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Characterising NO_2, Its Temporal Variability and Association with Meteorology A Case Study in Makkah, Saudi Arabia

Turki M. Habeebullah

Department of Environmental and Health Research, The Custodian of the Two Holy Mosques Institute for Hajj and Umrah Research, Umm Al-Qura University, Makkah, The Kingdom of Saudi Arabia

Abstract

Nitrogen dioxide (NO_2) is one of the most harmful pollutants in terms of its adverse effects on human health and natural environment. This paper intends to characterise NO_2 in Makkah, aiming to analyse its temporal variations and association with meteorological parameters. NO_2 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 NO_2 were collected at the PME site, whereas hourly data for 2012 were collected at both PME and Masfalah sites. NO_2 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 NO_2 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 μg^3/year) and NO_2 (-0.22 μg^3/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 NO_2/NO have increased and show positive trend (0.04 μg^3/year), however the trend is not significant. Temporal variations of NO_2 are analysed during various hours of the day and days of the week. Considerable lower levels of NO_2 were observed in the afternoon, which can be linked with high levels of solar radiation and temperature that accelerate photochemical dissociation of NO_2 into NO and atomic oxygen. Furthermore, the effect of temperature, wind speed and direction on NO_2 is analysed, which highlighted the importance of meteorological parameters in controlling the levels of NO_2.

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 (NOx) 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 (NO_2) is one of those atmospheric pollutants that have considerable adverse impacts on human health and natural environment (Harrison, 2001). NO_2 has attracted more attention throughout the world due to its increasing proportion in NOx as a result of new traffic technology (Carslaw, 2005). NO_2 is chemically related to nitric oxide (NO), and both NO_2 and NO together make nitrogen oxides (NOx). These species are formed during high temperature combustion processes from the oxidation of nitrogen in the air or fuel. The principal source of NOx in urban areas is road traffic (RoTAP, 2012). NOx is predominantly emitted in the form of NO, which reacts with ozone (O_3) in the atmosphere and is converted into NO_2. Therefore, NOx near the source is mainly in the form of NO but this ratio changes downwind from the sources and NO_2 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 NO_2, which has a variety of environmental and health impacts. NO_2 can irritate the lungs and lower resistance to respiratory infections, such as influenza. Long term exposure to high NO_2 concentrations may cause increased incidence of acute respiratory illness in children. Furthermore, in the presence of sunlight, NOx can react with Volatile Organic Compounds (VOCs) to produce photochemical pollutants, including O_3. NO_2 can also get further oxidized in air to acid gases, such as nitric acid (HNO_3), which contribute to the production of acid rain over regional scales (AQEG, 2004;RoTAP, 2012).

NOx and O_3 are chemically coupled, therefore the levels of O_3 and NO_2 are inextricably linked and any resultant reduction in the level of NO_2 is invariably accompanied by an increase in the level of O_3 (Clapp and Jenkin, 2001). Therefore, any policy or action that intends to address the problem of NO_2 has to consider the resultant increase in O_3 levels (for more details see, Munir *et al*., 2012). This paper intends to characterize NO_2 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 NO_2 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 usesNO$_2$ 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 NO_2 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 (SO_2), NOx, O_3, and meteorological parameters, including temperature, solar radiation, wind speed and direction. Masfalah is a roadside site and measures several air quality parameters, including NO_2. 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

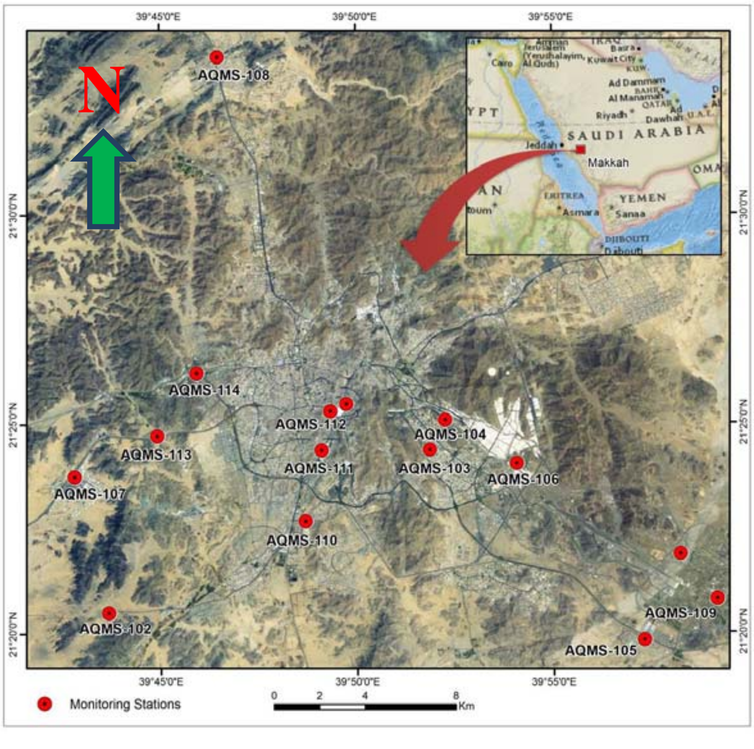

Figure 1. Map of air quality and meteorological monitoring sites in Makkah, Saudi Arabia, where AQMS 112 represents the PME, AQMS 111 the Masfalah site

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 NOx concentration in the atmosphere is based on the chemiluminescent energy emitted when NO reacts with O_3 in an evacuated chamber to form chemiluminescent NO_2. The NOx Monitor APNA-360 was used for monitoring the concentration of NO, NO_2 and NOx. The APNA-360 is designed for measuring the concentration of NOx in ambient air, based on the chemiluminescence method (CLD method) and hence is known as Chemiluminescent NOx Analyser. This analyser continuously measures NO, NO_2 and NOx. The concentration of NO_2 is calculated from the concentrations of NO and NOx. 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 NO_2 are40 and 100 $\mu g/m^3$, whereas 1 hour average standards are 200 and 660 $\mu g/m^3$, respectively. Fig. 2 compares annual average of NO_2 concentrations ($\mu g/m^3$) with the annual air quality standards for NO_2 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 NO_2 concentrations during the study period. Furthermore, the trend line (solid line) in Fig. 2 shows a decreasing trend in NO_2 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 NO_2 is considered a secondary pollutant which is formed in the atmosphere by the reaction of NO with O_3 (Clapp and Jenkin, 2001; Jenkin, 2004), however NO_2 is also emitted as a primary pollutant, which is directly emitted into the atmosphere by a combustion process. On roadside locations NOx is predominantly in the form of NO, whereas in areas away from combustion sources NOx predominantly exists in the form of NO_2 due to the conversion of NO into NO_2 in the atmosphere (Munir *et al*., 2012).

Fig. 3 shows the level of hourly NO_2 concentrations ($\mu g/m^3$) at both PME and Masfalah monitoring stations for year 2012, where it can be observed that NO_2 levels are below the PME hourly air quality standards (660 $\mu g/m^3$), whereas the WHO standard (200 $\mu g/m^3$) is exceeded only a few times. Probably this shows (Figs. 2 and 3) that short term NO_2 levels pose no threat to human health, however long term NO_2 levels are above air quality standards and are likely to pose threat to human health. In other words, it can be said that NO_2 levels are posing no threat to the health

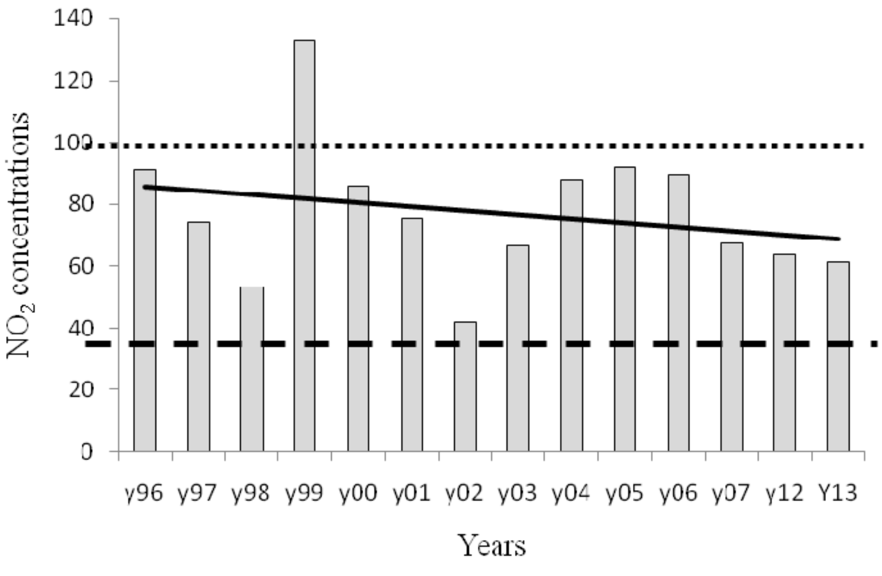

Figure 2. NO_2 concentrations ($\mu g/m^3$) annual averaged over the study period (1996 - 2007, 2012, 2013) at the PME site are compared with air quality standards. Note 2008 - 2011 data are missing as the monitoring station was not working due to some construction work at the Holy Mosque. The dotted and the dashed lines show NO_2 annual limits of PME (100 $\mu g/m^3$) and WHO (40 $\mu g/m^3$), respectively, whereas the solid line shows linear trend in the annual NO_2 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 Makkahto 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 μg^3/year) and NO_2 (-0.22 μg^3/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 $\mu g/m^3$ in case of NO and 300 $\mu g/m^3$ in case of NO_2 (Fig. 4). After the year 2000, NO levels have remained below 50 ($\mu g/m^3$) and that of NO_2 (with few exceptions) below 100 $\mu g/m^3$. The ratios of NO_2/NO (Fig. 4, bottom) have increased and show positive trend (0.04 $\mu g/m^3$ year), however the trend is not significant. The positive trend in NO_2/NO ratio shows that the proportion of NO_2 in NOx has increased as compared to NO. Carslaw (2005) has described increasing NO_2/NOx emission ratios from road traffic emissionsin 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

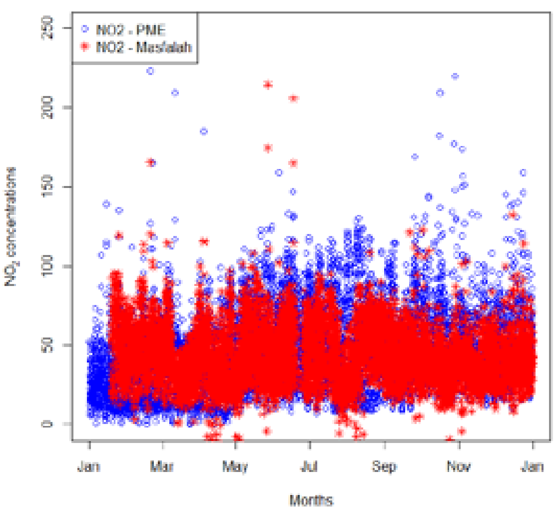

Figure 3. NO_2 hourly concentrations ($\mu g/m^3$) at the PME and Masfalah monitoring stations for year 2012

factors for increasing NO_2/NOx ratios. More recently, Carslaw *et al*. (2011) have analysed NOxan NO_2 trends in the UK and reported increased NO_2/NOx 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 $\mu g/m^3$ 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 NOx 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 NOx is mainly in the form of NO_2, which explains why NO_2 levels is 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°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

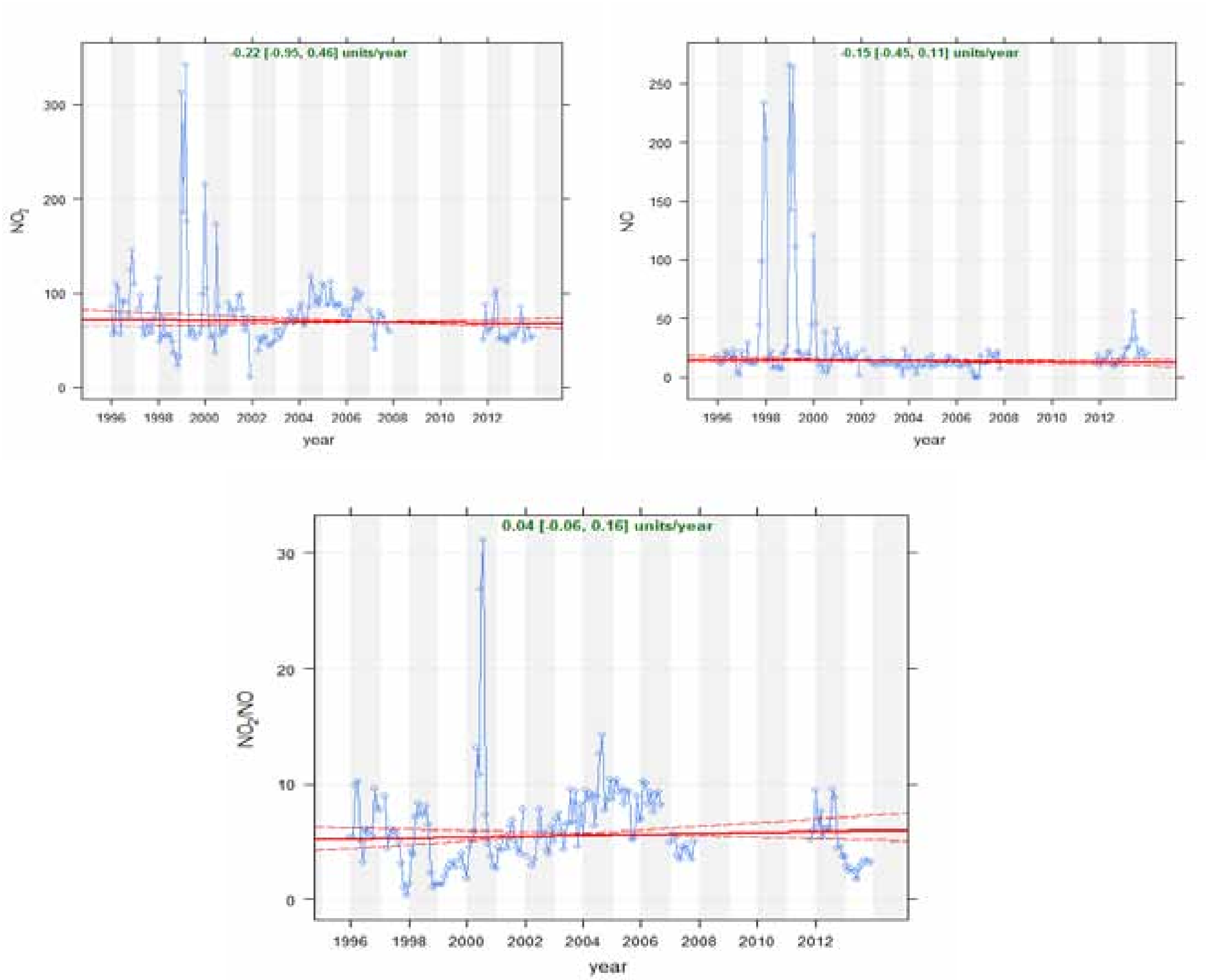

Figure 4. Temporal trends in NO (µg/m^3), NO_2 (µg/m^3) and NO^2/NO ratios during 1996 to 2013 at the PME monitoring station.

and therefore the levels of NO_2 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 NO_2 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 NO_2 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 (=> 2m/s), it can result in lower NO_2 concentrations (< 25 µg/m^3). In contrast, at Masfalah site the same wind speed and direction might result in much higher levels of NO_2. 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 pollutantsemitted to the atmosphere but also on meteorological parameters, such as temperature, wind speed and direction.

4. Conclusions

This paper analyses the levels of NO_2, 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

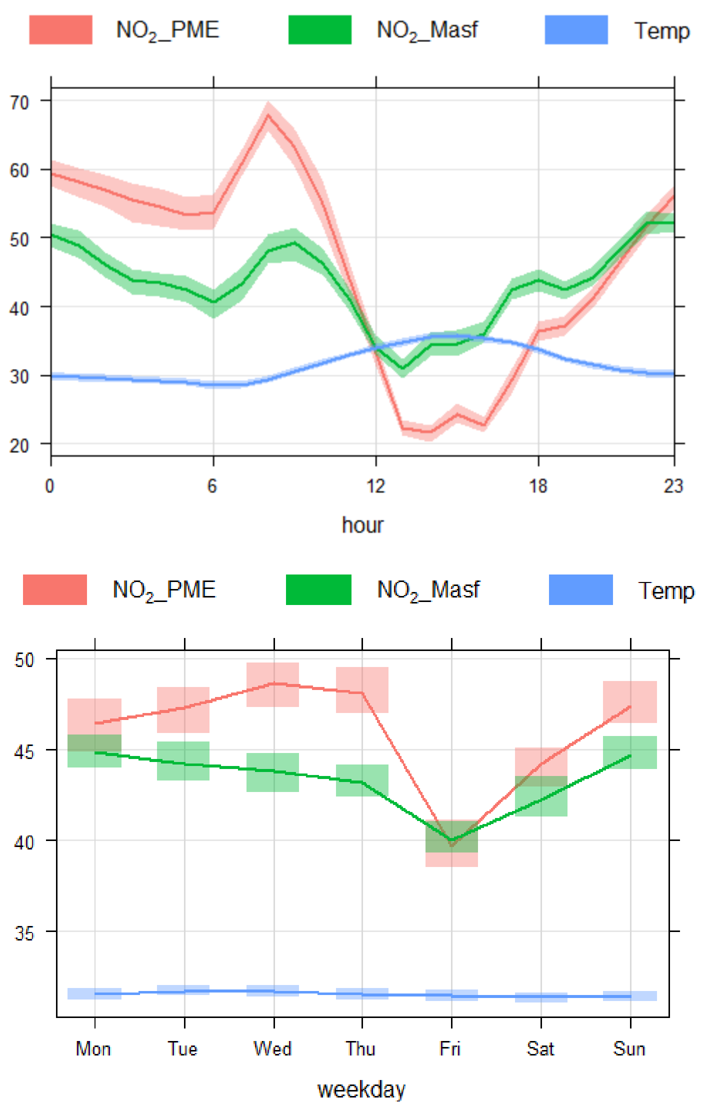

Figure 5. Temporal variations of NO_2 ($\mu g/m^3$) daily cycle (top) and weekly cycle (bottom) at PME and Masfalah monitoring stations during 2012.

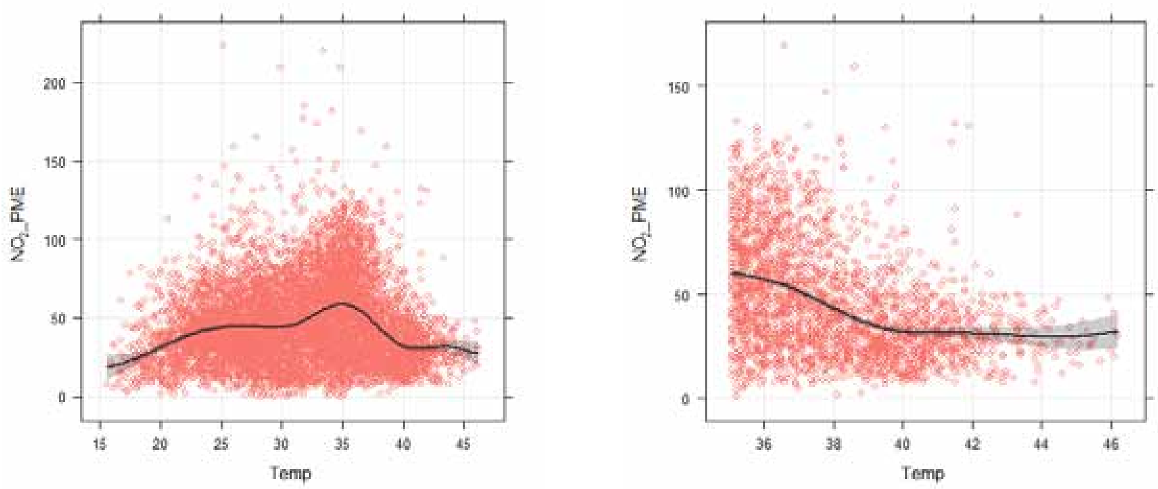

Figure 6. Scatter plots of NO^2 and temperature at the PME monitoring site: (a) whole dataset; (b) subset when temperature >35°C.

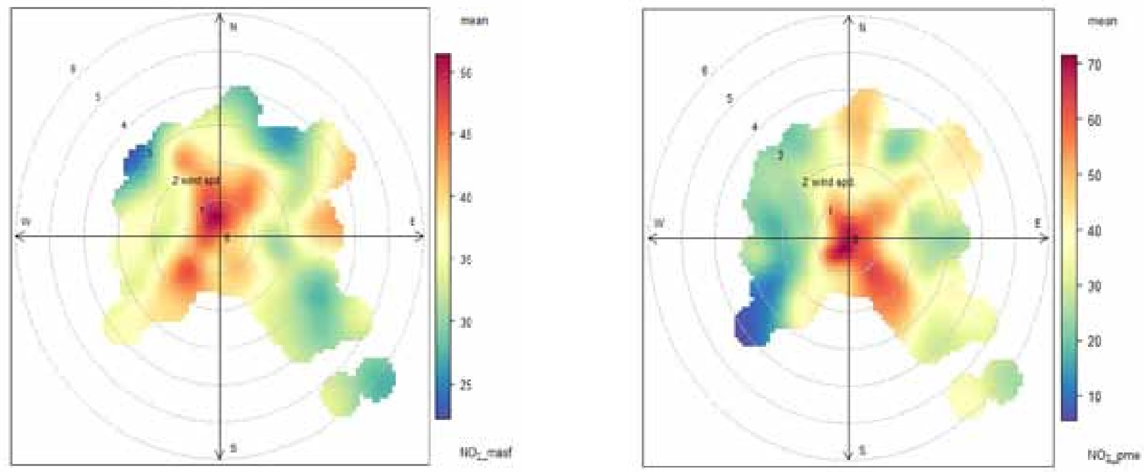

Figure7. Polar plots of hourly NO_2 concentrations (ug/m^3) at the Masfalah (left) and PME (right) monitoring station for 2012.

shown that in spite of the decreasing trends, long-term averaged NO_2 levels pose threat to human health, as the levels exceed WHO air quality standards. NO_2 concentrations have demonstrated both temporal and spatial variability. The spatial and temporal variability of NO_2 is analysed in light of the meteorological parameters. NO_2 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. NO_2 and NO have shown negative trends, however NO_2/NO have demonstrated positive trends. Further work is required to quantify primary NO_2 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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Correspondence to
Dr. Turki M. Habeebullah
Department of Environmental and Health Research,
The Custodian of the Two Holy Mosques Institute for Hajj and Umrah Research,
Umm Al-Qura University,
Makkah, The Kingdom of Saudi Arabia
P.O. Box: 6287, Sort Code: 21955
Tel: +966 25540504
Fax: +966 25564955
Mobile +966560033454
E-mail: t_habeebullah@yahoo.com