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Diurnal, seasonal and weekdays–weekends variations of ground level ozone concentrations in an urban area in greater Cairo

M. I. Khoder

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Abstract Ground level ozone (O_3) concentration was monitored during the period of December 2004 to November 2005 in an urban area in Greater Cairo (Haram, Giza). During the winter and summer seasons, nitrogen dioxide (NO_2) and nitric oxide (NO) concentrations and meteorological parameters were also measured. The mean values of O_3 were 43.89, 65.30, 91.30 and 58.10 ppb in daytime and 29.69, 47.80, 64.00 and 42.70 ppb in whole day (daily) during the winter, spring, summer and autumn seasons, respectively. The diurnal cycles of O_3 concentrations during the four seasons revealed a uni-modal peak in the mid-day time, with highest O_3 levels in summer due to the local photochemical production. The diurnal variations in NO and NO_2 concentrations during the winter and summer showed two daily peaks linked to traffic density. The highest levels of NOx were found in winter. Nearly, 75%, 100%, 34.78% and 52.63% of the mean daytime concentrations of O_3 during spring, summer, autumn and the whole year, respectively, exceeded the Egyptian and European Union air quality standards (60 ppb) for daytime (8-h) O_3 concentration. About, 41.14% and 10.39% of the daytime hours concentrations and 14.93% and 3.77% of the daily hour concentrations in summer and the whole year, respectively, exceeded the Egyptian standard (100 ppb) for maximum hourly O_3 concentration, and photochemical smog is formed in the study area (Haram) during a periods represented by the same percentages. This was based on the fact that photochemical smog usually occurs when O_3 concentration exceeds 100 ppb. The concentrations of O_3 precursors (NO and NO_2) in weekends were lower than those found in weekdays, whereas the O_3 levels during the weekends were high compared with weekdays. This finding phenomenon is known as the "weekend effect". Significant positive correlation coefficients were found between O_3 and temperature in both seasons and between O_3 and relative humidity in summer season, indicating that high temperature and high relative humidity besides the intense solar radiation (in summer) are responsible for the formation of high O_3 concentrations.

Keywords Ozone · Nitrogen oxides · Diurnal and seasonal variations · Weekdays/weekends · Meteorological parameters · Urban area

Introduction

Photochemical reactions in the troposphere transform primary air pollutants into secondary air pollutants. Photochemical oxidants are formed during the atmospheric photo-oxidation of a variety of trace gases (Kley et al. 1999). Ozone (O_3) is considered one of

M. I. Khoder (✉)
Department of Air Pollution Research,
National Research Centre,
Dokki, Giza, Egypt
e-mail: khoder_55@yahoo.com

the most important photo-oxidants that are produced from the photochemical reactions in the urban environment (McKee 1994). The elevated O_3 concentrations at the ground level have a particular concern due to their deleterious effects on public health, various natural materials, manufactured goods, vegetation and forest (NRC 1991; Xu and Zhu 1994; Brauer and Brook 1997; Krupa 1997; Hogsett et al. 1997; Wang and Georgopoulos 2001; Van Eijkeren et al. 2002; Ozen et al. 2002; Brönnimann et al. 2002; Wang et al. 2003). The tropospheric O_3 is also known to be one of the most important greenhouse gases (IPCC 2001). In addition, it plays a critical role in the tropospheric chemistry and is considered as a key element to control the chemical composition of the troposphere. Ozone is a key precursor of hydroxyl radical (OH) which control the oxidizing power of the atmosphere (Logan et al. 1981; Thompson 1992). The level of OH in the atmosphere in turn influences the levels of many primary air pollutants such as CH_4, CO and SO_2 (Poulida et al. 1991).

Ozone in the ground level may arise from tropospheric/stratospheric exchange that causes the transport of stratospheric air, rich in O_3, into the troposphere as well as production of O_3 by photochemical reactions taking place within the troposphere (Dueñas et al. 2002). It is formed through a series of complex photochemical reactions among its anthropogenic precursors that include industrial and vehicular emissions of nitrogen oxides (NOx) and volatile organic compounds (VOCs) in the presence of sunlight and temperature (Crutzen 1974; Gong and Demerjian 1997; Seinfeld and Pandis 1998; Derwent et al. 2003; Abdul-Wahab et al. 2005). VOCs are important precursors for the formation of O_3 (Kleinman et al. 2001; Zhang et al. 2004; Tie et al. 2006). The formation and concentration of ground level O_3 depends on the concentrations of NOx and VOCs, the ratio of NOx and VOCs, and the intensity of solar radiation (Nevers 2000). NOx emissions are mainly responsible for O_3 formation in the rural areas, whereas VOCs are responsible for O_3 formation in urban areas (EEA 1998). In the presence of sunlight, O_3 is formed through the photochemical destruction of nitrogen dioxide (NO_2) which creates nitric oxide (NO) and oxygen atom (O) that combines with molecular oxygen (O_2) to form O_3 (Vingarzan and Taylor 2003). Once formed, O_3 quickly reacts with NO regenerating NO_2 in the absence of VOCs. Increase the concentration of VOCs always increases O_3 formation, whereas increasing of NOx leads to more or less O_3, depending on the prevailing ratio between [VOCs] and [NOx] (Seinfeld and Pandis 1998; Barros 1999; Guicherit and Roemer 2000; Sadanga et al. 2003; Pereira et al. 2005). In the presence of VOCs, the oxidation processes of the VOCs play an important role in the oxidation of NO to NO_2 without consumption of O_3. VOCs oxidation mechanisms are mainly induced by OH radicals, which are formed from the reaction of O^1D radical that formed from the photo-dissociation of O_3 molecules by solar radiation with water vapour, during the day and by NO_3 radical during the night, leading to the production of hydroperoxy (HO_2) and organic peroxy (RO_2) radicals (Alvim-Ferraz et al. 2006). These radicals oxidize NO to NO_2 without consumption of O_3 and then the photolysis of the resulting NO_2 by sunlight leads to increase the accumulation of O_3 (Alvim-Ferraz et al. 2006). High levels of O_3 might be registered within city or at a distance downwind due to the high emissions of O_3 precursors in urban areas (Garcia et al. 2005). Ozone precursors may be transported over long distances under the effect of meteorological conditions, leading to O_3 formation far from the sources (Hastie et al. 1999; Brankov et al. 2003). Meteorological conditions have been shown to play an important role in O_3 formation and transport (Laurila and Lattila 1994; Laurila 1999; Thompson et al. 2001).

Ozone levels tend to be higher during weekends than on weekdays in some urban areas (Qin et al. 2004; Sakamoto et al. 2005; Pudasainee et al. 2006), despite what are believed about the lower emissions of O_3 precursors on weekends. This phenomenon is known as the "weekend effect". The mechanisms for the weekend effects on O_3 formation are still not well understanding. However, the California Air Resources Board (CARB) outlined six potential causes of the weekend effect for O_3 (2003), described by Heuss et al. (2003) and Jiménez et al. (2005) and the references therein. The causes are: (1) a reduction in NOx emissions on weekends that reduces the titration of O_3; (2) a weekend change in the timing of NOx emissions that allows for more efficient production of O_3; (3) increased sunlight caused by the reduction in the amount of soot in the air; (4) carryover of vehicle emissions near the ground; (5) carryover of vehicle emissions aloft; and (6) the increase in weekend

emissions, particularly from off-road sources such as lawnmowers.

Air pollution in Greater Cairo (Cairo and Giza Governorates and Shoubra El-Khiema city) is now recognized to be of significant environmental problems due to the presence of intensive anthropogenic activities. Industrial activities, big electrical power stations and more than 1.30 million vehicles running in the streets of the Greater city leading to an increase in the emission of O_3 precursors (NOx and VOCs). Therefore, the problem of pollution had been shifted towards the so called photochemical pollutants. The formation of those pollutants in Greater Cairo atmosphere is facilitated by the local climatic conditions (high temperature, intense solar radiation, clear sky), especially in the summer season. Giza city is very important part of Greater Cairo region due to the presence of the most important Egyptian monuments and historical places in it. The rapid urbanization, industrialization, and increased human activities in and around Giza city have led to an increase in O_3 precursors (Hassan 2000; Khoder 2007). Therefore, it is very important to evaluate the diurnal and seasonal variations of ground level O_3 concentration and its association with NOx and meteorological parameters. In addition, there is a lack of information on the ground level O_3 concentration on weekends in Greater Cairo. So, monitoring of ground level O_3 concentration on weekdays and weekends in an urban area in Giza (Haram) may provide insight into the effectiveness of control strategies of O_3, as such plans typically focus on reducing emissions of O_3 precursors.

Therefore, the main objectives of the present study are (1) assessment of the ground level O_3 concentrations in an urban area in Giza city (Haram), (2) study of the diurnal and seasonal variations in O_3 concentration and its relation with NOx, temperature and relative humidity during the lower and higher photochemical reaction periods (winter and summer seasons, respectively), and (3) study of the effect of the reduction of O_3 precursor (NOx) during weekends on the O_3 levels.

Materials and methods

Sampling site and periods of study

The narrow strip of Giza Governorate runs along the western side of the River Nile, opposite to the city of Cairo (Fig. 1). It lies between two big industrial areas, one in the north (Shoubra El-Khiema) and the other in the southeast (Helwan). Giza is located in the subtropical climatic region. The general climate of Giza city is cold, moist and rainy in winter, whereas it is characterized by high temperature, high solar radiation, clear sky and rainless during summer. Daily temperature ranged from 11.5°C to 17.8°C (with an average of 15°C) during winter and from 25.3°C to 34.8°C (with an average of 30.5°C) during summer season. Daily relative humidity ranged from 50.2% to 75.3% (with an average of 66.8%) during winter and from 31% to 72.5% (with an average of 61%) during

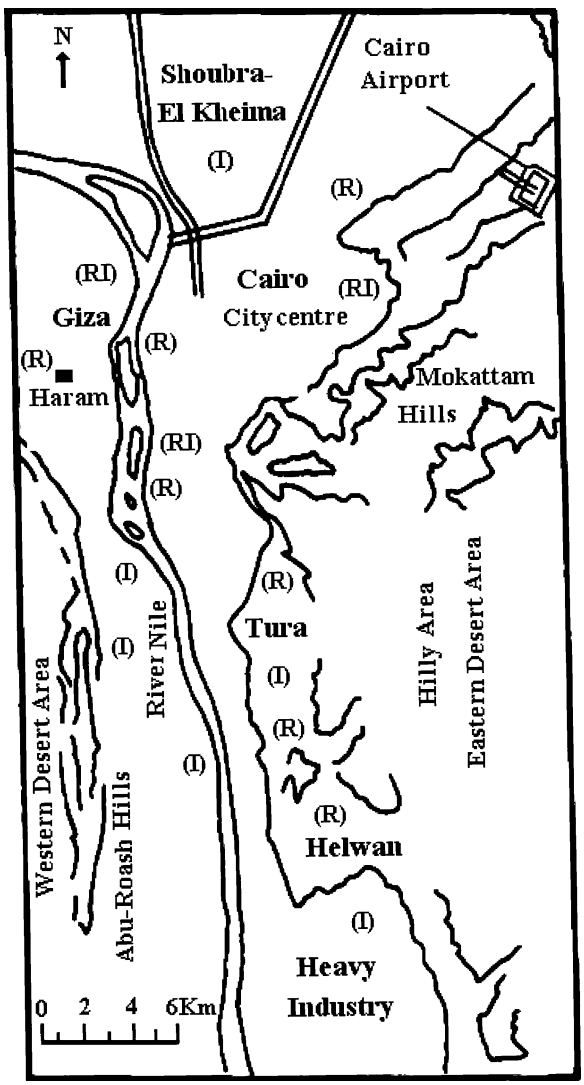

Fig. 1 Map of the greater Cairo areas showing districts of residentials (*R*), industrial (*I*), residential industrial (*RI*) activities and the sampling site (■)

summer. The prominent wind directions during the winter and summer seasons are north, north east and northwest. The average wind speeds were 8.68 km/h in the winter and 12.85 km/h in the summer. The mean values of global solar radiation were 10.99 MJ/m^2 in the winter and 24.98 MJ/m^2 in the summer.

The sampling location for measuring NO, NO_2, O_3 and meteorological parameters was installed in the urban area of Giza (Haram), located to the southwest of the Cairo city centre (Fig. 1). It is characterized by high traffic density, and parallel to the heaviest traffic street in Giza (Faisal Street). Sampling was carried out at a height of accurately 11.8 m above the ground level. Hourly ozone concentration was monitored from December 2004 to November 2005, two weekdays a week (without weekend days; Friday). However, NO, NO_2 and meteorological parameters were measured only during the winter and summer seasons to investigate the relationship between O_3 precursors and meteorological parameters and O_3 concentrations during the lower and higher photochemical reaction periods. The samples of NO and NO_2 were collected throughout 1 h intervals from 0600 to 0000 hours and one sample from 0000 to 0600 hours to observe the diurnal variations in NO and NO_2 concentrations. To study the weekend effect on the ground level O_3 concentration, NO, NO_2 and O_3 were measured during six weekends (Fridays) in summer season.

Sampling and analysis procedures

Dasibi ozone monitor (Dasibi, Model 1003-AH, Environmental Corp. Glendale, Calif. 91205) was used to monitor ozone concentration.

The NO and NO_2 gases were collected using a calibrated vacuum pump to draw 0.5 l min^{-1}. NO_2 was collected by bubbling air through a sodium hydroxide-sodium arsenite solution to form a stable solution of sodium nitrite (Harrison and Perry 1986). After scrubbing of NO_2, air sample was passed through oxidizing agent (acidic potassium permanganate) to oxidize NO to NO_2 (Stern 1968). The resulting NO_2 was collected by using the same method described above for NO_2 collection. The nitrite ion produced during sampling was reacted with phosphoric acid, sulfanilamide and *N*-(1-naphthyl)-ethylenediamine dihydrochloride to form an azo dye and then the absorbance of the sample against the reagent blank was measured at 540 nm by a spectrophotometer according to Harrison and Perry (1986). The air concentration of NO and NO_2 were calculated from the calibration standard curve and the volume of air.

Meteorological parameters

The temperature and relative humidity during winter and summer seasons were measured using a Sigma-II thermohygrograph (no. 7210, SK Sato Keiryoki MFG-Co., Ltd., Japan. Wind speed and direction, and solar radiation data were obtained from Egyptian Meteorological Organization.

Results and discussion

Monthly and seasonal variations of ground level ozone concentrations

The monthly variation of the daily 1 h maximum values, mean daytime (8 h from 0900 to 1700 hours) and daily (24 h) concentrations of O_3 during the period of study are graphically presented in Fig. 2. From this figure, it can be noticed that the highest monthly daytime and daily average O_3 concentrations were observed in the summer months (June–August), whereas the lowest concentrations were observed in the winter months (December–February). Monthly average values of ground level O_3 varied from 38.45 ppb (January) to 99.09 ppb (July) for daytime and from 26.38 ppb (January) to 68.14 ppb (July) for daily measurement. In addition, the highest daily 1 h maximum value of O_3 concentration was 143 ppb in July, whereas the lowest one was 50 ppb in January. The maximum hourly O_3 concentration in Haram is significantly high compared with those reported in other cities in the world, such as Sydney, 40 ppb (McKendry 1996), Los Angeles during 1994–1996, 50 ppb (Rizzo et al. 2002), Varanasi, India, 80 ppb (Pandey et al. 1992), Montreal, Canada, 45 ppb (McKendry 1993) and Conroe, 112 ppb (Kimura et al. 2008). In contrast, the maximum hourly O_3 concentration in Haram is lower than those found in downtown Houston (194 ppb) and La Porte (202 ppb; Kimura et al. 2008). In the present study, Table 1 shows the minimum, maximum, median and arithmetic mean daytime and daily concentrations of O_3 during the four seasons and the whole year of study

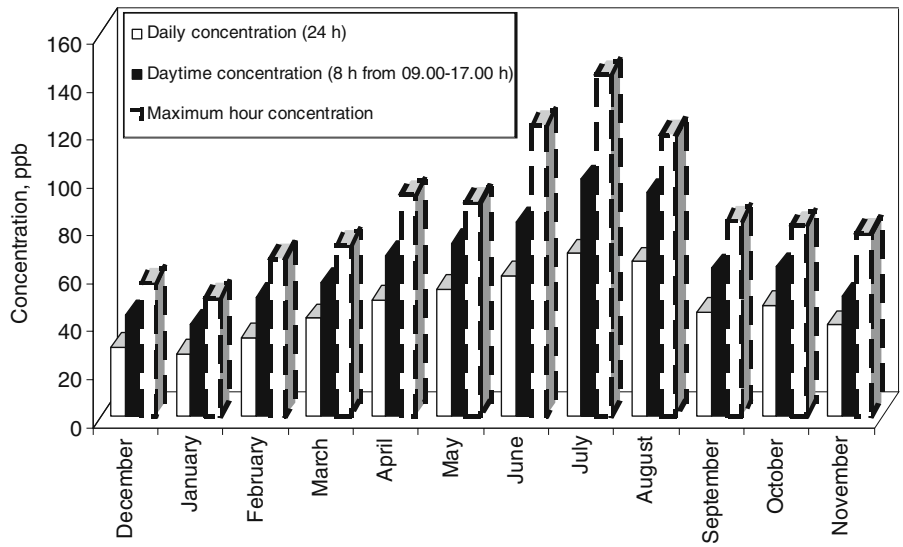

Fig. 2 Monthly variations of daily 1 h maximum, mean daytime and daily concentrations of ozone during the period of study

(annual), since the seasonal variation is the important characteristic of this pollutant. The highest daytime and daily O_3 concentrations were recorded during the summer, whereas the lowest levels were found during the winter season, and the difference in mean concentrations was statistically significant ($p<0.001$). The mean values of O_3 were 43.89, 65.30, 91.30 and 58.10 ppb in daytime (8 h) and 29.69, 47.80, 64.00 and 42.70 ppb in whole day (daily) during the winter, spring, summer and autumn seasons, respectively. The corresponding summer/winter ratios of O_3 concentrations were 2.08 and 2.16 during the daytime and whole day, respectively. The average daytime O_3 concentrations (8 h) exceeded the Egyptian air quality standard (60 ppb, 8 h average) and the European Union air quality standard (60 ppb, 8 h average) during the spring, summer and the whole year of study (annual; EEAA 1994 and Dueñas et al. 2002) and exceeded the National Ambient Air Quality Standards (NAAQS; 80 ppb, 8 h average) set by the US Environmental Protection Agency (Tong and Mauzerall 2006) during the summer season only.

Ground level O_3 concentrations can be determined as a result of source and sink mechanism, which relies on the prevailing levels of O_3 precursors (NOx and VOCs) and meteorological conditions in the environment such as, solar radiation intensity, temperature, relative humidity, wind speed and rain fall (Vukovich and Sherwell 2003; Pereira et al. 2005; Alvim-Ferraz et al. 2006; Pudasainee et al. 2006). Previous studies on the seasonal variations of O_3 concentration in other urban areas in Greater Cairo had observed that the highest levels of O_3 were in summer and the lowest levels were in winter (Rizk 1992; Khoder 1997, 2002 and 2004). The observed higher ground level O_3 concentrations during the summer months in the present study can be attributed to the higher solar radiation intensity and temperature that promote the photochemical generation of O_3. This agrees with the

Table 1 Mean daytime and daily concentrations of ozone during winter 2004–2005 to autumn 2005[a]

Season	Daytime (8 h)						Daily (24 h)				
	N	Minimum	Maximum	Median	Mean	S.D.	Minimum	Maximum	Median	Mean	S.D.
Winter	24	36.80	53.90	42.50	43.89	5.27	25.20	35.60	29.26	29.69	3.12
Spring	24	51.50	78.90	67.28	65.30	7.66	37.60	56.40	48.90	47.80	5.58
Summer	24	71.60	118.00	92.20	91.30	13.31	51.30	77.46	64.30	64.00	7.39
Autumn	23	47.80	71.13	54.75	58.10	8.23	33.60	51.10	42.60	42.70	4.43
Annual	95	36.80	118.00	63.40	64.70	19.56	25.20	77.46	45.30	46.10	13.48

S.D. Standard deviation, *N* number of sample

fact that O_3 in the summer season is associated with local photochemical production (Derwent and Davies 1994; Lin et al. 2001; Wolff et al. 2001; Kourtidis et al. 2002). The level of O_3 increases with the increase in the temperature and solar radiation intensity (Olszyna et al. 1997; Vingarzan and Taylor 2003; Vukovich and Sherwell 2003; Ribas and Peñuelas 2004; Garcia et al. 2005). On the other hand, the more stable atmospheric conditions and the increased frequency of nocturnal inversions in Greater Cairo during the winter months (Khoder 1997 and 2004) lead to an increase in the NOx concentration. In consequence, the destruction of O_3 is increased during the winter season as a result of higher NOx scavenging. Besides, the lower photochemical reactions in winter season due to the lower solar radiation intensity and lower ambient temperature lead to a decrease in the concentration of O_3. Low values of O_3 in winter months are attributed to low UV-radiation intensity and low ambient temperatures (Altshuler 1975).

Diurnal variations of O_3 and its precursors (NO and NO_2)

The study of the hourly variations of air pollutants within the day can provide valuable information about the sources, transport and chemical formation/destruction effects of such pollutants. The shape of O_3 cycles are strongly affected by levels of its precursors (NOx and VOCs) as well as the meteorological conditions (temperature and solar radiation; Rizk 1992; Khoder 1997; Alvim-Ferraz et al. 2006; Pudasainee et al. 2006). The diurnal variations in O_3 concentrations during the period of winter 2004–2005 to autumn 2005 are graphically presented in Fig. 3. From this figure, it can be noticed that, O_3 concentration reaches highest levels during the daytime and lowest levels in the nighttime during the four seasons. A uni-modal O_3 peak is seen for all seasons, with highest O_3 levels in summer followed by spring, then autumn and lowest levels in winter season. The broad peak of O_3 during daytime in summer season is attributed to higher temperature, higher solar radiation intensity as well as the longer sunlight hours, which are the favourable conditions to power the photochemical reactions, resulting high levels of O_3. Minimum values of O_3 concentrations appear in the nighttime and early morning hours (near sunrise). The O_3 concentration rises after the sun rises and reaches maximum levels at 1300 hours in winter and 1400 hours in spring, summer and autumn seasons, with mean values of 54.00, 73.92, 108.21 and 68.26 ppb during winter, spring, summer and autumn, respectively. After that time, a drop in O_3 concentration then begins. Variation in O_3 concentration had a tendency to follow the solar radiation intensity, resulting in higher O_3 levels during the daylight periods. This higher level in O_3 concentration during the daylight periods is attributed to the photochemical processes of O_3 formation. On the other hand, as the sun goes down in the evening and nighttime, the photochemical processing of O_3 is halted due to the absence of the photochemical reactions, and the O_3 that remains in the atmosphere is then consumed by deposition and/or reaction with NO which acts as a sink for O_3.

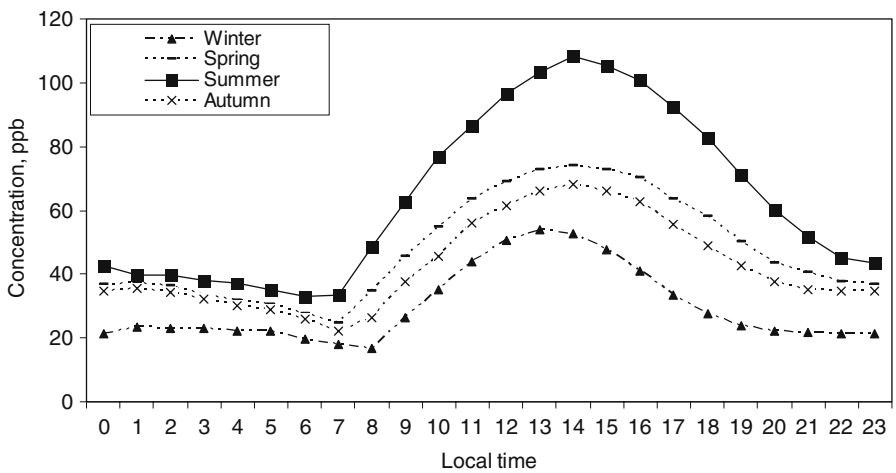

Fig. 3 Diurnal variations in ozone concentrations during winter 2004–2005 to autumn 2005

Consequently, the lower levels of O_3 in night can be attributed to in situ destruction of O_3 by deposition and/or reaction between O_3 and NO (Dueñas et al. 2002).

Diurnal variations in NO, NO_2 and O_3 concentrations during winter and summer seasons are graphically presented in Fig. 4. From this figure, it can be noticed that, the hourly concentrations of NO increases from 0600 to 0900 hours in winter (Fig. 4a) and from 0600 to 0800 hours in summer (Fig. 4b), then decreases in mid-day time. After that time, the concentration increases again to give a second peak in the evening. The morning peak is higher in magnitude than that of the evening peak. The trend of hourly concentrations of NO_2 was similar to that of NO concentrations with the exception of the times of the morning and evening peaks which are different (Fig. 4a and b). The diurnal cycle of these pollutants are related to the transportation/work cycle. During the morning time, the increase in the emission rate from traffic, accompanied with a poorer dispersive conditions due to the reduction of the thermal turbulence under the effect of low temperature and lower photochemical reaction lead to an increase in the concentrations of these pollutants. On the other hand, the lower concentrations of NO and NO_2 during mid-day time may be due to the high dispersion and high dilution conditions under the effect of high temperature, which increases the thermal turbulence currents. Moreover, the higher temperature and solar radiation intensity during mid-day time lead to increasing in the photochemical reactions and consequently increasing the chemical loss of these pollutants, the chemical loss of NO is titration with O_3, and photodissociation is the major loss of NO_2. This leads to decreasing the NOx concentrations at mid-day

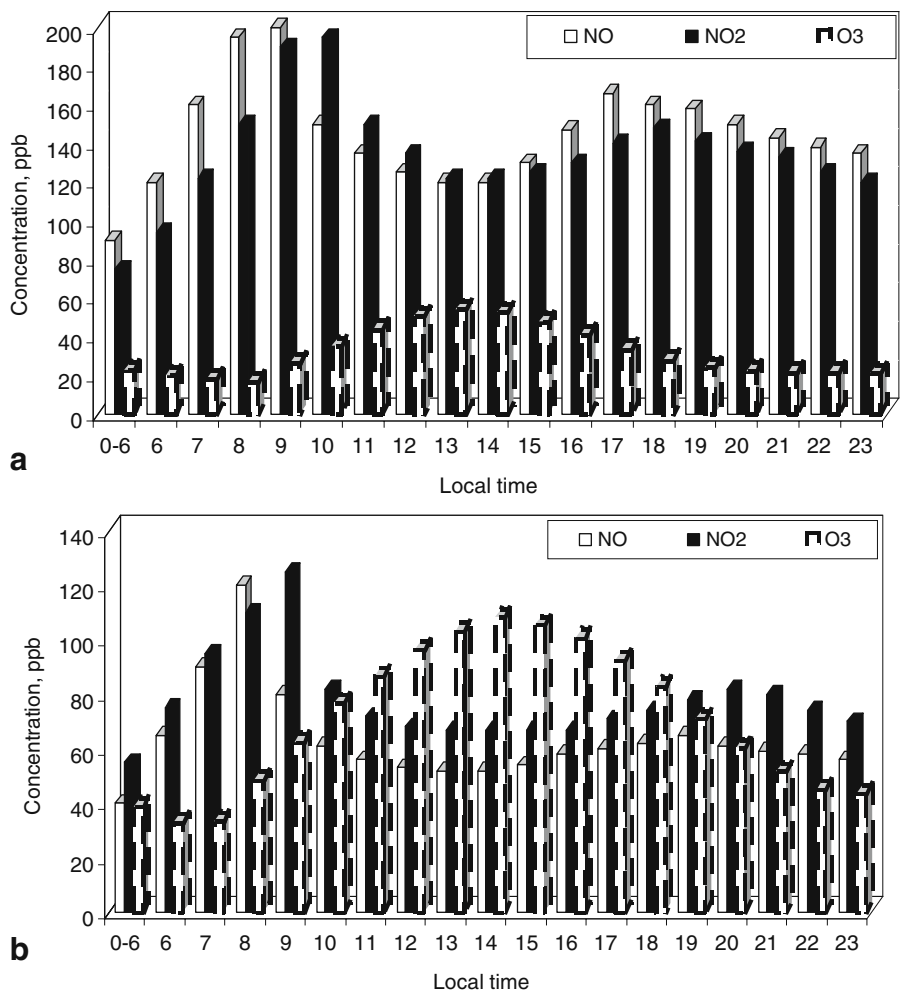

Fig. 4 Diurnal variations in NO, NO_2 and O_3 concentrations during winter (**a**) and summer (**b**) seasons

time. This is in agreement with Rao et al. (2002a, b) who found that the variations in NOx are caused by variations in boundary layer mixing processes, chemistry, anthropogenic emissions, and local surface wind patterns. In the present study, the peak formation of O_3 during winter is delayed by 4 and 3 h of the morning NO and NO_2 peaks, respectively (Fig. 4a). During summer, O_3 peak is delayed by 6 h of NO peak and 5 h of NO_2 peak (Fig. 4b). The high levels of NO during the morning hours in winter result in low concentrations of O_3 due to the rapid reaction between O_3 and NO.

In the present study, the highest levels of NO and NO_2 concentrations were found in winter. The corresponding winter/summer concentration ratios were 2.28 and 1.67 for NO and NO_2, respectively. The highest levels of NOx (NO and NO_2) during winter may be attributed to the meteorological conditions which are more favourable for the build-up of high NOx concentrations during that season. The highest levels of NO during the winter season lead to increased O_3 destruction, and correspondingly winter levels of ozone are depressed. This result confirms the high summer/winter concentration ratio of O_3 in the study area. Winter ozone levels are depressed due to the higher winter/summer NO concentration ratio (Bower et al. 1989). The reaction of NO with O_3 is about two orders faster than any other chemical loss reaction (LaI et al. 2000).

The frequency percentage distribution of the mean daytime (0900–1700 hours), daytime hour and daily hour concentrations of O_3 are graphically presented in Fig. 5. The Egyptian and European Union air quality standards for the mean daytime (8 h) O_3 concentration is 120 μg/m^3 (~60 ppb; EEAA, 1994 and Dueñas et al. 2002). About 75%, 100%, 34.78% and 52.63% of the mean daytime concentration of O_3 during spring, summer, autumn and the whole year, respectively, (Fig. 5a), exceeded the Egyptian and European Union air quality standards for maximum daytime (8 h) O_3 concentration. The Egyptian air quality standard for hourly O_3 concentration is 200 μg/m^3 (~100 ppb; EEAA 1994). Moreover, photochemical smog usually occurs when O_3 concentration exceeds 100 ppb (Guicherit et al. 1972). About, 41.14% and 10.39% of the daytime hours concentrations and 14.93% and 3.77% of the daily hours concentrations in summer and the whole year, respectively, exceeded the maximum hourly O_3 concentration set by EEAA, and photochemical smog is formed in the study area (Haram) during a periods represented by the same percentage (Fig. 5b and c).

Weekend/weekday variations in O_3, NO and NO_2 concentrations

The diurnal variations in NO, NO_2 and O_3 concentrations in the weekdays and weekends (Fridays) during the summer season are graphically presented in Fig. 6. As can be seen from this figure, the patterns of hourly variations in NO concentrations, i.e. the trend for increasing or decreasing, were similar during the weekdays and Fridays, with highest levels in the weekdays. The morning NO peaks were at 0800 hours for both weekdays and Fridays. During that

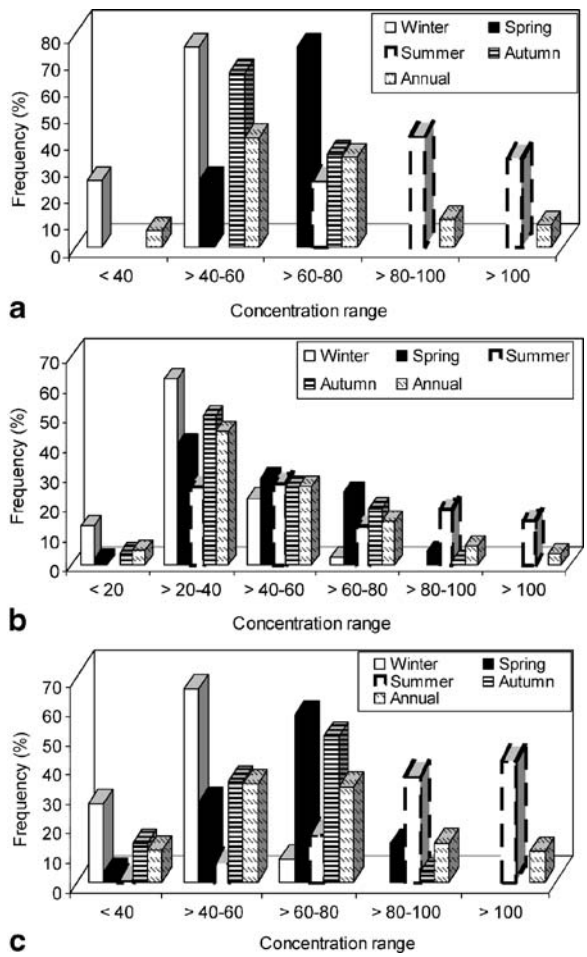

Fig. 5 Frequency percentage distribution of mean daytime (**a**), daily hour (**b**) and daytime hour concentrations of O_3 (**c**)

hour, the reduction of NO concentration on Fridays compared with the concentration of the weekdays during the same hour was 57.14%. Moreover, the average daily concentration of NO measured in weekdays was 35.89% higher than that measured in Fridays. NO_2 in ambient air originates mainly from the atmospheric oxidation of primary NO. The trend of NO_2 concentrations for increasing or decreasing in weekdays and Fridays is similar, with highest levels in the weekdays (Fig. 6). The highest values of NO_2 were at 0900 hours for both weekdays and Fridays. During that hour, the reduction of NO_2 concentration on Fridays compared with the concentration of the weekdays during the same hour was 43.26%. In addition, the daily average of NO_2 concentration measured in weekdays was 24.35% higher than that measured in Fridays. The reduction of NO and NO_2 levels in weekends (Fridays) is attributed to the reduction in the emission of these pollutants due to lower traffic density.

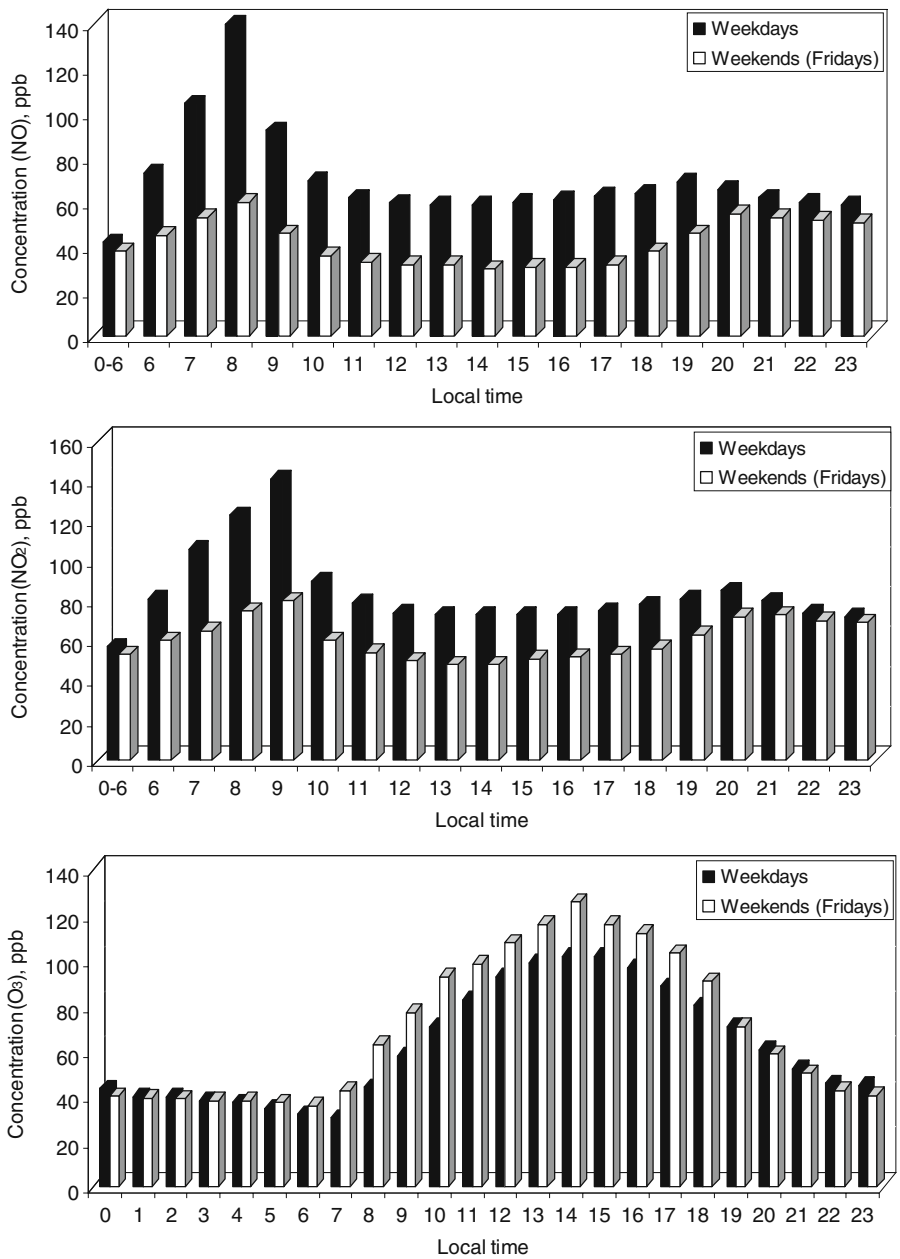

Fig. 6 Diurnal variations in NO, NO_2 and O_3 concentrations in weekdays and weekends (Fridays) during summer season

The formation and destruction mechanisms of O_3 determine the ground level O_3 concentration. The reduction in traffic density and consequently vehicle emissions on weekends compared with weekdays are used to examine the linkages between emitted O_3 precursors and ground level O_3 production. The phenomenon of weekend effect on O_3 occurs when O_3 concentrations tend to be higher during weekends compared to weekdays in some areas, despite the fact of lower emissions of O_3 precursors (NOx and VOCs) during weekends. The diurnal variations in O_3 concentrations during the weekdays and weekends (Fridays) showed a similar trend for increasing or decreasing in O_3 concentrations during the weekdays and Fridays, with high levels in Fridays (Fig. 6). The highest values were found at 1400 hours for both weekdays and Fridays. During that hour, O_3 concentration in Fridays was 19.05% higher than that found in weekdays. Moreover, the daytime (0900–1700 hours) average concentration of O_3 in Fridays was 16.78% higher than that found in weekdays. These results are in agreement with the previous studies which have reported high O_3 levels during weekends compared with weekdays, though, low concentrations of O_3 precursors (NOx and VOCs) at weekends (Qin et al. 2004; Sakamoto et al. 2005; Pudasainee et al. 2006). In the present study, O_3 concentrations during the weekends (Fridays) were higher compared with weekdays, whereas the levels of O_3 precursors (NO and NO_2) during weekends were lower than those found during weekdays. This phenomenon is known as the "weekend effect". The weekend effect on O_3 may be due to the decreased local emission of NO in weekends morning which consumes less O_3, and the latter cannot be further depleted during the daytime. In consequence, the accumulation of O_3 is increased during the daytime. The weekend effect on O_3 may be also due to difference in the reduction rate for the emission of NO_2 and VOCs during weekends and consequently on the prevailing ratio between [VOCs] and [NOx], since the formation of ground level O_3 depends on the concentrations of NOx and VOCs and the ratio between [VOCs] and [NOx]. Moreover, the relatively increase in the solar radiation intensity which results from the lower concentrations of fine particles in weekends due to the lower traffic density leads to an increasing in the photochemical formation of O_3 in weekends. This result is in agreement with Marr and Harley (2002a, b) who proposed that the less absorption of sunlight due to the lower fine particle concentrations at weekends results an enhanced O_3 formation during weekends. Altshuler et al. (1995) suggested that different dropped rate for NOx and VOCs emission inventories at weekends was a major cause of the weekend effect in the San Francisco Bay area. The most likely cause of higher levels of O_3 on weekends is a reduction in O_3 titration as a result of reduced vehicle emissions and hence, NOx levels (Atkinson-Palombo et al. 2006).

Association of O_3 with NOx, temperature and relative humidity

Ground level O_3 concentrations produced from photochemical reactions is influenced by the emission rates of the primary air pollutants (O_3 precursors) and meteorological parameters. Therefore, correlation coefficients between O_3 concentration and O_3 precursors (NOx) as well as meteorological parameters (temperature and relative humidity) during the winter and summer were calculated and summarized in Table 2. Statistically significant correlation coefficients ($p<0.001$) are highlighted in bold. Significant negative correlation coefficients were found between O_3 concentrations and NOx during both winter and summer seasons, indicating that an increase in O_3 level is associated with a drop in the concentration of NOx, since NOx is a precursor for O_3. Negative correlation coefficients were found between O_3 concentration and NO, NO_2 as well as NOx (Abdul-Wahab et al. 2005; Pudasainee et al. 2006). O_3 concentrations were positively correlated with temperature in the present study (Table 2), suggesting that high temperature leads to an increase in the formation of O_3. Higher temperatures are often associated with intense solar radiation, which would have a significant effect on the photochemical reactions and consequently on the O_3 formation. The favourable meteorological conditions (clear skies, warm temperature and soft winds) have a great influence on O_3 levels (Vecchi and Valli 1999). O_3 concentrations are positively correlated with temperature (Vukovich and Sherwell 2003; Pudasainee et al. 2006). In the present study, insignificant weak positive correlation coefficient was found between O_3 concentrations and relative humidity during the winter, whereas significant positive correlation coefficient was found during the summer season (Table 2). This result indicates that

Table 2 Correlation coefficients between nitrogen oxides (NOx), temperature, relative humidity and ozone concentrations during the winter and summer seasons

Season	N	Nitrogen oxides (NOx)	Temperature	Relative humidity
Winter	24	**−0.87**	**0.72**	0.32
Summer	24	**−0.75**	**0.88**	**0.68**

N Number of sample in statistical analysis

high relative humidity during summer season in the presence of high solar radiation intensity is an important factor for high O_3 concentration during that season. This result is in agreement with Vukovich and Sherwell (2003) who reported that high temperature and large concentrations of water vapor are a necessary, but not a sufficient, condition for high O_3. They added that the sufficiency condition is satisfied when significant amounts of solar radiation are reached and when stagnation conditions prevail in the surface layer during the same time. Positive correlation coefficients were found between monthly average concentrations of O_3 and relative humidity (Alvim-Ferraz et al. 2006).

Conclusions

Ground level O_3 is an important photochemical air pollutant. It is considered a key precursor of hydroxide radical which influences the concentrations of many primary air pollutants in the atmosphere.

Ground level O_3 concentrations were monitored during the period of December 2004 to November 2005 in an urban area in Greater Cairo (Haram, Giza). During the winter and summer seasons, NO_2 and NO concentrations and meteorological parameters were also measured. The highest daytime and daily O_3 concentrations were recorded during the summer, whereas the lowest levels were found during the winter. The summer/winter ratios of O_3 concentrations were 2.08 for the daytime and 2.16 for the daily levels. The diurnal cycles of O_3 concentrations during the four seasons revealed a uni-modal peak in the mid-day time, with highest O_3 levels in summer due to the local photochemical production. The lowest O_3 concentrations were found in the nighttime and early morning hours. The diurnal variations in NO and NO_2 concentrations during the winter and summer showed two daily peaks, one in the morning and the second in the evening, linked to traffic density. The morning peak is higher in magnitude than the evening peak. The highest levels of NOx were found in winter. The winter/summer concentration ratios were 2.28 for NO and 1.67 for NO_2. Nearly, 75%, 100%, 34.78% and 52.63% of the mean daytime concentrations of O_3 during spring, summer, autumn and the whole year, respectively, exceeded the Egyptian and European Union air quality standard (60 ppb) for daytime (8-h) O_3 concentration. About, 41.14% and 10.39% of the daytime hours concentrations and 14.93% and 3.77% of the daily hour concentrations in summer and the whole year, respectively, exceeded the Egyptian standard for maximum hourly O_3 concentration, and photochemical smog is formed in the study area (Haram) during a periods represented by the same percentages. This was based on the fact that photochemical smog usually occurs when O_3 concentration exceeds 100 ppb. The concentrations of O_3 precursors (NO and NO_2) in weekends were lower than those found in weekdays as would be expected, whereas the O_3 levels during the weekends were high compared with weekdays. Significant negative correlation coefficients were found between O_3 concentrations and NOx during both winter and summer seasons. The correlation coefficients between O_3 concentrations, temperature and relative humidity indicate that high temperature and high relative humidity in the presence of intense solar radiation (in summer) are responsible for the formation of high O_3 concentrations.

The results of this study indicate that O_3 concentrations at the study area violate the Egyptian air quality standard, especially during the summer season. However, the most important result obtained from the present study is that the weekend days have O_3 concentration exceed those of the weekdays. This finding phenomenon is known as the "weekend effect". So, O_3 control strategies should be applied in Greater Cairo in order to reduce the concentrations of O_3. In addition, more comprehensive study of the weekend O_3 effect would be required for better understanding of the sensitivity of O_3 formation to the emissions of NOx and VOCs and the causes of the weekend effect. This can be used to develop the corresponding emissions reduction policy for O_3 control strategies in Greater Cairo.

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