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Ground Level Ozone Fluctuational Characteristics from a Background Station of Malaysia

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Abstract

The fluctuational of ground level ozone (GLO) were investigated (year 2000 to 2011) in a rural site located in the central region of Peninsula Malaysia, far from direct sources of anthropogenic emissions. This study aims to analyse the fluctuation and transformation characteristics of GLO in rural area of Jerantut, Pahang. By using Critical Conversion Point and Time (CCP and CCT) and Critical Transformation Time (CTT) obtained from composite diurnal plot. CTT is important to understand the different processes responsible for GLO transformation. The CCT for ozone formation at Jerantut was identified occurring between 8.00 a.m. to 9.00 a.m. Jerantut hourly continuous monitoring recorded data was below 100 part per billion volume (ppbv). CTT fluctuational characteristics at the background station is important and provide an early signal to developed policies that manage nitrogen emission from background station that free from rapid development projects.

Keywords: *background station, ozone, ozone fluctuation, precursor, secondary air pollutant*

1. Introduction

Other pollutants concentration is known to cause ozone formation could be different depending on land use categories e.g. industrial, urban, suburban and rural. Rural background stations provide invaluable information on pollutant exposure to humans and vegetation at distances from a few km^2 to a few thousand km^2 [1]. USEPA [2] have addressed that rural station is also useful in providing air quality information on a regional scale. Background station must be located in an area with natural ecosystem, low population density and be a reasonable distance from anthropogenic emission sources [3]. Jerantut CAQMS was established by Department of Environment (DOE), Malaysia as a rural background station for comparison of observations from other land use categories such urban, suburban and industrial monitoring stations. In [1] find that many studies on air pollutant concentrations in Malaysia have included Jerantut for comparison with observation from other rural, urban, suburban and industrial monitoring stations. However, there as yet, no studies focus on the long term ground-level ozone concentration fluctuation at this station based on critical transformation time (CTT) for ozone transformation.

This study aims to analyse continuous monitoring data collected over a period of 11 years and to access the trends in fluctuational characteristics of ozone. CTT is obtained using the diurnal plot of ozone and the precursors. The Diurnal plot has information on photochemical reactions between the primary precursors. The relationship of the precursors such ozone and nitrogen oxides have to be studied. A number of researchers recently found that using critical conversion point (CCP) and critical conversion time (CCT) could understand well the formation and destruction of O_3 concentration from the diurnal plot [4], [5]. This particular aspect of investigating CCP and CCT has been motivated by the research conducted by [6] who presented and empirical study about CCT and explained why CCT often

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explain the relationship of NO and NO_2, where the NO_2 photolysis could be determined. This research focuses on Critical Transformation Time (CTT) where the exact time of ozone transformation is in the highest rate for modelling and prediction of ground-level ozone concentration.

2. Methodology

2.1. Study Area

The background location of continuous air quality monitoring stations (CAQMS) is located at *Pusat Meteorologi Batu Embun*, Jerantut, Pahang operated by a private company, Alam Sekitar Malaysia Sdn Bhd (ASMA) hired by Department of Environment (DOE) Malaysia have been chosen in this study. Fig. 1 and 2 show the map of the located background CAQMS.

The monitoring site is 200 kilometers from Kuala Lumpur, and 180 kilometers from Kuantan, the city of Pahang. Jerantut CAQMS is located in the middle of Peninsula Malaysia. The location is surrounded by the natural forest and agricultural activities. This monitoring station is located 8 kilometers from the town of Jerantut. Some short studies has shown that the main air pollution recorded here is influenced by local open burning, soil dust and a low number of motor vehicles [7], [8]. In addition, recent studies of short term monitoring of Particulate Matter, $PM_{2.5}$ particles sourced from two categorized which biological particles such as fungal spore, brochosome and fungal hypae where the other group frim anthropogenic particles such as soot [9].

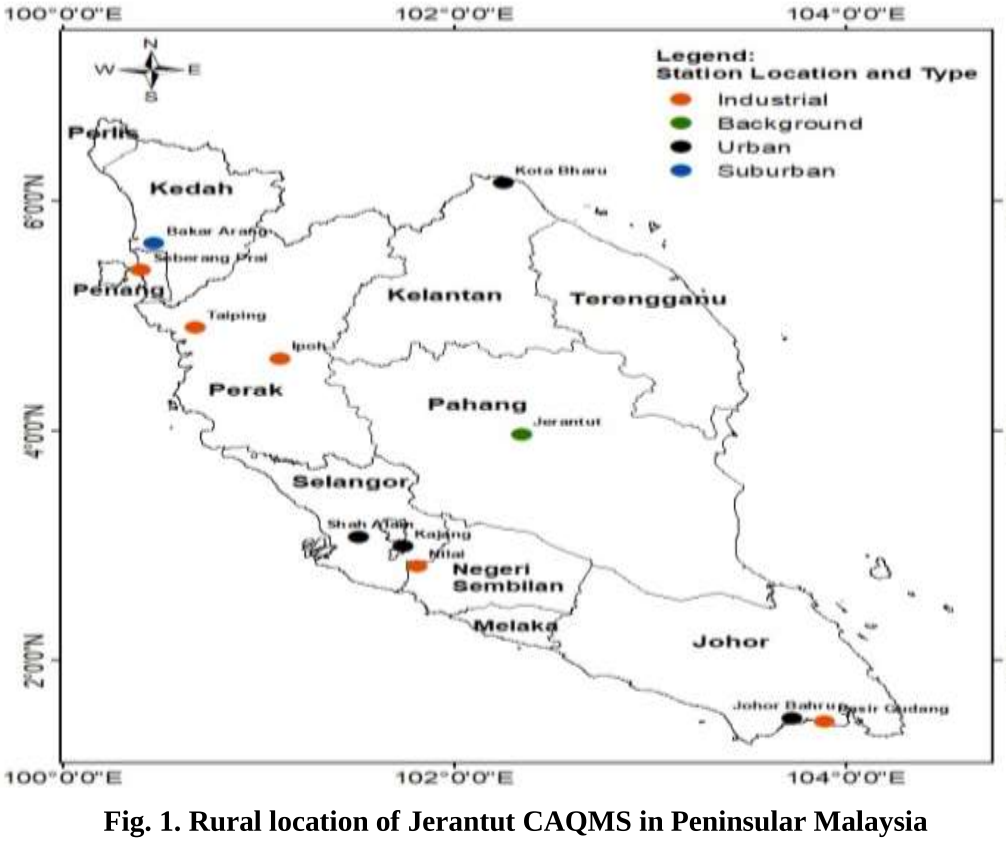

Fig. 1. Rural location of Jerantut CAQMS in Peninsular Malaysia

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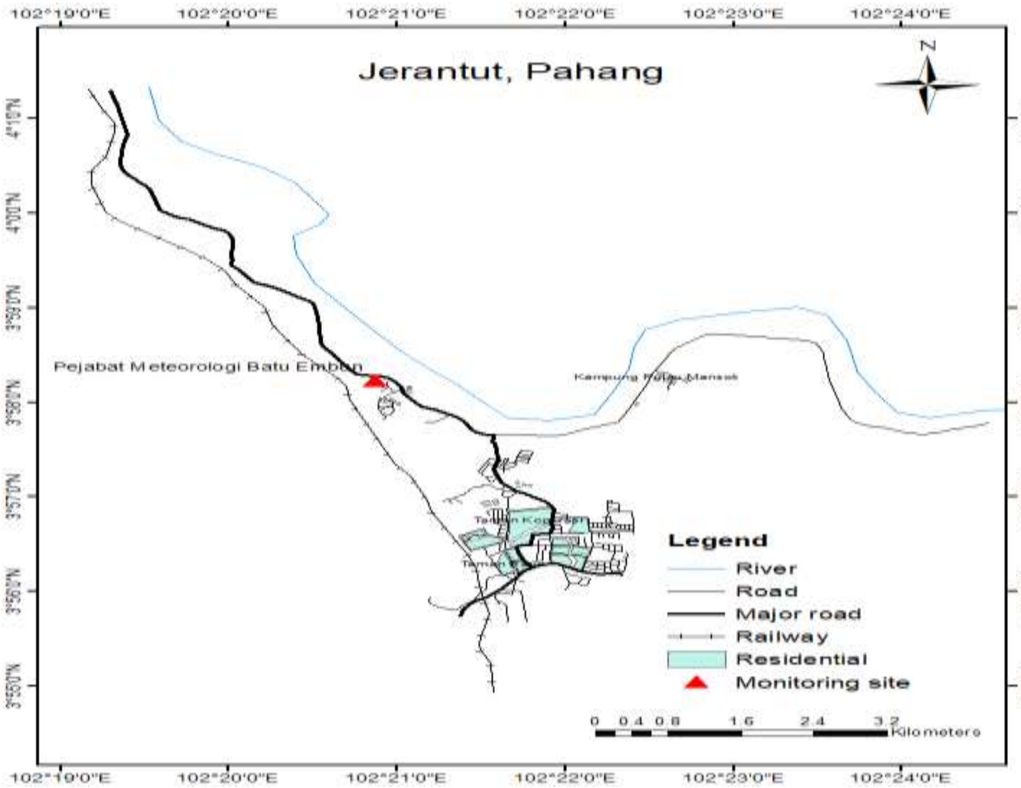

Fig. 2. Location of CAQMS in Jerantut

2.2. Secondary Data Collection

Twelve years of continuous hourly ground-level O_3 concentrations and other air pollutant levels starting from 1st January 2000 to 31st December 2011, was obtained from the Department of Environment, Malaysia.

The pre-treatment of hourly secondary data will be carried out to prepare the data for further analysis. Missing values will be directly omitted from analysis to avoid systematic error in dataset.

Hourly O_3 concentrations and other two air pollutants such NO and NO_2 will be plotted. Regular calibration of the monitoring instrument was done by Alam Sekitar Sdn. Bhd. (ASMA) for quality assurances and quality controls of the air monitoring data. According to [12], air monitoring instruments have been scheduled to have daily auto-calibration using zero air and standard gas concentration for gas monitoring such as O_3 and NO_2. At every two weeks interval, each of the instruments will be calibrated manually using its individual calibration gas. Before transferring to DOE, the hourly data was checked for validation. 0.6 ppbv and 0.4 ppbv were the lower detection limit for O_3 and NO_2, respectively.

2.3. Ground-Level Ozone Concentration

The ozone data were obtained from the air monitoring station by Department of Environment (DOE), which is managed by Alam Sekitar Sdn. Bhd (ASMA). The instrument used at the monitoring station was UV Absorption O_3 Analyzer Model 400A to measure the O_3 concentration. Beer-Lambert law was applied in the system to measure low ranges of O_3 in ambient air. The O_3 detection range of the analyser started from 0-100 ppb to 0-10 ppm. The ozone measurement was done when a UV light signal with a wavelength of 254 nm passed through the sample cell where it was absorbed in proportion to the amount of ozone present.

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2.4. NO_2 Concentration

Similar to ozone data collection, NO_2 concentration was obtained from DOE and the instrument used at the monitoring station was $NO/NO_2/NO_x$ Analyzer Model 200A. The chemiluminescence detection principle was used in the analyzer, which is coupled with state-of-art-electronics for NO_2 concentration measurement. The analyzer was equipped with a minimum detection range of 0-50 ppb to a maximum detection range of 0-20 ppm.

2.5. Diurnal Variations

The composite diurnal plot is used to study the long-term behaviour of the O_3 and its precursors. In this study, the average hourly concentration of O_3, NO and NO_2 were plotted to determine the relationship between the variables and to investigate the critical transformation time of O_3. Diurnal plots help to determine the critical conversion point where the interception of O_3, NO and NO_2 [4]. The CCT plays an important role in diurnal plot whereby the range of critical transformation time (CTT) has been investigated.

CTT is defined as the time range where the photochemical reaction reached the peak level (uni-modal shape) from the composite diurnal plot. CTT range occurred within the critical conversion time (CCT). Within the CCT, NO_2 photolysis rate started to surpass the NO titration rate. CTT was based on the composite diurnal plots of O_3, NO and NO_2. The interception point of O_3, NO and NO_2 concentration in a diurnal plot indicated the critical conversion point and the critical transformation time was determined through the relationship of O_3, NO and NO_2 concentration.

3. Results and Discussion

3.1. Descriptive Statistics

The descriptive statistics of hourly O_3 concentration from 2000 to 2011 at the background monitoring station; Jerantut (JTT) using Table 1.

Table 1: Descriptive data for hourly O_3 concentration from 2000 to 2011 of Jerantut CAQMS; JTT

Location	N Total	Mean	Standard Deviation	Minimum	Median	Maximum
JTT	99228	12	10.947	1	9	90

The O_3 concentration range was between 1 ppbv and 90 ppbv (Table 1). The hourly average concentrations of O_3 at the monitoring station was recorded at 12 ppbv, were found to be far lower than those recommended by RMAAQG guidelines suggested concentration under 100 ppbv. The maximum concentration for O_3 was found to be 90 ppbv.

3.2. Diurnal Variations

The diurnal plot for ozone along with its precursors (NO and NO_2) is presented in Fig. 3 at Jerantut continuous air quality monitoring station (CAQMS). O_3 diurnal variation shows the uni-modal shape. O_3 production is characterized by photochemical reaction of NO_x linked to UV_B intensity [10].

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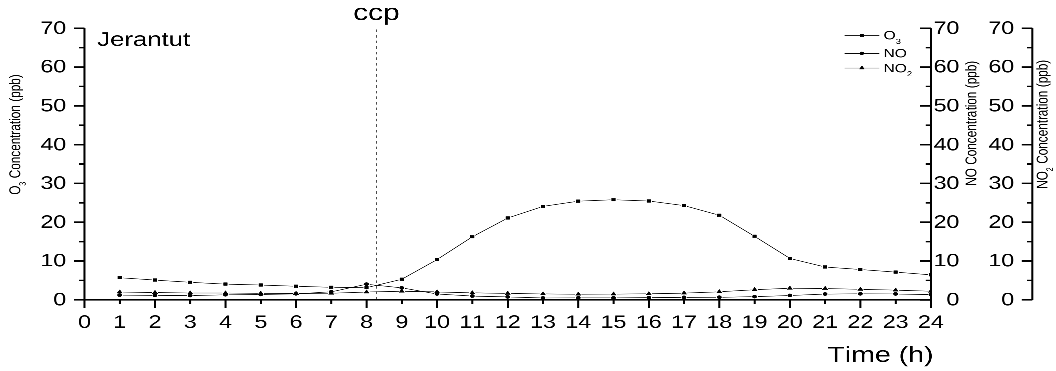

Fig. 3. Composite diurnal plot of O_3, NO and NO_2 concentration at rural CAQMS in Jerantut

The increasing trend of O_3 concentration after the sunrise, reaching a peak approximately between 12.00 p.m. to 4.00 p.m. Minimum concentrations were recorded in the afternoon between 7.00 p.m. to 7.a.m. The minima occurred at 8.00 a.m. The decrease of O_3 is due to the decrease of UV intensity as the sun radiation starts to decline. As the ozone decrease, NO_2 starts to increase, triggered by NO titrations. During morning rush hours (from 6.00 a.m. to 9.00 a.m.), NO is increase from vehicles thereby accelerating NO titration rates in ambient atmosphere [11]. Fig. 3 shows O_3 is low during this time as NO titrations during this time reduce O_3 concentration [8], [12]. O_3 concentration starting to increase gradually after the sun rises and reaches its maximum level between 2.00 p.m. and 4.00 p.m. O_3 concentration starts to decrease overnight because the lack of solar radiation and loss via NO titration and deposition [11].

CTT is introduced and the results showed the CTT in Table 2, which was between 8.00 a.m. to 9.00 a.m. During CTT, O_3 started to gradually increase as the increased rate of NO_2 photolysis at a point (CCP). At CCP show the time which indicate the highest rate of photochemical reaction rate.

Table 2: Critical conversion time (CCT) and critical transformation time (CTT) based on composite diurnal plots at Jerantut CAQMS

Year	Critical Conversion Time (CCT)
	Rural
Location	Jerantut
2000	9.00
2001	9.00
2002	8.30
2003	8.30
2004	8.30
2005	8.00
2006	8.00
2007	8.00
2008	8.00
2009	8.00
2010	8.00
2011	8.00
Critical Transformation Time (CTT)	8.00 am to 9.00 am

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3.3. Variations of O_3 Concentration Using Time Series Analysis

The hourly variations of O_3 concentrations throughout 12 years (2000 – 2011) were illustrated using the time series plot. Time series plot showed the data collected over a period time on one variable (O_3 concentration). Time series plot of hourly ozone concentration (ppbv) graphically used in describing fluctuation behaviour of the ground level O_3 concentration on monthly variation throughout the year.

Ozone demonstrates a clear seasonal pattern at Jerantut station. The variation of O_3 concentration is influenced by the seasonal monsoons. There are four monsoonal changes in Malaysia; North East monsoon (NE) occurs between December and March and South West monsoon (SW) occurs between June and September. NE monsoon is associated with the long-range transport of air mass from the east coast of Indo-China [13]. Researcher had find out that the other sources of substantial quantities of O_3 and other oxidants to Northeast Asia is due to the long range transport of air [14]. In order to understand the substantial quantities of O_3 and other oxidants, in [13] used trajectories clustered analysis where he indicate there were three groups of clusters of how high O_3 event. He first clustered the trajectories of the long range transport of O_3 and oxidants from East coast of Indo-China across the South China Sea. The northeasterly winds are common characteristics of surface circulation during winter monsoon. The polluted continental outflow air mass over East Asia usually has high concentration of O_3 and CO. As they flow across the sea, it will loss over water trajectories that occurs at the end of winter. The second group cluster trajectories are during the winter -spring transition. It is during the month of March when the northeasterly monsoon winds weaken. The long range transport of O_3 sources associated from the East Asian continent and Indo-China across the South China Sea. The polluted maritime air masses are the indicator of O_3 transformation from the precursors. Thus, it is critically important to understand the Asian continent as it will outflow the air mass to the near region such Klang Valley. The third group of clusters indicate that the high O_3 in Klang Valley is characterized by short-range air motion from irregular directions because at this time the monsoon transition (spring) with the weakest atmospheric circulation. As we know, O_3 is high with the presence of sunlight, and its precursors such as VOC and NOx.

During the inter monsoon periods (April-May and October-November), the atmospheric circulation is slower [1] and resulted the air mass travel to be shorter. The high O_3 concentration is believed to be from the long-range transport and from the local photochemical and transport process [13]. At this time of the year, (Feb-June) Malaysian Peninsular receive high radiation due to the hemispheric crossing of the sun. The intensity of solar radiation has the capability to increase the amount of O_3 due to the formation of O from NO_x and VOC [15], [16]. Fluctuational behaviour of ground level O_3 using composite diurnal plot will explain the inverse relationship with its main precursors that lead to the new information of O_3 transformation characteristics called critical conversion point and time critical conversion time [17], [18].

Jerantut O_3 concentration is higher in June and September during the South West monsoon. This is certainly true in the case of biomass burning emission from Sumatera, Indonesia [1], [19], [20] contributing factor when there is amount of particulate matter in the atmosphere. Previous studies by [21] has investigated the relationship of transformational characteristics of ground level ozone during high particulate events in urban area of Malaysia. There is some evidence that high particulate event (HPE) may affect the ozone concentration. The study shown that the concentration of ozone was high during HPE than those during non-HPE, and they were affected by the relatively higher temperature and lower relative humidity.

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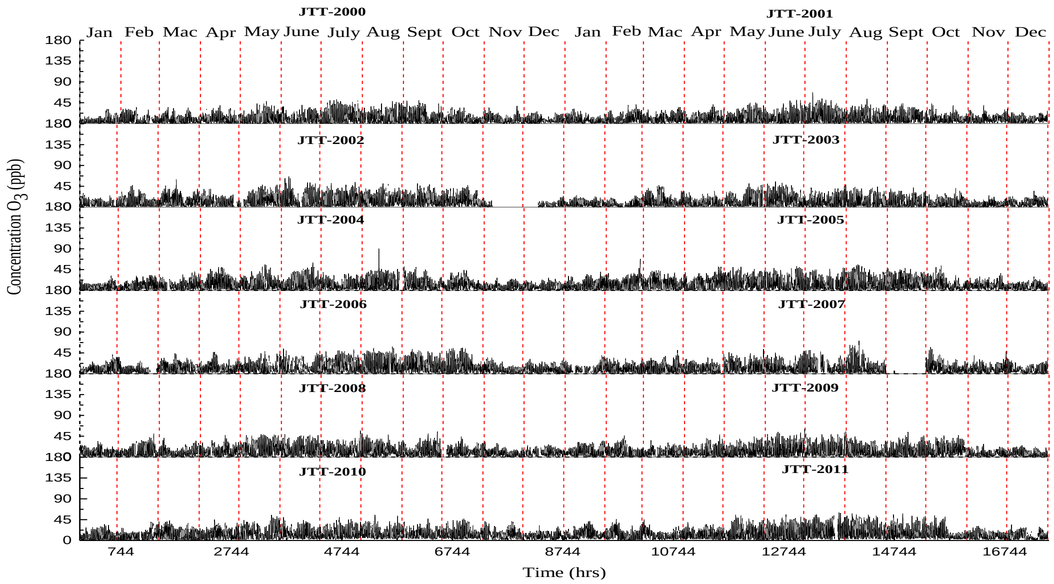

Fig. 4. Time series plot of O_3 concentration from 2000 to 2011 at rural background CAQMS in Jerantut

4. Conclusion

In conclusion, this study shows the CTT of long term O_3 concentration trends at a background station in Malaysia. The results demonstrate that the CTT is earlier (8.00 a.m. to 9.00 a.m.) and can be compared to other land use categories such urban, suburban and industrial. Jerantut recorded O_3 concentration is lower than the recommended levels suggested by RMAAQG. However, O_3 and other pollution levels at this background station should be assessed and monitored to maintain as background category station. Local sources, particularly at CTT time, should be monitored for example to avoid the traffic density during peak hours of CTT range time.

Acknowledgments

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