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Environmental Investigation and Determination of Heavy Metal Contamination Indicators in Dust Particles of Tehran-Iran (Case Study of Main City Squares)

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Abstract

In this study, dust samples were collected from 9 stations in Tehran during high-traffic summer hours and in dry climatic conditions and analyzed for elements identification using (ICP-OES). Enrichment factor (EF) and Mullergeoccumulation index (Igeo) were calculated for them. The results showed that lead (Pb), zinc (Zn), copper (Cu), arsenic (As) and bismuth (Bi) concentrations increased with respect to the earth crust. Examination of EF index shows that Pb, Zn, Cu, Bismuth, Arsenic and Molybdenum show the highest enrichment intensity in the environment. Other elements, such as chromium, cadmium, etc., show partial enrichment in the environment. The Mullergeoccumulation index indicates an increase in the concentration of lead, zinc and copper at all stations. Contamination of dust particles with heavy metals threatens the environmental condition of Tehran. Their main sources of emission reason are traffic of light and heavy traffic vehicles and emissions from factories and workshops in Tehran. Fe element has a positive and significant correlation coefficient with V and LOI since Fe is the soil index, LOI is the organic matter index as well as the V index for petroleum materials, so they have the same origin. Al and

Zn are linked to each other with positive and significant correlation coefficients as well as two elements are linked with positive correlation to As. So , the elements attached to it are probably of terrigenous origin. In the other branch, elements Ni and Cr are positively and significantly correlated with each other since Ni is an indicator of petroleum materials, so Cr is also of petroleum origin. The other branches asCa and Cd have positive and significant correlation coefficients and this branch is connected with Bi and Mo in significant range. The Ca element is an indicator of biogenic substances so the elements attached to it are antropogenic. According to the results, it is necessary to take necessary measures to control pollutant sources in Tehran.

Keywords Anthropogenic, Dust particles, Heavy metals, Pollution indicators, Tehran.

Introduction

Dust is called solid particles that enter the air by various processes and from various sources (Faiz et al., 2009). The main source of atmospheric dust in arid and semi-arid regions is soil erosion (Coz et al., 2009). Dust particles are fine-grained (clay and silt) and can be transported to very distances and elevations above the atmosphere and eventually depositedas dry or wet (Keramat et al., 2011). Dry subsidence in arid and semi-arid regions is the most important route of entry of pollutants into the environment. The importance of atmospheric dry subsidence is due to concerns related to sediment that enter the soil and aquatic environments and these particles have an adverseeffect on human health. This process is especially important in industrial and urban areas where the concentration of pollutants is high. In recent years, one of the major concerns of various communities around the world is the increase in the concentration of heavy metals in street dust due to their toxic effects Since heavy metals (Table 1) are bioaccumulative and as permanent and persistent environmental pollutants, their tendency to accumulate in living organisms has increased the risks associated with them (Shahbazi, 2012) Heavy metals in street dust is one of the major polluters of urban environments that can be caused by heavy traffic, industries, erosion of buildings, erosion of tires and parts used in cars, mining activities and Rcombustion of fossil fuels (Manasreh, 2010) Over the past few years, large amounts of atmospheric dust have also entered via the borders into some cities such as Tehran, where their exact origin have been disputed, but they are said to coming from deserts in neighboring countries. However, large amounts of them are deposited in the form of dust on urban areas (Fallah, 2012). The three main factors identified in increasing the amount of heavy metals in dusts, especially street dust and household dust, are traffic resulting from transportation, industry and weathering of materials (Karbassi et al., 2007). Lead, for example, originates from lead gasoline, while copper, zinc and cadmium come from tire wear, grease and lubricants, industrial

Table 1. Concentration of heavy elements along with statistical data on urban dust samples in 9 major Tehran squares (all elements are in mg / kg except Fe and LOI in% wt)

LOI	Fe	Bi	Mn	Cd	Cr	Ni	As	Cu	Zn	Pb	Sampling No.
15/74	3	2/7	805/4	0/2	64/8	27/2	3/8	130/8	402/9	96/3	S1
24/1	4/3	3/1	867/8	0/2	291/6	126/2	8/1	219/8	554/9	166/9	S2
14/62	3/8	2/7	807/1	0/2	84/4	32/4	4/1	760/4	526/8	132/4	S3
15/04	2/9	3/3	847/6	0/2	94	38	3/5	320/1	402	462/2	S4
14/04	3/2	2/1	862/5	0/1	57/4	20/3	9	135/2	290/8	70/2	S5
13/58	3/7	3/1	828/8	0/2	84/9	32/7	11/3	147	421/8	114	S6
18/42	3/4	0/6	969/2	0/1	63/9	50/8	16/5	240/4	1353	196/6	S7
15/75	3/1	2/4	811/9	0/2	67/7	22/4	3/5	281/3	314/7	75/2	S8
18/93	3/3	2/1	817/5	0/2	81/4	26/7	8	255/7	391/4	120/5	S9
13/58	2/9	0/6	805/4	0/1	57/4	20/3	3/5	130/8	290/8	70/2	Min
24/1	4/3	3/3	969/2	0/2	291/6	126/2	16/5	760/4	1353	462/2	Max
16/69	3/4	2/5	846/4	0/2	98/9	41/8	7/5	276/7	517/6	159/4	mean
_	5/6	0/1	1000	0/2	100	75	1/5	50	75	14	*earth crust
_	4	0/4	1000	0/4	70	50	6	30	90	35	Average in **soil

* Earth's crust: (wedepohl, 1974) ** Soil: (Bowen, 1979)

emissions and also from waste incinerators (Thorpe and Harrison, 2008). The origin of nickel and chromium in street dust is the corrosion of vehicle partsand the chromium plating of some parts of motor vehicles (Yazdi, 2013). Street dust has a significant contribution to urban environmental pollution. Many studies on street dust today focus on the concentration of elements present in them and their sources of emission. The type of compounds in street dust and their amount can be a good indicator for detecting environmental pollution (Tamrakar and Shakya, 2011). Humans and other living creatures are directly exposed to the heavy metals released into the environment. These metals are absorbed in three ways: adsorption through the skin, inhalation and ingestion of dust and contaminated soil. It should be noted that the most common concern is regarding the children age of 1-8 years, when the infection is transmitted via their hands and mouth (Moghaddas, 2013). In Modayish's studies,Hojati et al.,also studied the chemical and physical properties of dust particles (Hojati, 2012). Mahmoudiin a research on the atmospheric dust properties of Isfahan city stated that due to the similarity of chemical and mineralogical characteristics of dust with soils of eastern Isfahan region and considering the pattern of wind direction and particle size showing the average distance to the particle transport, we can consider the east of Isfahan as the main source for atmospheric dust in Isfahan(Mahmoudi, 2011). Tehran is one of the oldest cities in Iran and its capital. Its area is 730 sq km, with a population of more than 13 million and 260 isconsidered as one of the most populated cities (Iran Statistics Center, 2016).

Tehran is one of the largest cities in the world, located in the southern part of the Alborz highlands and is topographically divided into three regions, including the northern mountains, the hillside and the southern plain. The main geological feature of Tehran is its location between the Alborzgreatmountain (belonging to the third geological age) and the Iranian plateau (belonging to the fourth geological age). The most important aspect of this problem is the existence of active faults such as the Mesha, North Tehran and Ray faults, which have caused mild and small earthquakes are occurred at these faults. At the upper latitudes of the study area, which is the highlands of Tehran, the lithology of the region consists of Karaj formation with thick layers of tuff, with shale, siltstone, sandstone, limestone, marl, gypsum and gypsum carbonate rocks, Rhyolitic tuff, andesite, trachyte, dacite, lava flows, basaltic and finally dolomite of Soltaniehformation are distributed in the entire map of 1: 100000 Tehran. The bed of Tehran plain is made of current alluviums that are mostly alluvium of Hezardare including alluvium, debris, alluvial fans and glacial sediments with andinterlayers of clay and sand.

The main purpose of the present study is to determine the concentration of some metals in dust samples collected from the main squares of Tehran.

Materials and methods

Tehran is located in a relatively wide area is a city in Iran at longitude $51°6'$ to $51°38'$ East and latitude $35°34'$ to $35°51'$. North and its elevation is between 1800 meters north to 1050m on the south. Tehran metropolis as one of the largest cities in the world, is located in the southern part of the Alborz highlands and is about 20 kilometers (2,000 m) far from the 2000m mountains. Tehran is extended between the two valleys of the mountain and the desert and on the southern ranges of the Alborzmountni. It is bounded on the south by the mountains of Ray and BibiShehrbano and the flat plains of Shahriar and Varamin, and on the north by mountain.

Sampling

Dust sampling

Dust sampling was performed at 9 different areas (main squares of the city) using glass traps in Tehran (Hojati, 2019). The dust sampling traps used in this study consisted of square glass plates with the size $1\times 1\ m$ m and a plastic mesh with the pores $2\times 2\ mm$attached to it via 8 screws to trap the air dust. For sampling, 1 sediment trap was installed on the roof of a 4-storey building about 6 meters high above the ground. Based on the purpose of this project, much emphasis is on cars and heavy traffic as one of the polluting sources in Tehran. Therefore, nine main and high traffic areas were identified as sampling stations (Table 2). In selecting these stations, it was attempted to cover the four main geographical areas of Tehran (figure 1,2), for example Tajrish Square in the north, Azeri Square in the south, Azadi Square in the west, etc.

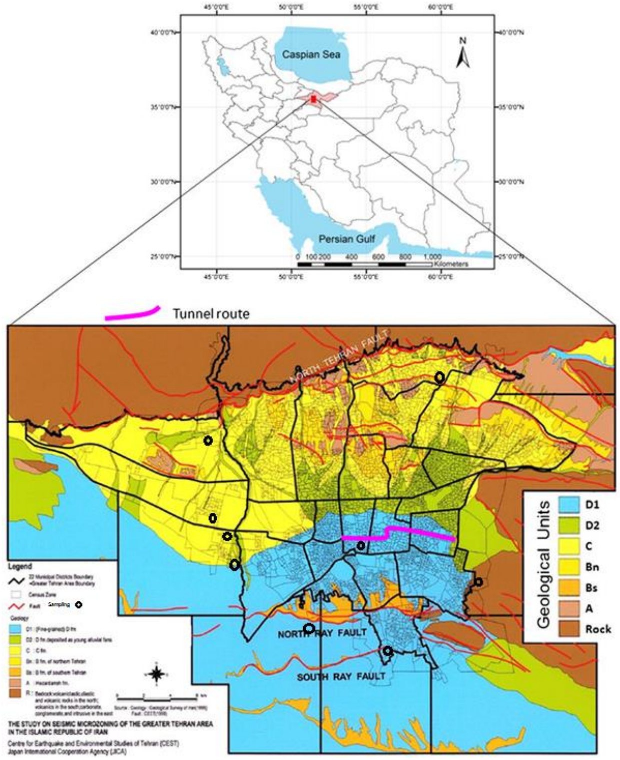

Fig 1. Geographical location of the study areas taken from Map 1: 100000 of Tehran

Fig. 2. A view of some sampling stations in Tehran (picture A view to the north and B view to the east)

Table 2. Specifications of sampling stations

Sampling area	Area	Station No.
East of Azadi sq.	Azadi sq.	Station 1
South of Enghelab sq.	Enghelab sq.	Station 2
North of second square of Sadeghie	Sadeqie second sq.	Station 3

West of Punak sq.	Punak sq.	Station 4
East of Valiasr sq.	Valiasr sq.	Station 5
South of Serahazari	Serahazari	Station 6
South of Rahahan sq.	Rahahan sq.	Station7
West of Tajrish sq.	Tajrish sq.	Station 8
South of Piroozi sq.	Piroozi sq.	Station 9

Laboratory studies

Samples were placed at 70 ° C for 24 hours in the laboratory. After drying, the specimens were passed through a sieve of 230 (63 μm) to remove the diluents of the elements concentration (sand, coarse silt) and to provide a specific equilibrium surface for further chemical analysis. The percentages of Walkley-Black Method Soil Organic Matter and the percentage of calcium carbonate equivalent (dissolved titration with a normal hydrochloric acid and recursive titration with 1 normal sodium were also measured in dust and soil samples (Khoshgoftarmanesh, 2007).Then, the samples were powdered using agate mortar. 0.5 g of the sieved and dried sample was taken, and in order to prevent carbonate boiling, first 2 drops of 0.1 N hydrochloric acidwas poured onto the sample inside Teflon Becker, and then 5 cc Hydrofluoric acid was added to decompose the soil silicates and heated on a sand bath at 125 ° C. Then, 7 cc of Aqua regia(HCland HNO 3 compound as 1:3 ratio) was added to each to decompose the nitrates and carbonates of the soil and was heated on the sand bath to 125 ° C, then cc3 perchloric acid was added to the sample to decompose the organic matter and again heated on the sand bath until near drying and finally reached 5 cc (50) in volumetric flask normal 0.1 hydrochloric acid and finally measured using ICP-OES (Yazdi, 2013).

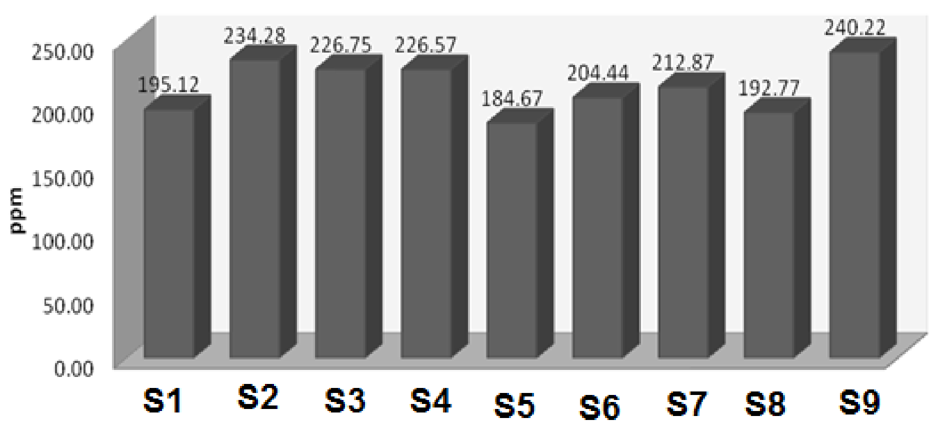

Chart (1) Comparison of the mean of metallic elements in the samples of 9 main squares of Tehran

Environmental pollution assessment methods

A: Enrichment factor (EF)

The enrichment factor of a metal is obtained by the following equation:

$$EF = \frac{[\frac{Cx}{Cref}]\ Sample}{[\frac{Cx}{Cref}]\ background}$$

Where , $[\frac{Cx}{Cref}]$sampleis the ratio of the metal concentration to the base metal (Fe) in the sample under study and the $[\frac{Cx}{Cref}]$backgroundis the ratio of the metal concentration in the crust to the base metal (iron) concentration in the crust The range of enrichment factor changes for analyzing the values obtained is presented in Table 3.

Table 3. Enrichment factor changes (Pekey 2006)

Amount of enrichment	Amounts of EF
No accumulation	EF≤1
Minor accumulation	1<EF≤3
Middle accumulation	3<EF≤5
Relatively severe accumulation	5<EF≤10
Severe accumulation	10<EF≤25
Very severe accumulation	25<EF≤50
Extremely high accumulation	EF>50

The calculated enrichment factor values for the samples are presented in Table 4 and Chart 2.

Table 4. Calculated EF values for the metals in the samples

Fe	Bi	Mn	Cd	Cr	Ni	As	Cu	Zn	Pb	EF
0/5	94/1	1/5	2/3	1/2	0/7	4/8	4/9	10/0	12/8	S1
0/8	73/2	1/1	1/4	3/8	2/2	7/0	5/7	9/6	15/4	S2
0/7	73/6	1/2	2/1	1/3	0/6	4/0	22/6	10/4	14/1	S3
0/5	117/9	1/6	2/9	1/8	1/0	4/5	12/2	10/2	63/1	S4
0/6	69/0	1/5	1/3	1/0	0/5	10/5	4/7	6/8	8/7	S5
0/7	86/1	1/3	2/0	1/3	0/7	11/4	4/4	8/5	12/3	S6
0/6	18/2	1/6	1/4	1/0	1/1	18/0	7/9	29/5	23/0	S7
0/6	80/9	1/4	1/8	1/2	0/5	4/2	10/0	7/5	9/6	S8
0/6	67/6	1/4	1/8	1/4	0/6	9/1	8/7	8/9	14/7	S9
0/6	75/6	1/4	1/9	1/6	0/9	8/2	9/0	11/3	19/3	mean

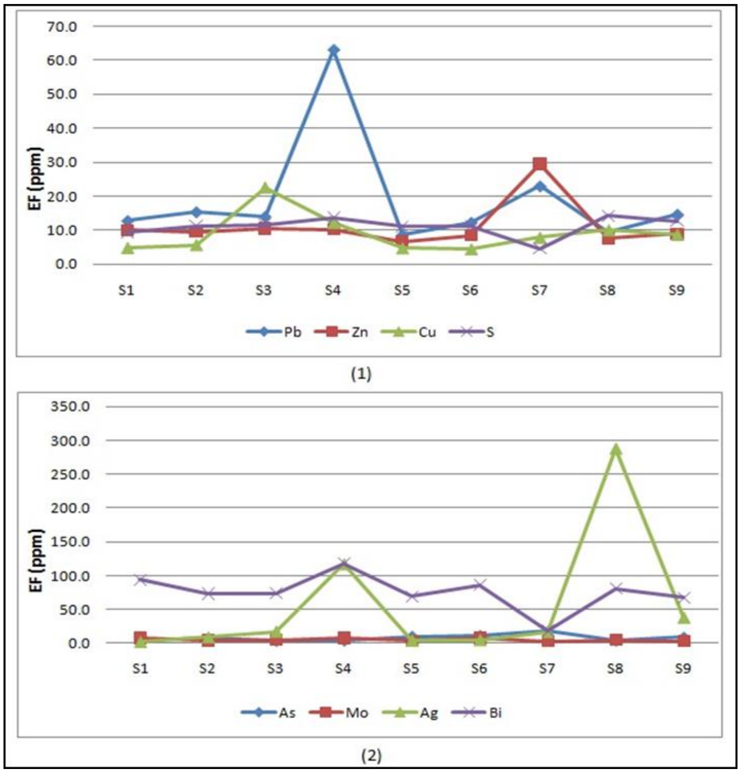

Chart (2) Figures 1 and 2 - EF Indicator for some elements in Tehran deposited dust

B: Muller index (Igeo)

In this study, in addition to the enrichment factor, the geoccumulation Index was also used to measure the heavy metal contamination ratecalculated from the following equation:

$$Igeo = log_2 \frac{Cn}{1.5Bn}$$

WhereCn is the average concentration of metal measured in the sample, Bn is the background concentration of the metal (hereinafter shale is used as the background) and the factor 1.5 is the shale correction factor.

In this formula,as theprevious concentration of element is obtained via the full decomposition, the shale concentration as a sedimentary rockshould be used since the previous concentration. Because the average element concentration in shale is lower than the average element concentration in non-contaminated sediments, thus it ismultiplied by 1.5 for equilibration. Descriptive classification criteria for geoccumulation index are presented in Table 5.

Table 5. Classification criteria for *geoccumulation* Index (Muller, 1979)

Igeo Range	Igeo Value	Igeo Class	Designation Of Sediment Quality
Igeo>5	>5	6	Extremely contaminated
3<Igeo<5	4-5	5	Strongly to extremely contaminated
3<Igeo<5	3-4	4	Strongly contaminated
1<Igeo<3	2-3	3	Moderately to strongly contaminated
1<Igeo<3	1-2	2	Moderately contaminated
Igeo<1	0-1	1	Uncontaminated to moderately contaminated
Igeo<1	0	0	Uncontaminated

Table 6 .The *geoccumulation* index for some elements in Tehran urban soil

Igeo	Pb	Zn	Cu	Cd	Cr	Bi	Ni	Mn	As	Mo
S1	1.68	1.5	0.95	0	0	2.08	0	0	0	0.72
S2	2.48	1.96	1.7	0	1.11	2.24	0.31	0	0	0.4
S3	2.14	1.89	3.49	0	0	2.05	0	0	0	0.4
S4	3.95	1.5	2.25	0	0	2.37	0	0	0	0.61
S5	1.23	1.03	1	0	0	1.73	0	0	0	0
S6	1.93	1.57	1.12	0	0	2.25	0	0	0	1
S7	2.71	3.25	1.83	0	0	0	0	0	0	0
S8	1.33	1.14	2.06	0	0	1.92	0	0	0	0.09
S9	2.01	1.46	1.92	0	0	1.73	0	0	0	0

The Mullergeochemicalindex for heavy metals in the samples is calculated and the results were classified according to the Muller criteria (Table 6, 7) and Chart 3 is plotted.

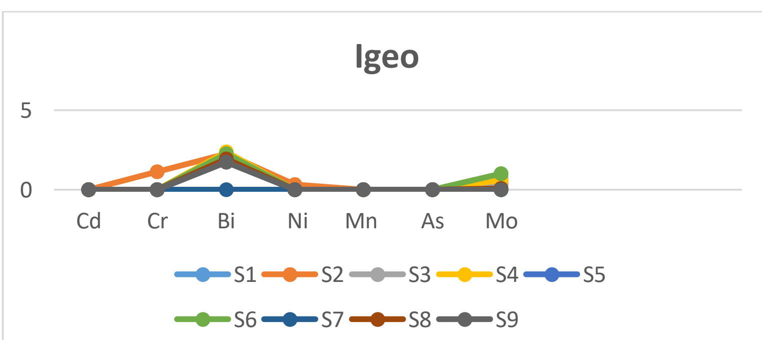

Chart 3. Igeo index for some elements in the deposited dust of Tehran

The results of multivariate statistical analysis

A: Cluster analysis and Pearsoncorrelation

Diagnosis of the relationship and correlation between different elements can help in more accurate assessment of environmental impacts. In this study, Pearson correlation coefficients were used to determine the relationships between different elements. Understanding these relationships can be helpful in identifying the source of the element and how it is transferred to the environment. The high correlation of elements in the sediment can be attributed to several factors such as: adsorption on clay minerals and organic matter, presence of elements in the structure of minerals especially clays, absorption of elements by oxides and iron and manganese hydroxides (Sam, 2011).

Table 7. Results of elements pollution intensity based on Igeo index in Tehran street dust

L.O.I.	Ca	Al	Fe	Co	Ni	Cd	Cr	Bi	Mo	V	As	Cu	zn	pb	
														1.00	pb
													1.00	0.16	zn
												1.00	0.06	0.14	Cu
											1.00	-0.35	0.74	-0.13	As
										1.00	0.47	-0.27	0.62	-0.27	V
									1.00	-0.17	-0.32	-0.03	-0.34	0.18	Mo
								1.00	0.75	-0.67	-0.70	0.09	-0.76	0.24	Bi
							1.00	0.36	0.15	-0.35	0.00	-0.04	0.01	0.13	Cr
						1.00	0.03	0.68	0.72	-0.32	-0.53	0.49	-0.25	0.51	Cd
					1.00	-0.06	0.96	0.14	0.07	-0.13	0.20	-0.06	0.28	0.18	Ni
				1.00	0.44	0.74	0.44	0.42	0.34	-0.26	-0.37	0.43	0.11	0.71	Co
			1.00	-0.22	-0.49	0.01	-0.53	-0.25	0.08	0.73	-0.05	-0.17	0.06	-0.45	Fe
		1.00	0.28	-0.08	0.11	-0.31	-0.16	-0.68	-0.16	0.81	0.57	-0.17	0.84	0.07	Al
	1.00	-0.33	-0.43	0.57	0.23	0.78	0.30	0.68	0.71	-0.50	-0.12	0.21	-0.18	0.59	Ca
1.00	-0.50	0.81	0.74	-0.26	-0.13	-0.32	-0.35	-0.67	-0.17	1.00	0.47	-0.27	0.62	-0.27	L.O.I.

Table 7 contd..Results of elements pollution intensity based on Igeo index in Tehran street dust

Pollution intensity	Element
Low to average pollution- station 4 high pollution	Pb
Low pollution-station 7 high pollution	Zn
Low pollution to average-station 3 high pollution	Cu
Practically non- contaminated	Cd
Practically non- contaminated	Cr
Practically non- contaminated	Ni
Practically non- contaminated	Mn
Practically non- contaminated	As
Practically non-contaminated	Mo
Low to moderate contamination	Bi

Figure (3) indicates a cluster analysis dendrogram of the elements present in the samples. Table (7) shows the correlation coefficients of the elements in the samples relative to each other.

For statistical interpretation of the relationship of the elements with each other and determine their origin in the dust particles, the correlation coefficients of the existing elements of the dust particles have been used. These coefficients are then transformed into cluster diagrams by which the similarity coefficients of the samples can be examined. These results are presented in Table (7) and Figure (3). By using cluster analysis we can divide the toxic elements in dust particles in Tehran into two main groups and sub-groups.

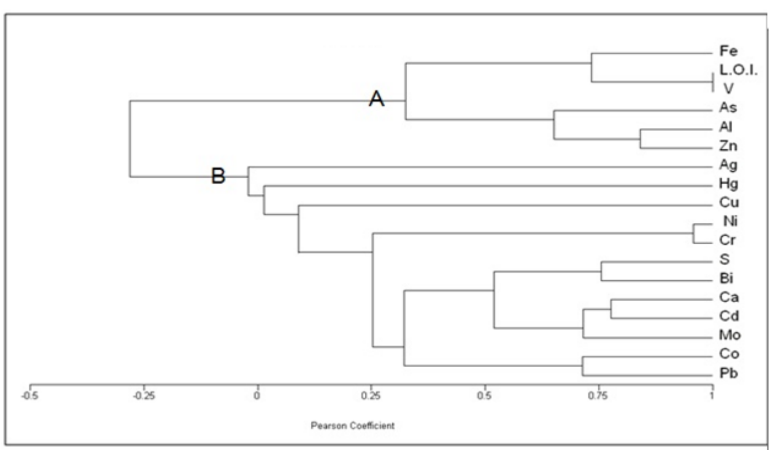

Fig. .3 Dendrogram of Cluster Analysis of Elements in Samples

Results and discussion

The Fe element with a significant positive correlation coefficient of 0.75 is connected to another branch containing elements V and LOI. Since element Fe is the index of soil materials, LOI is the index of organic matter and V is the index of petroleum, so the origin of the elements of these two branches is determined. The mentioned elements in the unexplained range are connected to their adjacent branch containing As, Al and Zn and cannot be interpreted but in this branch the elements Al and Zn with a positive and significant correlation coefficient are connected to each other as well as two elements with a positive correlation in the range of 0.7 to As. Since Al is a terrestrial index, therefore the elements attached to it are probably of terrestrial origin. The relationship of the aforementioned branches to the other branches is in non-interpreting range.

In the other branch, Ni and Cr elements are positively and significantly correlated with each other since Ni is an indicator of petroleum, so Cr is also of petroleum origin. The relationship of this branch to other branches is in non-interpreting range. In anotherbranch,Ca and Cd elements with positive and significant correlation coefficient of about 0.8 are connected to each other and this branch is connected with Bi and Mo in a significant range. The Ca element is an indicator of biogenic materials so the elements attached to it have a biogenic origin.

In general, heavy metal contamination in urban areas is often caused by road dust and automobile waste. The main role in pollution is dedicated toPb, Zn, Cu and Cd and the minor role is given to Cr, Co, Ni, V, Hg, As, Se , Fe and Mn. Meanwhile, Arsenic, is of primary importance in terms of being harmful to health and carcinogenicity. Factors such as soil particle size and its durability (soil durability in interaction with contamination sources) play an essential role in the uptake of elements. The adsorption of elements on silt particles is usually higher than sand.

Examination of EF data shows that Pb, Zn, Cu, Bismuth, Arsenic and Molybdenum show the highest enrichment intensity in the environment. Other elements, such as chromium and cadmium, etc. show partial enrichment in the environment.Igeo data show an increase in the concentration of lead, zinc, copper and silver in the environment. Fe has positive and significant correlation coefficients with V and LOI since Fe is the soil index, LOI is the organic matter index as and V is the petroleum index, so the origin of the elements of these two branches is determined. Al and Zn were linked to each other with positive and significant correlation coefficients as well as two elements with positive correlation are connected to As. So as a result the elements attached to it are probably of terrigenous origin.

In the other branch, Ni and Cr elements are positively and significantly correlated with each other since Ni is an indicator of petroleum, so Cr is also of petroleum origin. The other branches of Ca and Cd have positive and significant correlation coefficients and these branches are connected with Bi and Mo in significant range. The element Ca is an indicator of biogenic materials so the elements attached to it are of antropogenic.

Conclusion

The average data show that lead (Pb), Zinc (Zn), Copper (Cu), Arsenic (As), Bismuth (Bi) show higher concentration than the earth crust. The results of the enrichment factor calculations show that the bismuth element is in the high concentration range in all the squaresand the zinc element in Rahahansquare is very strong and in the rest of the squares, it is in the relatively intense range. The copper element in Sadeghiyeh and Punk squaresis in high accumulationrange, lead element in Punaksquare is strongly high and in other areas is in high concentration range, Arsenic also shows high concentration in Valiasr, Azeri and Rahahansquares. . Muller index calculations also show the contamination of lead, zinc, copper and bismuth. The elements mentioned are mostly the street and urban environments pollutants. The main source of urban lead is the use of lead-containing fuels and lead-containing paints. Arsenic and bismuth are sulfide-friendly and commonly present with sulfur in gasoline. Bismuth is also used in the manufacture of file and as a catalyst in the manufacture of tires. The asphalt used in the streets consists of sand, gravel and bitumen. Sand and gravel contains silicon, aluminum, and potassium, and bitumen contains various groups of asphaltenes, resin loops, saturates, and oils. Most resins are associated with sulfur, oxygen or azoth, and bitumen also contains very small amounts of vanadium and nickel. In addition, asphalt is usually associated with elements of sulfur, chromium, vanadium, manganese, uranium, cobalt. Asphalt is eroded by vehicles as well as the hot weather, so it is easily removed from the street surfaces and the associated elements enter the environment. Overall, the results show that street dust pollution to heavy metals threatens the environmental condition of Tehran considerably and their main sources of emissions are light and heavy traffic (fossil fuel combustion and corrosion of used car parts), and smoke from factories and workshops in Tehran. Fe has positive and significant correlation coefficients with element V and LOI, since Fe is the soil index, LOI is the organic matter index and V is dedicated to the index of petroleum, so the origin of the elements of these two branches is determined. Al and Zn are linked to each other with positive and significant correlation coefficients as well as two elements with positive correlation are connected to As. Thus, the elements attached to it are probably of terrigenous origin. In the other branch, Ni and Cr elements are positively and significantly correlated with each other since Ni is an indicator of petroleum, so Cr is also of petroleum origin. The other branches of Ca and Cd have positive and significant correlation coefficients connected to each other and these branches are connected with Bi and Mo in a significant range. The Ca element is an indicator of biogenic materials so the elements attached to it are anthropogenic. According to the results, it is necessary to take necessary measures to control pollutant sources in Tehran.

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