

Elemental Variability of PM 2.5 aerosols in Old Jeddah, Saudi Arabia

Abdallah A. Shaltout (✉ shaltout_a@hotmail.com)

National Research Centre

Safaa S. M. Ali

National Research Centre

Dhaif-allah R. Al-Malawi

Taif University

Eman Alzahrani

Taif University

Research Article

Keywords: Fine atmospheric aerosols, Elemental analysis, old Jeddah, EDXRF, statistical analyses

Posted Date: June 21st, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1752240/v1>

License:  This work is licensed under a Creative Commons Attribution 4.0 International License. [Read Full License](#)

Abstract

Air particulate matter with a diameter $\leq 2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) has been assembled from the historical old Jeddah district (downtown) throughout the whole year. Additional $\text{PM}_{2.5}$ aerosols have been collected during the autumn and winter seasons from another newly constructed district inside Jeddah city (Alnaeem). The annual concentrations of the total mass of the $\text{PM}_{2.5}$ aerosols from old Jeddah and Alnaeem sites were found to be 43 ± 6 and $61 \pm 14 \mu\text{g}/\text{m}^3$, respectively. These values are greater than the annual mass concentration of the air quality standards of the European Commission (EC, $25 \mu\text{g}/\text{m}^3$) and the world health organization (WHO, $10 \mu\text{g}/\text{m}^3$). The elemental analysis of the collected fine atmospheric aerosols has been achieved by an energy dispersive X-ray fluorescence (EDXRF) with three secondary targets (CaF, Ge, and Mo). Quantitative elemental analyses of twenty-two (22) elements have been achieved starting from the low Z element (Na) up to the high Z element (Pb). Although the old Jeddah site is not well organized, the elemental concentrations and total mass concentrations are lower than other sites. The statistical analyses including enrichment factors, the correlation analysis of Pearson, and the principal component analysis reveal more information about the source identification of the $\text{PM}_{2.5}$ aerosols collected from both locations. It was recognized that the quantified elements Al, Si, K, Ca, Ti, Mn, Fe, Rb, and Sr originate from a natural source. On the other hand, the elements Ta, Br, Pb, Sc, Ni, Cu, Zn, and S originate from anthropogenic source. Finally, the elements Na, Cl, and Br come mainly from the sea spray source.

1. Introduction

The intensification of anthropogenic sources of air pollution and other natural sources has a great concern on the air quality. There are negative effects of air pollution on human health, animals, plants, ecosystems, and global warming (Bascom et al., 1996; Bytnerowicz, Omasa, & Paoletti, 2007; Ramanathan & Feng, 2009). Based on the indoor and outdoor air pollution data, the annual premature deaths were found to be 3.7 and 4.3 million, respectively (WHO, 2014). Among the different criteria of air pollution, the atmospheric particulate matters represent the most important air pollutant especially the fine and ultrafine air particulates which are related to cardiovascular mortality and respiratory diseases (Heo et al., 2014; Ostro et al., 2010; Zeger, Dominici, McDermott, & Samet, 2008). Based on many epidemiological studies, the mass concentration of the fine particulate matter is proportional to the appearance of harmful and adverse diseases (Elmes & Gasparon, 2017; Pope 3rd, 2000; Silva et al., 2013). Fine particulate matter with a diameter equal to or less than $2.5 \mu\text{m}$ ($\text{PM}_{2.5}$) has gained a lot of attention in the literature because it can stay a long time in the atmosphere and travel thousands of kilometers (Boman, Shaltout, Abozied, & Hassan, 2013; Shaltout, Almallwai, Shehadeh, & Boman, 2012; Shaltout, Boman, Al-Malawi, & Shehadeh, 2013; Shaltout et al., 2015; Shaltout et al., 2014). Long-term exposure to the $\text{PM}_{2.5}$ aerosols may drastically influence lung function and cause chronic bronchitis, heart disease, and lung cancer especially for the elderly and children (Calderón-Garcidueñas et al., 2016; Chi et al., 2019).

The source apportionments and the characterization of the $\text{PM}_{2.5}$ aerosols assembled from several cities in the Middle East have been demonstrated (Boman et al., 2013; Shaltout, Ahmed, Harfouche, Hassan, & Eid, 2019; Shaltout et al., 2012; Shaltout et al., 2013; Shaltout, Boman, et al., 2020; Shaltout et al., 2015; Shaltout et al., 2014; Shaltout, Harfouche, Ahmed, Czyzycki, & Karydas, 2018; Shaltout, Harfoushe, et al., 2020; Shaltout, Hassan, Alomairy, et al., 2018). 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 $\text{PM}_{2.5}$ samples gathered from the city. Besides, there is a remarkable lack of information about the compositions and the source apportionments of the $\text{PM}_{2.5}$ collected from Jeddah. The morbidity risk associated with the $\text{PM}_{2.5}$ exposure collected from three sites for six weeks in Jeddah has been evaluated for cardiovascular and respiratory diseases. Based on the model of generalized linear time-series, the relative risk for cardiopulmonary morbidity was evaluated (Nayebare et al., 2019). It was found that the children and females less than 14 years are the more at risk for respiratory diseases whereas the risk of cardiovascular morbidity was higher in males above 40 years. After leaded gasoline phase-out in the years of 2008 and 2009, the lead (Pb) was determined in $\text{PM}_{2.5}$ aerosols collected from four sites in Jeddah using inductively coupled plasma mass spectrometry (ICP-MS). Although the lead concentrations in the $\text{PM}_{2.5}$ samples were considerably decreased, its concentration increased in the areas of high traffic density as well as those of industrial activities. Besides, the average concentration of lead was found to be $73.3 \text{ ng}/\text{m}^3$ (Aburas, Zytoon, & Abdulsalam, 2011). At fifteen elementary schools in south and north of Jeddah, the influence of schoolchildren's exposure to the mass concentration of outdoor and indoor $\text{PM}_{2.5}$ aerosols has been demonstrated. The indoor/outdoor ratios of the $\text{PM}_{2.5}$ aerosols were found to be 1.52, 1.63, and 1.59. High mass concentration was found in schools of south Jeddah whereas the $\text{PM}_{2.5}$ mass concentration was found to be $35.85 \mu\text{g}/\text{m}^3$. It was recognized that the indoor mass concentration of the $\text{PM}_{2.5}$ samples increased in presence of students and its average mass value was $25.42 \mu\text{g}/\text{m}^3$. Moreover, 100% of the $\text{PM}_{2.5}$ mass concentration exceeds the annual mean values of WHO and it has a great influence on schoolchildren (Alghamdi, 2013). Ultrafine and fine atmospheric aerosols ($\text{PM}_{0.5-0.25}$ and $\text{PM}_{2.0-1.0}$) 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. They found that the Cr species are mostly trivalent oxidation states whereas Mn species existed in divalent and trivalent oxidation states (Shaltout, Harfouche, et al., 2018). The elemental compositions and the source apportionments of PM_{10} and $\text{PM}_{2.5}$ sampled from different sites in Jeddah were investigated. An energy dispersive X-ray fluorescence (EDXRF) was utilized for the quantitative elemental analysis whereas the source apportionment was estimated using factor analysis. The main sources of the PM_{10} and $\text{PM}_{2.5}$ samples were found to be mainly from heavy oil combustion and soil dust as well as other secondary origins like industrial activities and vehicular emission sources (Khodeir et al., 2012). The concentration of the natural radioactivity and the associated internal inhalation effective dose of ^{40}K , ^{232}Th , ^{238}U , and Ra_{eq} were determined in $\text{PM}_{2.5}$ aerosols collected from four different locations in Jeddah. It was found that the effective inhalation dose in the $\text{PM}_{2.5}$ aerosols is greater than the world reference values in the air (Zytoon, Aburas, & Abdulsalam, 2014). Temporal variations including the seasonal and weekday/weekend variations of the total mass concentration, elemental contents, and source apportionments of PM_{10} and $\text{PM}_{2.5}$ and collected from Jeddah have been investigated. The main sources of the $\text{PM}_{2.5}$ samples were mainly the oil burning from oil refineries and road/soil dust (Lim et al., 2018).

The characterization of the $\text{PM}_{2.5}$ samples assembled from the oldest and historic district of Jeddah city (Old Jeddah), Saudi Arabia is the aim of the present study. The old Jeddah district represents the core of the city. The sampling area is characterized by several non-organized alleyways and the widths of the

roads are inconsistent. Also, the sampling area is closed to the sewer station and the coast of the Red Sea. To demonstrate the variance of air quality between the oldest and the modern districts of Jeddah, additional PM_{2.5} samples were collected from modern constructed sites (i.e. Alnaeem district). The elemental analysis of the collected fine particulate matter (PM_{2.5}) from the two sites has been carried out using multi-secondary target energy dispersive X-ray fluorescence spectrometry (EDXRF). In the present PM_{2.5} samples, CaF, Ge, and Mo secondary targets were used to cover the low, medium, and high Z elements, respectively. 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 source identification was discussed using different statistical tools including the principal components analysis, enrichment factors, and Pearson's correlation coefficients.

2. Experimental Setup

2.1. PM_{2.5} sampling

The PM_{2.5} sampling was carried out in Jeddah city, on the west coast of the Red Sea, Saudi Arabia. Jeddah is considered the most commercial area in the country. Also, it represents the second important location whereas it has the main airport and seaport of the country. The total population of Jeddah is estimated to be 3.58 million citizens (Nayebare et al., 2019). Over the last three decades, the development of the city was rapidly and severely in the field of building and manufacturing including an oil refinery, wastewater treatment, plants desalination, automobile fuels, metal industries, urbanization activities, and power plants. Also, other natural sources of air pollution could be found in Jeddah such as desert storms and soil erosion. Therefore, these natural and anthropogenic sources of air pollution could have resulted in environmental degradation and the air quality increasingly deteriorated. The PM_{2.5} samples have been collected from the roof of a residential area of the oldest and historic location of Jeddah "the old Jeddah" which historically served as the core of the city. Besides, the intensity of the population of the sampling location is relatively high comparing with other districts in the city. The sampling area is nearby to the seaport and shipyard of the city. Additional industrial activities are also close to the sampling location such as oil refinery, wastewater treatment, the industrial areas of the city, and power plants. It is located at a longitude of 39° 11' 15.9" N and latitude of 21° 29' 15.3" E. For comparison study, the limited number of PM_{2.5} samples have been sampled during winter and autumn seasons from the recently constructed district "Alnaeem" (longitude: 39°11'15.9" and latitude: 21°29'15.3") using the same procedure. The sampling locations are approximately 60 m above sea level to keep away from the direct influence of the road traffic. Figure 1 illustrates the sampling sites of the present work. One PM_{2.5} sample was collected every week for 24 h in the period from September 2014 to August 2015 covering the whole year. 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} collection. The present flow rate is optimized to achieve a particle with a diameter of 2.5 µm.

2.2. Instrumentation

An energy dispersive X-ray fluorescence spectrometry (EDXRF, Epsilon 5, PANalytical, Netherlands) with CaF, 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 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. Further information about the present EDXRF setup, limits of detection, and calibration curves of the quantified elements were illustrated elsewhere (Shaltout et al., 2019; Shaltout, Harfoushe, et al., 2020; Shaltout, Hassan, Alomairy, et al., 2018; Shaltout, Hassan, Karydas, et al., 2018; Shaltout, Hassan, et al., 2018).

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, 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 (Shaltout et al., 2019; Shaltout, Harfoushe, et al., 2020; Shaltout, Hassan, Alomairy, et al., 2018; Shaltout, Hassan, Karydas, et al., 2018; Shaltout, Hassan, et al., 2018).

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 old Jeddah site, the total mass concentration of the PM_{2.5} samples varied from 12 to 85 µg/m³ with an annual average of 42.5 ± 13.3 µg/m³. The individuals and the annual mass concentration of the PM_{2.5} samples exceed the annual mass concentration proposed by the world health organization (WHO) which is equal to 10 µg/m³ (WHO, 2006). However, 80% of the individual mass concentration of the present PM_{2.5} samples exceeds the 24 hours mean value of the WHO and the annual mean values of the European commission of air quality (25 µg/m³) (EU, 2019). For comparisons, additional PM_{2.5} samples were assembled from another site (Alnaeem district) which illustrates a high mass concentration and it varies from 19 to 135 µg/m³ with an average of 61 ± 14.6 µg/m³. Figure 2 illustrates the monthly variation of the mass concentration of the PM_{2.5} samples collected from old Jeddah and Alnaeem districts. Remarkable high standard deviations were found at Alnaeem district especially during the autumn months. Also, the

PM_{2.5} samples collected from the old Jeddah district during the spring have high standard deviations. At old Jeddah district, the highest mass concentration of the PM_{2.5} aerosols was found to be 54 ± 10 µg/m³ and 53 ± 3 µg/m³ during winter and spring seasons, respectively, Fig. 2. The high mass concentration of the PM_{2.5} aerosols in winter and spring could refer to the low wind speed and consequently the low atmospheric dispersion as well as the increase of the local burning activities.

The lowest mass concentrations of the PM_{2.5} samples were found during the months of the autumn (from September to November 2014), Figs. 2 and 3. The percentages of the individual mass concentration of the PM_{2.5} were depicted in Fig. 4. It was clear that about 95% of the collected PM_{2.5} samples from old Jeddah and Alnaeem districts is higher than the annual mean values of WHO, and 80% of them are also higher than the 24-hour values of WHO and the annual mean values of the European commission for air quality (EU, 2019; WHO, 2006). This illustrates that there is a remarkable challenge to decrease the mass concentration of the PM_{2.5} samples collected from old Jeddah and Alnaeem districts. However, only 10% of the total mass concentration of the PM_{2.5} samples collected from old Jeddah districts is higher than 60 µg/m³, Fig. 4. On the other hand, the old Jeddah district has a low mass concentration when comparing with the second location (Alnaeem). This could be due to the low density of the traffic inside the old Jeddah district as well as the decreasing of the number of inhabitants in the old Jeddah district whereas many residents prefer to move to the modern and new districts.

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. 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 old Jeddah is comparable with the previous work of Zytoon (Zytoon et al., 2014) and Aburas (Aburas et al., 2011). However, it seems to be higher than the values given by the others (Alghamdi, 2013; Khodeir et al., 2012; Lim et al., 2018). This present output result reflects the similarity and variability of the mass concentrations of the PM_{2.5} samples which depends on the nature of 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 of 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, µg/m ³	Location Nature
Present Work	Jeddah	2014/2015	42.5 ± 6.4	Residential (Old Jeddah)
			60.7 ± 14.4	Residential (Alnaeem)
WHO	10			Annual mean value
European Commission	25			Annual mean value
Aburas et al. (Aburas et al., 2011)	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 (Alghamdi, 2013)	Jeddah	2013	24.76 ± 8.71	South of Jeddah
			13.13 ± 3.65	North of Jeddah
Khodeir et al. (Khodeir et al., 2012)	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 (Zytoon et al., 2014)	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 (Lim et al., 2018)	Jeddah	2011/2012	21.9 ± 11.6	Residential

3.2. Elemental Analysis of PM_{2.5} Samples

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 CaF₂ secondary target. In this case, the low Z elements up to K (Z = 19) could be covered. Figure 5 illustrates an example of the XRF spectra of the low Z elements whereas the elements Al, Cl, K, Na, S, and Si can be identified. 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), Fig. 6. 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. One could recognize the L lines of W (L_{α1} = 8.398 keV, L_{α2} = 8.335 keV, L_{β1} = 9.672 keV, and L_{β2} = 8.398 keV) which originates mainly from the target of the X-ray tube, Fig. 7. According to the XRF spectra given by Figs. 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, Table 2 presents the minimum, maximum, and annual mean values for the elemental concentration in ng/m³ measured in the PM_{2.5} samples collected from old Jeddah and Alnaeem districts. The available air quality standard values of Pb and Ni were also presented in Table 2. Based on the elemental analyses of most elements illustrated in Table 2, the old Jeddah site has concentrations lower than the concentrations found at Alnaeem district. This indicates the low air pollution at the old Jeddah location in terms of elemental analysis. Also, the total mass concentration of the quantified elements represents 17.4% and 43% at old Jeddah and Alnaeem sites, respectively, Table 2. Therefore, the old Jeddah site has low concentrations of inorganic pollutants and high concentrations of volatile organic compounds (VOCs) in the PM_{2.5} samples. The situation is completely different in the Alnaeem district whereas the total mass concentration of the elements reaches 43%.

In the case of nickel (Ni), the average values observed in old Jeddah (25.8 ± 2.6 ng/m³) and Alnaeem (27.1 ± 3.4 ng/m³) districts are higher than the annual mean values of the air quality standards given by the European Commission (20 ng/m³). In addition, the individual quantitative analysis results of Ni in both locations 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. The release of Ni and its compounds in the atmosphere was originated from industrial and commercial activities. As the nickel (Ni) level in the atmosphere is higher than the maximum allowance level, it could have toxicity, carcinogenicity, and pathological effects (Cempel & Nikel, 2006; Haber et al., 2000).

In the case of Pb, the daily concentrations in the old Jeddah district vary from 4 to 232 ng/m³ and all of these values are less than the annual mean values of the European Commission (500 ng/m³). 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 has a concentration of 1177 ng/m³. However, the annual mean values of Pb at old Jeddah and Alnaeem districts are generally less than the annual mean values of air quality (500 ng/m³) and it equals 55 ± 70 and 371 ± 305 ng/m³, respectively.

The low concentration of Pb on both sides indicates the use of unleaded gasoline (Aburas et al., 2011). 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 old 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 and volcanic eruptions. It was recognized that the annual concentrations of these elements at Alnaeem district are always higher than their concentrations at the old Jeddah district. The concentrations of Si, K, and Fe at Alnaeem district are 4–6 times higher than that found at the old 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 old Jeddah district has a low level of inorganic pollutants comparing with the new districts of the city whereas the average values of the total mass concentration of the PM_{2.5} in old Jeddah are always lower than that found at Alnaeem district. In the case of Na and Cl, the average concentration of Cl is always higher than the average concentration of Na and which is in agreement with the literature (Rossby & Egnér, 2016; Thimonier, Schmitt, Waldner, & Schleppe, 2008).

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

El.	Old Jeddah District (S1), ng/m ³			Alnaeem district (S2), ng/m ³			Air Quality Standards
	Min.	Max.	Mean	Min.	Max.	Mean	
Na	65.1	1246.6	322.4 ± 292.8	121.9	916.9	394.0 ± 364.9	
Al	18.3	4819.0	830.4 ± 980.6	692.7	7993.5	3249.4 ± 2909.7	
Si	122.9	8424.6	1528.4 ± 1792.7	2177.6	15418.4	6597.8 ± 5256.3	
S	50.3	4128.5	980.0 ± 1015.8	404.0	4669.3	2665.2 ± 1092.0	
Cl	1.2	3584.4	832.0 ± 958.8	27.1	5256.5	1060.2 ± 1523.2	
K	6.9	1599.1	316.8 ± 321.3	591.4	2690.0	1193.2 ± 737.9	
Ca	46.2	6342.3	1777.3 ± 1598.8	1279.3	19787.1	7065.5 ± 5633.8	
Sc	1.8	31.6	11.3 ± 9.2	6.4	6.4	6.4 ± 0	
Ti	4.5	285.9	53.7 ± 61.3	102.4	755.5	289.5 ± 217.1	
V	0.0	23.0	6.8 ± 6.0	0.9	23.1	12.9 ± 7.6	
Mn	0.4	58.2	14.8 ± 15.3	22.6	197.6	82.4 ± 62.9	
Fe	12.4	2880.8	577.7 ± 663.5	1167.3	8880.5	3554.0 ± 2687.9	
Co	0.0	3.8	1.6 ± 1.1	0.0	6.0	2.6 ± 2.0	
Ni	22.2	35.0	25.8 ± 2.6	21.3	33.5	27.1 ± 3.3	20
Cu	11.5	33.2	15.7 ± 4.2	15.9	46.5	25.3 ± 10.2	
Zn	4.3	37.4	15.7 ± 12.3	3.6	107.2	28.0 ± 29.1	
Br	1.6	12.1	6.1 ± 2.5	2.3	36.6	10.7 ± 10.2	
Rb	0.1	6.2	1.7 ± 1.6	1.9	6.6	3.6 ± 1.4	
Sr	0.1	31.5	7.1 ± 6.9	9.5	84.4	32.7 ± 23.9	
Y	0.3	2.7	1.1 ± 0.7	0.7	1.2	0.9 ± 0.3	
Ta	0.0	31.6	14.9 ± 7.4	8.1	19.2	13.6 ± 7.8	
Pb	3.5	231.8	55.0 ± 69.9	14.8	1176.8	370.6 ± 304.7	500
Σ El.			7.40			26.74	
PM _{2.5}			42.49			60.74	
%			17.41			43.93	

The source of Cl on both sides is mainly from the sea spray and this could be expected whereas the annual 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 could be varied from 0.5 to 1.5 (Thimonier et al., 2008). Figure 8 shows the obtained seasonal Na/Cl ratios of the present work. At the old 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, Fig. 8. The highest value of the Na/Cl ratios was found in winter whereas the Na/Cl ratios of the other seasons are comparable, Fig. 8.

Furthermore, the elements Mn, V, and Co originate 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, iron ores, and steel industries (Moreno et al., 2011). Additional natural sources include the soil dust from wind erosion and suspensions of soils are also expected. The average values of Mn equal 14.8 ± 15.3 and 82.4 ± 63 ng/m³ at old Jeddah and Alnaeem locations, respectively. Mn increased 6 times at the Alnaeem site which indicates the traffic source. The annual mean value of Mn in old Jeddah is comparable with that found in Germany (Georgii & Muller, 1974). The average value of Mn found in the Alnaeem district is also comparable with that reported in Belgium (Kretzschmar, Delespaul, & de Rijck, 1980). The toxicity of Mn could depend on its oxidation states (Mn²⁺, Mn³⁺, and Mn⁴⁺) whereas the Mn²⁺ and Mn³⁺ oxidation states have a neurotoxic effect (Aschner & Aschner, 1991; Gavin, Gunter, & Gunter, 1990). Fortunately, a low concentration of Co was found at old Jeddah and Alnaeem locations (< 2.6 ng/m³) and it originates from the vehicular exhaust and the different industrial activities such as coal combustion and waste incineration. The high concentration of Co may cause health problems such as heart problems and Thyroid damage (Barceloux, 1999). The low concentration of Co at the old Jeddah site refers to the low traffic density. In the case of vanadium (V), it originates in the atmosphere mainly from anthropogenic sources such as petroleum refineries, steel industry, heterogeneous catalysts, and seagoing ships (Visschedijk, Denier

van der Gon, Hulskotte, & Quass, 2013). However, V also could be emitted into the atmosphere from natural sources whereas its concentration in the earth's crust reaches $100 \mu\text{g g}^{-1}$ (Schaller, 1994). It was also observed that the concentration of V at the Alnaeem location is twice its value at the old Jeddah location.

In the case of Sulfur (S), the highest concentration was found at Alnaeem district and it reaches 4669 ng/m^3 . The mean concentration of S at the Alnaeem location is four times higher than that found at the old Jeddah site. As mentioned earlier, the old Jeddah site has low traffic density whereas the Alnaeem location has high traffic density and close to oil refinery activities. Although sulfur is mainly released in the atmosphere from various anthropogenic sources such as oil and coal combustion, petroleum refineries, and smelting of non-ferrous ores, it also releases in the atmosphere from other natural sources such as biogenic and non-biogenic sources (geothermal emission, volcanoes, and sea spray) (Andreae, 1986; Cullis & Hirschler, 1980). Looking at Cu and Zn, there is a remarkably low concentration of these elements on the old 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 and these elements are Sc, Ti, Br, Rb, Sr, Y, and Ta. The average concentration of these elements, except Ti and Sr, in both sites, is 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 old Jeddah site. The scandium is rare in the earth's crust and exists as a trace in different minerals. 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 (Barksdale, 1966). 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 could be explained the origins of the anthropogenic activities on the quality of the atmosphere. The quantified elements naturally exist in the earth's crust and are crucial for humans, animals, and plants. The additional concentration of these elements could be released into the environment due to the different anthropogenic sources such as; industrial wastes, sewage sludge, and fertilizer impurities. As the concentration of these elements is equal to or less than its concentration in the earth's crust, it gives a clear indication of the natural sources. On the other hand, if the concentration of these elements is higher than its concentration in the earth's crust, it indicates anthropogenic origins. Therefore, the excess concentration of these elements in the earth's crust usually causes adverse effects on humans, animals, and plants and might have a different degree of toxicity. For a reference crustal element Y and element X, the enrichment factor for the element X is given by,

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

Where (X/Y) is the concentration ratio of X and Y elements in the $\text{PM}_{2.5}$ aerosols or the earth's crust, respectively. Additional details about the enrichment factors could be found elsewhere (Barbieri, 2016; Bern, Walton-Day, & Naftz, 2019; Iqbal & Shah, 2015; Sukri et al., 2018). The reference crustal element (Y) is usually stable in the soil with natural origins and is used to normalizing its concentration in the $\text{PM}_{2.5}$ aerosols. Aluminium (Al) has been selected as a reference element (Y) and it was previously considered as a conservative and low occurrence variability element (Ketterer, Lowry, Simon Jr, Humphries, & Novotnak, 2001; Schropp et al., 1990; Uduma, 2014; Yang et al., 2010). The chemical composition of the earth's crust was provided by Wedepohl (Hans Wedepohl, 1995). Figure 9 depicts the relationship between the annual mean values of the EFs versus the quantified elements in the $\text{PM}_{2.5}$ samples collected from the present two locations. If the values of the EFs 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 EFs 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 EFs are less than 2 ($EFs < 2$). The elements Fe, Ti, Rb, and Na quantified at the old Jeddah site have a natural origin with minimal enrichment values less than 2.

The moderate enrichment exists as the EFs range from 2 to 5 and this was found for Sr, Mn, and Y as illustrated in Fig. 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 originate from man-made sources. The high EF values of S, Cu, Zn, Ni, and Pb suggest the influence of traffic emissions, extensive mining, non-ferrous metal production, marine, fossil fuel combustion, and incinerator emissions (Aksu, 2015; Deboudt, Flament, & Bertho, 2004; Khodeir et al., 2012; Suvarapu & Baek, 2017).

3.3.2. Correlation Coefficients

As the elemental analysis of $\text{PM}_{2.5}$ aerosols was carried out for different seasons, sites, and elements, the interrelationship of the quantified elements and the sampling seasons was explored by Pearson's correlation coefficients. Therefore, the influence of the latent factors could be demonstrated. The calculations of Pearson's correlation coefficients were carried out in terms of the variations of the quantified elements and the seasons of the year. The formula of the Pearson's correlation coefficients r_{xy} is given by,

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

Where \bar{x} exhibits the average value of i number of x 's and \bar{y} expresses the average value of i number of y 's. The correlation coefficient values (r_{xy}) could be varying from -1 to $+1$. 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 ($r_{xy}=0$). As the correlation coefficient values vary from ± 0.5 to ± 1 , it gives a strong positive or negative correlation.

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

	<i>Al</i>	<i>Si</i>	<i>S</i>	<i>K</i>	<i>Ca</i>	<i>Ti</i>	<i>V</i>	<i>Mn</i>	<i>Fe</i>	<i>Co</i>	<i>Ni</i>	<i>Cu</i>	<i>Zn</i>	<i>Pb</i>	<i>Br</i>	<i>Cl</i>	<i>Rb</i>	<i>Sr</i>	<i>Na</i>
<i>Al</i>	1.00																		
<i>Si</i>	1.00	1.00																	
<i>S</i>	0.85	0.83	1.00																
<i>K</i>	0.97	0.96	0.89	1.00															
<i>Ca</i>	0.81	0.83	0.58	0.72	1.00														
<i>Ti</i>	0.98	0.99	0.84	0.96	0.81	1.00													
<i>V</i>	0.60	0.59	0.79	0.62	0.54	0.58	1.00												
<i>Mn</i>	0.82	0.84	0.72	0.76	0.86	0.83	0.61	1.00											
<i>Fe</i>	0.97	0.99	0.84	0.95	0.79	1.00	0.58	0.83	1.00										
<i>Co</i>	0.42	0.41	0.39	0.45	0.19	0.40	0.35	0.25	0.37	1.00									
<i>Ni</i>	0.87	0.87	0.80	0.88	0.72	0.87	0.63	0.73	0.86	0.38	1.00								
<i>Cu</i>	0.91	0.91	0.80	0.89	0.77	0.92	0.60	0.76	0.90	0.48	0.83	1.00							
<i>Zn</i>	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						
<i>Pb</i>	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					
<i>Br</i>	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				
<i>Cl</i>	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			
<i>Rb</i>	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		
<i>Sr</i>	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	
<i>Na</i>	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

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

	<i>Al</i>	<i>Si</i>	<i>S</i>	<i>K</i>	<i>Ca</i>	<i>Ti</i>	<i>V</i>	<i>Mn</i>	<i>Fe</i>	<i>Co</i>	<i>Ni</i>	<i>Cu</i>	<i>Zn</i>	<i>Pb</i>	<i>Br</i>	<i>Cl</i>	<i>Rb</i>	<i>Sr</i>	<i>Na</i>	
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	

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 ($< \pm 0.3$). Tables 3 and 4 illustrate the correlation coefficient values between the different quantified elements at the current two locations.

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 old 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 be 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 at 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 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 old 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, and leaded gasoline. 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 by high energy consumption, high vehicle emission, and low dispersion of the mass concentration of the PM_{2.5}aerosols.

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

<i>Seasons</i>	<i>Autumn 2014</i>	<i>Winter 2014/15</i>	<i>Spring 2015</i>	<i>Summer 2015</i>
Autumn 2014	1.00			
Winter 2014/15	0.96	1.00		
Spring 2015	0.97	0.88	1.00	
Summer 2015	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 old Jeddah and Alnaeem sites. For the separation of the component, the total variance of the analysis is based on Varimax rotation and Kaiser Normalization. Table 6 shows the contribution of each element in the component matrix. At the old 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 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. 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.

For comparison, four components represent 93% of the total variance of the analysis at Alnaeem district, Fig. 10, and Table 7. The first component approximately equals 64% of the total variation and it indicates the natural sources of the earth's crust elements. Although the elements S, V, Ta, Br, Cl, Y, and Na have anthropogenic and sea spray sources but they have a moderate contribution to the natural sources at the first component. Other anthropogenic elements have no contribution to the first component namely; Co, Pb, and Y. 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% and 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 component matrix for the quantified elements in PM_{2.5} collected from old Jeddah site.

	Component Matrix				
	1	2	3	4	5
Al	.983	.009	-.040	.041	.002
Si	.972	-.068	-.063	-.004	-.002
S	.878	-.114	.326	.086	-.099
K	.965	.029	.135	.128	.008
Ca	.820	-.210	-.397	-.061	.074
Ti	.980	-.074	-.046	.050	.037
V	.669	-.207	.300	-.083	.093
Mn	.856	-.197	-.236	-.019	-.090
Fe	.968	-.128	-.035	.057	.028
Co	.448	.404	.313	-.478	-.125
Ni	.887	-.060	.064	.105	.133
Cu	.944	.045	-.006	-.088	.030
Zn	.453	.451	-.334	-.395	-.147
Ta	-.216	-.116	.191	.753	.383
Pb	.482	-.430	.282	.157	-.435
Br	.091	.801	.337	.148	.194
Cl	.191	.838	.003	.341	-.122
Rb	.718	.040	-.339	.124	.384
Sr	.960	-.045	-.014	.057	.018
Y	.082	-.012	.367	-.602	.588
Na	.584	.734	.049	.139	-.131
Sc	.154	-.214	.780	-.018	-.127

Table 7. Four component matrix for the quantified elements in PM_{2.5} collected from Alnaeem district.

Component Matrix				
	1	2	3	4
Al	.885	-.045	.226	-.294
Si	.903	-.070	.211	-.287
S	.551	.653	.468	.139
K	.962	-.124	.070	-.134
Ca	.932	-.245	-.165	.067
Ti	.966	-.179	-.027	-.101
V	.754	.294	.387	.149
Mn	.938	-.229	.099	-.159
Fe	.955	-.227	.031	-.123
Co	-.372	.118	.698	.334
Ni	.924	.019	.096	-.023
Cu	.910	-.144	.186	.083
Zn	.862	.235	-.197	.349
Ta	.709	.689	.006	.003
Pb	-.045	.640	-.255	-.610
Br	.725	-.522	.294	-.034
Cl	.730	-.044	-.597	.223
Rb	.812	-.310	-.303	.281
Sr	.937	-.266	-.115	.036
Y	-.717	-.681	.008	-.011
Na	.580	.677	-.362	.163

Conclusion

Based on the quantified elements in the PM_{2.5} aerosols assembled from the old Jeddah and Alnaeem districts in Jeddah, the old Jeddah district (downtown of the city) has a low level of concentrations for the most quantified elements. Therefore, it has a low level of air pollution comparing with the other locations. The statistical analysis revealed that very and extremely high values of the enrichment factors were found for the elements Cl, S, Zn, Cu, Ni, Sc, Pb, Br, and Ta which indicates the anthropogenic sources of these elements from traffic emissions, extensive mining, non-ferrous metal production, incinerator emissions, fossil fuel combustion, and marine. Based on Pearson's coefficients calculations, the correlations between the quantified elements are different from one location to another which indicates the different anthropogenic activity for the same element. The principal component analysis confirmed that the primary sources of the quantified elements are the natural source followed by multi anthropogenic sources and sea salt spray.

Declarations

Author Contributions Statement

A.A.S.: Conceptualization, visualization, data curation, and writing original draft., **S.S.M.A.:** Conceptualization, visualization, review, and editing.
D.R.A.: Validation, review, and editing. **E.A.:** Project administration, Funding acquisition, review, and editing. All authors reviewed the manuscript."

Acknowledgment

The authors would like to thank Taif University Researchers Supporting Project number (TURSP-2020/136) Taif University, Taif, Saudi Arabia, for supporting this work.

Data Availability

The data of the present study are available from the corresponding author upon reasonable request.

Conflict of Interest

The authors declare that there is no conflict of interest.

References

1. Aburas, H.M., Zytoon, M.A., Abdulsalam, M.I.: Atmospheric Lead in PM_{2.5} after Leaded Gasoline Phase-out in Jeddah City, Saudi Arabia. *CLEAN. - Soil. Air Water*. **39**(8), 711–719 (2011). doi:10.1002/clen.201000510
2. Aksu, A.: Sources of metal pollution in the urban atmosphere (A case study: Tuzla, Istanbul). *J. Environ. Health Sci. Eng.* **13**(1), 79 (2015). doi:10.1186/s40201-015-0224-9
3. Alghamdi, M.A.: Indoor, Outdoor Particulate Matter Concentrations at Some Elementary Schools in Jeddah, Saudi Arabia. *J. King Abdulaziz University: Metrol. Environ. Arid Land Agricultural Sci.* **142**(579), 1–37 (2013)
4. Andreae, M.O.: The Ocean as a Source of Atmospheric Sulfur Compounds. In: Buat-Ménard, P. (ed.) *The Role of Air-Sea Exchange in Geochemical Cycling*, pp. 331–362. Springer Netherlands, Dordrecht (1986)
5. Aschner, M., Aschner, J.L.: Manganese neurotoxicity: cellular effects and blood-brain barrier transport. *Neurosci. Biobehav. Rev.* **15**(3), 333–340 (1991). doi:10.1016/s0149-7634(05)80026-0
6. Barbieri, M.: The Importance of Enrichment Factor (EF) and Geoaccumulation Index (Igeo) to Evaluate the Soil Contamination. *J. Geol. Geophys.* **5**, 1–4 (2016)
7. Barceloux, D.G.: Cobalt. *J. Toxicol. Clin. Toxicol.* **37**(2), 201–206 (1999). doi:10.1081/clt-100102420
8. Barksdale, J.: *Titanium: Its Occurrence, Chemistry, and Technology*. John Wiley & Sons Canada, Limited (1966)
9. Bascom, R., Bromberg, P.A., Costa, D.L., Devlin, R., Dockery, D.W., Frampton, M.W., Utell, M.: Health effects of outdoor air pollution. *Am. J. Respir. Crit Care Med.* **153**(2), 477–498 (1996)
10. Bern, C.R., Walton-Day, K., Naftz, D.L.: Improved enrichment factor calculations through principal component analysis: Examples from soils near breccia pipe uranium mines, Arizona, USA. *Environ. Pollut.* **248**, 90–100 (2019). doi:10.1016/j.envpol.2019.01.122
11. Boman, J., Shaltout, A.A., Abozied, A.M., Hassan, S.K.: On the elemental composition of PM_{2.5} in central Cairo, Egypt. *X-Ray Spectrom.* **42**(4), 276–283 (2013)
12. Bytnerowicz, A., Omasa, K., Paoletti, E.: Integrated effects of air pollution and climate change on forests: a northern hemisphere perspective. *Environ. Pollut.* **147**(3), 438–445 (2007). doi:10.1016/j.envpol.2006.08.028
13. Calderón-Garcidueñas, L., Jewells, V., Galaz-Montoya, C., van Zundert, B., Pérez-Calatayud, A., Ascencio-Ferrel, E., Solorio, E.: Interactive and additive influences of Gender, BMI and Apolipoprotein 4 on cognition in children chronically exposed to high concentrations of PM_{2.5} and ozone. APOE 4 females are at highest risk in Mexico City. *Environ. Res.* **150**, 411–422 (2016)
14. Cempel, M., Nikel, G.: Nickel: A Review of Its Sources and Environmental Toxicology. *Pol. J. Environ. Stud.* **15**(3), 375–382 (2006)
15. Chi, R., Chen, C., Li, H., Pan, L., Zhao, B., Deng, F., Guo, X.: Different health effects of indoor-and outdoor-originated PM_{2.5} on cardiopulmonary function in COPD patients and healthy elderly adults. *Indoor air.* **29**(2), 192–201 (2019)
16. Cullis, C.F., Hirschler, M.M.: Atmospheric sulphur: Natural and man-made sources. *Atmospheric Environ.* (1967). **14**(11), 1263–1278 (1980). doi:10.1016/0004-6981(80)90228-0
17. Deboudt, K., Flament, P., Bertho, M.-L.: Cd, Cu, Pb and Zn Concentrations in Atmospheric Wet Deposition at a Coastal Station in Western Europe. *Water Air Soil Pollut.* **151**(1–4), 335–359 (2004). doi:10.1023/b:wate.0000009906.55895.30
18. Elmes, M., Gasparon, M.: Sampling and single particle analysis for the chemical characterisation of fine atmospheric particulates: A review. *J. Environ. Manage.* **202**(Pt 1), 137–150 (2017). doi:10.1016/j.jenvman.2017.06.067
19. EU.: *Air Quality Standards*, (2019). <https://ec.europa.eu/environment/air/quality/standards.htm>. Retrieved from <https://ec.europa.eu/environment/air/quality/standards.htm>
20. Gavin, C.E., Gunter, K.K., Gunter, T.E.: Manganese and calcium efflux kinetics in brain mitochondria. Relevance to manganese toxicity. *Biochem. J.* **266**(2), 329–334 (1990). doi:10.1042/bj2660329
21. Georgii, H.W., Muller, J.: Schwermetallaerosole in der Großstadtluft [Heavy metal aerosols in the air of large cities]. *Schriftenreihe des. Vereins für Wasser-Boden- und Lufthygiene.* **42**, 39–50 (1974)
22. Haber, L.T., Erdreich, L., Diamond, G.L., Maier, A.M., Ratney, R., Zhao, Q., Dourson, M.L.: Hazard identification and dose response of inhaled nickel-soluble salts. *Regul. Toxicol. Pharmacol.* **31**(2 Pt 1), 210–230 (2000). doi:10.1006/rtph.2000.1377
23. Hans Wedepohl, K.: The composition of the continental crust. *Geochim. Cosmochim. Acta.* **59**(7), 1217–1232 (1995). doi:10.1016/0016-7037(95)00038-2
24. Heo, J., Schauer, J.J., Yi, O., Paek, D., Kim, H., Yi, S.M.: Fine particle air pollution and mortality: importance of specific sources and chemical species. *Epidemiology.* **25**(3), 379–388 (2014). doi:10.1097/EDE.0000000000000044
25. Iqbal, J., Shah, M.H.: Study of Selected Metals Distribution, Source Apportionment, and Risk Assessment in Suburban Soil, Pakistan. *J. Chem.* **2015**, 1–8 (2015). doi:10.1155/2015/481324
26. Ketterer, M.E., Lowry, J.H., Simon Jr, J., Humphries, K., Novotnak, M.P.: Lead isotopic and chalcophile element compositions in the environment near a zinc smelting–secondary zinc recovery facility, Palmerton, Pennsylvania, USA. *Appl. Geochem.* **16**(2), 207–229 (2001)
27. Khodeir, M., Shamy, M., Alghamdi, M., Zhong, M., Sun, H., Costa, M., Maciejczyk, P.: Source Apportionment and Elemental Composition of PM_{2.5} and PM₁₀ in Jeddah City, Saudi Arabia. *Atmos. Pollut. Res.* **3**(3), 331–340 (2012). doi:10.5094/apr.2012.037
28. Kretzschmar, J.G., Delespaul, I., de Rijck, T.: Heavy metal levels in Belgium: A five year survey. *Sci. Total Environ.* **14**(1), 85–97 (1980). doi:10.1016/0048-9697(80)90128-x

29. Lim, C.C., Thurston, G.D., Shamy, M., Alghamdi, M., Khoder, M., Mohorjy, A.M., Costa, M.: Temporal variations of fine and coarse particulate matter sources in Jeddah, Saudi Arabia. *J. Air Waste Manag Assoc.* **68**(2), 123–138 (2018). doi:10.1080/10962247.2017.1344158
30. Moreno, T., Pandolfi, M., Querol, X., Lavin, J., Alastuey, A., Viana, M., Gibbons, W.: Manganese in the urban atmosphere: identifying anomalous concentrations and sources. *Environ. Sci. Pollut Res. Int.* **18**(2), 173–183 (2011). doi:10.1007/s11356-010-0353-8
31. Nayebar, S.R., Aburizaiza, O.S., Siddique, A., Carpenter, D.O., Pope, A., Mirza, C. 3, Khwaja, H.M., H. A: Fine particles exposure and cardiopulmonary morbidity in Jeddah: A time-series analysis. *Sci. Total Environ.* **647**, 1314–1322 (2019). doi:10.1016/j.scitotenv.2018.08.094
32. Ostro, B., Lipsett, M., Reynolds, P., Goldberg, D., Hertz, A., Garcia, C., Bernstein, L.: Long-term exposure to constituents of fine particulate air pollution and mortality: results from the California Teachers Study. *Environ. Health Perspect.* **118**(3), 363–369 (2010). doi:10.1289/ehp.0901181
33. Pope, C. 3: Epidemiology of fine particulate air pollution and human health: biologic mechanisms and who's at risk? *Environ. Health Perspect.* **108**(suppl 4), 713–723 (2000)
34. Ramanathan, V., Feng, Y.: Air pollution, greenhouse gases and climate change: Global and regional perspectives. *Atmos. Environ.* **43**(1), 37–50 (2009)
35. Rossby, C.G., Egnér, H.: On the Chemical Climate and its Variation with the Atmospheric Circulation Pattern. *Tellus.* **7**(1), 118–133 (2016). doi:10.3402/tellusa.v7i1.8764
36. Schaller, K.-H.: Chapter 24 Vanadium. In: Herber, R.F.M., Stoeppler, M. (eds.) *Techniques and Instrumentation in Analytical Chemistry*, vol. 15, pp. 527–539. Elsevier (1994)
37. Schropp, S.J., Lewis, F.G., Windom, H.L., Ryan, J.D., Calder, F.D., Burney, L.C.: Interpretation of Metal Concentrations in Estuarine Sediments of Florida Using Aluminum as a Reference Element. *Estuaries.* **13**(3), 227 (1990). doi:10.2307/1351913
38. Shaltout, A.A., Ahmed, S.I., Harfouche, M., Hassan, S.K., Eid, K.A.: Lead speciation of PM_{2.5} collected from Greater Cairo, Egypt and Zarqa, Jordan: An energy dispersive X-ray fluorescence and X-ray absorption near edge structure study. *X-Ray Spectrom.* **48**(1), 38–45 (2019). doi:10.1002/xrs.2983
39. Shaltout, A.A., Almallwai, D.R., Shehadeh, Z.F., Boman, J.: Elemental composition of PM_{2.5} particles sampled in industrial and residential areas of Taif, Saudi Arabia, using energy dispersive X-ray fluorescence. *Environ. Sci.* **7**(6), 210–217 (2012)
40. Shaltout, A.A., Boman, J., Al-Malawi, D.R., Shehadeh, Z.F.: Elemental composition of PM_{2.5} particles sampled in industrial and residential areas of Taif, Saudi Arabia. *Aerosol Air Qual. Res.* **13**(4), 1356–1364 (2013)
41. Shaltout, A.A., Boman, J., Hassan, S.K., Abozied, A.M., Al-Ashkar, E.A., Abd-Elkader, O.H., Al-Tamimi, J.: Elemental Composition of PM 2.5 Aerosol in a Residential–Industrial Area of a Mediterranean Megacity. *Arch. Environ. Contam. Toxicol.* **78**(1), 68–78 (2020)
42. Shaltout, A.A., Boman, J., Shehadeh, Z.F., Dhaif-allah, R., Hemed, O.M., Morsy, M.M.: Spectroscopic investigation of PM 2.5 collected at industrial, residential and traffic sites in Taif, Saudi Arabia. *J. Aerosol. Sci.* **79**, 97–108 (2015)
43. Shaltout, A.A., Boman, J., Welz, B., Castilho, I.N.B., Ashkar, A., Gaita, S.M.: Method development for the determination of Cd, Cu, Ni and Pb in PM 2.5 particles sampled in industrial and urban areas of Greater Cairo, Egypt, using high-resolution continuum source graphite furnace atomic absorption spectrometry. *Microchem J.* **113**, 4–9 (2014)
44. Shaltout, A.A., Harfouche, M., Ahmed, S.I., Czyzycki, M., Karydas, A.G.: Synchrotron radiation total reflection X-ray fluorescence (SR-TXRF) and X-ray absorption near edge structure (XANES) of fractionated air particulates collected from Jeddah, Saudi Arabia. *Microchem. J.* **137**, 78–84 (2018)
45. Shaltout, A.A., Harfoushe, M., Ali, S.S., Karydas, A.G., Kregsamer, P., Wobruschek, P.,... El Orabi, N.F. Elemental composition and source apportionment of atmospheric aerosols collected from urban and residential areas of Jordan using multi-secondary targets energy dispersive X-ray fluorescence. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 105900. (2020)
46. Shaltout, A.A., Hassan, S.K., Alomairy, S.E., Manousakas, M., Karydas, A.G., Eleftheriadis, K.: Correlation between inorganic pollutants in the suspended particulate matter (SPM) and fine particulate matter (PM_{2.5}) collected from industrial and residential areas in Greater Cairo, Egypt. *Air Qual. Atmos. Health.* **12**(2), 241–250 (2018). doi:10.1007/s11869-018-0645-6
47. Shaltout, A.A., Hassan, S.K., Karydas, A.G., Harfouche, M., Abd-Elkader, O.H., Kregsamer, P., Strelci, C.: EDXRF analysis of suspended particulate matter (SPM) from residential and industrial areas in Cairo, Egypt. *X-Ray Spectrom.* **47**(3), 223–230 (2018). doi:10.1002/xrs.2830
48. Shaltout, A.A., Hassan, S.K., Karydas, A.G., Zaki, Z.I., Mostafa, N.Y., Kregsamer, P., Strelci, C.: Comparative elemental analysis of fine particulate matter (PM_{2.5}) from industrial and residential areas in Greater Cairo-Egypt by a means of a multi-secondary target energy dispersive X-ray fluorescence spectrometer. *Spectrochim. Acta B.* **145**, 29–35 (2018)
49. Silva, R.A., West, J.J., Zhang, Y., Anenberg, S.C., Lamarque, J.-F., Shindell, D.T., Folberth, G.: Global premature mortality due to anthropogenic outdoor air pollution and the contribution of past climate change. *Environ. Res. Lett.* **8**(3), 034005 (2013)
50. Sukri, N.S., Aspin, S.A., Kamarulzaman, N.L., Jaafar, N.F., Ghazi, M., Ismail, R.S., Zakaria, N.S., M. P: Assessment of metal pollution using enrichment factor (EF) and pollution load index (PLI) in sediments of selected Terengganu rivers, Malaysia. *Malaysian J. Fundamental Appl. Sci.* **14**(2), 235–240 (2018). doi:10.11113/mjfas.v14n2.1065
51. Suvarapu, L.N., Baek, S.O.: Determination of heavy metals in the ambient atmosphere. *Toxicol. Ind. Health.* **33**(1), 79–96 (2017). doi:10.1177/0748233716654827
52. Thimonier, A., Schmitt, M., Waldner, P., Schleppe, P.: Seasonality of the Na/Cl ratio in precipitation and implications of canopy leaching in validating chemical analyses of throughfall samples. *Atmos. Environ.* **42**(40), 9106–9117 (2008). doi:10.1016/j.atmosenv.2008.09.007
53. Uduma, A.U.: Aluminum as a Reference Element for the Elucidation of Pb Enrichment /Depletion in Selected Arable Soils of Nigeria. *IOSR J. Eng.* **4**, 15–22 (2014)
54. Visschedijk, A.J.H., Denier van der Gon, H., Hulskotte, J., Quass, U. *Anthropogenic Vanadium emissions to air and ambient air concentrations in North-West Europe*. Paper presented at the E3S Web of Conferences 1. (2013)

55. WHO.: WHO Air Quality Guidelines for Particulate Matter, Ozone, Nitrogen Dioxide and Sulfur Dioxide, Global Update 2005, Summary of Risk Assessment. Retrieved from (2006). http://whqlibdoc.who.int/hq/2006/WHO_SDE_PHE_OEH_06.02_eng.pdf
56. WHO.: *Burden of Disease From Household Air Pollution for 2012. Summary of Results.* Retrieved from 1211 Geneva 27, Switzerland www. (2014). who.int/phe/health_topics/outdoorair/databases/FINAL_HAP_AAP_BoD_24March2014.pdf
57. Yang, Y., Li, S., Bi, X., Wu, P., Liu, T., Li, F., Liu, C.: Lead, Zn, and Cd in slags, stream sediments, and soils in an abandoned Zn smelting region, southwest of China, and Pb and S isotopes as source tracers. *J. Soils Sediments.* **10**(8), 1527–1539 (2010). doi:10.1007/s11368-010-0253-z
58. Zeger, S.L., Dominici, F., McDermott, A., Samet, J.M.: Mortality in the Medicare population and chronic exposure to fine particulate air pollution in urban centers (2000–2005). *Environ. Health Perspect.* **116**(12), 1614–1619 (2008)
59. Zytoon, M.A., Aburas, H.M., Abdulsalam, M.I.: Determination of ⁴⁰K, ²³²Th and ²³⁸U activity concentrations in ambient PM_{2.5} aerosols and the associated inhalation effective dose to the public in Jeddah City, Saudi Arabia. *J. Environ. Radioact.* **129**, 148–156 (2014). doi:10.1016/j.jenvrad.2014.01.003

Figures

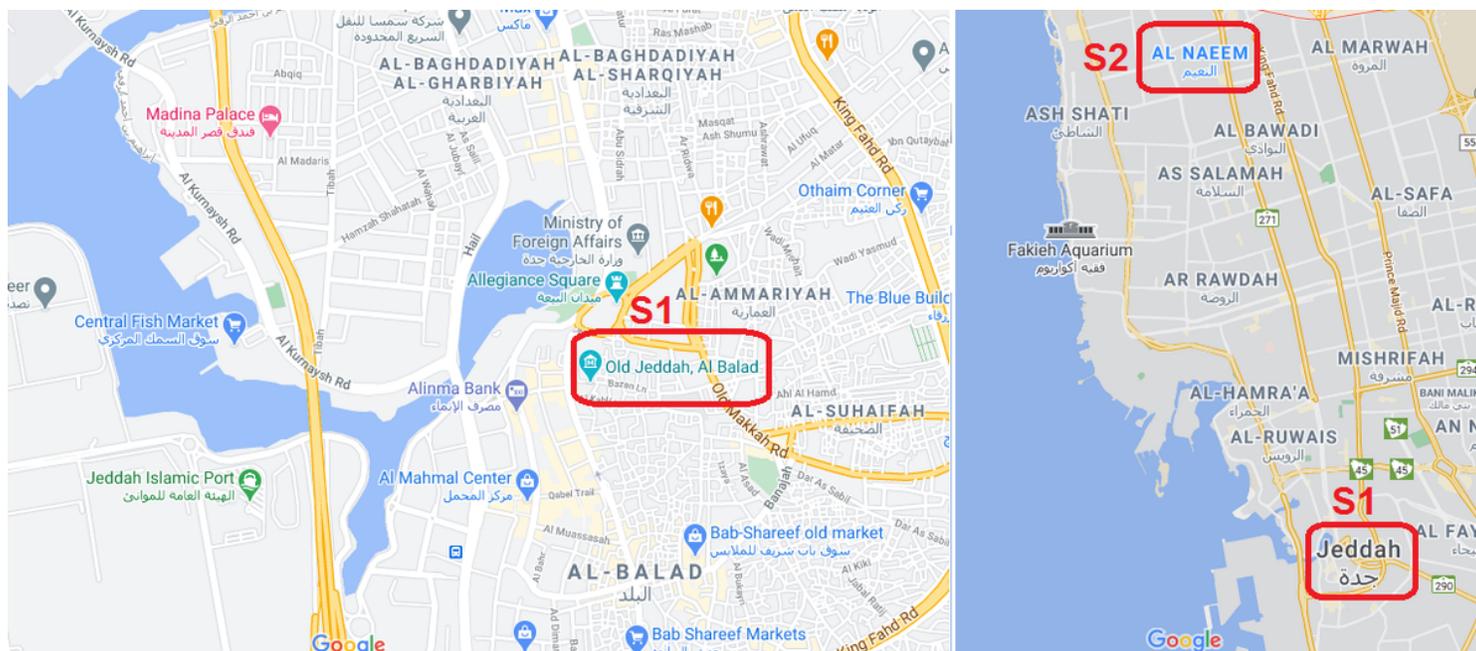


Figure 1

Sampling locations of the PM_{2.5} aerosols collected from old Jeddah district (S1) and Alnaeem district (S2).

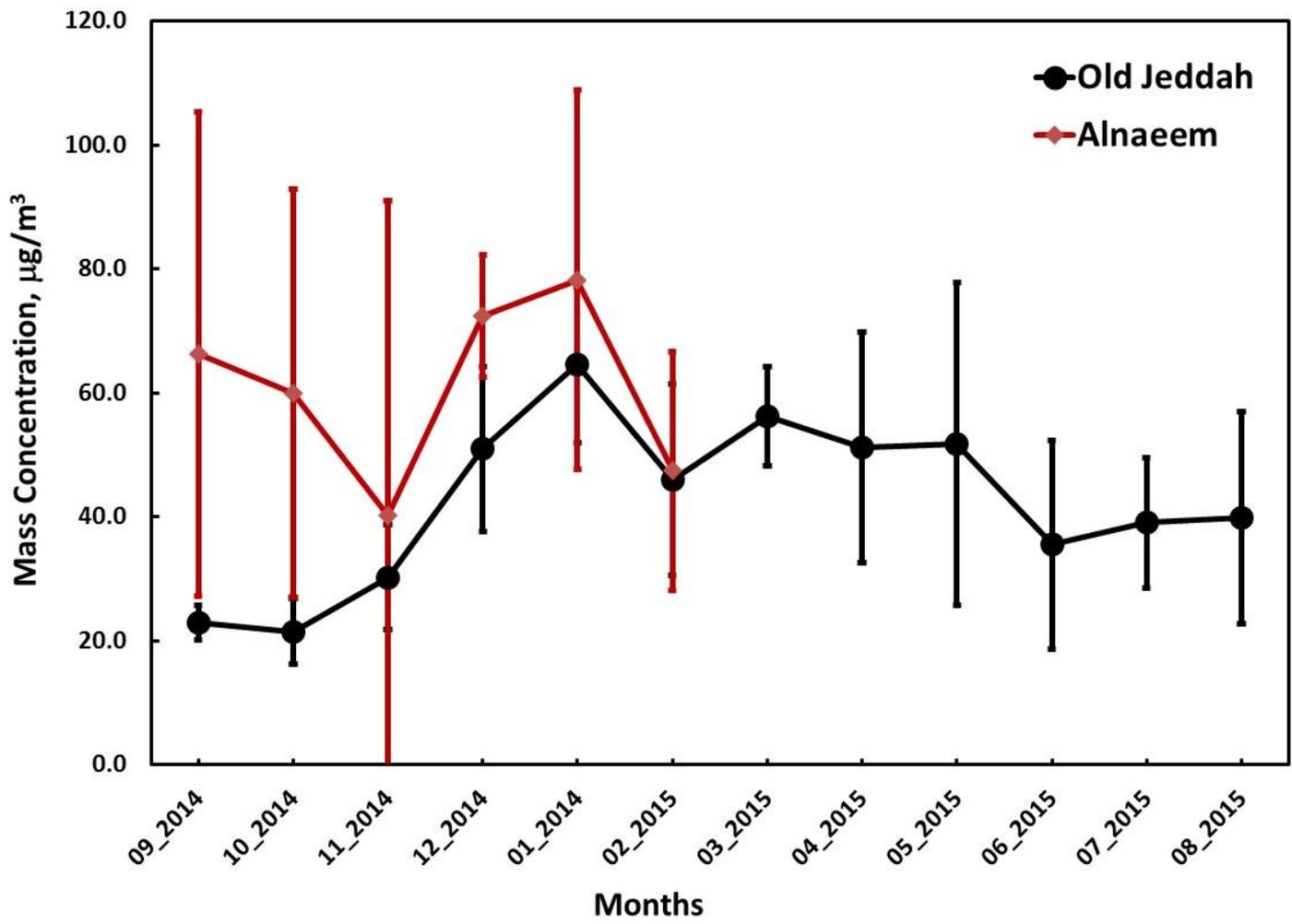


Figure 2
 Monthly variations of the PM_{2.5} samples collected from the “old Jeddah” district as well as PM_{2.5} samples collected from “Alnaeem” district for comparison.

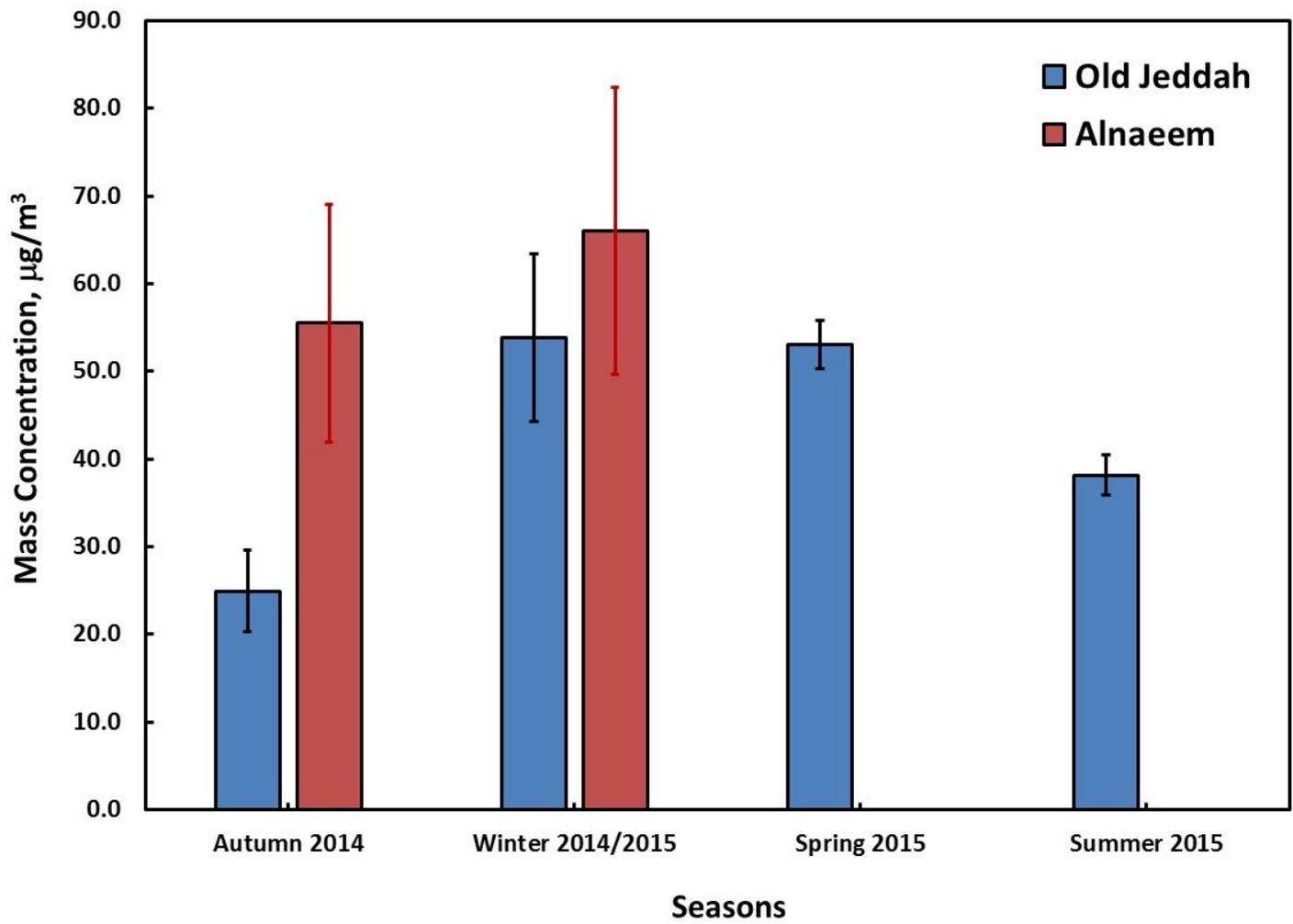


Figure 3
 The relationship between the seasons and the mass concentration of the PM_{2.5} samples collected from the old Jeddah and Alnaeem districts in Jeddah city, Saudi Arabia.

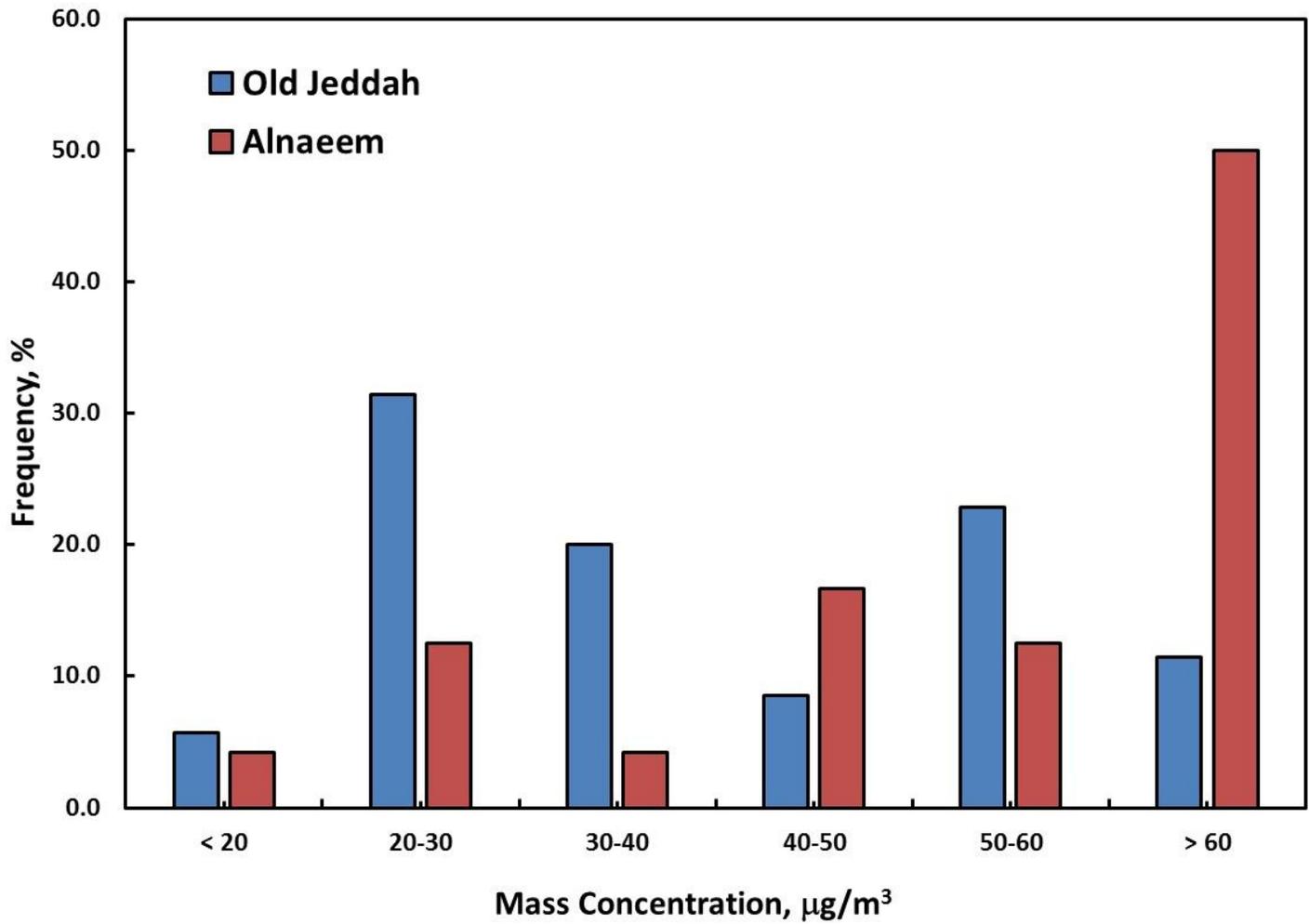


Figure 4

The frequency percentages of the daily mass concentration of the PM_{2.5} samples collected from the old Jeddah and Alnaeem districts

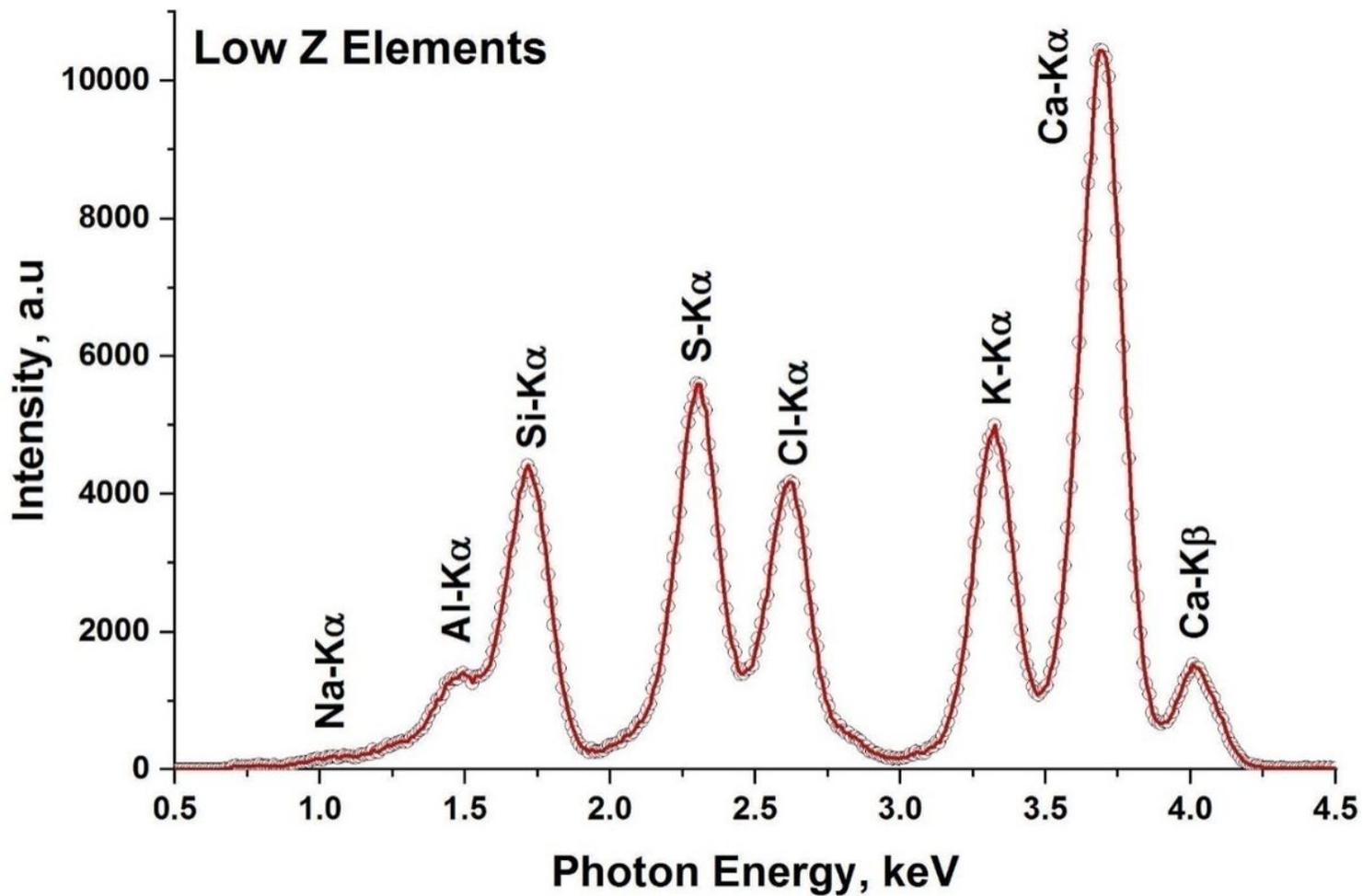


Figure 5

The EDXRF spectrum of the low Z elements using CaF₂ secondary target for selected PM_{2.5} sample from old Jeddah district, Saudi Arabia.

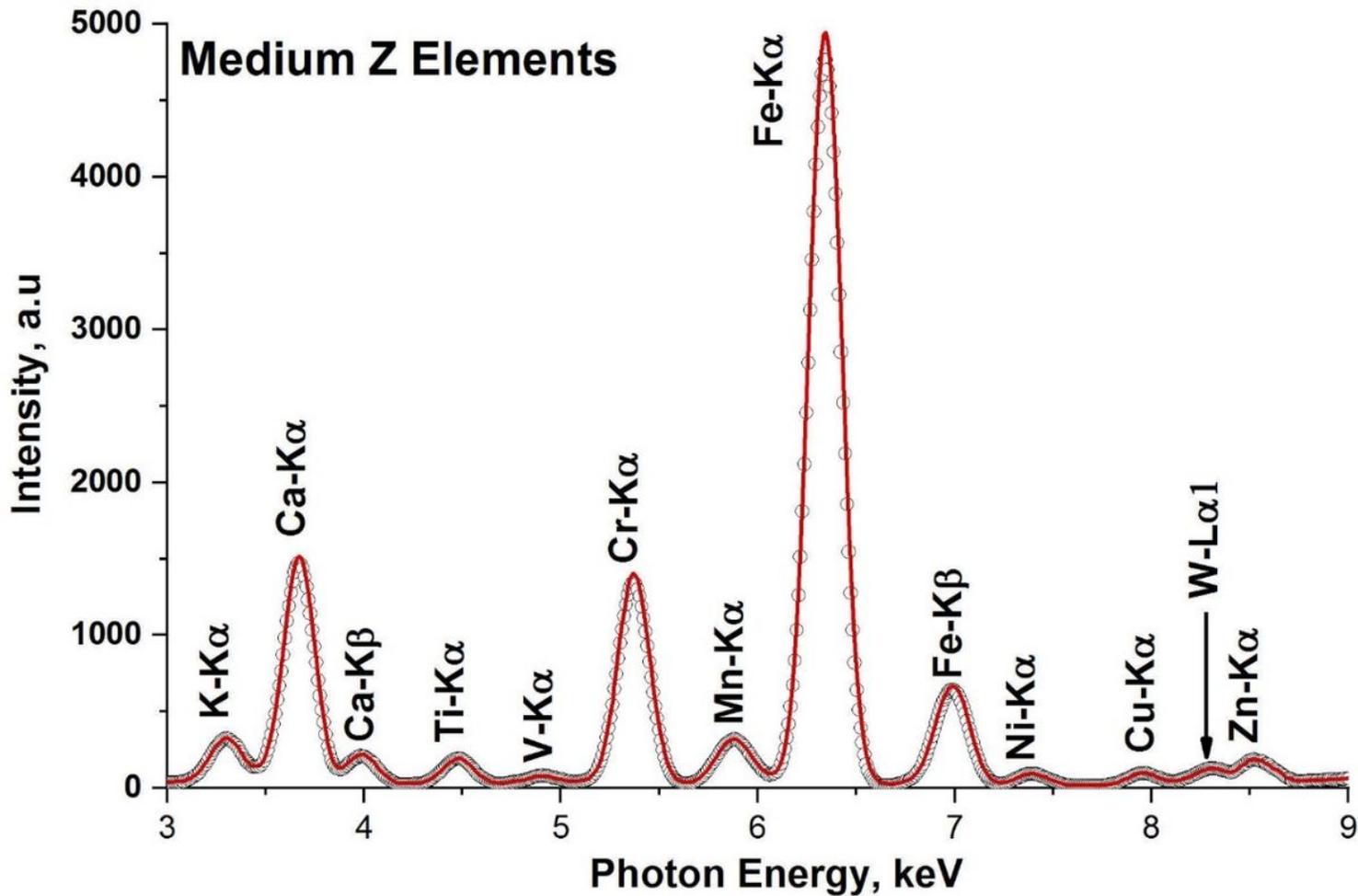


Figure 6

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

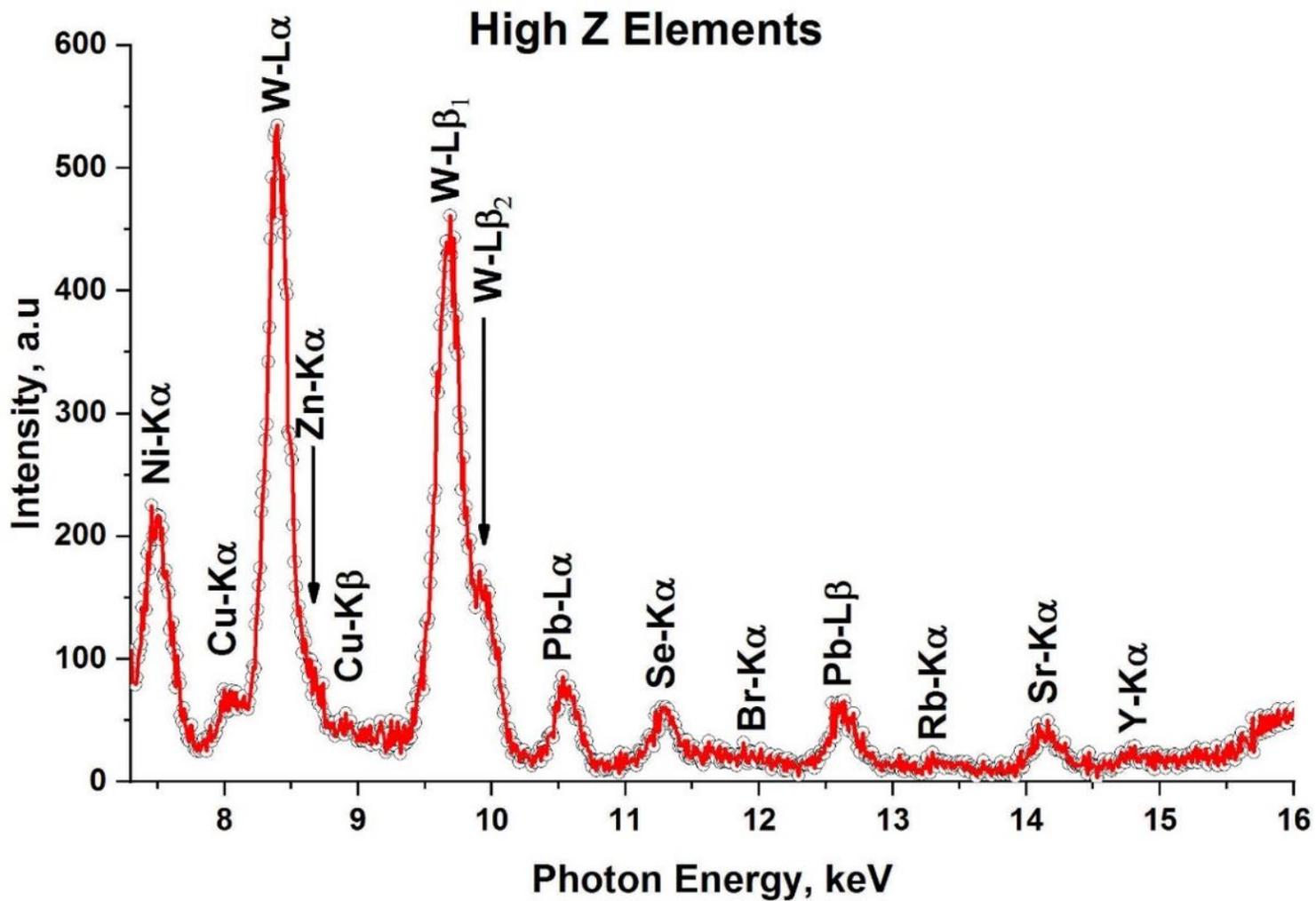


Figure 7

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

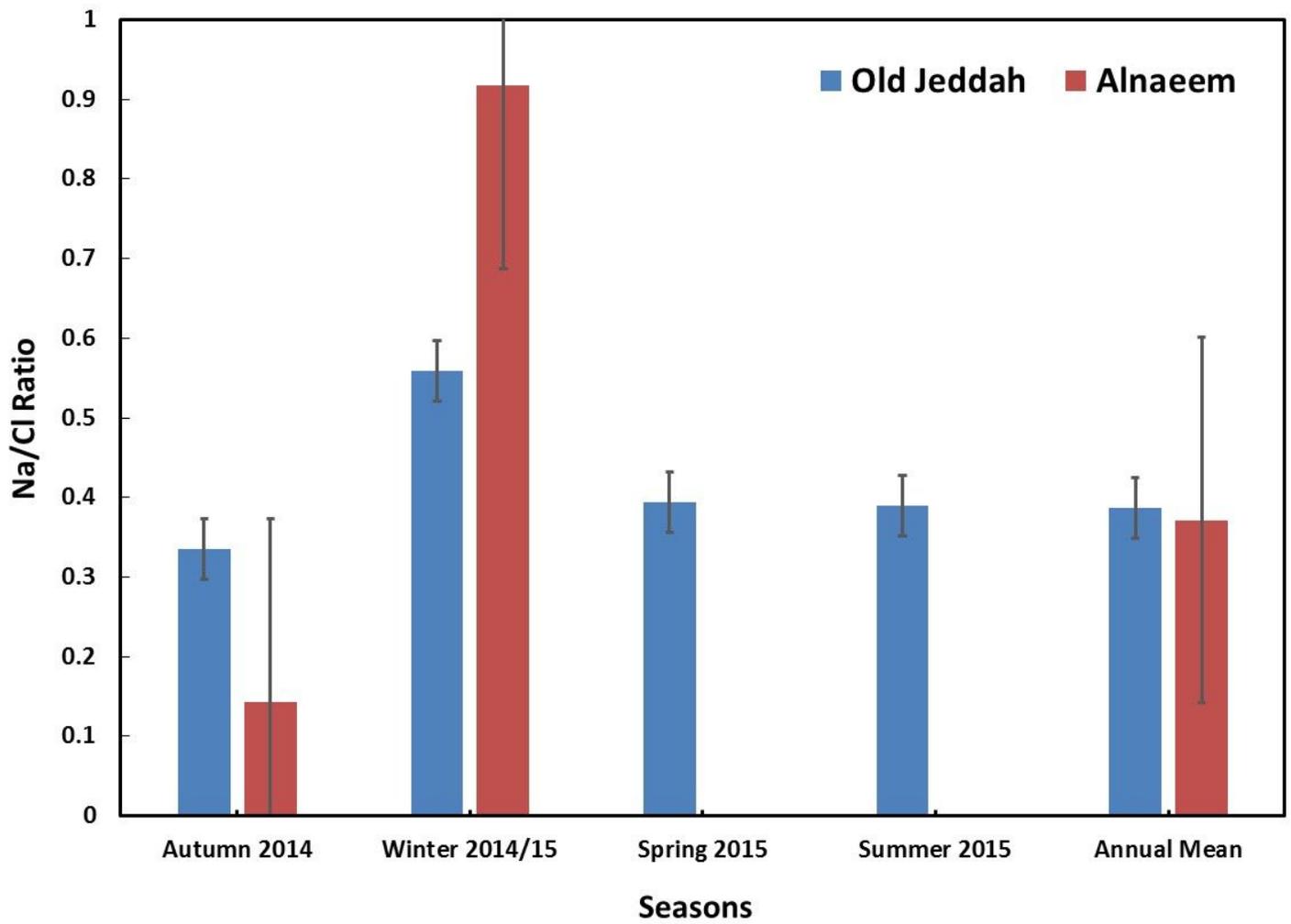


Figure 8

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

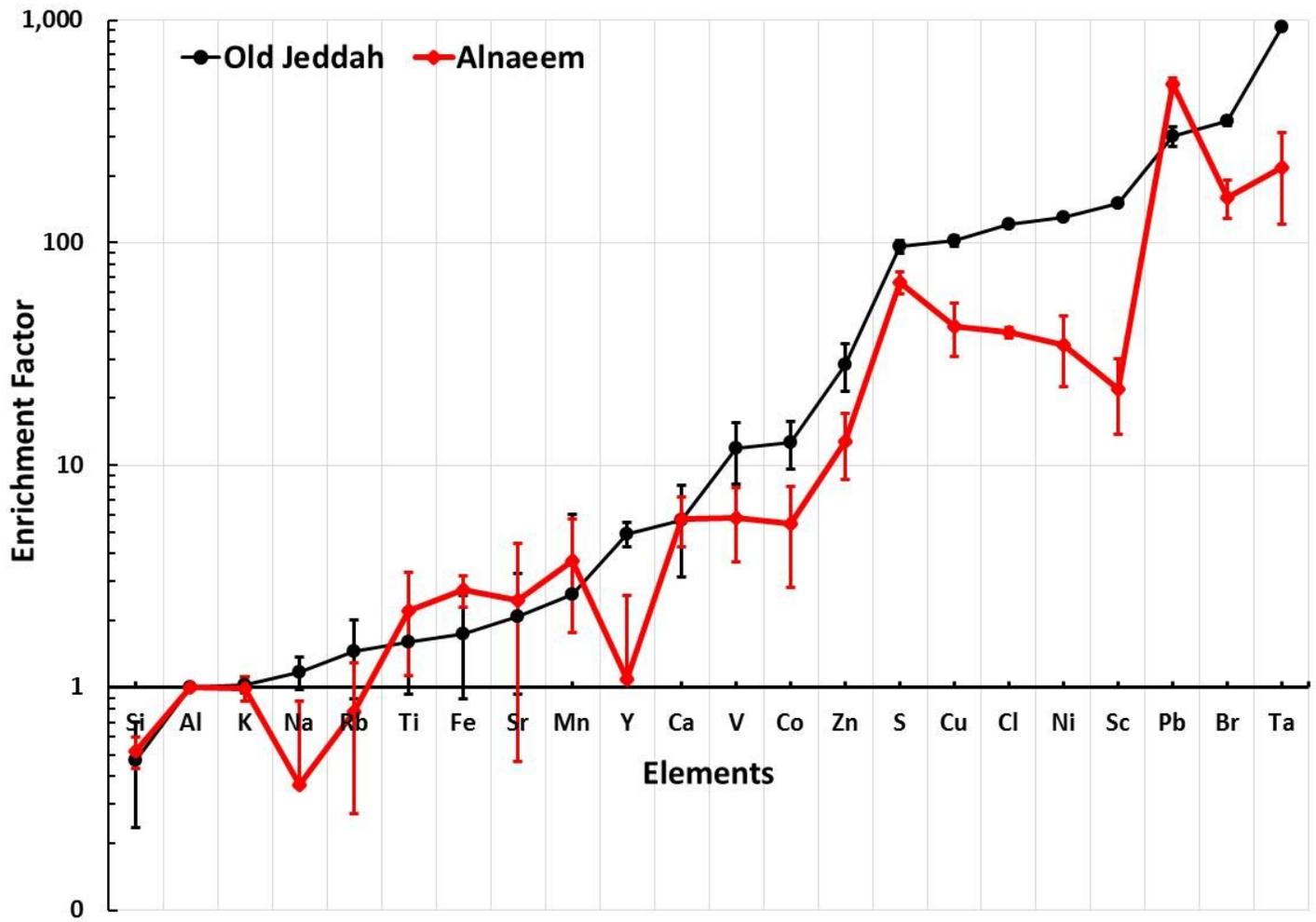


Figure 9

Enrichment factors of the determined elements in the PM_{2.5} samples assembled from the old Jeddah and Alnaeem locations

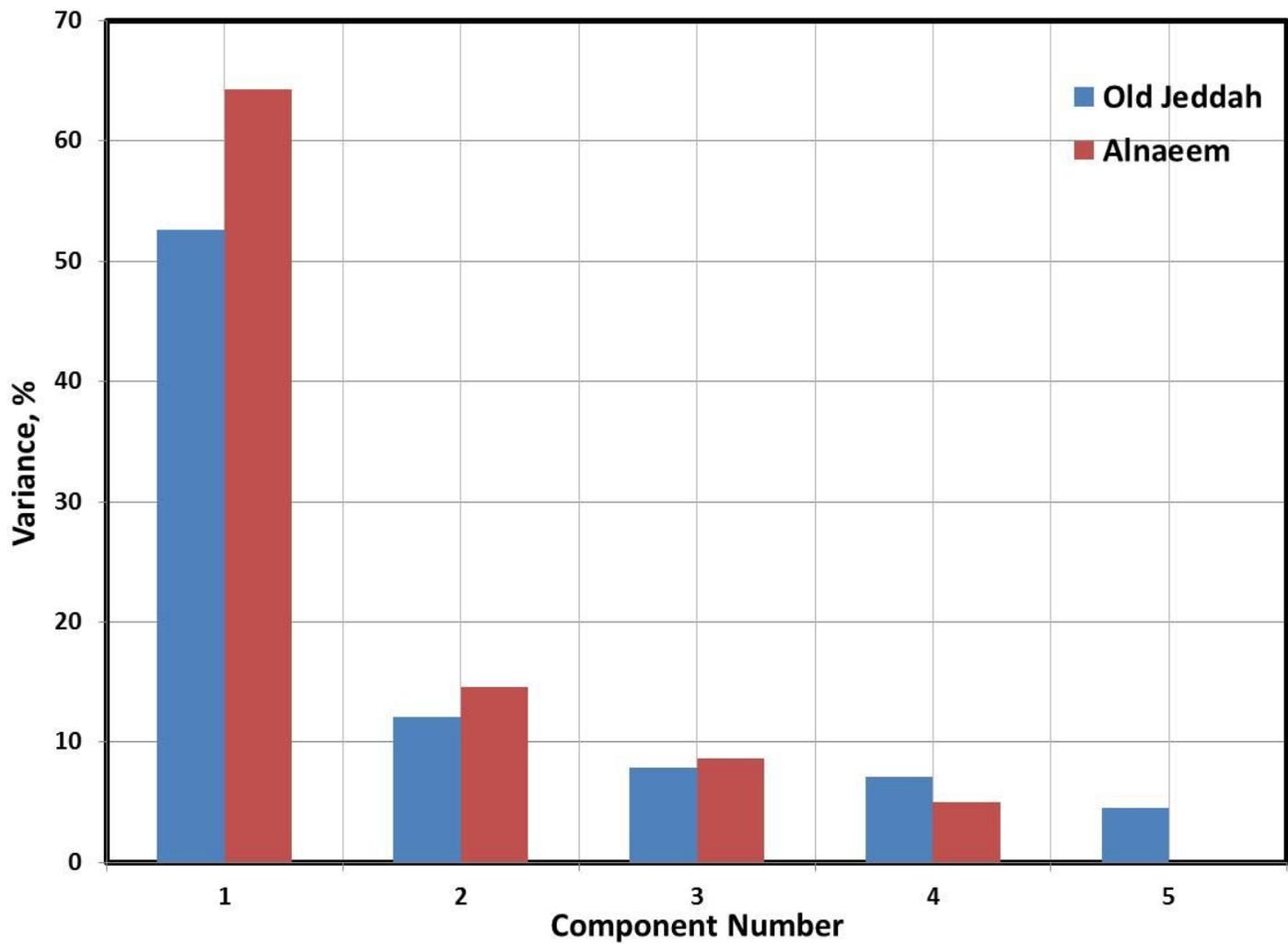


Figure 10

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