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Evaluation of heavy metals concentration in soil using GIS, RS and Geostatistics

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Abstract: *The objective of this study was to assess the effect of agricultural activities on heavy metal concentrations and spatial distribution using Geographical Information System (GIS), geostatistics and Remote Sensing (RS) techniques. The random systematic method was used for sampling strategy by dividing the study area into a grid of 5 km× 5 km and collecting 135 composite soil samples from 0-20 cm depth. These samples were analyzed for total concentration of heavy metals (Zn, Cd, Ni, Pb, Cu, Cr, Co, As and V), soil pH, organic matter and soil texture. Interpolation of heavy metals concentration was done by geostatistics methods and the appropriate method for interpolation was selected using spatial correlation analyzes and MAE and MBE functions. The interpolation maps of Zn, V and Pb were produced by discrete kriging method and exponential model, interpolation As map was produced using ordinary kriging and ovally model. For producing the interpolation maps of Cd, Cu and Cr, Co, Ni we used Radial Basic Function method and ordinary kriging method respectively and exponential model. For analyzing heavy metal distribution, we used landuse and geology maps. Landuse map was produced using multi teporal of satellite images IRS-P6 AWIFS. We used fuzzy method for classification of satellite images, have kappa and accuracy of 0.88 and 90% respectively. Analyzing the interpolation maps show that As, Cd, Zn and Pb have the geological and agricultural origin and Cr, Co, Ni and V originated from bedrocks. Agricultural activities such as over using of fertilizers can increase the amount of these elements in soil.*

Key words: *geostatistics, heavy metals, soil pollution, parent material, geographical Information System (GIS).*

I. Introduction

Because of limit sources of food, producing the safe food for increasing population of the word with minimum adverse effect on environment is one of the very important problems of word. Increasing the industrial and agricultural activities and producing the pollutants is one of the most important and developing problems of human in recent years (Torabian and Mahjouri, 2002). There are much expanded uses of chemicals in agriculture and industries. These chemicals enter the environment by agricultural and industrial activities (Amini et al, 2006). Because of wide distribution of chemicals and heavy metals in environment, which many of them are toxic, mutagen, carcinogenic; they can enter the food chain.

Soil is one of the most important natural sources of food. Intensive agricultural and industrial activities have the adverse effects on this important source. Therefore protection of soil quality and suppression of its downfall is very important and vital. Usually point and non- point pollutions produced by human activities (agriculture, industry, urban) affect the quality of soil and water drastically (Corwin and Wagenet, 1996). Such examples of these non- point pollutants are: fertilizers, pesticides, heavy metals and salts. These pollutants have widely distribution (Corwin et al, 1999). Non- point pollutants are the universal problems and don't be limited by political boundaries (Duda and Nawar, 1996). The non- point pollutants are known as the most important sources of pollution in soil and water and agriculture have the most contribution to produce these pollutants (Duda and Nawar, 1996 and Humenik et al , 1987).

These days, the importance of GIS, RS and geostatistics to soil pollution studies is well known. In recent years, GIS was used to managing and estimate the non- point pollution sources, by environment researchers (Walsh, 1988). Also, Satellite Image were used in natural resource, agriculture and environment studies. So it is necessary for accurate evaluation of non- point pollutions in wide scale to use of sum of sciences such as classical statistics, geostatistics, remote sensing, GIS, soil science, hydrology and biosciences.

The objective of this study is evaluating the total concentration of Cu, Zn, Cd, As, Cr, Co, Ni, V, Pb and evaluating the pollution of surface soil (0- 20 cm) in three catchment areas in Hamedan province, Iran: Kaboudarahang, Razan- Ghahavand and Khonjin- Talkhab, using classic statistics, geostatistics, GIS and RS. Hamedan provinve and these three catchment areas of this province are of the important centers of Iran agriculture.

II. Methods And Materials

- Study Site

The area of the study site is about 7262 Km^2 and located between 351074 and 360778 longitudes and 3545048 and 3956656 latitudes. As mentioned above this study area located in Hamedan province of Iran and contains three catchment areas: Kaboudarahang, Razan- Ghahavand and Khonjin- Talkhab (fig. 1). The predominant landuse of these catchment areas are: agriculture with predominant crops of wheat, barley, alfalfa and potato, garden and orchard.the minimum and maximum height of study area from sea surface is 1679 m and 2933m respectively. According to annual census of 15 recent years minimum and maximum precipitation of this region is 250 and 550 mm y^{-1} respectively. According to Domarten classification, the climate of this region is arid and semi- arid (Classification of soils of Hamadan Province.1997). The predominant geological structure of this area is quarteric sedimentary terraces and orbitalin lime, Shale and marls. The soils of this region are shallow and semi- deep, with gravels and lime. The texture of these soils is light to medium (Classification of soils of Hamadan Province.1997).

In this study we used the 1/50000 topographic maps for initial assessing of study site and recording the satellite image, geological maps (Fig. 2).

The landuse map of this region for year 2008 was produced using multi temporal of satellite images IRS-P6 AWIFS (Table. 1). Geometric and atmospheric corrections were done and growth phenologic stages of predominant crops (wheat, barley, alfalfa, potato, garden and orchard) were determined. Then after the classification of images using fuzzy method, the land use map with Kappa of 0.88 and accuracy of 90% was produced. We used this map for analyzing the heavy metals distribution in soils of study site (Fig. 2). Table 2 shows the area and area percentage of each landuse. Arc GIS software was used for interpolating the heavy metals.

Data acquisition

In this study we used the 1/50000 topographic maps for initial assessing of study site and recording the satellite image, geological maps that this map reflects the overall composition of the surface geology consists of five classes, alluvium, igneous and metamorphic rocks, limestone, sandstone and shale and Marl, has been prepared by the Geological Survey (Fig. 2).

Land use map: Mapping of land use and cropping pattern are essential for the study of soil contamination. That’s way in this study the land use map of this region in year 2008 was produced using multi temporal of satellite images IRS-P6 AWIFS (Table. 1). After determining the growth phenologic stages of predominant crops (wheat, barley, alfalfa, potato, garden and orchard) Images were acquired, first, satellite image geometric correction with a mean square error of less than 0.48 pixels was applied. For image classification, the method of fuzzy classification was used. Finally, the land use map of the study region was classified into eleven classes. To assess the classified land use map precision it was controlled for ground truths with a GPS. Kappa coefficient and overall classification accuracy of fuzzy classificotion were estimated 88 and 90 percent respectively. The results confirmed that the fuzzy classifier was capable to generate land use maps and cultivation pattern with high accuracy. We used this map for analyzing the heavy metals distribution in soils of study site (Fig. 2). Table 2 shows the area and area percentage of each land use. In this study we used Erdas Imagine software for Image processing and Arc GIS software for Geostatistics also Spsss software for statistics analysis.

Soil Sampling Analysis

135 composite soil samples were collected from 0 - 20 cm depth by dividing the affected area into a grid of 5 km×5 km using random systematic method. The area at each sampling point was about 20 m x 20 m grid and soil samples were taken of each corners and center of each grid. Soil samples were air dried and sieved a mechanically vibrating 2 mm stainless steel mesh. In these samples soil texture and organic carbon were determined using hydrometric and Walkley- Black methods respectively. EC and pH of these samples were determined in saturated extract and paste respectively (Klute, 1986). For determination of total Hg and As, one gram of soil sample was digested with a mixed acid (1:3:4 HNO_3:HCl:H_2O) (Shi et al., 2005). The total concentrations of other metals in soil samples were determined by digestion of 1 gram of soil with mixed acid (3:1 HNO_3:HCl) (Burt et al., 2003). The concentrations of the metals (except for As) in the soil extracts were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Demirak et al., 2006).

Concentrations of As in soil samples was determined by hydride generation atomic fluorescence spectrometry (HG-AFS) (Fu et al., 2008).

Statistical analyses

Basic statistical parameters for each variable, correlation matrices, histograms and boxplots were calculated using SPSS Statistical Software. Normality test for distribution of soil data was done at 95% confidence limit, using Klomogorov- Smirnov. Non- normal data were converted to normal data, using logarithm conversion method. We used box plots for assessing and correcting the outlier. For evaluating the effect of landuse on heavy metals concentration, the landuse map was classified in three groups of agriculture, urban- industrial and non- agriculture, then the mean of heavy metals concentration in these groups was compared using variance analyzing test. Correlation coefficients among heavy metals and among heavy metals and physical and chemical parameters of soil were calculated using Pearson correlation coefficient.

Kriging

Kriging is based on the idea that the value at an unknown point should be the average of the known values at its neighbors; weighted by the neighbors' distance to the unknown point. The method is mathematically closely related to regression analysis. The major aim of kriging is to find the statistical weights of observations with non- skew estimations and minimum variance of estimations. So kriging is called the best linear non- skew estimator (Webster and Oliver, 2000). In this study we used the ordinary kriging for evaluating the distribution of Co, Cr, Ni, As concentration (Webster and Oliver, 2000) and discrete kriging for evaluating the distribution of Pb, Zn and V concentration (Webster and Oliver, 2000). Also the distribution of Cd and Cu concentration was evaluated using radial basic function method (Webster and Oliver, 2000).

Evaluation of accuracy and deviation of interpolation methods

To evaluate interpolation methods, statistical indices of MAE (Mean Absolute Error), MBE (Mean Bias Error) and RMSE (Root Mean Square Error) were used. The MAE is an indicator of errors in the results and MBE indicates the bias of the results obtained through the applied method. When MAE and MBE are 0.00 or near to naught, the applied method simulates the fact well. However er, as far as its amount is farer than 0.00, it implies to less precise and more bias. Finally, we use the RMSE to evaluate model performances in cross-validation mode.

The smallest RMSE indicate the most accurate predictions. How the parameters MAE and MBE and RMSE are calculated, has been indicated as Eq 1-3.

$$MBE = \frac{1}{n}\sum_{i=1}^{n}\left[Z(x_i) - Z(x_i)\right] \qquad 1)$$

$$MAE = \frac{1}{n}\sum_{i=1}^{n}\left|Z(x_i) - Z^*(x_i)\right| \qquad 2)$$

$$RMSE = \sqrt{\frac{1}{n}\sum_{k=1}^{n}\left(Z(x_i) - Z^*(x_i)\right)^2} \qquad 3)$$

Where: Z(xi) is observed value at point xi, Z*(xi) is predicted value at point xi, N is the number of samples.

The validation and the sufficiency of the developed model variogram can be tested via a technique called cross validation. Cross validation estimation is obtained by leaving one sample out and using the remaining data. This test allows to assess the goodness of fitting of the variogram model, the appropriateness of neighborhood and type of kriging used. The interpolation values are compared to the real values and then the least square error models are selected for regional estimation (Leuangthong et al., 2004; Uyan and Cay, 2010).

III. Results And Discusion

Background concentration of heavy metals

The maps of background concentration of heavy metals were produced using mean of heavy metals concentrations in pristine areas regions such as pristine areas pastures and regions which are far from human activities. The mean concentration of each metal for each bedrock was calculated, using overlaying this pristine points and geological maps vector in Arc GIS that was calculated a geology map vector with mean of pristine points in each bedrock and we were converted geological map to raster dataset for overlaying and analysis with spatial distribution heavy metal. Then according to these maps, the background concentration maps of each metal were produced.

Heavy metals concentration in pristine areas show that the mean concentration of V and Cr is naturally high in all bedrocks and the lowest concentration in bedrocks of this region is related to Cd. The mean concentration of each metal in bedrocks and background concentration maps are shown in table 3 and Fig 3 respectively.

Statistical Description of Data

Table 4 shows the statistical description of data and some physical and chemical properties of soil. Coefficient of variance (CV) of Cd and As concentration is higher than 50%, is showing the high variance of these metals concentration in soils of study site. According to this table the least and the most CV is related to Co and As respectively.

The results of Klomogorov- Smirnov test show that the concentration of V, Cd and As don't follow the normal distribution (table 5). It is necessary for data in geostatistics to follow the normal distribution. Presence the high skewness and kurtosis in study data may disturb the variogram structure and kriging results. We used logarithm conversion for normalizing the concentration of Cd and As, because there is no negative data.

We replaced the data lower than ($\bar{x}$ ±3sd) with maximum or minimum of data which are lower than ($\bar{x}$ ±3sd). Also Pekey (2006) and Pereira et. al (2008) used this method to assess and correct the outlier in their studies.

After normalizing data, we used Pierson correlation coefficient for evaluating the correlations among heavy metals concentration and soil physical and chemical properties (table 6). According to Pierson correlation coefficient heavy metals were classified to three groups. In the first group, Co and Cr, Ni, V, Zn, in the second group, Cr, and Ni and V and in the third group Zn and Pb , V have the correlation higher than 0.6. High correlation among elements may be a result of derivation and enter soil from the same origin such as agricultural activities, atmosphere or parent materials. In this study and in all of these groups, according to background concentration and landuse maps (Fig. 2 and 3) parent materials and agricultural activities are the main origins of heavy metals in the soil. Many researchers such as Gurhan et al (2007) and Amini (2004) used Pierson correlation coefficient and stated that metals with high correlation coefficient may originate from the same origin (Gurhan Yalcin et al., 2007 and Amini et al., 2006).

Evaluating the Heavy Metals Concentration in Agriculture, Non- agriculture and Urban- Industrial Land Uses

For evaluating the relationships among heavy metals concentration distribution and landuse map, the landuse map was classified to 3 major landuses: agriculture, non- agriculture and urban- industrial. Table 7 shows the area and percentage of each landuse. Then the heavy metals concentration distribution and landuse maps were overlaid by Arc GIS software. Results indicate that the mean concentration of Cu, Cr, V, Zn and Cd in agriculture landuse is higher than other landuses but the mean concentrations of Co and Pb in urban-industrial and Ni in non- agriculture landuse are higher than agriculture landuse. For evaluating the significant difference among heavy metals concentration in different landuses we used one way variance analysis. The results showed that there is a significant difference in 95% confidence limit between Co concentration in agriculture and non- agriculture landuses, Pb concentration in agriculture and urban- industrial, agriculture and non- agriculture landuses, Zn concentration in agriculture and non- agriculture landuses. There is no significant difference among other heavy metals in different landuses. It seems that agricultural activities in study site affect the concentration of Pb and Zn in soils, also seems that the effect of urban- industrial activities on Pb concentration in soils is more than the effect of agriculture landuse.

Spatial Distribution

According to results of spatial correlation analysis for all variants the estimation error and the mean of Root mean square standardized are very closed to 0 and 1, respectively (table 8). This means that the accuracy of estimation is high. Also, table 8 shows that there is a high spatial correlation among heavy metals concentration (especially As, Ni, Cr, Co and V) in soil samples. This may be a result of the effect of natural factors such as parent material, topography and soil type on heavy metals concentration. It seems that human factors such as fertilizing may change the spatial distribution of some metals such as Cu and Cd (with weak spatial structure) and Zn and Pb with less range effect. The experimental semivariograms for the heavy metals in soil are compared with the fitted models in Fig. 4 and Fig.5. The results of empirical variograms and models fitted on heavy metals data show that spherical model fitted on As data and exponential model can represent the other metals distribution, except for Cd and Cu.

The results of evaluation of accuracy and deviation of interpolation methods using Mean Absolute Error (MAE) and Mean Bias Error (MBE) functions were shown in table 8. MAE is the absolute mean of difference between analyzed and estimated concentration and the closer to 0 MAE, the higher accuracy of method. MBE shows the mean difference between analyzed and estimated concentrations and the less MBE, the less difference between analyzed and estimated concentrations so the less deviation of the model (Webster and Oliver, 2000). Evaluating the strength of variants spatial structure using C/C0 (Sill/nuget)showed that the spatial structure of Cu and Cd is weak, therefore we used Radial Basic Function (RBF) for interpolation of these two metals. Other metals show the strong spatial structure and we used the kriging method for interpolation. After evaluating the kriging methods we used ordinary and discrete methods as the best interpolation methods (table 8).

Jiachun et al. (2007) used the ordinary and normal logarithm kriging methods for producing the spatial pattern of Cr, Hg, Pb, As, Cd and Cu and showed that Cd, Cr and other metals followed the linear, exponential and spherical models, respectively. They used the C0/ C+ C0 function for evaluating the variants spatial structures. Lado et al (2008) used the regression kriging for interpolation of heavy metals.

Interpolation Maps of Heavy Metals Concentration

Figure 6 shows the maps of As, Cr, Co and Ni total concentration distribution. The most concentration of As is 19.4- 38 mg kg^{-1} which occurs in the west of study region with The geological structure containing magmatic and metamorphic rocks, shale and marl. The highest concentration of Cr is 96- 140 mg kg^{-1} which occurs as the spots in the south and the west north of region, with geological structure containing shale and marl, sandstone, limestone and magmatic rocks. Natural concentration of Cr in magmatic rocks and shale is reported to be 90 and 35 mg kg^{-1} respectively (De vos et al., 2005). The highest concentration of Co is 19.9- 27 mg kg^{-1} and is observed in the west south and west north of region. These parts of study region have occurring on shale, marl, sandstone, limestone and metamorphic bedrocks. Magmatic bedrocks and shale naturally contains 150 and 19 mg kg^{-1} Co (De vos et al., 2005). The highest amount of Ni is 73- 110 mg kg^{-1} and is reported as three spots in the south, west south and west north of study region with geological structure containing shale, sandstone and limestone bedrocks. The natural concentration of Ni in shale and sandstone bedrocks is 90 and 20 mg kg^{-1} respectively (De vos et al., 2005).

The critical levels of soil pollution with As, Cr, Co and Ni are 10, 51, 10 and 50 mg kg^{-1} respectively (Pais and Benton jones, 2000, Kabata, 2001 and Merian, 1991). In the most parts of study region the soil concentration of these metals are higher than these critical levels, but the presence of lime in these soils may reduce the metals solubility, drastically.

Overlaying the maps of As, Cr, Co and Ni concentration distribution and land use, showed that soils with high concentration of metals don't follow the agricultural patterns. Also overlaying the interpolation maps of heavy metals concentration and background concentration maps showed that the highest concentration of these metals was observed in soils, which are deriving from shale and marl, magmatic and metamorphic and especially limestone bedrocks. Because of non-industrial distribution in study region, it seems that parent materials are the major factor affecting the high amount of metals in soil. Inácio et al. 2008 and Luo et al. 2007 stated that As concentration in soil is controlled by parent materials. Jiachun et al. 2007 showed that bedrocks control the As concentration in soil but there is a weak correlation between As in soil and anthropogenic resources.

Facchinelli et al (2001) and Mico et al. (2006) studied the heavy metals resources in soil and resulted that Cr, Co and Ni concentration in soil is controlled by bedrocks. Also the researches of Lado et al (2008) and Luo et al. (2007) resulted that bedrocks control the concentration of Cr and Ni in soil.

Distribution maps of total Cu, Zn, V, Cd and Pb in superficial soils of study region (Fig. 7 and Fig. 8) indicates that maximum concentration of Cu is 48.9- 57 mg kg^{-1} that is occurred at west of the study region. Overlaying the distribution and geology maps show that the maximum concentration of Cu underlay the shale bedrocks, which naturally is high in Cu content. Estimation of Cu background concentration (table3 and figure 3) upholds this result. This has been reported that the concentration of Cu in metamorphic and shale bedrocks is about 40 and 50 mg kg^{-1} respectively (De vos et al., 2005). Evaluating the distribution of total Cd in soil using radial basic function (Fig. 7) shows that minimum and maximum concentration of Cd in soils of study region is about 0.1 and 0.33- 0.55 mg kg^{-1} respectively. Overlaying the maps of Cd concentration distribution and geology of region shows that the soils with high concentration is in north, west, south and east south underlay the shale, marl and limestone bedrocks. This rocks naturally rich in Cd amount. The concentration of Cd in shale and limestone bedrocks can be rich as high as 0.8 and 0.2- 0.27 mg kg^{-1} respectively (De vos et al., 2005). Maximum concentration of Zn is about 87- 150 mg kg^{-1} which is occurred in north, east and south of the region. The parent materials of these parts are shale and metamorphic rocks. The concentration of Zn in limestone, shale and metamorphic rocks is naturally high (De vos et al., 2005). Figure 7 shows that regions which have 27 mg kg^{-1} Pb, occur at east south and north of study region and underlay the sandstone, limestone, magmatic and metamorphic bedrocks. These regions occupy the 10.8% of the total area of the study region. Natural Pb concentration in sandstone and shale bedrocks is 10 and 23 mg kg^{-1} respectively (De vos et al., 2005). The highest amount of V in soil was 112.8- 150 mg kg^{-1} which is occurred as a band at west north to east south and south to north and as a spot at west south of the study site. These bands and hot spot are occurring on the shale, sandstone, limestone and magmatic bedrocks. Shale and magmatic rocks naturally are rich in V amount (90- 260 and 150- 460 mg kg^{-1} respectively) (De vos et al., 2005).

The critical levels of total Cu, Zn, V, Cd and Pb in superficial soils are reported to be: 23, 60, 3, 0.76 and (De vos et al, 2005) mg kg^{-1} respectively (Angelone et al., 2002, Kabata, 2001, Kabata, 2001 and Merian, 1991). According to these levels the most areas of study site is polluted by Cu, Zn, V and Pb. Because of calcareous nature of these soils, the probability of these metals solubility is low. Overlaying the metals distribution and landuse maps show that there is high and unmanaged uses of fertilizers in the regions with high amounts of heavy metals (the rates of fertilizers use are: 500- 700 kg ha^{-1} y^{-1} urine, 200- 330 kg ha^{-1} y^{-1} potassium and 300- 558 kg ha^{-1} y^{-1} phosphorus fertilizers). These rates of fertilizing can cause the accumulation of metals in soil. Overlaying the heavy metals interpolation and background concentration maps (fig. 3) shows that highest amount of these metals is observed in soils derived from marl, shale, limestone, magmatic and metamorphic bedrocks. In addition because of non-developed industry in study site, it seems that the main effective factors on metals concentration in soils, are parent materials and agricultural activities. Facchinelli et al. (2001), Mico et al. (2006), Luo et al. (2007) and Jiachun et al. (2007) resulted that the amount of Cu and Zn in soil drastically affected by bedrock. Also Lado et al. 2008 showed that there is a high correlation between Cu, Cd, Zn and Pb concentration in European soils and lime stone bed rock and agricultural activity.

Mico et al. (2006), Luo et al. (2007) reported that Cd concentration in soil is controlled by human activities, such as use of phosphate fertilizers. Also Jiachun et al. (2007) studied the spatial distribution of heavy metals in soil and resulted that Cd concentration in soil is affected by natural and anthropogenic factors.

Facchinelli et al. (2001), Mico et al. (2006) and Luo et al. (2007) showed that Zn and Pb concentration in soil is controlled by human activities.

IV. Conclusion

Heavy metals are non- point pollutants which today because of undesirable effects on human and environment become the global problem. The most important results of this research are: there is a significant difference in 95% confidence limit between Co concentration in agriculture and non- agriculture landuses, Pb concentration in agriculture and urban- industrial, agriculture and non- agriculture landuses, Zn concentration in agriculture and non- agriculture landuses. There is no significant difference among other heavy metals in different land uses. It seems that agricultural activities in study site affect the concentration of Pb and Zn in soils, also seems that the effect of urban- industrial activities on Pb concentration in soils is more than the effect of agriculture landuse. Analyzing the interpolation maps of heavy metals and auxiliary gis layers (geology, landuse, background concentration of metals maps) shows that geology and agricultural activity are the origin of Cu, Zn, V, Cd and Pb in soils and Cr, Co, As and Ni derived from bed rocks. Also according to background concentration maps the main factors are effective on increasing the natural metals concentration in soils of study region are shale, sandstone, limestone and metamorphic bed rocks and the least back ground concentration of heavy metals is related to alluvium bedrock.

References

[1] Amini, M., Afyuni, M., Khademi, H., 2007. Mass balance modeling of Cd and Pb, in farms of Isfahan.Journal of Science and Technology of Agriculture and Natural Reasources.10(2),77-89.

[2] Amini, M., 2004. Modeling heavy metal accumulation and assessing its uncertainty in agro- ecosystems of Isfahan region. PhD thesis. Isfahan University of Technology. Isfahn. Iran.

[3] Angelone, M., Bellanca, A., Sprovieria, M., Neri, R., Salvagio, A., Manta, D., 2002. Heavy metals in urban soils: a case study the city of Palermo (Sicily), Italy. The since of the Total Environment. 300, 229-243.

[4] Cao, H. F., Chang, A. C., and Page, A. L., 1984. Heavy metal contents of sludge-treated soils as determined by three extraction procedures. J. Environ. Qual. 13:632–634.

[5] Corwin, D.L., Wagenet, R.J. 1996. Application of GIS to the modeling of nonpoint source pollutants in the vadouse zone: A conference overview. J .Environ. Qua. 25,403-411.

[6] Corwin, D.L., Loague, K., Ellsworth, T.R., 1999. Advanced information technologies for assessing nonpoint source pollution in the vaduose zone. J .Environ. Qual .28,357-37.

[7] Demirak, A., Yilmaz, F., Tuna, A.L., Ozdemir, N., 2006. Heavy metals in water, sediment and tissues of Leuciscus cephalus from a stream in southwestern Turkey. Chemosphere. 63, 1451–1458.

[8] De vos, W., Batista, M.J. Demetriades, A., Duris ,M.J., Lexa, J., Lis, J., Sina, K.,O' connor, P.J. 2005. Metallogenic Mineral Provinces and World Class Ore Deposits in Europe. In: Salminen, R. et al. (Eds.), Geochemical Atlas of Europe. Part 1 Background Information, Methodology and Maps.Geological Survey of Finland.[Online] Availability

[9] Duda, A.M, and Nawar, M. 1996. Implementing the World Bank, s water resources management policy: A priority on toxic substance from nonpoint sources. Water Sci. Technol. 33,45-51.

[10] Facchinelli, A., Sacchi, E., Mallen, L. 2001. Multivariate statistical and GIS –based approach to identify heavy metal sources in soils. Environ. Pollut. 114, 313-324.

[11] Fu, J. J., Zhou, Q. F., Liu, J. M., Liu, W., Wang, T., Zhang, Q. H., Jiang, G. B., 2008. High levels of heavy metals in rice (Oryza sativa L.) from a typical E-waste recycling area in southeast China and its potential risk to human health. Chemosphere. 71, 1269–1275.

[12] Gurhan Yalcin, M., Battaloglu, R. Ilhan, S. 2007. Heavy metal sources in Sultan Marsh and its neighborhood, Kayseri, Turkey. Environ Geol. 53, 399–415.

[13] Humenik, F.J., Smolen, M.D., Dressing, S.A. 1987. Pollution from nonpoint- sources: Where we are and where we should go. Environ. Sci. Technol. 21, 737-742.
[14] Jiachun, Sh., Haizhen, W., Jianming, X., Jianjun, W., Xingmei, L., Haiping, Z., Chunlan, Y. 2007. Spatial distribution of heavy metals in soils: a case study of Changxing, China. Environ Geol. 52,1–10.
[15] Kabata- Pendias, A., Pendias, H. 2001.Trace Elements in Soil and Plants, Boca Raton London, New York.
[16] Klute, A. 1986. Methods of soil analysis, part I, physical and mineralogical methods. Wisconsin.
[17] Lado, R.L., Tomislav, H., Hannes, I.R. 2008. Heavy metals in European soils: A geostatistical analysis of the FOREGS Geochemical database. Geoderma. 148, 189–199.
[18] Leuangthong O, McLennan JA, Deutsch CV. 2004. Minimum acceptance criteria for geostatistical realizations. Nat Resour Res 13:131–141.
[19] Luo, W., Wang, T., Lu, Y., Giesy, J.P., Shi, Y., Zheng, Y., Xing, Y., Wu, G. Landscape ecology of the Guanting Reservoir, Beijing, China: Multivariate and geostatistical analyses of metals in soils. Environ. Pollut. 146, 567_576.
[20] Merian, E. 1991. Metals and Their Compounds in the Environment, Occurrence, Analysis and Biological Relevance. Weinheim.
[21] Mico, C., Recatala, L., Peris, M., Sa´nchez, J. 2006. Assessing heavy metal sources in agricultural soils of an European Mediterranean area by multivariate analysis. Chemosphere. 65, 863–872.
[22] Pais, I., Benton jones, J. 2000. The handbook of Trace Elements. New York.
[23] Pekey, H. 2006. The distribution and sources of heavy metals in IzmitBay surface sediments affected by a polluted stream. Marine Pollut. Bulletin. 52, 1197–1208.
[24] Pereira, V., Inácio, M., Pinto, M. 2008. The Soil Geochemical Atlas of Portugal Overview and applications. J. Geochem. Exploration. 98, 22–33.
[25] Shi, A. B., Liang, L. N., Jiang, G. B., Jin, X. L. 2005. The speciation and bioavailability of mercury in sediments of Haihe River, China. Environ. International. 31,357–365.
[26] Soil and Water Reserch Institute. 1997. Classification of soils of Hamadan Province. Journal No. 625.
[27] Torabian, A., Mahjouri, M. 2002. Evaluating the effect of irrigation with sewage on uptake of heavy metals by leafy vegetables in south of Tehran. Iranian J. Soil and Water Sci. 16 (2), 189- 196.
[28] Uyan M, Cay T. 2010. Geostatistical methods for mapping grounwater nitrate concentrations. Paper presented at the 3rd international conference on cartography and GIS. Nessebar, Bulgaria. 15-20 June 2010.
[29] Walsh, S.J. 1988. Geographic Information Systems: An Instructional Tool for Earth Science Educators. J. Geography. 89, 17-25.
[30] Webster, R., Oliver, M.A. 2000. Geostatistics for environmental scientists. New York.

List of Tables

Table 1- data from satellite image

year	date	Sensor
2008	6 March	AWIFS
2008	3 April	AWIFS
2008	27 April	AWIFS
2008	18 july	AWIFS

Table 2- The area of landuse classes (% and ha)

Landuse type	Area (ha)	Area (%)
Potato and corn	27294	3.75
alfalfa	52810	7.3
Wheat and barley	140767	19.34
urban	3175	0.44
water	43	0.005
orchard	4586	0.6
Arid, fallow and pasture	351534	48.3
Salt land	5861	0.8
Mountain and pasture	87444	12.03
Calcareous regions	36276	4.99
plow	17480	2.4
total	727269	100

Table 3- back ground concentration of metals in bedrocks of study region (mg kg-1)

	bedrock				
metal	Alluvium	Magmatic and metamorphic rocks	limestone	sandstone	Shale and marl
Co	15/9	21	19	18/3	19/2
Cr	83/6	101	106/3	99/3	99/9
Cu	30/6	33/2	36/8	40/9	37/9
Ni	57/7	69/6	72/3	74	71/3
Pb	23/55	26	23/3	25	25/15
V	93/7	121/8	113/3	111/7	114/9
Zn	67/2	86/6	75/6	82	78/4
Fe	3/4	4/4	4/08	3/9	4/1
Cd	0/12	0/16	0/23	0/13	0/25
As	14/5	16/6	15/5	12/4	13/4

Table 4- statistical description of soil physical and chemical properties

Soil parameters*	Min.	Max.	mean	median	range	Std.	CV	skewness	Kurtosis
Co	8 /1	27	17/61	18	18/9	3/54	20/15	0/018	0/21
Cr	30	140	86/91	88	110	22/71	26/13	0/017	-0/36
Cu	13/5	57	34/37	34	43/5	9/11	26/50	0/118	-0/39
Ni	26	110	63/14	63	84	17/68	28/03	0/26	0/25
Pb	13	57	24/46	24	44	5/3	21/67	1/85	9/91
V	50	160	103/77	110	110	21/26	20/49	-0/22	0/23
Zn	35	150	76/71	76	115	17/49	22/79	0/65	1/61
As	4/65	85	14/65	13	80/35	8/52	58/15	4/72	34/68
Cd	0/1	0/55	0/15	0/1	0/45	0/07	50/07	1/96	5/44
pH	7/23	8/37	7/78	7/79	1/14	0/22	2/82	0/09	0/22
OM	0/03	2/69	0/64	0/55	2/66	0/51	79/68	1/78	3/74

* metals concentrations and organic matter are at mg kg^{-1} and percentage respectively.

Table 5- distribution of heavy metals concentration in soil of study region (Kolmogorov- Smirnov test)

	Co	Zn	V	Pb	Ni	Cu	Cr	Cd	As
N	135	135	135	135	135	135	135	135	135
Kolmogorov-Smirnov Z	0/94	0/68	1/55	1/18	0/55	0/54	0/78	3/5	2/15
Asymp. Sig. (2-tailed)	0/337	0/73	0/35	0/12	0/918	0/926	0/56	0	0

Table 6- Pierson correlation coefficient among heavy metals and soil physical and chemical properties

	Co	Cr	Cu	Ni	Pb	LogV	Zn	LogAs	LogCd	PH	LogOM	Clay
Co	1											
Cr	0.798**	1										
Cu	0.347**	0.331**	1									
Ni	0.778**	0.907**	0.413**	1								
Pb	0.573**	0.367**	0.099	0.318**	1							
LogV	0.869**	0.686**	0.216*	0.589**	0.590**	1						
Zn	0.772**	0.499**	0.233**	0.431**	0.661**	0.790**	1					
LogAs	0.108	0.147	0.106	0.170*	-0.005	0.067	-0.146	1				
LogCd	-0.388**	-0.377**	0.028	-0.243**	-0.260**	-0.522**	-0.312**	-0.197*	1			
PH	-0.036	-0.060	0.023	-0.024	0.000	0.032	0.011	0.058	-0.054	1		
LogOM	-0.025	0.064	-0.026	0.052	-0.001	-0.021	-0.033	0.009	-0.084	0.036	1	
Clay	0.028	0.012	-0.086	-0.009	0.052	0.067	0.047	0.105	-0.015	0.188*	0.198*	1

** $p < 0.01$, * $p < 0.05$, *OM* organic matter,

Table 7- landuses and their area

Landuse type	Area (ha)	Area (%)
agriculture	242617/082	33/4
Urban and industrial	6864/0768	0/94
Non- agriculture	481157/1072	65/7
total	727269/4464	100

Table 8- parameters of variograms fitted on study data

element	Interpolation method	Model	(C_0)	C	C_0+C	Mean	MS	RMSS	MAE	MBE
As	Ordinary Kriging	Spherical	0/038	0/4	0/438	0/35	0/037	1/123	4/6	-0/0076
Zn	Disjunctive Kriging	Exponential	0/22	0/77	0/99	0/18	0/009	1/03	11/7	-0/1874
Cu	Radial Basis Function	-	-	-	-	0/068	-	-	7/4	-0/0466
V	Disjunctive Kriging	Exponential	0/2	0/85	1/39	0/1	0/006	0/96	13/3	-0/0058
Ni	Ordinary Kriging	Exponential	157	212/77	369/77	0/0013	0/0006	1/138	12/5	-0/0015
Co	Ordinary Kriging	Exponential	5/96	7/75	13/71	0/0001	0/0007	1/019	2/5	-0/0089
Pb	Disjunctive Kriging	Exponential	0/46	0/53	0/99	0/013	0/00003	1/199	3/4	-0/0142
Cd	Radial Basis Function	-	-	-	-	0/002	-	-	0/65	-0/002
Cr	Ordinary Kriging	Exponential	226	333	559	0/003	0/00022	1/031		

C_0 nugget vaiance, C structral variance , C_0+C Sill variance
RMSs root- mean square standardized, MS mean standardized
MAE mean absolute error, MBE mean bayas eroor

List of Figures

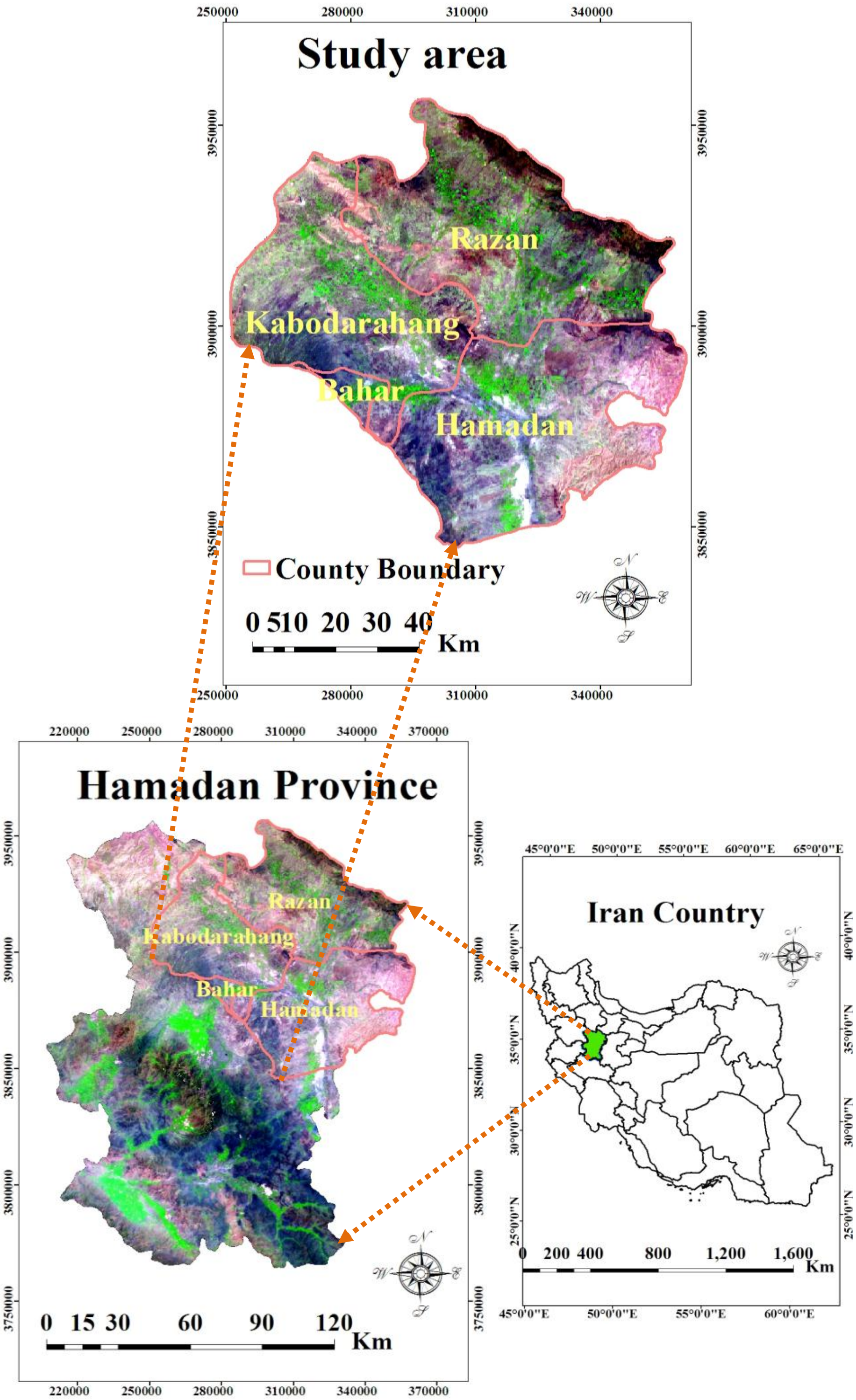


Fig. 1- The status of study region

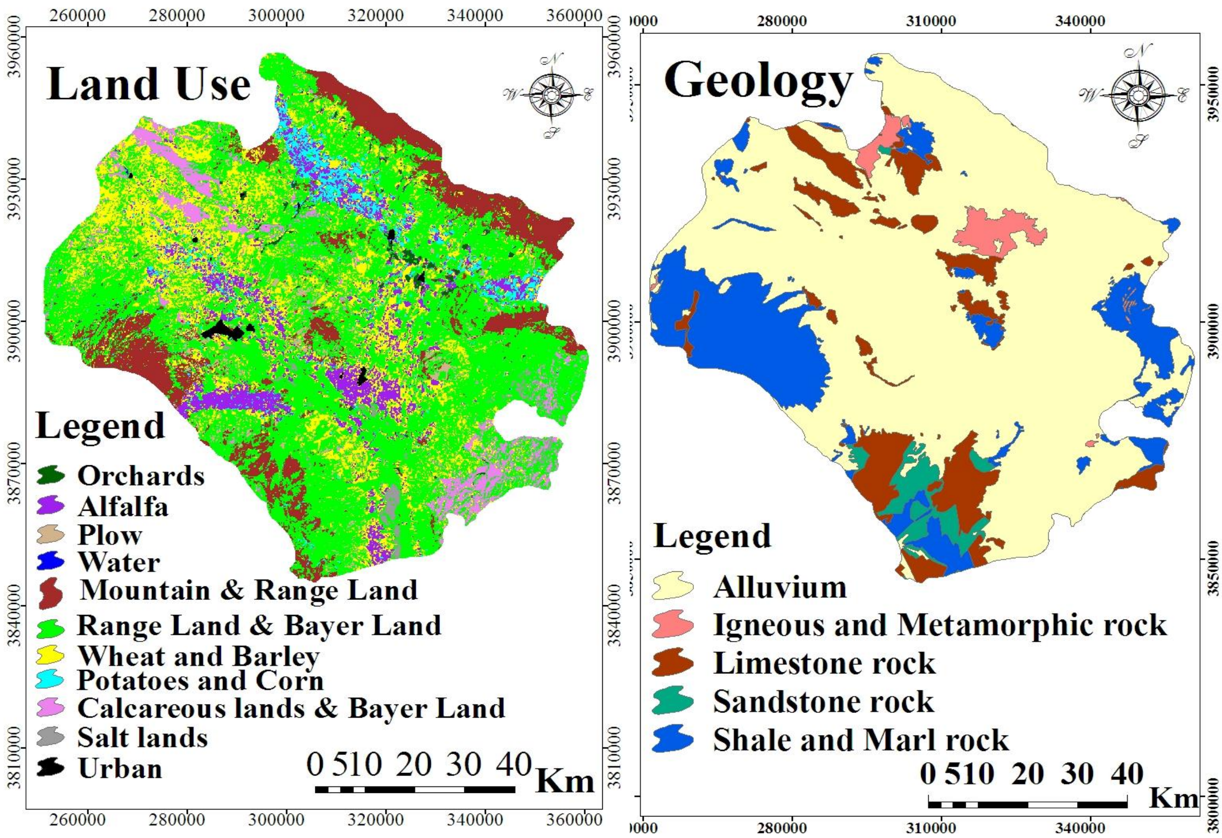


Fig. 2- Geology and land use maps of study region

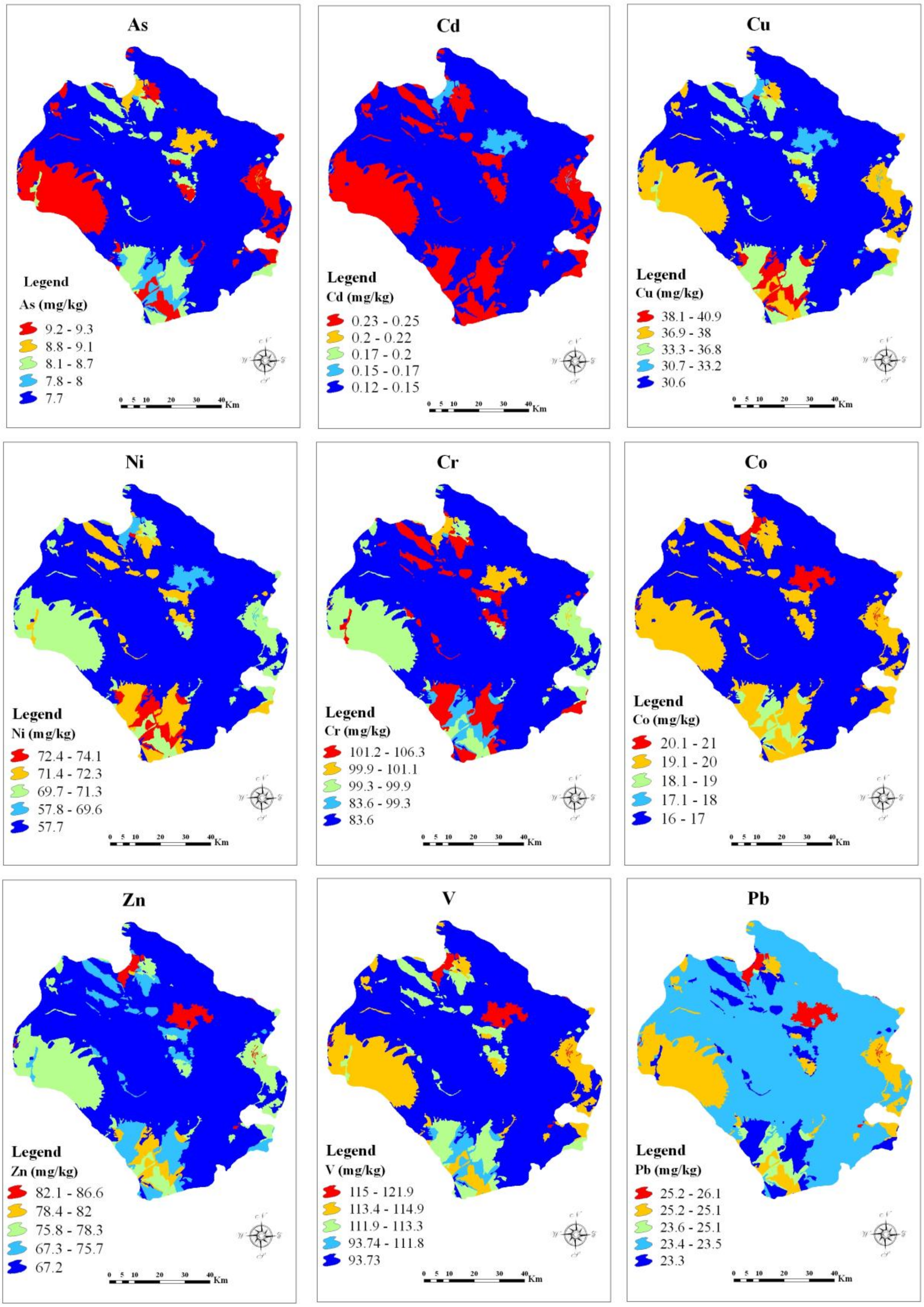
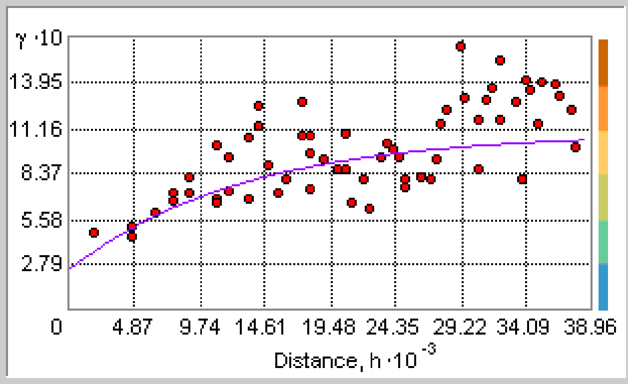
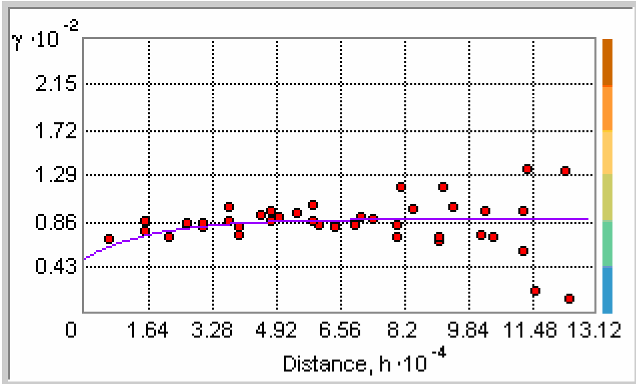


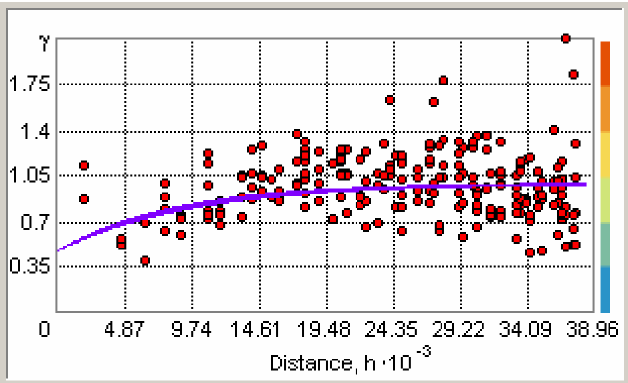
Fig. 3- estimation background concentration maps of Cu, Cd, As, Ni, Cr, Co, Zn, V and Pb.



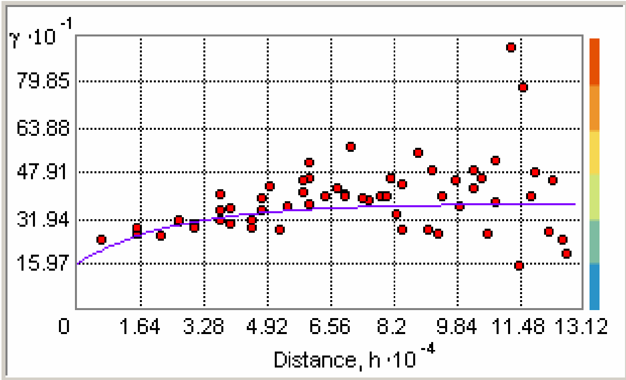
*Experimental semivariograms for **V***

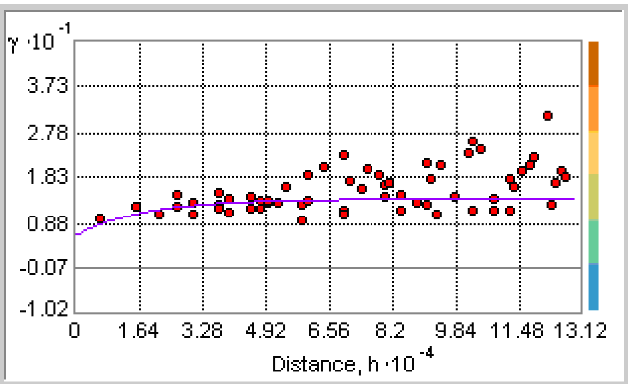


*Experimental semivariograms for **Zn***

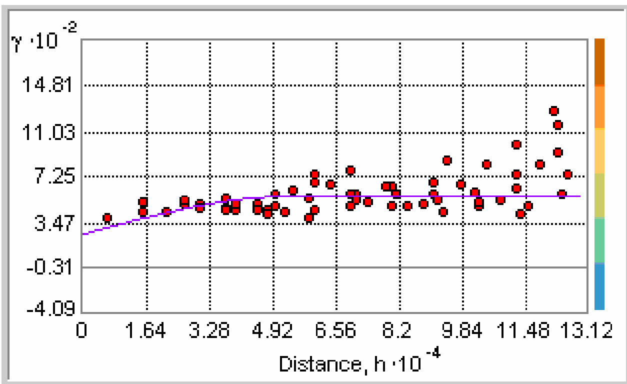


*Experimental semivariograms for **Pb***



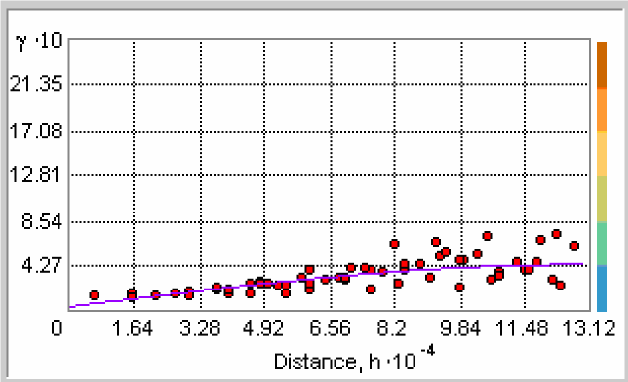


*Experimental semivariograms for **Co***



*Experimental semivariograms for **Cr***

Fig.4. Experimental semivariograms for heavy metals in soil compared with fitted models: Zn,V, Ni, Pb, Cr and Co (Exponential models)



Experimental semivariograms for ***As***

Fig.5. Experimental semivariograms for heavy metals in soil compared with fitted models: (As (Spherical models)

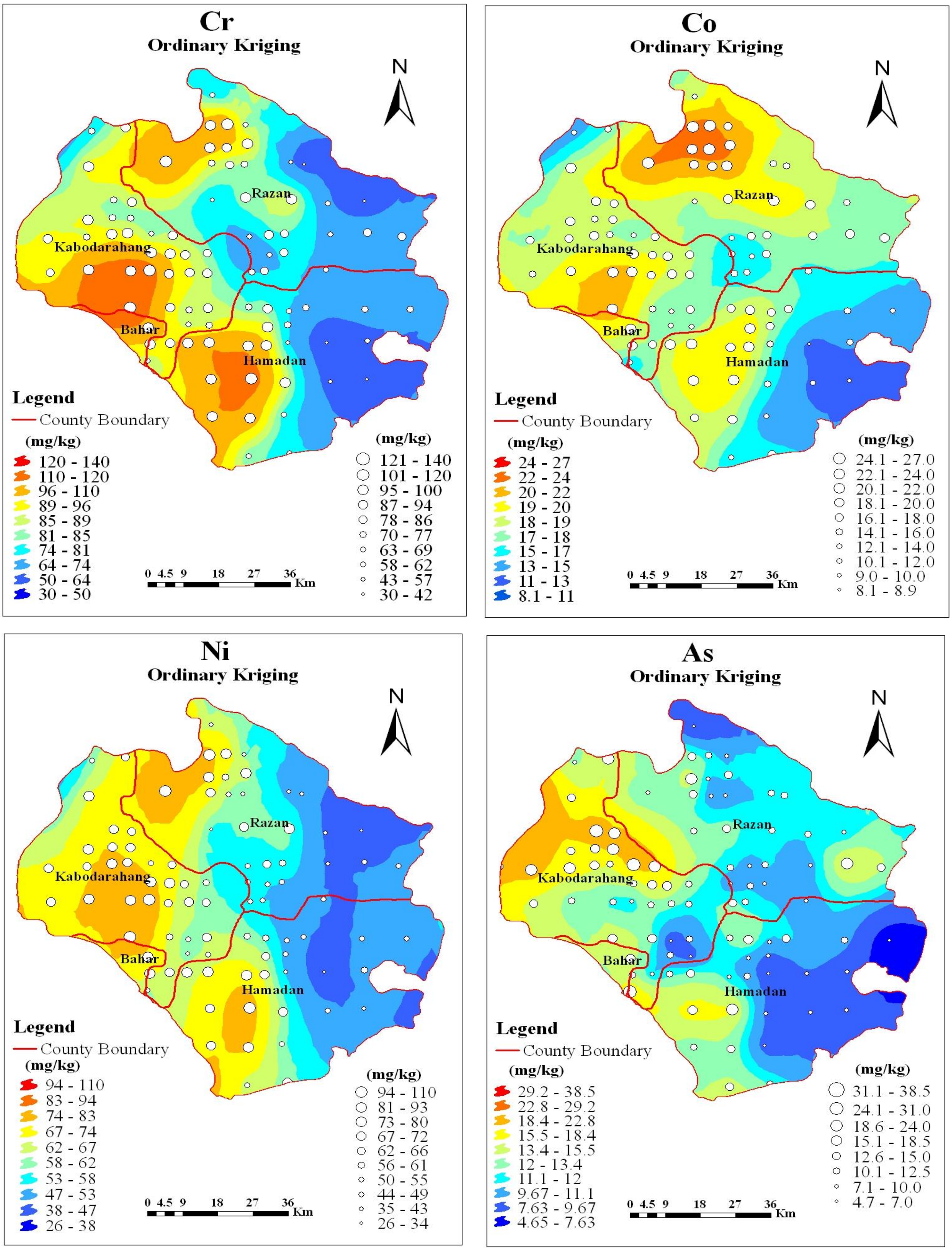


Fig. 6- distribution maps of Cr, Co, Ni and As.

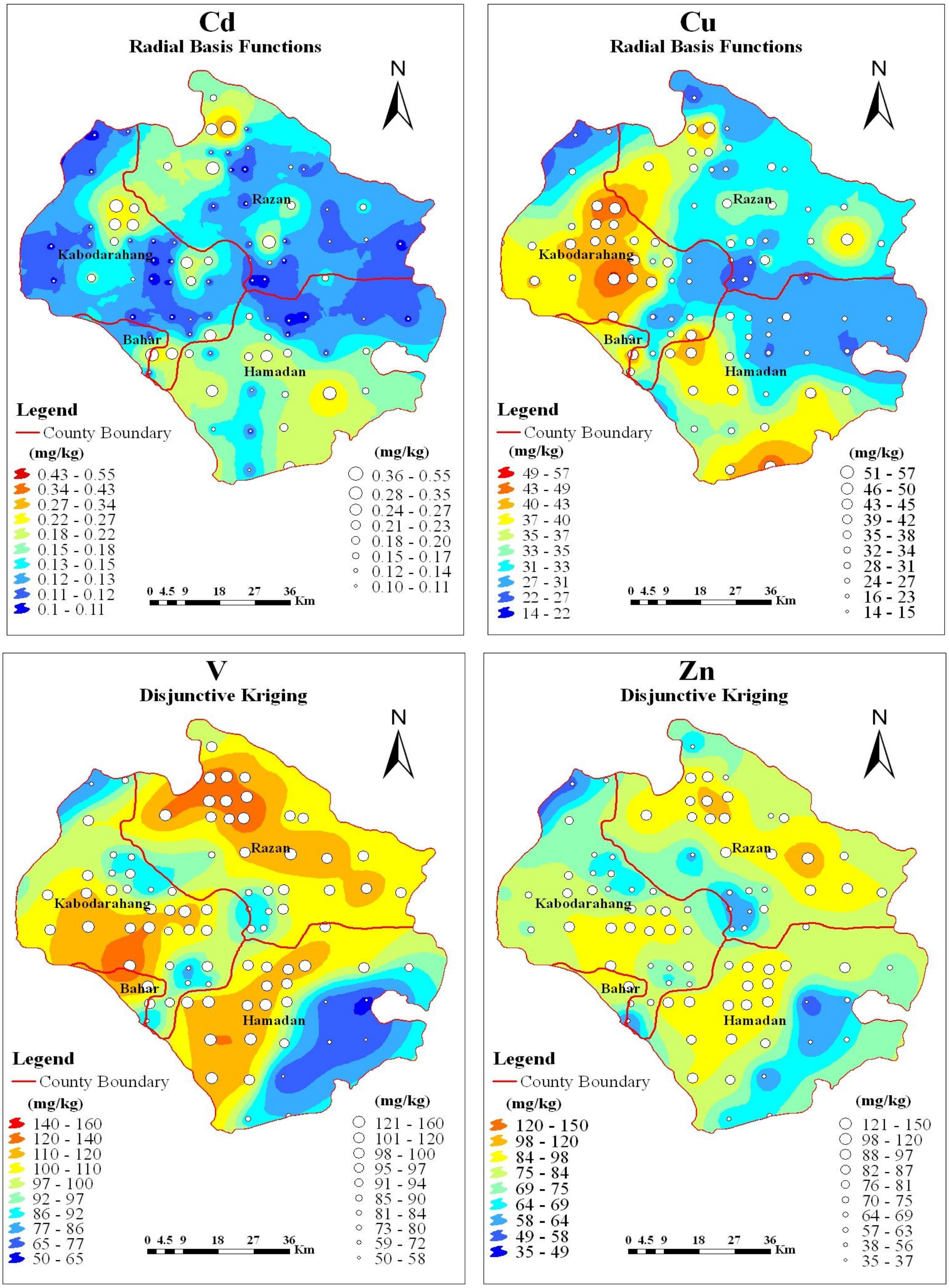


Fig. 7- distribution maps of Cd, Cu, V and Zn.

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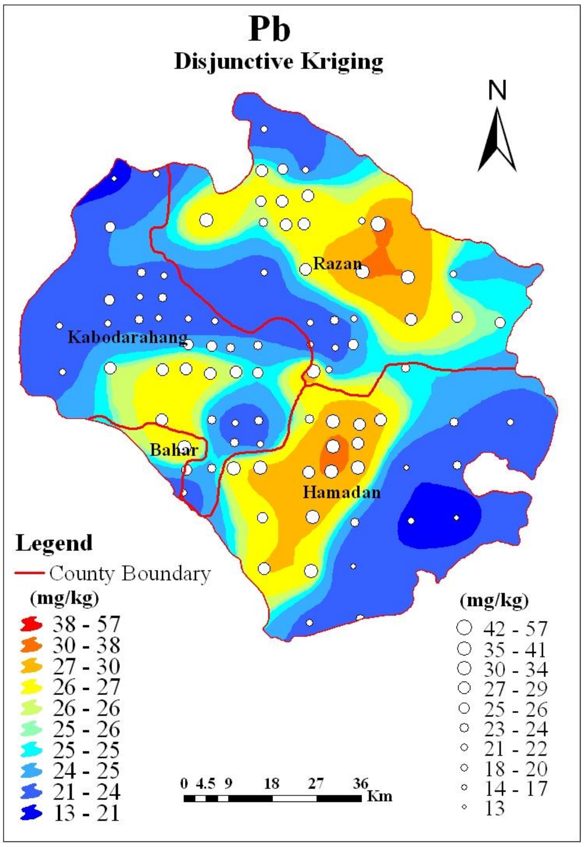

Fig. 8- distribution map of Pb.