ACKNOWLEDGEMENT

I wish to express my deep and sincere gratitude to my project supervisor, Associate Professor Dr. Nor Azam Ramli for his guidance, advice and encouragement during the course of this research and writing this dissertation. Furthermore I would like to thank my co-supervisor, Associate Professor Ahmed Shukri Yahaya for his guidance and advice.

The precious help given by Miss Nurul Isma bt. Mohammed in helping me in the site sampling is greatly acknowledged. Besides that, I would like to thank Miss Nurul Adyani bt. Ghazali for her advice in statistic and analysis.

Last but not least, I would like to express my love and appreciation to all my family members, course mates and friends.

ABSTRAK

Kajian ini bertujuan untuk menegtahui pegaruh pencemaran udara terhadap pengeluaran tanaman. Pencemaran udara adalah pencemaran utama yang boleh menyababkan kesan negatif terhadap tanaman mahupun kesihatan manusia. Ozon merupakan pencemar sekunder yang boleh menjejaskan hasil tanaman sayur dimana nitrogen dioksida pedahuluan bagi ozon. Terdapat tiga tempat yang terlibat dalam kajian ini , Taiping, Perai dan USM. Pengurangan hasil tanaman sayur kerana pendedahan ozon pada kadah kepekatan tertentu boleh ditentukan berdasarkan AOT40 dimana merupakan benchmark Eropah untuk penyelidikan tanaman. AOT40 boleh ditakrifkan sebagai akumulasi kepekatan ozon melebihi 40 ppb selama tempoh tiga bulan. Kehilangan hasil tanaman sayur sehigga 5% berlaku apabila AOT40 yang melebihi had akumulasi 3000ppb. Terdapat lima jenis tanaman terlibat dalam kajian iaitu bayam, kacang panjang, bendi, cili dan jagung. Jumlah kehilangan hasil tahun 2004 dan 2005 adalah 439,911 metrik tan dan 448,409 metrik tan masingmasing. Oleh itu, pembentukan ozon untuk ketiga tempat tersebut dianalisiskan dimana nitrogen dioksida sebagai pendahuluan. Model pembentukan ozon dihasilkan. Parameter meteorologi seperti suhu, kelajuan angin dan kelembapan juga terlibat dalam pemodelan. Model yang dihasilkan berdasarkan AOT40 dalam setiap tempoh tiga bulan. Dua puluh model dihasilkan untuk setiap tempat kaji tahun 2004 dan 2005. Ada beberapa langkah yang terlibat dalam proses pemodelan. Model dihasilkan diuji prestasinya dengan menggunakan plot tersebar dan penunjuk prestasi. Dengan ini, model terbaik untuk setiap halaman dapat ditentukan. Tempat kajian untuk setiap lokasi dilakukan untuk mengesahkan model.

ABSTRACT

This research is to investigate the effect of air pollution to crop production. Air pollution is the major pollution can cause adverse impact to the crops as well as human health. Ozone (O₃) is a secondary pollutant which may affect the crops yield lost where NO₂ act as precursor for O₃ formation. There are three sites involved in this study which are Taiping, Perai and USM. The crops reductions due to O₃ exposure in certain concentration standard were based on AOT40 which is the European benchmark for the crop study. AOT40 can be defined as the accumulations of the O₃ concentration exceed 40 ppm for three months period. Crops yield loss can go up to 5% when the AOT40 exceed 3000ppm accumulation limit. There are five crops involved in the study which are spinach, long bean, lady's finger, chili and maize. Total yield loss for the five crops is 439.911 metric tonnes and 448.409 metric tonnes for 2004 and 2005 respectively. Hence, O₃ formation for these three sites was analyzed where NO₂ is the precursor. The O₃ prediction models for each sites were generated. Other meteorological parameter such as temperature, wind speed and humidity were involved in the modeling. The models were generated based on the AOT40 values which are calculated in every three month period. Ten models were generated for each site for 2004 and 2005. There are some steps which involved in the modeling process. First, the model should be generated. Then, justification of the model was carried out to test the performance of the model by using scatter plot and performance indicator. From this step, the best model for each site can be determined. Site sampling for each site were carried out in order to verify the model.

TABLE OF CONTENTS

ACKNOWLEDGEMENT	i
ABSTRAK	ii
ABSTRACT	iii
TABLE OF CONTENTS	iv
LIST OF TABLE	vii
LIST OF FIGURE	viii
LIST OF ABBREVIATION	ix
LIST OF APPENDIX	X
CHAPTER 1	1
INTRODUCTION	1
INTRODUCTION	1
1.1 SOURCES OF AIR POLLUTANTS	2
1.2 PROBLEM STATEMENTS	2
1.3 OBJECTIVE	3
1.4 SCOPE AND REGION	4
CHAPTER 2	5
LITERATURE REVIEW	5
2.0 INTRODUCTION	5
2.1 AIR QUALITY OF NORTHERN AREA OF PENINSULAR MALAYSIA	6
2.2 AIR POLLUTION SOURCE	7
2.3 CROP STUDY AT NORTHERN AREA OF PENINSULAR MALAYSIA	8
2.4 TYPE OF POLLUTANT AND THEIR EFFECT TO THE CROP	9
2.4.1 OZONE	9
$2.4.2 \mathrm{~SO_x}$	11
$2.4.3 \text{ NO}_{x}$	12
2.4.4 VOC	12
2.5 AOT40	13
2.6 INTERNATIONAL AND NATIONAL AIR QUALITY STANDARD GUIDELINES	15
2.6.1 INTERNATIONAL AIR QUALITY STANDARD	15
2.6.2 MALAYSIA AIR QUALITY STANDARD	17

CHAPTER 3	19
METHODOLOGY	19
3.0 INTRODUCTION	19
3.1 DESCRIPTIVE STATISTICS	19
3.1.1 MEAN	19
3.1.2 VARIANCE	20
3.1.3 STANDARD DEVIATION	20
3.2 REGRESSION ANALYSIS	21
3.2.1THE SIMPLE LINEAR REGRESSION MODEL	22
3.2.2 THE MULTIPLE LINEAR REGRESSION MODEL	22
3.3 CALCULATION OF AOT40	23
3.4 PERFORMANCE INDICATOR	24
3.4.1 COEFFICIENT OF DETERMINATION	24
3.4.2 BIAS	25
3.4.3 PREDICTION ACCURACY	25
3.4.4 NORMALIZED ABSOLUTE ERROR (NAE)	25
3.4.5 ROOT MEAN SQUARE ERROR (RMSE)	26
3.5 INSTRUMENT	26
3.5.1 AEROQUAL	26
3.5.2 UV ABSORPTION OZONE ANALYZER MODEL 400A	27
3.5.3 ANALYSER CHEMILUMINESCENT NO/NO2/NOX ANALYZER MODEL 200A	27
3.6 SITE SAMPLING	28
CHAPTER 4	29
RESULT AND DISCUSSION	29
4.1 INTRODUCTION	29
4.1 AOT40 AND DIURNAL FOR STUDY AREA	29
4.1.1 AOT40 DETERMINATION FOR TAIPING	30
4.1.2 DIURNAL FLUCTUATION FOR TAIPING	31
4.1.3 AOT40 DETERMINATION FOR PERAI	33
4.1.4 DIURNAL FLUCTUATION FOR PERAI	34
4.1.5 AOT40 DETERMINATION FOR PENANG, USM	36
4.1.6 DIURNAL FLUCTUATION OF OZONE AND NITROGEN DIOXIDE (NO ₂) FOR USM	37

4.2 CROP REDUCTION CALCULATION	38
4.3 MODELING AND PREDICTION OF OZONE	42
4.3.1.1 MODELING OZONE FOR TAIPING	43
4.3.1.2 SCATTER PLOT	47
4.3.1.3 PERFORMANCE INDICATORS	51
4.3.2.1 MODELING OF OZONE FOR PERAI	52
4.3.2.2 SCATTER PLOT	56
4.3.2.3 PERFORMANCE INDICATORS	59
4.3.3.1 MODELING OZONE FOR USM, PENANG ISLAND	60
4.3.3.2 SCATTER PLOTS	64
4.3.3.3 PERFORMANCE INDICATOR	67
4.4 MODEL VERIFICATION	69
4.4.1DIURNAL FOR TAIPING	69
4.4.2 DIURNAL FOR PERAI	71
4.4.3 DIURNAL FOR USM, PENANG ISLAND	73
4.5 MODEL PERFORMANCE	75
4.5.1 SCATTER PLOT	75
4.6 PERFORMANCE INDICATOR	78
CHAPTER 5	79
CONCLUSION AND RECOMMENDATION	79
5.1 CONCLUSION	79
5.2 RECOMMENDATION	81
REFERENCE	82
APENDICES	86

LIST OF TABLE

Table 2.5.1 Group of crop due to sensitivity of crop (Mills et al., 2007)	14
Table 2.6.1.1 Air quality standard from WHO(2001) (Han and Naeher, 2006)	15
Table 2.6.1.2 Air quality standard from Environmental Protection Agency, US (US EPA, 2009)	16
Table 2.6.2.1 Malaysia air quality guideline (DOE, 2010)	18
Table 2.6.2.2 Malaysia API Scale (DOE, 2010)	18
Table 4.2.1 Crop lost in metric tonne (Mt) due to the ozone exposure 2004 (Agricultural department of Kedah, 2004)	39
Table 4.2.2 Crop lost in metric tonne (Mt) due to the ozone exposure 2005 (Agricultural department of Kedah, 2005)	41
Table 4.3.1.1 Developed model for Taiping year 2004	44
Table 4.3.1.2 Coefficient of the model variable Taiping for Januarry to March 2004	45
Table 4.3.1 3 Developed model for Taiping 2005	46
Table 4.3.1.4 Coefficient of the model variable Taiping Januarry to March 2005	47
Table 4.3.1.3.1 The model result of ozone model Taiping for the prediction	52
Table 4.3.2.1 Developed model for Perai 2004	53
Table 4.3.2.2 Coefficient of the Perai model October to December 2004	54
Table 4.3.2.3 Developed ozone model for Perai year 2005	55
Table 4.3.2.4 Coefficient of Perai model January to march 2005	55
Table 4.3.1.3.1 The best modeling result of Perai	60
Table 4.3.3.1 Model develop for USM 2004	61
Table 4.3.1.2 Coefficient of the model 2004 USM	62
Table 4.3.1.3 Model developed for USM year 2005	63
Table 4.3.1.4 Coefficient of the model 2005 USM	63
Table 4.3.3.3.1 The model result of ozone model USM for the prediction	68
Table 4.6.1 Performance indicator result of model for three sites	78

LIST OF FIGURE

Figure 1.4.1 Map for research location	4
Figure 4.1.2.2 Diurnal fluctuation of ozone for Taiping 2005	33
Figure 4.3.1.2.1 Scatter plot of the ozone at Taiping 2004 with prediction ozone 2005	48
Figure 4.3.1.2.2 Scatter plot of the ozone at Taiping 2005 with prediction ozone 2005	49
Figure 4.3.1.2.3 Scatter plot of the ozone at Taiping 2005 with prediction ozone 2006	50
Figure 4.3.2.2.1 Scatter plot of the ozone at Perai 2004 with prediction ozone 2005	56
Figure 4.3.2.2.2 Scatter plot of the ozone year 2005 with prediction ozone year 2005	57
Figure 4.3.2.2.3 Scatter plot of the ozone year 2005 with prediction ozone year 2006	58
Figure 4.3.3.2.1 Scatter plot of the ozone at USM 2004 with prediction ozone 2005	65
Figure 4.3.3.2.2 Scatter plot of the ozone USM 2005 with prediction ozone 2005	66
Figure 4.3.3.2.3 Scatter plot of the ozone year 2005 with prediction ozone year 2006	67
Figure 4.4.1.1 Diurnal fluctuation for NO ₂ and ozone of Taiping	70
Figure 4.5.1 Scatter plot of the ozone obtain with the predicted ozone at Taiping.	75
Figure 4.5.2 Scatter plot of the Ozone obtain with the predicted ozone at Perai	76
Figure 4.5.3 Scatter plot of the Ozone obtain with the predicted ozone at USM	77

LIST OF ABBREVIATION

NO₂ Nitrogen dioxide

 $\begin{array}{ccc} O_3 & Ozone \\ ws & Wind speed \\ Mt & Metric tonne \\ Ha & hectare \end{array}$

temp Temperature

NAE Normalized absolute error PA Prediction accuracy

R² Coefficient of determination RMSE Root mean square error IA Index of agreement

Rsq R-Square
ppb Part per billion
ppm Part per million

WHO World health organization

std Standard

API Air pollution index

AOT40 Accumulated of ozone exposure over a

threshold of 40ppb

LIST OF APPENDIX

Appendix A	86
Table A1 Scatter plot result for model for Perai	86
Table A2 scatter plot result for Taiping	87
Table A3 Scatter plot result for USM	88
Appendix B	89
Figure B1 Humidity for Perai 2004	89
Figure B2 Humidity for Perai 2005	89
Figure B3 Temperature for perai 2004	90
Figure B3 Temperature for perai 2005	90
Figure B6 Humidity for Taiping 2005	91
Figure B7 Temperature for Taiping 2004	92
Figure B8 Temperature for Taiping 2005	92
Figure B9 Temperature for USM 2004	93
Figure B10 Temperature for USM 2005	93
Figure B11 Humidity for USM 2004	94
Figure B12 humidity for USM 2005	94
Table B1 Average for annually data	95

CHAPTER 1

INTRODUCTION

INTRODUCTION

Generally, air is important to agricultural crops growth and production. Hence the composition of air was very important to make sure that the goodness of crop production due to their quantity and quality as well as yield. However, the findings over few decades had shown that ambient air pollution has the potential to cause adverse impacts on the growth and yield loss of agricultural crops (Ishii et al., 2007). There are many primary pollutant such as sulfur dioxide (SO₂), nitrogen oxides (NO_x), peroxyacetyl nitrate (PAN), and volatile organic compounds (VOCs) which may affect crops production (Tong et al., 2007). Photochemical reaction of O₃ formation started to occur between reaction of nitrogen oxides (NO_x) and volatile organic compounds (VOCs) which driven by high temperatures and presence of sunlight (Castellanos et al., 2009). It is found that O₃ is one of the secondary pollutants which can cause the yield lost of crop. Direct exposure of crops to O₃ can cause direct adverse impact to the crop. There has been a research whereby the selected rice species which are M7 & and M9 species were studied in order to determine the effect of O₃ and SO₂ to their yield. It was found that their yield were reduced due to the O₃ exposure (Chen and Li, 2003). Guidelines for air quality are necessary to solve this problem in order to protect human health and the crop. However, air pollution still happens every day and get worst especially in developing country (Van Dingenen et al., 2009).

1.1 SOURCES OF AIR POLLUTANTS

According to previous study, the dominant sources for the measured species were resuspended road dust, automobile and diesel emissions, combustion of oil and coal, ferrous and non-ferrous smelters and sea spray (Swietlicki et al., 1996). The dominant source can be categorized into natural and manmade sources. Manmade sources have mobile sources (motor vehicles), and stationary sources (power plants, industrial facilities, residential and commercial establishments, and a multitude of miscellaneous sources while the natural source is from plants. Determination of sources was very important in this study in order to control and identified the pollution and pollutants (Placet et al., 2000). However, it is also depend on the topography and meteorology condition (Cousin et al., 2005). Besides that, large high-intensity wildfire was also the source of air pollution. Large volume of the fine particles (PM_{2.5}) and O₃ can be generated (Preisler et al. 2010).

.

1.2 PROBLEM STATEMENTS

Malaysia which is a developing country is experiencing rapid change and evolution in technology and economy as well as industry to become a developed country. The dynamic change in industry has lead to the rapid increase of pollutants in the air due to the increase of vehicles and emission from factories. The increase in concentration of the pollutants can cause some effect to the plant (Bytnerowicz et al., 2007). The global demand for food has increased due to the dynamic increase in population. To achieve the demand, the yield per area of crop should be increased. However, environment problem especially air pollution can cause damage to crops and reduce the crops production (Gregory et al., 2002).

Malaysia is a country which is rich of natural material and food such as agriculture crop, plantation plant and many more. Hence, at the same time, the developing may bring along the adverse impact such as the over spent of material as well as pollution. The current major pollution is air pollution.

Pollutant in the air may change the climate characteristic such as the environment was getting wormer as impact of green house effect cause by the air pollution. The change in environment may lead to some crops which are less adaptability to the environment will going to be lost. For example, global warming increases the environment temperature which can lead to shortage of water in crop plantation and less production in consequence (Krupa and Kickert, 1989).

1.3 OBJECTIVE

The objectives of the research are:

- i. To analyze the past trend of ozone formation from 2004 to 2005
- ii. To estimate the effect of ozone exposure towards short term crops based on linear regression at Taiping, Perak, Perai and USM, Penang Island
- iii. Propose strategies to minimize crops reduction due to ozone exposure

1.4 SCOPE AND REGION

This research is the study of potential yield lost of the short term crops due to the ambient O₃ concentration in northern region of peninsular Malaysia. The study of O₃ formation, NO₂ as precursor was carried out. The study areas include the Penang Island, Seberang Perai and Taiping, north Perak. The data will be collected and analyzed. AOT40 was a benchmark of O₃ concentrations to determine the affect of O₃ to the crops. The yield loss of crops due to O₃ were calculated and estimated. Meteorological parameter such as wind speed, temperature and humidity are taking into consideration in this study.



Figure 1.4.1 Map for research location

CHAPTER 2

LITERATURE REVIEW

2.0 INTRODUCTION

Malaysia is experiencing rapid urbanization. Impact from the urbanization is exponentially increasing with population and industry. There is dynamic increase in population and industry as well as social-economic activity which may lead to the increase of materials usage and energy consumption. Power stations, factories and infrastructures were built to accelerate the country development and demand of the population. This may change the current environment and create some environmental impact such as as air pollution, acid rain, water pollution and land pollution (Atash, 2007).

Air pollution has become a major problem in the world which had created many environment problems. Among the factors which lead to air pollution is because of the increase in population and economy due to urbanization. It is reported that there are almost 500 compounds emitted from vehicles. However, there are only about 200 of the pollutants which have impacts to the environment were determined for an even smaller number (Fenger, 1999).

Among the major air quality parameter are PM_{10} ozone (O_3) Carbon dioxide (CO_2) , sulphur dioxide (SO_2) and oxides of nitrogen (NO_x) . The pollutants may affect the concentration of the compound above due to their reaction and transformation among each other. This may lead to the change in climate and affect the plant growth as well as human health (Percy and Ferretti, 2004). Air is the prime source for all the life on

the earth. Human must concern about it. The understanding of the human to the air quality was very important for the monitoring of environment and solution finding (Sharma et al., 2003).

2.1 AIR QUALITY OF NORTHERN AREA OF PENINSULAR MALAYSIA

API (Air Pollutant Index) was use to indicate the level of air pollution in Malaysia. It is important to determine and monitor the present air quality for the concern of public health and environment. API system was similar to the Pollutant Standard Index (PSI) developed by the United States Environmental Protection Agency (US-EPA) (DOE, 2010).

Northern areas of peninsular Malaysia refer to the state of Perak, Penang, Kedah and Perlis. The agriculture industry is the major economic in this area especially Kedah which are the home town of paddy. However, the developing of other industries was carried out in these areas due to the mission of the country to become a highly developed country such as industries area in Kulim, Bukit Minyak in Seberang Prai and Bayan Lepas, Pulau Penang. Infrastructures had been built for development purpose. Development leads to increase in vehicle volume which may derive air pollution. The factories in the industry areas will also contribute some pollutants to the atmosphere. As an impact, air quality in these areas will be affect (Ishii et al., 2007).

However, there was a haze period which the source came from Indonesia. From the history view, it showed that the worst haze episode happened in 1997. The smoke

haze from the land and forest fire affected Malaysia and even affected over 300 million of people which lead to economic lost (Afroz et al., 2003).

2.2 AIR POLLUTION SOURCE

In Malaysia, there are three major sources of air pollution which are mobile sources, stationary sources and open burning sources. The finding in past 5 year had shown that the emission from mobile sources have contributed 70-75% of the total air pollution. Stationary sources have contributed to 20-25% of the air pollution. Open burning or forest fires have contributed 3-5% to the total air pollution (Afroz et al., 2003).

Among the activities which lead to air pollution is fuel combustion from the residential, commercial/institutional, and small industrial space heating, steam, or process heat generation. Waste treatment and disposal method such as illegal open burning, apartment/institutional incinerators, landfills, agricultural and forest managed burning will also lead to air pollution problem. Besides that, in architectural coating, dry cleaning, equipment cleaning, graphic arts, pesticide application, auto refinishing, other surface coating and consumer products which used the organic solvent will also contributed to air pollution. The material handling and storage and miscellaneous which refer to transportation of petroleum, forest wildfires, dust, construction and other activities have created air pollution problem (Placet et al., 2000).

Mobile sources come from vehicles. There are large volumes of vehicles in Malaysia. There are 6.94 million of cars registered in Malaysia, while, 5.35 million of cars were

in-use. The registered motor were about 7.46 million, while, 4.66 million of the motors were in-use. For goods vehicle, there are 837 thousand of vehicles were registered, while, 706 thousand of good vehicles in-use (DOE, 2006). Base on the large volume of the vehicles, the emission from vehicles can be predicted and air quality can be estimated.

2.3 CROP STUDY AT NORTHERN AREA OF PENINSULAR MALAYSIA

Biotechnology has become a major technology to enhance the quality of plants or crops in order to increase the crops production and yield. As a result it can improve resistance of plants to pests and diseases which may lead to a reduction of expenditures on purchased inputs. The development of new technology has given benefit to the economic for the developing country as well as agriculture based country. In Malaysia, it will benefit the producers and consumers as a general economic effect of their country's adoption of improved planting material (Gotsch and Herrmann, 2000).

Most of the paddy agriculture crop located in the northern region of peninsular of Malaysia, more specific is in Kedah state. The entire paddy plantation in these areas are irrigated or rained. According to the analysis, there are relatively small difference in area estimates between the MOD_{rice} and NAS datasets. At the subnational state level, these two datasets were well correlated ($r^2 = 0.71$, RMSE = 350 km²) and had similar spatial distribution patterns of paddy rice field (Xiao et al., 2006)

Yield can be defined as the shifted from an energy ratio to the ratio between seed harvested and seed sown. Yield was very importance in calculate the economic benefit. Actual yield is the average yield of a district. It reflects the current state of soils and climate, average skills of the farmers, and their average use of technology. Actual yield also applies to the particular yield of a crop in a given paddock and season. Attainable yield is corresponding to the best yield achieved through skilful use of the best available of technology. Potential yield is 'the maximum yield that could be reached by a crop in given environments' as determined from physiological principles. Hence, the potential yield was refer to the crop physiology which deals with the structure and functioning of crops, and is therefore closely related to plant sciences and ecology. It means that air quality or the current environment was the sensitive part for the plant sciences in order to achieve the potential yield (Sadras et al., 2009).

2.4 TYPE OF POLLUTANT AND THEIR EFFECT TO THE CROP

2.4.1 OZONE

Ozone is normally located in the layer of 10-30 miles from the surface of the earth (US EPA, 2009). It contains 3 oxygen atoms (O₃) instead of the usual 2 oxygen atoms (O₂) which may block and protect human from the sun's ultraviolet radiation. The O₃ on the ground was toxic to human. Ozone can be produced by many reaction or process on the earth. The reaction compound involved are volatile organic chemicals, nitrogen oxides and sunlight (Curtis et al., 2006).

Surface O_3 can be found anywhere on the surface. It is because it can be transboundary transport in atmosphere in large region and experience rapid dynamic change. AOT40 was use to monitor the change of O_3 and the model was created. It

was found that the ambient O_3 concentrations at a given location are a product of topography, local scale photochemistry that is influenced by meteorology and by both natural and anthropogenic processes, and by transport of O_3 and/or its precursors from extraneous regions, although on occasions there may be intrusions from the stratosphere. It means that the model should come out with many factors such as temperature, wind speed, relative humidity and solar radiation (Krupa et al., 2003)

Ozone does not only damages the crop by accumulative effect (Krupa et al., 2003). Thus, there are also affected by climate, canopy position, leaf and tree age while varying between species. In addition, the ability detoxification of the plant also need to be taken into consideration (Matyssek et al., 2004). The damage of plant will happen when the O₃ on the ground achieved certain concentration, O₃ will damages plants primarily by entering plant leaves through the opening of the stomata. Once inside the plant tissue, O₃ can react to produce byproducts that cause crop losses via a reduction in either photosynthesis because of stomatal closure, or in carbohydrate used to produce detoxification systems (Tong et al., 2007)

Some visible symptoms of plant can be observed during the exposure under the O₃. The symptoms usually occur between the veins on the upper surface of the leaf. However, some of these are bifacial due to the species of plant. The symptoms include flecks (tiny light-tan irregular spots less than 1 mm diameter), stipples (small darkly pigmented areas approximately 2-4 mm diameter), bronzing, and reddening. The type and severity of injury is depends on several factors including duration and concentration of O₃ exposure, weather conditions and plant genetics (US DA, 2009)

$2.4.2 SO_{x}$

From previous study, it was found that there are approximately 100 million tons of SO₂ emissions per year result from human activity. The major man-made source of SO₂ is from the combustion of fuels (e.g. coal and oil) that contain sulfur(Greenstone, 2004). Many industrial produce hydrogen sulfide by processes and by decomposition of oil or dead vegetation. Sulfur type compounds like sulfur dioxide and mercaptans are produced in papermaking, rayon manufacturing, coke ovens, other industries as well as volcanic emissions. Acid gases like hydrochloric acid (HCl) and hydrofluoric acid (HF) are the side product produced by waste combustion and by several industries(Curtis et al., 2006). However, this emission can be successfully reduced using fuels with low sulphur content e.g. natural gas or oil instead of coal. On large plants in industrialized countries desulphurization of the flue gas is an established technique (Fenger, 1999).

Generally sulfur dioxide will accumulate in plant tissue as sulfur can cause effect to plant in certain period of time (Krupa et al., 2003). Many previous studies were focused on the acute exposure and the incidence of visible injury. However, there have no visible symptoms of the crop from the acute injury. But, it might tend to the result in subtle physiological changes such as reduction in plant growth and/or yield, premature senescence and abscission, accelerated fruit ripening, and can also give rise to visible chlorotic lesions. The physiological, chemical and anatomical changes can caused by long-term low-level exposures and increase plant susceptibility to other biotic and abiotic stresses such as frost, drought and pathogen attack (Garcia-Huidobro et al., 2001).

$2.4.3 \text{ NO}_{x}$

Nitrogen oxides (NO_x) are mainly came from the oxidation of nitrogen in atmosphere during combustion. The major source is come from vehicles. It is emitted in the form of the nontoxic nitric oxide (NO), which is subsequently oxidized in the atmosphere to the secondary "real" pollutant NO_2 . It can be reduced by optimization of the combustion. In other word, it is to increase the efficiency of the engine. Besides, the catalytic converters also can be installed in the exhaust as the conversion purpose of the compound into other more environmental friendly form (Fenger, 1999).

2.4.4 VOC

VOCs are referring to chemicals which are easily to be volatilized or evaporate into air. This may include petroleum refining, petrochemicals, vehicle exhaust, natural gas fields and distribution lines, storage of fuels and wastes, household products, pesticides, combustion, many industries and volatile emissions from coniferous forests (Curtis et al., 2006).

Methane is one of the common hydrocarbon gases in outdoor ambient air. There are about 40% of methane gases was produced by such non-human sources as wetlands, decaying vegetation, termites and oceans (US EPA, 2003). Pesticides also is a type of the VOC which can travel significant distances in the air (Curtis et al., 2006)

There is no standard of emission limit for VOC. However, OSHA regulates formaldehyde, a specific VOC, as a carcinogen. OSHA has adopted a Permissible Exposure Level (PEL) of .75 ppm, and an action level of 0.5 ppm. HUD has

established a level of .4 ppm for mobile homes. Based upon current information, it is advisable to mitigate formaldehyde that is present at levels higher than 0.1 ppm (EPA, 2009).

2.5 AOT40

Over the few decades, research in ambient O₃ has found that there are two main approaches to derive critical levels for O₃. There are concentration-based and stomatal flux-based methods (Mills et al., 2007). AOT40 is one of the methods to determine the O₃ level which are concentration-based. AOT40 was established by UN ECE (United Nation Economic Commission for Europe) by 1990s to achieve the environmental quality within the Europe region (Gerosa et al., 2007). The concept of AOT40 is based on the critical level of O₃. It can be defined as the exposure index or accumulated O₃ exposure above threshold of 40 nl O₃ l⁻¹. AOT40 is assume that the exceedance of the O₃ concentration would cause biomass production of plants to decline by more than 10% relative to that under pre-industrial O₃ regimes. In over view, AOT40 can assumes O₃ concentrations below 40 nl l⁻¹ and night-time exposure to be negligible (Matyssek et al., 2004). It can be written as AOTX. The term of AOTX (concentration accumulated over a threshold O₃ concentration of X ppb) has been adopted for this index where "X" is either 30 or 40 ppb for AOT30 and AOT40, respectively. AOTX is calculated as the sum of the differences between the hourly mean O₃ concentration (in ppb) and X ppb when the concentration exceeds X ppb during daylight hours, accumulated over a stated time period. The units for AOTX are parts per billion hours (ppb h or nmol mol⁻¹ h) and parts per million hours (ppm h, µmol mol⁻¹ h), respectively which were calculated on a volume/volume basis (Mills et al., 2007).

Table 2.5.1 show the previous study in Europe, there are 19 crops were tested with the exposure under the O_3 with certain concentration. Then, found that there are 3 types of independent groups from the tested crop. Critical levels of a 3 month AOT40 of 3 ppm h and a 3.5 month AOT40 of 6 ppm h were derived from the functions for wheat and tomato, respectively (Mills et al., 2007)

Table 2.5.1 Group of crop due to sensitivity of crop (Mills et al., 2007)

Group	Crops
Ozone sensitive crops	wheat, water melon, pulses, cotton, turnip, tomato, onion, soybean and lettuce
Moderately sensitive crops	sugar beet, potato, oilseed rape, tobacco, rice, maize, grape and broccoli
Ozone resistant	barley and fruit represented by plum and strawberry

However, the AOT40 exposure index was very high sensitive due to the quality of measured data. It might cause problem in calculation and estimation the AOT40 when errors occur in the set of data. For example, there are 5% overestimations in the mean concentration of O_3 results in a 10–50% overestimation in AOT40 (Hunov et al., 2003)

As we known, the AOT40 is based on the O_3 concentration in the air surrounding leaves and needles. However, it is widely recognized that only the O_3 molecules that enter the leaves through the stomata are harmful to plants. There are the questions there that the suitability of exposure index AOT40. The leaf detoxification systems which are able to cope with some of the oxidative stress induced by O_3 molecules

taken up by the leaves may take consideration to determine the concentration level of O_3 are harmful to the plant. This is very important in order to develop the different critical level exceedance for specific species of the crop (Karlsson et al., 2004).

.

2.6 INTERNATIONAL AND NATIONAL AIR QUALITY STANDARD GUIDELINES

2.6.1 INTERNATIONAL AIR QUALITY STANDARD

There were the international guidelines of the air quality. Usually, there are two sources to be a guideline. There are air quality standard from the WHO(world health organization) (Table 2.6.1) and the air quality standard of the Environmental protection Agency, US (Table 2.6.2). From the comparison, show that there is not much difference between these two guidelines.

Table 2.6.1.1 Air quality standard from WHO(2001) (Han and Naeher, 2006)

Pollutant	Average time	Value
СО	1 Hour	30 mg/m ³ (26 ppm)
CO	8 Hour	$10 \text{ mg/m}^3 (8.7 \text{ ppm})$
Lead	1 Year	$0.5 \mu\text{g/m}^3 (0.059 \text{ppb})$
NO_2	1 Hour	200 μg/m ³ (106 ppb)
NO ₂	1 Year	40 μg/m ³ (21 ppb)
O ₃	8 hour	120 μg/m ³ (61 ppb)
SO_2	24 Hour	125 μg/m ³ (47.7 ppb)
SO_2	1 Year	50 μg/m ³ (19.1 ppb)

EPA was establish the air quality standard under Clean Air Act in order protect public health, including the health of "sensitive" populations such as people with asthma, children, and older adults. EPA also sets limits to protect public welfare.

There are include the ecosystems (plants and animals), and protecting against decreased visibility and damage to crops, vegetation, and buildings (US EPA, 2009).

There are six common air pollutant were set by the EPA. There are nitrogen dioxide (NO2), ozone (O3), sulfur dioxide (SO2), particulate matter (PM), carbon monoxide (CO), and lead (Pb). Four of these pollutants (CO, Pb, NO2, and SO2) are emitted directly from a variety of sources. Ozone is not directly emitted, but is formed when oxides of nitrogen (NOx) and volatile organic compounds (VOCs) react in the presence of sunlight. PM can be directly emitted, or it can be formed when emissions of NOx, sulfur oxides (SOx), ammonia, organic compounds, and other gases react in the atmosphere (EPA, 2009).

For the EPA air quality standard, there have type of standards. Primary standards set limits to protect public health, including the health of "sensitive" populations such as asthmatics, children, and the elderly. Hence, secondary standards set limits to protect public welfare, including protection against visibility impairment, damage to animals, crops, vegetation, and buildings (EPA, 2009).

Table 2.6.1.2 Air quality standard from Environmental Protection Agency, US (US EPA, 2009)

Pollutant	Average time	Value
СО	1 Hour	35 mg/m ³ (26 ppm)
CO	8 Hour	9 mg/m ³ (8.7 ppm)
Lead	Quarterly Average	$1.5 \mu g/m^3$
Leau	1 Hour	$200 \mu \text{g/m}^3 (106 \text{ppb})$
NO ₂	1 Year	53 ppb
NO_2	8 Hour	120 μg/m ³ (61 ppb) (1997 std)
	8 Hour	0.075 ppm (2008 std)
O_3	8 Hour	0.12 ppm(1997 std)
	1 Hour	140 ppb
SO_2	1 Year	30 ppb

2.6.2 MALAYSIA AIR QUALITY STANDARD

51 stations were build by Department of Environment (DOE) to monitor the ambient air quality of Malaysia. These monitoring stations are strategically located in residential, traffic and industrial areas to detect any significant change in the air quality which may be harmful to human health and the environment. From the 51 station, can divide into 5 categories for monitoring purpose. Thus, 26% are industrial stations, 57% are residential, 2% traffic, 2% background and 13% PM10 stations. There are 5 pollutant were measured in those stations. The major pollutants are suspended particulate matters (PM10), sulphur dioxide (SO2), nitrogen dioxide (NO2), carbon monoxide (CO), and ozone (O3). These concentrations are measured continuously on hourly basis. The hourly value is then averaged over 24-hour running period for PM10 and SO2, 8-hour period for CO, whilst O3 and NOx are read hourly. An hourly index is calculated for each pollutant. The highest index value recorded is then taken as the API for the hour.

The calculation of the air pollution is based on the major air pollutant stated above. Then, the highest value among the pollutant was selected as API value. Usually, the PM_{10} was select due to the highest reading among the 5 pollutant. However, O_3 was very high in some places and trend to be the API reading. It was because the reaction of the nitrogen oxide and VOCs for vehicle or industries in present of the sunlight.

Table 2.6.2.1 Malaysia air quality guideline (DOE, 2010)

Pollutants	Averaging Time	Malaysia Guid	lelines
Ozone	1 Hour	0.10	200
	8 Hour	0.06	120
Carbon Monoxide	1 Hour	30.0	35
	8 Hour	9.0	10
Nitrogen Dioxide	1 Hour	0.17	320
	24 Hour	0.04	10
Sulphur Dioxide	1 Hour	0.13	350
	24 Hour	0.04	105
Particulate Matter(PMIO)	24 Hour	-	150
	I Year	-	50

Table 2.6.2.2 Malaysia API Scale (DOE, 2010)

API Scale	Air Quality
Good	0-50
Moderate	51-100
Unhealthy	101-200
Very Unhealthy	201-300
Hazardous	301 and above

CHAPTER 3

METHODOLOGY

3.0 INTRODUCTION

All the methods and instruments to obtain the result are show in this chapter. The data of crops and O_3 will be analyzed by using SPSS. The simple regression was applied and the outcomes are models for the O_3 formation as NO_2 as precursor. The yield loses of short term crop were calculated according to AOT40 which is the Europe standard. The O_3 and NO_2 verification also had been carried out at all the station by using gas sensor.

3.1 DESCRIPTIVE STATISTICS

Descriptive statistics is the mathematical method used to describe the set of the data. The descriptive statistics were used in this study which included mean, variance and standard deviation.

3.1.1 MEAN

Mean is known as arithmetic mean of set n measurement. All the data were added up and divide by the total number of added up data.

$$\overline{y} = \frac{\sum_{i=1}^{n} y_i}{n}$$

Where,

 $y_i = data of measured$

n = number of total data

3.1.2 VARIANCE

Variance is the square of the standard deviation.

$$s^{2} = \frac{\sum_{i=1}^{n} (y_{i} - \overline{y})^{2}}{n-1}$$

Where,

 \overline{y} =mean of the set number

 $y_i = \text{data of measured}$

n = number of the total data

3.1.3 STANDARD DEVIATION

Standard deviation is the square root of the variance. It used to measure the degree of dispersion of the data.

$$s = \sqrt{s^2} = \sqrt{\frac{\sum_{i=1}^{n} (y_i - \overline{y})^2}{n-1}}$$

Where,

y =mean of the set number

 $y_i = data of measured$

n = number of the total data

3.2 REGRESSION ANALYSIS

Normally, regression analysis was used in the prediction or estimation through the relation between independent and dependent variables (Sykes, 1992). The relationship can be formed among the variables. Simple regression is linear regression in other word where it is a straight line (Altman, 1991). It occurs in mathematic way as equation below:

$$Y = b_0 + b_1 X$$

Where,

Y is depend on variation in predictor (or independent or explanatory) variable,

X

Due to the equation above, a straight line might be plotted on the graph base on the data. Hence, the prediction can be made through the plotted line or generated equation (Altman, 1991). The linear graph of O₃ and others variable such as NO₂,

wind speed, humidity and temperature can be plotted by insert the data into the program and generate.

3.2.1THE SIMPLE LINEAR REGRESSION MODEL

Let $(X_1, Y_1), (X_2, Y_2), ..., (X_n, Y_n)$ be n pairs of random variables. Then the simple linear regression model is given by

$$Y_i = \beta_0 + \beta_1 X_i + \varepsilon_i$$
 $i = 1, 2, ..., n$

where

 Y_i is the dependent or response variable

 X_i is the independent or regressor or explanatory or predictor variable

 β_0 is the intercept of the regression model

 β_1 is the slope of the regression model

 ε_i is the random error term

3.2.2 THE MULTIPLE LINEAR REGRESSION MODEL

Let $x_1, x_2, ..., x_k$ be k independent random variables and $y_i, i = 1, 2, ..., n$ be the dependent variable. Then the multiple linear regression model is given by

$$y_i = \beta_0 + \beta_1 x_{1i} + \beta_2 x_{2i} + \dots + \beta_k x_{ki} + \varepsilon_i$$
 $i = 1, 2, \dots, n$

where

 y_i is the dependent or response variable

 $x_{1i}, x_{2i}, \dots, x_{ki}$ are the independent or regressor or explanatory or predictor

variables

 $\beta_0, \beta_1, ..., \beta_k$ are the coefficients of the regression model

 ε_i is the random error term

The multiple linear regression model can be written in matrix form as follows:

$$y_{(n\times 1)} = X_{(n\times p)}\beta_{(p\times 1)} + \varepsilon_{(n\times 1)}$$

with

$$y = \begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_n \end{bmatrix}, \quad X = \begin{bmatrix} 1 & x_{11} & \cdots & x_{1k} \\ 1 & x_{21} & \cdots & x_{2k} \\ \vdots & \vdots & & \vdots \\ 1 & x_{n1} & \cdots & x_{nk} \end{bmatrix}, \quad \beta = \begin{bmatrix} \beta_0 \\ \beta_1 \\ \vdots \\ \beta_k \end{bmatrix}, \quad \varepsilon = \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \vdots \\ \varepsilon_n \end{bmatrix}$$

where

y is a $(n \times 1)$ vector of observations

X is an $(n \times p)$ matrix of the independent variables with p = k + 1

 β is a $(k \times 1)$ vector of the regression coefficients

 ε is a $(n \times 1)$ vector of random errors (Yahaya, 2008)

3.3 CALCULATION OF AOT40

AOT40 is the benchmark of the Euro in the crop study. The index can be calculated as the sum of differences between the hourly O_3 concentrations higher than 40 ppb, for each daylight hour with global radiation \geq 50 Wm⁻²:

$$AOT40 = \frac{AOT40_{RAW}}{d_{v}t} d_{A}t$$

Where, $d_A t$ is the valid day of data collection

 $d_{y}t$ is the total day of data collection

 $\textit{AOT}\,40_{\textit{RAW}}$ is the accumulative of the O_3 which exceed 40 ppb in hourly

3.4 PERFORMANCE INDICATOR

Performance indicator was consist 6 indicators to investigate the goodness of the model. There are bias, coefficient of determination (R-square), prediction accuracy, normalized absolute error, root mean square error and index of agreement. Each of the indicator have their own formula to run the data.

3.4.1 COEFFICIENT OF DETERMINATION

Coefficient of determination is the R-square in other word. It measure of the fitness of the regression equation in estimation. It can explain the total variation of the Y that can explain by the regression equation. The value mu between zero to one. The vloser the value to the one is the better the regression equation.

Coefficient of determination,
$$r^2 = 1 - \frac{SSE}{SS_{yy}} = \frac{\sum_{i} (y_i - \hat{y})^2}{\sum_{i} (y_i - \hat{y})^2}$$

(Mendehall & Sincich, 1995)