

Characterising NO₂, Its Temporal Variability and Association with Meteorology A Case Study in Makkah, Saudi Arabia

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Abstract

Nitrogen dioxide (NO₂) is one of the most harmful pollutants in terms of its adverse effects on human health and natural environment. This paper intends to characterise NO₂ in Makkah, aiming to analyse its temporal variations and association with meteorological parameters. NO₂ data from two monitoring stations: (1) the Presidency of Meteorology and Environment (PME); and Masfalah monitoring stations were used in this paper. Long term daily data (1996 - 2013) used for determining historical trends of NO₂ were collected at the PME site, whereas hourly data for 2012 were collected at both PME and Masfalah sites. NO₂ levels were compared with WHO and Saudi National air quality standards, the former standards were violated in every single year, whereas the latter were exceeded only in 1999. Hourly NO₂ concentrations seem to be at acceptable levels and have not violated the air quality standards. Long term temporal trends determined by TheilSen function showed decreasing trend in both NO (-0.15 µg³/year) and NO₂ (-0.22 µg³/year) concentrations, which is probably an indicator of improvement in exhaust emissions from road traffic and other emission sources, most probably due to stringent emission policies by the government of Saudi Arabia. The ratios of NO₂/NO have increased and show positive trend (0.04 µg³/year), however the trend is not significant. Temporal variations of NO₂ are analysed during various hours of the day and days of the week. Considerable lower levels of NO₂ were observed in the afternoon, which can be linked with high levels of solar radiation and temperature that accelerate photochemical dissociation of NO₂ into NO and atomic oxygen. Furthermore, the effect of temperature, wind speed and direction on NO₂ is analysed, which highlighted the importance of meteorological parameters in controlling the levels of NO₂.

Keywords: nitrogen dioxide; air pollution; meteorological parameters; temporal trend; temporal variations; Makkah - Saudi Arabia

1. Introduction

Air pollution is one of the growing concerns in large urban cities of Saudi Arabia due to growing population and growing per capita income which has resulted in increased number of registered vehicles. Enhanced numbers of vehicles will lead to increased demand for gasoline and diesel and hence the emission of traffic related air pollutants, such as particulate matter, carbon monoxide (CO) and nitrogen oxide (NO_x) will increase. Previously several authors (e.g., Othman *et al.*, 2010; Habeebullah, 2013a; Alharbi, 2009; Seroji, 2011) have reported higher levels of air pollutants in Makkah. However, most of these studies have focused on particulate matters, which show particularly high levels and exceed air quality standards in Makkah. Recently, Habeebullah (2013b) has analysed various air pollutants in Makkah aiming at understanding emission sources. Furthermore, Munir *et al.* (2013a) have analysed long term trends in several air pollutants in Makkah and reported that the levels of some air pollutants have increased during the last decade or so. Therefore, there is

a need for further work to analyze the levels of various air pollutants in Makkah, investigate their association with meteorology, and prepare an action plan for effective air quality management.

Nitrogen dioxide (NO₂) is one of those atmospheric pollutants that have considerable adverse impacts on human health and natural environment (Harrison, 2001). NO₂ has attracted more attention throughout the world due to its increasing proportion in NO_x as a result of new traffic technology (Carslaw, 2005). NO₂ is chemically related to nitric oxide (NO), and both NO₂ and NO together make nitrogen oxides (NO_x). These species are formed during high temperature combustion processes from the oxidation of nitrogen in the air or fuel. The principal source of NO_x in urban areas is road traffic (RoTAP, 2012). NO_x is predominantly emitted in the form of NO, which reacts with ozone (O₃) in the atmosphere and is converted into NO₂. Therefore, NO_x near the source is mainly in the form of NO but this ratio changes downwind from the sources and NO₂ becomes the dominant fraction (e.g., AQEG, 2004; Clapp and Jenkin, 2001).

NO is not generally considered to be harmful to human health at the concentrations found in the ambient atmosphere. However, it is rapidly converted into NO₂, which has a variety of environmental and health impacts. NO₂ can irritate the lungs and lower resistance to respiratory infections, such as influenza. Long term exposure to high NO₂ concentrations may cause increased incidence of acute respiratory illness in children. Furthermore, in the presence of sunlight, NO_x can react with Volatile Organic Compounds (VOCs) to produce photochemical pollutants, including O₃. NO₂ can also get further oxidized in air to acid gases, such as nitric acid (HNO₃), which contribute to the production of acid rain over regional scales (AQEG, 2004; RoTAP, 2012).

NO_x and O₃ are chemically coupled, therefore the levels of O₃ and NO₂ are inextricably linked and any resultant reduction in the level of NO₂ is invariably accompanied by an increase in the level of O₃ (Clapp and Jenkin, 2001). Therefore, any policy or action that intends to address the problem of NO₂ has to consider the resultant increase in O₃ levels (for more details see, Munir *et al.*, 2012). This paper intends to characterize NO₂ in Makkah and aims to analyze its temporal variations and association with meteorological parameters. The aim is to better understand the factors that control the levels of NO₂ in a view to prepare an action plan for its effective management.

2. Materials and Methods

This study was conducted at the Hajj Research Institute, Umm Al-Qura University, Makkah, Saudi Arabia. The study uses NO₂ data from two monitoring stations: (1) the Presidency of Meteorology and Environment (PME); and (2) Masfalah monitoring stations. Long term daily data (1996 - 2013), used for determining historical trends of NO₂ were collected at the PME site, whereas hourly data for 2012 were collected at both PME and Masfalah site. PME is located near the Holy Mosque in Makkah. This is a continuous monitoring station and measures the concentrations of several air pollutants, such as CO, sulphur dioxide (SO₂), NO_x, O₃, and meteorological parameters, including temperature, solar radiation, wind speed and direction. Masfalah is a roadside site and measures several air quality parameters, including NO₂. The locations of the monitoring stations are shown in Fig. 1. The monitoring stations were previously described by Munir *et al.* (2013a&b).

At both monitoring stations strict QA/QC (Quality Assurance and Quality Control) measures are taken to ensure the quality of data. This process makes sure that the data are (a) Genuinely representative of atmospheric concentrations in the areas under investigation; (b) Representative over the period of measurement, a yearly data capture rates were typically over 90 %. Statistical

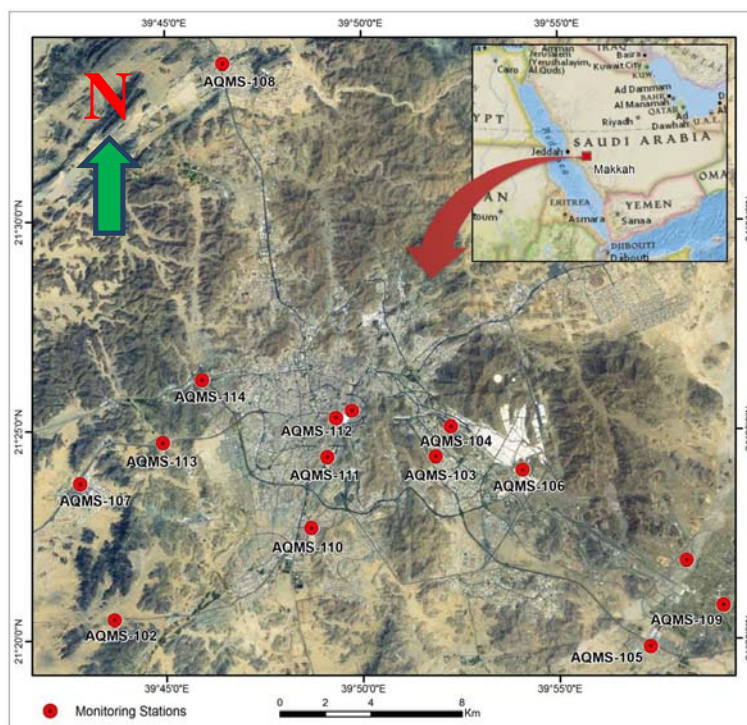


Figure 1. Map of air quality and meteorological monitoring sites in Makkah, Saudi Arabia, where AQMS 112 represents the PME, AQMS 111 the Masfalah site

data analysis was carried out in the statistical software R programming language (R Development Core Team, 2011), and associated package 'openair' (Carslaw and Ropkins, 2012). Temporal trend was quantified using TheilSen function described by Carslaw and Ropkins (2012).

The determination of NO_x concentration in the atmosphere is based on the chemiluminescent energy emitted when NO reacts with O₃ in an evacuated chamber to form chemiluminescent NO₂. The NO_x Monitor APNA-360 was used for monitoring the concentration of NO, NO₂ and NO_x. The APNA-360 is designed for measuring the concentration of NO_x in ambient air, based on the chemiluminescence method (CLD method) and hence is known as Chemiluminescent NO_x Analyser. This analyser continuously measures NO, NO₂ and NO_x. The concentration of NO₂ is calculated from the concentrations of NO and NO_x. The instrument is developed and calibrated by the Horiba, Ltd. In order to obtain stable and accurate data, the calibration procedure is carried out at regular intervals. Lower detectable limit of the instrument is 0.5 ppb.

3. Results and Discussion

Annual standards of World Health Organization (WHO) and Saudi Arabia national air quality standards set by the Presidency of Meteorology and Environment (PME) of Saudi Arabia for NO₂ are 40 and 100 µg/m³, whereas 1 hour average standards are 200 and 660 µg/m³, respectively. Fig. 2 compares annual average

of NO₂ concentrations (µg/m³) with the annual air quality standards for NO₂ set by WHO and PME. The WHO air quality standard is violated in every single year, however the PME standard is exceeded only in 1999, which showed the highest NO₂ concentrations during the study period. Furthermore, the trend line (solid line) in Fig. 2 shows a decreasing trend in NO₂ concentrations, which is probably an indicator of improvement in exhaust emissions from road traffic and other air pollution emission sources most probably due to stringent emission policies by the government of Saudi Arabia. Predominantly NO₂ is considered a secondary pollutant which is formed in the atmosphere by the reaction of NO with O₃ (Clapp and Jenkin, 2001; Jenkin, 2004), however NO₂ is also emitted as a primary pollutant, which is directly emitted into the atmosphere by a combustion process. On roadside locations NO_x is predominantly in the form of NO, whereas in areas away from combustion sources NO_x predominantly exists in the form of NO₂ due to the conversion of NO into NO₂ in the atmosphere (Munir *et al.*, 2012).

Fig. 3 shows the level of hourly NO₂ concentrations (µg/m³) at both PME and Masfalah monitoring stations for year 2012, where it can be observed that NO₂ levels are below the PME hourly air quality standards (660 µg/m³), whereas the WHO standard (200 µg/m³) is exceeded only a few times. Probably this shows (Figs. 2 and 3) that short term NO₂ levels pose no threat to human health, however long term NO₂ levels are above air quality standards and are likely to pose threat to human health. In other words, it can be said that NO₂ levels are posing no threat to the health

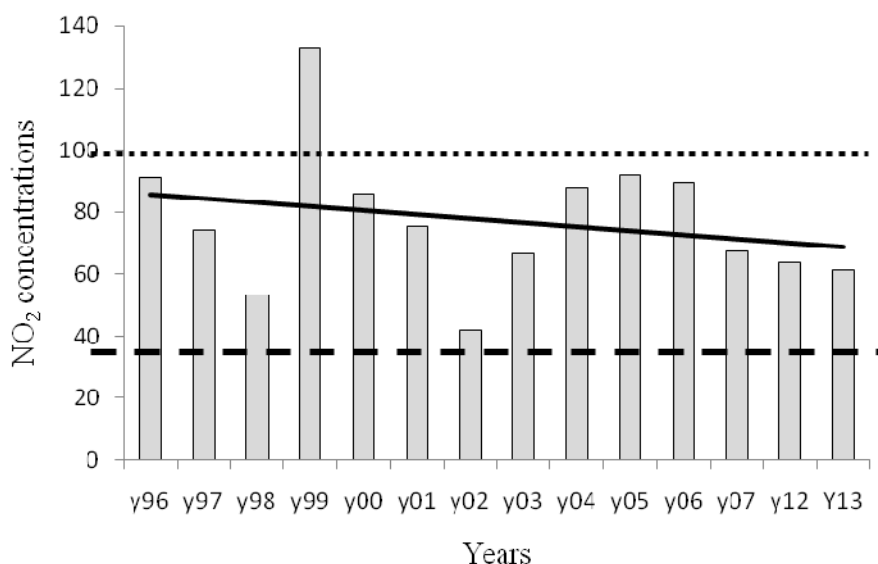


Figure 2. NO₂ concentrations (µg/m³) annual averaged over the study period (1996 - 2007, 2012, 2013) at the PME site are compared with air quality standards. Note 2008 - 2011 data are missing as the monitoring station was not working due to some construction work at the Holy Mosque. The dotted and the dashed lines show NO₂ annual limits of PME (100 µg/m³) and WHO (40 µg/m³), respectively, whereas the solid line shows linear trend in the annual NO₂ concentrations.

of the visitors (pilgrims) who come to Makkah for a short time, however it might pose risk to the health of residents of the Makkah city. It is worth re-emphasizing that every year millions of people from throughout the world visit the Holy City of Makkah to perform Umrah and Hajj (Pilgrimage) and stay here for several days, weeks, or months.

In Fig. 4 long temporal trends of NO_2 , NO and NO_2/NO are quantified, using TheilSen function (Carslaw and Ropkins, 2012). TheilSen function uses monthly average NO_2 concentrations to quantify annual trend. Both NO ($-0.15 \mu\text{g}^3/\text{year}$) and NO_2 ($-0.22 \mu\text{g}^3/\text{year}$) concentrations show negative trend, however the trend is insignificant. It can be seen in Fig. 4 that both NO and NO_2 levels were considerably higher in several months during 1998, 1999 and 2000. In some months the levels have reached a level as high as $250 \mu\text{g}/\text{m}^3$ in case of NO and $300 \mu\text{g}/\text{m}^3$ in case of NO_2 (Fig. 4). After the year 2000, NO levels have remained below $50 \mu\text{g}/\text{m}^3$ and that of NO_2 (with few exceptions) below $100 \mu\text{g}/\text{m}^3$. The ratios of NO_2/NO (Fig. 4, bottom) have increased and show positive trend ($0.04 \mu\text{g}/\text{m}^3 \text{ year}$), however the trend is not significant. The positive trend in NO_2/NO ratio shows that the proportion of NO_2 in NO_x has increased as compared to NO. Carslaw (2005) has described increasing NO_2/NO_x emission ratios from road traffic emissions in the UK using data from 36 monitoring stations during 1997 to 2003. Carslaw (2005) considered the following as the likely reasons for increasing NO_2/NO ratios: (a) increased use of certain types of diesel particulate filters fitted to buses; (b) increased penetration of diesel cars in the passenger car fleet; (c) new light and heavy-duty engine technologies; and (d) management approaches. The factors (a) and (b) are considered the most important

factors for increasing NO_2/NO_x ratios. More recently, Carslaw *et al.* (2011) have analysed NO_x and NO_2 trends in the UK and reported increased NO_2/NO_x ratios.

Temporal variations of NO_2 during different hours of the day and days of the week during the year 2012 at the Masfalah and PME monitoring stations are shown in Fig. 5. NO_2 levels at both monitoring stations vary during different time periods, however average NO_2 levels are slightly greater at the PME than the Masfalah monitoring station. Annual average NO_2 levels for year 2012 were 46 and $43 \mu\text{g}/\text{m}^3$ at PME and Masfalah monitoring stations, respectively. This is expected as Masfalah is a roadside, whereas PME is a background site situated within the boundary of the Holy Mosque. On roadsides freshly emitted NO_x is mainly in the form of NO. However, in the atmosphere NO reacts with O_3 and produces NO_2 , therefore by the time it gets to background locations NO_x is mainly in the form of NO_2 , which explains why NO_2 levels are greater at a background than a roadside site. In Fig. 5 it is shown that in the morning hours NO_2 levels are higher at the PME site, while after mid-day (about 12:00 hour) the NO_2 levels at the PME site decrease considerably more than that at the Masfalah site and the levels of NO_2 at PME become lower than the Masfalah site. In the afternoon very high temperature causes NO_2 levels to decrease considerably, probably due to photochemical dissociation of NO_2 and converting it to NO and atomic oxygen, however the reduction at the PME site is greater than at the Masfalah site. At a roadside location due to traffic, a continuous emission of NO and NO_2 is expected, which probably does not let the level of NO_2 to drop as much as on a background site. The negative correlation of NO_2 with temperature is shown in Fig. 6, which shows that NO_2 levels at PME monitoring site increase with temperature, however after about 35°C , the levels of NO_2 starts decreasing. In Fig. 6 (right-panel) NO_2 levels at a temperature greater than 35°C (temperature $> 35^\circ\text{C}$) is depicted, which clearly demonstrates the negative correlation between NO_2 and temperature at high temperature. Day *et al.* (2008) have analysed the negative correlation between NO_2 and temperature.

In Fig. 5 (bottom-panel) the weekly cycle of NO_2 is shown. Again, it is clearly shown that NO_2 levels are greater at the PME site than the Masfalah site, and that there is a considerable variation between the two sites at various days. The lowest NO_2 levels are shown on Friday at both monitoring sites, which is probably due to the weekend effect. Friday is a weekend day and governmental organisations, educational institutions, and private businesses remain close on this day. The second day of weekend was Thursday until 2012 and Saturday after 2013, however on both of these days most of the roads are almost as busy as normal weekdays

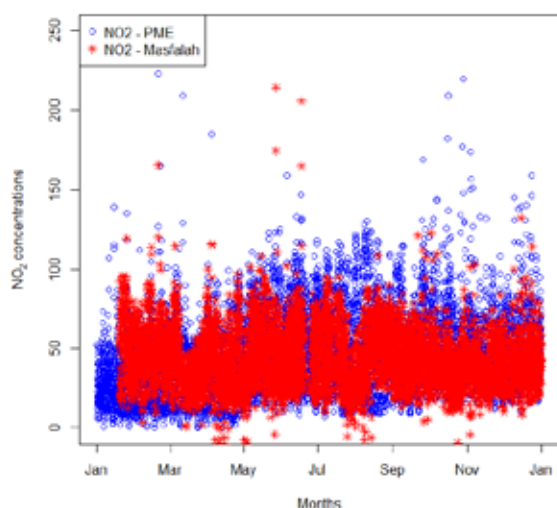


Figure 3. NO_2 hourly concentrations ($\mu\text{g}/\text{m}^3$) at the PME and Masfalah monitoring stations for year 2012

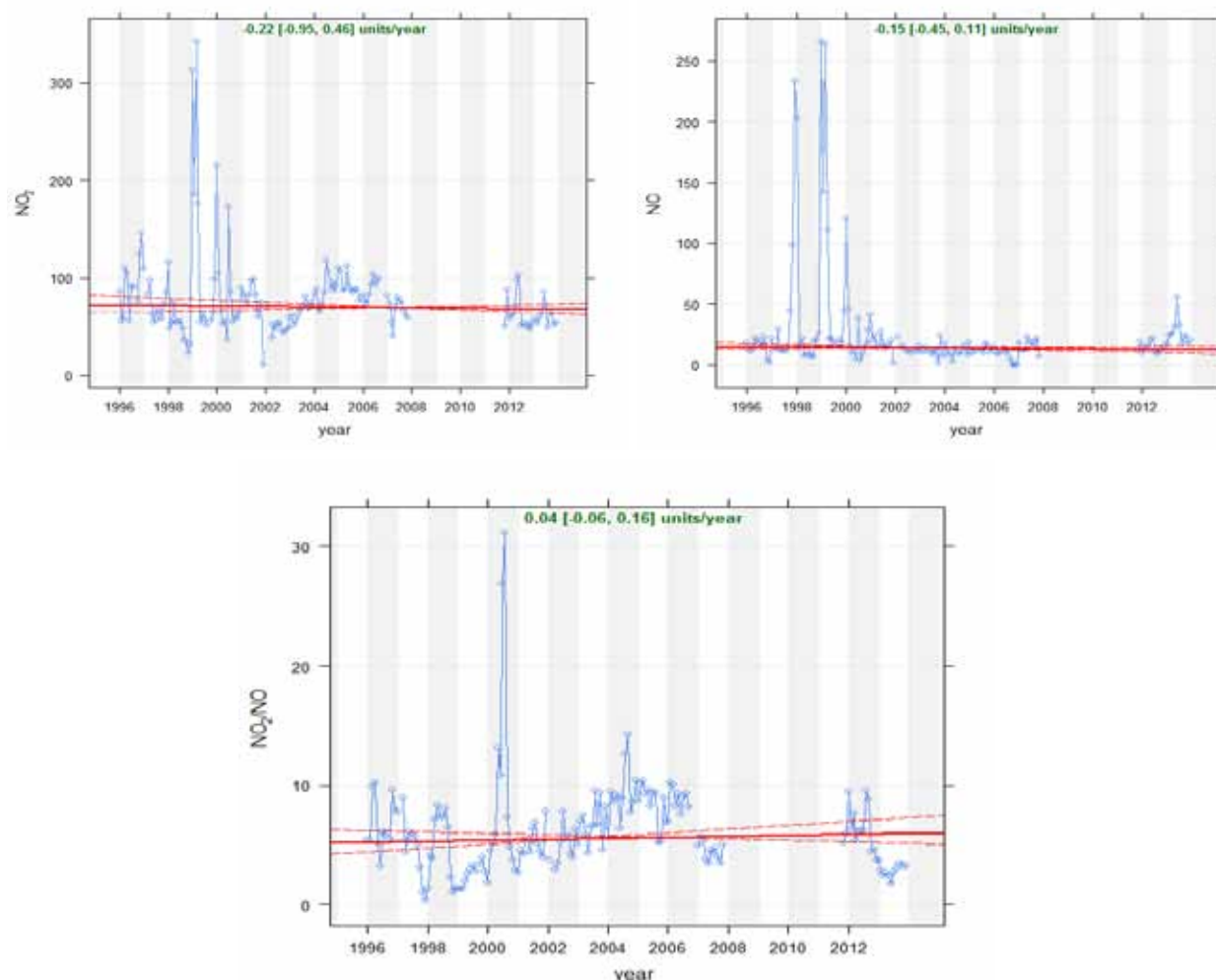


Figure 4. Temporal trends in NO ($\mu\text{g}/\text{m}^3$), NO₂ ($\mu\text{g}/\text{m}^3$) and NO₂/NO ratios during 1996 to 2013 at the PME monitoring station.

and therefore the levels of NO₂ on these days are not significantly different from other weekdays. Obviously, temperature is not related to daily traffic or other activities and is more related with time of the day or month of the year, therefore temperature curve on weekly cycle is almost a straight line (Fig. 5, bottom).

In Fig. 7 the effect of wind speed and direction on NO₂ is depicted with the help of polar plots. Meteorological parameters are not monitored at the Masfalah site, therefore wind speed and direction data used in both plots were collected at the PME site. Generally, at both sites high levels of NO₂ can be observed at low wind speed. This is because high wind speed plays an important role in the dispersion of locally emitted pollutants. In contrast at low wind speed, locally emitted pollutants remain undispersed and, therefore result in high levels of air pollutants. The effect of wind direction is related to the sources of emissions. Therefore various shades of colour can be observed in the polar plots in different directions, for example, opposite patterns of colour are shown in southeast and

southwest at both monitoring sites. At the PME site (Fig. 7, right) it can be clearly seen that when southerly wind blows at a speed of two meter per second or over ($\Rightarrow 2\text{m/s}$), it can result in lower NO₂ concentrations ($< 25 \mu\text{g}/\text{m}^3$). In contrast, at Masfalah site the same wind speed and direction might result in much higher levels of NO₂. This shows that the effect of wind speed and direction vary spatially depending on the distance of emission sources, the strength of emission source, local environment, and presence of barriers like buildings or trees. Furthermore, it indicates that air pollutant levels not only depend on amount of pollutant emitted to the atmosphere but also on meteorological parameters, such as temperature, wind speed and direction.

4. Conclusions

This paper analyses the levels of NO₂, its temporal trends and association with meteorological parameters, such as temperature, wind speed and direction in the arid climatic conditions of Makkah, Saudi Arabia. It is

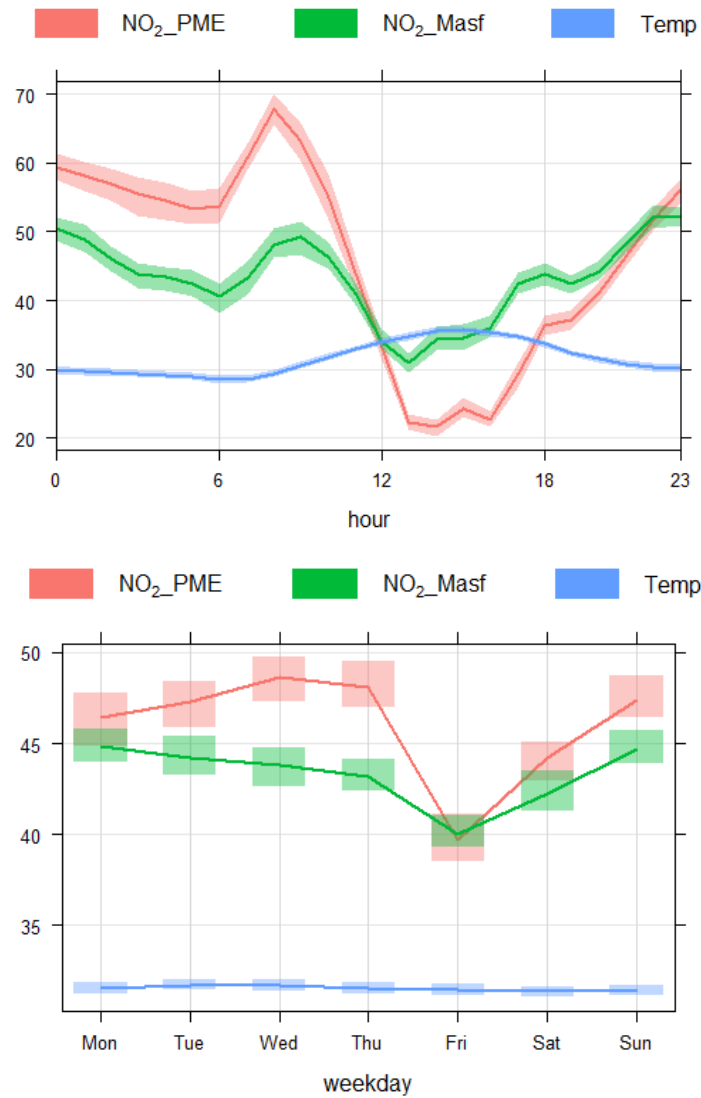


Figure 5. Temporal variations of NO₂ (µg/m³) daily cycle (top) and weekly cycle (bottom) at PME and Masfalah monitoring stations during 2012.

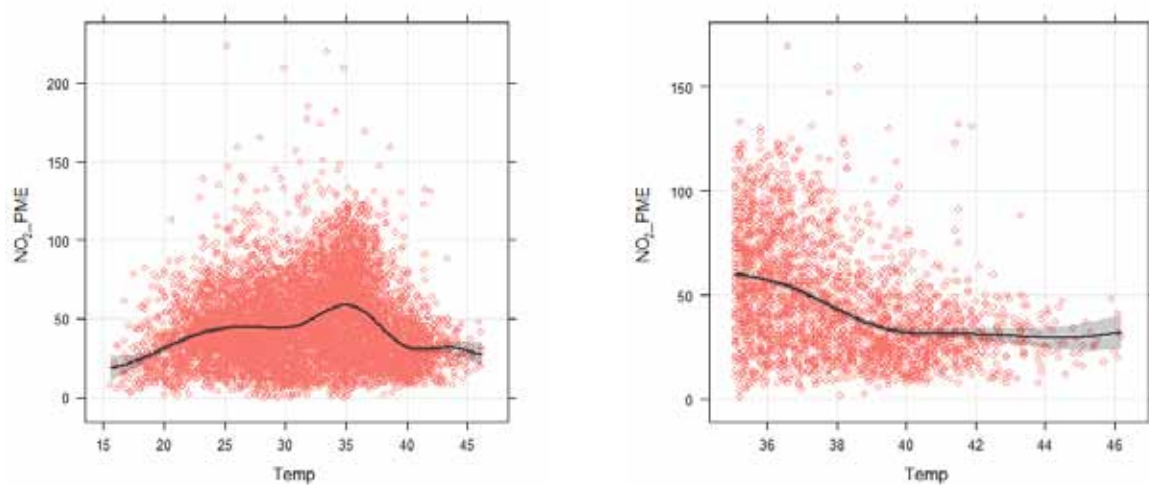


Figure 6. Scatter plots of NO₂ and temperature at the PME monitoring site: (a) whole dataset; (b) subset when temperature >35°C.

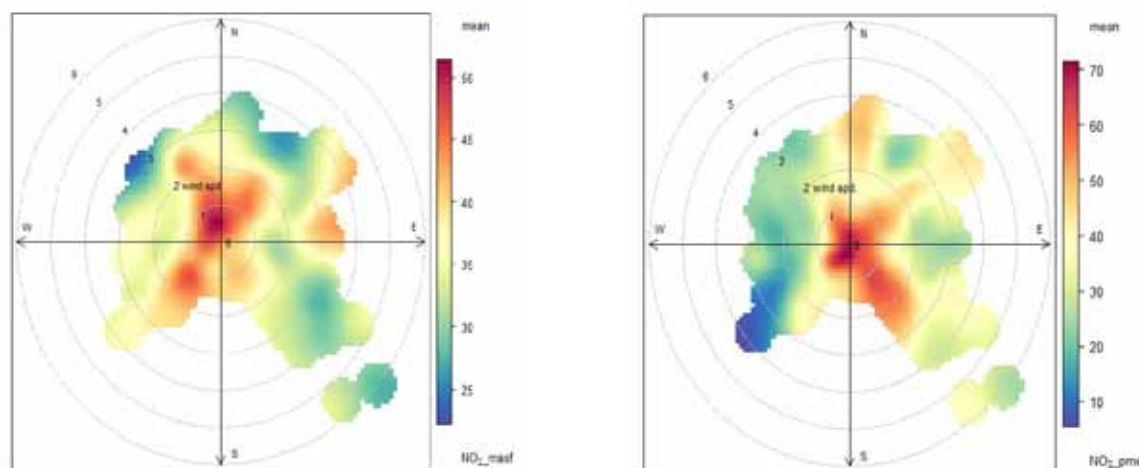


Figure7. Polar plots of hourly NO₂ concentrations (ug/m³) at the Masfalah (left) and PME (right) monitoring station for 2012.

shown that in spite of the decreasing trends, long-term averaged NO₂ levels pose threat to human health, as the levels exceed WHO air quality standards. NO₂ concentrations have demonstrated both temporal and spatial variability. The spatial and temporal variability of NO₂ is analysed in light of the meteorological parameters. NO₂ levels are observed to be lowest during the afternoon, probably due to high temperature and solar radiation levels and on Friday due to weekend effect. NO₂ and NO have shown negative trends, however NO₂/NO have demonstrated positive trends. Further work is required to quantify primary NO₂ concentration and its future implications for air quality in Makkah, which is part of the ongoing project for improving air quality in Makkah.

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