Investigation of Heavy Metalloid Pollutants in the Earth's Environment Using Kriging Method and Hydrus Model

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Research Letter

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Investigation of Heavy metalloid pollutants in the Earth's Environment Using Kriging Method and Hydrus Model

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Abstract:

The zoning of copper, nickel and lead heavy metals was investigated by using Kriging method in GIS environment using circular, spherical, exponential and Gaussian variograms. In addition, one-dimensional Hydrus modeling of water flow and heavy metals in the soil environment was simulated up to 50 cm depth for a 210-day period and the concentration of heavy metals to the root depth was simulated. Distribution of lead element in soil surface with spherical model showed that its variation was in the range of 20 to 70 mg / kg. These values were 50-60 mg / kg for copper and 30 mg / kg for nickel. Investigation of heavy metals in the soil using the Hydrus model showed that the simulated value at the initial 0-15 cm depth has the highest value and at lower depths is decreased. Comparison of the concentrations of these elements with the standard allowed by the WHO showed that the lead element in this region was higher than the permissible level.
Due to the scarcity of safe water resources in arid and semi-arid regions of the world, reuse of municipal and industrial wastewater for irrigation is one of the alternatives to agricultural activities. Despite providing part of the water needed for irrigation, it is one of the causes of soil contamination and agricultural crops. Qadir et al (2010) showed that irrigation with raw wastewater is expanding in some developing countries due to the mismatch of urban development with the infrastructure needed for wastewater treatment. Impact of irrigation with wastewater on accumulation of heavy metals in soil and crops in the region of Marrakech in Morocco were investigated, the results revealed high risks indexes, heavy metal contaminated food crops, is a great health risk to the local human and animal populations (Sana Chaoua, et al. 2019). Use of wastewater for irrigation has several benefits, including the use of nutrients in it and reducing its entry into nature. However, the use of wastewater is usually associated with microbial contamination and heavy metals. Which can affect different parts of nature and therefore human health. One of the important tools in environmental studies is GIS software. This tool has been widely used in soil studies, engineering and environmental issues. Kriging method in this software is one of the important capabilities that is able to interpolate the desired variable values based on its weight value relative to the adjacent points. One of the studies in this area is research that zoned the distribution of heavy metals zinc and copper by conventional kriging and exponential modeling (Khodakarami et al, 2011). Rahimpour et al (2014) modeled the spatial variations of heavy metals of copper, zinc, iron and manganese in the Harris County area using conventional kriging methods and basic radial functions. Sistani et al (2017) investigated heavy metal contamination around the Kerman steel industry. Their results showed that lead and cadmium concentrations increased under the influence of the steel industry. Borges et al (2014) investigated the distribution and zoning of heavy metals using GIS in Brazil and investigated the status of heavy metal contamination in the water and soil
resources of the study area. For spatial distribution of heavy metals in the middle Nile Delta of Egypt, contamination factor, pollution load Index and degree of contamination indices were used to assess the environmental risks of heavy metal contamination from the soils (shokr, M.S et al. 2016). Altan et al (2011) also distribution heavy metals cadmium, chromium, copper, nickel, zinc and Lead was investigated using GIS interpolation techniques. In addition to the surface distribution of heavy metals, their accumulation in soil due to the use of effluent for irrigation or fertilizers has also been reported in various studies (Khai Nm, et al, 2007). Results of their studied that heavy metal-contaminated soils of selected villages in Zamfara State, Nigeria were in the order Fe > Pb > Cr > Zn > Cd > Ni, with Pb and Cd having a concentration higher than permissible levels for soils and accounted for 98.64% of the total potential ecological risk (Sharhabil Musa, et al, 2021). To investigate the movement of heavy metals, different numerical models can be used to simulate their transport in unsaturated soil. One of these models is the one-dimensional Hydrus (Hydrus-1D) that has been used in various studies. This model is used to investigate the infiltration of water and pollutants into the soil as well as their one-dimensional transport within the soil with different boundary conditions. This model has also been used by various researchers to investigate heavy metal transport. Sayaad et al (2008) investigated the transfer of heavy metals in soil using Hydrus-1D under safflower and wheat cultivation. They concluded that the Hydrus model was able to give a good estimate of the metal transfer process in the soil. Dao et al (2014) simulated heavy metal transfer to soil using Hydrus-1D and concluded that this model was able to predict the heavy metal transfer in soil to an acceptable level. Also in another study by Behbahaninia et al (2014) to investigate heavy metal transport in unsaturated soil environment, the capability of the Hydrus-1D model to study the transfer and estimation of heavy metals of iron and zinc concentrations within soil was emphasized. Mohtar et al (2018) showed regional and local factors contribute to the different type of air pollutant concentrations in Urban environment. In general, the purpose of
this study was to investigate the distribution of heavy metals in lands irrigated with wastewater in south of Tehran by means of kriging interpolation in GIS environment and to identify areas with potential contamination of lead, copper and nickel. Also the purpose of this study is to study the risk of soil contamination and agricultural products and consequently the extent to which people's health is at risk. Also, considering the possibility of deep transfer of these pollutants, the deep penetration of these metals to the bottom layers of soil is evaluated using Hydrus-1D software. It is expected that by examining the horizontal and depth distribution of these metals in the soils of the study area, a comprehensive information on their distribution and concentration in the soil can be found.

**Material and method**

The present study was conducted on lands south of Tehran (Figure 1) that irrigated with municipal wastewater. The study area lies within the with approximate coordinates of 35 ° 30 '35 ° 34 north latitude and 51 ° 26 ° 29 ° east longitude with an average elevation of 1050 m above sea level. The main soil in the study area is clay-loam with 1.1% to 5.3% organic matter. The area receives large amounts of municipal wastewater as well as surface runoff of Tehran's streets during the rainy season, which has always been a cause of concern for heavy metal pollution in the area. The major crops in these areas include vegetable and garden crops, which is often surface irrigation method. Therefore, as a result of using this irrigation source (crude effluent), there is always a risk of soil contamination and agricultural crops and thus endangering human health.
Figure 1. The study area and sampling site

**Sampling and chemical analysis**

After field visits to cultivated areas in south of Tehran and sampling sites that were irrigated with raw wastewater, random sampling was performed. Thirty samples of surface soil at 0-15 cm depth were prepared from plots with approximate dimensions of 200 × 200 m. And after recording each sample information including sample number, location of the sample with GPS, time and date of sampling and area cultivation status, they were transferred to the laboratory for chemical analysis. In addition to soil samples, 30 samples were collected from the effluent entering the study area in different sections and intervals. After preparation of soil and wastewater samples, the concentrations of Pb, Ni and Cu were determined by atomic absorption spectroscopy (AAS). Also measured the amount of organic matter, acidity (pH) and electrical conductivity (EC) of the samples in Laboratory.

**Geostatistical analysis**
In order to study the distribution of copper, nickel and lead heavy metals, conventional kriging method in GIS environment was used. This method uses quantitative correlation between the measured points and then configures the space around the projected points based on the measured values. The computational function in kriging method for estimating the desired values is given by Equation 1:

\[
\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [z(x_i) - z(x_i + h)]^2
\]

In this equation, \( Z(x) \) is the value of the parameter \( i \) at the point \( X_i \), \( h \) is the distance between the pair of points and \( n \) is the number of pairs measured points that separated by \( h \) intervals. Estimated values using the above Semivariogram are then fitted to a theory model such as circular, spherical, exponential or Gaussian models. These models determine the spatial distribution as well as the parameters desired in the kriging method. The kriging method uses the weighted average of the points to estimate the unknown value.

The equation is given by Equation 2:

\[
z(x_0) = \sum_{i=1}^{n} \lambda_i z(x_i)
\]

In this equation, \( Z(X_0) \) unknown value of the parameter desired at point \( X_0 \) and \( z(X_i) \) measured at point \( X_i \) and \( \lambda \) is weight.

The initial condition for using the values measured for interpolation by kriging is their normal distribution. For this purpose, using the logarithmic function, the distribution) and data were normalized, and then interpolated with different variograms. Also, before selecting each of the circular, spherical, exponential and Gaussian models, their usability was evaluated and finally the best model was selected for interpolation. For this purpose, statistical the root mean square error indices (RMSE), Pearson correlation coefficient (R), mean absolute error( MAE) and
MBE were calculated (equations 3-6) by using IBM SPSS statistics 23 software or in Excel environment.

The closer the value of R to 1 number in these relationships, the greater the correlation between observed and estimated data. And the closer the index to zero, the better the results of the model.

\[
RMSE = \sqrt{\frac{\sum_{i=1}^{n}(Z^*(x_i) - Z(x_i))^2}{n}}
\]  

(3)

\[
R = \frac{\text{Cov}(Z^*(x_i), Z(x_i))}{\delta(Z^*(x_i))\delta(Z(x_i))}
\]

(4)

\[
MAE = \frac{1}{n} \sum_{i=1}^{n} |Z^*(x_i) - Z(x_i)|
\]

(5)

\[
MBE = \frac{1}{n} \sum_{i=1}^{n} [Z^*(x_i) - Z(x_i)]
\]

(6)

In these equations, the value \(Z^*(X_i)\) is equal to the estimated value of the parameter \(Z\) by the model at point \(X_i\) and \(Z(X_i)\) the measured value of \(Z\) at point \(X_i\) and Cov, is data covariance and \(n\) is the number of samples.

In addition to the mentioned indices, the Nugget, Range and Sill indices were also determined in the studied variograms.

The Range value is the distance after which the variogram value is fixed. Physically it indicates that the pair of samples after this value is not spatially correlated. The Sill value is equal to the maximum variability between the sample pairs. In addition, the modeling of deep water flow and heavy metal transport in the soil environment was performed using one-dimensional Hydrus model.
In one-dimensional Hydrus, the flow of water is described using the Richards equation. Pollutant changes in the soil are calculated based on the transfer-diffusion equation (CDE) as follows.

\[
\frac{\partial \psi c}{\partial t} + \frac{\partial \rho S}{\partial t} = \frac{\partial}{\partial x} \left( \theta D \frac{\partial c}{\partial x} \right) - \frac{\partial q c}{\partial x} \tag{7}
\]

In this equation, \(c\) the contaminant concentration in the soil solution, \(S\) the amount of contaminant absorbed, \(\theta\) is the soil volumetric moisture, \(D\) the diffusion coefficient, \(q\) the transient flow value, \(t\), the time and \(X\) is contaminant distance from initial point.

The correlation between the heavy metals in the soil solution and the amount of adsorbed to the soil particles (parameter \(S\) in the above equation) is explained by Freundlich's adsorption model (Dao CA et al., 2014) which is given in Equation 8:

\[
Q_s = K_F C_e^\beta \tag{8}
\]

In this equation, \(Q_s\) are equal to the amount of heavy metals absorbed, \(C_e\) concentration of heavy metals in soil solution, \(K_F\) and \(\beta\) are also constant coefficients Freundlich's equation. These coefficients can be estimated based on laboratory or based on previous studies and then calibrated the model.

The Hydrus model also uses the Van Genuchten-Mualem equation as follows to determine the hydraulic parameters of the soil.

\[
\theta(h) = \begin{cases} 
\theta_r + \frac{\theta_s - \theta_r}{[1+|\alpha h|^{1/n}]^m} & h < 0 \\
\theta_s & h \geq 0 
\end{cases} \tag{9}
\]

In this equation \(\theta_r\), the amount of residual soil moisture \(\theta_s\), saturated soil moisture, \(m\), \(n\), and \(\alpha\) coefficients of the model \(h\) soil moisture potential \(K_S\) soil saturated hydraulic conductivity and \(S_e\) is soil moisture effective content.
Simulation of water and heavy metal transfer in soil up to 50 cm depth of soil for a period of 210 days (mid-November to mid-June) was carried out as wheat growing period which is the dominant crop in the study area. The parameters m, n, α and Ks were estimated inversely in the Hydrus model. The Feddes function was selected as the main function of water uptake by the plant and its coefficients were selected from the default numbers in the model for the wheat crop. Boundary conditions and upstream initial values were considered for atmospheric water flow as well as irrigation water values.

Under these conditions, the height of soil water and rainfall amounts were considered equal to the depth of water required for irrigation, which were reduced by infiltration or evapotranspiration. Due to the low groundwater level and deep soil in the study area, downstream boundary conditions were considered as free flows. Soil moisture information for depths 0-15, 15-30 and 50-30 cm soil layers as input to the model were considered. In addition, the model boundary conditions for metal transport were also considered based on the initial concentration of heavy metal elements.

Results

Laboratory analysis-

The in laboratory analysis obtained from the measurement of Cu, Pb and Ni concentrations of soil samples of agricultural areas and crude effluent imported into the study area is presented in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Standard error is about 95% confidence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Element number of samples</td>
<td>Minimum Maximum Average Standard deviation</td>
</tr>
</tbody>
</table>
Comparison of the concentration values of these metals in all samples showed that Pb was higher than copper and nickel.

Statistical results and selection of the best model-

Statistical comparison of circular, spherical, exponential and Gaussian models to determine the best variogram is presented in Table 2. The results showed that the exponential model with minimum RMSE, MAE, MBE and maximum R has the best fit in drawing copper element compared to other models which was used as variogram used in heavy metal copper element zoning. Comparison of these indices for the nickel element showed that the spherical model was better as the desired variogram. The spherical model had the best fit for the copper element.

Also, comparison of other parameters showed that the selected variograms had minimum Sill Partial value, which means that the maximum variability between sample pairs was smaller.

Table 2. Comparing circle, shefdrd, Gussin model in different variograms.
After selecting the most suitable variogram, Cu, Ni and Pb zoning maps were prepared in the study area (Figures 2 to 4).

Evaluation of distribution of lead element showed that the highest concentration 70-50 mg / kg was found in central areas of study area that irrigated by crude effluent. Concentrations of this element in soils often used from well water for irrigation are in the range of 30-40 or 40-50 mg / kg. Also, with increasing distance from this area to the lands of Talibabad village (Figure 2), the concentration of this element decreases and reaches about 20-30 (mg / kg).

Similarly, the distribution of copper element showed that higher concentrations of this element were observed in the central areas of the study area, which is the major consumer of wastewater for irrigation, than elsewhere (Figure 3), the concentration of this element is about 50-60 mg / kg. However, in the vicinity of the city of Rey, the concentration of this element reaches 20-30 or less than 20 (mg / kg). In the surrounding areas of Talibabad village in Fig. 3, as in the case...
of lead, a minimal distribution of copper was observed at concentrations less than 20 (mg/kg). The distribution of nickel element in Fig. 4 showed that the concentration of this element was in the range of 30 (mg/kg). Study of the distribution of this element in the area shows a uniform distribution of this element and only in some of the central parts of the study area did the concentration of this element slightly exceed (30 mg/kg).

Fig 2. Distribution heavy metal lead in south Tehran.
Fig. 3. Distribution heavy metal copper in south Tehran.

Fig 4. Distribution heavy metal nickel in south Tehran.
Investigation of heavy metal concentrations in soil profiles using the Hydrus-1D model showed that the major accumulation of lead occurred in the surface layer of soil at a depth of 0-15 cm (Fig. 1). The simulated concentration of lead showed that the variations trend of this element versus depth of the soil is decreased, so that at depth of 15-30 cm, is about 25 mg / kg and at a depth of 30 cm below 15 mg / kg. Temporal changes in the transport of this element over a 210 day period from the soil surface to a depth of 50 cm (0-50) showed that the concentration of this element in the surface layer decreased from 45 mg / kg at the beginning of the period to 35 mg / kg at the end of the period. This decrease may be related to increased plant growth and consequently increased plant uptake. Study of the concentration changes in the downstream layer also shows a similar trend during the growth period as the concentration of Pb at the end of the period is reduced to less than about 15 mg / kg at the beginning of the simulation period to less than 5 mg / kg has reached the end of the period. The simulation of the deep transition of Cu and Nickel also showed similar results, with the major accumulation of these two metals in the surface layer and with increasing depth, the concentration of these elements decreased rapidly (Figure 5). The temporal variations of copper and nickel transfer in the upper boundary of the soil also show that although initially an increasing trend was observed, the amount of this element decreased over time and reached about 30 mg / kg at the end of the growth period. And at the lower boundary (50 cm depth), the amount of element transport reached a small amount of about 2 (mg / kg).

Discussion

Comparison of the mean concentration of heavy metals in soil with each other showed that the concentration of lead in these samples was higher than that of nickel and copper. On the other hand, comparing these values with the concentration of these elements in the effluent sample showed that the higher concentration of Pb in the soil samples may be related to the high
concentration of this element in the effluent used for irrigation. This may indicate the importance of raw wastewater treatment prior to use for agricultural purposes.
The findings of Harati et al (2010) also indicate high concentration of lead in the study area, which is consistent with the results of this study. The heavy metal pollution in the soil is very important, because of expensive measurement methods and low accuracy, the use of models is inevitable. In this regard, the use of conventional kriging based on different circular, spherical, exponential and Gaussian models is one of the most common methods for investigating heavy element distribution. In this study, spherical model for nickel and lead and exponential model for copper element allowed to study the dispersion and determination of contamination status of these elements. Comparing the results of this study is consistent with the study of Khaledan et al(2017) as well as Rahimpour et al(2014) who reported that the spherical model for the lead element and the exponential model for the copper element were the best fit. Toxic variogram analysis of these models showed a higher concentration of heavy metals in the central regions of the study area. One of the reasons for the higher concentration of these elements in this area could be related to the frequent use of wastewater, which is the most important source of irrigation in this area. It should be explained that due to the low concentration of nickel in the effluent of the inlet to the area and the uniform distribution of
the concentration of nickel in the entire study area, there is no strong relationship between the use of nickel and the nickel dispersion in this area. The results for the variations of this element are comparable to the results of the study by Fard Samiei et al (2016), who reported a uniform concentration of the element in the study area. Another similar study is the study of Barzin et al (2015), which investigated heavy metals in Hamadan province. Their research results also showed that lead element was affected by the activities agriculture is at a high level of pollution. It is important to determine the maximum permissible concentration of heavy metals in the soils of agricultural areas due to their potential absorption by the plant and its adverse effects on plant health and growth, as well as the possibility of their transmission through food cycles to plants and animals. Although an element such as copper is one of the necessary metals in the soil for plant growth, it is also found naturally in soil and is usually complexed with organic matter and is rarely free or exchangeable. It may even be due to a deficiency of this element as one of the micronutrients important for plant growth is the need to add it to the soil. However, due to the low boundary between the amount required and the amount of poisoning in the soil, increasing its concentration in the soil may cause environmental pollution. Therefore, excessive entry of this heavy element by abnormal factors such as the use of agricultural fertilizers, pesticides or wastewater into the soil can be a potential contributor to pollution. The maximum permissible values reported for lead, copper and nickel in different countries (Table 3) show that its permissible values for different countries are significantly different.

Table 3. Heavy metal standard in agricultural soils in different countries.

<table>
<thead>
<tr>
<th>Countries</th>
<th>Heavy metal standard in agricultural soils</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>100</td>
</tr>
<tr>
<td>Canada</td>
<td>150</td>
</tr>
<tr>
<td>China</td>
<td>200-50</td>
</tr>
<tr>
<td>Germany</td>
<td>200</td>
</tr>
<tr>
<td>Tanzania</td>
<td>200</td>
</tr>
<tr>
<td>Netherlands</td>
<td>190</td>
</tr>
<tr>
<td>New Zealand</td>
<td>10000</td>
</tr>
</tbody>
</table>
Therefore, it is necessary to use a globally acceptable index for this purpose, including the World Health Organization (WHO) index. The maximum permitted levels in agricultural soils for lead, copper and nickel are reported to be 60, 100 and 50 mg / kg, respectively, according to the WHO standard (Toth G, et al, 2016). Also, the permissible standard of agricultural soils in Iran has been introduced by the Environment Agency (Barzin M, et al, 2015) for these three elements, 75, 200 and 110 mg / kg, respectively. By comparing the concentrations of nickel and copper with the maximum permissible values based on WHO standards in agricultural soils, it can be said that there is no contamination of these two elements in the area.

Comparison of lead concentration with standard introduced by WHO as well as permissible value in agricultural soils of our country shows that its concentration in the central areas of the study area is due to repeated irrigation of this area by effluent above WHO value and also somewhat higher than permissible level in WHO agricultural soils are in Iran.

It is necessary to explain that lead is one of the most important metals that is widely used in parts of variety of vehicles, electrical equipment and buildings. Also, urban runoff that transports pollutants from city vehicles and small industrial wastewater and domestic wastewater to irrigated area and is increased heavy metals. Therefore, considering the higher concentration of this element compared to nickel and copper in the effluent entering this area, it seems important to control the concentration of this element. The results of hydrous model analysis of heavy metal concentrations in Soil profile showed that the accumulation of heavy metals in the soil surface layer was higher than the deeper layers.
The main reason for this is that the behavior of heavy metals depends on intermediate factors affecting the uptake of heavy metals in soil such as organic matter, iron oxides or clays which are higher in the surface layer (Rattan RK, et al., 2005). For example, examining the relationship between the concentrations of heavy metals measured in the samples and the amount of organic matter in them showed that, as the amount of soil organic matter increased, the concentration of heavy metals in the samples increased (Figure 2). Therefore, it can be said that one of the important factors is the accumulation of heavy metals in the surface layers and its non-transfer to the lower layers related to this parameter. Comparison of the findings of this study with the study by Dao et al. (2014) also indicates the important role of soil organic matter in controlling the transfer of heavy metals to the sublayers. The 0-15 cm layer of soil, due to its high percentage of organic matter and clay, tends to absorb heavy metals and delay their leaching to the lower layers. Decomposition of soil organic matter can release heavy metals and increase its concentration in soil solution. While the formation or accumulation of organic matter in the soil, the heavy metals can be absorbed by the soil and delay its leaching. This illustrates the importance of soil organic matter in preventing heavy metal transport to the lower layers and ultimately to groundwater. In addition, the uptake of heavy metals into soil colloids, including clay minerals, is one of the factors that reduce the rate of ion transfer (8). In contrast, soil organisms activity, plant root growth, and soil surface characteristics such as soil cracks in the dry season lead to preferential flow during irrigation. It can have a significant impact on the transmission of contamination to the lower layers of soil. The results also showed that the Hydrus model was able to predict the values of the elements to an acceptable level. The simulated values in the surface layer showed the highest and the lowest values in the lower layer, which was comparable to the measured values. Comparison of the performance of this model with research by Behbahaninia et al. (2014) also shows that by providing sufficient information needed for model inputs, one can accurately simulate element transfer. Another
similar comparable study is the study by Sayaad et al (2008), which concluded that the Hydros
model was able to simulate Cu and Pb transfer in the root environment.

Conlussion:

Due to the high cost in large-scale measurement of heavy metals, the use of statistical land
models and techniques is one of the appropriate ways to study their distribution and level of
pollution. In this study, Kriging Ordinary in GIS environment was used to analyze the values
of heavy elements of lead, copper and nickel in soils under effluent irrigation in the south of
Tehran. The findings showed that in general the highest concentration of elements was in the
central areas of the study area, where the source of irrigation was mainly raw effluent. Lead
was found to be above the allowable level in the central areas of the region, which are
frequently irrigated with effluent, and more control studies are needed. In addition to the
surface distribution of these elements, their deep transfer into the soil using one-dimensional
Hydus software showed that the highest accumulation of elements occurred in the surface
layer 0-15 cm. This is due to the presence of more organic matter, clay and iron and manganese
hydroxides as important factors in surface absorption in this layer, which indicates their
importance in preventing the transfer of these elements to the deeper layers. In this study, due
to the limitations of executive facilities, only the contamination of the three elements of lead,
nickel and copper was investigated, while the effluent may contain more heavy metals.

Therefore, considering this research shortcoming, conducting additional studies to more
comprehensively study heavy metals and zoning areas with excessive contamination limits can
be very beneficial.

*Availability of data and material:
"Data and material of our research is available and free for researchers, scientist and all of students".

*Competing interests

This paper is output a part of Ph.D research and there are not any competing interests between Authors.

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*Authors' contributions

Farhad mirzaei: conceiving, designing and analysis, performing the analysis, writing the paper

Yasser Abbasi: contributing data or analysis tools

Teymour Sohrabi: performing the analysis

Seyed Hassan Mirhashami: other contribution

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Figure 1

The study area and sampling site Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.
Figure 2

Distribution heavy metal lead in south Tehran. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.
Figure 3

Distribution heavy metal copper in south Tehran. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.
Figure 4

Distribution heavy metal nickel in south Tehran. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.
Figure 5

concentration of Pb, Cu and Ni in Depth right and Time left