Aerosol and Air Quality Research, 15: 1357–1366, 2015

ISSN: 1680-8584 print / 2071-1409 online
doi: 10.4209/aaqr.2015.01.0031

High Nighttime Ground-Level Ozone Concentrations in Kemaman: NO and NO_2 Concentrations Attributions

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ABSTRACT

High nighttime ozone (O_3) concentration levels were observed in Kemaman, Terengganu, and results were compared with those in other places in Malaysia. In this study, the contribution of precursors [nitric oxide (NO) and nitrogen dioxide (NO_2)] and meteorological factors wind speed, and wind direction) toward long-term high nighttime O_3 over the period of 1999 to 2010 was evaluated. During this period, the recorded highest nighttime O_3 ground level was 89 ppb with more than 25% surpassing 20 ppb. Analysis shows that minimal decreasing trends were measured in Kemaman. Lower nitrogen oxide (NO_x) concentrations restricted the sinking agents; thus, reducing the depletion rates allowed O_3 to remain in the atmosphere. Minimal associations were observed between the O_3 concentration level and the speed and direction of wind. Accordingly, the largest contributor toward high nighttime O_3 ground level concentration in Kemaman was most probably NO_x concentration.

Keywords: Long-term variations; NO_x concentration; Nighttime ozone chemistry.

INTRODUCTION

Ozone (O_3) is an important constituent of air that plays significant roles as an oxidant and greenhouse gas. Most of O_3 concentrations 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. At the ground level, O_3 is considered as a secondary air pollutant, which is typically associated with degrading air quality, and induces harmful effects on human health, crop production, material quality, and the ecosystem. O_3 is emitted from various anthropogenic activities. In particular, the formation and accumulation of O_3 are induced by the emissions of nitrogen oxide (NO_x) and volatile organic compounds (VOCs). At the ground level, NO_x plays an important role in the O_3 chemistry (Seinfeld and Pandis, 2006). In the 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). The variation in O_3 concentrations is influenced by meteorological factors. Such variation acts as a catalyst of photochemical reactions as well as a mixing and dispersion agent.

O_3 has received substantial attention worldwide because of its negative effects. Ghosh *et al.* (2013) reported that background O_3 has increased over the last decade and is expected to continuously increase in the subsequent years. Many countries, including Malaysia, monitor the current O_3 condition and have set guidelines against this air pollutant. Considerable research employed the variability of O_3 concentrations on daily, seasonal, weekend, and weekday bases. The variability of O_3 concentrations in urban (Alvarez *et al.*, 2000; Ghazali *et al.*, 2010; Hassan *et al.*, 2013), suburban (Reddy *et al.*, 2011; Swamy *et al.*, 2012), and rural (Duenas *et al.*, 2004) conditions were also described by several studies. Toh *et al.* (2013) and Ghozdic *et al.* (2011) explored the role of meteorology in the variation of O_3 concentrations and concluded that O_3 is significantly responsive toward temperature, UV radiation, relative humidity, as well as wind speed and direction. Intense solar radiation, high temperature, minimal rainfall, low wind speed, and low relative humidity can raise O_3 concentration (Toh *et al.*, 2013). Substantial research also realized the possibilities of adopting multivariate analysis to produce prediction and forecasting models of O_3 concentrations (Pires *et al.*, 2008; Kovac-Andric *et al.*, 2009; Jimenez-Hornero *et al.*, 2010; Ghozdic *et al.*, 2011). Ishi *et al.* (2007) and Mohammed *et al.* (2013) examined the phytotoxic effects of O_3 on crop production. At present, the number of studies that have investigated the variations

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of nighttime O_3 remain insufficient.

The increase of nighttime O_3 concentrations has gained scholarly attention. Such a phenomenon in different regions of the world has been observed and reported by several researchers. Sousa *et al.* (2011) studied the frequency, concentration, and time of the occurrence of high nighttime O_3 maxima in urban and suburban sites in Portugal from 2005 to 2007. Consequently, Sousa *et al.* (2011) discovered that the among meteorological parameters analyzed maxima scenarios were only correlated with wind direction with higher occurrences transpired in urban areas more than in suburban sites. According to Kulkarni *et al.* (2013), increasing nocturnal O_3 is associated with prevailing meteorological conditions and transport process because the photochemical production of O_3 ceases with the absence of sunlight. Meanwhile, Ghosh *et al.* (2013) explored the nighttime chemistry between O_3 and its precursors (NO_x) in terms of NO_2-NO_3-N_2O_5 cycle over urban Kolkata, India; the researchers found that 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.

This study primarily aims to determine the high nighttime O_3 concentrations in Kemaman, Terengganu. The magnitude, frequency, and time of high nighttime O_3 concentrations are analyzed with respect to the precursors of O_3 such as NO_2, NO, and CO concentration and its prevailing meteorological parameters, including of wind speed, and wind direction. The possible nighttime reactions of NO_x and O_3 are also critically explored and presented in this paper.

METHODS

O_3, NO_2, nitric oxide (NO) concentrations in Kemaman, Terengganu were progressively measured together wind speed and direction. Daylight hour was calculated based on the total number of hours between sunrise and sunset (Clapp and Jenkin, 2001), and the remaining hours were considered as nighttime. Based on the local time, the nighttime hours were between 7 PM and 7 AM (Mohammed *et al.*, 2013). The monitoring was conducted every hour for a period of twelve year, specifically from January 1, 1999 to December 31, 2010.

Sampling Site

Kemaman [N04°16.260, E103°25.826], one of the districts of Terengganu State, is located at the east coast of Peninsular Malaysia (Fig. 1). With a total area of 2535 km^2 or approximately 20% of the total area of Terengganu (Toriman *et al.*, 2009), Kemaman is known for the discovery of a petroleum site near its town Kerteh in the early 1980s. In general, this district is relatively underdeveloped, except for a few places along the coastline, in which steel and petrochemical plants are located (Sulong *et al.*, 2002). Only two major industrial sites (i.e., Kerteh Petrochemical and Gebeng Industrial Area) are located in and near Kemaman (Ismail *et al.*, 2011). In terms of weather conditions, this district experiences a wet equatorial climate characterized by high temperatures all year round, with seasonal heavy rains during the northeast monsoon from November to

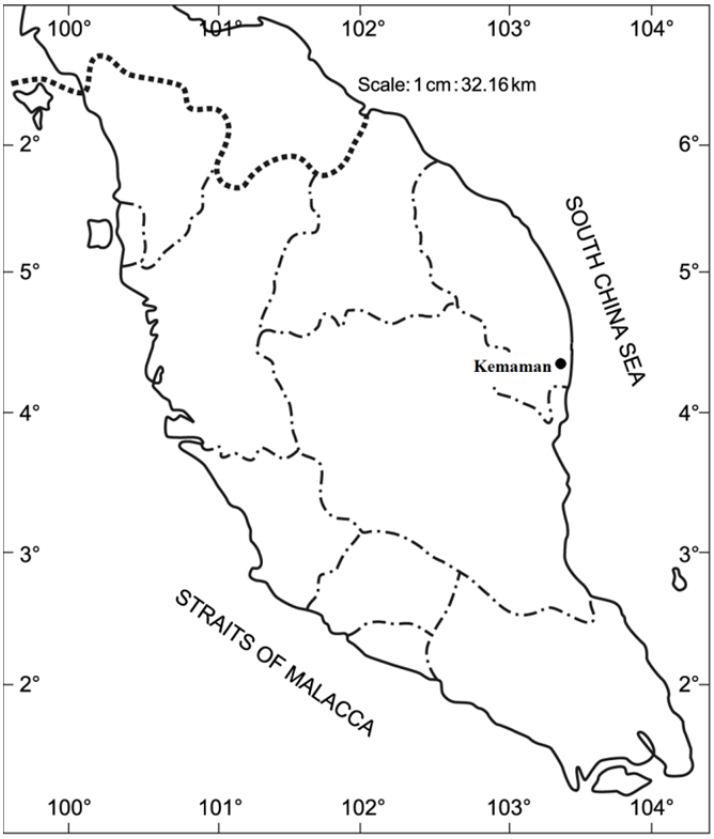

Fig. 1. The location of Kemaman monitoring station.

January (Sulong *et al.*, 2002). The annual rainfall in Kemaman is 2390 mm on average, with a standard temperature of 27°C and relative humidity at approximately 81% year-round (Toriman *et al.*, 2009; MMD, 2013). In 2010, the total population of Kemaman was 166,750.

Instrumentations

Continuous hourly ground level O_3 concentrations and other air pollution levels were established across Malaysia by the Department of Environment (DoE) to measure and detect significant changes in air quality. Mohammed *et al.* (2012) claimed that hourly O_3 concentrations can be measured with the UV absorption Ozone Analyzer Model 400A, a microprocessor controlled device. This O_3 analyzer applies a system based on the Beer–Lambert law to measure low ranges of O_3 concentrations in ambient air and gaseous media (Ghazali *et al.*, 2010). In this study, ambient O_3 concentrations were detected from the internal electronic resonance of O_3 molecules with the absorption of 254 nm UV light emitted from an internal mercury lamp (Teledyne, 1999). Meanwhile, the samples of hourly NO_2 were collected with the $NO/NO_2/NO_x$ Analyzer model 200A (Ghazali *et al.*, 2010). This analyzer applies the chemiluminescent detection principle to detect NO_2 concentrations in ambient air. Teledyne (1999) concluded that microprocessor technologies were incorporated into the analyzer to enhance its concentration monitoring ability. The analyzer has been proven to provide the sensibility, stability, and ease of use for ambient or dilution continuous monitoring requirement (DoE, 2008). Mohammed *et al.* (2012) reported that the secondary data obtained from the DoE, Malaysia were regularly subjected to standard quality control and quality assurance procedures. Wind speed (km/h) and wind directions (°), during nighttime were also included in the analysis. Wind speed and wind direction, were measured Met One 010C sensor, Met One 020C, respectively.

Cluster Analysis

Cluster analysis (CA) is a set of multivariate techniques commonly used to primarily assemble objects with similar characteristics. CA is a method to categorize objects into a number of clusters or groups, so that the objects in a cluster are similar to one another and the objects in different clusters are different from one another (Lau *et al.*, 2008; Pires *et al.*, 2008). CA maximizes the similarity of cases within each cluster while minimizing the dissimilarity between groups that are initially unknown (Lu *et al.*, 2011). In this analysis, each object is considered as a separate cluster before it is connected by Ward method agglomerate techniques and squared Euclidean distance. These approaches have been used by several researchers in air and water pollution studies (Shresta and Kazama, 2007; Lau *et al.*, 2009). Shresta and Kazama (2007) explained that Ward's method uses an analysis of variance approach to evaluate the distance between clusters in an attempt to minimize the sum of squares of any two clusters that are generated. The classifications of objects in CA are illustrated by a dendrogram (tree diagram), which shows the measured similarity or distance between any two variables. The variability of nighttime O_3 concentrations monitored from 1999 to 2010 was determined by conducting CA and with the linkage of reported distance in terms of Dlink/Dmax.

RESULT AND DISCUSSION

High Nighttime Ozone

The monitoring results reveal that O_3 exhibited strong day-to-day variations (Ghazali *et al.*, 2010). In the presence of sunlight, O_3 was formed by photochemical reactions, which involved its precursors and UV radiations. Maximum O_3 concentrations were observed during noontime that coincided with maximal UV radiation. By contrast, O_3 during nighttime was generally low and in a stable condition because of the absence of photochemical reactions. Further reduction in nighttime O_3 concentrations were also attributed to deposition processes and chemical reactions (Sousa *et al.*, 2011). Fig. 2 demonstrates the box plot of hourly average nighttime O_3 concentrations in Kemaman, Kuching, Taiping, Kajang, Kota Kinabalu, Gombak, Johor Bahru, Seberang Jaya, and Terantut. The findings suggest that nighttime O_3 concentrations were higher in Kemaman than in other stations. Mean nighttime O_3 in Kemaman surpassed was 14 ppb, whereas constant mean concentrations ranging from 5 ppb to 6 ppb were measured in other stations. The mean nighttime O_3 concentrations in Kemaman were twice as high as the concentrations in other stations, which verify the high nighttime O_3 occurrences in the district. Table 1 exhibits the mean concentrations of nighttime O_3 in Kemaman and several places. Nighttime O_3 concentrations in Kemaman were relatively higher than the reported nighttime concentrations in Kolkata and Portugal.

The variability of nighttime O_3 in Kemaman was further investigated by conducting CA using the hourly average nighttime O_3 concentrations over the period of 1999 to 2010. Nine monitoring stations (i.e., Kemaman, Kuching, Taiping, Kajang, Kota Kinabalu, Gombak, Johor Bahru, Seberang Jaya, and Jerantut) were applied to Hierarchical Agglomerative Cluster Analysis (HACA). A dendrogram in Fig. 3 illustrates the classification of the monitoring stations based on nighttime O_3. The results of the investigation confirm that Kemaman was solely grouped in Cluster 2 (C2) and all other stations were placed in the same cluster (C1). The differences between nighttime O_3 concentrations in Kemaman and other locations are believed to contribute to the results. Nighttime O_3 in Kemaman was high, whereas daytime O_3 was relatively low. The mean and median of daytime O_3 in the district were 26.9 and 26 ppb, respectively. Throughout the 12-year study period, zero exceedances were observed in Kemaman.

This specific finding clarifies that none of the daytime O_3 concentrations surpassed the Malaysian Ambient Air Quality Guidelines (MAAQG) for 1-hour averaging of O_3 concentration at 100 ppb. The maximum daytime O_3 in Kemaman was only 89 ppb, which was almost half of the maximum concentration recorded in Gombak (175 ppb). High daytime O_3 concentrations were observed in most of the urban stations, such as Kajang and Gombak (Azmi *et al.*, 2010; Ghazali *et al.*, 2010; Latif *et al.*, 2012; Banan *et*

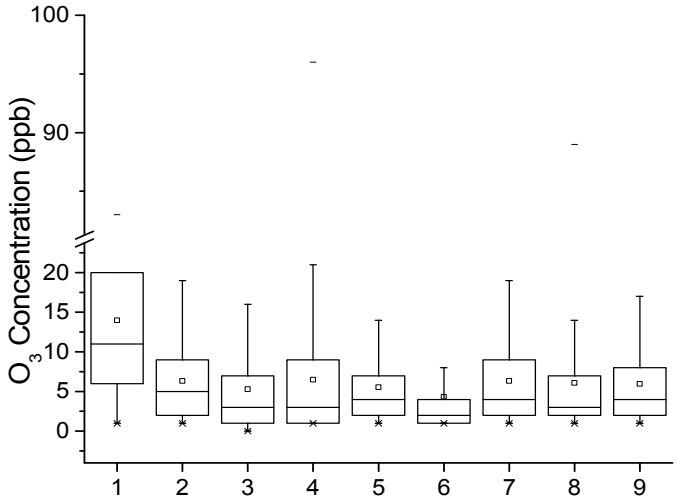

Fig. 2. Box of whisker plot with the error bars of nighttime ozone concentration at 1)Kemaman; 2) Kuching; 3) Taiping; 4) Kajang; 5) Kota Kinabalu; 6) Gombak; 7) Johor Bahru; 8) Seberang Jaya; 9) Jerantut on 1999–2010.

Table 1. Comparison of mean nighttime ozone between this study and reported studies.

References	Location	Duration	Mean Nighttime O_3
This study	Kemaman, Malaysia	Jan 1999–Dec 2010	14 ppb
Ghosh *et al.* (2013)	Kolkata, India	Oct 2010–Apr 2011	12 ppb
Kulkarni *et al.* (2013)	Portugal	2000–2010	10 ± 2.5 ppb
Pugh *et al.* (2010)	-	2008	8–12 ppb*

*median concentrations were used.

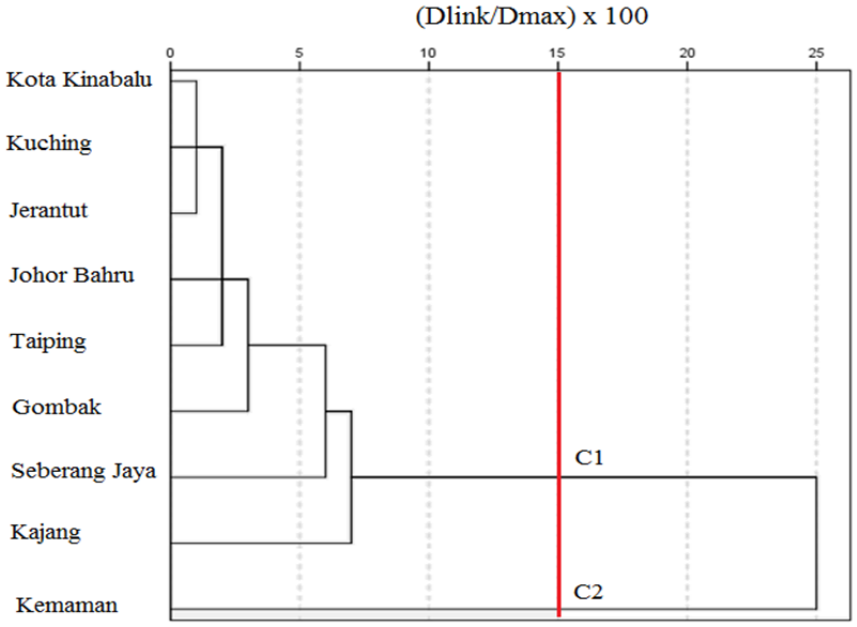

Fig. 3. Dendogram of classification of nighttime (7 PM–7 AM) ozone concentration of nine monitoring stations for 12 years period.

al., 2013), with frequent daytime O_3 surpassing the guideline limit. Through HACA, daytime O_3 concentrations in Kemaman were grouped together with those in Kuching, Taiping, Jerantut, Johor Bahru, and Seberang Jaya in C1, whereas C2 and C3 were solely represented by Gombak and Kajang, respectively as illustrated in Fig. 4.

Nighttime Ozone Concentration Variations

The fluctuations of nighttime O_3 concentrations over the 12-year study period are depicted in Fig. S1 (see the

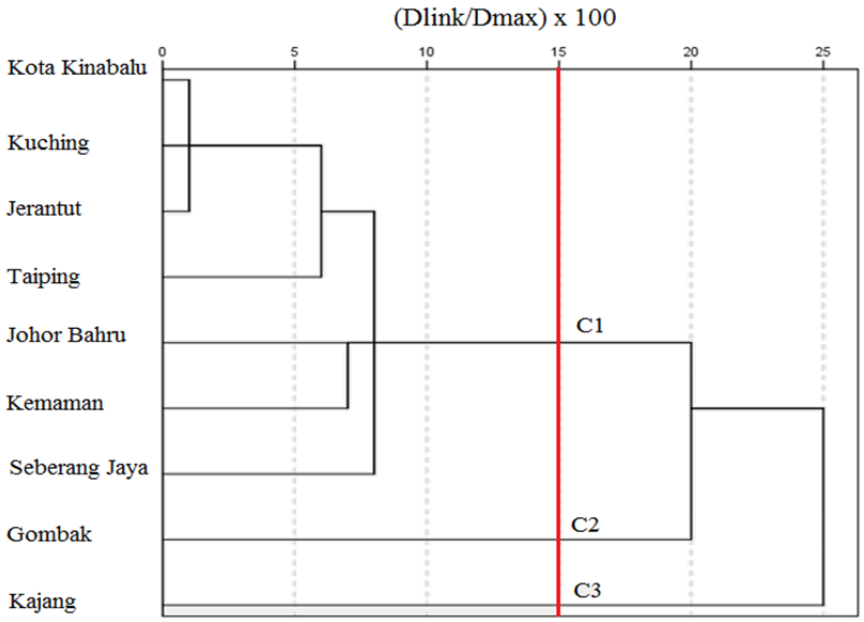

Fig. 4. Dendogram of classification of daytime (7 AM–7 PM) ozone concentration of nine monitoring stations for 12 years period.

Supplementary Material, SM). The figure exhibits that high nighttime O_3 concentrations were observed from June 2007 to February 2008, in which most concentrations were above 14 ppb (mean concentrations), as denoted by the red dash line. The highest mean nighttime concentrations at 20.3 ppb were observed in 2008. As shown by the time series plot in Fig. S1, numerous high concentrations were measured, as indicated by concentration spikes that could exceed 50 ppb. These high concentrations were generally measured early at night (7 PM to 10 PM), confirming the results reported by Sousa *et al.* (2011). Meanwhile, the monthly nighttime O_3 is illustrated in Fig. S2 (see the Supplementary Material, SM) with a box and whisker plot. The highest monthly average of nighttime O_3 was measured in January (19.2 ppb), but gradually decreased to the lowest concentration in April (8.9 ppb). The highest hourly average nighttime O_3 concentration was eventually observed in July with 40.2 ppb. The variation in monthly air pollutants is closely related to monsoonal changes (Md Yusuf *et al.*, 2010; Toh *et al.*, 2013).

Malaysia annually experiences four distinct monsoonal changes characterized by the northeast monsoon (November–March), southwest monsoon (June–September), first intermonsoon (April–May), and second intermonsoon (October–November). Nighttime O_3 concentration during intermonsoon is relatively low. According to Majid *et al.* (2012), late afternoon thunderstorms are frequently observed during the intermonsoon season. These thunderstorms are a localized phenomena, but they are periodically accompanied by heavy rainfall and gusty surface winds that are stronger and more turbulent than monsoon winds. Low O_3 concentrations were also observed at the beginning of the northeast monsoon (November). Suhaila and Jemain (2009) elucidated that the effect of the northeast monsoon is more prominent in east coast Peninsular Malaysia than in other locations. East coast Peninsular Malaysia is considered as the wettest location during the monsoon season. An increase in rainfall intensity promotes wet deposition process in the atmosphere, minimizing the pollutant concentration in ambient air, and strong and turbulent wind speed promotes the transport of air pollutants to other locations (Colls, 2002). The distribution of nighttime O_3 from 1999 to 2010 is displayed by a histogram in Fig. S3 (see the Supplementary Material, SM). The results of the investigation imply that most nighttime O_3 concentrations ranged from 5 ppb to 10 ppb, followed by 10 ppb to 15 ppb, and 15 ppb to 20 ppb. Few cases of nighttime O_3 were above 50 ppb.

Role of NO and NO_2 Concentrations

In Fig. 5, the diurnal variations of the hourly average of O_3 and its precursors (NO_2 and NO) illustrate their individual characteristics. O_3 production was photochemically driven; thus, the diurnal characteristic of O_3 concentrations displayed an increasing trend after sunrise, reaching the maximum around noon; minimum concentrations were recorded in the afternoon. In the troposphere, NO_x plays the most important role in forming and destroying O_3 concentration. The photochemical reactions of O_3 production are as follows:

$$NO_2 + h\nu\ (\lambda < 400\ \text{nm}) \rightarrow NO + O \quad \text{(R1)}$$

$$O + O_2 + M \rightarrow O_3 + M \quad \text{(R2)}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad \text{(R3)}$$

The lowest O_3 productions were observed in the morning around 8 AM. Similar characteristics of O_3 diurnal trends recorded by the current study have been reported by previous research (i.e., Duenas *et al.*, 2004; Kim and Guldmann, 2011;

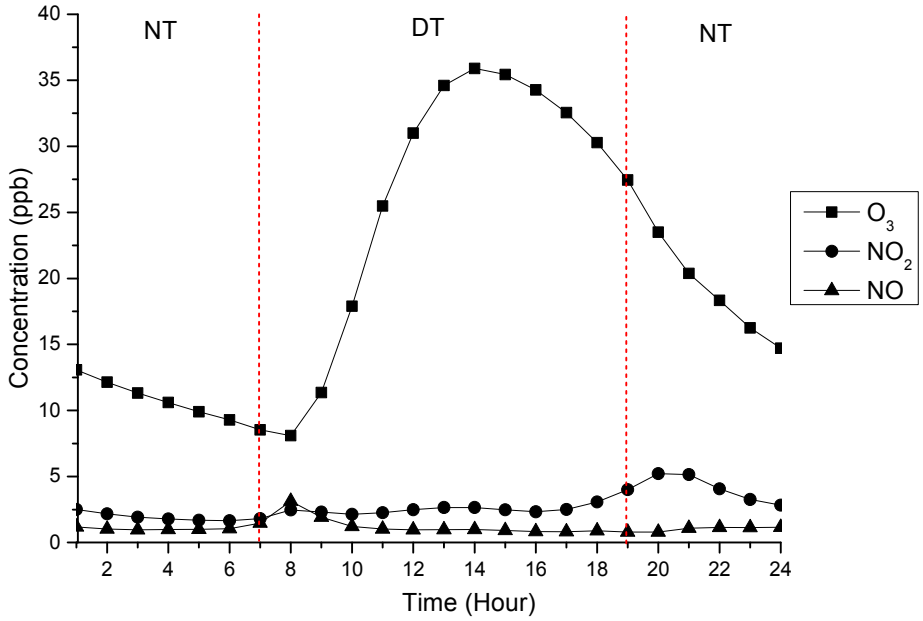

Fig. 5. 12 years average of diurnal variations of O_3, NO_2 and NO at Kemaman (*NT is nighttime;*DT is daytime).

Reddy *et al.*, 2011; Song *et al.*, 2011). O_3 concentrations at night are relatively low and more constant (Ghosh *et al.*, 2013). These low concentrations are primarily attributed to the absence of photochemical reactions, which convert O_3 precursors into O_3 (Seinfeld and Pandis, 2006). O_3 concentration during nighttime can also be reduced by chemical loss via NO titration (R3) and deposition process. The diurnal plot indicates that nighttime O_3 concentrations decreased significantly from 7 PM to 7 AM.

The test conducted in Kemaman revealed that NO and NO_2 concentrations were remarkably low with mean values of 1.1 and 4.5 ppb, respectively (Fig. 6). The plots also exhibited slightly unclear diurnal trends of NO_2 concentration. The maximum NO_2 and NO concentrations were recorded at 8 PM and 8 AM. In terms of magnitude and trends of NO_2 and NO concentrations, similarities were noted between Kemaman and Jerantut, which serve as background stations in Malaysia. Ghazali *et al.* (2010) posited that the typical NO_2 diurnal trends in Malaysia show two significant peaks at early morning (9 AM–10 AM) and in the evening (8 PM–10 PM), in which the second peak is lower because of emission intensity and prevailing meteorological parameters. Meanwhile, Banan *et al.* (2013) reported that the typical patterns of NO concentration diurnal trends are similar to that of NO_2 concentration, in which relatively high concentrations are observed at night and peak concentrations in the morning are attributed to vehicle emissions.

The absence of sunlight ceases O_3 production and enhances the efficiency of the removal mechanism of the pollutant concentration in the atmosphere. Ground level O_3 concentrations are removed from ambient air either via dry deposition or chemical reactions with NO_x and VOCs (Seinfeld and Pandis, 2006; Ghosh *et al.*, 2013). Principal reactions via R3 contribute to the destruction of daytime and nighttime O_3 concentrations. During daytime, the newly produced O_3 reacts with NO concentration to reproduce NO_2 concentration. Jenkin and Clemitshaw (2000) attested that R3 occurs at approximately 1 min at a typical boundary layer concentration of 30 ppbv. O_3 only accumulates when the rates of NO_2 photolysis (R1) are higher than those of R3. Nighttime O_3 chemistry is predominantly controlled by R3. However, the mean of nighttime NO concentrations in Kemaman is 1.1 ppb, which is extremely low and contributes to the reduction of NO titration rates. Reduction of NO titrations directly affects nighttime O_3 removal, thereby allowing O_3 to remain in the atmosphere. Consequently, the concentration of NO_2 eventually decreases with the decrease of NO titration, during which NO_2 is produced. Similar mechanism is believed to occur during high nighttime O_3 concentrations that were observed from June 2007 to February 2008 (Fig. S1). During that period, mean for nighttime ozone is 27.46 ppb, while mean NO_2 and NO concentration is 2.71 ppb and 0.80 ppb, respectively. Colls (2002) stated that, other than NO titration, NO_2 is another significant sink agent of nighttime O_3 via the following reactions:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad \text{(R4)}$$

$$NO_3 + NO_2 + M \leftrightarrow N_2O_5 + M \quad \text{(R5)}$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \quad \text{(R6)}$$

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). Ghosh *et al.* (2013) argued that R5 is thermally unstable and may disassociate N_2O_5 back into NO_2 and NO_3 radicals. However, N_2O_5 may also undergo reaction with H_2O to form nitric acid (HNO_3) (R6). The increase of water vapor at nighttime indicated by high relative humidity (Fig. 5) enhances R6. HNO_3 is highly soluble in water; thus, it

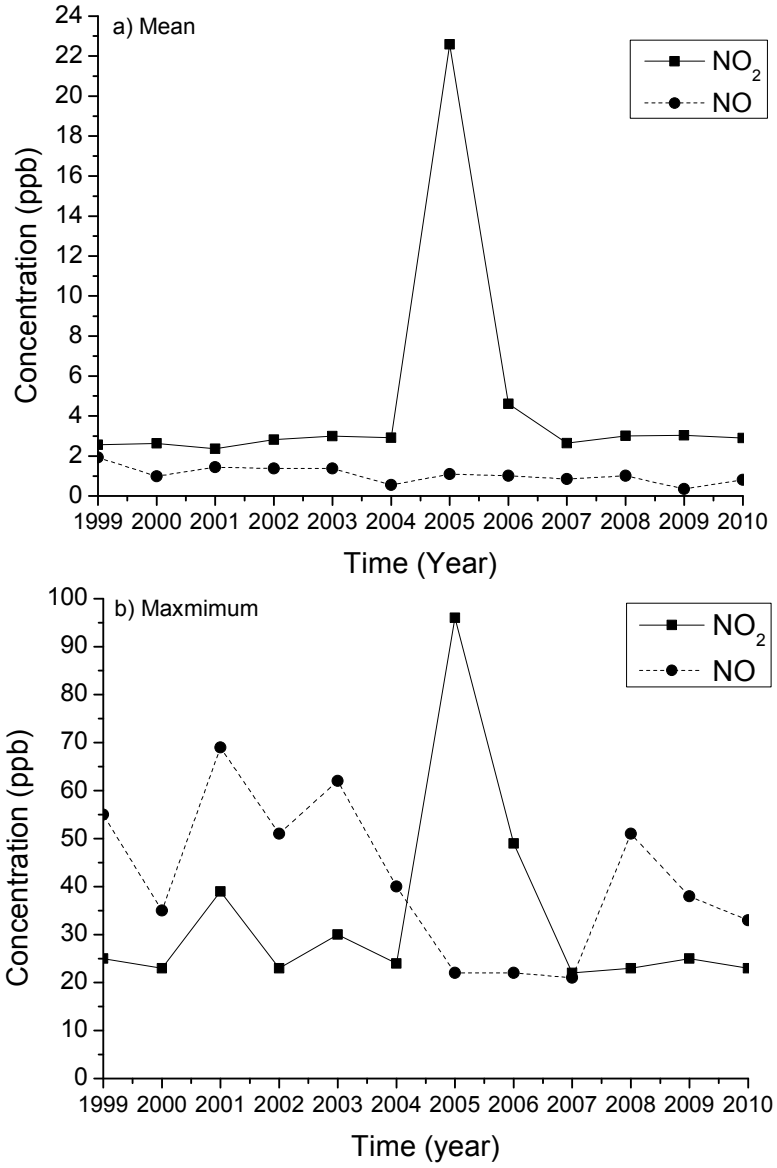

Fig. 6. The mean and maximum concentrations of NO_2 and NO during 1999–2010.

can be easily removed from the atmosphere via precipitation; in this case, HNO_3 becomes acid rain (Colls, 2002). The mean of nighttime NO_2 concentration in Kemaman was only approximately 4.6 ppb because of low NO titration rates and low emissions. Limited nighttime NO_2 concentrations directly reduce the reaction rates of R4 and R5. This study observed that interrupted removal reactions allowed O_3 to remain in the atmosphere. Fig. 5 exhibits that nighttime O_3 concentrations were still decreasing mainly because of dry deposition and some additional chemical reactions with hydrocarbons trough reaction with NO_3 (Jenkin and Clemitshaw, 2000). However, in the current studies effect of hydrocarbons is unconsidered due to limitation of monitoring data and understanding. Differed from other years, relatively higher nighttime NO_2 concentrations is measured on 2005 (Fig. 6). Mean and maximum NO_2 concentrations on 2005 is 22.58 ppb and 96 ppb, respectively. Result suggested that increasing in nighttime NO_2 concentrations will eventually enhancing R4, R5 and R6 reactions thus promote destructions of nighttime O_3. The mean concentrations of nighttime O_3 on 2005 is 12.51 ppb which is relatively smaller than average value for 12 years (14 ppb).

In summary, NO_x plays an important role in nighttime O_3 chemistry. In particular, low nighttime NO_x concentration in Kemaman evidently decreased O_3 removal rates, thereby allowing O_3 to remain at high concentration at night. This finding concurs with the observations reported by Ghosh *et al.* (2013) regarding the importance of O_3-NO-NO_2 chemistry in nighttime O_3. Jenkin and Clemitshaw (2002) mentioned that nighttime O_3 chemistry is predominately controlled by NO_3 and N_2O_5 concentrations; such control ceases at sunrise.

The observed high nighttime O_3 concentration in Kemaman was chiefly attributed by low nighttime NO_x concentration, which acts as the main component in the pollutants sinking process. During the 12-year study period, both NO_2 and NO were relatively at very low concentrations,

except in 2005. MAAQG sets the limit against NO_2 at 170 ppb, and the United States Environmental Protection Agency sets 100 ppb for 1-hour averaging. However, the mean concentrations of NO_2 in Kemaman ranged from 3 ppb to 22 ppb, and the maximum concentrations ranged from 22 ppb to 96 ppb (Fig. 6). Both values are far below the set limit. Meanwhile, NO concentration was considered at a minimal although no standard or guideline limit has been set against this particular pollutant. The mean concentrations of NO were relatively lower than those of NO_2, whereas in most years, the maximum concentrations of NO were higher than those of NO_2. The daily average of NO_2 in Kemaman is higher than that in Jerantut and is relatively similar to Sibu, Kota Kinabalu, and Tawau (Table 2). The NO_2 concentrations in urban cities such as Shah Alam, Kuching, Klang, Ipoh, and Johor Bahru were distinctively higher than those in Kemaman. Meanwhile, the daily average of NO concentration in Kemaman was the lowest among the selected locations listed in Table 2.

Sousa *et al.* (2011) claimed among several meteorological parameters which always been associated with ozone variations, wind speed and directions is the only significant factors that mays contributed to variations in nighttime ozone. Unlike daytime, cease in solar radiations during nighttime attributed to insignificant effect of UVB radiations, temperature and relative humidity towards ozone concentrations. The scenario is occur due relationship between ozone, temperature and relative humidity are depended on sunlight. However, wind speed and direction are significant agent that controlling ozone transport and dilution (Ghazali *et al.*, 2010; Kim and Guldman, 2011; Toh *et al.*, 2013) in both daytime and nighttime. Ghozdic *et al.* (2011) reported that lower wind speed is always associated with higher concentration of ozone and as well as other primary air pollutions.In abs Fig. S4 (see the Supplementary Material, SM) shows the monthly wind rose plot of nighttime wind speed and direction in Kemaman from January to December. In January, southerly and southwesterly winds accounted for more than 20% of wind directions, in which the majority of the winds blew between 3 and 6 km/h. Similar trends were also exhibited by the wind rose plot in February and March, in which most winds blew from the southerly and southwesterly directions. A slight change in wind direction was observed in April. More than 30% of the dominant wind direction came from southerly and southeasterly direction. During the second month of the first intermonsoon, most of the winds blew from the southerly and southeasterly direction (12%) but relatively higher wind speeds between 9 and 12 km/h were measured from northeast. Higher wind speeds blowing from north and northwest directions and up to 18 km/h were observed during the southwest monsoon, which Kemaman annually endures from June to September. However, during this monsoon, south and southeast dominate the wind blowing direction. Meanwhile, during the second intermonsoon (October–November), south and southeasterly is the dominant wind blowing direction. In December, southerly becomes the dominant wind blowing direction at Kemaman.

Fig. S5(a) and Fig. S5(b) illustrated composite plots of monthly average O_3, NO_2 and NO concentrations from 1999 to 2010. Figure suggested that highest monthly nighttime ozone is observed on January coincided with major air coming from southerly directions. Meanwhile, high nighttime ozone was also observed on August with average concentration of 18.35 ppb. On August wind speed relatively lower with most of wind is in the range of 3 to 6 km/h and may contributed to lower nighttime ozone transports. Low nighttime ozone also observed on April (10.32 ppb) coincided with relatively low wind speed which majorly blowing from south directions. However, on April, relatively higher NO concentrations (1.31 ppb) were measured which is believed significantly control nighttime ozone destructions via NO titrations reactions (R3). Similar conditions is most probably occurred on October. Wind factor is considered relevant in the transport of air pollutants (Kim and Guldmann, 2011; Toh *et al.*, 2013). Lower wind speed may contribute to high nighttime O_3 concentration because of low transport emissions of air pollutants, which allows O_3 to remain at one particular locations. The transport of air pollutants from other locations may also be one of the contributors of O_3 concentrations. The result of this study suggests that, high nighttime O_3 concentrations were observed in January that coincided with prevailing winds from the southerly direction. Kuantan City is located in the south of Kemaman and may influence the air pollution in the district via pollution transport. Kuantan is one of the biggest cities in east coast Peninsular Malaysia and characterized by high population and traffic density, numbers of industrials and residential establishments. From wind rose analysis (Fig. S4), the main direction of wind during northeast

Table 2. Comparison of mean NO_2 and NO between Kemaman and several locations in Malaysia.

References	Location	NO_2 (ppb)	NO (ppb)
This study	Kemaman	4.3	1.1
Latif *et al.* (2014)	Jerantut	1.9	1.3
Dominick *et al.* (2012)	Kuching	17	6
	Sibu	5	6
	Kota Kinabalu	5	4
	Tawau	5	7
	Klang	21	16
	Shah Alam	19	17
	Ipoh	10	6
	Johor Bahru	14	10

monsoon and first inter-moonson are from southerly and southwesterly, where will increase the O_3 concentrations that transferred from Kuantan to Kemaman.

CONCLUSION

O_3 production at ground level is highly influenced by its precursors which is oxides of nitrogen. In this study, the occurrences of high nighttime O_3 in Kemaman, Terengganu were explored in terms of the contribution of NO_x concentration and effect of wind speed and direction. The mean concentration of nighttime O_3 in Kemaman was 14 ppb, which was relatively higher than that in the major cities of Malaysia such as Kajang, Johor Bahru, Gombak, and Seberang Jaya. High nighttime O_3 concentrations were observed in from June 2007 to Febuary 2008 mainly attributed by lower NO titrations that capable in removing ozone from atmosphere. Whereas the lowest nighttime concentration was measured on April and October anually, which coincided with the intermonsoon period. This study discovered that low concentration of NO with mean concentration of 1.1 ppb significantly reduced NO titration reactions during nighttime in Kemaman. Lower rate of NO titration minimized the O_3 sinking process, which allowed high O_3 concentrations to remain in the atmosphere. Nighttime NO_2 might also contribute to high nighttime O_3. Significantly low NO_2 concentrations measured in Kemaman might cause the reduction in O_3 to sink via acid nitric production, inducing O_3 to remain in the atmosphere. Meanwhile, a small possibility of pollutant transport governed by wind speed and direction affected the nighttime condition in Kemaman. However, the role of NO_x concentration as nighttime O_3 sinking agent was the primary element that contributed to the high nighttime O_3 concentrations in Kemaman.

AKNOWLEDGMENT

The authors are grateful to Universiti Sains Malaysia for funding this study under grant 1001\PAWAM\811206 and to the Department of Environment Malaysia for providing air quality data. The authors also thank the Ministry of Education Malaysia for providing financial support to this study under the MyBrain15 program.

SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

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Received for review, January 18, 2015
Revised, January 18, 2015
Accepted, March 17, 2015

Supplementary Material (SM)

High Nighttime Ground-Level Ozone Concentrations in Kemaman: NO and NO2 Concentrations and Meteorology Attributions

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Fig. S1 Time series plot of yearly nighttime ozone variations at Kemaman during 1999-2010

Fig. S2 Box and whisker plot of monthly nighttime variations

Fig. S3 Histogram of nighttime ozone distribution on 1999-2010

Fig. S4 Wind rose (blowing from) of ground level wind speed (km/h) and wind direction (^{o}) measured for a span of 12 years in 1999-2010

Fig. S5 (a) Composite diurnal plot of monthly average O_3, NO_2 and NO from January to June

Fig. S5 (b) Composite diurnal plot of monthly average O3, NO_2 and NO from July to December

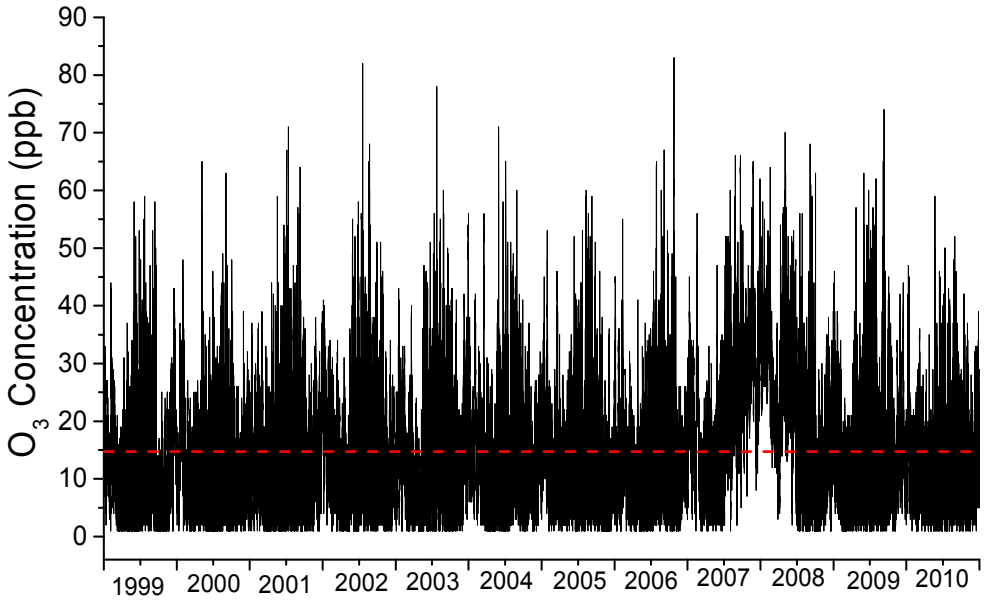
O_3 Concentration (ppb)
90
80
70
60
50
40
30
20
10
0
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010

Figure S1

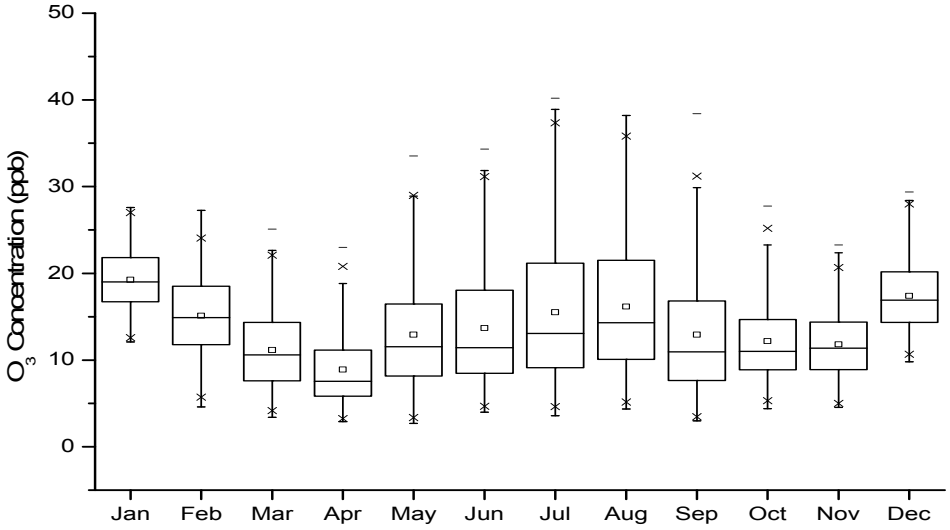
50
40
30
20
10
0
O_3 Concentration (ppb)
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec

Figure S2

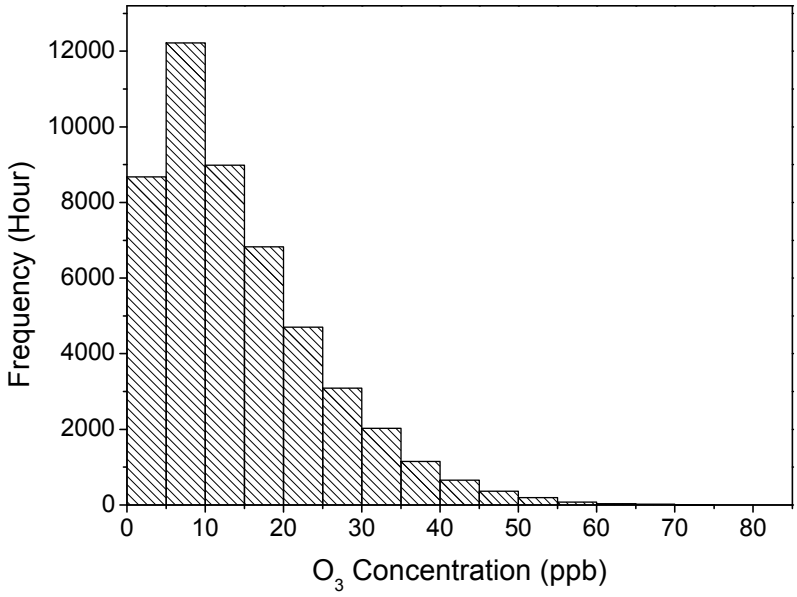
Frequency (Hour)
12000
10000
8000
6000
4000
2000
0
0
10
20
30
40
50
60
70
80
O3 Concentration (ppb)

Figure S3

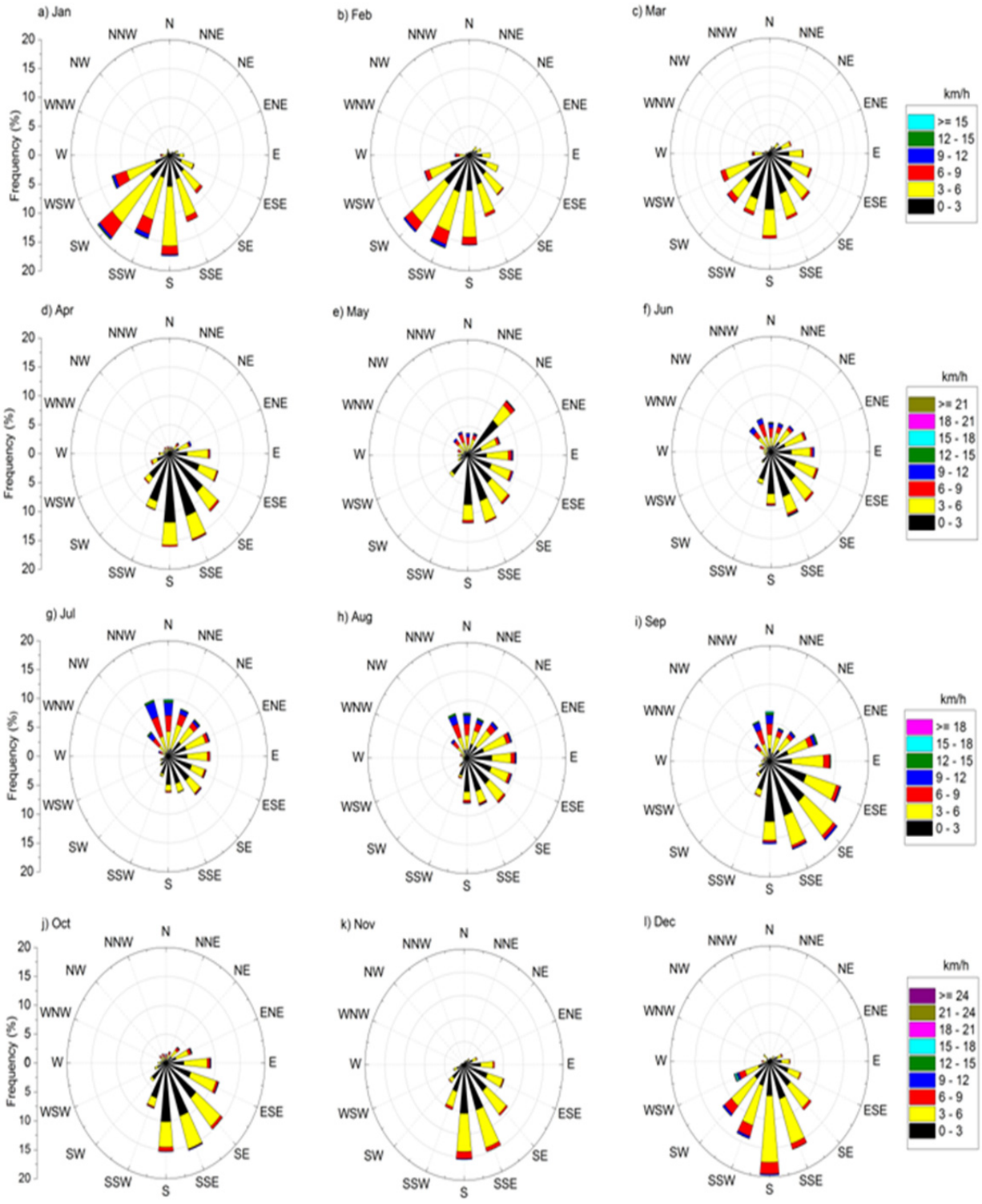
a) Jan
b) Feb
c) Mar
d) Apr
e) May
f) Jun
g) Jul
h) Aug
i) Sep
j) Oct
k) Nov
l) Dec
Frequency (%)
N
NNE
NE
ENE
E
ESE
SE
SSE
S
SSW
SW
WSW
W
WNW
NW
NNW
km/h
>= 15
12 - 15
9 - 12
6 - 9
3 - 6
0 - 3
>= 21
18 - 21
15 - 18
>= 18
>= 24
21 - 24

Figure S4

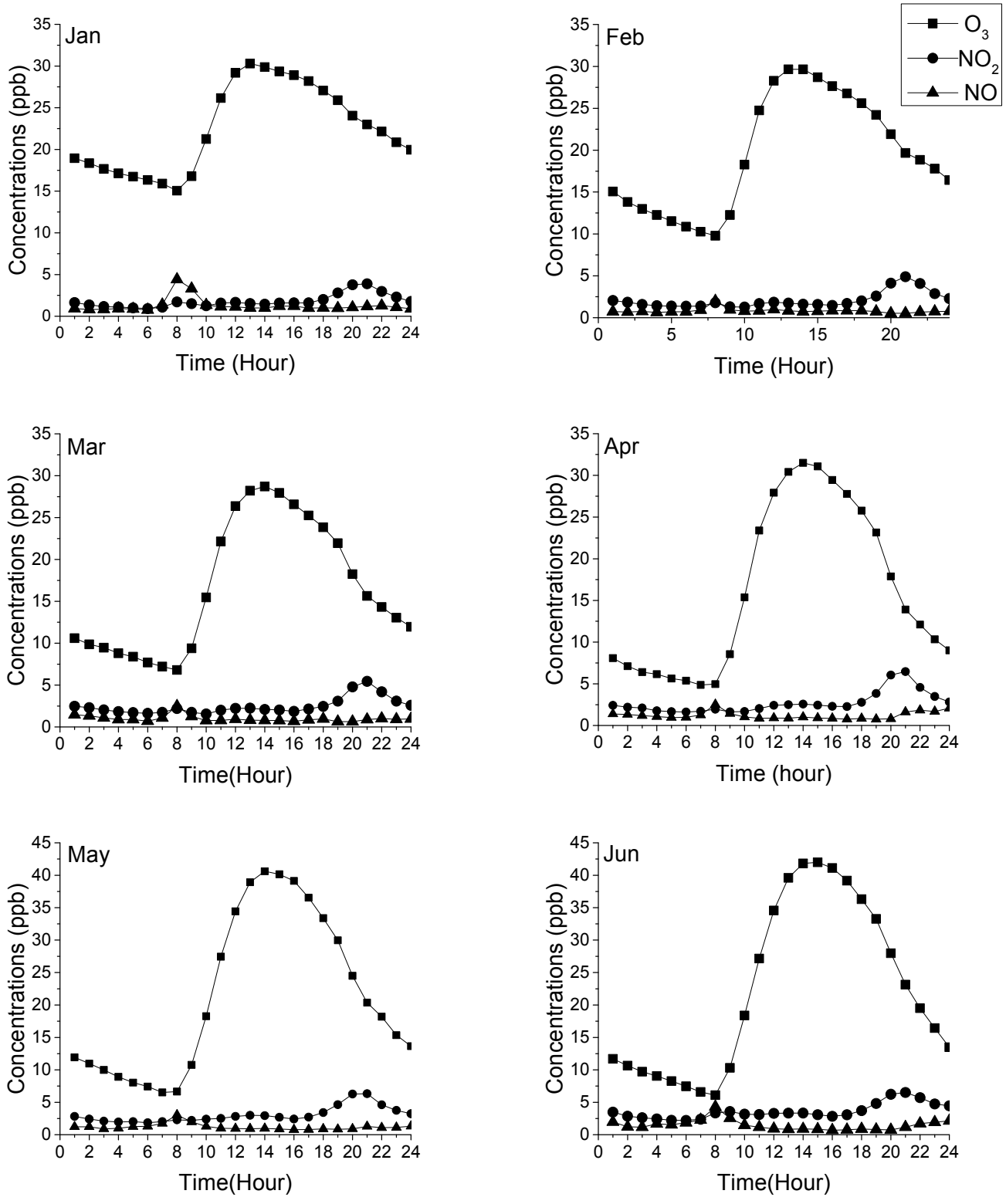
Jan
Feb
Mar
Apr
May
Jun
O3
NO2
NO
Concentrations (ppb)
Time (Hour)
Time(Hour)
Time (hour)

Figure S5 (a)

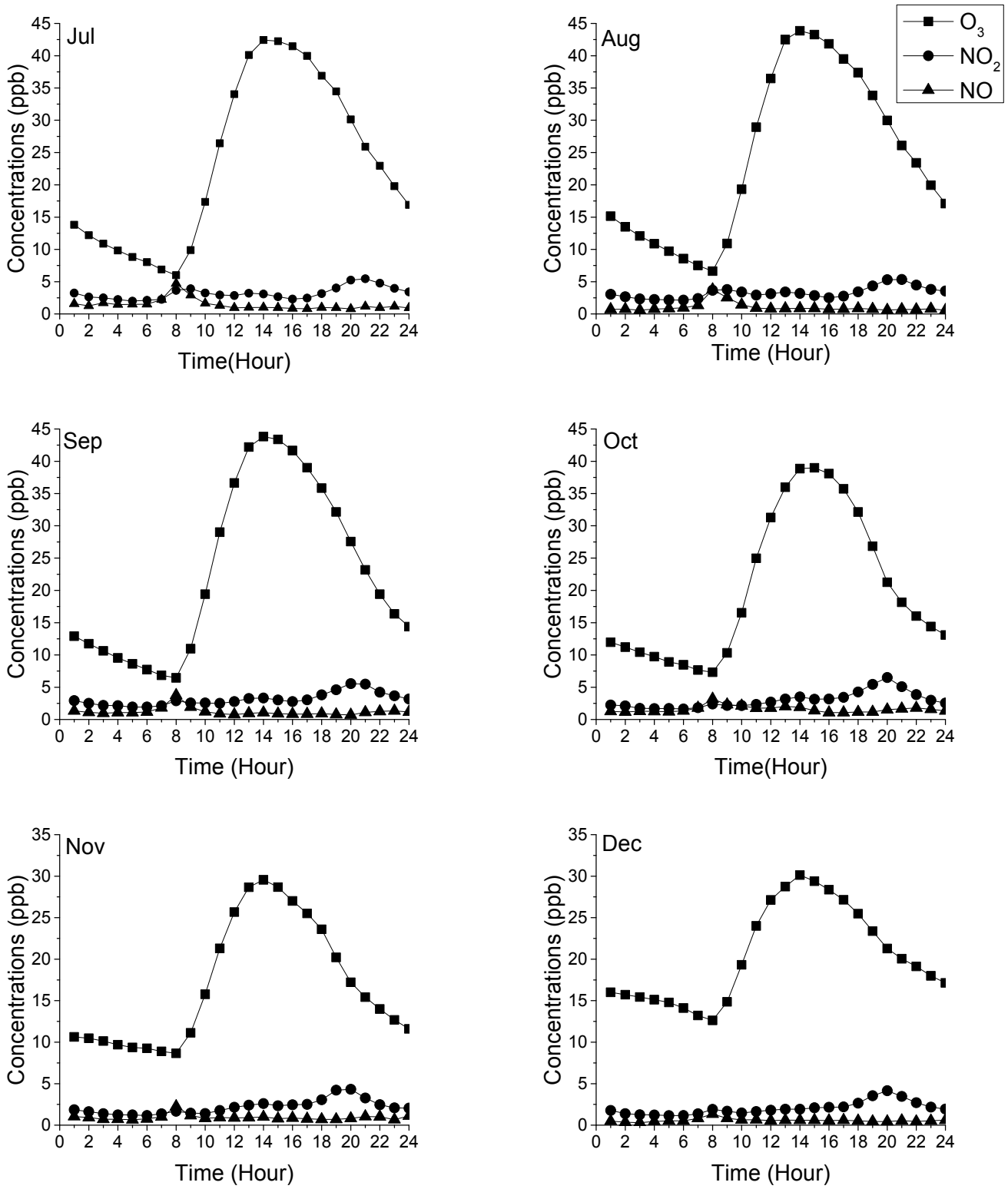
Jul
Aug
Sep
Oct
Nov
Dec
Concentrations (ppb)
Time(Hour)
Time (Hour)
O3
NO2
NO

Figure S5 (b)