MODELING OF OZONE PRECURSORS AND THEIR TRANSFORMATION INTO GROUND-LEVEL OZONE IN URBAN ENVIRONMENT IN MALAYSIA

by

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LIST OF ABBREVIATIONS

ANOVA	Analysis of Variance
AOT40	Accumulated Ozone Exposure over a Threshold of 40 ppb
API	Air Pollutant Index
AQI	Air Quality Index
ARBF	Adaptative Radial Basis Function
ARIMA	Auto-Regressive Integrated Moving Average
CAQM	Continuous Air Quality Monitoring Stations
CART	Classification and Regression Tree
CH_4	Methane
CO	Carbon Monoxide
CO_2	Carbon Dioxide
d_2	Index of Agreement
DHHS	Department of Health and Human Services
DoE	Department of Environment (Malaysia)
DU	Dobson Unit
EQR	Environmental Quality Report
FANN	Feedforward Artificial Neural Networks
FB	Fractional Bias
FV	Fractional Variance
hυ	Radiant Energy
IA	Index of Agreement
LOMP	Local Ozone Management and Prevention

LR	Linear Regression
MAAQG	Malaysian Ambient Air Quality Guidelines
MAQI	Malaysian Air Quality Index
MLR	Multiple Linear Regression
MSR	Regression Mean Square
MSE	Residual Mean Square
NAAQS	National Ambient Air Quality Standard
NAE	Normalised Absolute Error
NIOSH	National Institute for Occupational Safety and Health
NMSE	Normalised Mean Square Error
NN	Neural Network
NmHC	Non-methane Hydrocarbon
NO	Nitric Oxide
NO_2	Nitrogen Dioxide
NO_x	Nitrogen Oxides
O_3	Ozone
OH	Hydroxyl Radical
PA	Prediction Accuracy
PAN	Peroxyacetic Anhydride Nitric
PCR	Principle Components Regression
ppm	parts per million
PSI	Pollutant Standard Index
R^2	Coefficient of Determination
RH	Relative Humidity

RMG	Recommended Malaysia Air Quality Guidelines
RMSE	Root Mean Square Error
RO_2	Peroxy Radicals
SO_2	Sulphur Dioxide
STP	Standard Temperature and Pressure
SPSS	Statistical Product and Services Solution
Temp	Temperature
THC	Total Hydrocarbons
USEPA	United States Environmental Protection Agency
UVB	Solar Radiation
UV	Ultraviolet
VOCs	Volatile Organic Compound
WS	Wind Speed
WHO	World Health Organisation

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KAJIAN PERMODELAN PRAPENANDA OZON DAN PERUBAHANNYA KEPADA OZON ARAS PERMUKAAN DALAM PERSEKITARAN BANDAR DI MALAYSIA

ABSTRAK

Ozon (O_3) merupakan salah satu masalah utama dalam pencemaran udara di seluruh dunia kerana O_3 berupaya membawa masalah kesihatan kepada manusia dan persekitaran. Oleh sebab itu, kajian membentuk model ramalan kepekatan O_3 adalah penting untuk meramal kepekatan O_3 supaya dapat memberi amalan awal kepada masyarakat. Data kepekatan O_3 dan nitrogen oksida (NO_x) bersama-sama pembolehubah mateorologi dicerap dari stesen pencerapan untuk lima tempat kajian di Malaysia. Cerapan dibuat selama 5 tahun bermula daripada 2003 hingga 2007. Plot siri masa digunakan untuk menjelaskan transformasi daripada nitrogen dioksida (NO_2) kepada O_3. Keputusan membuktikan bahawa kepekatan puncak O_3 berlaku semasa tengahari apabila keamatan tertinggi UVB dan suhu direkodkan. Dengan menggunakan analisis regresi linear berganda, ramalan ozon model siang hari dan malam untuk setiap tempat kajian telah dijana berdasarkan kepekatan prapenanda O_3; NO_2, nitric oksida (NO), hidrokarbon bukan methane (NmHC), jumlah hidrokarbon (THC) dan parameter meteorologi seperti radiasi ultraviolet (UVB), suhu, kelembapan, kelajuan angin and arah angin sebagai ramalan. Data ini dianalisis dengan menggunakan kaedah regresi linear agar menghasilkan persamaan yang berguna untuk ramalan kepekatan O_3 pada masa hadapan. Pekali penentuan berganda (R^2) dikira untuk menunjukkan darjah kelinearan antara kepekatan O_3 dengan pembolehubah yang lain. Daripada model regresi yang dihasilkan, nilai ramalan kepekatan O_3 didapati. Ramalan kepekatan O_3 telah dijalankan dan plot tersebar kepekatan O_3 lawan ramalan O_3 telah diplot untul model yang dijanakan. Di antara parameter meteorologi, UVB dan suhu cenderung menyumbang kepekatan tertinggi O_3. Selain itu, kelajuan angin dan arah angin juga mempengaruhi akumulasi prapenanda dan kepekatan O_3 secara tidak langsung. Pengaruh daripada kepekatan O_3 berlainan jam sebelum kepada jam seterusnya juga ditunjukkan dan membuktikan bahawa kepekatan O_3 satu jam sebelum paling mempengaruhi kepekatan O_3 jam seterusnya. Seterusnya, analisis penunjuk prestasi telah dijalankan berdasarkan normalisasi ralat mutlak (NAE), ketepatan ramalan (PA), pekali determinasi (R^2), ralat min punca kuasa dua (RMSE) dan indeks perjanjian (IA). Model yang terbagus bagi ketiga-tiga tempat kajian telah ditentukan. Untuk menguji ketepatan nilai tersebut, graf nilai ramalan kepekatan melawan nilai cerapan dilakarkan. Selang keyakinan sebanyak 95 % dianalisa. Daripada kajian ini, pekali penentuan yang dicapai oleh kesemua model adalah berhampiran dengan 0.8; manakala ketepatan keseluruhan untuk model ramalan terbitan adalah berhampiran dengan 95 %.

MODELING OF OZONE PRECURSORS AND THEIR TRANSFORMATION INTO GROUND-LEVEL OZONE IN URBAN ENVIRONMENT IN MALAYSIA

ABSTRACT

Ozone (O_3) is one of the major problems of air pollution around the world due to its ability to cause adverse effect to human health and environment. Hence, it is important to develop O_3 prediction model to give the early warning to public. The hourly observations of O_3 and nitrogen oxides (NO_x) concentrations together with the weather parameters were monitored from five study areas in Malaysia. The observations were obtained over five year period from 2003 to 2007. Times series plot was used to explain the transformation of nitrogen dioxide (NO_2) into O_3 at urban environment of Malaysia. The findings proved that the peak concentration of O_3 occurs during noon when highest UVB intensity and temperature recorded. By using multiple linear regression analysis, O_3 prediction daytime and night time models for each study areas were developed based on its precursors; NO_2 concentration, nitric oxide (NO) concentration, Non-methane Hydrocarbon (NmHC), total hydrocarbon (THC) and also meteorological parameters such as ultraviolet radiation (UVB), temperature, humidity, wind speed and wind direction as the predictors. These data were analyzed using linear regression methods in order to set up the tool for future prediction of O_3 concentration. Coefficient of determination (R^2) was calculated to show the degree of linearity between O_3 concentrations with other prediction variables. From the regression model, the predicted values of O_3 concentration were observed. Prediction of O_3 concentrations was carried out and scatter plot of observed O_3 concentrations versus predicted O_3 concentrations was plotted for developed models verification. Among the meteorological parameters, UVB and temperature tend to contribute significantly to high O_3 concentrations. Besides that, wind speed and wind direction also affect the accumulation of precursor and affect the O_3 concentrations indirectly. The influences of the different previous hour O_3 concentrations on the next hour concentrations was also demonstrated and proved that previous one hour O_3 concentrations influence the most for the next hour concentrations. Performance indicators analysis was then carried out based on the normalised absolute error (NAE), prediction accuracy (PA), coefficient of determination (R^2), root mean square error (RMSE) and index of agreement (IA) and the best fit models for all the three study areas were determined. To determine the accuracy of the values, plots of predicted O_3 concentration against observed O_3 concentration were done. The 95 % confidence interval was found. From the study, the measured coefficients of determination for all models are above 0.8; however the overall accuracy for predicted models is approximately 95 %.

CHAPTER 1

INTRODUCTION

1.0 AIR POLLUTION IN MALAYSIA

Air pollution is now a problem for major conurbations throughout the world, in both developed and developing countries. In Malaysia, this was perhaps due to the associated rapid growth of the industrial sector, the increase in traffic volume, and the expansion in petroleum industry (Yahaya and Yusoff, 1999). The foremost air quality issue is whether or not urban air quality affect human, agricultural crops, forest and the ecosystem. Although the current situation in London is markedly less serious than it was during the smogs episode of the 1950s (Brimblecome, 1987) but in Malaysia, pollution concentrations regularly exceed the ambient air quality guideline especially in Klang Valley regions (DoE, 2000).

Air pollution is the presence of undesirable material in air, in quantities large enough to produce harmful effects to human health, vegetation, human property, or the global environment as well as create aesthetic insults in the form of brown or hazy air or unpleasant smells (de Nevers, 2000). Yang and Omaye (2009) defined atmospheric air pollution as any gaseous or particulate matter in the air that is not a normal air constituent or is not normally present in the air in high concentrations. However, such an implication ignores that the Earth's atmosphere has undergone substantial changes over time, and was influenced by many other variables, such as the effects of natural disasters, including volcanic eruptions and forest fires, on the atmosphere. Elsom (1992) gave a more thorough definition of air pollution as the presence in the atmosphere of substances or energy in such quantities and of such duration that is liable to cause harm to life, damage to man-made materials and structures, or changes in the weather and climate.

Air pollution has impacts at the local and regional levels. While atmospheric dispersion of airborne pollutants can reduce concentrations and localized effects, the impacts are often felt in places far from the source of emission. The long range impacts of air pollution were also evident in the recent Indonesian forest fires which spread over six countries affecting more than 3,200 km and about 70 million people (Dilip, 2006). Due to the transboundary movement of haze containing particulates and other pollutants, the air pollution index of PM_{10} in the Malaysian state of Sarawak hit record levels of 839 (DoE, 1997; Dilip, 2006).

Air quality in Malaysia is a major concern as the nation forged ahead to become an industrialized nation by the year 2020 (Dilip, 2006). Malaysia's environment in the field of air quality is fairly recent. Officially, its involvement began after the gazette of the Clean Air Regulations in 1978. The air quality monitoring work was first carried out by the Division of Environment in 1977 but it consisted mainly of short surveys (Amir, 2007). These surveys produced limited data in which little analysis could be done.

Subsequently, more air quality monitoring programs were conducted by the Division, although more often than not, these were directed at problematic areas (Amir, 2007). Related studies were also carried out from time to time by other interested bodies and individuals, notably Sham (1984). The findings from the studies conducted by Sham (1984) do give an indication of the air quality in Malaysia. However the sampling was not conducted continuously (Inouye and Azman, 1986). A continuously sampling system is necessary to obtain a more reliable and accurate information about the air quality in our atmosphere.

In line with that, in 1997, 16 new Continuous Air Quality Monitoring (CAQM) stations were set up by the DoE Malaysia in addition to the existing 13 stations (DoE, 1997). Parallel with the rapid development in Malaysia, the increasing numbers of industrial activities associated with the increasing numbers of vehicles increase the need of monitoring work. Therefore, up to 2006, the total monitoring stations in the country is 51 stations that are strategically located in both residential and industrial areas. These include one reference station located in Jerantut, Pahang. The CAQM stations are divided into five categories. Out of 51 stations established in Malaysia, 26% are industrial stations, 57% are residential, 2% traffic, 2% background and 13% PM_{10} stations. The parameters monitored include Total Suspended Particulates, Particulate Matter (PM_{10}), Sulfur Dioxide (SO_2), Nitrogen Dioxide (NO_2), Ozone (O_3), Carbon Monoxide (CO), and lead (DoE, 2006).

Air quality in Malaysia is reported based on air pollution index (API) system. Before the API system was adopted, in 1989, the DoE formulated a set of air quality guidelines, termed Recommended Malaysian Air Quality Guidelines (RMG) for air pollutants, defining the concentration limits of selected air pollutants which might adversely effect the health and welfare of the general public. Based on the RMG, the Department subsequently developed its first air quality index system, known as the Malaysian Air Quality Index (MAQI) in 1993 (DoE, 1996).

An index system plays an important role in conveying to both decision-makers and the general public the status of ambient air quality. In line with the need for regional harmonization and for easy comparison with countries the region, the department revised its index system in 1996, and the API was adopted. The API system of Malaysia closely follows the Pollutant Standard Index (PSI) system of the United States (DoE, 1996).

Table 1.1 shows the ambient standards adopted in MAAQG which forms the basis for calculating the API and compares them with the National Ambient Air Quality Standards (NAAQS) currently enforced in the United States and WHO guidelines.

Table 1.1 Ambient Air Quality Standards – Malaysia, United States and WHO

Air pollutants	Malaysia[a]		USEPA[b]		WHO[c]	
	(µg/m^3)	ppm	(µg/m^3)	ppm	(µg/m^3)	ppm
Carbon monoxide						
8-h average	10	9.0	10	9.0	10	9.0
1-h average	35	30.0	40	35.0	30	25.0
Nitrogen dioxide (NO_2)						
Annual	-	-	100	0.053	40	35.0
1-h average	320	0.17	-	-	200	0.10
Ozone (O_3)						
8-h average	120	0.06	150	0.075	100	0.053
1-h average	200	0.10	235	0.012	N/S	-
Particulate matter (PM_{10})						
24-h average	150	-	150	-	50	-
Sulfur dioxide (SO_2)						
Annual	-	-	80	0.03	N/S	-
24-h average	105	0.04	365	0.14	20	18.0

N/S – Not Specified
[a] DoE Malaysia (2007)
[b] USEPA (2009)
[c] WHO (2006) except for CO from WHO (2009)

Industrialization has been an important instrument for fast economic growth. This has triggered rapid urbanization and an exponential increase in motor vehicles. With the increasing industrialization and urbanization, the number of motor vehicles has also increased rapidly with attendant problems of air pollution. The growing use of motor vehicles aggravates the congestion and air pollution in the urban areas.

Figure 1.1 shows the number of registered motor vehicles in Malaysia from year 2000 to year 2008. The number of motor vehicle registration increasing steadily every year. The average percent increment of registered motor vehicles from 2000 to 2008 is 69.6%. In 2005, number of registered vehicles increase 39.0% from 2000 and reach the highest increment by percent up to 69.6% in 2008.

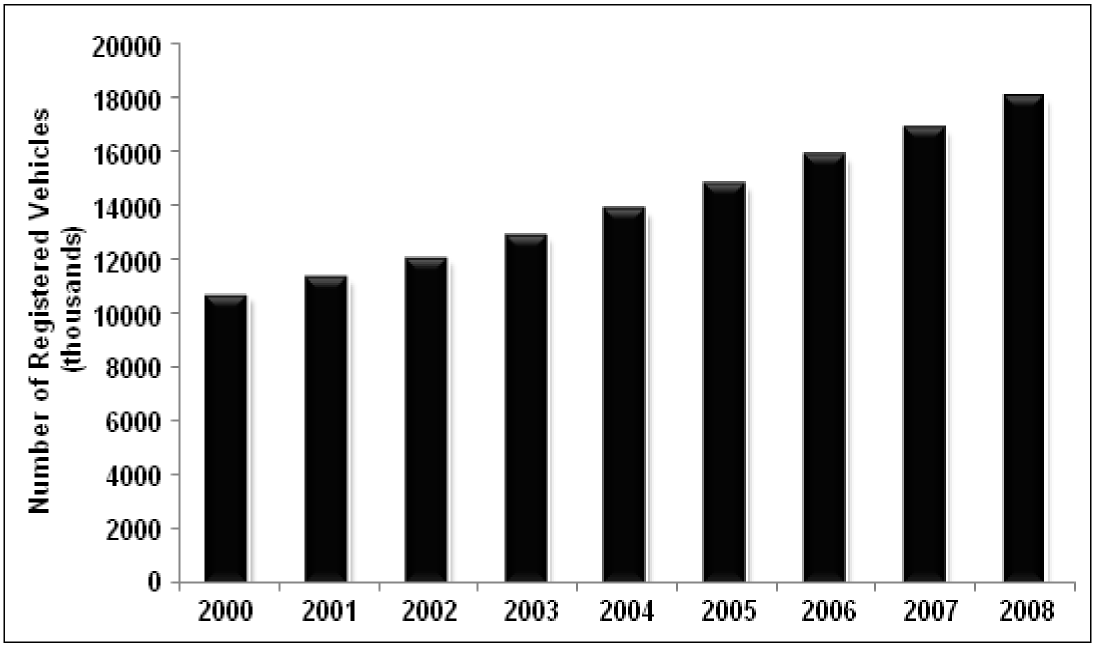

Figure 1.1 Number of registered motor vehicles in Malaysia
(Source: Department of Statistics, 2008)

Vehicle emissions were known to influence the concentration of O_3 in Malaysia. Number of vehicles will adversely affect the air quality. Figure 1.2 illustrates the number of new registered motor vehicles for five states where the monitoring sites were situated. It shows that Kuala Lumpur has the highest number of new registered motor vehicles for 2005 and 2006 followed by Selangor. Negeri Sembilan has the lowest registered motor vehicles among all five sites. However, all sites show the constant number of registered motor vehicles from 2005 to 2006.

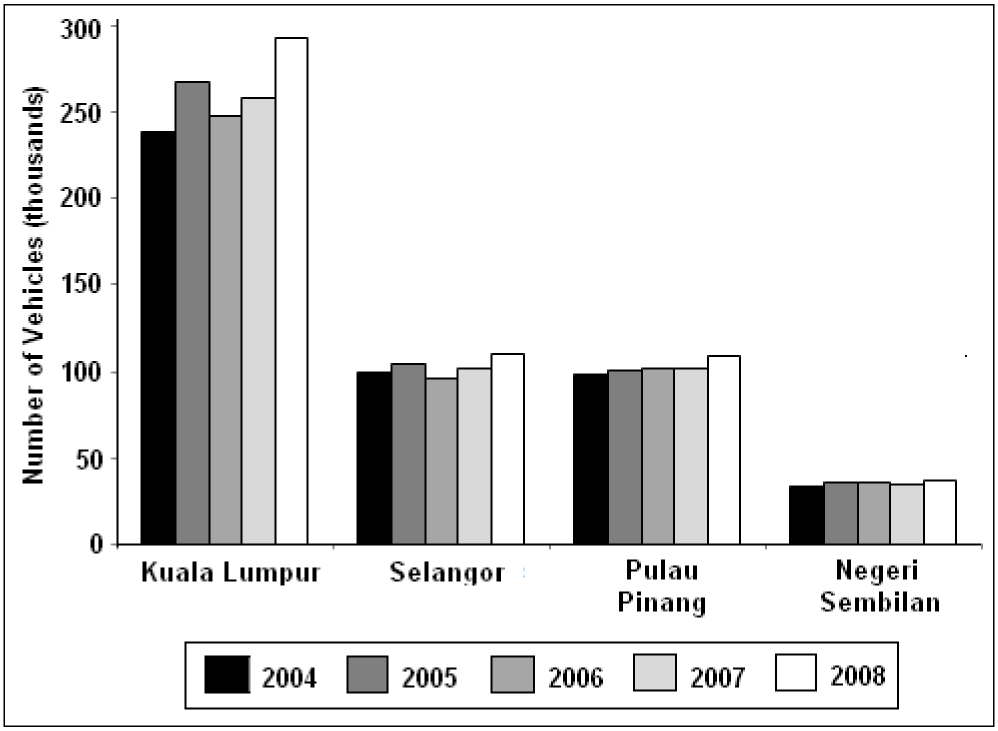

Figure 1.2 Number of new registered motor vehicles
(Source: Road Traffic Department of Malaysia, 2008)

Motor vehicles is the highest contributor to NO_x emission load in 2004 to 2007 which are 59%, 67%, 70% and 70% respectively. Figure 1.3 illustrates NO_x emission by sources in Malaysia in metric tonnes (mt) from 2004 to 2007. Industrial is the second highest contribution to NO_x for 2004 (31%), 2005 (27%) and 2006 (24%). While power station is the second highest contribution to NO_x emission for 2007 (16%) (DoE, 2008)

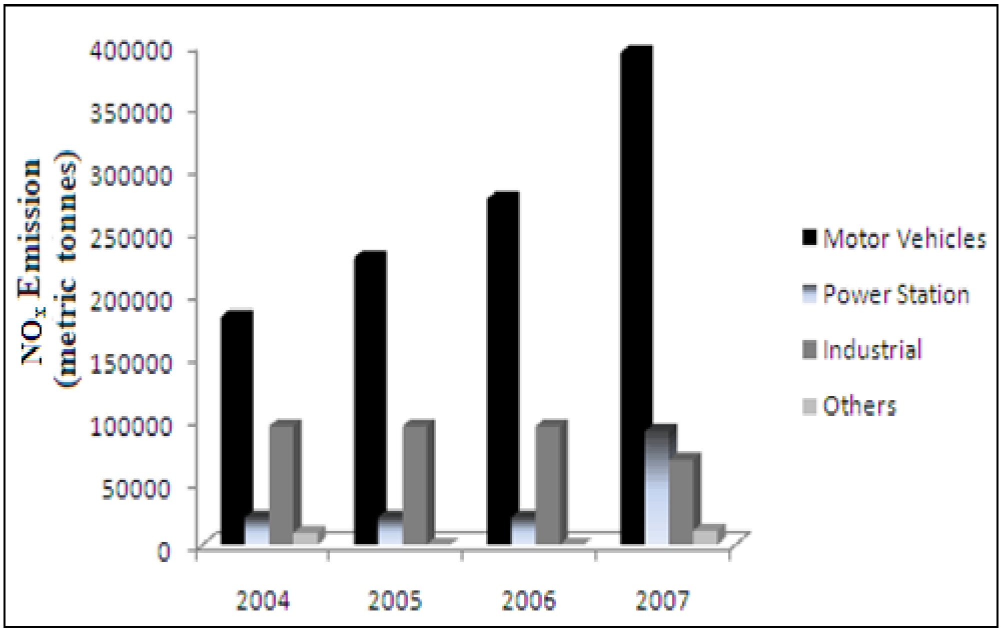

Figure 1.3 NO_x emissions by sources in Malaysia from 2004 to 2007 (DoE, 2008)

1.1 PROBLEM STATEMENT

The air pollution in Malaysia has not yet reached a critical level as in other metropolitan areas in Asia, like Jakarta or Manila (Amir, 2007). However, even outside extreme haze periods, pollution levels increased despite tight regulations and this is exacerbated by the increase in the number of vehicle, distance travelled and growth in industrial production. The haze phenomenon in Malaysia especially in the Klang Valley region is an important and serious problem. Since the early 1980s Klang Valley was reported to experience severe haze episodes (Soleiman et. al., 2003). The haze phenomenon in Malaysia which contribute to the air pollution event with most of the major air pollutant reading including O_3 concentration exceeds Malaysian standard (Awang et al., 2000) have already been observed in some urban and industrial regions of Malaysia (Nichol, 1998; Radojevic, 2001; Yusoff et al., 2009).

Nowadays, ground level ozone and photochemical smog are a worldwide problem at regional and continental scales, with specific geographic areas of agricultural, forestry and natural resources (Austin et al., 2002). It has been identified that ground level ozone poses adverse impacts on human respiratory systems and agricultural products, thus causes much concern to many metropolitan areas such as Los Angeles, London, and Hong Kong (Liu and Leung, 2008).

In Malaysia, ground level ozone were found to be one of the major pollutant from year 2004 to year 2008 (DoE, 2006; DoE, 2007; DoE, 2008; DoE, 2009). Most of the time, the O_3 concentrations in urban area exceeded the MAAQG for Klang Valley (DoE, 2008). Due to the capability of causing adverse effect towards human health, the ground level ozone should become the pollutant of concerned in Malaysia (DoE, 2006; DoE, 2007; DoE, 2008; DoE, 2009). Thus it is necessary and quite urgent to gain a good understanding of the characteristics of O_3 pollution in Malaysia.

Modeling the ozone's fluctuations and providing a good prediction are two of the most important tasks for the researchers. The development of effective prediction models of O_3 concentrations in urban areas is important. Management of control and public warning strategies for O_3 levels requires accurate forecast of the concentration of ambient O_3.

Eventhough an increasing number of studies on O_3 in Asia were reported, limited studies have been conducted on ground-level ozone in Malaysia. In Malaysia, statistical analysis using regression technique is rarely studied and has not been widely used for air pollution study. Moreover, air quality study in Malaysia basically focuses on the trends of air pollutant instead of statistical and modeling approach. The majority of attention on air pollution study in Malaysia has been focused on haze episode (Afroz et al., 2003; Afroz et al., 2007; Awang et al., 2000; Yusoff et al., 2009) and traditional pollutants such as $PM_{10,}$ SO_2 and CO, which are also the main air pollutants required to be monitored in major cities. The O_3 studies in Malaysia were mainly concentrated in Klang Valley (Sham, 1979; Azman et al., 1988). Their study only focused to the trends of O_3 during haze event in Malaysia. These studies used measurements over a short time period. Thus, they are not enough to provide an overall understanding of O_3 pollution in term of statistical method for prediction of O_3 concentration in Malaysia.

Empirical O_3 modelling and regression models in particular have been largely studied worldwide. Many linear regression (e.g. Robeson and Steyn, 1990; Ryan, 1995; Chaloulakou et al., 1999) and non-linear regression (e.g. Hubbard and Cobourn, 1998) models for O_3 prediction have been reported. Chaloulakou et al. (1997) proposed a simple regression model based on NO_2 and meteorological parameters to forecast 3h in advance the maximum O_3 concentration in Athens. Hubbard and Cobourn (1998) obtained very good results by applying a technique based on the selection between two non-linear regression equations. Burrows et al. (1995) used classification and classification and regression tree (CART) models to predict O_3 concentrations in three regions of Canada. On the other hand, Ryan (1995) found that a linear regression model produced more accurate forecasts than a CART model using the same set of inputs. In separate study on regression analysis, Garner and Dorling (2000) used automatic classification as in the CART method to predict O_3 concentration in UK.

Prediction model to predict the amount of ground level ozone include some input parameters that are meteorological variable (temperature, sun exposure or solar radiation, relative humidity, wind direction and wind speed) and concentration of the precursor emissions (NO_x, SO_x, VOCs and CO) which is influence by human activity (Abdul Raheem et al., 2009; Barrero et al., 2005; Castellano et al., 2009; Soja and Soja, 1999). Several studies had been done and prove that the O_3 level strongly depend on meteorological variable especially temperature and solar radiation and precursor emission such as NO_x and VOCs (Abdul Raheem et al., 2009; Barrero et al., 2005; Castellano et al., 2009; Soja and Soja, 1999). Several prediction models are created to predict the concentration of the ground level ozone by two main ways. One is created depending on the previous atmosphere condition and another one depending on theory related to physical and chemical reaction of the O_3 in atmosphere (Soja and Soja, 1999).

Eventhough several studies on diurnal variations of O_3 and NO_x were reported by Zhang and Oanh (2002) in Thailand and by Permadi and Oanh (2008) in Indonesia, but in Malaysia it is rarely studied due to lack of understanding of this process. Besides that, there is little work to studies about the effect or relationship between O_3 and its precursors in Southeast Asia especially in Malaysia. Although some study have been conducted by Awang et al. (2000) and Azmi et al. (2010) on O_3, however, their study only focused on trend of O_3 concentration. There is no prediction model on O_3 concentration have been developed to be implement in Malaysia. Therefore, this study focused on developing the best O_3 prediction model to be implementing in Malaysia scenario. As O_3 concentration form from an atmospheric photochemical processes involving O_3 precursors (NO_x and hydrocarbon), it is important to control the emissions of primary pollutants mainly produced by fossil fuel combustion. Thus it prudent to investigate this issue further that should change pertaining to NO_x emissions and O_3 formation, especially to the policy of inspection and maintenance of private vehicles in the country. Hence, this study is focused to create a prediction model which is suitable to be used in Malaysia.

1.2 OBJECTIVES

It is very important to ensure that this research will contribute to the environmental engineering field of studies. Therefore, this research was carried out with four main objectives, that is:

i. To determine the descriptive statistics of O_3 concentration and to investigate when the high O_3 concentration occurs using time series plot.
ii. To understand the influence of NO_x, incoming solar radiation, and temperature on the formation of O_3 using the diurnal fluctuations plot of ozone.
iii. To develop the multiple linear regression model to predict O_3 concentration using several performance indicator to identify the best prediction model describing O_3 in Malaysian urban areas.
iv. To propose possible framework to manage the impact of gaseous pollution to public.

1.3 SCOPE OF STUDY

Department of environment (DoE) recorded O_3 concentration at 51 monitoring stations throughout the country. From these, five years O_3 monitoring records (2003 to 2007) from five stations were selected to be analysed and modeled using multiple linear regression technique. The formation of O_3 did effect particularly those places within highly urbanized valley, such as Shah Alam, Gombak, Kuala Lumpur (Awang, 2000). Therefore, these 3 station were choosen together with station in Seberang Perai (Pulau Pinang) and Nilai (Negeri Sembilan) as these two station are also located in urban and industrial area.

As reported by Awang et al. (2000), improved in visibility thus more sunshine were also the triggering conditions for greater frequencies of formation of photochemical oxidant like O_3 at the back of highly urbanized river valley in Malaysia. About 50% of the places monitored O_3 were adversely affacted. Shah Alam recorded up to 1.8% readings exceeds the MAAQG followed by Gombak (1.1% exceeds MAAQG). On the other hand, Kuala Lumpur recorded 0.4% readings exceeds the MAAQG while Nilai (0.2%) and Seberang Perai (0.02%). Measurement from 2003 to 2007 were used to investigate the relationship between O_3 and their precursors (NO_2, NO, NmHC,THC) as well as meteorological parameters (temperature, solar radiation, humidity, wind speed and wind direction). Every variables of air pollutants and meteorological data have different characteristics and different influence to the formation of ground-level ozone. Therefore, in this research, all possible parameters that may influence the formation of O_3 was considered and added in construction of prediction model of O_3 concentration.

There are many types of regression analysis used by researcher all over the world to fit the air pollutant concentration data. Among these, the multiple regression analysis is one of the most widely used methodologies for expressing the dependence of a response variable on several independent (Al-Alawi et. al., 2008; Hassanzadeh et al., 2008; Sousa et. al., 2007; Barrero et al., 2006; Abdul Wahab et. al, 2005; Cobourn and Lin, 2004; Baur et.al., 2004; Soja and Soja, 1999; Hubbard and Cobourn, 1998). This method is a commonly used technique to obtain a linear input-output model for a given data set and were successfully implemented in predicting O_3 concentrations.

This study is focused on a relationship between nitrogen oxides (NO and NO_2), hydrocarbons, incoming solar radiation (UVB) and temperature which is a significant contributor to the formation of $O_{3.}$ In order to understand how these transformation occurs, the diurnal fluctuation between O_3 and nitrogen compounds were plotted. For the predcition purpose, multiple linear regrssion was used to predict previous one hour O_3 concentrations at those selected sites. The best models are selected based on several performance indicators such as normalized absolute error (NAE), root mean square error (RMSE), coefficient of determination (R^2), prediction accuracy (PA) and index of agreement (IA) to represent the O_3 monitoring records. It was then used to predict future O_3 concentration. The outcome model will allow government and any other related bodies to prepare and to take action to reduce the concentration of ground level ozone.

1.4 THESIS LAYOUT

Chapter 1 covers the introduction part of this thesis as well as the problem statement, objectives and scope of analysis of the thesis. Furthermore, this chapter gives an overview of air pollution in Malaysia.

Chapter 2 defines the characteristics of all pollutants of concern in this research as well as the effects of the pollutants to the environment that include humans and plant. Besides that, this chapter also discuss the weather influence to O_3 concentration. Furthermore, related studies on O_3 concentration were presented including all types of regression models used to fit O_3 concentration data.

Chapter 3 gives the information about the sites that involved in this research. In this chapter, all the procedures and all the materials involved in this research were also described. Besides, this chapter provides information on multiple linear regression and performance indicators analysis.

Chapter 4 present the statistical characteristics of every data. The descriptive statistic and time series plot of O_3 and other pollutants were discussed. It is also discuss the results of the MLR which are accompanied with the plots. The scatter plots of predicted O_3 concentration versus observed O_3 concentration were used the find the model accuracy. Besides, five different performance indicators which is normalised absolute error (NAE), root mean square error (RMSE), index of agreement (IA), prediction accuracy (PA) and coefficient of determination (R^2) were used to find the best prediction models that fits the observation. The best prediction model was find which varified using the new data sets..

Chapter 5 discusses the proposal for implementation of Local Ozone Management and Prevention (LOMP) scheme in Malaysia.

Chapter 6 concludes the research and listed the recommendations for further work.

CHAPTER 2

LITERATURE REVIEW

2.0 GENERAL

Ozone (O_3) is a reactive oxidant gas produced naturally in very trace amounts in the Earth's atmosphere. It was discovered by Christian Friedrich Schönbein in the middle of the nineteenth century (Seinfeld and Pandis, 2006). Schönbein also was first to detect ozone in air (Rubin, 2001) and it was first observed in the Los Angeles area in the 1940s. From the 1950s into the 1970s, California had the highest ozone concentrations in the world, due to its hourly average concentrations in Los Angeles reached its peak at 0.5 ppm and frequent smog alerts.

Depending on where it is located, O_3 can be beneficial ("good ozone") or detrimental ("bad ozone"). Ozone in the stratosphere, about 15-55 km altitude, plays a critical role in protecting humans from harmful UV radiation. However, O_3 in the troposphere between the Earth's surface and 10-15 km altitude is a harmful pollutant that causes human health problems (Liu and Johnson, 2002). On average, every ten million air molecules contains only about three molecules of O_3 (Roan, 1989). All O_3 in the atmosphere were collected in a layer at Earth's surface.

O_3 is mainly found in the two regions of the atmosphere that are closest to the earth's surface. About 10 percent of the atmosphere's O_3 is in the lowest-lying atmospheric region which is the troposphere (Yen, 2005). This O_3 is formed in a series of chemical reactions that involve the interaction of NO_x, VOCs, and sunlight. Most O_3 (about 90%) resides in the next atmospheric layer, the stratosphere. The O_3 in this region is commonly known as the ozone layer. Stratospheric O_3 is formed when the sun's ultraviolet (UV) radiation breaks apart molecular oxygen (O_2) to form O atoms, which then combine with O_2 to make ozone (Seinfeld and Pandis, 2006).

O_3 does not remain localized and it can be transported into a region by local winds and downward from the stratosphere. The different spatial distributions of NO_x and VOCs production, as well as NO destruction of ozone, often result in the largest ozone concentrations downwind of urban centers, rather than in urban areas themselves. Thus, urban area air pollution has direct impact on sub-urban area has due to dispersion of pollutants in all directions along the wind. This is because during transportation, primary pollutants often form secondary pollutants, causing greater adverse effects on crop production in sub-urban areas.

2.1 GROUND-LEVEL OZONE

Ground level ozone is ozone near the Earth surface in the troposphere region and it is produced naturally and reacts with gases emission from human activity. O_3 is an allotropic form (different elemental form with different properties) of O_2 and subsequently has different characteristics (Yang and Omaye, 2009). O_3 is heavier than O_2 and tends to accumulate around high-voltage apparatus. Although O_3 is more active than oxygen, it is much less stable and decomposes readily at ordinary temperatures when compared to O_2. It is also known as strong photochemical oxidants and is one of the major problems originating from air pollution in urban areas (Pires et al., 2008).

High O_3 concentration are hazard and bring challenge to the ecological life involve human, animals and plants because O_3 is reactive and oxidative pollutant and strong enough to alter other molecules. Excess amount of ground level ozone also bring adverse effect to agricultural crops and vegetation (Krupa et al., 1994). For human, O_3 degrades function of the respiratory system (Fahey, 2007; USEPA, 2010).

O_3 reacts with some gases, such as NO, and with some surfaces, such as dust particles, leaves, and biological membranes. These reactions can damage living cells, such as those present in the linings of the human lungs. High O_3 concentrations are strongly related to meteorological conditions and usually occur during sunny days, when primary pollutants (NO_x and NMHC) interact photochemically, supported by strong solar radiation and high temperatures (San Jose´ et al., 2005). Therefore, meteorological conditions strongly influence the efficiency of photochemical processes leading to ozone formation and destruction (Lengyel et al., 2004).

2.2 THE OZONE LAYER

The ozone layer is a layer in Earth's atmosphere which contains relatively high concentrations of O_3. This layer absorbs 97-99% of the sun's high frequency ultraviolet light, which is potentially damaging to life on earth (Yen, 2005). Ozone layer thickness is expressed in terms of Dobson units, which measure what its physical thickness would be if compressed in the Earth's atmosphere. In those terms, it's very thin indeed. A Dobson unit is the most basic measure used in O_3 research. One Dobson Unit (DU) is defined to be 0.01 mm thickness at standard temperature and pressure (STP) (Seinfeld and Pandis, 2006) as shows in Figure 2.1. A normal range is 300 to 500 Dobson units, which translates to an eighth of an inch.

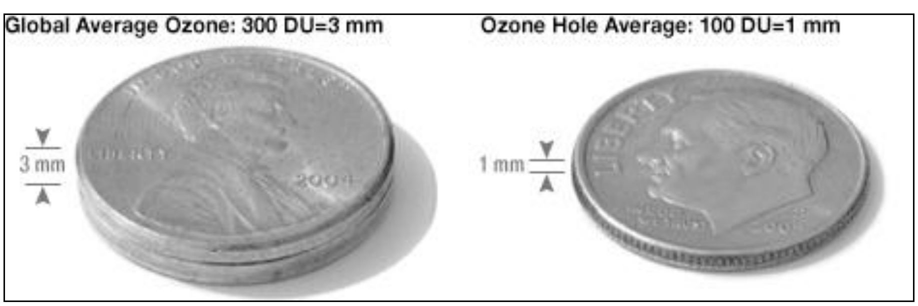

Figure 2.1 Thickness of Ozone Layer
(Adopted from: The Ozone Hole)

A thinning ozone layer leads to a number of serious health risks for humans. It causes greater incidences of skin cancer and cataract of the eye, with children being particularly vulnerable. There are also serious impacts for biodiversity. Increased UV-B rays reduce levels of plankton in the oceans and subsequently diminish fish stocks. It can also have adverse effects on plant growth, thus reducing agricultural productivity. Another negative effect is the reduced lifespan of certain materials (WHO, 2006).

2.3 PHYSICAL AND CHEMICAL PROPERTIES

Chemically, the ozone molecule consists of three atoms of oxygen arranged in the shape of a wide V and its formula is O_3 (Godish, 1997). Gaseous ozone is bluish in color and has a pungent, distinctive smell. The smell of ozone can often be noticed near electrical transformers or nearby lightning strikes (Colls, 2002). It is formed in these instances when an electrical discharge breaks an oxygen molecule (O_2) into free oxygen atoms (O), which then combine with O_2 in the air to make O_3.

The triangular-shaped ozone molecule (Fig 2.2) has a bond angle of 11.6° x 49° between the three oxygen atoms according to microwave studies, or 127° according to electron studies (Rubin, 2001). The bonding can be expressed as a resonance hybrid with a single bond on one side and double bond on the other producing an overall bond order of 1.5 for each side.

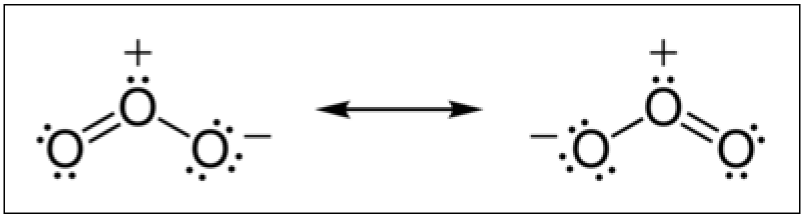

Figure 2.2 Ozone molecule
(Adopted from: The Ozone Hole)

2.4 OZONE FORMATION

There are no significant primary emissions of ozone into the atmosphere and all the O_3 found has been formed by chemical reactions that occur in the air (WHO, 2006). Ozone, therefore, is a secondary photochemical pollutant that is not polluting in its own right. It is produced from anthropogenic precursors that include industrial and vehicular emissions of VOCs and NO_x (Kovač-Andrić et al., 2009). 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; Al-Alawi et al., 2008; Hubbard and Cobourn, 1998).

O_3 results from complex chemical reactions when the primary pollutants, NO_x and NmHC, interact under the action of sunlight. Additional mechanisms for the formation of O_3 include stratospheric injection and processes that influence the abundance of NO_2 (Abdul-Wahab et al., 2005). The complex photochemical formation of this secondary pollutant is regulated by both natural and anthropogenic emissions and also by the meteorological conditions (Abdul-Wahab and Al-Alawi, 2002; Sadanga et al., 2003)

The formation of ozone in the upper atmosphere can be explained as a chemical process involving radiant energy (hυ) from the sun. Certain wavelengths in the ultraviolet range are able to break oxygen molecule (O_2) into monoatomic (reactive) oxygen atoms, O (reaction 2.1). These atoms can combine with an O_2 to form O_3 (Finlayson-Pitts and Pitts, 2000; Seinfeld and Pandis, 1998) as shows in reaction 2.2.

$$O_2 \xrightarrow{h\upsilon} O + O \tag{2.1}$$

$$O + O_2 \longrightarrow O_3 \tag{2.2}$$

Reaction (2.2) requires a third molecule to take away the energy associated with the free radical O and O_2, and the reaction can be represented by reaction (2.3);

$$O_2 + O + M \longrightarrow O_3 + M^* \tag{2.3}$$

M is any "body" with mass, primarily N_2 or O_2, but also particles, trace gas molecules, and surfaces of large objects. M absorbs energy from the reaction as heat; without this absorption, the combining of O and O_2 into O_3 cannot be completed (Finlayson-Pitts and Pitts, 2000). The absorption of UVB and C leads to the destruction of ozone as shown in reaction (2.4);

A dynamic equilibrium is established in reactions (2.4) and the following reaction (2.5). The O_3 concentration varies due to the amount of radiation received from the sun (Finlayson-Pitts and Pitts, 2000).

$$O_3 + h\nu \longrightarrow O + O_2 \tag{2.4}$$

$$O_3 + O \longrightarrow 2\,O_2 \tag{2.5}$$

Reaction (2.6) shows that radiant energy with a wavelength of 424 nm will break NO_2 into NO and O (Seinfeld and Pandis; 2006, Freedman, 1995). At high altitudes (above 20 km), O are produced by photolysis of O_2 by absorption of deep ultraviolet radiation. At lower altitudes, where radiation is no longer than 280 nm, the only source of O is the NO_2 photolysis. Then O combines with O_2 to form O_3 (reaction 2.7).

$$NO_2 \xrightarrow{h\nu\ (\lambda < 424\ nm)} NO + O \tag{2.6}$$

$$O + O_2 \longrightarrow O_3 \tag{2.7}$$

The ozone that forms, however, can react quickly with NO to produce NO_2 and O_2 (also known as a way of removing O_3) as shown in reaction (2.8).

$$NO + O_3 \longrightarrow NO_2 + O_2 \tag{2.8}$$

The cycle of reactions (2.6), (2.7) first generates and then destroys ozone (reaction 2.8). In lower atmosphere, net O_3 production would be very limited unless there is a process for turning NO into NO_2 without destroying O_3 at the same time. The reaction (2.3), (2.6) and (2.8) mentioned above occur rapidly and establish a stable ozone concentration (Finlayson-Pitts and Pitts, 2000). However, these reactions alone do not justify ozone levels measured in polluted urban areas.