



Spatial Distribution and Temporal Variation in Ambient Ozone and Its Associated NO_x in the Atmosphere of Jeddah City, Saudi Arabia

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ABSTRACT

Concentrations of ambient ozone (O₃) and nitrogen oxides (NO_x) were measured continuously for a period of 12 months in the city of Jeddah from December 2011 to December 2012. Meteorological parameters, wind speed, temperature, and relative humidity were also monitored. Concentrations of ground O₃ were found to be highly dependent on the NO_x diurnal cycle and wind speed. Nitrogen oxides were found to exceed air quality standards, especially in industrial sites, while O₃ concentrations were found to exceed 40 ppb, averaged over 1 h, on more than 24% of the measured days in the rural sites. Furthermore, they exceeded 30% in all other areas (i.e., the urban ones).

O₃ and NO_x were inversely related. The highest average NO_x concentration (96 ppb) occurred in a rural area downwind of a desalination plant, while the average O₃ concentration peaked in a rural area upwind of a desalination plant, reaching 63.5 ppb, although it also reached 72.6 in another rural area, and we consider this latter result as the background figure in the present study. The seasonal variations of O₃ were more distinct than those of NO_x. To the best of our knowledge, this is the first report providing comprehensive background information on air quality in an arid area of the developing world.

Keywords: Ambient ozone; Nitrogen oxides; Seasonal variation; Air quality; Jeddah.

INTRODUCTION

Air Quality in Urban areas is affected mainly by photochemical oxidants (Han *et al.*, 2011). Moreover, air pollution is a challenging problem as it would hinder sustainable development all over the globe (Akimoto, 2003; Molina and Molina, 2004). Increased combustion of fossil fuels in the last century is responsible for the progressive change in the atmospheric composition. Air pollutants, such as carbon monoxide (CO), sulfur dioxide (SO₂), nitrogen oxides (NO_x), volatile organic compounds (VOCs), ozone (O₃), heavy metals, and respirable particulate matter (PM_{2.5} and PM₁₀), differ in their chemical composition, reaction properties, emission, time of disintegration and ability to diffuse in long or short distances (Kampa and Castanas, 2008).

The relation between ozone and its two main precursors, NO_x (NO and NO₂) and volatile organic compounds (VOC), represents one of the major scientific challenges associated with urban air pollution (Sillman, 1999). The formation of ground level ozone depends on the intensity of solar radiation, the absolute concentrations of NO_x and VOCs, and the ratio of NO_x and VOCs (Nevers, 2000, Pudasainee *et al.*, 2006). Episodes of elevated O₃ are commonly associated with anticyclonic weather (Hassan *et al.*, 1995). The meteorological conditions associated with anticyclones such as high solar radiation, high temperature, low wind speed and low rainfall are favorable for tropospheric O₃ formation, and these are the conditions prevalent in KSA (Presidency of Environment & Meteorology, KSA, unpublished data). In addition to a complex system of chemical reactions, meteorological and topographical factors determine where ozone concentrations will be the highest. Maximum ozone concentrations often occur in locales more distance of the source emissions (Finlayson-Pitts and Pitts, 1997). Moreover, it is well known that the ozone concentrations in ambient air increase with increase in the intensity of radiation and temperature on the clear days (Nishanth *et al.*, 2012). Furthermore, the magnitude of ozone concentration variations is high in clear days than

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the cloudy days.

The formation of ozone in the troposphere begins with NO₂ photolysis, after which the NO product quickly reacts with ozone to regenerate the NO₂. Therefore, the ozone remains in a stationary state that depends on the speed of NO₂ photolysis and on the NO₂/NO ratio. If there were no other processes that transform NO into NO₂, the concentration of ozone would not increase significantly (Júnior *et al.*, 2009). However, in the presence of VOCs, the ozone concentration increases after NO is converted to NO₂ due to the formation of radicals (CETESB, 2003). NO_x is Produced formed in the atmosphere from both natural and anthropogenic sources, involving naturally occurring nitrogen and volatile organic compounds (VOCs) by the action of lightning (Brown *et al.*, 2006). However, NO_x emissions from anthropogenic sources exceed natural sources (Godish, 2004). Increased combustion of fossil fuels and exhaust fumes may be extremely pervasive, causing serious environmental degradation, illnesses and deaths (Ricciardolo *et al.*, 2004; Gurjar *et al.*, 2008; Roberts *et al.*, 2012).

Ozone is a major environmental concern because of its adverse impacts on human health (Bascomb *et al.*, 1996; sillman, 1999) and also because of its impact on crops and forest ecosystems (Hassan, 2010, Taia *et al.*, 2013).

A thorough understanding of the relationships among O₃ and NO_x under various atmospheric conditions is urgently needed to improve our understanding of the chemical coupling among these pollutants (Clapp *et al.*, 2001; Mazzeo *et al.*, 2005; Chou *et al.*, 2006; Costabile and Allegrini, 2007, Nishanth *et al.*, 2012). Seasonal variation effects on gaseous pollutants are of great significance to the life span and cycle of any pollutant in the lower atmosphere (Khan and Salem, 2007).

Saudi Arabia is one of the many arid lands in the world (e.g., Arizona, Nevada, South Africa, Peru, etc.). Very little attention was paid to areas having the same arid environmental condition as Saudi Arabia to monitor and measure the actual air pollution concentration in the atmosphere. Statistical analysis of such data may indicate air quality standards which are drastically different from those of non-arid areas (Sabbak, 1994). Industrial and vehicular emissions combine to give Jeddah a serious air pollution problem. Thousands of old vehicles crowd the city streets with poor regulation of emission levels, and the city's factories create additional environmental hazards (Kadi, 2009). Concentrations of heavy metals, gaseous air pollutants and particulate emissions far exceed internationally acceptable standards (Al-Jeelani, 2008; Hassan and Basahi, 2013).

Although monitoring of ozone is well established in USA and Europe, there is no a comprehensive study showing its seasonal, temporal and diurnal distribution in arid regions. Moreover, there is no enough background information for air quality standards for Jeddah as for the whole kingdom.

This study was undertaken in order to fulfil this gap of knowledge, and to describe the key observation of both diurnal and seasonal variation of ambient O₃ and its precursor NO_x and their variation with meteorological parameters in Jeddah. Moreover, we attempted in the present study to collect enough and significant data to estimate air quality

trends in Jeddah city atmosphere. Different metrological parameters (ambient temperature, relative humidity and wind speed and direction) and their influence on the air quality were also considered in the discussion of the results.

METHODOLOGY

Study Area

Jeddah is a coastal city lies at the Western coast of Saudi Arabia (N 21° 67', E 39° 15') 15 meter above sea level. Its population around 3.5 million, it represents one of the largest cities by population and industry in KSA. It has well established traffic networks because it is the maritime port of the kingdom, resulting in high population density and a dense urban and infrastructural network.

There were six monitoring locations chosen along transect representing different levels of urbanization in order to have a comprehensive study of spatial distribution and diurnal variation of O₃ and its precursors. The gradient extended over a distance of approximately 30 km within the boundaries of the city (Fig. 1).

All monitoring sites are characterized by prolonged hot sunny periods all the year around. Location (1) was at a rural area away from any source of pollution and it has a relatively low number of vehicles running there. Location (1) was 2 km up wind to a desalination plant at North of Jeddah, while location (2) was 5 km downwind of the factory. Other location; 4, 5 and 6 were located at the busiest highway (Madina Road) used by commuters and travelers as it leads to the airport, near the City Centre at a roof of King Abdulaziz University and at an industrial zone to the south of Jeddah, respectively (Fig. 1).



Fig. 1. Map of Jeddah showing different locations of sampling sites marked with black stars.

Table 1. Monitoring locations relevant to exposure assessment.

| Site classification | Description |
|---------------------------|---|
| 1 Rural | An open countryside location as far away as possible from roads and populated and industrial areas (<i>Usfan</i>). |
| 2 Rural area | Upwind of a desalination plant at Northern Jeddah. |
| 3 Suburban area | Downwind of a desalination plant at Northern Jeddah. |
| 4 City or urban centre | An urban location representative of general population exposure in the city centre (<i>Down Town, shopping Centre</i>). |
| 5 Other | A special source-oriented or microenvironment site located at a targeted receptor point, (<i>KAU Premises</i>). |
| 6 Industrial | An area where industrial sources make an important contribution to long-term or peak concentrations (<i>Industrial zone</i>). |

Ozone and NO_x Monitoring

Ground levels of O₃ were measured at all stations on a continuous daily basis and the automatic analyzers' response time was 1 min. O₃ concentrations were monitored by ozone automatic analyzers, operated on the principle of photometric detection of the specific absorption of UV light by ozone (O₃ analyzer Model 49i).

Ambient NO_x concentrations were measured simultaneously with chemiluminescence NO - NO₂ - NO_x analyzer Model 42i, in the range of 0–50 ppb to 0–100 ppm internal Zero/span Assembly with a detection limit of < 0.4 ppb

There were two types of calibration; manual one through gas cylinders of known pollutants concentration and autocalibration through permeation tubes (zero air is being generated *in situ*). The calibration was done manually once a month to ensure accuracy and to double check on the autocalibration (Winer *et al.*, 1974) for quality control.

Meteorology of the Study Areas

Unlike other Saudi Arabian cities, Jeddah retains its warm temperature in winter season, which can range from 25°C at midnight to 37°C in the afternoon. Summer temperatures are considered very hot and break the 40°C mark in the afternoon dropping to 30°C in the evening. Rain is very rare and usually falls in December and January. Humidity ratio is 45–53%.

Winds are north-eastern most of the year time. The prevailing locally measured winds in Jeddah lie in a sector between north and north-west. Air mass back trajectories calculated by the HYSPLIT online model for random dates in both January and June show trajectories approaching Jeddah from a NNE direction broadly following the Red Sea coast (Fig. 2.). Weather in Jeddah City is humid most of the year. Some unusual events often happen during the year, such as dust storms in summer, coming from the Arabian Peninsula's deserts or from North Africa.

Data analyses

Time series plotting techniques were used to visualize the seasonal, monthly, and diurnal patterns of NO, NO₂, NO_x and O₃ concentrations. Statistical Package for the Social Sciences (SPSS) version 18.0, Statistical Analysis System

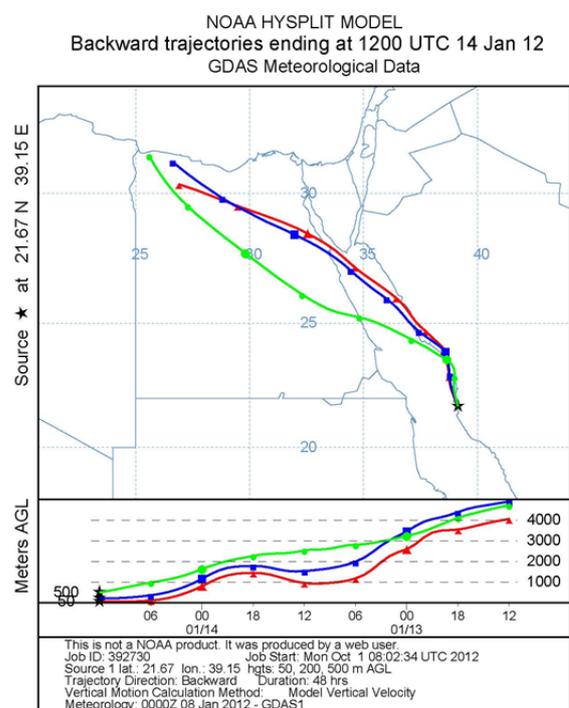


Fig. 2. Example of back trajectory for air mass arriving in Jeddah at 12.00 UTC on 14 January 2012. The red line (triangles) is the best representation of that sampled at ground level.

(SAS) 9.2, and MINITAB 16 software packages were used (Liu *et al.*, 2003).

RESULTS

Meteorological Conditions

The principal meteorological conditions recorded in the present study were wind speed, wind direction, temperature, relative humidity and atmospheric pressure in order to evaluate the influence they might have on ozone concentrations.

Monthly mean values of daytime (08:00–20:00) temperature (°C), relative humidity (%), and wind speed (km/h) at the station for January to December 2012 are shown in Fig. 3.

It was found Maximum temperature was recorded in August (47.6°C), while the lowest one was recorded during January (21.6°C).

The highest relative humidity was recorded during July (56%), while the lowest one was recorded during January (24%). On the other hand, wind speed was very high during winter season (January–February) where it was 24 km/h) while during summer it showed the minimum speed (11 km/h).

Diurnal Variations of O₃ and NO_x

Twelve-hour averages (08:00–20:00 h, KSA Standard Time, NST) ground level ozone concentrations measured are presented in Fig. 4.

During the entire period of study the surface ozone concentration varied from the minimum of 20 ppb in city centre and University premises sites in the morning to a maximum of 70 ppb at the rural site. The diurnal cycle of ozone was characterized by the maximum ozone concentration in the afternoon (between 14:00 and 16:00 hr) and minimum ozone concentration in the early hours of the morning (07:00 hr). A gradual decrease was observed in the evening hours (17:00 hr) in the study areas. After sunset, the concentration declining further and reached the

lowest level between 20:00 hr and 07:00 hr. The highest concentrations were recorded in Site 2 (averaged 54.9 ppb) which is a rural site while the lowest concentrations (averaged 25.1 ppb) were recorded in the city centre (site 4) “suburban area” (Fig. 4).

Diurnal variations in NO, NO₂ and NO_x concentrations are shown in Fig. 5. The Daily average peak emission of NO and photochemical formation of NO₂ and NO_x during the study period occurred at 7:00–9:00 h for sites 1, 5 and 6, 10:00–11:00 h for site 2 and 13:00–15:00 h for site 3, respectively. Site 4 “urban city centre” exhibited morning and evening peaks. The evening peaks occurred between 17:00 and 18:00 h, and it was higher in magnitude than morning peak which occurred between 08:00 and 09:00h.

In general, photochemical formation of ozone in air at a location is influenced by ambient temperature ($R^2 = 0.508$) and NO_x concentration (-0.372) (Table 2). It was clear that the ozone concentrations rises after 9:00 h and reached to peak value at about 14:00–16:00 h and then after it decreases slowly.

Association of Ozone with Meteorological Parameters and NO_x

Fig. 6 shows that the ozone concentration is at peak

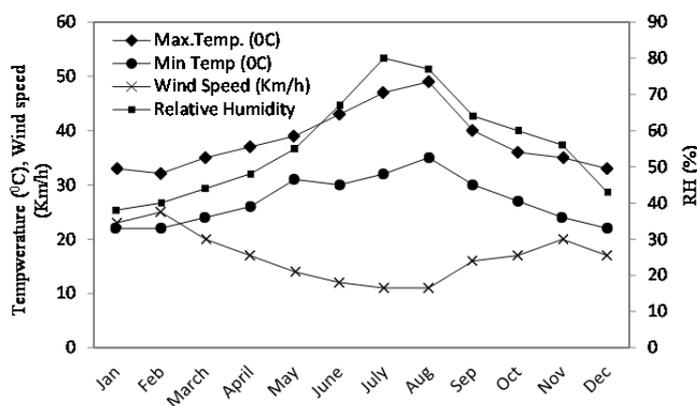


Fig. 3. Monthly Mean Values of meteorological conditions averaged between the different monitoring sites within Jeddah during the period of the observation.

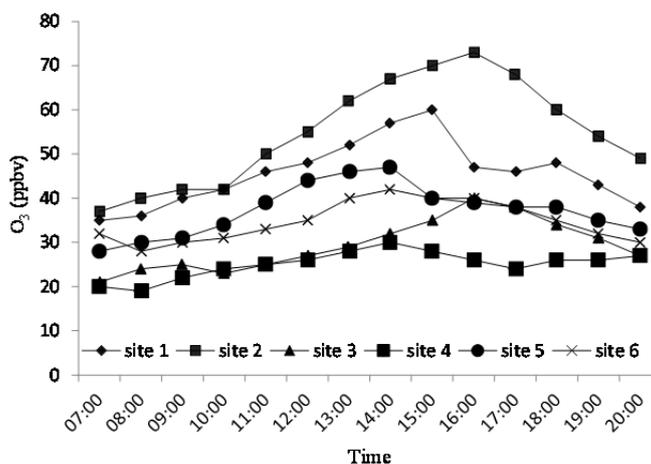


Fig. 4. Diurnal variation ozone concentration (ppbv) during daytime (07:00 – 20:00 h) at different monitoring sites.

when temperature is the maximum which indicates ozone concentration levels are directly related to temperature. There was a significant correlation between temperature and ambient O₃ concentrations ($R^2 = 0.508$, $P < 0.01$) (Table 2).

Photochemical formation of ozone in air at a location is influenced by ambient temperature and NO_x concentration. It was clear that the ozone concentrations rises after 9:00 h and reached to peak value at about 14:00–16:00 h and then

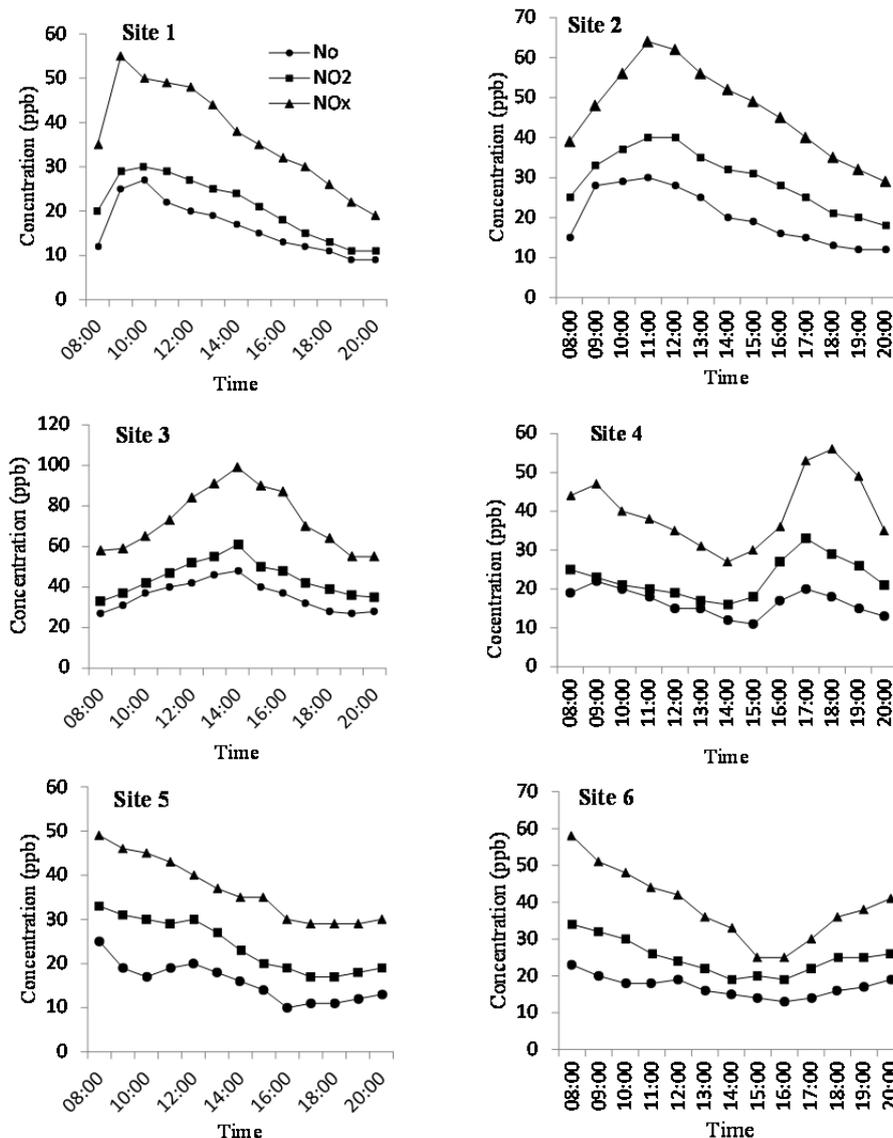


Fig. 5. Diurnal cycles of NO, NO₂ and NO_x in different monitoring sites.

Table 2. Correlation coefficients between hourly averaged ozone Concentration, NO_x and temperature (a) whole time period (08:00–20:00 h) and (b) day light time period (07:00–18:00 h).

| | Temperature | Wind speed | O ₃ | NO _x | Pressure |
|-----|-----------------|------------|----------------|-----------------|----------|
| (a) | Temperature | 1 | 0.508 | -0.254 | -0.107 |
| | Wind speed | -0.512 | 1 | 0.071 | 0.076 |
| | O ₃ | 0.508 | 0.297 | 1 | -0.561 |
| | NO _x | -0.254 | 0.071 | -0.372 | 1 |
| | Pressure | -0.107 | 0.076 | -0.561 | 0.216 |
| (b) | Temperature | 1 | 0.378 | -0.257 | -0.112 |
| | Wind speed | -0.625 | 1 | 0.437 | -0.108 |
| | O ₃ | 0.378 | 0.437 | 1 | -0.208 |
| | NO _x | -0.257 | -0.108 | -0.208 | 1 |
| | Pressure | -0.112 | 0.091 | -0.683 | 0.310 |

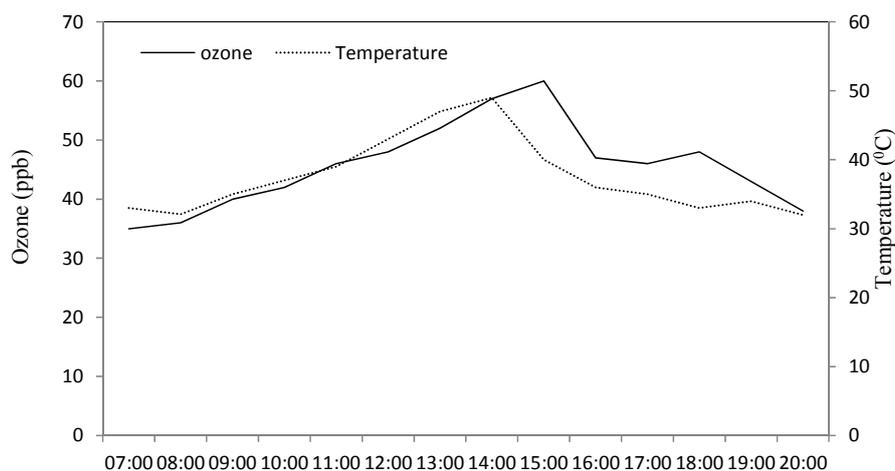


Fig. 6. Relationship between ambient levels of ozone and temperature.

after it decreases slowly. The concentrations decrease steadily after sunset. Therefore correlation coefficients between ozone concentration and temperature, as well as ozone precursors were calculated separately for two periods: (i) entire measured time (07:00–20:00 h) and (ii) day light hours (10:00–16:00 h). Correlation coefficients between hourly averaged O_3 concentration and NO_x for entire measured period and day light hours were -0.372 and -0.208 , respectively. Similarly, correlation coefficient between hourly averaged O_3 concentration and temperature for entire measured time was 0.508 . Moreover, multiple correlation coefficient between ozone and meteorological parameters (NO_x , and temperature, pressure and windspeed) were significant ($P \leq 0.05$). Statistical details of correlation studies showed that correlation coefficients improved slightly for day light hours. It was found that the most influencing parameters for formation of ozone in order are NO_x , followed by ambient temperature and wind speed at daylight hours, while for entire time period temperature is most influencing parameter (Table 2). There were strong correlation coefficients between pressure and O_3 (-0.561) as well as NO_x (0.216) over the whole period of the experiment (Table 2), which indicated the sensitivity to a single unit change. The minimum, maximum and average values of barometric pressure were 27.93, 31.06 and 30.11 Hg, respectively (data not shown).

Site - to - Site Variations

Fig. 7 summarises the results for each site for each month of the year. It shows that the daylight-averaged data from site 1 (typically rural area) (51.1 ppb), site 2 (a rural area upwind of a desalination plant) (56.4 ppb), site 3 (downwind of a desalination plant) (30.6 ppb), site 4 (City Centre) (28.5 ppb), site 5 (University premises) (37.7 ppb) and site 6 (Industrial one) (34.1 ppb). Whereas the local oxidant contributions at the two rural sites are comparable for most of the year, and were higher than the other four sites, the data provide clear evidence that the local source is substantially greater in midsummer (May–August) at all sites. Moreover, from the Fig. 6, it is evident that rural sites (1 and 2) recorded the highest O_3 mixing ratio during

midsummer (May–July). At Urban, residential and industrial sites (Sites 4, 5 and 6, respectively) O_3 concentrations show distinct maxima in late summer season (August) whereas at suburban area downwind of desalination plant (Site 3) it became high during autumn season (Sept.–Oct.).

Seasonal Variations

Fig. 8 shows variations in monthly average NO_x and O_3 concentrations. Average O_3 ranged from 11.1 ppb to 36.2 ppb, with wide distribution ranges from June through August, and increased in the winter. The annual average O_3 concentration was 40.3 ppb (averaged between different sites around Jeddah) while pronounced variations mainly in summer (between May to August). The daily mean O_3 values displayed summer highs with a gradual decline into autumn (Sep. to Nov.) and winter lows (Dec. to Feb.).

The monthly NO_x concentrations ranged from 29.7 to 53.1 ppb, while the annual average was 37.9 ppb (averaged between all sites), with a pronounced increasing trend towards the winter (Dec. to Feb.) to spring (March) (Fig. 8).

Frequency distribution of hourly means of O_3 showed that 40% of the data falls in the range between 10 to 30 ppb. The next highest frequency was 30% for the range 30 to 40 ppb; while the rest of the considered ranges (50 to 60 and 60 to 70ppb) form only 6.4 and 4.6%, respectively (Table 3).

DISCUSSION

Air pollution monitoring in Saudi Arabia is extremely limited, moreover, there is a lack of interest and awareness regarding air pollution problems. O_3 pollution has drawn much attention in Many Asian countries such as Hong Kong, Japan and China, in the last decade (Chan and Yao, 2008). However, O_3 pollution problems in Saudi Arabia and other Gulf countries were much less reported until recently. At present, ozone is measured in six studies in KSA; namely Jeddah (Sabbak, 1994), Makkah (Al-khalaf, 2006; Al-Jeelani, 2008, 2009; Seroji, 2010). Dhahran and Jubail (Amin and Husain, 1994) and Riyadh (Al-Dhowalia *et al.*, 1991). However, these studies were on fragmentary occasions.

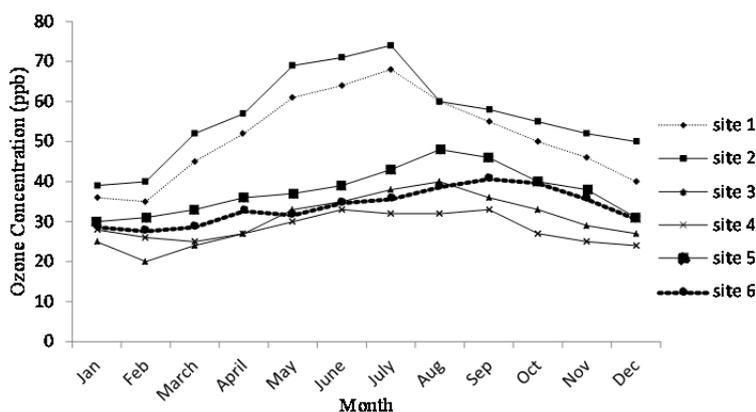


Fig. 7. Seasonal variations of monthly average O₃ concentrations (ppb) at different sites.

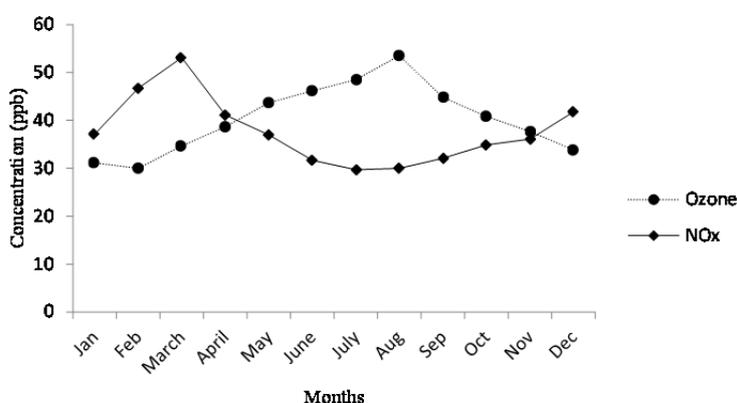


Fig. 8. Annual cycle of O₃ and NO_x concentrations (averaged between different sites).

Table 3. Frequency distribution of hourly mean O₃ concentrations (ppb) at different sites around Jeddah during 2012.

| Site | Concentration Range | | | | | | Total no. of hours |
|-------|---------------------|-------|-------|-------|-------|-------|--------------------|
| | 10–20 | 20–30 | 30–40 | 40–50 | 50–60 | 60–70 | |
| 1 | 0 | 0 | 2190 | 3285 | 1460 | 1825 | 8760 |
| 2 | 1086 | 0 | 730 | 2190 | 1095 | 0 | 5101 |
| 3 | 0 | 5475 | 730 | 0 | 0 | 0 | 6205 |
| 4 | 0 | 7200 | 0 | 0 | 0 | 0 | 7200 |
| 5 | 0 | 1460 | 4015 | 1825 | 0 | 0 | 7300 |
| 6 | 0 | 1085 | 4380 | 365 | 0 | 0 | 5830 |
| Total | 1086 | 15220 | 12045 | 7665 | 2555 | 1825 | 40396 |
| % | 2.7 | 37.6 | 29.8 | 18.9 | 6.4 | 4.6 | 100 |

Jeddah has numerous unregulated sources of particulates and gases (Sabbak, 1994). Most remarkable sources of pollutants are high number of vehicles, brick kilns, dusty roads and small industries. Our Previous study (Hassan and Basahi, 2013) indicated that most part of the city regularly experience total suspended particulates (TSP) and PM₁₀ concentration levels above their acceptable limits set by World Health Organization (WHO) (Khodeir *et al.*, 2012).

Observed average ozone concentrations are within WHO guideline values of 60 ppb through most of experimental sites. The concentrations exceeded the guideline value for 8% of the days monitored. Based on EPA classification, during the study period, ozone concentration remained good for most of the sites for about 90% of days, moderate

for 6.5% of the days, unhealthy for sensitive groups for 1% of the days for one site. These results are very similar to results of Pudasainee *et al.* (2006), who found similar results in Nepal. Recently, Reddy *et al.* (2012) stated that O₃ showed a well defined seasonal variation pattern on a diurnal scale with high levels (70.2 ± 6.9 ppbv) during the summer and low (20.0 ± 4.7 ppbv) during the monsoon with an annual mean of 40.7 ± 8.6 ppbv at a semi-arid rural site in Southern India.

Seasonal variation of O₃ observed in the present study show a typical pattern of rural site at sites 1 and 2, which is highly influenced by the seasonal changes, and this in agreement with results of other studies in Indian sub continent (Nishanth *et al.*, 2012), in Brazil (Júnior *et al.*, 2009), in

London (Clapp and Jenkin, 2001), in Nepal (Pudasainee *et al.*, 2006), in China (Chan and Yao, 2008) and in the USA (Song *et al.*, 2011; Roberts-Semple, 2012).

The diurnal variations of O₃ display a gradual increase in O₃ variations from February to May in all sites, with pronounced variations until August at rural sites and September in other sites, followed by a decrease through November. Such variations are apparently caused by photochemical differences across seasons and sites (Khoder, 2009). In months with relatively lower diurnal variations, the more prominent O₃ peaks were apparently obscured by lower peaks in months with relatively higher variations (Roberts-Semple *et al.*, 2012).

The pronounced variations in summer observed in this study were very common in several studies (Roberts-Semple *et al.*, 2012). Nevertheless, our measurements showed that 12-h average ozone concentration lies in between 11.1 and 56.6 ppb, which are higher than the expected values. However, our results contradict results of Amin and Husain (1994), who reported higher concentrations of O₃ and NO_x in Dhahran in the eastern region of the kingdom. They found mean daily concentrations of these pollutants were 84 and 89 ppb, respectively, while they recorded the maximum hourly concentrations of same pollutants to be 181 and 222 ppb, respectively. One explanation for their high records could be attributed to the fact that they recorded these measurements immediately after Gulf war during the period of oil well fires.

The formation of ozone presents a strong relationship with meteorological conditions. In large urban centers, high emissions of ozone precursors are associated with the burning of fossil fuels by light- and heavy-duty vehicles. The resulting high concentrations of ozone in the atmosphere are harmful to ecosystems (EPA, 1997; Taia *et al.*, 2013). While high O₃ concentrations are generally associated with conditions that suppress vertical mixing, such as relatively light winds and thermal inversions in the atmosphere (Sillman, 1999; Godish, 2004), previous studies have shown a non-linearity between concentrations of gas-phase pollutants and wind speed (Bigi and Harrison, 2010). In a two-stage model, Kim *et al.* (2004) found that downwind direction was an important determinant of increased exposure to traffic pollutants. Abdul-Wahab *et al.* (2005) reported that O₃ was weakly correlated with wind speed but was positively correlated with wind direction. Similar observations were made by Ainslie and Steyn (2007) of higher O₃ concentrations downwind in a multiple linear regression model. It is known that long-range transport of air masses contribute to the high O₃ levels in addition to photochemical formation (Nishanth *et al.*, 2012). In our study, air masses have a strong marine influence, the observed enhancement of ground O₃ could be only at the expense of photochemistry rather than the transport of pollutant. A similar pattern of back trajectory was observed in other areas of the world (Khemani *et al.*, 1995; Nishanth *et al.*, 2012).

The mid-day peak and low nighttime concentrations of O₃ are typical characteristics of the diurnal cycle of ozone (Pudasainee *et al.*, 2006; Han *et al.*, 2011; Roberts-Semple, *et al.*, 2012). The ozone concentration slowly rises after the

sun rises, attains maximum during daytime and then again decreases until the next morning. This is due to photochemical O₃ formation. The shape and amplitude of ozone cycles are strongly influenced by meteorological conditions (temperature, solar radiation) and prevailing levels of precursors (NO_x and HC). Daily cycle of NO level arising from vehicular emissions and its conversion to NO₂ possessed major impact on the daily cycle of ozone levels in the study areas (Pudasainee *et al.*, 2006).

The seasonal variation in NO_x with an increasing trend towards the winter has been reported by other authors in Cairo (Khodeir, 2009); Dallas (Smith *et al.*, 2011); Delhi (Guttikunda and Gurjar, 2011) and New Jersey (Roberts-Semple *et al.*, 2012). Such variations could be attributed to the poor dependence of NO_x on meteorological conditions. Similar trends observed for NO and NO₂ consisted of a winter peak and summer minima (Khodeir, 2009; Bigi and Harrison, 2010; Smith *et al.*, 2011). This enhanced seasonality of NO_x levels in winter may be partly attributed to increased fossil fuels for domestic heating and driving. Therefore, anthropogenic sources seem to play a greater role in NO_x build-up than local meteorological conditions in winter; NO from traffic emissions is converted to NO₂ while the photochemical formation of O₃ is inhibited by the lack of intense solar radiation in the early morning (Fig. 3) (Sadanaga *et al.*, 2008; Geddes *et al.*, 2009). Moreover, Low values of NO emissions in the morning consume less O₃, and in daytime, it cannot be depleted further. This could be associated with Low values of VOCs emissions (Pudasainee *et al.*, 2006) Therefore, there is accumulation of ozone. However, we have a unique situation here, during which anthropogenic emissions of both NO_x are low, yet ozone concentrations are higher. This effect cannot be explained easily. It requires more data particularly on VOC, which we lagged.

The diurnal variation of surface ozone is helpful to understand the different processes responsible for ozone formation and destruction at a particular location. It is regulated by chemical and atmospheric dynamic processes (Elampari and Chithambarathanu, 2011).

NO_x concentrations increased rapidly during morning hours at the observation sites, which is due to the photochemical processes and emissions-dilution balance of NO_x and O₃, reflecting increased emissions of motor vehicles during the morning rush hours and also from industrial activities, especially at industrial site. During the noon hours, the solar radiation increased greatly and the photochemical processes that produce O₃ dominated, especially after the sunrise. Oxygen atoms produced in the photolysis of NO₂ could react with O₂ and to produce O₃ through the chemical reactions (Reddy *et al.*, 2012).

O₃ showed peak values when NO_x had the lowest concentrations between 14:00 h to 16:00 h. During this time, NO_x accumulations were not significant because of high NO_x photochemical consumption and increased air mass dilution as the height of the boundary layer increases (Reddy *et al.*, 2012). The boundary layer height should reach a maximum in the afternoon and additional venting of the boundary layer by convection. After this, the photochemical

production of O₃ decreased while NO₂ level increased. The reduction in O₃ level is mainly due to the decrease of solar radiation which then would lower the level of the photochemical production. Finally during the night hours, the NO_x and O₃ were maintained balance quickly; as there was no solar radiation and both the source emission and dilution effects decreased significantly (Swamy *et al.*, 2012). Furthermore, the increasing traffic in the evening hours usually starts from 18:00 (site4) and 20:00 h (site 6). A combination of more stable atmospheric conditions and more vehicle emissions causes to second peak (Sites 4 and 6) of the precursors from the late evening to early night.

The average NO_x concentrations were much higher at a rural site downwind of a desalination plant, reflecting increased levels of vehicular and factory emissions. Conversely, average O₃ concentrations at this site were lower than others. The negative correlation in hourly average NO_x and O₃ concentrations suggested that NO_x is not the only factor contributed to elevated O₃ concentrations (Roberts-Semple *et al.*, 2012).

The present study provides important insight into seasonal variations of ground level ozone, its associations with meteorological parameters in the Jeddah atmosphere, nevertheless, inadequacies of meteorological and VOC data have limited our interpretation. Therefore, further studies on ozone chemistry are essential and urgently needed.

CONCLUSIONS

The present study analyzed the concentrations of NO, NO₂, NO_x and O₃ measured in Jeddah city over 365 complete days in 2012. The results indicate that the diurnal cycle of ozone concentration has a mid-day peak and lower nighttime concentrations. The ozone concentration slowly rises after the sun rises, reaching a maximum during the daytime and then decreases until the next morning. This is due to photochemical O₃ formation. The shape and amplitude of ozone cycles is strongly influenced by meteorological conditions and prevailing levels of precursors (NO_x). In the study areas, the daily cycle of NO concentration arises from vehicular emissions, and its conversion to NO₂, had a major impact on the daily cycle of ozone levels. It is worth, in future study, analyzing the relationship between NO₂ and NO_x, as well as NO and NO_x, and between O₃ and NO₂/NO, which could be useful in O₃ forecasting and air pollution control strategies. Moreover, the relationships between VOC, UV and O₃ during the daytime are still not well understood and warrant further study. Significant amount of research, including monitoring and modeling of surface ozone pollution, is urgently required to draft policies for its control.

The concentration of NO_x and O₃ were relatively high during May–July compared to other months of the year. Moreover, the concentrations of O₃, measured at rural areas were occasionally high. At other locations (Residential, Industrial and city centers) the concentration were found relatively low.

The diurnal pattern of surface ozone concentration clearly indicates its dependency on the photochemical

production process, while the seasonal variations were mostly due to the in-situ photochemistry.

The exposure of the population with the elevated level pollutants for several months needs further investigation using an appropriate risk analysis and human. Moreover, O₃ has the potential to be a problem in the future with increased anthropogenic activities.

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