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A Ten-Year Investigation on Ozone and It Precursors at Kemaman, Terengganu, Malaysia

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Abstract

10 years of continuous monitoring data (2000-2010) from Air Quality Division, Malaysian Department of Environment are used to investigate the relationships between ambient levels of ozone (O_3), nitric oxide (NO) and nitrogen dioxide (NO_2) as a function of NO_x, in Kemaman, Malaysia, wherewith the dominant sources of ozone precursors are industrial activities and road traffic. In addition, variation of oxidant OX (O_3 and NO_2) concentration with NO_x was also examined. The analyses established a weak linear relationship between O_3 and NO_x, signifying that Kemaman area is not NO_x sensitive but possibly VOC-sensitive area. The level of [OX] is influenced by NO_x-independent and NO_x-dependent contributions. The former is due to regional background O_3 concentration while the latter correlates to the local level of primary pollution. The measured concentrations of the pollutants varied as a function of time. The analyses also show that the diurnal cycle of ground level ozone concentration has a mid-day peak while lower concentration occurs at night time.

Keywords: ground level ozone; solar radiation intensity; diurnal cycle; oxidant; Kemaman

1. Introduction

Ozone is a secondary pollutant resulting from photochemical reaction of variety of natural and anthropogenic precursors; mainly volatile organic compound (VOC) and oxides of nitrogen (NO_x). The formation of ground level ozone depends on the intensity of solar radiation, the absolute concentration of NO_x and VOCs, and the ratio of NO_x to VOCs. Ground level ozone comes from two major sources namely regional background ozone primarily from the influx of ozone from the stratosphere and in situ local ozone production mainly via precursors, such as NO_x and VOC, emitted from variety of anthropogenic and natural sources (Clapp and Jenkin, 2001). Ozone at high concentrations could induce several adverse effects on human health and the environment (Kampa and Castanas, 2007). The concentration of photochemical oxidant (O_3 and NO_2) can be decreased by controlling their precursors; Nitrogen Oxides, NO_x (NO and NO_2) and VOCs (Geng *et al.,* 2007). However, the efficiency of emission control also depends on the relationship between primary and secondary pollutants, as well as ambient meteorological factors. Owing to the chemical coupling of O_3 and NO_x, the levels of O_3 and NO_2 are inextricably linked. The changes in the local level of O_3 and NO_2 will lead to an increasing background level. In this study, ten years ambient concentration data of O_3, NO, NO_2, and NO_x were used for the investigation of the hourly variation of NO, NO_2, NO_x and O_3. The variation of oxidant OX (O_3 and NO_2) concentration with NO_x was also investigated, contributing to a better understanding of the atmospheric sources of OX at this Kemaman area.

2. Materials and Methods

2.1. Site description

Kemaman (4°12' N, 103°18' E) is situated in the Terengganu State, a developing Malaysian town flanked by Kerteh Petrochemical Industrial Area at the north and the industrializing and urbanizing Gebeng Industrial Area at the south (Fig. 1). In this area, there are dominant sources of ozone precursors related to industrial activities and road traffic.

Figure 1. Location of air quality monitoring station in Kemaman

2.2. Source of data

In this study, the concentration of O_3, NO, NO_2, and NO_x data consisting of 120 months from January 2000 to December 2010 (excluding year 2008 due to the unavailable of the data for that particular year) acquired from the Air Quality Division, Malaysian Department of Environment for Sekolah Rendah Bukit Kuang Station (Station ID: CA 0002) located in Kemaman District, one of the earliest operational stations in Malaysia. The monitoring network was installed operated and maintained by Alam Sekitar Malaysia Sdn. Bhd (ASMA) under concession by the Department of Environment Malaysia (Afroz *et al.,* 2003). Tropospheric ozone concentrations data was recorded by using a system based on the Beer-Lambert law for measuring low ranges of ozone in ambient air manufactured by Teledyne Technologies Incorporated (Model 400E). A 254 nm UV light signal is passed through the sample cell where it is absorbed in proportion to the amount of ozone present. Every three seconds, a switching valve alternates measurement between the sample stream and a sample that has been scrubbed of ozone. The result is a true, stable ozone measurement. The concentration of ozone precursors, NO_x (NO and NO_2) were determined using the chemiluminescene measurement principal, couple with state-of-the-art microprocessor technology for monitoring high and medium levels of nitrogen oxides (Teledyne Models 200A). For quality control and quality assurance of the air monitoring data, all monitoring instruments were calibrated regularly by ASMA. For gas monitoring such as ozone and nitrogen oxides, the instruments were scheduled to have daily auto calibration using zero air (clean ambient air, free from contaminant) and standard gas concentration. The instruments have been calibrated manually using its individual calibration gas every two weeks. The hourly data was also checked for validation before it can be transferred to the Department of Environment.

2.3. Data analysis

In order to establish the hourly trend of selected pollutants, boxplot was performed by using Microsoft Excel Spreadsheet 2013. In descriptive statistics, a boxplot is a convenient way of graphically depicting groups of numerical data through their quartiles.

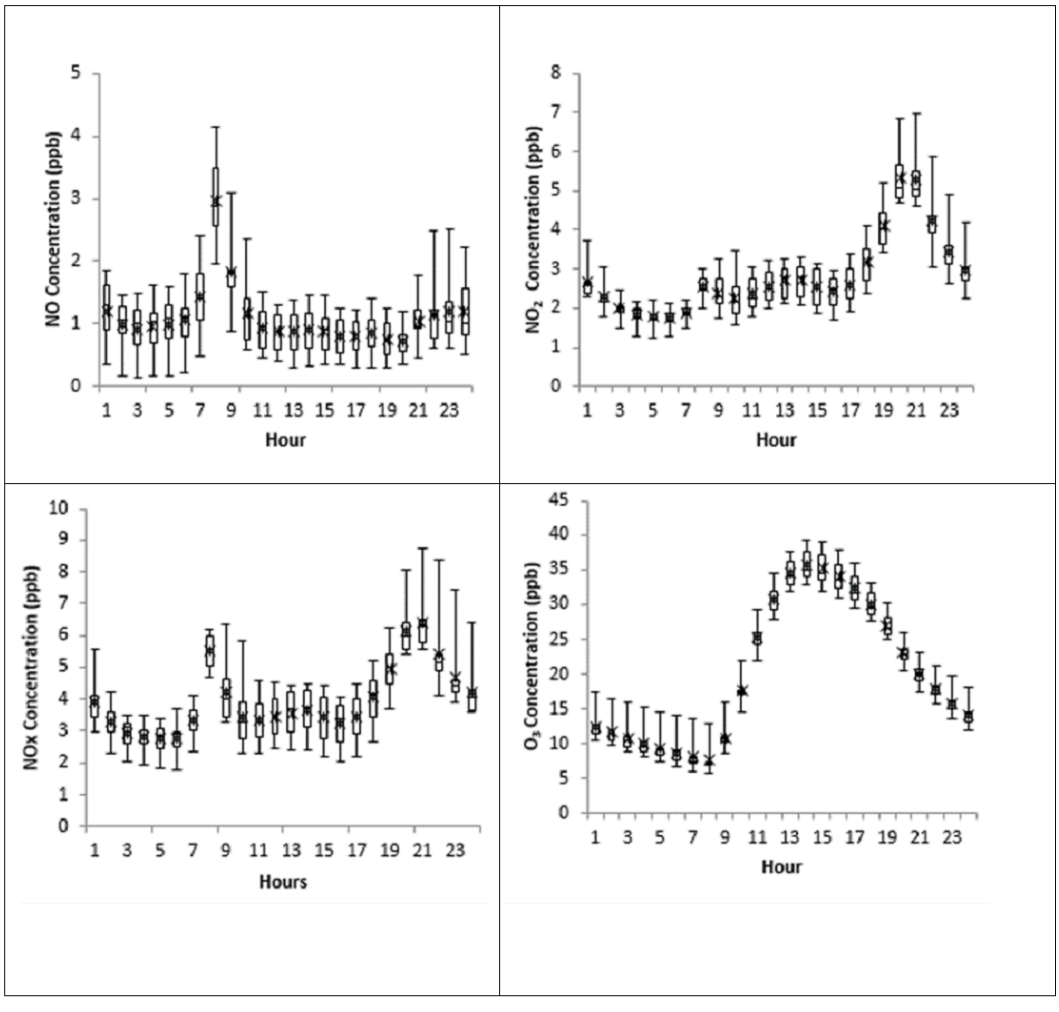

Figure 2. Hourly variation of mean values of NO, NO_2, NO_x, and O_3 concentrations from 2000-2010* (*excluding year 2008*)

Boxplot is a graphic representation of a distribution by a rectangle, the ends of which mark the maximum and minimum values, and in which the median and first and third quartiles are marked by lines parallel to the ends. The individual box plot is a visual aid to examining key statistical properties of a variable such as median, mean and quartiles. Analyses of variance and correlation analysis (the correlation is significant at the *0.05* level (2-tailed)) were conducted using STATGRAPHICS® Centurion XVI.I statistical software package.

3. Results and Discussion

3.1. Hourly variation of O_3, NO, NO_2 and NO_x concentrations

The 10 years (2000-2010, excluding year 2008) average diurnal variation of NO, NO_2, NO_x and O_3 concentrations were shown in Fig. 2.

Based on Fig. 3, the diurnal cycle of ozone concentration reaches a peak during the middle of the day, while there was a lower ozone concentration during nighttime (Ramli *et al.,* 2010). This is due to the photochemical reaction of O_3 precursors, such as volatile organic compound (VOC), with ambient air from natural sources and the long distance transport of NO_x (Pires *et al.,* 2012). The ozone concentration slowly increases after the sun rises until it reached its maximum during the daytime and then slowly decreases until the next morning. From 08:00 to 13:00-14:00 hours, an increase in solar radiation results in the increasing of ozone concentration (Ulke and Maezzo, 1998). The average data of ozone concentration and solar radiation shows that the ozone concentration is highly correlated to solar radiation (J/m^2.hr). It was found that the correlation coefficient between ozone and solar radiation was 0.67 from the statistical analysis, at the *0.05* level (2-tailed).

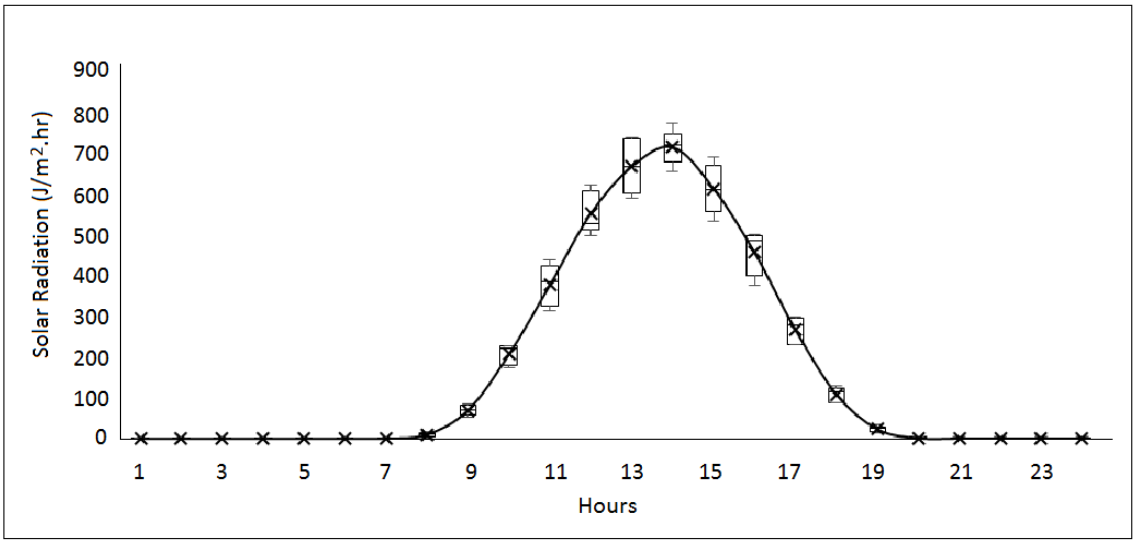

Figure 3. Hourly variation of mean values of solar radiation from 2000-2010* (*excluding 2008*)

The diurnal cycle of NO, NO_2 and NO_x are shaped like double waves. The morning peak of NO_2 occurs about two hours after the morning peak of NO (08:00). The O_3 peak occurs at 14:00 (Azmi *et al.,* 2010). It appears about 6 to 8 hours after the NO (08:00) and NO_2 (10:00) peak. After the morning peak (08:00), NO diminishes until it reaches lower value at (13:00-14:00). It was found that, both NO and NO_2 decreases correlate with an increase in O_3 (Ramli *et al.,* 2010). The increasing of NO_2 has caused the decreasing of O_3 concentrations (Ghazali *et al.,* 2008). NO is a primary contaminant, whereas O_3 and a large percentage of NO_2 are secondary contaminants, formed through a set of complex reaction. NO is converted to NO_2 via a reaction with O_3 as in Eq. (1). During daytime, NO_2 is converted back to NO as a result of photolysis, leads to regeneration of O_3 as in Eq. (2). The vertical mixing layer of also influenced the air pollution concentrations (Banan *et al.,* 2013). During the day, pollutants would be diluted when mixing layer rises and be limited to inside nocturnal planetary boundary layer (NPBL) during nighttime. Emitted pollutants such as NO and NO_2 are kept beneath this inversion, which may cause the hourly NO_x concentration to increase during the night (Han *et al.,* 2011)

3.2. Chemical coupling of O_3, NO and NO_2

The inter conversion of O_3, NO and NO_2 under atmospheric conditions is generally dominated by the following reactions (*Kenty et al., 2007*)

$$NO + O3 \longrightarrow NO2 + O2 \quad (1)$$
$$NO2 + hv\ (+O2) \longrightarrow NO + O3 \quad (2)$$

These equations form a cycle with no net chemistry; the overall effect of reaction Eq. (2) is the reverse of reaction Eq. (1). These reactions therefore represent a closed system which has the overall effect of partitioning NO_x between its component forms of NO and NO_2, and oxidant (OX) between its component forms of O_3 and NO_2, but leaving a total mixing ratio of both NO_x and OX unchanged. During daytime hours, NO, NO_2 and O_3 are typically equilibrated on the timescale of a few minutes, a condition usually referred to as photo stationary state. NO, NO_2 and O_3 concentrations are related by the expression $[NO].[O_3]/[NO_2] = J_2/k_1$, where J_2 is the rate of NO_2 photolysis and k_1 is the rate coefficient for the reaction of NO with O_3 (Han *et al.,* 2011).

The variation of the mean value of J_2/k_1 over time, obtained using 10 years data at Kemaman of NO, NO_2 and O_3 is shown in Fig. 4. The mean values of J_2/k_1 vary between 3.225 and 12.869 ppb and the maximum value occurred at 15:00. This provides adequate description of diurnal averaged observations, consistent with the chemical coupling of these species being dominated by reactions Eq. (1) and Eq. (2).

Fig.5 shows the variation in daytime O_3 concentration as a function of the NO_2/NO ratio. It was found that the level of O_3 increases with an increase in NO_2/NO ratio. O_3 increases rapidly with a small value of NO_2/NO ratio, this may be implicated that when O_3 was at low levels, the reactions of production of O_3 was dominated reaction (Han *et al.,* 2011). When O_3 reached at about 35 ppb, it tended to remains relatively stable. This shows that at higher levels, O_3 is close to reaching a photo stationary state. The output shows the results of fitting a logarithmic-X model to describe

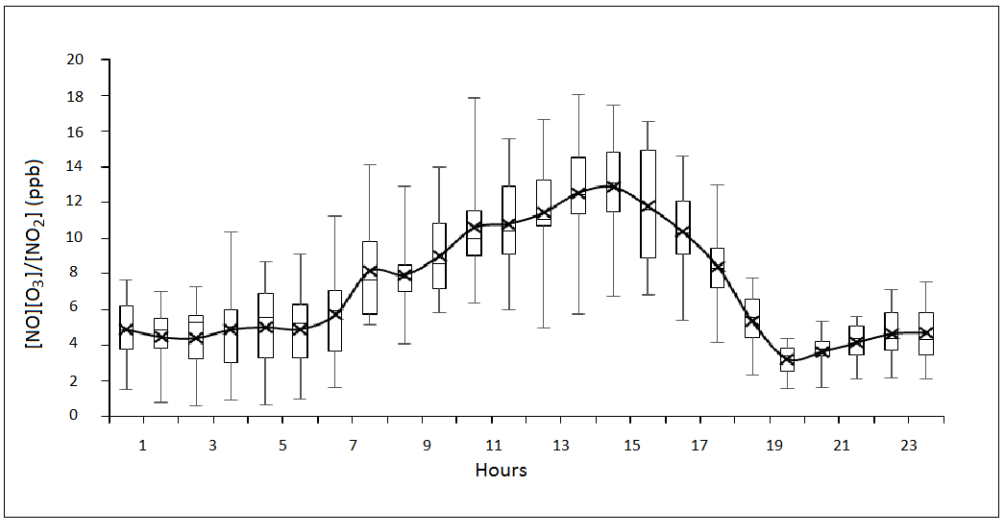

Figure 4. Variation of mean values of J_2/k_1

the relationship between O_3 concentrations and NO_2/NO. The equation of the fitted model is O_3 (ppb) = 13.6992 + 12.3397*ln (NO_2/NO). Since the result of *P*-value from the ANOVA is less than *0.05*, there is a statistically significant relationship between O_3 and NO_2/NO at the 95.0% confidence level. The logarithmic function can be used to forecast the [O_3] during the daytime. The correlation coefficient equals to *0.70*, indicating a moderately strong relationship between the variables.

3.3. Diurnal variation of [OX]

Fig. 6 shows the variation in the mean value of OX concentration. OX concentration shows a mid-day peak and lower nighttime concentrations which is similar to the variation of O_3 concentration. The OX concentration slowly raises after the sunrise, reaches a maximum during the day and then decreases until the next morning. This is due to the photochemical O3 formation (Pires *et al.,* 2012). Fig. 7 shows the variation of [NO_2]/[OX]. A smaller ratio of [NO_2]/[OX] is due to the higher concentration of O_3 during the day. This difference in the partitioning of NO_2 and O_3 may be related to the rate of chemical processes or the time available for them to occur. For instance, the higher ratio of [NO_2]/[OX] was due to the lower O_3 concentration during the day.

3.4. Local and regional contributions to oxidant

The variation of OX concentration against the level of NO_x is shown in Fig. 8. The total OX appears to increase linearly with NO_x over the entire range considered, such that the level of OX at Kemaman has NO_x-independent contribution and NO_x-dependent contribution. The NO_x-independent contribution can

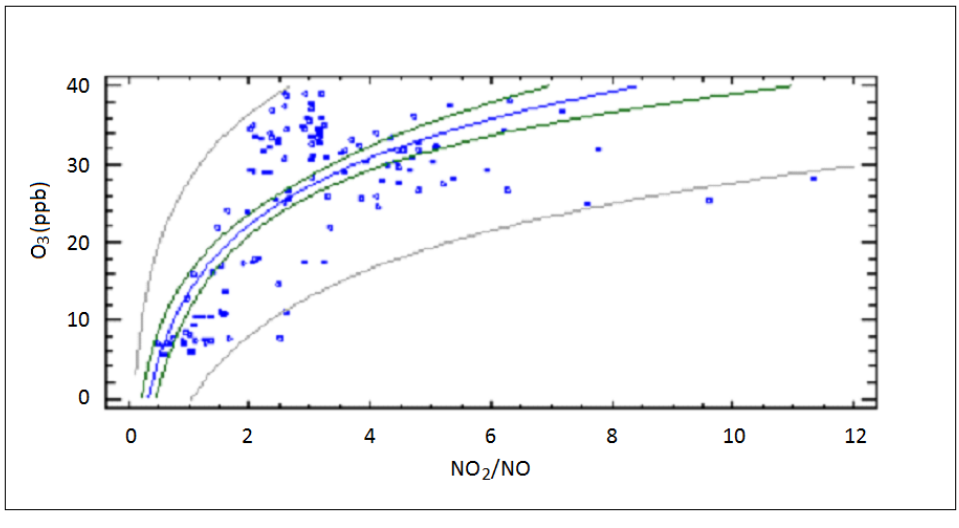

Figure 5. Relationship of O_3 concentration with the [NO_2]/[NO] ratio from 2000-2010* (*excluding year 2008*)

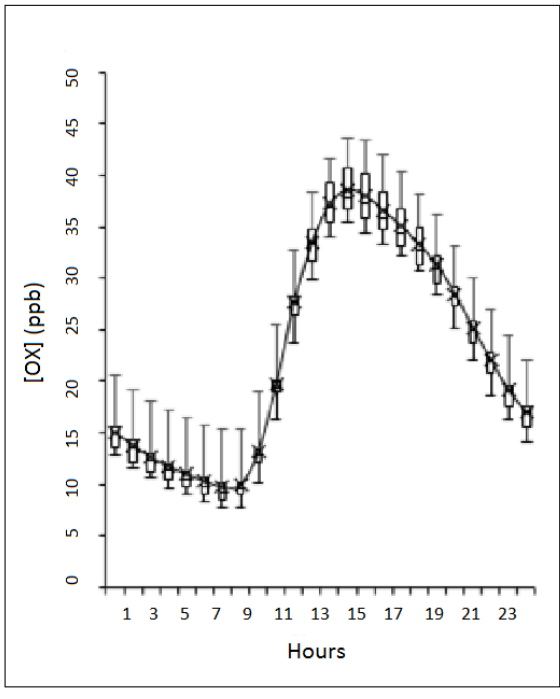

Figure 6. Variation of mean values of OX

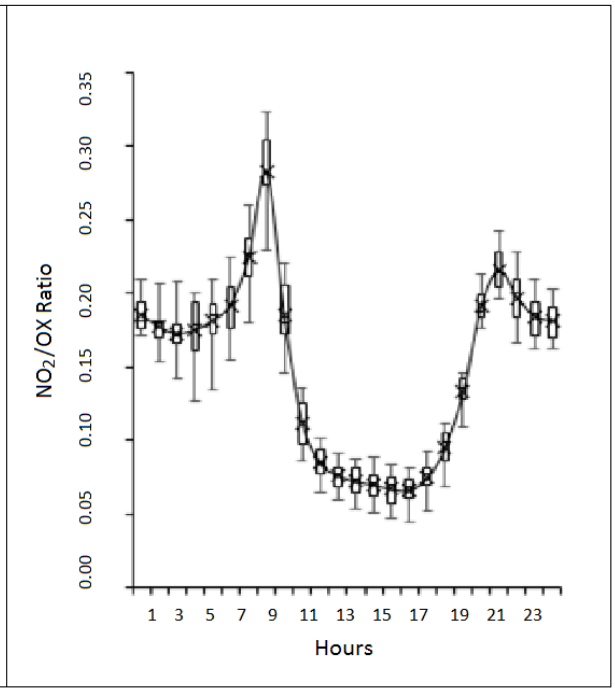

Figure 7. Variation of mean values of NO_2/OX ratio

be considered as a regional contribution which equates to the regional background of O_3 level, while the NO_x-dependent contribution can be considered as local contribution and is correlated with the level of primary pollution. The result of this study is similar as performed by Clapp and Jenkin (2001).

The local OX source has probable contributions from direct NO_2 emission, thermal reaction of NO with O_2 at high NO_x and common source emission of species which promote NO to NO_2 conversion. The regional contribution to O_3 concentration was known to be at about 18.22 ppb according to the intercept of the relationship between OX concentration and NO_x concentration.

3.5. Correlations between O_3 and NO_x

Fig. 9 shows that the concentration of O_3 and NO_x were linearly correlated. The correlation coefficient equals to *-0.165*, indicating a relatively weak relationship between the variables (O_3 and NO_x). A weak correlation between O_3 and NO_x indicates that Kemaman area is probably not NO_x-sensitive but possibly VOC-sensitive. This inverse relationship of O_3 and NO_x is due to the titration of O_3 during the daytime (Banan *et al.,* 2013; Nishanth *et al.,* 2014). Based on Fig. 10, the NO_2/NO_x ratio decreased greatly as NO_x increased that could be newly emitted could also support the VOC-sensitive nature in Kemaman. This finding is corresponding as

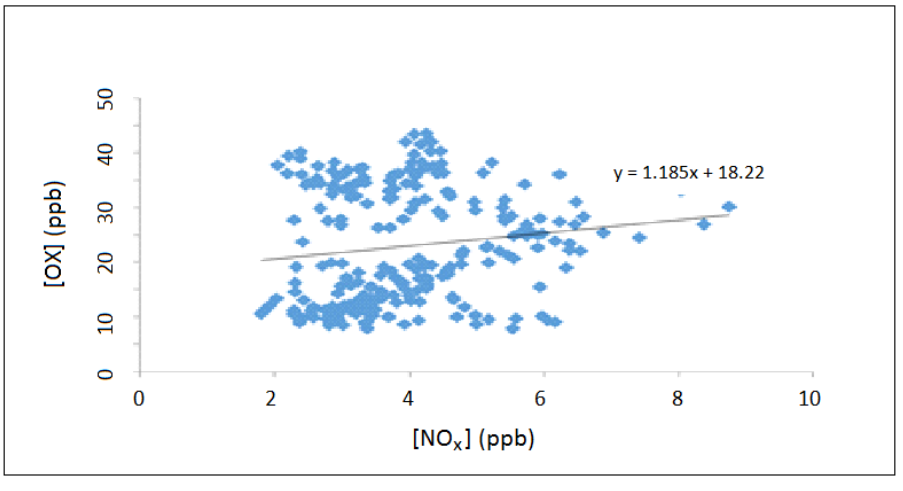

Figure 8. Relationship betwween [OX] with the level of [NO] from 2000-2010* (*excluding year 2008*)

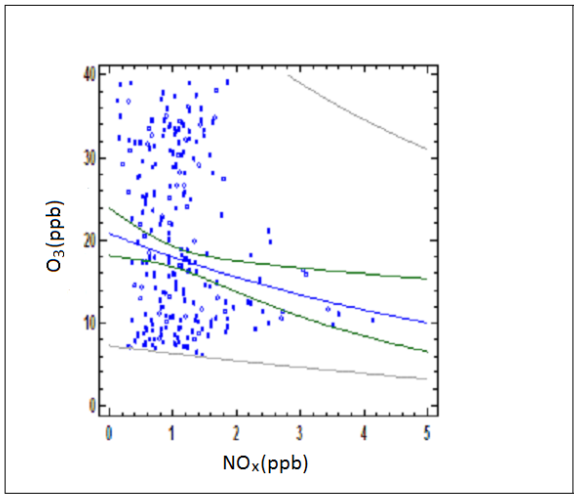

Figure 9. Correlations between [O_3] and [NO_x] from 2000-2010* (*excluding year 2008*)

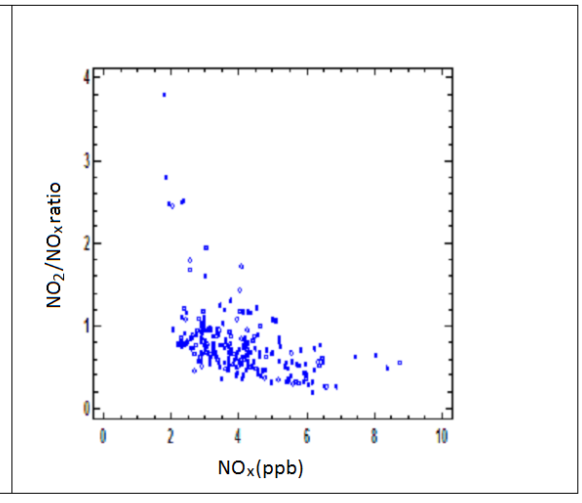

Figure 10. Relationship NO_2/NO_x ratio from 2000-2010* (*excluding year 2008*)

found by Song *et al.* (2011). VOC was emitted from the industrialized area and may also be emitted by traffic, and more detailed relationship among NO_x, VOC and O3 in this area need to be explored through future studies.

4. Conclusions

This study analyses the concentrations of NO, NO_2, NO_x and O_3 for 10 years from 2000 to 2010 (excluding year 2008). The results indicate that the diurnal cycle of ozone concentration has a mid-day peak (14:00) and lower nighttime concentrations. The ozone concentration slowly rises after the sun rises (08:00), reaching a maximum during daytime and then decreases until the next morning. This is due to the photochemical of ozone formation. In this study, it was also found a weak linear relationship between O_3 and NO_x, suggesting that this Kemaman area is not NO_x sensitive but possibly VOC-sensitive area. A logarithmic relationship between O_3 concentration and [NO_2]/[NO] ratio was also found which could be useful in [O_3] forecasting and air pollution control strategies. The level of [OX] is influenced by NO_2-independent and NO_2-dependent contributions. The former is due to regional background O_3 concentration and the latter correlates to the local level of primary pollution. The regional background O_3 concentration in Kemaman is about 18.22 ppb

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