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Temporal Variations of O_3 and NO_x in the Urban Background Atmosphere of the Coastal City Jeddah, Saudi Arabia

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ABSTRACT

Ozone is a pollutant of major concern because of its well recognised effects upon human health and crop yields. This study analyses in depth a new dataset for ozone from Jeddah, a coastal city in Saudi Arabia within the Middle Eastern region, for which very few ozone data are currently available, collected between March 2012 and February 2013. The measurements presented include NO, NO_2 and ozone as well as relevant meteorological variables. The data show a marked seasonal variation in ozone with highest concentrations in the summer months and lowest average concentrations in the winter. Concentrations also show a substantial difference between weekdays and weekends, with higher NO and NO_2 on weekdays, but lower concentrations of ozone. Plots of total oxidant versus NO_x concentration indicate background concentrations of ozone (at zero NO_x) ranging from 38.2 ppb in January to 59 ppb in May consistent with the northern hemisphere spring maximum in ozone concentrations. The slope of total oxidant/NO_x varies from 0.13 in March to 0.68 in August. The two summer months of July and August are anomalous with slopes of around double that of other months, suggesting a higher efficiency of ozone production at lower primary pollutant concentrations arising from much reduced daytime traffic. A substantial weekend/weekday difference in ozone which is higher at weekends appears to be attributable to lower daytime traffic activity and hence reduced emissions of NO_x to a "NO_x-saturated" atmosphere.

Keywords: Ozone; oxides of nitrogen; Saudi Arabia; total oxidant; weekend effect; meteorological parameters

1. INTRODUCTION

Tropospheric photochemical reactions transform primary air pollutants into secondary pollutants. Photochemical oxidants are amongst the most important products formed during these reactions. Among these, ozone (O_3) is particularly important because it is a major constituent of photochemical smog and has deleterious effects on public health, various natural materials, manufactured goods, vegetation and forests. O_3 is one of the important greenhouse gases and contributes to global warming and climate change (IPCC, 2007). Moreover, it plays a critical role in tropospheric chemistry and is considered one of the key species affecting the chemical properties of the atmosphere since it is a key precursor of hydroxyl radical (OH) which controls the oxidizing power of the lower atmosphere (Thompson, 1992).

Ground level O_3 may arise from troposphere/stratosphere exchange, as well as from photochemical reactions taking place within the troposphere (Monks, 2000). It is formed in the troposphere through a series of complex photochemical reactions among its anthropogenic precursors, which include industrial and vehicular emissions of nitrogen oxides (NO_x = NO + NO_2) and volatile organic compounds (VOCs) in the presence of sunlight. In urban areas, the relation between photochemical O_3 production and the concentration of its precursors is not linear; it depends upon the concentrations of NO_x and VOCs, the ratio of NO_x to VOCs, and the intensity of solar radiation (Kleinman et al., 2001; Zhang et al., 2004; Tie et al., 2006). In some cases, O_3 formation is controlled almost entirely by NO_x and is largely independent of the amount of VOC (NO_x-sensitive), while in other cases, it increases with increasing VOC (VOC-sensitive) (Sillman, 1999). Increasing the concentration of VOCs always increases O_3 formation, whereas increasing NO_x leads to more or less O_3, depending on the prevailing ratio between [VOCs] and [NO_x] (Guicherit and Roemer, 2000; Sadanaga et al., 2003). NO_x emissions are mainly responsible for O_3 formation in rural areas, whereas VOCs are primarily responsible for O_3 formation in urban areas (EEA, 1998).

Nitrogen monoxide (NO) is emitted from combustion processes and is short lived because it is oxidized to produce NO_2 which plays a major role in O_3 production. In the presence of sunlight, O_3 is produced by the reaction of an oxygen molecule (O_2) with a ground state oxygen atom (O), which originates from the photolysis of nitrogen dioxide (NO_2) by solar radiation. Once formed, O_3 quickly reacts with NO regenerating NO_2 in the absence of VOCs. This, so-called ‘null cycle’, does not lead to a net production or destruction of O_3. The presence of VOCs in the atmosphere interacts with this mechanism through reactions driven by the hydroxyl radical (OH), leading to oxidation of NO and therefore, to accumulation of O_3 (Seinfeld and Pandis, 1998). VOC oxidation reactions are

mainly induced by OH radicals leading to the production of hydroperoxy (HO_2) and organic peroxy (RO_2) radicals. These radicals oxidize NO to NO_2 without consumption of O_3 and the photolysis of the resulting NO_2 by sunlight leads to an increase the accumulation of O_3 (Seinfeld and Pandis, 1998).

Variations in O_3 concentration are controlled by a number of processes including photochemistry, physical/chemical removal, and transport. Precursor emissions (NO_x and VOCs) can lead to elevated levels of surface O_3 locally and downwind and cause large diurnal, day-to-day, seasonal and year-to-year variations in O_3 levels as a result of complex meteorological influences and photochemical mechanisms (Solomon et al., 2000). Meteorological conditions have been shown to play an important role in O_3 formation and transport (Laurila, 1999; Thompson et al., 2001). High levels of O_3 might be registered within a city or at a distance downwind due to the high emissions of O_3 precursors in urban areas (Garcia et al., 2005). O_3 concentrations increase also with solar radiation and temperature elevation (Tecer et al., 2003).

The O_3 ‘‘weekend effect’’ is a common phenomenon of O_3 behaviour in the urban atmosphere: higher O_3 concentrations may occur on weekends compared to weekdays despite lower concentrations of O_3 precursors at weekends. This phenomenon has been recognised in several countries (Marr and Harley, 2002b; Qin et al., 2004; Paschalidou and Kassomenos, 2004; Jimenez et al., 2005; Gao et al., 2005; Riga-Karandinos and Saitanis, 2005; Sakamoto et al. 2005; Pudasainee et al. 2006; Sadanaga et al., 2008; Khoder, 2009). The mechanisms for the weekend effects on O_3 formation are still not well understood. However, several photochemical modeling studies and a wide range of environmental analyses (Marr and Harley, 2002a; Yarwood et al., 2003; Blanchard and Tanenbaum, 2003; Heuss et al., 2003; Lawson, 2003) have suggested that the primary cause of higher O_3 on weekends is the reduction in NO_x emissions in a VOC-limited chemical regime. Marr and Harley (2002a, b) proposed that less absorption of sunlight due to lower fine-particle concentrations at weekends, resulting in enhanced O_3 formation might be a cause for the weekend O_3 effect. Qin et al. (2004) suggested that VOC sensitivity combined with a decrease of NO_x emissions at weekends was the cause.

The recent rapid increase in urbanization, industrialization and human activities has important impacts on air quality in Jeddah city. As a result, the emissions of O_3 precursors (NO_x and VOCs) have significantly increased. Therefore, the problem of pollution has been shifted towards the so-called photochemical pollutants. The formation of these pollutants in the Jeddah atmosphere is

facilitated by the local climatic conditions (high temperature, intense solar radiation, clear sky), especially in the summer season. Therefore, it is very important to evaluate the diurnal and seasonal variations of ground level O_3 concentrations and their association with NO_x and meteorological parameters. Moreover, the difference in O_3 concentrations between weekdays and weekends is also considered. This will help in understanding the atmospheric chemistry over the semitropical region within which very few studies have been conducted, and in informing a strategy to control ground level O_3 and other photochemical oxidants and their build-up in smog episodes in the future. A recent complementary study has examined spatial patterns of NO_x and O_3 (Hassan et al., 2013).

2. MATERIALS AND METHODS

2.1 Study Area

Jeddah is the most significant commercial centre and the second largest city in the Kingdom of Saudi Arabia. It houses more than 3.4 million inhabitants. The city is surrounded by mountains in the north-east, east and south-east. The growth of the city over the last thirty years has been rapid and diverse, and continues to date (Saudi Network, 2008). Unfortunately, due to lack of awareness and proper regulations, these development activities have been accompanied by environmental degradation, and over the years the air quality has progressively deteriorated. Like almost everywhere else in the world, the Jeddah environment and its citizens' health are affected by both mobile and stationary sources. More than 1.4 million vehicles are running in the streets of Jeddah city (Khodeir et al., 2012). Vehicle fuels used in Jeddah are mainly unleaded gasoline and diesel. The stationary sources in this city include an oil refinery, a desalinization plant, a power generation plant and several manufacturing industries.

2.2 Sampling Sites and Periods

The sampling site for monitoring of NO, NO_2, NO_x, O_3 and meteorological parameters was chosen in an urban background area of Jeddah city (Jamea district), located in the southeast of the city (Figure 1). The geographic co-ordinates of this site are 21.4869^{o}N; 39.2517^{o}E and the altitude is 38.7 m asl. Most of the air pollutant emissions arise from the surrounding traffic activities. The site is 105 metres from the nearest road, and 1700 metres from the closest major highway.

Sampling took place from March 2012 to February 2013. All times cited are local time (UTC+3).

2.3 Measurements and Instrumentation

Sampling was carried out at a height of 3.5 m for gaseous air pollutants and 6.7 m for meteorological parameters above the ground level. NO, NO_2, NO_x, O_3 and meteorological parameter data were monitored continously from March 2012 to February 2013. A UV Absorption Ozone Analyzer (Model 400E, Teledyne Technologies Company, San Diego) was used to monitor ozone concentration. It is a microprocessor-controlled analyzer that uses a system based on the Beer-Lambert law for measuring low ranges of ozone in ambient air. Accurate measurements are obtained in the ranges of 0-100 ppb to 0-10 ppm, with a lower detection limit of < 0.6 ppb. A chemiluminescence $NO/NO_2/NO_x$ analyzer (Model 200E, Teledyne Technologies Company, San Diego) was used to monitor NO, NO_2 and NO_x concentrations. It uses the proven chemiluminescence detection principle, coupled with state-of-the-art microprocessor technology to provide measurements of $NO/NO_2/NO_x$ in the ranges of 0-50 ppb to 0-20,000 ppb full scale, with a lower detection limit of < 0.4 ppb. Ozone calibration was checked with an ozone generator with that of $NO/NO_2/NO_x$ by seven point dilution of a standard gas mixture using mass flow controllers. Quality control checks were performed every three days including inspection of the shelter and instruments as well as zero concentration check, precision and span checks. The filter was replaced once every two weeks and calibration was conducted every month. The O_3, NO and NO_2 concentrations were recorded every one minute.

Air temperature, relative humidity, windspeed and direction were measured continuously using Lufft WS600-UMB Compact Weather Station, simultaneously with measurements of atmospheric pollutant concentrations. Solar radiation was measured continuously using a solar radiation sensor (Vantage Pro2^{TM} Accessories, Davis Instruments, USA).

Daylight hours are 6am to 7pm in spring and summer, 6am to 6pm in autumn and 7am to 6pm in winter. Traffic levels remain high throughout the day, and extend into late evending as many facilities remain open.

3. RESULTS AND DISCUSSION

3.1 Influence of Meterological Parameters on O_3 Concentration

Data are disaggregated by season, i.e. winter (DJF), spring (MAM), summer (JJA) and autumn (SON). Surface hourly air temperature is highest during summer and varied from 27 °C to 43 °C. In the winter season, the temperature profile is at a minimum and varies from 18 °C to 37 °C.

Figure 2 shows the monthly variation of average temperature (Figure 2a), relative humidity (Figure 2b) and wind speed (Figure 2c) during the study period. Monthly average ozone concentrations both for all hours and for daytime hours appear in Figure 3.

O_3 followed a close relationship with solar radiation; and hence surface temperature. The highest daytime average O_3 concentration (44.1 ppb) was observed in August with the highest average air temperature (35 ^oC) and a minimum of 23.5 ppb in December (26^oC). Hourly O_3 concentration was weakly but significantly correlated with temperature for hourly data ($r= 0.33$, $p< 0.001$) in the present study. The favourable meteorological conditions (clear sky, high temperature and light winds) have a great influence on O_3 levels (Vecchi and Valli, 1999). The separate influences of temperature and solar radition are too closely linked to allow disaggregation; neither shows a strong seasonal cycle (see Figures 2(a) and (d)).

Average relative humidity was observed to be maximum in autumn and winter seasons while minimum in summer. It varied from around 52% in winter to about 40% in summer (Figure 2b) and thus exhibits a significant negative correlation for hourly data ($r = - 0.27$, $p < 0.001$) with O_3 concentration. Therefore, the negative relationship arises simply from the fact that relative humidity is low in summer, when ozone production is most efficient.

Positive correlation ($r= 0.78$, $p < 0.001$) was found between hourly O_3 and wind speed. This is quite a strong relationship which seems unlikely to be related to the seasonal pattern in wind speed (Figure 2(c)), and is probably explained by low NO_x concentrations due to enhanced dilution at high wind speed, borne out by a strong reduction in both NO and NO_2 concentrations with increasing wind speed (Figure S1). Pollution roses also show an increasing gradient of NO_x gases with winds when moving from NW to SE, and inverse behaviour for ozone. This probably reflects stronger average winds from the NW sector diluting NO_x emissions, rather than proximity of local sources.

3.2 Monthly Variations of O_3 and NO_x Concentrations

The highest monthly daytime (8 h from 09:00 to 17:00) and daily average O_3 concentrations were observed in the summer, especially August, with values around 45 ppb and 30 ppb, respectively (Figure 3). The daily concentration had another maximum in March with a value around 26 ppb. The lowest concentrations were observed in the cooler months of October – February with values as low as 18 ppb and 24 ppb for the daily and daytime concentrations, respectively. Figure S2 shows

seasonally averaged data. In the present study, the average daytime O_3 concentrations (8 h) during the four seasons fell below the European Union air quality standard (60 ppb, 8 h average). These are also below the National Ambient Air Quality Standards (NAAQS; 75 ppb, 8 h average) set by the US Environmental Protection Agency. However, 20.6% of daytime 8-hourly ozone concentrations exceeded 50 ppb, and 3.4% exceeded the EU standard of 60 ppb. In the case of hourly concentrations, 7.3% of daily maximum hourly concentrations exceeded 60 ppb and 0.2% exceeded 75 ppb.

The monthly variation of mean daytime, nighttime and daily NO and NO_2 concentrations during the period of study are graphically presented in Figure 4. The highest daytime average NO and NO_2 concentrations were observed in May, whereas the lowest concentrations were observed in July and August. The mean daytime, nightime and daily concentrations of NO and NO_2 during the four seasons are graphically presented in Figure S3. The average concentrations of NO_2 in daytime and nighttime were similar, except in summer where the nighttime average concentration was higher than the daytime. On the other hand, the daytime concentration of NO was higher than the nighttime, except in summer where the nighttime average concentration was higher than the daytime. Data appear in Table S2. Because of high temperatures in daytime during the summer season in Jeddah city and the official days-off of government institutions, schools and colleges, most of the people stay home, and consequently the density of traffic during daytime is decreased. Therefore, low concentrations of NO_2 and NO are observed in daytime. On the other hand, after sunset the weather becomes more suitable for going out for shopping and travelling, and the traffic continues to flow until about midnight on weekdays. The traffic continues after midnight on Fridays and even longer until morning during Ramadan (20th July to 18th August). This led to greater emissions of NO_x at nighttime than daytime, and consequently the levels of these pollutants were higher at nighttime compared to daytime. Ratios of NO_2/NO_x are higher in the summer months (Figure 5) favouring higher ozone concentrations.

VOC are an important ozone precursor, but were not measured comprehensively in this study. However BTEX compounds, which contribute substantially to ozone formation were measured, and are being reported elsewhere (Alghamdi et al., 2014). Concentrations were broadly comparable with those of other cities and were highest overall in spring and summer. Although their potential for ozone formation is greatest in these seasons, it appears probable that NO_x concentrations are a greater determinant of ozone through the reaction of ozone with NO.

3.3 Diurnal Variation of O_3 and NO_x Concentrations

The study of diurnal variations of air pollutants can provide valuable information about the sources, transport and chemical formation/destruction effects of such pollutants. In addition, the diurnal variations have a major influence on exposure levels at sites nominally exposed to the same regional ozone distribution. The physical and chemical mechanisms which give rise to diurnal variations are detailed so that sites can be screened for different diurnal behavior characteristics (Derwent and Kay, 1988). The shapes of O_3 cycles are strongly affected by the levels of its precursors (NO_x and VOCs) as well as the meteorological conditions (temperature and solar radiation (Alvim-Ferraz et al., 2006; Pudasainee et al., 2006; Khoder, 2009). The diurnal variations in O_3 concentrations during the period of study are graphically presented in Figure 6. From this figure, it can be seen that the O_3 diurnal variation of each season showed a similar pattern, but the magnitudes of variations were different. O_3 concentrations reached a maximum during daytime and a minimum in the nighttime during all four seasons. The diurnal pattern of O_3 for each season is characterised by a maximum concentration in the afternoon. Its variation in different seasons generally coincides with the amount of solar radiation where O_3 reaches a peak value in the afternoon hours, and then continuously decreases until midnight. Rates of rise and fall are described in Table S1. 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 the winter season. The broad peak with higher amplitude of O_3 during daytime in the 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, and higher NO_2/NO_x ratios resulting in high levels of O_3. Minimum values of O_3 concentrations appear in the nighttime and early morning hours (near sunrise). The time of sunrise is a turning point of diurnal O_3. The O_3 concentration rises gradually just after the sun rises and reaches maximum levels at 1400- 1600 hours in winter and 1300-1400 hours in spring, summer and autumn seasons (Figure 6). After that time, O_3 concentrations decrease progressively until evening, and then keep decreasing more gradually, maintaining low values over night hours due to lack of solar radiation. O_3 production rate increases at low NO_x until a maximum is reached and then decreases at high NO_x (Sillman et al., 1990). This pattern occurs because high NO_x promotes removal of OH radicals by the reaction of OH with NO_2 (Zhang et al., 2004). 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 (Colbeck and Harrison, 1985) and/or reaction with NO which acts as a sink for O_3 (Dueñas et al., 2002). The decrease in O_3 during the early morning hours of the day at 0700–0800 h local time in winter, spring and autumn and at 0200 h local time in summer (Figure 6) is mainly due to the increase in traffic flow (rush

hours) and fresh NO emissions in all seasons. Measurements of traffic flow on a major North-South highway in Jeddah (Melibari, 2011) show a minimum at around 4 am followed by a rush-hour peak at 7 am, slightly reduced levels of traffic from 8 am to 4 pm, followed by an evening peak around 6 pm and high traffic levels until midnight, declining rapidly thereafter. Such a pattern, modified by better atmospheric mixing during daytime is seen in NO_x concentrations in Spring, Autumn and Winter (Figure 9).

Diurnal variations in NO and NO_2 concentrations during the period of study are graphically presented in Figure 6. From this figure, it can be seen that the hourly concentrations of NO increased from 0600 to 0800 hours in spring, autumn and winter and from 0000 to 0200 and 0500 to 0600 hours in summer (Figure 6a), then decreased in mid-day time. The apparently anomolous behaviour in summer results from human activity occurring mainly during nighttime hours when air temperatures are lower. After that time, the concentration increases again in the evening. Data appear in Table S3. The diurnal behavior of NO_2 was similar to that of NO, with a slightly different pattern (Figure 6). The diurnal cycles of these pollutants are related to the transportation/work cycle. During the morning time, the increase in the emission rate from traffic, accompanied by poorer dispersive conditions due to the shallower boundary layer, lead to an increase in the concentrations of NO_x. On the other hand, the lower concentrations of NO and NO_2 during mid-day time may be due to the better dispersion caused by increased convective activity. Moreover, the higher temperature and solar radiation intensity during midday leads to increases in the photochemical reactions and consequently increases in the chemical loss of these pollutants. 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. Apart from this, it is difficult to disentangle the effects of the various influencing factors.

Many facets of the data are comparable with those reported by Mavroidis and Ilia (2012) for urban background and suburban background sampling stations in Athens. Ozone in Jeddah shows a minimum during the morning rush hour, and an afternoon maximum (Figure 6), in reverse cycle to that of NO_x, as in Athens. Daytime ozone concentrations (Figure S1) show a similar seasonal cycle in both cities.

3.4 Concentrations of Total Oxidant (O_x)

Valuable insights into processes affecting ozone can be gained from application of the approach pioneered by Clapp and Jenkin (2001). This involves plotting the sum of ozone and nitrogen

dioxide (referred to as O_x) against the concentration of NO_x (Figure 7). The concentration of O_x at zero NO_x is the regional tropospheric ozone background and appears as the intercept in the plot. The gradient of $[O_x]/[NO_x]$ reflects sources of oxidant that increase with NO_x, which might include primary emissions of NO_2, or photochemical formation of ozone. Plots were conducted for each month of daytime data.

The oxidant intercept, or background ozone (Figure 7) ranged from 38.2 ppb in January to 59.0 ppb in May. This variation appears to be consistent with the spring maximum normally observed in northern hemisphere surface ozone measurements (e.g. Monks, 2000) and reported by Clapp and Jenkin (2001) in their UK dataset. These concentrations are higher than most concentrations measured in Jeddah, due to NO-related suppression of ozone in the city. The slope also shows substantial variation, from 0.13 in March to 0.68 in August. The two summer months of July and August are notably different from the other months, with slopes of around double the magnitude. This is consistent with the high average summer ozone concentrations seen in Figure S2. As the seasonal variation in solar radiation (Figure 2) is not great, it seems likely that this increase in daytime ozone may result predominantly from increased efficiency of ozone production at the lower NO_x concentrations seen in Figure S3. The alternative explanation of an increased NO_2/NO_x ratio in residual traffic emissions in summer seems unlikely.

3.5 Weekend/Weekday Variations in NO, NO_2, No_x and O_3 Concentrations

The formation and destruction mechanisms of O_3 determine the ground level O_3 concentration. The differences in NO_x and O_3 concentrations during the days of the week are observed mainly within areas with an influence from urban emissions, with lower NO_x levels and higher O_3 values at weekends than on weekdays. This is caused by weekly changes in emissions from human activities. This emission-concentration relationship at urban, suburban and rural sites is open to different interpretation (Jenkin et al., 2002; Fujita et al., 2003; Stephens et al., 2008). In regions where weekday and weekend O_3 values are approximately the same, the processes of background or long–range transport dominate, while sites dominated by regional or local anthropogenic O_3 production present weekday–weekend differences (Heuss et al., 2003). So, a study of weekday and weekend differences in O_3-NO_x levels is a valuable indicator of whether O_3 has its origin in local photochemical production or in transport processes. In Jeddah, weekdays are taken from Saturday to Thursday while weekend is Friday (an Islamic custom). In order to study the weekend effect in the study area, O_3 and NO_x daily evolution was examined on weekdays and at weekends in all four

seasons, as well as the daily average difference between weekend and weekdays (weekend minus weekdays).

The diurnal variations in NO and NO_2 concentrations on the weekdays and weekends (Fridays) and the weekday/weekend concentration ratios during the four seasons are graphically presented in Figure 8. The patterns of hourly variations in NO concentrations, i.e. the trend for increases or decreases, were similar during the weekdays and Fridays (except in Spring), with highest levels on the weekdays. NO_2 in ambient air originates mainly from the atmospheric oxidation of primary NO. The trend of the hourly concentration of NO_2 for increases or decreases during the weekdays and Fridays was also similar, with highest levels on the weekdays. The lower levels of NO and NO_2 at weekends (Fridays) are attributed to the reduction in the emission of these pollutants due to lower traffic density.

The reduction in traffic density and consequently vehicle emissions on weekends compared with weekdays is used to examine the linkages between emitted O_3 precursors and ground-level O_3 production. The phenomenon of a 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 (NO_x and VOCs) during weekends. The ground-level O_3 concentration over the urban areas of Jeddah city depends on photochemical production of O_3 related to NO_x concentration. Vehicle traffic is the major source of NO_x emission at the studied urban site, where it is assumed that the weekend traffic density is lower than on weekdays due to the official days-off of government institutions, schools and colleges. However, in spite of low weekend NO_x emissions, an elevated O_3 concentration was observed at the study site. Figure 9 shows the diurnal variations in NO_x and O_3 concentrations at the weekdays and weekends (Fridays) and the difference between weekends and weekdays (weekends minus weekdays) during the period of study. The O_3 concentration on weekends was greater than weekdays during all four seasons.

The occurrence of a weekend O_3 effect was determined by the differences in O_3 concentration between weekend and weekdays. Blanchard and Fairley (2001) and Fujita et al. (2003) classified the criteria used to identify the status of the weekend effect into three categories: a) intense weekend effect if O_3 difference is > 15 ppb; b) moderate weekend effect if O_3 difference is 5-15 ppb; and c) no weekend effect if O_3 difference is < 5 ppb. Using the above criteria, it can be seen that a moderate weekend effect was observed in all seasons. The mean hourly daytime difference between weekends and weekdays (weekends minus weekdays) ranged from 8.2 ppb to 16.2 ppb in

spring, 5.1 ppb to 8.8 ppb in summer, 4.2 ppb to 8.5 ppb in autumn, and 4.6 ppb to 13.4 ppb in winter (Figure 9 and Table S4). The weekend O_3 effect is significant in spring and winter. Meteorological conditions are also responsible to some extent for an intense weekend O_3 effect on a seasonal basis; however, it appears that differences in concentrations of O_3 precursors (NO_x and VOC) are a major cause for the weekend O_3 effect in the study area. At traffic influenced sites, increased vehicular traffic density from Saturday to Thursday leads to increased NO emission which is responsible for decreased O_3 concentrations on weekdays compared to weekends due to the rapid reaction of NO with O_3. Hence the weekend effect on O_3 is attributable to the decreased local emission of NO on weekend mornings which consumes less O_3, and the latter cannot be further depleted during the daytime (Atkinson-Palombo et al., 2006). In consequence, the accumulation of O_3 is increased during the weekend daytime. The different reduction rates for the emissions of NO and VOCs during weekends (Altshuler et al., 1995) and consequently the prevailing ratio between [VOCs] and [NO_x] may lead to increased O_3 at the weekend. The weekend O_3 phenomenon depends largely on differences in NO_x concentration between weekday and weekend; lower NO levels and VOC emissions on weekend mornings consume less O_3 which accumulates later by photochemical reactions (Pudasainee et al., 2006) which may be more efficient in a lower NO_x environment. Khoder (2009) also found many sites in Cairo with elevated O_3 on weekends when traffic and O_3 precursor levels were substantially reduced. Moreover, the relative increase in solar radiation intensity which results from the lower concentrations of fine particles at weekends due to the lower traffic density can lead to an increase in the photochemical formation of O_3 at weekends (Marr and Harley, 2002a, b). O_3 levels in the ambient air increased when emissions of NO_x decreased (Heuss et al., 2003; Bernstein et al., 2004; Sadanaga et al., 2008; Roberts-Semple et al., 2012). Similar observations were made in a potential non-attainment area of Cincinnati, Ohio where a reduction in NO emissions contributed to an increase in local O_3 (Torres–Jardon and Keener, 2006).

It is clear from the data that concentrations of NO_x, and especially NO are substantially lower at the weekend than on weekdays. This is also the case during daytime in the summer season. It is unclear to what extent VOC concentrations decrease as there are no data, or what compositional changes may occur between weekdays and the weekend. Qin et al. (2004), working in southern California also reported a reduction in NO_x at weekends, accompanied by an increase in ozone at most sites. VOC concentrations were reduced, but the mixture composition remained unchanged. It seems probable that motor vehicles are the main local source of VOC in Jeddah and that a similar situation prevails. If so, the main driver of the weekday-weekend effect and summer increase in ozone seems

likely to be the reduction in NO emissions and its effect upon the photostationary state through an increase in NO_2/NO_x ratio accompanying a reduced titration of ozone by NO. This reflects an atmosphere which is effectively "NO_x-saturated" with respect to ozone formation. It also seems likely that ozone production efficiency is enhanced by the reduction in NO_2 and VOC levels, as these are major sinks for the key free radical species involved in conversion of NO to NO_2 without consumption of ozone.

4. CONCLUSIONS

This is to our knowledge the most comprehensive analysis of an ozone dataset from a country of the Middle Eastern region. The concentrations of ozone are overall unexceptional for a polluted atmosphere, and some facets of the data are very similar to those in other parts of the world, whilst some are less so. An analysis of the total oxidant data following the method of Clapp and Jenkin (2001) reveals a typical northern hemisphere spring maximum in ozone although the background levels are exceptionally high for a low altitude site at over 50 ppb (Parrish et al., 2012). This may represent enhanced formation of ozone in background air due to the high photochemical reactivity of the region or enhanced vertical transport of stratospheric ozone. The data show the months of July and August to be exceptional in terms of ozone production efficiency (the gradient of the total oxidant/NO_x) plot which reflects the much lower daytime traffic activity and emissions of precursor pollutants during these months. There is also a substantial weekday/weekend difference with higher NO_x concentrations on weekdays accompanied by lower ozone than at weekends. It appears that the reduced titration of ozone with NO and consequent enhanced NO_2/NO ratio in July and August and at weekends is influencing the photostationary state, but also the oxidant plots suggest enhanced ozone production efficiency at the lower NO_x concentrations possibly because of the reduced influence of NO_2 and VOC as a sink for free radical species.

Overall, the data show the region to be in many ways similar to other areas with high traffic emissions and a photochemically reactive atmosphere, although there are some significant differences associated in the main with cultural factors affecting road traffic emissions. Further studies including both roadside and rural sites would lead to a deeper understanding of the ozone climate of the region. Collection of traffic data, unavailable to this study would also assist in data interpretation.

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FIGURE LEGENDS

Figure 1: Map of Jeddah with the sampling site marked with a star. Map data © Google, 2013 Terra Metrics.

Figure 2: Monthly variation of (a) temperature, (b) relative humidity, (c) wind speed and (d) solar radiation.

Figure 3: Monthly variations of mean daytime and daily concentrations of ozone during th period of study.

Figure 4: Monthly variations of daytime, nighttime and daily concentrations of NO and NO_2 during the period of study.

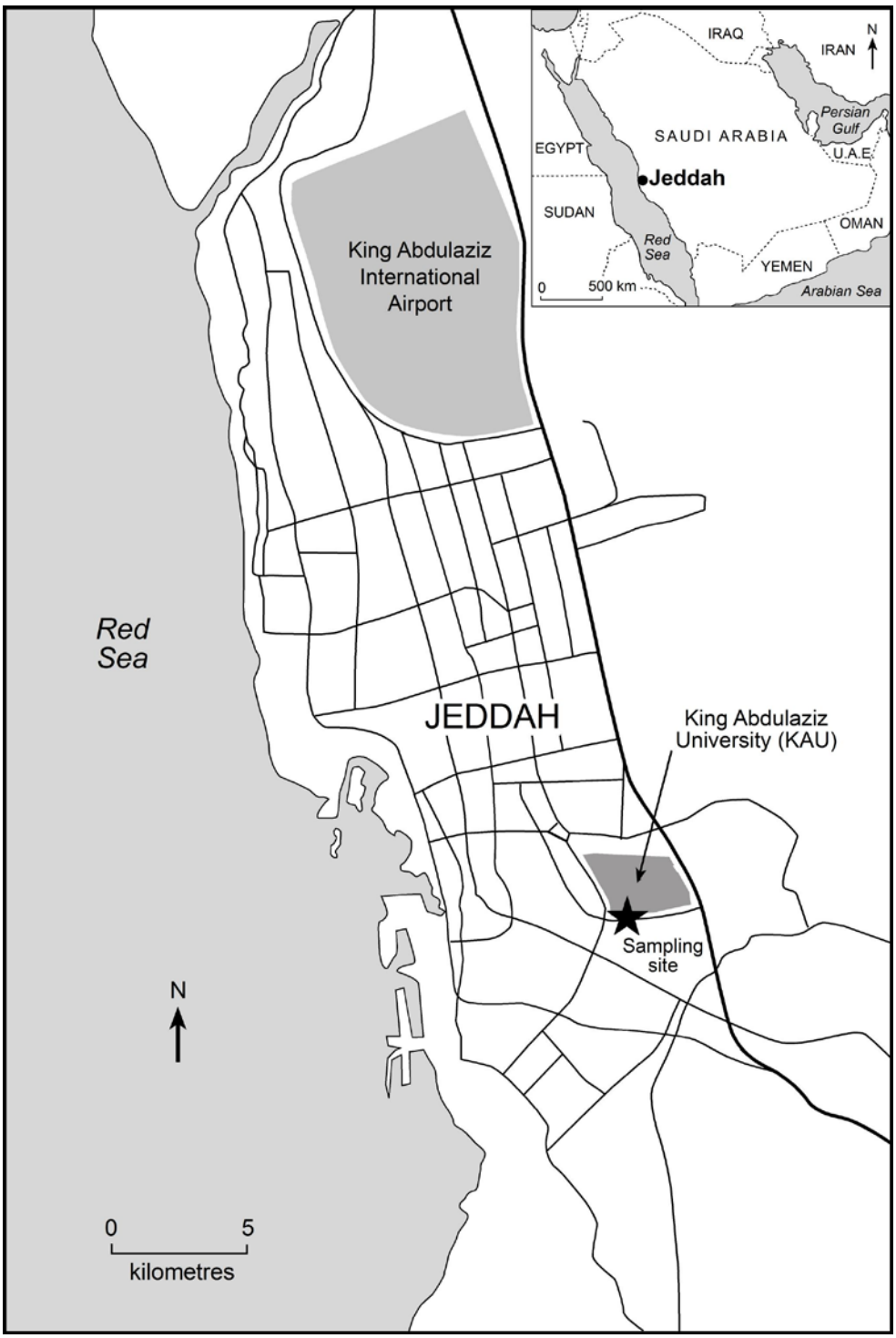
Figure 5: Monthly variations of NO_2/NO_x concentration ratios.

Figure 6: Diurnal variations in NO, NO_2 and O_3 concentrations during the different seasons.

Figure 7: Gradient and intercept of a plot of total oxidant ($O_3 + NO_2$) versus NO_x concentration for daytime samples for each month (equation $O_x = bNO_x + a$).

Figure 8: Diurnal variations of NO and NO_2 concentrations on weekdays and weekends (left column) and weekday/weekend concentration ratios (right column) during the different seasons.

Figure 9: Diurnal variations of NO_x and O_3 on weekdays and weekends and weekend minus weekday concentrations (ppb) during the different seasons.



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642 **Figure 1.** Map of Jeddah with the sampling site marked with a star. Map data © Google, 2013
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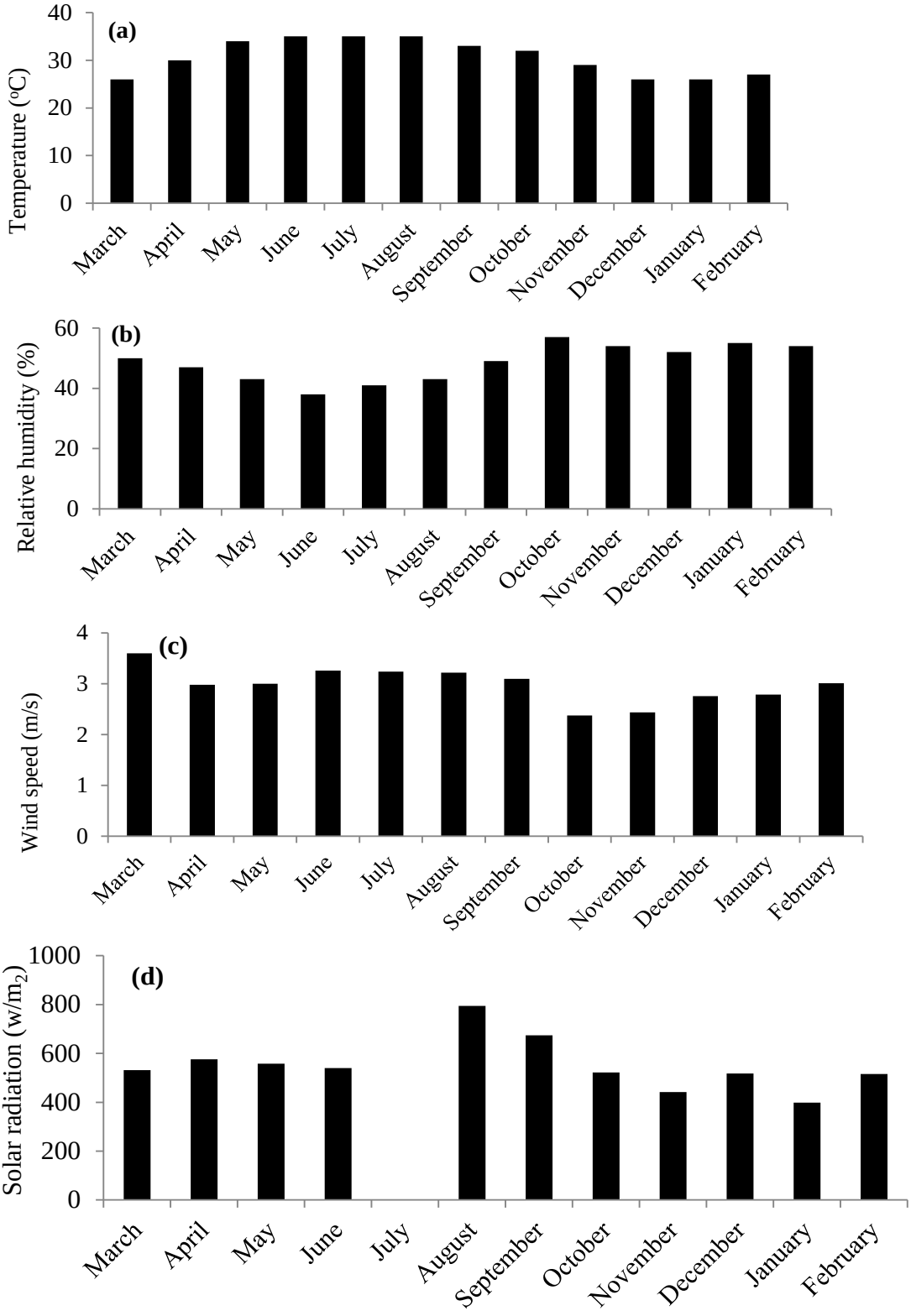
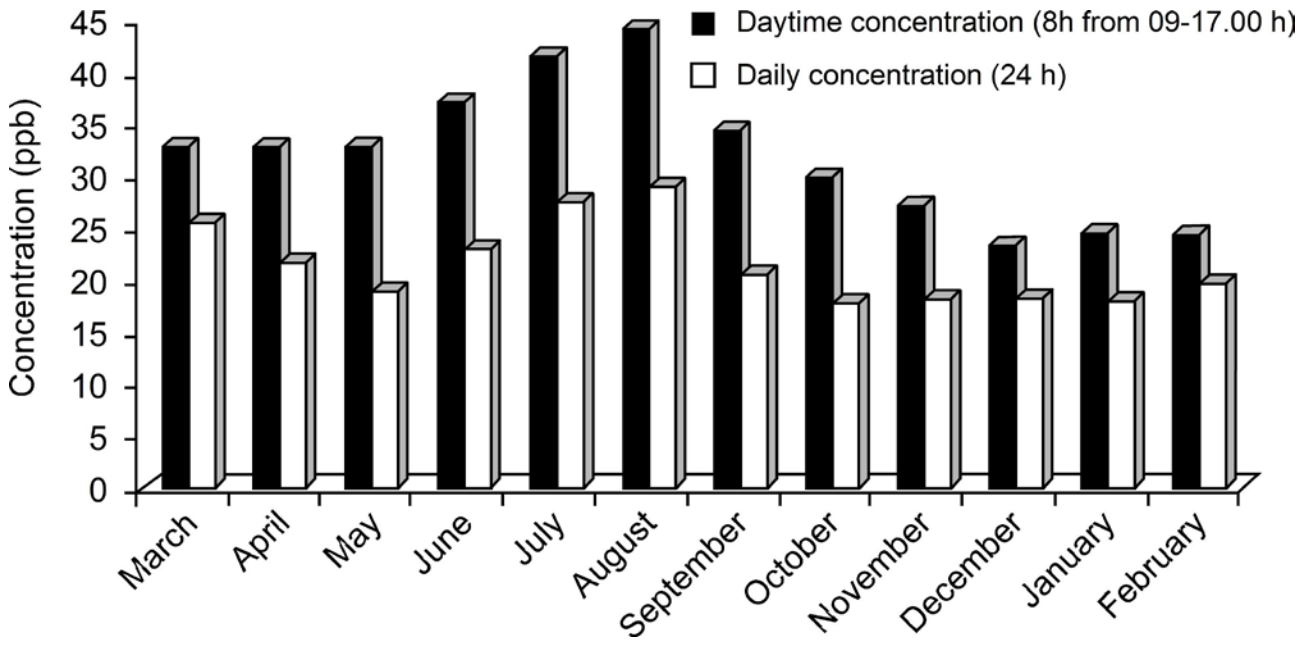


Figure 2. Monthly variation of (a) temperature, (b) relative humidity, (c) wind speed and (d) solar radiation



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651 **Figure 3.** Monthly variations of mean daytime and daily concentrations of ozone during the period
652 of study

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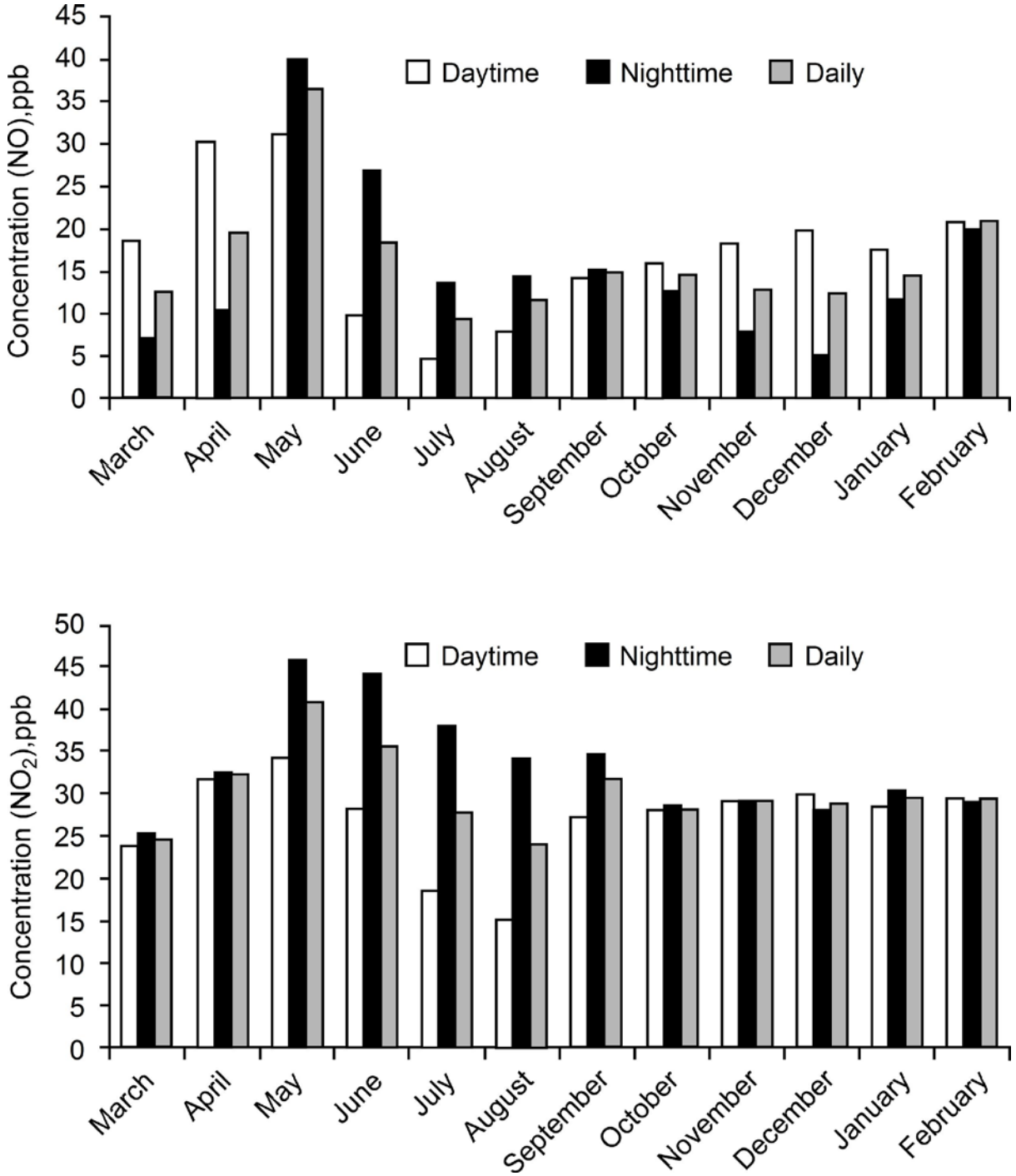

Figure 4. Monthly variations of daytime, nighttime and daily concentrations of NO and NO_2 during the period of study

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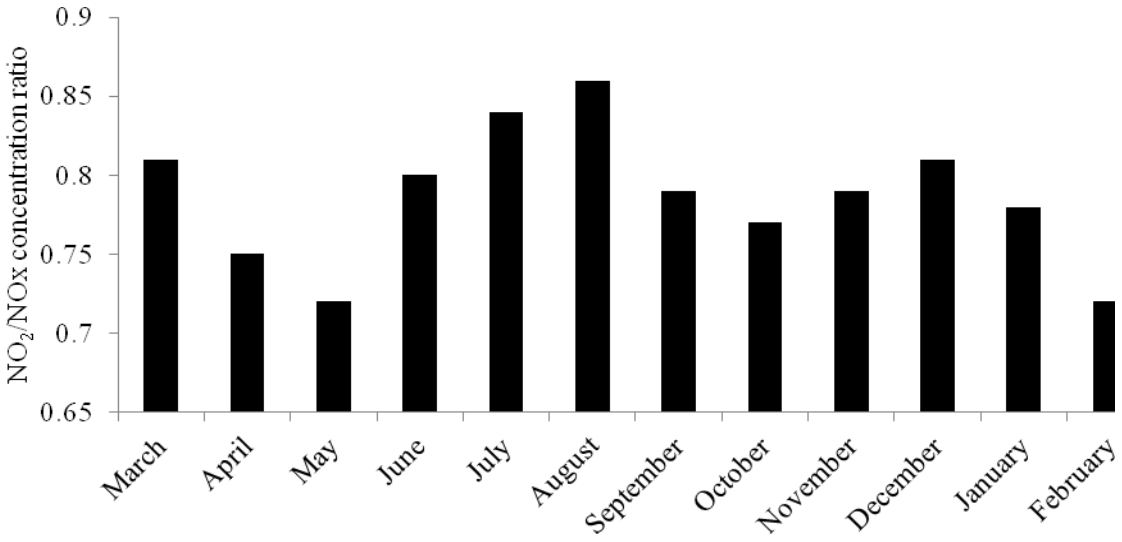

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665 **Figure 5.** Monthly variations of NO_2/NO_x concentration ratios

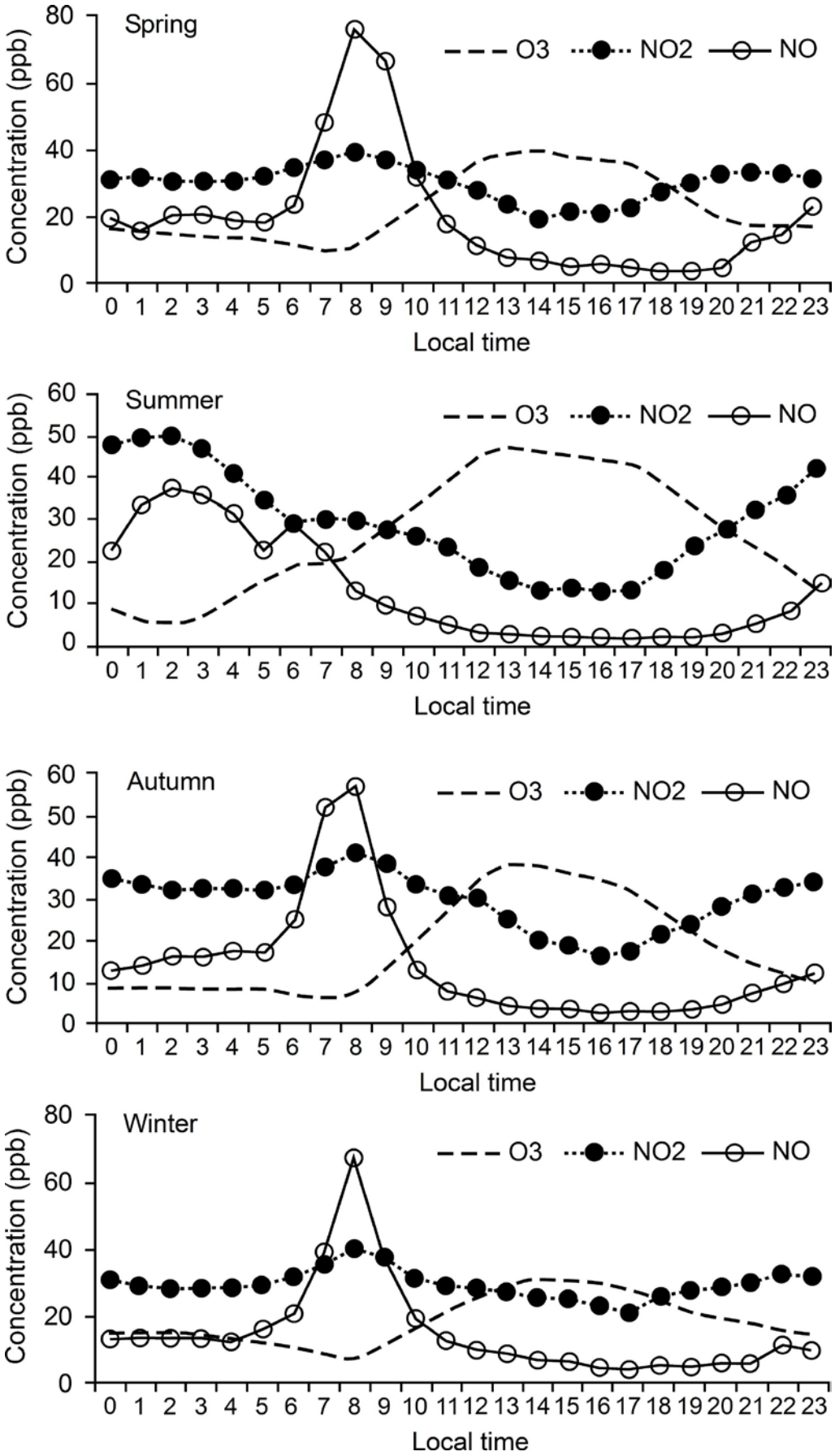
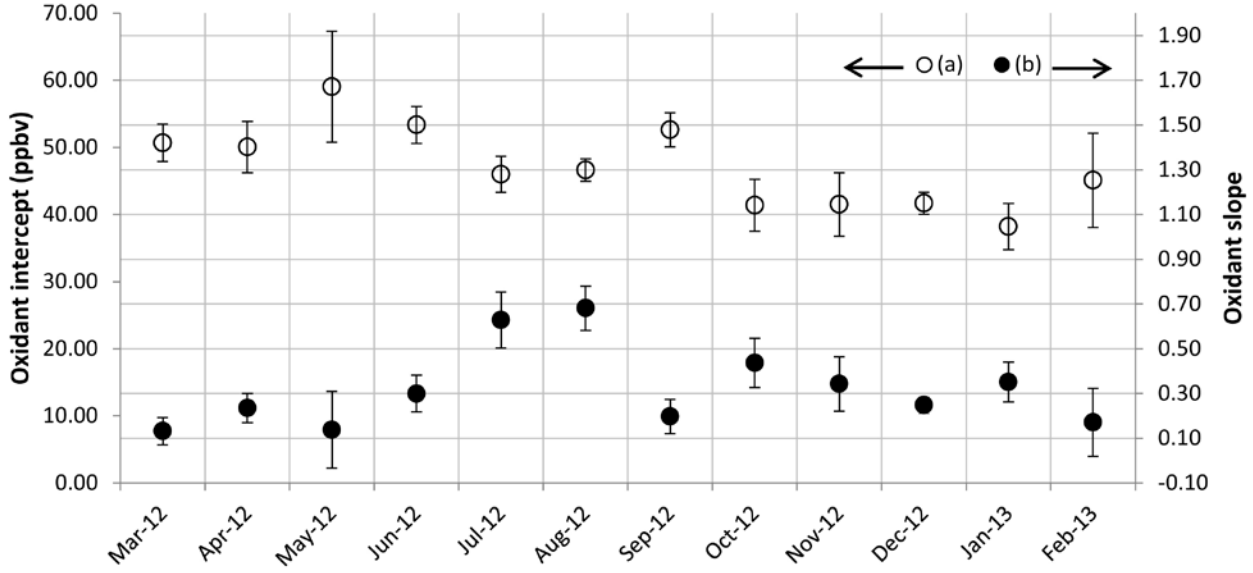


Figure 6. Diurnal variations in NO, NO_2 and O_3 concentrations during the different seasons



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671 **Figure 7.** Gradient and intercept of a plot of total oxidant (O_3 + NO_2) versus NO_x concentration for
672 daytime samples for each month (equation $O_x = bNO_x + a$)

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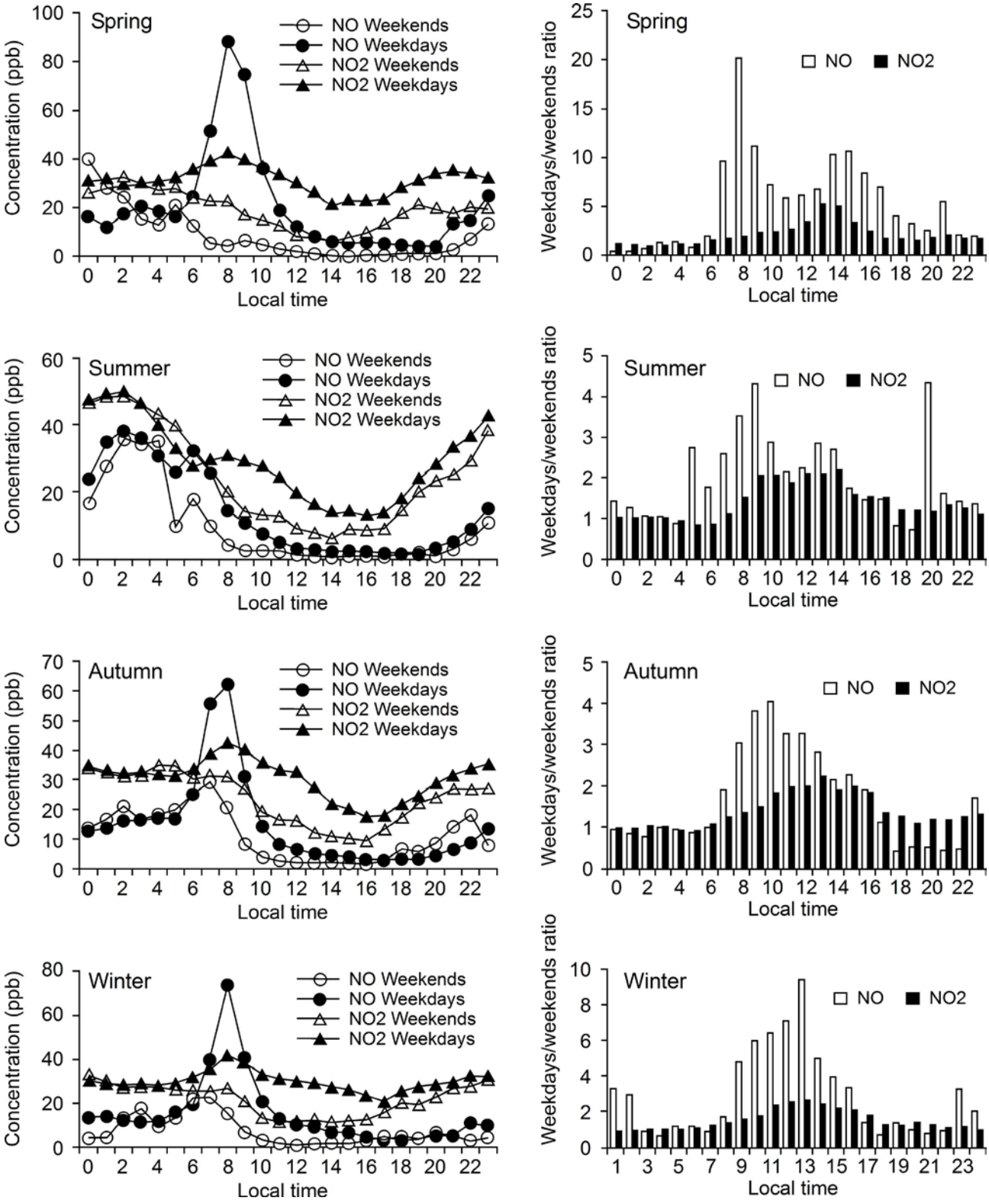
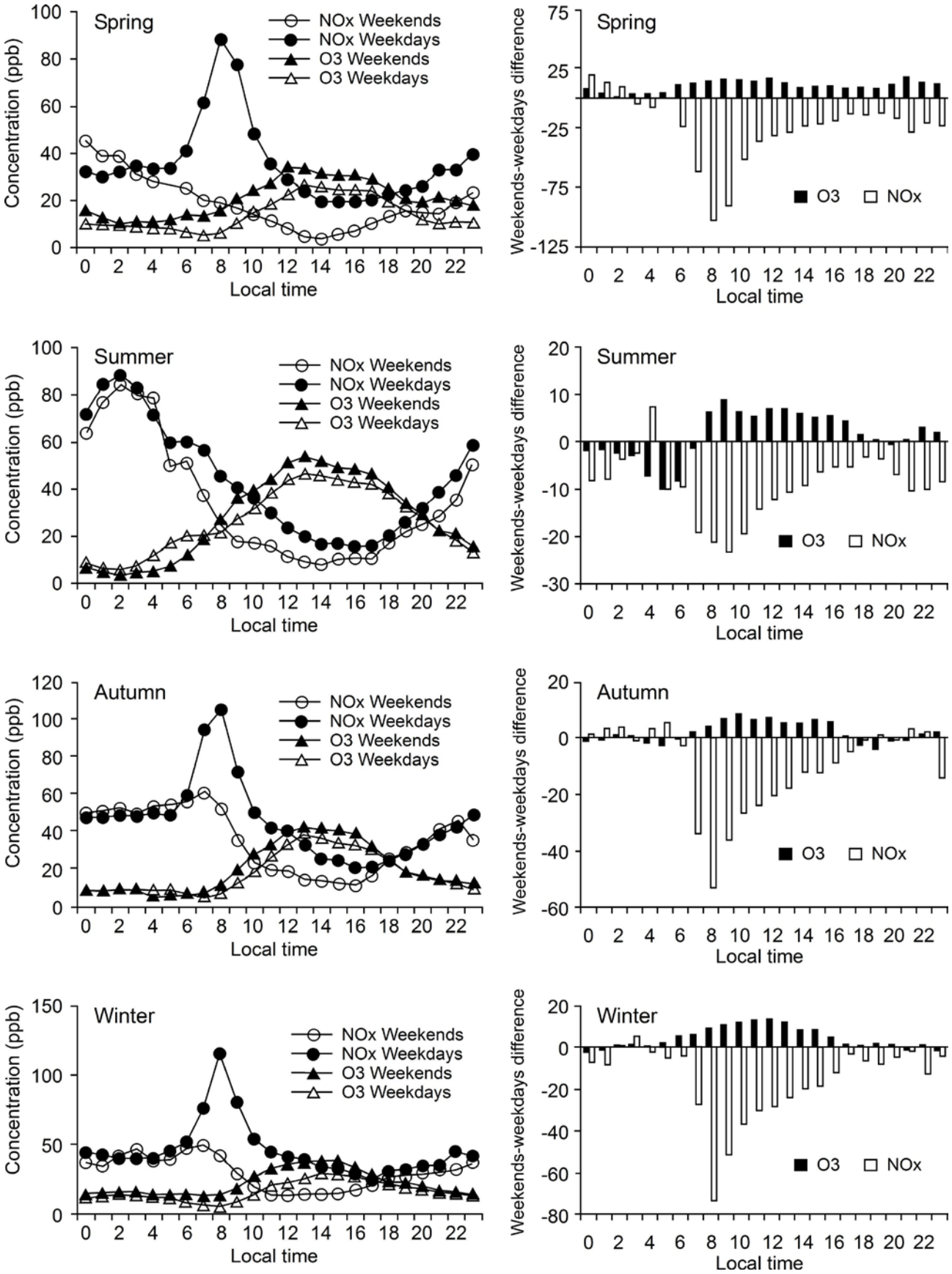


Figure 8. Diurnal variations in NO and NO_2 concentrations on weekdays and weekends (left column) and weekday/weekend concentration ratios (right column) during the different seasons



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