ABSTRACT: Presence of toxic metals in agricultural soils can impose adverse health impact on consumers. The main purpose of this study was to determine spatial distribution of elements Fe, Sb, Mn in agriculture soils and crops of Hamedan Province in Iran. Soil samples (0-20 cm depth) were collected from an area of 2831 km². Iron, Antimony and Manganese in samples of soil and agricultural crops were extracted and their amount was determined using atomic absorption spectrometer. The spatial distribution map of the studied elements was developed using Kriging method. The main concentration of Fe, Sb and Mn in the soil of the study area is about 3.8%, 2.5 and 403 mg/kg, respectively. According to chemical partitioning studies, the anthropogenic share of Fe, Sb and Mn is about 28.51%, 34.83% and 30.35%, respectively. Results of comparison of heavy metals pollution intensity in the agricultural soil with geo-accumulation index and also pollution index, illustrated that iron and manganese are classified in the Non-polluted class and antimony is in the moderately polluted class. Analysis of zoning map of pollution index showed that Fe, Sb and Mn are of geological sources. In fact, these metals are naturally found in soil. However, anthropogenic activities have led to more accumulation of these metals in the soil. The obtained health risk for metals in agricultural crops is indicative of safe value for consumers.

KEYWORDS: Agricultural yields; Health index ratio (HRI); Heavy metals; Soil; Zoning

INTRODUCTION

The levels of toxic metals is increasing in the agricultural soils due to over utilization of various chemicals for better yields. The pollutants can include metals, organic wastes and other organic and inorganic substances (Shetty and Rajkumar, 2009). The term “heavy metals” is very general but generally refers to any metallic element that has a relatively high density and is toxic even at low concentrations (Uba et al., 2009). Due to the adverse health impacts of metals, intensive research has been carried out to determine heavy metals in foods and other common food contaminants. The adverse health effects of heavy metals could mainly be due to their interference with normal body biochemistry through various metabolic processes (Okunola et al., 2011). Some of the heavy metals are extremely persistent in the environment (Taghinia Hejabi et al., 2011). They are not easily biodegradable and thus their accumulation reaches to critical levels (Khan et al., 2009). Metals have a high degree of toxicity that can be dangerous for both the human and the environment (Singanan et al., 2008). The soil pollution by heavy metals has received ample attention in the recent decades (Rafiei et al., 2010). Since soil is a thin part of the earth surface system that comes into direct contact with man (Kargar et al., 2012), therefore, it can transfer pollutants to food chain and
on the other hand it can be polluted by man’s activities. For instance, soil properties and quality can be adversely affected by the agricultural and industrial activities (Nasrabadi et al., 2010). Thus it is vital to preserve soil conditions for sustainable development (Ghaderi et al., 2012). For these reasons, more attention has been paid to the geochemistry of soil and also the intensity of pollutants (Soffianian et al., 2014; Karbassi et al., 2008). Since metals contents of soil can find their way into the agricultural crops, more awareness is built up in societies in connection health agricultural products (Akoto et al., 2008). Wastewater irrigation, solid waste disposal, sludge applications, vehicular exhaust and industrial activities are the major sources of metals in soil and an increased metal uptake by food crops grown on such contaminated soils is often observed (Nasrabadi et al., 2011). In general, farmers prefer to use wastewater for their beneficial nutrients and they ignore the presence of toxic metals (Chen et al., 2005; Singh et al., 2004). Although low concentrations of these metals are naturally found in soils, human activities have elevated their concentrations (Karbassi et al., 2015). Thus it is very important to assess soil pollution and take the necessary remediation measures (Romic et al., 2007). Mining, industries, road traffic, waste disposal, and agricultural use of fertilizers and chemicals are amongst human activities that can lead to heavy metal contamination of the soil (Karbassi et al., 2016). On the other hand, main natural factors contributing to metal contamination of the soil include volcanoes, fires in forests, and chemical composition of parent materials (Lado et al., 2008). Heavy metal accumulation in soils and plants is of increasing concern because of the potential human health risks (Karbassi et al., 2011). Heavy metal accumulation in plants depends on many factors that has brought out the subject of transfer factors of the metals (Rattan et al., 2005). The transfer factors of metals from soil to plant vary from soil to soil (Karbassi, 1998). The texture of soil, organic content of soil and also type of plant are among the main factors for transfer of metals from soil to plants (Kabata-Pendias and Pendias, 1984). As a general role, there should be a balance amongst uptake of various materials by plants to ensure health products for consumers as well as for the plants (Iyengar and Nair, 2000; Turkdogan et al., 2003). Thus, it will be wise to determine the elemental contents of soil before beginning new crop production. Thus, it is essential to set up a guideline to balance amongst heavy metals transfer in soil, the accumulation in vegetables and the health of consumers. Thus, it will be useful to assess health risk of metals in many ways (Raj Shakya and Malla Khwaounjoo, 2013). There are several studies in different countries for interpolation and determination of spatial distribution of heavy metals concentrations in soil (Biati et al., 2010; Karbassi et al., 2014). Lado et al. (2008) carried out modeling the distribution of eight critical metals (As, Cd, Cr, Cu, Hg, Ni and Zn) in European topsoil. They used regression-Kriging method and accuracy of predictions was evaluated by cross validation method. Spatial distribution of Cr, As, Cu, Pb, Cd and Hg in Changxing of Zhejiang Province in China was investigated by geo-statistics and log normal Kriging and ordinary Kriging for mapping (Juang et al., 2001). Juang et al. (2001) and Rodríguez et al. (2009) applied geo-statistics in their studies in order to prepare distribution map of heavy metals. Preparation of map to show the spatial distribution of metal contents in soils can help decision makers to select suitable areas for various land use. Hence, due to importance of Hamedan City as one of the main centers of agricultural activities in Iran, it is of utmost importance to determine the pollution of topsoil and agricultural crops of this area. Thus in the present investigation has tried to bring out the sources of Fe, Mn and Sb in agricultural soils of Hamedan. Subsequently the transfer factor of metals from soil to crops was determined. Finally the health risk of metals as a result of consumption of various agricultural products was computed. This study has been performed in Hamadan Province located in west of Iran in 2014.

MATERIALS AND METHODS

Hamadan Province occupies an area of 2831 km² (34° 35’ 34” N, 20° 49’13” E). Samples were taken from depth of 0-20 cm in accordance with systematic method. A total of 58 compound samples of topsoil and crops of wheat, barley, corn, alfalfa and potatoes were collected. Sampling was conducted in late September after harvest. Fig. 1 shows the location map of the study area and sampling points.

Soil samples were transferred to the laboratory for testing and measuring soil physical and chemical properties and were passed through 63-micron sieve. Phosphorus was measured by Olsen P extracting solution (0.5 M NaHCO3, pH 8.5); total nitrogen by
Kjeldahl digestion; pH was analyzed by glass electrode using a 1:1 soil: water ratio; and EC and salinity was measured by conductivity meter in a soil-water extract (1:2 soil: water ratio) (USDA, 2004; ASTM, 2000; Dewis and Freitas., 1984). For measuring soil-lime titration method was used (Gee and Bauder, 1986). Sodium and potassium were measured by a flame detector (AOAC, 2005). Soil texture was done in accordance with Gee and Bauder (1986). Total C were measured as described by Allison (1965) and Supaphol et al., (2006). Cation exchange capacity was measured according to standard methods (APHA, 2005; Aparna et al., 2010). Total organic carbon is an alternative analytical method for measuring hydrocarbons using the wet oxidation technique as previously reported by Nelson and Sommers (1975). Measurement of calcium and magnesium of soil was carried out by EDTA solution using complex metric (titrations) (AOAC, 2005; Gee and Bauder, 1986).

For digestion of soil samples, at first they were air dried and passed through a 63-micron sieve. Then 2g of soil was poured into a capped container and 15 mL of 4N nitric acid was added. Then the flasks were left for 12 h in a hot water bath at 80°C. Subsequently, the samples were filtered and concentrations of heavy metals were measured by atomic absorption spectrometer (Varian AA-400 model; available in laboratory of Environment Protection Organization of Hamedan Province). The reagents used include distilled water, 0.01M calcium chloride, 0.05M diethylene tri-amino penta-acetic acid (DTPA) (Black, 1965). The dry ash extraction method was used for digestion of plant samples (Shaw, 1989). Then concentration of iron, manganese and antimony of plant samples in the considered extraction was determined by atomic absorption spectrometer. The instrument was calibrated with diluted solution prepared from a known stock solution of each element. The accuracy and precision of the overall procedure have been determined and are estimated to be around 5% for most elements. The quality assurance of the analytical results was controlled with the use of certified reference marine organism IAEA-407 provided by International Atomic Energy Agency (Mzoughi and Chouba, 2012). Soil to plant metal transfer was computed as translocation factor (TF), which was calculated by using the equation TF = CPlant/CSoil where, CPlant is the concentration of heavy metals in plants and soil is the concentration of heavy metals in soil (Mahmood and Malik, 2014). Daily intake of vegetables in adult was calculated by data obtained during the survey though a questionnaire. DIM was calculated by the following equation: DIM = Cmetal × Cfactor × Dfood intake / Baverage weight (Chary et al., 2008).

Where Cmetal, Cfactor, Dfood intake and Baverage weight represent the heavy metal concentrations in plants (mg/kg), conversion factor: 0.085 (Chary et al., 2008), daily intake of vegetables and average body weight, respectively. In the present research work vegetables grown at the soils were collected from the study area and their metal concentration was used to calculate the health risk index (HRI). Value of HRI depends upon the daily intake of metals (DIM) and oral reference dose (RfD). RfD is an estimated per day exposure of metal to the human body that has no hazardous effect during life time (US-EPA IRIS, 2006). The health risk index for Sb, Mn and Fe by consumption...
of contaminated vegetables was calculated by following equation:

$$HRI = \frac{\text{DIM}}{\text{RfD}}$$  \hspace{1cm} (Akoto et al., 2014). \hspace{1cm} (1)

Where DIM represents the daily intake of metals and RfD represents reference oral dose. RfD value for Sb, Mn and Fe is 0.0004, 0.14 and 7000 (mg/kg bw/day) respectively (WHO, 1993; EPA, 2007). To quantify the degree of heavy metal pollution in soil, Igeo was calculated according to Muller and is given in Eq. 1 (Praveena et al., 2008). The results were interpreted using Igeo classes given in Table 1.

$$I_{geo} = \log_{2}\left(\frac{C_{n}}{1.5B_{n}}\right)$$  \hspace{1cm} (2)

Where $C_{n}$ is the concentration of the examined metal in the soil, $B_{n}$ is the geochemical background value of a given metal in the soil (Turekian and Wedepohl, 1961) and the factor 1.5 is used to account the possible variations in the background values.

To assess the intensity of metal contamination in Hamedan soils, the pollution index (Karbassi et al., 2008) was calculated using:

$$I_{p} = \log_{2}\left(\frac{C_{n}}{F_{n}}\right)$$  \hspace{1cm} (3)

Where, $C_{n}$ is the total elemental content in soils and $B_{n}$ is geochemical background of element.

Chemical fractionation method suggests that heavy metals form five bonds with soil and sediments including loosely bond, sulfide bond, organometallic bond, most resistant bond and within lattice bond among which loosely bond, sulfide bond and organometallic bond indicate anthropogenic elements of the environment and the other two bonds, namely, most resistant bond and within lattice bond indicate natural part of heavy metals in soil (Spencer and Macleod, 2002; Karbassi, Shankar, 2005). Five-stage chemical fractionation method was applied in this study in order to specify the anthropogenic part of heavy metals and the natural part of heavy metals. To understand the relationship amongst various metals and environmental indicators, Multi Variable Statistical Program (MVSP) was used. This analytical software is frequently used by various researchers (Karbassi et al., 2004 and 2008). Highest similarities are clustered/linked first. Two variables are connected only if they are highly correlated. After two variables are clustered, their correlations with all the other variables are averaged. The results of clustering are displayed in the form of a Dendrogram (Karbassi et al., 2007). Kriging interpolation method was applied in Arc GIS 9.3 software to show changes in concentration distribution of the investigated heavy metals (Johnston et al., 2001).

**RESULTS AND DISCUSSION**

Investigation of physicochemical parameters of soil showed that the parameters of electrical conductivity (EC), sodium, calcium carbonate (CaCO$_3$) and salinity have coefficients of variation above 50% which indicates the large variations of concentration of these variables in soil of Hamedan City. The rest of soil physicochemical parameters have coefficients of variation less than 50% which indicates its low variation in soil of Hamedan City. The average acidity of soil is 7.72 which indicates the soil of the study area is of alkaline nature. The dominant soil texture in the area is silty clay loam soil in accordance with USDA soil taxonomy. A summary of statistical status of some physicochemical properties of the soil of study area is presented in Table 2.

The results of Kolmogorov-Smirnov test showed that all data of soil and harvested crops are normal. A summary of statistical status of concentration of heavy metals in samples is presented in Table 3. The average concentration of heavy metals in soil of Hamedan City is as follows: iron (3.77 %), manganese (403.38 mg/kg) and antimony (2.44 mg/kg). It was concluded that among the investigated metals, concentration of manganese in soil is above the standard level. Table 4 compares concentrations of iron and antimony in the soil of study area with mean concentrations of Europe and the mean concentration of the world is soil. As it is seen, mean concentrations of iron and antimony in this study are more than those of Europe but mean concentration of iron is lower than that of the world.

<table>
<thead>
<tr>
<th>Igeo</th>
<th>Igeo class</th>
<th>Soil quality</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-0</td>
<td>0</td>
<td>Unpolluted</td>
</tr>
<tr>
<td>0-1</td>
<td>1</td>
<td>Unpolluted to moderately polluted</td>
</tr>
<tr>
<td>1-2</td>
<td>2</td>
<td>Moderately polluted</td>
</tr>
<tr>
<td>2-3</td>
<td>3</td>
<td>Moderately to highly polluted</td>
</tr>
<tr>
<td>3-4</td>
<td>4</td>
<td>Highly polluted</td>
</tr>
<tr>
<td>4-5</td>
<td>5</td>
<td>Highly to very highly polluted</td>
</tr>
<tr>
<td>5-6</td>
<td>&gt;5</td>
<td>Very highly polluted</td>
</tr>
</tbody>
</table>
and finally mean concentration of antimony is higher than that of the world. In this study, concentration of iron is much lower than the amount reported by in Jordan (5370.6 mg/kg), Malaysia (1790 mg/kg), England (2600 mg/kg), Spain (19300 mg/kg), and Canada (25660 mg/kg). The average concentration of iron in Earth’s crust is 41000 mg/kg (Rasmussen et al., 2001; De Miguel et al., 1997; Ramlan and Badri, 1989; Jiries, 2003; Schwar et al., 1988; Karbassi et al., 2005; Niencheski, 2002). also concentration of manganese in this study was more than reported by Jordan (144.6 mg/kg), Malaysia (153 mg/kg), Spain (362 mg/kg). Table 5 shows average concentration of iron, manganese and antimony in agricultural crops harvested in Hamedan City. International levels of iron, manganese and antimony in the agricultural crops are 5, 6.61 and 0.003 mg/kg, respectively (FAO/WHO, 2011; McGrath et al., 1997; Lone et al., 2008). In this study, concentration of manganese (in all crops) is higher than the standard level. According to the studies carried out by Tsafe et al. (2012) in Nigeria, concentration of iron and manganese in soil are 0.0142% and 195.25 mg/
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Table 6: Transfer factor (TF) of heavy metals in agriculture crops grown at Hamedan City

<table>
<thead>
<tr>
<th>Factor</th>
<th>Range</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Mean</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>644.00</td>
<td>124.00</td>
<td>768.00</td>
<td>403.3793</td>
<td>167.05696</td>
</tr>
<tr>
<td>Fe</td>
<td>2.80</td>
<td>2.20</td>
<td>5.00</td>
<td>3.7690</td>
<td>0.63057</td>
</tr>
<tr>
<td>Sb</td>
<td>4.50</td>
<td>1.00</td>
<td>5.50</td>
<td>2.4397</td>
<td>0.86814</td>
</tr>
</tbody>
</table>

Table 7: DIM and HRI of heavy metals in adults and children

<table>
<thead>
<tr>
<th>Heavy metal</th>
<th>Heavy metals in crops</th>
<th>DIM in adults</th>
<th>DIM in children</th>
<th>HRI in adults</th>
<th>HRI in children</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>43.834</td>
<td>0.023</td>
<td>0.0264</td>
<td>0.164</td>
<td>0.189</td>
</tr>
<tr>
<td>Fe</td>
<td>0.37</td>
<td>1.94×10^{-4}</td>
<td>2.23×10^{-4}</td>
<td>2.77×10^{-4}</td>
<td>3.18×10^{-4}</td>
</tr>
<tr>
<td>Sb</td>
<td>0.0275</td>
<td>1.44×10^{-5}</td>
<td>2.46×10^{-5}</td>
<td>0.036</td>
<td>0.0617</td>
</tr>
</tbody>
</table>

Table 8: Muller’s geochemical index, Karbassi modified geochemical accumulation index and contamination factor of studied soils (Karbassi et al., 2008)

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Background concentration of heavy metal</th>
<th>I_{poll}</th>
<th>I_{geo}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>850</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Fe</td>
<td>3800</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sb</td>
<td>0.6</td>
<td>2.025</td>
<td>1.439</td>
</tr>
</tbody>
</table>

Fig. 2: Cluster analysis amongst heavy metals and physico-chemical parameters in Hamedan soil

kg, respectively and the said concentrations in vegetables are 0.0044% and 54.05 mg/kg, respectively (Tsae et al., 2012). Concentrations of iron and manganese in vegetables might be very negligible (Anthony et al., 2007; Zhuang et al., 2009).

The ability of a metal species to migrate from the soil in to the plant parts is called as transfer factor (TF). Table 6 shows the transfer factor from soil to agricultural crops in Hamedan region. According to the studies carried out by Mahmood and Malik (2014), the transfer factor for manganese is less than the standard level. That is in accordance with the result of present study. The degree of toxicity of heavy metals to human being depends upon their daily intake (Anita et al., 2010). The population will pose no risk, if the ratio is less than 1 and if the ratio is equal or greater than 1 then population will experience health risk (Sajjad et al., 2009). Table 7, presents the daily intake and health risk of the studied metals in children and adults in Hamedan region. Given the daily intake of metals from agricultural products as well as considering the fact that health risk index is less than 1 for all metals, hence it will be safe for children and adults to consume the agricultural products. In a study performed by Mahmood and Malik (2014), HRI was found to be maximum for Spinacia oleracea (2.42 mg/kg) and Brassica campestris (1.22 mg/kg).

Intensity of soil pollution with heavy metals using
two indices of Muller’s geo-chemical index ($I_{geo}$) and Karbassi’s modified geochemical accumulation index ($I_{poll}$) is presented in Table 8. Results of comparison of heavy metals pollution in agricultural soil with Muller’s index and Karbassi’s modified index showed that iron and manganese fall within “no pollution- class” and antimony is classified as moderately polluted.

Fig. 2 shows the relationship amongst studied parameter. It should be pointed out that correlation coefficients obtained on the basis of Pearson formulae are used in cluster analysis. Hence, the similar parameters are linked together. The confidence level is set as 0.05 and Student’s Test is indicative of meaningful values over 0.45. These is not any meaningful relationship amongst parameters within Hamedan soil. This could be probably be due to human influence on soil chemistry by using various compost and fertilizers. There is only a rather acceptable relationship between
Fe and Sb that is indicative of the similar behavior in soil.

Table 9, shows the chemical fractionation of heavy metals in soil of Hamedan City. The results show that the highest concentrations of iron, manganese and antimony in the soil are related to the most resistant bonds and the lowest one is related to within lattice bonds. Fig. 3 shows the natural source and anthropogenic source of iron, manganese and antimony in soil. According to these curves, concentrations of all three metals are mostly affected by the parent materials.

In this study, Kriging method is applied on the studied elements to find out their spatial distribution (Figs. 4 to 6). According to the results, it was found that the highest concentration of iron in the soil of study area (4.25 %) is detected in the north, southwest and partly in the west of Hamedan City (Fig. 4). By overlaying various maps such as zone, geological and land use of the study area, it was found that this part of Hamedan City has agricultural and pastures use and its bed rock is composed of igneous rocks, shale rocks, sandstone and sedimentary rocks. In fact, it might be concluded that the iron in soil of Hamedan City is mostly of geological source. Anthropogenic sources of iron in soil include industrial activities such as steel industries, dust and wastes of iron mines, iron sulfate used in herbicides and chemical fertilizers (De Ves et al., 2005).
for use of herbicides and chemical fertilizers, these mentioned industries do not exist in the study area. Mico et al. (2006) applied multi-factor analysis in assessment of heavy metals sources in agricultural soils and concluded that iron concentration is controlled by the bed rock.

The highest concentration of manganese (about 457 mg/kg) in the soil of the study area is detected in the west of Hamedan City (Fig. 5). By overlaying the resulted zoning and geological and land use maps of the study area, it was found that this part of Hamedan City has mainly agricultural use and its bedrock is composed of igneous and metamorphic rocks. In fact, it may be said that manganese in soil of Hamedan City is mainly of geological source, however anthropogenic activities related to use of fertilizers and sewage in the agricultural lands may have led to increased amount of this heavy metal in the soil.

The highest concentration of antimony (about 3.2 mg/kg) in the soil of study area is detected in the southwest of Hamedan City (Fig. 6). By overlaying the zoning, geological and land use maps of the study area, it was found that the areas with high Sb concentrations coincide with cultivation pattern of the area. Its bedrock is composed of igneous, sandstone and shale rocks. In fact, it may be said that the antimony found in soil of Hamedan City is mainly of geological source, however anthropogenic activities related to use of fertilizers and sewage in the agricultural lands may have led to increased amount of this heavy metal in the soil.

The most important findings of visual adaptation of spatial distribution maps of heavy metals and land use and geological maps of the area suggests that the main cause of high concentration of iron, antimony and manganese in the study area is the parent material of soil. However, the possible increase in concentration of these elements in agricultural land is not far from expectation due to presence of heavy metals in chemical fertilizers, pesticides and sewage. Therefore, given the hazards of heavy metals intake especially in the existing agricultural lands, it is recommended to prevent further distribution of heavy metals by managing the use of chemical fertilizers and pesticides and non-utilization of sewage for irrigation of lands as well as to avoid cultivation of plants possessing high potential of heavy metals intake in the polluted areas.

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CONFLICT OF INTEREST
The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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