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Ground Level Ozone Fluctuational Characteristics within Two Industrial Areas in Malaysia

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Abstract. This study aims to investigate the fluctuation characteristics and source signature of ground level ozone (GLO) at a receptor site in commercial urban-industrial and suburban industrial area in Shah Alam, Selangor, and Bakar Arang are hot spots for industrialization. The fluctuation characteristics of ozone in industrial is determined using critical conversion time (CCT) and introduce the Critical Transformation Time (CTT) using secondary data from 2000 to 2011. We also use Principal Component Analysis (PCA) to determine the primary sources from atmospheric parameter and meteorological parameter. It was observed that suburban Bakar Arang has earlier CCT between 8.00 a.m. and 9.00 a.m. compared to Shah Alam where CCT occurred between 10.00 to 11.00 a.m. Results of PCA indicate ozone CCT fluctuation contribution in Shah Alam by primary air pollutants (CO, NO, NO_2, CH_4) and meteorological influence are 64.1% and 41.5%, respectively, higher than that in Bakar Arang. The use of CCT and CTT show specific time range of ozone production and destruction. These sources of compounds lead to formation of GLO and affecting the CCT. The application of CTT could be a signal of the urgent need to manage nitrogen emission from commercial industrial areas.

1. Introduction

As a developing country, Malaysia has experienced large scale land use change with increasing urbanization and industrialization [1] that lead to significant ozone pollution. Ground-level ozone (O_3) pollution is the second most significant prominent air pollution in Malaysia [2].

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 [3,4]. Ozone is produced by 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]. For example, in most urban environment, such as the Klang Valley,

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 [6].

In Malaysia, a number of previous studies have reported understanding the critical transformation characteristics of O_3 using NO_2 photolysis rate [6]. The critical conversion point (CCP) 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 critical conversion point (CCP) and critical conversion time (CCT) of precursors to O_3 could be deduced from them [6,7]. The findings of CCT make an important contribution to the exact time where the O_3 transformation is at its highest rate. The identification of Critical Transformation Time (CTT) in this study were set out to focus on the time range of O_3 transformational behavior before the O_3 reached it peaks level.

In this study, the CTT ozone fluctuation characteristics in two industrial areas with different background land use is presented to focus on the time range of O_3 transformational behavior before the O_3 reached it peaks level and highlight the challenges involved in ozone mitigation.

2. Methodology

2.1 Study Area

The study areas chosen for this are in Shah Alam (SA), Selangor, and Bakar Arang (BA), Kedah, where continuous air quality monitoring stations (CAQMS) are located. The CAQMS in these two locations are managed by a private company, Alam Sekitar Malaysia Sdn Bhd (ASMA) hired by Department of Envirnment (DOE) Malaysia. Figure 1 and 2 show the map of the location for CAQMS.

2.1.1 Shah Alam, Selangor.

Shah Alam (3.0733° N, 101.5185° E) is an established urban area in Selangor. It is the state capital of Selangor and a well-known industrial city in Malaysia with large coverage of industrial and transportation land uses [1]. The sampling station is located within 10 meters from the CAQMS located at Taman Tun Dr. Ismail residential area, connected by six major highways. Shah Alam is a heavily industrialized area with high human population and high traffic density, together with high pollutant emission. The temperature in Shah Alam varies between 33 °C and 27 °C throughout the year. March is the warmest month of the year at Shah Alam with little precipitation and November is the wettest month due to the northeast monsoon season. Shah Alam was chosen for analysis due to its high population density with urban-industrial environment hence an adverse affecting the health.

2.1.2 Bakar Arang, Sungai Petani, Kedah.

Bakar Arang, Sungai Petani, Kedah is located in Northern Peninsular Malaysia with 421,530 people. It is located on outskirts of Sungai Petani and 30 km from Penang Port. The CAQMS located at Sek. Keb. Bakar Arang near to industrial areas focused on the heavy industries from timber products, health products, electrical and electronics, plastics, textile, automotive, motor assemblies, pharmaceuticals and concrete products [8]. This area experienced uniformly high temperature in between 27°C to 30°C with mean rainfall of 267 cm. Population density and traffic density had increased therefore is expected that O_3 concentration in the sampling site will be high compared to other area. Awang *et al.* [9] reported that suburban Bakar Arang mean O_3 concentration is higher compared to urban mean O_3 concentration in Seberang Perai (industrial) and Kajang (urban). In conclusion, the mean O_3 concentration of Bakar Arang affected from vehicular emissions [9] and this study has focused on time range of O_3 accumulation associated with the rate of NO/NO_2 that has its time range variation in different land use environment.

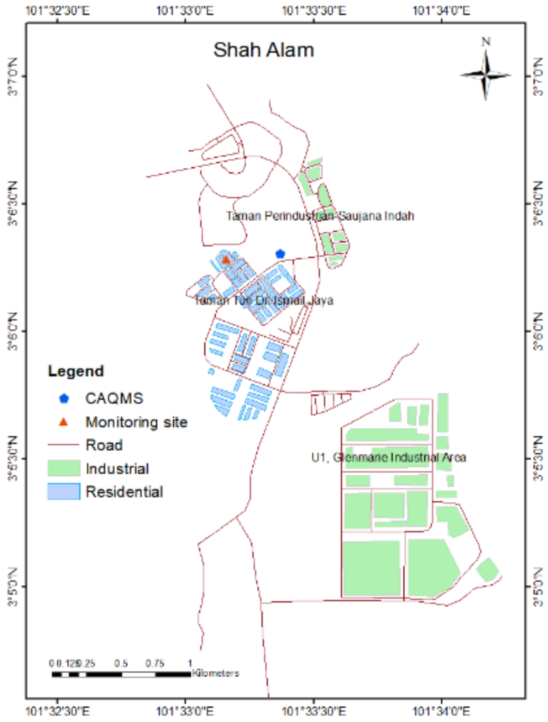

Figure 1. Location of monitoring site and Continous Air Quality Monitoring Station (CAQMS) in Shah Alam

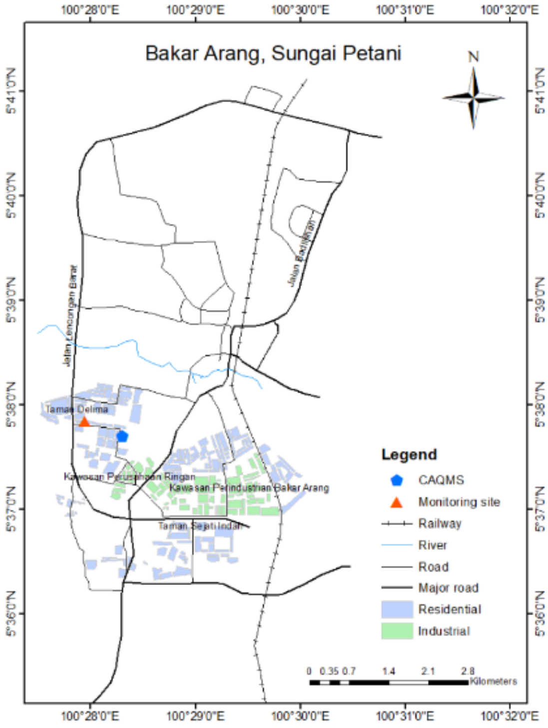

Figure 2. Location of monitoring site and Continous Air Quality Monitoring Station (CAQMS) in Bakar Arang

2.2 Secondary Data Collection

Twelve years of continuous hourly O_3 concentrations and other air pollutant levels starting from 1st January 2000 to 31st December 2011, was obtained from Department of Environment, Malaysia. There were two categories for data collection. First was to determine the fluctuation behavior O_3 concentration at the 2 CAQMS and identification of CTT of O_3 concentration using composite diurnal plot of NO-NO_2-O_3. Second was to determine the sources contribute the O_3 concentration using Principal Component Analysis (PCA) with 11 other variables were initially arrange by month and year based on CTT. The 11 variables studied were divide into two latent factors; air pollutants and meteorological parameters.

The first latent factor is air pollutants consisted of ground level ozone (O_3), carbon monoxide (CO), nitrogen oxide (NO), nitrogen dioxide (NO_2), sulphur dioxide (SO_2), the organic pollutant group consisted of methane (CH_4) and non-methane hydrocarbon (NMHC) while the second latent factor is meteorological parameters consisted of wind speed, ambient temperature, relative humidity and ultraviolet-B radiation (UVB). No imputation procedure was adopted for the treatment of missing data.

2.3 Primary Data Collection

This study used primary data that was collected to verify the secondary data that used to obtain the CCT (O_3 NO and NO_2). The monitoring set up is divided into three categories which the location for monitoring, the period and the monitoring equipment both for air pollutants and meteorological parameters

The important to do the primary data collection was to verify the secondary data to determine whether the secondary data is following the current trend of air quality. The location for monitoring site is located less than 1 km from CAQMS for SA and BA.

2.3.1 Monitoring Period and Equipment.

The monitoring period was started from 12.00 a.m. to 12.00 a.m. (24 hours) for 72 hours in Shah Alam and Bakar Arang. The primary data that were obtained at the studied site consists of ozone (O_3) and nitrogen dioxide (NO_2). They were monitored and collected by using the specific equipment (Table 1) which was run directly on the site.

Table 1. Specific equipment used for primary data's collection

Type of equipment	Parameter
Aeroqual S 500 Series	Ozone (O_3) and Nitrogen Oxides (NO, NO_2)
Automatic Weather Station (AWS) – RK900-01	Temperature, wind speed, relative humidity

The Aeroqual S 500 series typically used for short term air quality assessment and monitoring. It has an interchangeable sensor that attached to the monitor base. It consists of different sensor codes, types, detection range and has the minimum limit for the detection range. Aeroqual S 500 yielded close agreement with hourly average observations from a reference instrument used by DOE in temperate ambient conditions [10,11]. The concentration of O_3 and NO_2 were measured by using the same device with different portable sensor head. In term of quality control and quality assurances, Aeroqual provided a Calibration Accessory (R42) to enhance humidity control and delivery of calibration gas to the sensor head. Zero calibration is available whenever the sensors exhibited baseline reading higher than zero.

Automatic Weather Station RK900-01 is used for primary data collection for wind speed sensor with measurement accuracy at ± (0.3±0.3V) m/s. Wind direction sensor with measurement accuracy at ±3°, temperature with accuracy at ±5°C and relative humidity with accuracy level at ±3%, respectively.

2.4 Diurnal Variations

This study has used composite diurnal plots of O_3, NO and NO_2. Diurnal plot is representing the variation of ozone transformational behaviour together with its precursors- NO and NO2 during daytime and night time (24 hours).

CCP can be deduced from composite diurnal plot and showed O_3 production point that has introduced as critical conversion point (CCP). CCP was occurred at a specific time and has been introduced as critical conversion time (CCT) [6]. In addition, O_3 accumulation has the time range and could be different in different environment settings which has been introduced in this study as critical transformation time (CTT) and representing the novelty of this work.

The composite diurnal plot plays an important role in this study to determine at which point the three variables (O_3, NO and NO_2) intercept and causes the critical conversion point (CCP) to occur at specific time (CCT). From there, the critical transformation time (CTT) has been investigated. Previous research has only focused on time of NO_2 photolysis starts to accumulate (CCP). Through the use of CTT, the NO_2 photochemical reaction would be able to capture the O_3 accumulations before the O_3 decrease entering the phase of NO titration taken place. The time range of CTT could be highlighted to reduce the sources on the time range and could mitigate the exceedances of ozone concentration.

2.5 Principal Component Analysis (PCA)

PCA is widely used to reduce variables and to identify the relevant variables as sources of O_3 formation. It has capability to detect most significant variables in dataset with minimum loss of original information [6].

Equation 1 of Principal Components (PCs) as follow:

$$PC_i = l_{1i}X_1 + l_{2i}X_2 + \ldots + l_{mi}X_m \quad (1)$$

In this Equation 1, where PCi is the i^{th} PC, and l_{mi} is the loading of the observed variable X_m.

The first PCs is the linear combination of X having the largest variance [12]. The new variables known as PCs is defined by the eigenvectors od the covariance matrix of X. Ul-Saufie *et al.* [13] explained the eigenvalues shows the eigenvectors and PCs; for each PC, only eigen values larger or equal to 1 are considered as significant. Varimax rotation for PCA is important to ensure each variable is significant and correlate with only one component and has minimal association with other components. The load for each variable has significant where the factor loading is considered strong with the value 0.5, moderate with 0.4 and weak with the value 0.3.

3. Results and Discussion

The fluctuation of ozone concentration and its precursors during daytime and night time are linked to changes of critical conversion point (CCP), critical conversion time (CCT) and critical transformation time (CTT) in transformational behaviour of ozone concentration for SA and BA.

3.1 Diurnal Variations: Critical Conversion Point (CCP) and Critical Conversion Time.

The determination of CCP and CCT is analysed using composite diurnal plot from monitoring site is presented in Figure 3. O_3 diurnal variation shows the uni-modal shape at both locations. The O_3 concentration increased after sunrise, reaching a peak approximately between 12.00 p.m. and 4.00 p.m. O_3 production is characterized by photochemical reaction of NO_x linked to UV_B intensity [14].

Both SA and BA daily average concentration during monitoring do not exceed 100 part per billion (ppb) of Recommended Malaysian Ambient Air Quality Guideline (RMAAQG). The result of SA ozone started to rise around 10.00 a.m and the interception of ozone and nitrogen dioxide is obtained around 11.00 a.m to 12.00 p.m. The CCP is showing the time and known as CCT. While in BA, ozone started to rise up at 9.00 a.m. and CCT slightly earlier approximately between 8.00 a.m. and 9.00 a.m.

However, the formation fluctuation of ozone before reaching its peak has a certain time range. The time range can be obtained using the 12 years of secondary data and we represented the CCT and CTT as shown in Figure 4.

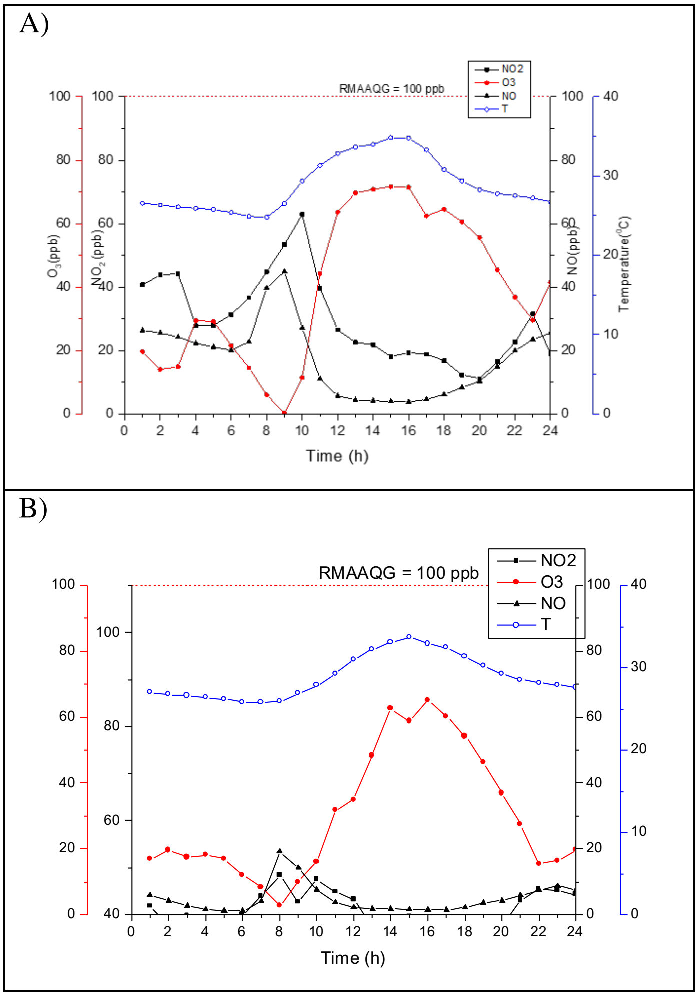

Figure 3. Composite diurnal plot from monitoring days (72 hours) of O_3, NO and NO_2 concentration at industrial monitoring site in a) Shah Alam b) Bakar Arang

3.2 Critical Transformation Time (CTT)

Diurnal plot giving the information of fluctuation of O_3. In Figure 4 (A and b) show the diurnal variation of the hourly average of O_3 and its precursors (NO and NO_2) at continuous air quality monitoring station (CAQMS). The fluctuational behaviour of individual illustrated using composite diurnal plot. O_3 production is characterized by photochemical processes. Overall O_3 diurnal variations show the uni-modal shape, mark the same pattern of primary data collection from monitoring days conducted as in Figure 3.

Based on previous studies where the researcher used diurnal plot to determine CCP of selected location [6]. Figure 4 (A and B) represent the industrial urban and sub urban CAQMS. Generally, at the beginning of the plot, NO_2 concentration was high while O_3 concentration remained low due to NO_x titration during night time [15]. 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, NO_2 was used up for the O_3 formation. CCP occurred when photochemical reaction rate started to surpass NO_x titration rate and it was represented by the interception point between O_3 and NO_2 concentration on the plot [6, 7, 15, 16,17].

The O_3 uni-modal peaks usually after CCT approximately between 12.00 p.m. to 4.00 p.m. For both areas, 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 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 in Equation (2), known as titration process.

Ozone starts to decrease started at 7.00 p.m. to 7.00 a.m. following reactions in equations (2) – (7):

$$NO_2 + hv(\lambda < 420nm) \rightarrow NO + O \quad (2)$$

$$O + O_2 + M \rightarrow O_3 + M \quad (3)$$

$$NO + O_2 \rightarrow NO_2 + O_2 \quad (4)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (5)$$

$$NO_3 + NO_2 + M \leftrightarrow N_2O_5 + M \quad (6)$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \quad (7)$$

During night time, the reaction between O_3 and NO_2 yield nitrate (NO_3) radicals through Equation (5). The produced NO_3 radicals directly react with NO_2, producing dinitrogen pentoxide (N_2O_5). It is unstable and will dissociated back to NO_2 and NO_3 radicals Equation (6). However, N_2O_5 may also undergo reaction with H_2O to form nitric acid (HNO_3). Increasing water vapour in night time relatively increase the RH will enhance the formation of nitric acid, HNO_3 Equation (7). HNO_3 is highly soluble in water and deposit thru precipitation as acid rain [3,18]. Limited night time NO_2 directly reduce the reaction rates of Equation (5) and Equation (6).

The decline continues until it reaches a stable concentration throughout the nights starting at 11.00 p.m. The interruption of removal reactions allowed O_3 to remain in the atmosphere [15].

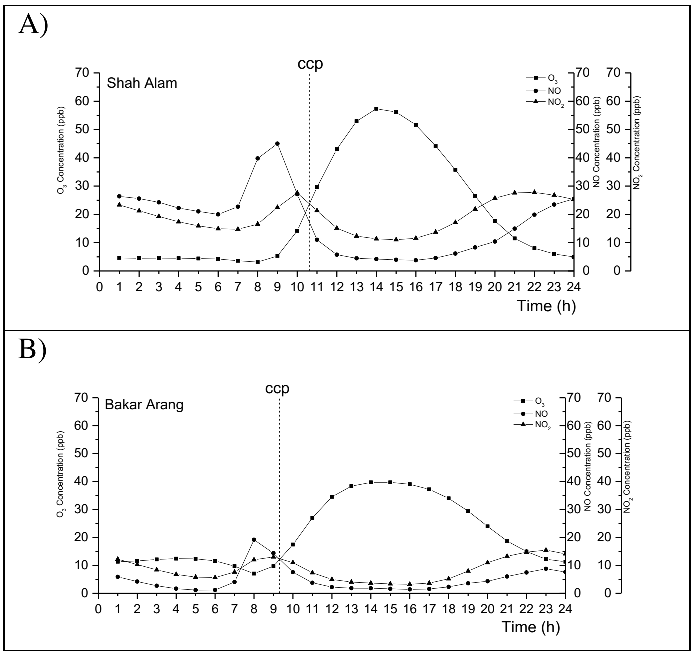

Figure 4. Composite diurnal plot of O_3, NO and NO_2 concentration at industrial urban CAQMS: (A) Shah Alam and industrial suburban (B) Bakar Arang in 12 years (2000-2011)

The results showed that the CCT in Table 4.2 of each location occurred within the CTT, which was between 8.00 a.m. and 11.00 a.m. CCT shown a time where a point that has intersection point of O_3 and NO_2 concentration. From the result, it was observed that the CCT at Kota Bharu occurred at ± 8.00 a.m. while CCT at Shah Alam, Kajang and Johor Bahru occurred at ± 10.00 a.m. These four locations are in the same categories of land use however the range of CCT in Kota Bharu slightly earlier while the other locations were in the same range. This finding confirming that the photochemical reaction depending on its sources and the temperature [19] which influencing the CCT to occurred early or later in different environment settings.

Table 2. Critical conversion time (CCT) and critical transformation time (CTT) based on composite diurnal plots at SA and BA.

Year	Critical Conversion Time (CCT)	
	Industrial-Urban	Industrial-Suburban
Location	Shah Alam	Bakar Arang
2000	10.45	9.15
2001	10.55	9.30
2002	10.55	9.45
2003	10.55	9.45
2004	10.55	9.15
2005	10.45	9.10
2006	10.15	9.40
2007	10.15	9.30
2008	10.45	8.55
2009	10.30	9.05
2010	10.30	9.00
2011	10.30	9.15
Critical Transformation Time (CTT)	10.00 a.m to 11.00 a.m	8.00 a.m to 10.00 a.m

3.3 Principal Component Analysis (PCA)

The PCs results in Table 3 show after varimax rotation. Varimax rotation in PCA is use to maximize correlation of a variable with one component only and minimize of the variables with the other component [19].

Table 3. Total Variance explained of diurnal ozone

		Diurnal Ozone		
		Rotated sum of square loading		
Location	Component	Eigenvalue	V (%)	C(%)
Shah Alam	1	7.195	64.10	85.43
	2	1.348	12.26	
Bakar Arang	1	4.565	41.498	86.12
	2	3.790	34.454	
	3	1.118	10.165	

Whereas, the factor loadings for each variable in Table 4 explained the ten significant parameters of the data set that influence the ozone fluctuation in SA and BA, respectively. Shah Alam diurnal ozone fluctuation is contributed by the first component with the biggest factor loading 7.195 with 64.1% of total variance. There are 8 variables listed as significant variables (e.g. NO_2, NO, CO, PM_{10}, CH_4, Temperature, Ultraviolet-B, Relative Humidity, Wind Speed). One variable has listed in second component (e.g. SO_2) with only 12.26%% of total variance.

Table 4. Rotated component matrix using varimax rotation

Location	Shah Alam		Bakar Arang		
PC	PC1	PC2	PC1	PC2	PC3
NO_2	-0.889		0.884		
NO	0.926			0.904	
CO	0.953			0.909	
PM_{10}	0.923			0.835	
SO_2		0.952		0.956	
CH_4	0.845		-0.812		
Temp	-0.926		0.807		
UVB	-0.806				0.611
RH	0.885		-0.859		
WS	-0.883		0.758		

Meanwhile in Bakar Arang, there are three PCs. The first factor loading is 4.565 representing 41.498% of the total variance. The first component listed are mixing of primary pollutants and meteorology parameters (NO_2, CH_4, Temperature, Relative humidity and Wind speed). PCs 2 comprise of other primary pollutants such NO, CO, PM_{10} and SO_2. The last variable into PCs 3 is only UVB with 10.165 total variance.

In conclusion of the results presented, the commercial industrial area in SA emits more oxides of nitrogen (NO and NO2) than in BA. These two main precursors have contributed to the time of ozone formation, the CCT and CTT. During CCT, NO_2 was used up for the O_3 formation. CCP occurred when photochemical reaction rate started to surpass NO_x titration rate and it was represented by the interception point between O_3 and NO_2 concentration on the plot [6,7,15,16,17]. Bakar Arang CCT and CTT slightly earlier while the other locations were in the same range. This finding confirming that the photochemical reaction depending on its sources and the temperature [18] which influencing the CCT to occurred early or later in different environment settings. CCT indicated the highest rate of photochemical reaction at that point. The diurnal plot showed that the NO_2 concentration decreased after CCT while O_3 concentration increased. This indicated that the transformation of NO_2 to O_3 occurred rapidly, which lead to accumulation of O_3 and concentration of O_3 increased. The O_3 maxima happened after CTT, usually between 12.00 p.m. and 4.00 p.m. After O_3 maxima, O_3 concentration tends to decrease due to the decrease of solar energy. NO_x titration takes place after sunset and causes NO_2 concentration to rise back and surpassed O_3 concentration.

4. Conclusion

O_3 concentration starts to increase after the sunrise, where a point for O_3 starts to produce has been introduce as CCP and CCT. The time range for O_3 to accumulate and increase had led in this study and known as CTT and being used to predict O_3 diurnal variation. The research has suggested factors need to be considered such the distribution of NOx with meteorological factors need to be addressed between the CAQMS. Thus, the importance of critical transformation time (CTT) could be highlight to explore the ground level ozone transformational behaviour for urban, industrial and suburban. In addition, the used of CTT in prediction of ozone variation could provide as an early signal of the urgent need to manage nitrogen emission from commercial-industrial areas that has detrimental effects on air quality and climate change and that has to be avoided.

Acknowledgements

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