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# ASSESSMENT OF FLUCTUATIONAL AND CRITICAL TRANSFORMATIONAL BEHAVIOUR OF GROUND LEVEL OZONE

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# ASSESSMENT OF FLUCTUATIONAL AND CRITICAL TRANSFORMATIONAL BEHAVIOUR OF GROUND LEVEL OZONE

**by**

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**Thesis submitted in fulfillment of the requirements**
**for the degree of**
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## LIST OF ABBREVIATIONS

| | |
|---|---|
| ANOVA | Analysis of variance |
| ANN | Artificial neural network |
| AOT40 | Accumulative ozone exposure over a threshold of 40 ppb |
| AOT50 | Accumulative ozone exposure over a threshold of 50 ppb |
| AOTX | Accumulative ozone exposure over a threshold value |
| AQLVs | Air quality limit values |
| API | Air Pollution Index |
| Ar | Argon |
| ASMA | Alam Sekitar Sdn Bhd |
| AT | Daily |
| CA | Cluster analysis |
| CAQM | Continuous Air Monitoring Stations |
| CARB | The California Resources Board |
| CCP | Critical conversion point |
| CEM | Continuous emission monitoring |
| $CH_4$ | Methane |
| CT | Critical conversion time |
| CO | Carbon monoxide |
| $CO_2$ | Carbon dioxide |
| CV | Coefficient of variations |
| *d* | Durbin-Watson |
| DT | Daytime |
| DFA | Detrended fluctuation analysis |
| DU | Dobson unit |

| | |
|---|---|
| EBIR | Equal benefit incremental reactivity |
| EQR | Environmental quality report (Malaysia) |
| EU | European Union |
| DoE | Department of Environment (Malaysia) |
| DoSM | Department of Statistics (Malaysia) |
| FEV | Forced expiratory volume |
| FVC | Forced vital capacity |
| GDP | Gross domestic product |
| GFC | Gas filter correlation |
| GIS | Geographical information system |
| GSE | Gas sensitive electrochemical |
| GSS | Gas sensitive semiconductors |
| $H_2$ | Hydrogen |
| He | Helium |
| $HO_2NO_2$ | Peroxynitric acid |
| HONO | Nitrous acid |
| $HNO_3$ | Nitric acid |
| *hv* | Radiant energy |
| $HO_2$ | Hydroperoxyl |
| IA | Index of agreement |
| IAQ | Indoor air quality |
| IR | Infrared |
| $J_{NO2}$ | $NO_2$ photolysis rate |
| $k_3$ | Reaction rate between NO and $O_3$ |
| KMO | Kaiser-Meyer-Olkin Measure |

| | |
|---|---|
| MAAQG | Malaysia Ambient Air Quality Guidelines |
| MAE | Mean absolute error |
| MIR | Maximum incremental reactivity |
| MLR | Multiple linear regression |
| Mo | Molybdenum |
| MOIR | Maximum ozone incremental reactivity |
| $N_2$ | Nitrogen |
| $N_2O$ | Nitrous oxide |
| $N_2O_5$ | Dinitrogen pentoxide |
| NAAQS | National Ambient Air Quality Standards |
| NAE | Normalized absolute error |
| Ne | Neon |
| NEM | North east monsoon |
| NO | Nitric oxide |
| $NO_2$ | Nitrogen dioxide |
| $NO_3$ | Nitrate |
| $NO_x$ | Nitrogen oxides |
| NRE | Ministry of Natural Resources and Environment, Malaysia |
| NT | Nighttime |
| O | Oxygen atom |
| O ($^1D$) | Excited single state oxygen atom |
| O ($^3D$) | Atomic oxygen |
| $O_2$ | Oxygen |
| $O_3$ | Ozone |
| OFP | Ozone formation potentials |

| | |
|---|---|
| OH | Hydroxyl |
| OLS | Ordinary least square |
| PA | Prediction accuracy |
| PCA | Principal component analysis |
| PCR | Principal component regression |
| PCs | Principal components |
| PI | Performance indicators |
| $PM_{10}$ | Particulate matter with aerodynamic diameter less than 10 micron |
| PMT | Photomultiplier tube |
| PNA | Poly-nuclear aromatic |
| POCP | Photochemical ozone creation potentials |
| ppb | Parts per billion |
| ppm | Parts per million |
| $R^2$ | Coefficient of determination |
| $\bar{R}^2$ | Adjusted coefficient of determination |
| RH | Relative humidity |
| RMSE | Root mean square error |
| $RO_2$ | Peroxy radicals |
| $SO_2$ | Sulphur dioxide |
| $SO_3$ | Sulphur trioxide |
| SPSS | Statistical Package for the Social Science |
| SWM | Southwest monsoon |
| T | Temperature |
| TSP | Total suspended particulate matter |
| TVOC | Total volatile organic compounds |

| | |
|---|---|
| USEPA | The United State Environmental Protection Agency |
| UV | Ultraviolet |
| UVB | Ultraviolet with wavelength (290 – 320 nm) |
| VIF | Variance inflation factor |
| VOCs | Volatile organic compounds |

## LIST OF APPENDICES


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# PENILAIAN TURUN NAIK DAN UBAH TAMPIL TINGKAH LAKU KRITIKAL OZON PARAS TANAH

## ABSTRAK

Ozon paras tanah merupakan pencemar udara yang berbahaya dan berupaya mendatangkan kesan negatif terhadap kesihatan manusia, hasil tanaman dan alam sekitar. Pemahaman mengenai ciri-ciri turun naik dan ubah tampil ozon adalah penting untuk merangka strategi pengurangan dan pengawalan. Oleh itu, kajian ini dijalankan bertujuan untuk mengenalpasti ciri-ciri turun naik dan ubah tampil ozon berdasarkan prapenandanya serta memperkenalkan titik perubahan kritikal (CCP) dalam pembentukan ozon menggunakan data yang dicerap di 18 kawasan seluruh Malaysia dari tahun 1999 sehingga 2010. Model ramalan ozon untuk jam berikutnya pada waktu harian, siang, malam dan perubahan kritikal juga dibentuk dengan menggunakan regrasi linear berganda (MLR) dan regrasi komponen utama (PCR) untuk meramal kepekatan ozon daripada kumpulan-kumpulan stesyen cerapan yang berbeza. Kumpulan-kumpulan ini adalah dari klasifikasi Jabatan Alam Sekitar, Malaysia dan dibentuk berdasarkan bacaan purata kepekatan ozon dan analisa kluster (CA). Walaupun majoriti cerapan data yang direkodkan adalah dibawah 100 ppb, sejumlah 1995 jam kepekatan ozon melebihi 100 pbb telah direkodkan yang mana 885 jam atau 44.5% disumbangkan oleh Shah Alam. Kitaran diurnal ozon menunjukkan puncak uni-modal diantara jam 12 tengah hari ke 4 petang, manakala kepekatan minimum yang direkodkan adalah konsisten pada jam 8 pagi. Analisis komponen utama (PCA) menunjukkan 80% daripada kepelbagaian ozon disumbangkan oleh $NO_2$, NO, suhu dan UVB manakala plot diurnal komposit mengesahkan kepelbagaian ozon sangat bergantung kepada kepekatan $NO_2$ and NO. CCP pembentukan ozon

dikenalpasti berlaku diantara jam 8 pagi ke 11 pagi. Model MLR kumpulan kluster harian mempamerkan prestasi paling optima berdasarkan kepada bacaan pekali penentu (0.9351), ketepatan ramalan (0.9671) dan indeks persetujuan (0.9831).

**ASSESSMENT OF FLUCTUATIONAL AND CRITICAL TRANSFORMATIONAL BEHAVIOUR OF GROUND LEVEL OZONE**


## ABSTRACT

Ground level ozone ($O_3$) is a noxious air pollutant that imposed adverse effects to human health, crop yield and the environment. Hence, it is important to understand their fluctuation and transformation characteristics in Malaysia in order to design abatement and control strategies properly. Therefore, this study aimed at investigating the characteristics of $O_3$ fluctuation and transformation from its precursors as well as to introduce the critical conversion point (CCP) of $O_3$ formation in 18 monitoring stations across Malaysia from 1999 to 2010. The next hour $O_3$ prediction models during daily, daytime, nighttime and critical conversion time were also developed using multiple linear regression (MLR) and principal components regression (PCR) to predict $O_3$ concentrations in different groups of monitoring stations. Groups of monitoring stations were based on the Department of Environment, Malaysia in terms of classification and newly developed groups using ranking of means and cluster analysis. Although majority of the recorded data was below 100 ppb, total of 1,995 hour of exceedances have been recorded, with Shah Alam contributed 885 hour or 44.5%. $O_3$ diurnal cycles suggested a uni-modal peak between 12 p.m. to 4 p.m., while minimum concentrations were consistently measured at 8 a.m.. Results of PCA showed the contributions to $O_3$ variation by $NO_2$, NO, temperature and UVB up to 80%, whereas the composite diurnal plots confirmed that variation is highly influenced by $NO_2$ and NO concentrations. The CCP of $O_3$ formation were identified to occur between 8 a.m. to 11 a.m.. The MLR model based on cluster group during daily exhibited optimal performance in terms of coefficient of determination, prediction

accuracy, and index of agreement with values of 0.9351, 0.9671 and 0.9831, respectively.

# CHAPTER 1

# INTRODUCTION

## 1.1 OVERVIEW

Unpolluted air comprised primarily of the gases of nitrogen ($N_2$; 78%), oxygen ($O_2$; 20.9%), argon (Ar; 0.93%) and the remaining 1% consisted of trace gases such as carbon dioxide ($CO_2$), neon (Ne), helium (He), methane ($CH_4$), hydrogen ($H_2$) and nitrous oxide ($N_2O$) (Prinn, 2003). USEPA (2008) gives the basic definition for air pollution as the presence of contaminant or pollution substances in the air that can interfere with human health or welfare, or produces other harmful environmental effects. In short, Kampa and Castanas (2008) defined air pollution as any substances that may harm humans, animals, vegetation or materials. At ground level, there are two groups of air pollutants which are primary air pollutants that are directly emitted from various sources such as anthropogenic and natural activities and secondary air pollutants resulted from photochemical reactions between primary air pollutants with a catalyst (Placet et al., 2000; Mohammed et al., 2013).

The history of air pollution began when men discovered fire. The pollution problems intensified during the Industrial Revolution as the result of coal burning as the prime energy source. Emissions of pollution from coal combustion were intense and coal smoke became a major atmospheric pollution problem (Godish, 1997). However, the biggest contributor to the changes in the atmospheric composition is primarily due to the combustion of fossil fuels in the power generation and transportation sector (Kampa and Castanas, 2008).

Air pollution is a major problem worldwide. Unlimited to urban and industrial areas, the effect of air pollution can spread out to the entire regions. Ramanathan and

Feng (2009) mentioned that every part of the world is connected through fast atmospheric transport, which open possibilities for pollutant to travel at longer distance. Ambient air pollution exists at all scales, from local, regional, continental to global (Vallero, 2008). Once the pollutants were emitted from their sources, it can travelled miles from the origin driven by wind. Under suitable conditions, some of pollutants such as nitrogen oxides ($NO_x$) and hydrocarbons also react to create secondary pollutants.

The detrimental effect of air pollution towards human health, crop productions, material quality, and surrounding environment being the major reasons for efforts to understand and control measures. The effects of air pollutant to humans vary based on susceptibility factors such as age, nutritional status and predisposing conditions (Kampa and Castanas, 2008). Thus, asthmatic patients, children, allergic individuals and elderly people are the group of individuals that were at higher risk (Bernstein et al., 2004). Over the centuries, a few major events proved that air pollution can be hazardous to the public health. Death and severe acute illness were reported during high pollutant concentration episodes in the Meuse Valley, Belgium in 1931, Danora, Pennsylvania in 1948 and in London, England in 1952 and 1956 (Folinsbee, 1993; Godish, 1997; Brimblecombe, 2006).

In Southeast Asia, severe high particulate events were recorded in 1983, 1990, 1991, 1994, 1997, 2005, 2006 and 2013 (Heil and Goldammer, 2001; Abas et al., 2004; Rahman, 2013; Othman et al., 2014). These high particulate events were triggered by the drastic increase in particulate matter with aerodynamic diameter less than 10 microns ($PM_{10}$), as well as total suspended particulate matter (TSP) from various sources including forest fire and anthropogenic emissions (Awang et al., 2000; Abas et al., 2004). During the high particulate events, air pollution concentrations which

include carbon dioxide ($CO_2$), carbon monoxide (CO), nitrogen oxides ($NO_x$), variety of hydrocarbons and ozone increased (Heil and Goldammer, 2001). Biomass burning during the events produced high concentrations of volatile organic compounds (VOCs) and contributed to surge in $NO_x$ concentrations which is the main ground level ozone precursors.

## 1.2 AIR POLLUTION IN MALAYSIA

Located in the centre of Southeast Asia, Malaysia experiences rapid development as the nation strived to become an industrialized nation by 2020. The World Bank (2014) established that Malaysian gross domestic product (GDP) growth in 2011 was 5.1% and increased approximately 0.5% in 2012. Urbanization process characterized by the increase in population, higher traffic density, changes in lifestyle and increase in energy demand has contributed to air pollution problem in Malaysia. Severe air quality problems were identified in highly urbanized areas in the Peninsular Malaysia contributed by mobile sources particularly motor vehicles (Azmi et al., 2010). Stationary sources such as power plant, industrial waste incinerators, dust emission from construction industry and quarries and open burning are also the major contributors towards the alarming state of air pollution in Malaysia (Dominick et al., 2012). Although, the current situation is not as severe as the smoke-haze episodes that happened in 1997, but the pollution concentration regularly exceeded the Malaysian Ambient Air Quality Guidelines (MAAQG) especially in urban areas.

Since the 1970s, Heil and Goldammer (2001) reported that there were regular (periodic) incidences of fire-related regional air pollution episodes that were experienced by the Southeast Asia nations including Malaysia that were considered as large-scale air pollution episodes. Serious high particulate event were recorded across

Malaysia in 1991, 1994, 1997, 2005 and 2013 (Rahman, 2013; Othman et al., 2014). Large scale forest and plantations open burning were identified as the main contributors towards the high particulate event (Mahmud, 2009) and local emissions by motor vehicle and industrial sites exaggerated the problems (Sansuddin et al., 2011). During the 2013 high particulate event, more than 600 schools in Johor that are located in areas with API exceeding the hazardous point of 300 had to be closed, while other areas with API reaching of more than 150 were advised to avoid outdoor activities. During the peak of the event, two southern districts (Muar and Ledang) were declared emergency as the API reached 700 (DoE, 2013; Rahman, 2013).

Regulations to regulate air pollution in Malaysia is enacted under Environmental Quality (Clean Air) Regulations, 2014. The regulation regarded air pollutants as smoke, cinders, solid particles of any kind, gases, fumes, mist, odours and radioactive. The main environmental regulatory agency in Malaysia is the Department of Environment (DoE) that is operated under the Ministry of Natural Resources and Environment (NRE), Malaysia.

Significant changes in ambient air pollution concentration for Malaysia are closely monitored by the DoE using 52 Continuous Ambient Air Monitoring Stations (CAQM), which have been installed across Malaysia. The stations were strategically placed at urban, sub-urban, industrial and background areas and the air quality were reported to citizens using the Air Pollution Index (API) system. The API values are calculated based on the average concentration of five criteria pollutants ($SO_2$, $NO_2$, CO, $O_3$, and $PM_{10}$) and the most dominant pollutant with the highest sub-index value is taken as the API (Awang, 2000; Dominick et al., 2012). In most cases, API values were determined based on $PM_{10}$, but occasionally API value was calculated based on

$O_3$ especially during afternoon and early evening. The Malaysian Ambient Air Quality Guidelines (MAAQG) are depicted in Table 1.1.

Table 1.1 Malaysian Ambient Air Quality Guidelines (DoE, 2010)

| Pollutant | Averaging Time | Malaysia Guidelines | |
|---|---|---|---|
| | | ppm | $\mu g/m^3$ |
| Ozone | 1 hour | 0.10 | 200 |
| | 8 hour | 0.06 | 120 |
| Carbon Monoxide | 1 hour | 30.00 | 35* |
| | 8 hour | 9.00 | 10* |
| Nitrogen Dioxide | 1 hour | 0.17 | 320 |
| | 24 hour | 0.04 | 10 |
| Sulphur Dioxide | 1 hour | 0.13 | 350 |
| | 24 hour | 0.04 | 105 |
| Particulate Matter ($PM_{10}$) | 24 hour | - | 150 |
| | 12 month | - | 50 |
| Total Suspended Particulate (TSP) | 24 hour | - | 260 |
| | 12 month | - | 90 |
| Lead | 3 month | - | 1.5 |

Note: *($mg/m^3$)

The API system categorizes the air quality status as good (0-50), moderate (51-100), unhealthy (101-200), very unhealthy (201-300), hazardous (301-500) and emergency (above 500). Annually, DoE reported the air quality status in Malaysia through the Environmental Quality Report (EQR), which concluded that air quality in Malaysia were from good to moderate levels at most of the time in 2004 to 2012 (DoE, 2013). However, the nation also experienced several unhealthy days mostly due to the increase in air pollution sources especially in the urban-industrial areas accompanied by favourable weather conditions.

Air pollution sources in Malaysia are mainly from anthropogenic emissions. Majority of air pollutants were emitted from motor vehicles, industrial sites, development activities, power generations, land clearing, open burning and forest fire

(Mohammed et al., 2013). Afroz et al. (2003) stated that 70-75% of total air pollution was generated by mobile sources (motor vehicle), 20-25% by stationery sources and approximately 3-5% by open burning and forest fires. On road cars, trucks and buses will always be important air pollution emitters in the cities (Chow et al., 2004). According to the Ministry of Transport, Malaysia (2012), by the end of 2012, there were about 22.27 million registered vehicles in Malaysia (Figure 1.1) approximately about 0.9 million (4%) higher than 2011.

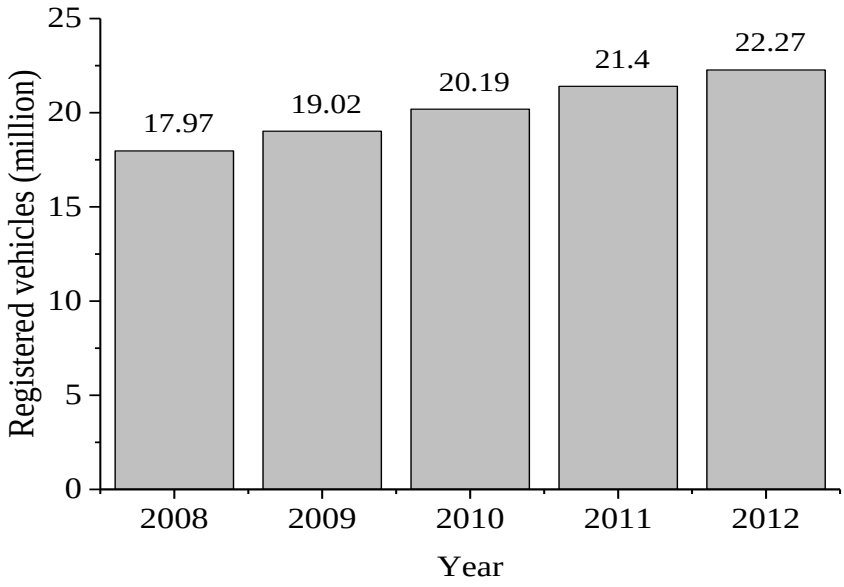


Figure 1.1 Number of registered vehicles in Malaysia (DoSM, 2012a)

Besides $PM_{10}$, $O_3$ is also the pollutant of concern due to favourable atmospheric conditions, high precursor emission from motor vehicles and industrial activities (DoE, 2013). $O_3$ is considered as one of the criteria air pollutants in Malaysia. According to USEPA (2008), criteria pollutant is the term used to describe a pollutant that have been regulated and continuously monitored due to adverse effect to human health. As a criteria pollutant, $O_3$ also used in API calculation as an indicators of air quality. Exposure to $O_3$ concentrations to a healthy human will result in a decreasing forced vital capacity (FVC) and forced expiratory volume (FEV), however $O_3$

exposure towards asthmatic person will result in chronic inflammations in the lower airways (Bromberg and Koren, 1995; Berstein et al., 2004). Plants reacts to $O_3$ exposure by showing flecking, stippling, bleached, spotting and pigmentations (Ishii et al., 2007; Ainsworth et al., 2012; Mohammed et al., 2013). $O_3$ also attacks carbon double bonds (C=C) in rubber materials and under additional stress, the bonds will eventually break (Lee et al., 1996; Vallero, 2008).

Studies revealed that there are increasing trends in the $O_3$ concentrations level in Malaysia especially in Klang Valley (Ghazali et al., 2010; Latif et al., 2012; Banan et al., 2013; Ahamad et al., 2014). Figure 1.2 clearly illustrated that $O_3$ pollution is more prominent in industrial and urban areas where the source of its precursors are more abundant.

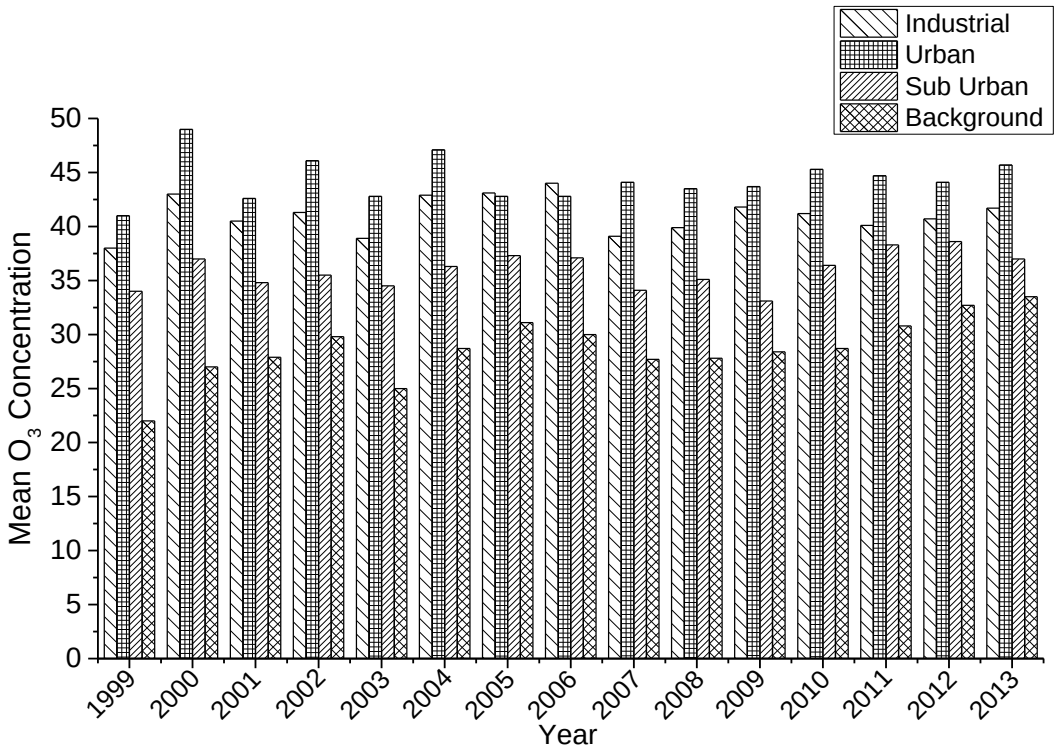


Figure 1.2 Annual average concentrations of $O_3$ by land use from 1999 to 2013 (Source: DoE, 2013)

In addition, Malaysia is located in the tropical regions where sunlight radiation is intense and constant. Sunlight acts as a catalyst to $O_3$ photochemical production (Atkinson, 2000; Seinfeld and Pandis, 2006; Tiwary and Colls, 2009), thus controlling variations in $O_3$ concentrations. $O_3$ showed strong day-to-day variations characterized by high daytime concentrations and low concentration during night and early morning (Ramli et al., 2010).

DoE (2013) stated that $O_3$ pollution becomes more prominent during the afternoon and early evening with concentrations occasionally surpassing the guidelines limit. Table 1.2 showed the total number of hours exceeding 1-hour-averaging of 100 ppb and annual maximum of $O_3$ concentrations at Klang Valley, Malaysia during 2004 to 2008. High numbers of exceedances indicated that $O_3$ were at an alarming state in Malaysia especially in the urban and industrial locations.

Table 1.2 Summary of hourly $O_3$ concentrations exceeding the MAAQG limit of 1-hour averaging around Klang Valley from 2004 to 2008 (Source: Latif et al., 2012)

| | 2004 | | 2005 | | 2006 | | 2007 | | 2008 | |
|---|---|---|---|---|---|---|---|---|---|---|
| Station | Σh | $O_3$ (ppb) | Σh | $O_3$ (ppb) | Σh | $O_3$ (ppb) | Σh | $O_3$ (ppb) | Σh | $O_3$ (ppb) |
| Gombak | 35 | 129 | 45 | 156 | 88 | 141 | 25 | 129 | 15 | 154 |
| Nilai | 12 | 138 | 8 | 119 | 4 | 113 | 4 | 117 | 2 | 112 |
| Klang | 1 | 103 | 6 | 118 | 4 | 127 | 0 | 99 | 0 | 99 |
| Petaling Jaya | 28 | 150 | 19 | 140 | 11 | 131 | 4 | 127 | 9 | 120 |
| Kajang | 94 | 159 | 80 | 157 | 76 | 161 | 41 | 127 | 21 | 127 |
| Shah Alam | 181 | 172 | 115 | 171 | 74 | 152 | 42 | 163 | 82 | 149 |
| Tanjung Malim | 14 | 117 | 7 | 115 | 20 | 127 | 4 | 104 | 31 | 122 |
| Putrajaya | NA | NA | 22 | 144 | 56 | 148 | 13 | 121 | 24 | 118 |
| Cheras | 157 | 196 | 148 | 181 | 64 | 145 | 33 | 131 | 45 | 135 |
| Jerantut | 0 | 90 | 0 | 68 | 0 | 58 | 0 | 71 | 0 | 57 |

Note: Σh is total hour of $O_3$ concentrations surpassing MAAQG limit of 100 ppb; NA is not available

## 1.3 PROBLEM STATEMENT

Fluctuations in $O_3$ concentrations in any given location resulted from the combinations of formations, destructions, transport and deposition process (Vingarzan, 2004). The combined effect of precursors and meteorological conditions contribute to complex $O_3$ studies and analysis. In Malaysia, $O_3$ is scarcely studied by several researchers focusing in different aspects such as concentration variations (Latif et al., 2012; Banan et al., 2013); guidelines exceedances (Ahamad et al., 2014); phytotoxicity risk (Ishii et al., 2007; Mohammed et al., 2013); effect of meteorological parameters (Toh et al., 2013); and $O_3$ transformations and prediction (Ghazali et al., 2010). These studies address the $O_3$ problems on highly urbanized areas in the country which is the Klang Valley.

However, Klang Valley is characterized by high population and traffic density, major roads and highways, residential and commercial establishments and surrounded by industrial parks. This scenario does not represent the whole picture as there are places which showed low rates of development and less anthropogenic emissions. In addition, the period of these studies are in between one to six years. The earliest data from 1998 to 2001 have been presented by Ishii et al. (2007), while Ahamad et al. (2014) used data from 2008 to 2010. Meanwhile, those studies will give a clear picture in the trend of $O_3$ if longer duration is used i.e over a decade.

Photochemical reactions is undeniably the most significant path of $O_3$ formations at the ground level. Intensive work have been carried out by several studies in order to gain understanding on the mechanism behind the formations of $O_3$ (Atkinson, 2000; Jenkin and Clemitshaw, 2000; Atkinson and Arey, 2003). The dependency of the $O_3$ formation towards UV light is associated with its clear daily variations. In the presence of sunlight, nitrogen dioxide ($NO_2$) undergoes photochemical reactions to produce free

oxygen atom (O), which later reacts with oxygen molecules ($O_2$) to form $O_3$ (Duenas et al., 2004; Azmi et al., 2010). $O_3$ concentration variations show an interesting pattern in the morning where $O_3$ level reaches the lowest concentration because of the higher rate of NO titration (Jiménez-Hornero et al., 2010). Once the minimal point is reached, $O_3$ starts to increase with the rise in $NO_2$ concentration, thereby promoting $NO_2$ photolysis. When the $NO_2$ photolysis rate is higher than the NO titration rate, critical conversion point (CCP) occurs. Therefore, CCP knowledge is very crucial in understanding ground-level $O_3$ chemistry because the difference in the chemical reaction's rate is expected to result in $O_3$ accumulation.

The literature review revealed that there are very limited studies on CCP where most of the studies were conducted only focusing on $NO_2$ photolysis rate (Clapp and Jenkin. 2001; Han et al., 2011). Moreover, various temporal, spatial and meteorological factors in Malaysia such as time of day, monsoonal changes, latitudes, clouds, and aerosols may influence the amount of UVB radiation received at the ground level. These will affect ground level $O_3$ formation and influence CCP formation. This type of study is limited and while other $O_3$ studies in Malaysia were rather focusing on variability of the pollutants (Azmi et al., 2010; Banan et al., 2013; Ahamad et al., 2014) than the other important characteristics of $O_3$. Studies related to CCP are scarce and further analysis in this area is required.

The usage of statistical modelling is capable in providing additional information in $O_3$ formations and fluctuations behaviour. The relationship between $O_3$, its precursors and meteorological conditions is frequently studied utilizing multiple linear regression (MLR) (Barrero et al., 2006; Ghazali et al., 2010). Some researchers also used a combination of MLR and principal component analysis (PCA) (Lengyel et al., 2004; Abdul-Wahab et al., 2005; Sousa et al., 2007; Özbay et al., 2011). In Malaysia,

only Ghazali et al. (2010) have attempted to develop the $O_3$ prediction models in urban areas using MLR. Even though good correlations were established between $O_3$ and $NO_2$, the absence of NO in the analysis were unable to completely explain the $O_3$ formation reactions as NO also plays significant roles equivalent to the $NO_2$ concentrations. Meanwhile, none of $O_3$ prediction models using the combination of PCA and MLR (PCR) were reported in Malaysia. Studies revealed that the PCR model is excellent in avoiding multicollinearity problems in $O_3$ analysis (Lengyel et al., 2004; Abdul-Wahab et al., 2005; Kovác-Andrić et al., 2009) and could be an important tool in predicting the $O_3$ concentrations.

Encouraged by lack of detailed $O_3$ studies in Malaysia, the aims of this study are to critically investigate the fluctuational and transformational behaviour of ground level $O_3$ in Malaysia. This study is carried out using a long period of monitoring records (12 years) and considering all types of land use (industrial, urban, sub-urban and background) across Malaysia. This study has also extended and improvised the usage of $O_3$ production rates ($J_{NO2}/k_3$) of earlier studies (Clapp and Jenkin, 2001; Gerasopoulos et al., 2006; Han et al., 2011) by introducing the critical conversion point (CCP) of $O_3$ formations. CCP is then used as the baseline in determining the critical conversion time (CT). CT is a period that is important in $O_3$ photochemical productions. In addition, this research also provides next hour $O_3$ prediction models using MLR and PCR during different periods of time.

## 1.4 OBJECTIVES

This research was carried out to accomplish four main objectives:

a) To determine the fluctuational behaviour of ground level $O_3$ and to investigate variation of $O_3$ exceedances using time series plot

b) To determine the critical conversion point (CCP) of $O_3$ transformation from its precursors and to introduce $O_3$ critical conversion time (CT)

c) To develop multiple linear regression (MLR) and principal component regression (PCR) models to predict $O_3$ concentration during 'daily' (AT), daytime (DT), nighttime (NT) and critical conversion time (CT) in different background criteria groups.

d) To identify the optimal next hour prediction models in describing $O_3$ fluctuation in Malaysia using several performance indicators.

## 1.5 SCOPE OF STUDY

This study was designed to investigate and explore long term ground level $O_3$ fluctuational and conversion behaviour from its precursors in the Malaysian climate using graphical and multivariate techniques from January 1999 to December 2010 (12 years). 18 out of 52 continuous air quality monitoring stations operated by Alam Sekitar Malaysia Sdn Bhd (ASMA) was selected in this study. The main criteria in selecting the studied locations are:

a) percentage of captured records was more than 80% for the concentration of $O_3$, $NO_2$ and NO

b) to represent categorical distribution of monitoring sites, which are urban (seven stations), sub urban (two stations) industrial (eight stations) and background (one station)

The remaining stations that are not selected are mostly due to low percentage of captured data and unavailability of UVB data.

This research utilized nine variables that were divided into two groups. One group comprised of air pollutants, such as ground-level ozone ($O_3$), nitrogen dioxide ($NO_2$), nitric oxide (NO), sulphur dioxide ($SO_2$) and carbon monoxide (CO). The other group composed of meteorological parameters, such as temperature, relative humidity, wind speed, and incoming solar radiation. These variables were selected based on their relationships with $O_3$. $NO_2$, NO and CO as the principle precursors to $O_3$ production (Clapp and Jenkin, 2001; Seinfeld and Pandis, 2006; Ahamad et al., 2014). Whereas, UVB is the main ingredient in $O_3$ photochemical reactions and without UVB, the reactions could not be completed (Tiwary and Colls, 2009). The relationship between $O_3$ and temperature is obtained through UVB and high relative humidity indicates wet or rainy conditions which can promote $O_3$ scouring. Wind is a dispersion agent to any air pollutants in the atmosphere. $SO_2$ are primary air pollutants that are being emitted from similar sources to $O_3$ precursors (De Nevers, 2010). Increasing in this pollutant may provide indication of $O_3$ increment due to excessive $O_3$ precursor concentrations.

Fluctuational behaviours of the $O_3$ concentrations are assessed during daily, diurnal (Duenas et al., 2004; Azmi et al., 2010; Ghazali et al., 2010; Banan et al., 2013) monthly and spatial using graphical analysis. The influence of $NO_2$, NO, temperature and incoming solar radiation towards $O_3$ formations and variations are explored using principal component analysis (PCA) and composite diurnal plot. This study is the first to introduce and explore the possibilities of explaining the variation in $O_3$ concentration using critical conversion point (CCP) of ground-level $O_3$ formation in the study area. CCP is defined as the point when $NO_2$ photolysis rate begin to surpass

NO titration rate during morning which corresponds to positive ozone production rates determined using composite diurnal plot and differences in $O_3$ production ($J_{NO2}$) and destruction rate ($k_3$).

According to the literature, research on $O_3$ prediction using PCA in tropical areas, such as Malaysia, are unavailable. The present study aimed to present the results of MLR analyses using the original variables and principal components (PCs) as the inputs for four different time periods, namely, 'daily' (AT), daytime (DT), nighttime (NT), and critical conversion time (CT). In this research, DT is defined as the complete hour falling between sunrise and sunset (Clapp and Jenkin, 2001). In Malaysia, Mohammed et al. (2013) used 7 a.m. to 7 p.m. (12 h) as DT, and 7 p.m. to 7 a.m. as NT, while AT is a whole day from 12 a.m. for 12 p.m. (24 h). In contrast to DT and NT, CT was determined based on CCP.

MLR is selected because of their capabilities to predict the contributions of selected variables to $O_3$ variations (Abdul-Wahab et al., 2005). Meanwhile, the use of PCs as input in MLR is intended to increase the prediction accuracy by removing multicollinearity problem. Next hour $O_3$ prediction models is developed based on different group of monitoring stations. Group of monitoring stations by DoE is analysed and new groups are developed using ranking of means and cluster analysis (CA). Index of agreement (IA), prediction accuracy (PA) and coefficient of determination ($R^2$) are used to measure the accuracy, while normalized absolute error (NAE), mean absolute error (MAE) and root mean square error (RMSE) are used to measure error in predicted $O_3$ concentrations.

## 1.6 THESIS LAYOUT

Chapter 1 covers the overview of the air pollution (section 1.1) and current state of air pollutions in Malaysia (section 1.2) as well as the introduction of this thesis. The details of the problem statement (section 1.3), objectives of the study (section 1.4) and the scope of the research (section 1.5) are provided in this chapter.

Chapter 2 discusses the details of $O_3$ fluctuation characteristics and transformation chemistry (section 2.2). In addition, the characteristics of their precursors (section 2.3), prevailing meteorological factors (section 2.4) and multivariate analysis are also highlighted (section 2.5).

Chapter 3 describes all materials and methodologies involved in this study. The information regarding the study areas (section 3.2), monitoring equipment (section 3.2), $O_3$ fluctuational analysis (3.3), $O_3$ transformational behaviour and critical conversion point identification (section 3.4) as well as statistical approaches (section 3.5) are discussed in this chapter.

Chapter 4 presents all the results in this research. The descriptive statistics provide an overview of $O_3$ concentrations (section 4.2). Fluctuation behaviour of $O_3$ concentrations during daily, diurnal, monthly and spatial are also discussed (section 4.3). Next, the established influence of $NO_2$, NO, temperature and incoming solar radiation towards $O_3$ formations is presented (section 4.4). After that, a discussion related to $O_3$ critical conversion point is discussed (section 4.4). In addition, results of MLR and PCR prediction models during different time periods and group of monitoring stations is presented (section 4.5). Lastly, selection of the best prediction model is made based on the performance indicators evaluation (section 4.6).

Chapter 5 provides conclusion to the research findings (section 5.1) and list the recommendations for future work (section 5.2).

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 INTRODUCTION

$O_3$ is a constituent of the Earth's atmosphere and is present in both the stratosphere and troposphere. It is a trace gas, which plays a key role in the oxidizing capacity of the atmosphere (Duenas et al., 2004). $O_3$ has a pungent odour that allows it to be detected even at very low concentrations (Fahey and Hegglin, 2010). In the history of mankind, $O_3$ is known as the accompaniments to the electrical storms before their distinct chemical compound was discovered by Christian Friedrich Schonbein in 1867 (Rubin, 2001). Farrell (2005) stated that $O_3$ is a very reactive allotrope of oxygen, which is recognized to be a strong oxidant, strong UV absorber, and an active molecule that participated in many important chemical reactions in the atmosphere. Due to these properties, $O_3$ has evoked researchers concerns on two environmental issues, which are the destructions of UV protector's stratospheric $O_3$ and photochemical formations of health compromising tropospheric $O_3$.

$O_3$ can be either 'good' or 'bad' depending on its functional location. Approximately 90% of $O_3$ are found in the upper part of the atmosphere in the ozone layer, while relatively small concentrations were found at ground level (Fahey and Hegglin, 2010). $O_3$ acts as the protective layer that shields the earth from the harmful UV radiation from the sun at the stratosphere level (15-55 km altitude). The concentration of $O_3$ in the ozone layer can be typically a few thousand ppb depending on the altitude and it is measured based on Dobson unit (DU) with one DU is equivalent to 0.01 mm of $O_3$ (Tiwary and Colls, 2009).

Whereas, the tropospheric $O_3$ is a secondary air pollutant formed in the atmosphere (0-15km altitude) which is a harmful air pollutant that is capable of causing detrimental effects to human health. The formation mechanisms of stratospheric and tropospheric $O_3$ are different as the wavelength of UV photons reach these atmosphere levels are different. Relatively weaker UV photons that reach the earth surface cause the tropospheric $O_3$ to require precursors to complete their formations, nevertheless the stratospheric $O_3$ are directly formed from oxygen molecule with availability of stronger photons (Seinfeld and Pandis, 2006).

## 2.2 GROUND LEVEL OZONE

Ground level $O_3$ present as a secondary pollutant in the lower atmosphere, where its formation and destruction can be enhanced by other pollutant that acts as its precursors (Ainsworth et al., 2012; Hassan et al., 2013; Alghamdi et al., 2014). Godish (1997) estimated that in a relatively clean environment during warmer seasons, ground level $O_3$ concentration ranges from 20 to 50 ppb, with background concentration of 10 to 20 ppb (Colls, 2002), while the mixing ratios in polluted urban areas often exceeds 100 ppb (Atkinson and Arey, 2003). Nolle et al. (2002) stated that the background of $O_3$ concentrations at the Central Mediterranean increased from 48.2 ppb in 1997 to 52.2 ppb in 2000. Vingarzan (2004) indicated that $O_3$ concentration over mid-latitudes of the Northern Hemisphere continue to rise about 0.5 to 2% per year for over the past three decades.

The seasonal mean of background of $O_3$ concentrations over North America ranged approximately from 20 ppb to 35 ppb at low latitudes sites, while at certain high latitudes the background concentrations could exceed 45 ppb (Dolwick et al., 2015). Mean of $O_3$ concentrations in Jerantut, Malaysia over 1997 to 2011 was 11.8

ppb (Latif et al., 2014). DoE, Malaysia designated Jerantut as the one and only background station in Malaysia to monitor the general background of air pollutants.

High concentrations of $O_3$ is associated with reduced visibility (Jacob, 2000) and claimed to be one of the major constituents of the photochemical smog (Zhang and Kim Oanh, 2002; Alghamdi et al., 2014; Pugliese et al., 2014). Photochemical smog was first discovered in Los Angeles in 1940s and it frequently occurred in major cities with high population density (Jenkin and Clemitshaw, 2000). He et al. (2002) mentioned that the formation of photochemical smog requires ambient temperature above 20$^{o}$C, low wind speed (< 3 m/s) and intense sunlight radiation.

### 2.2.1 Effect of Ozone

$O_3$ is a noxious air pollutant that is capable to induce harmful effects on human health, crop production, material quality and the ecosystem. $O_3$ is the second most hazardous air pollutant (after PM) in causing mortality and morbidity to human health (Ainsworth et al., 2012) and third most important greenhouse gas after carbon dioxide and methane (Toh et al., 2013).

At ground level, $O_3$ is toxic to both human and vegetation owing to its capability to oxidize biological tissue (Brimblecome, 2009; Pugliese et al., 2014). Vallero (2008) revealed that the most significant effect of $O_3$ to human is decrement of pulmonary function and increment of asthma attack. Phytotoxic nature of $O_3$ have also been related to crop yield on a global scale (Wang and Mauzerall, 2004; Ishii et al., 2007; Karlsson et al., 2007; Mohammed et al., 2013).

It is established that the human exposure to $O_3$ leads to respirator symptoms as $O_3$ targeted the pulmonary system thus, increased risk for hospital admissions (Ebi and McGregor, 2008; Kampa and Castanas, 2008; Brimblecome, 2009). Lippmann (1989)

claimed that the only significant exposure route of $O_3$ pollutant is through inhalation and inhalable concentration that is assumed to be at par with ambient concentrations recorded at monitoring stations. Once it is inhaled, the dose targeted the tissue in respiratory system and the effect of $O_3$ is intensified with more exercise as the breathing flow rate is increasing (Lippmann, 1989). Pires et al. (2008b) specified the concerning health effect from $O_3$ are damage to respiratory tract tissue, death of lung cells, inflammation of airways and increase in respiratory symptoms (cough, chest soreness and difficulty in taking deep breath). According to Bernstein et al. (2004) exposure to approximately 100 to 400 ppb of $O_3$ concentrations can cause neurophilic inflammations as early as an hour after the exposure and persisted up to 24 hours.

Various studies elucidated that the phytotoxic nature of $O_3$ air pollutant is the main criteria in affecting the plants (Ishii et al., 2007; Lindroth, 2010; Ainsworth et al., 2012; Banan et al., 2013; Mohammed et al., 2013). $O_3$ concentrations that were higher than 40 ppb may induce negative responds in terms of crops yields, biomass production, vitality and stress tolerance of the plants (Fuhrer et al., 1997). Ainsworth et al. (2012) listed that the major damaging effect of $O_3$ pollution towards plants include photosynthetic carbon assimilation, stomata conductance and reduction in crop yield. Normally plants show effect of $O_3$ when there is a speckle of brown spots on the flat areas of the plant's leaf in between the vein (Tiwary and Colls, 2009). $O_3$ is also capable to induce faster reduction of leaf area during crop senescence (Alvim-Ferraz et al., 2006; Kovač-Andrić et al., 2009).

In evaluating the $O_3$ impact on vegetation, accumulative exposure over a threshold value (AOTX) is introduced. European nations adopted AOT40 as the threshold limit starting from 1996. However, Mohammed et al. (2013) suggested that AOT50 index is more suitable to be implemented in Malaysia as currently there are no

guidelines limit designed against the effect of $O_3$ towards plant in this country and due to differences in the climate and amount of solar radiation.

Unlimited to biological entities, ground level $O_3$ can also effect the non-organic materials as well. Arif and Abdullah (2011) mentioned that some materials such as elastomers, textiles fibres, dye and paints are susceptible to $O_3$. Damage area usually takes the form of cracking leading to brittleness resulting in the reduction of the materials strengths and increased rate of wear (Lee et al., 1996). Studies have also revealed that paint pigments faded severely when it is exposed to high $O_3$ concentrations which that has been observed during Los Angeles photochemical smog (Solomon et al., 1992). According to Salmon et al. (2000) paint pigments and dye based on indigo family is more susceptible to $O_3$ damage. Additionally, $O_3$ is also capable in damaging the photographic materials and books (Godish, 1997) as well increase in corrosion of building material such as steel, zinc, copper, aluminium and bronze (Pires et al., 2008b).

### 2.2.2 Ground Level Ozone Fluctuational Behaviour

Ground level $O_3$ exhibited different fluctuation features compared to other primary air pollutants such as NO, $NO_2$, CO and $CO_2$. $O_3$ showed strong daily, weekly and seasonal variations (Jenkin and Clemitshaw, 2000; Duenas et al., 2004; Khoder, 2009; Han et al., 2012; Hassan et al., 2013). Hassan et al. (2013) claimed that diurnal variations are very important in understanding the different processes responsible for $O_3$ formation and destruction. $O_3$ showed clear diurnal trends which is very similar to solar radiation diurnal trends (Duenas et al., 2004). The $O_3$ concentration is normally low in the morning and gradually increase towards the afternoon (Ghazali et al., 2010; Alghamdi et al., 2014). Diurnal variation in $O_3$ shows a maximum concentration

around noon or early afternoon with the values gradually decreasing as evening approaches (Ghosh et al., 2013). Table 2.1 presents the summary of diurnal $O_3$ fluctuation in different locations. $O_3$ showed similar uni-modal trends that reach peak concentration around afternoon or early evening.

Table 2.1 Characteristics of $O_3$ diurnal trends

| Location | Duration | Diurnal cycle | Peak hour | References |
|---|---|---|---|---|
| Urban areas, Malaysia | 2006 | uni-modal | 1-2 p.m. | Ghazali et al. (2010) |
| Klang Valley, Malaysis | 2004-2008 | uni-modal | 2-4 p.m. | Latif et al. (2012) |
| Jerantut, Malaysia | 2005-2009 | uni-modal | 3 p.m. | Banan et al. (2013) |
| Malaga, Spain | - | uni-modal | 3 p.m. | Duenas et al (2004) |
| Rural, India | 2010 | uni-modal | 1 p.m. | Reddy et al. (2012) |
| Tianjian, China | 2010 | uni-modal | 2 p.m. | Han et al. (2011) |
| Jeddah, Saudi Arabia | 2012-2013 | uni-modal | 1 p.m. | Alghamdi et al. (2014) |
| Cairo, Egypt | 2004-2005 | uni-modal | 2 p.m. | Khoder (2009) |

Generally, $O_3$ concentration is higher during daytime as compared to nighttime because photochemical reactions only occurs during daytime (Ghazali et al., 2010; Reddy et al., 2011; Alghamdi et al., 2014). At night, $O_3$ concentration is constantly low primarily accounted for the absence of any photochemical production and further destruction by continuous chemical loss by NO titration and deposition (Ghosh et al., 2013). Considering the significant differences of $O_3$ concentrations between daytime and nighttime, several studies (Lengyel et al., 2004; Abdul-Wahab et al., 2005; Özbay et al., 2011) stressed that there are $O_3$ advantages of separating daytime and nighttime $O_3$ analysis due to different influencing factors. Table 2.2 summarizes the difference between daytime and nighttime of $O_3$ concentrations in Egypt, India and China.

$O_3$ also exhibited clear seasonal fluctuations with the highest and lowest $O_3$ concentrations observed during summer and winter seasons, respectively (Duenas et

al., 2004; Hassan et al., 2013; Iqbal et al., 2014). However, Md Yusof et al. (2010) alleged that seasonal variations in Malaysia that experience the tropical rainforest climate is different from the temperate countries that show four distinctive seasons every year. In Malaysia monsoonal changes showed more prominent effects to $O_3$ fluctuations (Ghazali et al., 2010; Latif et al., 2012) due to changes in the wind's flow pattern and rainfall intensity. Due to the difference in weather condition, Banan et al. (2013) claimed that monthly variations of $O_3$ in urban and sub-urban areas in Malaysia are strongly dependent on wind pattern.

Table 2.2 Review of daytime and nighttime $O_3$ concentrations

| Location | | Duration | Mean $O_3$ (ppb) | | References |
|---|---|---|---|---|---|
| | | | Daytime | Nighttime | |
| Cairo | Egypt | 2004-2005 | 64.70 | 27.50 | Khoder, 2009 |
| Kolkata | India | 2010-2011 | 26.00 | 9.00 | Ghosh et al., 2013 |
| Tieta | China | 2009 | 46.50 | 18.36 | Han et al., 2012 |
| Wuqing | China | 2009 | 65.91 | 18.08 | Han et al., 2012 |
| Anantapur | India | 2009 | 51.74 | 35.52 | Reddy et al., 2011 |
| Xi'an | China | 2009 | 23.64 | 7.10 | Reddy et al., 2011 |

### 2.2.3 Ground Level Ozone Transformational Behaviour

There are no significant anthropogenic emissions of $O_3$. The majority of ground level $O_3$ comes from photochemical reactions of methane, VOCs and $NO_x$, which are largely from anthropogenic emissions with the presence of sunlight (Ghazali et al., 2010). It is expected that a minor component (approximately 10%) of tropospheric $O_3$ are injected from stratospheric influx (Ainsworth et al., 2012), however the process is still unclear.

$O_3$ formation is influenced by the chemistry of its precursors, topography, type of terrain, vegetation and meteorological conditions (Kovác-Andrić et al., 2009). According to Alghamdi et al. (2014), some cases of $O_3$ formations are entirely controlled by $NO_x$ concentrations ($NO_x$-sensitive), while in other cases, it is totally

dependent on VOC concentrations (VOC-sensitive). Zhang and Kim Oanh (2002) added that the complexity of $O_3$ formation and destruction is also contributed by the involvement of physical and chemical processes in the lower troposphere and exchange air with stratosphere. As a result, $O_3$ is becoming the major pollutants that can induce serious environmental problems and yet their transformation behaviour is difficult to control and predict due to the effect of its precursors and meteorological changes (Abdul-Wahab et al., 2005; Pires et al., 2008b; Özbay et al., 2011).

### 2.2.3 (a) Daytime Chemistry of Ground Level Ozone Transformation

$O_3$ chemistry is much driven by the presence of sunlight as the pollutant itself is normally called a secondary pollutant (Jenkin and Clemitshaw, 2000). The sunlight initiated the photochemical reactions by providing near ultra violet radiation, which dissociates certain stable molecules into the formation of free radicals. Atkinson and Arey (2003), elucidated that the only significant formation route of $O_3$ in the troposphere began with photolysis of $NO_2$ (2.2).

$$O_2 + O + M \rightarrow O_3 + M \quad (2.1)$$

$$NO_2 + hv\ (\lambda < 400\ nm) \rightarrow NO + O \quad (2.2)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (2.3)$$

Where M is a third element, such as $N_2$ or $O_2$, which removes energy of the reaction and stabilizes the $O_3$ (Teixeira et al., 2009). The reactions in equations (2.1), (2.2), and (2.3) result in a photo-equilibrium between $O_3$, $NO_2$ and NO with no net formations and loss of $O_3$ (Atkinson, 2000; Nishanth et al., 2014). Jenkin and Clemitshaw (2000) expressed that in a typical boundary layer concentration of 30 ppb of $O_3$, the $O_3$ destruction reactions (2.3) occur on a timescale of around one minute. During daytime, the chemical inter-converting the $NO_x$ species involving the free

radicals either hydroperoxy radical ($HO_2$) or organic peroxy radicals ($RO_2$) is responsible in increasing the $O_3$ concentration. These free radicals are mainly produced in the troposphere as intermediates in the photochemical oxidation of carbon monoxide (CO) and volatile organic compounds (VOCs) (Jenkin and Clemitshaw, 2000; Atkinson and Arey, 2003). Both $HO_2$ and $RO_2$ are capable in providing additional $NO_2$ concentration in the atmosphere through reactions (2.4) and (2.5).

$$HO_2 + NO \rightarrow OH + NO_2 \quad (2.4)$$

$$RO_2 + NO \rightarrow OH + NO_2 \quad (2.5)$$

Where $HO_2$ is the hydroperoxy radical; OH is hydroxyl; $RO_2$ is organic peroxy radicals.

The additional $NO_2$ concentration will directly be converted into $O_3$ through reactions (2.2) and subsequently cycled to produce additional NO and $NO_2$ concentration. The production of $NO_2$ through the reactions in (2.4) and (2.5) does not consume $O_3$, subsequently together with reaction (2.1) and (2.2) represent the net source of $O_3$ at ground level (Atkinson, 2000; Jenkin and Clemitshaw, 2000; Seinfeld and Pandis, 2006; Tiwary and Colls, 2009).

Additional $O_3$ concentrations are also contributed by the CO concentrations. Reaction with OH oxidized CO into $CO_2$ through reactions (2.6) and generates $HO_2$ through (2.7). The chemical reaction between $HO_2$ and NO then take place to produce $NO_2$ (2.4), which is later converted into $O_3$ (Jacob, 2000).

$$OH + CO \rightarrow H + CO_2 \quad (2.6)$$

$$H + O_2 + M \rightarrow HO_2 + M \quad (2.7)$$

Where H is hydrogen atom; M is a third molecule ($N_2$ or $O_2$).

Nishanth et al. (2014) stated that the loss of $O_3$ concentration during daytime is mainly attributed by scavenge by NO titration (2.3) and their photolysis into O atom