

Anthropogenic share of metal contents in soils of urban areas

Fazeli, G.¹, Karbassi, A.R.^{2*}, Khoramnejadian, Sh.¹, Nasrabadi, T.²

1. Department of Environment, Damavand branch, Islamic Azad University,
Damavand, Iran

2. School of Environment, College of Engineering, University of Tehran, Tehran,
Iran

Received: 12.04.2018

Accepted: 18.07.2018

ABSTRACT: In the present investigation, 41 soil samples were subjected to single step chemical partitioning to assess the lithogenic and non-lithogenic portions of metals in Tehran's soils. The share of various studied metals in the anthropogenic portion ranges from as low as 0.2% to as high as 85% of bulk concentration. Geo-accumulation index (I_{geo}) showed that Cd falls within "heavily contaminated" soils. It might be inferred that Ni, Cu, Cr, Zn, Co and Ca fall within "Deficient to minimal" class in accordance with enrichment factor (EF) classification.. Enrichment factor values (to some extents) match with the chemical partition studies results (except for Ni and Cr). The very low Ca content of soil samples could be indicative of low biological productivity in the Tehran's soil. Also the very low concentrations of Mn could be indicative of reducing environment in soils of Tehran.

Keywords: Pollution, Indices, Metals, Contamination, Soil, Risk, Geochemistry, Environment, Urban area, Tehran

INTRODUCTION

Within a decade over one million people have migrated to Tehran megacity. Presently the day time population of Tehran is over 13 million. Similar trend can be found in many other capital cities worldwide. Such rapid migrations might leave adverse environmental impacts. Soils in urban areas can receive various forms of pollutants (Sobhan Ardakani 2018). These pollutants may include aromatic hydrocarbons as well as heavy metals Duruibe et al. (2007) reviewed metal pollution and their possible impacts on human. They concluded that heavy metals can threaten human life in many ways. A more detailed review on the

association of various illness and soil contents through inhalation and ingestion was presented by Oliver (1997). About 115 soil samples from Northeast China were analyzed to show that urban soils were polluted to various intensities by Cd, Zn, Cu, and Pb (Qing et al. 2015). Urban soils in parks of large cities can receive metals from various sources. Some studies have shown that pollution intensity decreases as the distance increases from the road sides (Madrid et al. 2002; Chen et al. 2005; Shi et al. 2008; Sun et al. 2010). This holds good for the forest roads near urban areas too (Pouyat and McDonnell 1991). The metal contamination of soils is more severe in cities where diverse activities exist or the infrastructure for receiving wastewaters within the urban area is weak (Singh and

* Corresponding Author ,Email: akarbasi@ut.ac.ir

Kumar 2006). In general, fleet fuels and wastewaters from residential sector are the main sources of various metal contents in urban areas (Möller et al. 2005; Imperato et al. 2003). Though microbial activities can play an important role in governing the metal contents in urban soils, it is found that such activities are rather weak near roadsides that may lead to higher accumulation of trace elements (Papa et al. 2010). Some studies have revealed that higher levels of metals in urban soils as well as urban agricultural zones can be attributed to both geology of area and the anthropogenic sources (Manta et al. 2002; Roudposhti et al. 2016). Association of metals with various phases of soil/sediment has been studied to differentiate between anthropogenic and lithogenic sources of metals (Ghaemi et al. 2015) in order to bring out environmental health effects.

The present investigation focuses on metal contents in urban area of a mega city where over 12 million liters of petrol per day is used. The number of various fleets is almost over 6 million. Thus, metals associated with fuel consumptions as well

as those associated with tires and oils can be accumulated in Tehran's soil. Subsequently, the soil pollution intensity will be brought out by the respective formulas.

MATERIALS & METHODS

District six of Tehran municipality is located in central to northern part of the city. Exact location of the study area in the capital city of Tehran in Iran is shown in Fig.1. The total area of district six is about 2138 hectare that is equal to 3.3% of total Tehran megacity area. About 240 thousand person put up in district six. The land use in district 6 is very diverse (29% residential, 29% roads, 14% urban green space, 8% administrative buildings, 9% educational centers, 6% commercial buildings, 3% hospital & military, 2% bare lands). This district is crowded with commercial and educational centers. About 8% of 13,599,817 urban trips within megacity of Tehran occur in district 6. Location of district 6 within Tehran city is shown in Fig. 1.

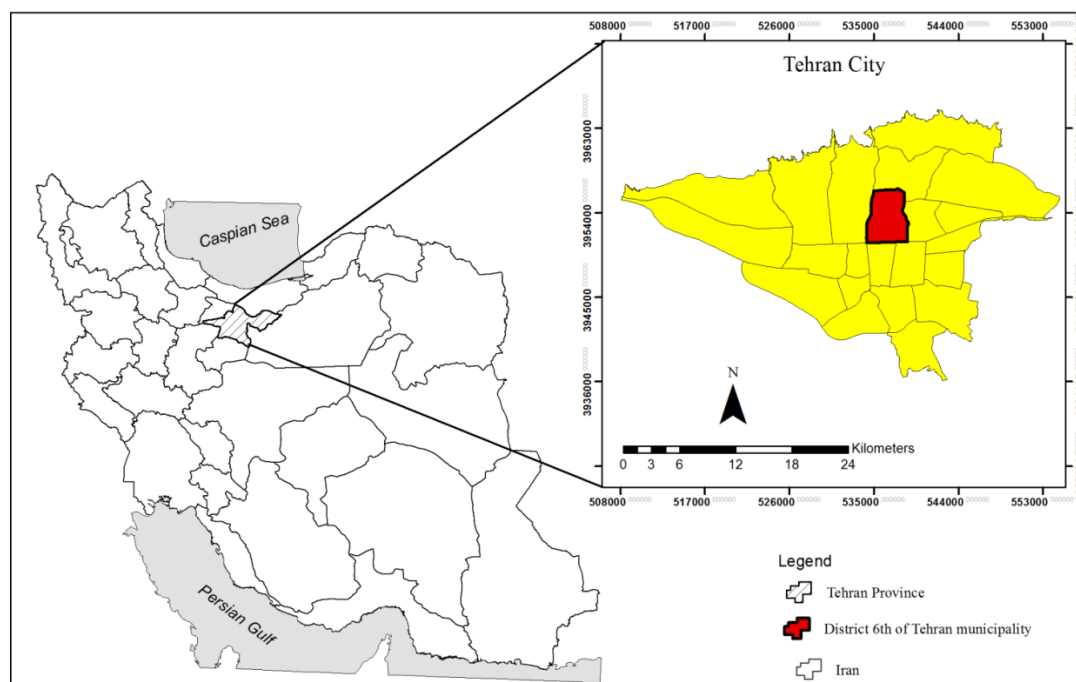


Fig. 1. Location of study area in Tehran City, Iran

About 41 soil samples were collected from district 6 (Fig.2). For this purpose, the area of study was divided into 41 grids and from each grid 4 samples (Z grid) were collected. Therefore, the total number of samples was initially equal to 164. Subsequently the 4 sub-samples from each grid were mixed to obtain a unique sample. All the samples were collected during the

summer of the year 2016. Spiral auger was used to collect the soil sample from top 50 cm of soil profile. The sampling locations encompass all possible land used within the area of study. All debris was removed before sampling to avoid misunderstandings from results. Soil samples were kept in plastic bags and sent to laboratory for further procedures.

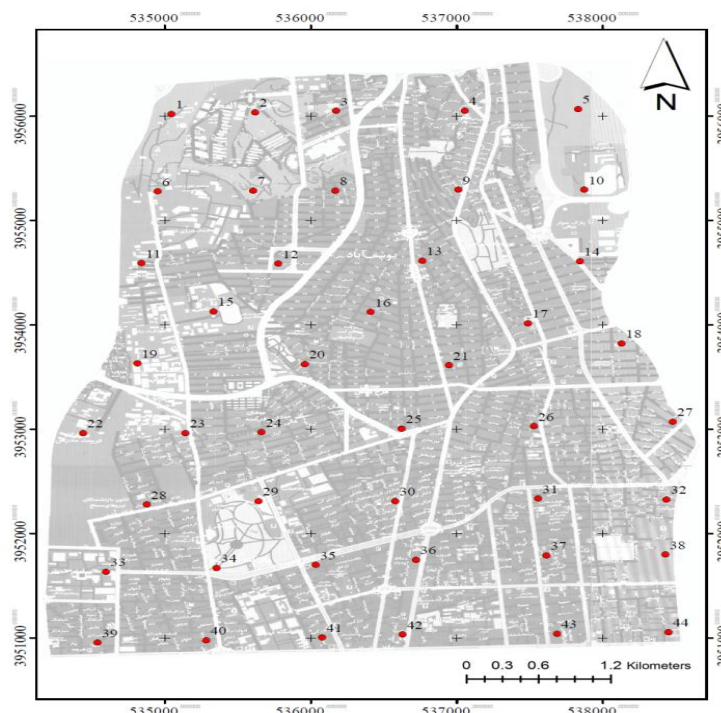


Fig. 2. Surface soil sampling locations within the municipality district

The collected soil samples were dried at 45°C in an oven for about 72 hours. Subsequently, all soil samples were passed through sieve to obtain fractions less than 63µm. About 0.5g of each soil sample was gently powdered using an agate mortar and pestle. The powdered samples were digested using strong acids (aqua regia and HClO₄). The volume of each digested soil sample was adjusted to 50 mL in a volumetric jar. To check out the quality control (QC) as well as the quality assurance (QA), certified reference material (MESS-1) and duplicate samples were used. The bulk metal contents of soil samples were measured by inductively coupled plasma mass spectrometer

(ICPAES). Further, single step chemical partitioning technique (Hosseini Alhashemi et al. 2011) was used to bring out the non-lithogenous portions of metals. For this purpose, about 2g of each soil sample was shaken for 30 minutes in a conical flask containing 15 mL of 0.53N HCl. The volume of aliquots was adjusted to 50 mL after filtering through Whatman filter No. 50. The metal contents in these solutions were analyzed by ICPAES. It should be pointed out QA/QC was carried out for this analysis as described for bulk analysis. The analysis of MESS-1 shows ±7% deviation from the published values.

For assessment of metal content accumulation/enrichment, two indices were

used. The degree of metal accumulation in the soil of study area was computed by the geo-accumulation index (I_{geo}). The formula for geo-accumulation is as follows;

$$I_{geo} = \text{Log}_2[C_n / (1.5 * B_n)] \quad (1)$$

where C_n and B_n are the metal concentrations in soil sample and shale, respectively (Muller 1979). Classification scheme of I_{geo} is shown in Table 1.

Enrichment of metals in soil samples was assessed by enrichment factor (Barbieri et al. 2016). In this formula, the metal contents in area of study are compared with that mean earth crust. Following is the formula for computation of enrichment factor;

$$EF = (C_n/C_{Fe})_{\text{sample}} / (C_n/C_{Fe})_{\text{crust}} \quad (2)$$

where $(C_n/C_{Fe})_{\text{sample}}$ is the ratio of the concentration of the element in soil samples (C_n) to that of Fe (C_{Fe}) in the soil sample and $(C_n/C_{Fe})_{\text{crust}}$ is the same ratio in an unpolluted reference sample (Pekey, 2006). The classification for enrichment factor is shown in Table 2.

RESULTS & DISCUSSION

In the present investigation Ni, Cu, Cr, Zn, Co, Cd, Pb, Mn, Fe and Ca in 41 soil samples of urban areas of Tehran megacity

were measured. The bulk metal content of soil samples is presented in Table 3. The concentration of Ni ranges from 39 to 78 mg/kg with a mean value of 57 mg/kg. Nickel concentration is low when compared with those of mean earth crust as well as mean shales. Though the mean value of Cu (about 39 mg/kg) is well within the published values for mean earth crust as well as mean shales, higher values (up to 60 mg/kg) can be seen in some sampling stations. The highest values for Cr (65 mg/kg) are lower than mean earth crust but much higher than shale values. Zinc also shows a similar trend as Cr does. Cobalt also shows similar trend and Ni when its mean value (12 mg/kg) is compared with mean earth crust and mean shales. Concentration of mean Cd (3 mg/kg) is 30 and 15 times higher than mean earth crust and means shales, respectively. Lead with a mean value of (31 mg/kg) is also higher than mean earth crust and shale values (almost 2 and 1.3 folds, respectively). The mean value of Mn (453 mg/kg) is almost twice lower when compared with mean earth crust as well as mean shales. The mean Fe content of soil samples (about 3 mg/kg) is lower than the values published for earth crust as well as shales.

Table 1. Classification of geo-accumulation index (I_{geo}) (Muller 1979)

| Class | Value | Degree of contamination |
|-------|-------------------|---|
| 0 | $I_{geo} \leq 0$ | Uncontaminated |
| 1 | $0 < I_{geo} < 1$ | Uncontaminated to moderately contaminated |
| 2 | $1 < I_{geo} < 2$ | Moderately contaminated |
| 3 | $2 < I_{geo} < 3$ | Moderately to heavily contaminated |
| 4 | $3 < I_{geo} < 4$ | Heavily contaminated |
| 5 | $4 < I_{geo} < 5$ | Heavily to extremely contaminated |
| 6 | $I_{geo} \geq 5$ | Extremely contaminated |

Table 2. Classification ladder for enrichment factor (EF) (Barbieri et al. 2016)

| Value | Enrichment class |
|----------------|----------------------|
| $EF < 2$ | Deficient to minimal |
| $2 < EF < 5$ | Moderate |
| $5 < EF < 20$ | Significant |
| $20 < EF < 40$ | Very high |
| $EF > 40$ | Extremely high |

Table 3. Bulk metal contents in soil samples of the study area (mg/kg, otherwise specified)

| Station | Ni | Cu | Cr | Zn | Co | Cd | Pb | Mn | Fe (%) | Ca (%) |
|--------------|-------|-------|-------|-------|-------|------|-------|--------|--------|--------|
| 1 | 60 | 40 | 35 | 90 | 12 | 4.1 | 25 | 560 | 3.3 | 1.7 |
| 2 | 56 | 25 | 20 | 70 | 10 | 3.6 | 22 | 230 | 2.9 | 2.2 |
| 3 | 40 | 40 | 50 | 55 | 11 | 2.7 | 26 | 360 | 2.8 | 3.2 |
| 4 | 78 | 32 | 19 | 45 | 10 | 1.9 | 16 | 290 | 3.2 | 2.9 |
| 5 | 40 | 50 | 42 | 44 | 12 | 3.3 | 35 | 390 | 3.3 | 2.3 |
| 6 | 63 | 35 | 44 | 52 | 15 | 2.2 | 25 | 320 | 3.1 | 2.3 |
| 7 | 58 | 55 | 33 | 50 | 14 | 3.2 | 20 | 600 | 3 | 2.3 |
| 8 | 56 | 30 | 32 | 70 | 10 | 2 | 44 | 400 | 2.9 | 3.1 |
| 9 | 55 | 30 | 29 | 87 | 9 | 1.9 | 12 | 750 | 2.9 | 1.8 |
| 10 | 48 | 33 | 45 | 63 | 8 | 3.3 | 20 | 450 | 2.8 | 2.5 |
| 11 | 78 | 45 | 44 | 52 | 11 | 2 | 33 | 420 | 3.2 | 2.5 |
| 12 | 65 | 27 | 46 | 72 | 10 | 2 | 20 | 315 | 3 | 2.8 |
| 13 | 65 | 30 | 45 | 49 | 12 | 3.8 | 14 | 350 | 2.9 | 2.1 |
| 14 | 45 | 32 | 50 | 58 | 11 | 3.9 | 14 | 255 | 2.9 | 2.8 |
| 15 | 58 | 50 | 36 | 67 | 12 | 3 | 12 | 460 | 2.8 | 1.9 |
| 16 | 66 | 40 | 33 | 56 | 9 | 2.5 | 25 | 450 | 2.9 | 2.2 |
| 17 | 56 | 35 | 36 | 65 | 8 | 4 | 35 | 520 | 2.8 | 2.3 |
| 18 | 63 | 39 | 39 | 63 | 11 | 3.2 | 23 | 623 | 3.2 | 1.9 |
| 19 | 62 | 32 | 38 | 62 | 14 | 2.1 | 25 | 654 | 3.3 | 2.7 |
| 20 | 49 | 31 | 56 | 49 | 9 | 2.9 | 25 | 754 | 3.1 | 1.8 |
| 21 | 59 | 45 | 45 | 58 | 15 | 4.1 | 30 | 423 | 3 | 3.2 |
| 22 | 58 | 45 | 56 | 54 | 15 | 3.3 | 40 | 523 | 3.3 | 3 |
| 23 | 59 | 36 | 49 | 80 | 12 | 2.2 | 20 | 780 | 2.9 | 2.7 |
| 24 | 58 | 39 | 50 | 68 | 9 | 3.2 | 45 | 325 | 2.8 | 2.3 |
| 25 | 53 | 45 | 40 | 78 | 9 | 2 | 52 | 350 | 3.2 | 2.6 |
| 26 | 56 | 32 | 65 | 58 | 7 | 1.9 | 25 | 250 | 3 | 1.9 |
| 27 | 65 | 33 | 35 | 65 | 12 | 1.9 | 66 | 298 | 2.9 | 2.2 |
| 28 | 67 | 39 | 25 | 95 | 13 | 4.3 | 75 | 235 | 2.9 | 2.2 |
| 29 | 62 | 50 | 32 | 35 | 15 | 3.8 | 60 | 550 | 2.8 | 2.2 |
| 30 | 55 | 30 | 22 | 63 | 11 | 2.1 | 25 | 750 | 2.9 | 3.2 |
| 31 | 65 | 50 | 32 | 48 | 19 | 2.9 | 30 | 650 | 2.9 | 3.4 |
| 32 | 39 | 30 | 19 | 56 | 17 | 4.1 | 20 | 500 | 2.8 | 1.7 |
| 33 | 65 | 45 | 35 | 65 | 12 | 3.3 | 35 | 445 | 3.2 | 2.6 |
| 34 | 54 | 55 | 26 | 69 | 10 | 2.2 | 23 | 520 | 3 | 2.3 |
| 35 | 56 | 35 | 29 | 75 | 9 | 3.2 | 22 | 235 | 2.9 | 2.9 |
| 36 | 62 | 60 | 28 | 73 | 13 | 2 | 14 | 219 | 2.9 | 3.2 |
| 37 | 39 | 40 | 31 | 69 | 12 | 3.7 | 45 | 780 | 2.8 | 2.9 |
| 38 | 47 | 30 | 19 | 86 | 14 | 4.2 | 42 | 425 | 3 | 2.3 |
| 39 | 49 | 25 | 42 | 81 | 12 | 3.6 | 36 | 320 | 2.9 | 2.4 |
| 40 | 45 | 30 | 61 | 87 | 15 | 4 | 45 | 396 | 2.9 | 2.2 |
| 41 | 62 | 55 | 44 | 63 | 15 | 3 | 48 | 450 | 2.8 | 2.2 |
| Min. | 39 | 25 | 19 | 35 | 7 | 1.9 | 12 | 219 | 2.8 | 1.7 |
| Max. | 78 | 60 | 65 | 95 | 19 | 4.3 | 75 | 780 | 3.3 | 3.4 |
| SD. | 9.27 | 9.17 | 11.51 | 13.73 | 2.63 | 0.81 | 14.80 | 165.20 | 0.16 | 0.46 |
| Mean | 56.98 | 38.54 | 37.98 | 64.51 | 11.80 | 2.99 | 30.95 | 453.05 | 2.98 | 2.46 |
| Earth crust* | 80 | 50 | 100 | 75 | 20 | 0.1 | 14 | 950 | 4.4 | -- |
| Shale** | 68 | 39 | 39 | 120 | 19 | 0.22 | 23 | 850 | 4.7 | -- |

* (Alloway 1995)

** (Turekian and Wedepohl 1961)

In general, the concentration of Ni, Cr, Zn, Co, Mn and Fe are lower than the published values for earth's crust (Alloway 1995). However, concentrations of Cd and

Pb are higher than mean values given for earth's crust as well as shales (Turekian and Wedepohl 1961). It should be pointed out the concentrations of Cr and Zn is also

higher than the mean values of shales (Turekian & Wedepohl, 1961). The very low Ca contents in the soils of Tehran's urban area might be indicative of lower biological productivity (Hirschi 2004). The higher concentrations of Cd and Cr might be attributed to the tires erosion by the traffic of urban areas; though various tires may contain different levels of metal contents (Shakya et al. 2006). The very lower concentrations of Mn in soils of area of study might be attributed to the redox potential prevailing in the soil profile (Karbassi et al. 2008).

The results of one step chemical partitioning for the assessment of anthropogenic metal contents are presented in Table 4. To calculate the percentile of anthropogenic and lithogenic fractions of metals, the bulk concentration of each metal was considered as 100%. Subsequently the anthropogenic portion was deducted from the bulk contents of metals to obtain the lithogenic fraction. Subsequently, percentile of lithogenic and anthropogenic fractions were computed by comparing to the total (bulk) metal contents.

The values in Table 4 clearly show that a considerable portion of Ni, Cr, Cd and Pb is derived from anthropogenic source. Therefore, in spite of lower concentration of Ni when compared with mean earth's crust and mean shale values, it might be concluded that a part of Ni is associated with the anthropogenic source. Generally, Ni could be considered as the indicator of oil contamination (Vaezi et al. 2015). Hence, it might be concluded that petrol used in Tehran's fleet is responsible for the

anthropogenic portion of Ni in soils of urban areas of Tehran megacity. Though Pb is totally eliminated from petrol for past 15 years, still its remains can be seen. The share of various studied metals in the anthropogenic portion of Tehran's soil shows the following trend: Cd>Cr>Pb>Ni>Co>Cu>Mn>Ca>Fe.

Table 5, shows the enrichment factor values for soil samples from district 6 of Tehran megacity. Considering the classification values given in Table 2, it might be inferred that Ni, Cu, Cr, Zn, Co and Ca fall within "Deficient to minimal" class. However Pb and Cd can be classified as moderate and extremely high, respectively. Therefore EF values to some extents match with the chemical partition studies results (except for Ni and Cr). Higher EF values are reported for soils of urban area in Palermo city in Italy (Manta et al., 2002).

Geo-accumulation formula proposed by Muller (1979) was further used to know about the possible metal contamination in urban soils of Tehran megacity. Since most of the values stand at zero; therefore the gist of results are presented in Table 6. In accordance with the classification (Table 1), it might be concluded that Ni, Cu, Cr, Zn, Pb and Mn are not accumulated within the soils of district 6. However, Cd falls within "heavily contaminated" soils. As discussed earlier the source of Cd in Tehran's soil might be the erosion of tires. A high I_{geo} value has been reported for Pb and Cd for the cities of China too (Wei and Yang 2010).

Table 4. Percentile of anthropogenic and lithogenic metal contents in Tehran's soil

| Station | (mg/kg) | | | | | | | (%) | | | |
|-------------------|---------|-------|-------|-------|-------|------|-------|--------|------|------|--|
| | Ni | Cu | Cr | Zn | Co | Cd | Pb | Mn | Fe | Ca | |
| Mean (bulk) | 56.98 | 38.54 | 37.98 | 64.51 | 11.80 | 2.99 | 30.95 | 453.05 | 2.98 | 2.46 | |
| Anthropogenic (%) | 25 | 5 | 35 | 2 | 7 | 85 | 26 | 2 | 0.2 | 0.7 | |
| Lithogenic (%) | 75 | 95 | 65 | 98 | 93 | 15 | 74 | 98 | 99.8 | 99.3 | |

Table 5. Enrichment factor (EF) values for surface soil samples in Tehran city

| EF | Ni | Cu | Cr | Zn | Co | Cd | Pb | Mn |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 1 | 1.00 | 1.07 | 0.47 | 1.60 | 0.80 | 54.67 | 2.38 | 0.79 |
| 2 | 1.06 | 0.76 | 0.30 | 1.42 | 0.76 | 54.62 | 2.38 | 0.37 |
| 3 | 0.79 | 1.26 | 0.79 | 1.15 | 0.86 | 42.43 | 2.92 | 0.60 |
| 4 | 1.34 | 0.88 | 0.26 | 0.83 | 0.69 | 26.13 | 1.57 | 0.42 |
| 5 | 0.67 | 1.33 | 0.56 | 0.78 | 0.80 | 44.00 | 3.33 | 0.55 |
| 6 | 1.12 | 0.99 | 0.62 | 0.98 | 1.06 | 31.23 | 2.53 | 0.48 |
| 7 | 1.06 | 1.61 | 0.48 | 0.98 | 1.03 | 46.93 | 2.10 | 0.93 |
| 8 | 1.06 | 0.91 | 0.49 | 1.42 | 0.76 | 30.34 | 4.77 | 0.64 |
| 9 | 1.04 | 0.91 | 0.44 | 1.76 | 0.68 | 28.83 | 1.30 | 1.20 |
| 10 | 0.94 | 1.04 | 0.71 | 1.32 | 0.63 | 51.86 | 2.24 | 0.74 |
| 11 | 1.34 | 1.24 | 0.61 | 0.95 | 0.76 | 27.50 | 3.24 | 0.61 |
| 12 | 1.19 | 0.79 | 0.67 | 1.41 | 0.73 | 29.33 | 2.10 | 0.49 |
| 13 | 1.23 | 0.91 | 0.68 | 0.99 | 0.91 | 57.66 | 1.52 | 0.56 |
| 14 | 0.85 | 0.97 | 0.76 | 1.17 | 0.83 | 59.17 | 1.52 | 0.41 |
| 15 | 1.14 | 1.57 | 0.57 | 1.40 | 0.94 | 47.14 | 1.35 | 0.76 |
| 16 | 1.25 | 1.21 | 0.50 | 1.13 | 0.68 | 37.93 | 2.71 | 0.72 |
| 17 | 1.10 | 1.10 | 0.57 | 1.36 | 0.63 | 62.86 | 3.93 | 0.86 |
| 18 | 1.08 | 1.07 | 0.54 | 1.16 | 0.76 | 44.00 | 2.26 | 0.90 |
| 19 | 1.03 | 0.85 | 0.51 | 1.10 | 0.93 | 28.00 | 2.38 | 0.92 |
| 20 | 0.87 | 0.88 | 0.79 | 0.93 | 0.64 | 41.16 | 2.53 | 1.13 |
| 21 | 1.08 | 1.32 | 0.66 | 1.13 | 1.10 | 60.13 | 3.14 | 0.65 |
| 22 | 0.97 | 1.20 | 0.75 | 0.96 | 1.00 | 44.00 | 3.81 | 0.73 |
| 23 | 1.12 | 1.09 | 0.74 | 1.62 | 0.91 | 33.38 | 2.17 | 1.25 |
| 24 | 1.14 | 1.23 | 0.79 | 1.42 | 0.71 | 50.29 | 5.05 | 0.54 |
| 25 | 0.91 | 1.24 | 0.55 | 1.43 | 0.62 | 27.50 | 5.11 | 0.51 |
| 26 | 1.03 | 0.94 | 0.95 | 1.13 | 0.51 | 27.87 | 2.62 | 0.39 |
| 27 | 1.23 | 1.00 | 0.53 | 1.31 | 0.91 | 28.83 | 7.15 | 0.48 |
| 28 | 1.27 | 1.18 | 0.38 | 1.92 | 0.99 | 65.24 | 8.13 | 0.38 |
| 29 | 1.22 | 1.57 | 0.50 | 0.73 | 1.18 | 59.71 | 6.73 | 0.91 |
| 30 | 1.04 | 0.91 | 0.33 | 1.27 | 0.83 | 31.86 | 2.71 | 1.20 |
| 31 | 1.23 | 1.52 | 0.49 | 0.97 | 1.44 | 44.00 | 3.25 | 1.04 |
| 32 | 0.77 | 0.94 | 0.30 | 1.17 | 1.34 | 64.43 | 2.24 | 0.83 |
| 33 | 1.12 | 1.24 | 0.48 | 1.19 | 0.83 | 45.38 | 3.44 | 0.64 |
| 34 | 0.99 | 1.61 | 0.38 | 1.35 | 0.73 | 32.27 | 2.41 | 0.80 |
| 35 | 1.06 | 1.06 | 0.44 | 1.52 | 0.68 | 48.55 | 2.38 | 0.38 |
| 36 | 1.18 | 1.82 | 0.42 | 1.48 | 0.99 | 30.34 | 1.52 | 0.35 |
| 37 | 0.77 | 1.26 | 0.49 | 1.45 | 0.94 | 58.14 | 5.05 | 1.29 |
| 38 | 0.86 | 0.88 | 0.28 | 1.68 | 1.03 | 61.60 | 4.40 | 0.66 |
| 39 | 0.93 | 0.76 | 0.64 | 1.64 | 0.91 | 54.62 | 3.90 | 0.51 |
| 40 | 0.85 | 0.91 | 0.93 | 1.76 | 1.14 | 60.69 | 4.88 | 0.63 |
| 41 | 1.22 | 1.73 | 0.69 | 1.32 | 1.18 | 47.14 | 5.39 | 0.74 |
| Min | 0.67 | 0.76 | 0.26 | 0.73 | 0.51 | 26.13 | 1.30 | 0.35 |
| Max | 1.34 | 1.82 | 0.95 | 1.92 | 1.44 | 65.24 | 8.13 | 1.29 |
| SD | 0.16 | 0.28 | 0.17 | 0.28 | 0.20 | 12.71 | 1.62 | 0.26 |
| Mean | 1.05 | 1.14 | 0.56 | 1.28 | 0.87 | 44.43 | 3.28 | 0.71 |

Table 6. Geo-accumulation index (I_{geo}) values for surface soil samples

| Igeo | Ni | Cu | Cr | Zn | Co | Cd | Pb | Mn |
|-------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Min | 0 | 0 | 0 | 0 | 0 | 2.53 | 0 | 0 |
| Max | 0 | 0.04 | 0.15 | 0 | 0 | 3.70 | 1.12 | 0 |
| Mean | 0 | 0 | 0.07 | 0 | 0 | 3.12 | 0.5 | 0 |

In the present investigation, Weight Pair Group (WPG) method was used to bring out cluster analysis. Fig. 3 depicts the dendrogram of cluster analysis. The dendrogram consists of four clusters namely a, b, c and d. In cluster "a" Ni, Fe, Cu and Ca are present. If Ni is taken into consideration as an indicator of oil pollution, then it might be concluded that Fe and Cu could have been derived from the same source. On the other hand, it could be concluded that Ca (as a biological indicator) can govern the behavior of Ni, Fe and Cu. Manganese has formed an individual cluster "b". Clusters "a" and "b" join at a rather very low similarity coefficient. This indicates that the mechanism control for Mn is different from other studied metals. As mentioned earlier, the very low Mn content in urban soils of Tehran megacity could be indicative of reducing environment. Under the reducing environment Mn totally acts different from the other metals (Karbassi et al. 2008).

Chromium also has developed a separated cluster "c". It joins clusters "a & b" at negative similarity coefficient. This might indicate the negative effects of Ni, Fe, Cu, Ca and Mn on Cr. That means as the concentrations of Ni, Fe, Cu, Mn and Ca increase, the concentration of Cr may decrease. Zinc, Co, Cd and Pb join each other at cluster "d". As earlier discussed these elements (except for Zn) are significantly present in anthropogenic portion of bulk metal contents.

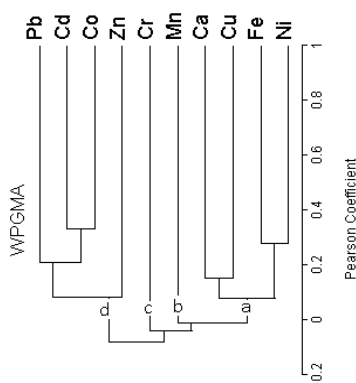


Fig. 3. Dendrogram of cluster analysis for metals of soils in Tehran city

Cluster "d" joins other three clusters "a, b & c" at negative similarity coefficient value and thereby, it could be inferred that the behavior of these metals is different from other studied metals in the soils of Tehran megacity. The very diverse clusters (a, b, c & d) itself is indicative of different sources and various controlling mechanisms of metals in Tehran's soil.

CONCLUSIONS

Urban areas are subjected to various sources of contaminations. The ever growing number of fleets in megacities of the developing countries might be considered as the most important source for soil pollution. In the present investigation, 41 soils of Tehran megacity have been subjected to chemical analysis. The results of present investigation showed that comparison of metal contents with those of earth's crust as well as shale may not furnish a true picture of contamination. Also, various pollution indices though having their own merits may not provide the real picture of metal accumulation in soils. In the present study, the single step chemical partitioning proved to provide ample information about the amount of metal contamination. The share of various studied metals in the anthropogenic portion (ranging from as low as 0.2% to as high as 85%) of Tehran's soil shows the following trend: $Cd > Cr > Pb > Ni > Co > Cu > Mn > Ca > Fe$. The very low Ca content of soil sample could be indicative of low biological productivity in the Tehran's soil. Also the very low concentrations of Mn could be indicative of reducing environment in soils of urban area of Tehran megacity. Among the studied metals, Igeo showed that Cd falls within "heavily contaminated" soils while other metals fall within "no pollution" classification. It might be inferred that Ni, Cu, Cr, Zn, Co and Ca fall within "Deficient to minimal" class in accordance with EF classification. However Pb and Cd can be classified as

moderate and extremely high contamination, respectively. Enrichment factor values (to some extents) match with the chemical partition studies results (except for Ni and Cr).

ACKNOWLEDGMENT

Authors would like to thank municipality of district 6 of Tehran city for their help in sample collection. We sincerely thank Mr. M. Sohrabi for his help during field works.

REFERENCES

Alloway, B. J. (1995). Heavy metals in soils, Blackie Academic & Professional, London.

Barbieri, M. (2016). The Importance of Enrichment Factor (EF) and Geoaccumulation Index (Igeo) to Evaluate the Soil Contamination. *J Geol Geophys* 5:237.

Chen, T. B., Zheng, Y. M., Lei, M., Huang, Z. C., Wu, H. T., Chen, H. et al (2005) Assessment of heavy metal pollution in surface soils of urban parks in Beijing, China. *Chemosphere*, 60(4), 542-551.

Duruibe, J. O., Ogwuegbu, M. O. C. and Ekwurugwu, J. N. (2007). Heavy metal pollution and human biotoxic effects. *Int J phys sci* 2(5), 112-118.

Ghaemi, Z., Karbassi, A., Moattar, F., Hassan, i A. and Khorasani, N. (2015). Evaluating soil metallic pollution and consequent human health hazards in the vicinity of an industrialized zone, case study of Mubarakheh steel complex, Iran. *J Environ Health Sci Eng* 13(1), 75.

Hirschi, K. D. (2004). The calcium conundrum. Both versatile nutrient and specific signal. *Plant physiol* 136(1), 2438-2442.

Hosseini Alhashemi, A. S., Karbassi, A. R., Hassanzadeh Kiabi, B., Monavari, S. M. and Nabavi, S. M. B. (2011). Accumulation and bioaccessibility of trace elements in wetland sediments. *Afr J Biotechnol* 10(9):1625–1636

Imperato, M., Adamo, P., Naimo, D., Arienzo, M., Stanzione, D. and Violante, P. (2003.) Spatial distribution of heavy metals in urban soils of Naples city (Italy). *Environ pollut*, 124(2), 247-256.

Karbassi, A. R., Monavari, S. M., Bidhendi, G. R. N., Nouri, J. and Nematpour, K. (2008). Metal pollution assessment of sediment and water in the Shur River. *Environ Monit Assess* 147(1-3), 107.

Madrid, L., Díaz-Barrientos, E. and Madrid, F. (2002). Distribution of heavy metal contents of

urban soils in parks of Seville. *Chemosphere*, 49(10), 1301-1308.

Manta, D. S., Angelone, M., Bellanca, A., Neri, R. and Sprovieri, M. (2002). Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. *Sci total environ* 300(1-3), 229-243.

Möller, A., Müller, H. W., Abdullah, A., Abdelgawad, G. and Utermann, J. (2005). Urban soil pollution in Damascus, Syria: concentrations and patterns of heavy metals in the soils of the Damascus Ghouta. *Geoderma* 124(1-2), 63-71.

Muller, G. (1979). Schwermetalle in den sediments des Rheins- Veränderungen Seit 1971. Umschau, 79, 778-783.

Oliver, M. A. (1997). Soil and human health: a review. *Eur J Soil Sc* 48(4), 573-592.

Papa, S., Bartoli, G., Pellegrino, A. and Fioretto, A. (2010). Microbial activities and trace element contents in an urban soil. *Environ Monit Assess* 165(1-4), 193-203.

Pekey, H. (2006). Heavy metal pollution assessment in sediments of the Izmir Bay, Turkey. *Environ Monit Assess* 123:219–231.

Pouyat, R. V. and McDonnell, M. J. (1991). Heavy metal accumulations in forest soils along an urban-rural gradient in southeastern New York, USA. *Water Air Soil Pollut* 57(1), 797-807.

Qing, X., Yutong, Z. and Shenggao, L. (2015). Assessment of heavy metal pollution and human health risk in urban soils of steel industrial city (Anshan), Liaoning, Northeast China. *Ecotoxicol environ saf* 120, 377-385.

Roudposhti, G. M., Karbassi, A. and Baghvand, A. (2016). A pollution index for agricultural soils. *Arch Agron Soil Sci* 62(10), 1411-1424.

Shakya, P. R., Shrestha, P., Tamrakar, C. S. and Bhattarai, P. K. (2006). Studies and determination of heavy metals in waste tyres and their impacts on the environment. *Pak J Anal Environ Chem* 7(2), 7.

Shi, G., Chen, Z., Xu, S., Zhang, J., Wang, L., Bi, C. and Teng, J. (2008). Potentially toxic metal contamination of urban soils and roadside dust in Shanghai, China. *Environ Pollut* 156(2), 251-260.

Singh, S. and Kumar, M. (2006). Heavy metal load of soil, water and vegetables in peri-urban Delhi. *Environ Monit Assess* 120(1-3), 79-91.

Sobhan Ardakani, S. (2018). Assessment of Pb and Ni contamination in the topsoil of ring roads' green spaces in the city of Hamadan. *Pollution*, 4(1), 43-51.

Sun, Y., Zhou, Q., Xie, X. and Liu, R. (2010). Spatial, sources and risk assessment of heavy metal contamination of urban soils in typical regions of Shenyang, China. *J Hazard Mater* 174(1-3), 455-462.

Turekian, K. K. and Wedepohl, K. H. (1961). Distribution of the elements in some major units of Earth's crust. *Bull Geol Soc Am* 72: 175-192.

Vaezi, A. R., Karbassi, A. R. and Fakhraee, M.

(2015). Assessing the trace metal pollution in the sediments of Mahshahr Bay, Persian Gulf, via a novel pollution index. *Environ Monit Assess* 187(10), 613.

Wei, B. and Yang, L. (2010). A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. *Microchem J* 94(2), 99-107.

