VARIATION OF GROUND LEVEL OZONE CONCENTRATIONS AND TOTAL COLUMN OZONE CONCENTRATIONS OVER KLANG VALLEY

By

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

FACULTY OF EARTH SCIENCE UNIVERSITI MALAYSIA KELANTAN

2021

THESIS DECLARATION

I hereby declare that the work embodied in this Report is the result of the original research and has not been submitted for a higher degrees to any universities or institutions.

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I certify that the report of this final year project entitled Variation of Ground Level Ozone Concentrations and Total Column Ozone Concentrations Over Klang Valley by Nur Aqilah Binti Azmi, matric number E17A0095 has been examined and all correction recommended by examiners have been done for the degree of Bachelor of Applied Science (Sustainable Science) with Honours Faculty of Earth Science, University Malaysia of Kelantan.

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ACKNOWLEDGEMENT

First and foremost, thanks and praises to the Almighty Allah, for His blessings throughout my research work to complete my final year project successfully.

It is a great pleasure to address my sincere gratitude to my supervisor Dr. Norrimi Rosaida Binti Awang for the continuous support of my final year project research, for her patience, motivation, advice, and immense knowledge. Her guidance helped me all the time of my research and thesis writing. Her help has enhanced my knowledge and skills in this research area. Her sincerity and motivation have deeply inspired me. I am truly grateful that I complete my final year project under her supervision and I could not have imagined having a better supervisor for my final year project.

Besides my supervisor, I would like to extend my gratitude to a few other lectures from the Faculty of Earth Science for helping me in understanding certain areas in the research such as statistics and remote sensing.

I would like to thanks my classmates for their support as we always encourage each other throughout completing our final year project. We always ready to support each other and share ideas in the research process. Indirectly, giving me the motivation to complete the final year project.

Finally, my thanks go to my family and all the people who have supported me and trusting me in completing my final year project directly or indirectly.

Variation of Ground Level Ozone Concentrations and Total Column Ozone Concentrations Over Klang Valley

ABSTRACT

Ozone exists in the upper atmosphere (the stratosphere) and the lower atmosphere (the troposphere). Ozone impacts life on the Earth either positively or negatively depending on where it is in the atmosphere. Ozone in the upper atmosphere absorbs harmful UV rays but ozone is consider as pollutant gas at the lower atmosphere. It is necessary to monitor both ground level ozone (GLO) and total column ozone (TCO). In this study, variations of ground level ozone (GLO) and total column ozone (TCO) concentrations over Klang Valley, Malaysia were determined. The GLO measurement data was acquired from Department of Environment (DOE) Malaysia and is measured using standard method instrument, UV Absorption Ozone Analyzer Model 400A while, TCO measurement using Ozone Monitoring Instrument (OMI) onboard the Aura satellite. The descriptive analysis shows GLO concentrations in all four stations in Klang Valley surpassed the 90 ppb recommended limit suggested in the Malaysia Ambient Air Quality Standard (NMAAQS) (2020). The diurnal variation of GLO exhibited highest maximum GLO concentrations is in Shah Alam (141 ppb). Meanwhile, Shah Alam observed the highest TCO (296 DU) followed by Petaling Jaya (294.20 DU), Klang (293.80 DU) and Nilai (290.50 DU). Analysis of TCO trend shows the existence of seasonal variation contributed by Northeast Monsoon (NEM) and Southwest Monsoon (SWM) as TCO concentration is the highest during SWM with average 290 DU and the lowest during NEM with average 230 DU. This is due to environmental condition such as low precipitation, low relative humidity, high temperature and long sunlight hours during SWM that favour towards an increase in TCO concentration. In contrast, high precipitation, high relative humidity, low temperature and short sunlight hours lead to lowest TCO concentration during NEM. GLO trend analysis shows peaks mostly in the end of March to April and October (40 to 50 ppb). This is during transitional monsoon period which also have lower precipitation than normal. The correlation between TCO and GLO shows weak positive relation in between 0.03 to 0.30, thus, an increase in GLO concentration not greatly influence the TCO concentration.

Variasi kepekatan ozon paras tanah dan kepekatan ozon lajur total di Klang Valley

ABSTRAK

Ozon berada di atmosfera atas (stratosfera) dan juga atmosfera bawah (troposfera). Ozon memberi kesan terhadap kehidupan di Bumi sama ada secara positif atau negatif bergantung pada kedudukannya di atmosfera. Ozon di atmosfera atas menyerap sinaran UV yang berbahaya tetapi apabila di atmosphera bawah, ozon dikira sebagai pencemar udara. Lantaran itu, pemantauan terhadap kepekatan ozon permukaan tanah (GLO) dan ozon lajur total (TCO) adalah penting. Dalam kajian ini, variasi ozon permukaan tanah (GLO) dan ozon lajur total (TCO) di Lembah Klang, Malaysia telah dikaji. Data kepekatan GLO diperolehi daripada Jabatan Alam Sekitar (JAS) Malaysia dan telah diukur menggunakan instrumen kaedah standard iaitu UV Absorption Ozone Analyzer Model 400A sementara, data kepekatan TCO diperolehi dari bacaan satelit Aura, Ozone Monitoring Instrument (OMI). Analisis deskriptif GLO menunjukkan kepekatan di keempat-empat stesen di Lembah Klang melebihi had yang disyorkan iaitu 90 ppb per jam yang disarankan dalam Standard Baru Kualiti Udara Ambien Malaysia (2020). Variasi GLO diurnal yang menunjukkan kepekatan GLO maksimum adalah di Shah Alam (141 ppb). Manakala, bacaan TCO tertinggi diperhatikan di Shah Alam (296 DU) diikuti oleh Petaling Jaya (294.20 DU), Klang (293.80 DU) dan Nilai dengan kepekatan maksimum terendah (290.50 DU). Analisis tren TCO menunjukkan variasi bermusim dipengaruhi oleh Monsun Timur Laut (MTL) dan Monsun Barat Daya (MBD). Di mana kepekatan TCO adalah tertinggi semasa MBD dengan purata 290 DU dan paling rendah semasa MTL dengan purata 230 DU. Ini dipengaruhi oleh keadaan cuaca semasa MBD dengan taburan hujan yang rendah, kelembapan udara relatif yang rendah, suhu udara yang tinggi dan sinaran cahaya matahari yang panjang, membolehkan kepekatan TCO meningkat. Sebaliknya, taburan hujan yang tinggi, kelembapan udara relatif tinggi, suhu udara yang rendah dan sinaran cahaya matahari yang kurang semasa MTL menyebabkan kepekatan TCO menurun. Analisisa terhadap trend GLO menunjukkan kepekatan maksima kebanyakannya dicatatkan pada hujung bulan Mac sehingga April dan juga di bulan Oktober (40 – 50 ppb). Ini berlaku semasa musim peralihan monsun yang juga mempunyai taburan hujan lebih rendah daripada biasa. Korelasi antara TCO dan GLO menunjukkan hubungan positif yang lemah antara 0.03-0.30, dimana peningkatan kepekatan GLO tidak terlalu mempengaruhi kepekatan TCO.

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LIST OF ABBREVIATIONS

CO_2	Carbon dioxide
BrO	Bromine oxide
DOE	Department of Environment, Malaysia
DU	Dobson Unit
EOS	Earth Observing System
FEM	Federal Equivalent Method
FRM	Federal Reference Method
GLO	Ground level ozone
GOME	Global Ozone Monitoring Experiment
H_2O	Water
H_2S	Hydrogen Sulphide
Hg	Mercury
IR	Infrared
NMAAQS	New Malaysian Ambient Air Quality Standard
MODIS	Moderate Resolution Imaging Spectroradiometer
N_2	Nitrogen
NASA	National Aeronautic Space Administration
NOx	Nitrogen oxides
NO_2	Nitrogen dioxide
O	Oxygen atom
O_2	Oxygen molecule
O_3	Ozone
OMI	Ozone Monitoring Instrument
$PM_{2.5}$	Particulate Matter with aerodynamic diameter less than 2.5 micron
SCIAMACHY	Scanning Imaging Absorption Spectrometer for Atmospheric Chartography
SO_2	Sulphur dioxide
SPSS	Statistical Package for the Social Science
TCO	Total column ozone
TOMS	Total Ozone Mapping Spectrometer

UV	Ultraviolet
VOCs	Volatile Organic Compounds

LIST OF SYMBOLS

%	Percentage
>	Greater than
<	Less than
+	Plus
hν	Radiation Energy
λ	Wavelength
μm	Micrometer
$\sum$	Sum of
$\bar{X}$	Mean
S	Standard Deviation
R	Pearson Correlation Coefficient

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Ozone gas (O_3) is a highly reactive gas that consists of three oxygen atoms. Ozone may occur naturally and also produce from human activities. Ozone exists in the upper atmosphere (the stratosphere) and the lower atmosphere (the troposphere). Ozone impacts life on Earth either positively or negatively depending on where it is in the atmosphere (USEPA, 2016a). The majority of the ozone concentration is found in the ozone layer (stratosphere), where the ozone layer acts as a protector for the Earth from harmful radiation from the sun. However, ozone that occurs in the troposphere is considered as a secondary pollutant known as ground level ozone or surface ozone. Ground level ozone is formed when primary pollutants, which are referred as ozone precursors such as nitrogen oxide (NOx) and volatile organic compounds (VOCs) react under the presence of sunlight (Mustafa & Mohammed, 2012). Ground-level ozone is generally correlated with air quality deterioration, which has adverse effects on human and crop health (Awang et al., 2016b).

Based on Ionel & Popescu (2010), the standard method that has been used to measure air contaminants are UV photometry, UV fluorescence, and chemiluminescence technique. However, USEPA (2006) has developed design and performance criteria for measuring ground level ozone. USEPA has developed gas-phase chemiluminescence for federal reference method (FRM) and UV photometry base for federal equivalent methods (FEM) (McElroy et al., 1997). Most countries in the world used the instrument that follows the reference or equivalent method to measure air contaminant including ozone (USEPA, 2016b) to ensure the reliability of the collected data. Department of Environment Malaysia (DOE) uses UV absorption Ozone Analyzer Model 400A, where this instrument is listed under USEPA Federal Equivalent Method (FEM). The method applied by this instrument is UV photometry method (Teledyne, 2018). This ozone measurement instrument is ground-based, and there are 68 continuous air monitoring stations available around the country (DOE, 2020). The UV photometry principle is where the UV radiation excites the electrons of the ozone gas. During the process, the gas molecule only absorbs energy in a certain range of wavelength or absorption bands. The depletion of the radiation intensity that is consumed by the gas molecule is thus measured (Ionel & Popescu, 2010).

The most widely used instrument for in determining vertical ozone distribution is ozonesonde. Ozonesonde are small, lightweight, balloon-borne instruments capable of making measurement from the surface to near 35 km in altitude. All of the ozonsonde data discussed in this report is from instrumentation using reaction of ozone with potassium iodide in an aqueous solution as the method of detection. Ozonesonde is known for its high accuracy and high vertical resolution in ozone measurement. This method is widely used in validation and comparison study for other derived ozone measurement from satellites, models, and ground observation (Akhil Raj et al., 2015).

Remote sensing has been applied in many fields including air quality monitoring. Remote sensing is a non-standard air quality monitoring technique for air quality monitoring (Ionel & Popescu, 2010). Remote sensing, however, has the advantages of minimizing the probability of the gas sample degrading during the path to and through the instrument, and of distributing the concentration across the space region rather than one sampling point (Ionel & Popescu, 2010). Remote sensors have two primary types which are active sensors and passive sensors where active sensors provide own sources of energy (radiation) to illuminate the target object which the radiation is in the microwave range of the electromagnetic spectrum while passive sensors detect natural energy (radiation) that is emitted or reflected by the object or scene being observed, sunlight is the most common source of radiation used by passive sensors (NASA, 2020a). Over the last three decades, different instruments were developed for remote sensing monitoring of aerosols and trace gases (Verma et al., 2019). Reflectance is the key to the retrievals of the atmospheric remote sensing data. Signals measured by the remote sensor influenced by optical atmospheric effects in two ways, which are radiometrically and geometrically. This means remote sensor collects data of air pollutants through its properties of scattering or absorption of radiation intensity and the direction of refraction of the radiation (Lim et al., 2009). Remote sensing instruments that normally use in ozone studies including SCIAMACHY (Chooi, et al., 2014), ozone monitoring instrument (OMI) (Tan et al., 2017), total ozone mapping spectrometer (TOMS) and Aura ozone monitoring instrument/microwave limb sounder (OMI/MLS) (Ziemke et al., 2018).

In this study, the remotely-sense data of total column ozone measurement is acquired from the Ozone Monitoring Instrument (OMI). OMI can distinguish between aerosol types and consist of products in different categories such as ozone products,

clouds, aerosols, and surface UV irradiance products, and trace gases products (NASA, 2012). In this study, the similarities, differences and correlation of data between the ground level ozone measured using standard method and total column ozone measured remotely-sensed were statistically analysed.

1.2 Problem Statement

Ground level ozone is one of the major air pollutions that has adverse impacts on human health and crop yield. Based on the New Malaysia Ambient Air Quality Standards (NMAAQS) (2020), the recommendation for ground-level ozone is limited to 90 ppb per 1 hour. High concentration of ozone has negative impacts on life on the Earth, the concentration of ozone has to be measured and monitored to ensure that it does not exceed the recommended limit by the standard. However, Awang et al., (2015) reported, that ozone concentration in Klang Valley showed the hourly average ozone concentration exceeds the recommended limit on several occasions. Hence, determining ozone concentration measurement is important for air quality status and guidelines compliances are important as ozone concentration measurement could provide useful information for the environmental and medical authorities to provide information and announcement for public health warnings (Tan et al., 2016).

In measuring ground level ozone, different methods are implemented by many researchers. Based on USEPA (2016b), the Federal Reference Method (FRM) for ozone is chemiluminescence, while the Federal Equivalent Method (FEM) is UV photometry. The chemiluminescence was established as the reference method as it meets the performance specifications and free of interferences (Long et al., 2014). The DOE Malaysia has been using UV Absorption Ozone Analyzer Model 400A which applies the UV photometry principle. The use of UV photometry is widespread

compared to chemiluminescence instrument. This is because as UV photometry instruments do not require external gas supply or other reagents and are convenient, compact, and easy to install (USEPA, 2014). However, there are some deficiencies in this FEM UV photometric method. For example, there might be sample degradation during transfer and passing through the instrument (Ionel & Propescu, 2010). Another shortcoming is UV photometry can be impacted by other interferences that have strong absorbance at 254 nm light. The interference might cause by water vapour (H_2O), hydrogen sulphide (H_2S), carbon dioxide (CO_2), meta-xylene, mercury (Hg), and aromatic hydrocarbon compounds found in ambient air (USEPA, 2014). In addition, ground level ozone measurement using standard method can only determine the ozone concentration at one sampling point. Hence, leaving many areas inaccessible for ozone concentration measurement. So, there is lacking spatial coverage using the standard method ozone measure.

Meanwhile, ozonesonde is a method in measuring the vertical ozone concentration. Ozonesonde has been use for validation of other ozone measurement from satellites, models and ground observation for its high accuracy and high vertical resolution (Akhil Raj et al., 2015). However, remote sensing is an alternative non-standard method that is used to measure ozone concentration. The operational theory of the remote sensing technique is a designed detector or sensor used to measure the optical properties of the ozone gas by the transmitted or reflected signal that is extended through the atmosphere. In recent years, detecting atmospheric profiles using remote sensing has gained popularity due to its large database, large spatial coverage, high-frequency data, and also accuracy has been improved all the time with many introductions of better algorithms (Muzammil & Hanan, 2017). However, the disadvantage of remote sensing is that it has difficulties to define the performance

standards of the data collected (Ionel & Propescu, 2010). This is due to the environmental factors that affect the instrument when used in the field. In most remote sensing instruments, the retrieval accuracy is affected by its noise detector and error calibrator which is usually caused by cloud contamination (Wetzel et al., 2003).

This study focused on assessing the variations of ground level ozone measured by standard method and total column ozone measured by remote sensing. The trend of similarities or differences between these two types of ozone measurements were analysed using statistical analysis.

1.3 Objectives

i. To determine ground level ozone measurement using the standard method and total column ozone using remote sensing technique.

ii. To investigate the concentration trend of ground level ozone and total column ozone.

iii. To determine the correlation between ground level ozone and total column ozone.

1.4 Scope of Study

The location of this study is Klang Valley, Malaysia. This study area is selected due to the availability of number of Department of Environment (DOE) continuous air monitoring stations in the location. This area was also selected as the area is under the reach of OMI coverage. Secondary data of ground level ozone acquired from DOE while remotely-sensed data of total column ozone is acquired from NASA Earth Data is used in this study. The period for which the data collected for this study is between January 2013 and December 2015. Descriptive analysis is obtained for both ground

level ozone and total column ozone. Diurnal variation of ozone concentration is plotted for the ground level ozone from standard method measurement to understand the data distribution and the diurnal variation of the ground level ozone. In performing the variation assessment, the daily concentration of both ground level ozone and total column ozone data is used, as OMI data for total column ozone only provide at certain time of the day and depending on the temporal resolution.

1.5 Significance of Study

The significance of this study is to understand the distribution of the ground level ozone and total column ozone data by descriptive analysis. The diurnal plot of ground level ozone concentration from standard method is determined to understand the ozone characteristics. Next, the relationship between ground level ozone concentration measured using standard method and remotely-sensed total column ozone concentration was determined by correlation analysis. Other than that, previous studies also reported that total column ozone condition and distribution affected the accumulation of ground level ozone (Lang ford et al., 2012; Tarasick et al., 2019). Besides, the formation, accumulation and destruction of ozone vary with altitude thus the ozone variation must be observed. In addition, ozone trend analysis is necessary to establish effective prevention and control measure to control ozone pollution. In this study, the similarities, differences and trend of the ground level ozone concentration measured using standard method and total column ozone measured remotely-sense were statistically analysed.

CHAPTER 2

LITERATURE REVIEW

2.1 Ozone

Ozone is a gas that plays important role in balancing the Earth's atmosphere thermal and chemical. Most ozone is located at the upper part of the atmosphere, which is called the stratosphere situated more than 10 km above the Earth's surface. Approximately, 90 % of the ozone in the atmosphere is contained in the stratosphere where the ozone layer is. Meanwhile, the remaining 10% of the ozone exists in the troposphere. The Earth's troposphere extends 10-18 km from the surface (Tiwary & Colls, 2010).

Ozone is capable of absorbing the harmful sun's ultraviolet (UV) radiation. Hence, stratospheric ozone has protecting humans and the ecosystems on Earth from solar radiation. However, tropospheric ozone has been related to secondary pollutants and greenhouse gases other than water vapour, carbon dioxide, and methane (Chooi et al., 2014).

2.1.1 Total Column Ozone (TCO) and Its Formation

Total column ozone (TCO) is the measurement of total atmospheric ozone that is given in the column which majorly exists in stratosphere and the remaining small portion in the troposphere. Usually, TCO is measure in Dobson Units (DU). Dobson Unit (DU) is the most common use in TCO research (Chooi et al., 2014; Shin et al., 2020). Measurement of DU compressed down all ozone over an area to 1 atm pressure and 0℃. The whole column ozone forms a slab 3 mm thick which corresponds to 300 DU.

The mechanisms of ozone formation are different in the troposphere and stratosphere. The formation in the stratosphere involves a chemical reaction using high radiation energy (hν) from the sun. The reaction only occurs at certain wavelengths within the ultraviolet range ($\lambda < 240$ nm) which able to split oxygen molecule (O_2) into two low energy oxygen atoms, $O(^3P)$ (Equation 2.1) (Seinfeld et al, 1998). Then each free low energy oxygen atoms $O(^3P)$ collided with an oxygen molecule with the presence of M to form ozone (O_3), where M is involved in the reaction without having chemical changes (Equation 2.2). M is another gas molecule either N_2 or O_2 that acts as reaction stabilizer.

$$O_2 + h\nu \rightarrow O(^3P) + O(^3P) \quad (2.1)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \quad (2.2)$$

2.1.2 Ground Level Ozone (GLO) and Its Formation

Ground level ozone (GLO) is the subset of total column ozone (TCO) and is considered as secondary air pollutants which not emitted directly into the air but created by photochemical reactions of its precursors with the presence of sunlight.

Nitrogen oxides (NOx) and volatile organic compounds (VOCs) are the main precursors of ground level ozone. The precursors emitted by human activities from automobiles, burning of fuel, power plants, industrials activities, and other sources then react in the presence of sunlight.

Troposphere receives lower solar radiation as the radiation could not enter the troposphere after being absorbed by the ozone layer. Hence in the troposphere, ozone is produced by series of reactions started with NO_2 photolysis (Awang et al., 2016b). The radiation involves in NO_2 photolysis is $\lambda < 430$ nm which break nitrogen dioxide (NO_2) into NO and $O(^3P)$ (Equation 2.3). Then, the single oxygen atom $O(^3P)$ combine with oxygen molecule O_2 that naturally exists in the air with the presence of a third body molecule denoted as M, where M usually another O_2 molecule or N_2 to form O_3 (Equation 2.4). However, O_3 which forms can be quickly destroyed by NO titration where NO rapidly reacting with O_3 to create NO_2 and O_2 (Equation 2.5). Net O_3 development will be very limited unless the process of turning NO into NO_2 occurs simultaneously without degrading O_3. Tiwary and Colls (2010) stated that another O_3 sinking agent other than NO is NO_2. NO_2 reacts with O_3 yield nitrate radicals (NO_3) (Equation 2.6). Production of radicals NO_3 reacts with NO_2 and yield dinitrogen pentoxide (NO_2O_5) (Equation 2.7). However, the reaction is thermally unstable and may disassociate back to NO_3 and NO_2 (Awang & Ramli., 2017). Though, NO_2O_5 may form nitric acid (HNO_3) by undergoing reaction with H_2O (Equation 2.8). HNO_3 is water-soluble, hence it can be easily eliminated from the atmosphere by precipitation, this situation causes HNO_3 becomes acid rain.

$$NO_2 \xrightarrow{h\nu\ (\lambda < 430\ nm)} NO + O(^3P) \quad (2.3)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \quad (2.4)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (2.5)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (2.6)$$

$$NO_3 + NO_2 + M \leftrightarrow N_2O_5 + M \quad (2.7)$$

$$NO_2O_5 + H2O \rightarrow 2HNO_3 \quad (2.8)$$

If there is participation of VOCs in the ground level O_3 formation, VOCs act as a free radical in the process of converting NO into NO_2 without degrading O_3 (Equation 2.9). NO_2 combines with radical (represent by hydroxyl radical, OH) in order to create a nonradical product (Equation 2.10). This reaction can be a permanent drain for both NOx and radicals (Cuciureanu & Dimitriu, 2006).

$$RO_2 + NO \rightarrow RO + NO_2 \quad (2.9)$$

Where R is a hydrocarbon (one of VOCs)

$$NO_2 + OH \rightarrow HNO_3 \quad (2.10)$$

2.2 GLO Precursor

As discussed before, the production chemistry between GLO and TCO is totally different due to the intensity of sunlight in the stratosphere and troposphere. Since high UV were received in the stratosphere TCO only required oxygen molecules and oxygen atoms to form ozone. Due to the unavailability of high UV in the troposphere, GLO formation required precursors as an ingredient to photochemically produced ozone. As reported by numerous research, NOx and VOCs are GLO main precursors (Banan et al., 2013; Awang & Ramli., 2017). NOx is emitted from the by-products of fossil fuels burning in automobiles and industrial activities (USEPA, 2006). Based on a study by Awang et al. (2015a), the diurnal trend of NO_2 shows two

noticeable peaks which at early in the morning (9 a.m. – 10 a.m.) and in the late evening (8 p.m. – 10 p.m.) where the second peak is smaller owing to the emission rate and current meteorology parameters. Besides, typically NO diurnal trend is similar to the NO_2 in which major peak concentrations are observed in the morning and also peak at night (Banan et al., 2013). Normally, due to an increase in traffic movement during morning rush hours, high concentration of NO released from vehicles. During this period, NO_2 concentration is similar to NO concentration because sunlight induced reaction to convert NO into NO_2 via reaction with O_3. NO concentration lower at night because NO that converted into NO_2 remained (Han et al., 2011). Sources of VOCs can be anthropogenic and biogenic which are emitted from various industrial and commercial activities and automobiles. VOCs emitted include all hydrocarbons such as alkanes, alkenes, and aromatic compounds (USEPA, 2006). VOCs produce NO_2 which produces a free O atom for the formation of GLO.

2.3 Meteorological Parameters that Affect GLO Variation

GLO formation or destruction indicates the whole mechanism is particularly controlled by meteorological parameters (Mustafa & Mohammed, 2012). Meteorological parameters that affect GLO variation are sunlight, temperature, relative humidity, and wind speed and direction. The GLO is photochemically driven, in which the diurnal trend of the GLO concentration increases after sunrise, reach maximum concentration around noon, and minimum in the afternoon (Awang et al., 2016a). The temperature affects the GLO formation indirectly. Temperature influences the amount and speed of GLO formation (Punithavathy et al., 2015). This is because the temperature is strongly correlated with solar radiation, where the temperature increases as the light intensity increases. Besides, relative humidity also affects the

GLO formation because hydroxyl radicals oxidized and contributed to the formation of GLO. This phenomenon can be associated with the increase of GLO concentration when the humidity decreased due to more hydroxyl radicals converted into GLO. Slower wind speed leads to the accumulation of GLO and increase of GLO concentration (Awang et al., 2018).

2.4 Effect of GLO

As mentioned before, GLO is considered a pollutant that is significantly related to the aspect of air quality associated with public health, has caused increasing concern among researchers. Ozone is well known as highly reactive oxidant. Ozone can impact human, plant and vegetation. High concentrations of GLO are predicted to have adverse effects on agricultural yield, forest output, and human health (Ghimire, 2018). Exposure of GLO to humans has been related to pre-maturity mortality and the number of morbidity endpoints such as the number of asthma attacks and hospital emergency visits (John et al., 1996). Ozone generates free radicals in human tissues. Severe irritation and headaches might be pe experience with inhalation of air mass containing 1 ppm of ozone (Mustafa & Mohammed, 2012). A study shows that high concentrations of GLO could cause respiratory dysfunction and cardiovascular also lead to higher rates of mortality, particularly for elderly people (Wang et al., 2017).

Besides, GLO also significantly affected agricultural and forest health. For some countries such as China and Canada, there is obvious change observe on crops and forests for the area with a high concentration of GLO such as the decrease in crop productivity and decline of forest. It causes injuries to shrubs and flowers due to their high oxidant characteristics (Ghimire, 2018; Li et al., 2018). Furthermore, GLO also causes damage to materials such as accelerate the degradation of some paints, speed

fading of some dyes, causing crack of rubber materials and also damage to textile products like cotton, polyester, nylon, and others (USEPA, 2016a).

2.5 GLO Standard Method Measurement

According to USEPA (2016b), the federal reference method (FRM) of measuring GLO concentration is chemiluminescence while the federal equivalent method (FEM) is using UV photometry. In UV photometry, the UV electrons excite by radiation. During this phase, the gas molecule absorbs energy in certain absorption bands (wavelength ranges) resulting in the loss of intensity of the radiation which therefore measured. The photometer principle consists of a radiation source lamp, a focused light beam that falls through a detector of a cell and radiation detector. The beam then became an electrical signal that can be read digitally. The gas concentration is measured by the loss of intensity of the radiation. The Beer-Lambert Law explained the relationship of radiation absorption and gas concentration. This UV photometry is the most widely used method in measuring O_3 concentrations as many modern devices use this method due to its accuracy and easy to use (USEPA, 2014).

Furthermore, chemiluminescence technique is closely related to UV fluorescence. However, the difference between chemiluminescence and UV fluorescence technique is that in chemiluminescence technique involves a chemical reaction that producing UV radiation. The principle of chemiluminescence measurement is chemo-physical. The concentration of the GLO gas measured is determined from the intensity of the radiation produce from the chemical reaction. Then the radiation produce is detected by the radiation detector in the instrument and recorded by the photomultiplier and transformed into electrical signals that can be saved (Ionel & Popescu, 2010). Other than O_3, the chemiluminescence technique is

also suitable for the measurement of NO and NOx. However, chemiluminescence method is not widely used because the instrument is no longer manufactured as this method is hard to handle (USEPA, 2014).

The concentration of hourly GLO measurement carried by DOE of Malaysia uses continuous air monitoring stations across the country. The Ozone Analyzer Model 400A which utilizes the UV absorption principle used to monitor GLO concentrations (Awang et al., 2018). The operation theory of this instrument follows the UV photometry technique. In this instrument, the ambient air sample is drawn into the mixing chamber of the device and the sample is exposed to the ultraviolet (UV) light at a wavelength of 254 nm. The UV light absorbed by the ozone molecule is in the proportion of its concentration and compared to the air sample with the absence of ozone. Since ozone unique absorption is at 254 nm, very small interference from other compounds with this method. However, some interference might occur from H_2O, H_2S, CO_2, meta-xylene, Hg, and aromatic hydrocarbon compounds, which also absorb UV light at 254 nm wavelength (USEPA, 2014). The resulting photocurrent from the detector is amplified and reads directly or is displayed on the recording. The operation theory of the instrument explained by USEPA, 2016b, as the UV Absorption Ozone Analyzer Model 400A used by DOE was listed in the FEM to measure GLO levels. The system of the instrument follows Beer-Lambert Law to measure low ranges of GLO concentration in the ambient air. (Awang et al., 2015a)

2.6 TCO Remote Sensing Measurement

Remote sensing technique to measure atmospheric aerosols has gained popularity due to its large database, spatial coverage, high-frequency data and also highly accurate data which improved by introductions of better algorithms all the time

(Muzammil & Hanan., 2017). Other than that, remote sensing technique has the advantage to eliminate the possibility of sample degradation when passaging into and through the instrument (Ionel & Popescu., 2010). Remote sensing broadens the study area by enabling the measurement of the concentration of selected substances over a region of space rather than one-point sampling. This technique measured the optical properties of the gas using a detector design to transmit or reflected signal that is received from an extended path-length through the atmosphere. Studies show that remote sensing has been used to detect many airborne pollutants (Ionel & Popescu., 2010). Remote sensing was used in many studies such to detect TCO in Peninsular Malaysia (Tan et al., 2016), SO_2 and NO_2 in golden energy triangle in Northwest China (Shen et al., 2016), PM_{10} in Malaysia (Kamarul Zaman et al., 2018) and $PM_{2.5}$ in China (Xue et al., 2017).

In remote sensing, many platforms can be used from ground-based sensors to the satellite platformed sensor. For the ground-based sensor, the measured concentration covered the area between the emitter and the receiver detector while the satellite sensor measured the total vertical concentration of the air pollutants. Some examples of ground-based remote sensing used to measure air contaminants are Light Detection and Ranging (LIDAR), Differential Absorption LIDAR (DIAL), Differential optical absorption spectroscopy (DOAS), and Fourier transform infrared (FTIR) absorption spectroscopy (Ionel & Popescu, 2010). However, this technique is partly having difficulties in defining the performance requirement which takes account of the environmental factors which impact the instrument in the field.

As for satellite-based remote sensing, the aerosols in the atmosphere acted as modifying agents in several ways. Each aerosol affected the absorption and scattering of solar or radiation directly (Ali et al., 2016). Passive remote sensing detects naturally

occurring energy from the sun while active remote sensing provided its source of electromagnetic energy. For both types, the sensor will detect the energy that had been emitted or scattered by the target. This remote sensing method also applied the Beer-Lambert Law, in which the amount of absorbed light is proportional to the number of the molecules. In fact, each gas has its specific absorption profile, it is possible for the sensor to detect multiple gases concentration simultaneously or one after another (Bassim et al., 2013).

In TCO remote sensing measurement, ozonesonde is the most widely used. Ozonesonde in a small lighweight balloon-borne instrument attached to a standard radiosonde and able to measure ozone vertical profile from the surface to about 35 km or about 4 hPa before the balloon burts. There are about 50 locations around the world that make regular measurement of TCO using ozonosonde approximately weekly. Ozonsonde data constitute a foundation to satellite calibration and use in many trend analysis and climatology (Thompson et al., 2019), especially for lower stratosphere study where the most uncertain from satellites measurement. Ozonesonde has been use for validation and comparison to other satellites derived TCO measurement due to its accurate values and high vertical resolution (Akhil Raj., 2015).

2.7 OMI Characteristics

Ozone Monitoring Instrument (OMI) is used in this study because it provides the atmospheric and radiometric quantities of the total column ozone (TOC). OMI data was also used in previous TCO research over Peninsular Malaysia (Tan et al., 2017) OMI is the successor of the Total Ozone Mapping Spectrometer (TOMS) instrument and provides in the monitoring of atmospheric ozone, aerosols, trace gases, and surface UV radiation (Buchard et al., 2008). OMI started collecting data since 9 August 2004

and one of the instruments that have onboard NASA's Earth Observing System (EOS) Aura satellite. Aura was launched on 15 July 2004 and orbit the earth in a polar Sun-synchronous pattern (NASA, 2012). This type of orbit allows the satellite to pass over a section of the earth at the same time of the day. However, the satellite has to shift its orbit by approximately one degree per day as there is 365 day in a year but 360 degrees in a circle. As they are sun-synchronous the satellite is always position relative to the sun. Table 2.1 summarize the characteristics of Aura satellite where OMI instrument onboard.

Table 2.1 Characteristics of NASA EOS Aura. (Source: ESA, 2020)

Characteristics	**Specification**
Orbit type	Sun-synchronous
Orbit height	705 km
Orbit period	98.8 minutes
Orbit inclination	98.7°
Repeat cycle	16 days

OMI has improved spatial resolution as compared to TOMS, GOME, and SCIAMACHY with larger number of wavelengths which has set a new standard for air quality and trace gases monitoring from space. OMI have the abilities to measure key air quality components including NO_2, SO_2, BrO and other aerosols characteristics. OMI have the spatial resolution of 13 x 24 km^2 and can be zoomed to 13 x 13 km^2 for urban scale pollution tracking and detection sources. OMI has two split channels for UV, the purpose is to increase the useful signal of the instrument (NASA, 2012). Table 2.2 summarize the general descriptions of OMI.

Table 2.2 Summarization the general descriptions of OMI. (Source: NASA, 2012)

Characteristics	Specification
Swath Width	2600 km
Wavelength Range	270 – 500 nm
Bands	UV-1: 264 - 311 nm UV-2: 307 – 383 nm VIS: 349 – 504 nm
Spatial Resolution	13 x 24 km 13 km x 13 km (zoom mode for detection of urban pollution)
Duty Cycle	60 minutes on daylight side, 10-30 minutes on the eclipse side (calibration)

TCO data acquired for this study is from the ozone products of OMI. These ozone products provide column ozone and ozone profiles. OMI ozone product of OMTO3 algorithm is selected this product consist of UV aerosol index, SO_2 index, cloud fraction, terrain and cloud pressure, and ozone concentration under the clouds. OMI OMTO3 reported to have similar quality of TCO measurement to TOMS (NASA., 2012) and showed a strong agreement to ozonesonde data expect for high altitude in winter-spring (Hu et al., 2017) which the errors may cause by the cloud cover, aerosol amount and solar zenith angle.

CHAPTER 3

MATERIALS AND METHODS

3.1 Study Area

The study focused on the area of Klang Valley, Peninsular Malaysia. Meteorologically, Klang Valley has a tropical rainforest climate. As located in the Peninsular Malaysia the study area affected by two monsoon seasons which are Northeast Monsoon (NEM) season from November to February and Southwest Monsoon (SWM) season from May to August (Azmi & Latif, 2010). Meanwhile transitional period is in April and October. Peninsular Malaysia will experience highest rainfall in December and lowest rainfall in February (Varikoden et al., 2010)

The borders of Klang Valley are not officially defined. However, it believed to consist of Kuala Lumpur, Putrajaya and its surrounding cities, such as Petaling Jaya, Shah Alam, Puchong, Klang, Sepang, Hulu Langat, and Gombak (Binyehemd et al., 2016). In its early development, Klang Valley was referred to the location close to the Klang River where its early development was a tin mining town in the late 19th century. Now, the Klang Valley area extends from the east (Gombak), west (Port

Klang), north (Rawang) and south (Negeri Sembilan). Figure 3.1 showed the map of study areas in Klang Valley.

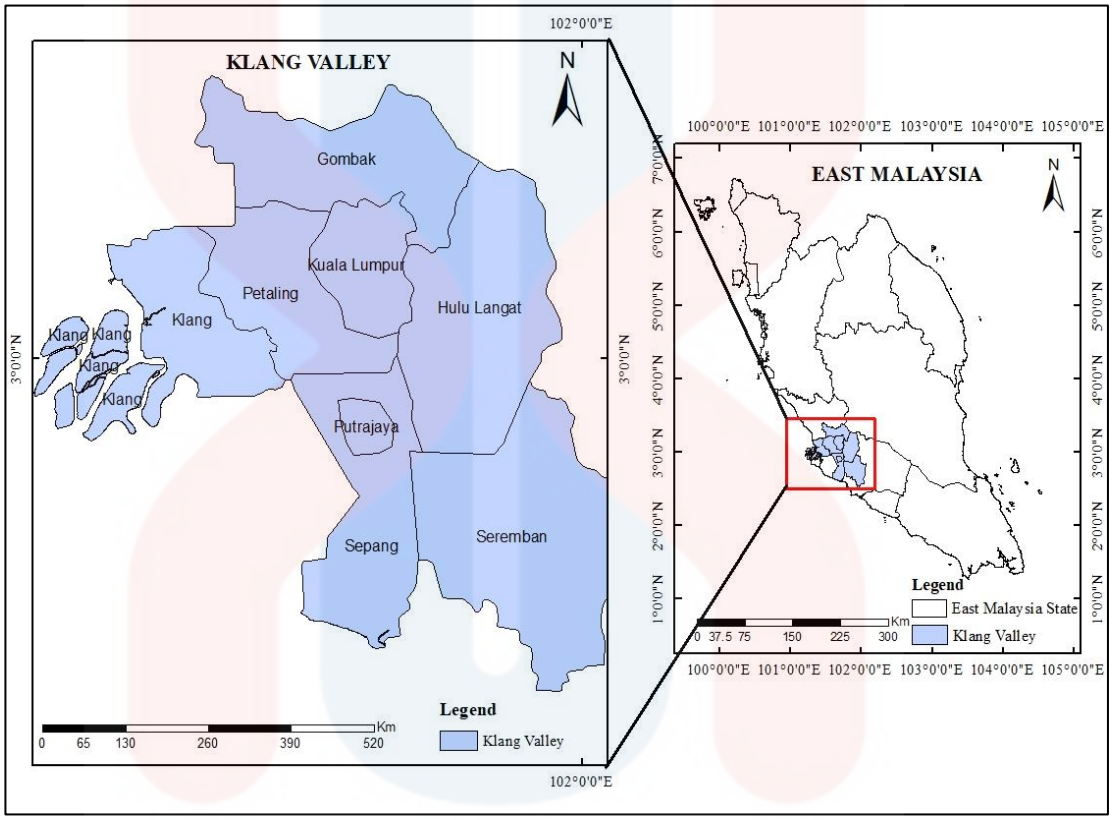

Figure 3.1 Map of Study Area, Klang Valley.

Klang Valley is a fast-growing metropolitan area of Malaysia, with dense population, industrials activities, numerous public transportation options, and highways which experience heavy traffic during the rush hour in the morning and late evening (Awang et al., 2015b). The transportations, roads, and highways served to link the city center of Kuala Lumpur with the suburbs area of Klang Valley. Other than that, Klang Valley is also known as industrial hot spots which include various types of industrial sectors. Over the years, the industrial market in Klang Valley has been rising steadily. Klang is one of the major contributors to Selangor's gross domestic product

and Klang Valley remain the choice for investment in Malaysia. From the industrial sectors in Klang Valley, it has contributed to 25% of Malaysia's total approved investment which has a total investment of RM3.1 billion from January to June 2018 (The Edge Malaysia, 2019). Klang Valley area also completed with residential including the planned residential area of Shah Alam. Besides, Klang Valley also have port activities in Port Klang.

Klang Valley maximum hourly ozone concentration recorded through the year of 2006 shows exceeding measure of 152 ppb of ozone concentration which surpasses the average recommended by Malaysia Ambient Air Quality Guideline which limit of 100 ppb per 1 hour (Ghazali et al., 2010) also the current limit by New Malaysia Ambient Air Quality Standard is 90 ppb. This occurs due to the higher emissions of ozone precursors in the area. This is because of the increase in ozone concentration effect by the elevation of precursor emissions level (Awang et al., 2016a). This precursor emitted into the air from the burning of fuels of automobiles and large industrials activities which massively developed in Klang Valley.

3.2 Monitoring Station

The GLO data acquired is from selected monitoring stations in Klang Valley. Those monitoring stations include Klang, Petaling Jaya and Shah Alam located in Selangor and Nilai, Negeri Sembilan (DOE, 2020). Figure 3.2 shows the selected monitoring stations in Klang Valley area.

The monitoring station for Klang is located at Sekolah Menengah Kebangsaan (P) Raja Zarina, with the coordinate N 3.0099° and E101.4084°. This station closes to the port area. The monitoring station for Petaling Jaya is located at Sekolah Kebangsaan Bandar Utama, with the coordinate N 3.1315° and E 101.6082°. Petaling

Jaya station is located in housing area, green areas, commercial and light industrial (Hashim et al., 2018). Shah Alam monitoring station located at Sekolah Kebangsaan Taman Tun Dr Ismail Jaya (N 3.1060°, E101.5573°). This station closes to industrial zone and residential areas (Hashim et al., 20018). The monitoring station for Nilai located at Taman Semarak (Phase II) with coordinate at N 2.8216° and E 101.8114°. Nilai station also surrounded by heavily industrialized area.

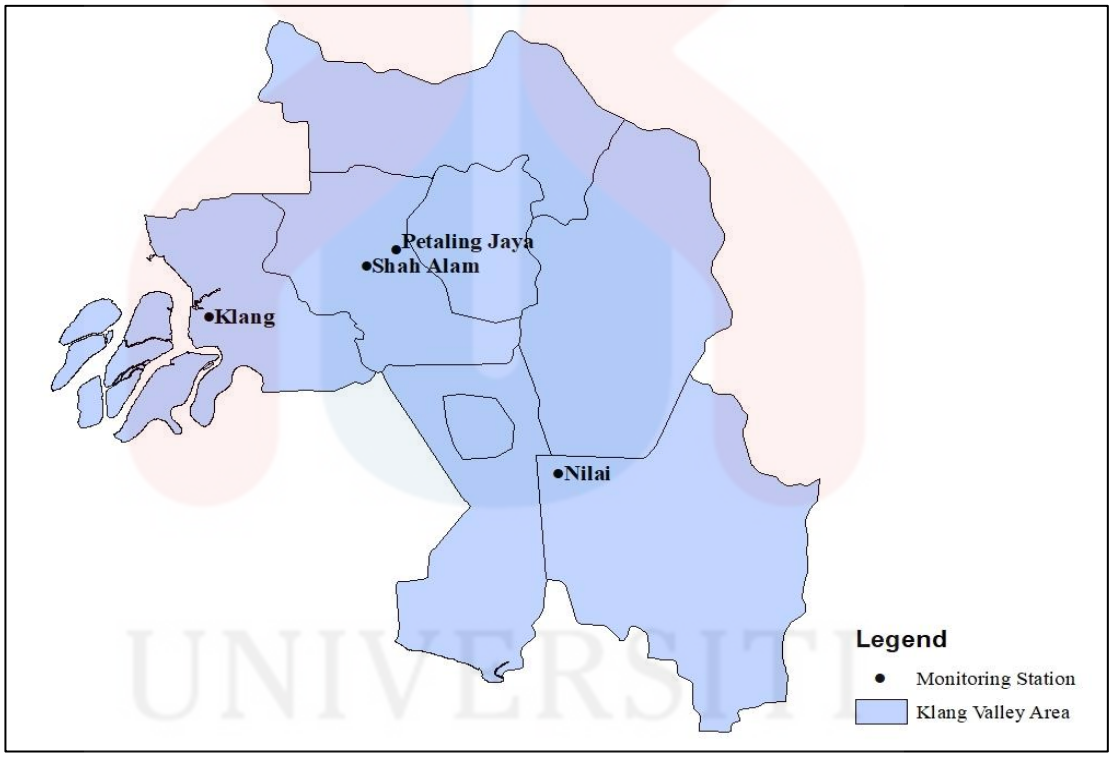

Figure 3.2 Selected Monitoring Stations in Klang Valley Area.

3.3 Secondary Data Collection

The secondary data of GLO obtained from the Department of Environment Malaysia. The data obtained is in the form of hourly average of GLO concentration for the year 2013-2015, from 1st January of 2013 until 31st December of 2015. The data were owned by Department of Environment (DOE) Malaysia, however, are

managed by Alam Sekitar Malaysia Sdn. Bhd. The instrument used by DOE is UV Absorption Ozone Analyzer Model 400A, where this instrument used for continuous monitoring follows the standard principle and procedures outlined by an internationally recognized agency, USEPA and listed under Federal Equivalent Method (FEM) which the method implement by this instrument is UV photometry method (Teledyne, 2018). The secondary data obtained have been put through standard quality control processes and quality assurance procedures (Awang et al., 2013). This study also encountered missing data and incomplete data matrices which usually the product of errors in measurement or data acquisition faults or inappropriate sampling (Junninen et al., 2004). All missing data contained in this study is deliberately excluded and not taken into account during the analysis.

The remote sensing data of TCO acquired from the NASA Earth Data from https://earthdata.nasa.gov//. Data of OMI OMTO3 is selected in the time frame of 1st January of 2017 until 31st December of 2019. The data acquired is a free source downloaded directly from the NASA Earth Data website. The OMI OMTO3 retrieval was accessed using Panoply software and the TCO data of each study point is extracted into a Microsoft Excel sheet. OMI OMTO3 data is available in daily average as the instrument onboard Aura satellite which cycles the Earth in orbit period of 98.8 minutes and the reading taken was average for a day. The OMI data of daily averaged TCO are grided at 0.25 x 0.25 degree, hence the TCO reading of each point is determined by the closes coordinates. Table 3.1 show the coordinate of the monitoring station and the closes coordinate chosen for OMI TCO data.

Table 3.1 The coordinate of the monitoring stations in Klang Valley and the closest coordinate from OMI data grid.

Station		Klang	Shah Alam	Petaling Jaya	Nilai
Coordinate	**Latitude**	N 3.0099°	N 3.1060°	N 3.1315°	N 2.8216°
	Longitude	E 101.4084°	E 101.5573°	E 101.6082°	E 101.8114°
Closest coordinate	**Latitude**	N 3.125°	N 3.125	N 3.125	N 2.875
	Longitude	E 101.375°	E 101.625°	E 101.625°	E 101.875°

3.4 Data analysis

3.4.1 Descriptive Analysis

In this study, the descriptive statistic of data of GLO using and TCO is determined to observe the overall distribution of data (Awang et al., 2015b). The descriptive measures which determine are mean, standard deviation, maximum, and minimum of the data. This analysis was done using the descriptive analysis built-in in Statistical Package for the Social Science (SPSS) Version 20. The mean is the most common statistic used. The mean is calculated by adding all data points (where X_i are individual values) and dividing the sum of the data by the number of samples (n) (Equation 3.1). Mean usually denoted by $\bar{X}$ (X bar) and calculated using the following formula:

$$\bar{X} = \frac{\sum Xi}{n} = \frac{X_1 + X_2 + \cdots + X_n}{n} \tag{3.1}$$

The standard deviation of the data is the measuring of spread of the values in the data set and computed by measuring the sum of differences between mean of individual values (X_i) divide by the number of individual data in the data set. The standard deviation can be computed by using Equation 3.2.

$$S = \sqrt{\frac{\Sigma_i (x_i - \bar{x}_i)}{n-1}} = \sqrt{\frac{(x_1 - \bar{x})^2 + (x_2 - \bar{x})^2 + \cdots + (x_n - \bar{x})^2}{r' - 1}} \tag{3.2}$$

3.4.2 Time Series Plot

The time-series analysis of GLO and TCO was plotted using Origin Pro 10. The time series plot of the ozone concentration is a graph where the ozone measurement data is plotted to some measure of time. From the time series graph, the trends of the GLO and TCO concentration have been identified. Sequential data of ozone measurement using the standard method for GLO and remote sensing for TCO at daily intervals plotted against the period of a year. The trend analysis of ozone measurement was obtained from the time scale.

3.4.3 Diurnal Plot

Diurnal variation of ozone concentration is plotted from the hourly average of standard method data (Awang et al., 2015b). The diurnal variation has plotted using the software OriginPro 9.1 64Bit. The distribution of ozone concentration shows more or less similar variability with different amplitudes. The ozone concentration shows high concentration during the daytime and low level during early morning and night. Low concentration of ozone appeared in the early morning, the rapidly increase as the solar radiation increase and reaches peaked value around noon. Afterward, the concentration will decrease after the maximum value and continuously decreases to lower values due to the absence of solar radiation. This similar diurnal variability of ozone concentration has been reported from the previous studies across Malaysia and also around the world (Hashim & Noor, 2017; Wang et al., 2017; Awang et al, 2018; Pancholi et al., 2018).

3.4.4 Pearson's Correlation Coefficient r

In finding the correlation between ground level data and remote sensing data, a built-in Pearson's correlation analysis in the OriginPro 9.1 is used. Pearson's correlation coefficient is the statistical test use to measure the statistical relationship or association between two data. Pearson's coefficient gives the magnitude of correlation as well as the direction of the relation. Equation 3.3 shows the calculation Pearson' correlation.

$$r = \frac{\sum(xi - x)(yi - y)}{\sqrt{\sum(xi - x)^2 (yi - y)^2}} \quad (3.3)$$

The Pearson's correlation coefficient, r limit ranges from 1 to -1, where 1 indicates perfect relationship, -1 indicates perfect negative relationship and 0 indicated no relationship exists. A high degree with coefficient values lies between ± 0.5 and ± 1 said to be a strong correlation. A moderate degree coefficient value lies between ± 0.3 and ± 0.49, then it is said to have a medium correlation. When the value lies below ± 0.29, it is a low degree relationship with a small correlation.

3.5 Research Flow Chart

Figure 3.3 shows the main research for this study. The correlation between GLO and TCO in Klang Valley, Malaysia from 2013 to 2015 is determined. The data of GLO measurement using standard method was acquired from DOE while data of TCO measurement using remote sensing is acquired from Nasa Earth Data. Throughout the study, a few analysis including descriptive analysis, diurnal variation, time series trend analysis and correlation analysis have been conducted. Descriptive statistic of both GLO and TCO is determine to understand the distribution of data. Diurnal variation of GLO is plotted to determine the characteristics of GLO. Time

series of GLO and TCO plotted to analyse the trend and correlation analysis between GLO and TCO is determine to quantify the relation.

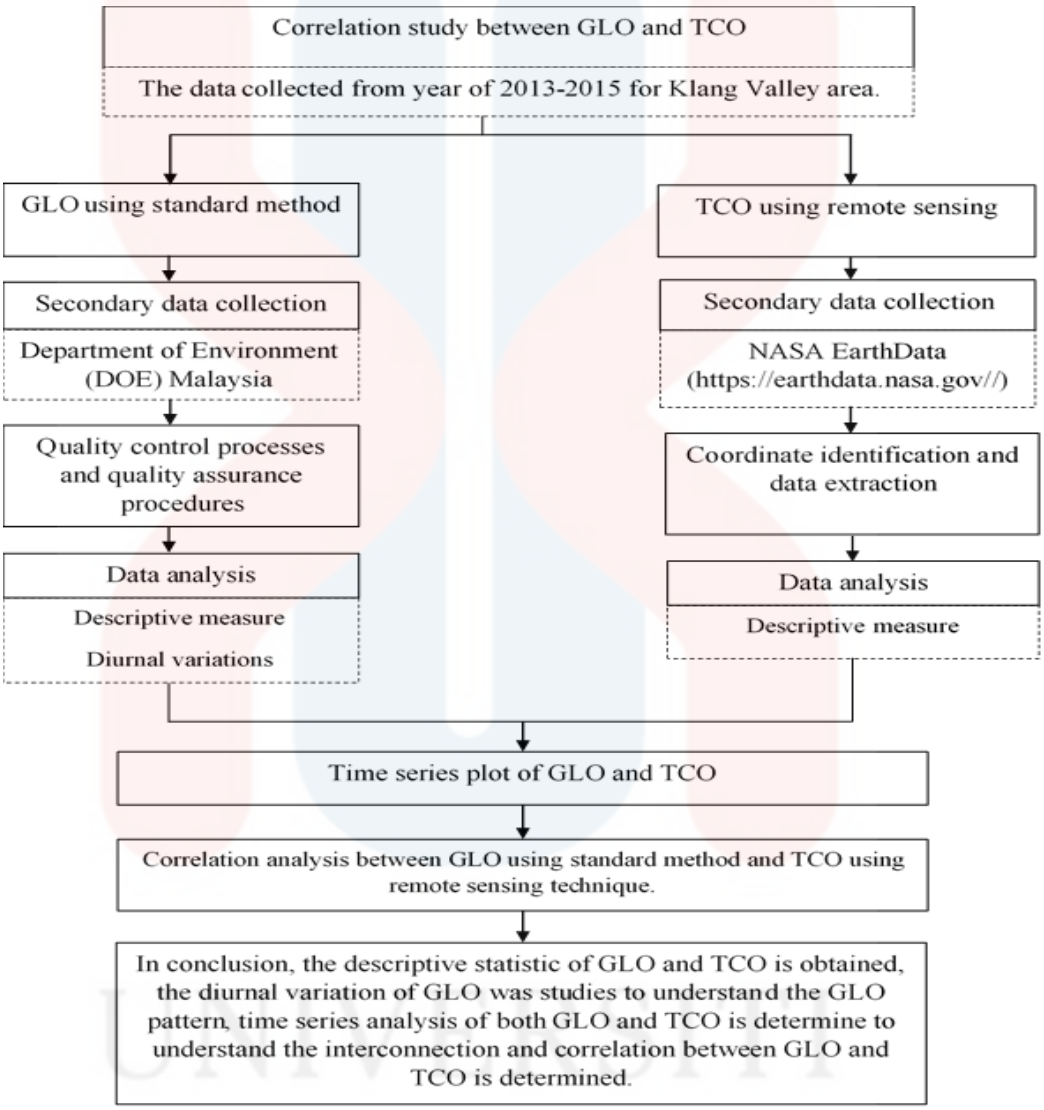

Figure 3.3 The flow chart of research methodologies.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Descriptive Statistic of Ground Level Ozone and Total Column Ozone

Descriptive statistics of GLO and TCO for the study area of Klang, Shah Alam, Petaling Jaya, and Nilai in 2013 to 2015 are depicted in Table 4.1. In Klang the highest maximum reading for GLO is 122 ppb in 2013. In Shah Alam, the highest reading is 161 ppb recorded in 2014. Whereas, in Petaling Jaya and Nilai the highest readings are 123 ppb in 2015 and 119 ppb in 2013, respectively. Overall, Shah Alam was seen to show the highest concentration followed by Petaling Jaya and Klang. Meanwhile, Nilai has the lowest maximum concentration compared to other stations. The analysis shows that all four areas have maximum readings exceed the 90 ppb per hour average recommended by NMAAQS (2020). This shows that there is concern about the increase in GLO concentration in those areas later in the future. GLO concentration is mainly highest in a location with increasing urbanization and industrialization which also related to the increase in human population (Aziz et al, 2020). Among these four locations, Shah Alam is a highly industrialized area with a high population and traffic. Hence, there is high emission of GLO main precursor, NO_2 compare to other areas

which increase the concentration of GLO in this area. Meanwhile, Nilai has still undergone development with lower population compared to the other three areas hence, lower GLO concentration was recorded for Nilai.

TCO measurement is taken from satellite hence, the TCO concentration measured from stratosphere to troposphere and GLO is the subset of the TCO. All four study areas show the TCO measurement higher than 290 DU in 2015. TCO descriptive statistic shows the highest TCO recorded in Shah Alam followed by Petaling Jaya in 2015 with 296.00 DU and 294.20 DU, respectively. High TCO in Shah Alam and Petaling Jaya suggested that these locations may be affected by high concentration of GLO in the area. According to a study by Chooi et al., (2020), between NEM and SWM, there is a strong fluctuation caused by the seasonal variation. As seen, there is an increasing trend of TCO from 2013 to 2015 for all locations. This occurrence may have related to the recovery of the ozone layer in the stratosphere as a study stated that the Montreal Protocol agenda in recovering ozone layer have indicated success as the thickness of ozone layer keep increasing by year and there is possibility that the ozone layer recovers with continuous mitigation from all country (Chipperfield et al., 2017). This might be the cause as to why TCO readings were the highest in 2015 for all four study areas.

Table 4.1 Descriptive statistics of ground level ozone (GLO) and total column ozone (TCO) concentration for Klang, Shah Alam, Petaling Jaya and Nilai in 2013-2015.

	GLO (ppb)				TCO (DU)			
	Mean	**SD**	**Min**	**Max**	**Mean**	**SD**	**Min**	**Max**
Klang								
2013	14.98	16.05	1.00	122.00	201.67	111.78	0.00	285.60
2014	16.26	16.82	1.00	115.00	194.90	110.29	0.00	272.30
2015	15.87	19.09	1.00	98.00	197.58	114.66	0.00	293.80
Shah Alam								
2013	16.44	19.59	1.00	141.00	193.74	116.19	0.00	284.95
2014	17.7	21.4	1.00	161.00	184.66	115.38	0.00	272.10
2015	13.5	21.11	1.00	119.00	186.09	120.58	0.00	296.00
Petaling Jaya								
2013	12.53	16.49	1.00	116.00	193.39	116.17	0.00	286.40
2014	13.93	17.21	1.00	108.00	186.13	114.75	0.00	272.80
2015	16.85	18.61	1.00	123.00	186.07	120.57	0.00	294.20
Nilai								
2013	14.04	15.16	1.00	119.00	193.01	115.92	0.00	283.00
2014	14.34	15.39	1.00	114.00	185.87	114.59	0.00	272.30
2015	18.35	17.53	1.00	106.00	185.08	120.69	0.00	290.50

4.2 GLO Diurnal Variation

The study on GLO diurnal variation include the observation on the sources of GLO and effect of GLO formation and destruction. Figure 4.1, 4.2, 4.3 and 4.4 shows the diurnal variation of GLO concentration in Klang, Shah Alam, Petaling Jaya and Nilai from 2013 to 2015, respectively. The GLO diurnal variation of each area shows similar unimodal shape but with different deviation degrees and maximum reading. The diurnal pattern of GLO concentration observed to have maximum concentration during the afternoon and minimum concentration during night-time and early morning. This result is consistent with previous studies (Banan et al., 2013; Awang et al., 2015b). The skewness of the diurnal variation for all four sites is similar which is skewed to the right. The variation of GLO concentration is higher during daytime compared to night-time due to the amount of solar radiation during the day, which empowers photochemical reactions and induces GLO formation.

In Klang (Figure 4.1), the highest peak in GLO concentration was 42 ppb in 2015 and 37.4 ppb in both 2013 and 2014. The maximum peak of GLO in 2013 and 2014 occurs at 3 p.m. However, in 2015 the GLO concentration in Klang reach maximum concentration at 2 p.m. The GLO achieve maximum concentration one hour earlier in 2015 as the lowest peak also occurs earlier during this year. The lowest peak of GLO concentration at Klang in 2013 and 2014 occurs at 8 a.m. while in 2015 at 7 a.m. Suggested that, this might cause by faster nigh-time GLO removal occur in 2015. Reported by Awang and Ramli (2017), high concentration of night-time NO enhanced further GLO night-time depletion.

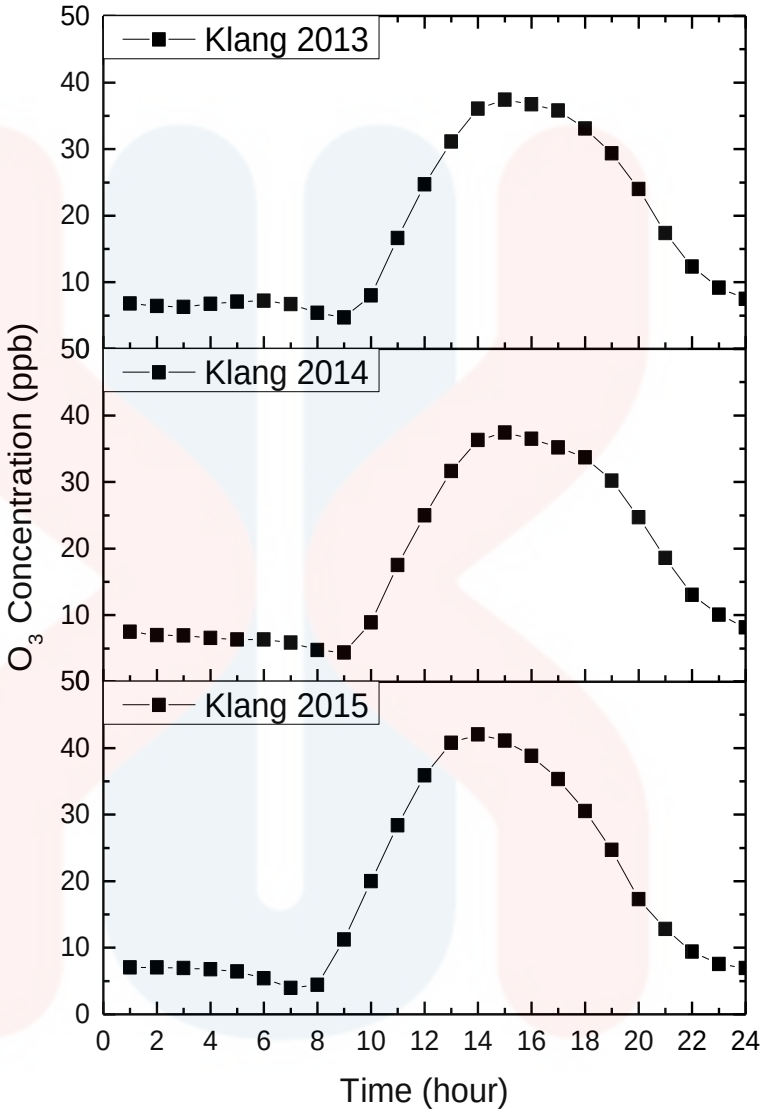

Figure 4.1 Diurnal plot of average O_3 concentration in Klang for 2013 to 2015.

Observed that in Figure 4.2 for Shah Alam, the GLO maximum peak in 2014 is the highest with 52 ppb followed by 2013 with 48.68 ppb and 2015 with 46.8 ppb. Other than that, observed that in the year 2013 the GLO concentration achieve the highest concentration at 4 p.m. Meanwhile, in the year 2014 and 2015 the GLO concentration at the highest during 3 p.m. The lowest peak of GLO concentration for Shah Alam are differed by time, in 2013 and 2014 the lowest peak is at 9 a.m. while in 2015 the lowest peak is as early at 5 a.m. This phenomenon is due to the faster

deposition of GLO in 2015, as observed that at 1 a.m. the concentration is already lower than 5 ppb but not in 2013 and 2014. This phenomenon might occur due to high concentration of night-time NO that enhance the GLO removal which allows the lowest peak achieved faster in 2015.

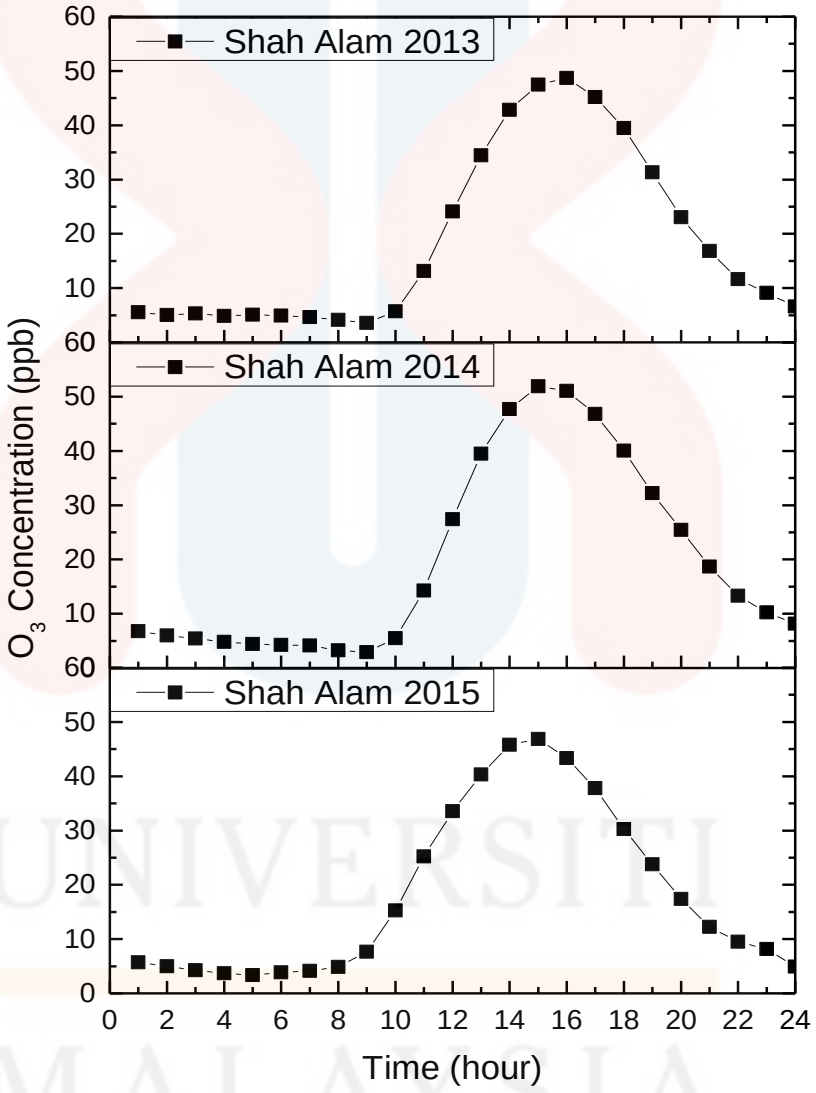

Figure 4.2 Diurnal plot of average O_3 concentration in Shah Alam for 2013 to 2015.

In Petaling Jaya, GLO concentration reached the highest concentration at 3 p.m. for all three years as observed in Figure 4.3. GLO has the highest maximum peak

in 2015 with 45.59 ppb while 2013 with 39.75 ppb and 2014 with 39.66 ppb. However, the lowest peak in 2013 and 2014 is at 8 a.m. while in 2015 is at 7 a.m.

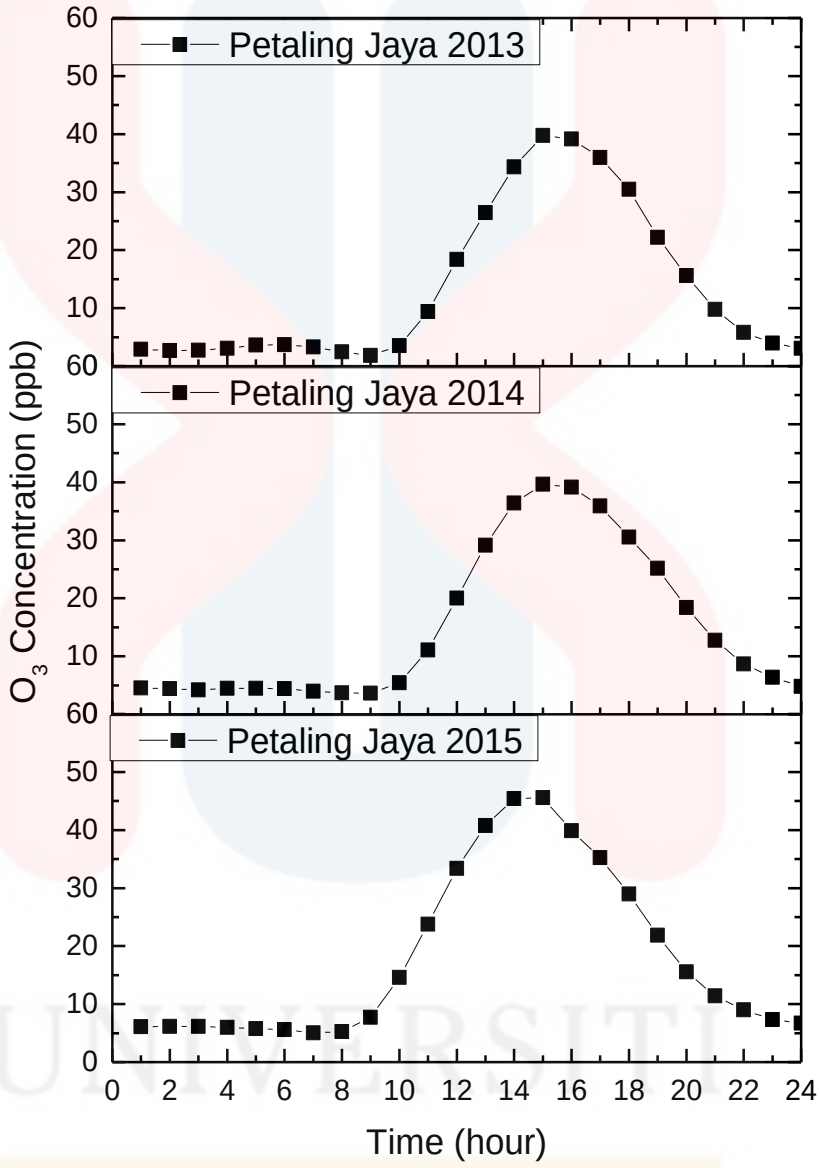

Figure 4.3 Diurnal plot of average O_3 concentration in Petaling Jaya for 2013 to 2015.

Referring to Figure 4.4 for GLO diurnal variation in Nilai, the highest maximum concentration is in 2015 with 43.53 ppb while in 2013 with 38.28 ppb and in 2014 with 35.60 ppb. In 2013 and 2014, GLO concentration achieved the maximum peak at 4 p.m. while in 2015 is at 3 p.m. During 2015, the GLO concentration also at

the lowest peak earlier at 8 a.m. compared to 2013 and 2014 which in both years the lowest peak is at 9 a.m.

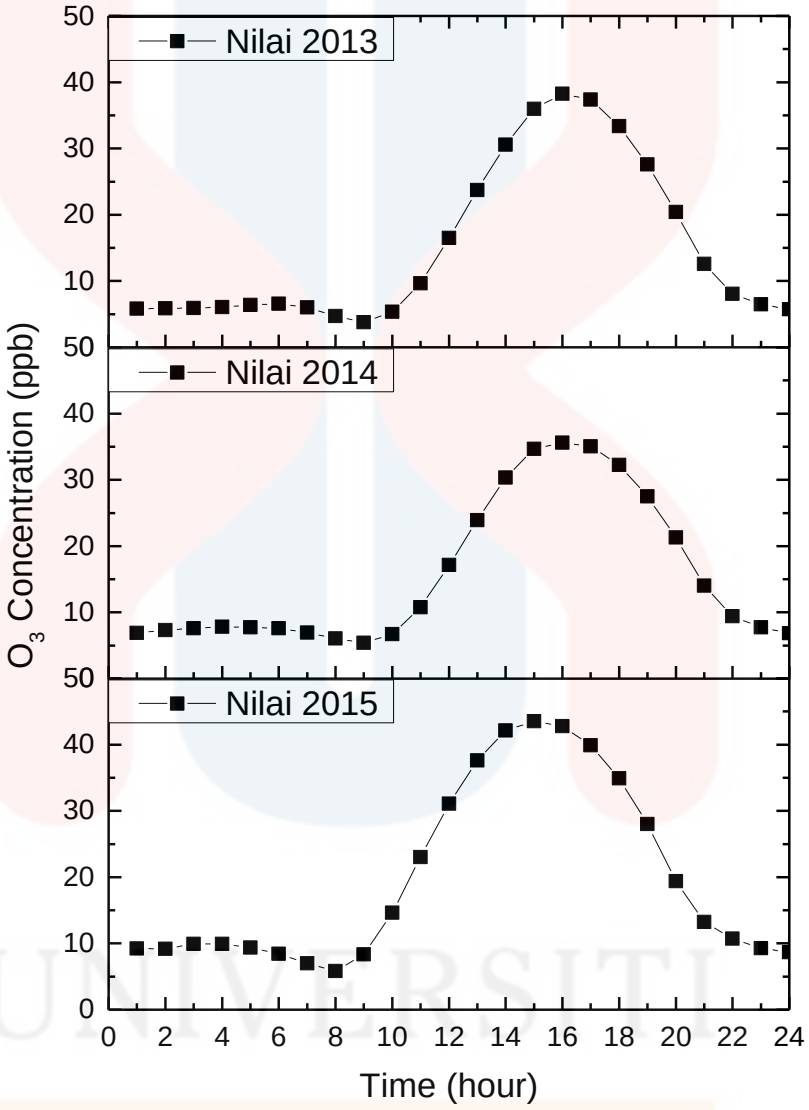

Figure 4.4 Diurnal plot of average O_3 concentration in Nilai for 2013 to 2015.

Overall, the highest peak of diurnal variation shown by Shah Alam followed by Petaling Jaya, Klang and Nilai with the lowest peak reading. Observed that the minimum concentration of GLO occurs in the night-time and early morning. The minimum concentration was consistently observed at around 8 a.m. to 9 a.m. This occurs due to titration of NO which contribute to night-time GLO sinks (Tiwary &

Colls, 2010). However, Klang in 2015 have an earliest low peak at 5 a.m., probably during this period, Klang has high rate of NO titration (Equation 2.5) which allows faster GLO sinking.

Normally during 6 a.m. to 9 a.m. is morning hustle durations, where high concentration of NO is released by vehicles. The NO released by vehicles will be oxidized and produce ozone precursor NO_2. Around 10 a.m. where sunlight intensity increases, enough energy triggers the photolysis reactions of NO_2 (equation 2.3) and resulting in GLO formation. Between 2 p.m. to 4 p.m. is when the maximum concentration is observed, as GLO concentration slowly rises after the sun rises and reaches peak concentration during these hours. After that, solar radiation intensity decreases and GLO concentration progressively decreases and remain low during night-time. Lack of solar radiation and NO deposition and titration lower the GLO concentration until early morning the next day.

4.3 Time Series Analysis of GLO and TCO

Time series of ground level ozone (GLO) and total column ozone (TCO) concentration of Klang, Shah Alam, Petaling Jaya and Nilai from 2013 to 2015 were shown in Figures 4.5 to 4.16, respectively. In this analysis, hourly data of GLO were averaged to get the daily average. Average concentration of daily GLO range between 0 ppb to 60 ppb, where lowest GLO concentration often occurs during night-time and early morning while the highest is during the afternoon. TCO have the range of concentration between 220 DU to 300 DU. This is normal for TCO as its concentration normally ranges from 200 to 400 DU and TCO lower than 220 DU indicates ozone layer depletion (Liou et al., 2002).

Klang in 2013, GLO concentration observed decreasing from January to early February. The situation can be explained as Peninsular Malaysia experiencing NEM during this month, where rainfall intensity is higher. As reported, humidity and GLO concentration have negative correlation as water washout GLO from the atmosphere (Mohamed Noor et al., 2018). However, TCO from January to early February showed an increasing trend, but still the lowest concentration of TCO throughout the year. In March the GLO and TCO show the increasing trend at usually after NEM season Peninsular Malaysia will be drier in February and more sunlight received, hence increase the GLO formation. During April the GLO and TCO drop again as this month is transitional monsoon period and rainfall increase. Then during SWM, May to September the TCO level is increasing and GLO trend dropping. In December the GLO and TCO concentration were also observed dropping.

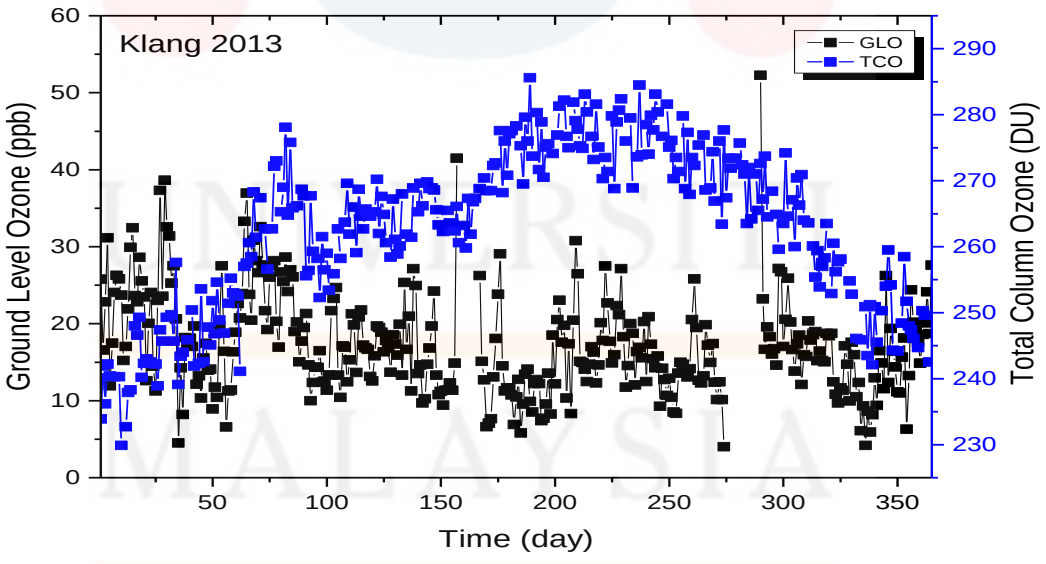

Figure 4.5 Time series of ground level ozone (GLO) and total column ozone (TCO) concentration at Klang in 2013.

In Klang 2014, the TCO concentration is obviously lower than in 2013 as the peak around 270 DU while in 2014 the peak is around 280 DU. TCO also observed an increase in March and start to drop in April then increase back in around September and October. Similarly, GLO has the highest peak in the same period as TCO. This may due to more sunny days experiences during those months. TCO concentration is on the lowest concentration at the end of the year, for Klang in the year 2014 has the lowest concentration compared to 2013 and 2015. This may be explained by heavier rainfall intensity during the end of 2014 as Malaysia also affected by tropical cyclones and typhoons (UN ESCP/WMO., 2014). Furthermore, huge flood phenomenon is also recorded in many states in Malaysia at the end of the year 2014 (UN ESCP/WMO., 2014).

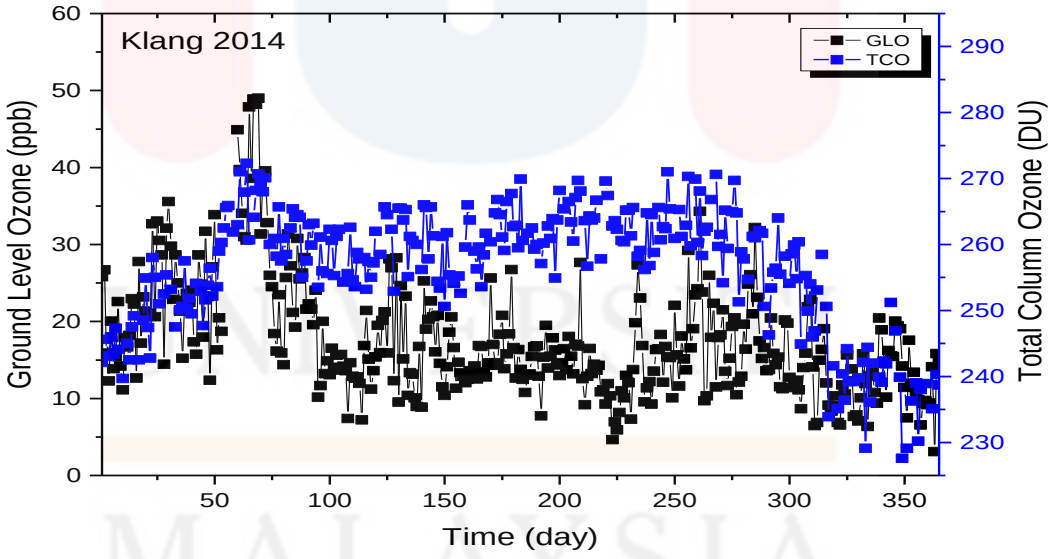

Figure 4.6 Time series of ground level ozone (GLO) and total column ozone (TCO) concentration at Klang in 2014.

In Klang 2015 (Figure 4.7), the TCO concentration gradually increases from January and reached the highest concentration in October. The highest peak of TCO in this year also raised to more than 290 DU. This situation due to the extreme El Nino which caused more sunny days and low rainfall in 2015 (Tan et al., 2017). Likewise, the GLO also have the highest concentration in October, this may be due to similar cause to high TCO concentration.

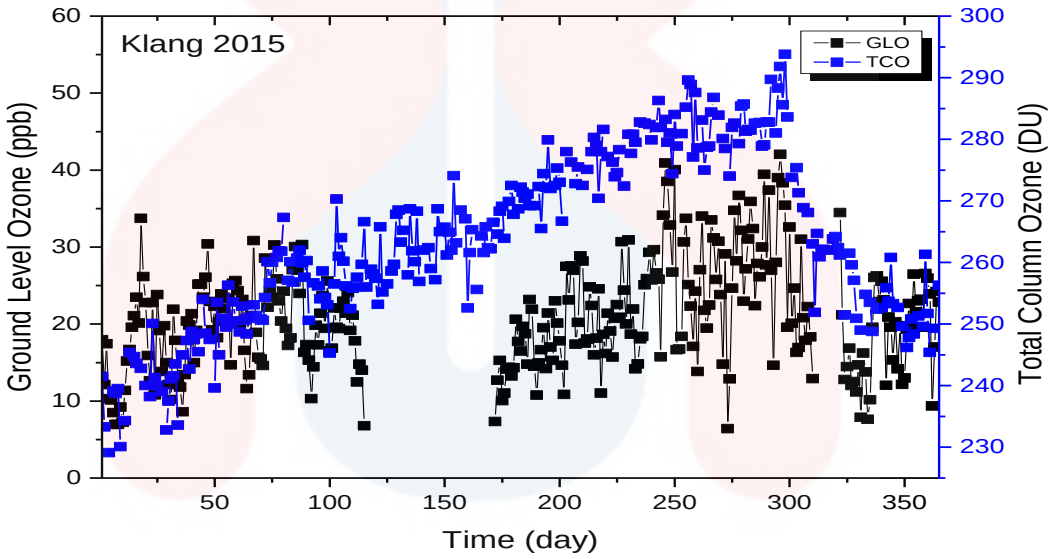

Figure 4.7 Time series of ground level ozone (GLO) and total column ozone (TCO) concentration at Klang in 2015.

Shah Alam in 2013 (Figure 4.8), GLO concentration observed decreasing from January to early February. Then, the GLO reached the highest concentration in March due to more sunny days experiences by Shah Alam throughout the year. However, TCO concentration is the lowest from January to February but with an increasing trend. In March, TCO also showed a high peak similarly to GLO. As of May to September TCO increases and started to decrease in December as rainfall increases due to NEM.

GLO also shows decrease concentration in December as the relative humidity increase and empowers GLO sinking.

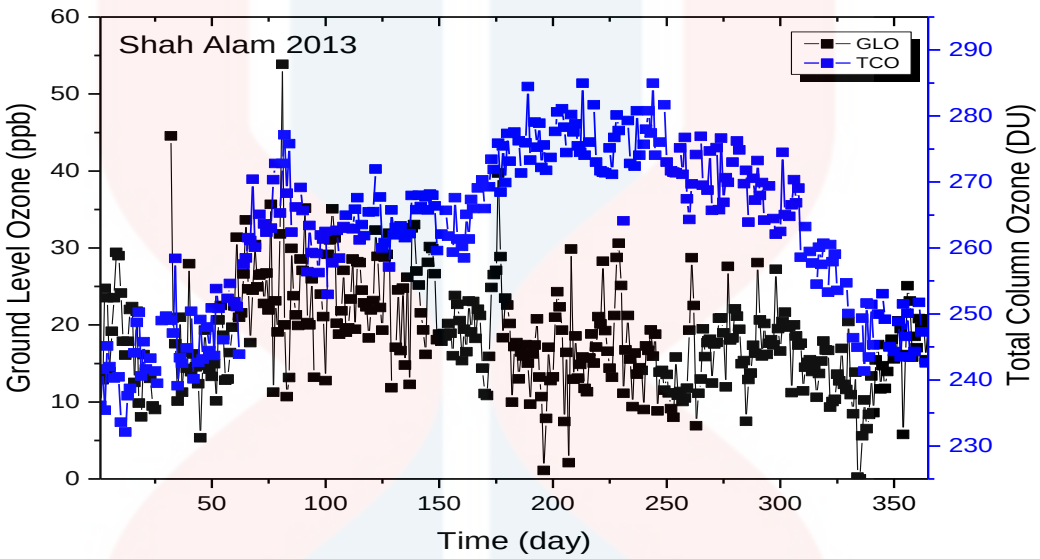

Figure 4.8 Time series of ground level ozone (GLO) and total column ozone (TCO) concentration at Shah Alam in 2013.

Likewise, in Klang, Shah Alam in 2014 (Figure 4.9) also observed with a noticeably lower peak of TCO compared to 2013 and 2015 with concentration lower than 270 DU. TCO also observed to increase in March and decline back in April. TCO observed to decrease from October to December, might be due to NEM. In contrast, GLO observed to incline in October and start to decline back after.

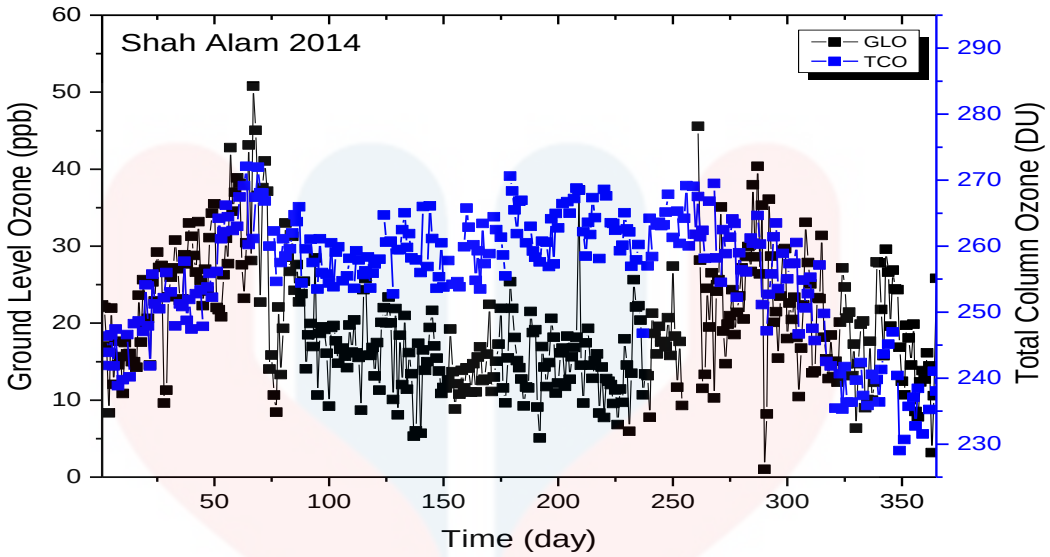

Figure 4.9 Time series of ground level ozone (GLO) and total column ozone (TCO) concentration at Shah Alam in 2014.

From the observation for time series of Shah Alam in 2015 (Figure 4.10), the TCO and GLO concentration had also gradually increased from January and reached the highest concentration in October with almost 300 DU concentration. Similarly to Klang, Shah Alam also affected by the extreme El Nino. El Nino causing the area to have more sunny hours which contributed to increase in TCO and GLO concentration. However, GLO concentration shows a declining trend in May, this causes by GLO deposition by rainfall or dilution by wind during SWM (Tan et al., 2017).

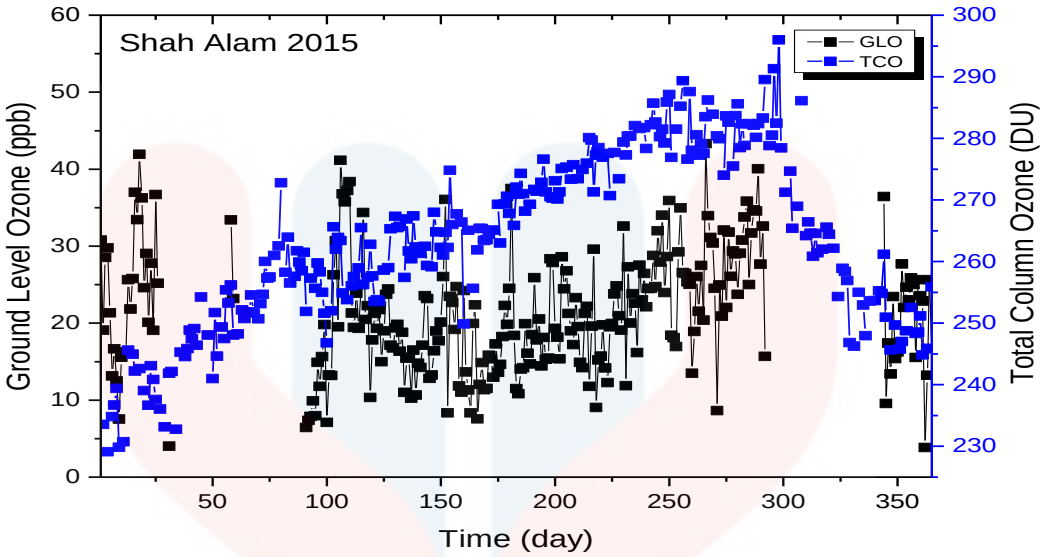

Figure 4.10 Time series of ground level ozone (GLO) and total column ozone (TCO) concentration at Shah Alam in 2015.

For Petaling Jaya in 2013 (Figure 4.11), in January and February, the GLO concentration decrease while the TCO concentration increase. TCO have the lowest concentration during early of the year. Then, TCO shows the first peak in March and decline back in April and increased from June to September. Meanwhile, GLO shows the highest concentration in August and lower concentration in September and December.

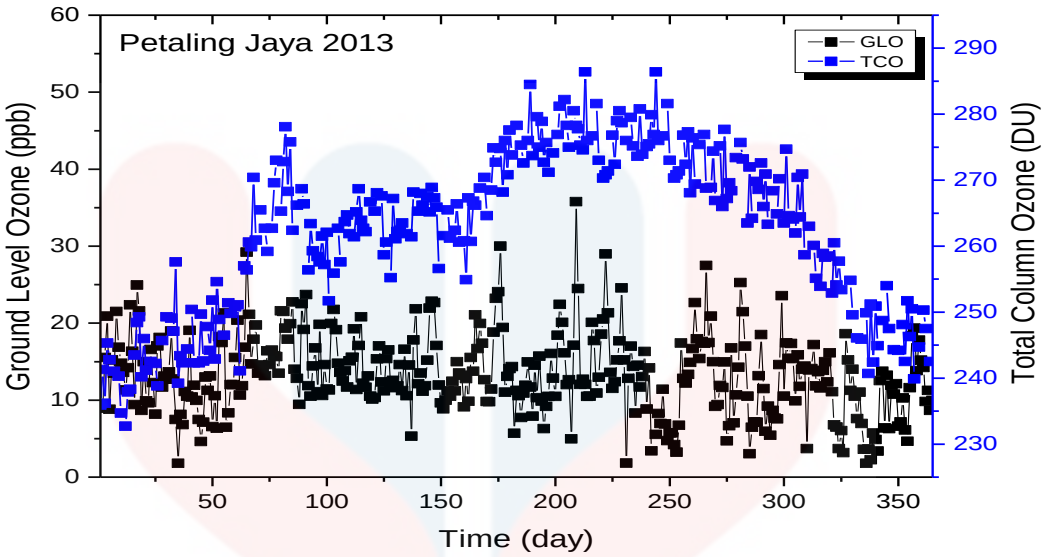

Figure 4.11 Time series of ground level ozone (GLO) and total column ozone (TCO) concentration at Petaling Jaya in 2013.

In Figure 4.12, TCO concentration in Petaling Jaya also the lowest compared to 2013 and 2015 with lower than 270 DU. However, the TCO also observed have noticeable peaks in March and October. During this year the lowest concentration of TCO observed in December and not in January which is vice versa for 2013 and 2015. GLO also observed to have noticeable peaks in March and October. Notice that both TCO and GLO increase in concentration in early December.

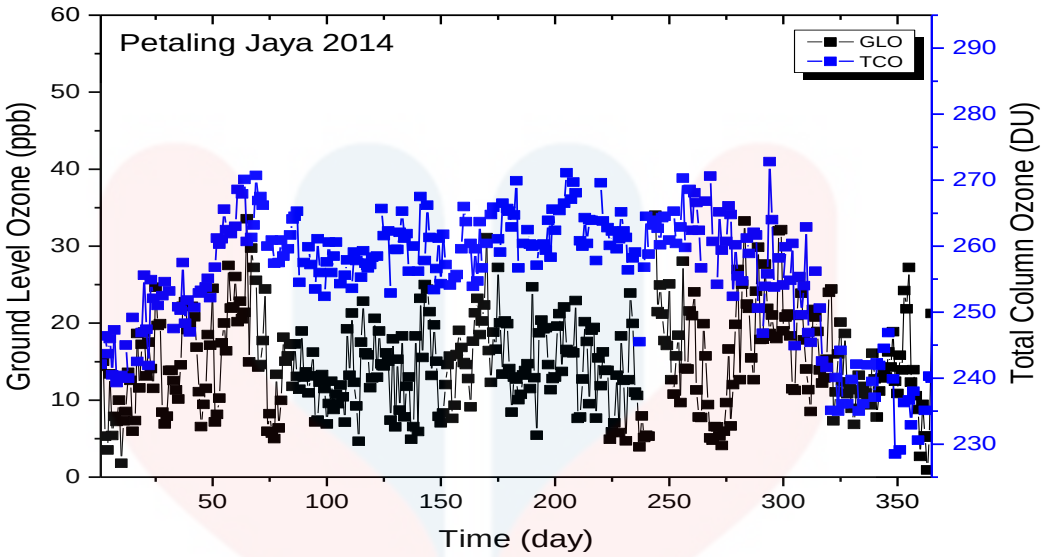

Figure 4.12 Time series of ground level ozone (GLO) and total column ozone (TCO) concentration at Petaling Jaya in 2014.

From the observation for time series of Petaling Jaya in 2015 (Figure 4.10), the TCO and GLO concentration had also gradually increased from January and reached the highest concentration in October with almost 300 DU concentration. The lowest TCO concentration is in the earlier of 2015 due to the extent of the increase of usual rainfall average during the end of the year 2014. GLO also shows observable peaks in February, May and October. This is because of during these months Petaling Jaya received more sunny days.

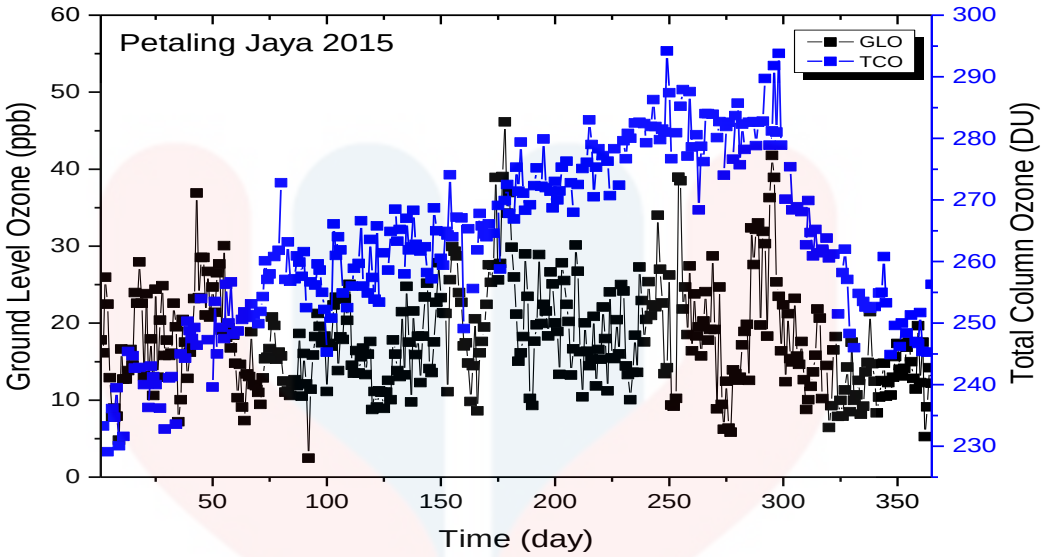

Figure 4.13 Time series of ground level ozone (GLO) and total column ozone (TCO) concentration at Petaling Jaya in 2015.

Nilai in 2013 (Figure 4.14), the TCO was shown to have the lowest concentration during early of the year. Then, TCO shows the first peak in March and decline back in April and increased from June to September. Meanwhile, GLO observed to have similar variation throughout the year.

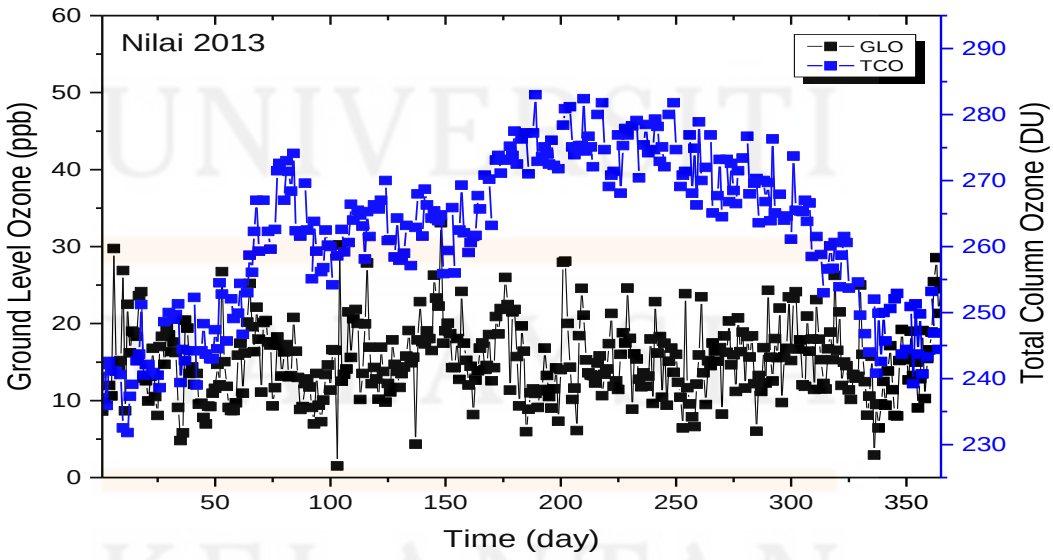

Figure 4.14 Time series of ground level ozone (GLO) and total column ozone (TCO) concentration at Nilai in 2013.

Figure 4.15 shows the time series of GLO and TCO concentration at Nilai in 2014. Similarly, Nilai also has the lowest TCO concentration in 2014 compared to 2013 and 2015 with lower than 270 DU. However, the TCO also observed have noticeable peaks in March and October. The lowest concentration of TCO observed in December and not in January which is vice versa for 2013 and 2015. GLO also observed to have noticeable peaks in January, March and October.

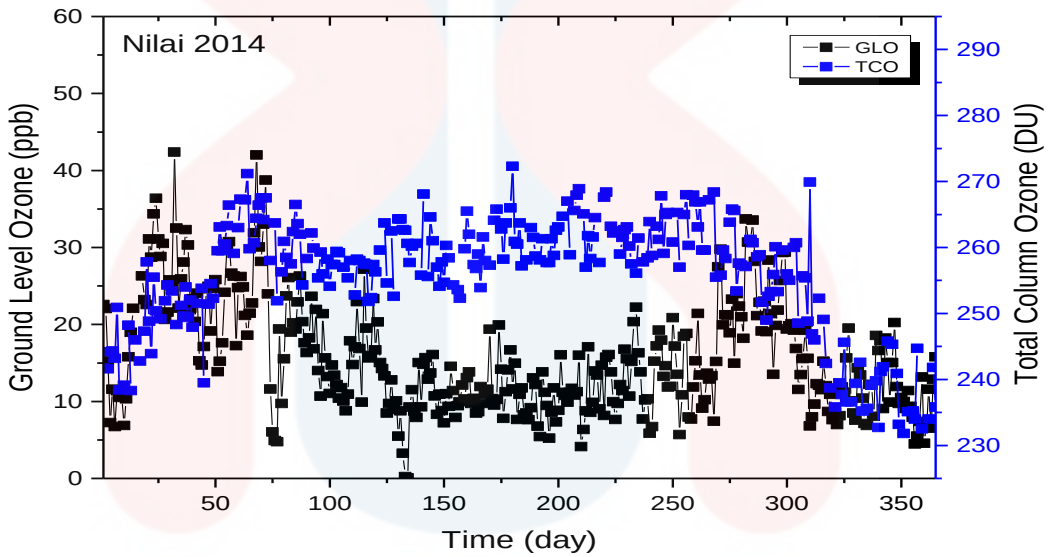

Figure 4.15 Time series of ground level ozone (GLO) and total column ozone (TCO) concentration at Nilai in 2014.

From the observation for time series of Nilai in 2015 (Figure 4.16), the TCO and GLO concentration had also gradually increased from January and reached the highest concentration in October with around 290 DU concentration. TCO also observed at the lowest concentration in January of 2015 due to the extend NEM from the end of the year 2014. GLO also shows observed show peaks in March and October.

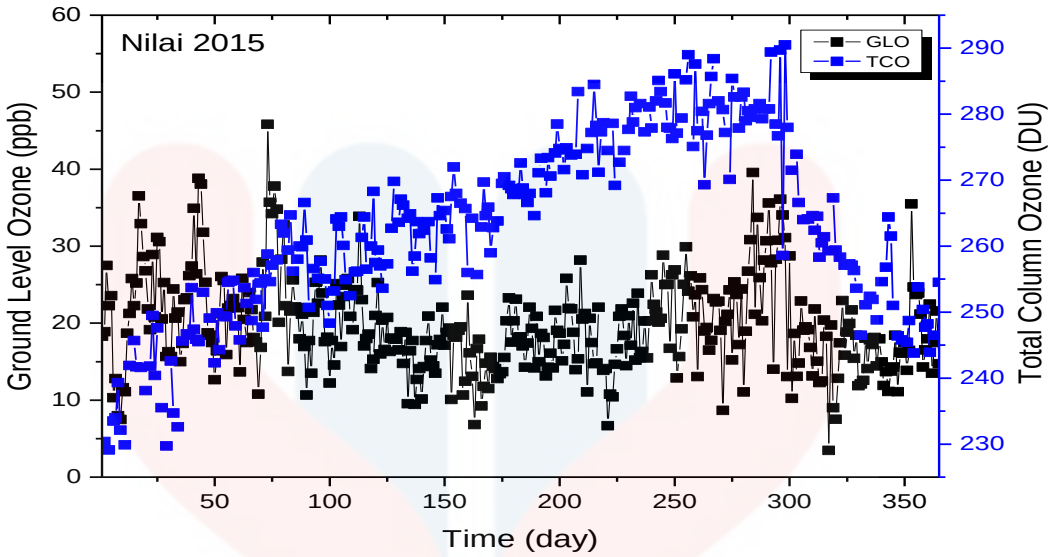

Figure 4.16 Time series of ground level ozone (GLO) and total column ozone (TCO) concentration at Nilai in 2015.

GLO concentration is correlated to temperature and wind speed but inversely correlated to humidity (Mohamed Noor et al., 2018). Normally, during monsoon seasons west coast of Peninsular Malaysia received less monthly rainfall compared to the east coast. As Klang Valley is located near to the west coast of Peninsular Malaysia, Klang Valley received less rainfall which allows high GLO concentration. However, the rainfall variation is more uniform throughout the year in spatially but differs by the monsoon season. NEM recorded more rainfall compare to SWM season (Varikonden et al., 2010). Thus, less GLO formation occurs during rainy days as the area is shielded by the thick cloud that filter UV radiation (Tan et al., 2017). Overall, GLO concentration has the highest concentration during the transitional monsoon period which may start at the end of March to April and October, where this period allows less rainfall intensity and longer sunny hours in the area. Hence, the GLO daily average higher than normal and solar radiation encourages more GLO production.

These trends of TCO are similar to a previous study (Tan et al., 2017). The values of TCO vary at different stations. TCO also affected the by NEM and SWM. TCO shows the highest concentration for all selected area during SWM because most areas in Peninsular Malaysia experience the highest temperature during this summer monsoon (Chooi et al., 2014). The peak followed by transitional monsoon period during April and October. The lowest TCO concentration observed during NEM or also known as winter monsoon. A similar trend also observed in a four-season country where TCO concentration is the highest during summer and lowest during winter (Shin et al., 2020).

As observed from figures before, the TCO concentration decline for all areas from early November and December. The declining TCO during this period caused by maximum rainfall, maximum relative humidity, minimum sunshine, and minimum temperature (Chooi et al., 2014). However, the TCO concentration starts to increase in March and April due to long sunny hours and higher temperature (Tan et al., 2017). Meanwhile, during SWM seasons from May to September for all areas the TCO increase significantly. The increasing trend even starts early SWM due to the long sunny hours with higher temperature and low rainfall.

Other than that, GLO and TCO is influenced by weather conditions and regional transport (Zhang et al., 2020). As in 2014, Malaysia weather affected by a few cyclones and typhoon throughout the year which causing higher rainfall intensity than usual and higher wind speed (UN ESCP/WMO., 2014). Rainfall and wind reduce ozone concentration by washout ozone from the atmosphere or diluted the concentration. This may have caused TCO concentration in 2014 for all areas decreased.

In 2015, El Nino has increased the ocean temperature and causes worse haze across neighbouring countries of Malaysia and Singapura. The El Nino phenomenon has delayed the monsoon rain from Indonesia cause Malaysia to received lower rainfall than usual normal. During SWM of the year 2015, Asia continent experienced summer season while Australia experience winter season. Hence, Australia exhibited low air temperature which causes high pressure. Therefore, this impacted the wind movement and forced the wind to move across the Indian ocean. Once the wind comes across equator it was deflected to the northwest before arriving Peninsular Malaysia (Masseran & Razali., 2016). Furthermore, forest fire in Indonesia during this time have transported to Peninsular Malaysia (Tan et al., 2017). This phenomenon has increased the TCO concentration in 2015 for all areas.

4.4 Correlation Analysis between GLO and TCO

The Pearson correlation is to determine the strength of linear relationship between two variables and is defined by r. Table 4.2 summarize Pearson's correlation coefficient of TCO to GLO concentration for Klang, Shah Alam, Petaling Jaya and Nilai in year 2013 to 2015.

The correlation coefficients between TCO and GLO in 2013-2015 show weak positive relation in all study areas except for Klang in 2013 and 2015which show a weak negative correlation and a moderate positive correlation, respectively. In Klang 2013, weak negative relation (r = -0.07965) would mean that GLO and TCO have inverse relation which supposedly impossible as GLO is a part of TCO. Reported in a study by Zhang et al., (2020), the tropospheric ozone have a strong positive correlation to stratospheric ozone. The negative correlation might be due to some errors in analysis. Klang in 2015 have a moderately strong correlation (r = 0.46939), the GLO

concentration moderately influencing the TCO concentration measurement. The correlation of TCO to GLO in Klang 2014, Shah Alam, Petaling Jaya and Nilai is considered weak positive correlation. That is GLO concentration only have small influences on TCO. The overall weak positive correlation is because TCO is overshadowed by the concentration of ozone in the stratosphere as 90% of the TCO is stratospheric ozone and only 10% is tropospheric ozone. However, ground level ozone may be less than 10% of the TCO as ground level only make up of 2 km above the ground (Tiwary & Colls, 2010). The correlation analysis also might have been affected by the missing data.

Table 4.2 Summary Pearson's correlation of total column ozone (TCO) to ground level ozone (GLO) concentration for Klang, Shah Alam, Petaling Jaya and Nilai in 2013-2015.

	Pearson's Correlation Coefficient r		
	2013	**2014**	**2015**
Klang	-0.07965	0.26101	0.46939
Shah Alam	0.09264	0.13820	0.21987
Petaling Jaya	0.19666	0.16365	0.29723
Nilai	0.12088	0.08943	0.04684

Figure 4.17 shows the scatter plot graph of TCO against GLO for Klang in 2013 (a), Shah Alam in 2013 (b), Petaling Jaya in 2013 (c) and Nilai in 2013 (d). This scatter plot is to visualize the slope of the graph. As discussed before Klang in 2013 (a) have a weak negative correlation between TCO and GLO, observed that the scatter plot showed a negative slope which indicated a negative or inverse relationship. Meanwhile the other scatter plot for Shah Alam in 2013, Petaling Jaya in 2013 and Nilai in 2013 (b, c and d) have a positive slope which indicated a positive relationship between TCO and GLO. All scatter plots in Figure 4.17 show that the steepness of the slope is low, which indicate a weak relation between TCO and GLO. In conclusion,

GLO and TCO have weak positive relation as GLO is only small part of TCO, however, increase in GLO still affected the TCO concentration.

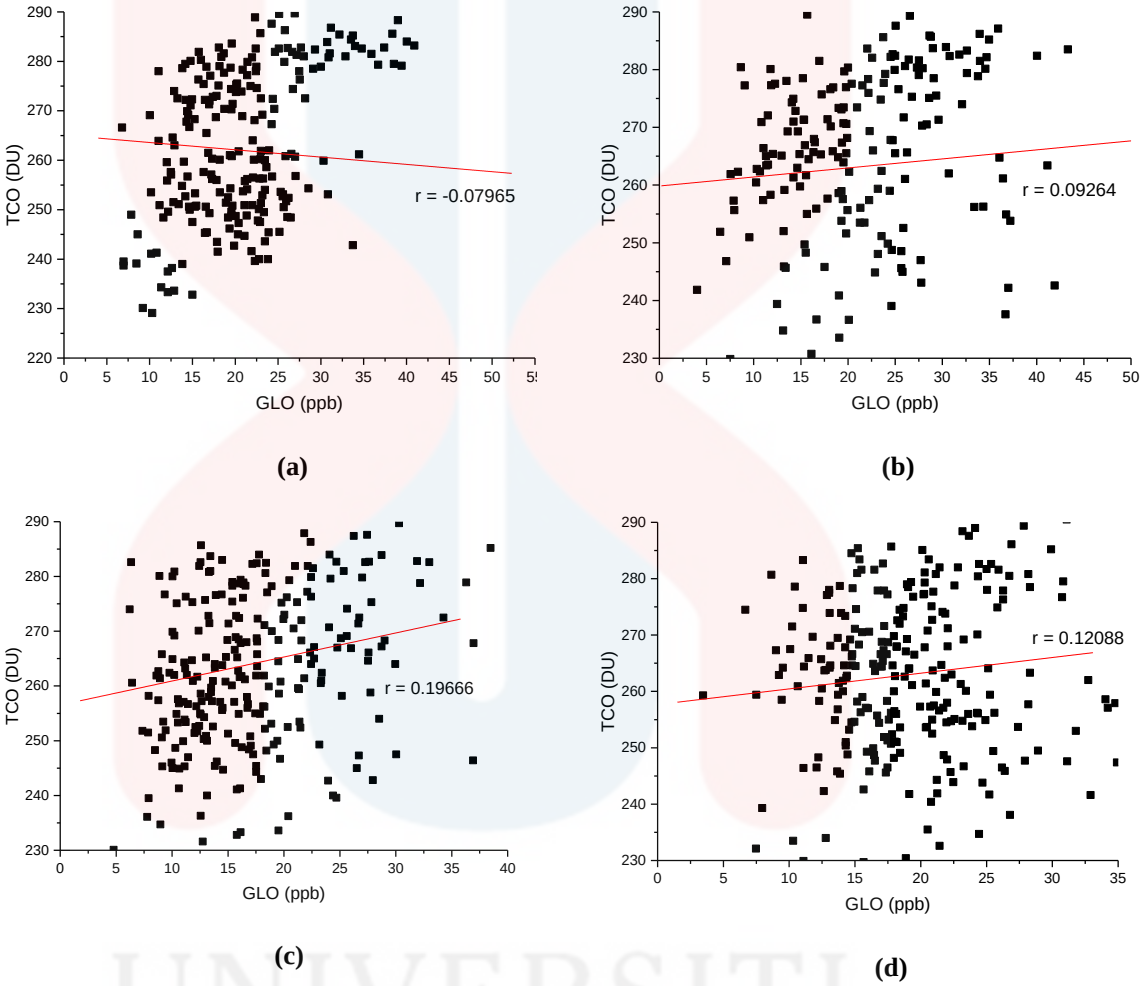

Figure 4.17 Scatter plot of TCO to GLO concentration for (a) Klang (b) Shah Alam (c) Petaling Jaya and (d) Nilai in 2013.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This study analysed the TCO and GLO concentration in Klang Valley, namely included Klang, Shah Alam, Petaling Jaya and Nilai from 2013 to 2015. In this study, the GLO concentration using standard method have been determined. Data of GLO concentration measured using UV absorption Ozone Analyzer Model 400A which applied the UV photometry method acquired from DOE. The study showed that all four location have maximum GLO concentration more than 90 ppb which are the recommended limit in NMAAQS (2020). Klang station exhibited GLO maximum concentration (98 to 122 ppb), Shah Alam (119 to 41 ppb), Petaling Jaya (116 to 123 ppb) and Nilai (106 to 119 ppb). Meanwhile, the daily TCO concentration has been retrieved from OMI satellite data range from (234 to 290 DU) over Klang Valley.

The diurnal variation of GLO is determined. GLO is highly influenced by its precursor NO and VOCs. The GLO diurnal cycle has peaked in the afternoon (2 p.m. to 4 p.m.) and lower concentration during night-time. GLO lowest peak is during the early morning (7 a.m. to 9 a.m.), the earliest lowest peak observed in Shah Alam 2015

at 5 a.m. The diurnal variation of GLO also have a higher peak in 2015 than in 2013 and 2014 for all location, which indicates increase in GLO over year.

The GLO and TCO trend in Klang Valley were investigated. The daily TCO and GLO concentration has been retrieved from OMI satellite data is used to investigate the annual trend of TCO over Klang Valley from 2013 to 2015. The TCO concentration for selected four stations shown seasonal variation. The trend resulting in seasonal change of NEM and SWM. TCO concentration observed to have higher concentration during the dry season or SWM. This is due to the high temperature and more sunny hours during SWM. Contrary, TCO concentration is lower during NEM. This is because of the low temperature, high rainfall, high relative humidity and less sunny hours which lead to lower TCO concentrations. In addition, TCO concentration influences by weather and regional transport. The higher concentration of TCO in 2015 affected by El Nino extreme hot weather and the transboundary haze from forest burning in Indonesia. Meanwhile, lower concentration in 2014 caused by colder weather with high rainfall and low temperature that leads to lower TCO concentration. GLO also observed to have the highest concentration mostly during the transition monsoon period, where these months received more sunny hours which contribute to high GLO formation and accumulation.

The correlation between GLO and TCO is determined. The correlation between TCO and GLO is weakly positive ($r = 0.05 – 0.30$). This may due to the small portion of GLO from TCO. GLO make up 2 km from the Earth surface, if tropospheric ozone is 10 % of the TCO, GLO is a smaller percentage than tropospheric ozone. Other than that, missing data of GLO and TCO may also affect the correlation between these two data sets.

5.2 Recommendation

As an extension to this study, appropriate risk assessment analysis might be needed due to the exceeding GLO concentration to the NMAAQS (2020) exposure to the human population in Klang Valley. This study is limited to the west coast of Peninsular Malaysia. As TCO is affected by NEM and SWM, further study must cover wider area in Malaysia as the monsoons affect the weather differently depending on the location in Malaysia such as the west coast, east coast and inland. Other than that, it is recommended to use interpolation to acquire the OMI data as the closest coordinate may not be accurate for the TCO data of selected location. Besides, validation of the OMI data to ozonesonde data is also recommended as ozonesonde is the baseline for remote sensing ozone measurement. Ozonesonde also has high vertical resolution and high accuracy. In addition, further studies can include investigations on the vertical distribution of ozone as vertical distribution is influenced by different parameters which could enhance the correlation analysis.

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