean concentration for ozone in Shah Alam and Nilai are almost same and it is indicate that the value is at alert level. From table, the roll-back means for Shah Alam are (O_3 = 8.5714, NO_2 = -10.6250) and for Nilai are (O_3 = 6.6942, NO_2 = -17.8089). The positive roll-back means of O_3 for both sites indicate that the background value is above the mean. Hence, care should be taken to ensure it does not go near to the guideline value more than the permissible occurrences in one year. The negative roll-back means of NO_2 for both sites indicate that the mean concentration is well below guideline value; hence pollution is not serious in this area.

Diurnal Fluctuations of Ozone and its Precursors Nitrogen Dioxide

The average diurnal profiles of O_3 and NO_2 concentrations for Shah Alam are shown in Figure 4. Diurnal profile for March 2005 and June 2005 represent the dry season while diurnal profile for September 2005 and December 2005 represent the wet season.
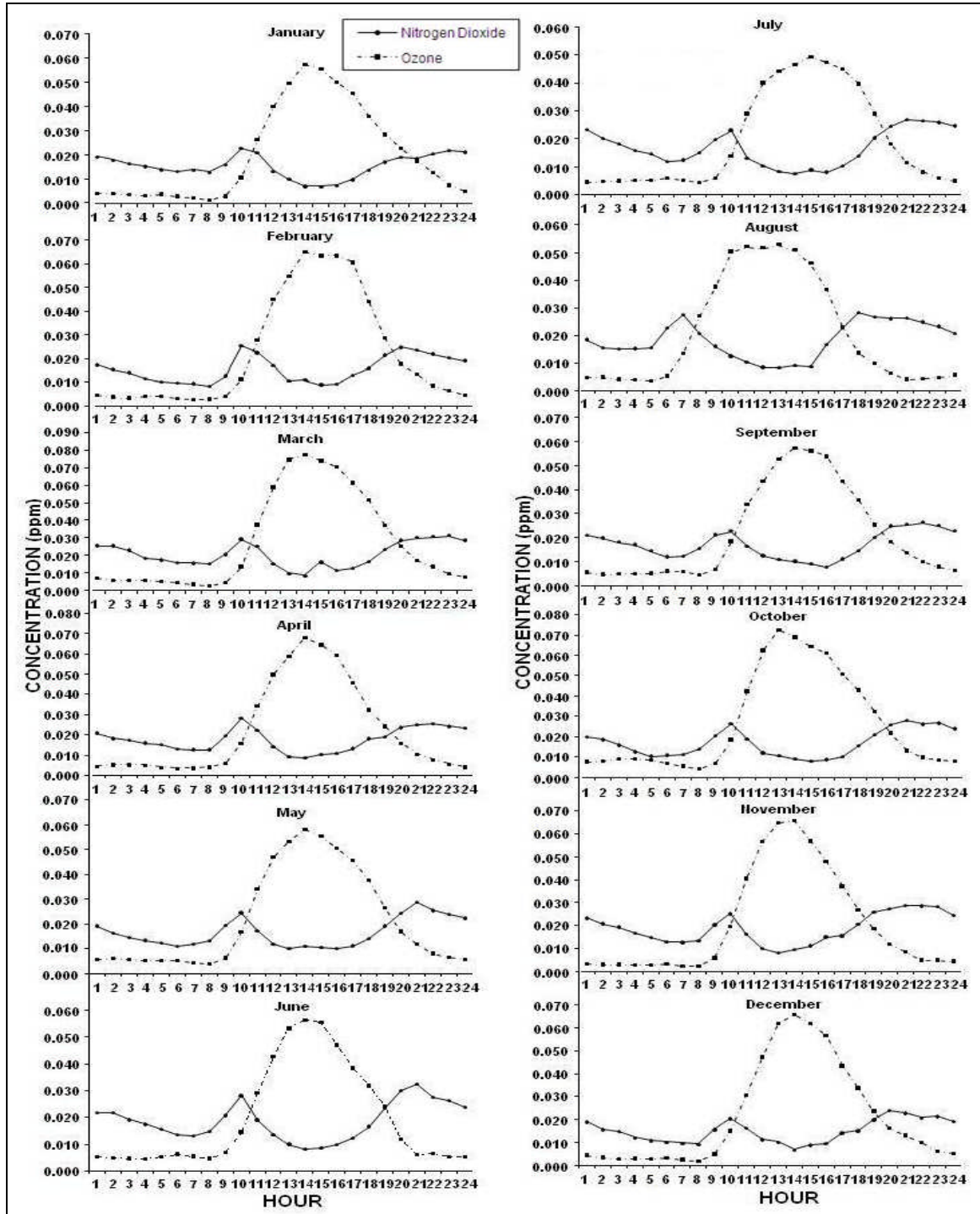

Figure 4. Diurnal fluctuations of ozone concentrations and its precursors Nitrogen Dioxide concentrations for Shah Alam

The diurnal variation of O_3 shows almost the same pattern at all five sites indicating a typical pattern for polluted urban areas characterized by high concentrations during daytime and low concentrations during late night and early morning. In contrast, the precursors, NO and NO_2 show an almost opposite diurnal variation pattern to O_3, which is characterized by high concentrations during night and early morning and low concentrations during daytime, especially noon and afternoon. An increase in the concentration of O_3 is closely corresponding to decrease in the concentrations of the precursors. The similar diurnal pattern in O_3 and precursors was observed in numerous urban areas around the world (Tu et al. 2007; Mazzeo et al. 2005; Dueńas et al. 2002; Zhang & Oanh 2002; Lal et al. 2000).

Ozone exhibits strong day-to-day variation and is sometimes virtually undetectable. Low wind speeds (<3 m/s) promote the build-up of high local ozone concentrations. The availability of NO and NmHC from local emissions such as vehicles and other anthropogenic activities must be considered to be among the contributing factors. Changes in O_3 amounts are closely linked to temperature, with colder temperatures resulting in more polar stratospheric clouds and lower O_3 levels. O_3 generates heat in the stratosphere, both by absorbing the sun's ultraviolet radiation and by absorbing upwelling infrared radiation from the lower atmosphere. Besides the photochemical reactions effected by solar radiation and variations in anthropogenic emissions, boundary layer processes and meteorological parameters also play important roles in the process of diurnal variations in O_3 and its precursors.

The average diurnal profiles of O_3 for both dry and wet season shows almost the same pattern with suggest that O_3 concentrations have lower concentrations at night. From Figures 4 and Figure 5 it was observed that, at 0100 hour until 0800 hour, the concentrations of O_3 are low due to the absence of sunshine and low NO_2. During morning hours, lower boundary layer height reduces the mixing processes between the O_3 surface layer (the bottom 10% of the boundary layer) and the O_3 upper layer largely in comparison to the noontime and contribute to early morning low O_3 levels (Lal et al. 2000). O_3 will increase following the high NO_2 due to traffic emissions during morning peak hours around 0800 to 0900 hour, the accumulated NO_2 concentration reached the maximum at 1000 hour. This is then followed by marked decrease in NO_2 concentrations towards midday until 1600 hour and then increased again in the late evening before reached second peak around 2100-2300 hours.

Conversely, after sunrise, sunlight intensity starts to increase and O_3 concentrations reaches peak concentrations at 1300 to 1500 hour coincided with the high UVB intensity and temperature. This was expected for a photochemical produced species such as O_3. Hence, production of O_3 by photochemical reaction is evidence. Moreover, O_3 concentrations will decreasing rapidly after peak until evening and then keeps decreasing gradually, maintaining low values over night due to the lack of solar radiation.

The diurnal variations in NO, NO_2 and O_3 concentrations during the four season observed exhibited a typical photochemical pollution situation. The peak was first reached by NO followed by NO_2 and finally O_3 several hours later. Subsequently, the after office traffic injected an additional burden of NO into the atmosphere which scavenged the remaining traces of O_3 by early evening and followed by the NO and other primary pollutants reaccumulated for the remainder of the night. This phenomenon seemed to suggest that the photochemical smog formation was able to occur in the city. Nonetheless, while humidity may affect oxidant formation both directly and indirectly, the magnitude of these effects has not been conclusively established.

The average diurnal profiles of O_3 and NO_2 concentrations for Nilai are shown in Figure 5. Diurnal profile for March 2005 and June 2005 represent the dry season while diurnal profile for September 2005 and December 2005 represent the wet season.

The overall average diurnal profile of O_3 for Nilai shows the same pattern with Shah Alam. Ozone production is strongly influenced by available of UVB radiation and air temperature. Night time concentration of O_3 is relatively low because the production of O_3 depends on the intensity of sunlight. After sunrise, sunlight intensity starts to increase, and

reaches a maximum value between hour 1300 hours and 1400 hours. From 0800 -1000 hours and 2000 – 2100 hours, the number of cars driven on the road is at its highest for the day, so the emission of pollutants from automobiles is maximized during these two periods. The maximum concentration of O_3 occurs about 1400 hours and drop just steadily to a low in the evening. On the other hand, the NO_2 concentrations exhibited two maxima, at about 0800-1000 hours and 2000-2100 hours, in correspondence with peaks in vehicular traffic density.
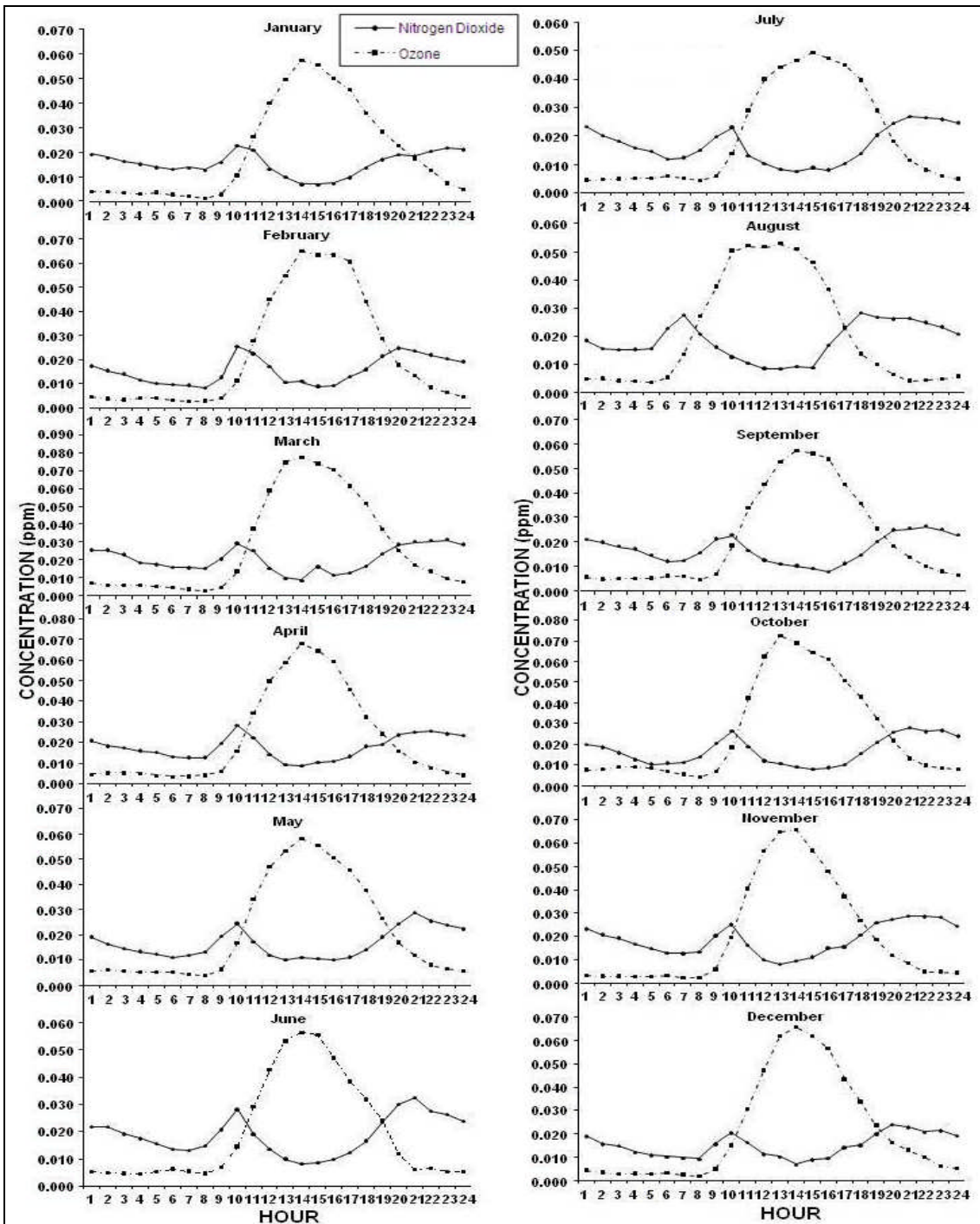

Figure 5. Diurnal fluctuations of ozone concentrations and its precursors Nitrogen Dioxide concentrations for Nilai

Comparison of diurnal O_3 profiles with NO_2 shows that minimum O_3 concentrations were coincident with concentration maxima of the NO_2 concentrations. In a typical day, primary pollutant concentrations exhibited two maxima in correspondence with peak in vehicular traffic density and minimal concentrations are observed in the first hours of the afternoon, reflecting favourable dispersion conditions of the atmosphere coupled with reduced vehicular traffic input. NO_2 have been destroyed from further chemistry by the present of sunlight to form O_3. This shows that the formation of ozone is chemically linked to the emissions of nitrogen oxides through oxidation of gaseous precursors such as NO_2. The occurrences of factors conducive for O_3 production, such as high atmospheric stability, high insolation and temperature, coupled with the availability of NO_x (> 90% constituted NO_2) and NmHC might have led to a higher rate of ozone formation.

Multiple Regression Analysis

A multiple linear regression modeling of ozone concentrations was carried out in order to find predictive equations for the concentration with the pollutant and meteorological variables as the predictor variables. Based on the information extracted from the correlation plots, a number of linear regression models containing several different combinations of predictor variables were developed and evaluated. Coefficient of determination (R^2) is use to determine the best model. The model with a high value of R^2 that does not contain too many variables is considered to be the best model.

Using regression analysis, only 5 factors, namely nitrogen oxides concentration, hydrocarbons concentrations (THC and NmHC), temperature, wind speed and previous hour O_3 concentrations ($O_{3,t-1}$) are observed to be statistically significant and theoretically meaningful and are therefore selected. Table 3 presents, for Shah Alam and Nilai, the results of the regression analysis with O_3 concentrations as the dependent variable and other pollutants and meteorological parameters as independent variables.

Table 3. Linear regression model for prediction of O_3 using the original independent variables for Shah Alam and Nilai

Predictors	Constant	$[O_{3,t-1}]$	$[NO_2]$	[NmHC]	Temp	WS
SHAH ALAM						
R square (0.897)						
Adjusted R square (0.897)						
Standardized coefficient		0.661	-0.084	-0.010	0.451	-0.081
Estimated regression coefficient	-0.075	0.662	-0.172	-0.001	0.003	-0.001
Standard Error	0.004	0.007	0.011	0.001	0.00	0.00
NILAI						
R square (0.890)						
Adjusted R square (0.890)						
Standardized coefficient		0.745	-0.141	-0.018	0.222	-0.081
Estimated regression coefficient	-0.022	0.737	-0.321	-0.001	0.001	-0.001
Standard Error	0.002	0.005	0.012	0.00	0.00	0.00

The R^2 gives the proportion of the variation in the ozone concentration explained by the independent variables in the model. The table shows that, when the six best variables are fitted to the ozone data, the values of R^2 and adjusted R^2 are about the same for both sites (Shah Alam = 0.897 and 0.897, Nilai = 0.890 and 0.890). This means that, close to 90% of the variation in the ozone concentrations are explained by the independent variables listed in the tables.

From Table 3, the highest value of standardized coefficient that shows the greater effect to O_3 for model Shah Alam is a previous hour O_3 concentration which is 0.661 followed by temperature (0.451), NO_2 (-0.084), ws (-0.081) and NmHC (-0.010). While for Nilai, the

highest value of standardized coefficient is a previous hour O_3 concentration (0.745) followed by temperature (0.222), NO_2 (-0.141), ws (-0.081) and NmHC (-0.018). It is shows that a previous hour O_3 concentration is the strongest variables that effect O_3 concentrations for both models. The final revised model was selected and the prediction model for Shah Alam and Nilai are shown in equation (4) and (5) respectively;

$$O_3 = -0.075 - 0.172NO_2 + 0.003Temp - 0.001ws - 0.001NmHC + 0.662O_{3,t-1} \quad (4)$$

$$O_3 = -0.056 - 0.315NO_2 + 0.001NmHC - 0.001THC + 0.002Temp + 0.699O_{3,t-1} \quad (5)$$

The fact that nitrogen dioxide and previous hourly ozone concentration influenced the ozone prediction values was evident. The model also suggested the influence of weather parameter i.e. windspeed and temperature on ozone concentrations. High insolation will result in an increase in temperature which will eventually provide suitable conditions for conversions of NO_2 into O_3. Increase in windspeed will promote dispersions hence reducing the ability of O_3 formations in ambient urban air.

Predictions of O_3 concentration have been done by using the predicted models to determine the accuracy of the models. The predicted hourly O_3 concentrations against the observed hourly O_3 concentrations for the model derived for Shah Alam and Nilai were plotted in Figure 6. This plotted were used to determine a goodness-of-fit of the model. The regression lines (A and C) indicate 95% confidence interval of the model was also drawn.

From Figure 6, it was found that, 89.7% of the point falls within this range suggesting the accuracy of the model developed at $R^2=0.897$. While the accuracy of the predicted model for Nilai is 89.0%. The R^2 values are 0.890.
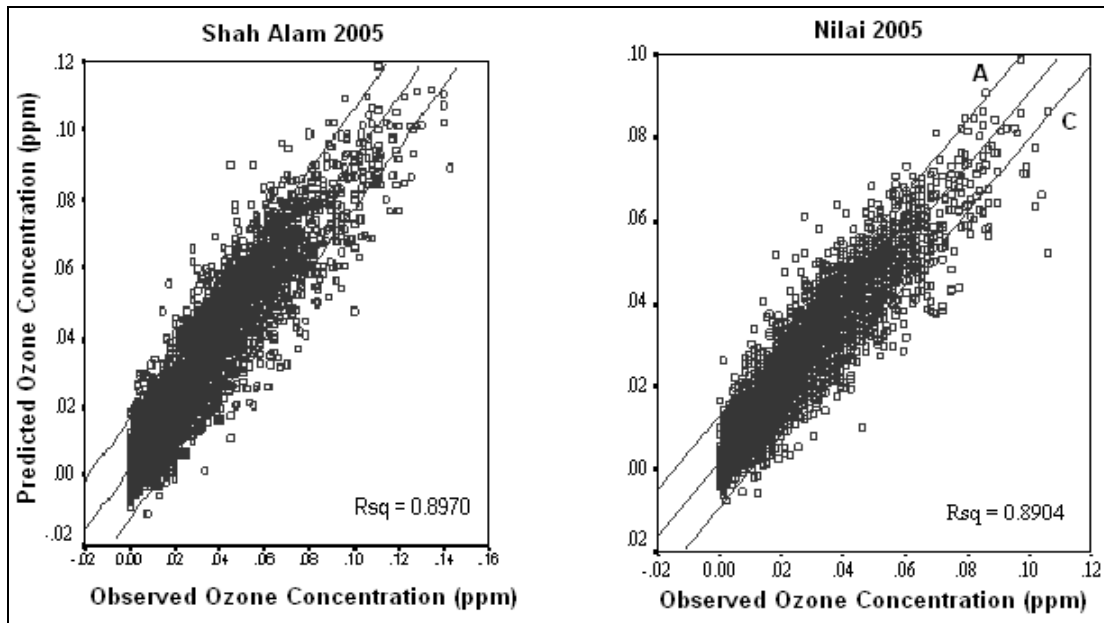

Figure 6. Scatter plot of predicted O_3 against observed O_3 for Shah Alam and Nilai 2005

CONCLUDING REMARKS

This study presents a multiple linear regression model for hourly O_3 concentrations. The model allows predicting O_3 concentrations maxima several hours in advance. Our model based on the

hour of the day and the day of the year, the relations between O_3, temperature, nitrogen oxides and hydrocarbons and previous hour O_3 levels. These variables take into account for the seasonal influences, photochemical and inertial components of O_3 levels, respectively. A traditional pattern of transformation of NO_2 into O_3 in atmosphere was justified through this study. It was observed that O_3 concentrations were negatively correlated to NO_2. This result was expected and confirmed the theory that NO_2 act as the precursors of O_3. This negative correlation is typical of on urban areas where the diurnal cycle of O_3 is impacted by traffic which releases NO_2, its precursor.

The result of fitting the best regression models on the O_3 data using six of the independent variables gave about the same values of adjusted coefficient of determination of around 0.89 for both sites. The prediction model shows the importance of previous hour O_3 concentrations, NmHC and temperature on determining the concentrations of O_3. These variables were used as a predictor variable in two separates multiple regression analyses to obtain the final models for the ozone concentrations.

Despite being linear model and therefore unable to account for non-linear behavior, it has an acceptable performance which is comparable to other, more complex, models found elsewhere in the literature. The model is easy to implement in association with automated pollution monitoring station systems, since the involved variables are commonly automatically measured therefore it will be a useful tool to public health protection because it can provide early warnings to the population. The availability of accurate and real time predictions of air pollutant concentrations level and limit value exceedences would give an early warning system for providing air quality information. It would support the action taken by government to achieve compliance with the air quality standards and to protect populations.

REFERENCES

Abdul-Wahab, S.A., Bakheit, C.S., Al-Alawi, S.M. 2005. Principle component and multiple regression analysis in modelling of ground-level ozone and factors affecting its concentrations. *Environmental Modelling & Softwares* 20: 1263-1271.

Steer, A.D. & Walton, T.E. 2003. Indonesia environment monitor 2003 special focus: Reducing pollution. Indonesia air quality report, World Bank Indonesia Office. http://www.worldbank.or.id

Barrero, M.A., Grimalt, J.O. & Canton, L. 2005. Prediction of daily ozone concentration maxima in the urban atmosphere. Chemometrics and Intelligent Laboratory Systems.

Department of Environment, Malaysia. 2007. *Malaysia environmental quality report 2007*. Kuala Lumpur: Ministry of Science, Technology and the Environment.

Dueñas, C., Fernández, M.C., Cañete, S., Carretero, J. & Liger, E. 2002. Assessment of ozone variations and meteorological effects in an urban area in the Mediterranean Coast. *Science of Total Environ.* 299: 97–113.

Elba, C.T., Eduardo, R.S., Flavio, W. & Jandyra, F. 2009. Measurement of surface ozone and its precursors in an urban area in South Brazil. *Atmospheric Environment* 43: 2213-2220.

Environmental Protection Agency (EPA). 2007. http://www.epa.gov. (09.03. 2007).

Environmental Protection Agency (EPA). 2009. http://www.epa.gov/air/criteria.html. (10.06.2009).

Freedman, B. 1995. Environmental ecology- *The ecological effects of pollution, disturbance and other stresses*. San Diego, California: Academic Press, Inc, 21-22.

Ghazali, N.A., Ramli, N.A., Yahaya, A.S., Yusof, N.F., Sansuddin, N. & Madhoun, W.A. 2009. Transformation of nitrogen dioxide into ozone and prediction of ozone concentrations using multiple linear regression techniques. *Environmental Monitoring & Assessment. Doi: 10.1007/s10661-009-0960-3.*

Ghazali, N.A., Ramli, N.A., Yahaya, A.S., Yusof, N.F., Sansuddin, N. & Madhoun, W.A. 2008. Regression modelling and temporal analysis of hourly ozone concentrations in urban environment of Malaysia. Jamaluddin Md. Jahi, Kadaruddin. Aiyub, Muhammad Rizal Razman, Kadir Arifin & Azahan Awang (eds.). *Proceedings International Conference on Human Habitat and Environmental Change 2008.* Bangi: Instite of the Malay World and Civilisation (ATMA), UKM and Environmental Management Society (EMS) Malaysia.

Lal, S., Naja, M., Subbaraya, B.H. 2000. Seasonal variations in surface ozone and its precursors over an urban site in India. *Atmospheric Environment* 34: 2713-2724.

Lawrence, C.L. 2003. The ozone weekend effect in California: Evidence supporting NO_x emission reductions. Technical Support Document. California Environmental Protection Agency: Air Resources Board.

Mazzeo, N.A., Venegas, L.E., Choren, H. 2005. Analysis of NO, NO_2, O_3 and NO_x concentrations measured at a green area of Buenos Aires City during wintertime. *Atmospheric Environment* 39: 3055–3068

Pudasainee, D., Sapkota, B., Shrestha, M.L., Kaga, A., Kondo, A. & Inoue, Y. 2006. Ground level ozone concentrations and its association with NOx and meteorological parameters in Kathmandu valley, Nepal. *Atmospheric Environment* 40: 8081–8087.

Seinfeld, J.H. & Pandis, S.N. (2006). *Atmospheric chemistry and physics from air pollution to climate change.* 2nd Edition. New Jersey: John Wiley & Sons Inc.

Tu, J., Xia, Z., Wang, H. & Li, W. 2007. Temporal variations in surface ozone and its precursors and meteorological effects at an urban site in China. *Atmospheric Research* 85: 310-337.

WHO. 2009. Photochemical oxidants: Environmental health criteria 7. World Health Organization, Geneva. Available online from World Wide Web: http://www.euro.who.int/Document/E87950.pdf

Zhang, B.N., Oanh, N.T.K. 2002. Photochemical smog pollution in the Bangkok Metropolitan Region of Thailand in relation to O_3 precursor concentrations and meteorological conditions. *Atmospheric Environment* 36: 4211-4222.

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