Review Article

Monitoring and Modelling the Trends of Primary and Secondary Air Pollution Precursors: The Case of the State of Kuwait

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Since the beginning of the industrial revolution, processes of different scales have contributed greatly to the pollution and waste load on the environment. More specifically, airborne pollutants associated with chemical processes have contributed greatly on the ecosystem and populations health. In this communication, we review recent activities and trends of primary and secondary air pollutants in the state of Kuwait, a country associated with petroleum, petrochemical, and other industrial pollution. Trends of pollutants and impact on human health have been studied and categorized based on recent literature. More attention was paid to areas known to researchers as either precursor sensitive (i.e., nitrogen oxides (NO_x), volatile organic compounds (VOCs)) or adjacent to upstream- or downstream-related activities. Environmental monitoring and modelling techniques relevant to this study are also reviewed. Two case studies that link recent data with models associated with industrial sectors are also demonstrated, focusing mainly on chemical mass balance (CMB) and Gaussian line source modelling. It is concluded that a number of the monitoring stations and regulations placed by the Kuwait Environment Public Authority (KUEPA) need up-to-date revisions and better network placement, in agreement with previous findings.

1. Introduction

It is of paramount importance to monitor and study the behaviour of primary and secondary precursors of air pollution, to establish a better understanding of their trends and impact on the surrounding environment. Human-related activities result in a number of airborne chemicals (i.e., primary pollutants), which include methane (CH_4) and nonmethane hydrocarbons (collectively known as total hydrocarbons-THC), total sulphur, nitrogen oxides and hydrogen sulphide (SO_x , NO_x , H_2S), carbon mono- and dioxide (CO and CO_2), BTEX (C_6H_6 , $\text{C}_6\text{H}_5\text{CH}_3$, $\text{C}_6\text{H}_5\text{C}_2\text{H}_5$ and $\text{C}_6\text{H}_4(\text{CH}_3)_2$), and other heavy metals (e.g., Hg, Pb, etc.). The interaction of such chemicals with the surrounding environment and the effect of photochemical reactions in the atmosphere results in what is known as secondary pollutants, a valid example of which is ozone (O_3).

Urban air pollution photochemistry is somewhat unique, and has been a matter of debate for a number of years amongst researchers [1–6]. One of the main characteristics of urban air pollution is the oxidation of SO_2 and NO_2 and their conversion to particulate sulphate (SO_4^{2-}) and gaseous and particulate nitrates (NO_3). Moreover, the rate of the conversion of NO_x to NO_3 affects ozone formation and the fate of the NO_x in the atmosphere. NO_x is oxidized to nitric acid (HNO_3) in the atmosphere, which in turn forms NO_3 particles [7].

Acidification of precipitation, visibility reduction, and deleterious effects on human health and plants are all effects associated with these secondary pollutants. Nonetheless, one of the main worries with regards to urban air pollution is the substitution of a pollutant with another in a reversible reaction. This could be witnessed in many Asian and European countries via the following nitric oxide reaction

FIGURE 1: Urban Kuwait map showing main locations in the stat. Image courtesy of satellite archives at the Kuwait Institute of Scientific Research.

with ozone

Hence, one pollutant (O_3) is substituted by another in the lower atmosphere (i.e., NO_2) [5]. In this paper, we review recent developments and trends associated with air pollution precursors, in terms of increase and diurnal patterns in the state of Kuwait and the surrounding region, mainly the Arabian Gulf peninsula. Environmental measuring techniques and modelling methods are reviewed within the scope of this paper.

1.1. Major Pollution Sources and Activities within the State of Kuwait. Kuwait is a principality state in the North-Eastern corner of the Arabian Gulf peninsula, currently with an estimated population of 2.8 million. Kuwait is characterized by a typical *desert climate* with long harsh summers, in which ambient temperatures exceed 55°C and mild winters. It is also a major exporter of crude oil (ranking forth in OPEC's producers list), where the 2.6 million barrels per day (mbbld) mark was crossed back in 2007 [8], with plans to increase production to 4 mbbld in 2020 [9]. Three major refineries process over 935,000 bbbld, situated in the southern part of the country, collectively referred to as the *refineries belt* [10].

Such characteristics make Kuwait a country with air pollution associated with down/upstream processes, namely, in southern parts of the country. In addition, petrochemical processing lines and conversion industries are all located, somewhat, in the vicinity of Al-Shuaibah industrial area (Figure 1). Border lines of the city, stretching to the fifth ring road, make Kuwait City an area cornered by the bay. The city area harbours both traffic-related airborne pollutants and southern sources emissions. In addition, activities within city

limits and harbour pollution from the northern stretch also contribute to the pollution load. Moreover, Kuwait has the largest and oldest power plant and desalination network in the region, dating back to the 1960s. The capacity of which is estimated at 16,095 MW and $2 \times 10^6 \text{ m}^3/\text{day}$, respectively [11].

Traffic congestion and rush hours within city limits and along major highways (i.e., King Abdulaziz (Fahaheel), 5th and 6th ring road) contribute mainly to the CO , NO_x and VOCs levels in the air. For every 33 residents in Kuwait, there are 100 cars registered [11]. Such estimates makes airborne pollution studies a must for concerned parties, namely, the Kuwait Environment Public Authority (KUEPA), which since 2001 is recognized as an independent government body with legal powers.

1.2. Primary Pollutants Monitoring. Compared to its neighbouring countries, Kuwait suffers from primary pollutants effects. This is witnessed clearly on the number of pollutants recorded in the KUEPA stations, which operate a number of fixed monitoring stations around the country. A previous study by Al-Rashidi et al. [12] stated that the stations were not appropriately distributed around the city limits, and there is a need to relocate them within residential areas to measure the actual impact of a number of primary pollutants (e.g., SO_2). Abdul-Wahab [13] compared two areas in the Gulf Council Countries (GCC), namely Al-Khalidya (Kuwait) and Qalhat (Oman), in terms of air pollutants and their load. Results showed higher levels of pollution in the urban residential area of Kuwait than in the suburban industrial area in Oman. The data recorded in Al-Khalidya showed that both nonmethane hydrocarbons (NMHC) and NO_2 have exceeded the Kuwait standards for residential areas. Furthermore, the results showed that the hourly distribution of NMHC, CO , and NO_x in Khaldiya was characterized by three peaks which were associated with the traffic loads on the main streets. The data recorded in the urban area of Kuwait showed marked day-of-week dependence also.

1.3. Secondary Pollutants. The major concern with secondary airborne pollutants is ground level ozone (O_3), namely, in a country with high ambient temperatures that induce (alongside radiation energy, volatile organic compounds (VOCs), and NO_x) ozone formation. In essence, controlling precursor emissions (i.e., VOCs and NO_x) coming from anthropogenic sources can minimize ozone formation [14]. The main contributor of such sources is combustion processes (local industries including power stations, gasoline and diesel operated vehicles, etc.). Transportation emissions control is hence considered crucial to ozone reduction.

Ground level ozone (O_3) formation is a continuous physical-chemical accumulation/destruction process [15]. Therefore, a diurnal ozone cycle/curve reflects the effects of all those underlying factors on ozone dynamics, which underlines the importance of monitoring such a chemical. Abdul-Wahab et al. [16–18] have used a mobile laboratory to study and analyse air pollution in Kuwait. Data analysis

TABLE 1: Standard USEPA methodology for annual population risk (APR) and hazard index (HI) calculations used by Al-Salem and Bouhamrah [27]; Al-Salem and Al-Fadhlee [28].

Equation/correlation	Notes
$OX = C_{O_3} + C_{NO_x} - C_{NO}$	Used for data filtration, where OX is the concentration of oxides in the ambient (ppb), C_{O_3} , C_{NO_x} and C_{NO} are the concentrations in ppb of ozone, NOx and nitric oxide, respectively.
$E = \frac{C \cdot CR \cdot EF \cdot ED}{BW \cdot AT}$	Where C is the contaminant concentration ($mg \cdot m^{-3}$); CR is the contact rate in $m^3 day^{-1}$; EF is the exposure frequency in days per year; ED exposure duration (year); BW is the average human body weight (kg); AT is the averaging time in hours/year.
APR = Risk factor $\times$ Population/lifetime	APR is the annual population risk
$HI = \sum (C_i/PEL_i)$	Where C_i is the concentration of i in mg/m^3 ; PEL_i is the permissible exposure limit for i in mg/m^3 .

showed that ozone concentration exhibited a maximum at 27°C as a function of ambient temperature. Increase in the ambient temperature above 27°C resulted in a decrease in the ozone concentration. Increase in power consumption in the summer, due to the increased use of indoor air conditioning, resulted in increase in emission rates of various pollutants.

It is also known that stratosphere ozone layer acts as a shield against all ultraviolet radiation approaching the planet Earth through absorption. Al-Jeran and Khan [19] analyzed data of ozone layer thickness obtained from Abu-Dhabi (UAE) station and detailed measurement of air pollution levels in Kuwait. The ozone layer thickness in stratosphere had been correlated with the measured pollution levels in the State of Kuwait. The influence of import of ozone depletion substances (CFCs) for the last decade had been evaluated. Other factor that strongly affects the ozone layer thickness in stratosphere is local pollution levels of primary pollutants such as total hydrocarbon compounds and nitrogen oxides. The dependency of ozone layer thickness on ambient pollutant levels presented in detail reflecting negative relation of both nonmethane hydrocarbon and nitrogen oxide concentrations in ambient air. The ozone thickness related to the ground level concentration of nonmethane hydrocarbon and can be used as an indicator of the health of ozone layer thickness in the stratosphere. The thinning of ozone layer on the poles was alarming that resulted into different protocols while near equatorial regions this phenomenon is not that much pronounced. The maximum thinning occurred in the month of June and the least in the month of December based on five years data from Abu-Dhabi monitoring station.

1.4. Health Impact. Increased levels of primary and secondary pollutants are known to have adverse effects on human health [20], to cause injury to plants [21], to reduce crops yield [22], and to negatively affect ecosystems [23]. Natural ecosystems adjacent to urban areas are exposed increasingly to air pollutants of urban origin. Air pollutants, particularly SO_2 , NO_2 and the major secondary photochemical oxidant O_3 , OH, and SO_4 are important threats to plants. Their effects comprise many physiological and biochemical changes in plants, which may result in growth reduction and yield loss, even at low levels chronic exposure. Concerning human health, tropospheric O_3 measured in urban regions and across regional airsheds are known to affect human health [24].

Air pollution in Kuwait is a major contributor to a number of health effects associated with many age groups in the city and around urban suburbia [25]. Local health reports show that 40% of the patients in one of the main hospitals in Kuwait during the period of August–October 1991 suffered from respiratory problems, baring first Gulf War effects and oil fields fires by retreating Iraqi troops. Statistical analysis showed that there was a highly significant correlation between the increased concentration of specific pollutants and symptoms of reactive and nonreactive airway diseases [26].

Al-Salem and Bouhamrah [27] studied a number of carcinogens and other primary pollutants in an industrial area in Kuwait. The main focus was on calculating the annual population risk (APR) to establish a better cancer risk assessment study by calculating APRs and hazard indices (HIs). Benzene (C_6H_6), di bromo-chloro methane, bromoform, chloroform, and methylene chloride were all measured using diffusive passive sampling techniques. Using the standardized USEPA methodology (Table 1), APR was increasing within winter months (mainly January) and had a proportional relationship with benzene levels in the atmosphere, wind direction, and location of site. On average, the industrial site in Kuwait exceeded the US average, city of St. Louis (US) and Modena (Italy), levelling at 6 cases on a 70 year average in population much less than the rest. Cases associated with leukaemia are attributed to benzene levels in the lower atmosphere. In a followup study investigating the south regions of Kuwait, Al-Salem and Al-Fadhlee [28] studied the APR and HI associated with benzene levels in the atmosphere in a residential area over the period of 3 years (2004–2006). The HI calculations were based on SO_2 , NO_2 , and NH_3 levels, which resulted in a value of 0.03, that is, fit for living conditions. Khan and Al-Salem [29] studied the effects of NO_x and NO on birth and still birth rates in Al-Ahamdi governorate in Kuwait. A relationship was proved based on statistical analysis performed using one and two way ANOVA. Based on the five years data collected, the still births in the area increased from 153 cases (2000) to 196 (2004), corresponding to an increase in the NO level.

The State of Kuwait oil fires and military operations associated with the 1991 Gulf War resulted in substantially increased levels of airborne particulate matter (PM) in the region around it, namely, the GCC. White et al. [30] used a quantitative risk assessment methodology to estimate

TABLE 2: Summary of recent studies conducted in the state of Kuwait focused on primary pollutants monitoring and source determination.

Reference	Primary pollutants studied	Notes
Al-Salem and Khan [10]	NO _x , NO, SO ₂ , CO, H ₂ S, NH ₃	Monitoring the trends and diurnal patterns of Al-Riqa and Fahaheel areas. A number of exceedences were recorded in violation of KUEPA rules and regulations.
Sebzali and Al-Salem [32]	NMHC, NO _x , SO ₂ , CO, H ₂ S, NH ₃	A neural network was developed based on multilayer processor modeling in Al-Mansoriah area. The study was used to estimate primary pollutants with a high accuracy.
Khan and Al-Salem [33]	C ₆ H ₆ , Cl ₂ , NO ₂ , NO _x , H ₂ S, CH ₄	Three years of data were assessed and filtered to execute concentration roses around a receptor point. Combustion and downstream activities were determined to be the major source.
Al-Salem [34]	CH ₄ , CO	A series of wind and concentration roses were executed to investigate the source of the two pollutants around Fahaheel. Patterns and shapes determined that the refineries belt side was the major contributor to the load.
Al-Salem et al. [35]	NO _x , NO, SO ₂ , CO, H ₂ S, NH ₃	Al-Mansoriah area was investigated and levels of NH ₃ were exceeding threshold limits. The area was determined to be a NO _x sensitive area in the state of Kuwait.
Albassam et al. [36]	CO, NO _x , NMHC	An assessment of air quality in the vicinity of a school was carried out, NMHC was above permissible limits. Statistical analysis was used to predict a number of primary pollutant.
Khan and Al-Salem [37]	C ₆ H ₆ , CO, NO _x	Seasonal variations and metrological conditions were affecting primary pollutants dispersion and fate in the atmosphere based on this study. Using executed roses around a receptor point and analysis the authors determined the effect.
Al-Adwani et al. [38]	CO, NO _x , THC	An intersection was monitored for automobile primary pollutants at the switch period of MTBE unleaded gasoline in Kuwait. CO and THC emissions increase as volatility increases.

the increase in premature deaths in citizens of Saudi Arabia associated with the Gulf War. Meta-analysis of daily time-series studies of nonaccidental mortality associated with increased PM₁₀ levels using two alternative methodologies yielded exposure response relative risk functions of 2.7% and 3.5% per 50 µg/m³ increase in PM₁₀ concentration. Combining these exposure-response functions with estimates of the magnitude and duration of the increased PM₁₀ exposure, the size of the exposed population and baseline mortality rates provided an estimate of approximately 1,080 to 1,370 excess nonaccidental deaths of Saudi citizens during 1991-1992 associated with the Gulf War-related increase in PM levels. Lange et al. [31] examined relationships between symptoms of respiratory illness present 5 years after the war and both self-reported and modeled exposures to oil-fire smoke that occurred during deployment of troops. Modeled exposures were exhaustively developed using a geographic information system to integrate spatial and temporal records of smoke concentrations with troop movements ascertained from global positioning systems records. Approximately 94% of the study cohort were still in the gulf theater during the time of the oil-well fires, and 21% remained there more than 100 days during the fires. There was modest correlation between self-reported and modeled exposures ($r = 0.48$, $P < .05$). Odds ratios for asthma, bronchitis, and major depression increased with increasing self-reported exposure. In contrast, there was no association between the modeled

exposure and any of the outcomes. These findings do not support speculation that exposures to oil-fire smoke caused respiratory symptoms among veterans.

2. Monitoring, Trends, and Diurnal Patterns

2.1. Pollutants Monitoring and Major Contributing Sources. In a country that is dominated by petroleum upstream/downstream industries, primary pollutants are of major concern, with regards to air quality. Other sources of primary pollutants in Kuwait include power stations (operating on fossil fuels) and road traffic. A recent study by Ramadan [39] was concerned with measurements of fortnightly average concentrations of a number of primary pollutants, namely: NO, NO₂, SO₂, H₂S, NH₃, and VOCs. The study location was in southern Kuwait (Al-Zour); an area influenced by petroleum refining and electrical generation activities. No violations of KUEPA standards were reported, but consistency of the results allowed the production of spatial distribution maps of the pollutants measured and consequently the comparison between levels of air pollution at different locations. A comparison between the measured concentrations and the applicable air quality standards promulgated by KUEPA showed that those compounds had low concentrations compared to both industrial and residential KUEPA standards. Table 2

FIGURE 2: Diurnal pattern of SO_2 recorded over the period 2000-2004 in Al-Mansoriah. Source: Al-Salem et al. [35].

summarizes a number of studies conducted in the state of Kuwait in the last decade, focused on primary pollutants monitoring.

A number of reasons drive researchers to study PM_{10} in an arid country like Kuwait, mainly for the abundance of surrounding sources around the city limits. Road traffic and frequent dust storm are proposed to be essential contributors to the total PM_{10} ambient load in urban areas [40]. Other sources include burning fuels (i.e., gasoline, oil, diesel, or wood) and blown dust. In a compiled study of seven European cities, Querol et al. [41] show that mineral dust, combustion, and secondary aerosols were important PM_{10} sources. They also show that PM_{10} levels were enriched at kerbsides relative to urban background, a fact that must be attributed to road traffic emissions. The same area (Fahaheel) was studied by Al-Salem and Khan [10] for its diurnal patterns of major primary and secondary pollutants. Al-Mansoriah residential area was monitored by Al-Salem et al. [35] for the same purpose (Figure 2). Similarities were found in typical airborne pollutants associated with both residential and industry adjacent sites. NO peaks were in contrast to ozone (titration effect) concentrations. And THC were associated with industrial sources at emissions strength hours. Heal et al. [42] point out traffic, combustion, and crustal material as the major sources in urban background. Studies on PM_{10} have been very limited in the state of Kuwait. A study by Al-Salem [43] over the period of two years considered PM_{10} data (January 2004–December 2005) and analyzed for Fahaheel urban area. The annual mean values exceeded (both years of continuous monitoring) the KUEPA permissible limit ($90 \mu\text{g m}^{-3}$), recording 291 in 2004 and $289 \mu\text{g m}^{-3}$ in 2005. 14 exceedances were recorded in 2004 based on daily rolling averages, while in 2005 15 exceedances were recorded. Engelbrecht et al. [44] initiated a study around Kuwait and other neighbouring countries, including UAE, Qatar and others. The study focused on providing information on the chemical and physical properties of dust collected over a period of approximately a year. By comparison, average PM_{10} and $\text{PM}_{2.5}$ mass and chemical concentration levels from the Middle East deployment sites areas many as 10 times greater than those from five rural

(IMPROVE) and five urban (CSN) sites in the southwestern US.

CO_2 is another important pollutant that has been a concern in the state for the last somewhat 20 years. The CO_2 concentrations also show a strong diurnal pattern with lowest values in the mid-afternoon when the local atmosphere is most unstable and highest concentrations in the early evening when the atmosphere becomes more stable and vehicular traffic is high. A secondary peak occurs in the early morning when traffic increases and the atmosphere is most stable [45]. In a study by Nasrallah et al. [46], measurements of an urban area in Kuwait were compared to the city of Phoenix (Arizona, USA). Analysis of this record reveals (a) an annual cycle with highest values in February and lowest values in September reflecting the growth and decay of vegetation in the Northern Hemisphere as well as fluctuations in motor traffic, (b) a weekly cycle with highest values during the weekdays and lowest values during weekends, and (c) a diurnal cycle with highest values after sunset when the local atmosphere becomes more stable following vehicular emission of CO_2 throughout the day and lowest values in late afternoon following several hours of relatively unstable conditions. During the daytime, CO_2 concentrations are related to wind direction, with westerly winds (coming from the desert) promoting lowest CO_2 concentrations. At night, lowest CO_2 levels are associated with higher wind speeds and winds from the north. Asia and more specifically the Middle East has become the largest contributor to mercury (Hg) in the atmosphere, responsible for over half the global emissions. A number of sources contribute to the Hg levels, such as Hg mining, gold mining, chemical industry, metal smelting, coal/crude oil combustion, natural, and agriculture resources. With the probable effects of a unique combination of climatic (e.g., subtropical climate), environmental (e.g., acid rain), economic (e.g., swift growth) and social factors (e.g., high population density), more effort is still needed to understand the biogeochemistry cycle of Hg and associated health effects in Asia. Li et al. [47] reviewed the Hg levels and sources in Asia. They have concluded that Kuwait was over contaminated by Hg due to chemical processing around the bay area due to salt and chlorine processing. BuTayban and Preston [48] conducted Hg pollution investigation in sediments in Kuwait Bay, which received wastewater from a Salt and Chlorine Plant (SCP) and untreated sewage. Highest T-Hg concentrations ($36,500 \pm 34,930 \text{ ng/gm}$) were observed around previous industrial outfall, where sediments were disturbed by shipping activities. T-Hg concentrations were lower in Shuwaikh Port area ($650 \pm 210 \text{ ng/gm}$) and decreased towards northern coastline of Kuwait Bay (wider Bay region, $50 \pm 30 \text{ ng/gm}$). These values were still above background concentrations of $15\text{--}20 \text{ ng/g}$. Calculation of T-Hg inventory in surface sediments indicated that 22.5 tons Hg was present which was similar to estimated industrial discharges of 20 tons, suggesting that the contamination is largely confined to the Bay. The distributions of Me-Hg were similar to those of T-Hg and represented ranges between 0.23% and 0.5% of T-Hg, indicating that surface sediments within Kuwait Bay contained 80 kg Me-Hg.

TABLE 3: Exceedences against KUEPA rules and regulations reported in Fahaheel and Al-Riq'a over the period between 2004-2005. Source: Al-Salem and Khan [10].

Pollutant	KUEPA hourly limit (ppb)	#Exceedences (year, area)	Reference
SO ₂	170	4 (2004, Fahaheel) 2 (2004, Al-Riq'a) 18 (2005, Fahaheel) 12 (2005, Al-Riq'a)	KUEPA [49]
H ₂ S	140	6 (2004, Fahaheel) 2 (2004, Al-Riq'a) 25 (2005, Fahaheel) 9 (2005, Al-Riq'a)	KUEPA [49]
O ₃	80	416 (2004, Fahaheel) 122 (2004, Al-Riq'a) 154 (2005, Fahaheel) 55 (2005, Al-Riq'a)	KUEPA [49]
NH ₃	800	None (2004, Fahaheel) None (2004, Al-Riq'a) 1 (2005, Fahaheel) None (2005, Al-Riq'a)	KUEPA [49]

2.2. Rules and Regulations. Rules and regulations that govern the emissions and concentration of airborne pollutants in the state of Kuwait are proposed and governed by Kuwait Environment Public Authority (KUEPA). In 2001, KUEPA was recognized as a separate entity with holding and legal power. It was previously considered as a division of the Ministry of Health in Kuwait. Residential and industrial areas are governed by threshold limits that regulate the emissions and sources strengths of all major primary and secondary precursors. A number of studies in Kuwait took place with the aim of recording exceedences against limits of certain airborne pollutants. Al-Salem and Khan [10] studied the outdoor air quality of two areas adjacent to upstream/downstream facilities in Kuwait. Table 3 shows the main findings of the study in terms of exceedences against KUEPA standards. In a residential area in mid-city borders, Al-Salem et al. [35] studied the exceedences of Al-Mansoriah area. Findings could be seen in Table 4.

3. Modelling Section

3.1. Related Studies, Principles, and Parameters. Ettouney et al. [11] used the ISCST (Industrial Source Complex Short Term) model to generate a numeric datasheet of an emission inventory in Kuwait. The model uses the steady-state Gaussian plume equation for a continuous elevated source, with the downwind hourly average concentration given in the following equation adapted from Wark et al. [2] and previously used by Al-Salem [50]:

$$C(x, y, z) = \frac{Q}{(2\pi)\sigma_y\sigma_z u} \cdot \exp\left[-\frac{1}{2}\left(\frac{y}{\sigma_y}\right)^2\right] \times \left\{ \exp\left[\frac{-(z-H)^2}{2\sigma_z^2}\right] + \exp\left[\frac{-(z+H)^2}{2\sigma_z^2}\right] \right\}. \quad (2)$$

Comparison of the ISCST model predictions and the data base showed reasonable agreement for the hourly averages. The ISCST model was also used by Abdul-Wahab et al. [51] to study SO₂ pollution pattern in the Al-Shuibah (southern Kuwait) industrial area in Kuwait. Some discrepancies were found, however, in the measured and predicted SO₂ concentrations at ground level. A similar approach was applied by Abdul-Wahab et al. [52] to study SO₂ pollution generated in an oil refinery in Oman over a 21 day period in January 2000. A model for the input of PM₁₀ dust has been constructed by Draxler et al. [53]. An assumption of the omnipresence of particles having sizes between 88 and 125 nm was verified by analyses of sampled desert sediments and published data. A well-tested function-related horizontal flux of all aeolian mass to friction velocity and threshold friction velocity. Finally, the ratio of vertical flux of PM₁₀ dust to the horizontal flux of all aeolian mass as a function of surface sediment texture was used to express the vertical flux of PM₁₀ dust. Textures of all sampled soils were quite close to "sand" texture and consequently only one ratio was used for all soils in the source areas of the area. The model domain is for Kuwait, part of Syria, Saudi Arabia, the United Arab Emirates, and Oman.

3.2. Chemical Mass Balance (CMB) Modelling. The chemical mass balance (CMB) model for source allocation based on receptor point measurements is a tool applied to (mainly) determine the contribution of sources surrounding a data collection point or site. To use CMB analysis, the researcher must assume that all sources affecting the airshed are identifiable, and that the pollution source profile associated with each source can be speciated. Back calculations are typically involved employing chemical fingerprinting of sources, that is, concentrations of certain pollutants associated with source strength or activity. A number of studies have been carried out in the past using CMB. Christensen and Gunst [54] have determined errors associated with CMB employed in a number of cases in air quality data. CMB equations have been used to apportion observed pollutant concentrations to their various pollution sources. Typical analyses incorporate estimated pollution source profiles, estimated source profile error variances, and error variances associated with the ambient measurement process. Often the CMB model is fit to the data using an iteratively reweighted least-squares algorithm to obtain the effective variance solution. CMB model was considered within the framework of the statistical measurement error model to minimize reported errors. Christensen [55] considered the performance of several solutions to the CMB equations for cases in which one or more solutions affecting the airshed are unknown. It was demonstrated that the presence of unknown sources in the airshed can lead to substantial (and sometimes surprising) errors when estimating the known source contributions. A simple illustration of the effect of unknown sources on the problem is given and the vulnerability of iterative estimators (such as the effective variance estimator) in the presence of unknown sources is explained. Six sediment cores were collected from Green Bay, Wisconsin, in order to identify

TABLE 4: Exceedences against KUEPA rules and regulations reported in Al-Mansoriah over the period between 2000-2004. Source: Al-Salem et al. [35].

Pollutant	Averaging period	Permissible limit (ppb)	#Exceedences/year	Reference
Ozone	8 hrs	60	6/2000 1/2004	KUEPA [49]
Ozone	Hourly	80	6/2000 5/2001 1/2002 1/2003 3/2004	KUEPA [49]
NO ₂	Daily	50	95/2000 48/2001 41/2002 93/2003 73/2004	KUEPA [49]
NO ₂	Hourly	100	234/2000 237/2001 342/2002 259/2003 323/2004	KUEPA [49]
NO ₂	Annual	30	5/(2000–2004)	KUEPA [49]
SO ₂	Hourly	170	5/2000 8/2002 12/2003 17/2004	KUEPA [49]
SO ₂	Annual	30	1/2003	KUEPA [49]
SO ₂	Daily	60	5/2003	KUEPA [49]
CO	Daily	8000	6/2004	KUEPA [49]

possible sources of polycyclic aromatic hydrocarbons (PAHs) using CMB model by Su et al. [56]. The cores had total PAH concentrations between 8.04 and 0.460 ppm. The results show that coke burning, highway dust, and wood burning are likely sources of PAHs to Green Bay. The contribution of coke oven emissions (CB) for the Green Bay cores is in the range of 5% to 90%. The overall highway dust (HWY) contribution is between 5% and 70%. Daily average PM₁₀, TSP (total suspended particulate matter) and their chemical species mass concentrations were measured at residential and industrial sites of an urban region of Kolkata during November 2003 through November 2004 by Gupta et al. [57]. Source apportionment using CMB model revealed that the most dominant source throughout the study period at the residential site was coal combustion (42%), while vehicular emission (47%) dominates at the industrial site to PM₁₀. Paved road, field burning, and wood combustion contributed 21%, 7%, and 1% at the residential site, while coal combustion, metal industry, and soil dust contributed 34%, 1%, and 1% at industrial site, respectively, to PM₁₀ during the study period. The contributors to TSP included coal combustion (37%), soil dust (19%), road dust (17%),

and diesel combustion (15%) at residential site, while soil dust (36%), coal combustion (17%), solid waste (17%), road dust (16%), and tyre wear (7%) at industrial site.

In light of the previously stated review, and importance of such methods in the execution of source allocation, the following section will demonstrate case studies of modelling nature performed in Kuwait. The first will be on the CMB model execution and the second is of a line source emission strength determination, all performed within state limits over the past 5 years, with the latter being of importance to industrial sectors concerned with green oil processing.

3.3. Case Study No. 1: On the Execution of CMB around Urban/Industry Adjacent Sites. The following work was carried out in two adjacent areas in Kuwait to a number of upstream and downstream facilities, alongside other medium-scale industries. Both urban areas are situated in Al-Ahmadi governorate (Figure 3). Fahaheel area (inhabited with about 100,000 residents) is considered one of five major areas in the state of Kuwait. The location of the area makes it a major point in work commuting and real estate ventures. The overly populated Fahaheel is adjacent to the largest in capacity oil refinery in the state (Mina Al-Ahamdi -MAA- refinery). Petrochemical industries; such as ammonia, urea, polyethylene, and polypropylene plants, as well as the newly proposed polystyrene and both of the aromatics project and the Olefins II project 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) which on the other hand is located somewhat on the west end of Fahaheel. However, Al-Riqqa area (inhabited with about 40,000 inhabitants) is less populated than Fahaheel. The residential area of Al-Riqqa host Kuwaiti residents of mid 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-Riqqa, the three refineries belt and Fahaheel area exist and the north eastern part is occupied by the downtown area of Al-Riqqa. Data were secured from KUEPA monitoring stations in both areas located on the roof of the main polyclinics.

The source allocation was ascertained by analyzing the data points collected and observing the wind directions of peak pollutants 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 to the ambient air quality. 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-Riqqa sectors were as follows: (1) downtown area, (2) refineries, petroleum, and petrochemical industries, and (3) traffic line sources (Fahaheel highway), gas stations, and sports clubs. Table 5 shows the distribution of these three sectors with respect to data collection point in Al-Riqqa (Polyclinic). As for Fahaheel, the primary pollution sources and each corresponding sector is shown in Table 6 [10, 58–60].

FIGURE 3: Satellite image showing both areas under investigation (Fahaheel and Al-Riqia) 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). Source: Al-Salem and Khan [10].

TABLE 5: Position distribution around outdoor data collection point in Al-Riqia 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

Based on the initial analysis and collected data, the CMB model was setup in Microsoft Office 2003 in an EXCEL program. Nonmethane hydrocarbons (NMHC), methane, carbon monoxide (CO), total hydrocarbons (HCT), and O_3 concentrations were also used in execution of CMB model. The standard approach was applied for apportioning observed pollutant concentrations to their sources. The model implements a least-square 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 pollutants contributions affecting the airshed and fraction of the wind sector. CMB model uses the chemical and physical characteristics of gases and particulate at a given receptor point to identify the presence of and/or quantify source contributions. Equation (3) is the basic relation corresponding to the selected receptor point. This equation expresses the relation between the concentrations of the chemical species measured at the receptor point (Main health center of Al-Riqia) and the chemicals emitted from the source.

$$\Delta C_i = \sum F_{ij} - S_i, \quad (3)$$

TABLE 6: Position distribution around outdoor data collection point in Fahaheel urban area.

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

where ΔC_i is the difference in 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 & 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; that is, the source. Equation (4) was used to calculate the wind speed contribution with respect to each source.

$$\%WS_i = \left(\frac{k_i}{K} \right) \times 100, \quad (4)$$

where $\%WS_i$ is the percent contribution of wind speed with respect to source i , k_i is the summation of wind speed points collected with respect to source i in (m/s) & 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 which is defined as the sum of squares of difference between measured and the sum of 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 [61, 62]. Equation (5) is the one set to solve

TABLE 7: source contribution in Al-Riqra and Fahaheel urban areas based on CMB model results averaged over the period of the study.

Source	Fahaheel (%SC)	Al-Riqra (%SC)
Petroleum downstream facilities	70	10
Petroleum upstream facilities	2	—
Fahaheel highway	18	70
Area's downtown	10	20

for the least linear square root. The linear function was introduced for the four major sources studied as well as, the receptor point, which represents the total cumulative concentration of a pollutant to be matched.

$$LF = \sum_{j=1}^m \sum_{i=1}^n C_i \cdot WS_i \cdot SC_i - \sum_{i=1}^n C_i \cdot WS_i \cdot SC_i, \quad (5)$$

where LF 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, $\%WS_i$ is the percent wind speed contribution at a certain wind direction range for source i , $\%SC_i$ is the percent source contribution for a source i & i represent pollutants, and j sources.

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 resulting from the sources under study for major pollutants. These two months were chosen to represent the two longest seasons in Kuwait, summer and winter for being severe in their metrological conditions. Fahaheel and Al-Riqra areas average contribution of the its four primary sources of air pollution over the period of study are shown in Table 7.

It can be noticed from the above stated results that in the case of Fahaheel, being more close to the three refineries belt, the downstream facilities were more dominant on the area ambient air quality were it had 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 to dispersing gaseous pollutants away from the two urban areas. Comparing the two downtown areas, Al-Riqra's was almost contributing 20% to the total ambient load where Fahaheel was exactly half of that percentage. Al-Riqra downtown (Although smaller in size than Fahaheel) is more populated and is occupied by all sorts of human related pollution activities that too contribute to the load. The effect of the downstream facilities was least effective in the case of Al-Riqra area.

3.4. Case Study No. 2: Line Source Modelling around Fahaheel Urban Area. To asses a better outdoor air quality an area, namely Fahaheel urban area, the second primary air pollution source around it (Fahaheel highway) was modelled

FIGURE 4: Imaginary axis lines for point source modelling around Fahaheel highway showing corresponding coordinates at: $X = 14.5$ cm and $Y = 2.1$ cm. The blue dot represents the source at the refinery (Tank farm) and the red and black circles represent, respectively, the receptor point and the point of calculation for the line source.

for its primary emission source (NO_2) due to its significant in contributing to the ambient load of pollution pool and assessing the air quality of it too. The highway was previously demonstrated to be the second most contributing source on the area's pollution levels [50]. Fahaheel highway (Figures 3 and 4) contribution was estimated to be 18% of the total concentration of all primary airborne pollutants. The primary source of NO_2 , NO_x , and CO is always considered to be urban traffic terrains and motorways.

In the case of the main highway, a continuous model was chosen for the dispersion of NO_2 . Assuming a northwest wind direction with respect to the receptor point. Equation (6) relates the concentration of a line source to the variables in hand [2]

$$C(x, 0) = \left[\frac{2q}{(2\pi)^{0.5} u \sigma_z} \right] \exp \left(-0.5 \left(\frac{H}{\sigma_z} \right)^2 \right), \quad (6)$$

where q is the source strength of pollutant emissions (i.e., SO_2) downwind per unit distance, C is the ground level concentration of the source (with respect to terrain) in ppb, H is the receptor point elevation (m).

The line source model described above, gives a wide range of application. The modification came in excluding the effective height and using the half full height at the tank farm [50]. The refinery side gave a $2 \text{ ngm/s} \cdot \text{m}^2$ NO_2 emission rate or strength, taking in perspective the total area of the refinery (MAA refinery total area = $10\,533\,400 \text{ m}^2$). This result combined with the line sources one, which is $0.15 \mu\text{gm}/\text{sm}^2$ per unit scale can give a clear view of the rate of NO_2 alone that is being emitted to the area. The calculations were based on the month of May 2004 with measurements taken from KUEPA Fahaheel monitoring station original 5 minutes data.

4. Final Remarks

After reviewing the subject matter, a number of conclusions could be withdrawn with regards to the monitoring of primary and secondary pollutants in the state of Kuwait.

- (i) Monitoring stations situated in residential and industrial areas by KUEPA, should incorporate better receptor point placement and modern prediction techniques that can aid in the data gathering.
- (ii) Metrological data gathered (as literature reviewed suggest) must be coherent with pollutants sources designed to be monitored.
- (iii) A number of pollutants are not being recorded when it comes to industrial sites, associated with health effect, which should be in the future plans of the state.
- (iv) A number of monitoring cases in Kuwait reveal different data than gathered by KUEPA, due to the lack of attention paid in placing mobile stations.

Modelling cases carried out reveal that Kuwait is a country influenced not only by chemical industries pollutants, but by traffic and other sources which should be regulated according to international rules and regulations. Concerned parties should start within the next few years in seriously revising state rules with regard to outdoor air quality, to provide better and healthier living conditions to the population. Airborne NO_2 was studied from a line source ($2 \text{ ngm/s} \cdot \text{m}^2$) taking in perspective the total area of the refinery considered. This result combined with the line sources one, which is $0.15 \mu\text{gm}/\text{sm}^2$ per unit scale can give a clear view of the rate of NO_2 alone that is being emitted to the area. Furthermore, chemical mass balance modelling (CMB) revealed that the three refineries belt of Kuwait was associated with higher contribution (70%) than other sources of pollution. This is particular to one case of a southern area in Kuwait. Whilst in the case of another part of the same Governorate, the contribution was mainly due to the Highway pollution load. Associated health impacts are also demonstrated by this study. In conclusion, findings in literature surveys and other aspects of air pollution modelling, lead to industrial sources and human factors as the main polluting source in the state of Kuwait.

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