CHARACTERISATION OF DIURNAL GROUND LEVEL OZONE CONCENTRATION IN URBAN AREA IN MALAYSIA

by

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A report submitted in fulfilment of the requirements for the degree of Bachelor of Applied Science (Sustainable Science) with Honours

FACULTY OF EARTH SCIENCE

UNIVERSITI MALAYSIA KELANTAN

2020

DECLARATION

I declare that this thesis entitled "Characterisation of Diurnal Ground Level Ozone Concentration in Urban Area in Malaysia" is the result of my own research except as cited in the references. The thesis has not accepted for any degree and is not concurrently submitted in candidature of any other degree.

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ACKNOWLEDGEMENT

It is a great pleasure to address people who helped me throughout this project to enhance my knowledge and practical skills especially in research area in order to completing the requirement Degree of Bachelor of Applied Science (Hons) Sustainable Science. First of all, I am grateful to The Almighty Allah for giving me strength and ability to understand throughout the research. Next, I would like to express my sincere appreciation to my supervisor, Dr. Norrimi Rosaida Binti Awang who support me in everything throughout the semester. Without her persistent help and guidance, this research would not been possible.

My gratitude also been extended to Amni Umirah Binti Mohamad Nazir, a PhD student who helped me a lot especially during fieldwork study and sharing her knowledge in my research. I would also like show my gratitude to my examiners for helping me to improve my research study. My fellow undergraduate students should also be recognised for their support. Finally, special gratitude to my family who always support and give the encouragement words to complete this research.

Characterisation of Diurnal Ground Level Ozone Concentration in Urban Area in Malaysia

ABSTRACT

Ground level ozone (O_3) can be classified as secondary air pollutant that impose harmful effects on human health, crop production and air quality. The formation of O_3 is induced by the emissions of its precursors (NOx and VOCs) in process of photochemical reaction with the presence of sunlight in daytime. Meanwhile, at nighttime, since there is no sunlight, those precursors of O_3 act as removal agents to reduce the O_3 concentration. An effective nighttime removal rate is believed to cause decrement in next day O_3 concentration, and vice versa. However, those interrelationship between daytime and nighttime O_3 reaction is scarcely studied and minimally understood. Therefore, this study focused on the determination of O_3, NO_2 and NO concentration and explore the relationship between daytime and nighttime of O_3 and its precursor in Shah Alam, Selangor. The primary data were collected by using Aeroqual S500 for 72 hours continuously. Meanwhile, the secondary data were obtained from Air Quality Division, Department of Environment (DoE), Malaysia for five years of continuous hourly average data of O_3, NO_2 and NO from 2006 to 2010. The obtained data were divided into daytime and nighttime and been analysed by descriptive analysis, box and whisker plot, time-series analysis, diurnal plot and multiple linear regression. The diurnal patterns of O_3 in Shah Alam were showing a consistent trend with slightly different magnitude. The maximum level of O_3 concentration was observed at noon time (1400 hour to 1500 hour), while its minimum level of O_3 concentrations occurred at night starting from 2000 hour until dawn which is around 0700 hour to 0800 hour due to NO titration. Most of the daytime O_3 concentration showed that it exceeds the permissible values recommended by MAAQG, which is 92 ppb compared to nighttime. The p-value obtained for the mean of O_3 concentration was 0.00. Since the p-value were less than 0.05, so there were significant differences for the mean of O_3 during daytime and nighttime in Shah Alam.

Pencirian Kepekatan Ozon Paras Tanah Harian di Kawasan Bandar di Malaysia

ABSTRAK

Ozon paras tanah (O_3) boleh diklasifikasikan sebagai bahan pencemar udara sekunder yang memberi kesan buruk terhadap kesihatan manusia, pengeluaran tanaman dan merosakkan kualiti udara. Pembentukan O_3 didorong oleh pelepasan prapenanda (NO_x dan VOC) dalam proses tindak balas fotokimia dengan kehadiran cahaya matahari pada waktu siang. Sementara itu, disebabkan tiada cahaya matahari pada waktu malam, prapenanda O_3 menjadi ejen penyingkiran untuk mengurangkan kepekatan O_3. Kadar penyingkiran waktu malam yang berkesan dipercayai boleh menyebabkan penurunan kepekatan O_3 pada hari berikutnya, dan sebaliknya. Walau bagaimanapun, hubungkait antara reaksi O_3 pada waktu siang dan malam kurang dipelajari dan difahami. Oleh itu, kajian ini memberi tumpuan kepada penemuan kepekatan O_3, NO_2 dan NO dan meneroka hubungan antara O_3 dan prapenanda pada waktu siang dan malam di Shah Alam, Selangor. Data utama dikumpulkan menggunakan Aeroqual S500 selama 72 jam secara berterusan. Sementara itu, data sekunder diperolehi daripada Bahagian Kualiti Udara, Jabatan Alam Sekitar (DoE), Malaysia selama lima tahun iaitu data purata setiap jam bagi O_3, NO_2 dan NO dari 2006 hingga 2010. Data yang diperoleh dibahagikan kepada siang dan malam dan dianalisis dengan analisis deskriptif, kotak dan plot kumis, analisis siri masa, plot harian dan regresi linear berganda. Corak harian O_3 di Shah Alam menunjukkan trend konsisten dengan magnitud yang sedikit berbeza. Tahap maksimum kepekatan O_3 diperhatikan pada waktu siang (1400 jam hingga 1500 jam), manakala kepekatan minimum O_3 terjadi pada waktu malam bermula dari 2000 jam dan menghampiri matahari terbit pada sekitar 0700 jam hingga 0800 jam disebabkan titisan NO. Kebanyakan kepekatan O_3 siang hari menunjukkan bahawa ia melebihi nilai yang disyorkan oleh MAAQG, iaitu 92 ppb berbanding dengan waktu malam. Nilai-p yang diperolehi untuk kepekatan purata O_3 ialah 0.00. Oleh kerana nilai-p kurang daripada 0.05, maka terdapat perbezaan yang signifikan untuk purata O_3 semasa waktu siang dan malam di Shah Alam.

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LIST OF ABBREVIATIONS

API	Air Pollutant Index
Cl	Chlorine
$ClNO_2$	Nitryl chloride
CO	Carbon monoxide
CO_2	Carbon dioxide
DoE	Department of Environment, Malaysia
H_2O	Water
HNO_3	Nitric acid
MAAQG	Malaysia or Malaysian Ambient Air Quality Guidelines
MLR	Multiple Linear Regression
N_2	Nitrogen
N_2O_5	Dinitrogen pentoxide
NaCl	Sodium chloride
$NaNO_3$	Sodium nitrate
NMHCs	Non-methane hydrocarbons
NO	Nitric oxide
NO_x	Nitrogen oxides
NO_2	Nitrogen Dioxide
NO_3	Nitrate radical
$O(^1D)$	Excited oxygen atom
$O(^3P)$	Oxygen atom
O_2	Oxygen molecules

O_3	Ozone
OH	Hydroxyl radical
$PM_{2.5}$	Particulate matter with aerodynamic diameter less than 2.5 micron
PM_{10}	Particulate matter with aerodynamic diameter less than 10 micron
PSI	Pollutant Standard Index
RH	Reactive volatile organic compound
RO_2	Peroxy radicals
SO_2	Sulphur dioxide
USEPA	United States Environmental Protection Agency
UV	Ultraviolet radiation
VOCs	Volatile organic compounds
WHO	World Health Organization

LIST OF SYMBOLS

%	Percentage
℃	Temperature (degree Celsius)
$\mu g/m^3$	Microgram per meter cubic
nm	Nanometer
λ	Wavelength
+	Plus
⇌	Reversible reaction
ppb	part per billion
hυ	Energy from solar radiation
km^2	Kilometre square
M	Inert body
nm	nanometer
R	Organic radicals
N	North
E	East
°	Degree (angle)
‘	Minute (angle)
$<$	Less than

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The atmosphere is very important for living organism as it is a mixture of the gases of 78 % of nitrogen (N_2), 21 % of oxygen (O_2) and 1 % of trace gases that surround the earth. Earth atmosphere is relatively transparent that shield earth to prevent from the adverse ultraviolet (UV) radiation from the Sun, keeps the surface of the Earth warmer by greenhouse effect by about 33℃ and the most important is to prevent the extreme difference between nighttime and daytime temperature (ESPERE, 2004).

Nowadays, the atmosphere can be and has been polluted by various pollutants. Pollutants can be from anthropogenic activities and natural sources. Air pollution can be described as the existence of the contaminant and adverse substance in the atmosphere that interfere with human health and the environment (Vallero, 2014). In Malaysia, the air quality was monitored by The Department of Environment (DoE) manually and continuously to identify any significant changes in the Malaysia encompassing air. Air Pollutant Index (API) is an index to measures the air quality status in Malaysia. The API scales and its status are shown in Table 1.1. The index is reflecting the effect of air pollutant to human health according to the scales of air pollutant either good or hazardous (DoE, 2019a).

Table 1.1: The API scales and status.

API	Status
0 – 50	Good
51 – 100	Moderate
101 – 200	Unhealthy
201 – 300	Very Unhealthy
>301	Hazardous

(Sources: DoE, 2019)

There are six air pollutants that are addressed by the Malaysia Ambient Air Quality Guidelines (MAAQG) (Table 1.2). This includes five current air pollutant which are particulate matter with aerodynamic diameter less than 10 micron (PM_{10}), ozone (O_3), nitrogen dioxide (NO_2), carbon monoxide (CO), sulphur dioxide (SO_2), and particulate matter with aerodynamic diameter less than 2.5 micron ($PM_{2.5}$) (DoE, 2019).

Table 1.2: New Malaysian Ambient Air Quality Guidelines (MAAQG)

Pollutants	Averaging Time	Malaysian Guidelines
		Level (ppb)
Particulate matter with aerodynamic diameter less than 10 micron (PM_{10})	1 Year	40
	24 Hour	100
Particulate matter with aerodynamic diameter less than 2.5 micron ($PM_{2.5}$)	1 Year	15
	24 Hour	35
Ozone (O_3)	1 Hour	92
	8 Hour	51
*Carbon monoxide (CO),	1 Hour	30
	8 Hour	10
Sulphur dioxide (SO_2)	1 Hour	96
	24 Hour	31
Nitrogen dioxide (NO_2)	1 Hour	149
	24 Hour	37

*mg/m^3 Sources: (DoE, 2019).

Ozone has become a burden in numerous nations because of its effect and become one of the major sources of air pollutant of the world. At ground level, air pollutant can be divided into two groups, primary and secondary air pollutant. Primary air pollutant is directly emitted from natural and anthropogenic activities. Meanwhile, secondary air pollutant form during photochemical reaction between primary air pollution and other components in the air (Yahaya et al., 2017). Ozone is identified as the as the secondary pollutant (Ghazali et al., 2010).

Ozone is a gas made of three atoms of oxygen and it can be both good and bad to living organism, depending on where it is located. The troposphere O_3 known as pollutant that hazardous to the environment, human health, and food production. Most of the O_3 in the troposphere known as ground level ozone occur from of the chemical reactions between nitrogen oxide (NO_x) and volatile organic compound (VOCs) that react in the presence of sunlight (Gautam et al., 2016; EPA, 2018b). VOCs and NOx are known as precursors of the O_3 production. Meanwhile, O_3 in the stratosphere make up a layer that acts as a sunscreen that protect living organism from exposed too much of UV radiation from the Sun (ESPERE, 2004; EPA, 2018a).

Furthermore, ozone also been classified as greenhouse gas has become main topic by previous research in recent years due to its impacts. Besides, in daytime and nighttime, it regulates nitrate radical (NO_3) and hydroxyl (OH) radicals in the atmosphere respectively. In Malaysia, it was reported that O_3 is one of the main air pollutants (Mohamad-Hashim et al., 2017; Yahaya et al., 2017). Basically, the concentration of O_3 in the urban area usually is higher especially during warm summer months compared to rural area because of the few factors that contribute to the production of O_3 such as climate condition, wind direction and wind speed (Ghazali et al., 2010). Typically, the concentration of O_3 is higher during daytime where it reaches their peak in mid to late afternoon and low concentration during nighttime and early morning due to the absence of the photochemical reaction process (Ghazali et al., 2010; Awang et al., 2017).

1.2 Problem Statement

Fresh air is the fundamental requirement for human wellbeing and the environment. Although, in numerous countries especially in developing countries, ground level ozone stays a standout amongst the most pervasive pollutant that gives negative effect to the environment, human health, and food production (Garthwaite et al., 2009; Gautam et al., 2016). According to the World Health Organization (WHO, 2018), in 2016, the ambient air pollution was assessed to cause 4.2 million premature deaths worldwide with 91 % of the total are happen in low and middle income countries.

Ground level ozone is a global air pollution problem that need to be addressed as it is an important greenhouse gas. Central Europe, Eastern United States of America (USA) and Eastern China record high concentrations of ground level ozone due to intensive industrial activities (Garthwaite et al., 2009). Ozone is formed by photochemical reaction between NO_2 and VOCs with presence of sunlight and it is a major constituent of photochemical smog (Ramli et al., 2010). NO_2 and VOCs are primary air pollutants resulted from various anthropogenic activities.

Ozone can influence the food production by entering the leaves through stomata. Continuing ozone exposure can cause several types of symptoms including flecking, stippling, reddening and bronzing (USDA, 2016). These symptoms commonly happen between the veins on the upper leaf surface of middle-aged and older leaves yet for some species may likewise include both leaf surfaces (bifacial). The severity of damage of the leaves is reliant on a few elements including plant genetics, weather condition, and duration and concentration of ozone exposure. According to Wilkinson (2012), soybean and wheat are especially sensitive plant to ozone exposure; potato, rice and maize are tolerably delicate plant; while barley has been observed to be ozone invulnerable. Exposure to ground level ozone cause all this global crop yields has declined every year due to increasing of O_3 concentration because of human activities.

Breathing the ground level ozone can cause damage to human lungs and narrows the flows of air in and out of the lungs (Malley et al., 2017). Furthermore, damage crop yields that will decrease the food supply (Chaiyakhan et al., 2017). The O_3 can actuate a sequence of negative health effects such as cardiovascular and respiratory disease, premature death even in a small amount. Mullins (2018) found that only 33.47 ppb of average daily O_3 concentration which is below ambient O_3 levels regulated. However, this concentration is still harmful if a person is exposed for longer duration. Besides, it may cause impact to vegetation production and environment.

High concentration of ozone can be monitored at noon time as the ozone formed due to the presence of sunlight for the photochemical reaction. Various researches emphasized that the concentration of ozone is in increasing trends due to the increment of its precursors. Most of the precursors of ozone are mainly come from large number of vehicles, coal combustion, and industrial activities (Monk et al., 2015). Mohamad-Hashim et al. (2017) found that Melaka have high concentration of O_3 in 2003-2012 due to large amount of solar radiation intensity amid that period. Meanwhile, Mohamed-Noor et al. (2018) found that the concentration of O_3 in Shah

Alam was surpass the MAAQG and frequency higher than other states due to its intensive industrial activities. Many industrial such Glenmarie located in Shah Alam.

The diurnal cycle of O_3 concentration has a mid-day unimodal peak around 1300 hour to 1500 hour and it became lower in nighttime due to the removal reaction of O_3. In Malaysia, O_3 concentration gradually increase after the sun rises at 0800 hour, reaching a higher during mid-day and decrease until the next morning (Ghazali et al., 2010; Mohamad-Hashim et al., 2017; Mohamed-Noor et al., 2018). The pattern was influenced by high rate of photochemical reaction of O_3 during daytime and the removal chemistry during nighttime. Brown et al. (2012) study that focused on O_3 nocturnal radical chemistry stressed that NO_3 and dinitrogen pentoxide (N_2O_5) reaction led to the loss of NOx and O_3 through its various heterogeneous and homogeneous reaction pathways. Since there is no sunlight, those precursors of ozone be a removal agent at nighttime. The high rate of chemical process will eventually affect the next day ozone concentration. An effective nighttime removal rate is believed to cause decrement in next day O_3 concentration, and vice versa. However, those interrelationship between daytime and nighttime O_3 reaction is scarcely study and minimally understood. Thus, this study would like to critically explore the characterisation of diurnal ground level ozone concentration between daytime and nighttime and any possibilities to use this relationship to reduce O_3 in ambient air.

1.3 Objectives

i. To determine the concentration of ground level ozone and its precursors during daytime and nighttime.

ii. To determine the relationship between daytime and nighttime ground level ozone concentration in urban area.

1.4 Scope of Study

This study is designed to investigate the interrelationship between daytime and nighttime ozone concentration in an urban area from 2006 to 2010 (5 years). The scope of study focuses mainly on identifying the relationship between daytime and nighttime ground level ozone concentration in urban area in order to understand the impact of daytime ground level ozone towards nighttime. The chosen area for this is Shah Alam, Selangor. This study utilized two type of data; primary data obtained from monitoring work and secondary data acquired from Department of Environment (DoE).

1.5 Significance of Study

In the past few years, ground level ozone issues remain a serious global air pollution problem and has grew out to be a major concern towards the public around the world. According to Liu et al. (2017), O_3 has been substituted PM_{10} and $PM_{2.5}$ as the main pollutant in three main cities in China from June 2016 to August 2016. The production of ground level ozone is due to high concentration of VOCs/NO_x and meteorological factor such as high temperature in that area (Ramli et al., 2010).

This study is important to investigate the characterisation of diurnal ground level ozone concentration between daytime and nighttime ground level ozone concentration in urban area. The daytime ground level ozone might be affecting the nighttime because nighttime usually focus on removal part of O_3 (Awang et al., 2017). The higher the removal process, the lower the ground level ozone. Thus, the study of the relationship between daytime and nighttime is necessary to develop a control strategy to reduce the effect of ground level ozone.

CHAPTER 2

LITERATURE REVIEW

2.1 Ground level ozone

Ozone is a gas that present in both the stratosphere and troposphere. Ozone that formed at the upper part of the atmosphere known as stratospheric ozone is approximately 90 % of its total, while a small amount of ozone is formed at the ground level known as ground level ozone or tropospheric ozone (Gautam et al., 2016). Stratospheric ozone acts as a shields to cover the Earth surface from the harmful UV radiation, while ground level ozone is a secondary air pollutant produce when the primary pollutant is reacting with other component in the atmosphere. Awang et al. (2015b) stated that due to the different wavelengths of the UV photon, the formation mechanisms of stratospheric and tropospheric ozone is different.

Basically, ground level ozone can be form in the troposphere which is the lowest layer of atmosphere. A combination of elimination combine with customary intrusion of ozone-rich stratospheric air and in-situ photochemical production is generally attributed to the ground level ozone (NAP, 1991). Department of Environment (DoE) (2019) stated that ground level ozone in urban area can be classified as one of the six major pollutants that set in MAAQG as a pervasive air pollution that can affect human wellbeing, environment, and crop yield. The major factors that contribute to the production of O_3 in urban area is due to emissions of NO_x

and VOC and meteorological conditions under photochemical reaction in the atmosphere (NAP, 1991; Souza et al., 2018). The major sources of VOCs are mainly from the vehicle exhaust, emission from the chemical, industries and from the use of solvent. On the other hands, NO_x is commonly emitted from the electricity generating stations, motor vehicles and combustion of fossil fuels.

Despite many years, problem that related with ground level issues is still not completely resolved. Malley et al. (2017) found that in 2010, almost 1.04 – 1.23 million respiratory death are among the global population higher than 30 years of age. The study highlights that exposure to ozone concentration can cause a global burden of disease among people.

2.2 Photochemical Reaction for Ozone Production

The production of ground level ozone is due to photochemical reaction of NO_x and VOCs which are mainly from anthropogenic emission with the existence of sunlight. Various studies reported that the maxima concentration of O_3 occurred at the late of afternoon between 1300 hour to 1500 hour in Malaysia (Ghazali et al., 2010; Azmi et al., 2010; Awang et al., 2015b). Abdul-Rani et al. (2018) found that the concentration of O_3 increases after sunrise around 0800 hour due to increasing solar radiation. Ozone molecules are composed of three atoms of oxygen (O), when O atom produced by the photodissociation of NO_2 in the troposphere combines with the molecular oxygen (O_2). Due to the expansions of the transportation, agricultural and industrial sectors, it has contributed to the production of waste gases, that particularly NO_x and VOCs, which will invade the atmosphere and aggravate the photochemical reaction of O_3.

2.2.1 Ozone chemical reactions during daytime

The formation of ozone starts when the organic radicals (R) are formed due to the reaction between reactive VOCs that expressed as RH with hydroxyl radicals (OH) (2.1).

$$RH + OH \rightarrow R\cdot + H_2O \qquad (2.1)$$

Then, peroxy radicals (RO_2) will be formed when the organic radicals are combined with molecular oxygen that usually requires M, an inert body either O_2 or N_2 to evacuate the energy from the reaction (2.2).

$$R\cdot + O_2 + M \rightarrow RO_2\cdot \qquad (2.2)$$

Nitrogen dioxide (NO_2) are formed when RO_2 reacts with nitric oxide (NO) (2.3).

$$RO_2\cdot + NO \rightarrow NO_2 + RO\cdot \qquad (2.3)$$

Then, solar radiation will photodissociated the NO_2 to evacuate ground state oxygen atoms, $O(^3P)$ and rebuild NO (2.4).

$$NO_2 + h\upsilon\ (\lambda < 420\ nm) \rightarrow NO + O(^3P) \qquad (2.4)$$

In equation (2.4), $h\upsilon$ represents the energy produce from solar radiation where v is the frequency of the electromagnetic wave of solar radiation and h is the product of Planck's constant. Finally, the O_3 formed when O atom from (2.4) is combined with molecular oxygen in the present of M (2.5).

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (2.5)$$

Then, near-ultraviolet wavelength will photodissociated O_3 to generate an excited oxygen atom, $O(^1D)$. Equation (2.6) is the key process of the tropospheric ozone because $O(^1D)$ has enough excitation energy to combine with water vapour (H_2O) to form two OH radicals.

$$O_3 + h\upsilon\ (\lambda<340\ nm) \rightarrow O_2 + O(^1D) \quad (2.6)$$

$$O(^1D) + H_2O \rightarrow 2OH \quad (2.7)$$

The resulting OH radicals leads to cycles of reactions. With enough VOCs and NO_x in the air, the chain reactions described above can enhance the formation of tropospheric ozone with the presence of sunlight (NAP, 1991; ESPERE, 2004).

2.2.2 Ozone chemical reactions during nighttime.

However, at nighttime, there is no incoming solar radiation. Therefore, the concentration of OH in nighttime at almost zero. Instead, there is another oxidant known as nitrate radical (NO_3) that is generated at night. NO_3 is formed from the reaction of O_3 and NO_2. Then, NO_3 radicals reacted further with NO_2 to form dinitrogen pentoxide (N_2O_5) (Mohamed-Noor et al., 2018). N_2O_5 in equation (2.9) may dissociate back into NO_3 and NO_2 because it is thermally unstable (Awang et al., 2015a; 2017).

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (2.8)$$

$$NO_3 + NO_2 \rightleftharpoons N_2O_5 \quad (2.9)$$

The chemical reaction in equation (2.8) also occurs during daytime but NO_3 is quickly photolyzed at daytime, and therefore NO_3 and its equilibrium partner N_2O_5 are both heavily suppressed during the day. Besides, the reaction between NO_3 and VOC generating secondary organic aerosol which also considered as a pollutant. Commonly, N_2O_5 occurs on the surface of or inside the aerosol particle that is readily taken up by water droplets and aqueous inorganic particles, where it will undergo hydrolysis process with water to form nitric acid that easily been removed by precipitation; acid rain (Awang et al., 2017). Moreover, N_2O_5 could reacting with chloride ions in sea salt aerosol at nighttime to form nitryl chloride ($ClNO_2$) that will be photolyze the next morning (Ball, 2014).

$$N_2O_5 + NaCl \rightarrow ClNO_2 + NaNO_3 \quad (2.10)$$

$$ClNO_2 + h\upsilon(\lambda<840 \text{ nm}) \rightarrow Cl + NO_2 \quad (2.11)$$

The NO_2 formed in equation (2.11) remains available for photochemical ozone production the next day. Meanwhile, Cl atom is more reactive than NO_3 and OH, so it leads to the oxidation of VOCs that do not react with NO_3 directly (Ball, 2014).

Generally, ozone concentration is maximum amid daytime instead of nighttime due to the photochemical reaction only occur during daytime as sunlight is needed in the photochemical reaction. At night, the concentration of ozone is commonly low because of the absence of sunlight and further elimination by continuous chemical loss by NO deposition and titration (Awang et el., 2015a).

2.3 Ozone Precursors

In the formation of ozone, VOCs and NO_x and plays important role as its precursors (Ghazali et al., 2010; Awang et al., 2015a; 2015b; 2017; Wang et al., 2017). In addition, the meteorological conditions also enhance the formation, distribution and destruction of ozone (Souza et al., 2018). Most significant sources of O_3 precursors are fossil fuel combustion from power generation and transportation. In urban areas, both natural and anthropogenic VOCs and NO_x are important as they emitted by combustion and evaporation process. NO_x mainly from the combustion process, stratospheric instruction, soils, wildfires and lighting (Portmann et al., 2012). The concentration of ozone in eastern China has increase in recent year due to the vigorous economic development and rapid urbanization (Wei et al., 2014; Wang et al., 2017).

2.3.1 Nitrogen oxides

Nitrogen oxides plays important roles for the formation and destruction of O_3 concentration. Nitrogen oxides that include NO and NO_2 are the most crucial nitrogen compound that commonly occurs in urban area and approximately 90 % of the emission of combustion is contain of NO (Ghazali et al., 2010). At nighttime, NO_3 is formed and control the chemistry of the nighttime atmosphere. Awang et al. (2015a) claimed that high concentration of O_3 at nighttime in Kemaman is due to low nighttime NO_x concentration that cause low O_3 removal rates. Besides, when the NO_x is reacts with H_2O, it will form nitric acid (HNO_3) which is the major contributor of acid rain (ESPERE, 2004). In addition, N_2O_5 is formed when NO_3 and NO_2 in nighttime acts as a store for NO_3 that can react with H_2O to form HNO_3 or decompose back into NO_2 and NO_3 (ESPERE, 2004).

2.3.2 Volatile Organic Compounds

Similar to NO_x, VOCs also play crucial roles in O_3 formation. Even though exposure to VOCs gives acute harm to human health, but long-term exposure could result in carcinogenic and cardiovascular effect (Ras et al., 2009). VOCs play an important role as a free radicals that convert NO into NO_2 without destroying the O_3 (Ghazali et al., 2010). Volatile organic compound usually emitted directly to the atmosphere from various sources of natural and anthropogenic activities and vegetation. The main group of atmospheric VOCs are non-methane hydrocarbons (NMHCs) that also acts as precursor to O_3 production through hydroxyl (OH) radical-initiated oxidation (Banan et al., 2013). The sources of NMHCs includes industrial operations, landfills, motor vehicle combustion, natural gas leakages, power plants and solvent usage. Ras et al. (2009) found that there is positive correlation between VOCs and O_3 where VOCs has higher potential of O_3 formation in the Tarragona, Spain especially in the summer time because there is more sunlight to promote the formation of O_3.

2.4 Effect of Ground Level Ozone Pollution

Ozone is an air pollutant that associated with adverse health effect. Exposure to ground level ozone for short-term or long-term giving negative impact to human health, crop production and the environment (Azmi et al., 2010; Azid et al., 2015). Various studies have been reported that O_3 are harmful to vegetation, human health and the environment due to its precursors and meteorological condition (Ghazali et al., 2010; Awang et al., 2015a; 2015b; 2017).

2.4.1 Effect on human health

Breathing ozone can trigger various health impacts to children, people who are active with outdoors, the elderly and people with respiratory health issues. EPA (2018a) states that children are riskier from exposed to ozone because their lungs are still in developing process. Furthermore, Bell et al. (2014), found that woman has high risk to O_3 exposure compare to man in aged group of youngest and oldest. Most serious effect of O_3 to human is related to cardiovascular disease. Breathing O_3 can trap air in the alveoli and can cause muscle in the airways to constrict which cause to shortness of breath and wheezing. Long term exposure to O_3 can cause permanent lung damage and death from respiratory causes (Wang et al., 2017). Factors that may affect the human health is their smoking habit, occupation baseline health status and other health-related factors that increase the risk of ozone exposure (Bell et al., 2014).

2.4.2 Effects on vegetation

Ground level ozone that exceed 40 ppb have potential impact on the production of vegetation (NAP, 1991). High concentration of ozone reducing the plant photosynthesis and retard the plant growth that resulting in reduction of carbon storage by vegetation and finally rising the formation of carbon dioxide, CO_2 in the atmosphere. Sicard et al. (2017), stated that North America, Northern Asia and Central Africa have the strongest impact of O_3 on vegetation due to the climate on that area. The damaging effect of O_3 includes reduction in crop yield, photosynthetic carbon assimilation and stomata conductance.

CHAPTER 3

MATERIALS AND METHODS

3.1 Flow chart of research methodologies

Figure 3.1 shows the research flow chart of the methodologies of investigation of inter-relationship between daytime and nighttime of ground level ozone in Shah Alam, Selangor. The primary data are collected in 21–26 July 2019 for 72 hours continuously while secondary data are obtained from DoE in hourly average data from 2006-2010. The secondary data are verified by primary data by using a suitable statistical analysis.

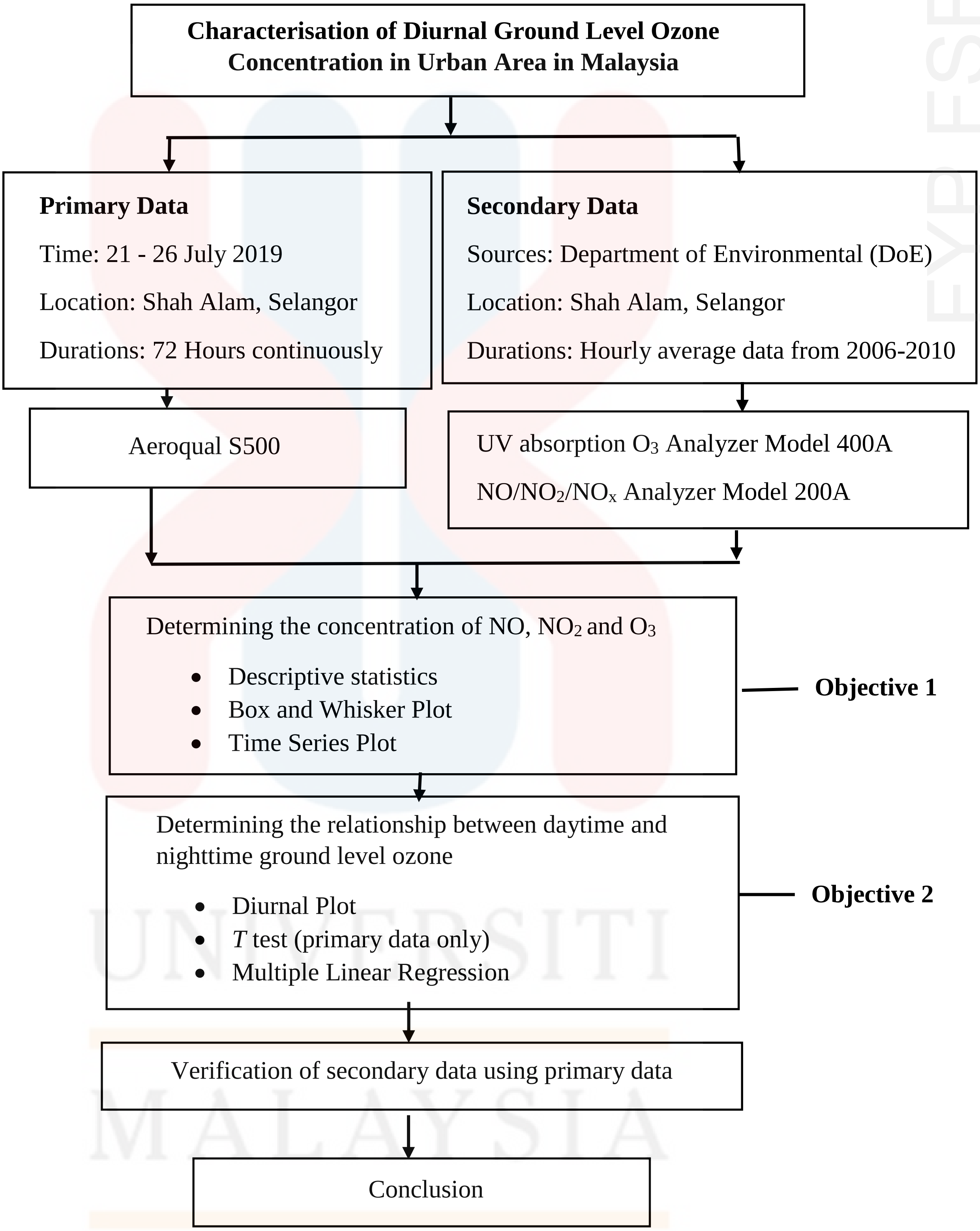


Figure 3.1: Flow chart of research methodologies

3.2 Study Area

The study area selected is Shah Alam, Selangor with the coordinate of 3°4’20” N 101°31’00” E. This location is chosen because it is categorised as urban area with numbers of industrial park and has among the best communication facilities and infrastructure in the region (Ramli et al., 2010; MBSA, 2017). Shah Alam is the state capital of Selangor, located in the Klang Districts within Petaling with a total area of 290.3 km^2 (Figure 3.2). Table 3.1 showed the detail of monitoring station in Shah Alam, Selangor.

Table 3.1: Details of Study Area

Station	**Location**	**Coordinate**	**Area (km^2)**	**Type of area**	**Population**
Taman Tun Dr Ismail Primary School (TTDI) Jaya	Shah Alam, Selangor	N03°4’20”, E101°31’00”	290.3	Urban area	481,654

Shah Alam is an urban area in Selangor with a population of 481,654 people in 2019 and is one of the main cities within the Klang Valley (Abdul-Rahman et al., 2015). Climatically, Shah Alam experiences a tropical rainforest with consistent temperature throughout the year, where the average temperature ranges between 23.2℃ and 31.9℃ (Awang et al., 2015). The rapid urbanisation and industrialisation process in Shah Alam indirectly degrade the air quality status in that area due to the increasing anthropogenic emissions that are released to the atmosphere (Mohamed-Noor et al., 2018).

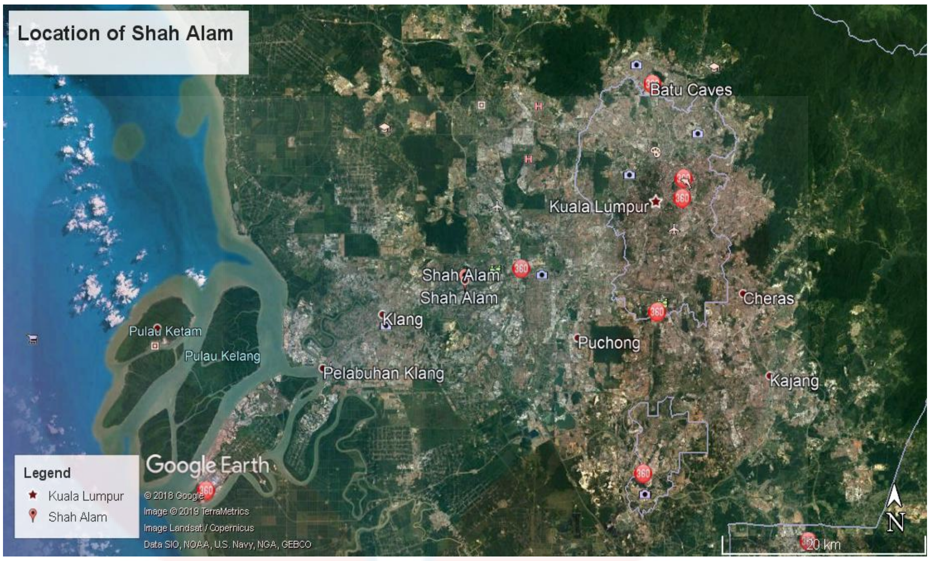


Figure 3.2: Location of Shah Alam. Sources: (Google Earth, 2018).

3.3 Primary Data Collection

The monitoring was done in urban area that located in Siti Homestay TTDI Jaya, Jalan Esei Tiga U2/41c, Taman TTDI Jaya, 40150 Shah Alam, Selangor that consists of parameters O_3 and NO_2. The primary data is collected by using Aeroqual S500 for 72 hours continuously as showed in Table 3.2. Aeroqual S500 is an ultra-portable handheld monitor that enable the accurate real-time surveying the outdoor air pollutant. The components that supplied with the Aeroqual S500 are sensor heads, monitor base, lithium smart charger, USB to monitor cable, battery pack and optional for temperature and relative humidity sensor. Aeroqual S500 is typically used for short-term air quality that suitable for this research that has interchangeable cartridge (head) sensor attached to the monitor base (Aeroqual, 2019a). The sensor heads can be replaced and removed to measure as many as pollutants interested. The concentration of O_3 and NO_2 are determined using the same instrument but with different sensor head. The sensor heads need to warm-up at least three minutes to burn off any contaminants from surrounding (Aeroqual, 2019b).

Table 3.2: Specific equipment used for primary data's collection

Type of equipment	The parameters that are measured
Aeroqual S500	O_3 and NO_2 concentration

3.4 Secondary Data Collection

The secondary data obtained from the Air Quality Division, Department of Environment (DoE), Malaysia for five years of continuous hourly average data of O_3, NO, and NO_2 from 2006 to 2010 for Shah Alam, Selangor. The list of equipment used by DoE are showed in Table 3.3.

Table 3.3: List of Equipment used by DoE

Parameter	Monitoring equipment	Detection Principle
O_3	UV Absorption O_3 Analyzer Model 400A	Applied a system based on the Beer-Lambert law
$NO/NO_2/NOx$ concentration	Chemiluminescent $NO/NO_2/NO_x$ Analyzer Model 200A	Applied a chemiluminescent detection principle

3.4.1 Ground Level Ozone

The instrument used by DoE to detect the O_3 concentration was UV Absorption O_3 Analyzer Model 400A where it applied a system to measured low-range O_3 concentration in ambient air based on Beer-Lambert law (Ghazali et al., 2010; Awang et al., 2015a; 2017). The amount of ozone detected using 254 nm UV light signal and it has multi-tasking software that allows it to view the test variables during operation (Teledyne, 2015b).

3.4.2 Nitrogen Oxides

The sample of hourly NO and NO_2 was detected by chemiluminescent NO/NO_2/NO_x Analyzer Model 200A (Ghazali et al., 2010; Awang et al., 2015a;2017). The instrument is attached with state-of-the-art microprocessor technology that allow for accurate detection low-level measurement for use as dilution CEMS monitor and an ambient analyser (Teledyne, 2015a).

3.5 Data Analysis

The data was analysed with a few statistical analyses. The collection of data of O_3, NO_2 and NO were analysed using descriptive analysis, time series plot, diurnal plot, linear regression and *t* test.

3.5.1 Descriptive analysis

Descriptive analysis is used to study the basic features of the data by summaries about the data and the measures (Kaur et al., 2018). The data obtained are analysed descriptively in terms of measures of variability and central tendency. Measures of variability includes skewness, standard deviation, minimum and maximum variables while, central tendency are means, mode and median. Thus, in this study, descriptive analysis was used to obtain the minimum, maximum, mean, and standard deviation of all the continuous data obtained from the DoE for secondary data and primary data.

3.5.2 Box and Whisker Plot

Box and whisker plot is a simple plot that presents a quick sketch of the distribution of the underlying data of five sample quartile which are include the minimum, the maximum, the median, the lower quartile and the upper quartile (Wilks, 2006). It is a graphical representation of a distribution in a rectangle shape with the maximum and minimum values mark at the ends. Since data of O_3, NO_2 and NO concentrations were continuous hourly, box and whisker plot were suitable to represent the result.

3.5.3 Time series plot

Time series plot is used to understand the relationship between the cause and effect of environmental pollution by plot the concentration of ozone and its precursors against time. The goal of time series plot is to identify the pattern of O_3 and its precursor over time. The data collected was hourly average data from 2006 until 2010 (5 years) so, time series plot is suitable analysis to see the change of pattern of each parameter in long duration.

3.5.4 Diurnal Plot

Diurnal plot is an analysis that involved symbol and line to illustrate the pattern of diurnal variation of O_3 and its precursors during daytime and nighttime and used to study the differences between daytime and night time ground level ozone as it is being used for long-time studies of behaviour. Diurnal plot is chosen to plot the average hourly value of the time on a 24 hour scale (Mohamed-Noor et al., 2018) to graphically determine the relationship between daytime and nighttime variation. It can produce the minimum and maximum peak that indicate the concentration of O_3 and NO_2.

3.5.5 Multiple Linear Regression Analysis

Regression analysis is a statistical technique for estimate the relationship between a dependent variable and one independent variable and formulates the linear relation equation between both variable. Linear regression was applying to summarize the linear relationship between two variables, x and y by a single straight line (Daniel, 2006). Multiple linear regression is a regression model that have one dependent variable and more than one independent (Uyanik and Guler, 2013).

Formula:

$$y = \beta_0+\beta_1x_1+\beta_2x_2+...+ \beta_px_p \quad (3.1)$$

where,

y = dependent variable

x = independent variables

β_0 = y-intercept (constant term)

β_p = slope coefficients for each explanatory variable

3.5.6 *T* test Analysis

The *t* test analysis are used to compare the values of the mean from two variables and test whether there is different between two independent sample means. *T* test is a parametric method that used when the samples satisfy the conditions of independence, normality, and equal variance. It can be divided into two group which is independent *t* test where it been utilized when the two groups under comparison are independent of each other and another one is paired *t* test that used when two groups under comparison are dependent on each other (Kim, 2015). This analysis was operated using Statistical Packages for Social Sciences (SPSS) version 20.0.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

The result of analyses that have been done in this study, which are descriptive analysis, plot and whisker plot, time series plot, diurnal plot, and multiple linear regression were detailed and discussed in this chapter.

4.2 Descriptive analysis of ozone, nitrogen dioxide and nitrous oxide concentration during daytime and nighttime.

The overall variation concentration of O_3, NO_2 and NO in Shah Alam were studied by using descriptive analysis. Descriptive analysis was used to show the trend and pattern of ground level ozone and its precursors by obtaining the maximum, minimum, standard deviation and mean for each parameter of primary and secondary data. For secondary data, it involves five years data from 2006 to 2010 with total 21,912 data included leap year in 2008. The result of descriptive analysis of O_3, NO_2 and NO in Shah Alam during daytime and nighttime are shown in Table 4.1. The results significantly showed that mean concentration of ozone during daytime in 2006 is significantly higher than in 2007, 2008, 2009 and 2010, with 35.85 ppb, 32.83 ppb, 33.94 ppb, 34.11 ppb, and 32.86 ppb, respectively. It seems that during this period, ozone concentration is high because coincidence with the period where Malaysia experienced short periods of moderate haze mainly due to transboundary pollution from July until October (Latifa et al., 2018; DoE, 2019c).

There are several unhealthy air quality regions were recorded in Malaysia particularly in Klang Valley, Terengganu, Perak, Johor, Negeri Sembilan, Pahang, Sarawak and Melaka (DoE, 2007). The air quality levels in Malaysia is determined by the Air Pollutant Index (API) as shown in Table 1.1 as it is the air pollutant index scale that easily to understand (DoE, 2019a). Apart from the haze episodes that occur in 2006, the pollutant that remained in the air caused by the transboundary pollution coupled with conducive atmospheric condition enhances the formation of O_3 in few locations in Malaysia that includes Shah Alam (DoE, 2007).

The results showed that O_3 concentration recorded in Shah Alam is higher during daytime, that is exceed the Malaysian Ambient Air Quality Guideline (MAAQG) which is 92 ppb. Thus, it means there were higher contribution of NO_2 concentration into the atmosphere that commonly due to vehicles emission. Shah Alam is the well-known industrial park in Malaysia and the air quality monitoring station is surround by residential areas (Mohamad-Hashim et al., 2017). The emission from the industry and vehicle around that area contribute the most to the O_3 formation. The oxidation of NO concentration during daytime producing NO_2, consequently increasing the amount of O_3 concentration. From the Table 4.1, the concentration of NO_2 is less compared to O_3 concentration due to the efficiently used up for the formation of O_3 in the atmosphere during daytime (Awang et al., 2017). For O_3 formation, the intensity of sunlight is very important for NO_2 to undergoes photochemical reaction to form free oxygen atom (O) and reacts with O_2 to form O_3 (Awang et al., 2015b). High temperature during daytime indicates high solar intensity that encourage the photochemical reaction (Mohamad-Hashim et al., 2017).

Meanwhile, the mean concentration of O_3 during nighttime in 2006 is lower than 2007, 2008, 2009 and 2010, which were 8.63 ppb, 9.31 ppb, 9.37 ppb, 10.98 ppb, and 8.70 ppb, respectively. The O_3 concentration during nighttime is lower compared to the daytime due to the absence of sunlight as the catalyst for photochemical reaction to occurs. Awang et al. (2015b) stated that in nighttime, the O_3 concentration is commonly low and in stable condition due to absence photochemical reaction and attributed to deposition processes and chemical reaction via NO titration (2.8). The results showed NO concentration was higher compared to daytime. This is because NO play important role during nighttime O_3 chemistry as the increase of NOx evidently increase the O_3 removal rates, thereby it decreases the concentration of O_3 during nighttime.

Table 4.1: Descriptive analysis of ground level ozone and its precursors during daytime and nighhttime in Shah Alam.

Year	Parameter	Daytime				Nighttime			
		Min	**Max**	**Mean**	**SD**	**Min**	**Max**	**Mean**	**SD**
2006	O_3 (ppb)	0	152.0	35.85	28.13	0	83.0	8.63	10.90
	NO_2 (ppb)	0	66.0	14.18	10.62	0	80.0	20.37	11.86
	NO (ppb)	0	161.0	14.96	19.61	0	184.0	21.45	23.70
2007	O_3 (ppb)	0	163.0	32.83	25.69	0	79.0	9.31	11.24
	NO_2 (ppb)	0	66.0	13.19	9.50	0	69.0	18.78	10.76
	NO (ppb)	0	207.0	15.56	20.90	0	177.0	20.38	23.41
2008	O_3 (ppb)	0	149.0	33.94	27.55	0	85.0	9.37	10.98
	NO_2 (ppb)	0	70.0	15.86	11.00	0	70.0	22.67	13.22
	NO (ppb)	0	162.0	16.61	22.64	0	138.0	20.31	22.85
2009	O_3 (ppb)	0	145.0	34.11	26.92	0	91.0	10.98	11.91
	NO_2 (ppb)	0	141.0	15.54	11.98	0	88.0	22.59	14.00
	NO (ppb)	0	153.0	15.07	20.35	0	231.0	18.37	23.39
2010	O_3 (ppb)	0	148.0	32.86	26.43	0	72.0	8.70	10.98
	NO_2 (ppb)	0	142.0	16.39	11.84	0	130.0	22.55	12.99
	NO (ppb)	0	129.0	14.34	18.57	0	143.0	17.68	21.47

*Note: Min= minimun, Max= maximum, SD= standard deviation

4.3 Box and Whisker Plot of O_3, NO_2 and NO Concentration during Daytime and Nighttime

Box and whisker plot is a simple plot that presents a quick sketch of the distribution of the underlying data of five sample quartile which are include the minimum, the maximum, the median, the lower quartile and the upper quartile (Wilks, 2006). The fluctuation of daytime and nighttime O_3, NO_2 and NO concentration from 2006 until 2010 were depicted in Figure 4.1 (a) and Figure 4.1 (b), respectively. Box and whisker plot show the similar result with descriptive analysis with additional that could give illustrates clear difference of O_3, NO_2 and NO between daytime and nighttime. The result showed daytime O_3 concentration is significantly higher compared to O_3 concentration during nighttime for all years due to the availability of sunlight for photochemical reaction (Awang et al., 2017). In contrast to O_3 concentration, the concentration of NO_2 and NO are higher in nighttime compare to daytime as there no photochemical reaction to occurs for ozone production, thus allowed NO_2 and NO to accumulate to higher concentration.

In Figure 4.1 (a), it showed that when O_3 concentration reached it maximum concentration, the amount of NO_2 concentration was depleted. This is because NO_2 have been efficiently used up for the formation of O_3 (Awang et al., 2017). The highest amount of O_3 concentration was detected in 2007 with 163 ppb that exceed the permissible values recommended by MAAQG as shown in Table 1.2. Meanwhile, in Figure 4.1 (b) it shows that NO concentration was higher compared to O_3 concentration. Warmiński and Bęś (2018) stated that O_3 and NO is the most important parameter that takes place in nighttime reaction.

Besides, the box and whisker plot exhibit the skewness of the data. The data would be symmetrical when the median is located roughly in the middle of the box (Rumsey, 2019). Figure 4.1 and Figure 4.2 showed that O_3 and NO_2 concentration were in symmetrical data while, NO show the unsymmetrical data as the median is not located at the middle of the box. The data was skewed to the right as the longer part of the box is appeared to be longer above the median line but skewed to the left when the box was below the median line. The results showed all the data for daytime and nighttime in Shah Alam are skewed to the right. Once the result of O_3 concentration showed skewed to the right, it indicates that the O_3 data leads to high concentration. Apart from that, there were outlier detected in each dataset of box and whisker plot. An outlier can be defined as a data point that located outside of the fences of the box and whisker plot. In Figure 4.1 (a), the outliers are contributed from the highest of O_3 concentration throughout the year. The outlier's presence is indicated that there are certain days that O_3 concentration was significantly higher than any other normal days.

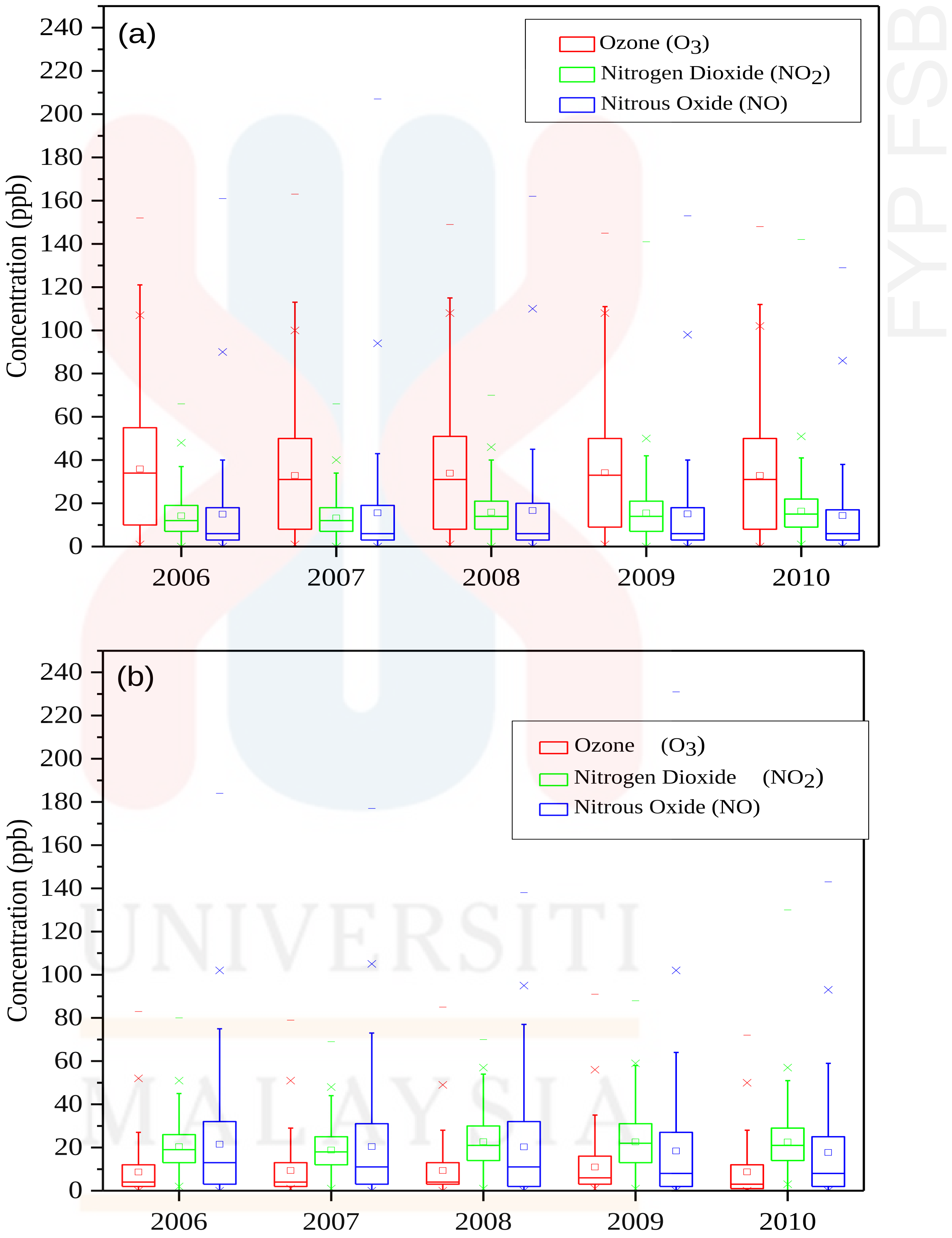


Figure 4.1: Box and whisker plot of (a) daytime; (b) nighttime of O_3, NO_2 and NO concentration.

4.4 Hourly variation of O_3, NO_2 and NO concentration during daytime and nighttime.

Time series plots are used to determine the hourly trend and pattern of O_3, NO_2 and NO concentration variation over time. Time series plots of O_3, NO_2 and NO concentration during daytime and nighttime for Shah Alam from 2006 to 2010 are illustrated in Figure 4.2, Figure 4.3, Figure 4.4, Figure 4.5 and Figure 4.6, respectively to determine their annual trends.

The result illustrated that daytime O_3 concentration is higher compared to nighttime and exceed the permissible values recommended by MAAQG as shown in Table 1.2. There a few occasions when the O_3 concentration exceed the MAAQG, which is 92 ppb. The daytime O_3 concentration have different maximum concentration from 2006 to 2010 which are 152 ppb, 163 ppb, 149 ppb, 145 ppb and 148 ppb, respectively. It been expected that the higher of O_3 concentration is due to the industrial parks' emissions and high traffic density as the location of Shah Alam is located at urban area and surround by industrial park. Meanwhile, there is no peaks of NO_2 concentration that beyond permissible limit outlined by MAAQG of 149 ppb. This is due to the efficiently used up of NO_2 concentration for O_3 formation in daytime (Awang et al., 2017). There is no guidelines limit for NO because NO does not include and categorize as 6 major air pollutants in Malaysia which are $PM_{2.5}$, PM_{10}, CO, NO_2, O_3, and SO_2 (DoE, 2019b).

The time series pattern of O_3 concentration during daytime and nighttime for Shah Alam are slightly different with NO_2 concentration. The concentration of O_3 during daytime were higher compare to NO_2 concentration as it been expected to be use efficiently for O_3 formation (Awang et al., 2017). Apart from that, throughout the whole year, the O_3 concentration during nighttime is lower beyond the MAAQG as there is no sunlight for photochemical reaction and increasing in O_3 removal rates (Ramli et al., 2010). The results showed that O_3 formation during daytime is strongly influenced by the solar radiation, temperature and its precursor that involved in the photochemical reaction (Tsai et al., 2008). Besides, the gap that in Figure 4.5 are considered as missing data maybe due to the failure of the monitoring tools to function on that time.

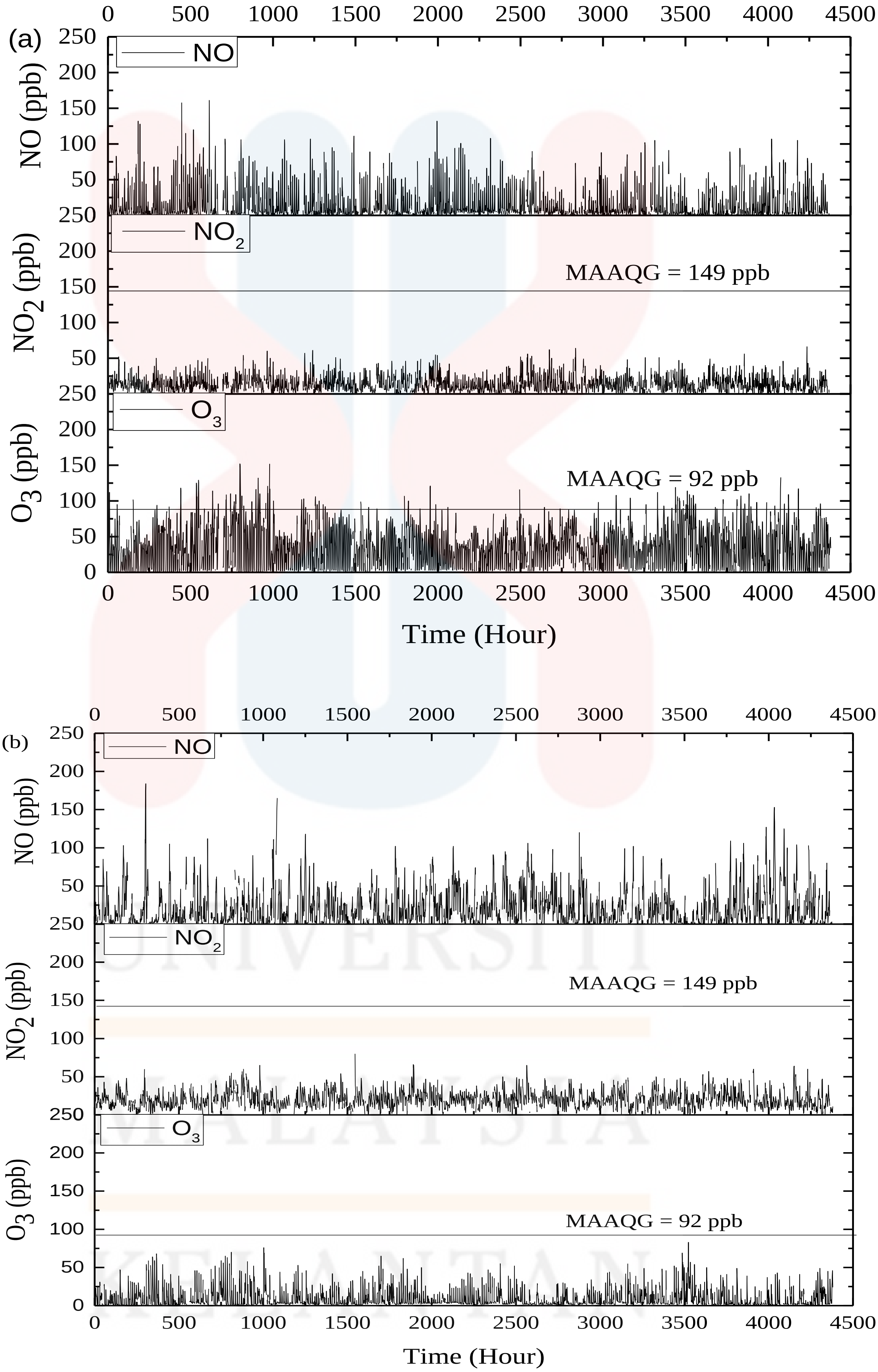


Figure 4.2: Time series plot of (a) daytime; (b) nighttime of O_3, NO_2 and NO concentration in 2006.

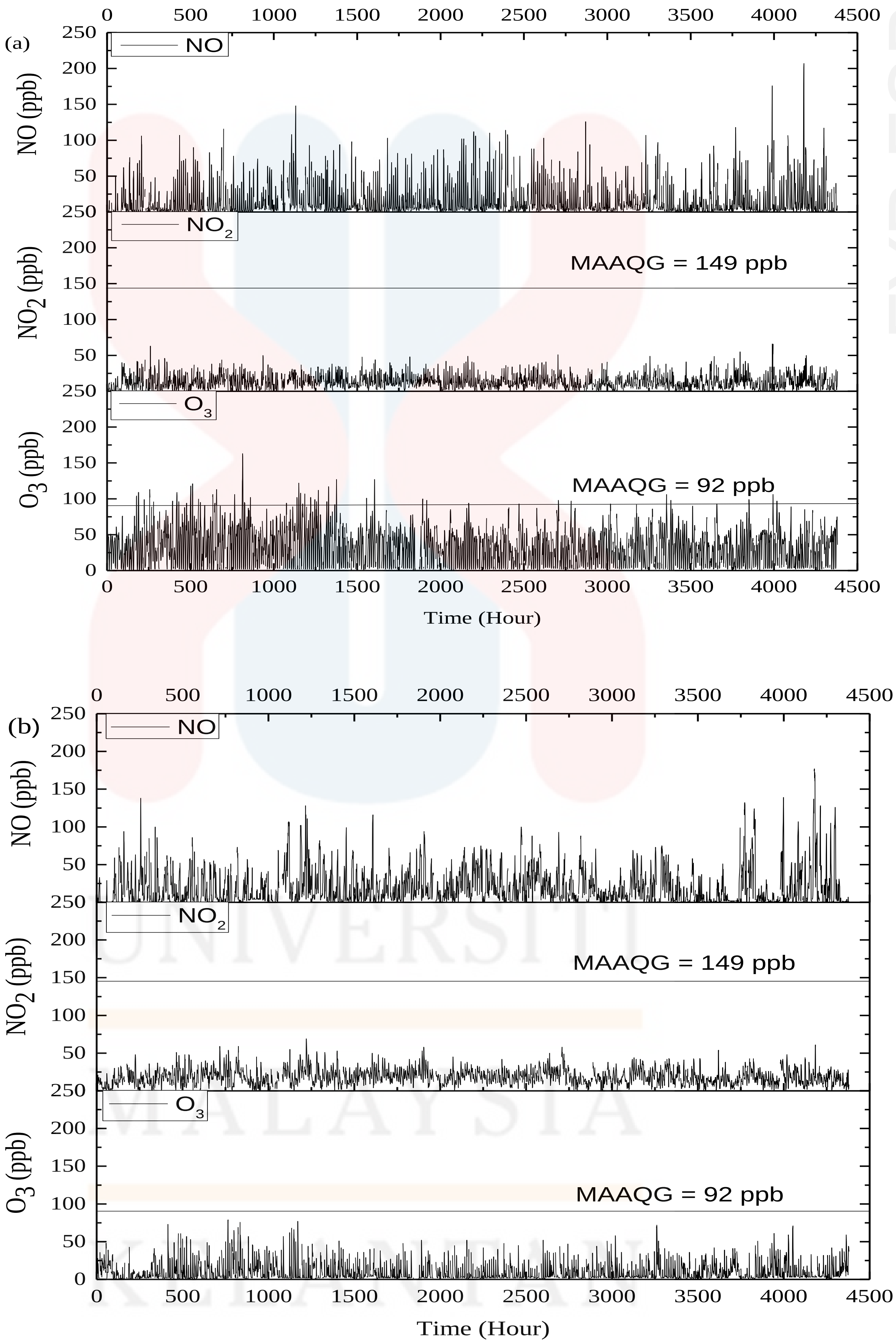
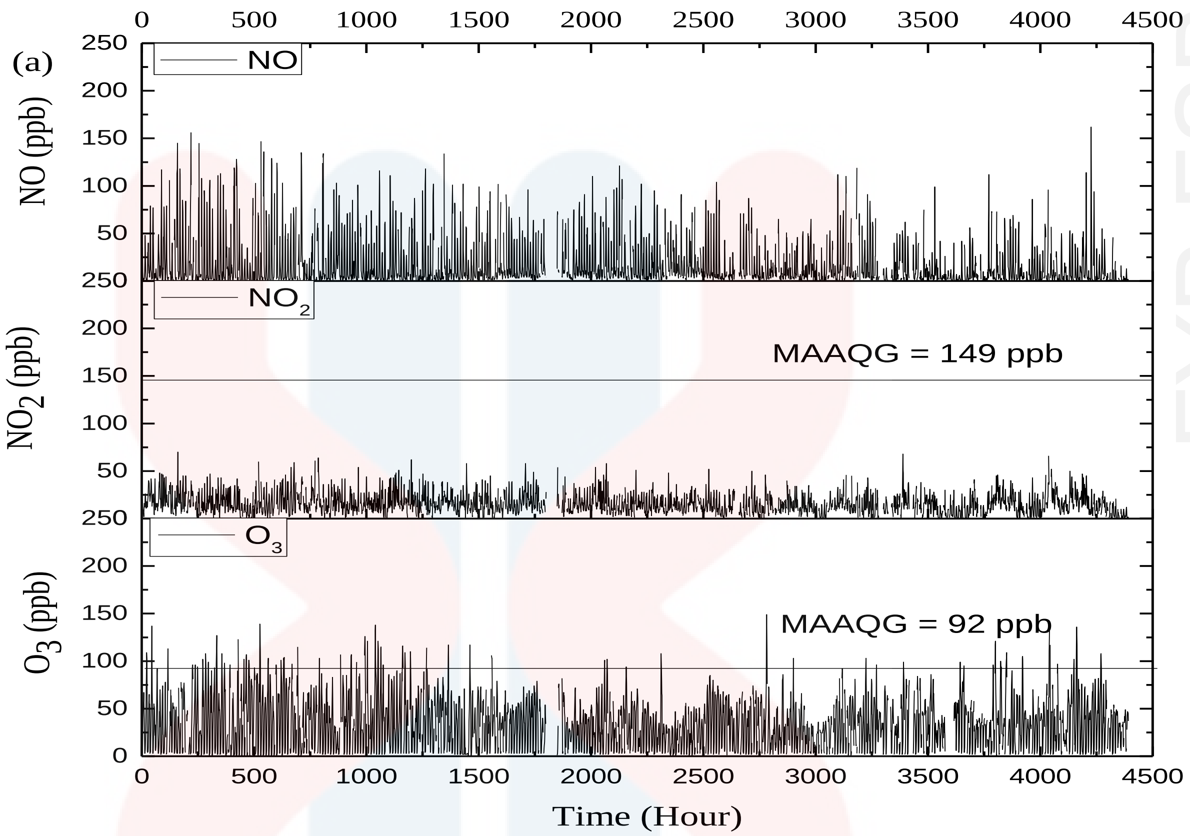


Figure 4.3: Time series plot of (a) daytime; (b) nighttime of O_3, NO_2 and NO concentration in 2007.



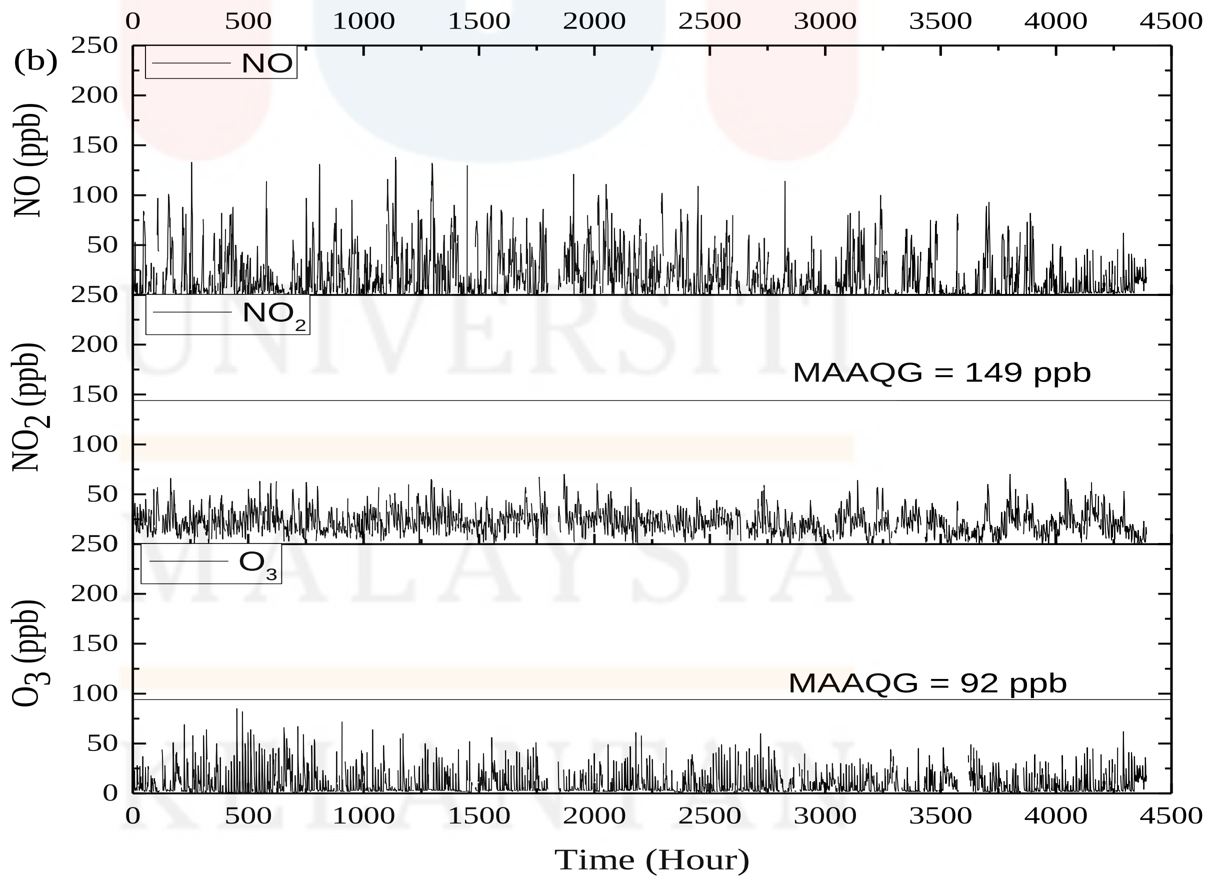


Figure 4.4: Time series plot of (a) daytime; (b) nighttime of O_3, NO_2 and NO concentration in 2008.

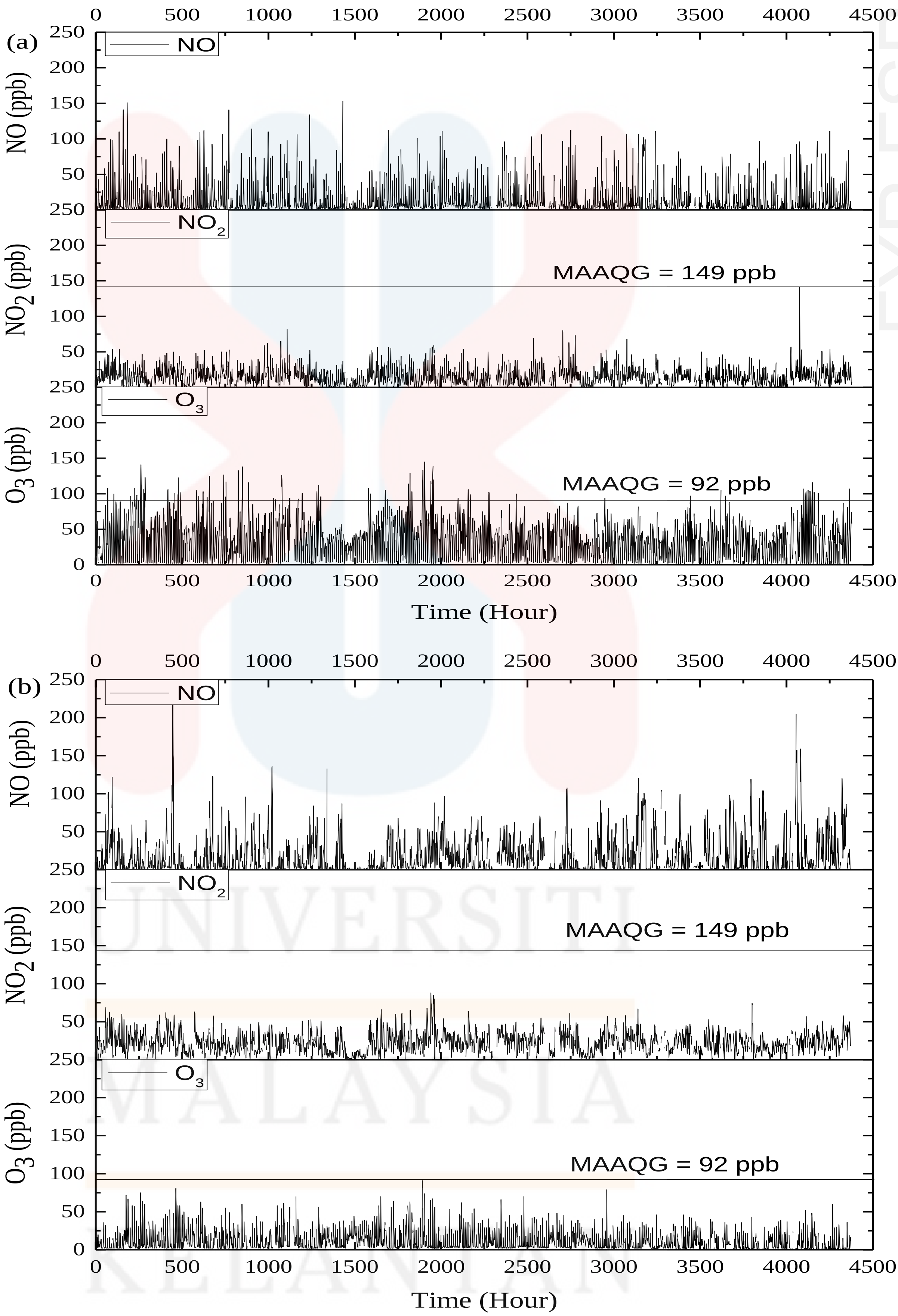


Figure 4.5: Time series plot of (a) daytime; (b) nighttime of O_3, NO_2 and NO concentration in 2009.

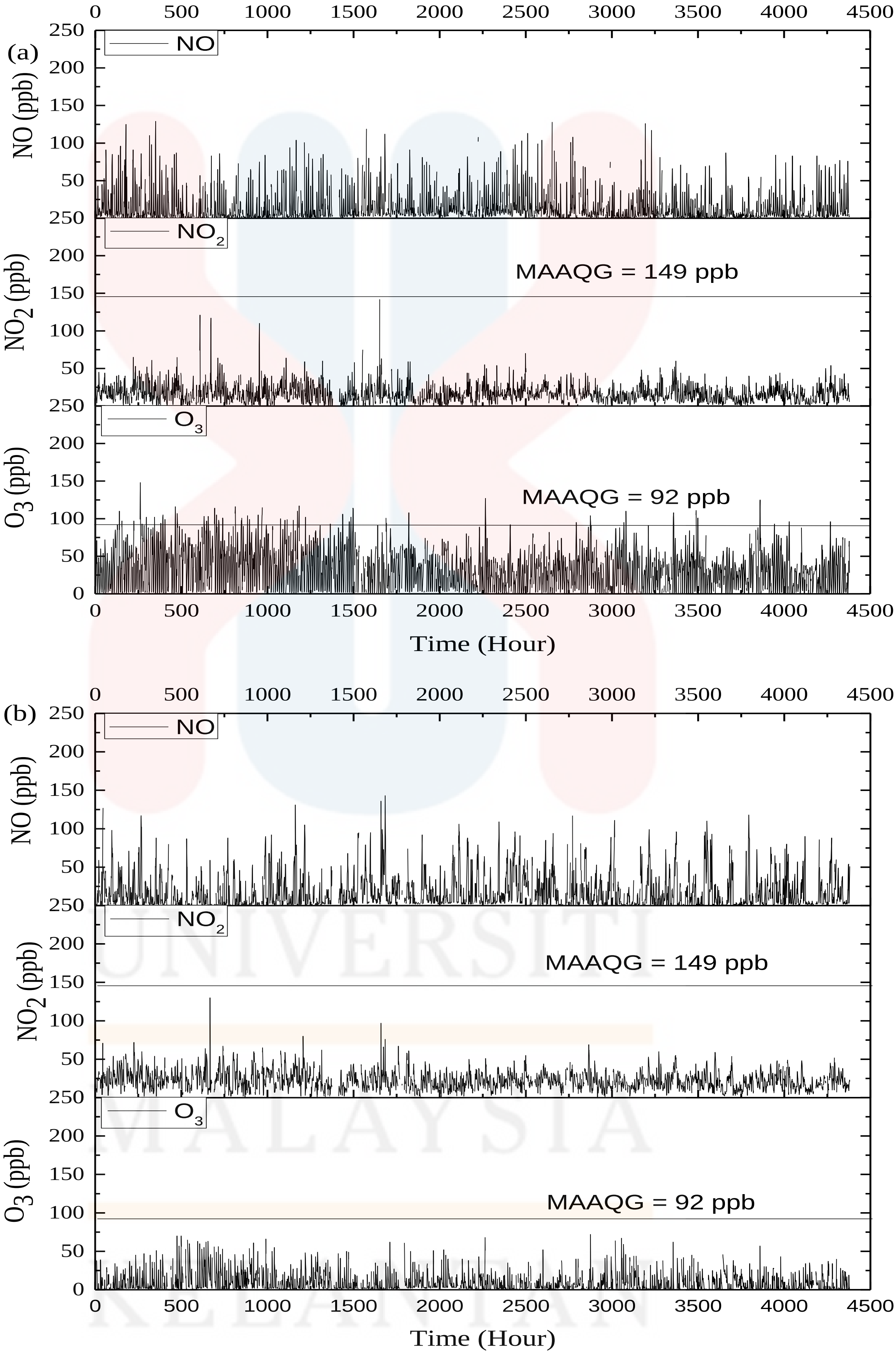


Figure 4.6: Time series plot of (a) daytime; (b) nighttime of O_3, NO_2 and NO concentration in 2010.

4.5 Diurnal variation of O_3, NO_2 and NO concentration during daytime and nighttime.

Diurnal variability of O_3, concentration and its precursor during daytime and nighttime in Shah Alam were analysed using diurnal plot. Diurnal variation is used to analyse the daily variation of O_3, and its precursor. The diurnal pattern of O_3, NO_2 and NO concentration in 2006 to 2010 are showed in Figure 4.7 to 4.11, respectively with differentiate of their daytime and nighttime.

In each year, the O_3, NO_2 and NO concentration showed relatively same diurnal pattern during daytime and nighttime, but with different magnitude. The diurnal pattern of 5 years O_3 concentration showed that the maximum concentration occurred during noon time between 1400 hour to 1500 hour and the minimum concentration occurred during nighttime. This statement was supported by Ghazali et al. (2010) and Awang et al. (2015b) in their study about the diurnal variation of O_3 concentration during daytime. However, Ramli et al. (2010) found that the concentration of O_3 in Shah Alam reaches peak concentration at 1300 hour to 1500 hour due to high temperature and UVB intensity. The results illustrated that O_3 concentration started to rise after sunrise which is around 0800 hour as their production of O_3 were enhanced by higher rate of photochemical reaction coupled with busy roads of vehicles. Minimal values of O_3 concentrations occurred at night starting from 2000 hour and near the sunrise which is around 0700 hour to 0800 hour due to NO titration.

In the morning rush hour that usually starting from 0800 hour, relatively high amount of NO_2 concentrations was produced by traffic emissions which contributed to higher photochemical reactions as the amount of sunlight received increase at that time (Azmi et al., 2010). The solar radiation received in daytime is encourage the photochemical reaction for O_3 production and provide enough energy for photolyze NO_2 into NO and O atom. All 5 years diurnal pattern of O_3 in Shah Alam reached its maximum concentrations around 1400 hour to 1500 hour. This pattern occurred due to high emission of NO_2 concentration into the atmosphere coupled with intensity of solar radiation during noon time. This statement is supported by Ramli et al. (2010), where the photochemical reaction is affected by the variation of anthropogenic activities and solar radiation.

In the evening, starting 1800 hour, the O_3 concentration were slowly reduce as the NO_2 concentration in the atmosphere during the noon time has been completely used up and reduced for O_3 formation. At nighttime, the O_3 concentration are tends to be more uniform with low concentration compared to daytime due to absence of photochemical reaction. This finding is supported by Awang et al. (2015b), which the reduction O_3 concentration in nighttime is due to chemical reaction and deposition processes.

Apart from that, the diurnal pattern of NO_2 in daytime showed that it was at lowest level when O_3 concentration at their maximum level. This is due to the NO_2 concentration had been used up efficiently for O_3 formation. Ramli et al. (2010) stated that increasing of O_3 concentration are closely corresponding to decrease in the concentration of precursors. In contrast to O_3 trend in diurnal variation, that there are two significant increasing trends of NO_2 concentration in Shah Alam, which started from 0700 hour to 1000 hour and from 1800 hour to 2200 hour which known as morning and evening peak, respectively. The second peak of NO_2 concentration seemed to be much lower than the first peak due to low intensity of vehicle emission and unfavourable meteorological condition during nighttime. The diurnal pattern of NO_2 concentration during nighttime showed a higher magnitude compared to daytime.

The rises of human activities will increase traffic and cause traffic congestions especially in city center like Shah Alam. Slow movement of vehicles in traffic congestions can increase the NO emissions and it will continuously be emitted into the atmosphere, causing the NO_2 concentration started to increase within the time. After the peak hour, the NO_2 concentration will decrease and reached its lowest level around noon until early evening as it involves in NO_2 photolysis reaction in O_3 formation, as stated in Equation 2.4. The level of traffic during working hour are expecting to be lower and at the same time lower the concentration of NO_2 in that area (Azmi et al., 2010).

Nitrogen dioxide concentration started to rise once again in the evening, which is starting from 1800 hour. There is less sunlight being radiate in the evening subsequently reduce the rate of photolysis reaction as well as O_3 production. Thus, during nighttime the O_3 concentration would not be as efficient as during daytime and in stable condition. This is due to the absence of sunlight and increased the O_3 removal rates as the higher concentration of NO_2 and NO are crucial for removal mechanism of O_3 in nighttime. Awang et al. (2017) stated that the O_3 concentration during nighttime can be reduced by the chemical loss via transportation process and deposition, and NO titration as stated in Equation 2.8.

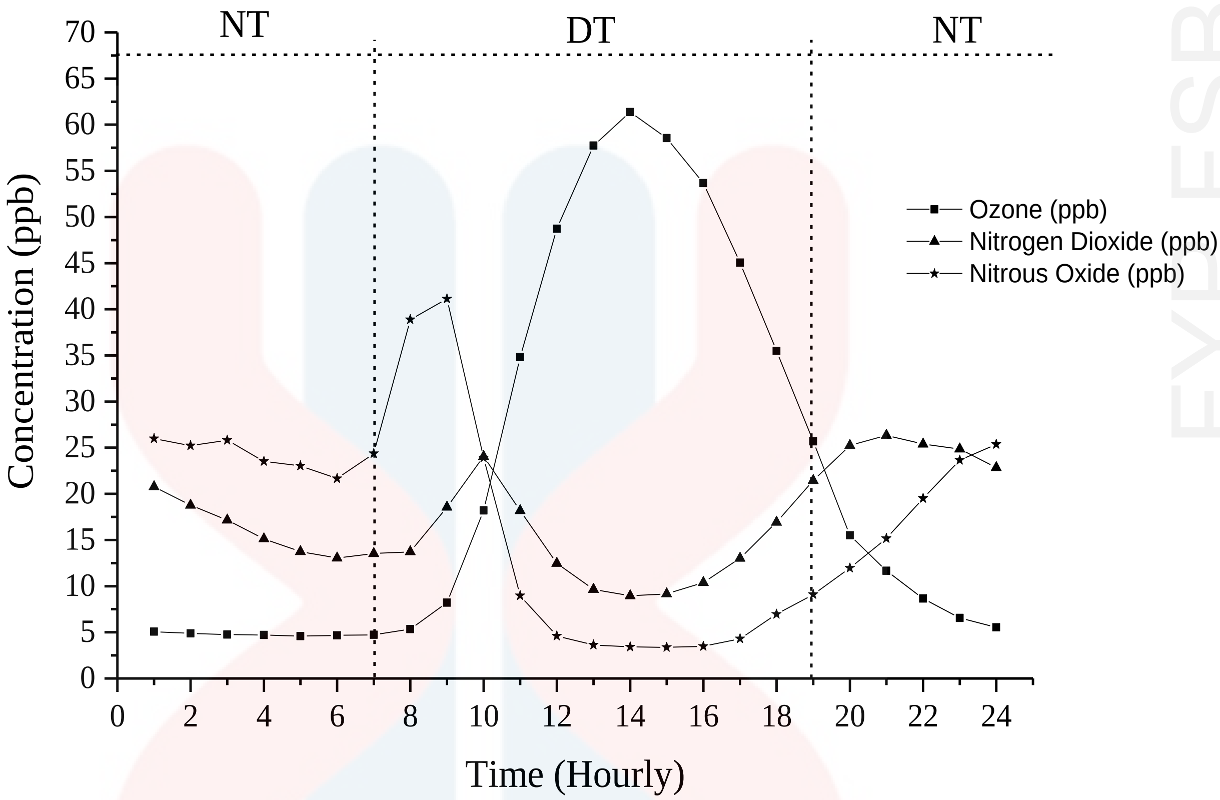


Figure 4.7: Diurnal plot of O_3, NO_2 and NO concentration in 2006 (Notes: DT is daytime; NT is nighttime)

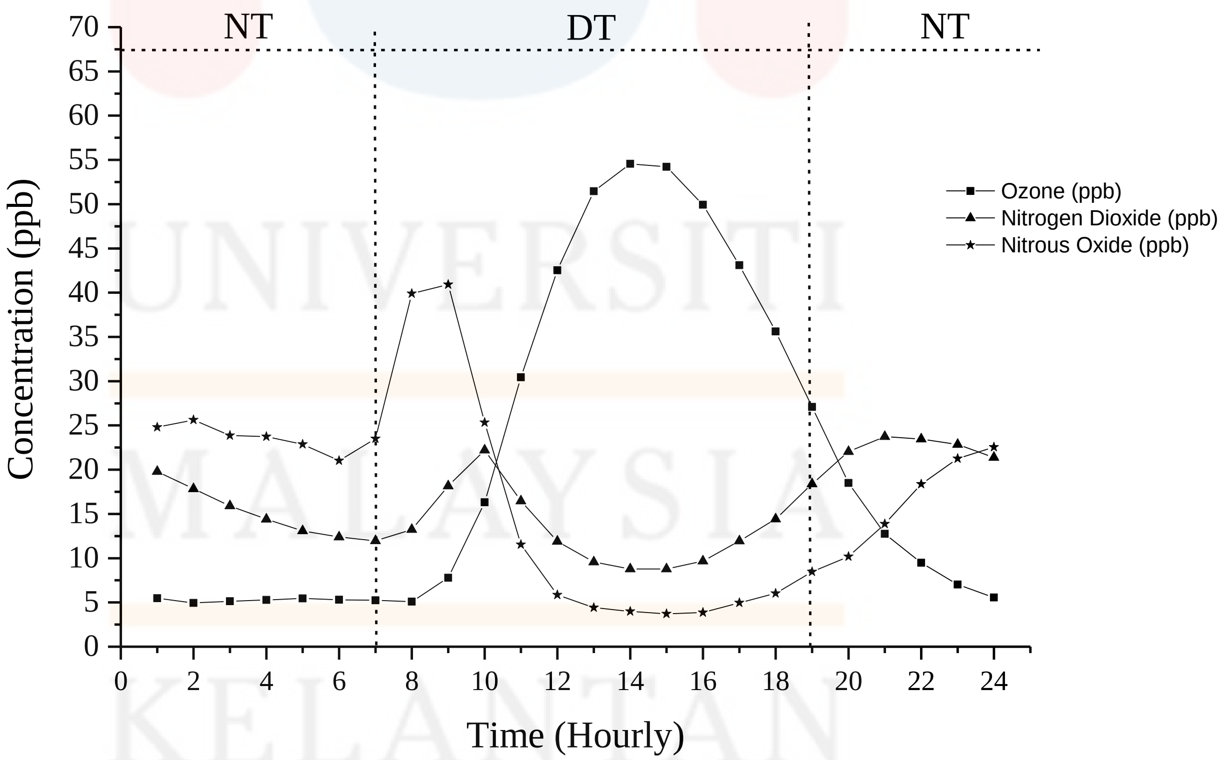


Figure 4.8: Diurnal plot of O_3, NO_2 and NO concentration in 2007 (Notes: DT is daytime; NT is nighttime)

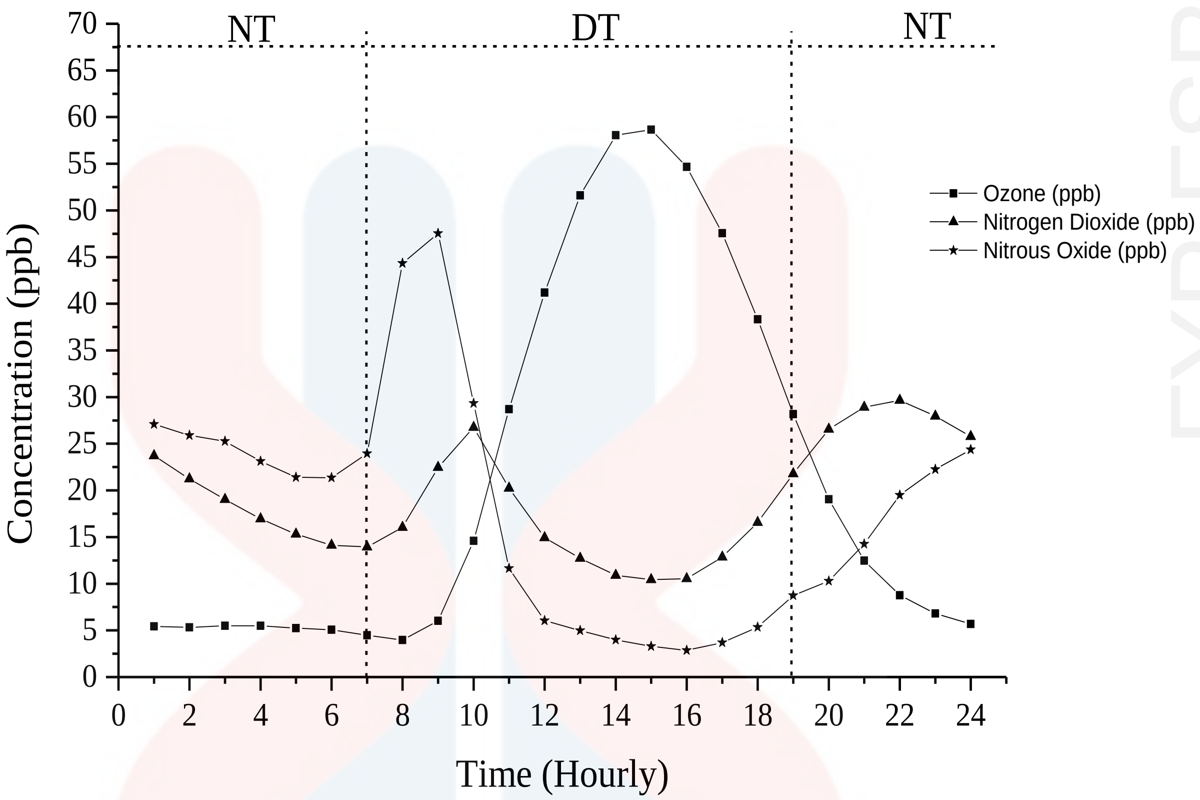


Figure 4.9: Diurnal plot of O_3, NO_2 and NO concentration in 2008 (Notes: DT is daytime; NT is nighttime)

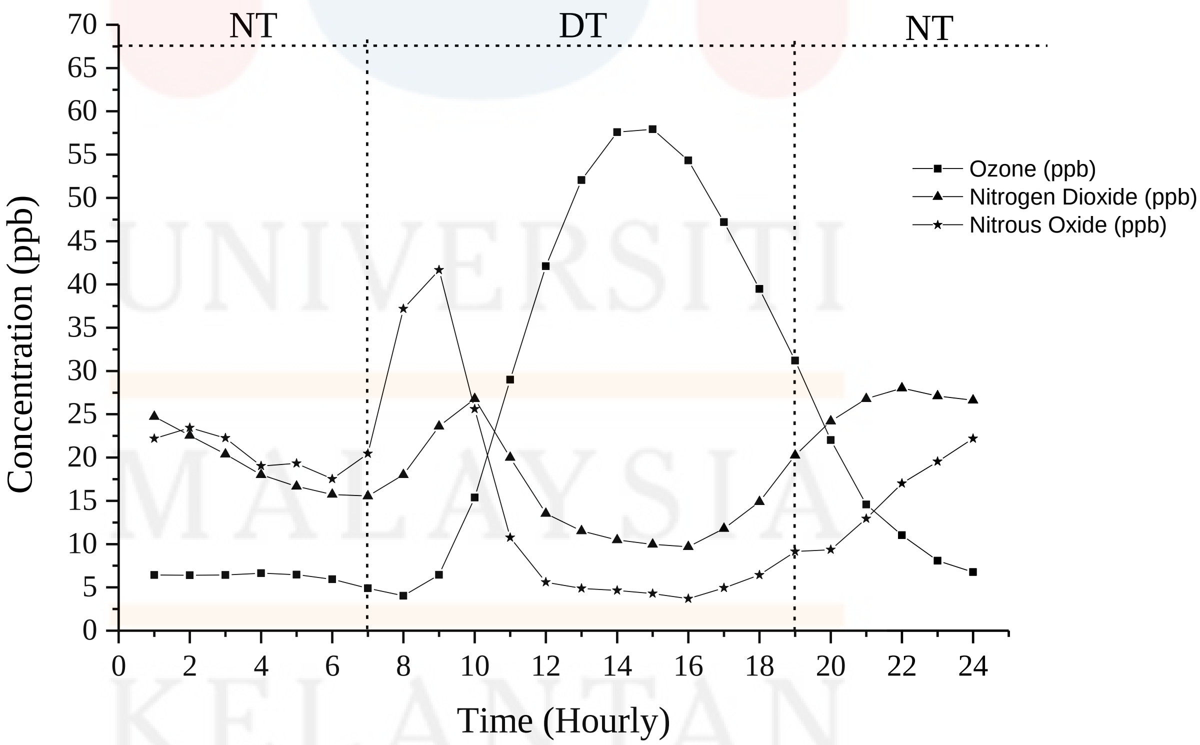


Figure 4.10: Diurnal plot of O_3, NO_2 and NO concentration in 2009 (Notes: DT is daytime; NT is nighttime)

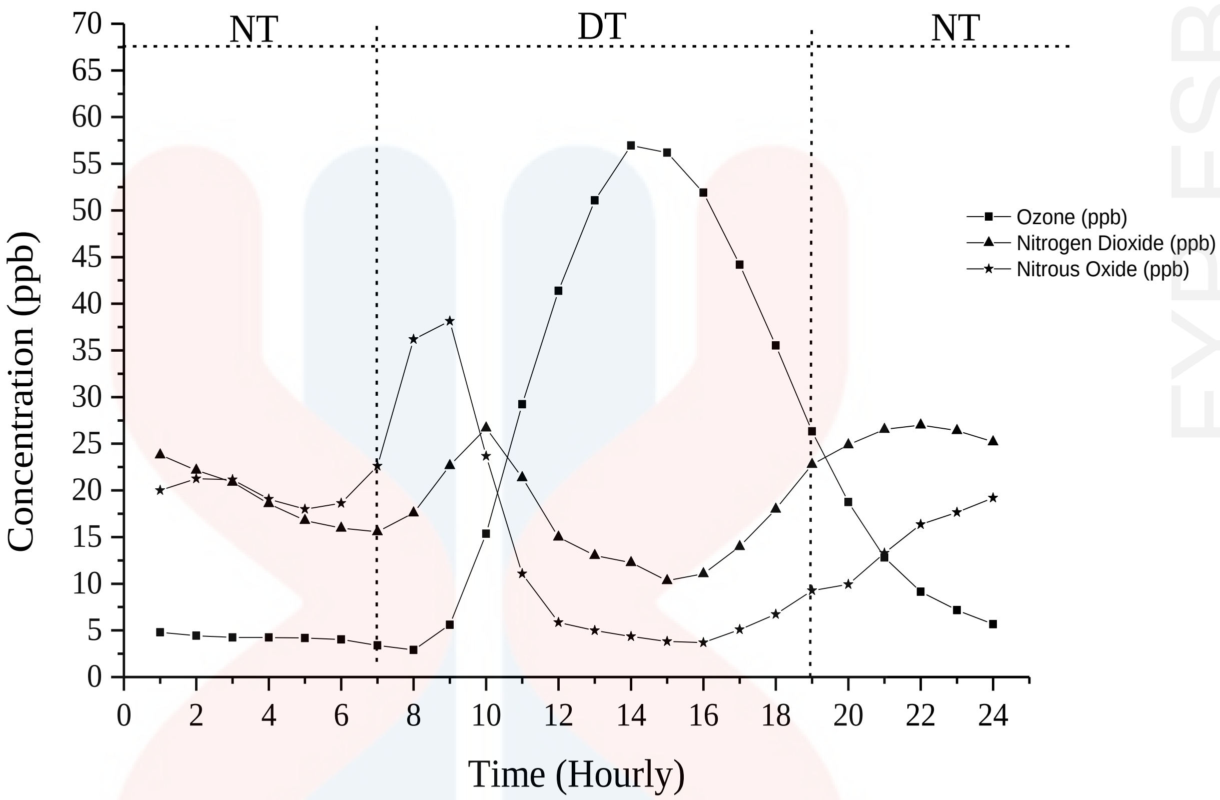


Figure 4.11: Diurnal plot of O_3, NO_2 and NO concentration in 2010 (Notes: DT is daytime; NT is nighttime)

4.6 Multiple Linear Regression (MLR) of Daytime Fluctuations towards Nighttime Ground Level Ozone Variations

A multiple linear regression analysis of O_3 concentration was carried out to determine the variation of O_3 concentration due to changes in NO_2 and NO concentration. Table 4.2 present the result of the multiple linear regression analysis with O_3 concentration as the dependent variable while NO_2 and NO as the independent variables.

Table 4.2: Multiple Linear Regression Equation for O_3 concentration using the independent variables for Shah Alam.

	R^2	Models	VIF	Durbin-Watson
Daytime	0.333	$O_3 = 46.164 – 0.187NO_2 – 0.666NO$	1.226	0.653
Nighttime	0.156	$O_3 = 14.664 – 0.128NO_2 – 0.155NO$	1.077	0.987

The table displays the values of the R^2, VIF and Durbin-Watson. R^2 is used as indicator to identify the best model with high value of R^2 which nearing 1.0 that does not contain too many variables (Ghazali et al., 2010). The model was developed with the data subset covering a complete year from 2006 to 2010 for both daytime and nighttime. The R^2 gives the proportionality of variation in ozone concentration as explained by the independent variables in the model. The results showed that MLR during daytime and nighttime have significantly lower R^2 which are 0.333 and 0.156, respectively. Thus, only 33 % during daytime and 16 % during nighttime of the O_3 variations were explained by the selected variables. A significantly lower R^2 exhibited that fewer possibilities of O_3 variations were explained by the independent variable.

In this study, the autocorrelation and multicollinearity existed in the developed models were evaluated by variance inflation factor (VIF) and Durbin-Watson. The result showed that the developed models did not encounter multicollinearity problems as the VIF is than 10 (Awang et al., 2015b). However, Durbin-Watson may indicate positive autocorrelation problems for both daytime and nighttime because the values are 0.653 and 0.987, respectively which less than 2. The Durbin-Watson statistic will always have a value between 0 and 4 (Awang et al., 2015b).

4.7 Verification of Secondary Data Analysis using Primary Data

The secondary data was verified using primary data which has been monitored at Siti Homestay TTDI Jaya, Jalan Esei Tiga U2/41c, Taman TTDI Jaya, 40150 Shah Alam, Selangor (Appendix A). The parameters monitored are O_3 and NO_2 concentration by using Aeroqual S500 for 72 hours continuously. The same analysis methods were used to verified which are descriptive table, box and whisker plot, time series analysis, diurnal plot and *t* test.

During the monitoring, the Aeroqual S500 with O_3 and NO_2 sensor attached was placed on an iron stand which approximately one meter above asphalt pavement under the tent (Appendix B). The set up was designed to prevent direct sunlight that may affect the sensors. The position of both aeroqual must be oppositely from each other sensor to make sure that it does not affect the reading (Appendix C).

4.7.1 Descriptive analysis of O_3 and NO_2 concentration during daytime and nighttime

Descriptive statistics was illustrated in Table 4.3, where the mean O_3 concentration is higher during daytime compared to nighttime O_3 concentration. The maximum O_3 was recorded in Day 2 compared to Day 1 and Day 3 which is 84 ppb, 86 ppb, and 74 ppb, respectively.

The study area was surround by the residential area and near with the industrial park. That area is quite busy and regularly experienced traffic congestion especially during weekday because there are school nearby and high residential population surround the area that used the road to go to the workplaces or other destinations. High traffic density is indicated high emissions of NO_2 which is the main O_3 precursors. However, there no peaks of O_3 concentration that beyond permissible limit outlined by MAAQG of 92 ppb. Similar with secondary data, the NO_2 concentration is less compared to O_3 concentration during daytime due to efficiently used up for the O_3 formation. The nighttime O_3 concentration in Day 1 showed the lowest mean value compared to Day 2 and Day 3 with 6.34 ppb as there a rainfall on that day from 0600 hour to 0700 hour. Overall, mean O_3 concentration during nighttime was lower as there is no sunlight that contributed for photochemical reaction except in Day 3 where it slightly higher than NO_2 concentration. However, there are peaks where O_3 concentration reached maximum value compared to NO_2 concentration during nightime.

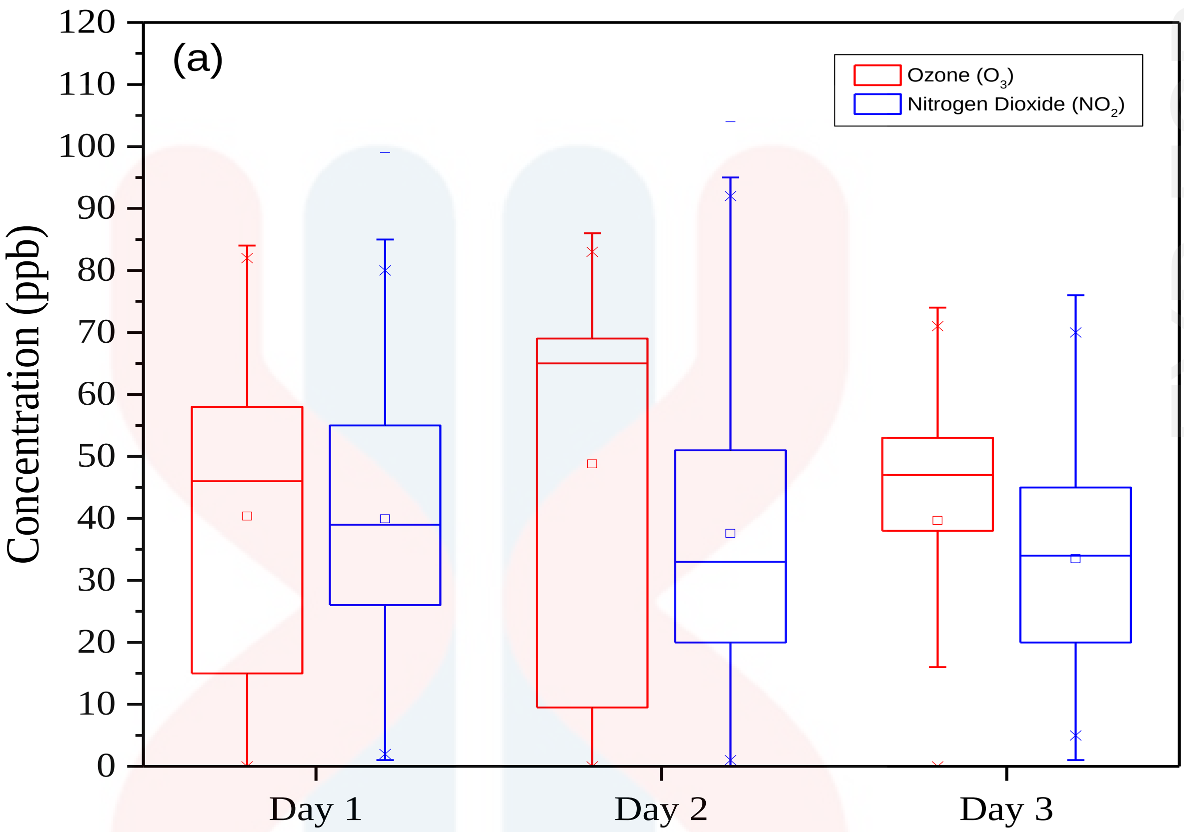
Table 4.3: Descriptive analysis of ground level ozone and nitrogen dioxide during daytime and nighttime in Shah Alam.

Day	Parameter	Daytime				Nighttime			
		Min	Max	Mean	SD	Min	Max	Mean	SD
1	O_3 (ppb)	0	84	40.37	25.56	0	62	6.34	13.54
	NO_2 (ppb)	1	99	39.94	19.69	0	78	50.43	14.38
2	O_3 (ppb)	0	86	48.79	30.33	0	66	19.55	22.42
	NO_2 (ppb)	0	104	37.58	22.75	6	61	36.72	13.78
3	O_3 (ppb)	0	74	39.65	21.85	5	55	28.88	11.21
	NO_2 (ppb)	1	76	33.50	16.27	1	53	25.62	13.53

*Note: Min= minimun, Max= maximum, SD= standard deviation

4.7.2 Box and Whisker Plot of O_3 and NO_2 Concentration during Daytime and Nighttime

Figure 4.12 showed the result of box and whisker plot that demonstrates the O_3 and NO_2 concentration during daytime and nighttime in Shah Alam. The plot showed similar result with secondary data where the daytime O_3 concentration is significantly higher compared to nighttime while NO_2 concentration is higher during nighttime as there is no photochemical reaction to occurs, thus allowed the NO_2 concentration to accumulate to higher concentration. Most of the NO_2 concentration in both daytime and nighttime showed symmetrical data compared to O_3 concentration as the median is located roughly in the middle of the box.



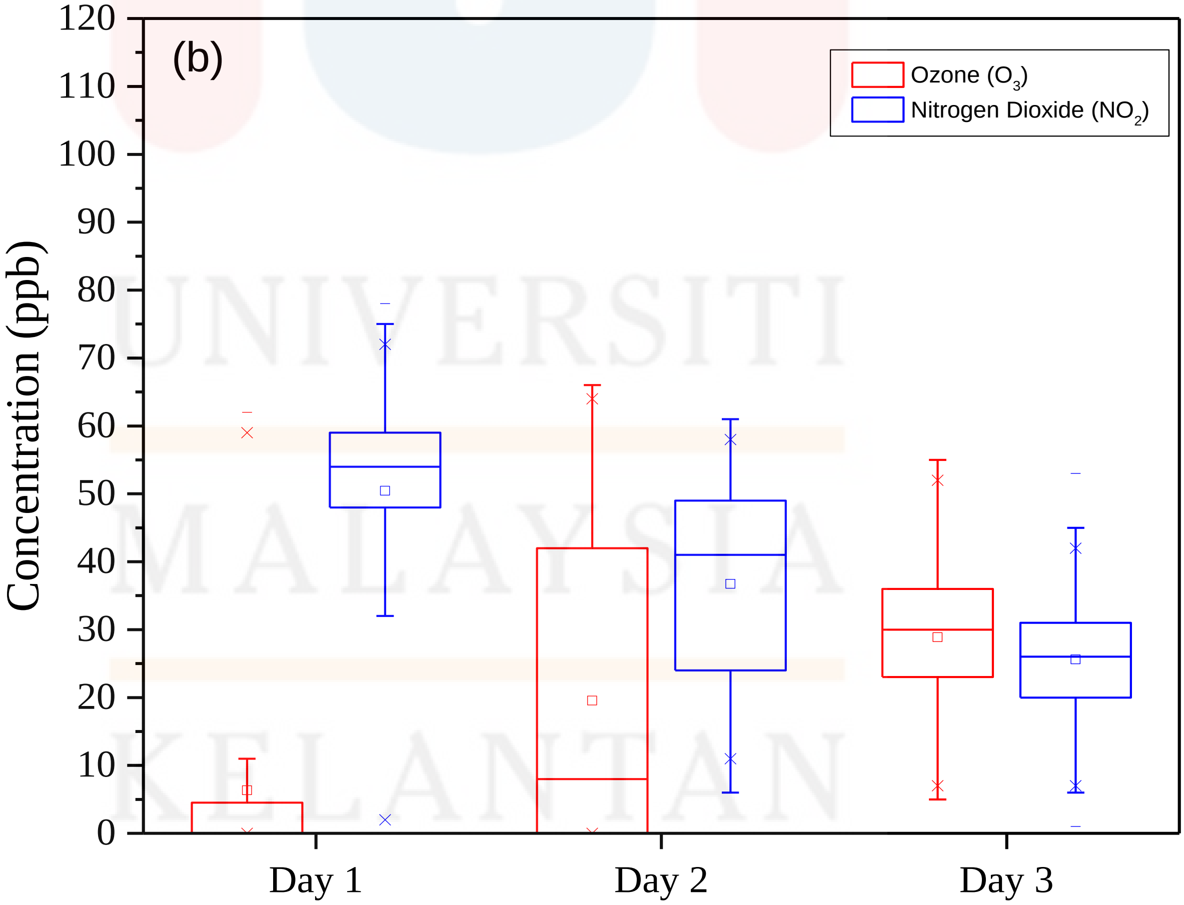


Figure 4.12: Box and whisker plot of (a) daytime; (b) nighttime of O_3, and NO_2 concentration.

4.7.3 Hourly variation of O_3 and NO_2 concentration during daytime and nighttime

Figure 4.13 to 4.15 illustrates the time series plot of O_3 and NO_2 concentration from 3 days. O_3 and NO_2 concentration were differentiated using different line color; black line indicated O_3 concentration and red line indicated NO_2 concentration, respectively. Time series plot for O_3 concentration in Figure 4.13 to 4.15 showed similar fluctuational pattern as the secondary data as the O_3 concentration during daytime were higher compare to NO_2 concentration as it been used up to accumulate the O_3 concentration. Besides, the gap that found in the result are considered as missing data due to the failure of the aeroqual to functional well during the monitoring time as it been shut down due to low battery.

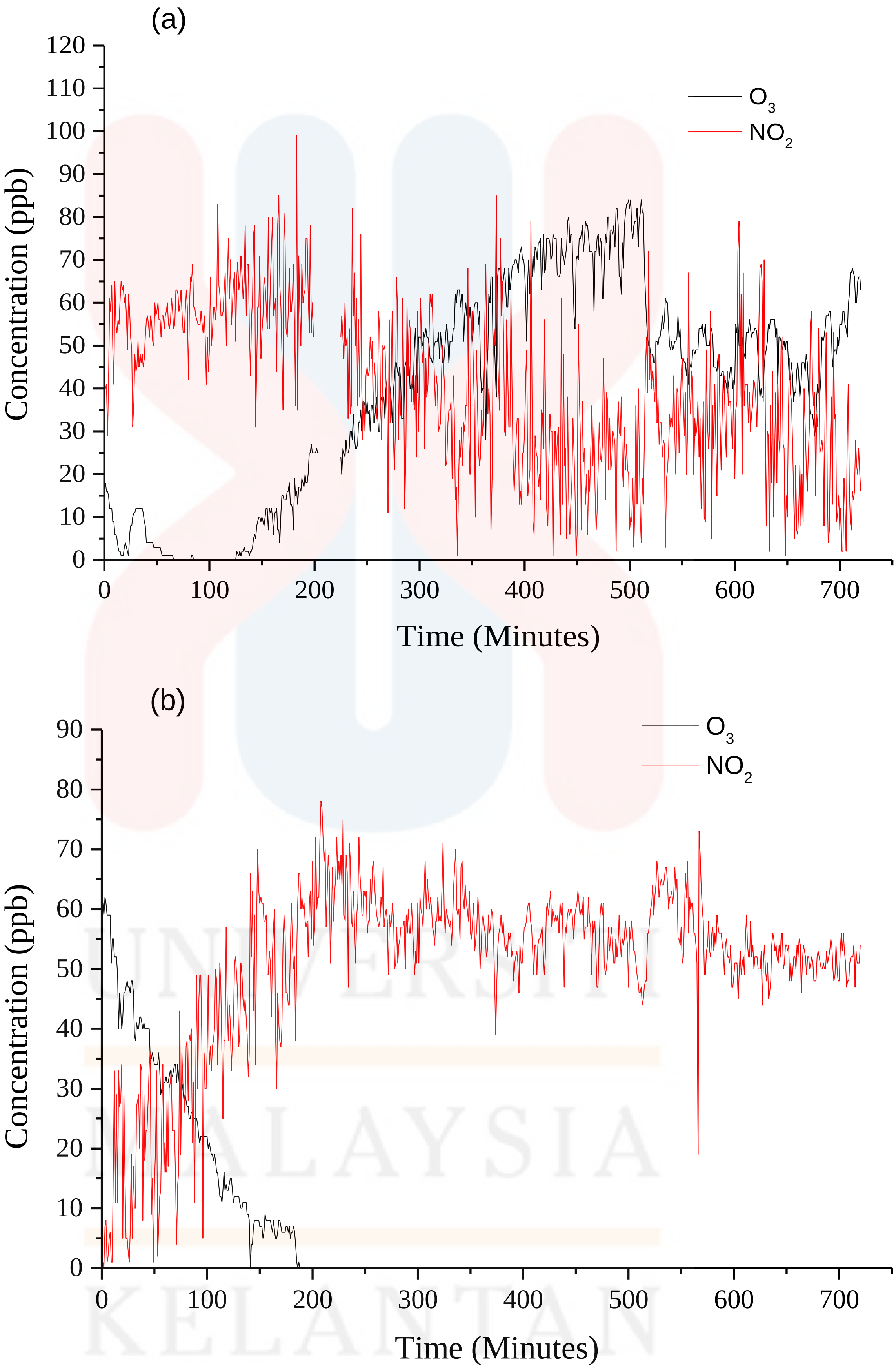


Figure 4.13: Time series plot of (a) daytime; (b) nighttime of O_3, and NO_2 concentration in Day 1.

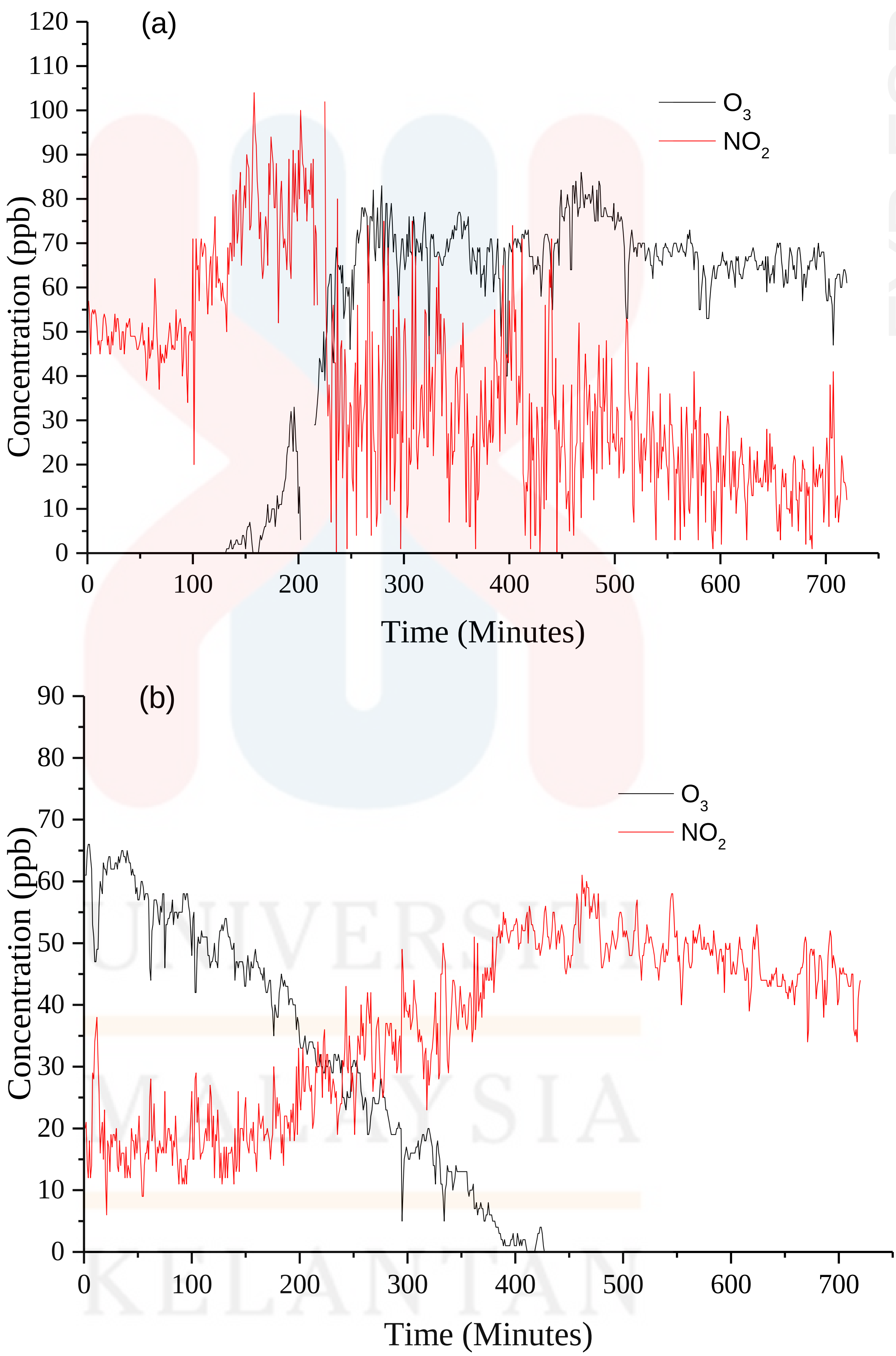


Figure 4.14: Time series plot of (a) daytime; (b) nighttime of O_3, and NO_2 concentration in Day 2.

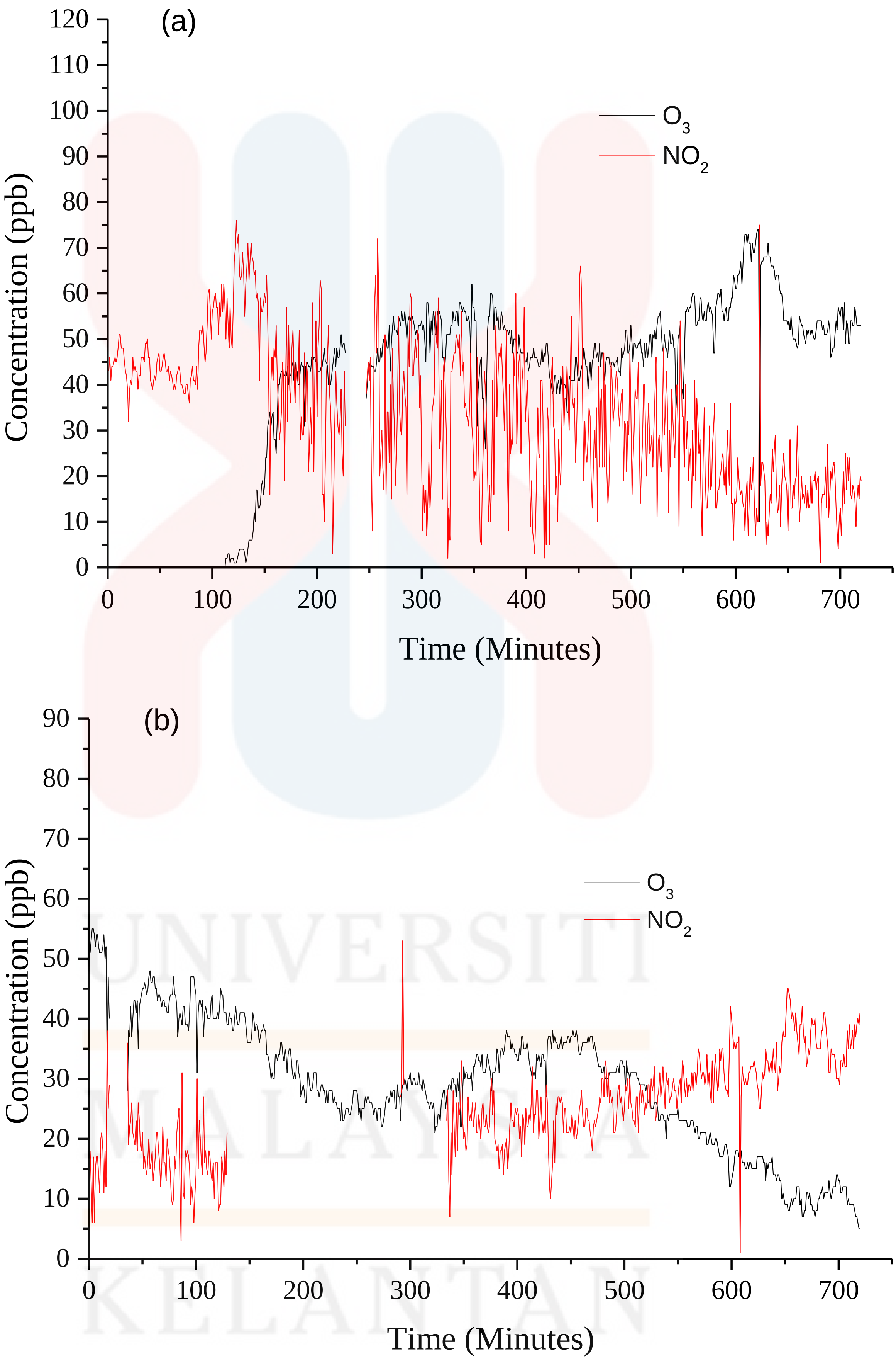


Figure 4.15: Time series plot of (a) daytime; (b) nighttime of O_3, and NO_2 concentration in Day 3.

4.7.4 Diurnal variation of O_3 and NO_2 concentration during daytime and nighttime

Diurnal variability of O_3 and NO_2 concentration for primary data were analysed using diurnal plot as shown in Figure 4.16 to 4.18. The diurnal pattern of three days O_3 concentration showed the higher concentration during daytime and the minimum concentration during nighttime. The results illustrated that O_3 concentration started to increase around 0900 hour as their production were enhanced by higher rate of photochemical reaction coupled with busy roads from the residential areas. Minimal values of O_3 concentration occurred at night starting from 1800 hour until 0900 hour. Diurnal variation of O_3 concentration in Day 1 and Day 2 showed it reached maximum peak at 1500 hour with different magnitude while in Day 3, it showed the maximum peak is at 1600 hour. At nighttime, the O_3 concentration tend to low concentration compared to nighttime due to absence of photochemical reaction as it occurs the O_3 reduction due to chemical reaction and deposition process (Awang et al., 2015b).

Apart from that, the diurnal pattern of NO_2 in daytime showed that it was at lowest level when O_3 concentration at maximum level. This is due to the NO_2 concentration had been used up efficiently for O_3 formation. Besides, the diurnal pattern of NO_2 concentration in nighttime showed a higher magnitude compared to daytime. The rises of human activities around that area have increase traffic and cause traffic congestion especially in main road of Shah Alam.

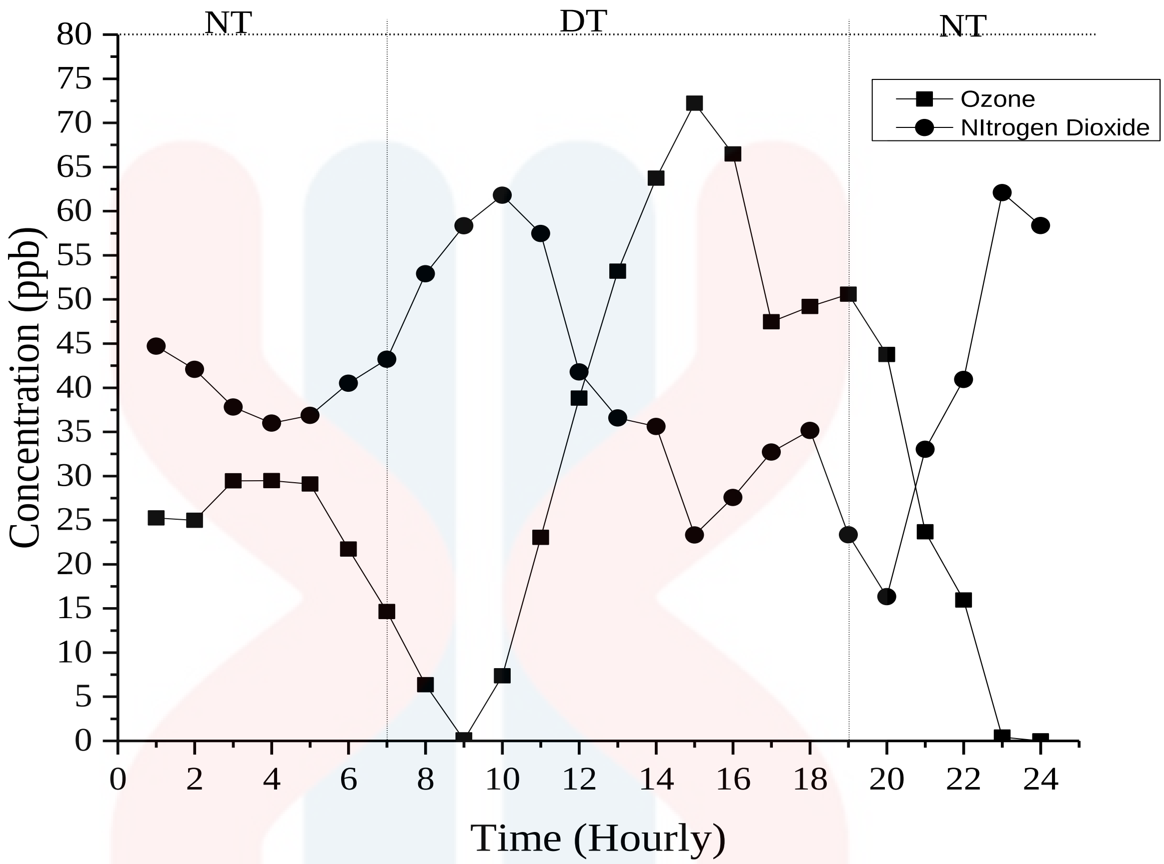


Figure 4.16: Diurnal plot of O_3 and NO_2 concentration in Day 1 (Notes: DT is daytime; NT is nighttime)

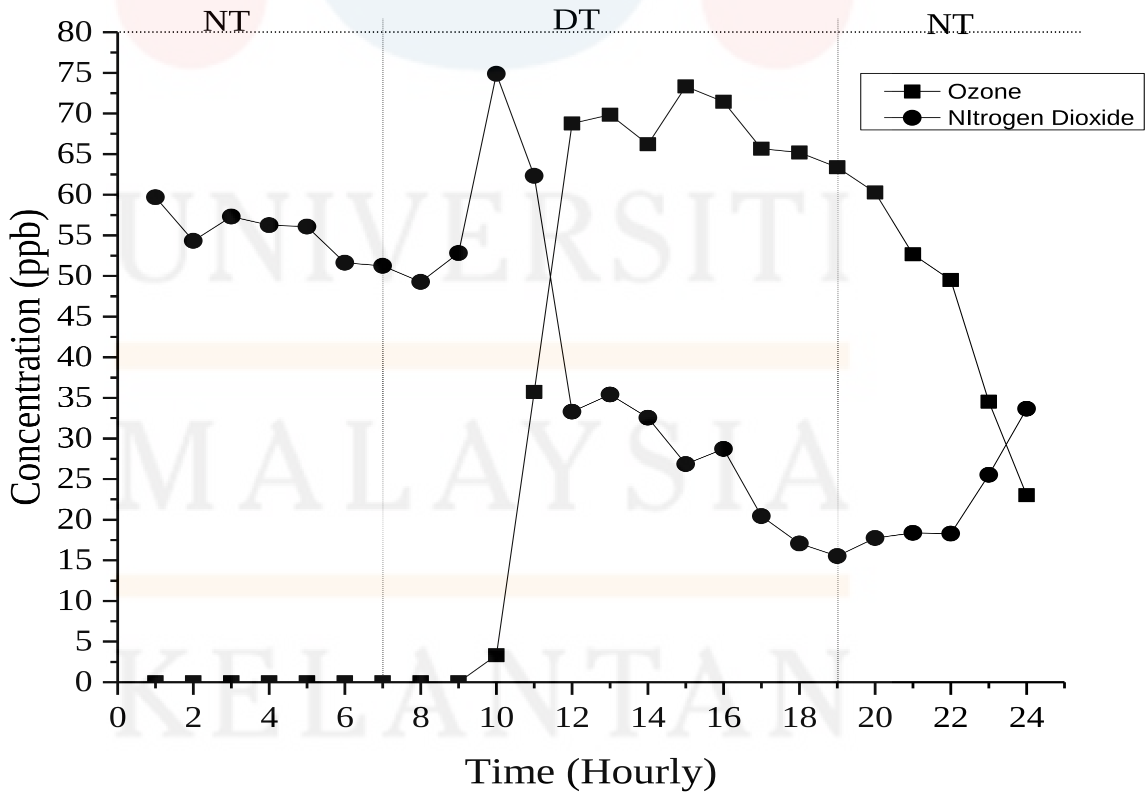


Figure 4.17: Diurnal plot of O_3 and NO_2 concentration in Day 2 (Notes: DT is daytime; NT is nighttime)

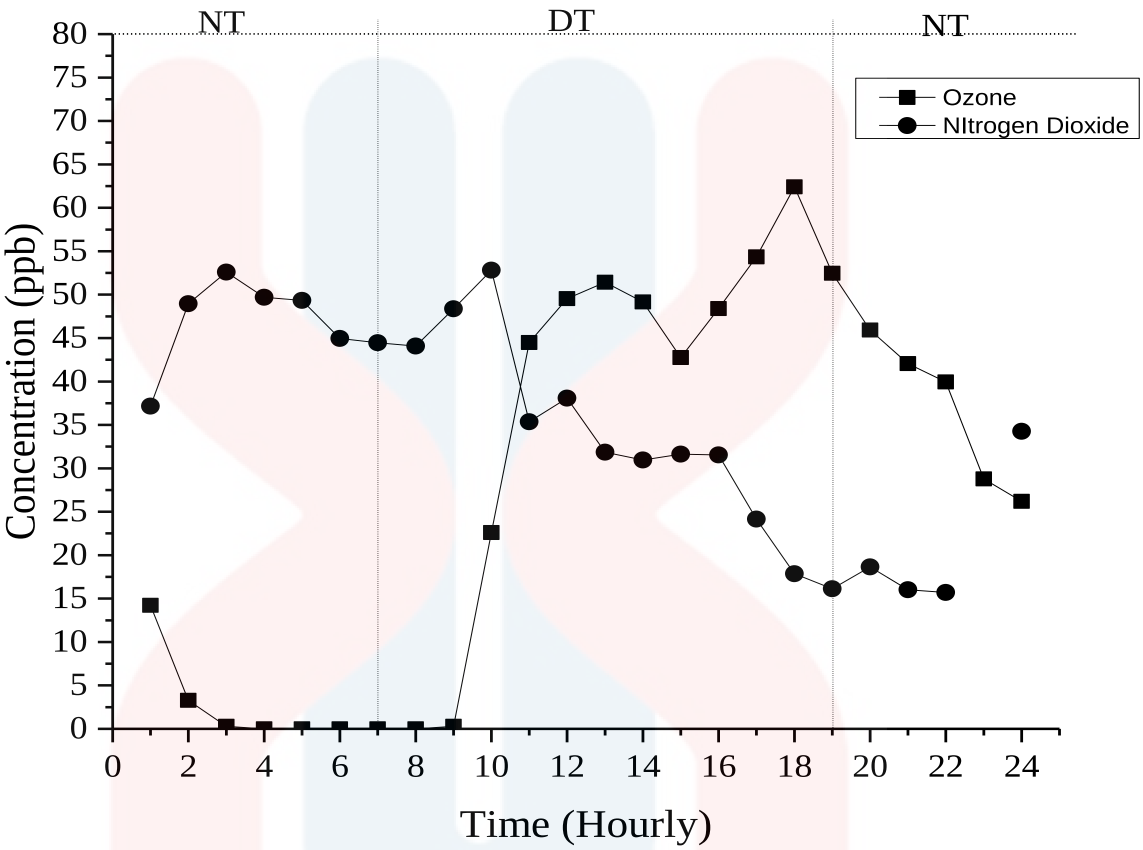


Figure 4.18: Diurnal plot of O_3 and NO_2 concentration in Day 3 (Notes: DT is daytime; NT is nighttime)

4.7.5 Independent *T* Test of O_3 Concentration during Daytime and Nighttime

Independent *t* test was done to statistically compare the means of O_3 during daytime and nighttime. The test adequate to give the information about the significant difference of O_3 concentration between daytime and nighttime thus their relationship can be statistically determined. The result of independent *t* test of O_3 concentrations for daytime and nighttime in Shah Alam were showed in Table 4.4.

The mean of O_3 during daytime and nighttime will be proven to be statistically different if the p-value obtained is less than 0.05 which translate to 95% confident intervals. The p-value obtained for the mean of O_3 concentration was 0.00. Since the p-value were less than 0.05, so there were significant differences for the mean of O_3 during daytime and nighttime in Shah Alam. The mean of O_3 concentration during nighttime were higher than daytime with concentration 41.96 ppb while during daytime 18.16 ppb, respectively.

Table 4.4: The independent *t* test O_3 concentration at Shah Alam.

Variable	Classification	Mean	Standard Deviation	p-value
O_3 (ppb)	Daytime	18.16	18.49	0.00
	Nighttime	41.96	26.48	

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This study investigated the interrelationship between daytime and nighttime ozone concentrations in Shah Alam, Selangor using secondary data from 2006 to 2010 and been verified using primary data of 2019. The study shown that O_3 were fluctuated which are higher during daytime with the maximum mean concentration with 35.85 ppb in 2006. The time series result showed there a few occasions when O_3 concentration exceed the permissible values prescribed by the MAAQG, which is 92 ppb during daytime due to strongly influenced by its precursors involved in the photochemical reaction that coupled with high solar radiation and temperature. Among the studied, the results of this study suggest that during daytime, it produced the highest O_3 concentration compared to nighttime in Shah Alam.

The O_3, NO_2, and NO concentration for 2006 to 2010 suggest typical diurnal pattern where O_3 concentration showed that the maximum concentration occurred during noon time between 1400 hour to 1500 hour and the minimum concentration occurred during nighttime. Apart from that, the diurnal pattern of NO_2 in daytime showed that it was at lowest level when O_3 concentration at their maximum level. In contrast to O_3 trend, there are two significant increasing trends of NO_2 concentration in Shah Alam, which started from 0700 hour to 1000 hour and from 1800 hour to 2200 hour which known as morning and evening peaks, respectively. In MLR analysis, the models develop showed a positive autocorrelation problem for both daytime and nighttime because the values are 0.653 and 0.987, respectively which less than 2 and the models showed no multicollinearity existed. Also, the results showed that MLR during daytime and nighttime have significantly lower R^2 which are 0.333 and 0.156, respectively. The independent *t* test result also demonstrated that there were significant differences for the mean of O_3 during daytime and nighttime in Shah Alam.

5.2 Recommendations

In this study, there a few recommendations need to be considered. Firstly, the location of the air quality equipment during monitoring period in Siti Homestay. It should be placed in front of homestay area which is much closer to the road that far from higher building and trees so that more accurate measurements will be obtained. Since this study is scarcely study and minimally understood thus, further study should be done critically to explore more the characterisation diurnal of ground level ozone concentration between daytime and nighttime O_3 concentration in urban area.

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APPENDICES

Appendix A: Monitoring area in Siti Homestay TTDI Jaya, Jalan Esei Tiga U2/41c, Taman TTDI Jaya, 40150 Shah Alam, Selangor

Appendix B: The Aeroqual S500 with O_3 and NO_2 sensor attached was placed on an iron stand which approximately one meter

Appendix C: The position of both aeroqual with O_3 and NO_2 sensors