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Variations in Surface Ozone and NO_x at Qena a Subtropical Site in Upper Egypt

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Abstract Measurements of surface ozone (O_3), NO_x ($NO + NO_2$) and meteorological Parameters have been made in South Valley University campus, Qena, Upper Egypt (26.20° N, 32.75° E), from January 2014 to December 2015. The main objective of this study is to investigate the diurnal, monthly and seasonal variations of O_3 and nitrogen oxides (NO_x). The meteorological factors impacts on O_3 and NO_x levels have been under taken. The measurements of O_3 and NO_x showed distinct diurnal and seasonal variability at this site. The hourly average pattern of O_3 over the study period showed a maximum value (49.9±5.6) ppbv in the afternoon (12.00 h LST) and minimum one (22.2±8.47) ppbv during early morning (6.00 h). In addition, for NO_x, the maximum concentration (8.96±3.3) ppbv was observed during night time and minimum (3.44±0.5) ppbv during daytime. The variability of O_3 and NO_x, during day time, reflect the photolysis of nitrogen dioxide. This study also indicates the maximum value of O_3 was recorded in hot months (Apr.-Sept.) and minimum during cold months (Oct. – Mar.). A negative correlation coefficient of - 0.47 for the relationship between O_3 and NO_x reveals the role of NO_2 photolysis that generates O_3 at this site. The correlation between O_3 and meteorological parameters indicate that the ambient air temperature solar radiation and wind speed have positives correlation (0.62, 0. 51 and 0.22), respectively. On the other hand, the relative humidity has a negative effect on ozone level with a correlation coefficient equals -0.53. The relationship between NO_x and meteorological parameters have negative correlations (-0.30, -0.25 and -0.41) with temperature, solar radiation and wind speed, respectively and positive relation (0.34 with relative humidity).

Keywords Surface ozone, Nitrogen oxides, Meteorological factors, Semi-urban area

1. Introduction

Surface ozone (O_3) is a secondary pollutants and is formed through a series of photochemical reactions in the presence of volatile Organic compounds (VOCs) and nitrogen oxides (NO_x) under intense solar radiation [1]. O_3 is produced by the reaction of oxygen molecule (O_2) with an oxygen atom, which originates from the photolysis of nitrogen dioxide (NO_2) by solar radiation. O_3 is destroyed by reacting with NO to form NO_2 and O_2. O_3 is capable of causing damage to human health via respiratory disease [2-6]. High concentrations of surface ozone also affect vegetation and forests [7].

The main sources of NO_x is complete combustion of fossil fuel particularly from vehicle emissions [8, 9]. VOCs are emitted directly into the atmosphere from vegetation and a variety of natural and anthropogenic sources [10]. Non-methane hydrocarbons are the main group of atmospheric VOCs and a precursor to O_3 production via hydroxyl (OH) radical-initiated oxidation, and subsequent reactions with NO_x [11-14]. O_3 levels in the atmosphere have been widely studied for many locations in the world [15-30]. On the other hand, very few studies have been conducted in Qena particularly outside the city campus. Most of the previous studies have been conducted inside an urban area or in rural area and most of them reported that there is a obvious relationship between O_3 level and its precursors_(NO_x, VOCs). In addition, most of the previous studies, related to ozone, reported that the ozone concentrations during the daytime were found to be significantly different from those of night time. During daytime hours, higher concentrations of ozone were recorded than during the night time. The concentrations would build up rapidly from the early hours of the day, to peak around noon, and then drop to a low in the evening. [27-30]. An analysis of the influences of meteorological parameters on O_3 and its precursors can contribute to a better understanding of the local and regional causes of O_3 pollution [31]. The seasonal and diurnal variations of surface O_3 and its precursors and the related meteorology have been extensively studied around the world [32, 33]. These studies showed that O3 chemistry and the effects of meteorological conditions could vary depending on the characteristics of the climate and air pollutants emissions in the place of interest. The main objective of this study is to investigate the diurnal, monthly and seasonal

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variations of O_3 and nitrogen oxides (NO_x). The metrological factors impacts on O_3 and NO_x levels have been under taken.

2. The Location of the Sampling Site

The location of the sampling site at South Valley University (SVU) metrological research station (26°17' N, 32°43' E, 97 m asl) is shown in Fig. 1. South Valley University is located about 6 K northeast of Qena city in eastern desert. Also, the station is located about 0.5 km from the University Campus and 1 km from red sea road (Qena – El Hurghada high way). In general, the site lie within the subtropical region and its terrain is semi-desert where a little establishment and vegetation are found around the site The location is characterized with no major industrial activities The climate of Qena city is characterized by cold winter, and very hot but non-humid in summer, a hot season from March to October and a cold season from November to February. During summer time, temperatures could reach 46°C, while winter temperatures drop to sub-zero levels. Table 1 shows the monthly mean variations of meteorological parameters like wind speed, temperature, and relative humidity at present location during the period of observations. The wind speed was high during the period from April to Aug. and low from Nov. to Jan. The maximum average wind speed ranged from 2.4 to 3. 16 m/s.

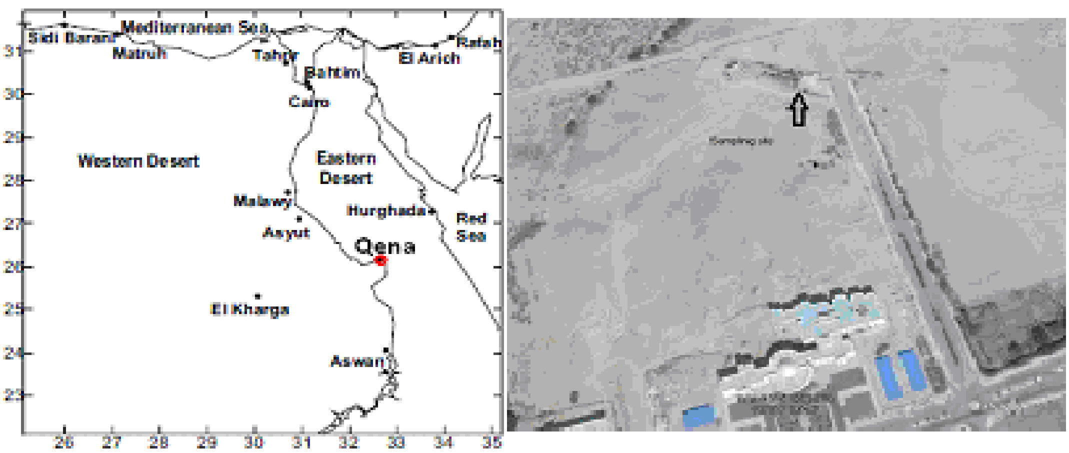


Figure (1). The location of the sampling site

Table (1). Monthly mean variations of meteorological parameters during the period of study at Qena

Temperature °C	Jan.	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct.	Nov	Dec
Average	14.7	17.5	22.6	24.6	30.6	32.8	33.5	33.9	33.3	26.8	21.2	18.2
Maximum	28.8	33.0	39.8	41.9	45.5	45.3	43.1	45.6	42.6	40.2	32.9	30.0
Minimums	3.0	1.6	1.8	2.2	2.2	21.6	22.9	24.7	9.5	16.1	10.1	7.0
STDV	5.7	5.6	6.0	6.6	5.7	5.0	5.0	4.9	4.9	5.1	5.0	5.1
Relative humidity %												
Average	46.5	37.1	30.8	18.3	16.7	17.8	20.7	23.5	25.8	31.2	42.6	49.6
Maximum	100.0	83.0	93.0	58.0	56.0	52.0	56.0	54.0	63.0	66.0	95.0	100.0
Minimum	9.0	7.0	3.0	4.0	3.0	3.0	2.0	5.0	5.0	8.0	9.0	5.0
STDV	17.8	15.3	17.0	10.4	8.9	9.4	9.7	10.1	11.7	12.3	14.9	16.7
Wind speed ms^{-1}												
Average	1.6	1.7	2.1	2.4	2.80	3.16	2.6	2.60	1.8	1.6	1.4	1.1
Maximum	9.1	9.1	10.2	9.2	8.16	10.7	7.5	8.8	8.2	6.0	7.0	7.2
Minumum	0.0	0.0	0.0	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
STDV	1.7	1.6	1.8	2.1	2.03	2..04	1.7	1.8	3.1	1.1	1.4	1.4
Solar radiation W/m^2												
Average	249.8	245.7	312.4	336.	343	361.6	355.6	362	322.9	305	243	246
Maximum	527.7	537.4	687.7.	727	628.	678	643.6	622	654.9	585.2	541	563
Minumum	10.8	12.3	20.4	25.9	34.2	54.6	59.2	65.2	47.6	37.7	15.5	13.5
STDV	151.7	148.4	173.9	178.1	152.	168.1	153.6	181	163	148.7	167	171

3. Results and Discussion

3.1. Diurnal Variation of O_3 and NO_x

The hourly average of O_3 variations within day over a period from January 2014 to December 2015 are graphically in Fig. 2. The vertical bars represent the standard deviation. The figure shows highest levels of O_3 concentration during the daytime and lowest levels in the nighttime. The maximum surface O_3 (49.9±5.6) ppbv was observed in the late afternoon (12.00 h LST, local standard time) and minimum one (22.2±8.47) ppbv was observed during early morning (6.00 h). The daytime increase in O_3 concentration is mainly from the photoxidation of carbon monoxide, hydrocarbons, and methane in the presence of sufficient amount of NO_x. In the our location, the main sources of carbon monoxide and hydrocarbons are motor vehicle exhaust and some man activities in the university. Also, it is clear that with the start of sunshine, O_3 concentration gradually increases and it reaches a maximum value at noon time (12.00 h). O_3 may be produced according the following reaction:

$$NO_2 + h\gamma \rightarrow NO + O$$
$$O + O_2 + M \rightarrow O_3 + M \quad (1)$$

The present data shows that the O_3 concentrations started to decline after 1700 h in the evening on all days. The low concentration of O_3 observed during nighttime is, may be, due to the absence of photolysis of NO_2 and loss of O_3 by NO, may be through the following titration reaction.

$$NO + O_3 \rightarrow NO_2 + O_2 \quad (2)$$

Figure 3 shows the hourly average of NO_x variations during the period of study. Nitrogen oxides can be caused by photochemical, transport and emission processes whose strength varies between day and night. It was found that NO_x concentration was higher during nighttime (21.00 h) and lower during daytime (13.00 h). During night, the boundary layer descends and remains low till early morning; hence, in the absence of solar radiation, NO_x gets trapped in the shallow surface layer and become at high levels.

At this location, the maximum and minimum average concentration of NO_x are found to be about 8.96±3.3 ppbv and 3.44±0.5, respectively. These concentrations are relatively small compared to that of other sites in Egypt such as Cairo and Alexanderia [23, 27].

The present results show similar behavior of both surface ozone and oxide of nitrogen with other studies, that have been proposed in other urban and rural locations. Also, it is clear that the NO_x concentration is mirror image of O_3 concentration during the sunshine duration. Fig. 2 and Fig. 3 are indicating that an increase in O_3 level is associated with a drop in the concentrations of NO_x [17, 24, 26, 27, 30, 36, 37, 38].

In order to better understand the relationship between surface O_3 with NO_x, relationships were examined. The Scatter diagram of hourly O_3 and NO_x is shown in Fig. 4. Significant negative correlations were found between NO_x and O_3 as shown in Table 2 and Fig. 4. The present result shows that the correlation coefficients between NO_x and O_3 varying from -0.35 to - 0.63 with average values equals -0.47. In urban stations in Istanbul, Topeu and Incecik [39, 40] (2002, 2003) are stated that the correlation coefficients varying from −0.54 to −0.84 for summer months in the years of 1998 and 1999. A similar relationship between NO_x and O_3 in Istanbul between 2001 and 2005 have been found by Im et al [41] (2008).

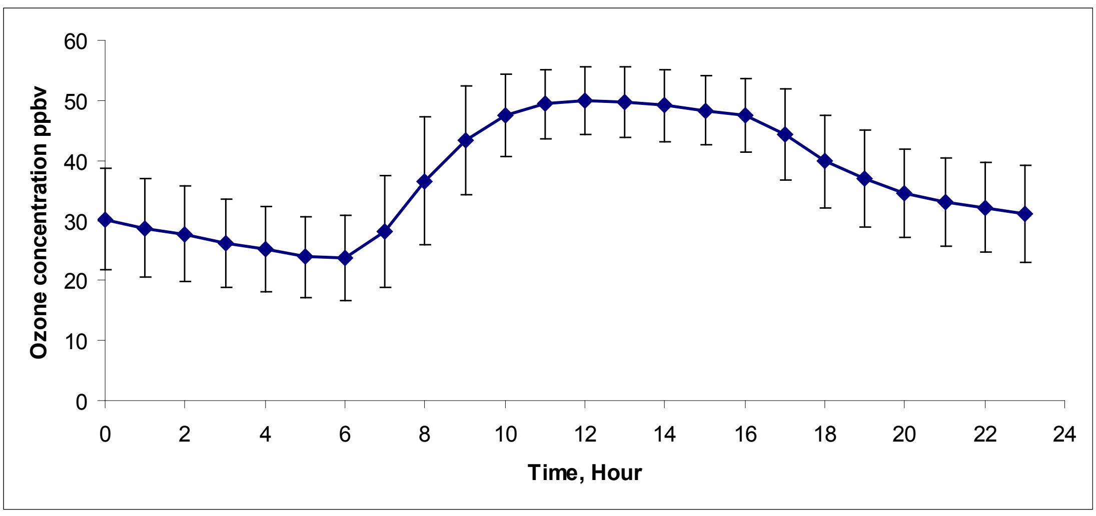


Figure (2). Daily average diurnal variations of O_3 from January 2014 to December 2015

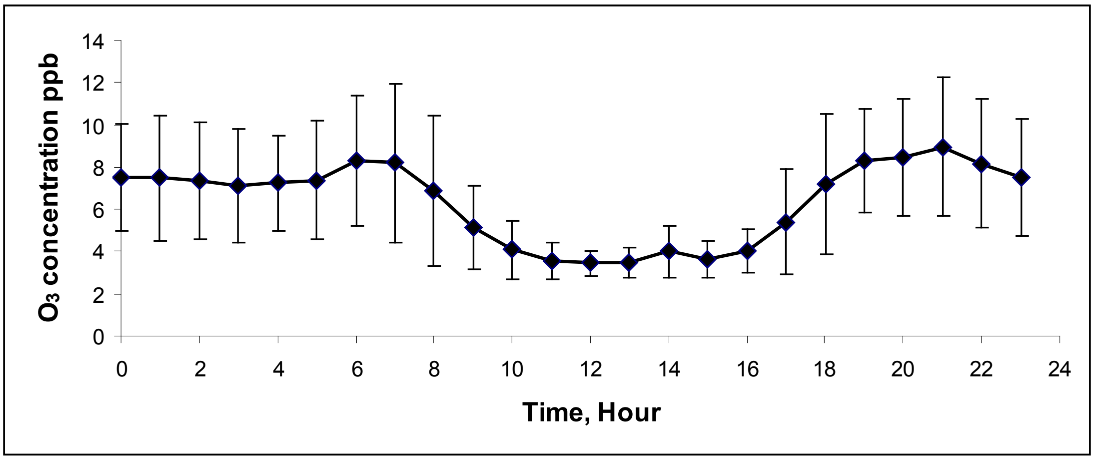


Figure (3). Daily average diurnal variations of NO_x from January 2014 to December 2015

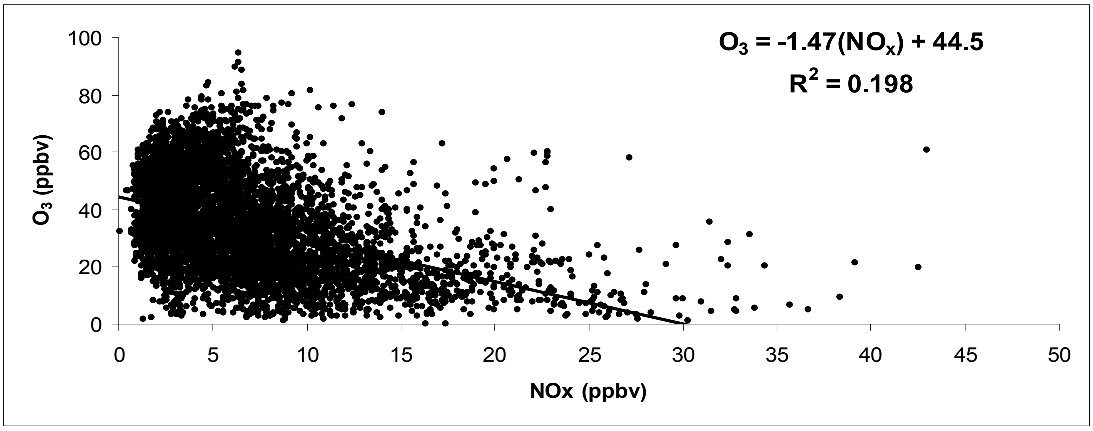


Figure (4). Scatter diagram of hourly O_3 and NO_x concentrations

Table (2). Correlation coefficient between NO_x and O_3

Months	Correlation coefficient all period
Jan.	-0.63
Feb.	-0.35
Mar.	-0.55
Apr.	-0.55
May	-0.50
Jun.	-0.54
July	-0.39
Aug.	-0.42
Sep.	-0.47
Oct.	-0.49
Nov.	-0.45
Dec.	-0.48
All	-0.47

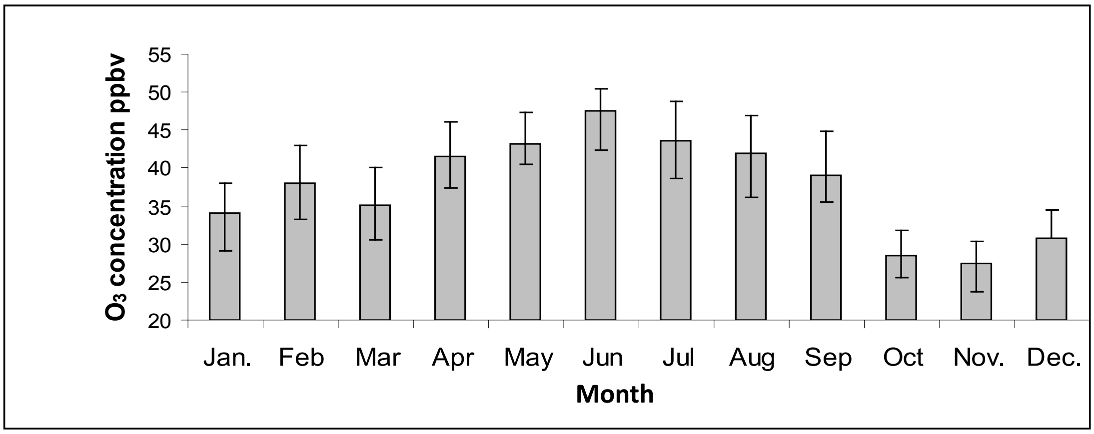


Figure (5). Monthly variations of O_3 at Qena city during the period (2014-2015)

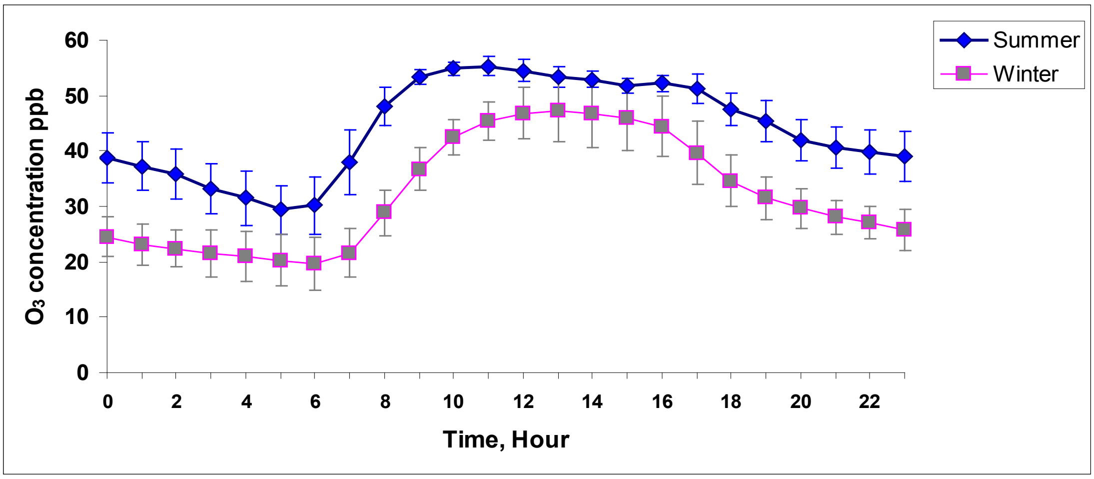


Figure (6). Diurnal variation of O_3 in Qena city during summer and winter of the period 2014-2015

3.2. Monthly and Seasonal of O_3 and NO_x

The monthly mean O_3 concentrations at Qena, averaged over each month in the 2014–2015 periods are shown in Fig. 5. The highest value of concentration was found in hot months (Apr.-Sep) while the minimum one was found in cold months (Oct- Mar). The highest level of averaged O_3 (47.6 ppbv) was observed in Jun. and the lowest one was found in Nov. (27.4 ppbv).

In this study, the diurnal variations of O_3 observed at Qena are highly influenced by the seasonal changes that depend on the site characteristics and emissions. At this site O_3 levels tend to follow the solar radiation intensity, resulting in higher O_3 concentration during the daylight period (9.00 - 17.00 h) in summer days and during period (11.00-16.00 h) in winter days (see Fig. 6). The diurnal pattern of O_3 for each season is characterized by minimum concentration during early morning hours (4.00-6.00 h). At the present location, the maximum average value of O_3 (55.28 ppbv) during summer season was observed at 11.00 h while the minimum one (29.42 ppbv) was observed at morning (6.00 h). On other hand, during winter season, the maximum average of O_3 was 47.3 ppbv and it is recorded at 13.00 h while, the minimum one was 19.63 ppbv (recorded at 6.00 h).

Fig. 7 represents the monthly mean NO_x concentration at Qena, averaged over each month in the 2014–2015 periods. It is clear that the highest value of nitrogen oxide was found in cold months and the minimum one in hot months. The results show that the highest averaged value of NO_x (10.17 ppb) was observed in January and the lowest one (3.8 ppbv) was in Sept. NO_x level shows almost opposite diurnal variation pattern compared to O_3, characterized by high concentrations during morning and afternoon and low concentration during noon. With increasing solar intensity, the photolysis rate of NO_2 increases, leading to decreased NO_2 and increased O_3 As seen in Fig. 8, the highest values of NO_x were monitored in early morning (6.00-8.00 h) and afternoon (17.00 - 23.00 h). The highest values in early morning and afternoon are attributed to increasing the human activities and traffic flow with very low solar radiation intensities.

3.3. Ozone and NO_x Variations with Meteorological Parameters

The pollutants variability is influenced by the changes in meteorological parameters such as temperature, humidity, wind speed and solar radiation. A detailed account of variations of O_3 with and meteorological parameters is described in present section. Figure (9) and Table (3) show the correlation coefficients between hourly averaged O_3 concentration, NO_x and meteorological parameters. It was found a positive relationship between the ambient temperature, solar radiation and wind speed with O_3 concentration where the correlations coefficient (r) are 0.62 0.22 and 0.51, respectively. The increasing ambient temperature is associated with increasing solar radiation intensity, particularly during day light hours. We can say that the photochemical formation of ozone in air at a location is influenced by ambient temperature, solar radiation, and NO_x concentration. On other hand, relative humidity has a negative effect on O_3 concentrations where the correlation coefficient (r) is -0.53. The effect of relative humidity can be explained as follow: an increase in humidity reduces the amount of solar radiation reaching the earth's surface, thus led to reduce the photochemical formation of ozone.

As we mentioned before, in Fig. 2 and Fig. 3, the O_3 concentrations are increasing with a drop in the concentrations of NO_x. The correlation coefficient between NO_x and meteorological parameters confirm this relation where NO_x concentrations have a negative correlations (-0.30, -0.25 and -0.41) with temperature, solar radiation and wind speed, respectively and positive relation (0.34) with relative humidity.

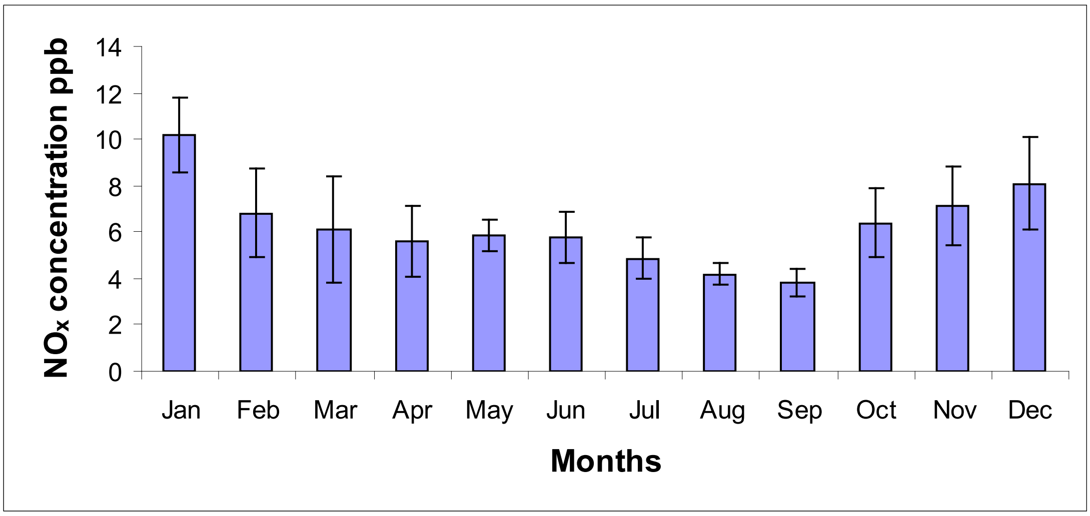


Figure (7). Monthly variations of NO_x at Qena city during the period (2014-2015)

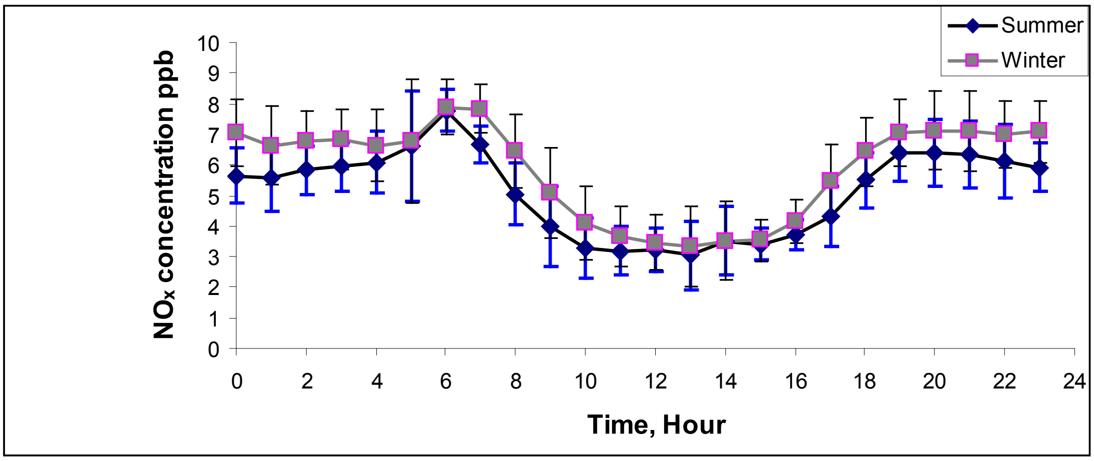
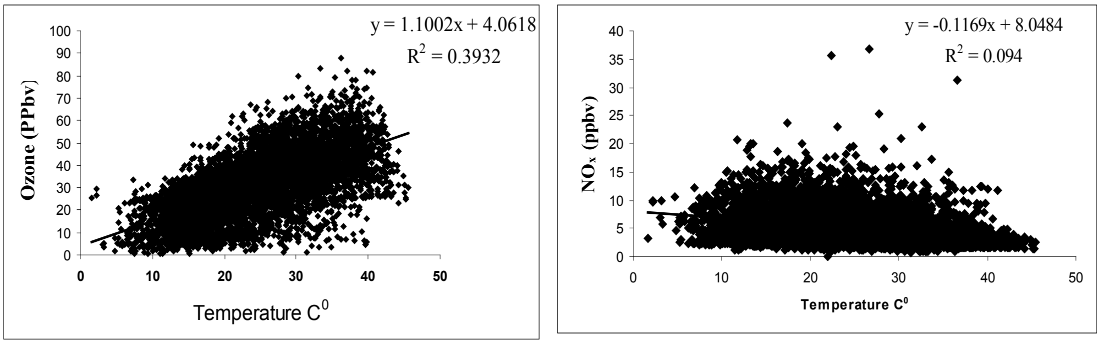


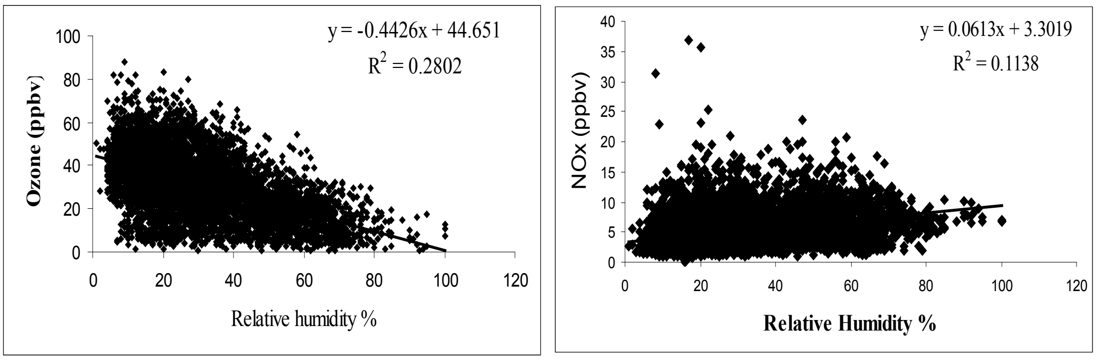
Figure (8). Diurnal variation of NO_x in Qena city during summer and winter of the period 2014-2015

Table (3). Correlation coefficients between hourly averaged O_3 concentration, NO_x and meteorological parameters (temperature, relative humidity, wind speed and solar radiation)

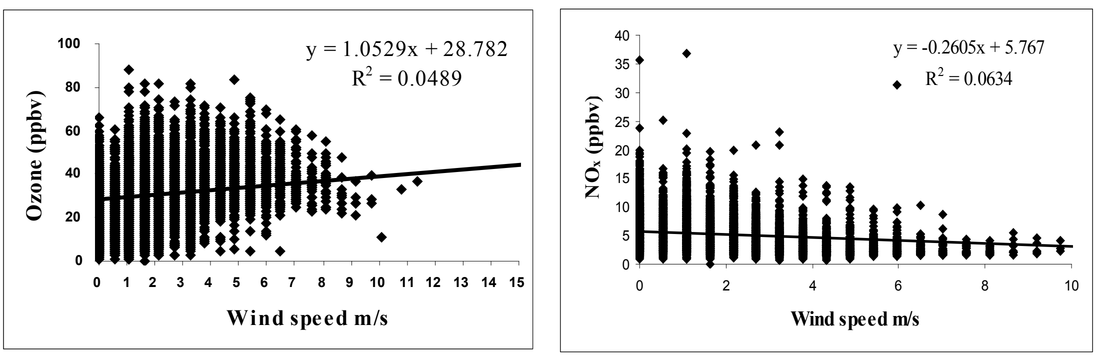
Correlation coefficient r	O_3	NO_x	RH	Temp	W.s	Solar radiation
O_3	1	-0.47	-0.53	0.62	0.22	0.51
NO_x	-0.47	1	0.34	-0.30	-0.25	-0.41



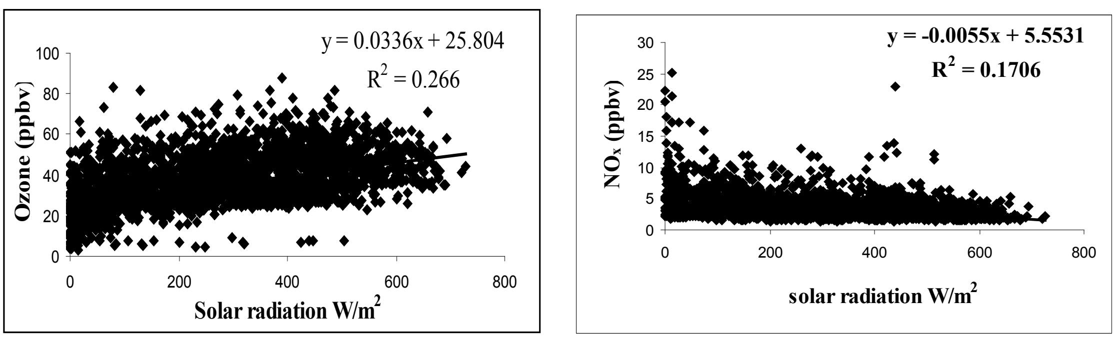
a-Effect of Temperature



b-Effect of relative humidity



c-Effect of wind speed



d-Solar radiation

Figure (9). Relations of both O_3 and NO_x vs a- Air temperature, b-Relative humidity, c-Wind speed and d-Solar radiation

4. Conclusions

In this study, the variations of both surface ozone O_3 and oxide of nitrogen NO_x are investigated in site lie within the subtropical region with terrain is semi-desert where a little vegetation is found around the site. The location is characterized with no major industrial activities. The site lie within South valley university campus, Qena, Upper, Egypt. The investigation involves: diurnal, monthly, seasonal variations and the effect of metrological parameters on both O_3 and NO_x. The investigation showed the following:

- The highest levels of O_3 concentration (49.9±5.6 ppbv) were during the daytime (12.00 h LST) and lowest levels (22.2±8.47ppbv) early morning (6.00 h).
- NO_x concentration was higher (8.96±3.3 ppbv) during nighttime (21.00 h) and lower (3.44±0.5 ppbv) during daytime. (13.00 h)
- The study shows that the NO_x concentration is mirror image of O_3 concentration, particularly particularly during the sunshine duration.
- The monthly variation shows that the highest value of O_3 concentration was found in hot months (Apr.-Sep) while the minimum one was found in cold months (Oct-Mar).
- Also, the monthly variation of NO_x, shows the highest value of nitrogen oxide in cold months and the minimum one in hot months.
- A positive relationship between the ambient temperature, solar radiation and wind speed with O_3 concentration where the correlations coefficient (r) are 0.62, 0.22 and 0.51, respectively. On other hand, relative humidity has a negative effect on O_3 concentrations where the correlation coefficient (r) is -0.53.
- A negative relationship between the ambient temperature, solar radiation and wind speed with NO_x concentration where the correlations coefficient (r) are -0.30, -0.25 and -0.41, respectively.
- The variability of O_3 and NO_x, during day time, reflect the photolysis of nitrogen dioxide.

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