INTERRELATIONS AMONG OZONE, ITS PRECURSORS AND METEOROLOGICAL PARAMETERS

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgments, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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(NUR LIYANA BTE LOKMAN)

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ABSTRACT

Air is one of the basic elements needed for survival of any living things on earth. The quality and cleanliness of air is vital to sustain life and prevent health problems. Air pollution has long been recognized as an international problem as air may move from one place to another without boundaries. A secondary air pollutant, lower ground ozone, brings a threat to humans, plants and animals. According to Awang et.al (2013), there are areas in Malaysia which recorded high number of ozone gas case exceedences. Despite massive and costly control efforts, even countries in Europe and North America still experience severe ozone problems (Wu & Chan, 2001). The increase in human activities, development and urbanization contributes in increasing the ground level ozone. In this study, the interrelations among ozone, its precursors and its meteorological parameters in oil and gas industry is determined. This study is conducted in an oil and gas environment where the data of concentrations of nitrogen oxide, nitrogen dioxide, ozone and meteorological parameters such as temperature, humidity, wind speed and direction are obtained from Department of Environment Malaysia. The equipment used at air quality stations is the Aeroqual AQM60 Environmental Station. This instrument is custom built to measure common air pollutants including ozone, nitrogen dioxide, carbon monoxide, sulphur dioxide, particulate matter and meteorological parameters. Data is taken from 5 different air quality stations which have been identified closest to oil and gas industry area. 3 years of data was analyzed and modelled using time series analysis. From the analyzed data, the concentration of ozone gas and its precursors at oil and gas industry was found to have exceeded the Malaysian Ambient Air Quality Guidelines (MAAQG) quite a number of times in a year period. It was also concluded that surrounding temperature is related to the concentration of pollutants.

CHAPTER 1

PROJECT BACKGROUND

1.1 Introduction

Air is a mix of natural gases that surrounds the earth atmosphere. It is the basic need of all living things on earth. Generally, air consists of 78 % nitrogen, 21 % oxygen and the other 1 % is a mix of other inert gases (Wakamatsu et al., 1974). Carbon dioxide is another important constituent in air which covers around 0.1 % to 0.3 %. Oxygen gas allows mankind to breathe, and its byproduct, carbon dioxide allows plants to respire, therefore allowing life. Besides sustaining life, air plays a role in combustion, energy production, allows chemical reactions to occur etc. Thus, maintaining the quality of air has never been more vital. However, rapid development and urbanization globally has caused the quality of air to be compromised.

Air pollution occurs when the air contains gases, dust, fumes or odor in harmful amounts which might cause health problem or discomfort to humans or animals or might cause damage to plants and materials (Harrop, 2003). Pollutants may be of natural origin or man-made. Man-made pollutants for example carbon dioxide and sulphur dioxide are coming from combustion while natural origin pollutants may originate from natural disasters such as volcanic eruptions. However, man-made pollutants from human activities are the ones causing air pollution to become one of the major threats to the world. These pollutants come from the industry, motor vehicles, open burnings, fumes from hair spray and aerosol spray, waste deposition in landfills and military sources such as nuclear weapons.

In Malaysia, the monitoring of air quality is done by The Department of Environment (DoE) continuously and manually. This is done by a network of 51 Continuous Air Quality Monitoring (CAQM) stations placed strategically around the country (Department of Environment, 2014). These stations are divided into 5 categories; industrial, residential, traffic, background and particulate matter (PM_{10}). Parameters measured by CAQM stations and their categories are shown in Table 1.

Table 1: Parameters Measured by Different Categories of CAQM (Department of Environment, 2014)

Category	Sulphur Dioxide	Nitrogen Dioxide	Carbon Monoxide	Ozone	Hydrocarbon	PM_{10}	UV
Industrial	X	X	-	-	X	X	-
Residential	X	X	X	X	X	X	X
Traffic	X	X	-	X	X	X	-
Background	X	X	X	X	X	X	X
PM_{10}	-	-	-	-	-	X	-

Air pollution index (API) measures the ambient air quality and is developed for easy reporting and documentation of the quality of air daily. The index gives ranges and its effect on human health rather than the actual concentrations of air pollutants for the public's ease of understanding. The Malaysian API system closely follows the Pollutant Standard Index (PSI) developed by the United States Environmental Protection Agency (US-EPA). API is calculated based on 5 major pollutants; sulphur dioxide, nitrogen dioxide, carbon monoxide, particulate matter less than 10 micrometers (PM_{10}) and ground level ozone. Ranges of API and its status are shown in Table 2.

Table 2: Air Pollution Index Flowchart (Department of Environment, 2014)

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

In Malaysia air pollutant has been seriously monitored which leads to the implementation of an air quality standard, Malaysia Ambient Air Quality Guideline (MAAQG) to address major air pollutants (Table 3) in the country. Measurements of air pollutants are monitored and reported for assessment of human health effects. An average time of 1 hour, 8-hours, 24 –hours, 12-months and 3-months are the time-

weighted average exposure standards which gives the average airborne concentration of a particular pollutant that is permitted over a time.

Table 3: Malaysian Ambient Air Quality Guideline (MAAQG) (Department of Environment, 2014)

Pollutant	Average Time	ppm	($\mu g/m^3$)
Ozone	1 Hour 8 Hour	0.10 0.06	200 120
Carbon Monoxide	1 Hour 8 Hour	30.0 9.0	35** 10**
Nitrogen Dioxide	1 Hour 24 Hour	0.17 0.04	320
Sulphur Dioxide	1 Hour 24 Hour	0.13 0.04	350 105
Particulate Matter (PM_{10})	24 Hour 12 Month		150 50
Total Suspended Particulate (TSP)	24 Hour 12 Month		260 90
Lead	3 Month		1.5

Note, **= mg/m^3

In general, air pollutants can be divided into two categories, primary and secondary pollutant. Primary pollutants such as carbon monoxide and sulphur dioxide are pollutants emitted directly from a source whereas secondary pollutants are those formed when primary pollutants react with sunlight in the atmosphere. Secondary pollutants such as lower ground ozone are less given attention as it is an indirect pollutant.

On a global basis, the World Health Organization (WHO) estimates 800,000 people per year die from the effects of air pollution (EPA, 2013). Air pollution causes many different types of diseases mainly involving respiratory. Besides health threats, air pollution are also responsible to effect the environment by contributing to global warming. Air pollution also accounts for an estimated of several billion dollar crop loss every year in the United States alone (Mc. Kee, 1993).

The presence of this secondary pollutant in the air increases the risk of both acute (short term) and chronic (long-term) health effects to humans (McKee, 1993; Afroz et al., 2003). Even at low levels, ozone can affect those with lung disease, children, elderlies and people who are active outdoors by reducing lung function and inflame the linings of the lungs. Constant exposure may permanently scar lung tissue. Besides that, high and long term exposure to ozone will damage agricultural crops, forests and ecosystems. Malaysia's Department of Environment has set Malaysian Ambient Quality Guidelines (MAAQG) which addresses major air pollutants including ozone and nitrogen dioxide to monitor and assess the quality of air. However, there are no law enforcements to reduce the emission of ozone gas.

Ozone is high in concentration mainly in industrial areas due to the production and emission of its precursors; nitrogen dioxides and volatile organic compounds. This also includes the oil and gas industry. The oil and gas industry are one of the main sources of nitrogen oxides. The air quality impacts of oil and gas exploration and production are the subject of increasing scrutiny (Olaguer, 2012). The maintenance, startup, shutdown, emissions and flares emit large amounts of nitrogen oxides. Flares releases approximately 82 % off all pollutants discharged into ambient air by the oil industry in the region of Mexico (Villasenor et al., 2003). Given the possible impact of large facilities, they may contribute several parts per billion to 8-hr ozone during exceedances.

1.2 Problem Statement

Ozone has been recognized as a major air pollutant and a threat to humans, plants and animal life (Hewitt et al., 2009). According to Awang et.el (2013), there are areas in Malaysia which recorded high number of ozone gas case exceedences. Despite massive and costly control efforts, even countries in Europe and North America still experience severe ozone problems (Wu & Chan, 2001). The increase in human activities, development and urbanization contributes in increasing the ground level ozone. Even though it has been half a century since ozone was first identified as a significant, phytotoxic, gaseous air pollutant in South California (Lefohn, 1992), the interrelations among ozone and its precursors is relatively less researched here in Malaysia. Kuwait, being one of the major oil exporting country did a study regarding the emissions of gaseous pollutants to minimize the emissions of major pollutants to the state of Kuwait and neighbors countries (Al-Hamad & Khan, 2008). The Mexican oil industry in Campeche Sound, southeast Mexico also did an air quality emission inventory for their offshore operations. The precursor of ozone, nitrogen oxides, was one of the air pollutants screened during this study. In addition, the Houston Advanced Research Center did a study on the decreasing air quality due to increased drilling of oil and gas industries in Texas. In this study, ozone modelling was done to show ozone attainment at areas significant with oil and gas industries. However, till today, there are no studies done regarding ozone concentrations in oil and gas facilities in Malaysia. To safeguard the environment, one should have a thorough knowledge of gaseous emissions resulting from the daily basis combustion activities under different operational conditions in oil and gas industry (Al-Hamad & Khan, 2008). Thus, to predict and avoid non-desirable effects of ozone and reduce ozone pollution, it is vital to understand the relationship of ozone and its precursor, nitrogen oxides.

1.3 Objectives

This study has four main objectives:

i. To obtain the levels of nitrogen oxides (NO and NO_2) and ozone gases in an oil and gas industry
ii. To determine the relationship between nitrogen oxides (NO and NO_2) and ozone as its precursor over a time period
iii. To study the relationship of meteorological parameters such as wind, temperature and humidity and the levels of nitrogen oxides (NO and NO_2) and ozone gases.
iv. To model the concentrations of ozone in oil and gas industry by using time series analysis

1.4 Importance of Study

Air is one of the basic elements needed for survival of any living things on earth. The quality and cleanliness of air is vital to sustain life and prevent health problems. Air pollution has long been recognized as an international problem as air may move from one place to another without boundaries. The understanding and full knowledge of a certain pollutant is important. By research and studies, method of reducing or prevention of high emission of any pollutant may be developed. In this case, the study of ozone is crucial as the number of case exceedences in Malaysia is quite high (Ishii, Bell, & Marshall, 2007). As the oil and gas industry is one of the major contributors to lower ground ozone, detailed studies and researches must be done. This secondary pollutant will cause many health problems towards the oil and gas workers and also to the surrounding civilians if no precaution is taken. Besides that since air pollutants are airborne particles, the destruction of crops will occur in the future if no control over the amount of nitrogen oxides and volatile organic compounds emitted are taken. In the booming industry of oil and gas, the environmental effects, mainly air pollution has always been looked out to.

1.5 Scope of Study

This study will take place nearby an oil and gas onshore platform, located in Kerteh, Terengganu. The data taken from Department of Environment is a 4 year period data. For this study, three pollutants will be analyzed; nitrogen oxide, nitrogen dioxide and ozone. The study of ozone at oil and gas platforms has never been done before in Malaysia, thus will help the oil and gas companies in their health, safety and environment knowledge.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

The oil and gas industry contributes a number of air pollutants such as nitrogen dioxide, sulphur dioxide, carbon monoxide, carbon dioxide and VOC's. Since nitrogen dioxide is a precursor of ozone, the probability of high ozone concentrations in the oil and gas industry will be high. The meteorological factors such as sunlight presence and favorable wind conditions at the oil and gas industry environment helps promote the formation of ozone. Thus, understanding the precursors of ozone is vital in order to improve the quality of air.

2.2 Ozone

Ozone is a highly reactive, colorless, secondary pollutant gas consisting of three atoms of oxygen. A German-born professor of chemistry at the University of Basel, Switzerland, Christian Friederich Schönbein was first to discover ozone in 1839 (Nardo, 1991). Nardo (1991) described ozone as two-faced as it is considered a pollutant at the troposphere but at the upper level ozone, it is considered essential to the existence of life. Ozone at the upper atmosphere is considered as good ozone as it helps protect the earth from UV rays. However, the lower ground ozone is taken as bad ozone as it affects human health and the environment (Hewitt et al., 2009). Ozone is an odorless but highly reactive gas which is 1.6 times heavier than air (Ghazali, et al., 2009). Lower ground ozone is a result of photochemical reaction of volatile organic compounds (VOCs) and oxides of nitrogen with the presence of sunlight under preferable meteorological conditions. Nitrogen oxides and volatile organic compounds both are produced mainly from vehicle and industry emissions. Due to the increase in both pollutants by time, the amount of ozone produced increases causing ground level ozone to be the most significant air pollutant (Awang, 2013). Besides being a threat by its own, ozone also contributes in the global warming as it is a greenhouse gas.

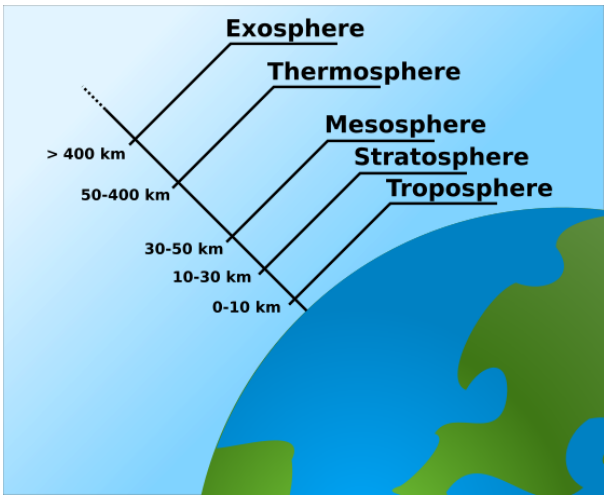

Figure 1: The Earth Atmosphere Layers

The earth's atmosphere can be divided into five main layers, as shown in Figure 1; exosphere, thermosphere, mesosphere, stratosphere and troposphere. Ozone is present in both the stratosphere and troposphere layer. However, stratosphere ozone should not be considered a photochemical air pollutant (Ghazali et al., 2009), even though it contains relatively high concentrations of the gas. Stratosphere ozone serves as a protective layer that shield's the earth from the sun's dangerous ultraviolet radiations. It filters out sunlight wavelengths from about 200 nm UV rays to 315 nm. Ozone in the stratosphere is produced when high energy ultraviolet rays of wavelengths less than 240 nm hits oxygen, splitting it into two single atoms. The free oxygen atoms then combine with oxygen molecules to form ozone (ESRL, 2010). The formation is illustrated in equation (1) and (2). hν in the equation refers to radiant energy from the sun

$$O_2 + h\nu \rightarrow O\ (^3P) + O\ (^3P) \qquad (1)$$

$$O\ (^3P) + O_2 \rightarrow O_3 \qquad (2)$$

Troposphere is the lowest layer of the earth's atmosphere where life exists. It composes of 80 % of atmosphere mass and 99 % of its water vapor and aerosol. The air in the troposphere contains primary and secondary pollutants. Primary pollutants are emitted directly from the sources whereas secondary pollutants are produced by reaction of those primary pollutants with the environment. The two main precursors of the formation of ozone are VOCs and nitrogen oxides which are both emitted mainly from the industry. Other mechanisms for the formation of tropospheric ozone

include stratospheric injection and processes that influence the abundance of nitrogen dioxide (Ghazali, 2010). Surrounding conditions which are favorable in the production of ozone such as high temperatures and low wind may lead to higher concentrations of ozone gas. This explains why ozone concentrations vary throughout the year and from year to year (Ghazali et.al, 2009).The formation of ozone begins with the exposure of nitrogen dioxide to radiant energy (sunlight) to break it down into nitric oxide and two low energy oxygen atoms (Ramli et al.,2010). When nitrogen dioxide is exposed to UV light of wavelength less than 424 nm, an oxygen atom and a nitrogen oxide molecule are generated via the nitrogen dioxide photolysis reaction (Lawrence, 2003). The free oxygen atom will then combine with oxygen in the air to form ozone. The formed ozone will then react with nitrogen oxide to produce nitrogen dioxide and oxygen. The formation is illustrated in equation (3), (4) and (5).

$$NO_2 + h\nu\ (\lambda<430\ nm) \rightarrow NO + O\ (^3P) \quad (3)$$

$$O\ (^3P) + O_2 \rightarrow O_3 \quad (4)$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (5)$$

VOC plays the role of converting nitrogen oxide into nitrogen dioxide without breaking ozone by combining 'free radicals' to produce a product that is not a radical thus preventing the cycle to repeat (Ghazali et al., 2010). Equation (6) and (7) illustrates the process. R in the equation refers to hydrocarbons, a class of VOCs.

$$RO_2 + NO \rightarrow RO + NO_2 \quad (6)$$

$$NO_2 + OH \rightarrow HNO_3 \quad (7)$$

Based on recent research, the tropospheric ozone levels in the country are reportedly high and there are a number of exceedences cases where the levels are higher than the Malaysian Ambient Air Quality Guideline (MAAQG). According to EPA, studies show that ozone causes many respiratory problems such as uncomfortable sensation in chest, reduce in lung function, aggravate asthma, inflame and damage the lining of the lungs. In addition to that, ozone may also aggravate chronic lung diseases such as emphysema and bronchitis. Literally thousands of studies have described a wide array of effects ranging from transient reductions in

lung function and symptoms to the irreversible changes in lung structure which may result in accelerated decline in lung capacity and premature mortality (McKee, 1993). Figure 2 illustrates the death attributes to outdoor air pollution in the year 2008. Malaysia has around 6-10 deaths per 100000 population and a part of it might be caused by ozone either due to short term or long term effect.

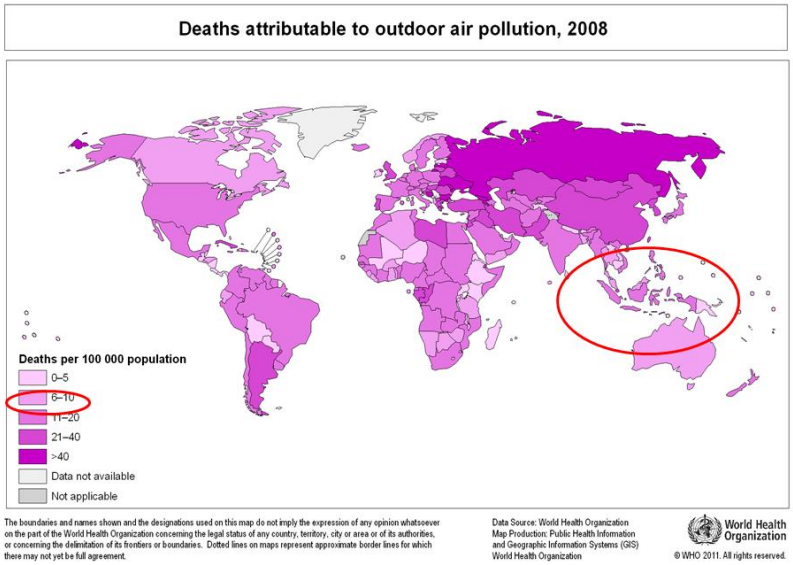

Figure 2: Death Attributes to Outdoor Pollution (WHO, 2010)

2.3 Nitrogen Oxides (NO_x)

Nitrogen oxide is referred to nitric oxide and nitrogen dioxide. Approximately 90 % of the emissions from combustion sources are nitrogen oxide rather than nitrogen dioxide, however, since nitrogen oxide can potentially oxidize to nitrogen dioxide they are collectively referred as nitrogen oxides (NO_x) (Ghazali et al., 2009). Nitrogen dioxide is the product of industrial synthesis of nitric acid which is produced millions of tons per year. It has a reddish-brown color with a characteristic sharp biting odor. Nitrogen dioxide is mainly sourced from internal combustion engines, thermal power system, and from the household, kerosene and gas heaters. Nitrogen dioxide is known for its toxicity even by inhalation. However, due to its odor, nitrogen dioxide inhalation can be avoided. According to World Health Organization (WHO), epidemiology studies show that symptoms of bronchitis in asthmatic children in association with long term exposure to this gas

and will reduce lung function growth (WHO, 2011). Short term exposure may cause significant inflammation of the airways.

Nitric oxide (NO) is a by-product of combustion from automobile engines, fossil fuel power plants and is produced naturally during electrical discharges of lightning in thunderstorms. It is a colorless gas which can rapidly oxidize into nitrogen dioxide. The process is illustrated in equation (8).

$$2\ NO + O_2 \rightarrow 2\ NO_2 \qquad (8)$$

The levels of nitrogen oxides in the air keep rising due to the increase number of vehicles and the progress of urbanization in the country. The increasing level of urbanization can be seen in Figure 3. Besides causing health problems, nitrogen oxide in the air may convert into nitric acid which causes acid rain.

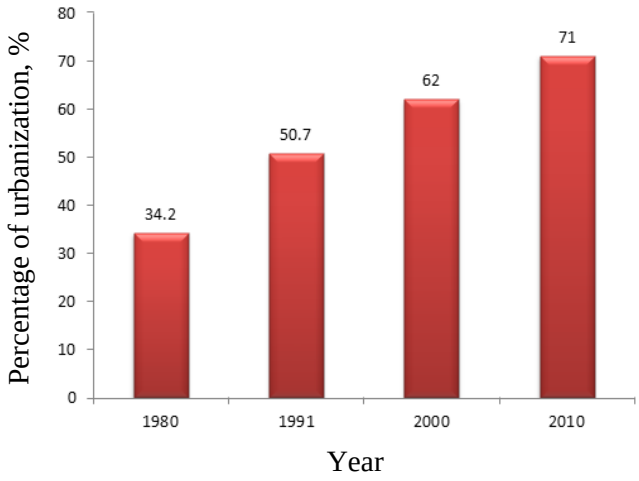

Figure 3: Level of Urbanization in Malaysia (Department of Statistics Malaysia, 2010)

The Environmental Protection Agency (EPA) in the United States has defined VOC as any compound that participates in atmospheric photochemical reactions and has vapor pressure greater than 10 Pa at 25 ˚C, a boiling point of up to 260 ˚C at atmospheric pressure and 15 or less carbon atoms (Koppman, 2007).

2.4 Issues Related to Ozone

Ozone is currently emerging to become one of the main pollutant concerns in Malaysia (Awang et al., 2013). The increase in sources of ozone precursors has been increasing the production of ozone under the influence of sunlight and other meteorological precursors. In Malaysia, the levels of ozone in urban, industrial areas are the highest in concentration as to rural areas (Ramli et al., 2010; Ghazali et al., 2010) due to its airborne properties. Some of the studies in Malaysia demonstrate that ozone concentrations and predictions modelling are best done using linear regression models and time series. Both methods are beneficial in indicating maximum ozone concentrations due to its simplicity (Ghazali et al., 2008).

Ozone precursor arises from natural mobile and stationary sources (Mohammed et al., 2012; Awang et al., 2013; Afroz et al., 2003) which also includes from the oil and gas industry. From previous research, it is sure that oil and gas activities may have significant impact to low ground ozone, through either regular emissions or flares and other emission event associated with process upsets, and perhaps also maintenance, startup and shutdown of oil and gas facilities (Olaguer, 2012). Among the most important emission sources from the oil and gas industry are flares, discharges to water, cuttings from drilling activities and crude oil spills (Villasenor et al., 2003). A mixture of nitrogen dioxide and nitric oxide are emitted during combustion processes with largest part being nitrogen oxide (Hofele, van Velzen, Langenkamp, & Schaber, 1996).

The study by Olagues, E.P. (2012) done in Texas produced a model that predicts the ambient ozone emissions associated with compressor engines from oil and gas industry in the Barnett Shale under average midday conditions in June. The study showed that the amount of peak 1-hr ozone in the oil and gas industry may exceed 3 ppb approximately 2 km or more downwind, depending on the extend of nitrogen oxides titration and inhibition. Flare volumes of 100000 cubic meters per hour of natural gas over a 2-hour period also contributes over 3 ppb to peak 1-hour ozone 8 km away downwind of the oil and gas facility.

A four month research by Sonibare et al. (2009) at petroleum production facilities around Niger Delta, Nigeria at a distance of 50 – 500 m from the petroleum flow stations showed that over 97% of the measured concentrations of nitrogen

dioxide were below 0.66 ppm which implies that the air quality is in the good category of air with no health alarm. However, at the distance of 60 m away from the flow stations, the air quality was described as very unhealthy with an AQI (air quality index) of 210. Nigeria is presently the leading gas flaring country in the world which can be identified as a major source of air pollutants for the country.

In addition to that, an air quality emission inventory study was done by the Mexican oil industry to assess the impacts of emissions from their offshore operations in the area of Campeche Sound, southeast of Mexico. This study considered 174 offshore platforms and a few compression stations (Villasenor et al., 2003). This study focused more on sulphur dioxide emissions, however, nitrogen dioxide was still measured and modelled. The maximum hourly of nitrogen dioxide concentrations recorded were well below the regulatory limit of 0.21 ppm. However, this only represents a glimpse of the range of nitrogen dioxide concentrations at the monitoring site. Villasenor et al. (2003) stated that nearly 660000 tons of pollutants are emitted into ambient air per year from that area itself and 52 % of total emissions are nitrogen oxides.

Kuwait is also a major oil producing country and their economy depends on export of crude and refined products. A study by Al Hamad and Khan (2008) to find out the total emissions of pollutants from flaring activity in Kuwait was done to minimize the amount of gas flared and reduce the emission of pollutants in the state of Kuwait and neighboring countries. Similar to the study by Villasenor, this study does not focus on lower ground ozone pollution and its precursors, but to all main pollutants emitted during flaring such as carbon dioxide, carbon monoxide, sulphur dioxide, nitrogen oxides, methane and VOC's. It was found out that total emissions of pollutants from flaring activity in the oil and gas industry continues to increase by year due to the increase in demand.

In addition to that, as much as ozone affects human health, it is also currently the most important air pollutant that negatively affects growth of both agriculture and native species in most parts of the world (Feng & Kobayashi, 2009). The study area for this project is located near to agriculture areas therefore; the effects of ozone towards the crops must be taken into account. Many researches have been done to study the yield reduction of crops such as paddy, wheat, corn and other plants due to

the concerns of increasing concentrations of ozone in the ambient air which would largely reduce food production in the future. The food demand of the global population will be affected. Ozone affects the crops by increasing respiration rates, reduced photosynthesis and growth and much more (Feng & Kobayashi, 2009; Ishii, Marshall, Bell, & Abdullah, 2004). In Selangor, studies showed that the ozone level is above the given European limits and the extent of yield losses could have ranged from 1.6 to 5.0 % (by weight) in 2000 (Ishii et al., 2004). An experimental study done on paddy cultivars at Klang Valley has shown a yield reduction of 6.3 % when grown in the non-filtered air from that area. Although not all crops shows equal effect towards ozone, this issue must be taken seriously as it involves the food supply for the population and directly affects global economy (Reilly, 2007). In contrast to that, a study by Hewitt et al. (2009), showed that oil palm plantations in Malaysia also gives a hand in the emission of oxides of nitrogen and volatile organic compounds at a high rate instead of being affected by ozone. It is sourced from vehicle exhaust, combustion at the palm oil processing plant and substantial soil nitrogen fertilization in the plantation.

To conclude, to date, there are no researches done in Malaysia on air pollution in oil and gas industry. Thus, this research is done to understand the formation of ozone due to the activities of oil and gas industry in Malaysia.

CHAPTER 3

METHODOLOGY

3.1 Location of Study

This study is to model the concentrations of ozone gas in the oil and gas industry in Malaysia. It will be done at PETRONAS Kerteh Refinery located in Kerteh, Terengganu. The refinery processes 49,000 barrels of Malaysian light, sweet crude oil per day making it a suitable study area. Figure 4 shows the location of the study area. Kerteh is located in Peninsular Malaysia; in the state of Terengganu which is about 2 hours' drive to the south of Kuala Terengganu. Started with a small town, the booming oil and gas industry has made Kerteh an oil and gas town. Besides oil and gas, Kerteh is located nearby to Teluk Kalong's industrial area which makes Kerteh a suitable location for this study.

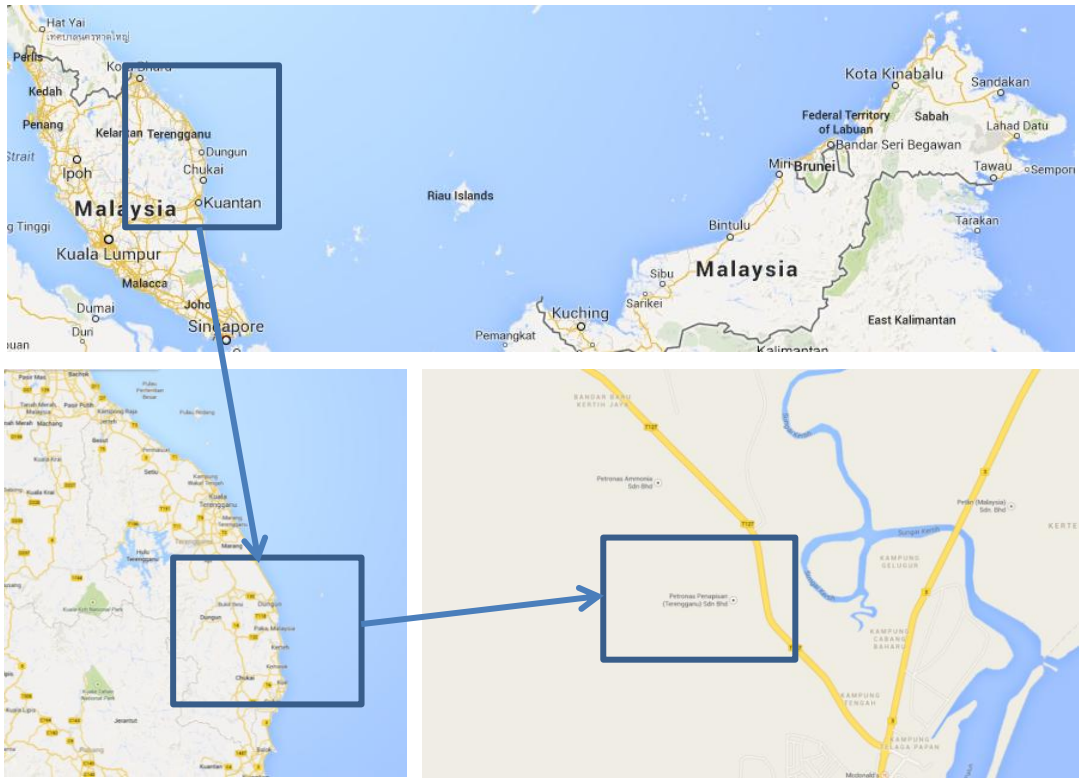

Figure 4: Study Area

3.2 Data Obtained from Department of Environment

The concentration of pollutants (ozone, nitrogen oxide and nitrogen dioxide gas) is obtained from DoE where the equipment used is the Aeroqual AQM60 Environmental Station as shown in Figure 5. This instrument is custom built to measure common air pollutants including ozone, nitrogen dioxide, carbon monoxide, sulphur dioxide and particulate matter. It is also capable to measure and record meteorological parameters such as temperature, humidity, wind speed and direction. Ozone module the nitrogen oxides module of the AQM 60 uses the principle of gas sensitive semiconductor (GSS).

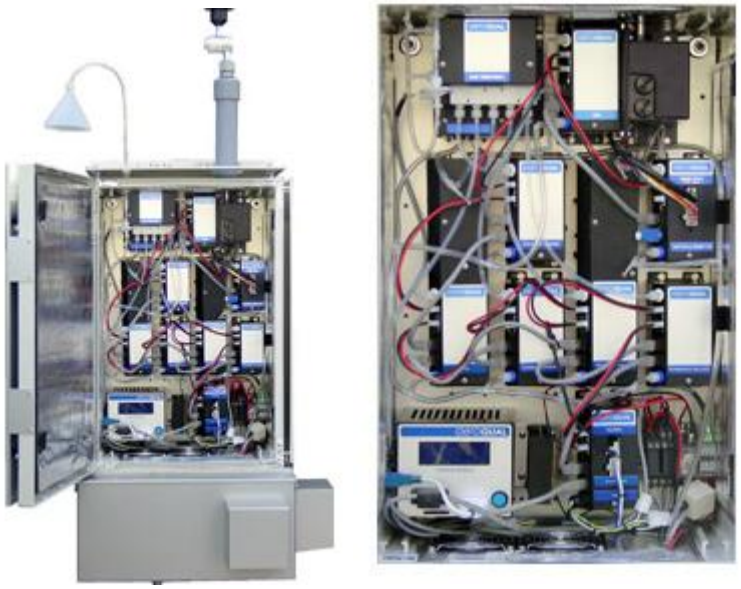

Figure 5: Aeroqual AQM60 Environmental Station

3.3 Analysis of Data

3.3.1 Time Series Analysis

Time series is a collection of observations of well-defined data items obtained through repeated measurements over time. Usually time series data contains repeated patterns of variation, and identifying and quantifying the scale of the repeated pattern is often the focus of the analysis. The objective of time series analysis includes, to obtain data compression, explanatory on seasonal factors (wind) and relationships with other variables (temperature, humidity) and the prediction of future values.

In this study, nitrogen oxides and ozone data of 3 years are analyzed. Thus, the fluctuation of ozone, its precursors and meteorological parameters can be observed.

3.4 Gantt Chart and Key Milestone

This study flow will be according to the Gantt chart in Table 4 and Table 5 to ensure the project is progressing according to the time frame given.

Table 4: Project Gantt Chart and Key Milestone for FYP 1

No		1	2	3	4	5	6	7	MID SEMESTER BREAK	8	9	10	11	12	13	14
1	Selection of project topic	■	■													
2	Preliminary research work		■	■	■	■										
3	Submission of extended proposal						○									
4	Proposal defense									■	○					
5	Project work continues											■	■	■		
6	Submission of Interim Draft Report														○	
7	Submission of Interim Report															○

○ Key milestone ■ Process

Table 5: Project Gantt Chart and Key Milestone for FYP 2

No		1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Project Work Continues	■	■	■	■	■	■	■	MID SEMESTER BREAK								
2	Submission of Progress Report																
3	Project Work Continues						○			■	■	■	■	■			
4	Pre-SEDEX												○				
5	Submission of Draft Report													○			
6	Submission of Dissertation (soft bound)														○		
7	Submission of Technical Paper														○		
8	Oral Presentation															○	
9	Submission of Project Dissertation (Hard Bound)																○

○ Key milestone ■ Process

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

Data on the concentration of ozone, nitrogen oxide, nitrogen dioxide, surrounding temperature and humidity were obtained from Department of Environment Malaysia (DOE). Sampling is done hourly for each pollutant and meteorological parameter at 5 different Continuous Air Quality Monitoring (CAQM) stations located at Paka, Jerantut, Bintulu, Miri, and Station B. Data has been analysed from 2008 to 2010. The coordinates for Paka, Jerantut, Bintulu and Miri stations are stated in Table 6.

Table 6: CAQM Locations

Station ID	Station name	Longitude	Latitude
CA0007	Pej. Kajicuaca Batu Embun, Jerantut	N03°58.238	E102°20.863
CA0024	Kaw. Industri Paka	N04°35.880	E103°26.096
CA0028	Sek. Men. Dato Permaisuri Miri, Sarawak	N04°25.456	E114°00.731
CA0027	Balai Polis Pusat Bintulu, Sarawak	N03°10.587	E113°02.433

Figure 6: Location of Continuous Air Quality Monitoring Stations

These four stations are located around 2 km to 12 km away from oil and gas industry facilities, however, due to the distance and meteorological factors, the

concentration of pollutants recorded were quite low. The raw data received from DOE were processed into hourly data and the readings from the four stations stated in Table 6 is attached in Appendix A. Throughout the analysis of three years (2008 to 2010), the year 2010 was chosen for detail analysing as it has the highest pollutant records from the four years. Thus, records from stations namely Station B which is located much closer to oil and gas facilities, in Kerteh, Terengganu will be used and analysed in this study.

4.2 Comparison of Air Pollutants Concentrations from Station B with Background Station

4.2.1 Concentration of Air Pollutant at Station B

Figure 7 shows the monthly average concentration of ozone, nitrogen oxide and nitrogen dioxide gases for Station B for the year 2010. It is observed that the concentration of ozone is the highest in June with the reading of 0.29 ppm. The next month, July, the concentration of ozone drops to the lowest value for the entire year with a reading of 0.14 ppm. In January and February, the concentrations of ozone were higher than the average values with 0.20 ppm and 0.24 ppm respectively. However, for the rest of the year, the average monthly concentration of ozone does not changes much as it ranges around 0.14 ppm to 0.16 ppm. The average monthly concentration of ozone for 2010 recorded at Station B is all above the Malaysian Ambient Air Quality Guideline (MAAQG), 0.06 ppm.

Average daily concentrations of nitrogen oxide and nitrogen dioxide for the year 2010 at Station B both are the highest in the month of April with 0.024 ppm and 0.027 ppm respectively and lowest in the month of July with 0.012 ppm nitrogen oxide concentration and 0.015 ppm nitrogen dioxide concentration. Comparing the three gases, nitrogen dioxide has the highest concentration throughout the year, except for the month of June where ozone's concentration increased tremendously. However, the concentrations of nitrogen dioxide in 2010 are still below the MAAQG limits of 0.04 ppm.

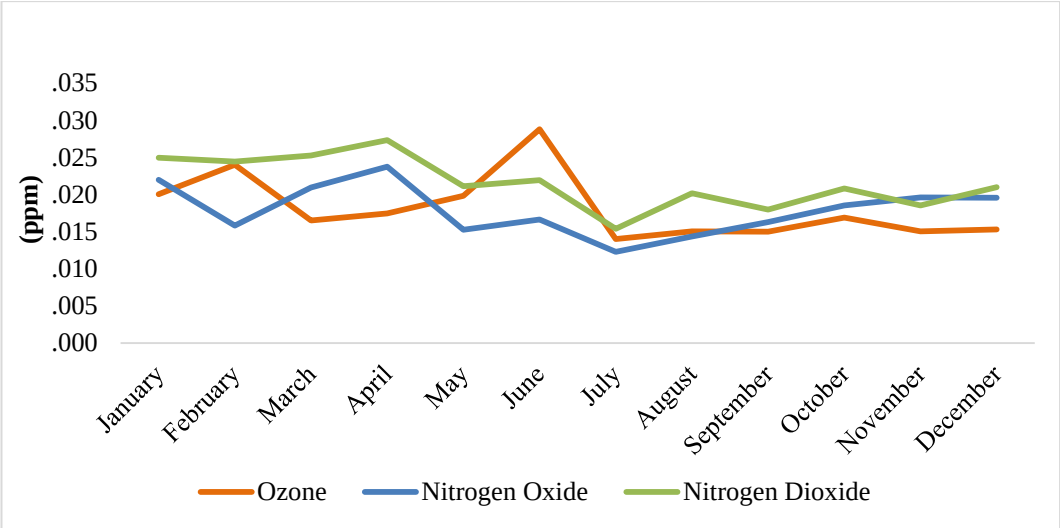

Figure 7: Concentration of Air Pollutants at Station B

4.2.2 Concentration of Air Pollutant at Background Station

DOE has designated its CAQM in Jerantut, Pahang as a background station to provide insight into seasonal variations in pollutant concentrations and for any comparison purposes and benchmarking with other stations nearer to anthropogenic emissions (Latif et.el, 2013). It is located at an area of natural ecosystem and low population. Figure 8 represents the monthly average concentration of air pollutants at Jerantut Station for the year 2010. Throughout the whole year, it can be observed that the concentrations of the three gases maintains at an average level. The concentrations of nitrogen oxide and nitrogen dioxide are too low and can be disregarded. The concentration of ozone gas was recorded the highest during the month of August with readings of 0.015 ppm and lowest during the month of December with readings of 0.009 ppm.

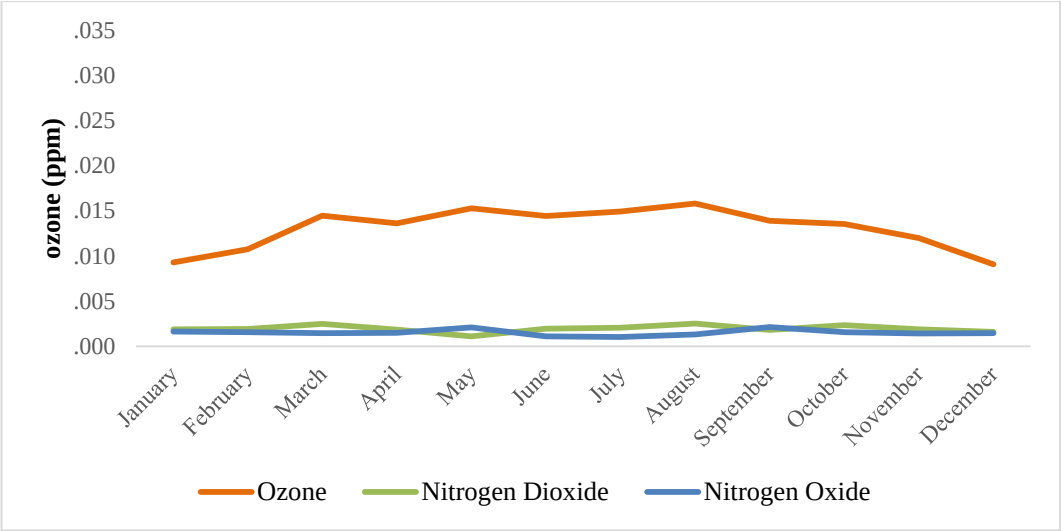

Figure 8: Concentration of Air Pollutants at Jerantut Station

4.2.3 Discussion

The concentrations of ozone, nitrogen oxide and nitrogen dioxide gas in the air is higher at Station B compared to samples at Jerantut Station. The levels of nitrogen oxide and nitrogen dioxide are multiple times higher at Station B than of Jerantut Station. The location of Station B which is close to Kerteh's industrial area which is mainly oil and gas industries may be one of the main factor of the high level of pollutants. Nitrogen dioxide levels are higher compared to nitrogen oxide as oxidation occurs. This reaction is then promoted with favourable meteorological conditions. In addition to that, the formation of ozone is also higher in Kerteh. Ozone levels in Kerteh almost triple the levels in Jerantut Station. The high amount of the main ozone precursors coming from the industry nearby may result in this high formation of ozone gas. However, it is observed that even at the background station, Jerantut still has measurable amounts of ozone gas which may be brought over by wind factors. The Meteorological Service Singapore reported of increased number of hotspot counts in Peninsular Malaysia for June 2010 together with the developing stages of El Nino (dry season) which may cause the levels of ozone increased abruptly. Since there are obvious differences in concentrations of air pollutants when comparing Station B to the background station, the discussion at the next part will use Station B for analysing.

4.3 Ozone

Ozone concentrations vary throughout the year due favourable conditions such as high temperatures and low winds. Figures 9 to 12 show the daily maximum ozone concentrations, surrounding temperature and humidity for months in the year 2010. The figures for the rest of the months are in Appendix B. From the figures, it can be seen that the concentration of ozone is directly proportional to temperature. However, the concentration of ozone is not directly affected by humidity. In most months, the pattern of ozone concentrations is likely to follow the pattern of surrounding temperature. Taking for example Figure 9, in January, the days when the maximum hourly temperature is high, the concentration of ozone is also high and vice versa. However, ozone is also affected by other precursors and meteorological parameters. Thus, in Figure 10 and Figure 11, for the month of May and June, there are days where even though the temperature is lower than normal, the ozone concentration still remains.

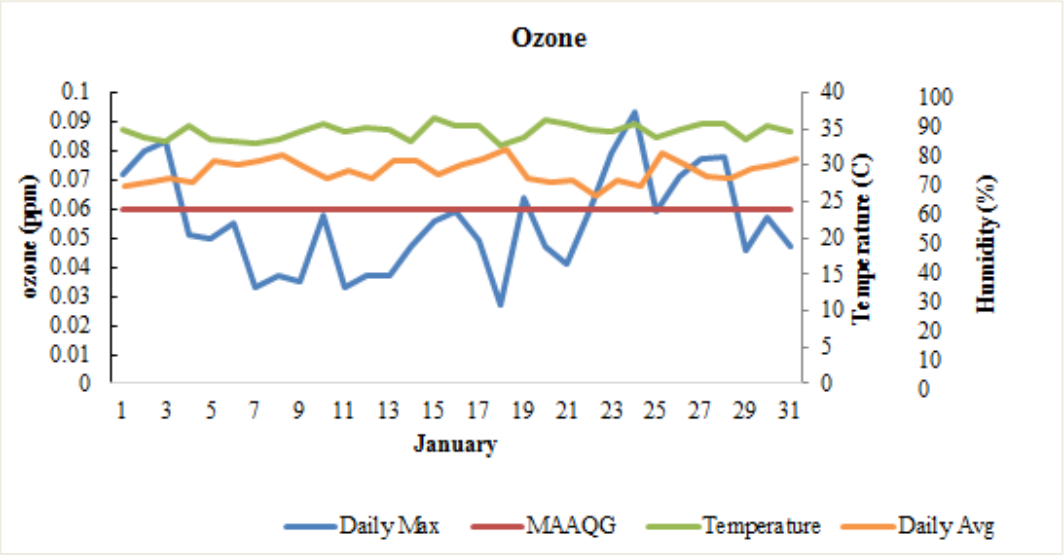

Figure 9: Ozone concentration for January 2010

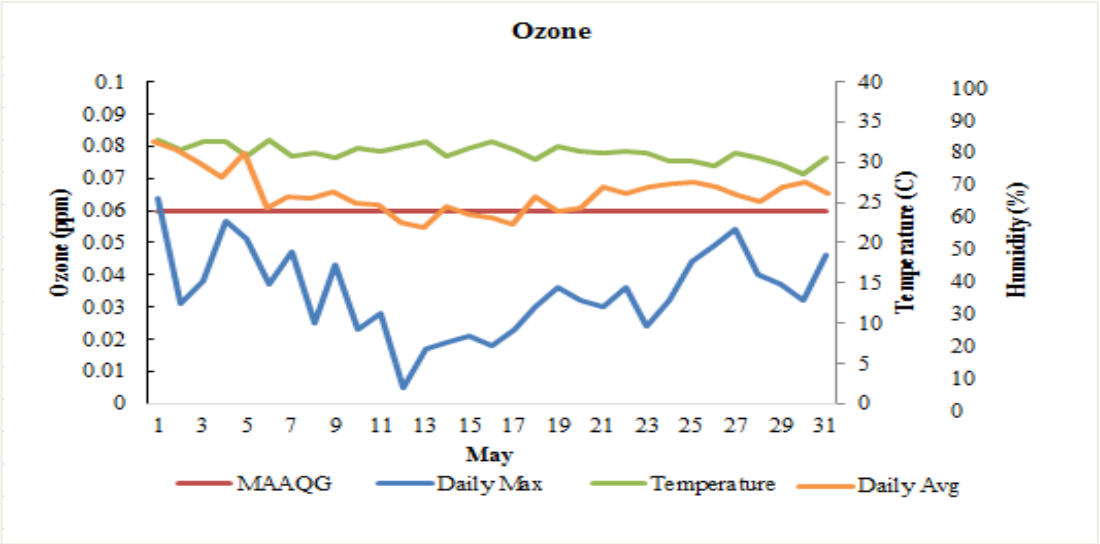

Figure 10: Ozone concentration for May 2010

The month with the highest average daily concentration of ozone for the year 2010 is June with 0.029 ppm shown in Figure 11. The highest concentration recorded for this month is on 20th June, with the concentration of 0.064 ppm and the lowest is 0.04 ppm which occurred on the 7th, 17th, 24th and 30th June. The highest concentration exceeded the MAAQG by 0.004 ppm. Even though June is recorded as the highest daily average for ozone concentration in 2010, there are only two days that it exceeds MAAQG 8-Hour Average Time. The month with the lowest average monthly concentration recorded is in July (Figure 12), with a concentration of 0.014 ppm. Due to technical error, there are some missing data for July. The highest daily concentration recorded for this month is 0.049 ppm on 1st July and the lowest concentration is on the 19th, with 0.005 ppm.

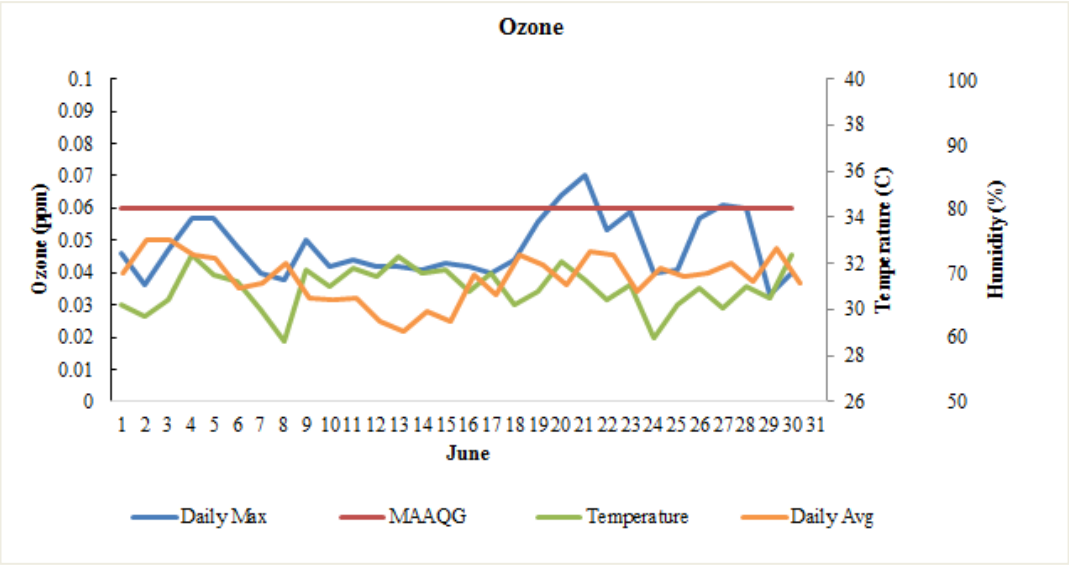

Figure 11: Ozone concentration for June 2010

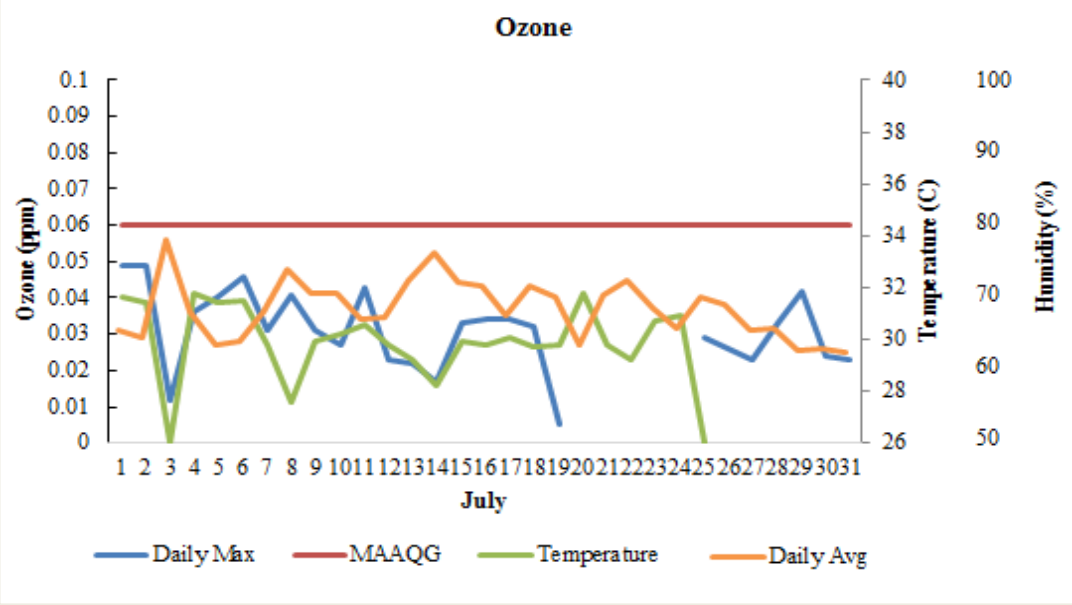

Figure 12: Ozone concentration for July 2010

4.4 Nitrogen Oxide

The concentration of nitrogen oxide keeps rising throughout the years due to increase urbanization and the increase in number of vehicles. Nitrogen oxide may convert into nitric acid which causes acid rain or oxidizes to nitrogen dioxide. The oil and gas industry are one of the main contributors of nitrogen oxide to the air. Data for nitrogen oxide were recorded and sorted into daily maximum concentrations. MAAQG does not have any guidelines for this particular gas. Figure 13 and Figure 14 shows the daily maximum concentrations of nitrogen oxide, surrounding temperature and humidity for the highest and lowest concentration months in the year 2010. The rest of the results are in Appendix B.

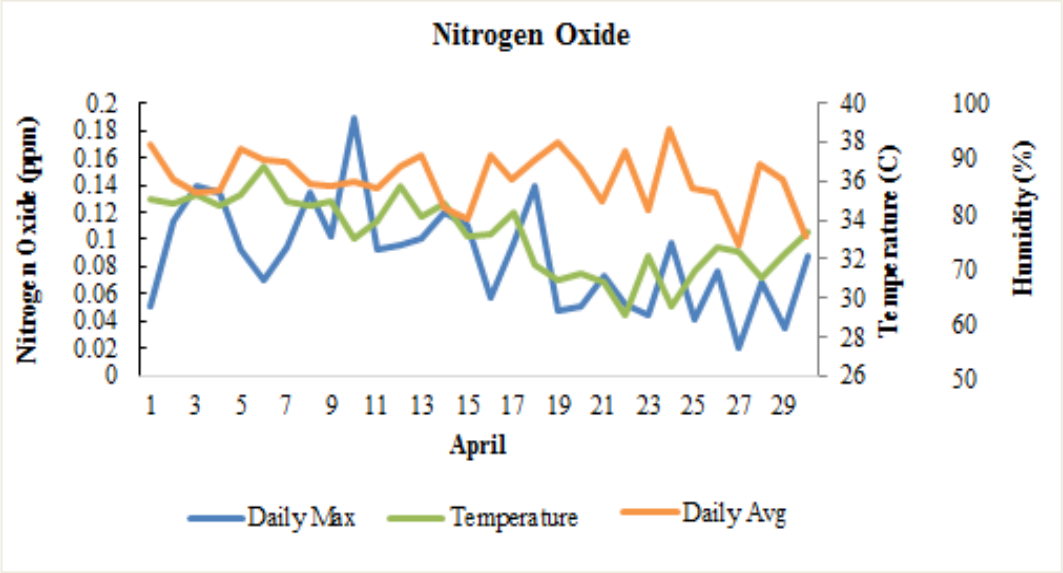

Figure 13: Nitrogen Oxide Concentrations for April 2010

In 2010, April had the highest monthly average concentration for nitrogen oxide with 0.024 ppm. Figure 13 shows the daily maximum and daily concentration of nitrogen oxide for April. Daily maximum concentration pattern shows two peaks of 0.189 ppm on the 10th of April and 0.097 ppm on the 24th. The lowest daily nitrogen oxide recorded on the 27th, with 0.02 ppm. For the lowest monthly concentration, July recorded a 0.012 ppm concentration. There are two peaks as seen in Figure 14 which occurred on the 2nd and 12th July with concentrations of 0.095 ppm and 0.097 ppm respectively. The results show that the concentration of nitrogen oxide is not affected by the surrounding temperature and humidity of the area.

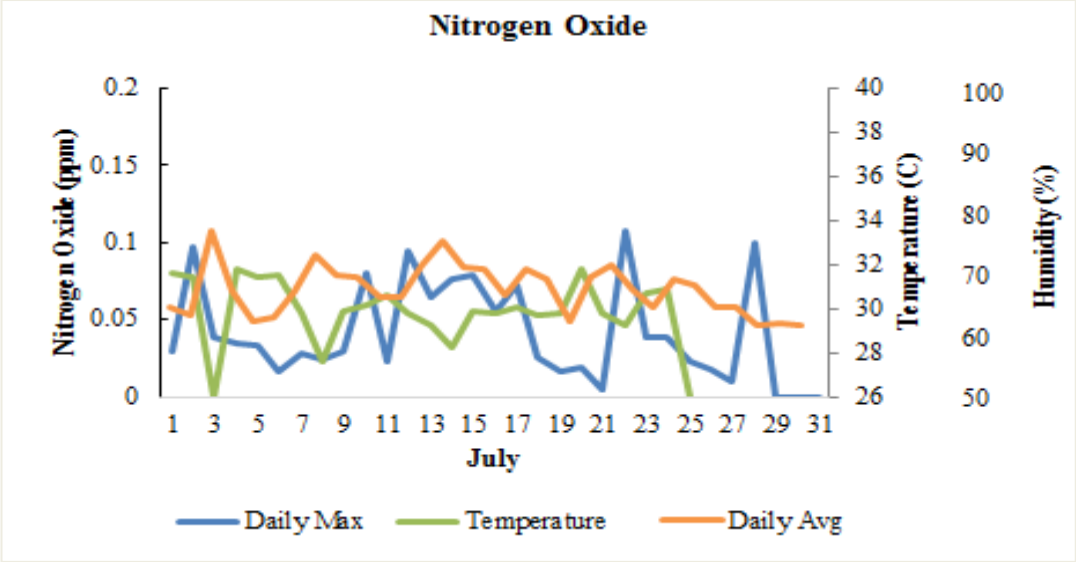

Figure 14: Nitrogen Oxide Concentrations for July 2010

4.5 Nitrogen Dioxide

Figure 15 and Figure 16 illustrates the daily maximum concentration of nitrogen dioxide for the months with the highest and lowest concentration in the year 2010 recorded by Station B. Daily maximum concentration pattern for each month shows a high number of exceedance above the MAAQG given limit of 0.04 ppm for every 24 hour average time. In 2010, the month with the highest monthly average concentration is April (Figure 15), which also recorded the highest monthly concentration of nitrogen oxide. The concentration during April was 0.027 ppm. The daily maximum concentration for April shows exceedance for most days in the month except for 11th, 19th, 20th, 25th, 29th and 30th. The highest concentration recorded was on the 14th with 0.062 ppm followed by a concentration of 0.058 which occurred two days before 14th.

The lowest concentration recorded in 2010 was in July (Figure 16) with 0.015 ppm, which is also similar to nitrogen oxide and ozone, recording the lowest concentration in the year. Figure 16 illustrates that the concentration of nitrogen dioxide only exceeds MAAQG limits thrice in the month on the 2nd with 0.054 ppm, the 22nd with 0.053 ppm and 23rd with 0.049 ppm. The rest of the month shows a

concentration below the guideline limits in the range between 0.039 ppm to the lowest concentration recorded, 0.018 ppm on 27th July.

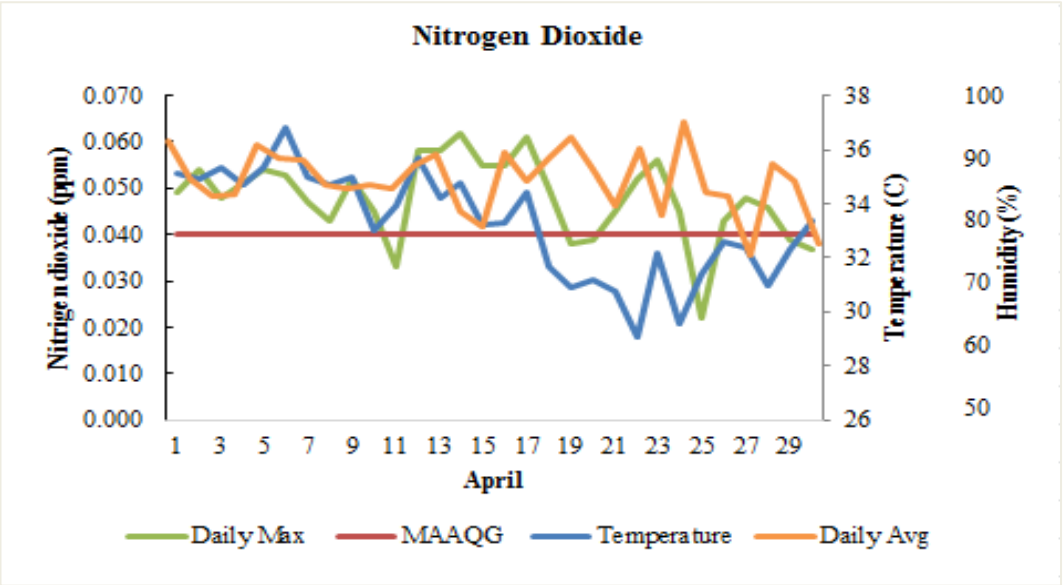

Figure 15: Nitrogen Dioxide Concentrations for April 2010

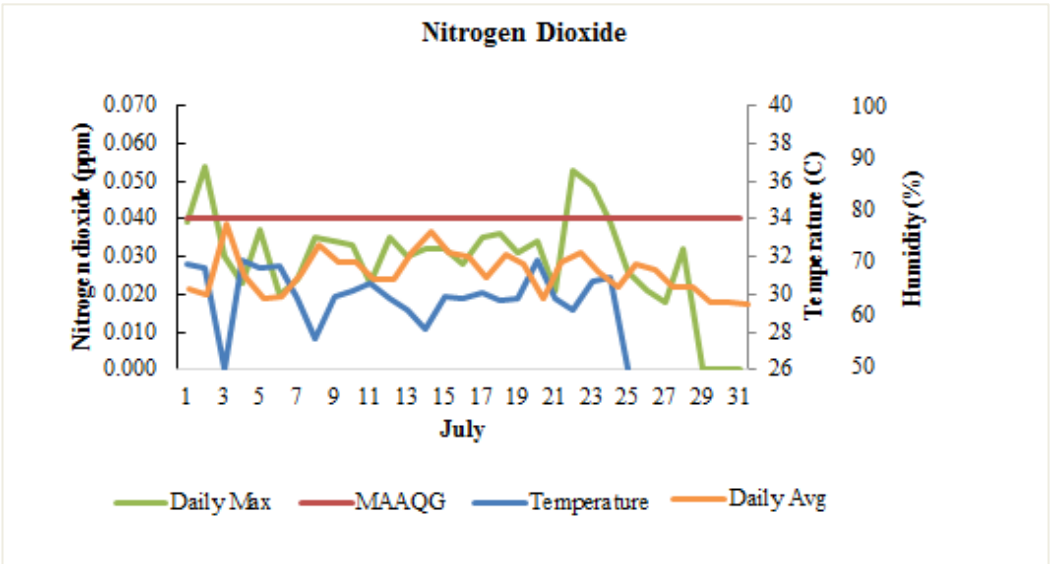

Figure 16: Nitrogen Dioxide Concentrations for July 2010

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The effect of lower ground ozone pollution must not be taken lightly. The effects are dangerous especially towards human health and also effect crops. This study examined the concentrations of ozone, its precursors and relationship with meteorological parameters in an oil and gas industry environment. The concentrations of ozone, and its precursors; nitrogen oxide and nitrogen dioxide are shown to be higher at the oil and gas industry. In this study, the objectives were achieved. Firstly, the levels of nitrogen oxides and ozone gas have been measured nearby an oil and gas industry area, with ozone gas levels higher compared to its precursors. Secondly, the relationship between nitrogen oxides and ozone over a time period of a year was determined. It is seen that the levels of nitrogen oxide are usually the lowest (due to oxidation to nitrogen dioxide) followed by nitrogen dioxide and with ozone the highest. Third, the relationship between surrounding temperature is directly proportional to the levels of nitrogen dioxide and the formation of ozone. However, humidity does not affect the levels of all three gases.

Air pollution is considered an international problem as it cannot be contained within an area. The levels of ozone precursors emitted from oil and gas industry might be a major contributor to the pollution of ozone. There should be a guideline or standard made up specifically for the oil and gas industry for the air pollutants emitted from the plant. HSE departments of the industry should be aware of the effects of these pollutants especially towards their workers. This study can be more accurate if some modifications and additions were done such as:

1) Obtain wind speed and wind direction data
2) Obtain UV radiation data
3) Obtain air samples from within the oil and gas industry area
4) Increase the duration of sampling
5) Analyse samples at other oil and gas areas to compare
6) Compare the trends at oil and gas industry with trends at other industry areas

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APPENDICES

Appendix A

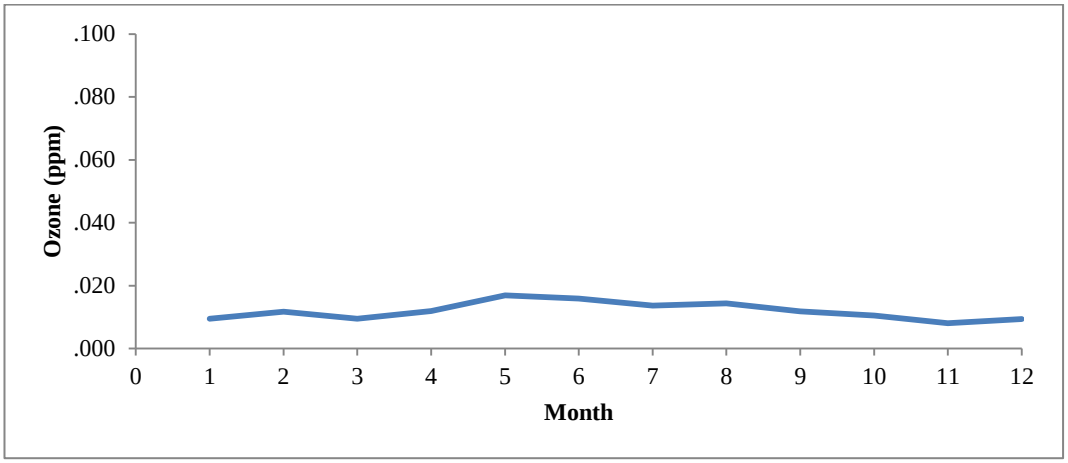


Figure A-1: Concentration of ozone gas at Jerantut Station the year 2008

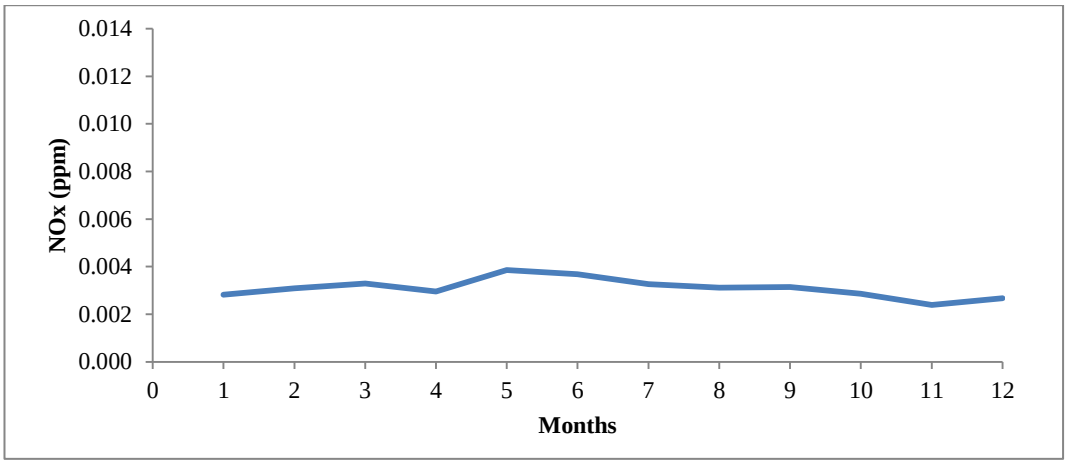


Figure A-2: Concentration of nitrogen oxides gas at Jerantut Station the year 2008

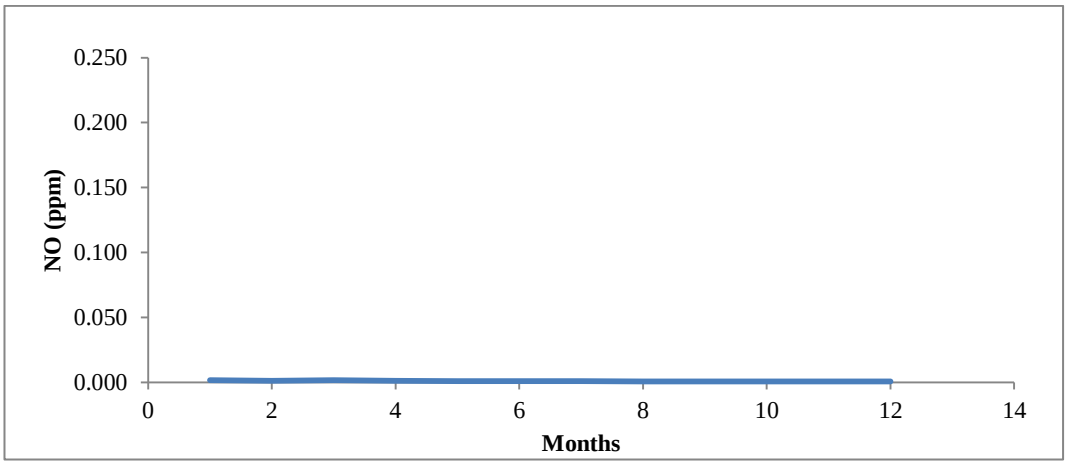


Figure A-3: Concentration of nitrogen oxide gas at Jerantut Station in year 2008

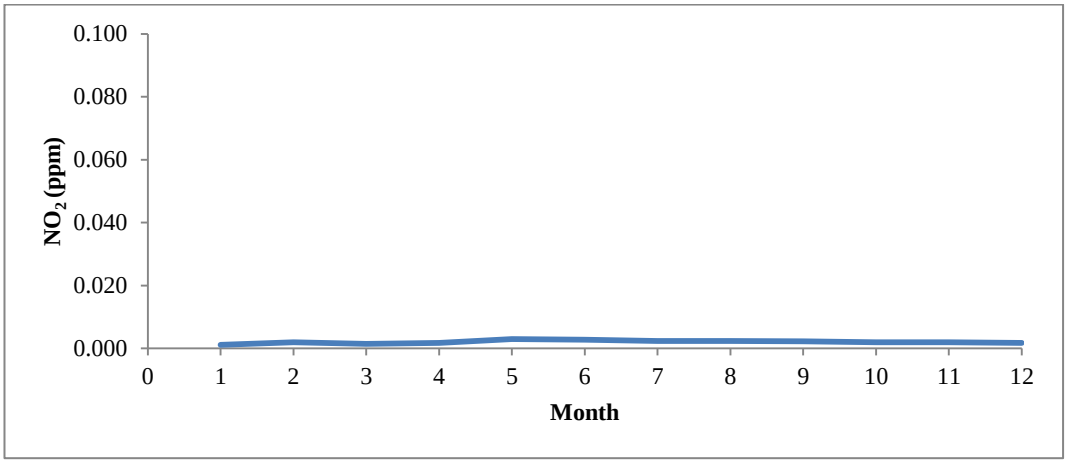


Figure A-4: Concentration of nitrogen dioxide gas at Jerantut Station in year 2008

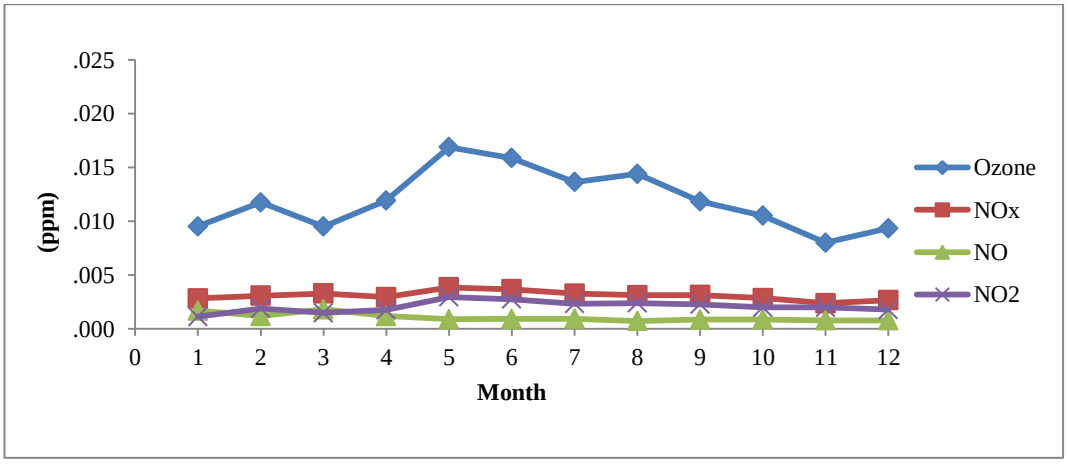


Figure A-5: Comparison of gases concentration at Jerantut Station in year 2008

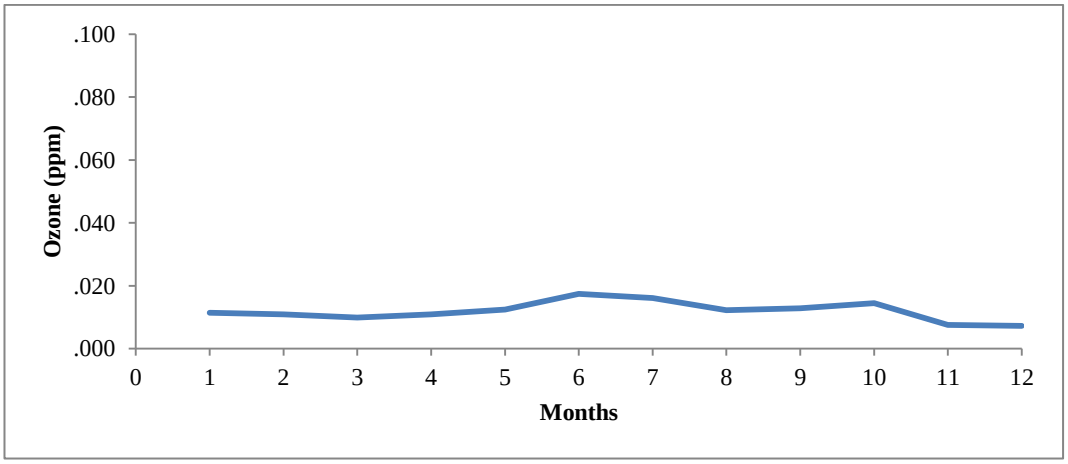


Figure A-6: Concentration of ozone gas at Jerantut Station the year 2008

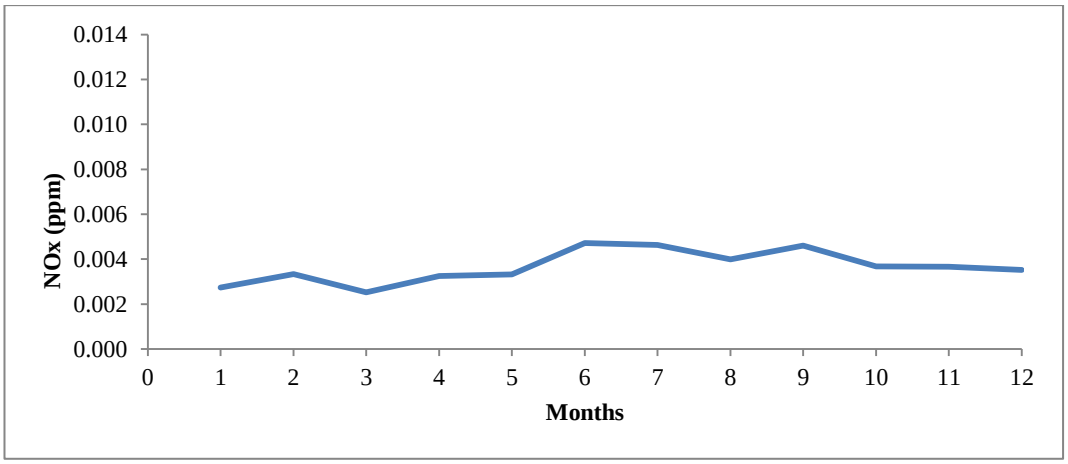


Figure A-7: Concentration of nitrogen oxides gas at Jerantut Station the year 2009

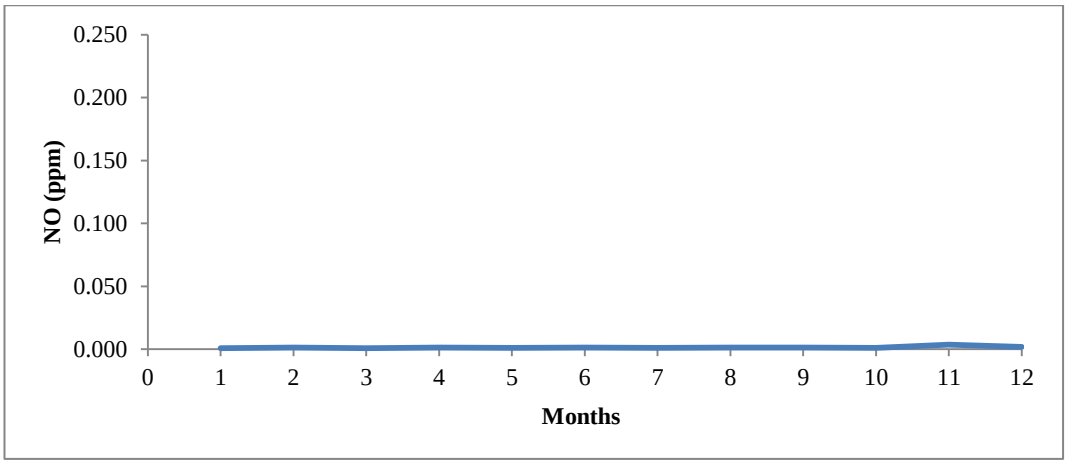


Figure A-8: Concentration of nitrogen oxide gas at Jerantut Station in year 2009

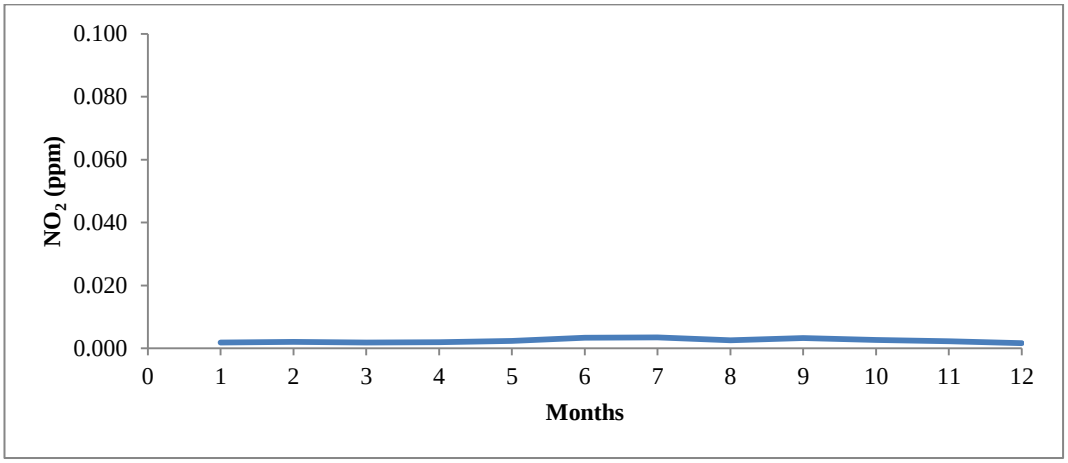


Figure A-9: Concentration of nitrogen dioxide gas at Jerantut Station in year 2009

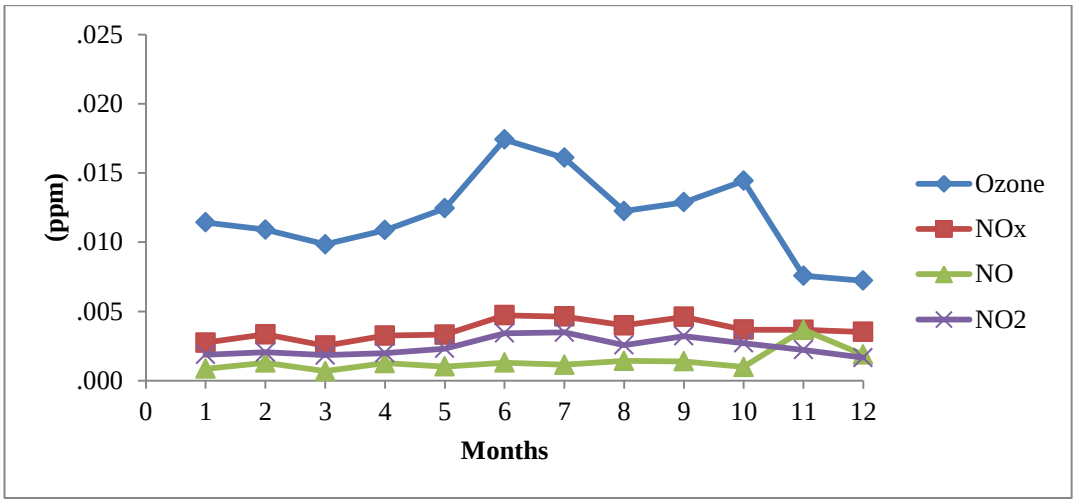


Figure A-10: Comparison of gases concentration at Jerantut Station in year 2009

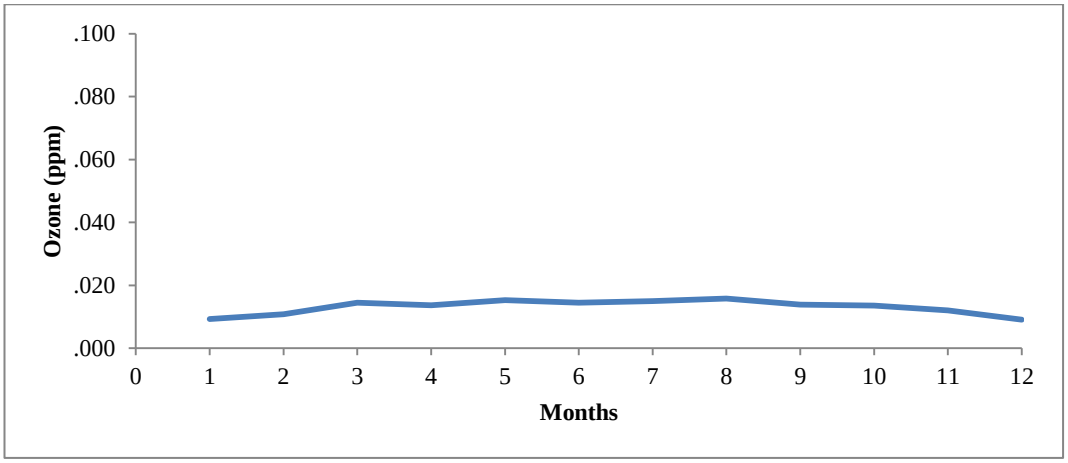


Figure A-11: Concentration of ozone gas at Jerantut Station the year 2010

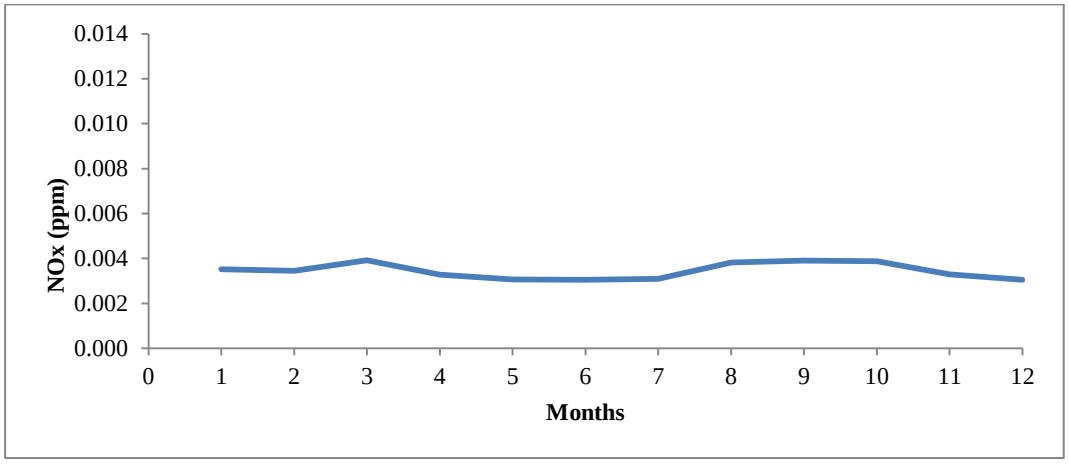
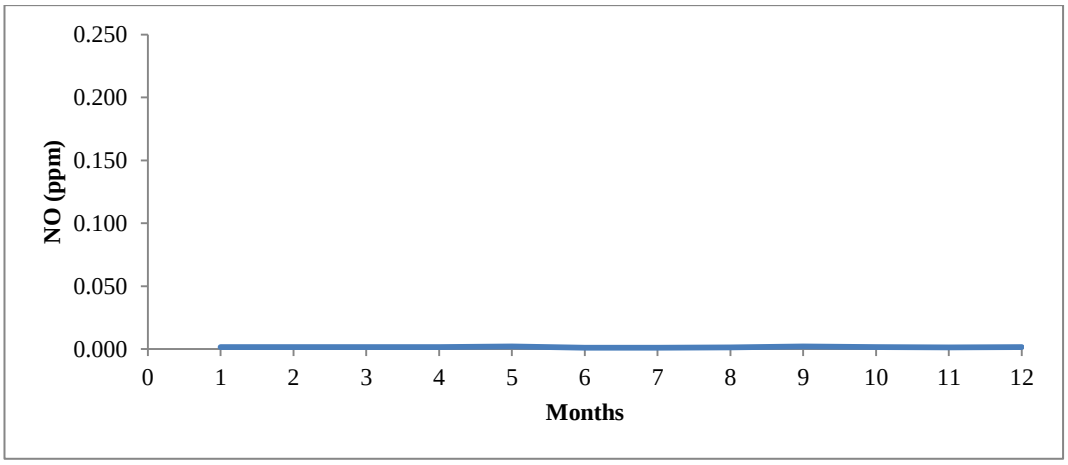


Figure A-12: Concentration of nitrogen oxides gas at Jerantut Station the year 2010



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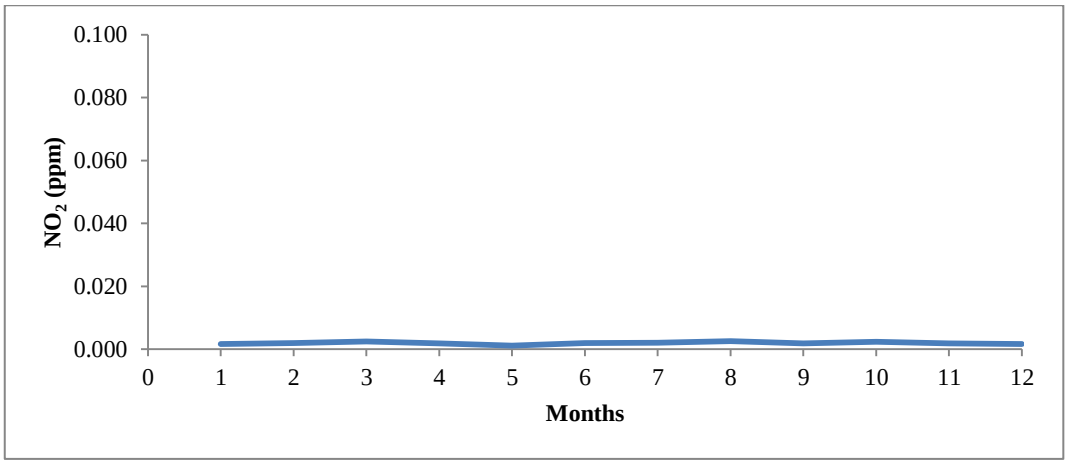

Figure A-14: Concentration of nitrogen dioxide gas at Jerantut Station in year 2010

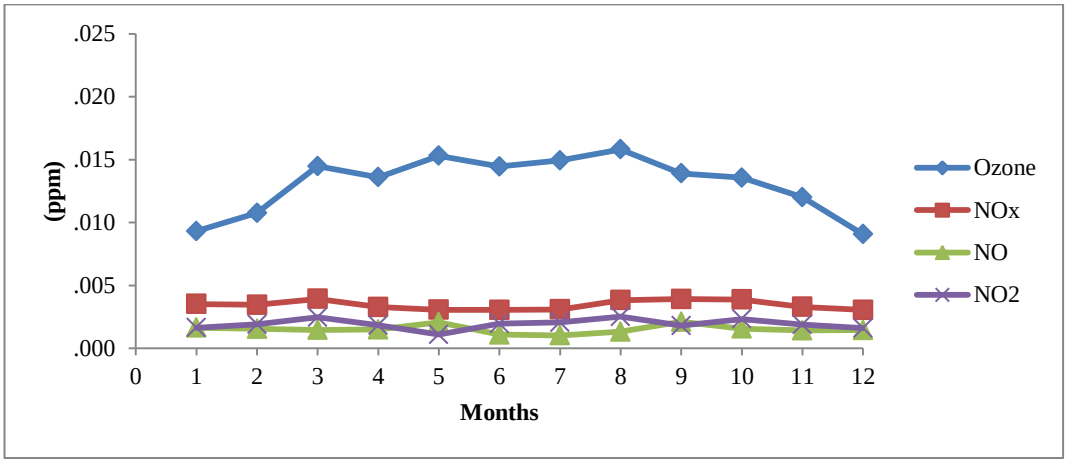

Figure A-15: Comparison of gases concentration at Jerantut Station in year 2010

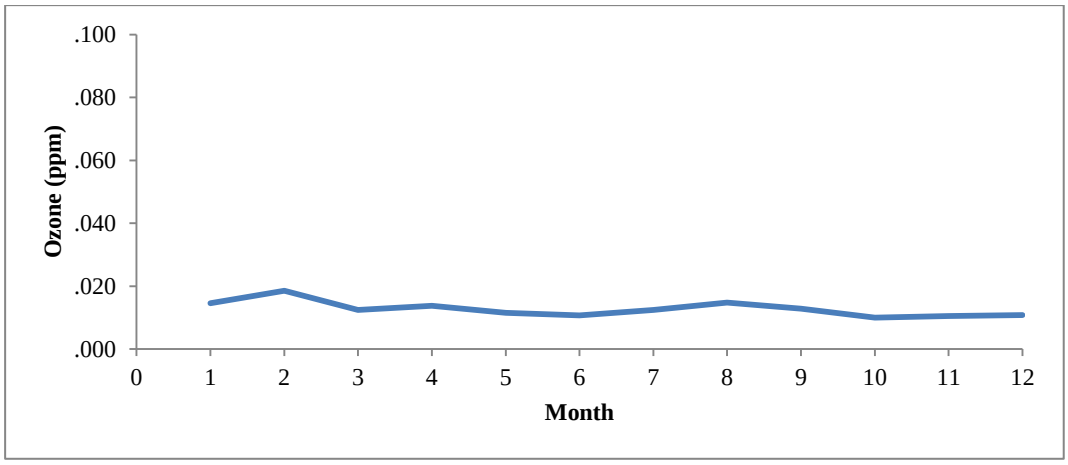

Figure A-16: Concentration of ozone gas at Bintulu Station the year 2008

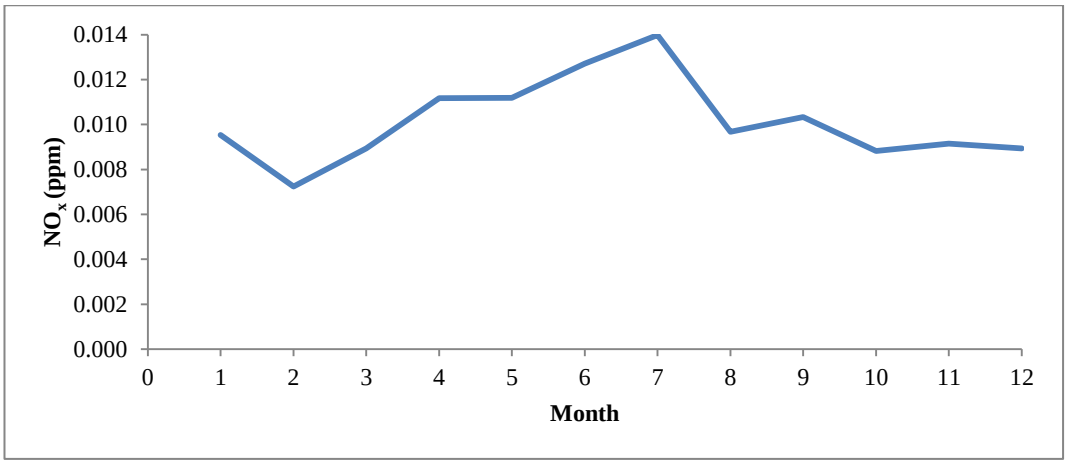

Figure A-17: Concentration of nitrogen oxides gas at Bintulu Station the year 2008

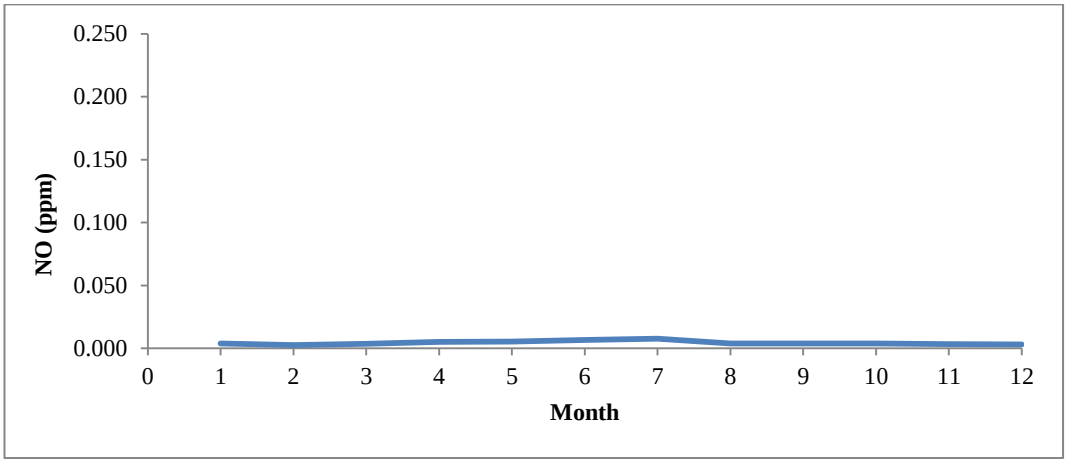

Figure A-18: Concentration of nitrogen oxide gas at Bintulu Station in year 2008

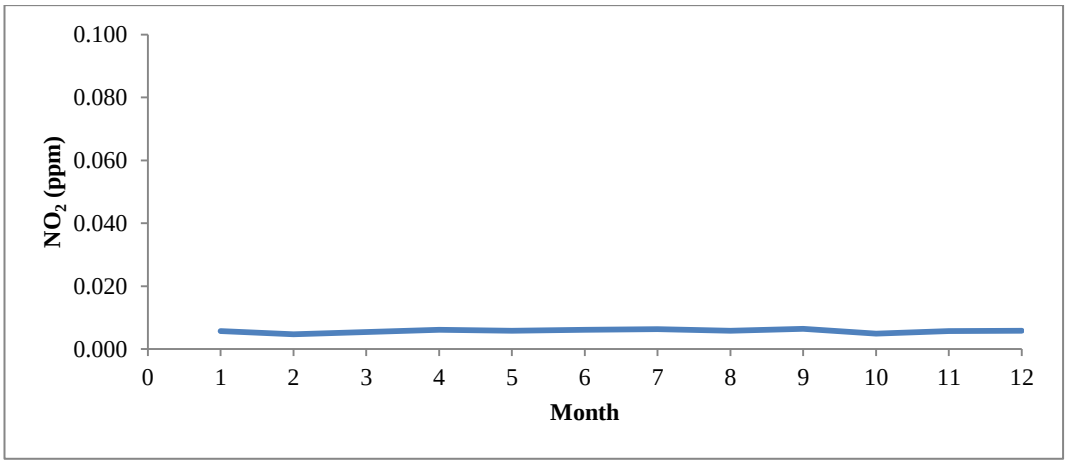

Figure A-19: Concentration of nitrogen dioxide gas at Bintulu Station in year 2008

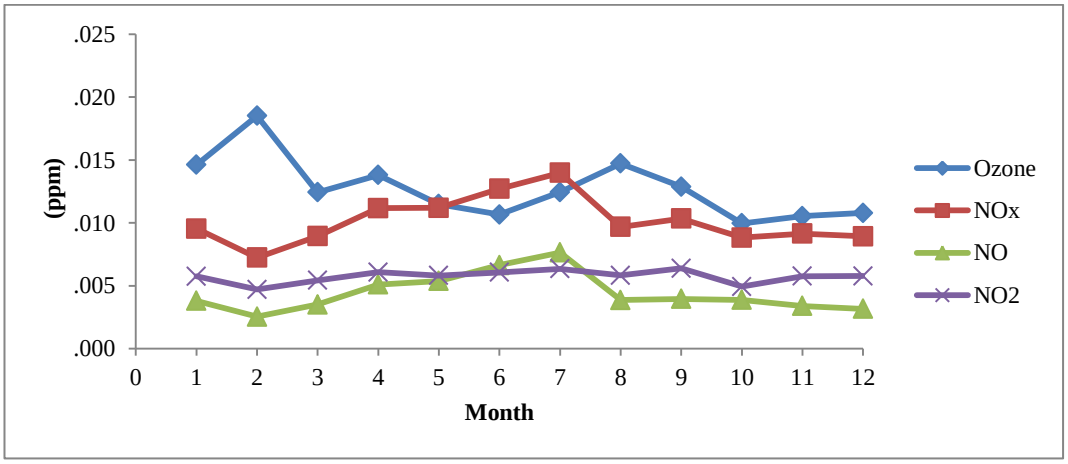

Figure A-20: Comparison of gases concentration at Bintulu Station in year 2008

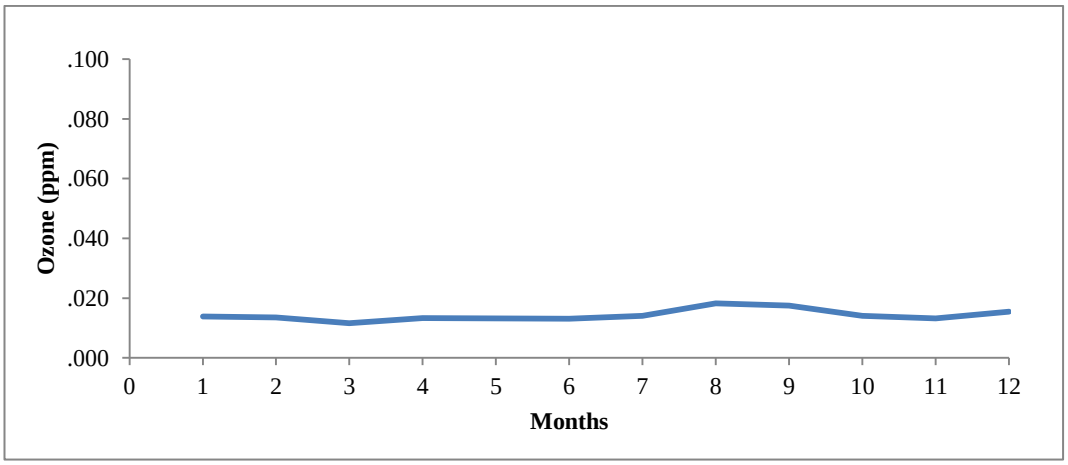

Figure A-21: Concentration of ozone gas at Bintulu Station the year 2009

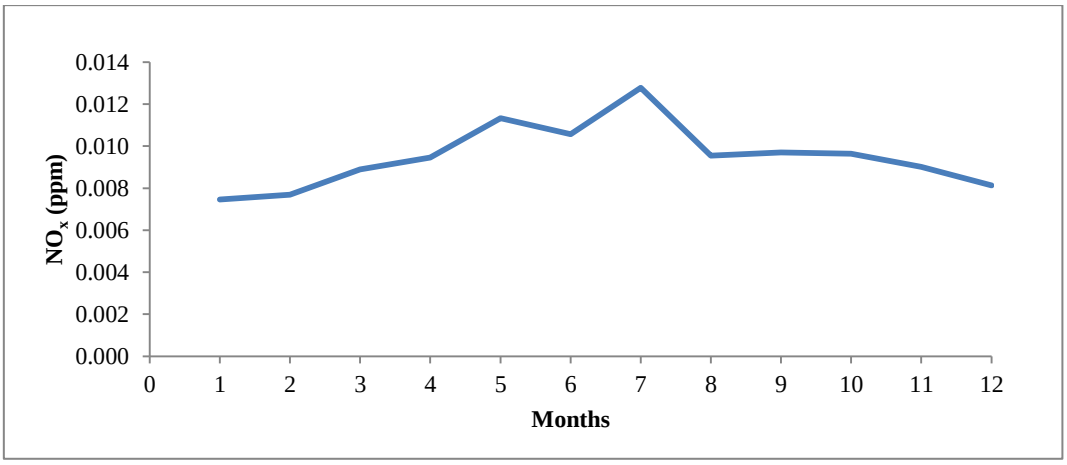

Figure A-22: Concentration of nitrogen oxides gas at Bintulu Station the year 2009

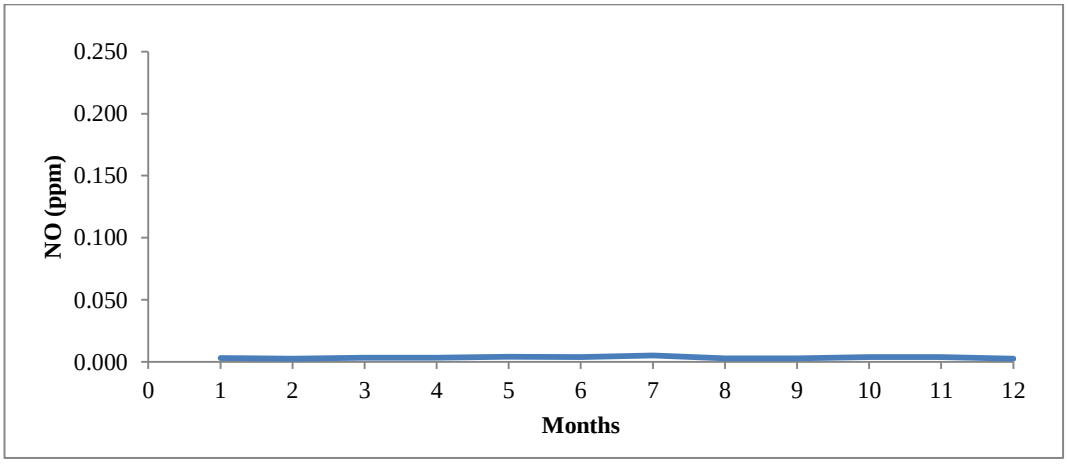

Figure A-23: Concentration of nitrogen oxide gas at Bintulu Station in year 2009

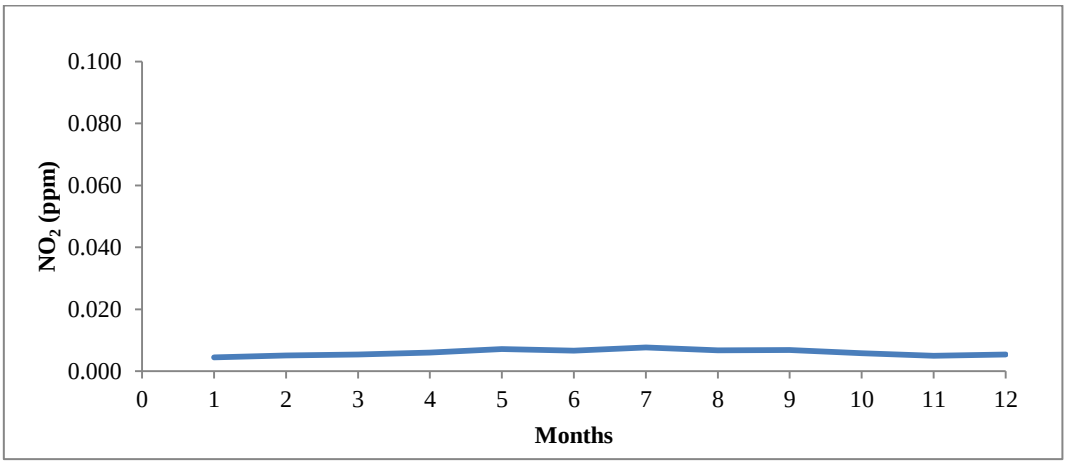

Figure A-24: Concentration of nitrogen dioxide gas at Bintulu Station in year 2009

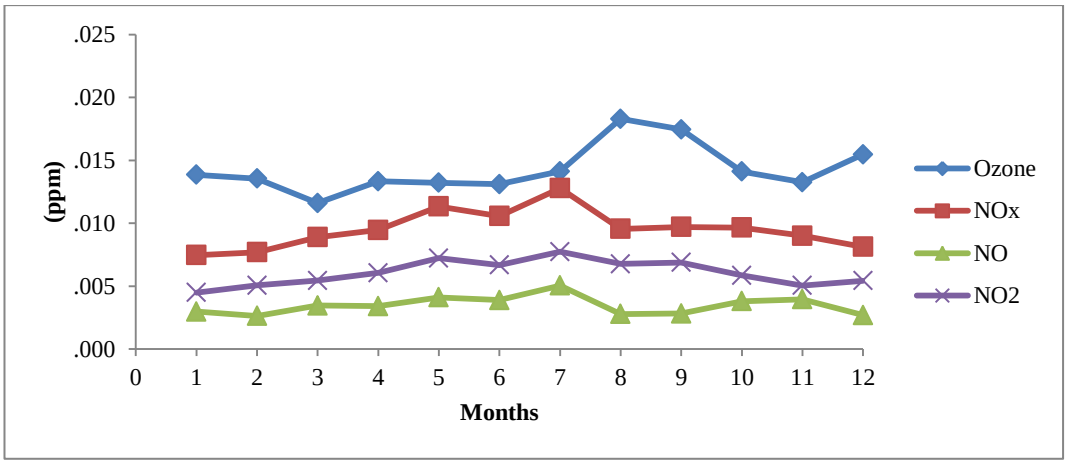

Figure A-25: Comparison of gases concentration at Bintulu Station in year 2009

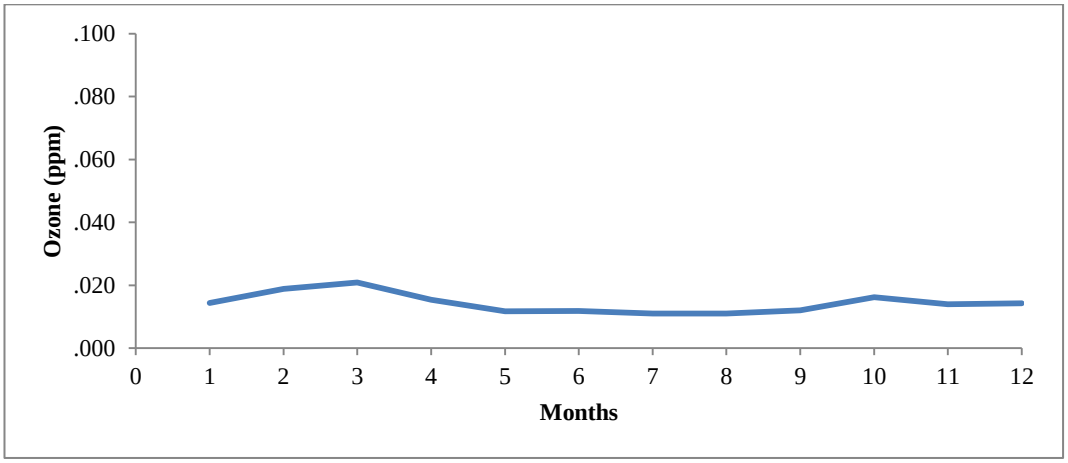

Figure A-24: Concentration of ozone gas at Bintulu Station the year 2010

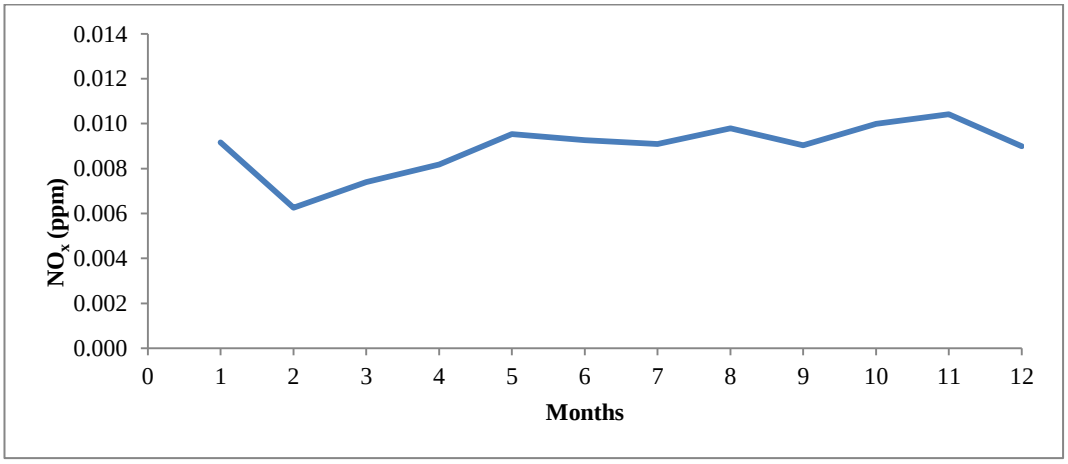

Figure A-25: Concentration of nitrogen oxides gas at Bintulu Station the year 2010

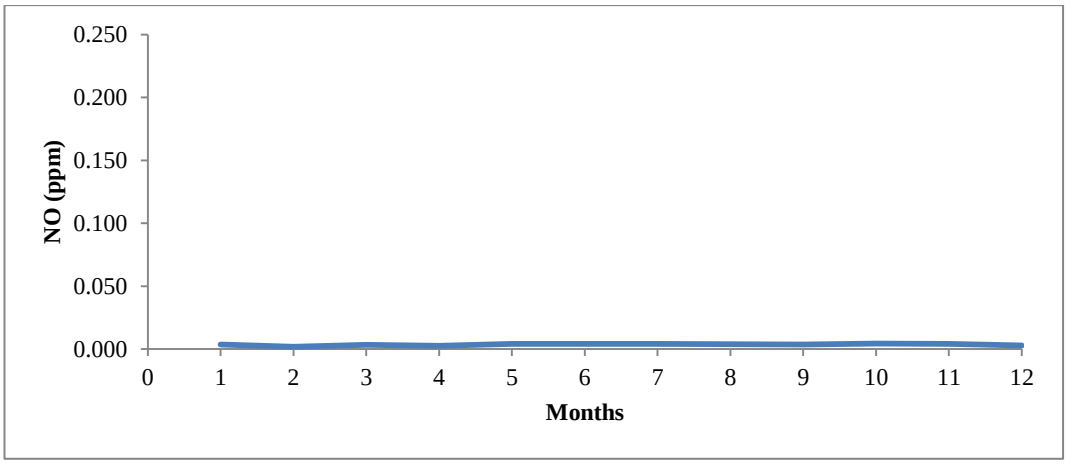

Figure A-26: Concentration of nitrogen oxide gas at Bintulu Station in year 2010

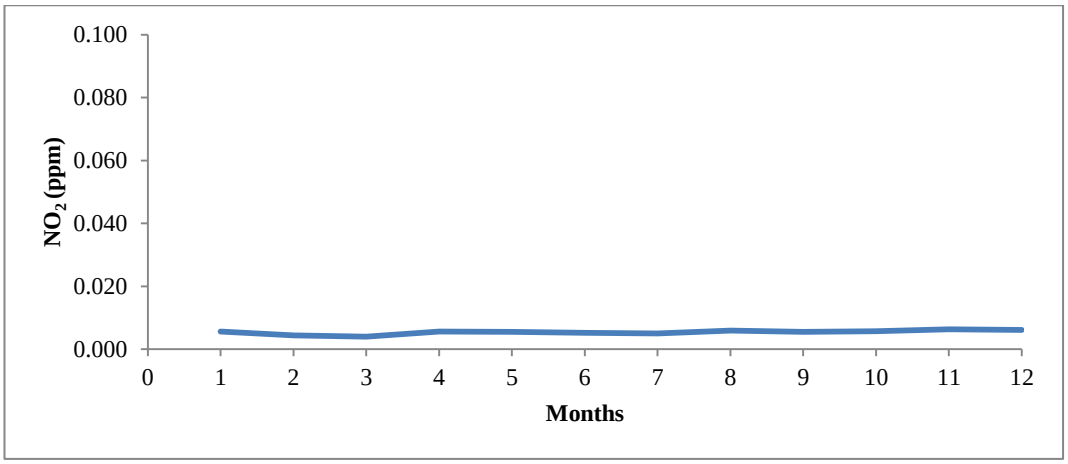

Figure A-27: Concentration of nitrogen dioxide gas at Bintulu Station in year 2010

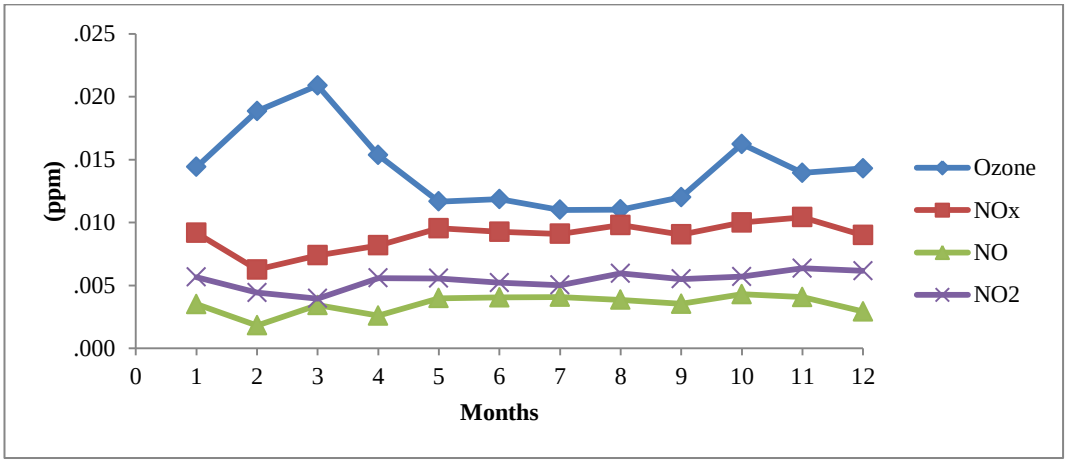

Figure A-28: Comparison of gases concentration at Bintulu Station in year 2010

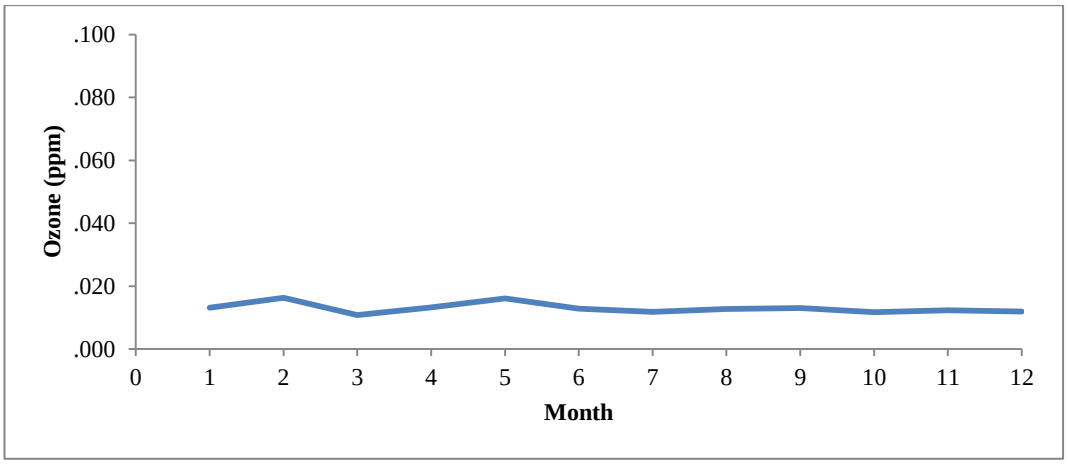

Figure A-29: Concentration of ozone gas at Miri Station the year 2008

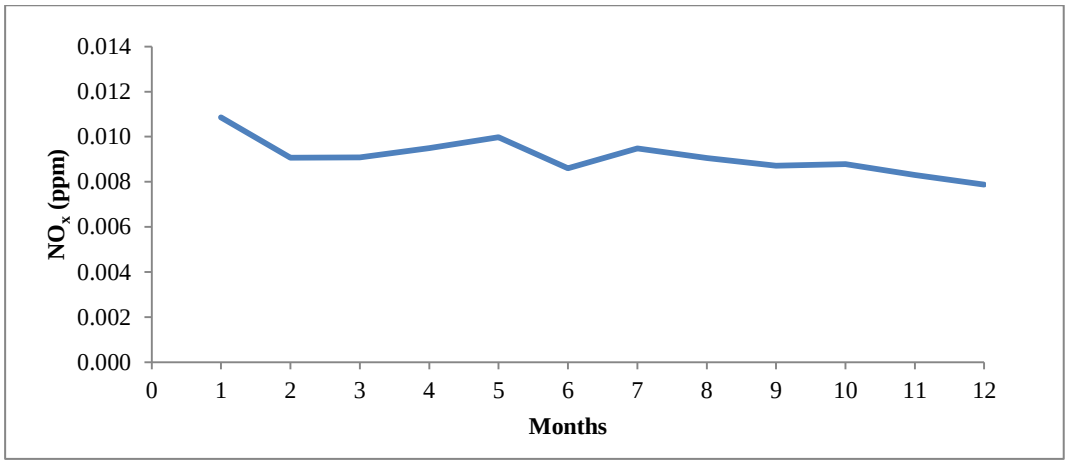

Figure A-30: Concentration of nitrogen oxides gas at Miri Station the year 2008

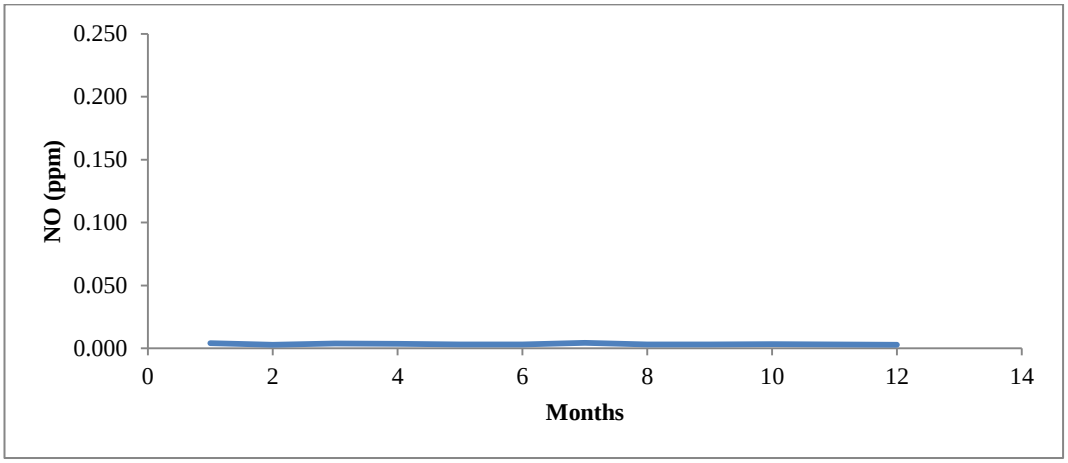

Figure A-31: Concentration of nitrogen oxide gas at Miri Station in year 2008

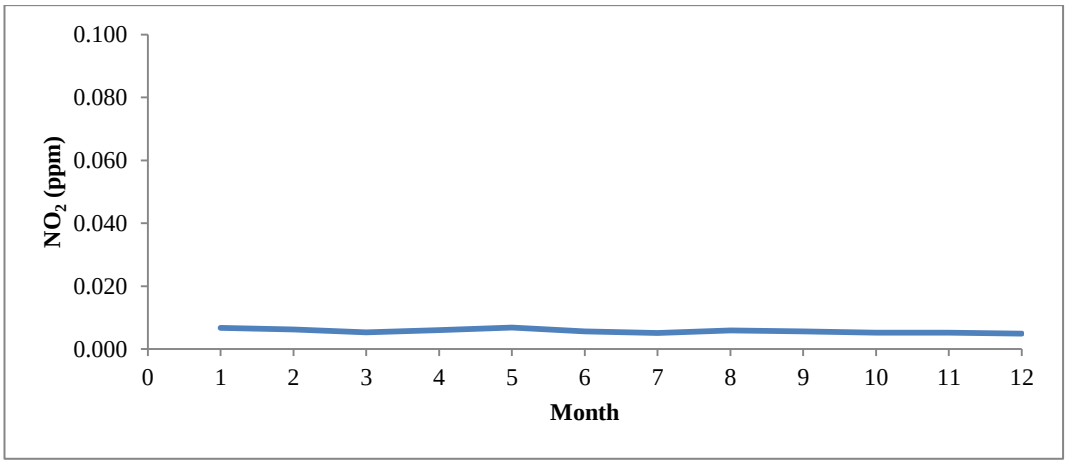

Figure A-32: Concentration of nitrogen dioxide gas at Miri Station in year 2008

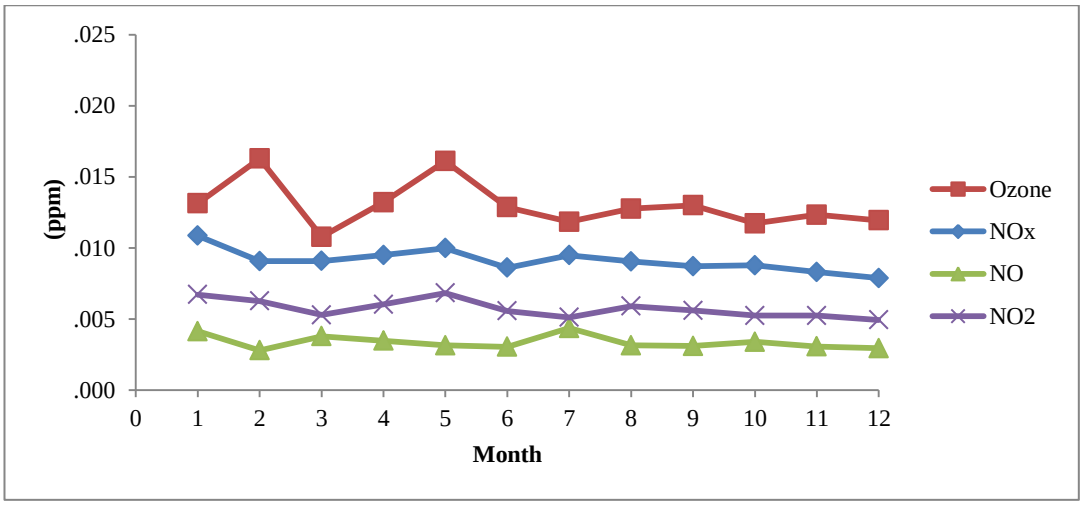

Figure A-33: Comparison of gases concentration at Miri Station in year 2008

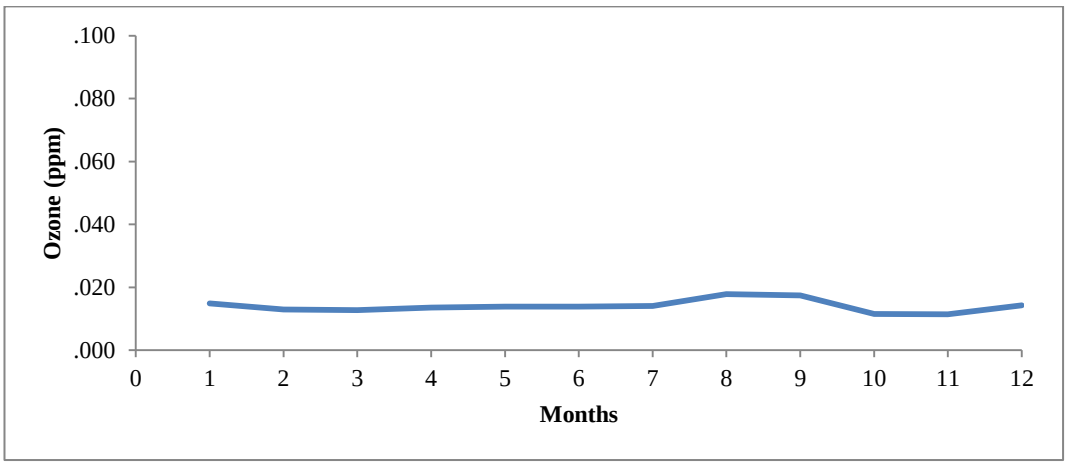

Figure A-34: Concentration of ozone gas at Miri Station the year 2009

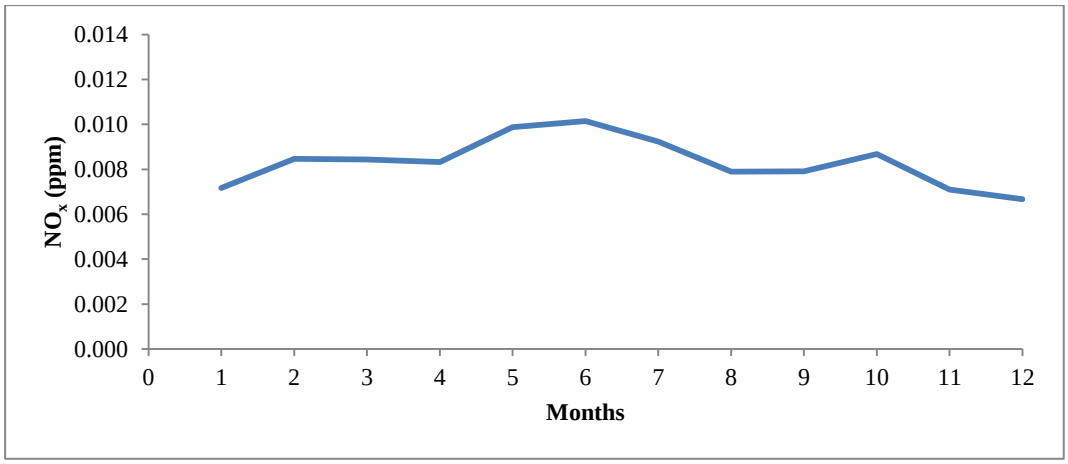

Figure A-35: Concentration of nitrogen oxides gas at Miri Station the year 2009

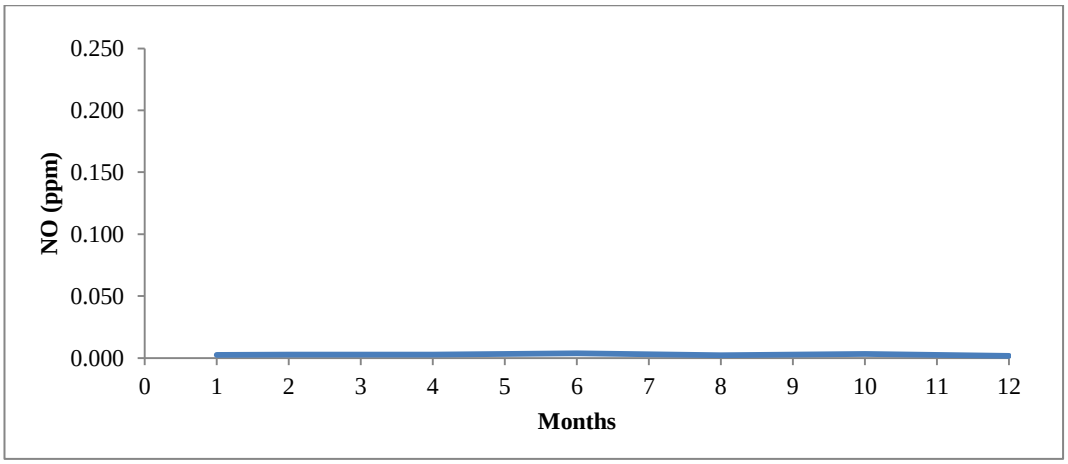

Figure A-36: Concentration of nitrogen oxide gas at Miri Station in year 2009

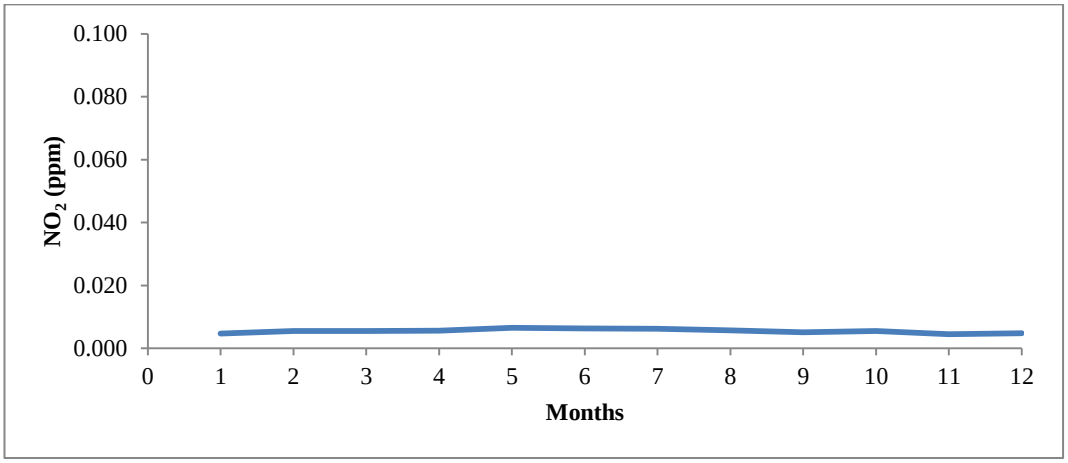

Figure A-37: Concentration of nitrogen dioxide gas at Miri Station in year 2009

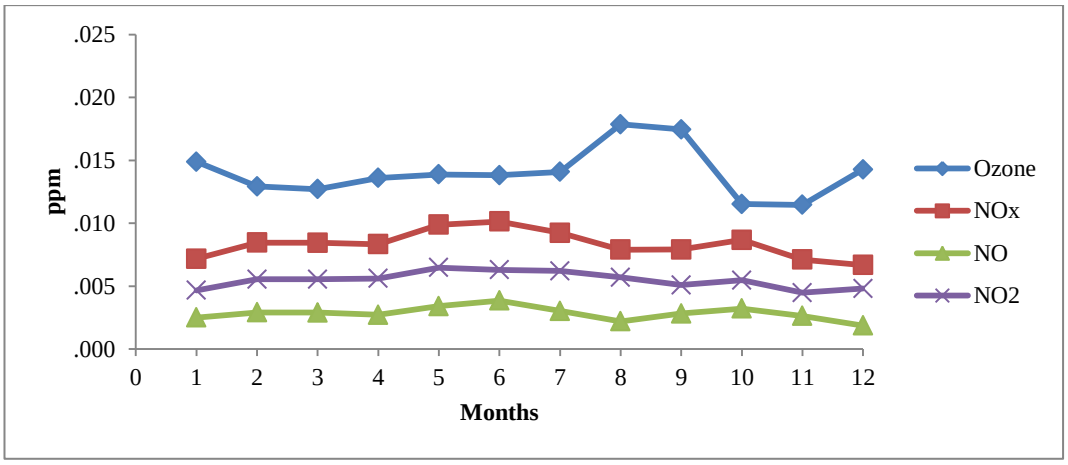

Figure A-38: Comparison of gases concentration at Miri Station in year 2009

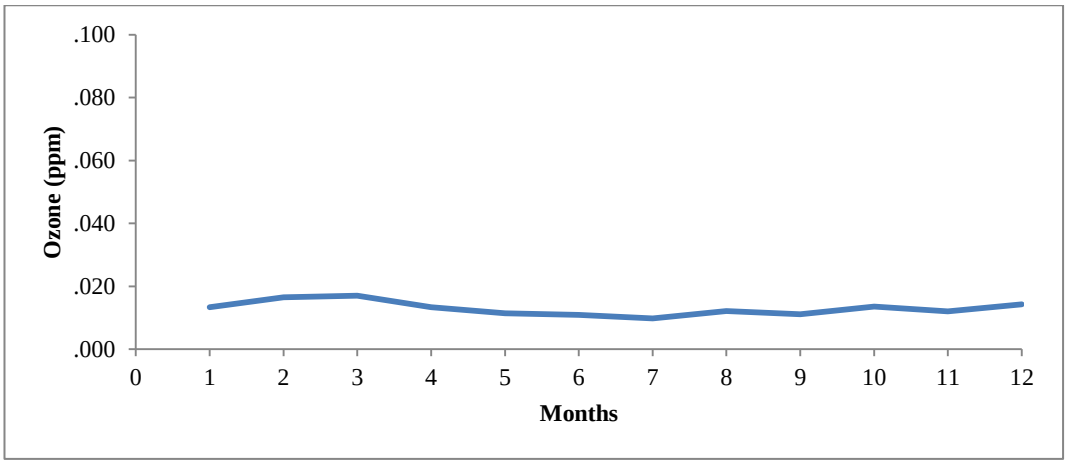

Figure A-39: Concentration of ozone gas at Miri Station the year 2010

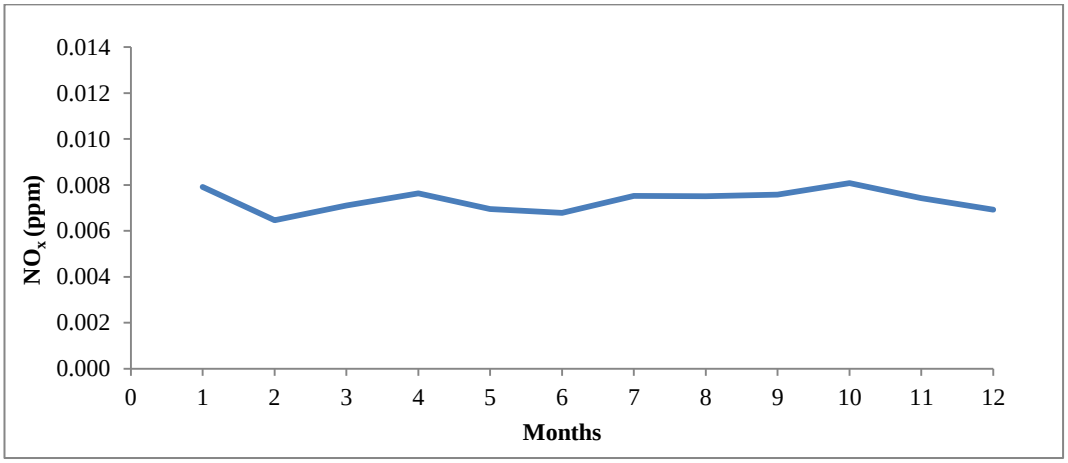

Figure A-40: Concentration of nitrogen oxides gas at Miri Station the year 2010

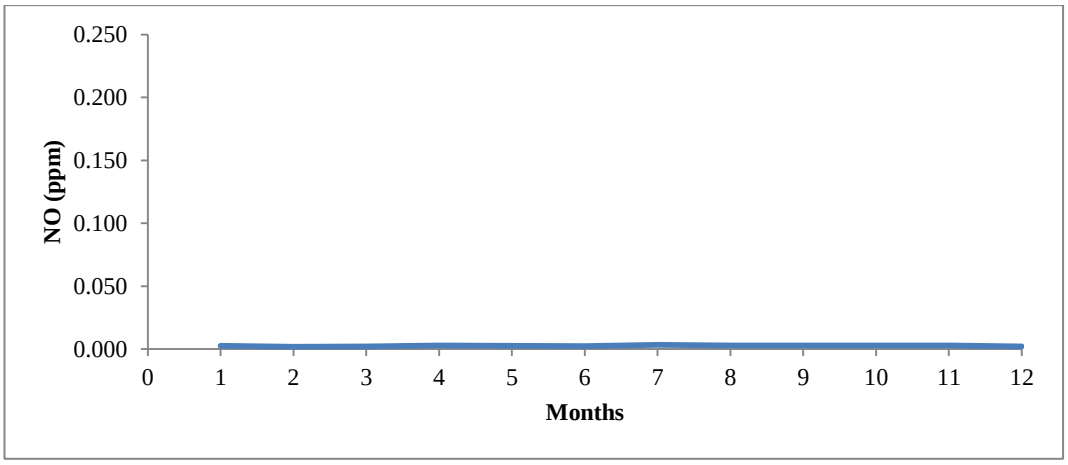

Figure A-41: Concentration of nitrogen oxide gas at Miri Station in year 2010

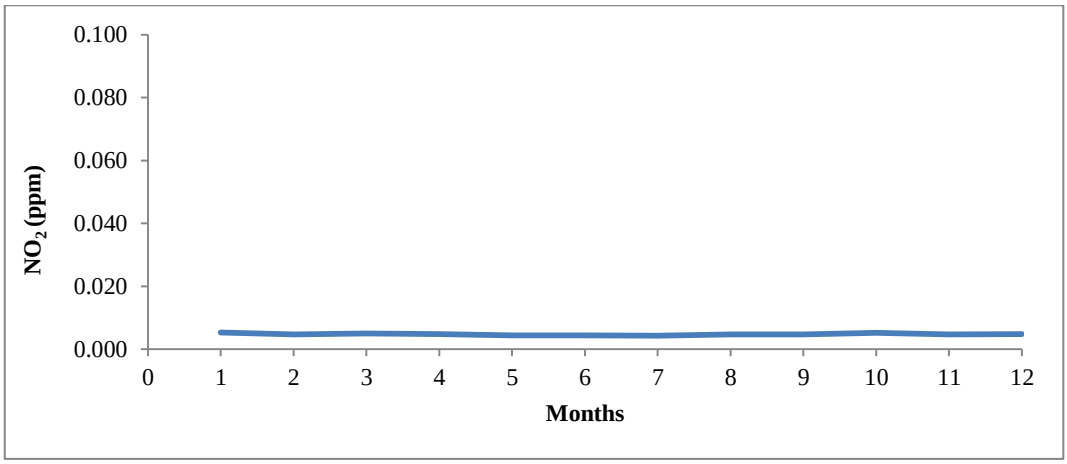

Figure A-42: Concentration of nitrogen dioxide gas at Miri Station in year 2010

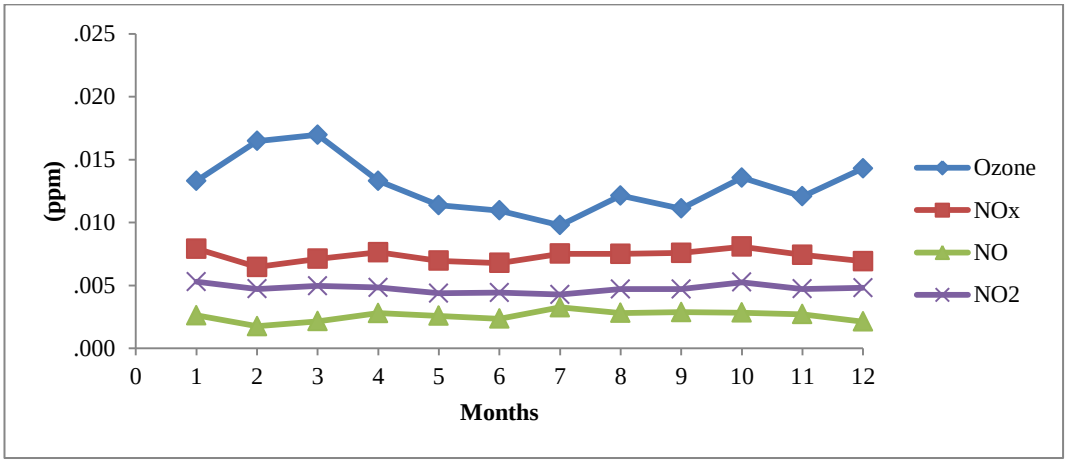

Figure A-43: Comparison of gases concentration at Miri Station in year 2010

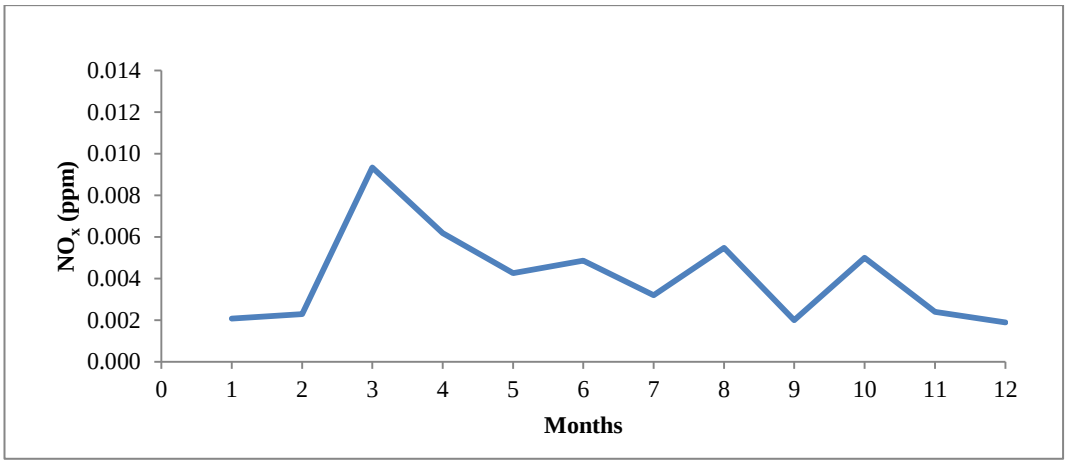

Figure A-44: Concentration of nitrogen oxides gas at Paka Station the year 2008

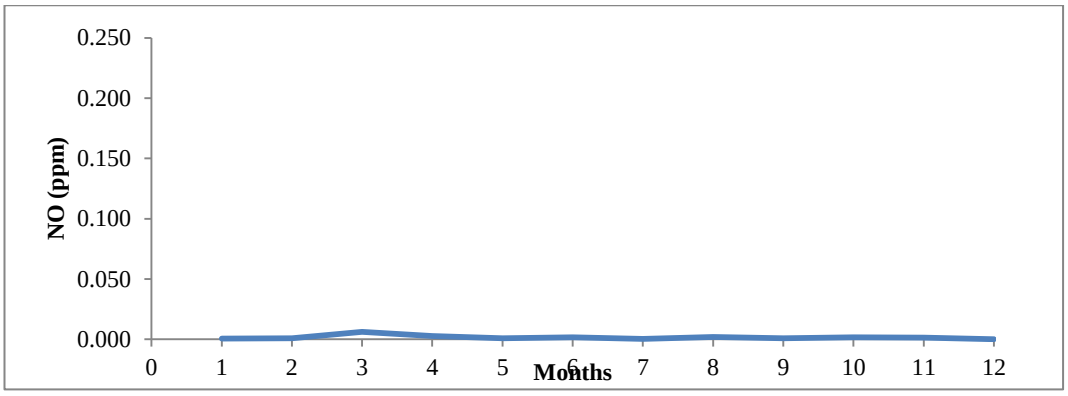

Figure A-45: Concentration of nitrogen oxide gas at Paka Station in year 2008

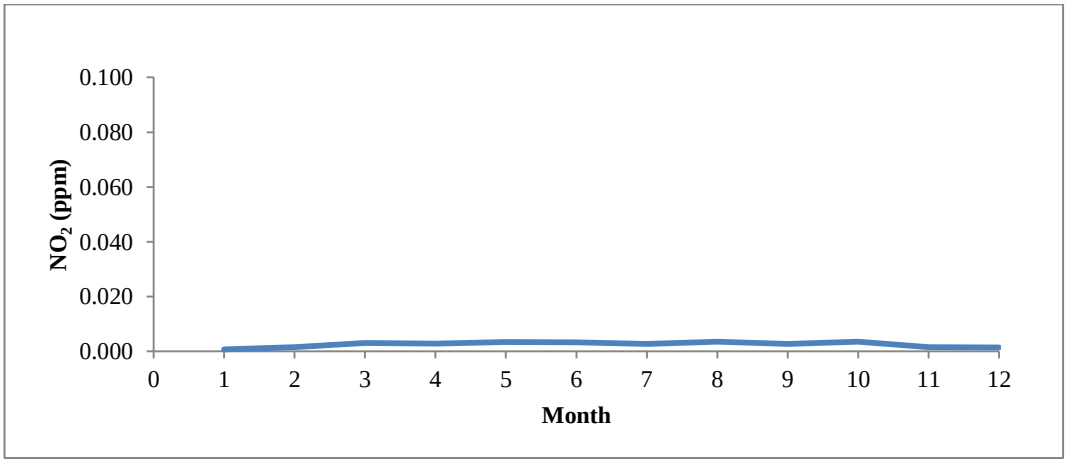

Figure A-47: Concentration of nitrogen dioxide gas at Paka Station in year 2008

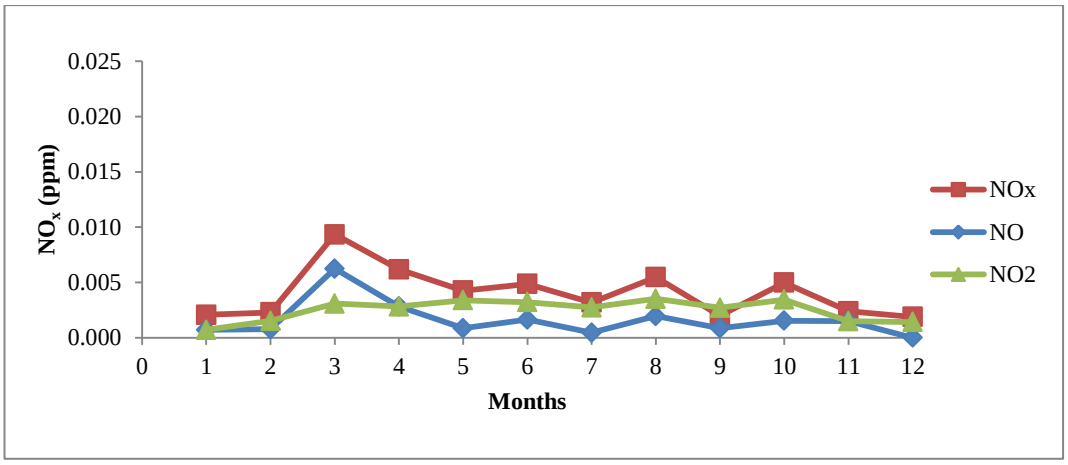

Figure A-48: Comparison of gases concentration at Paka Station in year 2008

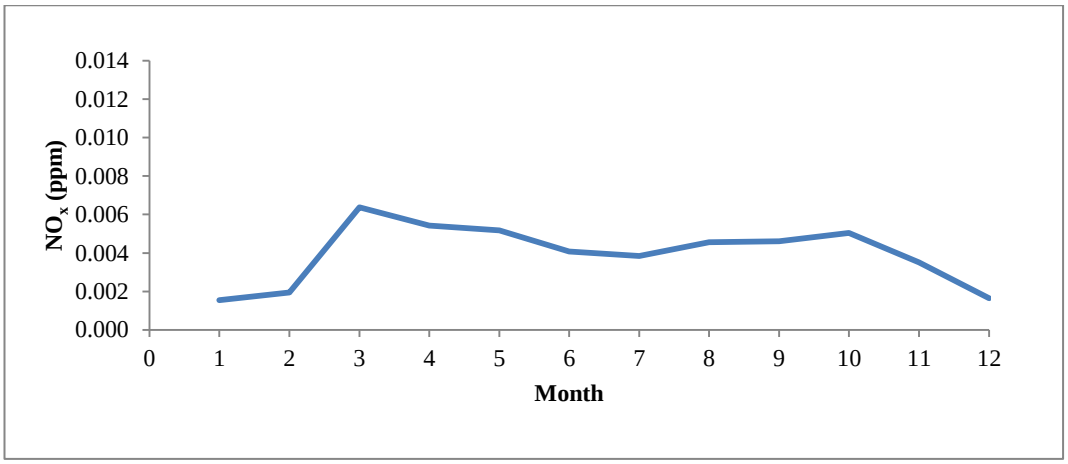

Figure A-49: Concentration of nitrogen oxides gas at Paka Station the year 2009

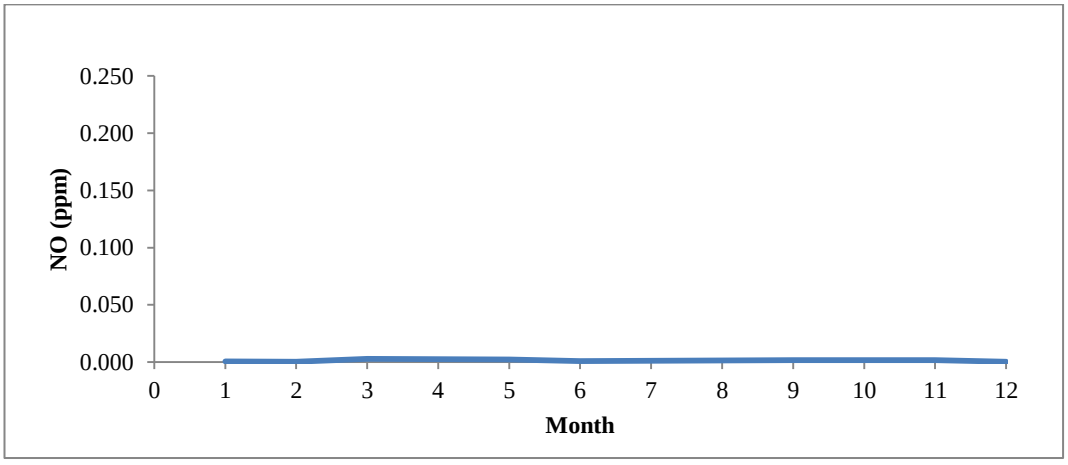

Figure A-50: Concentration of nitrogen oxide gas at Paka Station in year 2009

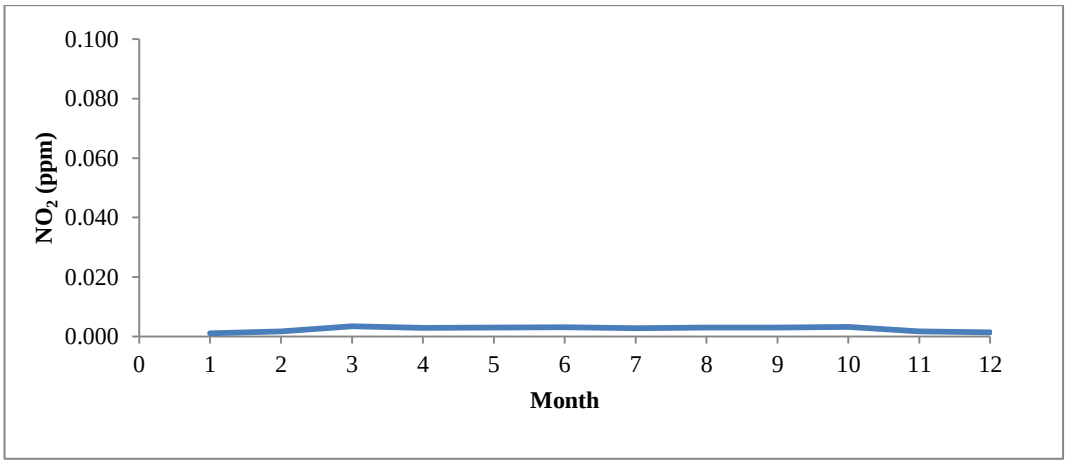

Figure A-51: Concentration of nitrogen dioxide gas at Paka Station in year 2009

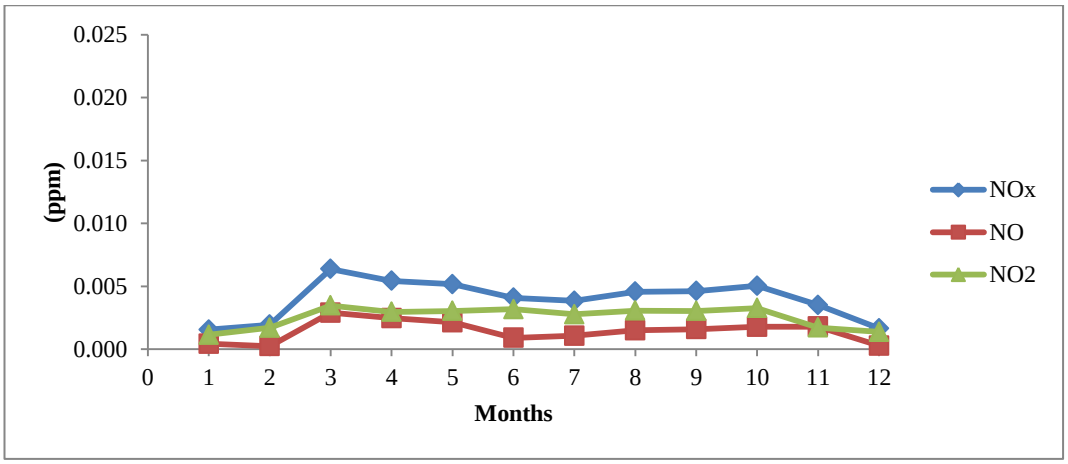

Figure A-52: Comparison of gases concentration at Paka Station in year 2009

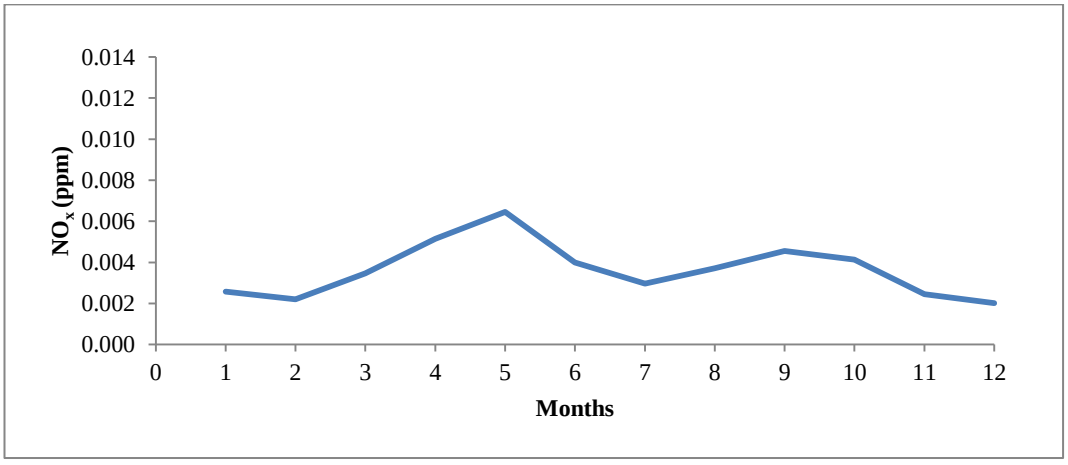

Figure A-53: Concentration of nitrogen oxides gas at Paka Station the year 2010

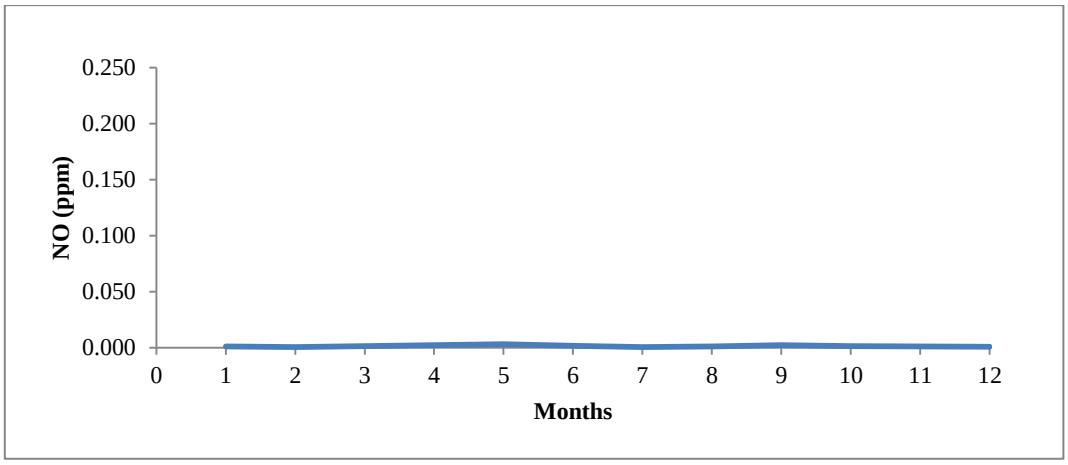

Figure A-54: Concentration of nitrogen oxide gas at Paka Station in year 2010

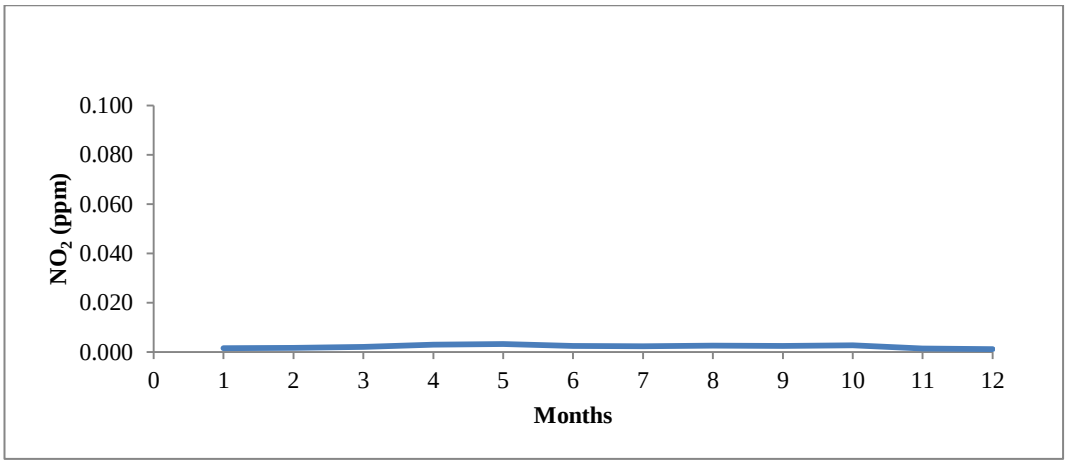

Figure A-55: Concentration of nitrogen dioxide gas at Paka Station in year 2010

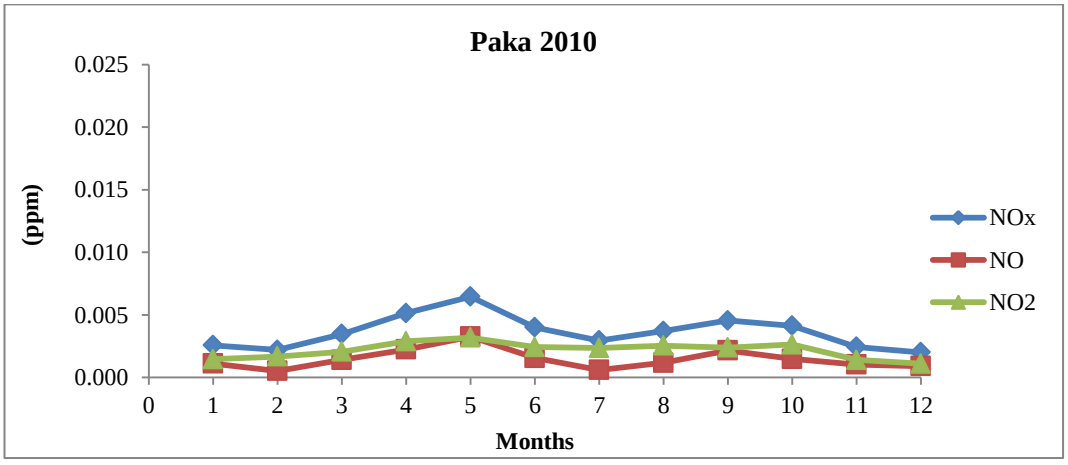

Figure A-56: Comparison of gases concentration at Paka Station in year 2010

Appendix B

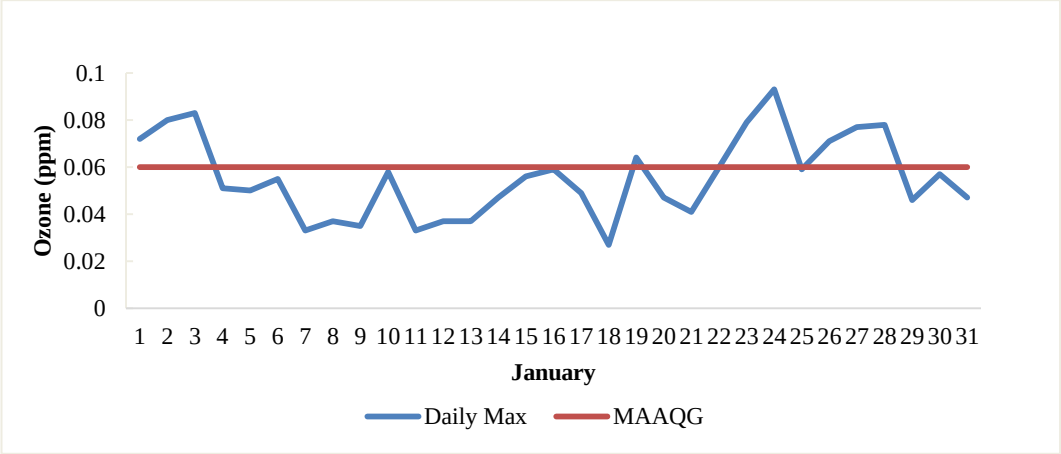

Figure B-1: Concentration of ozone gas at Station B for January 2010

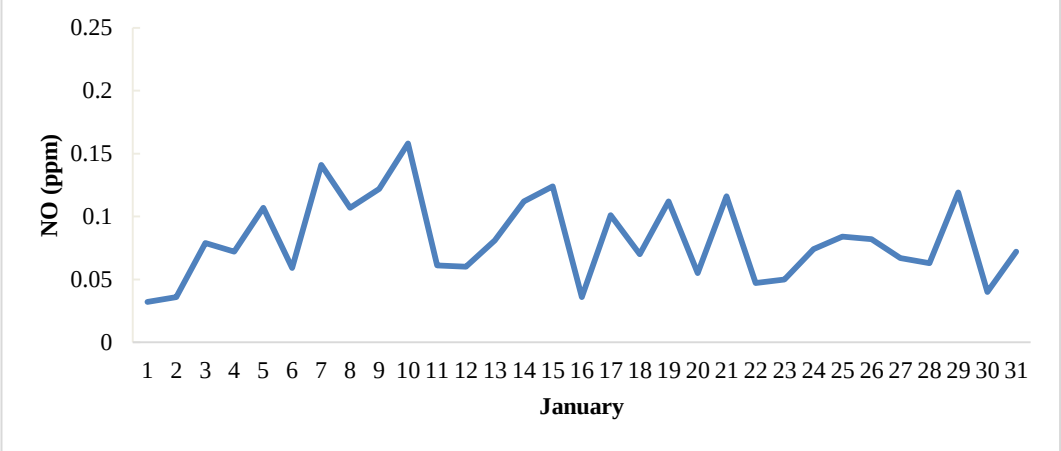

Figure B-2: Concentration of nitrogen oxide gas at Station B for January 2010

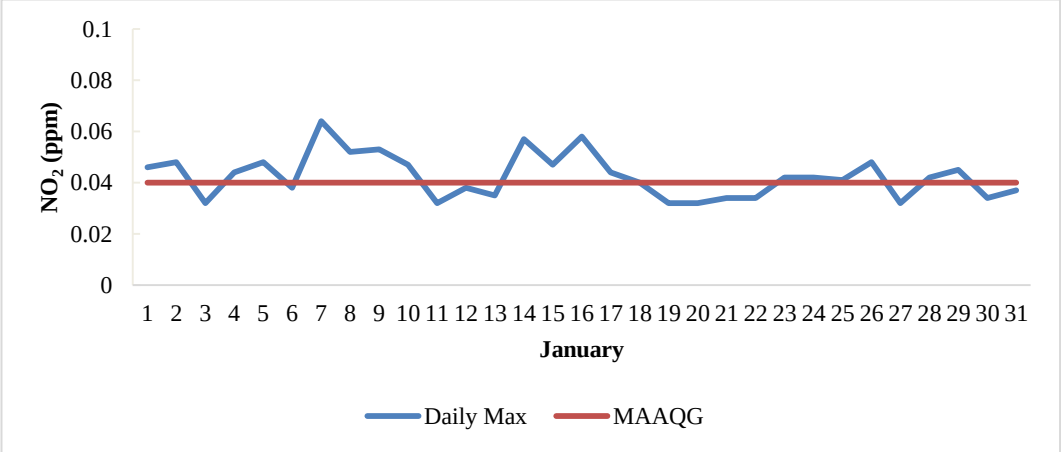

Figure B-3: Concentration of nitrogen dioxide gas at Station B for January 2010

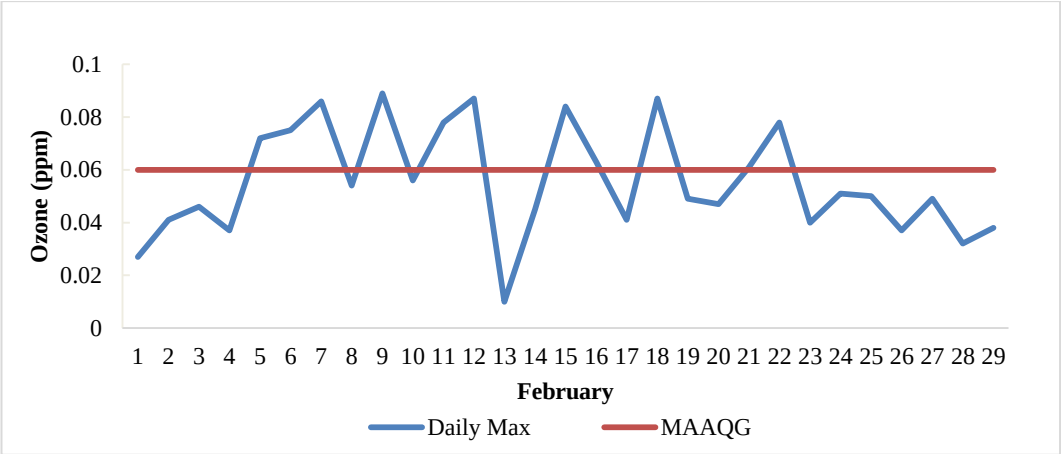

Figure B-4: Concentration of ozone gas at Station B for February 2010

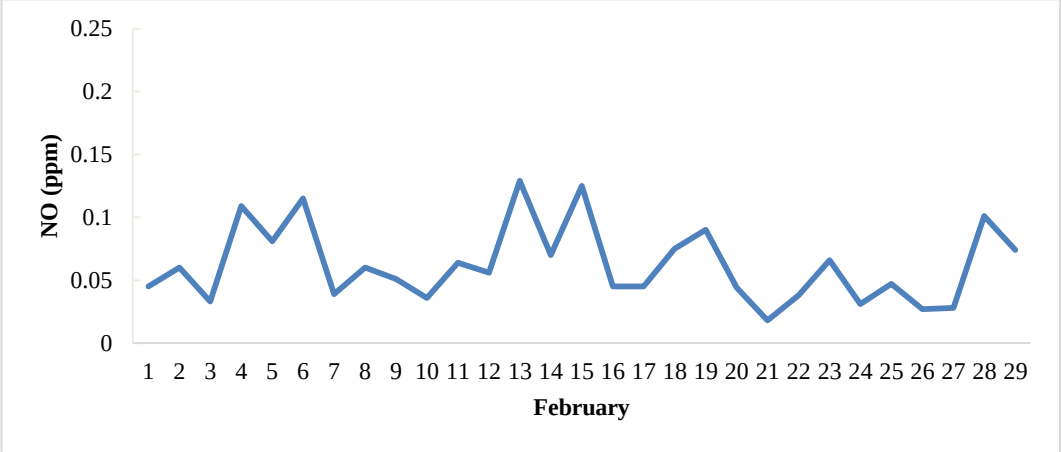

Figure B-5: Concentration of nitrogen oxide gas at Station B for February 2010

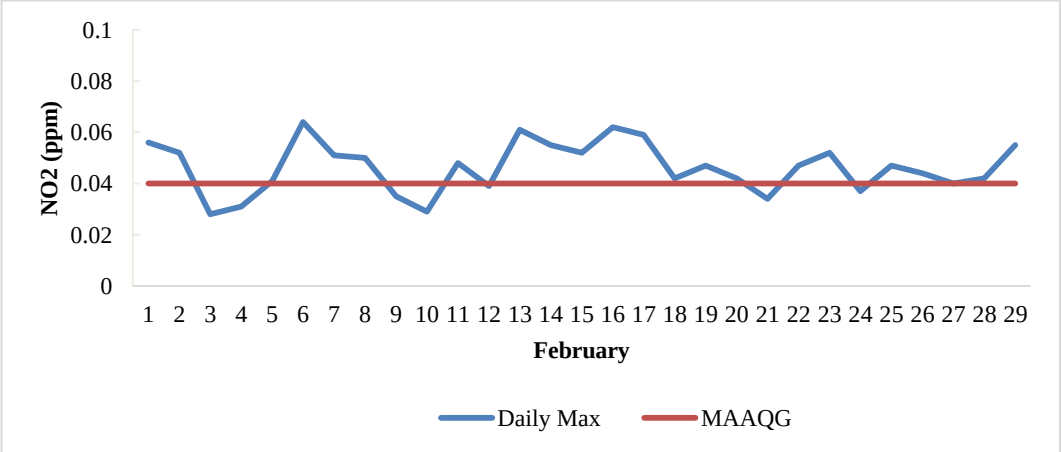

Figure B-6: Concentration of nitrogen dioxide gas at Station B for February 2010

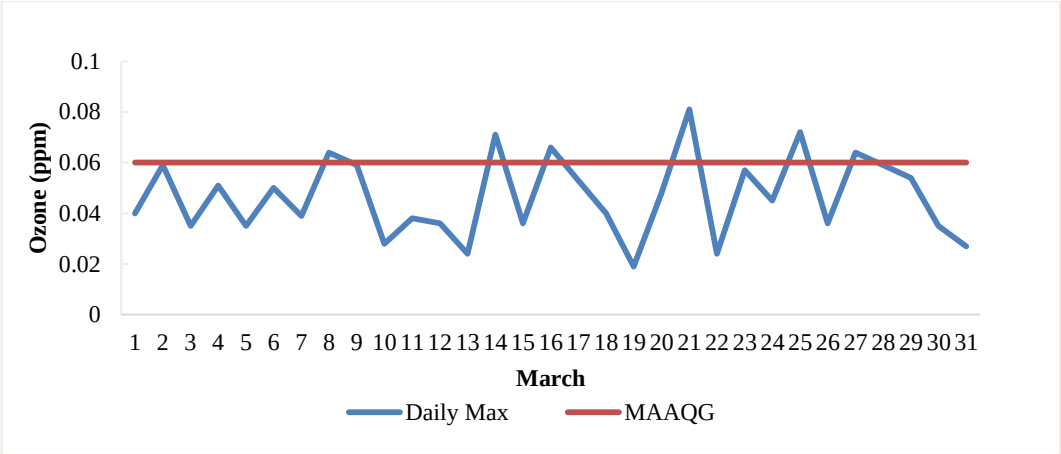

Figure B-7: Concentration of ozone gas at Station B for March 2010

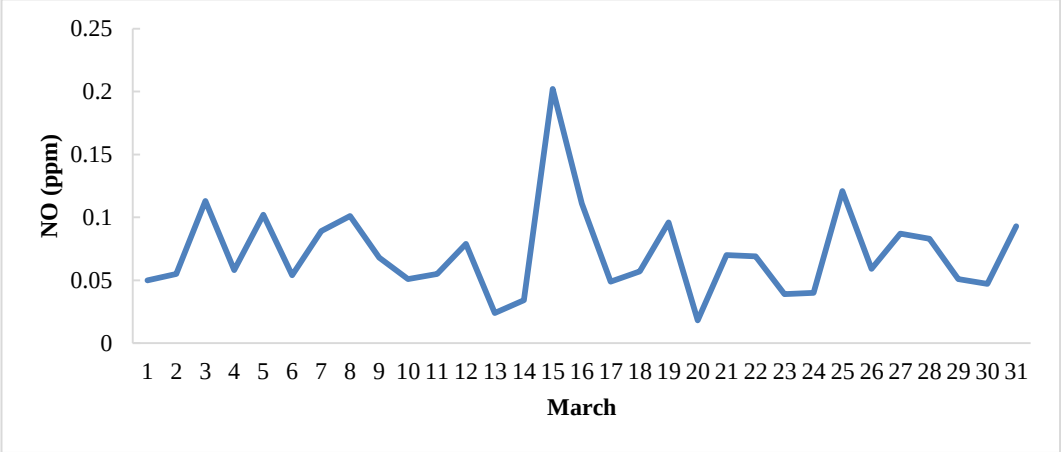

Figure B-8: Concentration of nitrogen oxide gas at Station B for March 2010

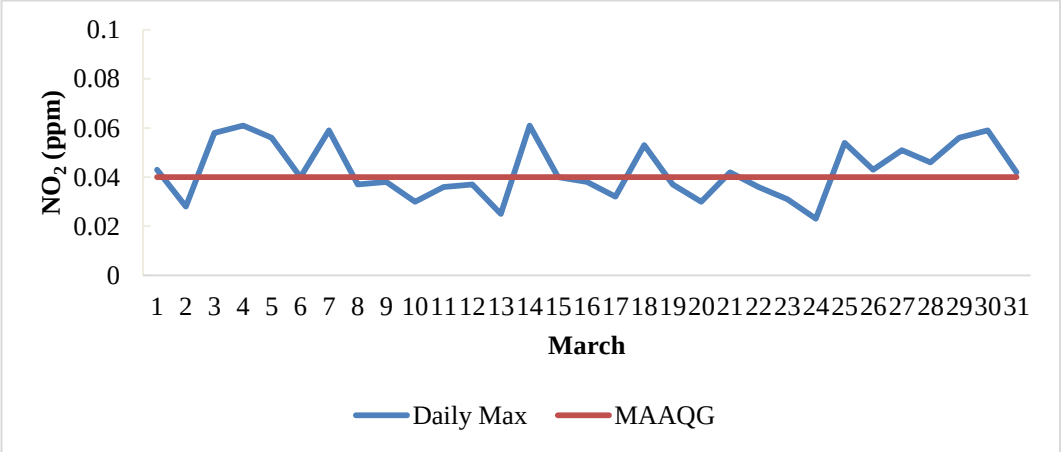

Figure B-9 Concentration of nitrogen dioxide gas at Station B for March 2010

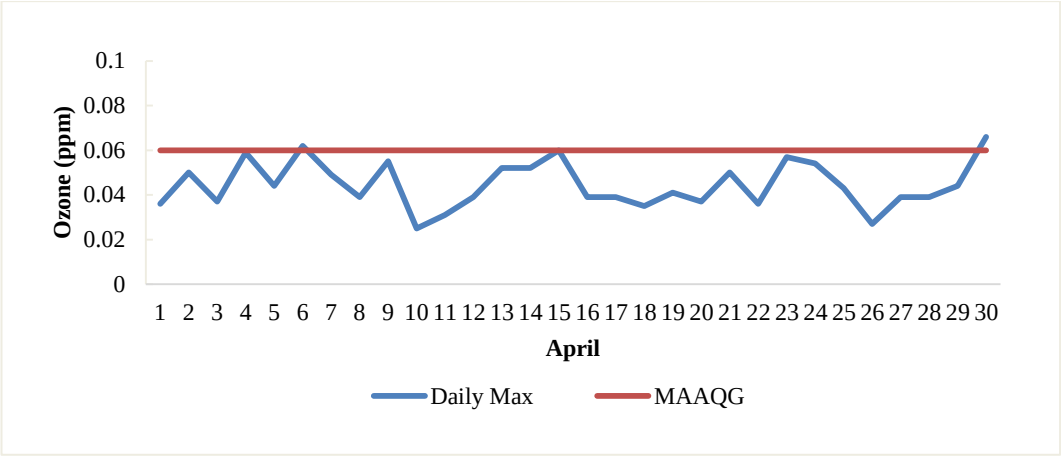

Figure B-10: Concentration of ozone gas at Station B for April 2010

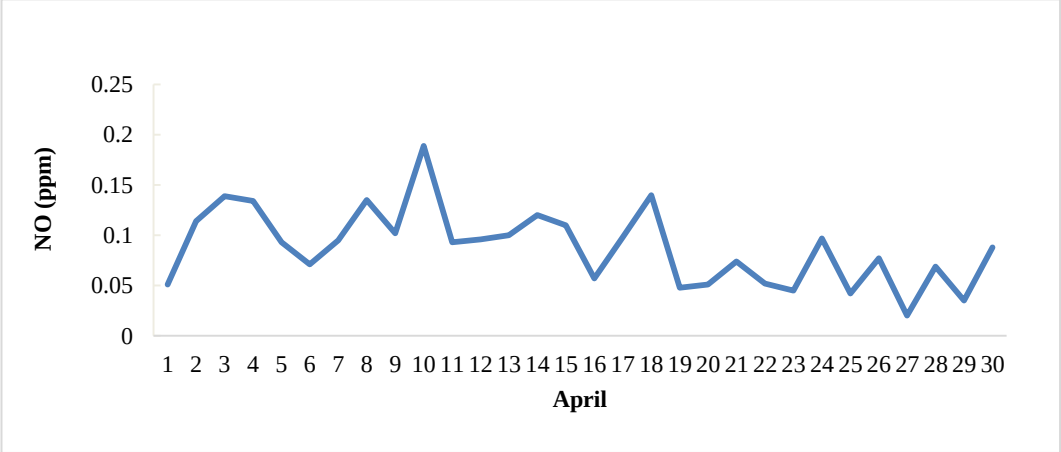

Figure B-11: Concentration of nitrogen oxide gas at Station B for April 2010

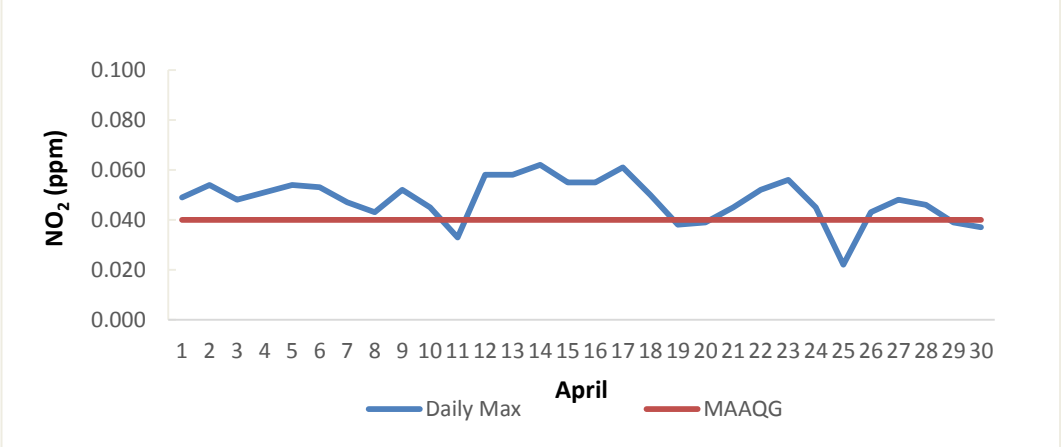

Figure B-12 Concentration of nitrogen dioxide gas at Station B for April 2010

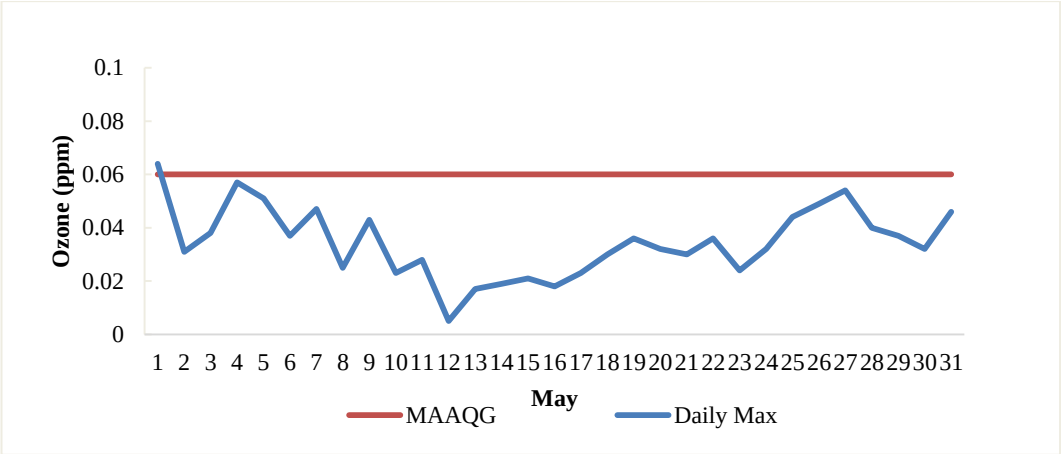

Figure B-13: Concentration of ozone gas at Station B for May 2010

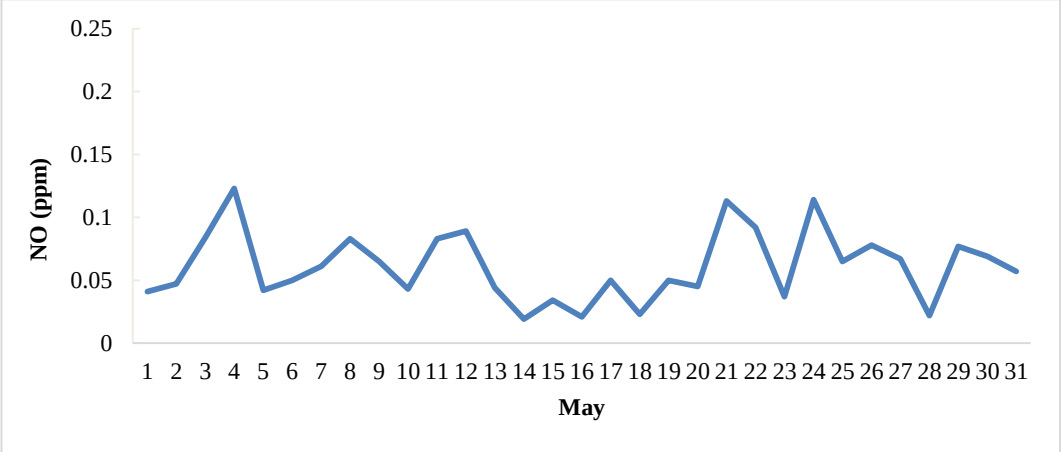

Figure B-14: Concentration of nitrogen oxide gas at Station B for May 2010

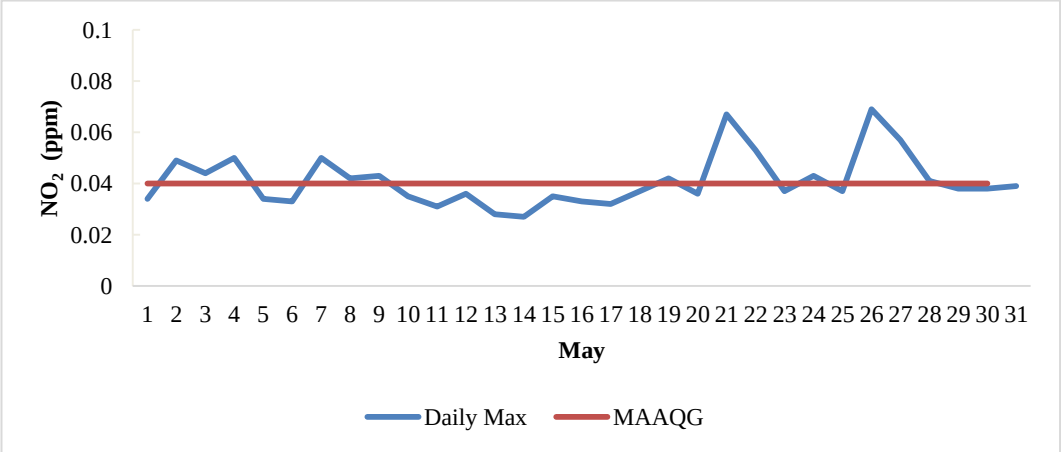

Figure B-15 Concentration of nitrogen dioxide gas at Station B for May 2010

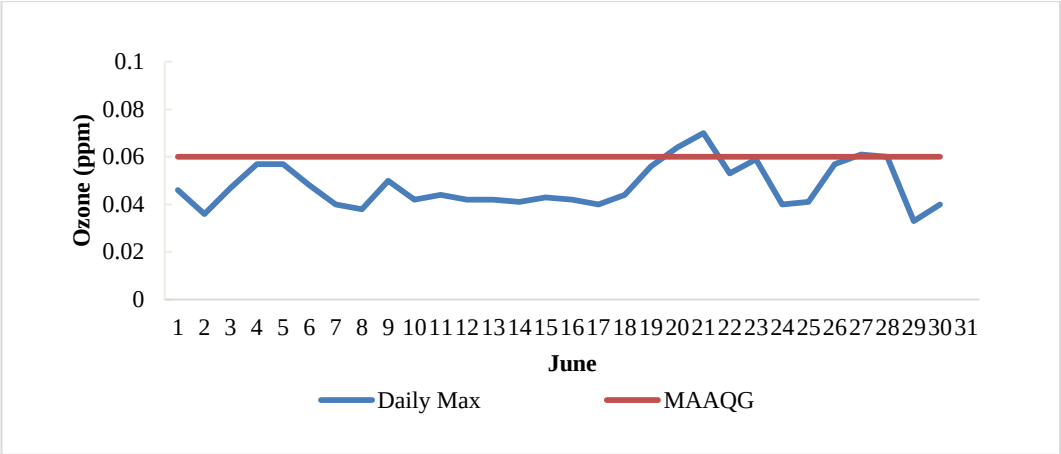

Figure B-16: Concentration of ozone gas at Station B for June 2010

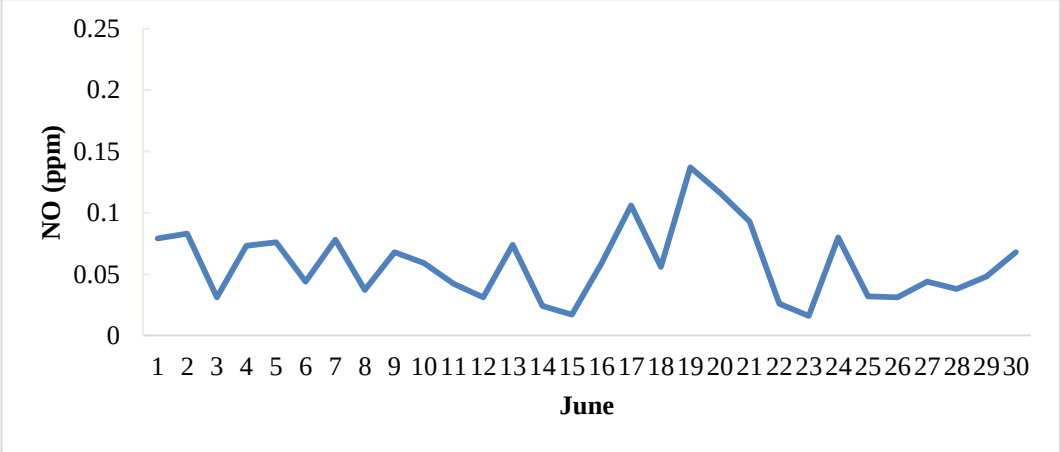

Figure B-17: Concentration of nitrogen oxide gas at Station B for June 2010

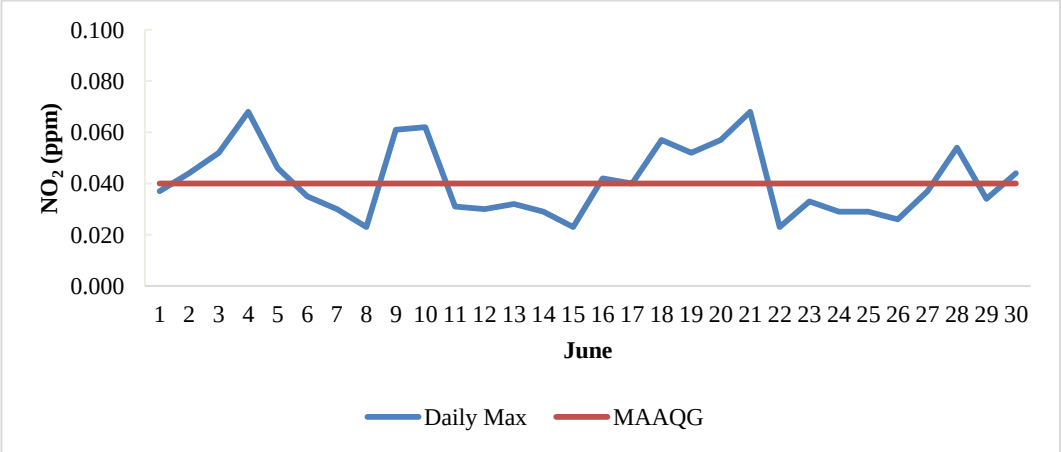

Figure B-18 Concentration of nitrogen dioxide gas at Station B for June 2010

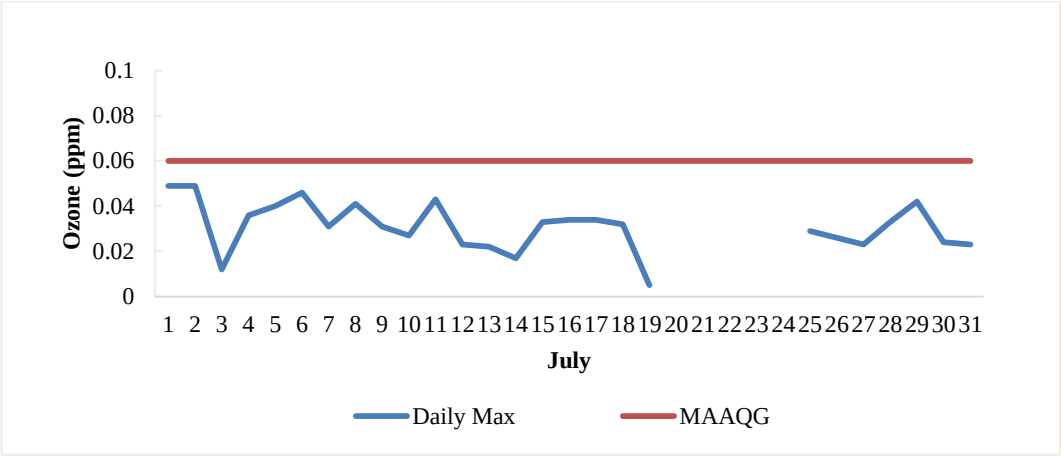

Figure B-19: Concentration of ozone gas at Station B for July 2010

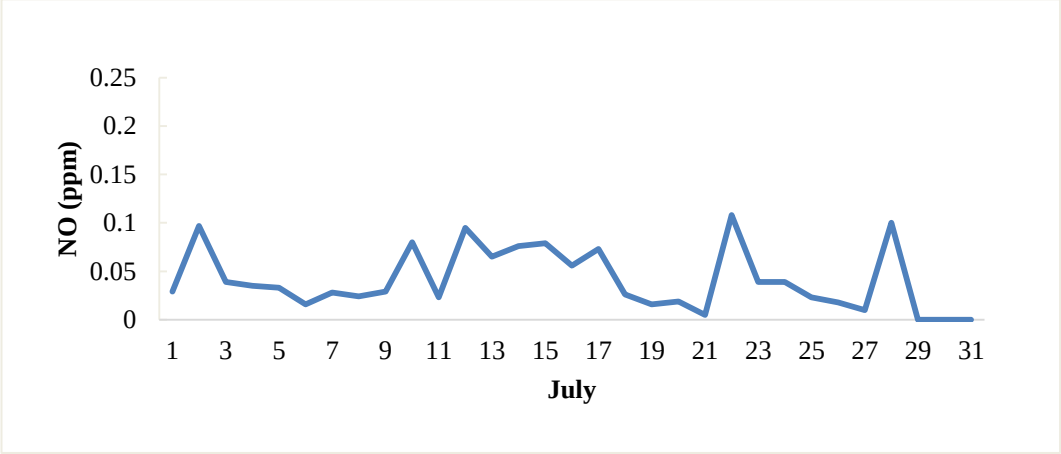

Figure B-20: Concentration of nitrogen oxide gas at Station B for July 2010

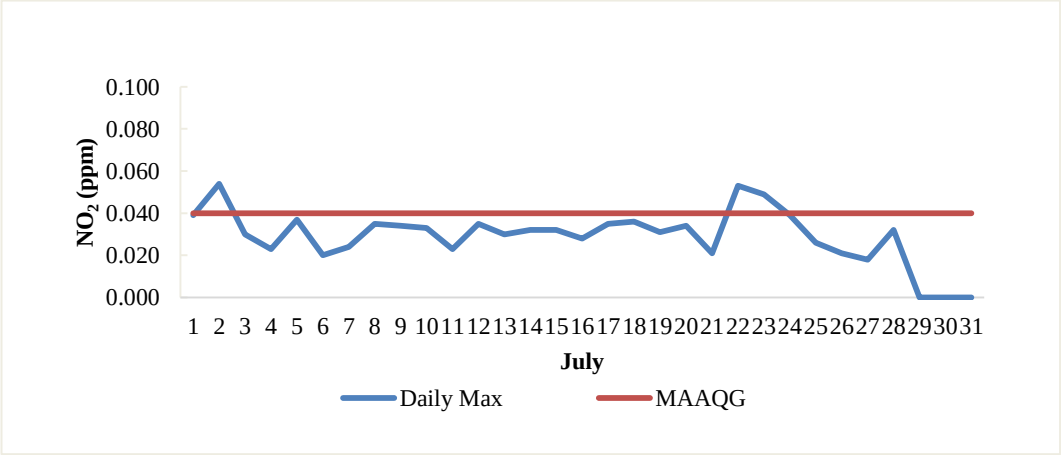

Figure B-21 Concentration of nitrogen dioxide gas at Station B for July 2010

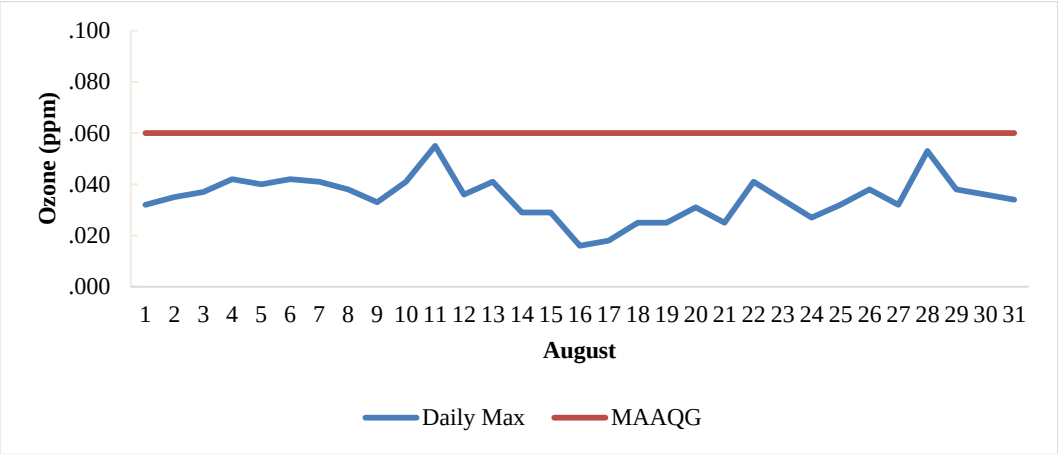

Figure B-22: Concentration of ozone gas at Station B for August 2010

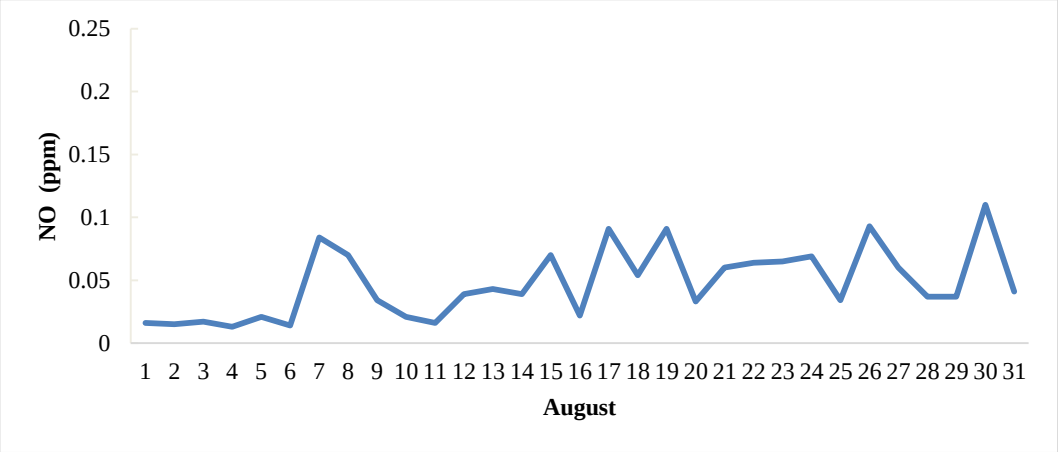

Figure B-23: Concentration of nitrogen oxide gas at Station B for August 2010

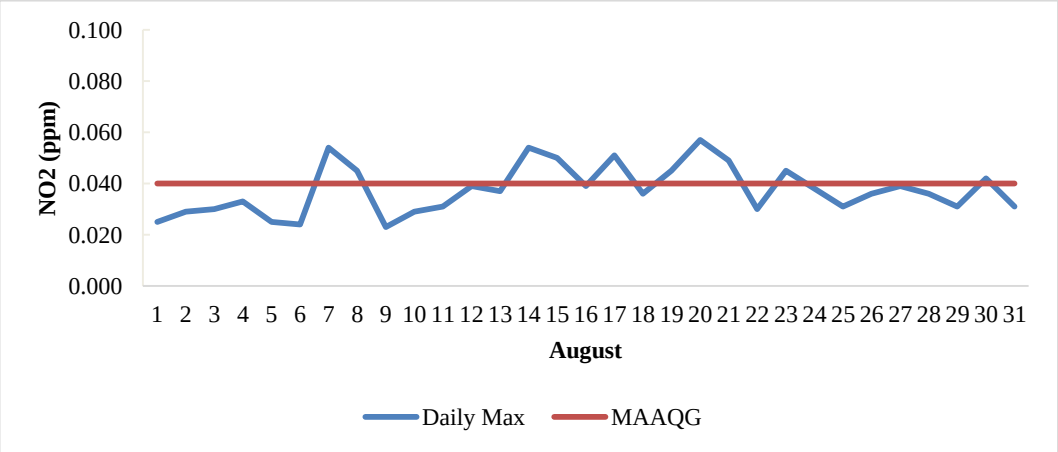

Figure B-24 Concentration of nitrogen dioxide gas at Station B for August 2010

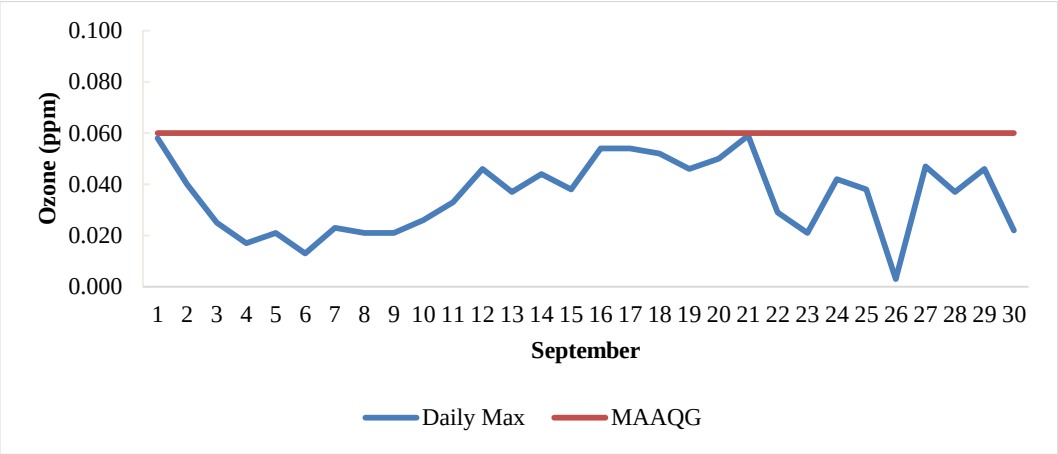

Figure B-25: Concentration of ozone gas at Station B for September 2010

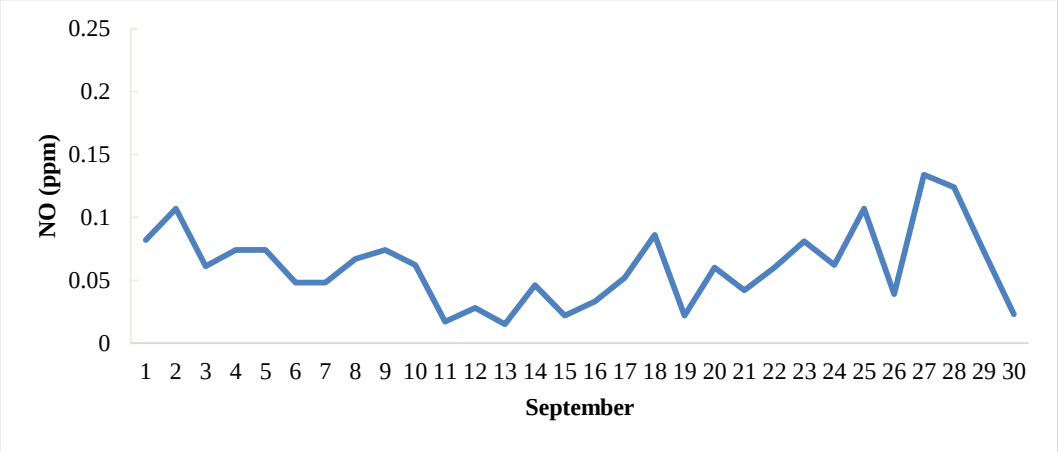

Figure B-26: Concentration of nitrogen oxide gas at Station B for September 2010

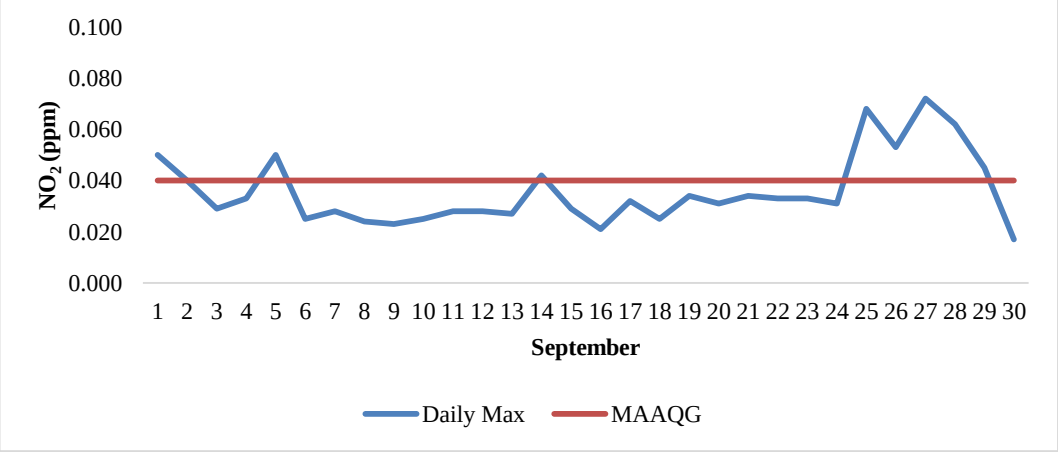

Figure B-27 Concentration of nitrogen dioxide gas at Station B for September 2010

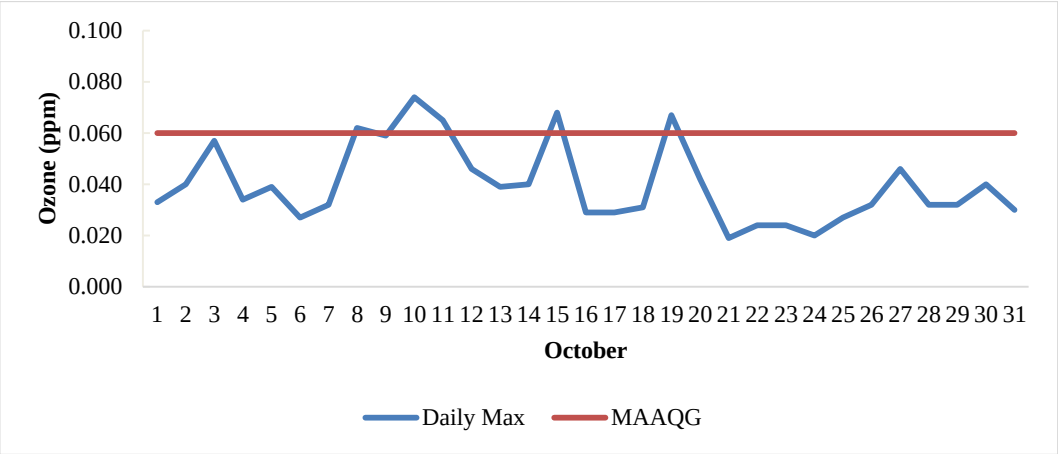

Figure B-28: Concentration of ozone gas at Station B for October 2010

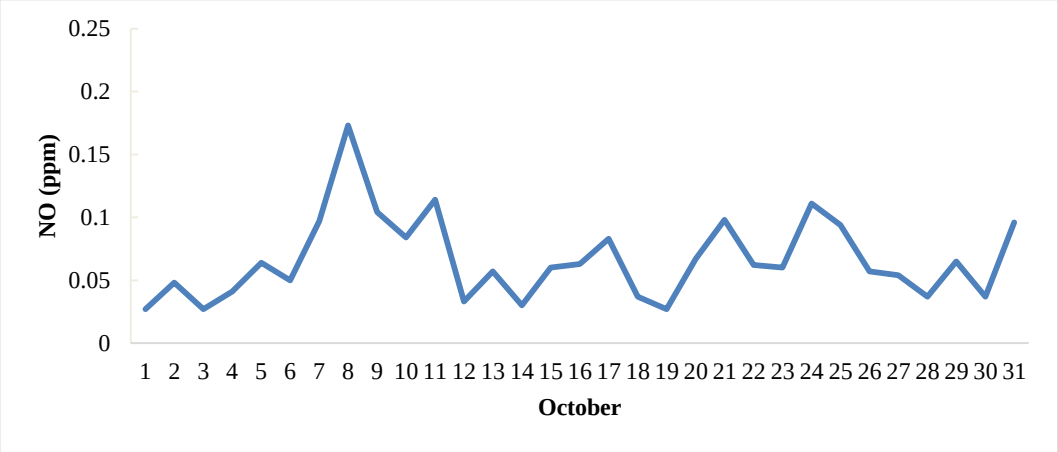

Figure B-29: Concentration of nitrogen oxide gas at Station B for October 2010

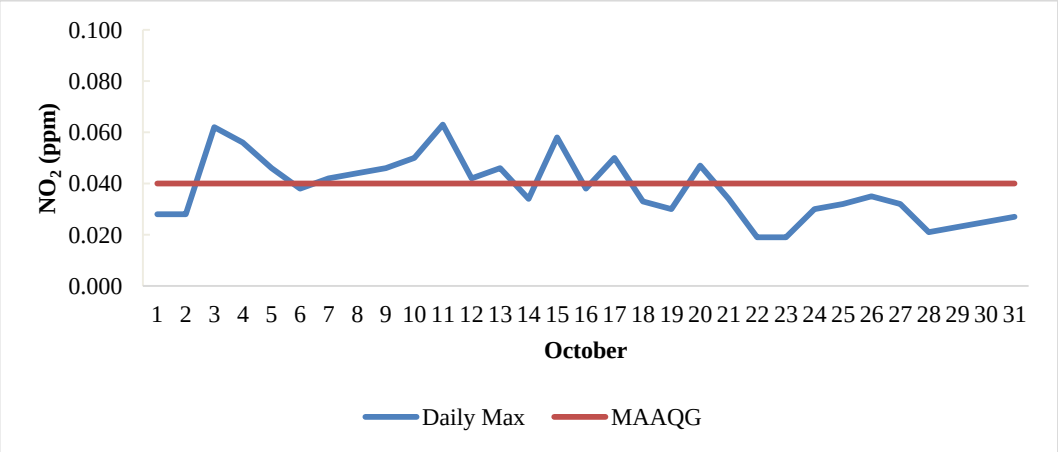

Figure B-30 Concentration of nitrogen dioxide gas at Station B for October 2010

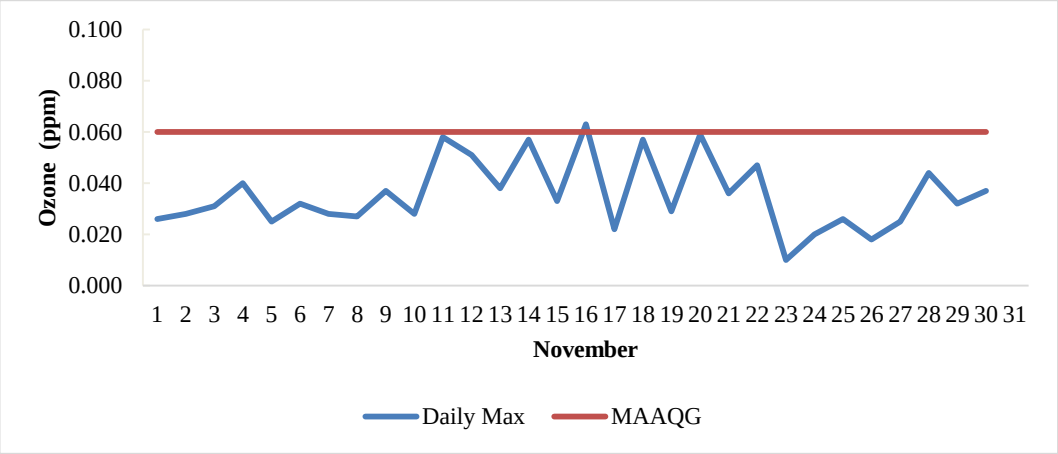

Figure B-31: Concentration of ozone gas at Station B for November 2010

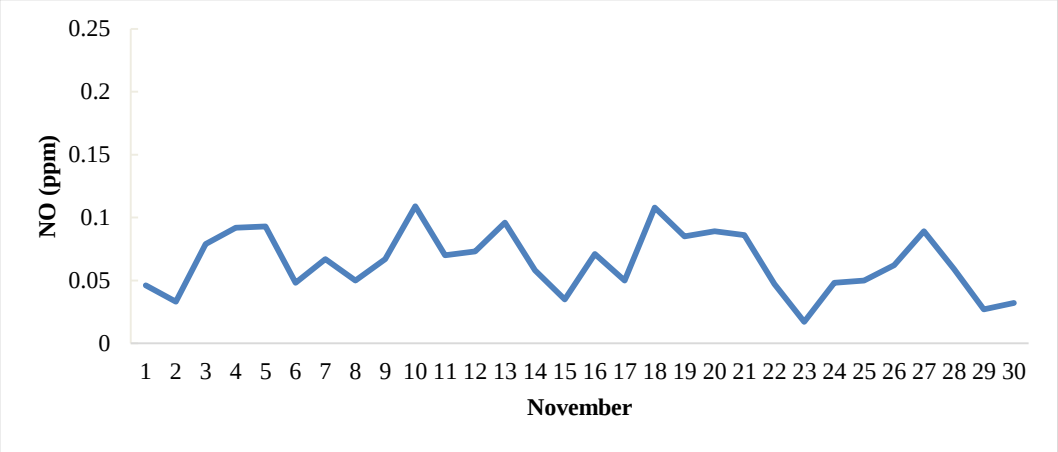

Figure B-32: Concentration of nitrogen oxide gas at Station B for November 2010

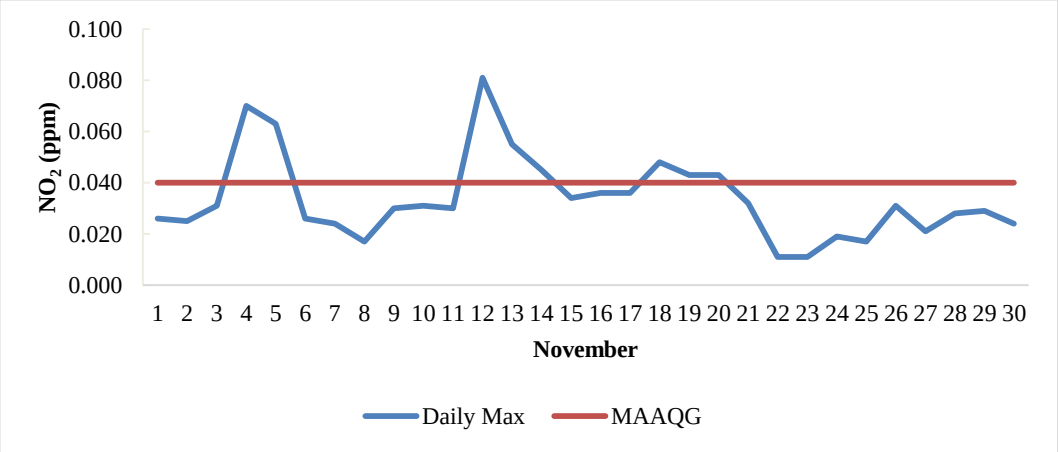

Figure B-33 Concentration of nitrogen dioxide gas at Station B for November 2010

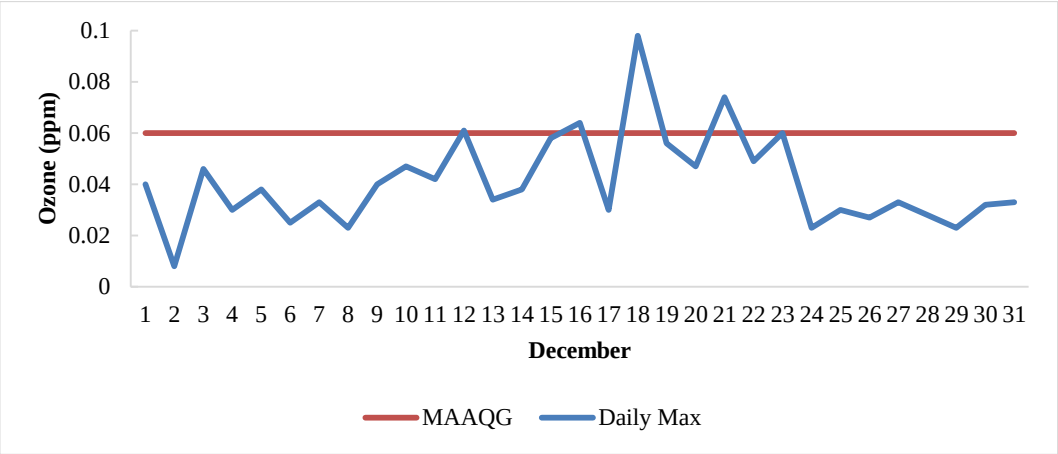

Figure B-34: Concentration of ozone gas at Station B for December 2010

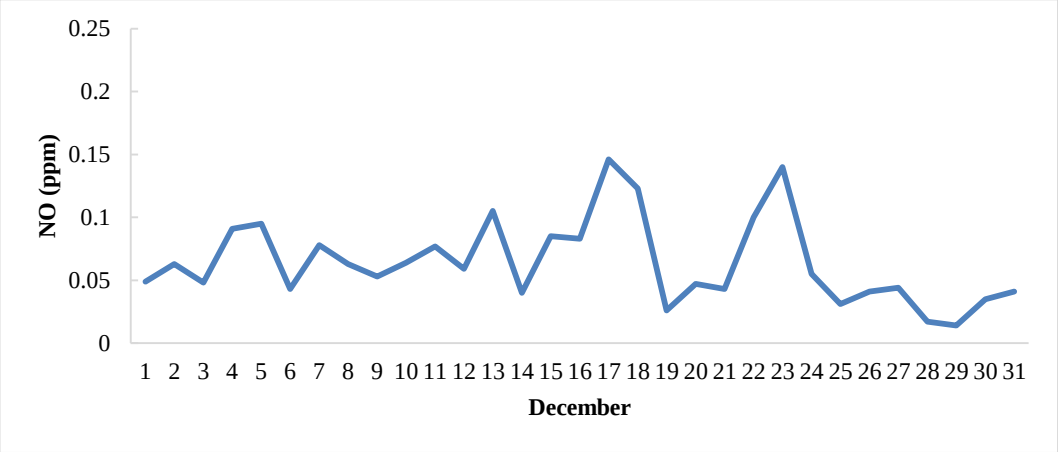

Figure B-35: Concentration of nitrogen oxide gas at Station B for December 2010

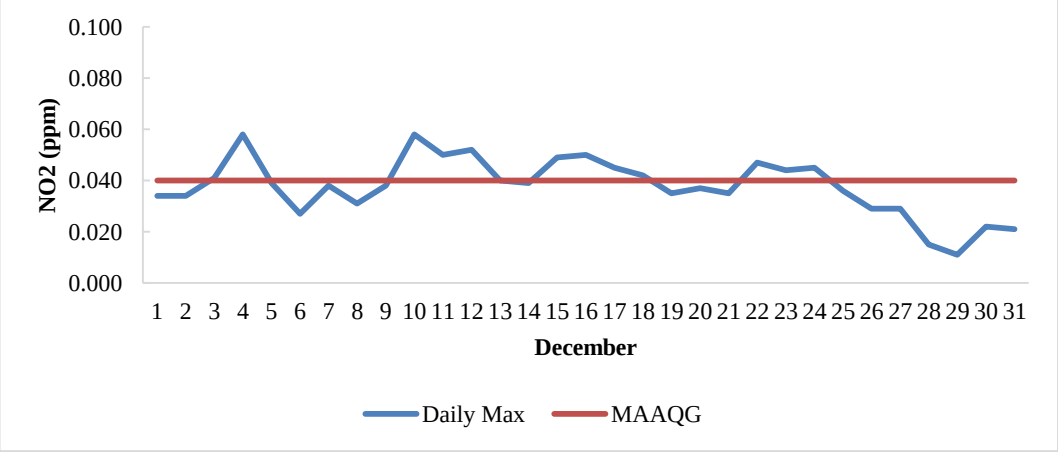

Figure B-36 Concentration of nitrogen dioxide gas at Station B for December 2010