Annual and Diurnal Trend of Surface Ozone (O$_3$) in Industrial Area

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Abstract. Malaysia is a developing country that facing air pollution issues due to industrialization, urbanization activities and population growth. Ozone (O$_3$) is one of the pollutants that can give adverse effects to human health either in long-term or short-term effect. Moreover, it also can interrupt the normal ecosystem and cause extinction in species. This study aims to analyse the annual trends of the concentration of ozone (O$_3$) level for 3-year and the diurnal trends of ozone at Kemaman, Terengganu. One-way Analysis of Variance (ANOVA) revealed that there exists statistically significant different (p<0.05) of O$_3$ concentrations during year 2012-2014. Meanwhile, diurnal trend showed the lowest O$_3$ concentration values in the morning and the highest average concentration values of O$_3$ in the noon, but it starts to decrease gradually in evening and night. The understanding of the ozone trend, yearly and hourly, can helps in tackling the atmospheric pollution problems due to industrialization in Malaysia.

1. Introduction

Recently, in a developing country such as Malaysia, air quality is one of the environmental concern due to anthropogenic activities. The sources of air pollution typically come from industrial emission, open burning and land transportation. This air pollution can affects human health. Since 1970, air quality in Malaysia was decline and no countermeasures have been initiated [1]. Emission from vehicles that caused by motor traffic and anthropogenic activities such as urbanization and industrial activities are the main air pollutant sources in Malaysia [2]. The major pollutant elements that pollute the air quality are carbon monoxide (CO), nitrogen oxides (NO$_x$), sulphur dioxide (SO$_2$), surface ozone (O$_3$), benzene (C$_6$H$_6$) and particulate matter (PM) that contribute negative impacts to the population health and economic, ecosystem and climate [3-4]. Moreover, the growth of population is one the factors that cause a decrease in air quality through rapid urbanization and contribute lots of air pollutant sources such as in mining activities, services, heavy industries and agriculture [5-6].

Ozone (O$_3$) is one of the predominant pollutants that can be present in the troposphere layer and stratosphere layer of the earth. Troposphere ozone or also known as ground-level ozone is highly phytotoxic pollutants, which it particularly generates by photochemical reaction process and with the presence of its precursors that generally produced by human activities and natural process [7] as shown
in Figure 1. Furthermore, the perfect formation of ozone is involved hydrocarbon, nitrogen oxide gases and ozone itself with the presence of sunlight. The main source formation of ozone is through fossil fuel combustion. It also can be destroyed by reaction with synthetic chemical, natural chemical reaction and reaction with the various surface. The formation of stratosphere ozone is also involved the presence of solar ultraviolet radiation with a natural and synthetic chemical produced by a human at the stratosphere. There are two steps of formation ozone at the stratosphere. The oxygen (O\textsubscript{2}) was split up by ultraviolet radiation and produce to an atom of oxygen. Then, highly reactive oxygen atoms come together with oxygen molecules (O\textsubscript{2}) and form ozone molecules (O\textsubscript{3}). Stratosphere ozone will play a big role in the future due increase of input in stratospheric to tropospheric ozone in climate change scenario [8]. Furthermore, O\textsubscript{3} and its precursors were also transport from source of mixing, deposition, advection and convection process at stratosphere and troposphere layers by destructive process. Based on the previous study, the Figure 1 showed the formation and destruction of O\textsubscript{3} on the earth [9].

![Figure 1. The Formation and Destruction Process of the Ozone (O\textsubscript{3}) that occurs on the Earth][10]

In conjunction with uncontrolled dissemination of ozone to the atmosphere, it harms to human health, ecosystem and environment. In the previous study, it showed that the increase of O\textsubscript{3} could cause morbidity and mortality on human [9]. It also promotes respiratory and cardiovascular system problems for short-term effects and respiratory mortality and asthmatics problem especially in children for long-term effect but there is no crucial evidence for long-term effect of ozone [11]. The high concentration of O\textsubscript{3} also can interrupt the ecosystem by interfering the normal development of plant grown, symbiotic relationship between parasite and plant interaction and increase in species extinction [12]. Besides, it also causes global climate change to our environment [13].

The aim of this study is to determine the annual and diurnal trend of ozone (O\textsubscript{3}) concentration at one of industrial area in Terengganu. We expect to provide information of the concentration of O\textsubscript{3} to the responsible parties to take the precaution and mitigation measure to improve air quality and synchronized with sustainable development goal for year the 2030 under sustainable cities and communities goal and climate change goal.
2. Materials and Methods

Kemaman is one of the industrial parks that is located at Terengganu State in the East Coast Peninsular Malaysia. Overall, Kemaman has an area of 2,535.60 km², which administered by the Kemaman Municipal Council. In terms of population, Kemaman has a population of 201,100 people as estimated in 2014. The main industrial activities are the oil, petroleum and steel production [14]. Thus, producing many anthropogenic pollutants to the atmosphere. This study emphasized on the criteria pollutant that is well known to affects the human health and the deterioration towards environment, which is ozone. The monitoring data of ozone concentrations is perform under the responsibility of the Malaysian Department of Environment (DOE), Ministry of Energy, Science, Technology, Environment and Climate Change (MESTECC). The location of study area is specifically located at the Bukit Kuang Primary School, Teluk Kalung,Kemaman (N04° 16.260’; E103° 25.826’).

This study is based on the data measured data from January 2012 until December 2014 (3 years period). The concentration of O$_3$ was measured and monitored hourly by Teledyne API Model 400/400E instrument through UV absorption (Beer- Lambert) method with 0.4 ppb detection limit and 0.5 % of precision level [10]. The data were arranged in Microsoft Excel Spreadsheet® 2016 and analysed using Statistical Packages for Social Sciences (SPSS®) version 25. The data were analysed through the boxplot and the evaluation of central of tendency via summary statistics.

3. Results and Discussion

The summary of descriptive statistics for the 3-year data starting from January 2012 until December 2014 at industrial area in Terengganu as shown in Table 1. The highest maximum average concentration of O$_3$ is 0.098 ppm in the year 2013 as compared to the year 2012 (0.095 ppm) and 2014 (0.085 ppm). The trend is shown via boxplot representation as in Figure 2. The boxplot contains many information that was compiled together such as mean, median, maximum and minimum values. Although the trend shows the non-fluctuating shape, but the Analysis of Variance (ANOVA) confirms that there exists statistically significant different (p<0.05) of the ozone concentration during the study period. This can be confirmed through Figure 2 as there exists extreme events in the year 2012 and 2013, make it dissimilar pattern as compared with the year 2014. Although the extreme events occurred in the year 2012 and 2013, the mean concentration of ozone was dominated in the year 2014 with 0.022 ppm. The study area is very popular with the heavy industrial areas at Terengganu that involved the production of polymer, petrochemical, steel and others. Industrial activities are believed in emitting the precursors of ozone such as nitrogen oxides (NO$_x$) and volatile organic compound (VOC) to the atmosphere [15] which promotes the production of ozone in that particular area. Previous study of surface O$_3$ have shown that local variations of O$_3$ can be influenced by NO$_x$ and VOCs. VOC, for example those including C6 to C8 aromatics, isoprene, monoterpenes, acetone and especially those from biogenic sources, may also contribute to the concentration of O$_3$ in the atmosphere due to the formation of organic peroxides. The formation and concentration of ground level O$_3$ depends on the concentrations of NO$_x$ and VOCs, the ratio of NO$_x$ and VOCs, and the intensity of solar radiation. In the presence of sunlight, O$_3$ is form through the photochemical destruction of nitrogen dioxide (NO$_2$) which creates nitric oxide (NO) and oxygen atom (O) that combines with molecular oxygen (O$_2$) to form O$_3$. Once formed, O$_3$ quickly reacts with NO regenerating NO$_2$ in the absence of VOCs.

| Year | 2012 | 2013 | 2014 |
|------|------|------|------|
| Mean (ppm) | 0.021 | 0.021 | 0.022 |
| Median(ppm) | 0.018 | 0.018 | 0.200 |
| Maximum(ppm) | 0.095 | 0.098 | 0.085 |
| Minimum(ppm) | 0.000 | 0.001 | 0.000 |
| Interquartile range (ppm) | 0.021 | 0.020 | 0.021 |

The diurnal pattern of hourly ozone concentration is shown in Figure 3. The ozone concentration started to increase from 0900 hours, continuously until 1500 hours. The sunny day which resulted in high temperature would induces the production of ozone. In Malaysia, the dry monsoon is characterized
with the weather parameters of increased in temperature and sunny hours. During this time, the ozone concentration is found to increase. Solar radiation and emission from vehicles play important roles in increasing the average O$_3$ concentration. In the previous study, the high population growth also is notified as the one of the contributors to increase values of O$_3$ concentration through human activities such construction activities, open burning activities, mobile sources and others [15] and [16]. The diurnal concentrations of O$_3$ are influence by the intensity of solar radiation and the amount of its precursors as well the titration processes. The trend of ozone concentrations is decline gradually during 1600 hours. Meanwhile, the boxplot had shown that the O$_3$ average concentration is lowest in the morning compared to noon and evening. Usually, the ozone concentration is lower during the rainy season, lower temperatures, lesser sunny hours, and relatively high humidity such as in the early morning and nighttime [16].

![Boxplot analysis of average concentration of ozone trends for the period of 2012-2014](image1)

**Figure 2.** The boxplot analysis of average concentration of ozone trends for the period of 2012-2014

![Diurnal boxplot analysis of average concentration of ozone (ppm) trends for the period of 2012-2014](image2)

**Figure 3.** Diurnal boxplot analysis of average concentration of ozone (ppm) trends for the period of 2012-2014
4. Conclusion
In conclusion, there is a non-fluctuating annual trend of ozone during the year 2012-2014. Unfortunately, due to the existence of some extreme ozone concentration events, the result shows significant difference among the three years. The diurnal pattern shows that the ozone concentrations were increase towards the noon, and decreases slowly towards the evening and nighttime. In the morning, the ozone concentrations were kept constant until the incoming solar radiation is appear for the production of ozone.

5. References

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