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COMPARATIVE ASSESSMENT OF AMBIENT AIR QUALITY IN TWO URBAN AREAS ADJACENT TO PETROLEUM DOWNSTREAM/UPSTREAM FACILITIES IN KUWAIT

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Abstract - Air quality data (ground level ozone (O_3), NO, NOx, SO_2, CO, H_2S and NH_3) of two Kuwaiti urban areas adjacent to petroleum processing facilities, Fahaheel and Al-Riqa, were analyzed and compared to evaluate: (1) the exceedances of the Kuwait Environment Public Authority (KUEPA) air quality limits, (2) primary air pollution sources and their contribution to the ambient load, (3) diurnal patterns of air pollutants and (4) the "weekend effect" on O_3 levels. High O_3 levels, above the threshold limit for human health, were observed in both urban areas. CO, NOx and NO levels in Fahaheel were higher than in Al-Riqa. Combustion sources (which exist close to Fahaheel) drive both NOx and NO diurnal patterns in both areas. Emissions from downstream facilities and the activity of Fahaheel highway affect the CO levels in the areas. Concentration roses were plotted for annual durations to examine the primary dominant sources of air pollution in both study areas. By establishing a Chemical Mass Balance (CMB) model around the two receptor points in both areas, it was revealed that the downstream facilities sector was the main contributor of air pollutants in Fahaheel. CMB model gave a 70% average contribution of the sector to the Fahaheel receptor point. However, 70% of the total contribution of the studied sources in Al-Riqa urban area was from the traffic and line sources side. The examination of the rate of O_3 accumulation, during the high O_3 period in Kuwait (April-October), revealed the occurrence of two phases, a fast and a slow one, with different durations in each urban area. Regression equations were used to study the midweek effect of O_3 levels. This study supports the hypothesis that O_3 weekend variation is due to an NOx emission difference between weekends and weekdays and VOCs sensitivity.

Keywords: O_3, NO, CO, SO_2; Weekend effect; Chemical Mass Balance; Concentration roses.

INTRODUCTION

Since the establishment of new rules and regulations governing all environment-affecting industries emerged in the state of Kuwait back in 2001 (KUEPA, 2001), there has been a growing concern about air quality in urban areas. To improve urban air quality, policy makers express widespread interest in controlling major airborne pollutants such as ground level ozone (O_3), CO, NO, NO_2, SO_2, H_2S, NH_3, Volatile Organic Compounds (VOCs) and Polycyclic Aromatic Hydrocarbons (PAHs).

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Deleterious effects on human health (Brunekreef and Holgate, 2002), injury to plants (Saitanis et al., 2001) and reduction of crop yield (Nali et al., 2002) are known to be caused by increased levels of these pollutants. Besides, elevated levels of VOCs and ground level O_3, measured across regional airsheds are known to affect human health (Seinfeld and Pandis, 1998; Al-Salem and Bouhamrah, 2006; Al-Salem and Al-Fadhlee, 2007). In many countries across Asia, North America and Europe, the air quality has been improved over the last two decades. However, it is estimated that in 2010 the European urban population will still be exposed to high concentrations of air pollutants (EEA, 2003).

The number of reactions involved in air pollutant formation is very large, and has kept scientists occupied for many years. The oxidation of SO_2 and NO_2 and their conversion to particulate sulfate (SO_4^{42}) and gaseous and particulate nitrates (NO_3^4) are important characteristics of urban air photochemistry (Monn and Shaeppi, 1993; Matsumoto et al., 1998). NO_2 is oxidized to nitric acid (HNO_3) in the atmosphere, which in turn forms NO_3^4 particles. The effects of these secondary pollutants (including O_3) are associated with acidification of precipitation, visibility reduction and effects on human health (Riga-Karadinos and Saitanis, 2005). Many attempts have been made by scientists to monitor and control such gaseous pollutants. Khan and Al-Salem (2007a) have studied airborne pollutants in an urban area in Kuwait in order to assess the ambient air quality and its suitability for urban living development. With data collected for three years it was discovered that hydrogen sulfide (H_2S) was the pollutant with the major annual increase due to the abundant sources surrounding the area under investigation. Major violations against the KUEPA were recorded in that study. A strict strategy was proposed to monitor urban area air quality in Kuwait, with constant monitoring tools and methods.

Seasonal variation effects on gaseous pollutants are of great significance to the life span and cycle of any pollutant in the lower atmosphere. Ozeki et al. (2006) characterized seasonal and regional variations of gaseous pollutants in transportation. Precipitation samples were collected from nine areas in Japan (2000 and 2001) to profile the pollutants in each of the four seasons of the year. Khan and Al-Salem (2007b) have selected three pollutants (methane (n-CH_4), benzene (C_6H_6) and NOx) to be seasonally monitored and studied for a period of three years in an urban estate in Kuwait. The elevated temperatures and strong winds of the summer seasons over the study period affected methane levels drastically due to the increase of dust levels in the summer periods in Kuwait. Dust adsorption effect and break down of methane particles all resulted in low levels of methane gas in the summer seasons.

The objective of this work was to investigate the air pollution of two urban areas in Kuwait, namely Fahaheel and Al-Riqa. The two areas are in the vicinity of many industrial sites, petroleum downstream/upstream facilities (including Kuwait's three refineries belt, petrochemical complexes, crude oil production points …etc) and many small industries. For this purpose we explore the air pollution levels in these areas, with emphasis paid to O_3, NO, NOx, CO, H_2S and NH_3. The exceedances of the air quality limits of the KUEPA were calculated and the sources were detected around each area and their significance and contribution to the total load of air pollution were determined using concentration rose plotting and a Chemical Mass Balance (CMB) model established around each area at a chosen receptor point. The diurnal patterns and seasonal variations of these gaseous pollutants were studied and the relationships between them were explored. In addition, the rate of O_3 accumulation and the so called "weekend effect", concerning the variation of O_3 levels between weekdays and weekends, were investigated. The metrological parameters (ambient temperature, relative humidity and wind speed and direction) and their influence on the air quality were also considered in the discussion of the results.

STUDY AREAS

Both urban areas (Al-Ahmadi governorate, state of Kuwait) are characterized by prolonged sunny hot periods from late spring to autumn. Fig.1 shows both study areas with respect to the coastline of Kuwait and southern downstream facilities and the upstream facilities of the greater Burgan area (second largest oil filed in the world). The image also shows Fahaheel highway, which is considered one of the two busiest highways in Kuwait, used by work commuters and travelers to other Gulf Council Countries (GCC). The highway is also used by Al-Ahmadi governorate residents to commute to their work places or Kuwait city. Fahaheel highway passes through both study areas.

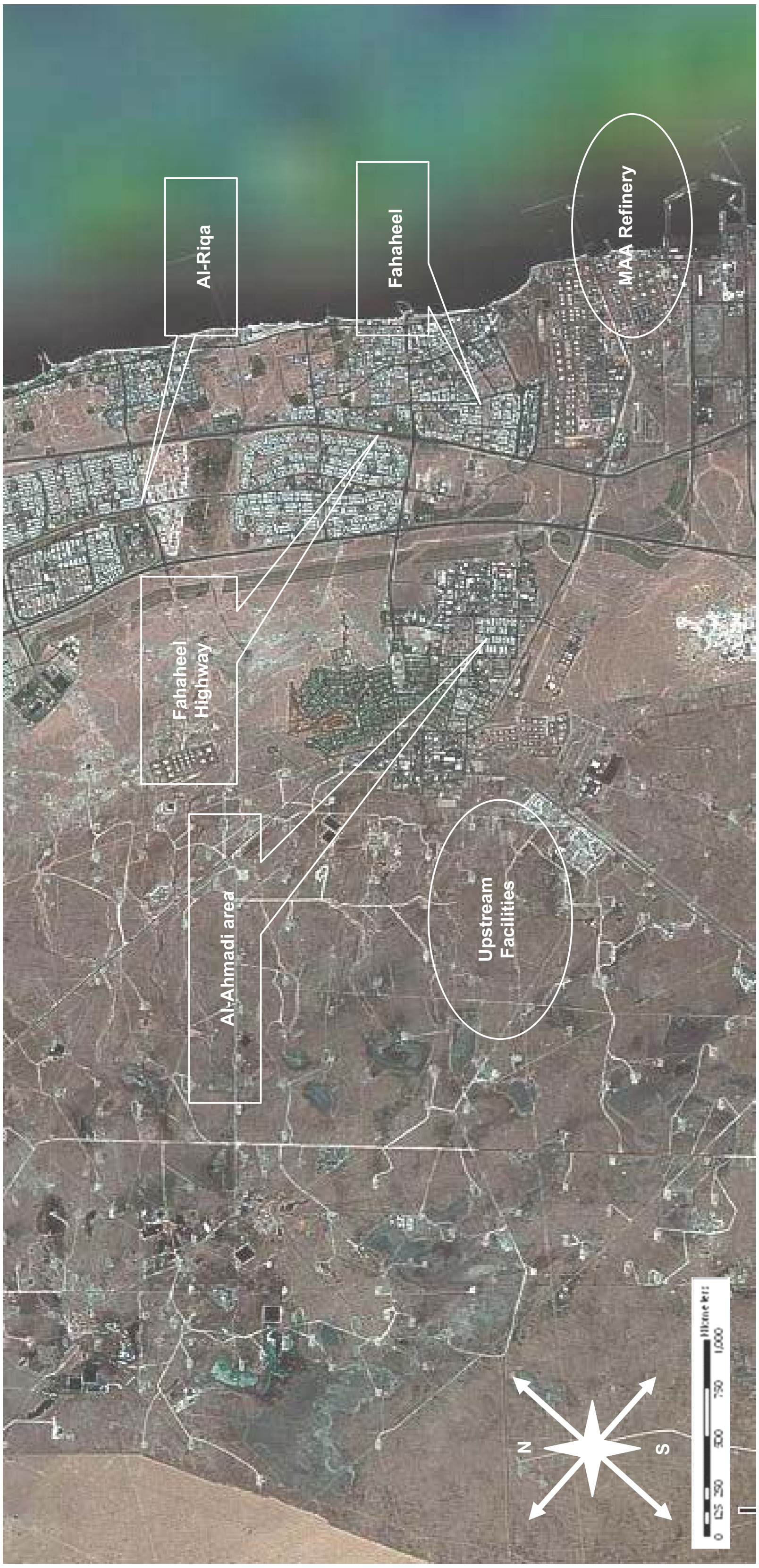


Figure 1: Satellite image showing both areas under investigation (Fahaheel and Al-Riqa) with respect to the main petroleum downstream, namely MAA refinery and upstream facilities in the state of Kuwait. Source: image adapted from KISR satellite archives (Kuwait).

The Fahaheel area (inhabited by about 100,000 residents) is considered to be one of five major areas in the state of Kuwait. It is located on the south of the coastal urban development of Kuwait city. The location of the area makes it a major point for work commuting and real estate ventures. The overly populated Fahaheel is adjacent to the highest capacity oil refinery in the state (Mina Al-Ahamdi - MAA- refinery). All the refineries, including MAA (three refineries belt), are located on the south side of the main Fahaheel shopping area (downtown). Petrochemical industries such as ammonia, urea, polyethylene and polypropylene plants, as well as the newly proposed polystyrene (proposed year of commissioning 2008), aromatics (proposed year of commissioning 2009) and Olefins II projects (proposed year of commissioning 2008) and other private small cottage industries also exist on the south side of the area. Background concentrations are associated with the second largest oil field in the world (The Greater Burgan Field) located somewhat on the west end of Fahaheel. By comparison, Al-Riqa area (inhabited by about 40,000 inhabitants) is less populated than Fahaheel. The residential area of Al-Riqa concentrates Kuwaiti residents of the middle and working classes. It is situated to the north side of Fahaheel and is dominated by inner roads that lead to the downtown of the area. To the south of Al-Riqa are the three refineries belt and Fahaheel area and the northeastern part is occupied by the downtown area of Al-Riqa. The polyclinics of Fahaheel and Al-Riqa were chosen to be the receptor points of both study areas, serving as the data collection point and the best location surrounded by the main air pollution sources.

DATA AND METHODS

The data used in this study were provided by the Air Pollution Monitoring Division, Kuwait Environment Public Authority (KUEPA) from both Fahaheel and Al-Riqa monitoring stations (15 and 7.5 m above ground level, respectively). The available data concern both five minute interval original data points and hourly averages of continuous measurements of the concentrations of the pollutants O3 (ppb), NO (ppb), NO2 (ppb), NOx (ppb), CO (ppm), H2S (ppb) and NH3 (ppb), total methane hydrocarbons (ppm), CH4 (ppm), (not all used in this study) and of the metrological parameters of ambient temperature (0C), relative humidity (%) and wind speed (m/s-1) and direction. The ambient air samples were drawn from a fixed probe (Group Tek. Model, 3-5 m, fixed photolytic converter, Environment SA and Thermo Models) located on the top of the polyclinics and were analyzed by using different primary pollutant and secondary precursor analyzers (Whatman 41, Air sample Grasbey-Anderson Ltd., 1% tolerance, weather station), all connected with a central online data acquisition system managed and controlled by EnviDAS software. For both urban areas, the data set covered the period from 1st January, 2004 to 31st December, 2005. Data points were filtered by discarding span check points, NULL and mechanical error sequences. The recovered data points were 97% of the original magnitude.

From those data the average diurnal pattern profiles were constructed for each pollutant and the exceedances of the limits/threshold values, over which they were considered injurious for human health, were calculated. Two receptor points (i.e. polyclinics in both urban areas) were chosen to establish a Chemical Mass Balance (CMB) model, to determine the percent contribution of the primary sources of air pollution around each urban area. The rates of the O3 accumulation, as described by both Fuijita et al. (2003) and Riga-Karadinos and Saitanis (2005) were discussed for the high O3 months in Kuwait (i.e. April-October). The NO and O3 concentrations were further analyzed to reveal any differences between midweek and weekends.

The source allocation was ascertained by analyzing the data points collected and by observing the wind directions of peak pollutant concentration values. Many researchers in their investigations have used CMB models to identify the predominant sources with respect to wind direction and their impact on the ambient air quality (Christensen and Gunst, 2004 and Christensen 2004). Various major airborne pollutants were present in the current pool of data. Sectors around each data collection point (receptor point) were divided to ease the analysis part of the constructed CMB model. Al-Riqa sectors were as follows: 1) downtown area, 2) refineries, petroleum and petrochemical industries, 3) traffic line sources (Fahaheel highway), gas stations, and sports clubs. Table 1 shows the distribution of these three sectors with respect to the data collection point in Al-Riqa (Polyclinic). As for Fahaheel the primary pollution sources and each corresponding sector is shown in Table 2 (Al-Salem and Khan, 2006).

Table 1: Position distribution around the outdoor data collection point in Al-Riqa urban area.

Position in degrees	Potential Air Pollution Source
300-130	Downtown area
131-260	Refineries, petroleum and petrochemical industries
261-299	Traffic line sources (Highway), gas stations, and sports clubs

Table 2: Position distribution around the outdoor data collection point in the Fahaheel urban area, Source: Al-Salem and Khan, 2006.

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

The above distribution of sectors (i.e. primary air pollution sources) will be identified in the CMB Modelling step as to how they affect the receptor points of the area. It was assumed that the sources were in the following directions, corresponding to the closest degree of each sector, in the case of Al-Riqa urban area, downtown area [0^0-135^0], refineries [136^0-270^0] and line sources [271^0-360^0].

Based on the initial analysis and collected data, the CMB model was setup in Microsoft Office 2003 in an EXCEL program. Non-methane Hydrocarbons (nm-HC), methane, carbon monoxide (CO), total hydrocarbons (HCT) and O_3 concentrations were also used in the execution of CMB model. The standard approach was applied for apportioning observed pollutant concentrations to their sources. The model implements a least squares solution to a set of linear equations, expressing each source as a linear sum product of the source percent contribution with predominant wind sector.

The CMB equations were based on the assumption that the observed ambient quantity of a chemical species is the simple sum of the product of pollutant contributions affecting the airshed and fraction of the wind sector. The CMB model uses the chemical and physical characteristics of the gases and particulates at a given receptor point to identify the presence of and/or quantify source contributions. Chemical degradation is excluded from the CMB analysis since NO and ozone convert photochemically very fast. Equation 1 is the basic relation corresponding to the selected receptor point. This equation expresses the relation between the concentrations of the chemical speicies measured at the receptor point (Main health center of Al-Riqa) and the chemicals emitted from the source.

$$\Delta C_i = \sum F_{ij} - S_i \qquad (1)$$

Where ΔC_i is the difference in concentration of a chemical compound i at the receptor point, Fij 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 wind speed contribution must be calculated in order to get the percent wind speed contribution with respect to the desired range of wind directions, i.e., the source. Equation 2 was used to calculate the wind speed contribution with respect to each source.

$$\%WS_j = (k_j / K) \times 10 \qquad (2)$$

Where $\%WS_j$ is the percent contribution of wind speed with respect to source j, k_j is the summation of wind speed points collected with respect to source j in (m/s) and K is the total summation of wind speed points in (m/s) excluding calm period.

In order to match the concentrations at the receptor point, predefined linear functions were solved with an objective function. The objective function, defined as the sum of squares of differences between measured and fractional concentrations of different sources chemical fingerprints including the influence of wind sector, is minimized The chemical fingerprints were average readings of concentrations reflecting the recorded inventories of the sources (Al-Bassam and Khan, 2004, Al-Hajraf et al., 2005). Equation 3 was used to solve for the least linear square root. The linear function was introduced for the four major sources studied as well as the receptor point, which represent the total cummulative concentration of the pollutant to be matched.

$$LF = \sum_{j=1}^{m}\left(\sum_{i=1}^{n} C_i.WS_j.SC_j - \sum_{i=1}^{n} C_i.WS_j.SC_j\right)^2 \qquad (3)$$

L.F. is the linear function set to match the percent contribution of each source, C_i is the concentration of airborne chemical i at a certain source or receptor point, $\%WS_j$ is the percent wind speed contribution at a certain wind direction range for source j, %SCj is the percent source contribution for a source j, where i represent pollutants and j sources.

RESULTS AND DISCUSSION

Exceedances of Air Quality Limits/Threshold Values

In order to assess the air quality in the two urban areas, measured concentration values of the pollutants were analyzed and compared with the limits and guidelines specified by the latest regulations (Law 210/2001) of the Kuwait Environment Public Authority (KUEPA, 2001).
Hourly concentrations of the pollutants monitored (O_3, SO_2, H_2S and NH_3) were compared with the limits specified by KUEPA. For the protection of human health, the KUEPA sets a limit of 80 ppb as an hourly rolling average for ground level O_3. Inhabitants of both areas in our study were exposed to O_3 levels above the limit. In 2005, the Fahaheel area had 154 exceedances of the O_3 limit. Compared to 2004, the exceedance number was reduced by more than half (the number of exceedances in 2004 was 416). Both SO_2 and H_2S exceedances had increased in 2005, exceeding the limits of 170 ppb and 140 ppb, respectively. There were no ammonia gas violations in 2004, while in 2005 there was only one.

Al-Riqa urban area was exposed to better air quality conditions in the period of study. Generally, the conditions in Al-Ahmadi governorate are similar. In the case of the monitored parameters, when a certain pollutant level is high in the Fahaheel area, the same pollutant will be high in Al-Riqa as well as the number of exceedances. SO_2 in 2004 had two exceedances, which had increased to 12 in the following year. There were no ammonia violations in Al-Riqa area in both years of study. Ozone levels were very high in Al-Riqa too, but the number of exceedances had decreased from 122 (2004) to 55 (2005). Two violations were recorded in 2004 for H_2S and had increased to 9 in the following year.

Primary Pollution Sources Determination Step and Percent Contribution Calculation Using CMB

The data collected in this study were used to construct concentration roses for the monitored pollutants. After the filtration process, a series of concentration roses were plotted for both areas of Fahaheel and Al-Riqa. Concentration roses were constructed for an annual average to determine the predominant wind and air pollution sources. All concentration roses were plotted in a blowing-from fashion. Fig.2 shows the concentration roses constructed for ground level O_3 (2004) in both study areas.

In Al-Riqa, the O_3 levels were predominantly blowing from the north-northeast sector of the area exceeding -40ppb. The shape and direction of O_3 in 2005 was very similar to 2004, when the two roses were compared. The Fahaheel area too had a similar ground level O_3 direction (north-northeast). Levels reaching above 40 ppb were noticed in both years of monitoring (2004 and 2005). Concentration roses for NOx, NO_2 and NO gases were executed in a single plot. Fig.3 shows the concentration roses executed for the year 2004 (Al-Riqa urban area).

Table 3: The air quality data of Fahaheel and Al-Riqa in comparison with the air quality limits determined by KUEPA.

Pollutant	KUEPA hourly limit (ppb)	Number of exceedances (year, area)	Reference
SO_2	170	4 (2004, Fahaheel) 2 (2004, Al-Riqa) 18 (2005, Fahaheel) 12 (2005, Al-Riqa)	KUEPA, Appendix 533, law 210/2001.
H_2S	140	6 (2004, Fahaheel) 2 (2004, Al-Riqa) 25 (2005, Fahaheel) 9 (2005, Al-Riqa)	KUEPA, Appendix 533, law 210/2001.
O_3	80	416 (2004, Fahaheel) 122 (2004, Al-Riqa) 154 (2005, Fahaheel) 55 (2005, Al-Riqa)	KUEPA, Appendix 533, law 210/2001.
NH_3	800	None (2004, Fahaheel) None (2004, Al-Riqa) 1 (2005, Fahaheel) None (2005, Al-Riqa)	KUEPA, Appendix 533, law 210/2001.

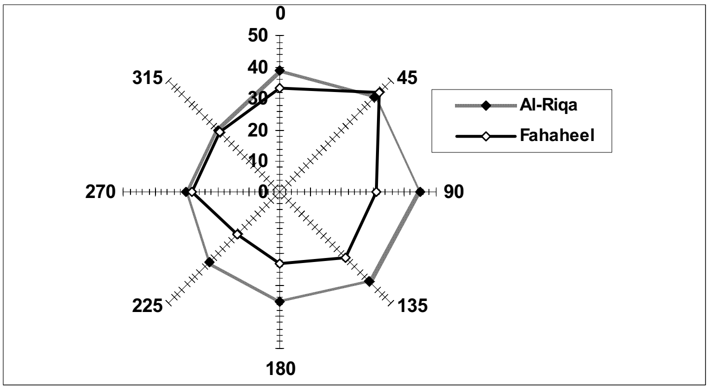


Figure 2: Annual O_3 (ppb) accumulated concentration rose executed for the year 2004 for Al-Riqa and Fahaheel urban areas (Al-Ahmadi Governorate-Kuwait).

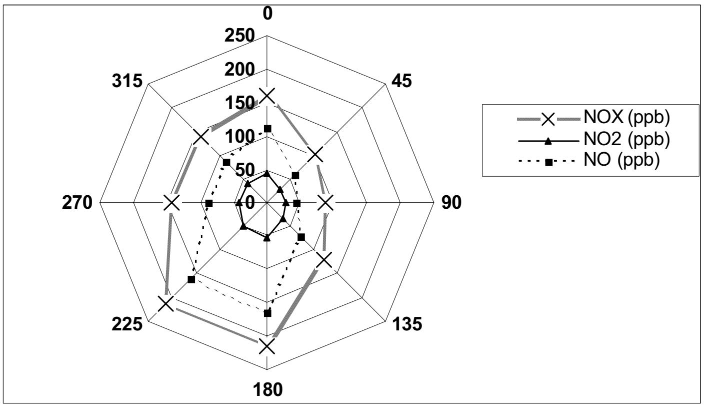


Figure 3: Annual NOx, NO_2 and NO (ppb) accumulated concentration rose executed for the year 2004 for Al-Riqa urban area (Al-Ahmadi Governorate-Kuwait).

Observed ozone levels from the north-northeast wind sector were high due to the fact that it is nearly undisturbed by man-made emissions, which makes NOx minimal in the same sector (Fig.3). In both areas, NOx ($NO+NO_2$) were mainly blowing from the petroleum downstream facilities side, i.e., Kuwait's three refineries belt. In Al-Riqa, NOx levels were blowing from the mentioned sector, exceeding 200 ppb on an annual mean basis. The Fahaheel area experienced a similar NOx behavior. The main NOx blowing sector is the southern one, which is occupied by the petroleum downstream facilities. Adding to the background concentrations resulting from the inner roads, heavy vehicle emissions and power station emissions, the sector emits NOx regularly from combustion sources in the three refineries adjacent to Fahaheel. As for the other pollutants (SO_2, CO, H_2S and NH_3), the same mentioned sector was the main contributor to the bulk of the concentration rose in both years of the study. SO_2 levels detected by the concentration roses plotted for 2004 and 2005 had reached 30 ppb from the above mentioned sector in Fahaheel. However, Al-Riqa concentration roses showed levels of 28 ppb (2004) and 29 ppb (2005) from the downstream facilities. Sulfur based components in the chemical processes (from stacks in refineries) and hydrodesulphurization processes and sulfur recovery units are considered to be the main contributors from that sector. Overworking conditions in the three refineries of the state of Kuwait resulting from continuous shutdowns of the smallest refinery (Al-Shuibah refinery) because of the fourth refinery project taking place at the moment resulted in the above violations and sector dominance on the plotted concentration roses. CO in Al-Riqa reached the level of almost 1.2 ppm (2004 and 2005) and in Fahaheel it exceeded 1.5 in 2004 and reached 1.7 in 2005. Incomplete combustion in flaring as well as the upstream facilities emissions (southern ones) all result in such accumulation of CO in the ambient air. H_2S levels in 2004 and 2005 exceeded 4 ppb in

Fahaheel. Al-Riqa showed similar values for H_2S (3.5 in 2004 and 3.8 in 2005). NH_3 exceeded 60 ppb in both areas, resulting from the downstream facilities sector (in both years of the study). Prilling processes (currently replaced) were in operation at that time (2004). With the replacement of urea prilling, the ammonia levels were produced from the bypass lines of the ammonia processing plant of the Petrochemicals Industries Company (Kuwait, P.I.C.).

The CMB model developed in this study was based on the values obtained in the months of January and July; since both months recorded variations of many airborne pollutants and had many maximum readings of the concentrations of major pollutants arising from the sources under study. These two months were chosen to represent the two longest seasons in Kuwait; summer and winter for being the most severe in their meterological conditions. The average percent contribution of the four primary sources of air pollution in the Fahaheel and Al-Riqa areas over the period of study are shown in Fig. 4.

The resulting portions of the source contribution varied between 78 and 111%. This behavior was always expected due to the associated errors for each source contribution which yield total contributions of less than or larger than 100%. In the results shown in Fig.4, mismatch points were excluded from the calculation. It can be noticed from the above stated results that, in the case of Fahaheel, which is closer to the three refineries belt, the downstream facilities were more dominant in the ambient air quality of the area, where it contributed 70% of its total pollution load. The least affective air pollution source was the upstream facilities of the Greater Burgan area (2%). The distance and winds are the strong influencing parameters for the dispersal of gaseous pollutants away from the two urban areas. Comparing the two downtown areas, Al-Riqa's was contributing almost 20% to the total ambient load, while Fahaheel was exactly half of that percentage. Although smaller in size than Fahaheel, Al-Riqa downtown is more populated and is occupied by all sorts of human-related pollution activities that also contribute to the load. The effect of the downstream facilities was least effective in the case of Al-Riqa area.

Diurnal Patterns of Monitored Pollutants

The dynamics of gaseous air pollutants were examined by their diurnal patterns. The average diurnal patterns (2004-2005) of the O_3, NO and CO levels for each month of the year and for each urban area were plotted and are shown in Fig.5. Significant variations were observed between the two urban areas in the level of pollutants and, in some cases, the diurnal pattern itself.

Concerning the level, the primary pollutants NO and CO occur at higher concentrations in Fahaheel. The same was observed for O_3. The higher levels of NO (evidently NOx) and CO in Fahaheel could be attributed (along with the reasons described in the previous sections) to its bigger size and to its larger population, as well as its busy eastern harbor. In Fahaheel, NO levels were higher during cooler periods in Kuwait (Jan-March and Oct-Dec), the same as in Al-Riqa. Regarding the diurnal patterns, it was interesting that all pollutants monitored in both cities exhibited two peaks in the exact same time frame. In the early morning (between 6 to 8 am) and evening (4 to 6 pm) times, two peaks existed in both cities, coinciding with the typical Kuwaiti urban activity (traffic, open shops, restaurants and markets, and central heating).

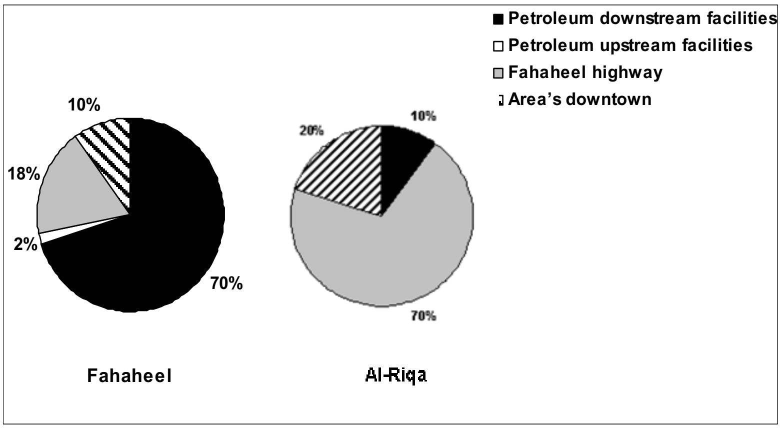


Figure 4: Contribution of air pollution sources studied in both area under investigation.

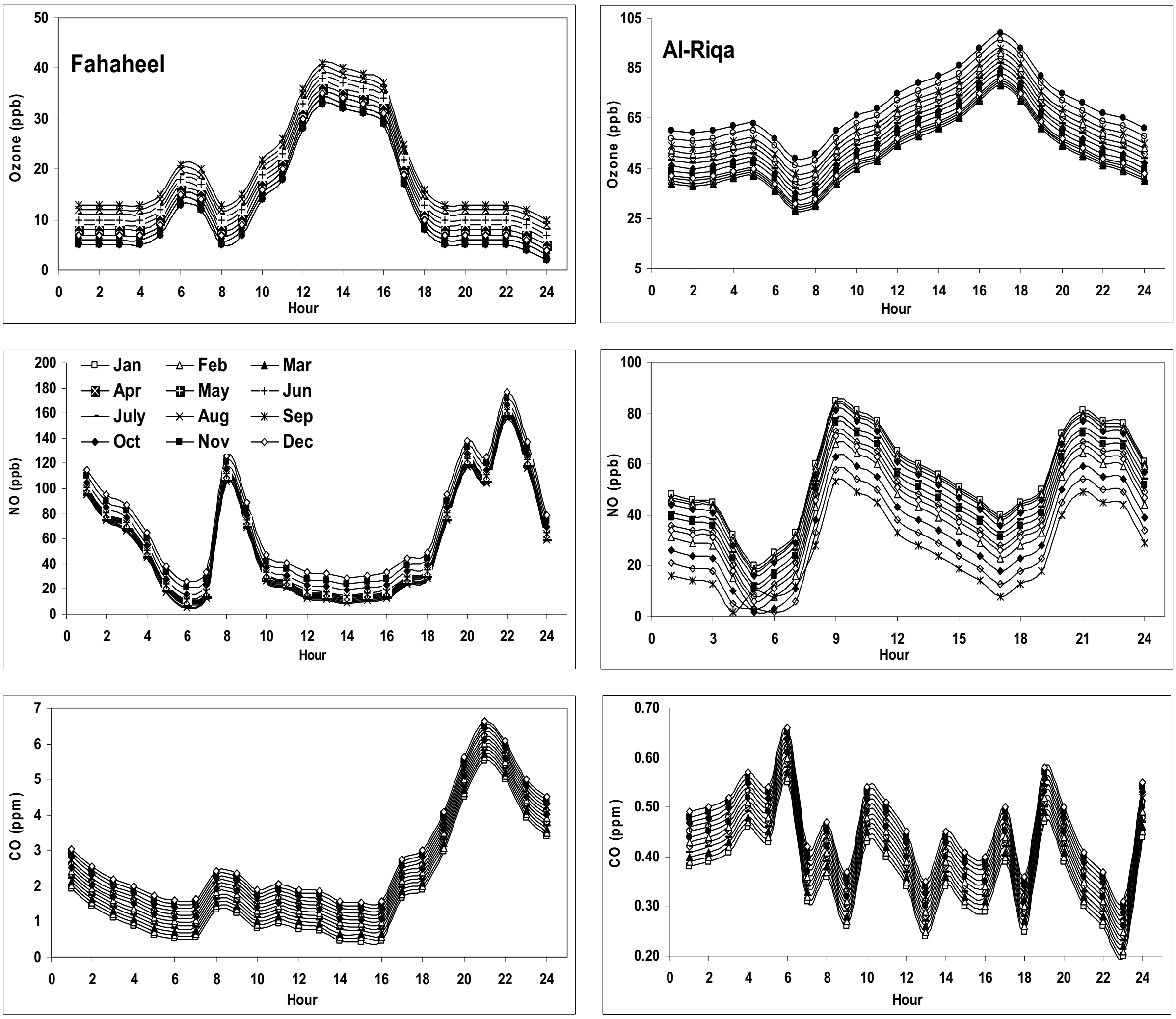


Figure 5: The plots of the monthly diurnal patterns of air pollutants (NO, O_3 and CO) in Fahaheel (left) and Al-Riqa (right) urban areas based on the two years (2004-2005) averages.

The diurnal patterns had a parallel pattern along the months studied, as clearly shown in the Figure 5, which can be explained by the load of pollutants in every month. NO, O_3 and CO differ in ambient levels monthly and are associated directly with either source emissions or photooxidation rate. In the case of O_3 (Fig.5), the levels were clearly more elevated in summer months, increasing gradually until reaching the month of September in both years. This period (April-September) has intensely higher solar radiation and is characterized by higher ozone levels.

NO increased gradually (April-March) as seen in Fig.5. NO peaks in both cities were noticed to be stronger in the months between October to February, mainly in Al-Riqa. During these months, the low solar radiation intensity, temperature and inversion do not cause intense photochemical reactions, which would lead to NO destruction (Riga-Karadinos and Saitanis, 2005, Al-Salem and Khan, 2006, Al-Salem, 2007). The generally lower concentrations of NO exhibit a lower peak in Al-Riqa between 6 to 9 am in the morning, compared to Fahaheel. At both urban areas, NO had a strong peak at around 22:00. Other than being the second rush hour time on Fahaheel highway, associating NO emissions with the area, this time (8-11 pm) is the time that Kuwait Car Association (KCA) activities are at their peak. Cars with NOs (Nitric Oxide System) installed contribute greatly to the general NO levels, mainly at Al-Riqa (since it is closer to KCA). NO is pumped into the burning chamber of the engines with air and gasoline, giving higher engine explosion. Night-time inversion is another contributing factor since a lower inversion layer hinders dilution processes, resulting in higher concentration levels of those species with ground-based sources, *i.e.* NO.

The observed diurnal patterns of CO in the two areas were very different. CO levels increased gradually throughout the year in Al-Riqa urban area. Excluding the two common peaks of all monitored pollutants, at around 4:00 AM a small peak in the CO levels was noticed. Fluctuation throughout the rest of the day was observed as well. The main CO contributing source (70% contribution from Fahaheel highway as established previously) can explain the observed pattern. For the 6:00 AM and 2:00 PM peaks, the highway is at rush hour because of the work commuters and school students. The 10:00 AM peak could be the result of the end shift workers commuting back to Al-Riqa from Kuwait's three refineries belt area. The increasing levels throughout the year are a direct result of the O_3 inverse effect (Riga-Karadinos and Saitanis, 2005). The CO levels in the troposphere exhibit an inverse behavior to O_3 seasonal fluctuation, with a maximum occurring in winter and minimum in summer, which is enhanced by the seasonal variations in the rates of CO production. Although O_3 levels are more intense in summer, the elevated temperatures and high radiation in a desert climate (Kuwait) produce the background concentrations of ground level O_3 to overcome this phenomenon in the summer (Fig.7). During the period of lower solar radiation (*i.e.* winter), it is enriched in the atmosphere due to lower OH^- concentrations, which is the only reactant for CO. Ozone, on the other hand is produced rapidly from VOC removal during the photochemical active season. This finding was observed previously in Ali Sabah Al-Salem residential area in Kuwait (Al-Hajraf et al., 2005).

The patterns for O_3 mixing ratios were very similar in both urban areas, but different in levels, particularly in summer months. In both urban areas there was an increase in the O_3 levels during the months from April to September and a strong daytime photochemical buildup due to photooxidation of ozone gas, indicating more active photochemical processes during the luminous hours of the early morning exceedances and middle of the day (maximum temperatures and radiation intensity) and in sunny seasons.

Concerning the relative humidity (RH), an increase in the humidity was noticed in the cooler periods in both cities and especially during ozone accumulation times, i.e. early morning and mid day. This suggests that a reduced loss of ozone by photoassociation may occur (Tisgaridis and Kanakidou, 2002, Riga-Karadinos and Saitanis, 2005). This may contribute to the different ozone levels in both urban areas.

Rate of Ozone Accumulation

In this study, particular attention was paid not only to diurnal ozone patterns but to it accumulation behavior. Since ozone is a photochemical oxidant, its concentrations cannot begin increasing until sufficient sunlight is present. Therefore, before sunrise, auto emissions (particularly NO) actually break down ozone present in the atmosphere. After sunrise, ozone concentrations gradually increase due to the photoassociation of nitrogen dioxide (NO_2) (also a constituent of automobile exhaust) and the resultant reaction of the atomic oxygen (O) and molecular oxygen (O_2) already present in the atmosphere (Seinfeld and Pandis, 1998, Riga-Karadinos and Saitanis, 2005).

As described by both Fuijita et al. (2003) and Riga-Karadinos and Saitanis (2005), the time when the mixing ratio of ozone equals the mixing ratio of NO could be regarded as the starting time for the daily ozone build up, referred to as the NO-O_3 crossover time ($t_{NO=O3}$), and should be considered as a marker for the end of the morning inhibition period and the beginning of the ozone accumulation. The rate of O_3 accumulation (ppb/hr) could be calculated as the difference of the ozone mixing ratio divided by the corresponding period of O_3 accumulation, as shown in equation 4.

$$\text{rate} = [O_{3\,\text{Tmax}} - O_{3\,t\,\text{NO=O3}}] / [T_{\max} - t_{\,\text{NO=O3}}] \qquad (4)$$

where $O_{3\ \text{Tmax}}$ is the ozone concentration in the ambient air (ppb) at maximum temperature, $O_{3\ t\ \text{NO=O3}}$ is the ozone concentration at the NO-O_3 crossover time (ppb), T_{max} is the time (hr) of maximum temperature; and $t_{\ \text{NO=O3}}$ is the crossover time (hr).

Following the approach used by Fuijita et al. (2003) and Riga-Karadinos and Saitanis (2005), the differences in ozone accumulation during the ozone build up period, for the high ozone months in Kuwait (April-October), were comparatively examined in the areas of Fahaheel and Al-Riqa. In both urban areas, the rate of O_3 accumulation increases from May up to September (not shown). It was found that, in Fahaheel, the crossover occurs about two hours earlier and lasts about an hour longer compared to Al-Riqa. This occurs because of the higher rates of NOx in Fahaheel, which help break down the ozone at ground level but still cannot lower its levels to those of Al-Riqa because of the initial high ozone levels existing in the area's lower atmosphere.

In the current study, another approach was used based on comparing the diurnal pattern (2004 and 2005) for the high ozone months in Kuwait (April – October) to the NO and ozone mixing ratios. In Fahaheel, the comparison used confirmed that the crossover occurs about two hours earlier (Fig.6, point A). Levels of NO and ozone were much higher in Fahaheel compared to Al-Riqa in the high ozone level months. The duration of ozone build up in both cities differs (Fig.6), due to the fact that the initial ozone levels in the study were much higher in Fahaheel than in Al-Riqa, which could be explained by transportation of high levels of ozone (70-80 ppb) from the southern direction. The fact that high levels of ozone are observed together with non-vanishing NO emissions can be explained (the reaction NO + ozone ⇓ NO_2 takes place within minutes) if one assumes long term transport of high ozone levels and the existence of nearby sources of NO prior to ozone titration (which is typical for Fahaheel). In the case of Al-Riqa, most of the ozone is already titrated, which yields much lower ozone values during nighttime for the area.

The constant rate of O_3 accumulation from morning to its peak concentration found by Fujita et al. (2003) does not seem to be applicable to our data, which exhibit two rather distinct phases of O_3 accumulation with their respective maxima in the two cities (Fig.6): (a) a fast phase (from points B and C to point D), suggesting a high rate of ozone accumulation, and (b) a slow-phase (from point D to points F and E), suggesting a low rate of ozone accumulation. The duration of each phase is different in the two cities and seems to depend on the local photochemistry. Probably, the approach of Fujita et al. could be applicable to places where the ozone accumulation curve exhibits a bell-shaped pattern with a clear peak and where ozone accumulation reaches its maximum almost linearly, as described in their article, but it is rather inappropriate for places, like in Fahaheel and Al-Riqa, where the ozone diurnal pattern exhibits a plateau. The present findings in this study agree with those of Riga-Karadinos and Saitanis (2005) in two Greek Mediterranean costal cities.

Weekday/Weekend Variations

Human activities cause emissions of all sorts of airborne pollutants. These emissions are bound to affect the weekly cycle of ambient pollutant concentrations. Weekday and weekend differences in ambient concentrations of air pollutants such as NOx and CO have been the subject of research interest in the past decade. During weekends, the levels of ozone are believed to be lower compared to those occurring during weekdays because of car traffic emissions (line sources are lower and several plants may be inactive during that time (Riga-Karadinos and Saitanis, 2005)). In Kuwait, back in 2004 and 2005, weekends were on Thursdays and Fridays. In this study, monthly averages of the mean hourly ozone and NO concentration mixing ratios vs. the corresponding mixing ratios on Wednesday, Thursday, Friday and Saturday, recorded in both Fahaheel and Al-Riqa, were plotted. As an example, the plots of Wednesday and Thursday in Al-Riqa area shown in Fig.7. In Table 4, the relevant linear regression equation and the corresponding correlation coefficients are given for both urban areas.

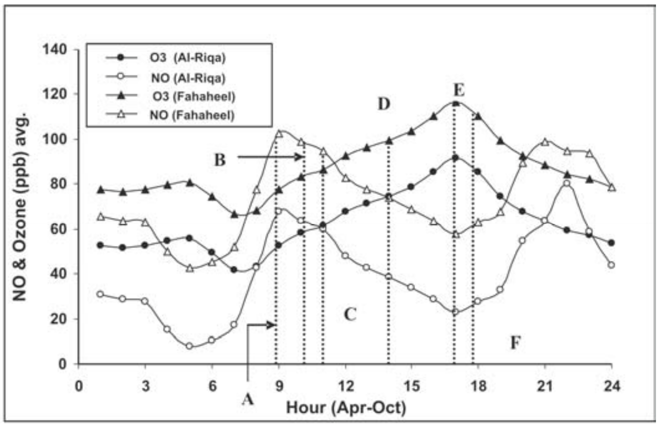
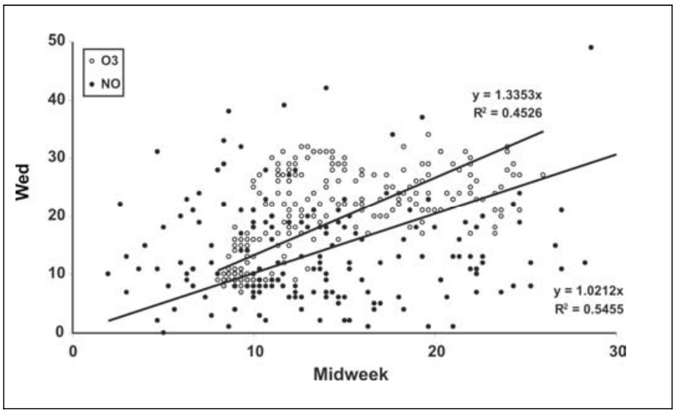


Figure 6: The average (April-October) diurnal pattern of ozone and NO in Fahaheel and Al-Riqa urban areas (Kuwait): (A) the time of onset of photochemistry; (B, C) the crossover in Fahaheel and Al-Riqa; (D) the end of fast phase ozone accumulation in both urban areas; (E, F): show the maximum mixing ratios of ozone and the end of the slow phase of ozone accumulation in Fahaheel and Al-Riqa. The afternoon and night photochemistry phases follow.



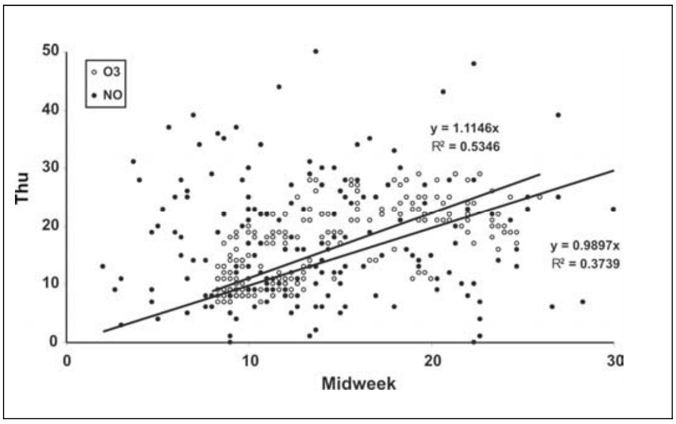


Figure 7: Correlation plots of the monthly averages of the mean hourly ozone and NO mixing ratios (Wed. Thu. – Al-Riqa) during midweek (Sun-Tues) vs. the corresponding mixing ratios of the rest of the week.

Table 4: Regression equations of the summer mean hourly ozone mixing ratios at Fahaheel and Al-Riqa during midweek (Sun-Tues) vs. the corrosponding mean hourly ozone mixing ratios on Wednesday, Thursday, Friday, and Saturday (X).

	Fahaheel		Al-Riqa	
Wednesday O_3	Y = 2.390X	r = 0.843	Y = 1.335X	r = 0.672
Wednesday NO	Y = 0.173X	r = 0.424	Y = 1.021X	r = 0.738
Thursday O_3	Y = 0.946X	r = 0.809	Y = 1.114X	r = 0.731
Thursday NO	Y = 0.417X	r = 0.276	Y = 0.989X	r = 0.611
Friday O_3	Y = 1.625X	r = 0.898	Y = 0.851X	r = 0.433
Friday NO	Y = 1.762X	r = 0.431	Y = 0.684X	r = 0.582
Saturday O_3	Y = 0.200X	r = 0.846	Y = 1.028X	r = 0.189
Saturday NO	Y = 1.985X	r = 0.998	Y = 0.26X	r = 0.998

Concerning O_3, the slopes of the linear regressions for Fahaheel urban area during Thursdays and Fridays revealed that, they were similar; however, the O_3 slopes for Wednesdays were much higher (Table 4). In Al-Riqa, O_3 slopes were very similar for Wednesdays and Thursdays and were lower for Fridays and Saturdays.

Regarding NO in Fahaheel, during Saturdays and Fridays the slopes were clearly closer to one compared to those of Thursdays and Wednesdays (Table 4), while in Al-Riqa slopes were closer for Wednesdays and Thursdays. These results suggest the occurrence of a weekend effect in both areas. Obviously, the weekend effect is stronger in Fahaheel than in Al-Riqa and more intense on Wednesdays than on Thursdays. High NOx levels can inhibit the production of O_3 either by NO titration of O_3 or by reaction of NO_2 and OH to form nitric acid (HNO_3), a sink for both radicals and NOx. Because of complex chemistry, O_3 does not respond linearly to the levels of precursors. In NOx sensitive regions (i.e. abundant VOCs relative to NOx), O_3 decreases more rapidly with reductions in NOx emissions than with reductions in VOCs. In VOCs-sensitive regions (i.e. abundant NOx relative to VOCs) a decrease in NOx emissions may cause an increase in O_3 because of reduced titration or reduced formation of HNO_3. Locations where ozone increases during weekends, but NOx emissions are significantly lower, should be considered VOCs-limited (Blanchard and Tanenbaum, 2003, Riga-Karadinos and Saitanis, 2005). Thus, the increase of O_3 levels during weekends in both urban areas suggests that both cities may be VOCs-sensitive. The reduction of anthropogenic emissions during weekends is expected to reduce proportionately equally anthropogenic VOCs (AVOCs)

In addition to the above-discussed role of VOCs in the ‘‘weekend effect’’, it is the low early morning rush-hour traffic on weekends that allows ozone concentrations to begin rising from a significantly higher concentration and therefore reaching higher overall weekend concentrations. Different studies demonstrate a wide range in the weekday/weekend O_3 behavior: a little variation among weekdays, but Saturdays and Sundays (which corresponded to Thursdays and Fridays in Kuwait at that time) having higher O_3, with Sundays having the highest levels in and around major cities such as Los Angeles and San Francisco (US), or Paratas and Volos (Greece). On the other hand, in many other sites the weekday and weekend O_3 concentrations are approximately equal (Fujita et al., 2003; Heuss et al.,2003). Marr and Harley (2002) suggest that NOx concentrations are consistently lower on weekends relative to weekdays by approximately 30–40%, while VOC changes are less pronounced (<10%). The explanation of weekday/weekend variation, due to NOx reduction, is supported by a wide range of analyses of ambient air data and several photochemical studies. Changes in the timing and location of emissions and meteorological factors play smaller roles in weekend O_3 behavior (Heuss et al., 2003). Analysis of ambient air quality data and emissions forecasts for weekdays and weekends may improve considerably our understanding of the effects of control strategies and of future changes in emissions on future ambient O_3 concentrations.

CONCLUSION

Synoptically, the primary pollutants NO, CO, H_2S and SO_2 occurred at higher levels in Fahaheel than in Al-Riqa. Concerning the exceedances of the pollutants monitored, in terms of human health regulations in Fahaheel and Al-Riqa, the number of exceedances of the gaseous pollutants were much higher in Fahaheel. A Chemical Mass Balance (CMB) model was established around both receptor points, i.e. polyclinics. This model revealed that, in the case of Fahaheel, petroleum downstream facilities were the main contributor to the ambient load, while in Al-Riqa urban area, Fahaheel highway was the main contributor to the ambient load of pollutants. Examination of O_3 accumulation rate from April to October revealed two phases: a fast and a slow one, with different durations in each of the two cities due to different levels of precursors and to different local photochemistry. A strong weekend effect was observed in Fahaheel, but less intense in Al-Riqa. Both urban areas seem to be VOCs limited. The causes of the weekend O_3 effect were probably the weekend/weekday differences in NOx emissions and the complex non-linear photochemistry of ozone. The relatively lower NO and NO_2 concentrations on weekends result in less OH radical loss and more O_3 formation. Lower NOx emissions on weekends decrease NO titration of the O_3 newly formed at the surface and the ozone transported from aloft. The data of this study would be useful for future comparisons. It is obvious that, for future air quality management strategies, the development of accurate, temporally and spatially resolved day-of-the-week emission inventories, including separate inventories for weekends can promote a better understanding. Regarding the role of local agencies involved in making air quality conditions better in urban living locations, the Kuwait Environment Public Authority (KUEPA) must enforce their rules and regulations of the industrial sectors around urban areas. Emissions from upstream and downstream industries cause a number of problems in the general population regarding human health and welfare. The Kuwait Public Authority of Industry (KUPAI), must monitor the activities of small industries and their role in contributing to the general pollution load around urban areas in the state.

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