

The Concentration of Heavy Metals in Precipitated Particles on the Leaves of Street Side Trees in the Urban Environments (Tehran– Iran)

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Received: 29 July 2017 / **Accepted:** 20 September 2017 / **Published:** 30 October 2017

ABSTRACT: The present study investigated heavy metals located on the leaves of street side trees in crowded areas of Tehran in order to evaluate the metal pollution caused by cars. Contamination factor, Index of geo-accumulation, enrichment factor, modified degree of contamination, and Pollution load index were used to describe the pollution of the environment and probable sources of metal emissions. The potential ecological risk of exposure to metals in the areas was measured. Leaves are useful and low-cost collectors of aerosols which are produced by transportation. According to the results of the present study, Pb, Cu, Cd, Co, Ni and Zn elements are the main pollutants within the study area; Cr and Hg, also, turned out to produce pollution in the environment. Pb and Cr have probably been emitted from depreciation of vehicles and corrosion of parts and industries; probable origins of Zn and Cu are the industrial combustion sources and alloys of automobile parts. Mn is emitted from anthropogenic sources and further studies are required to identify its emission sources. Mo and V are probably the result of natural sources. The origin of Al, Co and Hg is a combination of natural and man-made sources, with high proportion for man-made activities. Due to high concentrations of Hg and Cr in areas outside and inside the city, further studies are required to find the source of origin of Hg and Cr elements. The ecologic risk of Pb, Cd and Cu was higher in different study areas. The risk of exposure to heavy metals in high density areas, and especially in Geisha, turned out to be high. Traffic of old cars and the traffic flow are effective in the pollution changes in different areas, and decrease in wind speed and direction causes pollution escalation in central areas of Tehran, compared to Western and Northern areas.

Keywords: metal pollution, geochemical indicators, tree leaves, urban environments.

INTRODUCTION

Investigation on the concentration of metal particles, identifying their sources, estimating their distributive power, and qualitative assessment of air pollutants are essential in assessing the quality of the urban environment (Lu et al., 2009). The majority of metals emitted in the air precipitate under the influence of gravity in the closest area to the emission source. Generally, vegetation is planted in streets side in urban environments. Plants are able to precipitate the aerosols set on themselves (Maher et al., 2008. Moreno et al., 2003). Metals accumulate, in a dry manner, on the surface of leaves (Nowak and Daniel, 2006); they, also, can be preserved both

inside and on the surface of the leaf (Gratani et al., 2000).

Due to the high surface area per weight unit, leaves are considered as collectors of aerosols produced by transport in urban environments (Nowak and Daniel, 2006). Collection and decomposition of the metal content on the tree leaves is a low-cost, effective and useful way to study the quality of urban environment and monitor the rate and degree of metal pollution (Kardel et al., 2010; Balasooriya et al., 2009). High and wide distribution of trees in the city, and the variety of planted trees, provides favorable condition for spatial and temporal resolution of collected samples; it must be mentioned that easy implementation and



low cost of sampling is the important benefit of using tree leaves (Kardel et al., 2010; Norouzi and Khademi, 2015).

Tehran's biggest environmental problem is the air pollution issue that is caused by, both, natural and human factors. Most important natural factors involved in producing pollution include being surrounded by mountains, lack of sustained winds with suitable speed, and low precipitation. Human factors, such as the consumption of fossil fuels by different industries and factories, various commercial and constructional activities, home heating system and, most importantly, the large number of cars which are equipped with no suitable particle filters and catalysts are also hugely responsible for current pollution with which the city is struggling (Kermani et al., 2003; Kermani et al., 2016; Naddafi et al., 2012). There is limited information in regard with metals in the aerosols of Tehran (Kermani et al., 2016). The present study investigated heavy metals located on the leaves of street side trees in crowded areas of Tehran in order to evaluate the metal pollution caused by cars. The structural and morphological diversity of tree leaves is effective in the rate of aerosols precipitation (Kardel et al., 2010; Balasooriya et al., 2009).

Hence, *Platanus orientalis*, *Ulmus minor* 'Umbraculifera', and *Robinia pseudoacacia* leaves with varying blade structure were collected from the street sides to achieve the objectives of this study. These trees are the most abundant species in urban green spaces, which functioned as the sampling points in the present study. Environmental quality and potential sources of metals were interpreted using geochemical parameters in order to identify and describe environmental pollution and changes in metals.

MATERIALS AND METHODOLOGY

Study area

Tehran is the capital of Iran. The prevailing wind flow in Tehran is in the East-West direction and most industries are located in the Western part of the city (Alijani and Safavi, 2005). A short analysis of topography of Tehran shows that North and East of Tehran are blocked with mountains which, unfortunately, function as barriers against the transmission of contaminants. Moreover, since the area is flat and open, suburban pollutants enter the city from West with the help of winds (Alijani and Safavi, 2005).

The density of industrial centers is high in West and South-west, in which about 28% of the total industry in Tehran and 7% of the country's industry, such as thermal power plants, refineries of Tehran, factories and workshops of construction

products such as cement and ceramic, and airport can be mentioned, is located (Golbaz et al., 2010). 4 stations were selected in the west and central Tehran for the completion of the present research (Figure.1). Site.1 is located within the dense green space at the Chitgar highlands in the West of Tehran (outside of city area), in which park traffic is very low due to semi-forest function of Chitgar. The horizontal distance between the sampling area in this site and the Tehran-Karaj highway (one of the most crowded highways in Iran) is over 1000 meters. However, due to its location in the west of Tehran and the abundance of large and small industries, as well as specific topographic, and wind blowing conditions in Tehran, this area is, also, affected by the consequences of air pollution. Since most of the particles are produced by vehicles, they precipitate in the shortest distance from the source. Thus, the samples of tree leaves in site1 were collected from the dense cover of green areas at the edge of road within the park. Site1 was considered as a low-traffic area. And sites 2, 3 and 4 were considered, and almost turned out to be, high-traffic sites. Samples at site 2 were collected from marginal areas of the Azadi Square in the West and Southwest of Tehran. Azadi Square is struggling with heavy traffic in Tehran. This area is the closest sampling site (in this study) to Tehran-Karaj highway. There are numerous wide streets and sidewalks in this area and, consequently, the lower density of residential and commercial buildings caused to have better air flow and ventilation, in comparison to site 3. Samples in site3 are collected from the Gisha Bridge (Jalal Al Ahmad Street and Chamran highways). Site3 is located in the center of Tehran. The existence of Vehicles Bridge, the intersection of two highways, proximity to residential and commercial buildings and higher education institutions and administrations have caused high traffic in this area; the presence of structures in this area has reduced air ventilation, which makes the case more serious. Samples in site 4 were collected from the Hemmat highway margin adjacent to the Pardisan Park. This highway is the main E-W and W-E connection in Tehran. Site 4 is the Northernmost study area in the study. Despite high traffic in this highway, the location of this site and direction of wind flow towards Tehran, have caused relatively good air conditioning in this area; additionally, the density of commercial and residential buildings is very low and they are located far from the highway.

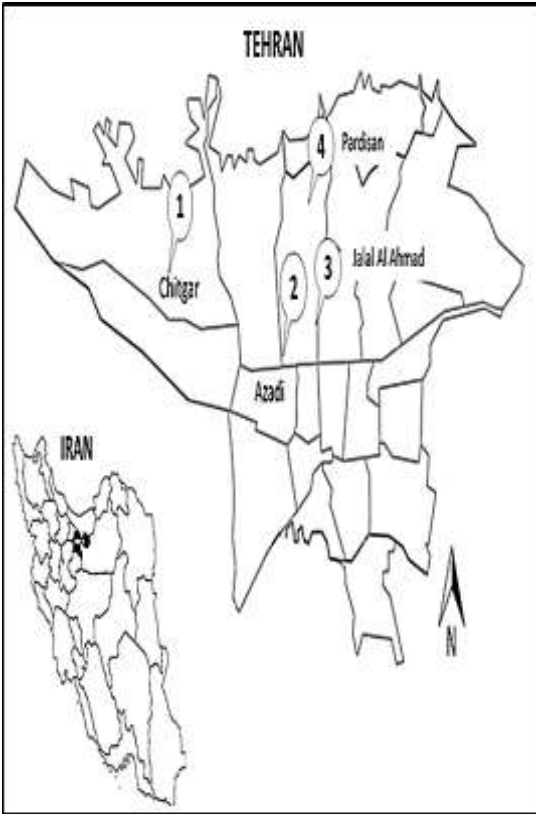


Figure1. Sampling areas in this study. September 2014

Sampling and Analysis

Leaves of *Platanus orientalis* and *Ulmus minor* 'Umbraculifera' and *Robinia pseudoacacia* trees were collected randomly of each site with a minimum distance from the street. Orientation of trees were considered identical relative to the streets and the sun and wind directions. The sampling of trees was carried out at the end of the growing season in the second half of September 2014. The last rainfall in the area happened months ago. Completely fresh leaves from the outermost part of each tree's crown were collected from the street; leaves were placed within the wrapped bags in ice tank with minimal hand contact and transported to the laboratory in the shortest time. 0.5 grams of each sample was put in 12 ml of nitric acid within a Teflon polymer container coated by aluminum foil for 1 hour at room temperature. Then it was placed on asbestos heater with indirect heat. After drying on paper, it was reached to volume by in 50 cc balloon and then filtered by Whatman 42 filter the concentrations of metals of 1st periodic Group were measured by ICP- MS device. Reference materials were used to calibrate the numbers. After measuring the concentration of metals, the average for each element was calculated in each site, and also the

concentrations of metal in all collected samples from high-traffic sites (2, 3 and 4) were summed together and the average of each element concentration was considered as its total concentration.

The present study used Contamination factor(Cf), Modified degree of contamination(mDf), Pollution load index(PLI), Enrichment Factor(EF)and potential ecological risk(RI) indices to determine the likelihood of potential ecological risks of each metal element in the intended sites(Muller, 1979. Thomilson et al., 1980. Salmanzadeh et al., 2015. Lu et al., 2010. Hakanson, 1980 .Addo et al., 2012). Previous information for elements is limited in Iran and the background concentrations of elements for different areas of Iran in different environments are not provided by relevant organizations (Salmanzadeh et al., 2015; Khosheghbal and Charkhabi, 2012). No previous study is carried out on measuring the concentrations of precipitated metals on the leaves of street side trees in this area. We used the values suggested by Hakanson, 1980, for terrestrial plants as background values for calculating the indices. Aluminum was used as reference metal.

The indices of Cf and mCd were used in order to determine and express the environmental contamination status of a particular metal. These indices were calculated by Formula 1.

Cd (Contamination Degree)is an index to measure the severity of total environmental degree of contamination which is obtained by the sum of Cf(Contaminatio factor)of all metals(Formula2). Later, mCd(Modified Contamination Degree) developed(Formula3). Furthermore, PLI(Pollution Load Index) was measured through Formula 4.

Formula1: $Cf = C_n/C_b$

Formula 2: $Cd = \sum C_f$

$\sum C_f/n = mCd$ Formula 3

Formula 4: $PLI = \sqrt[n]{C_{f1} * C_{f2} * ... * C_{fn}}$

In which C_n is the measured concentration of the element in the sample tested and C_b is background value of the element.

The levels of Cf and mCd and PLI is shown in Table 1.

Table 1. Levels of Cf, mCd, and PLI

Cf	grade Cf	mCd	mCd grade	PLI	PLI grade
Cf < 1	Low polluted	mCd < 1.5	Low	PLI value of >1	is polluted
1 ≤ Cf < 3	Moderate polluted	2-4	Moderate	PLI value of <1	indicates no pollution
3 ≤ Cf < 6	strongly polluted	4- 8	Considerable		
6 < Cf	extremely polluted	8- 16	High		
		16-32	Extremely polluted		
		mCd > 32	ultra high polluted		

Potential ecological risk index (RI) is defined as 5 and 6 formulas (Hakanson, 1980).

Formula 5: $E_i = Tr * Cf$

Formula 6 : $RI = \sum_i^p E_i$

Where E_i is the potential ecological risk factor of metal i , T_i is the toxic response factor of metal $C_o = Cu = Ni = Pb = 5, cd = 30$ and $Zn = 1$ (Xu et al., 2015.

Hakanson, 1980), C_f represents the pollution factor of metal i , C_b is the background value of metal I , RI represents the sensitivity of the biological community to the toxic metals and illustrates the potential ecological risk caused by the overall contamination (Xu et al., 2015. Hakanson, 1980) (table2).

Table 2: Grade of ecological risk. E_i , The ecological risk factor of metal i ; RI , the ecological risk index.

E_i	Ecological risk grade	RI	Ecological risk grade
$E_i < 15$	Low	$RI < 50$	Low
$15 \leq E_i < 30$	Moderate	$50 \leq RI < 100$	Moderate
$30 \leq E_i < 60$	Considerable	$100 \leq RI < 200$	Considerable
$60 \leq E_i < 120$	High	$200 \leq RI$	High
$120 \leq E_i$	Very high		

RESULTS AND DISCUSSION

Average concentrations of metals were measured in four sites and the average concentration of elements in high-traffic areas (Sites 2, 3, 4) were also determined (Table3). The hierarchy of metals in terms of concentration in high-traffic areas was like this: Metals $Al > Mn > Cu > Zn > Pb > Cr > Ni > Co >$

$Cd > MO > V > Hg$. Al is not affected by human activities; so, its high value in an environment has natural origin and is the most abundant element in the crust and form stable relationship with other elements of the crust (Turekian and Wedepohl, 1961).

Table 3. The average concentration (ppm) of elements measured at different sites of this study

site / metal	Al	Cd	Co	Cr	Cu	Hg	Mn	MO	Ni	Pb	Zn	V
background values *	500	0.6	0.5	0.23	14	0.01	630	0.9	3	2.7	100	1.6
high-traffic stes(2,3,4)	154.4	0.4	0.9	10.5	47.2	0.1	126.0	0.1	2.7	15.7	45.6	0.1
Site1(Chitgar)	89.7	0.2	0.3	5.7	24.4	0.0	79.5	0.1	1.7	6.9	25.1	0.1
Site 2(Azadi)	163.7	0.4	0.8	11.4	49.7	0.1	142.0	0.1	3.6	15.1	68.1	0.1
Site 3(Gisha Bridge)	168.8	0.5	1.1	11.9	59.7	0.1	117.4	0.2	2.8	18.8	41.8	0.2
Site 4(Pardisan)	130.7	0.3	0.7	8.3	32.0	0.0	118.5	0.1	1.7	13.1	26.7	0.1

* Land Plant(Hakanson,1980)

Since the presence of element in an area can have natural or human origin, high concentration of any specific element does not necessarily mean an unnatural pollution in an environment (Grzebisz, 2002).

To determine the quality of sample locations and pollution level of elements in various areas of the study, PLI and mCD indicators were determined (Fig.2).

CF values and their change levels are provided in Table 4 to describe the degree of pollution of each element.

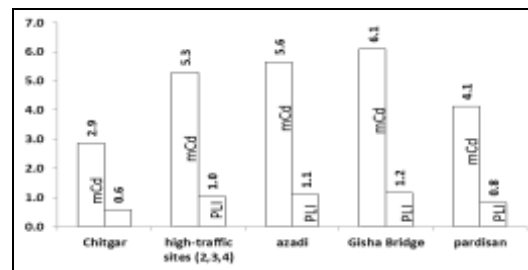


Figure2. MCD and PLI indices (the background elements concentration Hakanson,1980)

Table 4. CF values of elements in the samples. (CF values are based on background values of Hakanson, 1980)

Cf	Al	Cd	Co	Cr	Cu	Hg	Mn	Mo	Ni	Pb	Zn	v
Chitgar	0.18	0.26	0.58	24.68	1.74	3.3	0.13	0.13	0.58	2.54	0.25	0.06
HighTraffic	0.31	0.67	1.75	45.84	3.37	3.9	0.2	0.16	0.91	5.8	0.46	0.09
Azadi	0.33	0.64	1.65	49.6	3.55	4.03	0.23	0.15	1.21	5.6	0.68	0.08
Gisha	0.34	0.81	2.18	51.75	4.27	5	0.19	0.18	0.94	6.95	0.42	0.1
Pardisan	0.26	0.57	1.42	36.17	2.29	2.67	0.19	0.19	0.57	4.85	0.27	0.09

MCD and PLI results show that metals have polluted the environment in low to moderate rate and the amount of pollution is intensified in high-traffic areas. Environment quality in areas with high traffic volume and density of residential structures is further declined.

In Gisha Bridge, factors such as traffic density and commercial and residential structures have increased metals and caused the degradation of the environment. Decrease in wind speed and the lack of consistent winds, as well as the density of buildings in the central parts of Tehran, have caused an increase in aerosol content and, consequently, metals in high-traffic areas in central area of Tehran (Leili et al., 2008, Shamsipour et al., 2013, Salamzadeh et al., 2012). In this study, the toxicity and pollutions of Pb, Hg, Cr, Co and Cd turned out to be more than other metals. The inherent properties of some metals intensify their toxicity in the environment.

Enrichment factor (EF), the levels of which are shown in Table 5 and Figure 3, is calculated for each individual element. It should be noted that when the elements enrichment factor is calculated in proportion with values measured in Chitgar, no elements seems to belong to polluted class.

The EF value of elements showed that Cr, Hg, Pb, Cu, Zn, Co and Ni have an increasing trend in high traffic areas. EF values of Pb, Cr, Hg and Cu were higher than 10 and, thus, the contribution of human sources in the production of these elements is probably higher (Yongming et al., 2006).

In general, high EF values and their ascending trend reflect the increasing risk of the element. Zhang and Liu, 2002 suggest that elements with enrichment factor value about 0.5-1.5 are from terrestrial origin and enrichment factor value above 1.5 show the contribution of human sources.

Table 5: EF values of elements in samples, (values are measured in proportion with background values of Hakanson, 1980)

location	Unpolluted	Low	Moderately	Strongly	Extremely
Chitgar	other metals	Co-Ni	Cu - Pb	Hg	Cr
high-traffic sites	other metals	Cd - Ni	Co	Cu - Hg - Pb	Cr
Azadi	other metals	Cd - Ni - Zn	Co - Cu - Hg	Pb	Cr
Gisha bridge	other metals	Cd - Ni	Co - Cu - Hg	Pb	Cr
Pardisan	other metals	Cd - Ni	Co - Cu - Hg	Pb	Cr

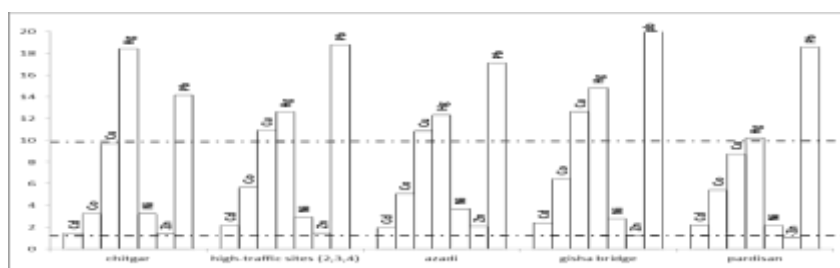


Figure3: EF index(the background elements)

Concentration Hakanson,1980) Co is produced by the combustion of fuels, as well as aerial, ceramic and glass industries (Shahar and Majid, 2008). The main source of Hg emission is coal, petroleum, coke and few studies have been conducted regarding this metal in the air. Ni is used in manufacturing alloys for plating tire ring, in exterior parts of the vehicles, and plating the engine cylinder and piston for

enabling them to withstand long-term contact with heat Corrosion of auto parts and auto oi; petroleum combustion and power plants are other sources for Ni emission (Shahar and Majid, 2008; Norouzi and Khademi, 2015).

Although Cd is found in low quantities in the earth's crust, it is increased by human activities (Wei and Yang, 2010). Construction materials, such as cement, as well as mechanical wearing-out of tires are the main sources of Cd emission (Ellis and Revitt, 1982). Pb is mainly resulted from transportation in urban areas (Addo et al., 2012). Pb is found within the particles from vehicles (Ellis and Revitt, 1982). High traffic, high volume of light, heavy vehicles, and high speed of vehicles cause burning more petrol and, therefore, increase the rate of Pb emission into the environment (Duong and Kyu Li, 2010). Emissions from the head hoses of fuel tanks and the igniters (Maher et al., 2008), balance weights for vehicles wheels, as well as the wearing-out of tires (Shahar and Majid, 2008) release Pb particles into the environment. Additionally, vehicles which use inappropriate and undesirable catalytic converters are also a source of Pb emissions. Pb and S affect the performance of catalytic converters adversely. Pb causes delays in the ignition and reduces thermal efficiency (Shahar and Majid, 2008). Other factors responsible for Pb emission are construction materials, such as cement, bricks, wood, and painting (Mandal and Voutchkov, 2011) and erosion of asphalt covers of roads and vehicle tires. Contrastingly, the ignition source of Cd is scarce (Wei and Yang 2010). Cr is used to enhance the hardness and resistance of alloys used in vehicles and their metal surfaces against mechanical abrasion (Wei and Yang, 2010); it is also used in cement industry (Banat et al., 2005). Cr can be emitted from cooling materials used in thermal power plants which burn coal, as well as power plants and corrosion of metals (Shahar and Majid, 2008). Cu particles are released from engine wearing-out and amortization of metals and parts (Shahar and Majid, 2008). Copper is produced due to oil pump corrosion and grease contact with car parts at high temperatures (De Miguel et al., 1997); it is, also, emitted from car exhaust. Cu is used in the car igniters to increase the flammability and as anti-corrosion on motor surfaces to reduce friction between engine parts (Shahar and Majid, 2008). Particles resulted from the industrial lubricants (Jiries et al., 2001) as well as tire and engine wearing out (Lu et al., 2009) are the largest sources of Cu production in urban environments (Lu et al., 2009). Cement dust and exhaust fumes are two important emissions sources for Zn into the environment (Ellis and Revitt, 1982). Tire wearing out, industrial lubricants (Jiries et al., 2001), the burning of tires (Kermani et al., 2016) and electrical industries of galvanized parts (Norouzi and Khademi, 2015) release Zn particles into the environment. Smelting industry is one of the other sources of Zn emission (Shahar and Majid, 2008).

The contribution of human activity in the emission of Hg and Co turned out to be very high in the present study. Hg pollution was high in low-traffic areas (Chitgar site). Hg pollution varied in high-traffic areas under the influence of traffic in different sites. Hg had the highest toxicity in Gisha Bridge and the lowest pollution in Pardisan. In other words, industries are the major sources of Hg emissions and emissions from cars intensify the level of Hg emissions within the city. Co emissions, also, follow the same trend. Based on geochemical indices identified in this study, the contribution of anthropogenic sources in Ni emission is low. However, Ni has shown an increase in the Azadi site. Azadi site is the closest study site to the power plant in Tehran; on the other hand, there are old worn-out cars consuming heavy fuel in this site. Increase of the concentration and enrichment of Pb and Cd in high-traffic areas indicates the important role of car parts wearing-out, corrosion, physical abrasion of vehicles, and also abrasion of materials, such as street asphalt caused by vehicle traffic. In addition to vehicle depreciation and amortization of construction materials, the method of traffic flow management can increase particle emissions.

The concentration change and the pattern of pollution intensification of Cd and Pb represents the increasing trend of these elements, and their higher toxicity, in areas with high traffic density and high density of buildings; Furthermore, the reduction of wind speed in central parts of Tehran has increased the concentration of these elements in Gisha Bridge area.

The results of the geochemical parameters indicate that Cr emission is most likely from combustion sources and industrial lubricants used in numerous industrial units in the West and Southwest of Tehran. However, based on the results, the concentration of Cu is intensified in the city, and since the samples were collected from street sides in the city and no industrial unit was analyzed in sampling areas, it can be concluded that the source of Cu is mainly old and worn out cars, industrial oils and lubricants and alloys used in car parts, while some of the sources of Cr emission are similar to the sources of Cu particle sources. Since the fluctuations of Zn concentration did not turn out to be significant in the city, and its main contamination is found in Azadi area with Gisha Bridge in the second place, so the probability of Zn emission from fuel by vehicles is decreased. Mn may be released from a separate source of other metals in this branch.

Hakanson, 1980, states that the estimation of RI and Ei of each metal in different areas along with the quantitative description of the severity of degree of contamination based on geochemical indices can

clearly reveal the potential ecological risk of metals and indicate the degree of environmental contamination with metals.

Figure 4 shows different values of Eri for each individual element.

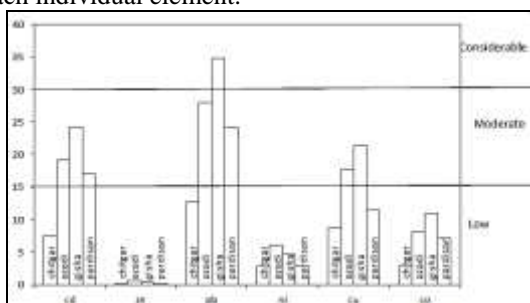


Figure 4. Eri index values of each metal in each of the studied areas

Figure 5 represents values of RI index in different studies areas.

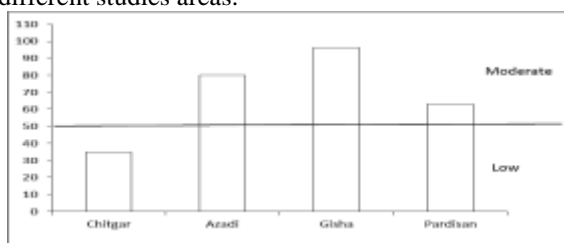


Figure 5. Ecological risk potential of metals in different studies areas

CONCLUSION

The results of changes in metal concentrations and the ranging of geochemical indicators in this study show that Pb, Cu, Cd, Zn and Co are the main, and most dangerous, metal pollutants in the study area. In addition, Cr and Hg can also create pollution in the environment. Hg and Co involve a combination of natural and anthropogenic sources, with higher contribution of human activities. The concentration of Hg and Cr were high in Chitgar; so, some parts of their concentration may be due to the increase of natural sources. Therefore, it is necessary to conduct complementary studies in this area. Due to the elimination of Pb from gasoline in recent years, although its emission into the urban environment is significantly declined, its former accumulation still remains in the environment. Changes in the quality of vehicle fuel and the use of solvents and catalysts can Pb to the reduction of Pb in the environment; however, Pb is a very stable isotope that stays in the environment for a long time (Atiemo et al., 2011). The assessment of potential ecological risks of metals against the health of living creatures provides the community health planners with a powerful tool for

processing and analyzing ecological information (Zhao and Li, 2013).

The results of the present study show that the risk of exposure to metals is, respectively, higher for Pb, Cd and Cu metals in perforated areas. The risk of the presence of metals is higher in Giesha and Azadi, in comparison to Pardisan. Therefore, troubles resulted from Pb-bearing oil and fuel will remain for a long time in the environment. Various parameters, such as parameters related to street conditions and its bordering buildings, the number of road lines and traffic flow which ventilates the adjacent air along with its pollutant metal particles and effects on the distribution of pollutants in the road edges, affect the emission of vehicle pollutants.

The most important factor in vehicle pollutant emission is the traffic flow that includes traffic volume, speeds and density as main factors, as well as other factors, such as drivers' behavior in starting to move, the vehicle types, traffic management method, and traffic signs locations in the streets.

Environmental parameters include climatic conditions such as temperature, rainfall, wind direction and speed and roadside soil characteristics. Giesha Bridge area had the highest traffic rate in this study and the presence of administrative and residential buildings in this area has reduced air ventilation and increased pollutants. Metal pollutants are higher in the center of Tehran. The second site was Azadi area, where traffic had produced high concentrations of pollutants. Pardisan, in the northernmost part of the study area, has the lowest contamination rate. High speed of vehicles, lesser use of brakes and wind conditions, as well as distance from residential and administrative buildings in Pardisan, have reduced the pollutants rate. Despite the proximity of Chitgar area to numerous industrial units in the West of Tehran, dense green spaces were significantly effective in reducing the pollutants.

Time and cost restrictions hindered the study of speciation and sequential extraction of metal phases in the present study. In environments where basic standards are not defined for background concentrations, it is desirable to use the modified Mueller index after separation of metals and study the speciation of various phases in order to obtain more precise results (Karbassi et al., 2008). Therefore, it is recommended to find the sources of elements through this method in order to provide more obvious description for element emission sources in future studies.

ACKNOWLEDGMENTS

Hereby, we extend our gratitude to the President of Geological Survey and Mineral

Exploration in Iran and its Research Council for providing the facilities for this research.

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