Abdolhossein Parizanganeh[1], Robab Saberinia[1], Ali Hajabolfath[2], Abbas Ali Zamani[1]

CONCENTRATION AND SPATIAL DISTRIBUTION OF TOTAL AND BIOAVAILABLE HEAVY METALS IN TOP SOILS IN TAHAM DISTRICT OF ZANJAN PROVINCE-IRAN

[1]Department of Environmental Science, Faculty of Science, University of Zanjan, Zanjan-Iran, h_zanganeh@znu.ac.ir , Tel : +982414269056

[2]Department of Geology, Faculty of Science, University of Zanjan, Zanjan-Iran

h_zanganeh@znu.ac.ir

Abstract. Toxic elements like heavy metals are natural constituents of the earth's crust and a number of these elements are biologically essential at trace levels and play an important role in human health. Heavy metal contamination of soil is a widespread problem in Zanjan province located in North West Iran due to natural pedogeochemical background and anthropogenic sources. Taham district was selected for detail study and the objectives of the study were set to evaluate the total as well as bioavailable fraction of heavy metals in surficial soils within the studied area. 57 surficial soil samples were collected and analyzed for heavy metal contamination by Atomic Absorption Spectrometry (AAS). The obtained results when compared with WHO and EPA standards show a very high concentration of some toxic metals notably As, Pb and Cd. Bioavilable fraction of studied metals was also measured with formation of metal complex with Diethylene Tri Amine Penta Acid (DTPA) agent. To find the share of the anthropogenic sources in the contamination of soils, the Enrichment factor (Ef) and Geological accumulation index were measured and the distribution maps were drawn using Arc GIS (9.3). High concentrations of some toxic metals like As, Pb and Cd were found in isolated patches in North West, East and South West of the studied area originating both from pedogenic as well as anthropogenic sources. Soil contamination by metals was very high around industrial town and agricultural lands within the studied area. The most effective factors responsible for high concentrations of other elements like Cu, Co, Ni and Fe in soil were found to be pedogenic in nature.

Key words: Heavy metals, Enrichment factor, Geological accumulation index, Taham district, Zanjan-Iran.

INTRODUCTION

Heavy metal contamination of soils is widespread and there is a risk of transfer of toxic and available metals to human, animals, and agricultural crops (Gaetke and Chow, 2003). Heavy metals are natural constituents of the Earth crust. A number of these elements are biologically essential at trace levels and play an important role in human health (Juvanovic, et al., 1995). The potential risk for the environment and population due to soil heavy metals arising from metallic mining has been well described (Abrahams, 2002). Heavy metals can induce toxicity in wildlife if the soil level reaches critical values; also plant accumulation in above-ground tissues can result in an increase of metal accumulation in top-soil, via leaf deposition, or can create an exposure pathway for metal introduction into the food chain (Unterbrunner et al., 2007). Two main sources of heavy metals in soils can be considered: (i) the natural pedo-geochemical background, which represents the heavy metal concentration inherited from the parent rock and (ii) anthropogenic contamination, which can be directed via wastes, animal manure, compost, sewage sludge, or diffuse via aerosol deposition (Parizanganeh, et al., 2012).

Zanjan province located in North West Iran has a large metalliferous site and has been considered as a traditional mining region since antiquity. There are still large reserves of lead (Pb) and zinc (Zn) in the area. Both mines and smelting units in the province present a risk of contamination of soils, plants, surface and ground water by dissemination of the particles carrying metals by wind action and/or by runoff from the tailings. Heavy metal contamination in different parts of Zanjan province has been previously reported specially in the vicinity of Lead and Zinc mining and smelting sites (Abbasi, et al., 2000) (Chehregani, et al., 2009). The total heavy metal contents can indicate the extent of contamination, but is not usually an accurate indication of the phyto-toxicity; so many latest studies investigated the heavy metal fractions of mine soils (Vega, et al., 2004) and evaluated the phyto-toxic risk for human receptors. However, the determination of heavy metal fractions is a more complex task than the determination of the total contents of heavy metals (Li, et al., 2005). The main purpose of this research is to measure the quantity of heavy metals in top soils of the studied area, the determination of the rate of the bioavailable elements in top soil is also one of the pillars of this research, since this part aside from polluted or unpolluted soils; show the absorption ability of the plants.

MATERIALS AND METHODS

The study site

In this study the Taham district located near the city of Zanjan was selected for detailed study. Soil samples were collected from the studied area during October 2012 (figure 1).

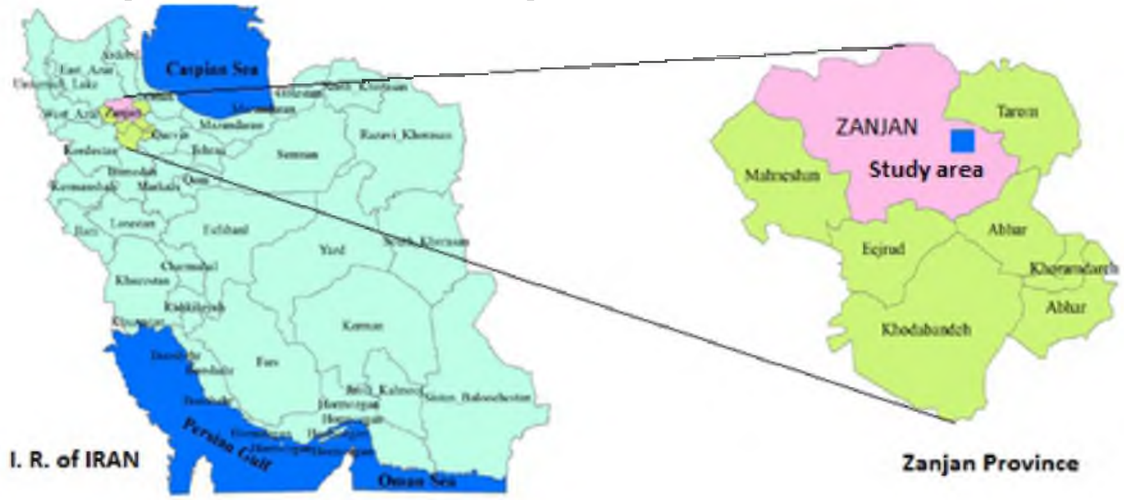

Figure 1- Location map of the studied area

Sample collection

Fifty seven soil samples were collected through systematic random sampling. The study area was divided into a 4x4 km grid and samples were collected from every corner of the grid. Based on the information gathered through field trips and taking into account the type of landuse and the population density, the number of samples was increased by subdividing the grid in selected locations (2x2 km grid).

Soil samples were collect from the surface of the soil (0-30 cm deep) and preserved by using the method of soil analysis (Mohammadi and Eslami, A., 2007). From each sampling points, four soil samples were gathered and mixed properly to obtain a composite sample mixture. The soil sampling spots were cleared of debris before sampling. Each composite soil samples were placed in cellophane bags labeled then taken to the laboratory for pre-treatment and analysis. The sampling tools, were washed with soap and rinsed with distilled water after each sampling (Whitten and Ritchie, 1991).

Soil analysis

In the laboratory, bulk soil samples were spread on trays and were air dried at ambient conditions for two weeks. The samples were then grounded by mortar and pestle, sieved through a 2 mm mesh, and oven-dried at 50 °C for about 48 hours. The samples were then stored in polyethylene bags and re-homogenized before being used. The soil samples were digested using the 11466 ISO standard methods (the aqua regia digestion method) (ISO 11466, 1995). The bioavailable content of metals were determined using Lindsey method (Lindsay, 1978).

The metals (Pb, As, Zn, and Cd,) in the soil extracts were analyzed by Atomic Absorption Spectrometry (AAS). Three analytical replicates were measured for each sample. Data with replicates were presented as mean-standard error and difference test was made using SPSS 14 software. The pH and EC (solid: distilled water=1:5) of the soil samples were also measured by with pH and EC meters (Metrohm, Germany). Finally, using the geostatistical methods with Arc GIS (9.3) the heavy metal distribution maps were drawn.

RESULTS AND DISCUSSION

Total heavy metal in soils

Comparing the results with standard range shows that the concentrations of heavy metals Pb, Zn, Cu, Cd in the studied area are higher than standards. Summary statistics for the analyzed elements in all the studied samples are presented in table 1. Though, Cadmium has the lowest mean concentration (11.2 mg/kg), it is well above the maximum permissible limits given by all existing standards. While the highest contents are for Pb (122.8 mg/kg), As, Zn, and Cd are also much higher than standards and are somehow related to the pedo geochemical sources. Zinc industries are the major anthropogenic source for the enrichment of these heavy metals in the top soil. The extremely high metal levels in tailings from these industries made them a potentially hazardous source of soil contamination. Soil pH averaged 7.93 (from 6.67 to 8.57) indicating a neutral to alkaline nature. Electrical conductivity (EC) in the samples is quite variable ranging from 127.5 to 686.0 µs.cm-1. The concentration of the studied metals are in the order of Pb> Zn> As>Cd.

Table 1 - The nature of the soil samples and total metal concentrations in the top soil (mg.kg-1)

	pH	EC (µs.cm^{-1})	Pb	Zn	Cd	As
Avg.	7.93	353.3	122.8	79.2	11.2	62.6
Max.	8.57	686.0	176.7	227.6	19.8	97.8
Min.	6.67	127.5	61.7	32.8	3.7	26.7
Median	7.98	362.0	124.2	71.9	11.0	64.7
STDEV	0.31	108.2	27.4	36.3	0.3	13.5
World Avg.*	-	-	20.0	50.0	0.3	5-10
WHO Standards	-	-	20.0	50.0	0.3	

*Kelepertsis, et al. 2001

The bioavailable heavy metals (Lindsay and Norvell, 1978) content in soil samples are much less than total metal content. With increasing total heavy metal content in soils, the bioavalaible content of metals are also increase and there are a significant correlation between them (table 2).

Table 2 - Bioavailable heavy metal contents in the top soil. (mg. kg-1)

	Pb	**Zn**	**Cd**	**As**
Avg.	5.6	3.74	0.19	1.28
Max.	13.6	21.81	0.56	1.50
Min	2.7	0.04	0.13	0.86
Median	5.0	2.23	0.18	1.30
STDEV	2.3	4.68	0.06	0.12

Figure 2 shows the concentration and distribution of each metal within the studied area. Arsenic concentrations (figure 2.a) is very high in north and central parts of the district coinciding with some geological formations (igneous metaliferous shale and tuffs) and are purely pedogenic. High concentrations of As in some localized patches in southern parts of the district close to the Zanjan industrial town may be of anthropogenic origin. Lead, Cadmium and Zinc concentrations in top soil within the studied area (figures 2.b, 2.c and 2.d) also show a similar distribution pattern as that of As. i.e. very high concentrations of all three metals are found in north and central parts of the districtunder investigation and are mainly natural with pedogeochemical background. Similarly, higher concentrations of all the studied metals are also found in southern parts of the district with industrial and agricultural landuses and are probably of anthropogenic origin.

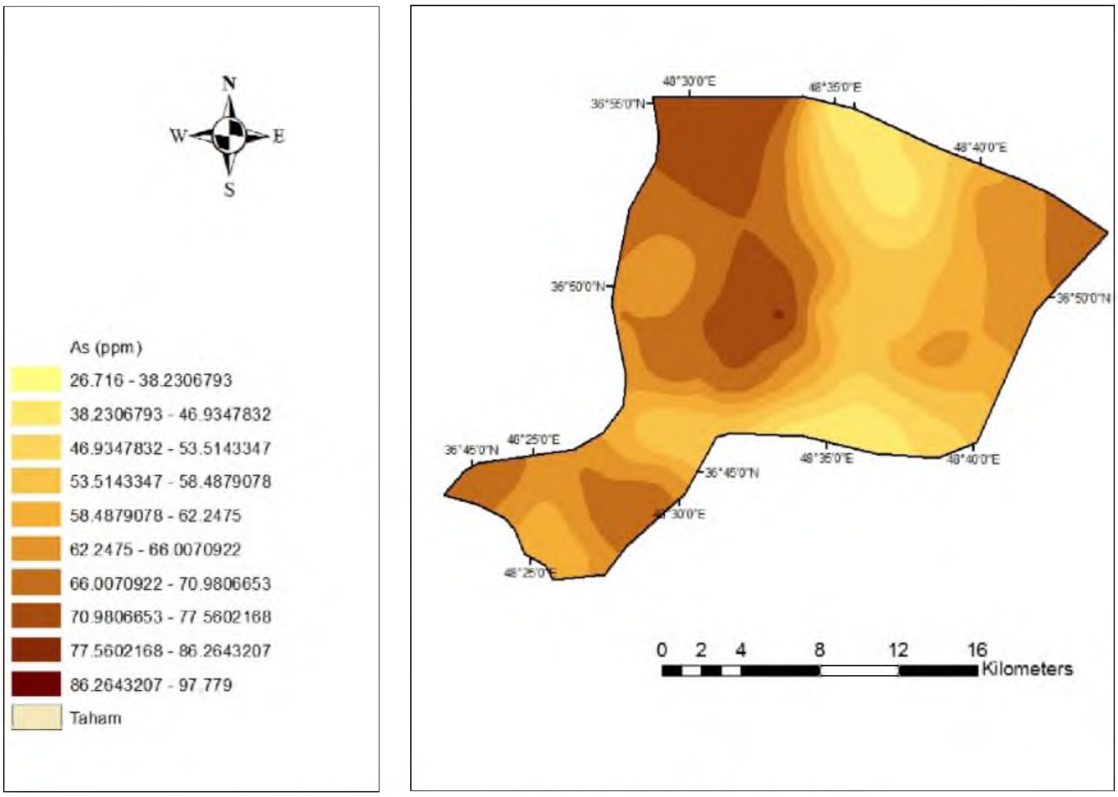

Figure 2a - Concentration & distribution of total Arsenic

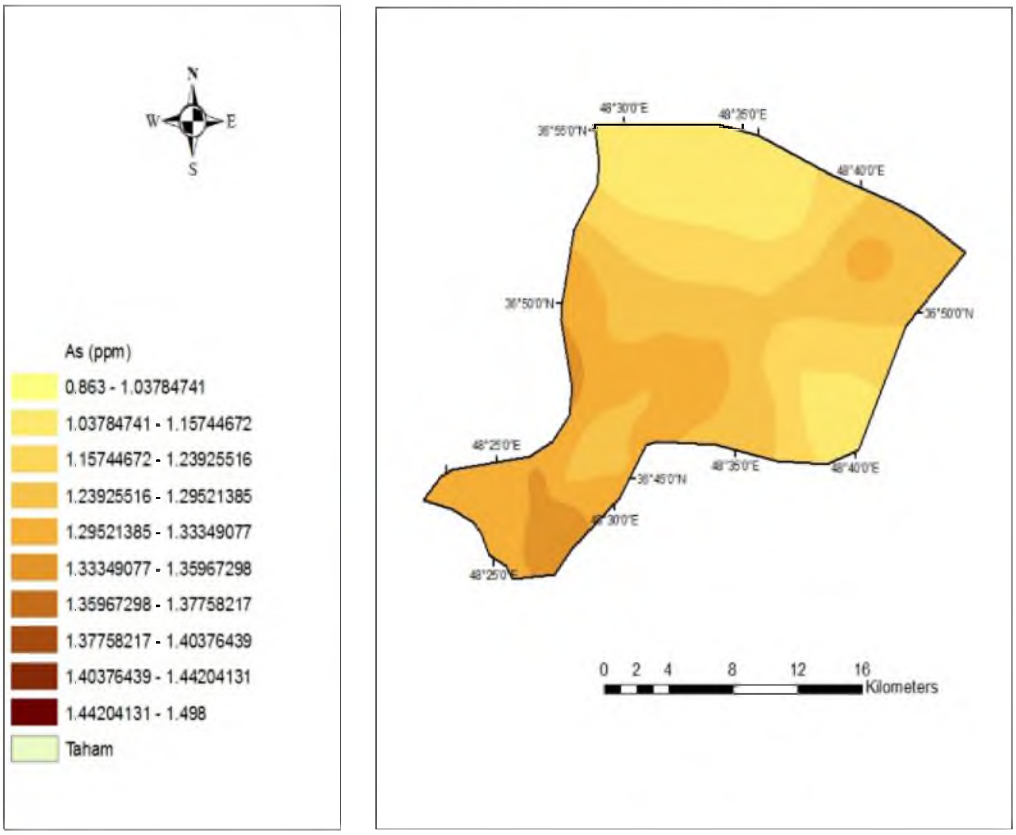

Figure 2b - Concentration & distribution of bioavailable Arsenic

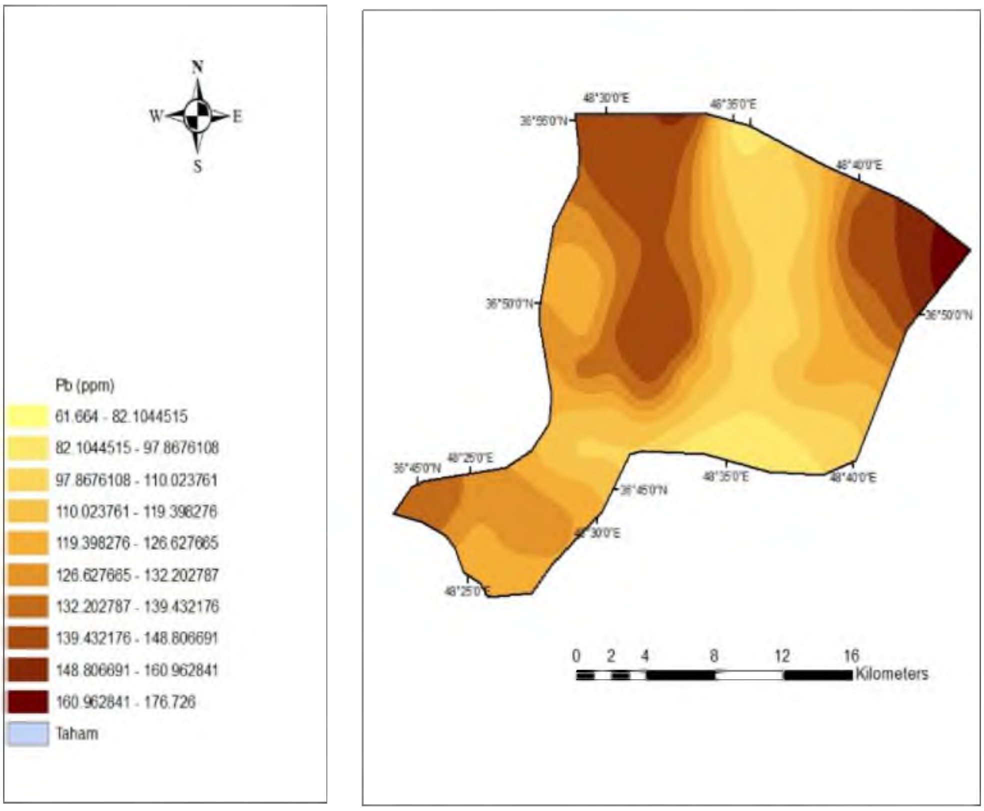

Figure 2c - Concentration & distribution of total lead

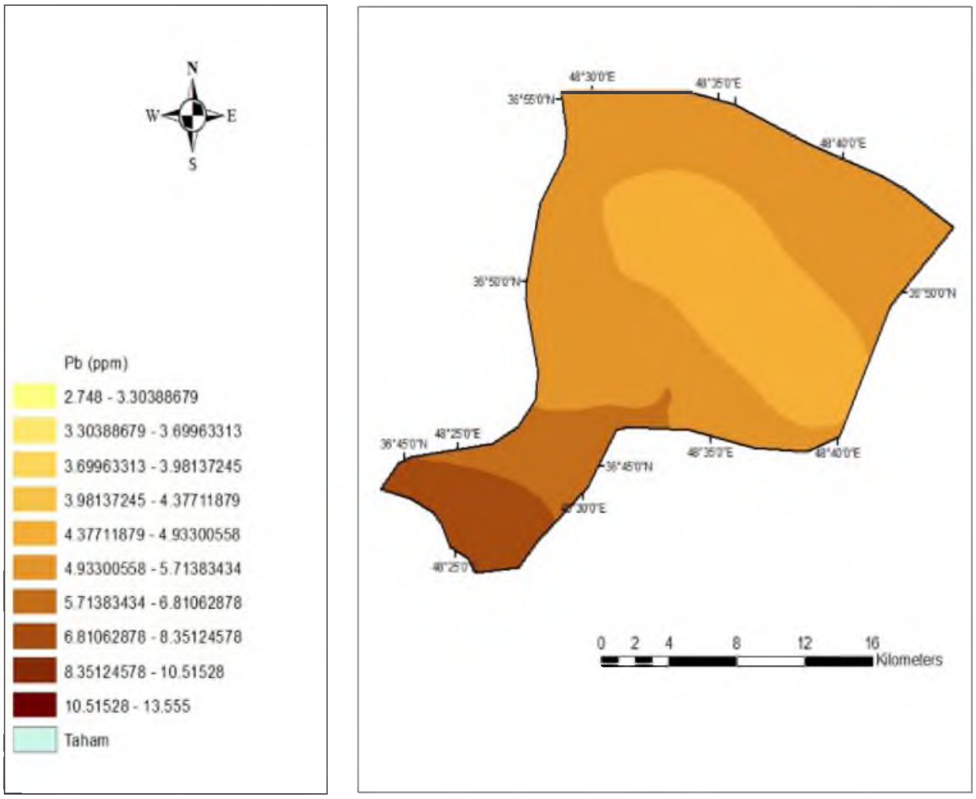

Figure 2d - Concentration & distribution of bioavailable lead

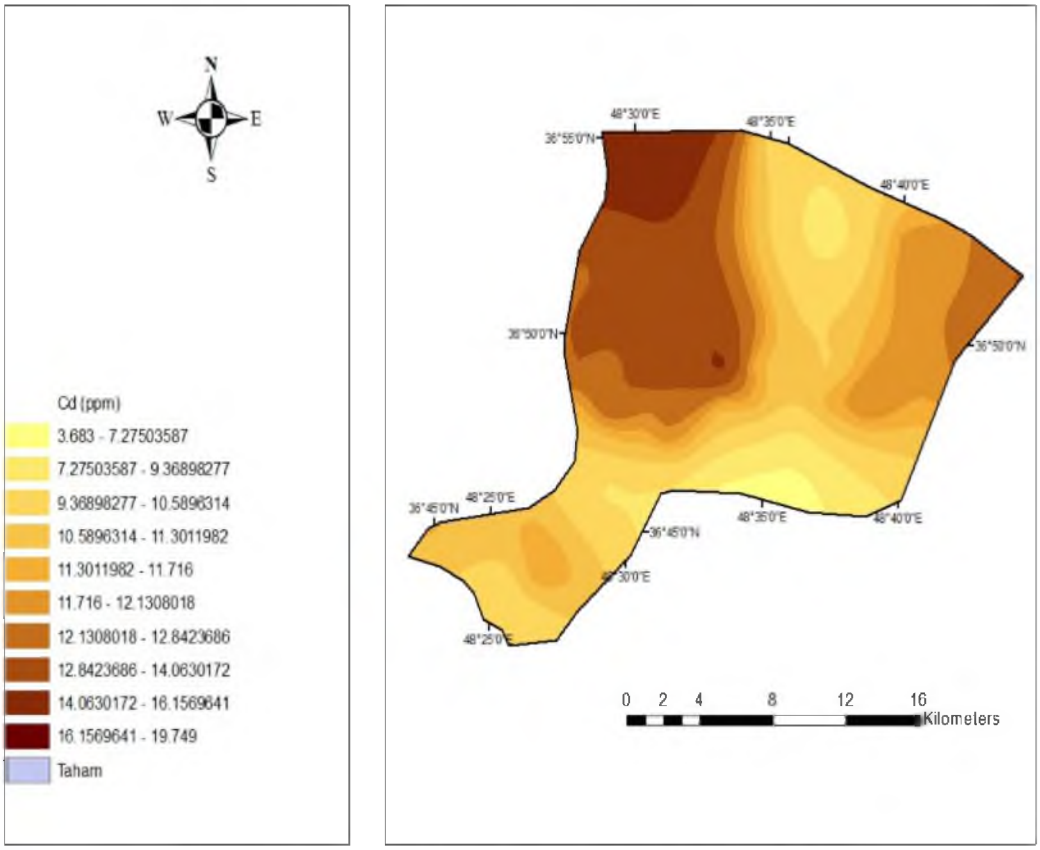

Figure 2e - Concentration & distribution of total Cadmium

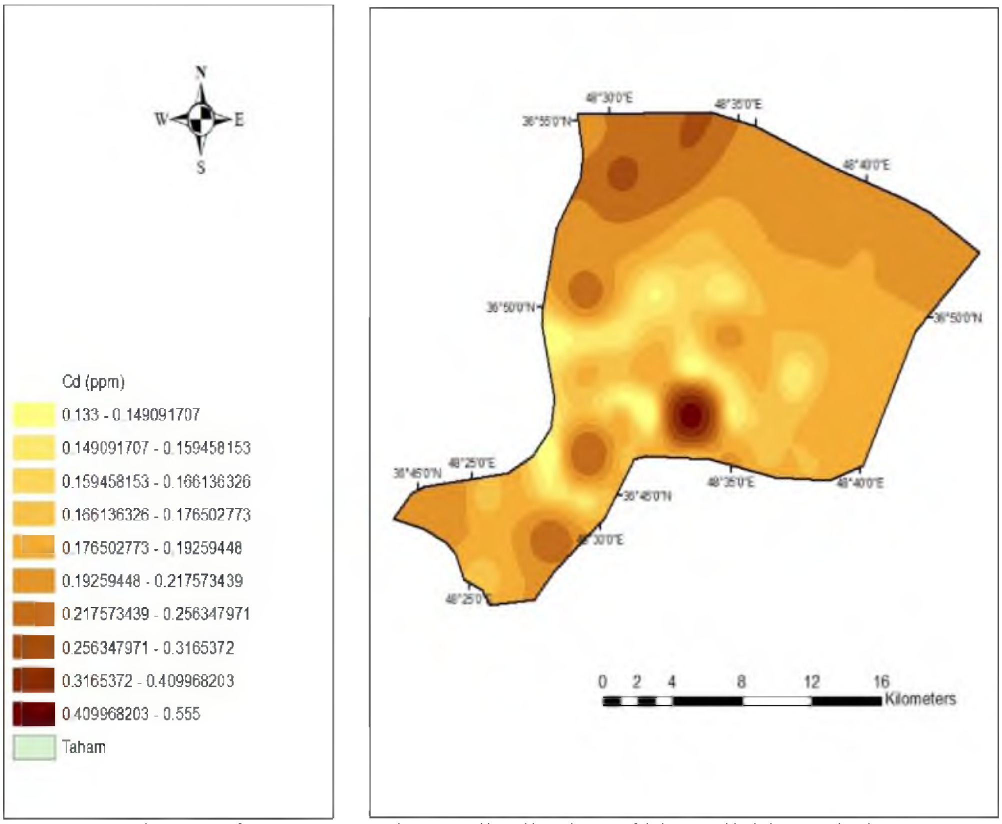

Figure 2 f - Concentration & distribution of bioavailable Cadmium

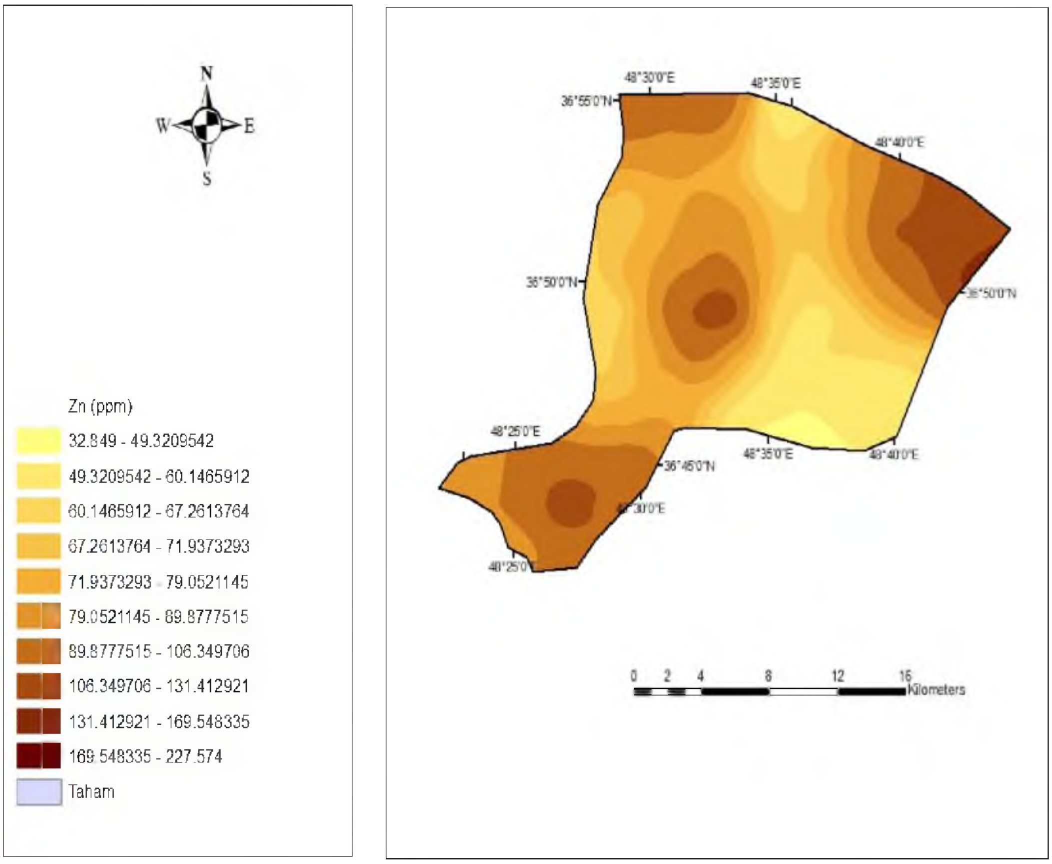

Figure 2g - Concentration & distribution of total zinc

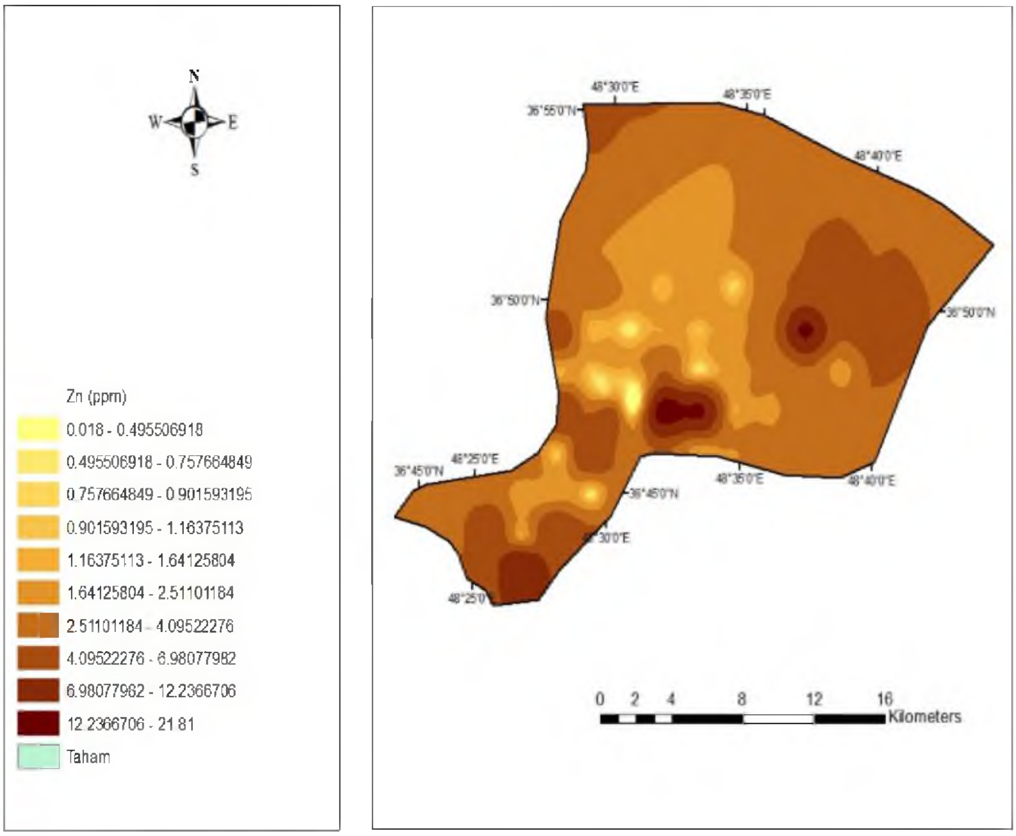

Figure 2h - Concentration & distribution of bioavailable zinc

Enrichment Factor (EF)

A common approach to estimate how much the sediment is impacted (naturally and anthropogenically) with heavy metal is to calculate the Enrichment Factor (EF) for metal concentrations above uncontaminated background levels (Huu, et al., 2010). Pollution will be measured as the amount or ratio of the sample metal enrichment above the concentration present in the reference station or material (Mediolla, et al., 2008; (Abrahim and Parker, 2008). The EF method normalizes the measured heavy metal content with respect to a sample reference such as Fe, Al or Zn (Mediolla, et al., 2008). The EF of a heavy metal in sediment can be calculated with the following formula (Huu, et al., 2010).

$$EF = \frac{C_{metal} / C_{normalizer}}{C_{metal\ control} / C_{normalizer\ control}}$$

Where Cmetal and Cnormalizer are the concentrations of heavy metal and normalizer in sediment and in unpolluted soil. Enrichment factor (EF) can be used to differentiate between the metals originating from anthropogenic activities and those from natural procedure, and to assess the degree of anthropogenic influence. Five contamination categories are recognized on the basis of the enrichment factor as follows: (Sutherland, 2000).

EF < 2 is deficiency to minimal enrichment

EF 2 – 5 is moderate enrichment,

EF 5 – 20 is significant enrichment,

EF 20 – 40 is very high enrichment,

EF > 40 is extremely high enrichment.

As the EF values increase, the contributions of the anthropogenic origins also show an increase (Abrahim and Parker, 2008). Based on the enrichment factors calculated for different studied heavy metals in the studied area (figures 3.a, 3.b, 3.c and 3.d), cadmium shows extremely high enrichment, Arsenic and lead show significant enrichment and zinc is moderately enriched in the district.

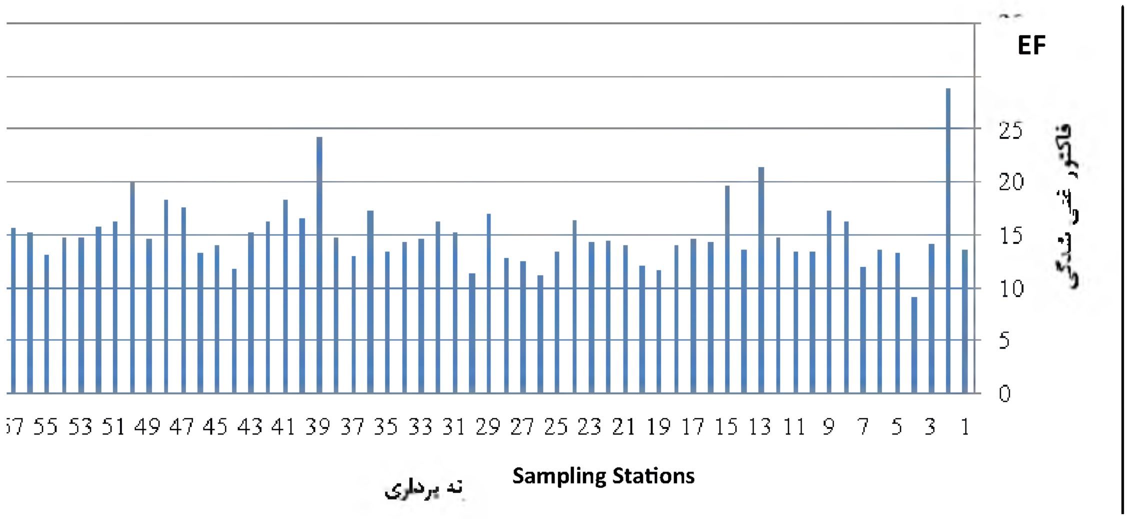

Figure 3a - Enrichment factor for As

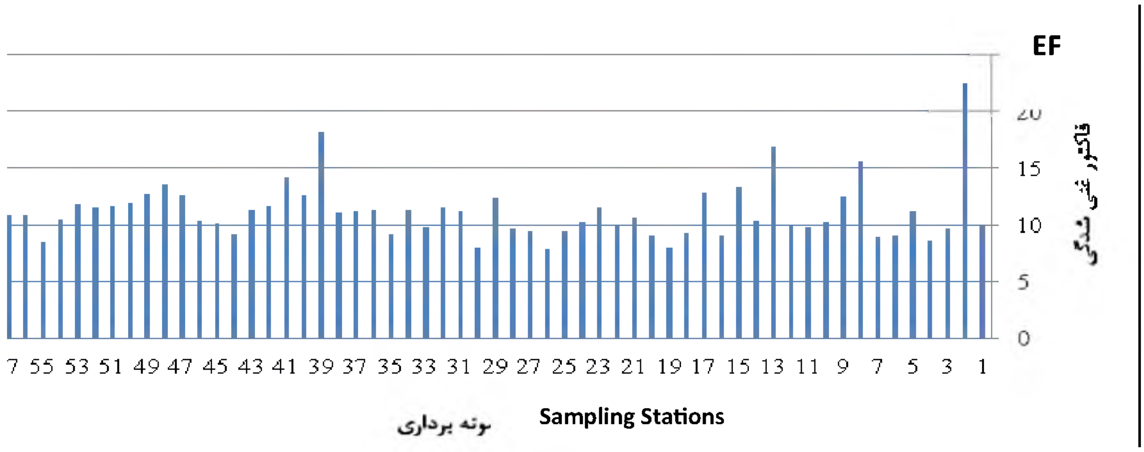

Figure 3b - Enrichment factor for Pb

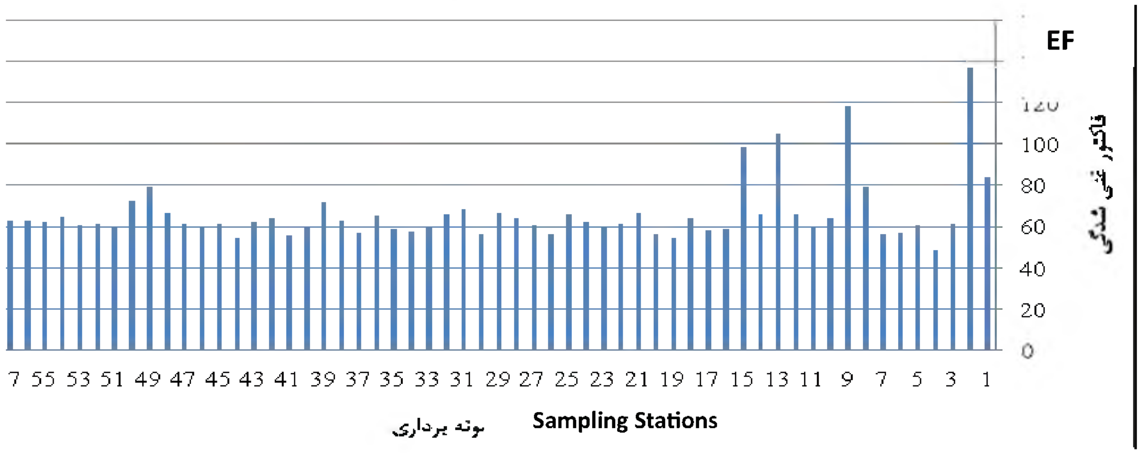

Figure 3c - Enrichment factor for Cd

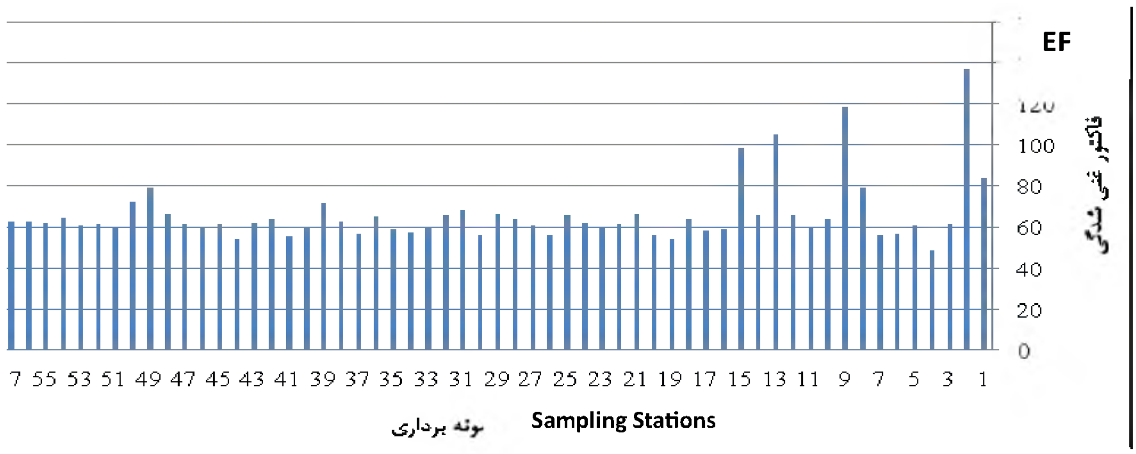

Figure 3d - Enrichment factor for Zn

Figure 3 - Enrichment Factor(EF) for heavy metals As (a), Pb (b), Cd (c), and Zn (d) in the study area

CONCLUSION

57 soil samples were analyzed to determine the concentration and distribution of heavy metals (Cd, Pb, As, and Zn) in top soil of Taham district in Zanjan-Iran. Determination of bioavailability of heavy metals in soil with DTPA method has been shown that by increasing total amount of heavy metals in soil, the bioavailable content of metals also show an increase. The dispersion maps provided for all studied heavy metals show that the highest concentrations of all metals almost coincide and are observed in northern and central parts of the district and their high concentrations are extremely related to natural pedo-geochemical background. While the highest total concentration of all studied metals are found in north and central parts of the district, the highest bioavailable content of the same metals are mostly observed in the southern parts of the studied area. This observation along with the degree of enrichment in southern parts further supports the anthropogenic nature of these elements in this part of the district.

REFERENCES

Abbasi, M., Mohammadi, H., Peyda, M., 2000. Heavy Metal Contamination of Surface-water and Groundwater of Vicinity Region of Zanjan Zinc and Lead Smelting Plant. Research report, Zanjan Department of the Environment.

Abrahams, P. W., 2002. Soils: their implications to human health. The Science of the Total Environment. Vol. 291, No. 1-3, pp. 1–32.

Abrahim, G. M. S., Parker, P. J., 2008. Assessment of heavy metal enrichment factors and the degree of contamination in marine sediment from Tamaki Estuary. Auckland, New Zealand. Environ. Monit. Assessment, Vol. 136, pp. 227-238.

Chehregani, A., Noori, M., Lari Yazdi, H., 2009. Phytoremediation of heavy-metal-polluted soils: Screening for new accumulator plants in Angouran mine (Iran) and evaluation of removal ability. Ecotoxicology and Environmental Safety, Vol. 72, No. 5, pp. 1349–1353.

Gaetke, L. M., Chow, K., 2003. Copper toxicity, oxidative stress, and antioxidant nutrients. Toxicology, Vol. 189, No. 2, pp.147-163.

Huu, H. H., Rudy, S., and An Van Damme. 2010. Distribution and contamination status of heavy metals in estuarine sediments near Cau Ong harbor. Ha Long Bay, Vietnam. Geology,

ISO 11466, 1995. Soil quality-Extraction of trace elements soluble in aqua regia. International standard, pp. 1–6.

Juvanovic, S., Carrot, F., Deschamps, N., Vukotic, P., 1995. A study of the air pollution in the surroundings of an aluminum smelter using Epiphytic and Lithophytic Lichens. Journal of Trace Microprobe Techniques, Vol. 13, pp. 463–471.

Kelepertsis, A., et al. 2001. The Environmental geochemistry of soils and waters of Susaki area, Korinthos, Greece, Environmental Geochemistry and Health, Vol. 23, pp. 117-135.

Li, J., Xie, Z. M., Zhu, Y. G., Naidu, R., 2005. Risk assessment of heavy metal contaminated soil in the vicinity of a lead/zinc mine. J. Environ. Sci. Vol. 6, pp. 881–885.

Lindsay, W. L., Norvell, W. A., 1978. Development of a DTPA soil test for zinc, iron, manganese, and copper. Soil Sci. Soc. Am. J. Vol. 42, pp. 421–428.

Mediolla, L. L., Domingues, M. C. D., Sandoval, M. R. G., 2008. Environmental Assessment of an Active Tailings Pile in the State of Mexico (Central Mexico). Research Journal of Environmental sciences, Vol. 2, No. 3, pp. 197 – 208.

Mohammadi, H., Eslami, A., 2007. Quantity and Quality of Special Wastes in Zanjan province. Research report, Zanjan Department of the Environment. pp. 2-3.

Parizanganeh, A. H., Bijnavand, V., Zamani, A. A., and Hajabolfath, A., 2012. Concentration, Distribution and Comparison of Total and Bioavailable Heavy Metals in Top Soils of Bonab District in Zanjan Province. Open Journal of Soil Science, 2, 7-16.

Sutherland, R. A., 2000. Bed sediment-associated trace metals in an urban stream. Oahu, Hawaii. Environmental Geology, Vol. 39, pp. 611 – 637.

Unterbrunner, R., Puschenreiter, M., Sommer, P., Wieshammer, G., Tlustoˇs, P., 2007. Heavy metal accumulation in trees growing on contaminated sites in Central Europe. Environmental Pollution. Vol. 148, No. 1, pp. 107–114.

Vega, F. A., Covelo, E. F., Andrade, M. L., Marcet, P., 2004. Relationships between heavy metals content and soil properties in mine soils. Analytica Chimica Acta., Vol. 524, No. 1-2, pp. 141–150.

Whitten, M. G., Ritchie, G. S. P., 1991. Calcium chloride extractable cadmium as an estimate of cadmium uptake by subterranean clover. Aust. J. soil Res. Vol. 29, pp. 215–221.

РЕЗЮМЕ

А. Паризанганех[1], Р. Сабериниа[1], А. Хаджаболфат[2], А.А. Замани[1]

КОНЦЕНТРАЦИЯ И ПРОСТРАНСТВЕННОЕ РАСПРЕДЕЛЕНИЕ ОБЩИХ И БИОДОСТУПНЫХ ТЯЖЕЛЫХ МЕТАЛЛОВ В ВЕРХНИХ СЛОЯХ ПОЧВЫ В ТАХАМСКОМ РАЙОНЕ, ЗАНДЖАНСКОЙ ПРОВИНЦИИ, ИРАН

[1]*Кафедра экологии, факультет естественных наук, Университет Занджан, Занджан-Иран, h_zanganeh@znu.ac.ir ,Тел : +982414269056*

[2]*Отделение геологии, Факультет наук, Университет Занджан, Занджан-Иран*

Токсичные элементы, такие как тяжелые металлы, являются естественными составляющими земной коры и некоторые из этих элементов являются биологически важными на уровне микроэлементов и играют важную роль в укреплении здоровья человека. Загрязнение почвы тяжелыми металлами является широко распространенной проблемой в Зенджанской провинции, которая находится на северо-западе Ирана. Вследствие естественного педогеохимического фона и антропогенных источников Тахамский район был выбран для детального изучения и были установлены задачи исследования по оценке общей, а также биодоступной фракции тяжелых металлов в поверхностных горизонтах почв. Было отобрано 57 образцов с поверхности почвы, которые были проанализированы на предмет загрязнения тяжелыми металлами при помощи атомно-абсорбционной спектрометрии (ААС). Полученные результаты, по сравнению со стандартами ВОЗ и EPA показывают очень высокую концентрацию некоторых токсичных металлов в частности, As, Pb и Cd. Биодоступную часть исследованных металлов также измеряли при помощи формации комплекса металлов с веществом Диэтилен Три Амин Пента Кислотой (DTPA). Чтобы определить долю антропогенных источников в загрязнении почв были измерены коэффициент обогащения (EF) и индекс геологического накопления, а также были созданы карты их распределения с помощью Arc GIS 9.3. Высокие концентрации некоторых токсичных металлов, таких как As, Pb и Cd были найдены в изолированных пятнах на северо-западе, востоке и юго-западе изучаемой территории, происхождение которых связано с почвообразующими и антропогенными источниками. Загрязнение почвы металлами было очень высоким вокруг промышленного города и сельскохозяйственных угодий в пределах изучаемой территории. Наиболее эффективные факторы, вызывающие высокую концентрацию других элементов, таких как Cu, Co, Ni и Fe в почве имели почвообразующую природу.

Ключевые слова: тяжелые металлы, коэффициент обогащения, геологический индекс накопления, Тахамский район, Занджан-Иран.

ТҮЙІН

А. Паризанганех[1], Р. Сабериниа[1], А. Хаджаболфат[2], А.А. Замани[1]

ТАХАМ АУДАНЫ, ЗАНЖАН ПРОВИНЦИЯСЫНЫҢ БЕТКІ ТОПЫРАҚ ҚАБАТЫНДАҒЫ ЖАЛПЫ ЖӘНЕ БИОАШЫҚ АУЫР МЕТАЛДАРДЫҢ ШОҒЫРЛАНУЫ ЖӘНЕ КЕҢІСТІКТЕ ТАРАЛУЫ, ИРАН

[1]Экология кафедрасы, табиғи ғылымдар факультеті, Занжан университеті, Занжан-Иран, h_zanganeh@znu.ac.ir , Тел : +982414269056

[2]Геология бөлімі, Ғылымдар факультеті, Занжан университеті, Занжан-Иран

Ауыр металдар сияқты уытты элементтер жер қыртысының табиғи құрамдас бөлігі болып табылады және осы элементтердің кейбіреуінің микроэлементтер деңгейінде биологиялық маңызы болуымен қатар, адам денсаулығын нығайтуда маңызды рөл атқарады. Топырақтың табиғи педогеохимиялық фон мен антропогендік көздер салдарынан ауыр металдармен ластануы Иранның солтүстік-батысында орналасқан Занжан провинциясындағы кеңінен таралған проблема болып табылады. Тахам ауданы егжей-тегжейлі зерттеу үшін таңдап алынды, зерттелетін аумақ шеңберінде топырақтың беткі қабатындағы ауыр металдардың ортақ, сондай-ақ биоашық түйірлерін бағалау бойынша зерттеу міндеттері белгіленді. Топырақтың беткі қабатынан 57 үлгі алынып, атомдық-сіңірілу спектрометрия (ААС) көмегімен ауыр металдармен қаншалықты ластанғаны сараланды. Алынған нәтижелер, Дүниежүзілік денсаулық сақтау ұйымы мен Қоршаған ортаны қорғау агенттігінің стандарттарымен салыстырғанда As, Pb және Cd секілді кейбір уытты металдар құрамының мөлшерден тыс екенін көрсетеді. Зерттелген металдардың биоашық бөлігі Диэтилен Три Амин Пента Қышқылы (DTPA) затымен металдар кешенін құру көмегімен де өлшенді. Топырақтың ластануындағы антропогендік көздер үлесін айқындау үшін Байыту коэффициенті және геологиялық түзілу индексі өлшеніп, ArcGIS (9.3) көмегімен бөлу картасы құрылды. As, Pb және Cd секілді кейбір уытты металдардың көптеп шоғырлануы солтүстік-батыс, шығыс және оңтүстік-шығыстағы зерттелетін аумақтан топырақ құрушы және антропогендік көздердің әсерінен болатын оқшауланған жерлерден табылды. Зерттелетін аумақтағы ауыл шаруашылық жерлер мен өндірістік қала төңірегіндегі топырақтың ластану деңгейі өте жоғары болды. Cu, Co, Ni және Fe секілді басқа элементтердің жоғары шоғырлануын тудыратын барынша тиімді факторлар топырақ түзгіш сипатта болды.

Кілтті сөздер: ауыр металдар, байыту коэффициенті, Геологиялық түзілу индексі, Тахам ауданы, Занжан-Иран.