

Original Research Paper

Elemental Composition and Concentration of Atmospheric Particulate Matter in Kuwait

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Abstract: Hourly PM₁₀ and PM_{2.5} samples were simultaneously collected at 10 and 3 urban sites, respectively in Kuwait from March 2014 to February 2015, to study the air quality and heavy metals content and Total Petroleum Hydrocarbons (TPHs) in PM₁₀ samples. The annual average concentrations of PM₁₀ and PM_{2.5} were 152 and 97.3 µg/m³, respectively, with an average PM_{2.5}/PM₁₀ ratio of 70%. The contamination level of heavy metals in PM₁₀ samples was assessed in terms of Enrichment Factor (EF) using mathematical models. The elements associated with an anthropogenic activity in the PM₁₀ samples; i.e., Pb, Cu, Co, Cd and Zn, were 2.4, 12.9, 14.6, 42.6 and 156.2 times higher than the corresponding background values in Kuwait soil. TPH was the dominant pollutant in the PM₁₀ samples. In general, most daily average Air Quality Indices (AQI) of PM₁₀ concentrations fell under the categories of “good” and “moderate”.

Keywords: PM₁₀, PM_{2.5}, Heavy Metals, TPHs

Introduction

Atmospheric particulate Matter (PM) consists of a mixture of solid particles and liquid droplets from a variety of sources and can be divided according to particulate size into dust fall (with an aerodynamic diameter of 100-1000 µm), Total Suspended Particulate (TSP, with an aerodynamic diameter of less than 100 µm), inhalable particulate matter (PM₁₀, with an aerodynamic diameter of less than 10 µm), coarse particulate (PM_{2.5-10}, with an aerodynamic diameter of 2.5-10 µm) and fine particulate (PM_{2.5}, with an aerodynamic diameter of less than 2.5 µm) (SEP, 2003). In general PM₁₀ originates from mineral dust, while PM_{2.5} and finer PM, which have more serious health effects compared to coarser PM, have various sources, normally dominated by combustion.

PM is composed of various heavy metal elements, most of them having toxic effects that have been extensively studied in urban areas. The determination of heavy metal element concentrations in the ambient suspended particulate matter of major urban areas is an important component of pollution studies (Goyer, 1996; Donaldson and MacNee, 1998; Singh, 2001). Wind-blown dust generally contributes to the release of heavy metals in the ambient atmosphere (USEPA, 1999a;

AMAP, 1997). Hazardous suspended PM pollutants are released by various sources like factories, refineries, automobiles, power plants, sewage plants, etc. (Dannecker *et al.*, 1990). Pollution of this nature is a worldwide problem, including in Kuwait's urban areas, since these metals persist in the environment and most of them are toxic to living organisms. Although considered essential for various human biological functions in trace quantities, several of these heavy metals pose serious toxicological risks at high levels (Addo *et al.*, 2012).

Emissions of PM in Kuwait have been increasing remarkably in the past two decades; thus, it has become a problem of significant concern (Al-Awadhi and Al-Awadhi, 2006; KEPA, 2014). The PM levels in Kuwait's cities have been on the rise, attributable to a significant increase in vehicular traffic—the number of vehicles in 2004 was 1.042 million, whereas this number reached to 1.916 million in 2014 (KEPA, 2014). Traffic remains the main source of air pollution in Kuwait's cities, while upstream/downstream industrial sources such as power plants, oil fields and various other industries contribute to a much lesser degree (Al-Salem and Khan, 2008). Table 1 shows the total PM₁₀ and PM_{2.5} emission rates from various sources in Kuwait city.

Although real-time monitoring of suspended PM is a vital means for predicting pollution levels, it does not describe the composition of the pollution. Accordingly, this study aims to investigate the air quality at ten sites in Kuwait, in terms of concentrations of suspended PM (PM₁₀ and PM_{2.5}) and the elemental composition of PM₁₀ in terms of heavy metals. The measured PM₁₀ levels are compared with the Kuwait Environment Public Authority (K-EPA) guideline limits.

Prototype Data Collection

The PM₁₀ and PM_{2.5} data were collected from ten and three Air Quality Monitoring (AQM) stations, respectively, set up by K-EPA, using Met-One (USA) Model Beta Attenuation Mass (BAM)-1022 monitors. Continuous measurements of PM₁₀ and PM_{2.5}, corresponding to a period between March 1st, 2014 and February 28th, 2015 (i.e., 12 months), were collected. For correlation purpose, the major meteorological parameters, including wind speed m/s and direction (degrees), relative humidity (%) and ambient temperature (°C), were also obtained from the AQM stations (Gill Instruments, UK) over the same monitoring period. The monitoring stations for PM₁₀ are: Mutla (MU), Al-Jahra (J), Saad Al-Abdullah (SA), Shuwaikh (SH), Mansuria (MA), Al-Salam (S), Rumaithiya (R), Al-Ahmadi (A), Fahaheel (F) and Ali Al-Salem (AS) (Fig. 1), while the monitoring stations for PM_{2.5} are: Al-Jahra (J), Saad Al-Abdullah (SA) and Al-Ahmadi (A). Each of these stations is located in a residential area which differs in its surroundings, geographical characteristics and sources of air pollution.

Each station is provided with a continuous gas monitor. The monitors are operated automatically and measurements are normally recorded every five minutes continuously, 24 h a day, throughout the year. PM concentrations are measured by the beta-gauge method. A span calibration is used to check the validity of the data, where a sample of known concentration of pollutants is tested by the machine. This is done every three to four days to check for the behavior and accuracy of the monitors. Also, full system checks are routinely carried out once every three months by specialists.

Ambient PM measurements were retrieved from a central online data acquisition system managed and controlled by EnviDAS software. The data was filtered manually by discarding NULL values and the total percentage of filtered data recorded was about 96.5%: i.e., 3.5% of the data values were cleaned), which is considered an acceptable percentage of data recovery for air quality assessment (Khan and Al-Salem, 2007).

Table 1. Total PM₁₀ and PM_{2.5} emission rates from various sources in Kuwait city (ton/year)

Source	PM _{2.5}	PM ₁₀
Transport	9,750	11,450
Aviation	50	50
Port	150	200
Road dust	7,000	46,650
Power plants	1,400	1,700
Industries	900	1,100
Gathering centers	1,000	100
Total	19,350	61,250

Source: KEPA (2014)

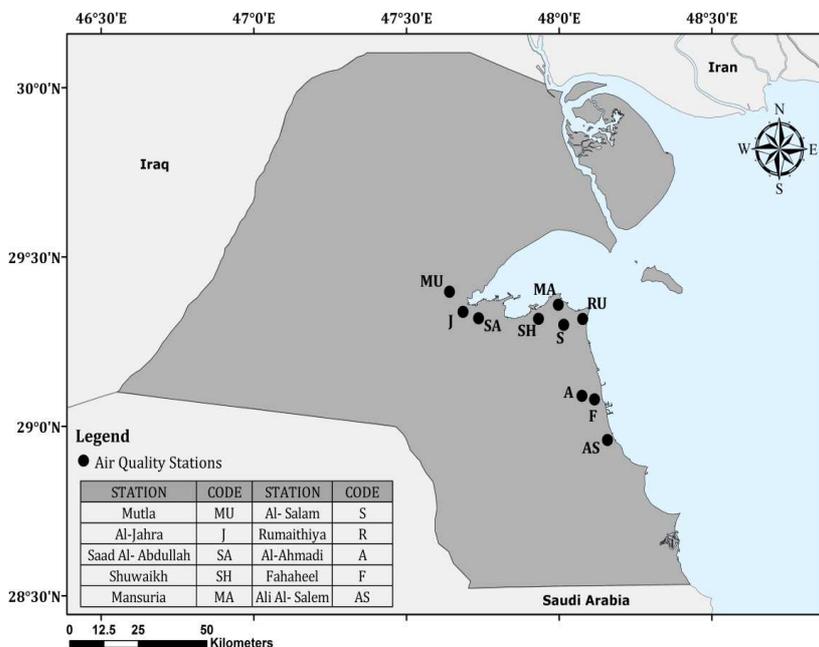


Fig. 1. Locations of the air quality monitoring stations set up by K-EPA

Fifteen PM₁₀ filters were collected from the ten stations for a preliminary quantification of the metal content. Five duplicate samples were collected from J, SH, F, Mu and A stations. The collections were carried out on two different days: May 1st and 7th, 2014.

Methodology

Inductively Coupled Plasma Optical Emission Spectrometry (ICPOES) was used for determining element presence in 15 PM₁₀ samples. The sample containers (PTFE flasks) were soaked overnight with 10% HNO₃, followed by rinsing thrice with the same acid and thrice with de-ionized water and finally dried in an oven at 50°C. For chemical analysis, the extraction and analysis of heavy metals was carried out as per the US EPA method IO-3.2 (USEPA, 1999b). As per the method, PM₁₀ samples collected on glass fiber, along with their respective blank filter papers (1 blank per sample), was digested by Mars 6 Microwave Digestion system using aquaregia (3HCl + 1HNO₃) for 23 min at about 180°C. After digestion the solutions were neutralized with 2% boric acid and gauged. The advantage of using hydrochloric acid is the dissolution of the quartz filter, which avoids the need for filtration. Field blanks and certified urban dust (NIST 1648) were digested and analyzed along with the samples. For quality assurance, only samples with a recovery value >95% were considered for analysis, ensuring the precision and reproducibility of the measurements.

Total Petroleum Hydrocarbons (TPHs) in the PM₁₀ samples were measured using the US-EPA 8015C method (GC analysis) and US-EPA 3540C (Extraction) procedure. The filter samples containing particulates matters were extracted on Soxhlet Extraction unit (7890A GC system with flame Ionization Detector-Agilent) for 4 h with 60 mL dichloromethane, filtered with hexane, concentrated to 1 mL and analyzed on GC

system equipped with fused silica capillary column, operated in split mode using carrier gas, helium. Then, the samples were heated at 50°C and gradually increased through 3 ramps up to 330°C. The GC system was calibrated using C8-C40 standards from 175 to 1750 µg mL⁻¹ and the samples were quantitated against the curve generated through calibration.

The Enrichment Factor (EF) equation (Sutherland, 2000) was employed for calculating the level of PM contamination by heavy elements:

$$EF = \frac{[C_n(\text{sample}) / C_{ref}(\text{sample})]}{[B_n(\text{baseline}) / B_{ref}(\text{baseline})]} \quad (1)$$

Where:

- $C_n(\text{sample})$ = The content of the examined element in the PM sample
- $C_{ref}(\text{sample})$ = The content of the reference element in the PM
- $B_n(\text{baseline})$ = The baseline content of the examined element in Kuwait soils
- $B_{ref}(\text{baseline})$ = The baseline content of the reference element in Kuwait soils

The persistency of pollutant exceedances; hourly, daily and monthly averages; pollutant ratios (PM_{2.5}/PM₁₀) and correlation coefficients between various locations and PMs were investigated using the SPSS software package (Version 19).

Air quality in terms of PM₁₀ was also assessed through the use of the Air Quality Index (AQI) developed by Al-Shayji *et al.* (2008), for Kuwait, based on the guidelines proposed by the US Environmental Protection Agency (USEPA, 2006). Table 2 shows the AQI category codes, suggested for the Kuwait EPA and their ranges for PM₁₀, based on health effects.

Table 2. AQI range (after Al-Shayji *et al.* (2008) and the US Environmental Protection Agency (2006)

Categories	AQI sub-index	PM ₁₀ (µg/m ³) 24 h
Good	0-50	0.0-90 ^a (0-54) ^b
Moderate	51-100	90.1-350.0 (55-154)
Unhealthy for sensitive groups	101-150	350.1-431.3 (155-254)
Unhealthy	151-200	431.4-512.5 (255-354)
Very Unhealthy	201-300	512.6-675.0 (355-424)
Hazardous1	301-400	675.1-837.5 (425-504)
Hazardous2	401-500	837.6-1000 (505-604)

Results

Basic Analysis for PM₁₀

Table 3 describes the statistic of average all measured concentration of PM₁₀. The results indicate that the variation in the PM₁₀ concentrations ranges between 5 and 9.6% and the mean values are greater than the median values having positive skewness values, i.e., values approaching to zero from the positive direction. Thus under these circumstances, PM₁₀ pollutants can be considered as a stable condition.

The range of the two percentile points, defining the upper and lower tails of data, indicates a clear difference between the maximum and minimum measured values. Such difference is also shown in the inter quartile (difference between the 75th and 25th percentile) and the skewness number indicates that the data deviates from symmetry around the mean, while positive kurtosis value indicates a shape flatter of data than normal.

The Arithmetic Mean Concentration

The monthly average concentrations of PM₁₀ at each station are shown in Fig. 2. It is noticed that SA station has the maximum monthly average concentration among all stations, with a concentration of 387.5 µg/m³, which is 1.1 to 2.5 times higher than at other stations. The monthly average concentration at the 10 stations varied from 23.1 µg/m³ (in November) to 387.5 µg/m³ (in February), with an average of 152 µg/m³ (Fig. 3). The highest concentration observed in February deviates from the normal trend associated with dusty days, which peak annually in June. The concentrations by season varied from 107 µg/m³ (autumn) to 173-174 µg/m³ (spring and summer). High PM₁₀ concentrations in summer can be attributed to the effects of northwesterly winds, which carry dust from the Iraqi Desert into Kuwait. High winter averages for PM_{2.5} and PM₁₀ occur due to various factors that account for elevated amounts

of PM₁₀ in that season, such as the noticeable increase in the traffic volume due to the influx of workers and students during winter season; moreover, the normal lower mixing heights with stable boundary layers (inversion layer) during the winter season, results in trapping more PM and limiting its dispersion in the atmosphere. The annual average PM₁₀ concentration for Kuwait's cities reached 152.2 µg/m³, with minimum and maximum concentrations of 112.0 µg/m³ (J) and 190.5 µg/m³ (AS), respectively.

Exceedance of PM₁₀ Permissible Limits

A comparison between the daily mean concentrations and applicable air quality standards promulgated by K-EPA (350 µg/m³) for residential areas and the proposed standard (150 µg/m³) reveals that the data in all monitoring stations exceeded the permissible limits. With respect to effective K-EPA rules and regulations (350 µg/m³), the percentage of data exceeding the limit at the 10 stations varied from 3.3 to 10.1%, with an average of 6.7%, while on the proposed value by K-EPA (150 µg/m³), the percentage of data exceeding the limit at the 10 stations varied from 15.3 to 34.0%, with an average of 26.2% (Fig. 4). On average, 24 and 96 exceedances were recorded per year during the period between March 1st, 2014 and February 28th, 2015 applying PM₁₀ standard values of 350 and 150 µg/m³, respectively. Considering the proposed PM₁₀ permissible limit of 150 µg/m³, the total average percentage of exceedances during spring, summer, fall and winter were 28.4, 37.8, 13.5 and 24.9%, respectively. Note that highly elevated levels of PM₁₀ are known to occur in Kuwait (mainly in summer) resulting in a reduction of visibility (Al-Hajraf *et al.*, 2005). The annual limit value of 90 µg/m³, specified by K-EPA, was exceeded at all monitoring stations over the 12 months of monitoring. The annual mean concentration averaged over all 10 stations was 152.2 µg/m³.

Table 3. Statistic descriptive of PM10 concentration (µg/m³) at the 10 stations during March 2014 to February 2015

Location	95% Confidence Interval for Mean		Trimmed Mean	Median	Variance	Std. Deviation	Minimum	Maximum	Range	Interquartile Range	Skewness	Kurtosis	25 th Percentile	75 th Percentile	
	Lower Bound	Upper Bound													
MU	130.4	125.4	135.4	98.4	73.0	53948.8	232.3	1.0	4274.0	4273.0	86.0	9.0	107.9	48.0	134.0
J	111.9	108.6	115.3	89.4	77.0	25469.7	159.6	1.0	4064.0	4063.0	52.0	9.7	144.9	58.0	110.0
SA	143.3	136.0	150.6	95.3	78.0	117280.1	342.5	1.0	7946.0	7945.0	98.0	9.9	135.6	37.0	135.0
SH	154.8	150.8	158.8	129.5	111.0	35414.3	188.2	2.0	3538.0	3536.0	86.0	7.9	94.3	81.0	167.0
MA	170.8	163.8	177.8	126.4	108.0	98710.9	314.2	1.0	6135.0	6134.0	98.0	9.1	109.9	70.0	168.0
S	183.3	176.3	190.3	135.2	113.0	110963.9	333.1	9.0	6827.0	6818.0	93.5	9.0	108.6	79.0	172.5
R	141.5	137.6	145.5	118.2	83.5	34613.8	186.0	1.0	4399.0	4398.0	88.0	7.6	108.7	56.0	144.0
A	175.3	168.2	182.3	132.3	118.0	101224.1	318.2	2.0	8045.0	8043.0	97.0	10.3	154.9	76.0	173.0
F	123.7	119.1	128.3	93.8	83.0	47366.7	217.6	1.0	4546.0	4545.0	63.0	9.4	115.6	57.0	120.0
AS	189.7	182.2	197.2	138.6	116.0	122964.1	350.7	12.0	4994.0	4982.0	95.0	8.1	80.5	80.0	175.0

The range of the two percentile points, defining the upper and lower tails of data, indicates a clear difference between the maximum and minimum measured values. Such difference is also shown in the inter quartile (difference between the 75th and 25th percentile) and the skewness number indicates that the data deviates from symmetry around the mean, while positive kurtosis value indicates a shape flatter of data than normal

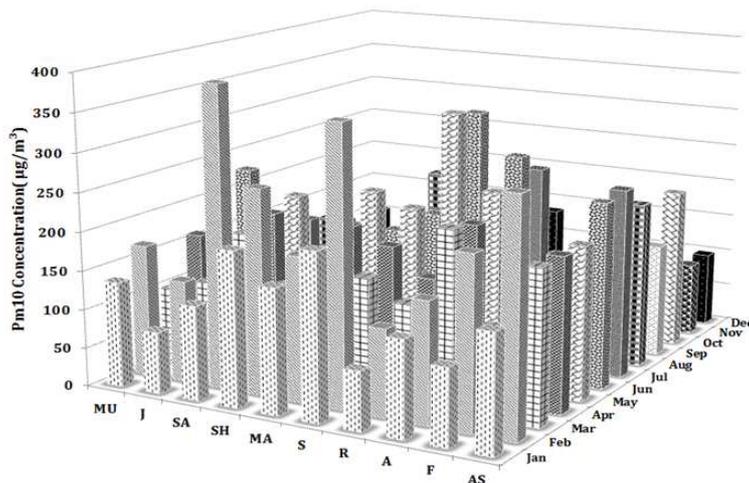


Fig. 2. Monthly average concentration of PM₁₀ at the AQM stations

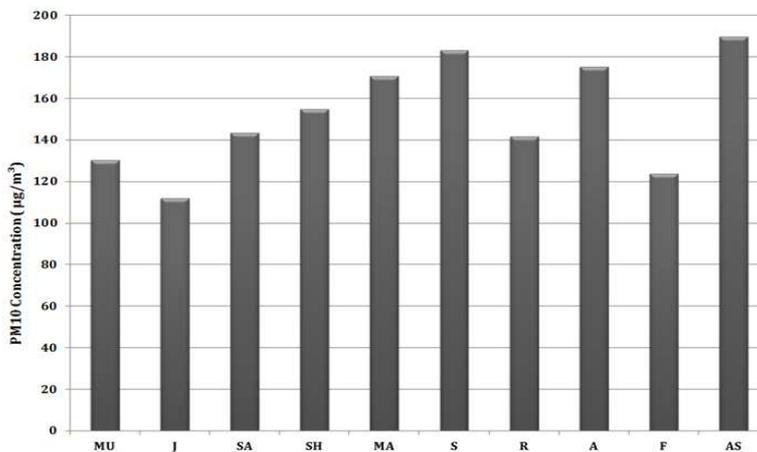


Fig. 3. Annual average concentration of PM₁₀ at the AQM stations

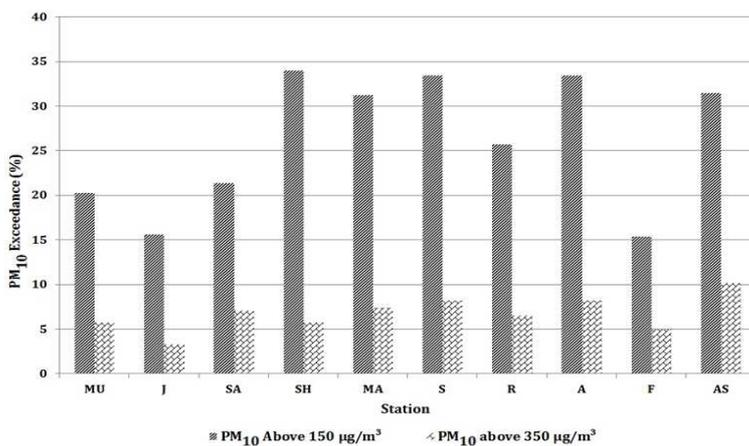


Fig. 4. Percentages of PM₁₀ exceedances of effective and proposed permissible limits promulgated by K-EPA during the monitoring period at the 10 stations

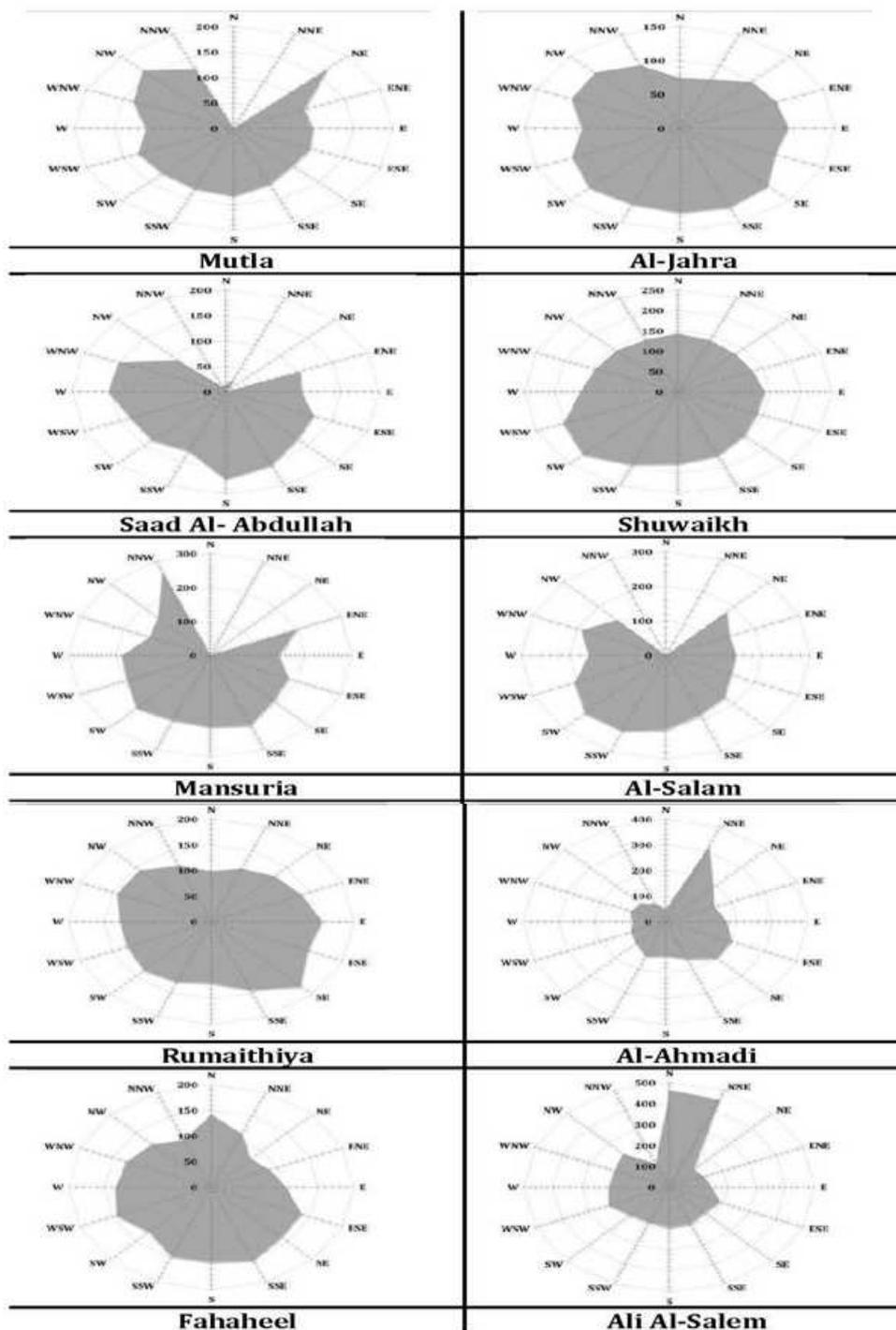


Fig. 5. Annual mean PM₁₀ concentration roses for all monitoring stations

Annual mean PM₁₀ concentration roses were constructed with 16 wind directions in order to investigate the relative contributions of winds blowing PM₁₀ from each direction (Fig. 5). The plots revealed that winds blowing PM₁₀ came predominantly from between the northwest and south-west corridors at the

monitoring stations located near the edge of the open desert (i.e., MU, SA and AS). This suggests that dust potentially contributes to the ambient PM₁₀ load in these open areas. Rising/suspended dust and dust storms in Kuwait are generated by the prevailing northwesterly winds, representing 60% of wind-direction

measurements taken in Kuwait; moreover, these winds are dominant in the summer season (Al-Basri, 1993). On the other hand, the stations that are located in the inner cities (i.e., R, SH, F and J), were subjected to PM₁₀ blowing in from all directions with generally elevated levels from the southwest side. In Ahmedi station (A), located to the east of the Burgan oil field, winds blowing PM₁₀ came predominantly from the northeast and southeast corridors, suggesting that PM₁₀ from the oil field contributes significantly to the ambient load in this area.

The concentrations of PM₁₀ at all stations showed a high correlation, ranging from 0.91 to 0.03 ($r = 0.75$) (Table 4), implying that PM₁₀ may have common sources, such as traffic, at all stations. The highest correlation occurred between Ahmadi (A) and Ali Al-Salem (AS); these two areas are located near the boundary of the Shuaiba petro-industrial area and the Burgan oil field. Shuwaikh (SH), which is located in the seaport zone near Kuwait city, at a distance of approximately 100 km from these two areas, showed a lower correlation with A and AS, i.e., 0.8 and 0.4, respectively. The prevailing northwesterly winds are likely to influence the diffusion of PM₁₀ concentrations generated from the petro-industrial area away from the other sites:

- Correlation is significant at the 0.05 level (two-tailed)
- Correlation is significant at the 0.01 level (two-tailed)

Variation of PM₁₀ Levels during the Day

The evolution of hourly pollutant concentrations measured during the day is presented in Fig. 6a and 6b. Figure 6a indicates that an elevation in concentrations occurs during noontime and around midnight. Similarly, Fig. 6b confirms that this finding is applicable during all months. The noontime elevation may be a result of a substantial secondary component beside the exhaust

component, such as suspended dust. The midnight elevation may be associated with the inversion layer behavior during the midnight hours (cooling time) resulting in limited dispersion of pollutants and increasing the potentiality of trapping them the air atmosphere; this is due to the relatively calmer conditions from around midnight until the early morning hours favoring the accumulation of pollutants and causing them to reach the ground.

Figure 7 shows an inverse correlation between the hourly average variation in relative humidity and PM₁₀ concentration. This indicates that as the humidity increases, the potentiality of PM₁₀ emissions from various sources reduces. Figure 8 shows a positive correlation between the hourly average variation in temperature and PM₁₀ concentration, suggesting that high temperatures during the day impact PM₁₀ pollution levels in the air. These high temperatures play a major role in rising convective motions, turbulent flows and atmospheric diffusion capacity in the lower part of the atmosphere and as a consequence higher emissions of fine particles is achieved.

Ambient Concentrations of PM_{2.5}

The variation in PM_{2.5} concentrations during the data collecting period is presented in Table 5; these range from 47.1 to 177.1 µg/m³ at three monitoring stations (A, J and SA), with an average concentration of 97.3 µg/m³. These measurements are 4.7 and 17.7 times more than the annual US NAAQS standard of PM_{2.5} (10 µg/m³), respectively (Fig. 9). The results obviously indicate that fine PM should be seriously considered as a health impact factor in Kuwait's urban areas. Hourly averages of PM₁₀ and PM_{2.5} pollutants show that both pollutants follow a relatively similar trend of variations during a day (Fig. 10). The calculated ratios of PM_{2.5}/PM₁₀ varied spatially, ranging from 0.31 to 1.4 with an average of 0.7, indicating that fine PM at urban sites is also a concerning problem.

Table 4. Correlation coefficient (r) of PM₁₀ between the sites

	Mu	J	SA	SH	MA	S	R	A	F	AS
MU	1.000									
J	0.552**	1.000								
SA	0.695**	0.789**	1.000							
SH	0.200	0.470*	0.300	1.000						
MA	-0.300	0.100	0.000	0.300	1.0					
S	0.713**	0.441*	0.470*	0.435*	0.2	1.000				
R	0.300	0.200	0.300	-0.100	0.3	0.487*	1.000			
A	0.729**	0.400	0.554**	-0.100	0.0	0.761**	0.636**	1.0		
F	0.781**	0.531**	0.601**	0.400	-0.1	0.762**	0.300	0.649**	1.000	
AS	0.609**	0.300	0.430*	0.000	0.2	0.796**	0.686**	0.909**	0.594**	1.0

* Correlation is significant at the 0.05 level (two-tailed)

** Correlation is significant at the 0.01 level (two-tailed)

Table 5. Statistical descriptive of measured of PM_{2.5} concentration (µg/m³) at the monitored sites

Location	Mean	95% Confidence Interval for Mean		5% Trimmed Mean	Median	Variance	Std. Deviation	Minimum	Maximum	Range	Interquartile Range	Skewness	Kurtosis	25th Percentile	75th Percentile
		Lower Bound	Upper Bound												
J	47.1	46.1	48.2	40.3	38.0	2375.0	48.7	1.0	1059.0	1058.0	15.0	8.7	103.9	32.0	47.0
SA	177.2	168.2	186.1	123.9	97.0	113976.7	337.6	1.0	4679.0	4678.0	112.0	6.8	59.7	55.0	167.0
A	67.7	64.4	71.1	54.6	49.0	12974.2	113.9	1.0	2991.0	2990.0	46.0	14.1	286.7	29.0	75.0

Table 6. The correlation coefficient (r) of PM_{2.5} and PM₁₀ between the monitoring stations

		J		SA		A	
		PM10	PM2.5	PM10	PM2.5	PM10	PM2.5
J	PM10	1					
	PM2.5	0.583**	1				
SA	PM10	0.789**	0.633**	1			
	PM2.5	0.725**	0.685**	0.845**	1		
A	PM10	0.391	0.180	0.554**	0.235	1	
	PM2.5	0.349	0.398	0.608**	0.411*	0.798**	1

* Correlation is significant at the 0.05 level (two-tailed); ** Correlation is significant at the 0.01 level (two-tailed)

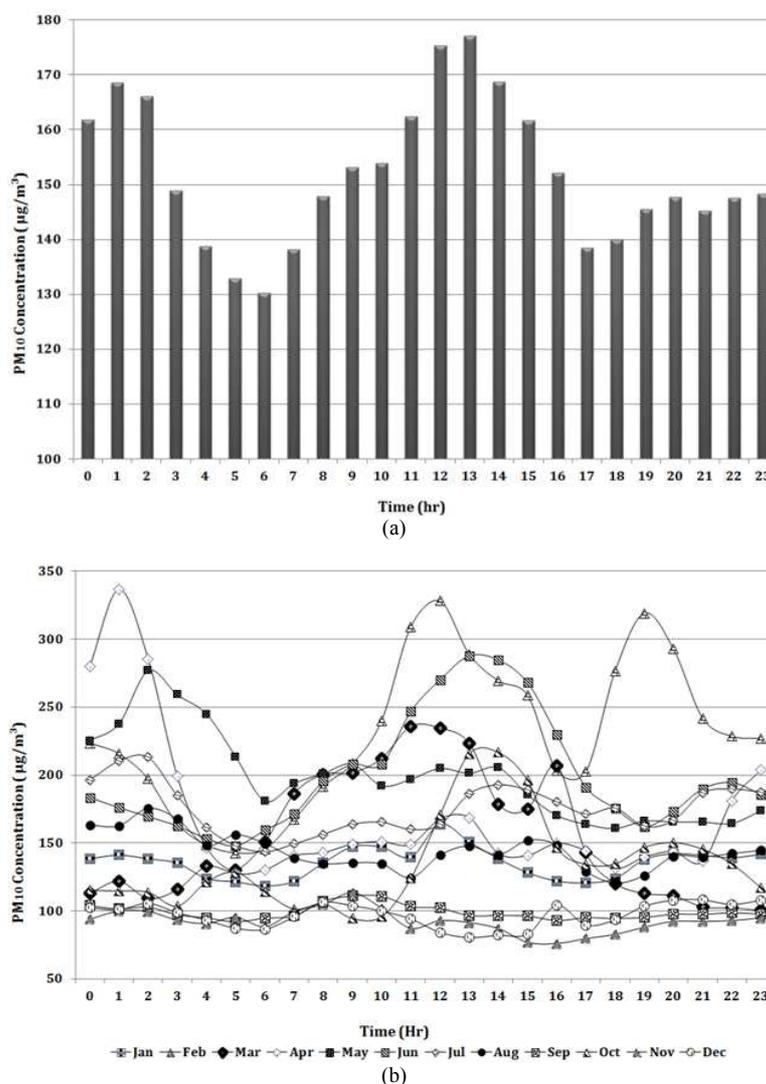


Fig. 6. Overall hourly average PM₁₀ concentrations (a) Annual average (b) Monthly average

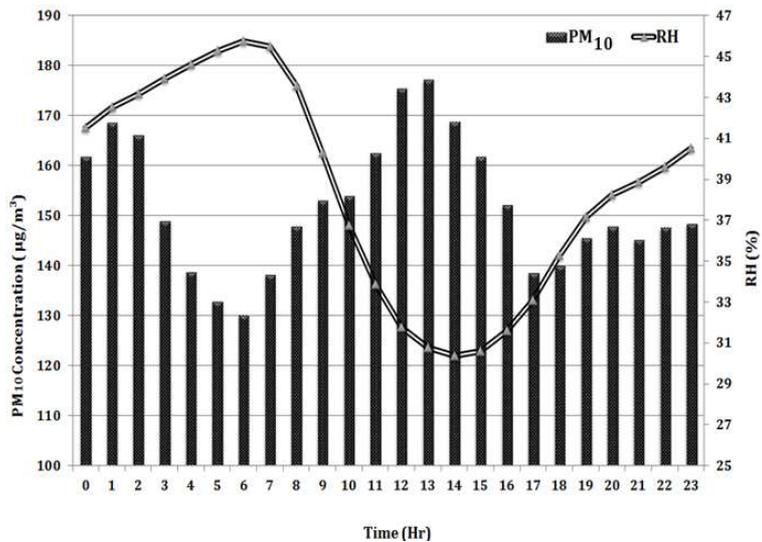


Fig. 7. Hourly average variation in relative humidity and PM₁₀ concentration

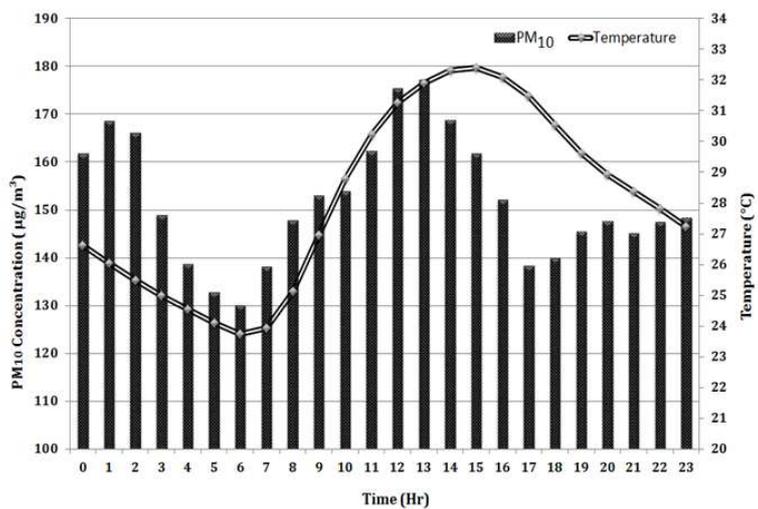


Fig. 8. Hourly average variation in temperature and PM₁₀ concentration

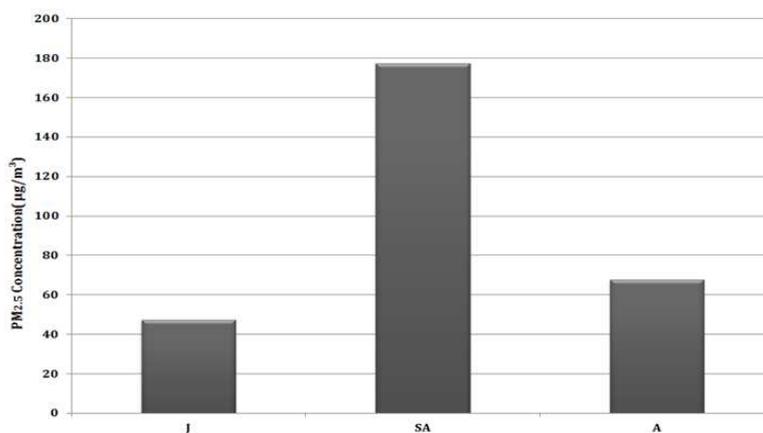


Fig. 9. The annual average concentration of PM_{2.5} at monitored stations

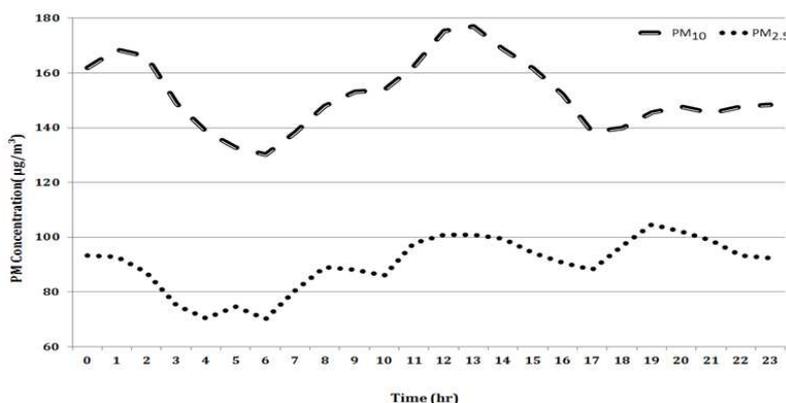


Fig. 10. Hourly averages of PM₁₀ and PM_{2.5} concentrations

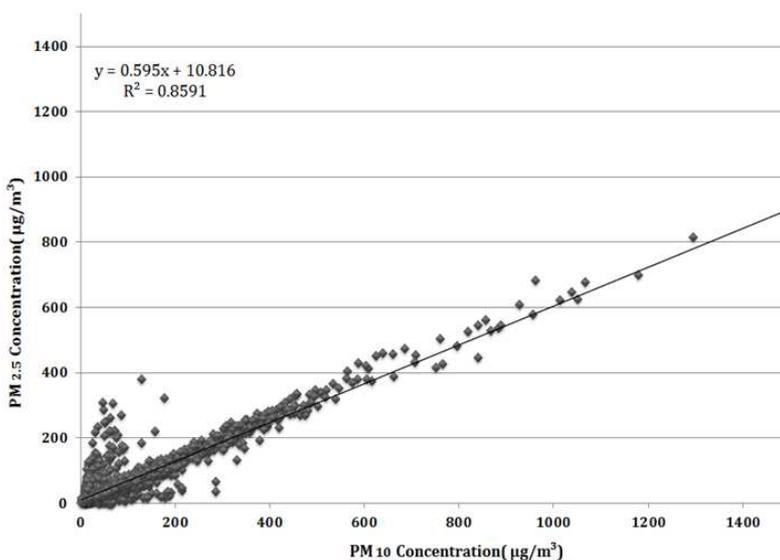


Fig. 11. Relationship between PM₁₀ and PM_{2.5} at Ahmadi (A) station

According to Duan *et al.* (2006), high ratios (larger than the average value) are generally associated with the secondary particulate formation of species and organics, while low ratios are associated with the primary particulate formation of fugitive dust or sand dust blowing from far sources; i.e., long-distance transport. Table 6 presents the hourly analysis of correlations of the PM₁₀ and PM_{2.5} pollutants. The correlation analysis showed that PM₁₀ and PM_{2.5} are strongly correlated ($r > 0.4$ and reaches 0.8), indicating common sources (traffic emissions or dust). The simple linear model method was employed to estimate the mathematical relationship between PM₁₀ and PM_{2.5}. A positive correlation between the PM₁₀ and the PM_{2.5} is recognized through the following relationship (Fig. 11):

$$PM_{2.5} = 0.6PM_{10} + 10.8 \quad (2)$$

The value of R^2 for this relationship was 0.86 with a significant correlation coefficient of $r = 0.8$:

- Correlation is significant at the 0.05 level (two-tailed)
- Correlation is significant at the 0.01 level (two-tailed)

Elemental Concentration in PM₁₀

The elements were categorized into two groups; namely, anthropogenic activity and typical crustal elements. Table 7 shows the concentration of 15 identified elements in the PM₁₀ samples. Al-Awadhi and Al-Shuaibi (2013) determined the elemental composition of Kuwait top sediments through the analysis of 184 top surface sediment samples collected from various existing aeolian sediments found across the Kuwaiti desert. The calculated ratios of the average crustal elements in the

PM₁₀ sample to crustal elements in the background surface sediment of Kuwait for Ca, Al, Fe and Mg ranged from 0.2 to 0.4, while for Na and K the ratios were found to be 16.3 and 6.6, respectively. This implies that the main source of fine particulate pollution at the urban sites could be from traffic and industrial sources with partial contributions from dust fallout. Average concentrations of the indicator elements associated with an anthropogenic activity that come primarily from industrial sources; i.e., Pb, Cu, Co, Cd and Zn, were 2.4, 12.9, 14.6, 42.6 and 156.2 times higher than corresponding sediment background values (measured from local aeolian sediments), respectively. The average concentrations of Cr, Ni and V were found to be 80, 70 and 60% less than their corresponding sediment background values, respectively. This may lead to the fact that most of the pollutants in the PM₁₀ samples are produced from anthropogenic sources.

Enrichment Factor Analysis

A cluster analysis using average linkage clustering was performed on the standardized elemental content of 15 PM₁₀ data with the help of a Statistics Toolbox function (Fig. 12). Figure 12 displays four clusters at a level around 1.5: (1) Co-Cr-Be-Cd-V-Pb-Ni-Mn-Cu; (2) Zn-Mg-K; (3) Fe-Ca-Al; and (4) Na. The analysis shows that clusters 1 and 2 are linked at a higher level (~2), potentially pointing to a common source, while the large separation of Na in cluster 4 suggests that Na might not share the same source as the other elements. Accordingly, this study uses Na as a reference element. To calculate the Enrichment Factors (EFs) for the various elements in the PM₁₀ samples, the average concentration of Na in the Kuwait sediment is used as the reference element baseline (B_{ref}), while the average content of each element in the samples is selected as that element's baseline (B_n). Table 8 lists the EFs for 10 elements identified in the PM₁₀ samples. Table 8 indicates that the mean EFs increases in the following order: Cr, Ni, V, Fe, Mn, Pb, Cd, Cu, Co and Zn., while only Cu, Co and Zn, have mean EFs higher or equal than 2.

The EF helps to identify which elements may have originated from human activities as opposed to natural processes and to assess the degree of this anthropogenic influence. Based on specific EF range, Table 9 presents

five contamination categories (Sutherland, 2000; Loska and Wiechuya, 2003). Usually, an EF of 10 and above (high level of enrichment) indicates an anthropogenic origin (Lee *et al.*, 1994; Liu *et al.*, 2003; Balasubramanian and Qian, 2004; Meza-Figueroa *et al.*, 2007). Thus, Co, Cu and Zn in the PM₁₀ samples, can be attributed mainly to anthropogenic activity.

Table 7. Comparison between elemental contents in soils of Kuwait and PM₁₀ samples collected in Kuwait (mg/kg)

Metals	PM ₁₀ sample	Background value	Ratio
Fe	1,610.30	4,115.70	0.39
Al	2,209.20	5,469.20	0.40
Mn	41.20	119.60	0.34
Zn	2,868.60	18.35	156.30
V	7.90	19.10	0.41
Na	14,972.10	915.12	16.36
K	4,159.90	630.20	6.60
Cd	17.95	0.42	42.60
Mg	1,230.10	4,916.10	0.25
Co	64.40	4.40	14.66
Cu	362.10	28.05	12.94
Ni	7.72	25.40	0.30
Cr	5.50	24.90	0.22
Ca	6,196.30	29,707.10	0.21
Pb	12.67	5.21	2.42

Table 8. Enrichment factors for elements in PM₁₀ in Kuwait

Elements	Enrichment Factor		
	Min	Max	Ave
Fe	0.003	0.94	0.19
Mn	0.046	0.58	0.22
Zn	2.29	33.53	9.19
V	0.057	0.44	0.18
Cd	0.006	4.98	1.96
Co	0.001	71.91	8.15
Cu	0.10	29.95	5.90
Ni	0	0.71	0.13
Cr	0	0.41	0.09
Pb	0.024	3.14	0.75

Table 9. Contamination categories based on EF values

Enrichment factor (EF)	Comment
EF < 2	Deficiency to minimal enrichment
EF = 2-5	Moderate enrichment
EF = 5-20	Significant enrichment
EF = 20-40	Very high enrichment
EF > 40	Extremely high enrichment

Table 10. Gross mineralogy (XRD) of the PM₁₀ samples (%)

Site/ Sample No.	Calcite	Quartz	Rutile	Orthoclase	Albite	Dolomite	Kamacite	Halite	Braunite
F (S1)	16.9	12.3	20.1	-	-	23.6	-	-	13.6
MU (S2)	32.6	11.3	15.6	-	-	20.0	10.9	9.6	-
A (S3)	40.1	18.1	-	9.6	9.5	16.0	-	-	-
Ave	29.9	13.9	17.9	9.6	9.5	19.9	10.9	9.6	13.6

Table 11. TPH concentrations in the PM₁₀ samples

Site	TPH (µg/filter)
MU	238
J	189
SA	205
SH	197
R	274
A	284
F	246
AS	296
Average	241

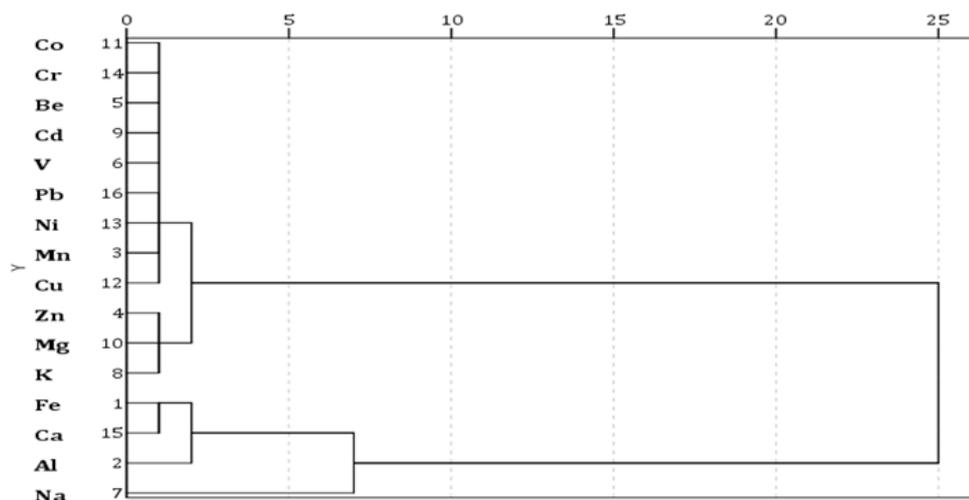


Fig. 12. Hierarchical dendrogram for measured pollutants in PM₁₀ (the distances reflect the degree of correlation between different elements)

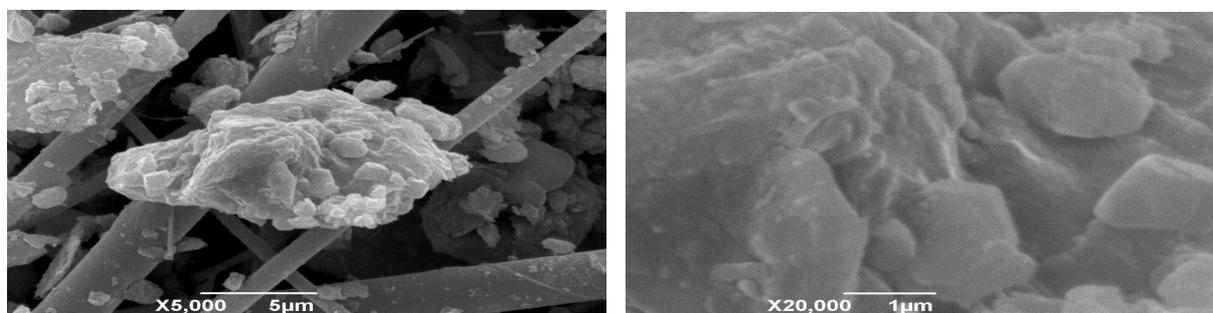


Fig. 13. SEM images of PM₁₀ collected at station A; showing both grain sizes and morphology of the particulate matter

The PM₁₀ samples are moderately contaminated by Pb and Cd, since their maximum EF values range between 2 and 5. However, the PM₁₀ samples are highly contaminated by Zn and Cu, since their maximum EF values fell between 20 and 40, while Co had a maximum EF of more than 40, thus indicating extremely high contamination. Cu and Pb can be emitted from fossil fuel combustion, metal processing, tires abrasion, brake linings, exhaust catalysts, road pavement and corrosion of galvanized protection barriers (Al-Awadhi and Al-Awadhi, 2013). The

maximum EFs of other elements were low, indicating that these elements are insignificant contaminants.

Mineralogical and SEM Analysis

Mineralogical analysis of three PM₁₀ samples showed that all samples consisted of calcite (29.9% on average), dolomite (19.9% on average) and quartz (13.9% on average) minerals, with an appreciable amount of illite, dolomite and albite and rare percentages of orthoclase (Table 10). Khalaf (1989) and Al-Awadhi and Al-Shuaibi (2013) found

appreciable percentages of calcite and quartz within fine size fractions of surface sediments and dust samples collected in Kuwait. Accordingly, the genesis and composition of the local dust and aeolian sand should have a direct influence on the mineralogical composition of PM₁₀.

The grain size and morphological characteristics of one of the 20 collected PM₁₀ samples, as observed by the SEM, is illustrated in Fig. 13. The figure distinctly shows different morphological structures and sizes of the grains. Most of the samples generally contain quartz, calcite, dolomite and clay particles. A few samples contain gypsum and feldspars. Fibrous cyan bacteria occur in most samples as well as some pollen grains. Clay particles are commonly less than 0.5 μm in size, while the other minerals (i.e., quartz, calcite, dolomite, gypsum and feldspars) occur as grains or clustered grains of more than 4 μm in size. No significant difference in the sample composition was recognized; however, samples from Ahmadi (A) and Mutla (M) stations, near north and south oil fields, respectively, are relatively rich in carbonates.

Total Petroleum Hydrocarbon (TPH) Analysis

An attempt was made to investigate the toxicity of the persistent organic contaminants in the PM₁₀ via measuring the TPH at 8 monitoring stations. The qualitative concentrations of TPHs in the PM₁₀ samples are presented in Table 11. The areas located near oil field/industrial area exhibits higher PM₁₀ contaminations

of TPH than in other areas. Higher mean TPHs concentrations are recorded in AS (296 μg/filter), F and A stations, while lower mean concentration is recorded in J station (189 μg/filter). The elevated mean concentration of TPH in PM₁₀ samples at R station may be associated with high emission rate due to vehicle movements in this area. Such finding may indicate that while the traffic remains a main source of PM₁₀ pollution in the residential areas in Kuwait, petrochemical industries and oil fields/refineries are also possible sources in the vicinity of these areas.

Air Quality Index (AQI)

Figure 14 illustrates the results of AQI values for the daily average of PM₁₀ concentrations for the period from March 2014 to February 2015 at the AQM stations. On average, 39.6 and 53.64% of the daily calculated AQI values for PM₁₀ concentrations are categorized as “good” and “moderate”, respectively. The moderate values were more abundant in areas with heavy traffic, such as SH, MA and S, as well as in AS, which is located downwind of the Shuaiba industrial area. In the winter season, 43% of the daily average data was categorized as “moderate”, while in the summer season, this percentage increased to 80% (Fig. 15). The percentage of elevated values in the “moderate” category in summer, in some cases, may be directly associated with regular dust phenomenon during this season; roadside dust may be another possible source.

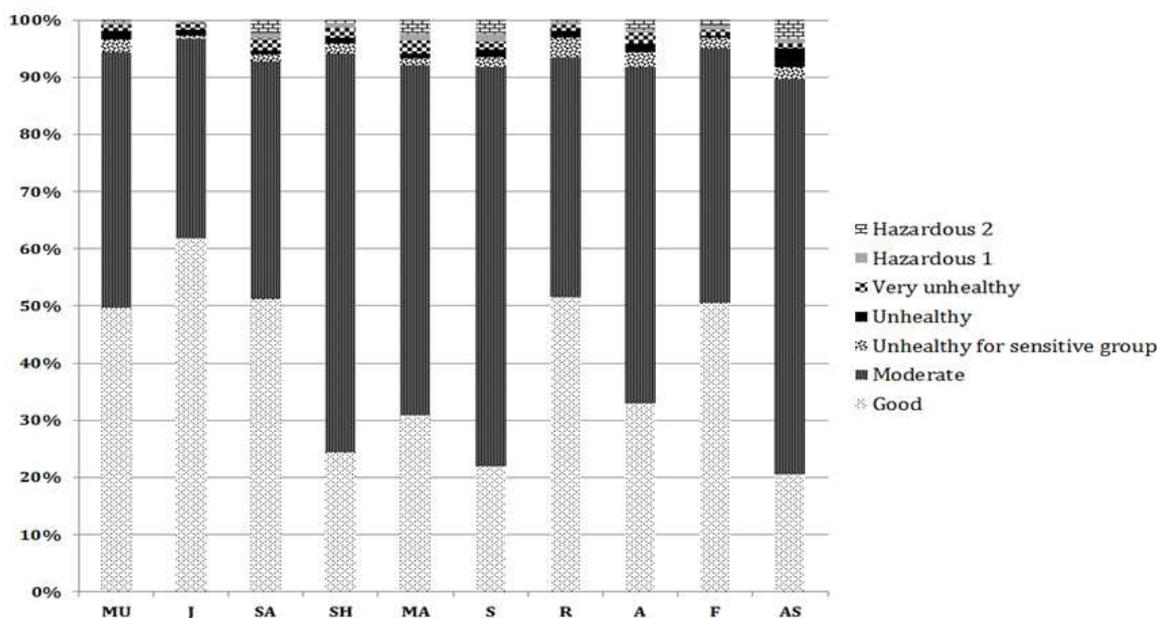


Fig. 14. Annual AQI for PM₁₀ concentrations at the 10 stations

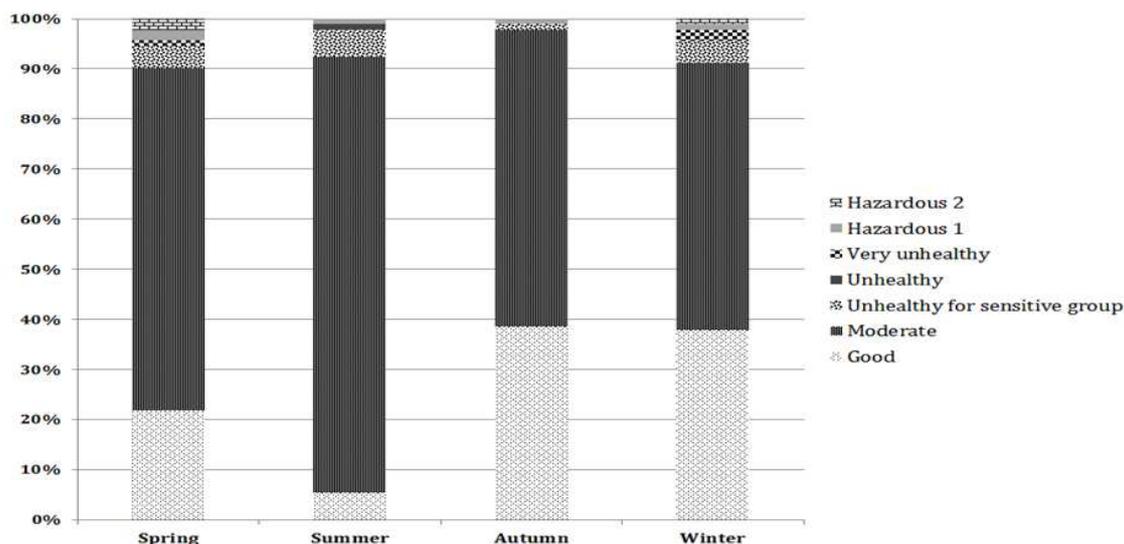


Fig. 15. Seasonal AQI for PM₁₀ in Kuwait

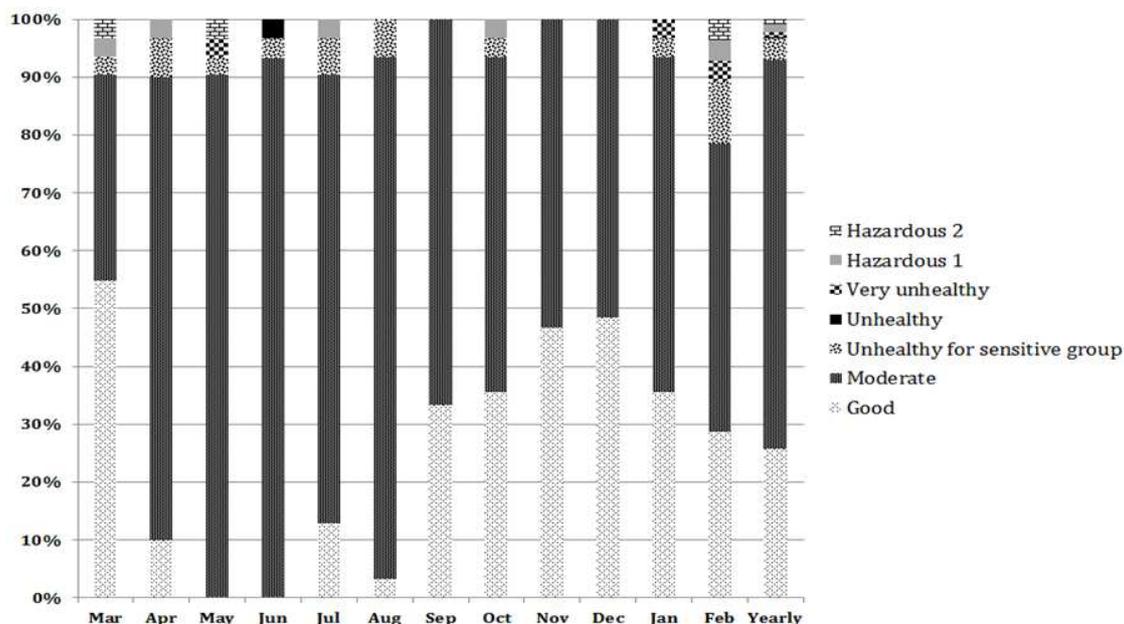


Fig. 16. Monthly AQI for PM₁₀ in Kuwait

The overall monthly assessment of the PM₁₀ in Kuwait (Fig. 16), indicates that about 7.3% of AQI values are categorized as “unhealthy” and “very unhealthy”, while 1.3 and 3.8% of AQI values are categorized as “hazardous 1” and “hazardous 2”, respectively. This indicates that PM₁₀ is a worrying pollutant in the cities of Kuwait.

Conclusion

In this study, one-year PM₁₀ and PM_{2.5} data set (March 2014 to February 2015) was evaluated and analyzed for different urban areas of Kuwait. In some

areas, 68.4 % of daily mean values of PM₁₀ exceeded the Kuwait EPA permissible limit (350 µg/m³), while the average concentration of PM_{2.5} is found to be 9.7 times more than the annual US NAAQS standard (10 µg/m³). Beside the traffic emissions, the prevailing northwesterly winds are likely to influence the diffusion of PM₁₀/PM_{2.5} concentrations generated from the oil fields and industrial areas, towards the urban areas. The high percentages of calcite and the appreciable amount of quartz found in the PM₁₀ samples may indicate that dust fallout and the roadside dust are other possible sources. A number of toxic

metal were noticeably enriched in the PM₁₀ samples due to anthropogenic activities. Enrichment factor analysis revealed that PM₁₀ being contaminated by the following metals with an increase in the order of Cr, Ni, V, Fe, Mn, Pb, Cd, Cu, Co and Zn. The TPH results also show relatively higher values in PM₁₀ samples collected near oil industrial areas than in other areas.

Seasonal variability of PM levels was clearly noticed. In winter season, lower concentrations in PM levels is attributed to low wind velocity that likely results in lower concentrations of re-suspended roadside dust particles, while higher concentrations in PM levels during summer season are accounted to the effects of frequent dust storms. However, in some summer days, under certain circumstances when there is no dust storm, the PM levels were likely lower due to either perfect atmospheric mixing or reduced number of the vehicles on the road. The analysis of hourly variation in the PM₁₀ concentrations during the day, also, showed elevation and reduction in the level with respect to the temperature and humidity, respectively.

Although site-to-site differences in PM₁₀ and PM_{2.5} were found, a strong relationship between them was observed, this may indicate similar source origination from either local traffic or industrial sources. In general, the result of AQI shows that PM₁₀ levels can be characterized as “moderate”. With such unappreciated levels of PM₁₀ as well PM_{2.5} pollutants in Kuwait’s urban areas, mitigations should be implemented to minimize emission rate and health and environmental impact assessment study is recommended to investigate long-term impacts. To decrease PM emission rates, concerned parties (Kuwait EPA) must regulate car emissions and force PM₁₀ and PM_{2.5} regulations governing emissions from industries such as refineries, cement, ceramic and stone factories.

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Author’s Contributions

Jasem M. Al-Awadhi: Participated in data collection and analysis and contributed to the writing of the manuscript (Percentage of contribution 70%).

Anwar B. Al-Helal: Participated in data-analysis and contributed to the reviewing of the manuscript (Percentage of contribution 30%).

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues involved.

References

- Addo, M.A., E.O. Darko, C. Gordon, B.J.B. Nyarko and J.K. Gbadago, 2012. Heavy metal concentrations in road deposited dust at ketu-south district. Ghana. *Int. J. Sci. Technol.*, 2: 28-39.
- Al-Awadhi, F.A. and S.A. Al-Awadhi, 2006. Spatial-temporal model for ambient air pollutants in the state of Kuwait. *Environmetrics*, 17: 739-752. DOI: 10.1002/env.791
- Al-Awadhi, J.M. and A.A. AlShuaibi, 2013. Dust fallout in kuwait city: Deposition and characterization. *Sci. Total Environ.*, 461: 139-148. DOI: 10.1016/j.scitotenv.2013.03.052
- Al-Basri, A., 1993. Dust Phenomena and their environmental impacts in Kuwait. MSc Thesis, Arabian Gulf University.
- Al-Hajraf, S., D. Al-Ajmi, A. Khan, H. Tang and A. Wahner *et al.*, 2005. Air quality assessment of Ali Sabah Al-Salem urban community. *Kuwait Ins. Scient. Res. (KISR)*.
- Al-Salem, S.M. and A.R. Khan, 2008. Comparative assessment of ambient air quality in two urban areas adjacent to petroleum downstream/upstream facilities in Kuwait. *Brazilian J. Chem. Eng.*, 25: 683-696. DOI: 10.1590/S0104-66322008000400006
- Al-Shayji, K., H.M. Lababidi, D. Al-Rushoud and H. Al-Adwani, 2008. Development of a fuzzy air quality performance indicator. *Kuwait J. Sci. Eng.*, 35: 10-26.
- AMAP, 1997. Arctic pollution issues: A state of the arctic environment report. Arctic Monitoring and Assessment Programme (AMAP), Olsen and Olsen Academic Publishers, Oslo, Norway.
- Balasubramanian, R. and W.B. Qian, 2004. Characterization and source identification of airborne trace metals in Singapore. *J. Environ. Monit.*, 6: 813-818. DOI: 10.1039/B407523D
- Dannecker, W.B., B.H. Schroder and S.T. Stechmann, 1990. Organic and inorganic substances in highway tunnel exhaust air. *Sci. Total Environ.*, 93: 293-300. DOI: 10.1016/0048-9697(90)90119-F
- Donaldson, K. and W. MacNee, 1998. The mechanism of lung injury caused by PM₁₀. *J. Sci. Technol.*, 1: 10-16. DOI: 10.1039/9781847550095-00021

- Duan, F.K., K.B. He, Y.L. Ma, F.M. Yang and X.C. Yu *et al.*, 2006. Concentration and chemical characteristics of PM_{2.5} in Beijing, China: 2001-2002. *Sci. Environ.*, 355: 264-275.
DOI: 10.1016/j.scitotenv.2005.03.001
- Goyer, R.A., 1996. Results of lead research: Prenatal exposure and neurological consequences. *Environ. Health Perspectives*, 104: 1050-1054.
- Khalaf, F.I., 1989. Desertification and Aeolian processes in the Kuwait Desert. *J. Arid Environ.*, 16: 125-145.
- Khan, A. and S. Al-Salem, 2007. Seasonal variation effect on airborne pollutants in an urban area in the state of Kuwait. *J. Environ. Res. Dev.*, 1: 215-218.
- Lee, D.S., J.A. Garland and A.A. Fox, 1994. Atmospheric concentrations of trace elements in urban areas of the United Kingdom. *Atmospheric Environ.*, 28: 2691-2713.
DOI: 10.1016/1352-2310(94)90442-1
- Meza-Figueroa, D., M.D.I. O-Villanueva and M.L.D.I. Parra, 2007. Heavy metal distribution in dust from elementary schools in Hermosillo, Sonora, México. *Atmospheric Environ.*, 41: 276-288.
DOI: 10.1016/j.atmosenv.2006.08.034
- KEPA, 2014. Pollution load assessment. Kuwait Environmental Action Program. Published by Kuwait Environment Public Authority (K-EAP) in collaboration with the World Bank, Kuwait.
- SEP, 2003. Monitoring and Method of Air and Waste Gases 4th Edn., Environment Science Press, Beijing, China, pp: 9.
- Liu, Q.T., M.L. Diamond, S.E. Gingrich, J.M. Ondov and P. Maciejczyk *et al.*, 2003. Accumulation of metals, trace elements and semi-volatile organic compounds on exterior window surfaces in baltimore. *Environ. Pollut.*, 122: 51-61.
DOI: 10.1016/S0269-7491(02)00286-5
- Loska, K. and D. Wiechula, 2003. Application of principal component analysis for the estimation of source of heavy metal contamination in surface sediments from the Rybnik Reservoir. *Chemosphere*, 51: 723-733.
DOI: 10.1016/S0045-6535(03)00187-5
- Singh, S.R., 2001. Concentration of fine silica and heavy metals in respirable suspended particulate matter small-scale foundries in Chandigarh. *J. Occup. Environ. Med.*, 5: 196-200.
- Sutherland, R.A., 2000. Bed sediment-associated trace metals in an urban stream. Oahu, Hawaii. *Environ. Geol.*, 39: 611-627. DOI: 10.1007/s002540050473
- USEPA, 2006. Guideline for reporting of daily air quality-Air Quality Index (AQI). Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711, USA.
- USEPA, 1999a. National air toxics program, the integrated urban strategy. United States Environm. Protection Agency's, Federal Reg.
- USEPA, 1999b. Compendium of methods for the determination of inorganic compounds in ambient air. Compendium of Method IO-3.1, EPA/625/R-96/010a.