

Temporal variations of O₃ and NO_x in the urban background atmosphere of the coastal city Jeddah, Saudi Arabia

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4 **Temporal Variations of O₃ and NO_x in the Urban**
5 **Background Atmosphere of the Coastal City Jeddah,**
6 **Saudi Arabia**

7
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36

37 **ABSTRACT**

38 Ozone is a pollutant of major concern because of its well recognised effects upon human health and
39 crop yields. This study analyses in depth a new dataset for ozone from Jeddah, a coastal city in
40 Saudi Arabia within the Middle Eastern region, for which very few ozone data are currently
41 available, collected between March 2012 and February 2013. The measurements presented include
42 NO, NO₂ and ozone as well as relevant meteorological variables. The data show a marked seasonal
43 variation in ozone with highest concentrations in the summer months and lowest average
44 concentrations in the winter. Concentrations also show a substantial difference between weekdays
45 and weekends, with higher NO and NO₂ on weekdays, but lower concentrations of ozone. Plots of
46 total oxidant versus NO_x concentration indicate background concentrations of ozone (at zero NO_x)
47 ranging from 38.2 ppb in January to 59 ppb in May consistent with the northern hemisphere spring
48 maximum in ozone concentrations. The slope of total oxidant/NO_x varies from 0.13 in March to
49 0.68 in August. The two summer months of July and August are anomalous with slopes of around
50 double that of other months, suggesting a higher efficiency of ozone production at lower primary
51 pollutant concentrations arising from much reduced daytime traffic. A substantial
52 weekend/weekday difference in ozone which is higher at weekends appears to be attributable to
53 lower daytime traffic activity and hence reduced emissions of NO_x to a “NO_x-saturated”
54 atmosphere.

55

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

58

59

60 1. INTRODUCTION

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

70

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

85

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

94 mainly induced by OH radicals leading to the production of hydroperoxy (HO₂) and organic peroxy
95 (RO₂) radicals. These radicals oxidize NO to NO₂ without consumption of O₃ and the photolysis of
96 the resulting NO₂ by sunlight leads to an increase the accumulation of O₃ (Seinfeld and Pandis,
97 1998).

98

99 Variations in O₃ concentration are controlled by a number of processes including photochemistry,
100 physical/chemical removal, and transport. Precursor emissions (NO_x and VOCs) can lead to
101 elevated levels of surface O₃ locally and downwind and cause large diurnal, day-to-day, seasonal
102 and year-to-year variations in O₃ levels as a result of complex meteorological influences and
103 photochemical mechanisms (Solomon et al., 2000). Meteorological conditions have been shown to
104 play an important role in O₃ formation and transport (Laurila, 1999; Thompson et al., 2001). High
105 levels of O₃ might be registered within a city or at a distance downwind due to the high emissions
106 of O₃ precursors in urban areas (Garcia et al., 2005). O₃ concentrations increase also with solar
107 radiation and temperature elevation (Tecer et al., 2003).

108

109 The O₃ “weekend effect” is a common phenomenon of O₃ behaviour in the urban atmosphere:
110 higher O₃ concentrations may occur on weekends compared to weekdays despite lower
111 concentrations of O₃ precursors at weekends. This phenomenon has been recognised in several
112 countries (Marr and Harley, 2002b; Qin et al., 2004; Paschalidou and Kassomenos, 2004; Jimenez
113 et al., 2005; Gao et al., 2005; Riga-Karandinos and Saitanis, 2005; Sakamoto et al. 2005;
114 Pudasainee et al. 2006; Sadanaga et al., 2008; Khoder, 2009). The mechanisms for the weekend
115 effects on O₃ formation are still not well understood. However, several photochemical modeling
116 studies and a wide range of environmental analyses (Marr and Harley, 2002a; Yarwood et al., 2003;
117 Blanchard and Tanenbaum, 2003; Heuss et al., 2003; Lawson, 2003) have suggested that the
118 primary cause of higher O₃ on weekends is the reduction in NO_x emissions in a VOC-limited
119 chemical regime. Marr and Harley (2002a, b) proposed that less absorption of sunlight due to lower
120 fine-particle concentrations at weekends, resulting in enhanced O₃ formation might be a cause for
121 the weekend O₃ effect. Qin et al. (2004) suggested that VOC sensitivity combined with a decrease
122 of NO_x emissions at weekends was the cause.

123

124 The recent rapid increase in urbanization, industrialization and human activities has important
125 impacts on air quality in Jeddah city. As a result, the emissions of O₃ precursors (NO_x and VOCs)
126 have significantly increased. Therefore, the problem of pollution has been shifted towards the so-
127 called photochemical pollutants. The formation of these pollutants in the Jeddah atmosphere is

128 facilitated by the local climatic conditions (high temperature, intense solar radiation, clear sky),
129 especially in the summer season. Therefore, it is very important to evaluate the diurnal and seasonal
130 variations of ground level O₃ concentrations and their association with NO_x and meteorological
131 parameters. Moreover, the difference in O₃ concentrations between weekdays and weekends is also
132 considered. This will help in understanding the atmospheric chemistry over the semitropical region
133 within which very few studies have been conducted, and in informing a strategy to control ground
134 level O₃ and other photochemical oxidants and their build-up in smog episodes in the future. A
135 recent complementary study has examined spatial patterns of NO_x and O₃ (Hassan et al., 2013).

136

137 **2. MATERIALS AND METHODS**

138 **2.1 Study Area**

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

150

151 **2.2 Sampling Sites and Periods**

152 The sampling site for monitoring of NO, NO₂, NO_x, O₃ and meteorological parameters was chosen
153 in an urban background area of Jeddah city (Jamea district), located in the southeast of the city
154 (Figure 1). The geographic co-ordinates of this site are 21.4869°N; 39.2517°E and the altitude is
155 38.7 m asl. Most of the air pollutant emissions arise from the surrounding traffic activities. The site
156 is 105 metres from the nearest road, and 1700 metres from the closest major highway.

157

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

159

160

161 **2.3 Measurements and Instrumentation**

162 Sampling was carried out at a height of 3.5 m for gaseous air pollutants and 6.7 m for
163 meteorological parameters above the ground level. NO, NO₂, NO_x, O₃ and meteorological
164 parameter data were monitored continuously from March 2012 to February 2013. A UV Absorption
165 Ozone Analyzer (Model 400E, Teledyne Technologies Company, San Diego) was used to monitor
166 ozone concentration. It is a microprocessor-controlled analyzer that uses a system based on the
167 Beer-Lambert law for measuring low ranges of ozone in ambient air. Accurate measurements are
168 obtained in the ranges of 0-100 ppb to 0-10 ppm, with a lower detection limit of < 0.6 ppb. A
169 chemiluminescence NO/NO₂/NO_x analyzer (Model 200E, Teledyne Technologies Company, San
170 Diego) was used to monitor NO, NO₂ and NO_x concentrations. It uses the proven
171 chemiluminescence detection principle, coupled with state-of-the-art microprocessor technology to
172 provide measurements of NO/NO₂/NO_x in the ranges of 0-50 ppb to 0-20,000 ppb full scale, with a
173 lower detection limit of < 0.4 ppb. Ozone calibration was checked with an ozone generator with
174 that of NO/NO₂/NO_x by seven point dilution of a standard gas mixture using mass flow controllers.
175 Quality control checks were performed every three days including inspection of the shelter and
176 instruments as well as zero concentration check, precision and span checks. The filter was replaced
177 once every two weeks and calibration was conducted every month. The O₃, NO and NO₂
178 concentrations were recorded every one minute.

179

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

184

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

188

189 **3. RESULTS AND DISCUSSION**

190 **3.1 Influence of Meteorological Parameters on O₃ Concentration**

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

194 Figure 2 shows the monthly variation of average temperature (Figure 2a), relative humidity (Figure
195 2b) and wind speed (Figure 2c) during the study period. Monthly average ozone concentrations
196 both for all hours and for daytime hours appear in Figure 3.

197

198 O₃ followed a close relationship with solar radiation; and hence surface temperature. The highest
199 daytime average O₃ concentration (44.1 ppb) was observed in August with the highest average air
200 temperature (35 °C) and a minimum of 23.5 ppb in December (26°C). Hourly O₃ concentration was
201 weakly but significantly correlated with temperature for hourly data ($r = 0.33$, $p < 0.001$) in the
202 present study. The favourable meteorological conditions (clear sky, high temperature and light
203 winds) have a great influence on O₃ levels (Vecchi and Valli, 1999). The separate influences of
204 temperature and solar radiation are too closely linked to allow disaggregation; neither shows a strong
205 seasonal cycle (see Figures 2(a) and (d)).

206

207 Average relative humidity was observed to be maximum in autumn and winter seasons while
208 minimum in summer. It varied from around 52% in winter to about 40% in summer (Figure 2b) and
209 thus exhibits a significant negative correlation for hourly data ($r = -0.27$, $p < 0.001$) with O₃
210 concentration. Therefore, the negative relationship arises simply from the fact that relative humidity
211 is low in summer, when ozone production is most efficient.

212

213 Positive correlation ($r = 0.78$, $p < 0.001$) was found between hourly O₃ and wind speed. This is
214 quite a strong relationship which seems unlikely to be related to the seasonal pattern in wind speed
215 (Figure 2(c)), and is probably explained by low NO_x concentrations due to enhanced dilution at high
216 wind speed, borne out by a strong reduction in both NO and NO₂ concentrations with increasing
217 wind speed (Figure S1). Pollution roses also show an increasing gradient of NO_x gases with winds
218 when moving from NW to SE, and inverse behaviour for ozone. This probably reflects stronger
219 average winds from the NW sector diluting NO_x emissions, rather than proximity of local sources.

220

221 **3.2 Monthly Variations of O₃ and NO_x Concentrations**

222 The highest monthly daytime (8 h from 09:00 to 17:00) and daily average O₃ concentrations were
223 observed in the summer, especially August, with values around 45 ppb and 30 ppb, respectively
224 (Figure 3). The daily concentration had another maximum in March with a value around 26 ppb.
225 The lowest concentrations were observed in the cooler months of October – February with values as
226 low as 18 ppb and 24 ppb for the daily and daytime concentrations, respectively. Figure S2 shows

227 seasonally averaged data. In the present study, the average daytime O₃ concentrations (8 h) during
228 the four seasons fell below the European Union air quality standard (60 ppb, 8 h average). These
229 are also below the National Ambient Air Quality Standards (NAAQS; 75 ppb, 8 h average) set by
230 the US Environmental Protection Agency. However, 20.6% of daytime 8-hourly ozone
231 concentrations exceeded 50 ppb, and 3.4% exceeded the EU standard of 60 ppb. In the case of
232 hourly concentrations, 7.3% of daily maximum hourly concentrations exceeded 60 ppb and 0.2%
233 exceeded 75 ppb.

234

235 The monthly variation of mean daytime, nighttime and daily NO and NO₂ concentrations during the
236 period of study are graphically presented in Figure 4. The highest daytime average NO and NO₂
237 concentrations were observed in May, whereas the lowest concentrations were observed in July and
238 August. The mean daytime, nighttime and daily concentrations of NO and NO₂ during the four
239 seasons are graphically presented in Figure S3. The average concentrations of NO₂ in daytime and
240 nighttime were similar, except in summer where the nighttime average concentration was higher
241 than the daytime. On the other hand, the daytime concentration of NO was higher than the
242 nighttime, except in summer where the nighttime average concentration was higher than the
243 daytime. Data appear in Table S2. Because of high temperatures in daytime during the summer
244 season in Jeddah city and the official days-off of government institutions, schools and colleges,
245 most of the people stay home, and consequently the density of traffic during daytime is decreased.
246 Therefore, low concentrations of NO₂ and NO are observed in daytime. On the other hand, after
247 sunset the weather becomes more suitable for going out for shopping and travelling, and the traffic
248 continues to flow until about midnight on weekdays. The traffic continues after midnight on Fridays
249 and even longer until morning during Ramadan (20th July to 18th August). This led to greater
250 emissions of NO_x at nighttime than daytime, and consequently the levels of these pollutants were
251 higher at nighttime compared to daytime. Ratios of NO₂/NO_x are higher in the summer months
252 (Figure 5) favouring higher ozone concentrations.

253

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

260

261 3.3 Diurnal Variation of O₃ and NO_x Concentrations

262 The study of diurnal variations of air pollutants can provide valuable information about the sources,
263 transport and chemical formation/destruction effects of such pollutants. In addition, the diurnal
264 variations have a major influence on exposure levels at sites nominally exposed to the same
265 regional ozone distribution. The physical and chemical mechanisms which give rise to diurnal
266 variations are detailed so that sites can be screened for different diurnal behavior characteristics
267 (Derwent and Kay, 1988). The shapes of O₃ cycles are strongly affected by the levels of its
268 precursors (NO_x and VOCs) as well as the meteorological conditions (temperature and solar
269 radiation (Alvim-Ferraz et al., 2006; Pudasainee et al., 2006; Khoder, 2009). The diurnal variations
270 in O₃ concentrations during the period of study are graphically presented in Figure 6. From this
271 figure, it can be seen that the O₃ diurnal variation of each season showed a similar pattern, but the
272 magnitudes of variations were different. O₃ concentrations reached a maximum during daytime and
273 a minimum in the nighttime during all four seasons. The diurnal pattern of O₃ for each season is
274 characterised by a maximum concentration in the afternoon. Its variation in different seasons
275 generally coincides with the amount of solar radiation where O₃ reaches a peak value in the
276 afternoon hours, and then continuously decreases until midnight. Rates of rise and fall are
277 described in Table S1. A uni-modal O₃ peak is seen for all seasons, with highest O₃ levels in
278 summer followed by spring, then autumn and lowest levels in the winter season. The broad peak
279 with higher amplitude of O₃ during daytime in the summer season is attributed to higher
280 temperature, higher solar radiation intensity as well as the longer sunlight hours, which are the
281 favourable conditions to power the photochemical reactions, and higher NO₂/NO_x ratios resulting in
282 high levels of O₃. Minimum values of O₃ concentrations appear in the nighttime and early morning
283 hours (near sunrise). The time of sunrise is a turning point of diurnal O₃. The O₃ concentration rises
284 gradually just after the sun rises and reaches maximum levels at 1400- 1600 hours in winter and
285 1300-1400 hours in spring, summer and autumn seasons (Figure 6). After that time, O₃
286 concentrations decrease progressively until evening, and then keep decreasing more gradually,
287 maintaining low values over night hours due to lack of solar radiation. O₃ production rate increases
288 at low NO_x until a maximum is reached and then decreases at high NO_x (Sillman et al., 1990). This
289 pattern occurs because high NO_x promotes removal of OH radicals by the reaction of OH with NO₂
290 (Zhang et al., 2004). On the other hand, as the sun goes down in the evening and nighttime, the
291 photochemical processing of O₃ is halted due to the absence of the photochemical reactions, and the
292 O₃ that remains in the atmosphere is then consumed by deposition (Colbeck and Harrison, 1985)
293 and/or reaction with NO which acts as a sink for O₃ (Dueñas et al., 2002). The decrease in O₃
294 during the early morning hours of the day at 0700–0800 h local time in winter, spring and autumn
295 and at 0200 h local time in summer (Figure 6) is mainly due to the increase in traffic flow (rush

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

302

303 Diurnal variations in NO and NO₂ concentrations during the period of study are graphically
304 presented in Figure 6. From this figure, it can be seen that the hourly concentrations of NO
305 increased from 0600 to 0800 hours in spring, autumn and winter and from 0000 to 0200 and 0500 to
306 0600 hours in summer (Figure 6a), then decreased in mid-day time. The apparently anomolous
307 behaviour in summer results from human activity occurring mainly during nighttime hours when air
308 temperatures are lower. After that time, the concentration increases again in the evening. Data
309 appear in Table S3. The diurnal behavior of NO₂ was similar to that of NO, with a slightly different
310 pattern (Figure 6). The diurnal cycles of these pollutants are related to the transportation/work
311 cycle. During the morning time, the increase in the emission rate from traffic, accompanied by
312 poorer dispersive conditions due to the shallower boundary layer, lead to an increase in the
313 concentrations of NO_x. On the other hand, the lower concentrations of NO and NO₂ during mid-day
314 time may be due to the better dispersion caused by increased convective activity. Moreover, the
315 higher temperature and solar radiation intensity during midday leads to increases in the
316 photochemical reactions and consequently increases in the chemical loss of these pollutants. The
317 high levels of NO during the morning hours in winter result in low concentrations of O₃ due to the
318 rapid reaction between O₃ and NO. Apart from this, it is difficult to disentangle the effects of the
319 various influencing factors.

320

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

326

327 **3.4 Concentrations of Total Oxidant (O_x)**

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

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

335

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

348

349 **3.5 Weekend/Weekday Variations in NO , NO_2 , NO_x and O_3 Concentrations**

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

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

365

366 The diurnal variations in NO and NO₂ concentrations on the weekdays and weekends (Fridays) and
367 the weekday/weekend concentration ratios during the four seasons are graphically presented in
368 Figure 8. The patterns of hourly variations in NO concentrations, i.e. the trend for increases or
369 decreases, were similar during the weekdays and Fridays (except in Spring), with highest levels on
370 the weekdays. NO₂ in ambient air originates mainly from the atmospheric oxidation of primary NO.
371 The trend of the hourly concentration of NO₂ for increases or decreases during the weekdays and
372 Fridays was also similar, with highest levels on the weekdays. The lower levels of NO and NO₂ at
373 weekends (Fridays) are attributed to the reduction in the emission of these pollutants due to lower
374 traffic density.

375

376 The reduction in traffic density and consequently vehicle emissions on weekends compared with
377 weekdays is used to examine the linkages between emitted O₃ precursors and ground-level O₃
378 production. The phenomenon of a weekend effect on O₃ occurs when O₃ concentrations tend to be
379 higher during weekends compared to weekdays in some areas, despite the fact of lower emissions of
380 O₃ precursors (NO_x and VOCs) during weekends. The ground-level O₃ concentration over the urban
381 areas of Jeddah city depends on photochemical production of O₃ related to NO_x concentration.
382 Vehicle traffic is the major source of NO_x emission at the studied urban site, where it is assumed
383 that the weekend traffic density is lower than on weekdays due to the official days-off of
384 government institutions, schools and colleges. However, in spite of low weekend NO_x emissions, an
385 elevated O₃ concentration was observed at the study site. Figure 9 shows the diurnal variations in
386 NO_x and O₃ concentrations at the weekdays and weekends (Fridays) and the difference between
387 weekends and weekdays (weekends minus weekdays) during the period of study. The O₃
388 concentration on weekends was greater than weekdays during all four seasons.

389

390 The occurrence of a weekend O₃ effect was determined by the differences in O₃ concentration
391 between weekend and weekdays. Blanchard and Fairley (2001) and Fujita et al. (2003) classified
392 the criteria used to identify the status of the weekend effect into three categories: a) intense
393 weekend effect if O₃ difference is > 15 ppb; b) moderate weekend effect if O₃ difference is 5-15
394 ppb; and c) no weekend effect if O₃ difference is < 5 ppb. Using the above criteria, it can be seen
395 that a moderate weekend effect was observed in all seasons. The mean hourly daytime difference
396 between weekends and weekdays (weekends minus weekdays) ranged from 8.2 ppb to 16.2 ppb in

397 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
398 winter (Figure 9 and Table S4). The weekend O₃ effect is significant in spring and winter.
399 Meteorological conditions are also responsible to some extent for an intense weekend O₃ effect on a
400 seasonal basis; however, it appears that differences in concentrations of O₃ precursors (NO_x and
401 VOC) are a major cause for the weekend O₃ effect in the study area. At traffic influenced sites,
402 increased vehicular traffic density from Saturday to Thursday leads to increased NO emission
403 which is responsible for decreased O₃ concentrations on weekdays compared to weekends due to
404 the rapid reaction of NO with O₃. Hence the weekend effect on O₃ is attributable to the decreased
405 local emission of NO on weekend mornings which consumes less O₃, and the latter cannot be
406 further depleted during the daytime (Atkinson-Palombo et al., 2006). In consequence, the
407 accumulation of O₃ is increased during the weekend daytime. The different reduction rates for the
408 emissions of NO and VOCs during weekends (Altshuler et al., 1995) and consequently the
409 prevailing ratio between [VOCs] and [NO_x] may lead to increased O₃ at the weekend. The weekend
410 O₃ phenomenon depends largely on differences in NO_x concentration between weekday and
411 weekend; lower NO levels and VOC emissions on weekend mornings consume less O₃ which
412 accumulates later by photochemical reactions (Pudasainee et al., 2006) which may be more efficient
413 in a lower NO_x environment. Khoder (2009) also found many sites in Cairo with elevated O₃ on
414 weekends when traffic and O₃ precursor levels were substantially reduced. Moreover, the relative
415 increase in solar radiation intensity which results from the lower concentrations of fine particles at
416 weekends due to the lower traffic density can lead to an increase in the photochemical formation of
417 O₃ at weekends (Marr and Harley, 2002a, b). O₃ levels in the ambient air increased when emissions
418 of NO_x decreased (Heuss et al., 2003; Bernstein et al., 2004; Sadanaga et al., 2008; Roberts-Semple
419 et al., 2012). Similar observations were made in a potential non-attainment area of Cincinnati, Ohio
420 where a reduction in NO emissions contributed to an increase in local O₃ (Torres-Jardon and
421 Keener, 2006).

422

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

431 likely to be the reduction in NO emissions and its effect upon the photostationary state through an
432 increase in NO₂/NO_x ratio accompanying a reduced titration of ozone by NO. This reflects an
433 atmosphere which is effectively “NO_x-saturated” with respect to ozone formation. It also seems
434 likely that ozone production efficiency is enhanced by the reduction in NO₂ and VOC levels, as
435 these are major sinks for the key free radical species involved in conversion of NO to NO₂ without
436 consumption of ozone.

437

438 **4. CONCLUSIONS**

439 This is to our knowledge the most comprehensive analysis of an ozone dataset from a country of the
440 Middle Eastern region. The concentrations of ozone are overall unexceptional for a polluted
441 atmosphere, and some facets of the data are very similar to those in other parts of the world, whilst
442 some are less so. An analysis of the total oxidant data following the method of Clapp and Jenkin
443 (2001) reveals a typical northern hemisphere spring maximum in ozone although the background
444 levels are exceptionally high for a low altitude site at over 50 ppb (Parrish et al., 2012). This may
445 represent enhanced formation of ozone in background air due to the high photochemical reactivity
446 of the region or enhanced vertical transport of stratospheric ozone. The data show the months of
447 July and August to be exceptional in terms of ozone production efficiency (the gradient of the total
448 oxidant/NO_x) plot which reflects the much lower daytime traffic activity and emissions of precursor
449 pollutants during these months. There is also a substantial weekday/weekend difference with higher
450 NO_x concentrations on weekdays accompanied by lower ozone than at weekends. It appears that
451 the reduced titration of ozone with NO and consequent enhanced NO₂/NO ratio in July and August
452 and at weekends is influencing the photostationary state, but also the oxidant plots suggest
453 enhanced ozone production efficiency at the lower NO_x concentrations possibly because of the
454 reduced influence of NO₂ and VOC as a sink for free radical species.

455

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

462

463

464

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469

470

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608

609

610 **FIGURE LEGENDS**

611

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

614

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

617

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

620

621 **Figure 4:** Monthly variations of daytime, nighttime and daily concentrations of NO and NO₂
622 during the period of study.

623

624 **Figure 5:** Monthly variations of NO₂/NO_x concentration ratios.

625

626 **Figure 6:** Diurnal variations in NO, NO₂ and O₃ concentrations during the different seasons.

627

628 **Figure 7:** Gradient and intercept of a plot of total oxidant (O₃ + NO₂) versus NO_x concentration
629 for daytime samples for each month (equation $O_x = bNO_x + a$).

630

631 **Figure 8:** Diurnal variations of NO and NO₂ concentrations on weekdays and weekends (left
632 column) and weekday/weekend concentration ratios (right column) during the
633 different seasons.

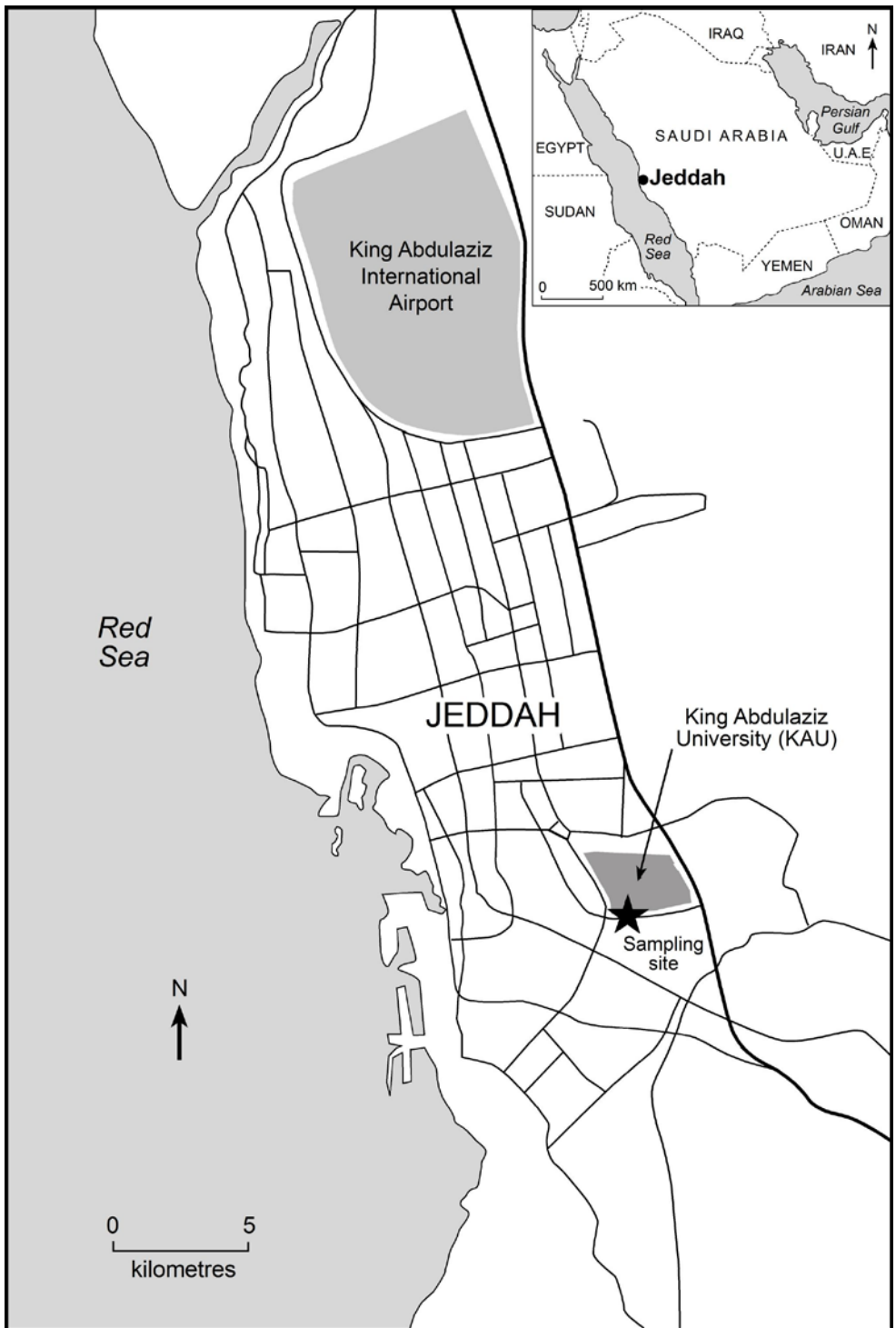
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635 **Figure 9:** Diurnal variations of NO_x and O₃ on weekdays and weekends and weekend minus
636 weekday concentrations (ppb) during the different seasons.

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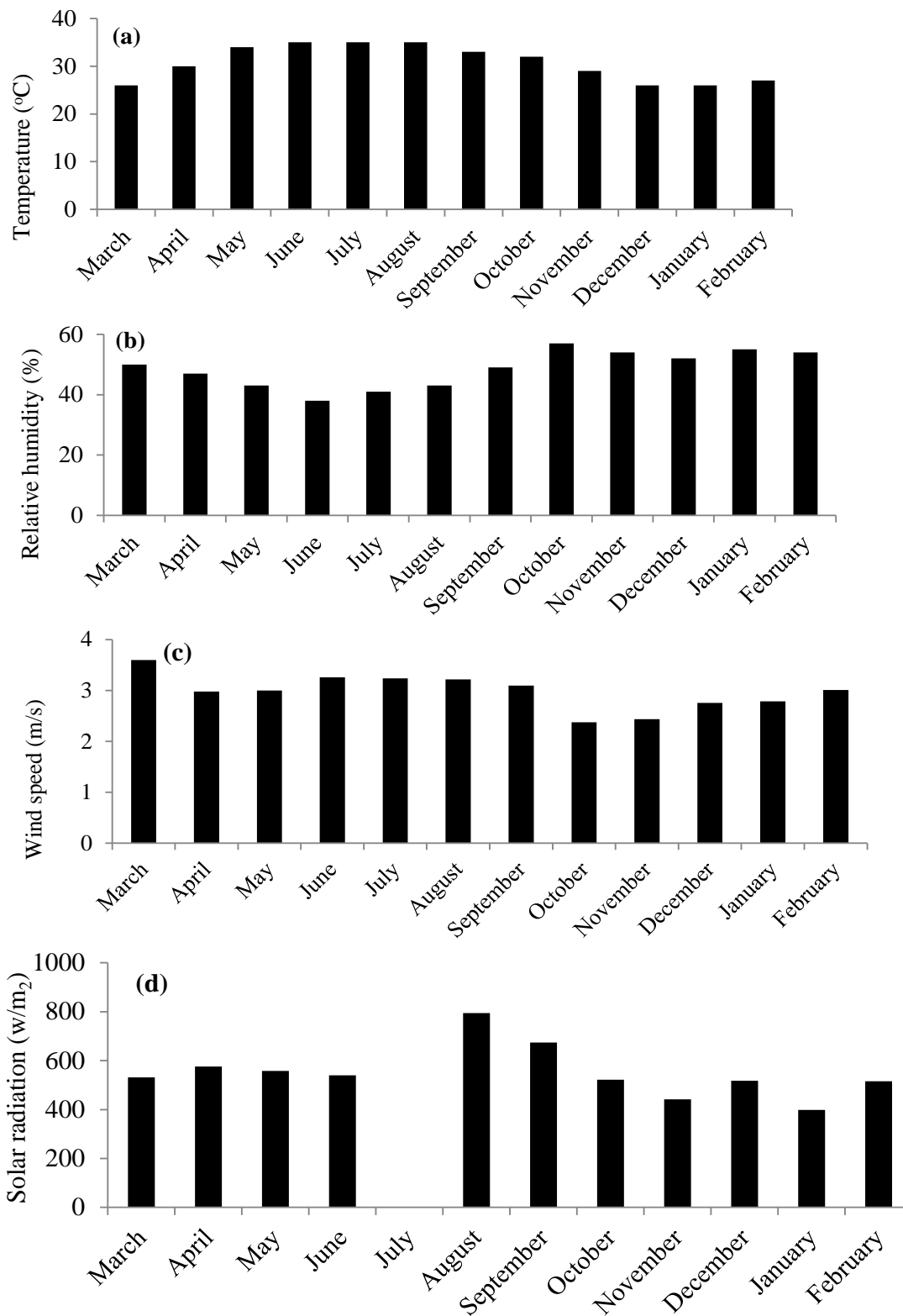


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642 **Figure 1.** Map of Jeddah with the sampling site marked with a star. Map data © Google, 2013
 643 Terra Metrics

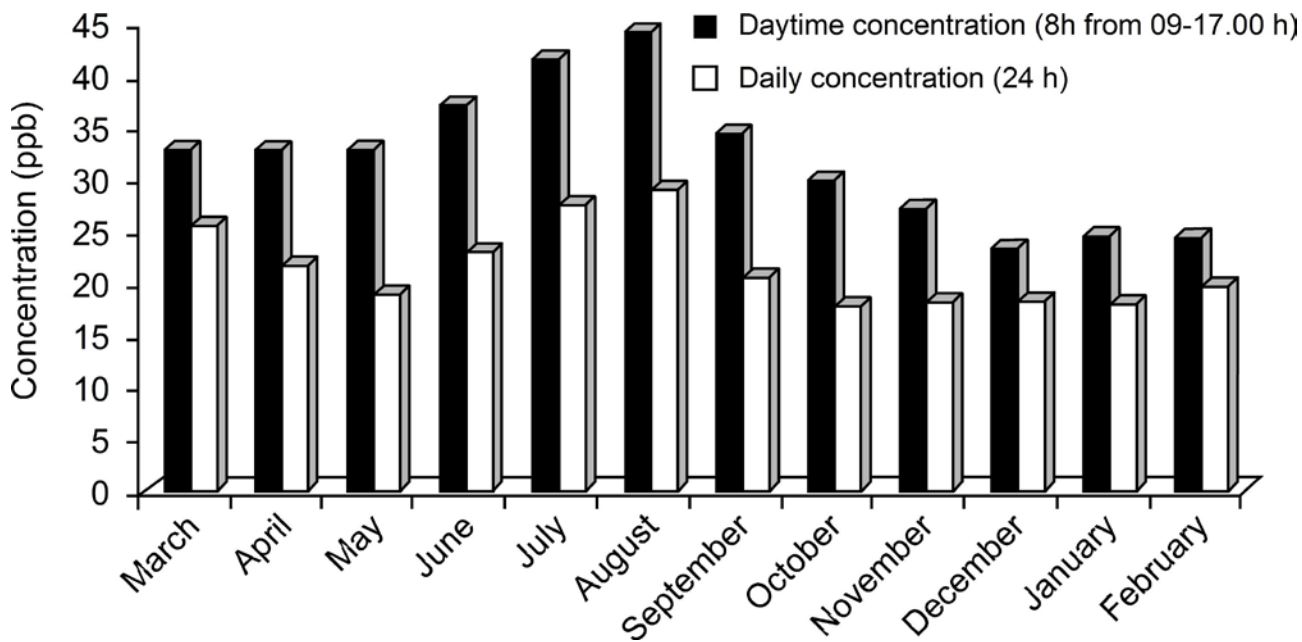
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646 **Figure 2.** Monthly variation of (a) temperature, (b) relative humidity, (c) wind speed and (d) solar
 647 radiation

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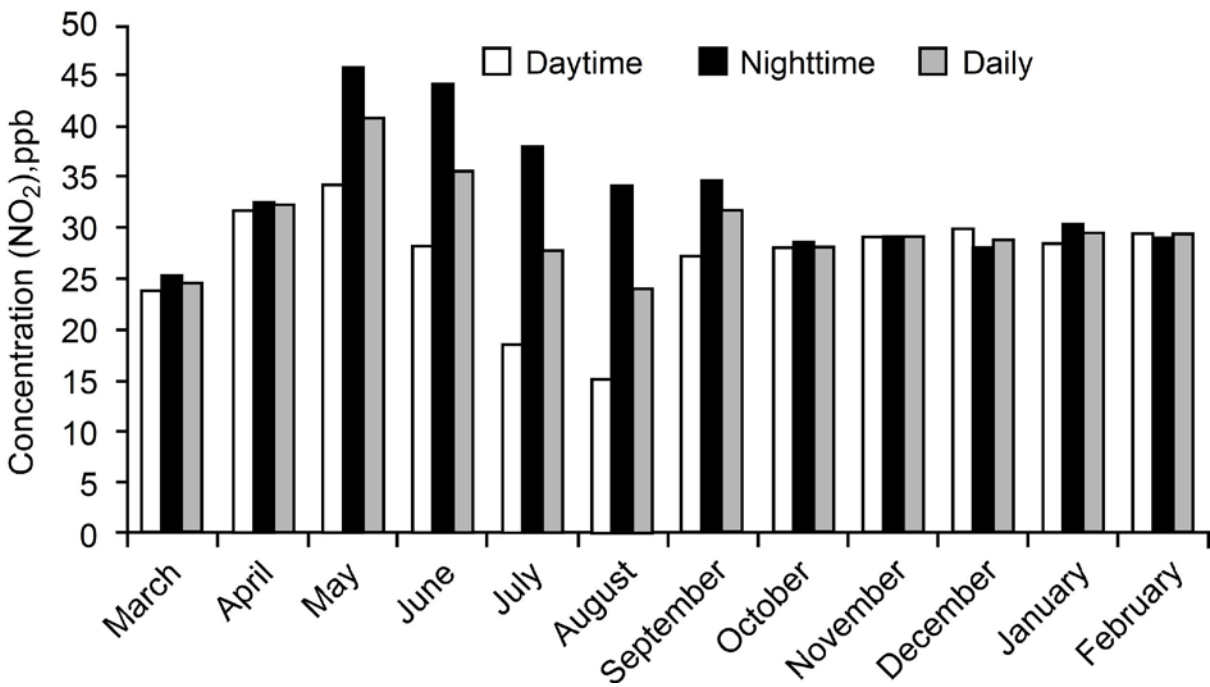
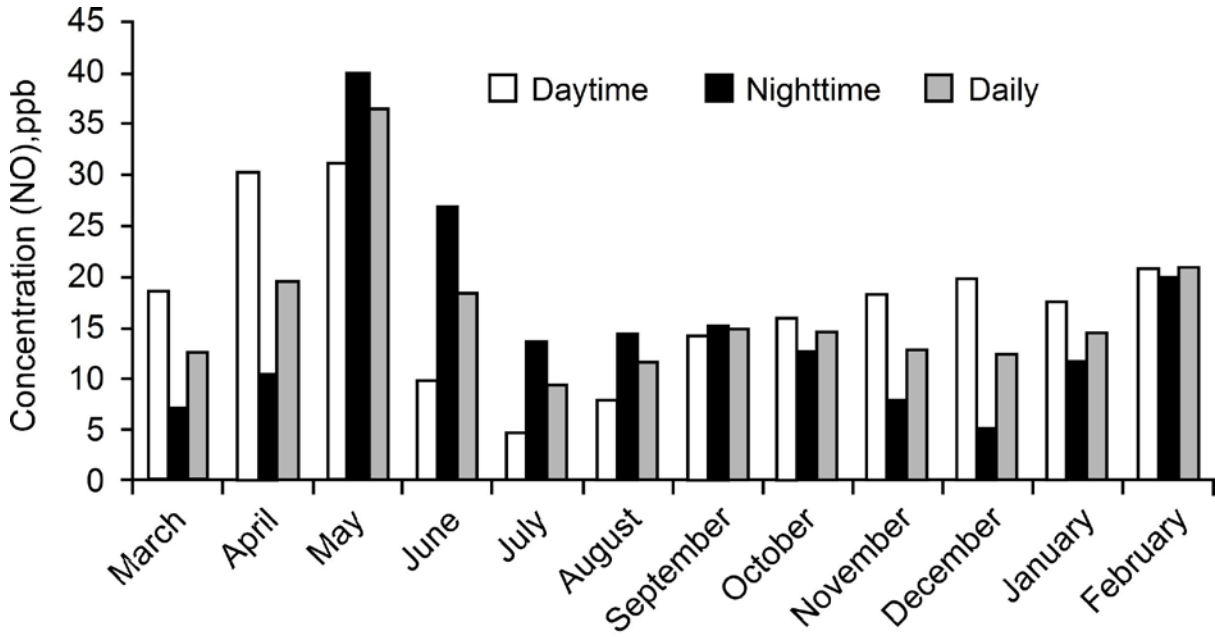
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651 **Figure 3.** Monthly variations of mean daytime and daily concentrations of ozone during the period
 652 of study

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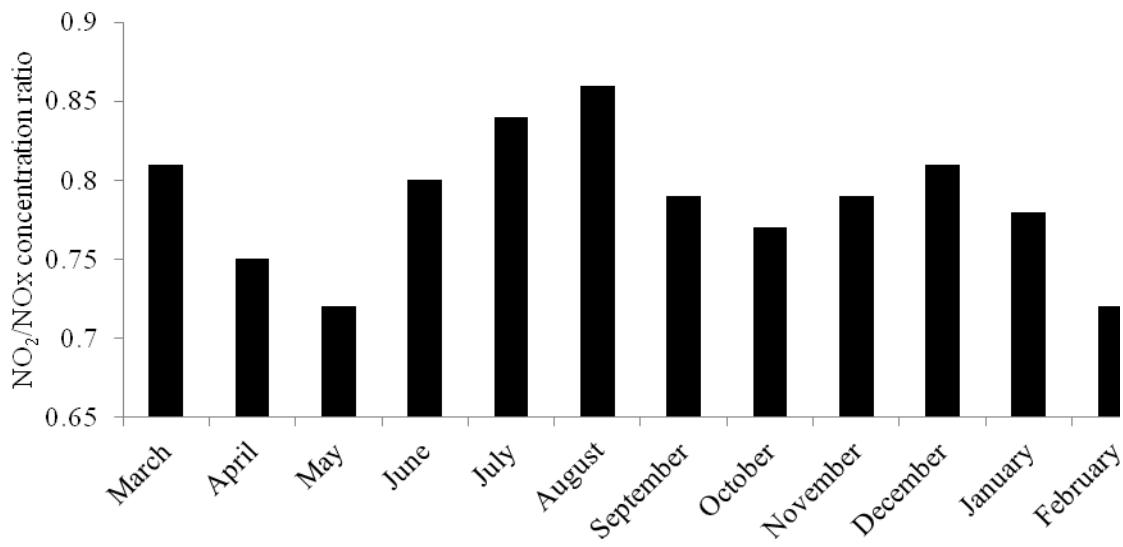
658 **Figure 4.** Monthly variations of daytime, nighttime and daily concentrations of NO and NO₂ during
659 the period of study

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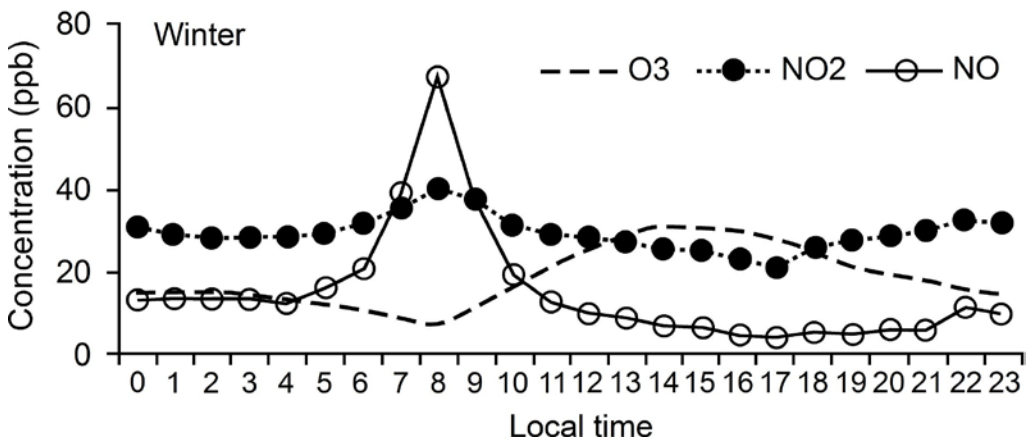
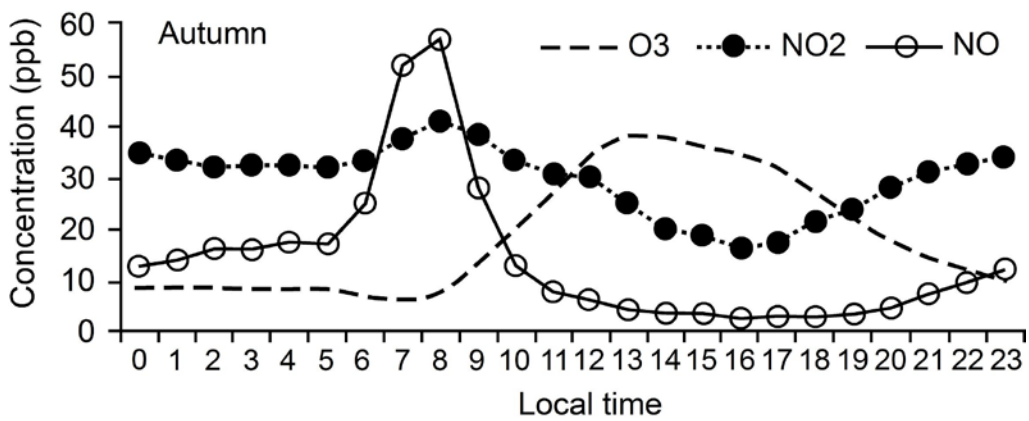
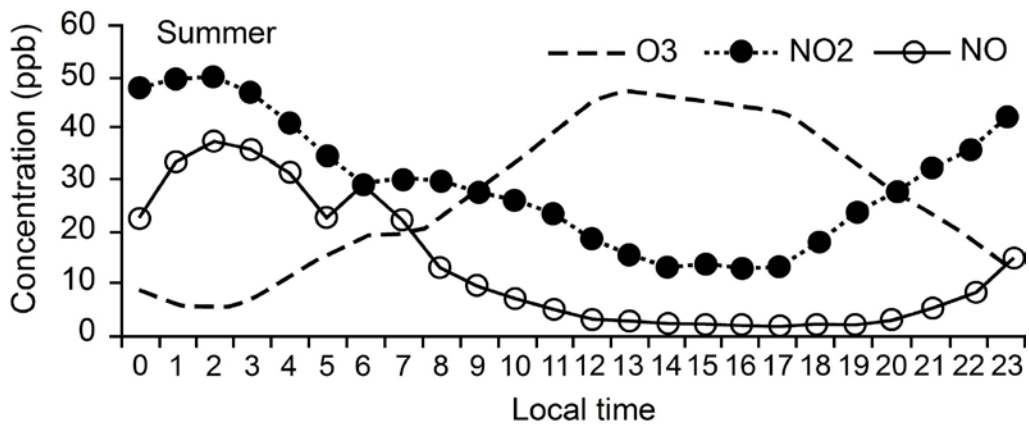
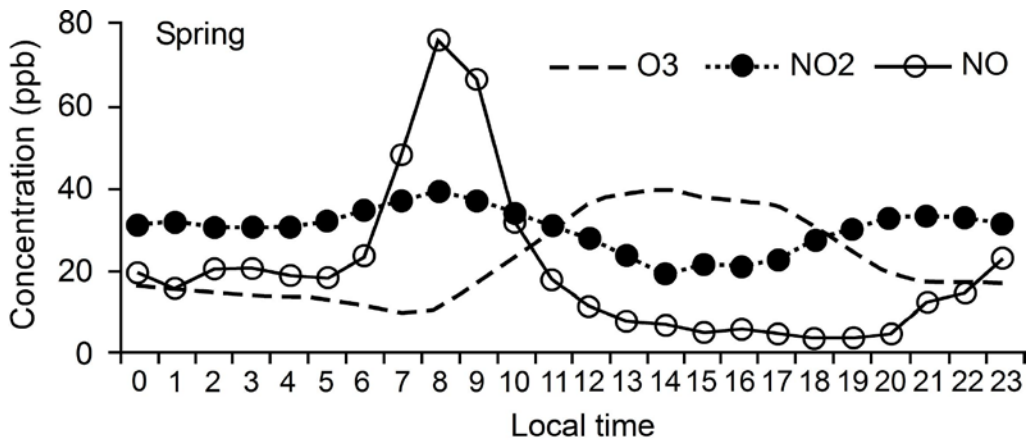
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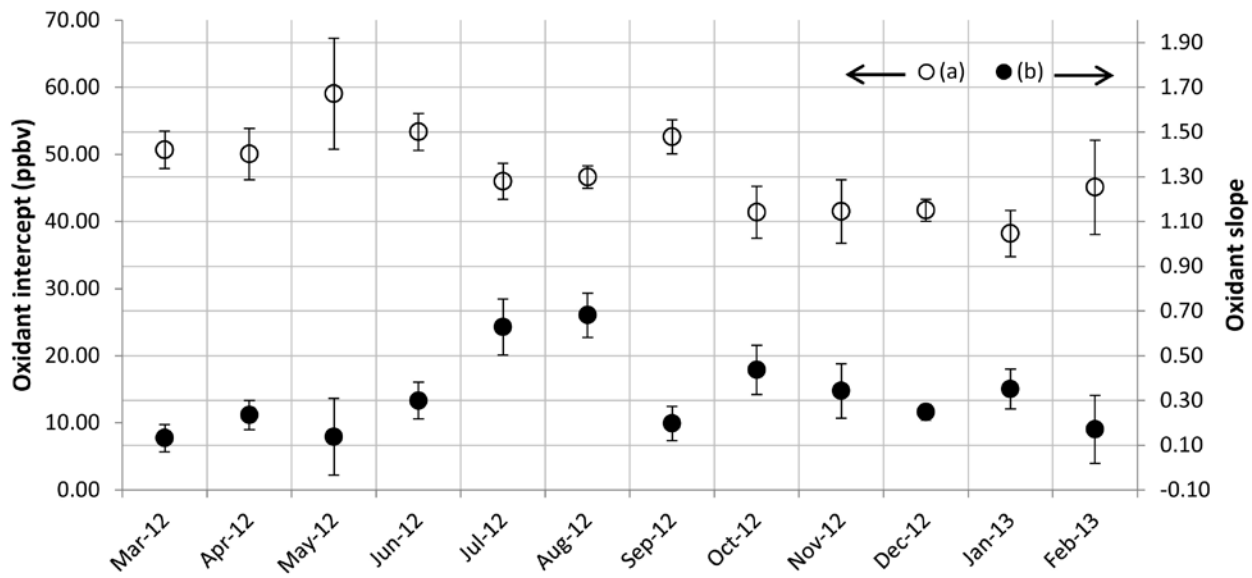
665 **Figure 5.** Monthly variations of NO₂/NO_x concentration ratios



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668 **Figure 6.** Diurnal variations in NO, NO₂ and O₃ concentrations during the different seasons

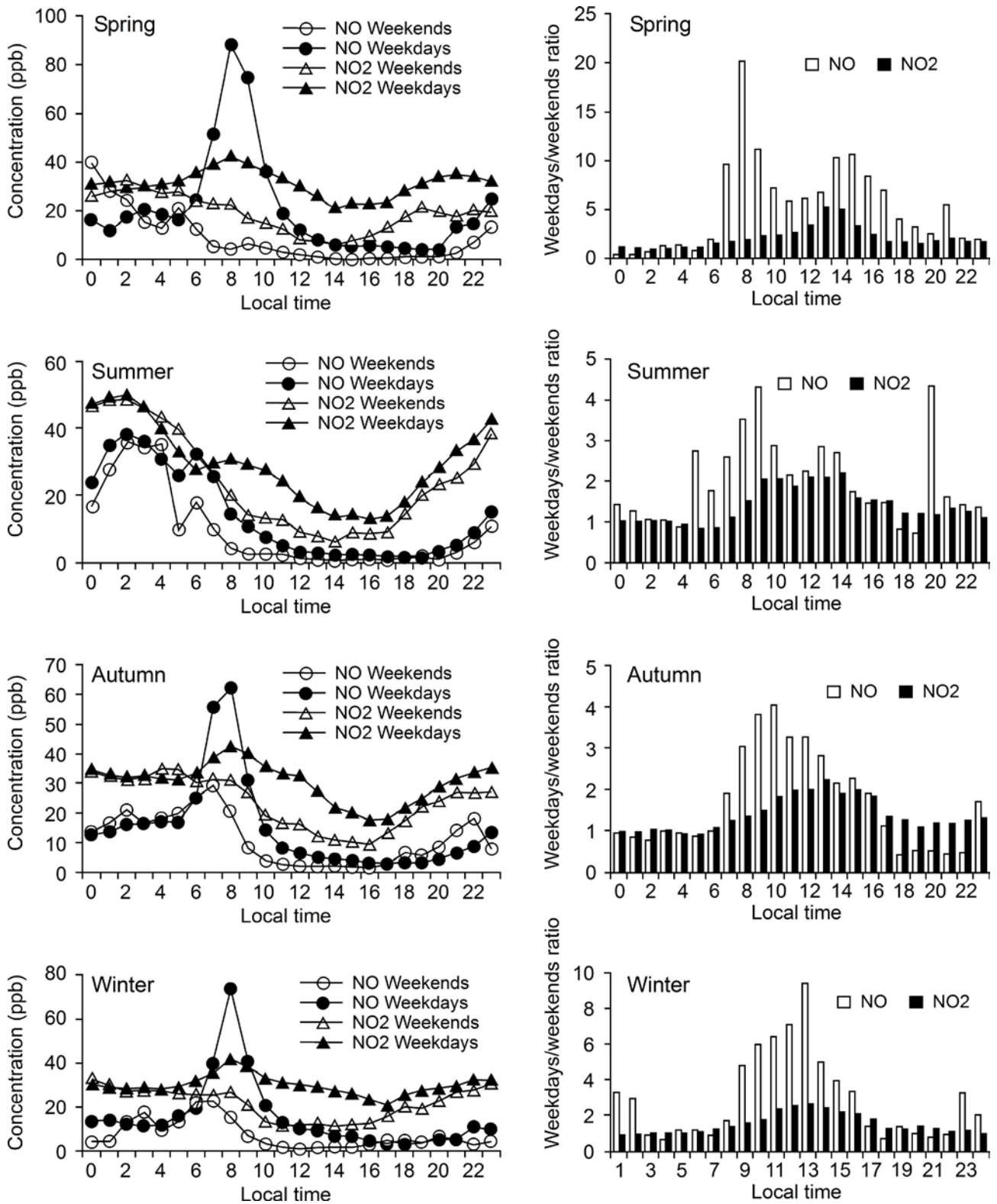


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671 **Figure 7.** Gradient and intercept of a plot of total oxidant ($O_3 + NO_2$) versus NO_x concentration for
 672 daytime samples for each month (equation $O_x = bNO_x + a$)

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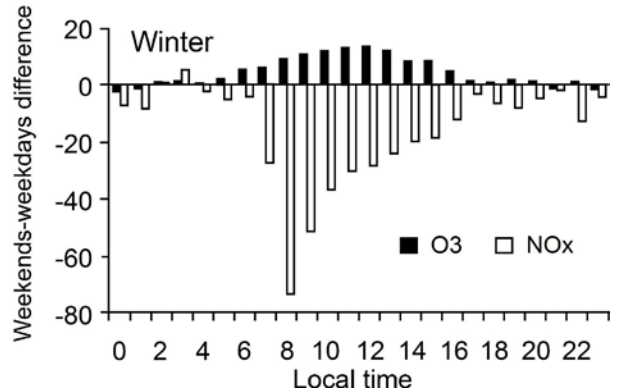
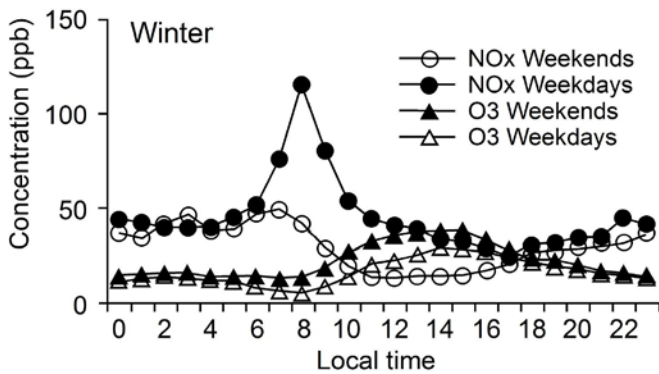
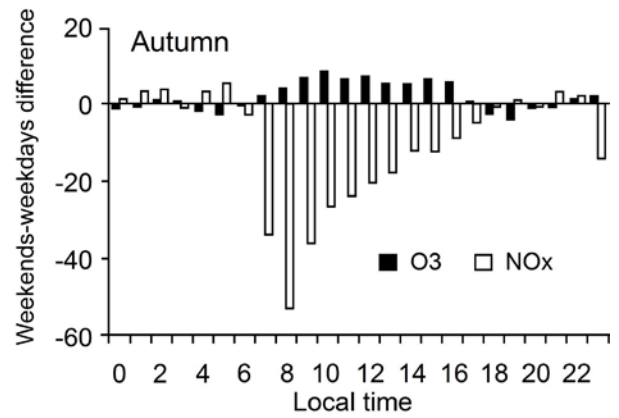
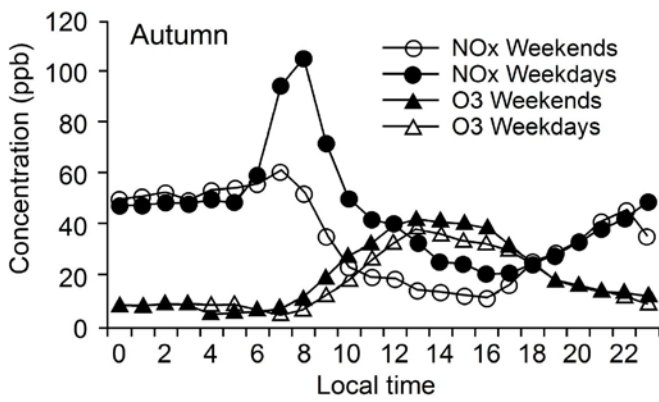
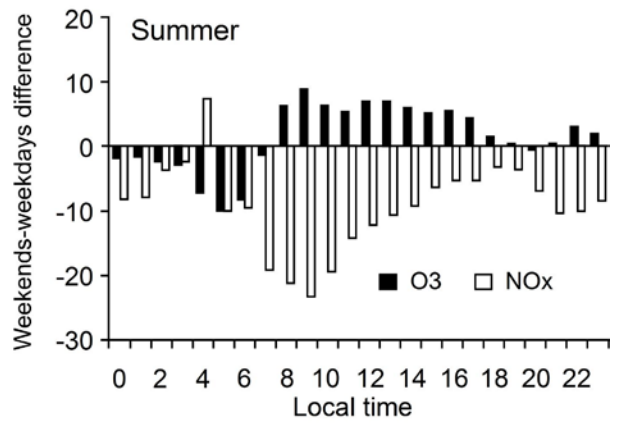
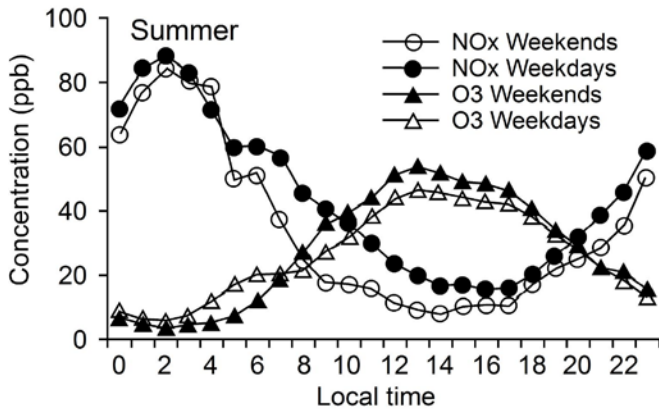
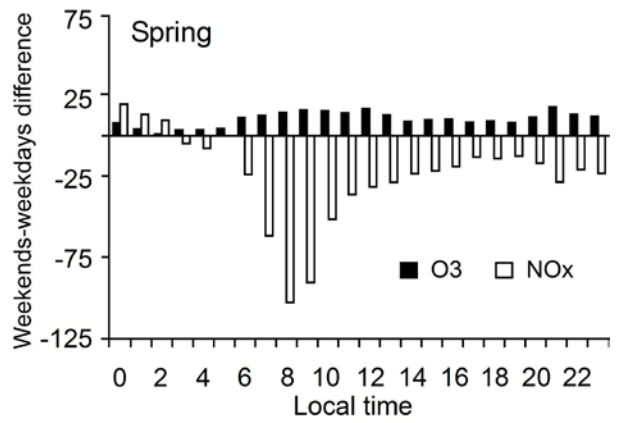
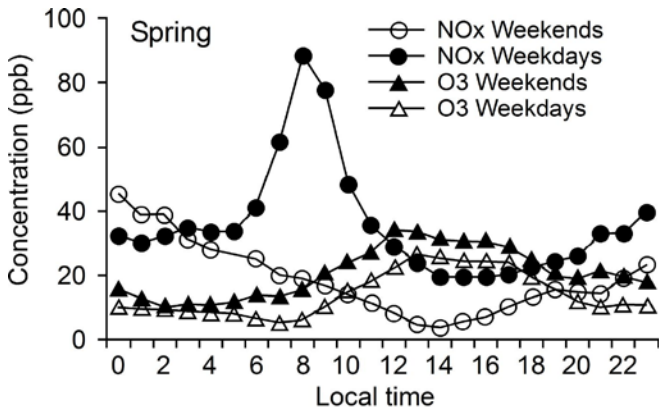
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Figure 8. Diurnal variations in NO and NO₂ concentrations on weekdays and weekends (left column) and weekday/weekend concentration ratios (right column) during the different seasons



681 **Figure 9.** Diurnal variations in NO_x and O₃ on weekdays and weekends, and weekend minus
 682 weekday concentrations (ppb) during the different seasons