Modelling Ozone-Temperature Slope under Atypically High Temperature in Arid Climatic Conditions of Makkah, Saudi Arabia

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ABSTRACT

Ground level ozone concentration is dependent on its precursors, such as Nitrogen Oxides (NOₓ) and hydrocarbons (HCs) and meteorological parameters, most importantly air temperature. Positive ozone-temperature slope at average temperature is well-documented. However, how this relationship breaks at extremely high temperature in hotter climates is still debatable. As this could have implications for long term global modelling predictions, this paper explores evidence for a negative ozone-temperature slope during atypically high temperature events in Makkah, Saudi Arabia, where temperature levels as high as 50°C are recorded. At temperature levels (15–42°C) statistical analysis showed positive ozone-temperature slopes, however the slopes became negative at atypically high temperature levels (> 42°C). Using data when hourly mean temperature was greater than 42°C, Quantile Regression Model (QRM) showed negative ozone-temperature slopes. The negative slopes at quantile 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9 were –1.88, –5.83, –7.89, –7.08, –11.11, –15.00, –18.28, and –28.57 µg/m³/°C, respectively. Mean slope determined by linear regression was –11.51 µg/m³/°C. Furthermore, the negative slopes were stronger at higher quantiles of ozone distribution, indicating non-linearities in the association of ozone and temperature. Reduction in the levels of ozone precursors, such as total hydrocarbons (THCs) and nitrogen dioxide (NO₂) is probably the most likely reason for the negative ozone-temperature slope at extremely high temperature. Previously concerns have been expressed that under the warming climate scenario increasing temperature may further increase ozone levels, particularly in urban areas during pollution episodes, however this study suggests the opposite at extremely high temperature in hot arid climatic conditions.

Keywords: Ground level ozone; Extremely high temperature; Quantile regression model; Ozone-temperature slope; Makkah.

INTRODUCTION

Ozone (O₃) is a secondary air pollutant and is formed by photochemical oxidation of Volatile Organic Compounds (VOCs) and Nitrogen Oxides (NOₓ) in the presence of solar radiation (AQEG, 2009). Ozone is a reactive oxidant and is actively involved in many chemical reactions, including biochemical reactions. It plays a vital role in atmospheric chemistry and contributes to the greenhouse effect (IPCC, 2001). At higher concentrations ground level ozone has been linked with various health problems, damage to agricultural crops and other materials (e.g., Bell and Treshow, 2008). Ozone adversely affects human health due to its irritant properties and induction of an inflammatory response in the lungs, causing health problems and premature deaths (AQEG, 2009). Analysing the health impacts of ozone World Health Organisation (WHO, 2008) has reported that high levels of ground level ozone causes about 21000 premature deaths and 14000 respiratory hospital admissions annually in 25 European Union countries. Atmospheric ozone levels are dependent on the amount of ozone precursors (sources), the amount of reactants (sinks) and meteorological conditions. High ozone concentrations are usually observed during periods with sustained high temperatures and sunshine because such conditions favour photochemical ozone formation.

Ground-level ozone at a specific location is dependent on several mechanisms: (a) photochemical ozone formation which is dependent on the level of ozone precursors, such as VOCs and NOₓ; (b) chemistry with other air pollutants that can affect ozone concentration in different ways, such as particles can provide a surface for ozone dry deposition, carbon monoxide (CO) can react with hydroxyl radical (OH) to produce peroxy radicals that consume nitric oxide (NO), and freshly emitted NO acts as a sink for ozone; (c) meteorological conditions, e.g., solar radiation, temperature,
relative humidity, wind speed and wind direction play a significant role in ozone formation and dispersion; and (d) vertical transport known as Strato-Tropospheric Exchange (STE) and horizontal transport including global (hemispheric), regional and local-scale transport (Jenkin, 2008; Munir, 2013). The individual contribution of each of these mechanisms varies both spatially and temporally. If the conditions of ozone transport, precursors concentrations and solar radiation are kept the same, the variation of ground-level ozone can be simply explained by air temperature. On this condition, the ozone concentration is typically proportional to the temperature because chemical reaction rate constant increases with temperature.

The slope of the ozone-temperature relationship is referred to as the climate penalty factor and is investigated by several authors (e.g., Camalier et al., 2007; Bloomer et al., 2009). Temperature has a positive association with ozone and ground-level ozone concentration typically increases with increasing temperature (Bloomer et al., 2009). Intergovernmental Panel on Climate Change (IPCC, 2007) has reported that temperature has been rising globally, as a result ground-level ozone is expected to rise as well, assuming everything else remains the same (Cape, 2008). Several researchers have investigated the effect of rising average temperature on ground-level ozone (e.g., Wu et al., 2008; Bloomer et al., 2009; Jacob and Winner, 2009). However, the effect of extremely high temperature on ground is analysed by a small number of studies, all based in the USA, for example Steiner et al. (2010). They investigated the effect of extremely high temperature on ozone and reported negative climate penalty factor during 1980–2005 in California, USA. This paper explores the negative ozone-temperature slope at extremely high temperature and its significance further using data from arid climatic conditions of Makkah, Saudi Arabia applying an advanced statistical model.

Several authors have reported high levels of air pollutants in Makkah (e.g., Seroji, 2011; Habeebullah, 2013a, b; Munir et al., 2013a, b). Makkah is a densely populated city and is considered the holiest city in the Muslim world, and millions of Muslims visit the city every year. Clean air is therefore a particularly sensitive issue in Makkah, especially during Hajj and Ramadan which may occur in the hottest months (June and July) when both pilgrims and the residents of Makkah often face the combined challenge of extremely high temperature and reduced air quality. The question is as to what is the effect of extremely high temperature on air pollution, particularly on secondary air pollutants like ground-level ozone, which is formed in the presence of solar radiation and high temperature. This needs to be investigated in detail. Makkah is subject to high temperatures throughout the year, especially during summer months when temperature reaches up to 50°C. The levels of ground-level ozone and its association with climatic factors are not well characterised in Makkah.

In this paper the aim is to analyse the effect of atypically high temperature on ground-level ozone in Makkah, focusing on summer months. The study mainly focuses on atypically high ozone and temperature levels using data collected in Makkah by continuous monitoring stations during the last few years. The finding of this research will be important not only for local air quality modelling, but also will feed into the long-term climate change models for forecasting future levels of ozone and its potential implications.

**METHODOLOGY**

**Data Source**

This study was carried out at the Hajj Research Institute, Umm Al-Qura University, Makkah, Saudi Arabia. The data for 2012 were collected at the Presidency of Meteorology and Environment (PME) and Masfalah monitoring stations. PME is located near the Holy Mosque in Makkah. This is a continuous monitoring station and measures the concentrations of several air pollutants (e.g., PM$_{10}$, NO$_x$, ozone) and meteorological parameters (e.g., temperature, solar radiation, wind speed and direction). Masfalah is a roadside site and measures only air quality parameters. Long-term (2003–2012) temperature data used for temporal analysis of temperature were available at Azizia, Shara’ai and Leeth monitoring sites. The locations of the monitoring stations are shown in Fig. 1. The monitoring stations were previously described by Munir et al. (2013a, b).

Ozone was measured using a UV Photometric Ozone Analyser (Model – APOA360). This is the most commonly used instrument for measuring ground-level ozone concentration. Ambient air is drawn through a cell in which the absorption of UV radiation is measured at 254 nm. The strong absorption by ozone at this wavelength produces a detectable absorption measurement when ozone is present in the cell. The absorption cell alternately samples ambient air coming directly from the atmosphere and ambient air diverted through a manganese dioxide scrubber that converts ozone catalytically to oxygen but leaves all other trace gases intact and the relative humidity almost constant. The UV irradiance is therefore measured in the presence and absence of ozone in the ambient air. The measured irradiance in the presence of ozone is related to the measured irradiance in the absence of ozone, by the Beer-Lambert law. By comparing the two irradiance signals it is possible to determine the concentration of ozone in the cell, provided that the length of the cell and the absorption cross-section for ozone are known. Ozone measurements are reported as parts per billion volume or partial pressure. 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 rate were typically over 90%.

Statistical data analysis was carried out in the statistical software R programming language (R Development Core Team, 2012), and associated packages openair (Carslaw and Ropkins, 2012), and Quantreg (Koenker, 2013).

**Modelling**

In this paper a quantile regression model (QRM) was
developed to investigate the effect of atypically high temperature on ground level ozone. QRM divides the dependent variable (here ozone concentrations) into several quantiles (percentiles) and analyses the effect of independent variables on each quantile. Ordinary multiple regressions are based on mean, which could be biased by outliers in the dataset and therefore are not suitable for ozone data analysis. Quantile regression is based on median and other quantiles which are robust to outliers and therefore can provide a better model fit. Furthermore, QRM allows the covariates to have different contribution at different quantiles of the ozone distribution and is robust (insensitive) to departures from normality and to skewed tails. Readers are referred to Koenker (2005) and Hao and Naiman (2007) for the details of QRM; and to Munir et al. (2011), Munir et al. (2012), Sousa et al. (2008), Baur et al. (2004) for the applicability of QRM to ground level ozone concentrations.

To model the effect of atypically high temperature on ozone concentrations a QMR model was applied as shown in Eq. (1). The model was run three times: (a) using whole dataset for 2012 collected at the PME site; (b) using a subset of 2012 data when temperature was greater than 42°C; (c) using a subset of 2012 data when temperature was less than 42°C.

\[
[\text{ozone}] = \beta_0 + \beta_1 p \text{ temperature} + \delta_i \tag{1}
\]

In Eq. (1), \(\beta_0\) represents the intercept, \(\beta_1\) the slope (gradients) of the temperature, and \(\delta_i\) the error term. The \(p\) shows the \(p\)th quantile and its value lies between 0 and 1.

Eq. (1) can have numerous quantiles and will require a separate equation for each quantile and therefore will produce numerous coefficients for each variable. This study adopts 9 quantiles (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9) and therefore 9 equations will generate the same number of quantile regression coefficients (\(\beta_{0.1}^1, \beta_{0.2}^1, ..., \beta_{0.9}^1\)).

RESULTS AND DISCUSSIONS

Annual cycles of temperature at three monitoring sites
(Leeth, Sharaai, and Azizia) in Makkah averaged over ten years (2003–2012) are depicted in Fig. 2, where it can be observed that although observed temperature is slightly different at various monitoring stations, they follow the same annual cycles. In Makkah summer season is typically May, June, July, August, and September. In Saudi Arabia the other seven months are designated as winter months, however the average monthly temperature in most of these months is higher than 25°C, which might not be considered as winter months in some other colder countries like United Kingdom. In Fig. 2 considerable difference in summer and winter months can be observed, typical of the region. June shows the highest whereas January shows the lowest temperature in the annual cycle. For comparison with temperature, the annual cycle of ozone concentrations (µg/m³) using 2012 data from the PME site is depicted in Fig. 3. Assuming positive linear association between temperature and ozone concentration (e.g., Bloomer et al., 2009), ozone levels should have been highest in June due to highest temperature level in this month. However, this is not the case and highest ozone levels are rather observed in September. This might indicate that in arid climatic conditions like in Makkah, ozone levels decline in extremely hot months, which requires further analysis (discussed below). Temporal variations of ground level ozone have been characterised by several researchers (e.g., Coyle et al., 2002; Jenkin et al., 2002; Jenkin, 2008; AQEG, 2009; Munir et al., 2012; Hassan et al., 2013), and are therefore not discussed in further detail here. Rather, here the aim is to highlight that ozone and temperature cycles have different trends and use this as a starting point for an analysis of how the observed relations between ozone and temperature vary in different months.

For further analysis, we used scatter plots and bivariate correlation analysis. In Fig. 4 the association of ozone and temperature is depicted for the months of June and July. The aim for selecting these two months is that these have highest temperature levels (as shown in Fig. 2) and are most suitable for this study. It can be observed in Fig. 4 that ozone has positive correlation with temperature until temperature reaches about 42°C, above this level the association becomes negative. Fig. 4 (bottom row) shows scatter plots when temperature is greater than 40°C (temp > 40), here the negative correlation is much clearer. Using whole dataset for June and July correlation coefficients were 0.49 and 0.39 at the PME and Masfalah monitoring sites, respectively. However, when only temperature levels greater than 40°C were considered, correlation coefficients became negative: PME = –0.28 and Masfalah = –0.08. The curve at the Masfalah site rather looks flat at temperature > 40°C, however it still shows that ozone levels are not increasing.

**Fig. 2.** Annual cycles of temperature (°C) at 3 monitoring sites (Leeth Road, Sharaai and Azizia University in Makkah, averaged over 10 years (2003–2012).
Fig. 3. Annual cycle of ozone ($\text{O}_3 \text{ µg/m}^3$) and temperature (temp °C) at the PME monitoring station in Makkah, 2012.

with increasing temperature. The strength of correlation was considerably stronger at the PME than at the Masfalah site. This is probably because that PME has collocated temperature and ozone data and hence shows stronger correlation between ozone and temperature. This shows that ideally meteorological and air quality data should be collected at the same site. The negative correlation between ozone and atypical high temperature is interesting and might play more significant role in the future in the light of changing climatic conditions.

To further analyse the association of extremely high temperature and ozone, QRM model (Eq. (1)) was applied using three different sets of data collected at the PME site: (a) whole dataset for 2012; (b) using a subset of 2012 data when temperature was less than 42°C (temp < 42°C); (c) using a subset of 2012 data when temperature was greater than 42°C (temp > 42°C). QRM helps analyse the effect of temperature on various quantiles of ozone distribution. For model (a) all quantile regression coefficients were positive. The values of coefficients for quantiles 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9 were 0.68, 2.12, 3.30, 3.91, 4.23, 4.68, 4.92, 5.43, and 6.06, respectively. For model (b) the slopes were also positive and their values were 0.54, 1.88, 3.18, 3.95, 4.34, 4.81, 5.02, 5.50, and 6.12 at quantile 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9, respectively. Model (c) which used temperature data above 42°C and the corresponding ozone data, the outputs of QRM are shown in Table 1. The coefficients along with upper and lower bounds of QRM for different quantiles are shown in Table 1, where it can be seen that the values of coefficients are negative at quantile 0.2 to 0.9 and range from $-1.88$ to $-28.57$, showing a strong negative effect of temperature on ozone concentrations. Mean slope determined by ordinary least square regression model was $-11.51$. In simple words it means that at atypically high temperature (> 42°C) on average, ozone levels decrease by 11.51 µg/m$^3$/°C. At higher quantiles of ozone (0.9) the slope reaches to 28.57 µg/m$^3$/°C (see Table 1 for details).

Previously Steiner et al. (2010) analysed ozone-temperature relationship from 1980–2005 for four air basins in California and reported significant negative ozone-temperature slopes at extremely high temperatures (>39°C). However, Steiner et al. (2010) have reported consistent ozone-temperature slopes across five different percentiles of the ozone distribution, suggesting that the high-temperature ozone response is not dependent on the level of ozone. This is in contrast to the finding of this study that suggests the opposite. The finding of this study suggests that ozone-temperature slope is not linear at different levels of ozone at any temperature level. Furthermore, slopes are stronger at higher quantiles of the ozone distribution. Bloomer et al. (2009) and Camalier et al. (2007) have reported significant spatial and temporal variability in ozone-temperature relationship, probably due to variations in chemical and meteorological environments which strongly influence ground level ozone formation.

A warming climate is expected to exacerbate ground level ozone pollution in many regions of the world, possibly offsetting the benefits from reduction in precursor’s emission and increasing exceedences of air quality standards (IPCC, 2007). However, this study suggests that extremely high temperature in arid climatic conditions like in Makkah might have the opposite effect, which needs to be considered in future air quality projections. We suggest further investigation to this matter over large spatial and temporal range.

In Makkah due to data constraints and the unavailability of previous work on this issue, it is rather hard to fully evaluate the reasons for negative ozone-temperature slope...
Fig. 4. Showing scatter plots of ozone concentrations (µg/m³) and temperature (°C) in Makkah during June and July, 2012 at the PME and Masfalah monitoring sites.

Table 1. Outcomes of quantile regression model (QRM) between ozone and temperature for 2012 from PME site, when temperature > 42°C. Coefficients are in µg/m³/°C.

<table>
<thead>
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<th>Quantile</th>
<th>Coefficient</th>
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<th>Lower bound</th>
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<td>-9.62</td>
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<td>-7.08</td>
<td>-10.81</td>
<td>-4.77</td>
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<tr>
<td>0.6</td>
<td>-11.11</td>
<td>-15.76</td>
<td>-6.75</td>
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<tr>
<td>0.7</td>
<td>-15.00</td>
<td>-18.92</td>
<td>-10.94</td>
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<tr>
<td>0.8</td>
<td>-18.28</td>
<td>-22.44</td>
<td>-15.81</td>
</tr>
<tr>
<td>0.9</td>
<td>-28.57</td>
<td>-32.78</td>
<td>-3.28</td>
</tr>
<tr>
<td>Mean</td>
<td>-11.51</td>
<td>-16.01</td>
<td>-6.91</td>
</tr>
</tbody>
</table>
at atypically high temperature. To find a reason why ozone-temperature slope turns negative at extremely high temperature, we analysed the levels of ozone precursors, such as Total Hydrocarbons (THC) and nitrogen dioxide (NO$_2$) to see how they interact at extremely high temperature. Both of these species are monitored at the PME monitoring site. Unfortunately, various species of hydrocarbons, such as non-methane hydrocarbons (NMHC) and isoprene are not monitored in Makkah. Both THC and NO$_2$ show a declining trend at extremely high temperature in Makkah. Both THC and NO$_2$ are considered the precursors of ozone and reduction in their levels at extremely high temperature may cause reduction in photochemical ozone formation. In Fig. 5 scatter plots of THC vs. temperature (top) and NO$_2$ vs. temperature (bottom) are depicted. THC levels start decreasing after approximately 35°C, whereas NO$_2$ levels decrease after approximately 40°C. Steiner et al. (2010) has reported that the emission of VOCs, especially isoprene - emitted by vegetation, is temperature dependent. According to Steiner et al. (2010) isoprene concentrations increased with increasing temperature in the range of 16–38°C and decreased with further temperature increase. On the other hand, the concentrations of NO$_2$ is dependent on its chemistry such as photochemical formation and photo-dissociation of NO$_2$, and its dispersion (horizontal and vertical transport). NO$_2$ chemistry is affected by the amount of precursors (e.g., NO), temperature and solar radiation, whereas its transport is dependent on wind speed, direction and temperature. Thus, temperature can affect NO$_2$ negatively in two ways: firstly through direct effect by enhancing the photo-dissociation; and secondly through affecting other meteorological parameters, such as wind speed and atmospheric stability to enhance the dispersion process. Jayamurugan et al. (2013) have also reported negative association between temperature and

![Fig. 5. Scatter plots showing the association of total hydrocarbons (THC $\mu$g/m$^3$) (top) and NO$_2$ $\mu$g/m$^3$ (bottom) with temperature (°C) during 2012 at PME site in Makkah.](image-url)
NO\textsubscript{2}, stating that heating of earth by the sun induces thermal turbulence during summer and increases the mixing height and therefore help increase the dispersion process of NO\textsubscript{2}. Therefore, it seems likely that reduction in the levels of NO\textsubscript{2} and THCs at extremely high temperature are causing ozone level to decrease and is the likely reason of the negative ozone-temperature slopes at extremely high temperature.

For further analysis, to determine the reason for negative ozone-temperature slope we used wind speed and wind direction data to analyse their effect on ozone and temperature. Fig. 6 depicts the association of wind speed and direction on temperature and ozone. Firstly we used the full-dataset for year 2012 from the PME site to show the average relationship between wind speed, wind direction, temperature and ozone (Fig. 6, top-row). Here we can observe a typical positive relationship between ozone and temperature, showing that both high temperature and high ozone levels are observed when wind is blowing from the north, northwest or west direction at a speed of about 1 to 4 m/s. However, when we took a subset of the data i.e., when temperature > 40°C, the relationship between ozone and temperature changed (Fig. 6, bottom-row). Here the high levels of ozone are linked with wind blowing from the west direction, whereas the high levels of temperature are associated with wind blowing from the east, especially from the northeast direction. This again provides an evidence that at extremely high temperature the association between ozone and temperature changes to negative. Furthermore, this association is linked with wind speed and direction, which reveals that at high temperature the transport of ozone changes. Furthermore, temperature levels may play an important role in changing the boundary layer height and hence affecting the Strato-Tropospheric Exchange (STE) of ozone. The summer afternoon periods, which observed the highest temperature are the periods of intense convective mixing in the boundary layer (Aneja et al., 2002), which affects the STE of ozone. Therefore, in light of the above discussion we may conclude that high temperature levels affect the levels of ozone precursors, wind speed and wind direction and atmospheric stability which are probably causing the negative ozone-temperature slope at extremely high temperature.

**Fig. 6.** Polar plots showing the association of ozone and temperature with wind speed and wind direction in Makkah: top-row shows all data, whereas bottom-row shows a subset when temperature > 40°C.
Jacob and Winner (2009) have published a detailed review of the effect of climate change on air quality, particularly on ground level ozone. They concluded that climate change alone will increase summertime surface ozone in polluted regions by 1–10 ppb over the coming decades, with the largest effects in urban areas and during pollution episodes. This climate penalty means that stronger emission controls will be needed to meet a given air quality standard. Furthermore, they reported that higher water vapor in the future climate is expected to decrease background ozone, so that pollution and background ozone have opposite sensitivities to climate change. In this paper using monitored ozone and temperature data, we suggest that ozone will probably behave differently at extremely high temperature in arid climatic conditions. The findings of this study require further investigations over a greater temporal and spatial range.

CONCLUSIONS

Makkah is part of an arid region where extremely high temperature (>42°C) occurs frequently. Under warming climate scenarios temperature is supposed to further increase and may further signifies the importance of the ozone-temperature relationship and its implications in the future. Several studies suggest that under warming climate scenario ozone levels will be positively affected by increasing temperature levels, reducing the benefits of reduction in ozone precursors. This study agrees that ozone and temperature have positive association at average temperature range, however at extremely high temperature (>42°C) ozone levels decline due to chemical and meteorological parameters. Using a QRM model, in this paper we have shown that ozone-temperature slopes turn negative at various quantiles of ozone distribution. Reduction in the levels of ozone precursors, such as hydrocarbons and NO\textsubscript{2} changes in wind characteristics and atmospheric stability at extremely high temperature seem to be the main cause. However, further investigations over a large spatial-temporal range are required to conclusively confirm the outcomes of this study and their impacts on future air quality projections in arid climatic conditions, like in Makkah.

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REFERENCES


Habeebullah, T.M. (2013b). Health Impacts of PM\textsubscript{2.5} Using AirQ2.2.3 Model in Makkah. J. Basic Appl. Sci. 9: 259–268.


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