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Preliminary Study of Ground Level Ozone Nighttime Removal Process in an Urban Area

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Abstract

The depletion processes of nighhtime ground level Ozone (O_3) concentrations in an urban area in Malaysia were evaluated. Annual monitoring records of O_3 in Kota Bharu, Kelantan, were obtained from Department of Environment, Malaysia and separated into daytime and nighttime concentrations. In Malaysia, daytime starts from 7 a.m. until 7 p.m., and 7 p.m. to 7 a.m. is deemed as nighttime. The annual hourly average concentrations of O_3 were 15.13±9.23 and 5.76±5.58 ppb for daytime and nighttime, respectively. The diurnal cycles of ground-level O_3 concentrations suggests that a uni-modal peak occurs at 1 p.m. and high O_3 concentrations was observed on December 2010 as a result of the higher rate of local photochemical production. Absence of photochemical reactions during nighttime identified as the main factor that contributed to low nighttime O_3 concentrations. This study discovered that NO and NO_2 play important role in O_3 depletion process during nighhtime. Result confirmed that high nighttime NO concentration enhanced further destruction of nighttime O_3 concentrations.

1. Introduction

Ozone (O_3) is an important constituent of the atmosphere that plays important roles as an oxidant as well as greenhouse gas. The O_3 is known to occupy in ozone layer which, is located in the middle of the stratosphere and acts as a shield that protecting Earth from harmful radiation. However, a small concentration of O_3 also exists in the troposphere and considered as a secondary air pollutant due to their production mechanism. At ground level, the formation and accumulation of O_3 are induced by the emissions of nitrogen oxide (NO_x) and volatile organic compounds (VOCs). With presence of sunlight, nitrogen dioxide (NO_2) undergoes photochemical reactions to produce free oxygen atom (O), which mainly reacts with oxygen molecule (O_2) to form O_3 (Duenas et al., 2004; Abdul-Wahab et al., 2005; Ghazali et al., 2010). O_3 has received substantial attention worldwide because of its negative effects. Under certain conducive atmospheric conditions, O_3 can build into high concentration and capable to impose negative impacts on human health, crop production, material quality and the ecosystem.

Ground level O_3 exhibited different fluctuation features compared to other primary air pollutants such as NO, NO_2, CO and CO_2. Ozone showed clear diurnal trends which is very close to solar radiation diurnal trends (Duenas et al., 2004). The O_3 concentration is normally low in the morning and gradually increases towards the afternoon (Ghazali et al., 2010; Alghamdi et al., 2014). Diurnal variation in O_3 shows the highest concentration around noon or early afternoon and the values gradually decreasing as evening approaches (Ghosh et al., 2013). Various studies reported that O_3 shows similar uni-modal trends that reach peak concentration around afternoon or early evening and the same trend were also observed in Malaysia (Ghazali et al., 2010; Latif et al., 2012; Banan et al., 2013; Awang et al., 2016).

Generally, O_3 concentration is higher during daytime as compared to nighttime because photochemical reactions only occurs during daytime (Ghazali et al., 2010; Reddy et al., 2011; Alghamdi et al., 2014). At night, O_3 concentration is constantly low primarily accounted for absence of any photochemical production and further destruction by continuous chemical loss by NO titration and deposition process (Ghosh et al., 2013). Considering the significant differences of O_3 concentrations between daytime and nighttime, several studies (Abdul-Wahab et al., 2005; Özbay et al., 2011) stressed that there are O_3 advantages of separating daytime and nighttime O_3 analysis due to different influencing factors.

The variations of nighttime O_3 concentrations have gained scholarly attention. There are small numbers

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of studies that have been published focusing on nighttime O_3 concentrations. Due to absence of photochemical reactions, Sousa et al. (2011) and Kulkarni et al. (2013) relates the variations in O_3 concentrations over Portugal from 2005 to 2007 with variations in prevailing meteorological conditions and transport process. Among the literatures, Ghosh et al. (2013) reported interesting finding in nighttime O_3 chemistry. According to Ghosh et al. (2013), the NO_2-NO_3-N_2O_5 cycle plays a significant role in the nighttime O_3 chemistry as the cycle heavily affects the depletion process. In Malaysia, Awang et al. (2015) reported high nighttime O_3 concentrations recorded in Kemaman, Terengganu due to inefficient removal mechanism. Low removal or depletion mechanism cause the O_3 concentration remained in the atmosphere at high concentration and posed possible negative impact.

This study primarily aims to determine the nighttime depletion process of O_3 concentrations in Kota Bharu, Kelantan. The possible nighttime reactions of NO_x and O_3 are also critically explored and presented in this paper.

2. Materials and Methods

2.1. Description of O_3 Measurement Sites

Measurements of O_3 concentration carried out at Sekolah Menengah Tanjung Chat, Kota Bharu, Kelantan [N06º09.520'; E102º15.059'] (Figure 1). Kota Bharu is Kelantan's capital city at the river mouth of Kelantan. It has an estimated population of 314,964 (2010 census) and covers an area of 394 km^2 (Shaari et al., 2012). The major land use in Kota Bharu is for agriculture, with one industrial park at Pengkalan Chepa (Azlan et al., 2011). Climatically, Kota Bharu experiences tropical rainforest climate distinguished by high temperature and relative humidity with heavy seasonal rains during northeast monsoon (November to January) (Sulong et al., 2002), while the driest months are June and July.

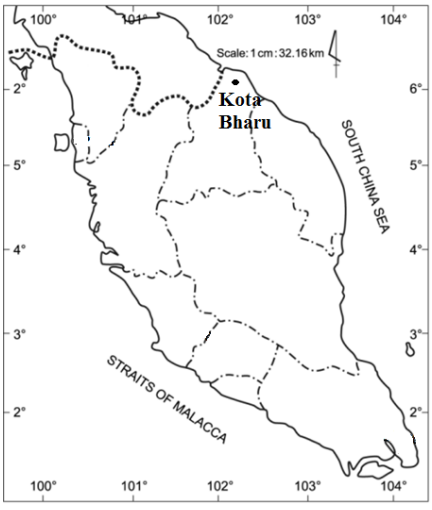

Figure 1: Location of continuous ambient air monitoring stations in Kota Bharu (DoE, 2015)

2.2. Measurements and Instrumentations

Continuous hourly O_3, NO_2 and NO concentrations data for 2010 starting from 1st January to 31st December 2010 obtained from the Air Quality Division of the Department of Environment, Ministry of Natural Resources and Environment of Malaysia. The obtained secondary data are regularly subjected to standard quality control processes and quality assurance procedures (Mohammed et al., 2013). The procedures used for continuous monitoring are in accordance with the standard procedures outlined by internationally recognized environmental agencies such as the United States Environmental Protection Agency (Latif et al., 2014).

Hourly O_3 concentration was monitor using the Model 400E UV Absorption Ozone Analyzer (DoE, 2015). The analyzer utilizing the Beer-Lambert Law, which based on the internal electronic resonance of O_3 molecules with absorption of 254 nm UV light in measuring low ranges of O_3 concentration in ambient air (Ghazali et al., 2010; Mohammed et al., 2013). Ambient NO_2 and NO concentrations were collect using the Model 200A NO/NO_2/NOx Analyzer (Ghazali et al., 2010; Latif et al., 2014). This analyzer applies chemiluminescence detection principles to detect NO_2 concentrations in ambient air and has been proven to produce sensible, stability, and ease of use for ambient or dilution continuous monitoring (DoE, 2015).

In this study, daylight hour were calculated based on complete hours falling between sunrise and sunset (Clapp & Jenkin, 2001) and the remaining hours were considered as nighttime. Based on local time, nighttime hours are lies between 7 p.m. to 7 a.m. (Mohammed et al., 2013). Ozone measured between 7 a.m. to 7 p.m. is considered as daytime ozone, while ozone measured between 7 p.m. to 7 a.m. is deemed as nighttime ozone.

3. Results and Discussion

3.1. Nighttime Ozone Concentration Variations

The fluctuations of daytime and nighttime O_3 concentrations over 2010 are depicted in Figure 2. The box and whisker plot illustrates clear differences between daytime and nighttime O_3 concentrations, which daytime O_3 is significantly higher than nighttime O_3. Result is in line with the theory of O_3 photochemical reactions that stated that O_3 production only occurred during daytime. O_3 photochemical reactions are limited during daytime due to availability of sunlight which acts as the catalyst in the reaction. The mean values of daytime and nighttime O_3 concentration are 15.13 ppb and 5.76 ppb, respectively. Higher variations observed in daytime compared to nighttime indicated by higher standard deviation which is 9.23 ppb for daytime and 5.58 ppb for nighhtime. Even though large differences between

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daytime (15.0 ppb) and nighttime (4.0 ppb) median value was observed, the maximal value for both duration of time is comparative similar with 49 ppb for daytime and 41 ppb for nighttime.

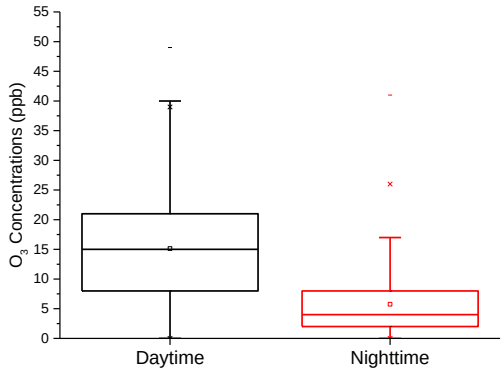

Figure 2: Box and whisker plot of daytime and nighttime O_3 concentrations

The monthly variation of mean for daytime and nighttime O_3 concentrations during the period of study is graphically presented in Figure 3. The highest daytime average O_3 concentrations observed on December with 11.16 ppb whereas the lowest concentrations observed on October with 1.83 ppb. Result suggested that nighttime O_3 is comparatively low in Kota Bharu with monthly average were lower than 10 ppb except for December 2010.

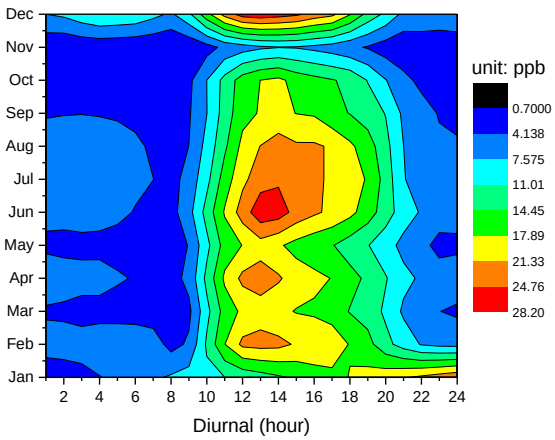

Figure 3: Contour plot of monthly average of O_3 concentrations in 2010

Variation in monthly air pollutants is closely related to monsoonal changes (Yusuf et al., 2010; Toh et al., 2013). Similar to any other places in Malaysia, Kota Bharu experiences four distinct monsoonal changes characterized by the northeast monsoon (November to March), southwest monsoon (June to September), first inter-monsoon (April to May), and second inter-monsoon (October to November). Low concentrations of O_3 observed on April (4.62 ppb), September (3.69 ppb) and October (1.83 ppb) coincided with inter-monsoon period. Late afternoon thunderstorms are usually observed during the inter-monsoon season. These thunderstorms are a localized phenomenon, but they are periodically accompanied by heavy rainfall and gusty surface winds that are stronger and more turbulent than monsoon winds.

3.2. Main precursor attribution

The diurnal variations of the hourly average of O_3, NO_2 and NO illustrated in Figure 4 showed their individually diurnal characteristics. O_3 production was photo-chemically driven; thus, the diurnal characteristic of O_3 concentrations displayed an increasing trend after sunrise, reaching the highest concentration around noon; while minimal concentrations recorded in the afternoon. The lowest O_3 concentration observed in the morning around 8 a.m. Similar characteristics of O_3 diurnal trends recorded by the current study have been previously reported (Duenas et al., 2004; Kim & Guldmann, 2011; Reddy et al., 2011; Song et al., 2011). The diurnal plot indicates that nighttime O_3 concentrations decreased significantly from 7 p.m to 7 a.m. Ghosh et al. (2013) also reported similar finding as O_3 concentrations at night in Kolkata, India are relatively low and more constant. These low concentrations are primarily attributed by absence of photochemical reactions, which convert O_3 precursors into O_3 (Seinfeld & Pandis, 2006). O_3 concentration during nighttime can also be reduced by chemical loss via NO titration, deposition and transportation process.

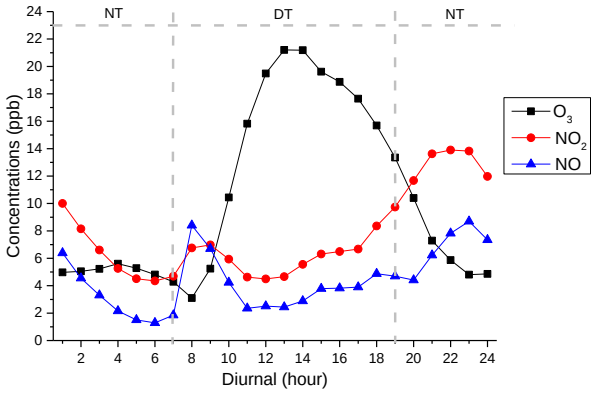

Figure 4: Diurnal plot of O_3, NO_2 and NO concentration in Kota Bharu (Notes: DT is daytime; NT is nighttime)

The plot suggested that diurnal trends of NO_2 and NO concentrations in Kota Bharu is similar and in line with other finding reported by earlier research (Banan et al., 2013). Both pollutants exhibited two peaks in concentrations which measured at 8 a.m and 10 p.m. The daily maximum concentrations of NO_2 and NO in Kota Bharu recorded at 10 p.m. Ghazali et al. (2010) posited that the typical NO_2 diurnal trends in Malaysia show two significant peaks at early morning (9 a.m to 10 a.m) and in the evening (8 p.m to 10 p.m) which the second peak is lower because of emission intensity and prevailing meteorological parameters. However, this study found that the second peak which measured at 10 p.m is profoundly higher than the first peak indicating that the nighttime concentrations of NO_2 is higher than daytime. The finding is re-confirm with box and whisker plot of

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daytime and nighttime NO_2 concentration shown in Figure 5. The average NO_2 concentrations during daytime and nighttime is 6.40 ppb and 9.04 ppb, respectively.

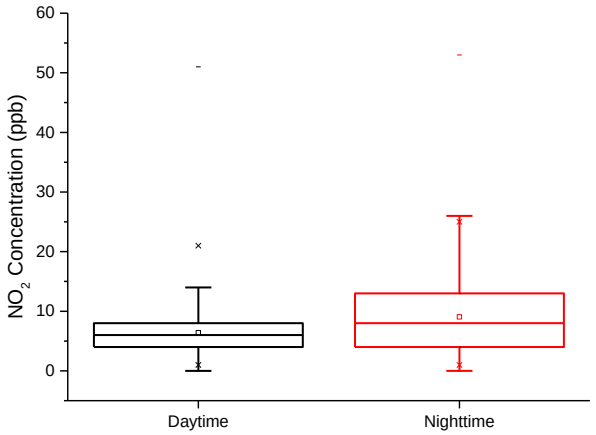

Figure 5: Box and whisker plot of daytime and nighttime NO_2 concentration

Even though, NO concentrations also showed two peaks concentrations, the morning peak that had been observed around 8 a.m is slightly higher than evening peak which also observed at 10 p.m. According to Banan et al. (2013), vehicle emission during morning rush hour play the most important rule in regulated NO concentrations variations because most of the NO concentrations in ambient air produced by vehicle emissions. The box and whisker plot of daytime and nighttime NO concentrations in Figure 6 shows that daytime concentrations are higher than the nighttime concentrations with an average concentration of 4.23 ppb and 4.59 ppb, respectively. However, the maximal NO concentrations for 2010 recorded during nighttime with 137 ppb.

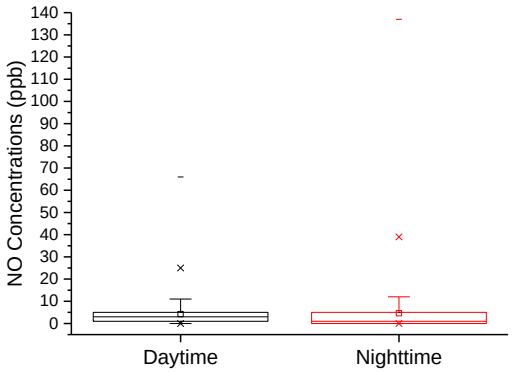

Figure 6: Box and whisker plot of daytime and nighttime NO concentration

The concentrations of ground level O_3 normally low and minimal during nighttime compare to daytime. The nighttime variations of O_3, NO_2 and NO concentrations are illustrated in Figure 7. During nighttime, absence of sunlight ceases O_3 production and enhances the efficiency of the removal mechanism of the O_3.

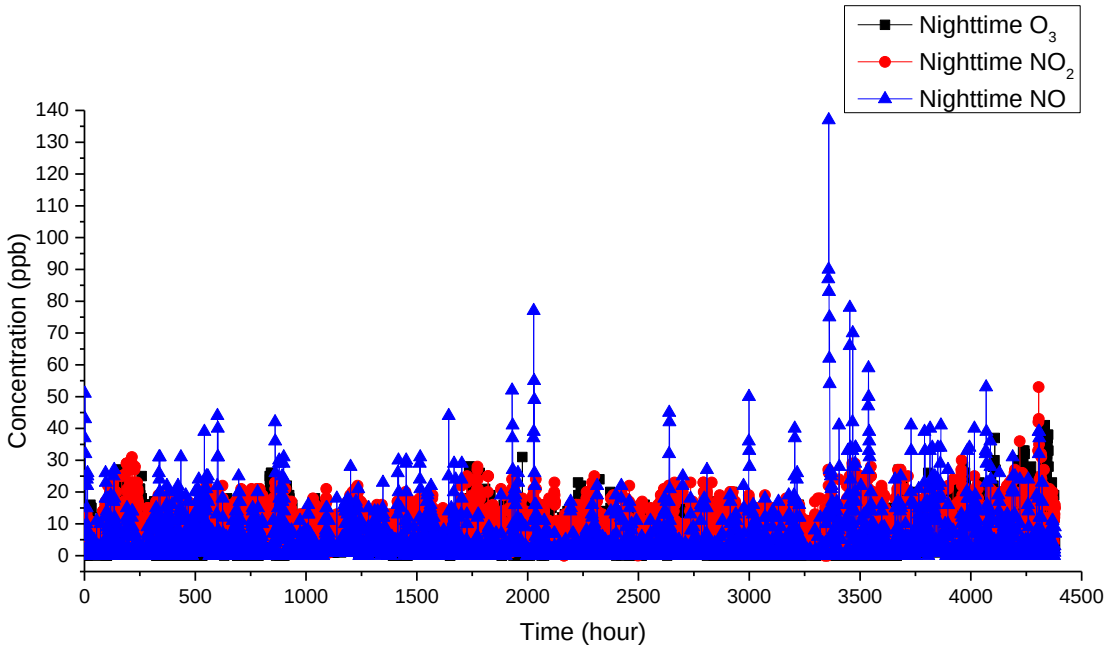

Figure 7: Time series plot of O_3, NO_2 and NO concentrations during nighttime

Nighttime O_3 chemistry is predominantly controlled by reaction by NO and O_3 concentrations which NO titration process/reaction (R1). High NO concentration will promote O_3 removal reactions, thus diminished O_3 from ambient air. In contrast, reduction of NO titrations directly affects nighttime O_3 removal, thereby allowing O_3 to stay in the atmosphere. Similar mechanism believed to occur during high nighttime O_3 concentrations that observed from June 2007 to February 2008 in Kemaman, Terengganu (Awang et al., 2015). During that period, mean for nighttime ozone is 27.46 ppb, while mean NO_2 and NO concentration is 2.71 ppb

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and 0.80 ppb, respectively. Tiwary and Colls (2010) stated that, other than NO titration, NO_2 is another significant sink agent of nighttime O_3 via R2.

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (R1)$$

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (R2)$$

$$NO_3 + NO_2 + M \leftrightarrow N_2O_5 + M \quad (R3)$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \quad (R4)$$

At night, the reactions between O_3 and NO_2 yield nitrate (NO_3) radicals through R4. The produced NO_3 radicals directly react with NO_2, producing dinitrogen pentoxide (N_2O_5). The R5 is thermally unstable and may disassociate N_2O_5 back into NO_2 and NO_3 radicals (Ghosh et al., 2013). However, N_2O_5 may also undergo reaction with H_2O to form nitric acid (HNO_3) (R6). The concentrations of HNO_3 are highly soluble in water; thus, it can easily be removed from the atmosphere via precipitation; in this case, HNO_3 becomes acid rain (Colls, 2002).

4. Conclusion

O_3 production at ground level is highly influenced by its precursors which is oxides of nitrogen. In this study, the depletion mechanism of nighttime O_3 concentrations in Kota Bharu, Kelantan explored in terms of contribution of NOx concentration. Result suggested that O_3 clearly showed differences between daytime and nighttime indicated by differences in each time mean concentration. The mean of daytime concentration is 15.13 ppb compare to 5.76 ppb for nighttime. Absence of photochemical reactions during nighttime is identified as the main reason that contributed to low O_3 concentrations. This study discovered that NO and NO_2 plays the most important role in O_3 depletion process during nighhtime. Result confirmed that the high nighttime NO concentration enhanced further destruction of nighttime O_3 concentrations.

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