

Trends of Transformation Characteristics of Ground-Level Ozone in Urban Peninsular Malaysia

Hasifah Abdul Aziz, Norrimi Rosaida Awang, Mohamad Faiz Mohd Amin

Abstract:- Ozone (O_3) is the second prominent air pollution in Malaysia. The annual variation of ozone concentration depends upon several conditions such as the sources of its precursor, the land use type and meteorological parameter. This study aims to understand the trends and issues of transformation characteristics of O_3 in 4 urban area (Shah Alam, Kajang, Johor Bahru and Kota Bharu) during specific critical conversion time (CCT) as well as to introduce the critical transformation time (CTT) of O_3 in 4 selected continuous air quality monitoring stations (CAQMS) from the year 2000 to 2011. The identification of CTT for O_3 formation was identified occurring between 8.00 a.m and 11.00 a.m., and the O_3 uni-modal peaks usually after CTT at approximately between 12.00 p.m and 4.00 p.m. The results indicated that the CTT of O_3 in the Kota Bharu is slightly earlier occurring between 8.00 a.m to 10.00 a.m whereas Shah Alam, Kajang and Johor Bahru the CTT later occurring between 10.00 a.m to 11.00 a.m. Only Kota Bharu recorded data was below 100 part per billion volume (ppbv), while Shah Alam, Kajang and Johor have recorded exceedances above 100 ppbv. This research elucidates that CTT is adequate to control ozone concentration. Ozone might exceed Recommended Ambient Air Quality Guideline (RMAAQC) unless nitrogen emissions are adequately managed, due to the detrimental effects for those who are at risk of respiratory health problems resulting from air pollution.

Index Terms: Diurnal variations, ozone fluctuation, precursor, secondary air pollutant.

I. INTRODUCTION

The unpolluted Earth's atmosphere is a mixture of gases consisting of nitrogen (N_2) and Oxygen (O_2), comprising approximately 78% and 21% respectively of atmospheric mass and volume. The 1 % remaining consists of a number of trace gases. Contamination of the air began to be affected by human activities with the introduction of gas or particulate-phase substances or energy forms (heat, noise, radioactivity) so that the locally, regionally, or globally altered atmosphere may pose harm to humans, biological systems, materials or the atmosphere itself [1]. Many cases of air pollution problems affecting the world are of local or near-field origin and hence amenable to local fixes/solutions [2]. Example of these includes severe urban pollution by nitrogen oxide (the precursor of ground-level ozone) or particle matter. Both can be solved, at least partially, by curbing local scale emissions from vehicles, factories and

power plants. In [2] has reported that researchers must find the particles that are most dangerous to health in each place so policies can reduce levels of those pollutants first. Ground-level ozone (O_3) pollution is the second significant prominent air pollution in Malaysia [3].

Troposphere ozone, otherwise known as ground-level ozone, is formed in the atmosphere by complex photochemical reactions involving precursors; the oxides of nitrogen and volatile organic compounds [4], [5]. Ozone becomes harmful at ground level as its unstable and reactive oxidant that can deposit onto most surfaces including biological tissues, for example, lungs, eyes or plants [6], [7]. Ozone form from its precursors; both nitric oxide (NO) and nitrogen dioxide (NO_2) are directly involved in O_3 photochemical reactions to produce O_3 . The lifetime of these precursors, the rates of their reaction in the atmosphere and the lifetime of O_3 in the troposphere combine to make tropospheric O_3 a regional-global scale problem [5].

The concentration of other pollutants (its precursor) is known to cause ozone formation, the extent of which could be different depending on the specific land use categories, e.g. urban, suburban and rural. The diurnal cycles of surface ozone have a uni-modal shape, which is controlled by various processes including photochemistry, physical/chemical removal, and the rate of deposition and transport [9], [10]. In Malaysia, a number of previous studies have reported understanding the critical transformation characteristics of O_3 using NO_2 photolysis rate [8]. The critical conversion time (CCT) could be utilised to explain the various fluctuation characteristics of O_3 and predict their diurnal variations. Literature has emerged that shows the entire process of photochemical reactions which involve NO_2 photolysis and NO titration reactions where it can determine the CCT of precursors to O_3 [10], [11]. This study, therefore, set out to focus on trends of critical transformation time (CTT) characteristics where the exact time range of ozone transformation is in the highest rate in urban peninsular Malaysia.

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II. METHODOLOGY

A. Study area

4 urban areas (Shah Alam, Kajang, Kota Bharu and Johor Bahru) of continuous air quality monitoring stations (CAMQS) 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 shows the map of the located monitoring station.

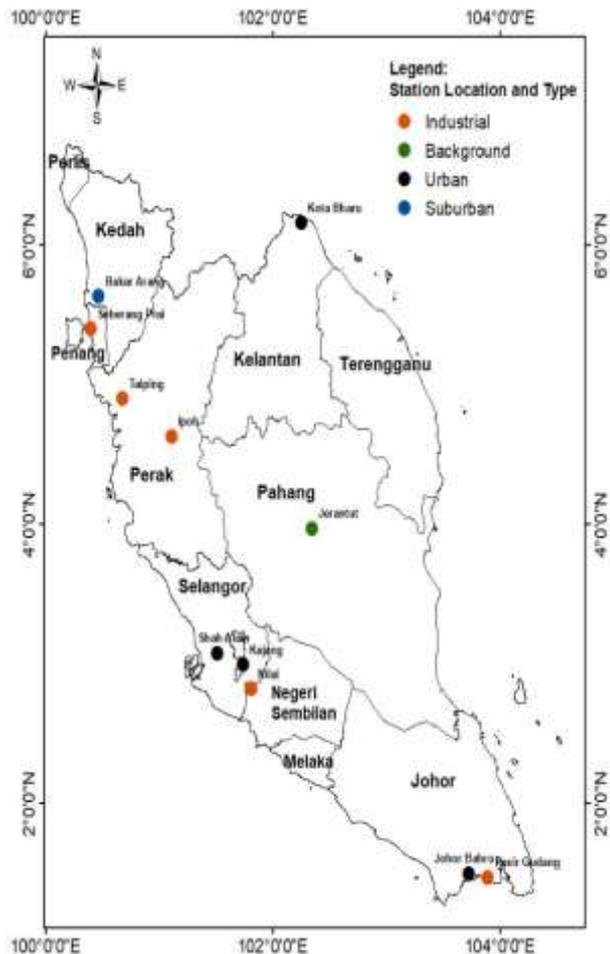


Fig. 1: Selected urban location of CAQMS in Peninsular Malaysia

B. 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 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.

C. Ground-level ozone concentration

The ozone data were obtained from the air monitoring station by DOE, which is managed by 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.

D. NO_2 concentration

Similar to ozone data collection, NO_2 concentration were 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.

E. 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 [10]. The CCT plays an important role in diurnal plot whereby the range of 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 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.

III. RESULTS AND DISCUSSION

A. Descriptive statistics

The descriptive statistics of hourly O_3 concentration from 2000 to 2011 at the 4 monitoring station; urban- Kota Bharu; KB, Shah Alam; SA, Kajang; KJG and Johor Bahru; JB using Table 1 and boxplot, illustrated below (Fig. 2). The hourly average concentrations of O_3 at the monitoring stations were recorded between 13 and 20 ppbv. Shah Alam (SA) station recorded the highest average concentration of O_3 (20 ppbv).

This was followed by Kajang (19 ppbv), Johor Bahru (14 ppbv) and Kota Bharu (13 ppbv) respectively. The highest

maximum recorded at Kajang with maximum value up to 175 ppbv, followed by Shah Alam (174 ppbv), Johor Bahru (141 ppbv) and Kota Bharu (69 ppbv).

Table 1: Descriptive data for hourly O₃ concentration from 2000 to 2011 of 4 CAQMS; KB, SA, KJG and KB

Location	N total	Mean	Standard Deviation	Minimum	Median	Maximum
KB	99602	13	10.341	1	12	69
SA	99717	20	23.730	1	11	174
KJG	92047	19	21.582	1	12	175
JB	99694	14	14.256	1	9	141

The variations of O₃ concentrations at the 4 monitoring stations because of the different background of the presence of its precursors; the oxides of nitrogen (NO_x) and volatile organic compounds (VOCs) thru photochemical reactions in the presence of sunlight [11], [12].

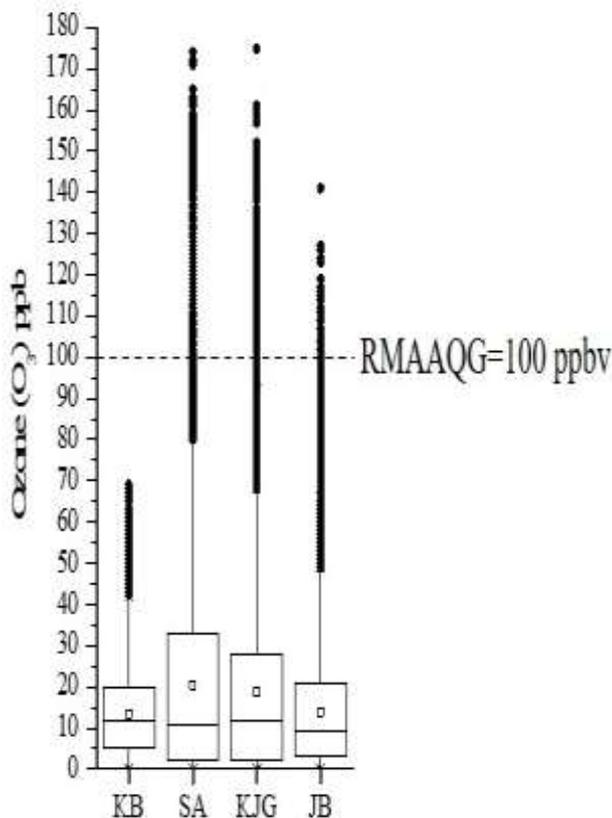


Fig. 2: Box and Whisker Plot of hourly average of O₃ concentration for Kota Bharu, Shah Alam, Kajang and Johor Bahru

Results from box and whisker plot suggest that distribution of the data at SA, KJG and JB were skewed to the right (median < mean), while KB was uniformly distributed (median = mean). The median values vary to the average O₃ concentration (between +/- 9 ppbv and 12 ppbv), while the standard deviation for the dataset was between 10 and 21 ppbv for all the stations. Results of distribution have several violations of distribution assumptions of parametric tests; alternative nonparametric techniques can be used to detect long-term air pollutants when sample of data does not satisfy normal distribution assumptions. This exemplified in work undertaken by [13] demonstrates that ozone distribution in 6

monitoring station of United Kingdom are not normally distributed and hence non-parametric statistic should be used. Other than that, there were also outliers detected in each of the data set. Outliers are the data that lies far from the other value in a random sample and do not belongs to the main population. The outliers in Fig. 2 contributed from the highest O₃ concentration recorded throughout the 12 years. The presence of the outliers indicated that there are certain days when the O₃ transformation was much higher than the other days. Most of the maximum concentrations were outliers sources from external pollutant factors [14].

B. Diurnal variations

Diurnal plot giving the information of fluctuation of O₃. Fig. 3 shows the diurnal variation of the hourly average of O₃ and its precursors (NO and NO₂) at 4 continuous air quality monitoring station (CAQMS). The fluctuational behaviour of individual illustrated using composite diurnal plot (Fig. 3). Overall, O₃ diurnal variations show the uni-modal shape. The increasing trend of O₃ 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 at all stations. Several recent studies exhibit that O₃ exhibits strong diurnal variations [8], [15]–[17] at different locations. Day time surface ozone [18] and nocturnal surface ozone [17] variations depending on its precursors and meteorological conditions. The study of ozone variation is complex. In [18] have addressed some key challenge in mitigating ozone based on surface ozone. There is large difference in the frequency of total daily maximum ozone concentration between CAQMS stations that are close. Thus, in this study, critical conversion point (CCP) that show the exact time (CCT) is used to explain in more details of photochemical processes involved in fluctuational and transformation of O₃. CCP and CCT can be obtained from composite diurnal plot. The different location has a different time for CCP. CCP is assumed to be the interception point between O₃, NO₂ and NO line in the composite diurnal plot [10]. Generally, at the beginning of the plot, NO₂ concentration was high while O₃ concentration remained low due to NO_x titration during nighttime [16]. Changes started to occur when entering CCT, starting around 8.00 a.m., due to the increasing solar radiation that triggers photochemical reactions. During CCT, NO₂ was used up for the O₃ formation. CCP occurred when photochemical reaction rate started to surpass NO_x titration rate and it was represented by the interception point between O₃ and NO₂ concentration on the plot [10], [11], [19]–[21]. The O₃ uni-modal peaks usually after CCT approximately between 12.00 p.m. to 4.00 p.m.

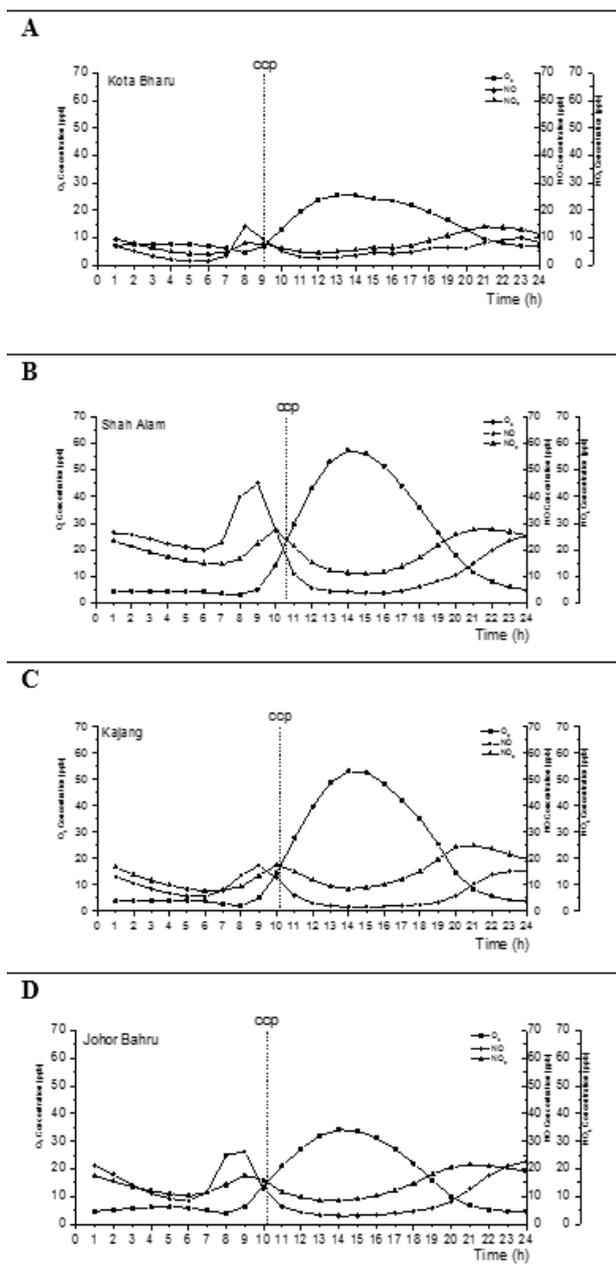
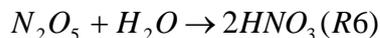
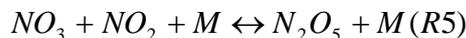
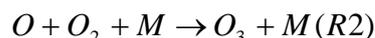


Fig. 3: Composite diurnal plot of O₃, NO and NO₂ concentration at urban CAQMS: (A) Kota Bharu (B) Shah Alam (C) Kajang and (D) Johor Bahru

CCT was considered based on the photochemical reactions of O₃ formation. CCT is the process where the rate of NO₂ photolysis was higher than the rate of NO titration [20]. Higher rate of NO₂ photolysis than NO titration will accumulate the O₃ production [22]. Thus, CCT can be used to explain the O₃ formation and destruction (Table 2) which can be used to represent diurnal the variations of O₃ during daytime and nighttime.

Fig. 3 represents diurnal variations for the urban CAQMS. The CCP of each location is obtained based on the average of hourly data for 12 years. For all regions, the ozone concentration starts to decrease after the CCT time (the uni-modal peaks) around 2.00 p.m. to 5.00 p.m. The decrease of O₃ is due to the decrease of UV intensity as the sun radiation starts to decline. As the ozone decrease, NO₂ starts to increase (R4), the titration process. Ozone starts to

decrease started at 7.00 pm to 7.00 a.m at all locations following reactions:



During nighttime, the reaction between O₃ and NO₂ yield nitrate (NO₃) radicals through R4. The produced NO₃ radicals directly react with NO₂, producing dinitrogen pentoxide (N₂O₅). It is unstable and will dissociate back to NO₂ and NO₃ radicals (R5). However, N₂O₅ may also undergo reaction with H₂O to form nitric acid (HNO₃). Increasing water vapour in nighttime relatively increase the RH will enhance the formation of nitric acid, HNO₃ (R6). HNO₃ is highly soluble in water and deposit thru precipitation as acid rain [7], [23]. Limited nighttime NO₂ directly reduce the reaction rates of R4 and R5. The decline continues until it reaches a stable concentration throughout the nights starting at 11.00 p.m. The interruption of removal reactions allowed O₃ to remain in the atmosphere [16]. The high concentration of NO₂ will enhance the reaction in R4, R5 and R6 to destruct the O₃.

The monthly diurnal variation analysis revealed the second peaks of surface ozone during night time happened at more than 50% of all CAQMS occurring around 3.00 a.m. to 5.00 a.m and the ratio mean of nighttime to daytime ozone concentration was the highest in the east coast region and lowest in the central region while the other regions were in average. This could explain the highest is due to horizontal transport while the lowest is due to titration [17].

C. Critical Transformation Time (CTT)

CTT is introduced to assess the trends of ozone transformation for urban area. The results showed that the CTT in Table 2, which was between 8.00 a.m. and 11.00 a.m. From the result, it was observed that the CTT at Kota Bharu occurred between \pm 8.00 a.m to 10.00 a.m. while CCT at Shah Alam, Kajang and Johor Bahru occurred between \pm 10.00 a.m to 11.00 a.m. These 4 locations are in the same categories of land use however the range of CTT in Kota Bharu slightly earlier. During CTT, O₃ concentration only started to accumulate due to the increased rate of NO₂ photolysis at a point time called CCT that indicated the highest rate of photochemical reaction at that point. The diurnal plot showed that the NO₂ concentration decreased after CCP while O₃ concentration increased. This indicated that the transformation of NO₂ to O₃ occurred rapidly, which lead to accumulation of O₃ and concentration of O₃ increased. Hence the mean value both NO₂ and NO were higher during CCT [10]. The O₃ maxima happened after CCT, usually between 12.00 p.m. and 4.00 p.m. which is at different time range.

Table 2: Critical conversion time (CCT) and critical transformation time (CTT) based on composite diurnal plots at 4 CAQMS

Year	Critical Conversion Time (CCT)			
	Urban			
Location	Shah Alam	Kajang	Johor Bahru	Kota Bharu
2000	10.45	10.00	10.30	9.10
2001	10.55	10.00	10.20	9.10
2002	10.55	10.00	10.00	9.10
2003	10.55	10.00	10.20	9.15
2004	10.55	10.00	10.15	9.05
2005	10.45	10.00	10.15	8.30
2006	10.15	10.00	10.10	8.50
2007	10.15	10.00	10.00	8.50
2008	10.45	10.10	10.00	9.00
2009	10.30	10.00	10.10	9.30
2010	10.30	N/A	10.15	9.00
2011	10.30	N/A	10.00	8.30
Critical Transformation Time (CTT)	10.00 a.m to 11.00 a.m	10.00 a.m to 11.00 a.m	10.00 a.m to 11.00 a.m	8.00 a.m to 10.00 a.m

IV. CONCLUSION

In conclusion, CTT can be used to characterize the behaviour of ground-level ozone. The concentration of O₃ pollution depending on its ambient environment decided by their transport in the atmosphere depending on atmospheric dispersion or diffusion. The rate of this process depending on atmospheric turbulence, which varies with both location and time. Therefore, pollutants and particulates released from industrial, vehicular and other sources into the atmosphere get dispersed by different mechanisms governed by meteorological parameters. The CTT of O₃ has the information of source reaching the receptor location and information of the local meteorology. The parameters of interest are the local wind speed, wind direction and temperature vary from time-to-time becomes essential for interpretation of air quality data and modelling of pollutant in the atmosphere.

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