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Elemental Variability of $PM_{2.5}$ Aerosols in Historical and Modern Areas of Jeddah, Saudi Arabia

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Abstract: Air particulate matter with a diameter of 2.5 μm ($PM_{2.5}$) were assembled for a whole year from the historical Jeddah district. Additional $PM_{2.5}$ aerosols were collected during the autumn and winter seasons from another newly constructed district in Jeddah city (Alnaeem). The annual concentration of the total mass of the $PM_{2.5}$ aerosols from the historical Jeddah site was found to be 43 ± 6 μg/m^3. In addition, the average of the total mass concentration at the Alnaeem site was 61 ± 14 μg/m^3. These values were greater than the annual mass concentration of the air quality standards of the European Commission (25 μg/m^3) and the World Health Organization (10 μg/m^3). The elemental analysis of the collected fine atmospheric aerosols was achieved by energy dispersive X-ray fluorescence (EDXRF) with three secondary targets (CaF_2, Ge, and Mo). Quantitative elemental analyses of twenty-two (22) elements were achieved starting from the low atomic number element (Na) up to the high atomic number element (Pb). Although the historical Jeddah site is not well organized, the elemental concentrations and total mass concentrations were lower than those of the other site. The statistical analyses including enrichment factors, correlation analysis, and the principal component analysis revealed more information about the source identification of the $PM_{2.5}$ aerosols collected from both locations. It was recognized that the elements Al, Si, K, Ca, Ti, Mn, Fe, Rb, and Sr originated from a natural source. On the other hand, the elements Ta, Br, Pb, Sc, Ni, Cu, Zn, and S originated from anthropogenic sources. Finally, the elements Na, Cl, and Br came mainly from the sea spray source.

Keywords: fine atmospheric aerosols; elemental analysis; historical Jeddah; EDXRF; statistical analyses

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1. Introduction

The intensification of anthropogenic sources of air pollution and other natural sources is of great concern with regard to air quality. Air pollution has negative effects on human health, animals, plants, ecosystems, and global warming [1–3]. Based on indoor and outdoor air pollution data, annual premature deaths were found to be 3.7 and 4.3 million, respectively [4]. Among the different criteria of air pollution, atmospheric particulate matters represent the most important air pollutant, especially fine and ultrafine air particulates which are related to cardiovascular mortality and respiratory diseases [5–8]. Based on many epidemiological studies, the mass concentration of fine particulate matter is proportional to the appearance of harmful and adverse diseases [9–11]. Fine particulate matter with a diameter equal to or less than 2.5 μm ($PM_{2.5}$) has gained a lot of attention in the literature because it can persist for a long time in the atmosphere and travel thousands of

kilometers [12–16]. Long-term exposure to $PM_{2.5}$ aerosols may drastically influence lung function and cause chronic bronchitis, heart disease, and lung cancer, especially for the elderly and children [17,18].

The source apportionments and the characterization of the $PM_{2.5}$ aerosols assembled from several cities in the Middle East have been demonstrated [12–16,19–23]. However, there is a remarkable lack of information about the composition and the source apportionments of the $PM_{2.5}$ collected from Jeddah, Saudi Arabia. At three sites in Jeddah, the morbidity risk associated with the $PM_{2.5}$ exposure collected for six weeks has been evaluated for cardiovascular and respiratory diseases [24]. It was found that the children and females less than 14 years are more at risk for respiratory diseases, whereas the risk of cardiovascular morbidity was higher in males above 40 years [24]. At fifteen elementary schools in south and north of Jeddah, the influence of schoolchildren's exposure to the mass concentration of outdoor and indoor $PM_{2.5}$ aerosols has been demonstrated [25]. It was found that, 100% of the $PM_{2.5}$ mass concentration exceeds the annual mean values of WHO [25]. The average mass concentration of the $PM_{2.5}$ in schools in south and north Jeddah was found to be 35.85 $\mu g/m^3$ and 20.98 $\mu g/m^3$, respectively [25]. In addition, the overall average of the indoor mass concentration in all schools of Jeddah was 25.42 $\mu g/m^3$. The indoor/outdoor ratios of the $PM_{2.5}$ aerosols ranged from 1.52 to 1.63 [25]. It was recognized that the indoor mass concentration of the $PM_{2.5}$ samples increased in the presence of students [25]. After the leaded gasoline phase-out at Jeddah in the years of 2008 and 2009, the lead (Pb) was determined in $PM_{2.5}$ aerosols collected from four sites in the city using inductively coupled plasma mass spectrometry (ICP-MS) [26]. The average concentration of lead was found to be 73.3 ng/m^3 [26]. Although the lead concentrations in the $PM_{2.5}$ samples were considerably decreased, lead concentration increased in the areas of high traffic density as well as in areas of industrial activities [26]. In another study, ultrafine and fine atmospheric aerosols ($PM_{0.5–0.25}$ and $PM_{2.0–1.0}$) were collected from Jeddah and characterized employing X-ray absorption near edge structure (XANES) and synchrotron radiation total reflection X-ray fluorescence (SR-TXRF) for Cr and Mn species [19]. It was found that the Cr species are mostly trivalent oxidation states, whereas Mn species existed in divalent and trivalent oxidation states [19]. A comprehensive study about the elemental compositions and the source apportionments of PM_{10} and $PM_{2.5}$ sampled from different sites in Jeddah was conducted [27]. An energy dispersive X-ray fluorescence (EDXRF) was utilized for the quantitative elemental analysis, whereas the source apportionment was estimated using factor analysis [27]. The main sources of the PM_{10} and $PM_{2.5}$ samples were found to be mainly from heavy oil combustion and soil dust as well as other secondary origins, such as industrial activities and vehicular emission sources [27]. In the natural radioactivity point of view, the concentration, and the associated internal inhalation effective dose of ^{40}K, ^{232}Th, ^{238}U, and Ra_{eq} were determined in $PM_{2.5}$ aerosols collected from four different locations in Jeddah [28]. It was found that the effective inhalation dose in the $PM_{2.5}$ aerosols is greater than the world reference values in the air [28]. Additionally, temporal variations including the seasonal and weekday/weekend variations of the total mass concentration, elemental contents, and source apportionments of PM_{10} and $PM_{2.5}$ and collected from Jeddah have been investigated [29]. The main sources of the $PM_{2.5}$ samples were mainly the oil burning from oil refineries and road/soil dust [29].

Over the last three decades, the development of the city increased rapidly and severely in the field of building and manufacturing, including the development of an oil refinery, wastewater treatment, plants desalinization, automobile fuels, metal industries, urbanization activities, and power plants. Also, other natural sources of air pollution can be found in Jeddah, such as desert storms and soil erosion. Therefore, these natural and anthropogenic sources of air pollution may have resulted in environmental degradation, and the air quality increasingly deteriorated. Although Jeddah city represents one of the largest cities in Saudi Arabia, an insufficient number of articles have been conducted on the characterization and the health effects of the $PM_{2.5}$ samples gathered from the city. Therefore, the characterization of the $PM_{2.5}$ samples assembled from the historical and

modern districts of Jeddah city, Saudi Arabia is the aim of the present study. The historical Jeddah district represents the core of the city. The elemental analysis of the collected $PM_{2.5}$ from the two sites was carried out using multi-secondary target energy dispersive X-ray fluorescence spectrometry (EDXRF). Further investigation about the source identification was demonstrated using different statistical tools, including principal components analysis, enrichment factors, and Pearson's correlation coefficients.

2. Experimental Setup

2.1. $PM_{2.5}$ Sampling

Jeddah is considered the most commercial area in the country. Also, it represents the second most important location in the country, as it has the main airport and seaport of the country. The total population of Jeddah was estimated to be 3.58 million citizens [24]. The $PM_{2.5}$ sampling was carried out in historical Jeddah district, on the west coast of the Red Sea, Jeddah, Saudi Arabia. The sampling site of historical Jeddah is characterized by several non-organized alleyways and the widths of the roads. Also, it is nearby to the the wastewater treatment station, desalination plant, oil refinery, power plant, and activities at the seaport and shipyard. In addition, the intensity of the population of the sampling location is relatively high compared with other districts in the city. The historical Jeddah site is located at a longitude of 39°11′15.9″ N and latitude of 21°29′15.3″ E. One $PM_{2.5}$ sample was collected every week for 24 h in the period from September 2019 to August 2020, covering the whole year. The total number of the collected $PM_{2.5}$ samples was 48 samples (12 sample/season). For comparison study, a limited number of $PM_{2.5}$ samples were collected during the same autumn and winter seasons 2019/2020 from a recently constructed district "Alnaeem" (longitude: 39°11′15.9″ and latitude: 21°29′15.3″) using the same procedure (12 sample/season).

The two $PM_{2.5}$ sampling setups are approximately 12 m above ground level, on selected roof buildings of the two sites, to keep away from the direct influence of the road traffic and windstorms, Figure 1. The $PM_{2.5}$ samples were accumulated on polycarbonate filters (25 mm diameter, pore size 0.4 µm, Whatman, Maidstone, UK) loaded inside a Dewell-Higgins type cyclone (Casella CEL, Bedford, UK) operated at a flow of 3 L min^{-1}. The polycarbonate filters are characterized by a low level of impurities and high efficiency for $PM_{2.5}$ collections. The present flow rate is optimized to achieve a particle cut-off of 2.5 µm.

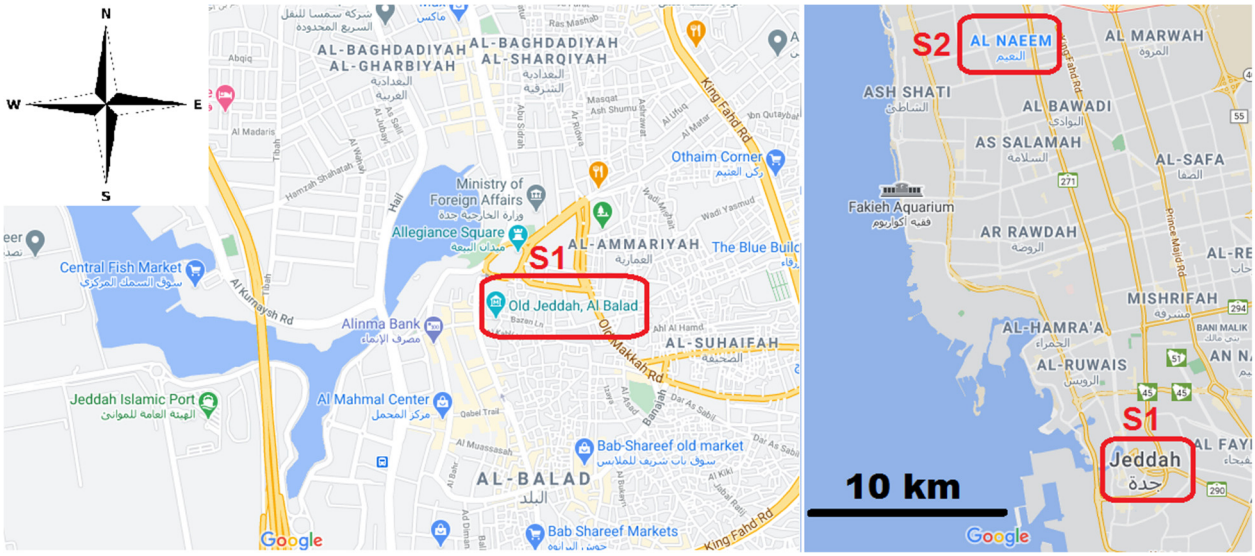


Figure 1. Sampling locations of the $PM_{2.5}$ aerosols collected form the historical Jeddah district (S1) and Alnaeem district (S2).

2.2. Instrumentation

An energy dispersive X-ray fluorescence spectrometry (EDXRF, Epsilon 5, PANalytical, Almelo, Netherlands) with CaF_2, Ge, and Mo secondary targets was used for the quantitative elemental analysis of the blank and $PM_{2.5}$ filters. By using multi-secondary targets, the low, medium, and high atomic number (Z) elements can be quantified in the $PM_{2.5}$ samples. The deposited $PM_{2.5}$ samples on the polycarbonate filters were directly analyzed without any prior sample preparation since the present method is completely nondestructive. The X-ray tube with the dual anode (Sc/W) was used as the main excitation source at different power settings. The X-ray fluorescence spectra were measured by a Germanium detector with a nominal resolution of 144 eV for Mn-Kα. At three photon energy ranges, the XRF spectra of the $PM_{2.5}$ samples were counted. For low Z elements, the excitation energy of the X-ray tube was carried out at a current of 15 mA and a voltage of 40 kV using a CaF_2 secondary target. In this case, the low Z elements up to K (Z = 19) could be covered. Besides, the excitation energy of the X-ray tube for the medium Z elements was executed using a germanium (Ge) secondary target at a maximum current and voltage of 8 mA and 75 kV, respectively. The medium Z element can be identified up to Zinc (Zn = 30). Using a current of 7.5 mA, applied voltage of 80 kV, and Mo secondary target, the high Z elements could be quantified, and these elements are Pb, Se, Br, Rb, Sr, and Y. The developed analytical method presents extremely excellent limits of detection in terms of the low Z elements. Additional refinement in the instrumental sensitivity was elucidated. Further information about the present EDXRF setup, limits of detection, and calibration curves of the quantified elements were illustrated elsewhere [20,21,23,30,31].

2.3. Method Verification

The verification and the validity of the current method were assured by analyzing a standard reference material of air particulate (#2783, National Institute of Standard and Technology, Gaithersburg, MD, USA) using the present EDXRF setup. An excellent agreement between the measured and certified concentration of most of the elements was achieved, which emphasizes the validity of the present method. Further details about the validity of the current method were depicted elsewhere [20,21,23,30,31].

3. Results and Discussions

3.1. $PM_{2.5}$ Mass Concentration

The deposited mass concentration of the $PM_{2.5}$ samples was calculated by weighting the polycarbonate filters before and after the sampling using a microbalance of six digits (Sartorius CC50). At the historical Jeddah site, the total mass concentration of the $PM_{2.5}$ samples varied from 12 to 85 $\mu g/m^3$ with an annual average of 42 $\pm$ 13 $\mu g/m^3$. The individuals and the annual mass concentration of the $PM_{2.5}$ samples exceeded the annual mass concentration proposed by the World Health Organization (WHO) which is equal to 10 $\mu g/m^3$ [32]. However, 80% of the individual mass concentration of the $PM_{2.5}$ samples exceeded the 24 h mean value of the WHO and the annual mean values of the European commission of air quality (25 $\mu g/m^3$) [33]. For comparisons, additional $PM_{2.5}$ samples were assembled from another site (Alnaeem district) which illustrated a high mass concentration, and it varied from 19 to 140 $\mu g/m^3$ with an average of 61 $\pm$ 15 $\mu g/m^3$. Figure 2 illustrates the monthly variation of the total mass concentration of the $PM_{2.5}$ samples collected from the historical Jeddah and Alnaeem districts. Remarkably high standard deviations were found at Alnaeem district, especially during the autumn months. Also, the $PM_{2.5}$ samples collected from the historical Jeddah district during the spring had high standard deviations. At historical Jeddah district, the highest mass concentration of the $PM_{2.5}$ aerosols was found to be 54 $\pm$ 10 $\mu g/m^3$ and 53 $\pm$ 3 $\mu g/m^3$ during winter and spring seasons, respectively, Figure 2. The high mass concentration of the $PM_{2.5}$ aerosols in winter and spring could refer to the low temperature and wind speed and consequently the low atmospheric dispersion, as well as the increase of the local fuel and coal burning activities. The temperature during the winter ranges from 18.9 °C to 29.4 °C and it ranges from 20 °C to 36.7 °C during spring.

On the other hand, the wind speed in winter ranges from 3.8–4.5 m/s and it increases slightly in spring (4.1–4.6 m/s).

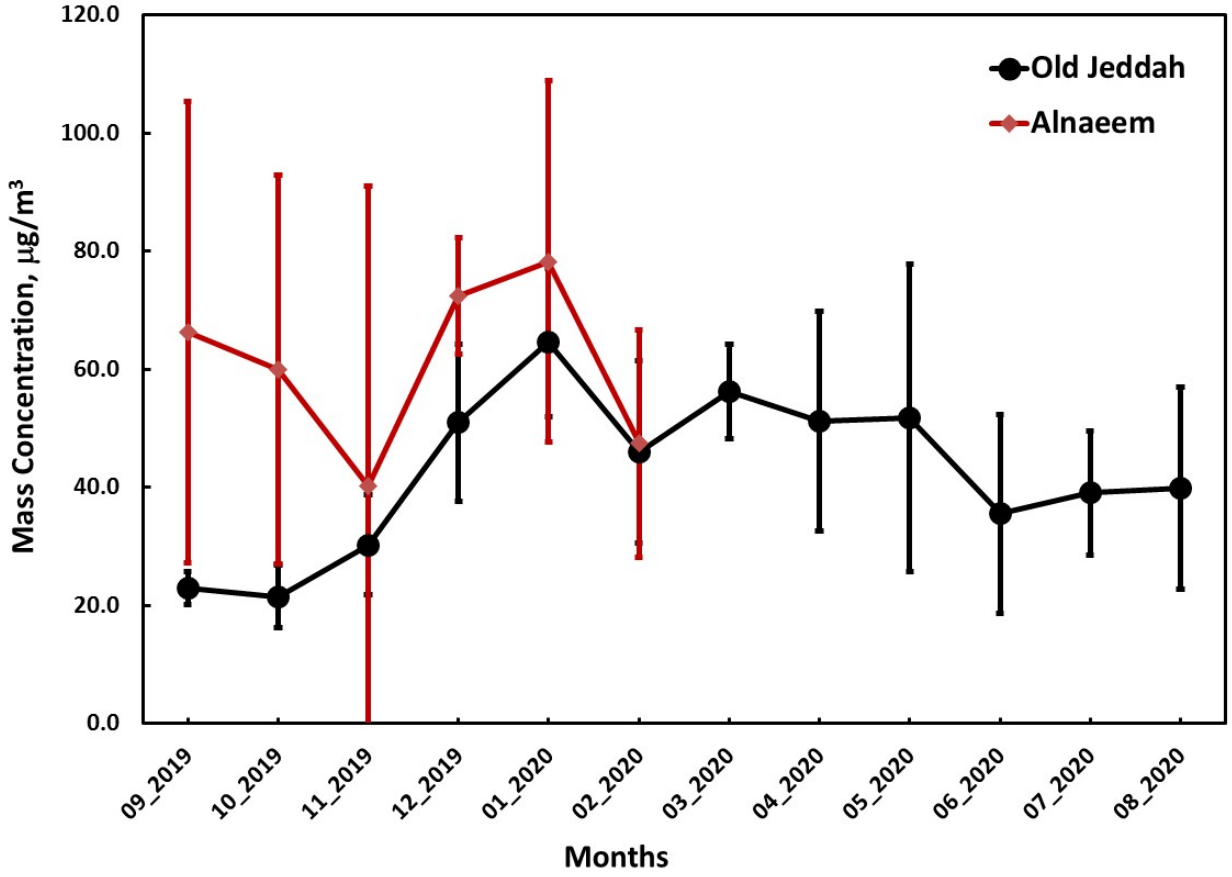


Figure 2. Monthly variations of the $PM_{2.5}$ samples collected from the "historical Jeddah" district as well as from "Alnaeem" district for comparison.

The lowest mass concentrations of the $PM_{2.5}$ samples were found during the months of the autumn (from September to November 2019), Figures 2 and 3. This is due to the meteorological factors especially the increasing of relative humidity and temperature [34], whereas the relative temperature and humidity reaches to 91% and 37.2 °C, respectively. The percentages of the individual mass concentration of the $PM_{2.5}$ are depicted in Figure 4. It was clear that about 95% of the collected $PM_{2.5}$ samples from historical Jeddah district were higher than the annual mean values of WHO, and 80% of them were also higher than the 24-h values of WHO and the annual mean values of the European commission for air quality [32,33]. This illustrates that there is a remarkable challenge to decreasing the mass concentration of the $PM_{2.5}$ aerosols in Jeddah, especially from historical Jeddah district. However, only 10% of the total mass concentration of the $PM_{2.5}$ samples collected from historical Jeddah district were higher than 60 µg/m^3, Figure 4. On the other hand, the historical Jeddah district had a low mass concentration when compared with the second location (Alnaeem). This could be due to the low density of the traffic inside historical Jeddah, whereas the capacity of the streets in the historical Jeddah was lower than at the other site (Alnaeem).

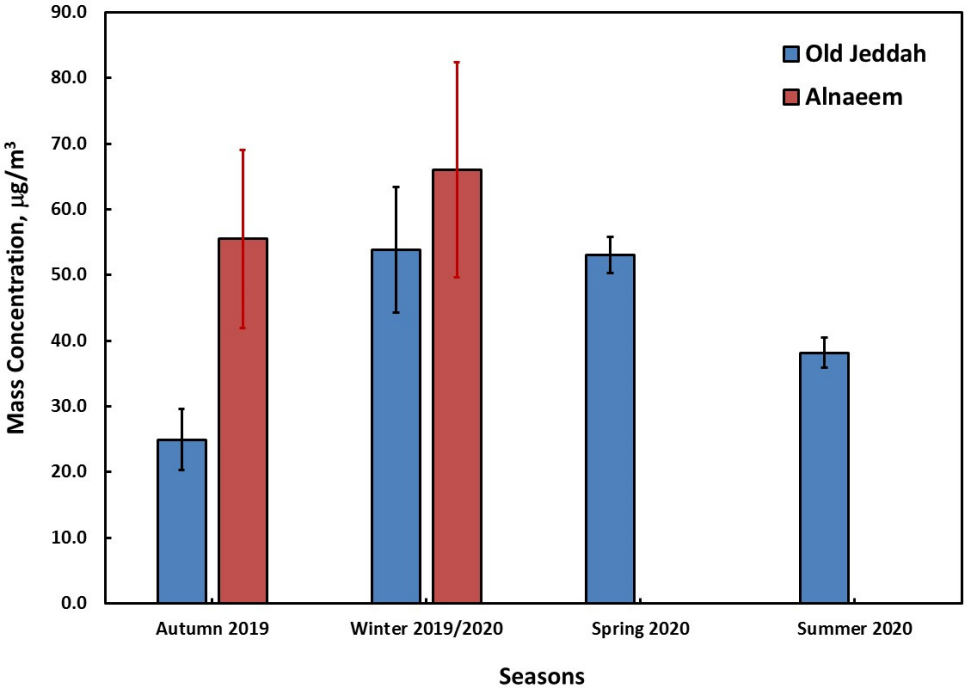


Figure 3. The relationship between the seasons and the mass concentration of the $PM_{2.5}$ samples collected from the historical Jeddah and Alnaeem districts in Jeddah city, Saudi Arabia.

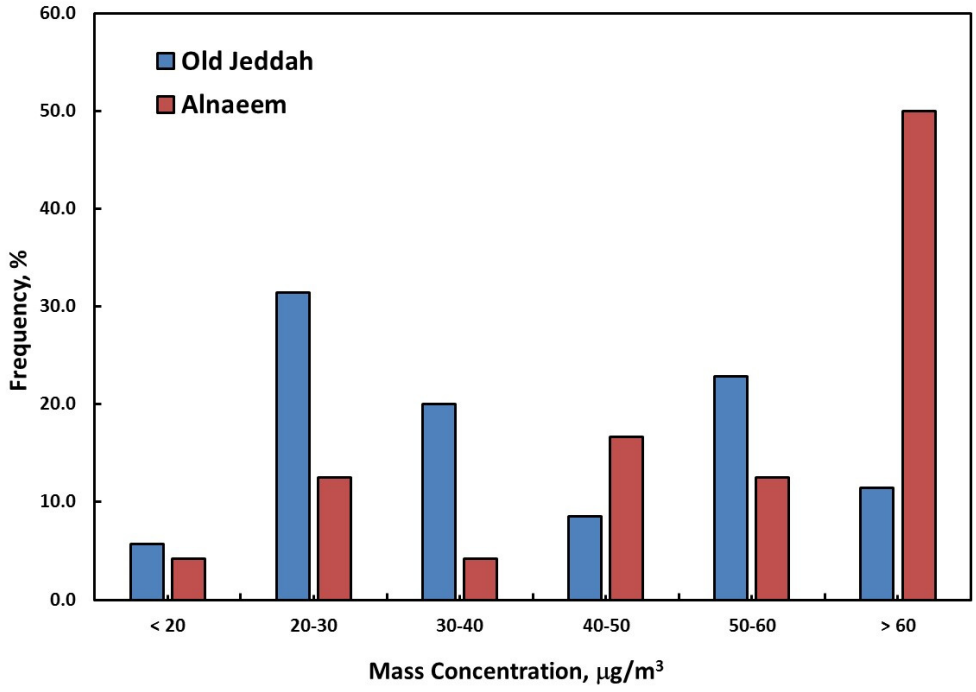


Figure 4. The frequency percentages of the daily mass concentration of the $PM_{2.5}$ samples collected from the historical Jeddah and Alnaeem districts in Jeddah, Saudi Arabia.

The high mass concentration of the $PM_{2.5}$ samples at the Alnaeem district could refer to the high density of the traffic as well as the industrial activities around the sampling location such as power plants, oil refinery, and seawater desalination plant. For comparisons of the present results with other published works in Jeddah, Table 1 presents the annual mean values of the $PM_{2.5}$ found in the present work and the other published data in Jeddah. The present annual mean value of the $PM_{2.5}$ mass concentration of historical Jeddah is

comparable with the previous work of Zytoon [28] and Aburas [26]. However, it seems to be higher than the values given by the others [25,27,29]. The output result reflects the similarity and variability of the mass concentrations of the $PM_{2.5}$ samples which depends on the natural and anthropogenic sources during the sampling collection. Meanwhile, most of the published works regarding the atmospheric pollution in Jeddah city confirm that more than 70% of the total mass concentration of the $PM_{2.5}$ samples is higher than the annual mean values of WHO and the European Commission for air quality. Therefore, there is an urgent need for scientific tools to decrease the mass concentration level of the $PM_{2.5}$ aerosols in Jeddah.

Table 1. The average mass concentration of the $PM_{2.5}$ samples reported in the present work and in the previous published works in Jeddah, Saudi Arabia.

Reference	City	Year	Mass Concentration, $\mu g/m^3$	Location Nature
Present Work	Jeddah	2019/2020	42 ± 6.4	Residential/commercial (Historical Jeddah)
			61 ± 14	Residential (Alnaeem)
WHO		10		Annual mean value
European Commission		25		Annual mean value
Aburas et al. [26]	Jeddah	2008/2009	47.7 ± 16.5	Residential
			67.8 ± 65.3	King Abdulaziz University
			41.2 ± 4.8	Residential/commercial
			47.3 ± 26.1	Residential
Alghamdi [25]	Jeddah	2013	24.76 ± 8.71	South of Jeddah
			13.13 ± 3.65	North of Jeddah
Khodeir et al. [27]	Jeddah	2011	15.8 ± 3.1	Residential
			18.0 ± 4.0	Residential
			73.2 ± 65.1	Suburban
			23.8 ± 11.7	Urban
			29.1 ± 14.1	Urban
			31.1 ± 5.8	Urban
			24.5 ± 11.8	Residential
Zytoon et al. [28]	Jeddah	2008/2009	47.02 ± 19.15	Residential
			41.15 ± 8.51	Residential/commercial
			47.32 ± 25.37	Residential
			67.77 ± 61.27	Industrial/commercial
Lim et al. [29]	Jeddah	2011/2012	21.9 ± 11.6	Residential

3.2. Elemental Analysis of $PM_{2.5}$ Samples

Figures 5–7 illustrate an example of the XRF spectra of the low, medium and high Z elements using CaF_2, Ge and Mo secondary targets, respectively. According to the XRF spectra given by Figures 5–7, twenty-two (22) elements were quantified in most of the $PM_{2.5}$ samples and these elements are Al, Br, Ca, Cl, Co, Cu, Fe, K, Mn, Na, Ni, Pb, Rb, S, Sc, Si, Sr, Ta, Ti, V, Y, and Zn. As shown in Figure 7, one could recognize the L lines of W ($L_{\alpha 1}$ = 8.398 keV, $L_{\alpha 2}$ = 8.335 keV, $L_{\beta 1}$ = 9.672 keV, and $L_{\beta 2}$ = 8.398 keV) which originates mainly from the target of the X-ray tube. Table 2 presents the minimum, maximum, and annual mean values for the elemental concentration in ng/m^3 measured in the $PM_{2.5}$ samples collected from historical Jeddah district. Additionally, the minimum, maximum and the average of the collected $PM_{2.5}$ samples from Alnaeem site is included in Table 2. The available air quality standard values of Pb and Ni are also presented in Table 2 [33]. Based on the elemental analyses of most elements illustrated in Table 2, the historical Jeddah site has concentrations lower than the concentrations found in Alnaeem district.

This indicates the low air pollution at the historical Jeddah location in terms of elemental analysis. Also, the total mass concentration of the quantified elements represents 17% and 43% at the historical Jeddah and Alnaeem sites, respectively, Table 2. Therefore, the historical Jeddah site has low concentrations of inorganic pollutants in the $PM_{2.5}$ samples.

In the case of nickel (Ni), the annual mean value observed in historical Jeddah (26 ± 2.6 ng/m^3) district is higher than the annual mean value of the air quality standards given by the European Commission (20 ng/m^3) [33]. In addition, the individual and the average (27 ± 3.4 ng/m^3) quantitative analysis results of Ni at Alnaeem location are also higher than the value of the air quality standard. It was also recognized that there is remarkable stability of Ni in both sites during the whole year whereas the variations of the standard deviation values are within 10%. This indicates that the weathering conditions in the city have no influence on the increasing or decreasing the concentration of Ni in $PM_{2.5}$ samples. Therefore, the changing of the meteorological factors (temperature, relative humidity, and wind speed) has no influence on the variations of Ni concentration. The release of Ni and its compounds in the atmosphere was originated from industrial and commercial activities [35,36]. As the nickel (Ni) level in the atmosphere is higher than the maximum allowance level, it could have toxicity, carcinogenicity, and pathological effects [35,36]. In the case of Pb, the daily concentrations in the historical Jeddah district vary from 4 to 230 ng/m^3 and all of these values are less than the annual mean values of the European Commission (500 ng/m^3) [33]. At Alnaeem district, the daily concentration of Pb was also less than the annual mean values of the European Commission except for one sample that had a concentration of 1200 ng/m^3. However, the Pb values of the annual mean at historical Jeddah and the average of individuals at Alnaeem districts were generally lower than the annual mean values of air quality (500 ng/m^3) and it equals 55 ± 70 and 370 ± 310 ng/m^3, respectively.

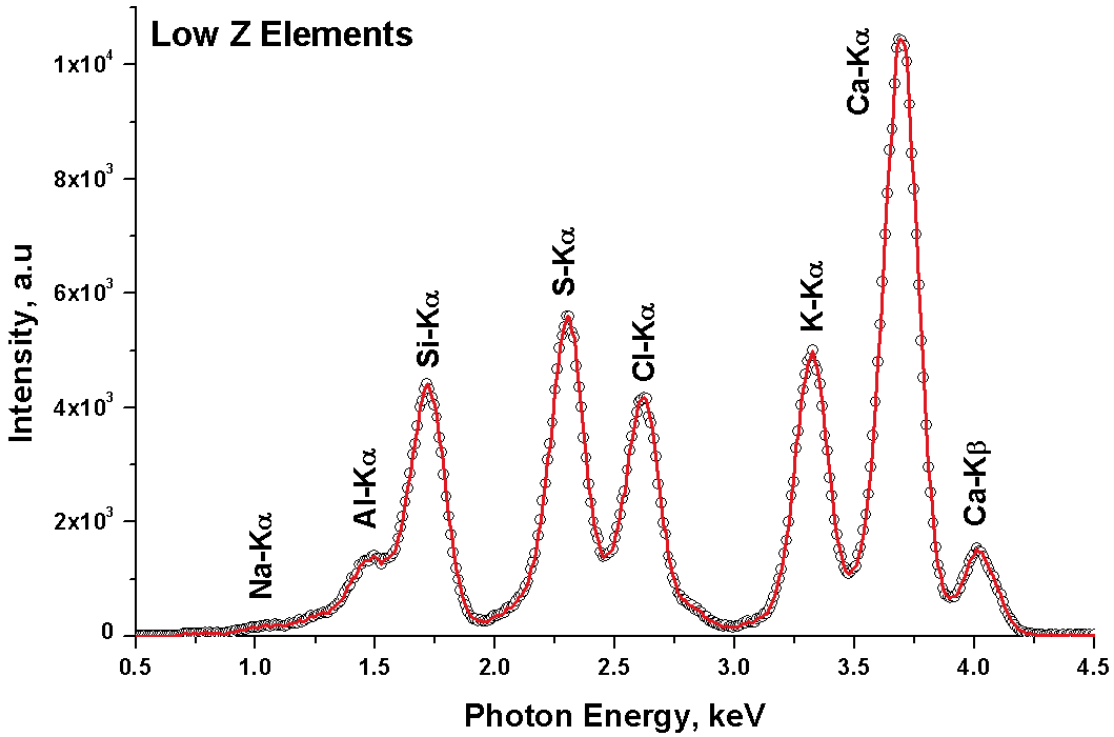


Figure 5. The EDXRF spectrum of the low Z elements using CaF_2 secondary target for selected $PM_{2.5}$ sample from historical Jeddah district, Saudi Arabia.

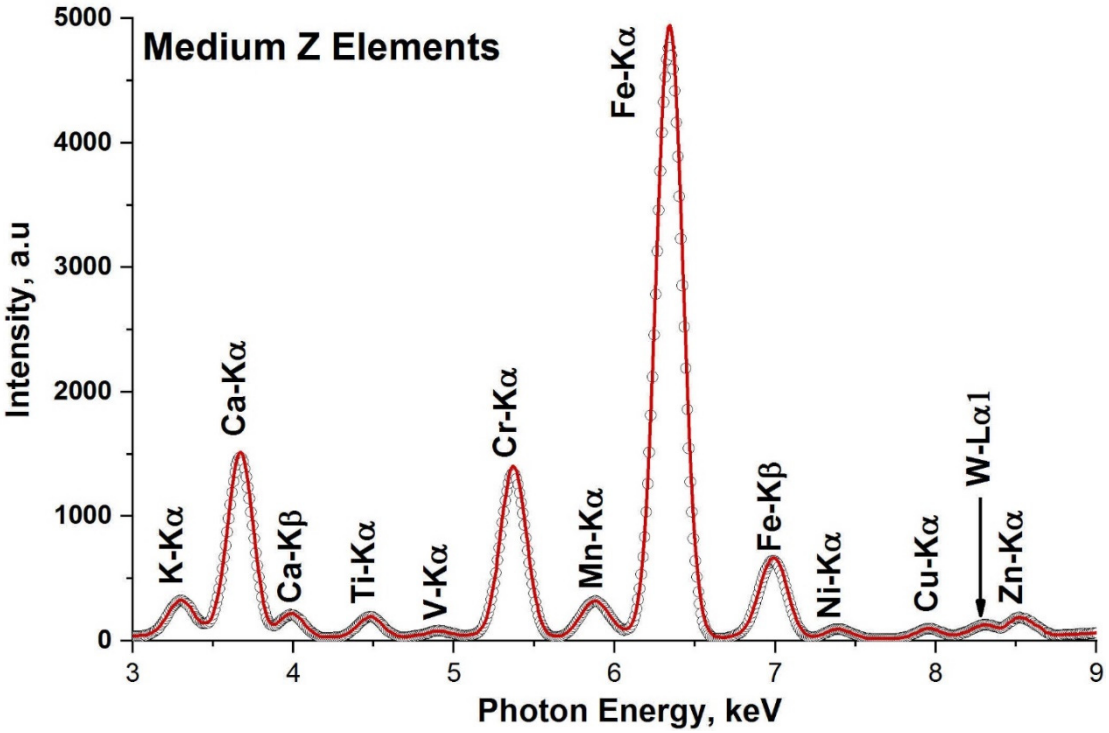


Figure 6. The EDXRF spectrum of the medium Z elements using Ge secondary target for selected $PM_{2.5}$ sample from historical Jeddah district, Saudi Arabia.

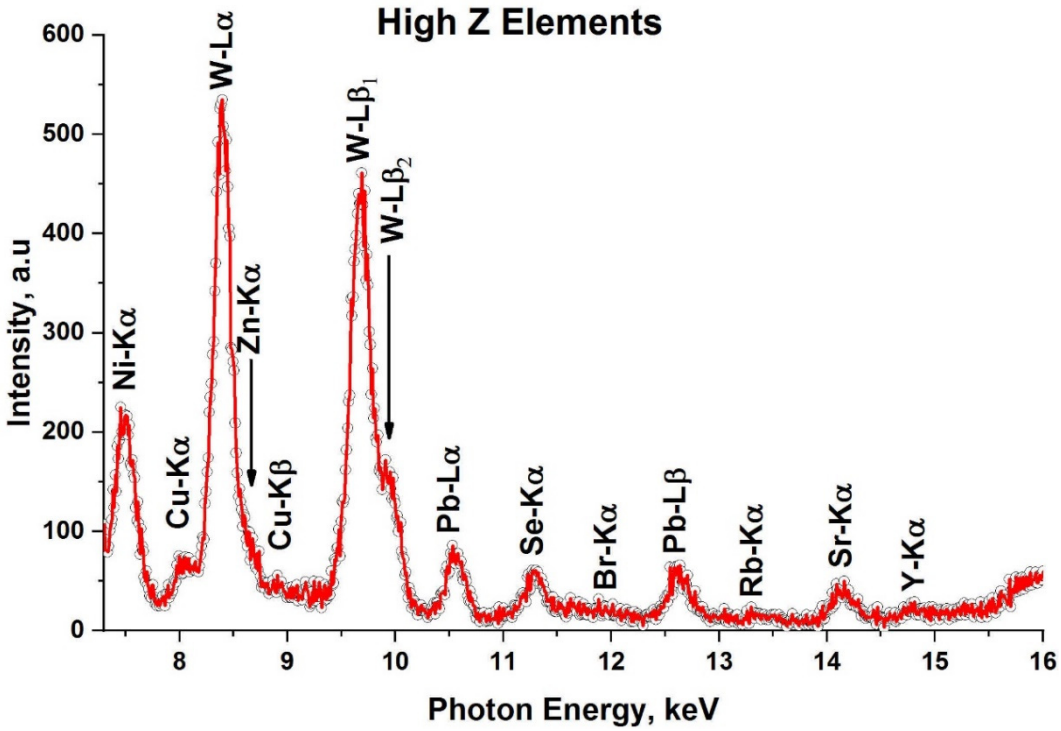


Figure 7. The EDXRF spectrum of the high Z elements using Mo secondary target for selected $PM_{2.5}$ sample from historical Jeddah district, Saudi Arabia.

The low concentration of Pb on both sides indicates the use of unleaded gasoline [26]. However, the high concentration of Pb at Alnaeem district could refer to the proximity of the different industrial activities including high traffic density. The low concentration of Pb in historical Jeddah districts refers to the low traffic density since most of the trucks

cannot pass inside the district. Seven major elements were determined in the $PM_{2.5}$ samples, namely Al, Ca, Cl, Fe, K, Na, and Si. These major elements are considered crustal elements and their origin from the sea spray and soil dust including dust storms. It was recognized that the average of the individual concentrations of these elements at Alnaeem district are always higher than the annual mean concentrations at the historical Jeddah district.

The concentrations of Si, K, and Fe at Alnaeem district are 4–6 times higher than that found at the historical Jeddah location, Table 2. The high concentrations of Al, Ca, Fe, and Si at the Alnaeem district originate not only from the soil dust but also from the cement industries in the city. Jeddah has many locations specified from the cement industry, where these elements represent the main ingredients. Therefore, the historical Jeddah district has a low level of the pollutants of the elemental mass concentration compared with the new district of the city, whereas the average values of the total mass concentration of the $PM_{2.5}$ in historical Jeddah are always lower than that found in the Alnaeem district. In the case of Na and Cl, the average concentration of Cl is always higher than the average concentration of Na, which is in agreement with the literature [37,38].

Table 2. The minimum, maximum and the mean values of the elemental analysis in the $PM_{2.5}$ assembled from historical Jeddah and Alnaeem districts.

El.	Historical Jeddah District (S1), ng/m^3			Alnaeem District (S2), ng/m^3			Air Quality Standards
	Min.	Max.	Mean	Min.	Max.	Mean	
Na	65	1200	320 ± 290	120	920	390 ± 360	
Al	18	4800	830 ± 980	690	8000	3200 ± 2900	
Si	120	8400	1500 ± 1800	2200	15,000	6600 ± 5300	
S	50	4100	980 ± 1000	400	4700	2700 ± 1100	
Cl	1.2	3600	830 ± 960	27	5300	1000 ± 1500	
K	6.9	1600	320 ± 320	590	2700	1200 ± 740	
Ca	46	6300	1800 ± 1600	1300	20,000	7100 ± 5600	
Sc	1.8	32	11 ± 9.2	6.4	6.4	6.4 ± 0	
Ti	4.5	290	54 ± 61	100	760	290 ± 220	
V	0.0	23	6.8 ± 6.0	0.9	23	13 ± 7.6	
Mn	0.4	58	15 ± 15	23	200	82 ± 63	
Fe	12	2900	580 ± 660	1200	8900	3600 ± 2700	
Co	0.0	3.8	1.6 ± 1.1	0.0	6.0	2.6 ± 2.0	
Ni	22	35	26 ± 2.6	21	34	27 ± 3.3	**20** [33]
Cu	12	33	16 ± 4.2	16	46	25 ± 10	
Zn	4.3	37	16 ± 12	3.6	110	28 ± 29	
Br	1.6	12	6.1 ± 2.5	2.3	37	11 ± 10	
Rb	0.1	6.2	1.7 ± 1.6	1.9	6.6	3.6 ± 1.4	
Sr	0.1	32	7.1 ± 6.9	9.5	84	33 ± 24	
Y	0.3	2.7	1.1 ± 0.7	0.7	1.2	0.9 ± 0.3	
Ta	0.0	32	15 ± 7.4	8.1	19	14 ± 7.8	
Pb	3.5	230	55 ± 70	15	1200	370 ± 300	**500** [33]
***ΣEl* *.**			***7.4***			***27***	
***PM*$_{2.5}$ ***			***42***			***61***	
Elemental mass, %			***17***			***44***	

* The mass concentration is in μg/m^3.

The source of Cl at both sites is mainly from the sea spray and this could be expected, whereas the average concentrations of Cl and Na on both sides are comparable. Considering other natural and anthropogenic sources as well as the sea spray, the Na/Cl ratios be varied from 0.5 to 1.5 [38]. Figure 8 shows the obtained seasonal Na/Cl ratios of the present work. At the historical Jeddah site, 30% of the Na/Cl ratios are within the range from 0.5 to 1.5 whereas 36% of the Na/Cl ratios of Alnaeem district are with the same range. The variation of the Na/Cl ratio far from the restricted range could be an indication of the existence of other sources rather than the sea spray. However, the seasonality of most of the Na/Cl ratios approaches the minimum restricted range, Figure 8. The highest value of the Na/Cl ratios was found in winter whereas the Na/Cl ratios of the other seasons were comparable, Figure 8.

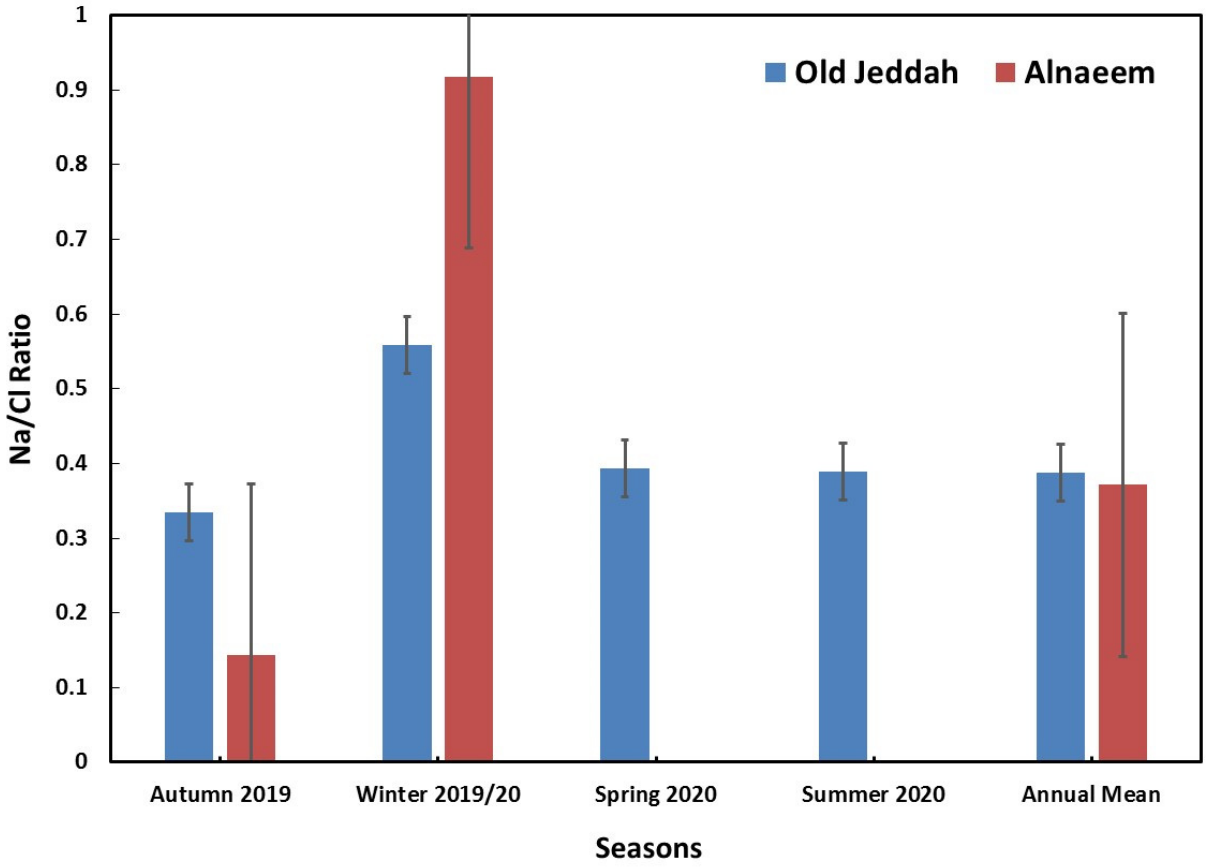


Figure 8. The Na/Cl ratios at historical Jeddah and Alnaeem districts versus the seasons of the year as well as the overall average values.

Furthermore, the elements Mn, V, and Co originated from anthropogenic and natural sources. The expected anthropogenic sources have different contributions to these elements in the atmosphere, such as traffic, power plants, coal, crude oil, and steel industries [39]. Additional natural sources include the soil dust from wind erosion and suspensions of soils are also expected. The average values of Mn equal 15 ± 15 and 82 ± 63 ng/m^3 at historical Jeddah and Alnaeem locations, respectively. Mn increased six times at the Alnaeem site, which indicated a traffic source. The annual mean value of Mn in historical Jeddah is comparable with that found in Germany [40]. The average value of Mn found in the Alnaeem district is also comparable with that reported in Belgium [41]. Fortunately, a low concentration of Co was found at historical Jeddah and Alnaeem locations (<2.6 ng/m^3) and it originated from vehicular exhaust and different industrial activities, such as coal combustion and waste incineration. The low concentration of Co at the historical Jeddah site refers to the low traffic density. In the case of vanadium (V), it originated in the

atmosphere mainly from anthropogenic sources such as petroleum refineries, steel industry, heterogeneous catalysts, and seagoing ships [42]. However, V also could be emitted into the atmosphere from natural sources, whereas its concentration in the earth's crust reaches 100 μg g^{-1} [43]. It was also observed that the concentration of V at the Alnaeem location was twice as high at the historical Jeddah location.

In the case of Sulfur (S), the highest concentration was found at Alnaeem district and it reaches 4700 ng/m^3. The mean concentration of S at the Alnaeem location is four times higher than that found at the historical Jeddah site. As mentioned earlier, the historical Jeddah site has low traffic density whereas the Alnaeem location has high traffic density and is close to oil refinery activities. Therefore, the high concentration of sulfur at Alnaeem site originated from the different anthropogenic sources namely exhaust combustion from vehicles, power plants, and petroleum refineries, and smelting of non-ferrous ores.

Looking at Cu and Zn, there is a remarkably low concentration of these elements on the historical Jeddah site as illustrated in Table 2. The origins of Cu and Zn in the atmosphere could be the brass and alloy industries, vehicular emission, and galvanized metals. Other minor elements were quantified on both sites, including Sc, Ti, Br, Rb, Sr, Y, and Ta. The average concentration of these elements, except Ti and Sr, in both sites, was less than 15 ng/m^3. The average mass concentrations of Br, Rb, Y, and Ta on both sides are comparable and the variations are among the standard deviations. The behavior of scandium (Sc) is completely different from all other elements whereas it has a higher concentration at the historical Jeddah site. The scandium is rare in the earth's crust. The expected sources of Sc in the air of historical Jeddah could be the wastes of the house hold equipment (glasses, fluorescent and energy saving lamps) and the oil industry [44,45]. The natural origins of Ti and Sr seem to be dominating whereas they have the same behavior as the major elements like Ca and their highest concentrations were found at the Alnaeem site. Titanium (Ti) varies from 0.5 to 1.5% in the earth's crust, and it occurs in a form of different minerals such as brookite, anatase, ilmenite, and perovskite [46]. However, Ti also releases into the atmosphere from the coal and oil combustion and titanium industry especially the production of TiO_2 pigment.

3.3. Statistical Analysis

3.3.1. Enrichment Factor Calculations

Using the quantitative elemental analysis and the established information of the earth crust composition, the calculations of the enrichment factor (EF_X) could explain the origins of the anthropogenic activities and their influence on the quality of the atmosphere. For a reference crustal element Y and element X, the enrichment factor for the element X (EF_X) is given by,

$$EF_X = \frac{(X/Y)_{air}}{(X/Y)_{crust}} \quad (1)$$

where (X/Y) is the concentration ratio of X and Y elements in the $PM_{2.5}$ aerosols or the earth's crust, respectively. Additional details about the enrichment factors can be found elsewhere [47–50]. The reference crustal element (Y) is usually stable in the soil with natural origins and is used to normalize its concentration in the $PM_{2.5}$ aerosols. Aluminium (Al) has been selected as a reference element (Y) and it was previously considered as a conservative and low occurrence variability element [51–54]. The chemical composition of the earth's crust was provided by Wedepohl [55]. Figure 9 depicts the relationship between the mean values of the EFx versus the quantified elements in the $PM_{2.5}$ samples collected from the present two locations. If the values of the EF_X equal to or less than 1, it indicates that the element of interest has a natural source from the earth's crust. The elements Si, Al, and K originate from the natural source from the earth's crust whereas the EF_X values of these elements equal or less than 1. Also, there is no enrichment for Na and Rb found at the Alnaeem site which indicates the natural origins. Minimal enrichment could be observed as the values of the EF_X are less than 2 ($EF_X < 2$). The elements Fe, Ti, Rb, and Na quantified

at the historical Jeddah site have a natural origin with minimal enrichment values less than two.

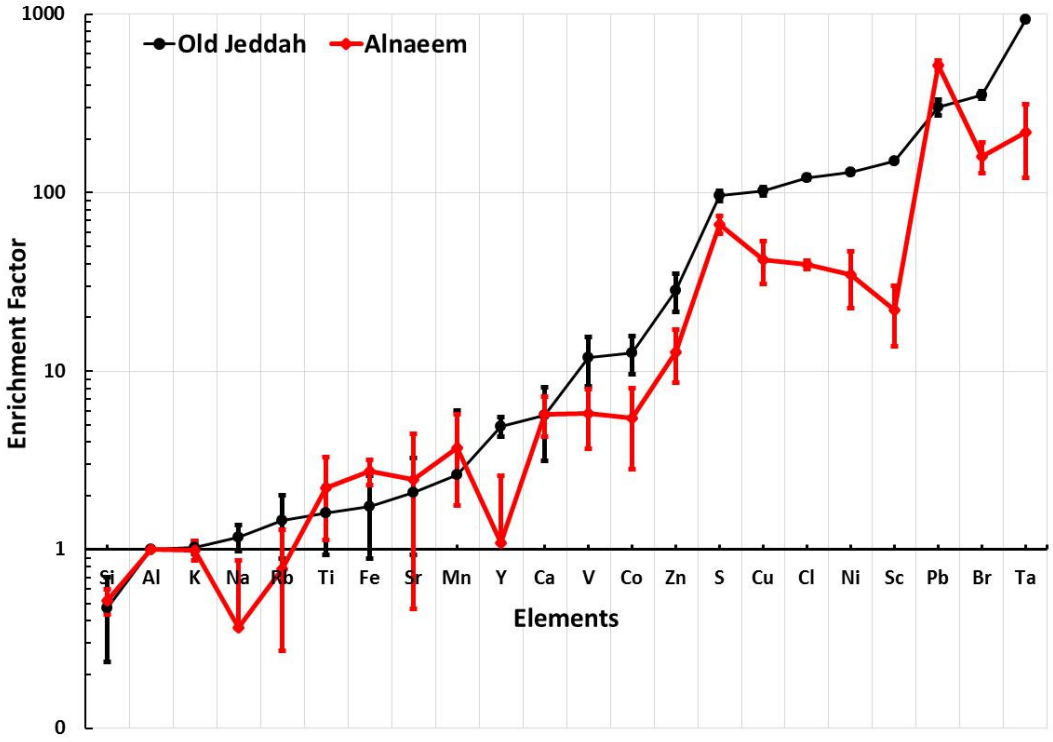


Figure 9. Enrichment factors of the determined elements in the $PM_{2.5}$ samples assembled from the historical Jeddah and Alnaeem locations.

The moderate enrichment exists as the EFs range from 2 to 5 and this was found for Sr, Mn, and Y as illustrated in Figure 9. The elements Sr, Mn, and Y have mainly natural origins such as seawater, but it also releases into the atmosphere from other anthropogenic sources like coal combustion. A significant enrichment is expected when the EFs vary from 5 to 20. The main elements that have significant enrichment factors are Ca, V, and Co. A very high and extremely high enrichments could be expected when the EFs range from 20–40 and >40, respectively. The enrichment factor of very and extremely high values (>20) was found for the elements Cl, S, Zn, Cu, Ni, Sc, Pb, Br, and Ta. This illustrates that these elements originated from man-made sources, except Cl and Br where the marine and Sea water could be expected to be the main sources. The high EF values of S, Cu, Zn, Ni, Sc and Pb suggest the influence of traffic emissions and fuel combustion, extensive mining, and oil refinery [27,56–58].

3.3.2. Correlation Coefficients

The interrelationship of the quantified elements and the sampling seasons was explored by Pearson's correlation coefficients. The formula of the Pearson's correlation coefficients r_{xy} is given by,

$$r_{xy} = \frac{\frac{1}{N}\sum_{i=1}^{N}(x_i - \overline{x})(y_i - \overline{y})}{\sqrt{\frac{\sum_{i=1}^{N}(x_i - \overline{x})^2}{N-1}}\sqrt{\frac{\sum_{i=1}^{N}(y_i - \overline{y})^2}{N-1}}} \quad (2)$$

where $\overline{x}$ exhibits the average value of i number of x's and $\overline{y}$ expresses the average value of i number of y's. As the correlation coefficients approach +1 or −1, it indicates the perfect

positive or perfect negative correlations, respectively. There is no correlation between the variables when the coefficient values equal to zero (r_{xy} = 0). A moderate negative or positive correlation could be obtained when the correlation coefficient values vary from ±0.3 to ±0.49. The low degree of correlation could be expected as the correlation coefficient values less than ± 0.3 (<±0.3). Tables 3 and 4 illustrate the correlation coefficient values between the different quantified elements at the current two locations.

Table 3. The correlation coefficients of Pearson between the quantified elements in the $PM_{2.5}$ samples collected from historical Jeddah site.

	Al	Si	S	K	Ca	Ti	V	Mn	Fe	Co	Ni	Cu	Zn	Pb	Br	Cl	Rb	Sr	Na
Al	1.00																		
Si	1.00	1.00																	
S	0.85	0.83	1.00																
K	0.97	0.96	0.89	1.00															
Ca	0.81	0.83	0.58	0.72	1.00														
Ti	0.98	0.99	0.84	0.96	0.81	1.00													
V	0.60	0.59	0.79	0.62	0.54	0.58	1.00												
Mn	0.82	0.84	0.72	0.76	0.86	0.83	0.61	1.00											
Fe	0.97	0.99	0.84	0.95	0.79	1.00	0.58	0.83	1.00										
Co	0.42	0.41	0.39	0.45	0.19	0.40	0.35	0.25	0.37	1.00									
Ni	0.87	0.87	0.80	0.88	0.72	0.87	0.63	0.73	0.86	0.38	1.00								
Cu	0.91	0.91	0.80	0.89	0.77	0.92	0.60	0.76	0.90	0.48	0.83	1.00							
Zn	0.46	0.44	0.30	0.37	0.38	0.42	0.27	0.45	0.37	0.37	0.31	0.50	1.00						
Pb	0.43	0.44	0.61	0.47	0.29	0.47	0.42	0.46	0.50	0.14	0.42	0.45	−0.12	1.00					
Br	0.07	−0.01	0.12	0.15	−0.20	0.01	0.08	−0.14	−0.04	0.37	0.13	0.12	0.23	−0.25	1.00				
Cl	0.20	0.12	0.08	0.25	−0.03	0.14	−0.15	0.01	0.10	0.28	0.11	0.18	0.24	−0.09	0.63	1.00			
Rb	0.71	0.71	0.44	0.67	0.71	0.74	0.28	0.63	0.73	0.21	0.64	0.68	0.25	0.15	0.07	0.21	1.00		
Sr	0.94	0.96	0.82	0.92	0.80	0.95	0.58	0.80	0.95	0.41	0.84	0.92	0.35	0.48	0.05	0.20	0.74	1.00	
Na	0.58	0.52	0.49	0.61	0.29	0.51	0.27	0.34	0.47	0.50	0.44	0.56	0.54	0.08	0.60	0.81	0.40	0.52	1.00

Sodium (Na) on both locations has low and/or moderate correlations with most of the quantified elements except Cl, whereas there is a strong correlation between Na and Cl in both locations which indicates the sea spray sources. Low negative and positive correlations were found between Co and other elements in most of the quantified elements at the two sites. Perfect and strong positive correlations ranging from 1 to 0.70 were found for most of the crustal elements, namely; Al, Ca, Fe, K, Mn, Si, and Ti. The correlation of sulfur (S) with other elements at the two sampling locations is completely different. In the historical Jeddah district, S has strong correlations with most crustal elements and anthropogenic elements, namely; Ca, Cu, Fe, K, Mn, Na, Ni, Sr, Ti, Pb, and V. The strong correlation of S with the anthropogenic elements such as Cu, Ni, and Pb could have originated from the different mobile and stationary sources like trucks, cars, and power plants. However, S has only strong correlations with V, Ni, Ta, and Na in Alnaeem district, and these elements are mostly produced from oil combustion and sea spray. Therefore, it seems that S in the current two sites has different anthropogenic origins rather than just oil combustion at each site. The same behavior was found for Pb, whereas it has moderate correlations with all elements except S whereas there is a strong correlation between Pb and S at historical Jeddah. At the Alnaeem location, Pb has low correlations with all elements without exception. Therefore, Pb has also different origins at both locations and stays in the atmosphere for a long time. These sources are the industrial processes, coal, and

oil combustion. The correlation coefficients of the seasons of the year illustrate a strong correlation between the different seasons, Table 5. However, the lowest correlation was found between the winter and summer seasons whereas the winter season is characterized low dispersion of the mass concentration of the $PM_{2.5}$ aerosols.

Table 4. The correlation coefficients of Pearson between the quantified elements in the $PM_{2.5}$ samples assembled from Alnaeem site.

	Al	Si	S	K	Ca	Ti	V	Mn	Fe	Co	Ni	Cu	Zn	Pb	Br	Cl	Rb	Sr	Na
Al	1.00																		
Si	0.99	1.00																	
S	0.25	0.20	1.00																
K	0.94	0.97	0.15	1.00															
Ca	0.70	0.76	0.01	0.88	1.00														
Ti	0.88	0.92	0.08	0.98	0.94	1.00													
V	0.51	0.48	0.87	0.48	0.36	0.42	1.00												
Mn	0.89	0.93	0.06	0.97	0.91	0.99	0.40	1.00											
Fe	0.88	0.92	0.06	0.97	0.93	1.00	0.41	1.00	1.00										
Co	-0.03	0.02	−0.04	0.01	0.17	0.05	−0.15	0.11	0.08	1.00									
Ni	0.74	0.75	0.50	0.81	0.75	0.79	0.67	0.77	0.79	0.13	1.00								
Cu	0.76	0.80	0.19	0.86	0.84	0.87	0.58	0.88	0.88	0.01	0.80	1.00							
Zn	0.62	0.64	0.25	0.75	0.76	0.79	0.49	0.72	0.75	−0.18	0.68	0.77	1.00						
Pb	0.08	0.08	−0.01	−0.02	−0.08	−0.01	−0.08	−0.01	−0.02	−0.15	−0.05	−0.01	0.04	1.00					
Br	0.66	0.70	0.06	0.75	0.73	0.77	0.47	0.82	0.81	−0.01	0.63	0.86	0.49	−0.29	1.00				
Cl	0.48	0.51	−0.05	0.65	0.83	0.73	0.22	0.63	0.69	−0.10	0.56	0.61	0.79	0.08	0.36	1.00			
Rb	0.50	0.54	0.09	0.71	0.86	0.74	0.42	0.67	0.72	0.00	0.76	0.72	0.67	−0.30	0.61	0.82	1.00		
Sr	0.72	0.78	0.04	0.89	0.99	0.95	0.40	0.93	0.95	0.13	0.76	0.86	0.75	−0.10	0.79	0.79	0.84	1.00	
Na	0.39	0.39	0.43	0.45	0.43	0.45	0.41	0.34	0.38	−0.15	0.48	0.30	0.75	0.33	−0.09	0.63	0.39	0.40	1.00

Table 5. The correlation coefficients of Pearson between the seasons of the year in the $PM_{2.5}$ samples from historical Jeddah site.

Seasons	Autumn 2019	Winter 2019/20	Spring 2020	Summer 2020
Autumn 2019	1.00			
Winter 2019/20	0.96	1.00		
Spring 2020	0.97	0.88	1.00	
Summer 2020	0.89	0.75	0.89	1.00

3.3.3. Source Identification Using Principal Component Analysis (PCA)

The source identification could be explored from the relation between the quantified elements in the $PM_{2.5}$ aerosols. The principal component analysis (PCA) was applied to reduce the number of variables (the quantified elements) into a few components that explain the origins and the relationship among the quantified elements. The principal components are the eigenvectors of the data's covariance matrix. Figure 10 illustrates the relationship between the total variance (%) versus the principal components for the quantitative elemental analysis of the $PM_{2.5}$ assembled from the historical Jeddah and Alnaeem sites. For the separation of the component, the total variance of the analysis is based on Varimax rotation and Kaiser normalization. Tables 6 and 7 show the contribution of each element in the component matrix for both sites. At the historical Jeddah site, five

components explain 84% of the total variance of the analysis. The first component represents ~53% of the total variation and it refers mostly to the natural sources of the earth's crust elements. Most of the quantified elements contribute to the natural origins except Ta, Br, Cl, Y, and Sc which originate from marine, shipyard, and oil industry. Also, the elements Co, Zn, Pb, and Na have mixed natural and anthropogenic origins whereas they have a moderate contribution to the first component. The second component represents 12% of the variation and it represents the sea spray sources whereas Na, Br, and Cl are the main contributors, Table 6. The third component represents ~8% of the variation and it could be originated from traffic-related air pollution such as the combustion of heavy fuel oils and vehicle exhausts. A moderate and low contribution of the elements S, K, V, Co, Ni, Pb, and Br represent the main source, Table 6. The elements S, Co, Ni, and Pb could be released into the atmosphere from the traffic with diesel-fuelled vehicles. The fourth and fifth components represent 7% and 5%, respectively. They represent the mixed origins between the natural, anthropogenic, and sea spray sources.

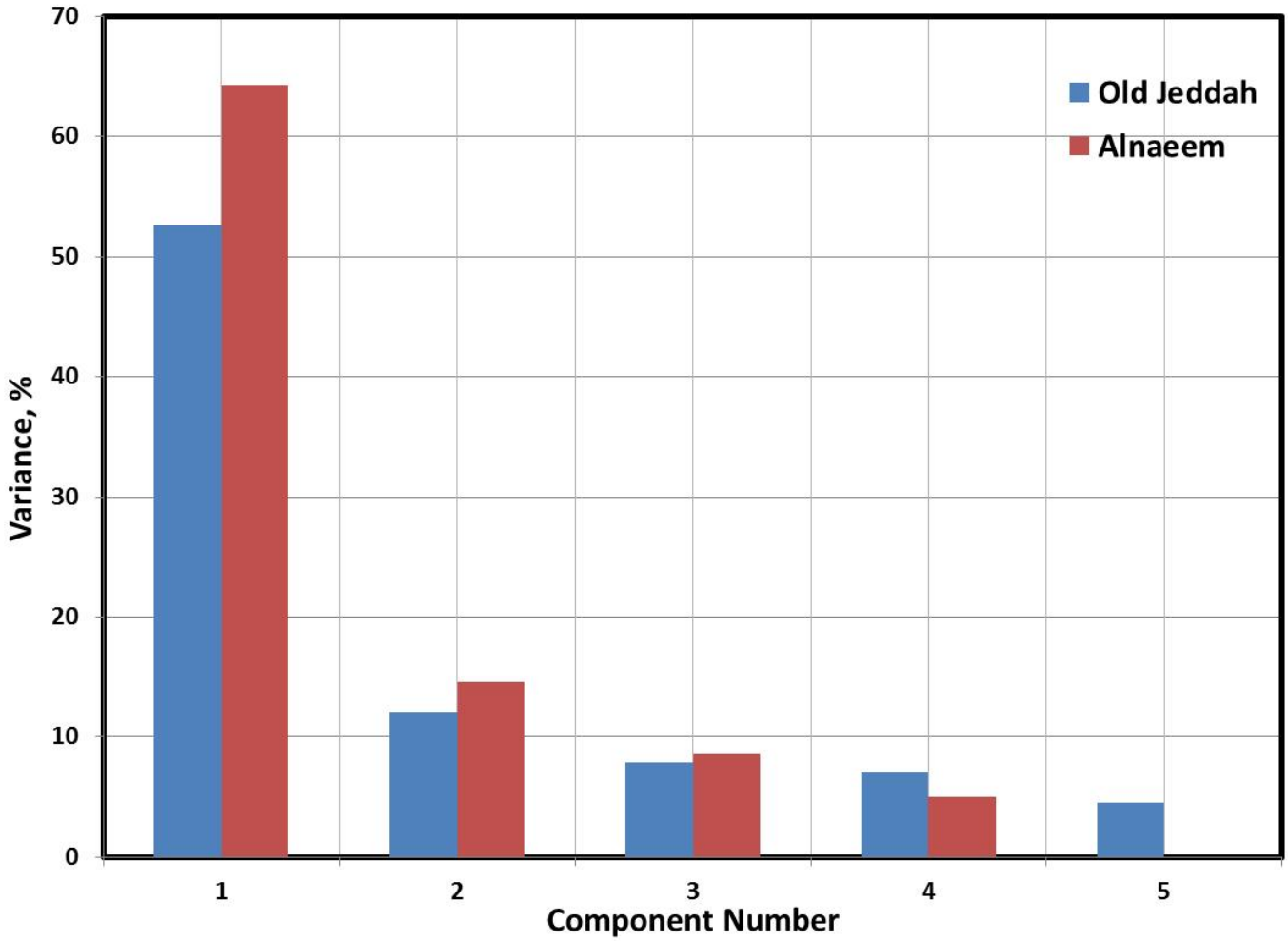


Figure 10. Relationship between the total variance (%) versus the components for the quantitative elemental analysis of the $PM_{2.5}$ assembled from the historical Jeddah and Alnaeem sites.

For comparison, four components represent 93% of the total variance of the analysis at Alnaeem district, Figure 10, and Table 7. The first component approximately equals 64% of the total variation and it indicates to the natural sources of the earth's crust elements, sea spray and fuel combustion, and oil industry. The sources of Br, Cl and Na originates mainly from the marine and sea spray sources where S, V, Ta, Y originates from fuel combustion and oil industry. The second component represents ~15% of the variation and it originates

mainly from anthropogenic sources including, alloy smelters, vehicle exhausts, and oil and coal combustions. The main contributed elements for the second components are S, V, Co, Ni, Zn, Ta, and Pb, Table 7. The third component represents ~9% an originates from other anthropogenic sources such as mining activities, power plants, metal production, mineral production, manufacturing industries, and construction. The main contributed elements for the third component are Al, Si, S, V, Mn, Fe, Co, Cu, and Br. The fourth component represents 5% and it could refer to the sea spray, power plants, and the released smoke from automobile exhausts. The contributed elements for the fourth component are Al, Ca, V, Co, Cu, Zn, Br, and Cl.

Table 6. Five components matrices for the quantified elements in $PM_{2.5}$ collected from historical Jeddah site.

	Component Matrix				
	1	**2**	**3**	**4**	**5**
Al	0.983	0.009	−0.040	0.041	0.002
Si	0.972	−0.068	−0.063	−0.004	−0.002
S	0.878	−0.114	0.326	0.086	−0.099
K	0.965	0.029	0.135	0.128	0.008
Ca	0.820	−0.210	−0.397	−0.061	0.074
Ti	0.980	−0.074	−0.046	0.050	0.037
V	0.669	−0.207	0.300	−0.083	0.093
Mn	0.856	−0.197	−0.236	−0.019	−0.090
Fe	0.968	−0.128	−0.035	0.057	0.028
Co	0.448	0.404	0.313	−0.478	−0.125
Ni	0.887	−0.060	0.064	0.105	0.133
Cu	0.944	0.045	−0.006	−0.088	0.030
Zn	0.453	0.451	−0.334	−0.395	−0.147
Ta	−0.216	−0.116	0.191	0.753	0.383
Pb	0.482	−0.430	0.282	0.157	−0.435
Br	0.091	0.801	0.337	0.148	0.194
Cl	0.191	0.838	0.003	0.341	−0.122
Rb	0.718	0.040	−0.339	0.124	0.384
Sr	0.960	−0.045	−0.014	0.057	0.018
Y	0.082	−0.012	0.367	−0.602	0.588
Na	0.584	0.734	0.049	0.139	−0.131
Sc	0.154	−0.214	0.780	−0.018	−0.127

Table 7. Four components matrices for the quantified elements in $PM_{2.5}$ collected from Alnaeem district.

	Component Matrix			
	1	**2**	**3**	**4**
Al	0.885	−0.045	0.226	−0.294
Si	0.903	−0.070	0.211	−0.287
S	0.551	0.653	0.468	0.139
K	0.962	−0.124	0.070	−0.134
Ca	0.932	−0.245	−0.165	0.067
Ti	0.966	−0.179	−0.027	−0.101
V	0.754	0.294	0.387	0.149
Mn	0.938	−0.229	0.099	−0.159
Fe	0.955	−0.227	0.031	−0.123
Co	−0.372	0.118	0.698	0.334
Ni	0.924	0.019	0.096	−0.023
Cu	0.910	−0.144	0.186	0.083
Zn	0.862	0.235	−0.197	0.349
Ta	0.709	0.689	0.006	0.003
Pb	−0.045	0.640	−0.255	−0.610
Br	0.725	−0.522	0.294	−0.034
Cl	0.730	−0.044	−0.597	0.223
Rb	0.812	−0.310	−0.303	0.281
Sr	0.937	−0.266	−0.115	0.036
Y	−0.717	−0.681	0.008	−0.011
Na	0.580	0.677	−0.362	0.163

4. Conclusions

The present work confirms the elevation of the total mass concentration of $PM_{2.5}$ at two sites in Jeddah where ~80% of the collected $PM_{2.5}$ samples was higher than the maximum allowance level of the air quality standards of WHO and the European commission. Based on the quantified elements in the $PM_{2.5}$ aerosols assembled from the historical Jeddah and Alnaeem districts in Jeddah, the historical Jeddah district (downtown of the city) had a low level of mass concentrations for the most quantified elements. Therefore, Jeddah has a low level of air pollution compared with the other location (Alnaeem). The statistical analysis revealed that significant, very high, and extremely high values of the enrichment factors were found for the elements Ca, V, Co, Cl, S, Zn, Cu, Ni, Sc, Pb, Br, and Ta which indicates the anthropogenic origins of these elements. The elements Cl and Br originate from the marine, seawater spray, and seagoing ships. The main anthropogenic sources of other elements could be traffic emissions, fuel combustion, oil refinery, and non-ferrous metal production (cement industry). Based on Pearson's coefficients calculations, the correlations between the quantified elements are different from one location to another which indicates the different anthropogenic activities for the same element. In the case of the crustal elements (Al, Ca, Fe, K, Mn, Si, and Ti), there are perfect and strong positive correlations ranging from 1 to 0.70. The principal component analysis confirmed that the primary sources of the quantified elements are natural sources followed by multi-anthropogenic sources and sea spray. The remarkably high concentration of sulfur (S) at the Alnaeem site confirms the origins of the many anthropogenic sources, such as exhaust combustion from

vehicles, power plants, and petroleum refineries. More attention should be considered to Ni as the average concentrations of Ni in both sides are higher than the annual value of air quality standards.

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