**Ozone (O₃) ambient levels as a secondary airborne precursor in Fahaheel urban area, the State of Kuwait**

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**Abstract**

Two years of continuous monitoring data over two time-spans (2004–2005 and 2014–2015) were used to investigate the relationship between ozone (O₃) and nitrogen oxides (NOₓ ≈ NO + NO₂) in Fahaheel urban area (Kuwait). Their relationship was used to understand their chemical reactions and the NO₂ and O₃ concentration ratio to gain an insight into the sources of total atmospheric oxides (OX = O₃ + NO₂) levels. A Chemical Mass Balance (CMB) model was developed to detect likely point sources around the monitoring station and quantify their contribution to the overall air pollution load. Hourly diurnal variations in O₃ ground level concentrations during weekends showed a slight increase in O₃ levels. In addition, it was observed that overall hourly average O₃ concentration reached higher levels during weekdays and weekends in 2004–2005 compared to 2014–2015. The concentration of photochemical oxidants (e.g., O₃ and NO₂) can be decreased by controlling the emissions of their precursors; NOₓ and VOCs. The net effect of NOₓ emissions on O₃ concentrations was negative with a weak exponential decline correlation between NOₓ and O₃, indicating Fahaheel urban area’s VOC-sensitive characteristics. For all years considered, the slopes of the linear OX–NOₓ relationships were higher during daytime compared to night-time, showing that NO₂ oxidations were dominant during daytime and that O₃ net production was high. The study also showed the high NOₓ oxidation level and the possible presence of O₃ net production. The slopes during night-time indicated that NO₂ consumption exceeded its formation rate. During day and night-time, the NO₂/NOₓ ratio was found to decline significantly as newly emitted NOₓ increased, supporting the area’s VOC-sensitive nature. By setting up a CMB model around the Fahaheel receptor point, it was revealed that downstream petroleum facilities

**Abbreviations:** C, concentration of airborne pollutant; CMB, chemical mass balance; CO, carbon monoxide (ppb); CO₂, carbon dioxide (ppb); H₂S, hydrogen sulphide (ppb); HC, hydrocarbons; HO₂, hydroperoxy; J, rate (kinetic velocity constant) of NO₂ photolysis reaction at equilibrium; ME, middle-eastern; NMHC, non-methane hydrocarbon; NO, nitrogen oxide (ppb); NO₂, nitrogen dioxide (ppb); NOₓ, nitrogen oxides (ppb); O₃, ozone level (ppb); OX, total atmospheric oxides; SC, source contribution (%); Temp., ambient temperature (°C); VOCs, volatile organic compounds; WD, wind direction (°); WS, wind speed (m s⁻¹).
have been the major contributor to pollutants environmental load over the years.

**KEYWORDS**
air quality, chemical mass balance, modelling, ozone (O₃), pollution, volatiles

1 | INTRODUCTION

Photochemical oxidants and their atmospheric by-products are two of the major air pollution problems in urban areas. Photochemical oxidants are secondary air pollutants formed as precursors by complex photochemical reactions (photolysis) containing nitrogen oxides (NOₓ ≈ NO + NO₂) and a wide range of volatile organic compounds (VOCs) under the influence of sunlight (Adame et al., 2012). Ground level O₃ formation depends on solar radiation intensity, absolute NOₓ and VOCs concentrations and the NOₓ to VOCs ratio (Jaffe and Wigder, 2012). Typically, O₃ formation increases proportionally with increasing concentrations of VOCs. Carbonyl compounds within the C1 to C8 range comprising formaldehyde, acetaldehyde, and isovaleraldehyde, were recently reported as contributors to OH reactivity and O₃ production (Yang et al., 2017).

The increase in NOₓ levels results in concentration changes of O₃ depending on the dominant ratio of VOCs to NOₓ (Tiwari et al., 2015). Reduction in NO₂ levels is always accompanied by an increase in O₃ levels (Mazzeo et al., 2005).

In some areas, there is a trend towards higher levels of O₃ concentration on weekends compared to weekdays. This is despite the typically lower weekend VOCs and NOₓ emissions. This phenomenon is known as the ozone weekend effect and was first reported back in the 1970s in the United States (Cleveland et al., 1974). It is understood that the combined effect of VOC sensitive regimes and NO titration with the different magnitude and timing of emissions (e.g., decreasing NOₓ/VOC morning ratios on weekends) causes O₃ to rise in weekends (Jimenez et al., 2005).

In the Middle East (ME) region, vertical ozone profiles were studied using a chemical-transport model by Li et al., (2001). A maximum regional summertime O₃ in the middle troposphere was predicted to exceed 80 ppbv. Recent studies examining temporal and spatial patterns of O₃ and NOₓ in Jeddah (Saudi Arabia) showed a clear variation in O₃ levels with the highest concentrations reported during the summer season (Mazzuca et al., 2016). In general, O₃ production tends to be more sensitive to VOC in the morning, along with high production rates of O₃. The production of O₃ was found to favour NOₓ in the afternoon due to increased volumes of traffic (Mazzuca et al., 2016).

Studies related to O₃ and NOₓ chemistry have been widely conducted at numerous locations around the world, including the Indian Peninsula, Southeast Asia and North America (Kumar et al., 2017; Pancholi et al., 2018; Sharma et al., 2016). There is a lack of such in-depth analysis of O₃ and its precursors in the State of Kuwait, where primary and secondary airborne pollutants are associated with the oil and gas industry and unsanitary waste management. The aim of this study is to investigate the fate of O₃ as a secondary pollutant by evaluating the photochemistry in one of Kuwait’s major urban areas (Fahaheel). The study also reports on the daytime and night-time relationships between O₃ and NOₓ and investigates the O₃ weekend effect in Fahaheel area. It further quantifies sources contributing to the studied area’s ambient air pollution by developing a chemical mass balance (CMB).

2 | MATERIALS AND METHODS

2.1 | Site description

The state of Kuwait is a West Asian Country categorised by the World Bank as a high-income developing country. It occupies 17,818 km² of land on the ME Arabian Gulf, with a population reaching 4.1 million in 2017 (PACI, 2018). The Fahaheel urban area (29°05’00”N lat. and 48°07’36”E long.) is one of the state’s major cities, which is associated with petroleum industries supporting the oil based economy of Kuwait. It is characterised by arid/harsh climate with ambient temperatures reaching above 55°C during the summer season. The area of Fahaheel is adjacent to the state’s largest oil refinery (Mina Al-Ahmadi, MAA). Background concentrations are associated with the greater Burgan oil field on the west end of Fahaheel alongside other downstream and chemical industries (Al-Salem, 2015; Al-Salem and Khan, 2008). The Fahaheel area is shown in relation to the Kuwaiti coastline in Figure 1. More details on commuting routes and industrial sites around Fahaheel can be found elsewhere (Al-Qassimi and Al-Salem, 2019; Al-Salem and Khan, 2010).
2.2 | Data acquisition and processing

Continuous data for the years 2004–2005 and 2014–2015 was acquired from the Fahaheel monitoring station (15 m above ground level) by Environment Public Authority, Kuwait (EPA). The samples were examined using various primary pollutant and secondary precursor analysers (Whatman 41, Air sample Grasbey—Anderson Ltd., 1% tolerance, weather station), all linked to EnviDAS software’s central online data system. OX is consequently a more stable entity to study as it shows the potential for renewed production of O3 (Song et al., 2011). Therefore, work on nitrogen-based pollutants encompassed the OX filtration procedure for NO and ozone titration established previously by other authors and depicted as follows (Al-Salem and Khan, 2008, 2010; Pancholi et al., 2018; Tiwari et al., 2015; Al-Qassimi and Al-Salem, 2019):

\[ O_X \text{ [ppb]} = O_3 + NO_2 \quad (1) \]

where \( O_X \) is the total oxidant concentration in the ambient atmosphere (ppb) and values falling below the estimated baseline of \( O_X \) were discarded due to photo-oxidation reactions, particulate accumulation, choking or OH ion presence malfunctioning of the instruments.

2.3 | Patterns establishment of pollutants

It is well established that the reactions shown below generally dominate the interconversion of \( O_3, NO, \) and NO\(_2\) under atmospheric conditions (Adame et al., 2012; Al-Qassimi and Al-Salem, 2019):

\[ NO_2 + h\nu (\lambda < 398 \text{ nm}) \rightarrow NO + O \quad (2) \]
\[ O + O_2 + M (N_2, O_2) \rightarrow O_3 + M \quad (3) \]
\[ NO + O_3 \rightarrow NO_2 + O_2 \quad (4) \]
\[ \frac{[NO][O_3]}{[NO]} = \frac{J}{k} \quad (5) \]

where \( h\nu \) is the sunlight (solar) intensity; \( J \) is the rate of NO\(_2\) photolysis reaction in Equation (2); \( k \) is the rate coefficient for the reaction of NO with \( O_3 \) in Equation (4) (Han et al., 2011). In this study, diurnal variation of NO, NO\(_2\), NO\(_X\), O\(_3\), and O\(_X\) along with variation of seasonal regional and local O\(_X\), and surface plots of NO\(_X\) and O\(_X\) annual daily mean variation, were examined.

FIGURE 1 Pictorial satellite image showing study area with respect to (1) MAA refinery, (2) SHU refinery, (3) MAB refinery, (4) Fahaheel urban area, (5) Burgan oil field, and (6) Al Ahmadi area. The dotted line represents route no. 55. Map Source: KISR GIS
3 | RESULTS AND DISCUSSION

3.1 | Diurnal patterns of monitored pollutants

The plots of the O3, NO, NO2, and NOX diurnal variations of hourly averages for the years 2004–2005 and 2014–2015 are shown in Figure 2. The air quality in Fahaheel urban area was investigated during the high O3 period (April to September) for all years. The hourly averaged data in each day were divided into two parts: daytime (7:00 to 21:00) and night-time (21:01 to 6:59). This was the analysis period of choice for most Kuwaiti seasonal primary pollutant studies (Al-Awadi et al., 2015).

It is well established that the inversion layer, solar intensity, wind patterns and sources of emissions have a significant influence on the daily variability of any pollutant (Han et al., 2011; Tiwari et al., 2015). Based on the analysis shown in Figure 2, the daily average maximum level of O3 reached 69 ppb during the years 2004 to 2005 compared to 47 ppb in 2014 to 2015. The diurnal patterns of NO, NO2, and NOX established in Figure 2 showed two daily peaks during morning and evening periods. The peak values of NO and NO2 occurred at the same time during morning hours (e.g., 6:00 to 8:00). This coincides with work and school rush hour vehicle emissions. The evening peaks occurred between 19:00 to 21:00 in 2004–2005 and in 2014–2015.

The diurnal patterns of O3, NO, NO2 and NOX for 2004–2005 and 2014–2015, differed in their monthly ambient levels. This is directly related to the emissions from the source and the rate of photo-oxidation. For the years 2004 to 2005 and 2014 to 2015, NO levels were elevated during cooler periods in Kuwait (December to March). In general, it was observed that NO and NO2 were rising inversely with the decrease in O3 levels. The increase in NO2 levels is associated with the decrease of O3 concentrations (Ramli et al., 2010). In general, the lower NO emissions in 2014–2015 are related to the use of catalytic convertors in modern vehicles in addition to lower combustion sources concentration build-up around the vicinity of Fahaheel area. The lower NO emissions in 2014–2015 are likely related to the increase in catalytic converters use as part of new environmental regulations to mandate such for automobiles.

3.2 | Diurnal variation and chemical coupling of O3, NO, and NO2

The mixing ratio of NO2, O3, and the rate of NO2 photolysis (J4) was determined to aid in investigating the photolysis of the pollutants. The average variations of the value of J4/k3 from Equation (6), was obtained for the years 2004–2005 and 2014–2015 data at Fahaheel urban area (Figure 3). The mean J4/k3 values varied between 4.71 and 17.74 ppb in 2004–2005, and the maximum value occurred at 15:00. In addition, the mean values of J4/k3 varied between 4.18 and 9.38 ppb in 2014–2015 and the maximum value occurred also at 15:00. Han et al. (2011) reported mean J4/k3 values ranging from 0.176 to 5.513 ppb in Tianjin, China, and a maximum value at 10:00. In the results reported by Ismail et al. (2016) for the ambient monitoring work conducted in Kemaman, Malaysia, the maximum J4/k3 value was recorded at 15:00 and the mean J4/k3 values varied between 3.225 and 12.869 ppb. The

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**Figure 2** Diurnal variations of hourly averaged concentrations of O3, NO, NO2, and NOX in Fahaheel urban area based on the 2 years averages (a) (2004–2005) and (b) (2014–2015)
The seasonal variability of these pollutants was examined further and shown in Figure S1 showing the total average concentrations of O₃, NO, NO₂, and NOₓ during summer, autumn, winter and spring (excluding winter of 2004). Overall, concentrations of nitrogen oxides (NO, NO₂, and NOₓ) were highest during the Autumn of 2004 and higher during the cold seasons (autumn and winter) in 2005. In 2014, nitrogen oxides were higher during the winter and spring seasons and in 2015 they were higher during the cold seasons (autumn and winter). In addition, the O₃ concentrations were higher during warm seasons (summer and spring) in all years due to high temperatures and abundance of solar radiation.

The variation in the Oₓ concentration mean values in Figure 4a for the years 2004–2005 and 2014–2015 showed that the concentration of Oₓ in 2004 to 2005 was characterised by a midday peak and lowest at night-time. Similar results to the Oₓ pattern observed in 2004–2005 have been previously reported in many locations including Saudi Arabia, India, and Malaysia and it was due to the rapidity of the photochemical formation of O₃ (Alghamdi et al., 2014; Pires et al., 2012).

The NO₂/Oₓ concentration ratio variation is shown in Figure 4b to explain the NO₂ and O₃ partition differences through photochemical processes. The behavioural difference between NO₂ and O₃ may be related to the time they have to react in the atmosphere or the rate of chemical processes in the studied area. The variation in concentration of O₃ in daytime and night-time as a function of the ratio of NO₂/NO is shown in Figure 5.

**FIGURE 3** Variation in the mean values of $J/k$ during (□) 2004 to 2005 and (*) 2014 to 2015

**FIGURE 4** Variation of (a) mean values of Oₓ and (b) mean values of NO₂/Oₓ ratio in 2004–2005 and 2014–2015
It was observed that O₃ daytime and night-time levels increased with the increase in the NO₂/NO ratio between 2004 to 2005 and 2014 to 2015. These observations are in line with the findings of Ismail et al. (2016). In addition, it was found that O₃ increased rapidly with minor variations in the NO₂/NO ratio. This may be explained by the dominance of the O₃ generation reactions that occurred when O₃ was at low levels as noted previously by Pires et al. (2012). The analysis shown in Figure 5 resulted in fitting a logarithmic function to describe the relationship between O₃ concentration and NO₂/NO concentration ratio. The equations of the fitted models were found to be:

\[
O₃ \text{ (ppb)} = 26.68 + 17.62 \ln \left( \frac{\text{NO}_2}{\text{NO}} \right), \quad r^2 = 0.29 \text{ (Daytime 2004–2005)}
\]

\[
O₃ \text{ (ppb)} = 5.09 + 12.83 \ln \left( \frac{\text{NO}_2}{\text{NO}} \right), \quad r^2 = 0.27 \text{ (Night-time 2004–2005)}
\]

\[
O₃ \text{ (ppb)} = 9.31 + 14.39 \ln \left( \frac{\text{NO}_2}{\text{NO}} \right), \quad r^2 = 0.20 \text{ (Daytime 2014–2015)}
\]

\[
O₃ \text{ (ppb)} = 1.26 + 9.22 \ln \left( \frac{\text{NO}_2}{\text{NO}} \right), \quad r^2 = 0.29 \text{ (Night-time 2014–2015)}
\]

When O₃ concentration reached around 60 ppb, it continued to remain relatively stable during daytime in 2004–2005 and 2014–2015. This indicates that concentration of O₃ is close to reaching photostationary state at higher levels. The dataset was investigated using regression analysis for linearity to determine whether it is best to represent it using a linear function for ease in interpretation and analysis (Figures S2–S5). Regression analysis for linear functions is also shown in the Supplementary Material File. However, logarithmic fitted data was used to regress the O₃ concentration during the daytime as it provided the best fit and showcased the photostationary behaviour. The correlation coefficients were found to be equal to 0.29 and 0.20 during daytime 2004–2005 and 2014–2015, respectively, indicating a weak relationship between the variables. The low correlation coefficient during daytime is explained by the increase in O₃ production. (Figure 5). The variation of O₃ and the NOₓ mean ambient levels in daytime and night-time were also assessed in this study. O₃ formation and destruction with
NO\textsubscript{X} variation were examined for the day and night-time durations. The equations shown above were found to best represent the studied data. The values of the two time periods were observed using the daytime and night-time hourly averages (Figure 6). The 2004–2005 daytime analysis shows a relatively low value of \( r^2 \) (0.006) with a significance value of 0.145. This is also significantly above the typical threshold of 5% for significance. The plots indicated a relatively weak relationship between the \( O_3 \) and NO\textsubscript{X}, which was more evident during night-time for 2014–2015 (Figure 6b,d. The 2014–2015 statistical shows an \( r^2 \) value of .0004, and a significance value of 0.71, which supports the null hypothesis (no correlation). The observed behaviour can also be related to the titration of \( O_3 \) within the atmosphere during daytime hours and reflects the related mixed effect of meteorological conditions with chemical reactions, transport patterns and atmospheric dispersion (Nishanth et al., 2014). Similar behaviour has been reported previously by Hassan et al. (2013) in Jeddah city (Saudi Arabia), where negative correlations between \( O_3 \) and NO\textsubscript{X} during whole time period (20:00 to 8:00) and day light time period (7:00 to 18:00) were found to be in the range of −0.21 to −0.37, respectively.

To further confirm the VOC sensitive nature of Fahheel urban area, Figure 7 shows the NO\textsubscript{2}/NO\textsubscript{X} ratio variation with NO\textsubscript{X} during daytime and night-time, which was found to decrease greatly as the emitted NO\textsubscript{X} increased during night-time in 2004–2005 (Song et al., 2011). The net NO\textsubscript{X} emission and the original ratio of NO\textsubscript{2}/NO\textsubscript{X} are found to control the direct input of NO\textsubscript{2} that could be estimated by the lower end rations at increased NO\textsubscript{X} levels (Seinfeld and Pandis, 2006). The decrease in the NO\textsubscript{2}/NO\textsubscript{X} emissions confirms the VOC sensitive nature of Fahheel urban area and the findings are in agreement with those found by Ismail et al. (2016) in Kemaman, Malaysia. The variations in daytime and night-time O\textsubscript{X} concentrations against NO\textsubscript{X} levels are shown separately in Figure 8. Two types of air pollution impact loads, namely NO\textsubscript{X}-dependent and NO\textsubscript{X}-independent, influence the levels of O\textsubscript{X} at a certain location (Clapp and Jenkin, 2001). NO\textsubscript{X}-dependent impact explains the influence of local contributions of mainly the primary pollutants by the net increase of NO\textsubscript{2} through NO\textsubscript{X} emissions (Song et al., 2011). This is followed by the oxidation of NO to NO\textsubscript{2} by radical species such as OH, RO\textsubscript{2} (where R is a hydrogen atom or carbon-based moiety) and others (Seinfeld and Pandis, 2006). NO\textsubscript{X}-independent impact relates to regional contribution equivalent to O\textsubscript{3} background concentration which is the intercept of the relationship between O\textsubscript{X} and NO\textsubscript{X} concentrations. The slopes of the linear O\textsubscript{X}–NO\textsubscript{X}

\[
y = 40.425e^{0.0009x} \\
R^2 = 0.0018
\]

\[
y = 37.728e^{-0.021x} \\
R^2 = 0.2696
\]

\[
y = 27.485e^{0.0004x} \\
R^2 = 0.0007
\]

\[
y = 20.104e^{-0.01x} \\
R^2 = 0.2743
\]

**FIGURE 6** Correlations between \( O_3 \) and NO\textsubscript{X} concentration in 2004–2005 for (a) daytime and (b) night-time and in 2014–2015 for (c) daytime and (d) night-time.
**FIGURE 7** Correlations between NO$_2$/NO$_x$ ratio and NO$_x$ concentration in 2004–2005 for (a) daytime and (b) night-time and in 2014–2015 for (c) daytime and (d) Night-time

**FIGURE 8** Correlations between O$_x$ and NO$_x$ concentration in 2004–2005 for (a) daytime and (b) night-time and in 2014–2015 for (c) daytime and (d) Night-time
relationships in Figure 8 averaged at about 0.76 and 0.42 during daytime and night-time, respectively. This showed that O₃ levels in Fahaheel area were mainly controlled by the net NOₓ emissions, whereas the contribution of NOₓ and O₃ photochemical reactions to O₃ was much less. The intercepts during daytime were 43.66 and 28.78, respectively, in 2004–2005 and 2014–2015 and were 39.68 and 24.99 during night-time in 2004–2005 and 2014–2015, respectively. This showed that O₃ levels in Fahaheel area were mainly controlled by likely contributions from direct NO₂ emission, thermal reaction of NO with O₂ at high NOₓ and species source emissions that promote NO to NO₂ conversion. Statistical analysis including regression analysis for linear functions is shown in Figures S6 and S7 as an example.

### 3.3 Weekday/weekend differences

During weekends the increase in O₃ levels compared to the levels observed during weekdays is known as the weekend effect (Domínguez-López et al., 2014). The weekend effect phenomena may occur during weekends despite lower levels of O₃ precursors; NOₓ and VOCs (Alghamdi et al., 2014). Furthermore, the California Air Resource Board (CARB) stated a hypothesis that the VOCs become sensitive to O₃ formation when NOₓ emissions decrease on weekends (Blanchard and Fairy, 2001). In other words, areas are considered to be VOCs-sensitive when O₃ levels are high on weekends but NOₓ emissions are considerably lower (Blanchard and Tanenbaum, 2003). Higher NO, NO₂ and NOₓ concentrations and lower O₃ concentration on weekdays were observed during daytime in Fahaheel area in 2004 to 2005 and 2014 to 2015 as seen in Tables S1 and S2, respectively. The details are presented in the Supplementary Materials File for the aforementioned tables. This corresponds to the change in weekends in Kuwait, and complements the analysis conducted in this study. Thus, the slightly elevated weekend O₃ levels in Fahaheel urban area during daytime and the negative correlation seen earlier between O₃ and NOₓ, confirm that Fahaheel is VOC-sensitive.

It can be seen from Figure 9 that O₃ and NOₓ’s hourly diurnal variation patterns also differed between weekdays and weekends. The same was also observed in previous study showing higher vehicle emissions during rush hours in major cities around the world (Qin et al., 2004; Alghamdi et al., 2014).

**FIGURE 9** Diurnal variations of hourly averaged O₃ and NOₓ concentration in 2004–2005 for (a) weekdays and (b) weekends and in 2014–2015 for (c) weekdays and (d) weekends
3.4 Development of the chemical mass balance (CMB) model

The use of CMB models to identify the predominant sources impacting a particular point source or receptor point in relation to wind direction and their effect on air quality, was adopted by many researchers in the past (Christensen and Gunst, 2004; Christensen, 2004; Al-Salem and Khan, 2008; Al-Salem and Khan, 2010). To facilitate the analysis of the built CMB model, the sectors around the receptor point (i.e., Fahaheel polyclinic) were selected (Table 1). In the CMB model step, the distribution of sectors was identified as to how they would impact the area’s receptor point. A least-square solution was implemented by the model to a set of linear equations, taking each source as a linear sum product of the percentile source contribution with predominant wind sector (Al-Salem, 2008). Equation (10) is the corresponding basic relationship to the designated receptor point.

\[
\Delta C_i = \sum F_{ij} - S_i
\]  

where \(\Delta C_i\) is the difference in the concentration of a chemical compound \(i\) at the receptor point, \(F_{ij}\) is the fraction of concentration of the species \(i\) starting from the source \(j\), and \(S_i\) is the concentration of pollutant \(i\) at the receptor point. The total contribution of the WS was estimated to receive the percentage contribution of wind speed thus.

\[
\% WS_i = (k_i/K) \times 100
\]

| Position in degrees | Source |
|---------------------|--------|
| 0–135               | Downtown area |
| 136–255             | Refineries, petroleum, and petrochemical industries |
| 256–300             | Oil production facilities (Burgan) |
| 301–360             | Traffic line sources (highway), gas stations, and sports clubs |

Source: Al-Salem and Khan (2008)
where \( WS \) is the wind speed contribution in terms of source \( i \) (%), \( k \) is the summation of wind speed points collected in terms of source \( i \) in \((\text{m s}^{-1})\); and \( K \) is the total summation of wind speed points in \((\text{m s}^{-1})\) excluding calm periods. To match receptor point concentrations, predefined linear functions were resolved with an objective function (OF) defined as the sum of squares of the difference between the measured concentrations and the sum of fractional concentrations of different sources chemical fingerprints (including wind sectors influence). Equation (12) was solved for the least linear square root as follows:

\[
LF = \sum_{j=1}^{m} \sum_{i=1}^{m} C_i \cdot WS_i \cdot SC_i - \sum_{i=1}^{n} C_i \cdot WS_i \cdot SC_i
\]

where \( LF \) is the linear function set to match each source’s percentage contribution; \( C \) is the airborne chemical \( i \) concentration at a given source or receptor point, \( SC \) is the percent source contribution for a source \( i \) and \( i \) denotes a certain pollutant and \( j \) denotes sources.

The main difference noticed among all years can be seen in the concentration roses (radar plots) shown in Figures 10 and 11. In 2004–2005, NO was found to be present in a significant proportion on the MAA refinery side (Figure 10b). The solution obtained for the CMB equations for each source studied is shown in Tables S3 and S4. The CMB model results summarized in the tables were based on the July 2014 and January 2015 readings. These were then compared to the CMB model results obtained by Al-Salem and Khan (2008) and Al-Salem (2008) during the month of July 2004 and January 2005, respectively.

The CMB model's objective function represented the four major sources contributing to the receptor point in July 2014 with a match of 60%. A 44% mismatch (i.e., 56% match) was estimated for the January 2015 model. The MAA refinery source contributed to the solution obtained in July 2014 by a total of 61% and the Fahaheel highway was the least contributing to the area by only 5%. The refinery side contributed a total of 65% to the receptor point. Burgan, downtown, and highway

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**FIGURE 11** Annual concentration rose of air pollutants (a) \( \text{O}_3 \), (b) \( \text{NO} \), (c) \( \text{NO}_2 \), and (d) \( \text{NO}_x \) in Fahaheel urban area based on the 2 years averages (2014–2015)
provided contributions of 21, 10, and 4%, respectively. On the other hand, at the receptor point, the CMB model provided a 91% match for the four identified sources in the data fitted in July 2004, and 89% match for the January 2005 model representing winter periods in Kuwait. Comparing the 2-month results for the years in the model, it was noticed that the significant contribution to background concentrations still came from the petroleum refineries and petrochemical industries. The contribution in 2004–2005 was about 70% compared to about 65% in 2014–2015. The CMB model was validated by estimating the statistical correlation between the emission strengths (based on wind directional) and the maximum emission of each component (emission of chemical compound) following the methodology previously depicted by Scheff et al. (1984). This yielded a strong and moderate regression coefficients ($r^2$) which equals 0.89 and 0.65 for the months of July 2014 and January 2015, respectively. These results are paramount in developing strategies for upcoming regulations governing residential and urban areas within the State of Kuwait.

4 | CONCLUSION

Results from this study on the variation of $O_3$ and NOX at Fahaheel urban area (Kuwait) for the period of 2 years over two time-spans (2004–2005) and (2014–2015) led to the determination of their behaviour in the atmosphere. $O_3$ levels were clearly higher in the summer months, gradually increasing until reaching the month of July in 2004–2005 and the month of August in 2014–2015. In addition, it was observed that $O_3$ reached higher overall weekdays and weekends concentrations in 2004–2005 compared to 2014–2015.

In Fahaheel urban area, the $O_3$ and NOX hourly diurnal variation patterns varied between weekdays and weekends and $O_3$ concentrations were seen to increase over the weekends. The NOX weekday concentration morning peaks were slightly higher than those over the weekends in 2004–2005 and 2014–2015 revealing higher traffic emissions during rush hours. The net effect of NOX emissions on $O_3$ concentration was negative with a weak exponential decline correlation between NOX and $O_3$, indicating Fahaheel urban area’s VOC-sensitive characteristics. Heavy traffic from Fahaheel highway and the industrial area can also emit VOCs. During the study period, the slopes of the $O_3$−NOX linear relationships were higher during the day than during the night-time, indicating that NOX oxidations were dominant during the daytime and that $O_3$ net production was high. The smaller slopes during the night-time indicated that NO2 consumption exceeded its formation. During night-time, the NO2/NOX ratio was found to decline sharply as the newly emitted NOX increased, which also supported Fahaheel’s VOC-sensitive nature.

The established CMB model about the receptor point revealed that the downstream petroleum facilities in all years have been the major contributor to the pollutants load. VOCs and NOX form complicated interactions with $O_3$, so examining the relationship between $O_3$, VOCs and NOX is important to verify the photochemical $O_3$ production as well as the ozone weekend effect in Fahaheel urban atmosphere. The present study provided insight into ground level ozone variations in urban Fahaheel, yet the interpretation was limited by meteorological and VOCs data inadequacies. Future studies need to explore more detailed relationships between NOX, VOCs, and $O_3$ in the Fahaheel area. In addition, direct observation of the reactivity of VOCs using the OH reactivity measuring system (Kovacs and Brune, 2001; Sadanaga et al., 2004) is worth further investigation. Emission forecasts and analysis of ambient air quality data on weekdays and weekends can significantly improve our understanding of the impacts of emission control strategies and future changes in $O_3$ concentrations.

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**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section at the end of this article.

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