Algerian Journal of Environmental Science and Technology
December edition. Vol.2. Nº3. (2016)
ISSN : 2437-1114
www.aljest.org

Evaluating and determining of heavy metals in the atmospheric dust by using statistical methods (PCA and CA)

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ARTICLE INFO

Article History:

Received : ***12/11/2016***
Accepted : ***21/12/2016***

Key Words:

Heavy metals;
Multivariate statistical analysis;
Atmosphere dust.

ABSTRACT/RESUME

Abstract: *Today with the galloping rate of population air pollution has recently become an inherent part of human life. In fact no one can turn a blind eye to the enormous effect of this issue on human health. Street dust is an indicator of air pollution status in cosmopolitan atmosphere. It is very valuable for measuring the amount of air pollution. In this research a spatiotemporal trend has been conducted on heavy metals including Pb, Cd, Co, Zn, Mn, Fe, Cu and Ni existing in Isfahan atmospheric area. In this study temporal trend analysis of concentrations of heavy metals through sampling during 7 months (May to November 2014) revealed the fact that highest concentration of heavy metals Pb, Cd, Zn, Ni and Cu showed in the last month of sampling (November). Spatial trend of heavy metals variations in this area also showed that the highest concentrations of Zn, Cu, Ni, Cd and Pb exist in the center and southern part of the city (High traffic, and Population); but, the concentration of Co, Mn and Fe were almost uniformly distributed in all parts of the city. Normalized elemental content of soil dust in ratio to their corresponding value in reference soil has displayed the following enrichment order: Zn> Cu> Co> Pb> Ni> Fe> Mn. The results show that there are three main sources for heavy metals available in atmospheric dust in Isfahan city. The first group is metals with industrial-traffic source that contain Pb, Cd, Zn, Ni and Cu. The second group comprises metals from natural soil that contains Fe and Mn; and the third includes Co that originates from various manufacturing industries.*

I. Introduction

The drought, which in recent years increasingly intensified due to the climate change and desertification phenomenon in the Middle East, has played an important role in increasing dust. Due to the dissertation which resulted in dried soil, smaller particles have been increasing, then they are converted to the form of aerosol; thereby by wind currents or other physical processes they join the two air flow. The very small particles are known as the dust [1]. The main air pollution issues in cosmopolitans area are dust emissions since a certain amount of dust will be produced during a short period of time [2]. The most percentage of dust particles containing clay and silt (especially silts) because of the fact that these particles are very low weight, and most of the time in arid and semi-arid area they don't have any flocculation materials, so it's possible for these particles to dispersion. These can be transmitted long distance and high altitude in atmosphere and ultimately could be deposited in dry or wet form [3].

Due to the high emissions of dust in the environment, heavy metals attaching to the particles can be released on a large scale [4], and because of this, dust can be considered as an important source of heavy metals [5].

Generally, urban dust reflects the state of pollution in urban areas [6]. At the same time, when the dust phenomenon happens, the concentration of some heavy metals (including Lead) rises three times [7]. Generally, heavy metals enter to the urban environment from the various human sources including industrial plants, combustion of fossil fuels, use of energy [8] and agricultural activities. Heavy metals can cause serious environmental hazard. Metals such as Lead, Cobalt, Cadmium, Copper, and chromium are defined as dangerous pollutants which can be accumulated in the human body with a relatively long half-life existence. In addition, some ions of Cadmium, chromium and Copper lead to skin diseases and types of cancer [9]. Therefore, the study and understanding of the heavy metals behavior is significant for different reasons. One of the main studies about any pollutant understands the value and source of pollution. For this reason, determining the amount and source of heavy metals contained in dust as one of the factors of urban atmospheric pollution is very important. In a study on the distribution and identification of sources of heavy metals about particulate matters in atmosphere in India, it was found that the metals such as Cadmium, Lead, Zinc, Copper and Nickel are highly enriched in comparison with the same metals in crust of the earth. The industrial activities, exhaust from vehicles and fuel combustion were introduced as the main sources of these metals in the atmosphere under the study [10]. In one study Mohair et al revealed the fact that, it is crystal clear that the main source of contamination of agricultural soils in relation to Zinc, Lead and Arsenic is dust association with mining of these metals [11]. In another study Pandey et al revealed the fact that the mean concentrations of heavy metals in PM10 were found in the order of Fe> Cu> Zn> Mn> Pb> Cr> Cd> Ni. In this study the major sources contributing to air pollution were firstly coal mining related activities and active mine fires, and secondarily vehicular emissions, while wind-blown dust through unpaved roads also contributed to some extent [12]. In this study, the time and location trends of heavy metals pollution is examined. On the other hand, the identification of sources of heavy metals in dust was analyzed using statistical methods. The population, heavy traffic of vehicles and proximity to industrial centers along with biological contaminants existing in Isfahan are known to be the permanent sources of environmental pollutions.

II. Materials and methods

II.1. Study area

The area under study of this research is Isfahan urban (Iran) which is located between longitudes 51° 32' to 51° 47' east and latitudes 32° 38' to 32° 46' north. The city is one of the largest and most populous cities in Iran. Furthermore, in terms of industrial activities, Isfahan is in the second rank of industrial cities in Iran. The Meteorological Organization Statistics show that the wind direction in Isfahan is mainly from the southwest, but; in summer the wind direction is from the East and northeast that causes the transmission of the dust created in the East of Isfahan into urban area **[13]**.

II.2. Field method

For collecting dust, the traps suggested by Menendez et al. were used **[14]**. These traps consist of a 1 m^2 glass on which a plastic 2 mm mesh is located (Figure 1). Twenty-two zones in the city for traps dust samples were selected (Figure 2). When determining the dose-response of an environmental exposure, it is valuable to have a sample size large enough that participants in the study will experience the health outcome **[15]**. At each site, two glass traps are placed on a floor building. The sampling was conducted during seven months (May to November 2014). At the beginning of each month, glass surface is completely washed using water and sponge; and at the end of each month dust of both glass by bladed spatula were collected in each area and were collected in clean plastic bags and were transferred to the laboratory.

II.3. Laboratory methods

Dust samples, after transferring to the laboratory, were passed from 2 mm sieve. The purpose of this study is determining the concentration of contained heavy metals Zinc (Zn), Manganese (Mn), Cobalt (Co), Iron (Fe), Copper (Cu), Nickel (Ni), Lead (Pb) and Cadmium (Cd) in dust samples. Therefore, 6 normal nitric acid added to 0.5 g of dry dust samples. After 48 hours, samples are located at 80 ° C of heat for half an hour and later, we use a balloon full a volume of 25 mL with nitric acid 1% **[16]**. Perkin-Elmer atomic absorption spectrometry 3030 is used for measuring the concentration of Zinc, Manganese, Cobalt, Iron, Copper and Nickel; and Perkin-Elmer atomic absorption spectrophotometer A-ANALYST 200 is implemented for the measurement of Lead and Cadmium.

II.4. Statistical analysis

Basic and multivariable statistical analysis on the concentration of heavy metals of dust was conducted in this study. In order to compare the

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concentrations of heavy metals contained in dust with each other and with comparison to the concentrations of these metals with the other reported studies, basic statistical analysis has been used. Time trend concentration of heavy metals of dust during the 7 months of sampling with the help of box plot of statistical comparison is displayed using Duncan method. Also, Location trend of concentration of heavy metals of dust in the 22 sampling zones in Isfahan, through implementing a bubble graph, is illustrated. In this study, in order to determine the source of heavy metals in dust, multivariate statistical analysis (CA & PCA) have been used. It is required to optimize the air quality monitoring network using the practical alternative methods such as Principal Component Analysis (PCA) and Cluster Analysis (CA). PCA is a multivariate statistical technique that creates new variables, commonly known as principal components (PCs) that are orthogonal and uncorrelated to each other. These PCs are linear combinations of the original variables **[17]**.

Figure *Glasses traps of dust samples*

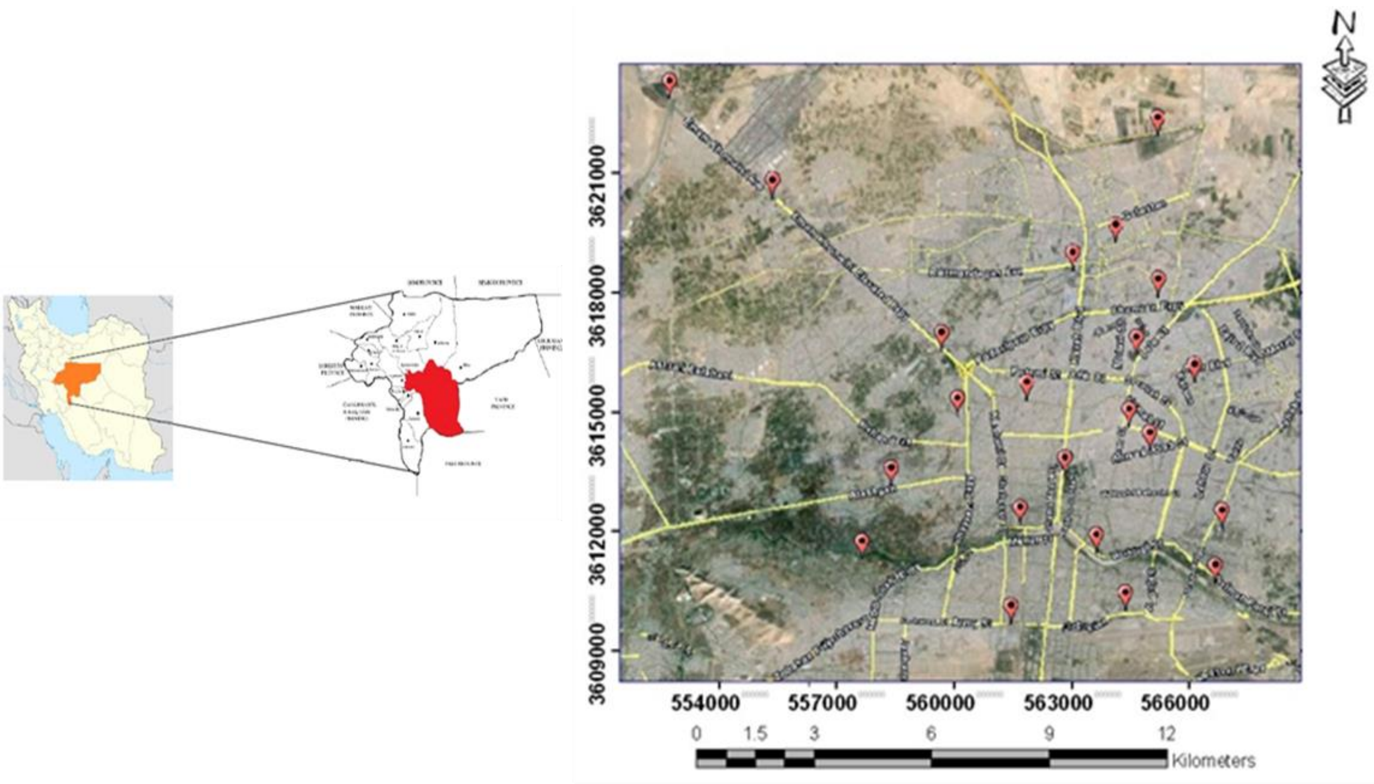

Figure 2. Location of sampling in Isfahan city (Iran)

III. Results and discussion

III.1. the concentration of heavy metals

By comparing the average concentrations of studied heavy metals in this experiment with an average concentration of these metals in the soil, it can be seen that the concentration of all metals, except for Iron and Manganese dust, is more than that of the soil. The ratio of the concentration of dust to soil is as follow: Zn> Cu> Co> Pb> Ni> Fe> Mn. This table shows that, heavy metals like Zinc, Copper, Cobalt, Lead and Nickel in urban dust are enriched by polluting elements but Iron and Manganese, which remain unchanged. In one study in the China The concentration of Cu, Zn, Pb, Cd and Cr in road dust were higher than their local soil background values to different extent, furthermore this research revealed the fact that an anthropogenic input is of vital importance for increasing the amount of heavy metals in dust, so that so much the concentration of Cd was 15.2 times higher than its secondary standard value of the Chinese Environmental Quality Standard for soils **[18]**. Based on previous studies, maximum concentrations of heavy metals in atmosphere dust attributed to industrial and residential areas; the density depends strongly on traffic, the number of vehicles and their speed of movement **[19]**. Iodice et al (2016) in one study reveals the fact that combined analysis of the different data sets clearly shows that for the investigated municipalities in Campania, a considerable part of total emissions is due to road traffic **[20]**.

III.2. Comparing concentrations of heavy metals in the dust with some other cities

Street dust is a major source of heavy metals in big cities. In this stupendous machine age in metropolises atmosphere high concentration of heavy metals causes deleterious effect on various terrestrial creatures and human beings **[21, 22]** .A common method is the comparison of average concentration of heavy metals in urban areas with each another **[19]**. Nevertheless, this method is not widely accepted **[23]**. In this study the comparison of the average concentration of heavy metals during seven months of sampling, with reported concentration of some heavy metals in various cities across the world has been done. The concentrations of heavy metals in the Baoji China, Ottawa Canada, Hong Kong, Calcutta India, Oslo Norway, Madrid Spain, London England and Tehran Iran are given in Table 2. By comparing Tables 1 and 2, it seems that the concentration of Cobalt and Nickel in the dust of Isfahan is more than that of all mentioned cities. The same trend is true for Zinc, with the exception of Hong Kong and London. The amount of Manganese and Iron of dust in Isfahan is lower than all cities of Table 2. The amount of Lead of dust in Isfahan is more than Hong Kong, Ottawa and Oslo; and the amount of Copper of dust is less than all cities with the exception of Ottawa and Calcutta. The concentration of Cadmium in the dust in Isfahan is less than Calcutta, London and Tehran and it is more than that of Ottawa and Oslo.

III.3. Temporal trend concentration of heavy metals

To investigate the effects of significant industrial structure and pollution controls change, temporal trend analysis with dynamic emissions factors are very valuable **[2]**. Temporal trend of average concentration of heavy metals is shown in Figure 3. Cobalt, during seven months of sampling contains a large monthly variation. This indicates that sources of this metal of dust in the atmosphere are different in each period. After Cobalt, two metals namely Manganese and Iron are not different in monthly sampling compared to another months. According to Figure 3, the last month of Sampling (T7) indicates the highest concentration of Cadmium, Copper, Nickel, Lead and Zinc. In this month, because of the cold weather and increasing traffic vehicles due to the reopening of schools and universities; fossil fuel consumption has increased. This reflects that the main source of these metals in the dust of urban is fuel consumption for producing thermal and kinetic energy. Resulting from one research about air pollution monitoring revealed the fact that all of the major air pollutions and the following heavy metals: like Cr, Cu, Ni, Pb and Zn, caused by the anthropogenic activities affecting **[20]**. A research about the trends of atmospheric heavy metals deposition in Lithuania shows that Pb and Zn in the air are observed during the cold Period because of large fuel consumption during cold season **[31]**. A research on heavy metals of dust in Kayseri, Turkey revealed that the heavy metals like Copper, Nickel, Cadmium and Zinc arise from industrial activities; while origin of Lead is related with traffic **[32]**.

III.4. Spatial trend concentration of heavy metals

Figure 4 shows the spatial trend of concentration of heavy metals of dust in each area during seven months of sampling. According to this figure, the Location trend of heavy metals Zinc, Cadmium, Copper, Nickel and Lead in the center and south of the city is more than the otherparts. This indicates

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www.aljest.org

Table 1: *Descriptive statistics of average concentrations of heavy metals in the dust during seven months of sampling with average concentration of heavy metals in soil (mg/Kg)*

Element	Ni	Cu	Fe	Mn	Zn	Co	Cd	Pb
Max	94	139.2	13738.6	394.8	1060.2	28.7	2.7	230.3
Min	46.9	82.5	7997	219.2	774.3	21.4	2.1	183
Rang	47	56.7	5741.6	175.5	285.8	7.3	0.5	47.3
Mean	70.8	102.6	10250	325	935.2	25.6	2.4	198.1
Median	77.7	100	9406.9	334.5	904.2	26	2.4	193
S.D	16.6	17.8	2422.6	59.6	101.8	2.3	0.2	16.6
CV	23.4	17.4	23.6	18.3	10.8	9	9.9	8.4
Skewness	-0.2	1.6	0.4	-0.7	-0.2	-0.8	0.1	1.3
Kurtosis	-0.9	3.5	-1.9	0.4	-0.8	1.3	-2.4	1.7
Reference Value*	51.2	31.6	12986.5	487.7	69.3	9.7	-	133

The average concentration of heavy metals in the surface soil of the region* *[24]****.*

Table 2: *A comparison of heavy metals concentration (mg/Kg) in street dust of Isfahan and other cities*

City	Ni	Cu	Fe	Mn	Zn	Co	Cd	Pb	Reference
Baoji	48.8	123.2	NA	804.2	715.3	15.9	NA	433.2	**[23]**
Hong Kong	28.6	110	14100	594	3840	9.5	NA	120	**[25]**
Ottawa	15.2	65.8	18948	431.5	112.5	8.3	0.37	39	**[26]**
Calcutta	42	44	26700	619	159	15.6	3.1	536	**[27]**
Oslo	41	123	NA	833	412	19	1.4	180	**[28]**
Madrid	44	188	NA	362	467	3	NA	1927	**[28]**
London	NA	191	22800	379	1176	7.3	5.2	2008	**[29]**
Tehran	34.8	225.3	NA	NA	837.2	NA	10.7	257.4	**[30]**
Isfahan	70.8	102.6	10250	325	935.2	25.6	2.4	198.1	**This study**

** NA: not available*

that these metals, in areas of the city with more urban population and traffic, have higher concentrations compared to the other regions; and most likely, these metals arise from the traffic of vehicles while the location trend of Manganese, Iron and Cobalt is almost identical across the study area. This indicates that these metals are influenced by other factors. Assessment of air quality monitoring data in one study showed the fact those significant spatial variations in concentrations of PM10, PM 2.5, PM1, SO2, NO2 and heavy metals in PM10 depending on pollutant emission or formation and pollutant dispersion mechanisms, which are also influenced by meteorological conditions and distance of the site from sources **[12]**. A study of heavy metals and polycyclic aromatic hydrocarbons in road dust of Isfahan shows that the Lead, Zinc, Cadmium and Copperhave the origin of urban vehicle traffic and these metals in crowded areas of the city have higher concentrations compared to other regions **[33]**.

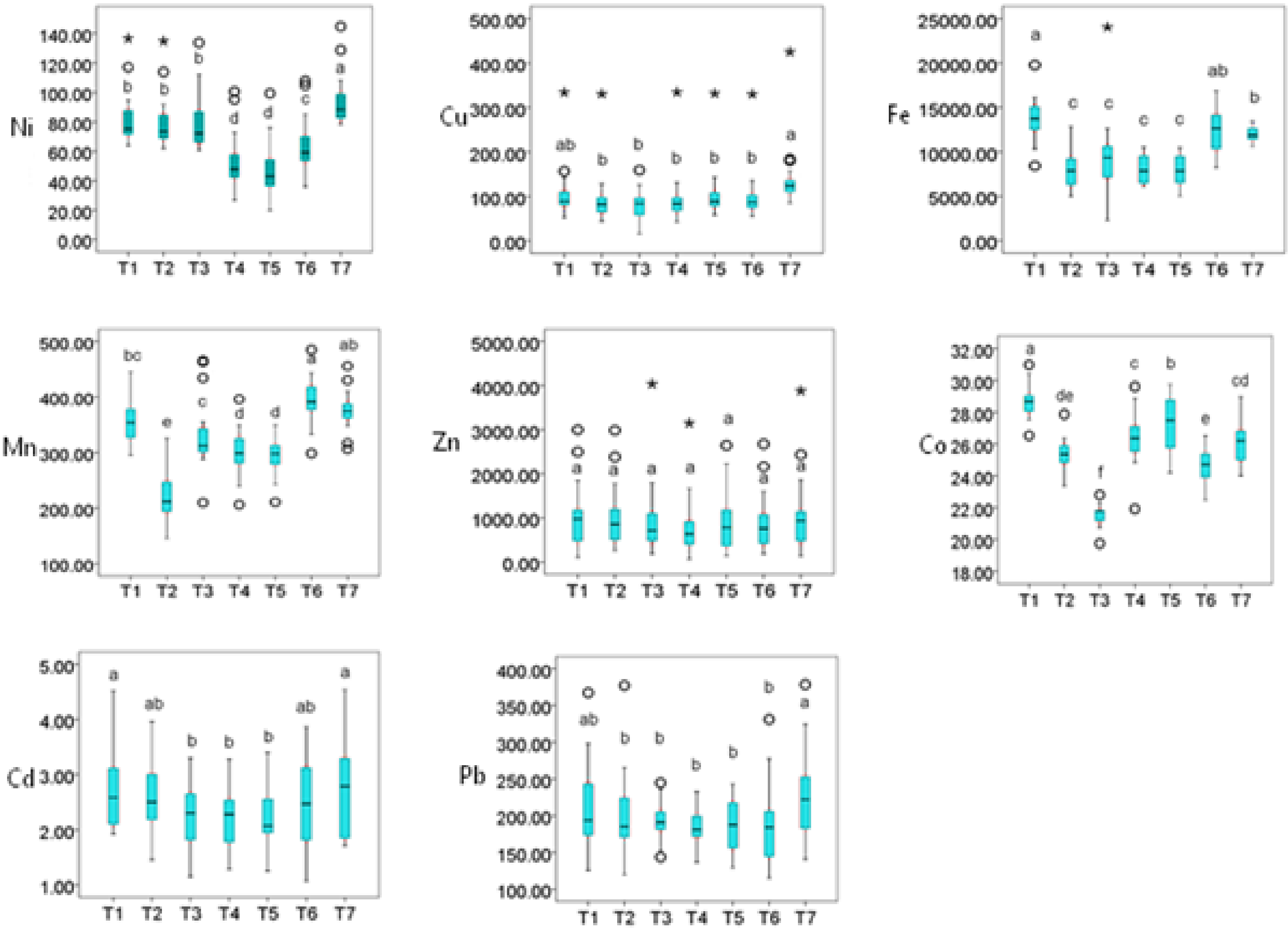

Figure 3: Box plot of subsidence rate changes during the sampling period(mg/Kg). (Months with same letters, at 5% level of Duncan test have not significant Difference).

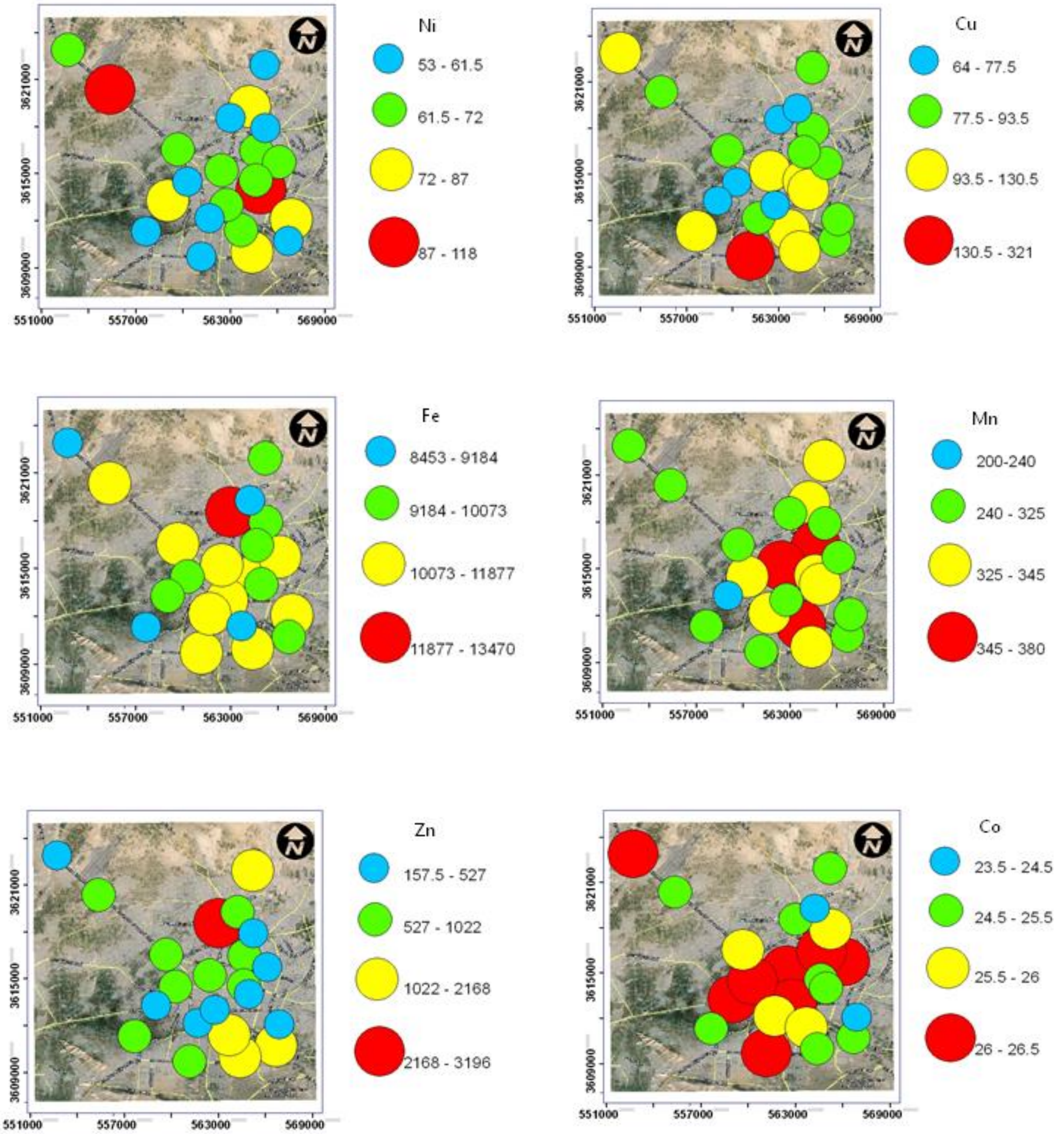

Figure 4: *Bubble chart of distribution of heavy metals (mg/Kg) in dust of each 22 area during seven months of sampling*

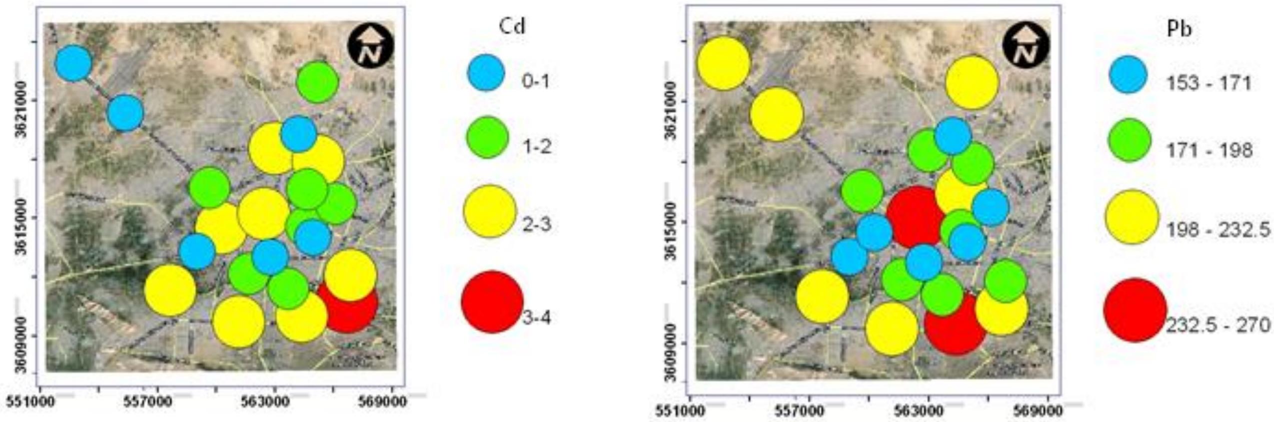

Figure 4: *Continue* (mg/Kg)

III.5. Multivariate statistical analysis results

Clustering and principal components analyses are the most common methods of the multivariable statistical methods that are used in environmental studies **[34, 35]**. PCA also widely is applied for reducing the use of data and extracting small number of hidden factors for analysis of the relationship between variables **[36, 37]**. PCA is a classification method that includes both measuring distance and the similarity between the objects among clusters. Objects in the clusters are grouped in terms of similarities; and the basic assumption is that the proximity of objects in space by variables represents similarity of their properties **[38]**.

III.6. Clustering Analysis

Figure 5 shows dendrogram of studied variables using cluster analysis. The distance of clusters represents the correlation between the variables. Little distance indicates strong correlation and long distance presents weak correlation between the variables. Regarding the dendrogram, it can be seen that variables are placed in three major groups. The first group consists of Lead, Cadmium, Zinc and Nickel. The second group of metals includes Manganese and Iron and the third group has Cobalt. Copper also has considerable similarities with the first group and Cadmium.

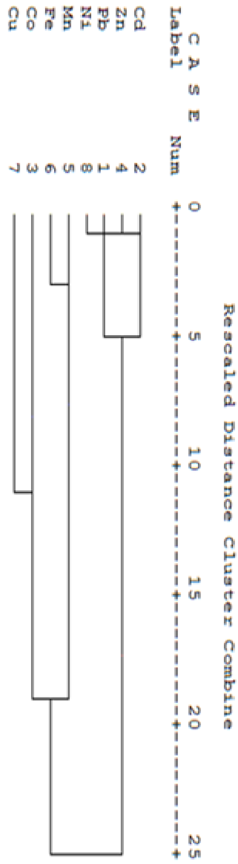

Figure 5: *Dendrogram of clustering analysis, the average concentrations of heavy metals in the dust during 7 months sampling*

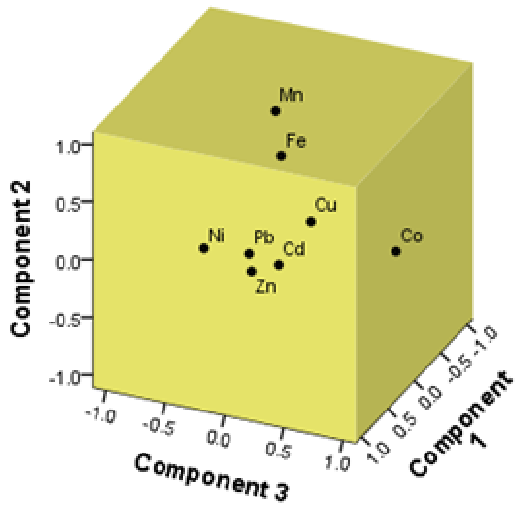

Figure 6. *Three-dimensional graph of distribution factors for heavy metal of dust*

III.7. Principal components analysis

PCA is a multivariate statistical to transform the original data set into a smaller one that account for most of the variance of the original data **[39]**. Table 3 shows result of principal component analysis on the studied heavy metals of the dust. In this table, results of principal components from one to eight are given. In addition, load of each variable is presented in Table 4. According to Table 4, eight factors are required to justify 100% of the variability of these elements, but only three of the eight factors are justified about 91.3%. In principal component analysis, Varimax rotation was used. Varimax command is one of the most common methods of rotation orthogonal, which maintains independence of extractive factors. This method reduces the variables with bigger load to the minimum number. As can be seen, the primary factor is very strong component, because it justifies about 58.5% of the total variability. The load of Lead, Cadmium, Zinc and Nickel, after rotation state, is more than the other variables. The second factor States about 17.1% of the total distribution variation. According to Table 4 in eigenvectors, Iron and Manganese are placed in this factor. The third factor (6.15% of total variation) is under the influence of Cobalt. Therefore, for expounding principal component analysis, the first factor includes Lead, Cadmium, Zinc and Nickel. The second factor consists of Iron and Manganese and the third factor is related to Cobalt. This result is shown in Figure 6. It can also be said that Copper has similar behavior to the first and third factors respectively. According to the classification available in Figure 6, Copper also belongs to the first factor and has the same origin as with Lead, Cadmium, Zinc and Nickel. Likewise present study Norouzi et al (2016) in study of biomagnetic monitoring of heavy metals contamination in deposited atmospheric dust in Isfahan revealed the fact that The presence of traffic-related heavy metals (Fe, Pb, Zn and Cu) in the dust deposited on leaves and their coexistence in ferromagnetic phases, based on the highest correlation of these metals with magnetic parameters, explains the proximity of the magnetic hot spots with high traffic sites in the city **[40]**. Davila et al (2006) revealed the fact that Mn had no correlation with magnetic parameters, so they concluded that this element in samples derived from natural accumulation in environment **[41]**.

IV. Conclusion

Today with the galloping rate of population no one can turn a blind eye to the enormous effect of air pollution on human's life, so the investigations about air pollution are widely varied from place to place so that so much Air pollution studies, methods and technologies are continually evolving. In present study this issue research by statistical methods like Principal Component Analyze and Cluster Analyze. The first factor in this study is called "Anthropogenic". This factor includes Lead, Cadmium, Zinc, Nickel and Copper. Exhaust fumes of vehicles, steam of various industries and coal mines are the main source of Lead. Zinc in various industries such as batteries, tire manufacturing and electrical equipment is used. Copper originates from depreciation of brake insulation and Nickel arises from released fossil fuels into the environment. A lot of study in all over the word shows that there is a high correlation between Lead and Cadmium. Therefore, it can be concluded that these contaminants have common emission source. The second factor has natural source (probably non-contaminated soils). This factor belongs to the Manganese and Iron- that in terms of the amount in the dust- is less than local soil. In this study research on the sources of heavy metals in dust by using principal component analysis method and cluster analysis revealed the fact that Manganese has a natural origin from local soil. The third factor has the origin of the combination of industrial activities, because the Cobalt is separate from other two groups, but due to the higher amount of Cobalt in dust in comparison with soil, there is the possibility of getting rich from different industries.

Table 3: *Special values of studied variables in the dust based on principal component analysis*

Component	Initial eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %
1	4.6	58.5	58.5	4.6	58.5	58.5	3.8	48.3	48.3
2	1.3	17.1	75.6	1.3	17.1	75.6	1.9	24.6	73.02
3	1.2	15.6	91.2	1.2	15.6	91.2	1.4	18.2	91.3
4	0.5	6.7	98.09						
5	0.08	1.09	99.1						
6	0.06	0.8	100						
7	4.56×10^{-17}	5.71×10^{-16}	100						
8	-1.4×10^{-16}	-1.7×10^{-15}	100						

Table 4: *Special vectors or load factors of the variables in the dust*

Element	Before rotated			After rotated		
	Principle Components			Principle Components		
	1	2	3	1	2	3
Ni	0.83		- 0.48	**0.93**		
Cu	0.78		0.31	0.56	0.4	0.48
Fe	0.75	0.56		0.4	**0.83**	
Mn	0.44	0.88			**0.99**	
Zn	0.89	- 0.33		**0.94**		
Co			0.93			**0.98**
Cd	0.9			**0.86**		0.35
Pb	0.93			**0.92**		

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Please cite this Article as:
Aghaei A., Khademi H., *Evaluating and Determining of heavy metals in the atmospheric dust by using statistical methods (PCA and CA)*, ***Algerian J. Env. Sc. Technology***, ***2*:3 (2016) 224-234**