Heavy Metals Contamination in Soil, Surface Water and Groundwater of an Agricultural Area Adjacent to Tehran oil Refinery, Iran

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ABSTRACT: Concentrations of six heavy metals including Cr, Mn, Ni, Pb, V and Zn were determined in top soil (from 47 grid cells), surface water (4 streams) and groundwater (8 wells and 4 qanats) from an agricultural area located at south part of the Iranian capital, near the Tehran oil refinery. Concentrations of the elements were measured using flame and flameless atomic absorption spectrometry. Based on the results of agglomerative hierarchical method for clustering of the soil grid cells, some similarities between the dendrograms of Mn and Ni, Pb and V, and Zn and Cr were observed. The pattern of metal occurrence exhibited the following descending order: Mn> Zn > Cr > V > Ni > Pb for soil, Pb, Ni, Mn > Zn, V, Cr for wells and Ni, Pb > Cr, V > Mn, Zn for streams. Significant positive correlations were found among Zn, Cr and Ni as well as between Mn and Zn, Ni and V, and Pb and Zn in soil. Significant positive associations were also observed in the case of Mn-Ni and Mn-Cr in wells and streams, respectively. The mean concentrations of the heavy metals in the soil exceeded the normal uncontaminated soils (with the exception of V). In the case of Cr, Zn and V, our results were above the soil critical range. The mean levels of all the elements in the surface and groundwater were considerably lower than the related guidelines and limits.

Key words: Heavy metals, Agricultural soils, Surface water, Groundwater,Tehran

INTRODUCTION

Heavy metals have been well documented as they are amongst the most hazardous materials threatening the environment worldwide and are characterized by its long period of residual, high invisibility, little transfer, high toxicity, and complexity of chemical behaviors and eco-reaction (Alloway, 1995; Khairiah *et al.*, 2006). Soils can have a natural input of heavy metals from parent rock in concentrations that do not represent any risk to animal or plants (Ross, 1994; Serrano *et al.,* 2005). However, geochemical cycles and biochemical balance of heavy metals have drastically altered in some areas by anthropogenic sources (human activities), such as mining, smelting, waste disposal, domestic and industrial effluents, vehicle exhausts, sewage sludge, pesticides, agrochemicals and inorganic fertilizers (Labrecque *et al.,* 1995; Nicholson *et al.,* 1998; Weber and Karczewska, 2004; Kachenko and Singh, 2006; Montagne *et al.,* 2007). Unlike organic pollutants, heavy metals do not biodegrade and are usually not mobile, so the soil acts as a long-term sink for heavy metals, which can have residence times ranging from hundreds to thousands of years depending on the element and the physicochemical properties of the soil (Alloway, 1995; Mortvedt, 1996; Brunetti *et al.,* 2009).

The accumulation of heavy metals in agricultural soils is of increasing worldwide concern because of food safety issues and potential human health and ecosystems risks, due to their carcinogenic and mutagenic effects (Alloway, 1995; Zheng *et al.,* 2007). Excessive accumulation of heavy metals in agricultural soils through wastewater irrigation may not only result in soil contamination but also leads to elevated heavy metal uptake by plants. In addition, there is also the possibility of transfer of these metals into environmental media, most especially shallow groundwater systems through leaching (Behbahaninia *et al.,* 2009)**.** The main objective of this study was to determine the levels of Cr, Mn, Ni, Pb, V and Zn in soils, surface water and groundwater. The other main purpose of this investigation was to provide reliable data, which can be compared with previous or future results from other areas of the world as well as existing guidelines and limits. Before conducting the present study, no relatively comprehensive research on trace

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elements concentration in soil and water resources of the area (that is the main site of providing vegetables for Tehran, the most populated city of the country) has been done. Hence, the results of this project can be very important from health and environmental point of view. The other objectives of the research were: (a) to evaluate the possible relationships among the levels of the metals in soils, surface water and groundwater samples from the region, (b) to determine inter-elemental relationships (associations among the elements).

MATERIALS & METHODS

The study area (Fig. 1) is located at south part of the Iranian capital, immediately east and south of Tehran oil refinery (Latitude 35° 29' 49.87" to 35° 33' 7.36" N, Longitude 51° 26' 50.73" to 51° 26' 50.99" E) and near the Tehran-Qom highway. The area covers about 2.5×6 km (from east to west and south to north, respectively).

The refinery, located at south part of the Iranian capital, produces a variety of petroleum and chemical products such as liquid gas, ordinary gasoline, light and heavy naphtha, kerosene, gas oil, furnace oil, mineral oil since about 36 years (Mesdaghinia *et al.,* 2005).

The large city of Tehran produces about 2 millions m³/day of wastewater, which is planned to be treated in wastewater treatment plants and the effluent and sludge from treatment plants is going to be used for the irrigation of crops in more than one hundred thousands hectare of agricultural lands in the plains south of Tehran (Behbahaninia and Mirbagheri, 2008). Long-term use of this wastewater, which is mainly used for cultivation of leafy and other vegetables, has resulted in the accumulation of heavy metals in the soil and their transfer to the various crops under cultivation (Yargholi *et al.,* 2008).

The soil sampling was based on the grid point sampling system. The study area (Fig. 1) was divided into 50 grids (each one covered an area of about 500 × 500 m) defined by a Global Positioning System (GPS) receiver. Sampling was conducted using plastic spade (to avoid any contact with metal) during August 2010. The samples were taken from all of the grid cells, except for the cells numbers 26, 37 and 47 (due to local utilities and industries). A total of 141 surface soil samples (47 composite samples × 3 replications) were collected from the area. Three composite samples were collected from each grid cell. The composite samples consisted of 25 to 30 sub-samples collected in a 3 to 6 m radius from the center point, placed in clean plastic bags and transported to the laboratory the same day of sampling. After removing visible plant residues, the samples were

air-dried and sieved using a 2 mm mesh stainless steel sieve. Following this the samples (about 20g) were dried in an oven at 105°C overnight (at least 12 h until constant weight was achieved) and stored in pre-washed labeled polyethylene bags at room temperature before analysis (Mason, 1992; URBSOIL, 2004; Micó *et al.,* 2008~ Peris *et al.,* 2008).

The surface water and groundwater samples were collected from 16 sampling sites (eight wells, four qanats and four streams) during August 2010 (Fig. 1a). Total number of the samples was 48 (16 sampling sites × 3 replications). The samples were collected at Teflon capped brown glass vessels, pre-cleaned with HNO_3 and deionized water. Upon sampling, the samples were acidified with concentrated HNO_3 (65%, supra pure) and transported to the laboratory within the same day of collection and kept refrigerated (4 °C) prior to analysis (<24 h). For collection, preservation and analysis of the samples, the standard methods (APHA, 2005; DHEC, 2005) were followed.

Approximately 1g of the soil samples were digested using aqua regia (HCl/HNO_3, 3:1 solution)-$HClO_4$ (Huang and Jin, 2008). The water samples were digested with aqua regia (3:1, HNO_3: HCl) to release its trace metal contents using standard methods (APHA, 2005), by transferring 100ml of well-mixed, acid preserved sample to a 250 ml flask. A 10 ml aqua regia was added. The flask was covered with a glass watch, placed on a hot plate and the solution cautiously evaporated to about 25 ml, making certain that the sample did not boil. The solution was cooled, the wall of the flask and the watch glass were washed down with deionized water then, the solution was filtered to remove insoluble material that could clog the nebulizer. The reagents were Merck supra-pure grade, and deionized water (18.2 μScm^{-1}) was used from a Millipore Milli Q system. All glassware was soaked in concentrated acid solution both before and after use. The digested samples were transferred to tightly sealed linear polyethylene (Nalgene) containers to avoid adsorption of metals from digested solution and kept at 4°C prior to further analysis (Betti and Papoff, 1988). Soil samples were first analyzed by flame atomic absorption spectrometry (FAAS; Perkin-Elmer Model 5000); samples giving Pb and Ni results below the detection limit by FAAS were subsequently analyzed by graphite furnace atomic absorption spectrometry (GFAAS; Thermo Electron-M5). All the water samples were analyzed by GFAAS.

Quality assurance and quality control of metal analyses were assessed using triplicate, reagent blanks and standard reference materials (SRMs) for each batch of analyses. Four SRMs (NIST 2709, NIST 2711, NIST 1643d and CWW-TM-G), representing sandy soil,
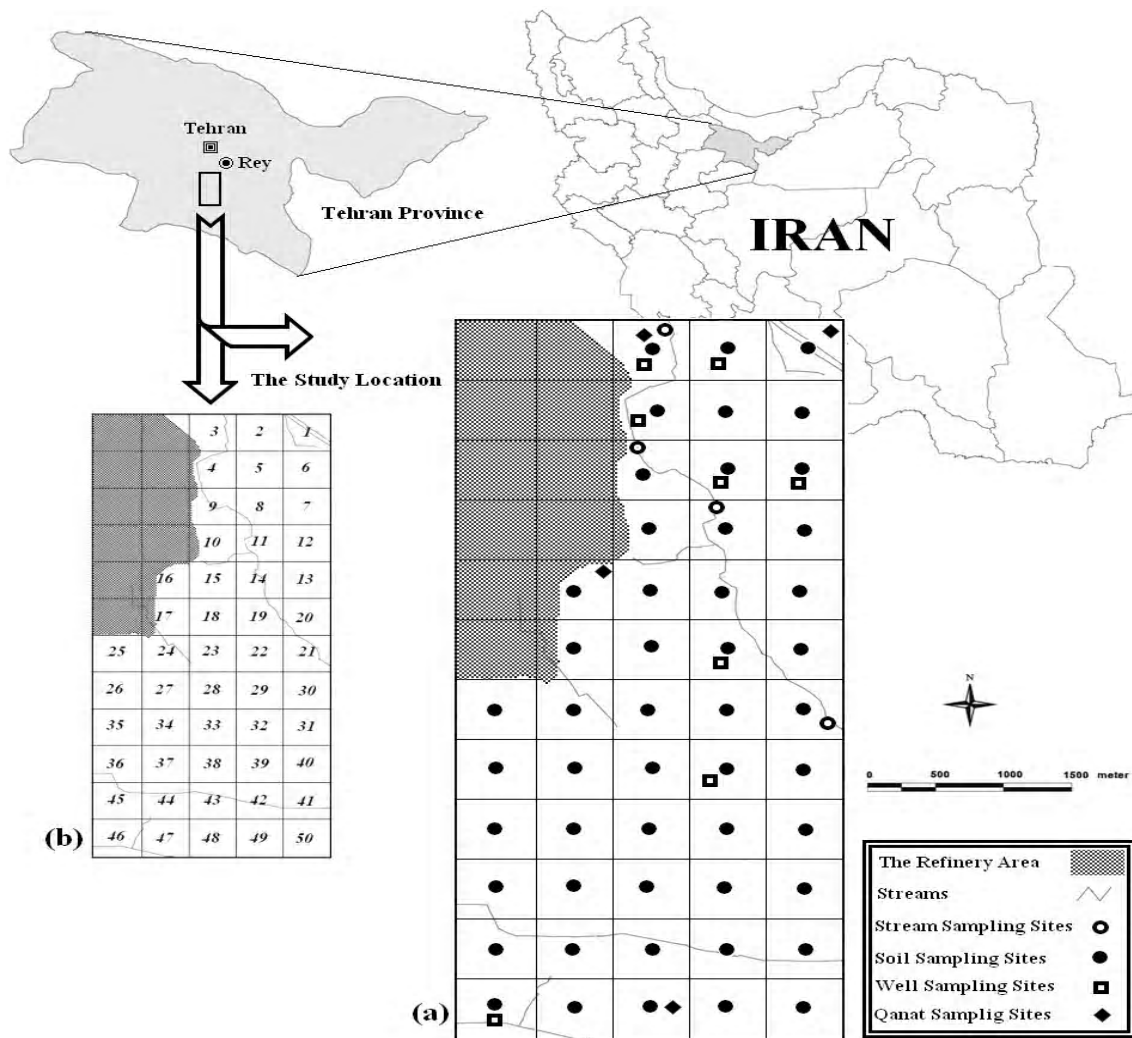
Fig. 1. Map of the study area showing location of soil, surface water and groundwater sampling sites (a) and numbers of the grid cells (b)

contaminated soil, freshwater and wastewater, respectively, were used in this study. The digestions were prepared in a similar manner as samples. The recoveries were consistently in the range 95.7-103.6%, and the relative standard deviation of triplicate measurements was less than 10% for all metals. The detection limits (three times the standard deviation of the blank, n = 10) for FAAS and GFAAS were (µg/L): 3 and 0.003 (Cr), 1.5 and 0.005 (Mn), 5 and 0.06 (Ni), 15 and 0.05 (Pb), 40 and 0.10 (V), 1.5 and 0.02 (Zn), respectively.

One-sample Kolmogorov-Smirnov (K-S) goodness of fit test was applied to test the null hypothesis that the samples come from a normal population (Zar, 2010). Since the null hypothesis was accepted, parametric statistical methods could be applied. To detect homogeneity of variances Levene's test (Sokal and Rohlf, 1995) was used and because the variances were heterogeneous, Taylor's power law (Perry, 1981~ Southwood and Henderson, 2000) applied to determine appropriate data transformation. As a result all data were ln (n+1) transformed. Four one-way ANOVAs were employed to test for significant differences in heavy metal levels in soil, qanats, wells and streams samples. In cases that the differences were significant, Duncan's new multiple range test was used to determine which group means did not differ from one another (Steel *et al.,* 1997; Zar, 2010). Pearson's correlation coefficients were used to examine relationships between the elements in soil as well as water (wastewater and groundwater) samples. Moreover, the relationships between the levels of metals in soil and water samples (for those grid cells where both water and soil samples could be collected) were assessed by Pearson's correlation coefficients.

Agglomerative hierarchical clustering method (using Euclidean measures) was used to classify the grid cells based on the level of the elements in the soil and water samples (Ludwig and Reynolds, 1988; Gnanadesikan, 1997). Data analyses were performed using new versions of statistical packages especially SPSS (Version 18.0) .

RESULTS & DISCUSSION

Fig. 2 shows dendrograms derived by average linkage clustering of the grid cells. Generally, comparison among the six clusters shows the highest similarities between Mn and Ni. In both cases if an arbitrary vertical line crosses the horizontal lines at a distance about 14, two distinct cluster groups can be observed, so that the grid cells 36, 42, 43, 44 and 48 can be clustered into one group while the remaining cells (with exception of 35 and 49) clustered into another group. Some similarities were also observed between the dendrograms of Pb and V because, if an arbitrary line drawn at a distance of about 24, the grid cells can be divided into two general groups, including the grid cells 2, 3, 5, 6, 8, 9, 10, 13, 15, 16 and 48 in one group and the other grids (except few cases) in another group. On the other side, after drawing arbitrary vertical lines at a distance about 17 on the dendrograms of Zn and Cr, two distinct groups can be detected (the grid cells 1, 2, 3, 4, 6, 7, 10, 11, 13, 14, 15, 17, 30 and 39 in one group and the others, with exception of 9, 16, 23 and 29, in another group).
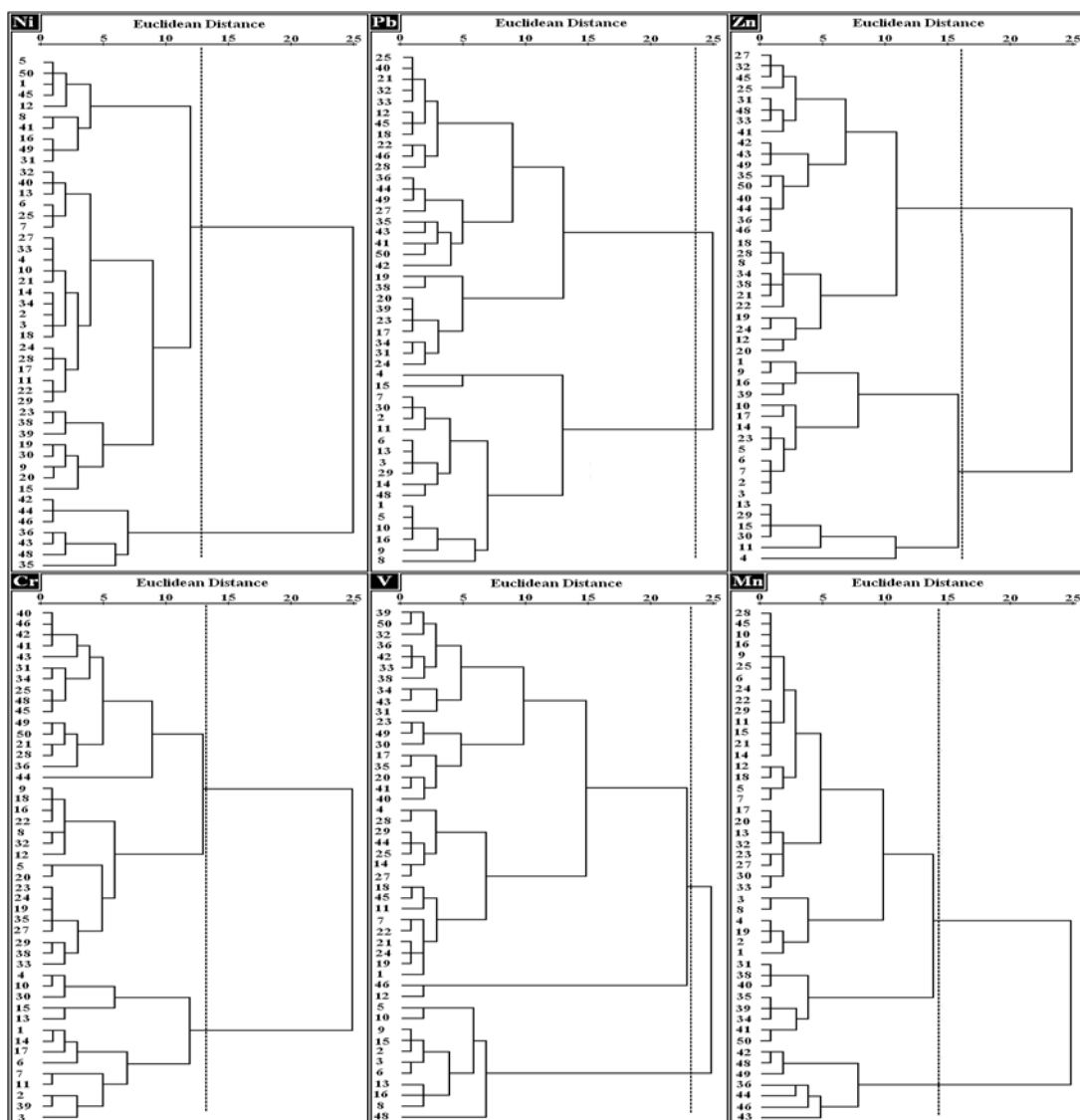

Fig. 2. The dendrograms for hierarchical cluster analysis of the grid cells (derived by average linkage clustering), based on the heavy metal levels in the soil samples

Generally, before interpretation of the above mentioned results, it should be noted that in the case of each dendrogram, the grid cells that can be categorized in one group, most probably have the same major source of the metal distribution.

Since the main activity in the study area is agriculture, the observed similarities between Mn and Ni dendrograms (Fig.2) can be attributed to the soil organic matter which is derived mainly from recent plant residues (Van-Camp *et al.,* 2004). In this regard, it is important to note that some plant species are known to naturally accumulate high levels of metals including Mn and Ni (Baker *et al.,* 2000). In soils with normal Mn levels, Ni and Mn can be simultaneously accumulated to very high levels within *Alyssum* trichome bases (Broadhurst et al. 2004; Tappero et al. 2007). Broadhurst et al. (2009) also found that *Alyssum* leaves begin to hyperaccumulate Ni and accumulate Mn as soon as they emerge and continue to do so as they grow and age. Manceau et al. (2002) reported a close association of Ni and Mn in soil ferromanganese micronodules collected from a French agricultural soil. Varga et al. (1999) noted that Ni contamination hinders the transport of K and Zn, and leads to accumulation of Mn in root tissue.

On the other side, the mentioned similarities between Pb and V dendrograms (Fig.2) seems to be mainly due to input from the same pollution sources, particularly oily sludge generated by Tehran oil refinery. Similar cases have been reported by other researchers (Al-Sarawi *et al.,* 1998). The observed similarity between Zn and Cr dendrograms may be attributable to application of chemical fertilizers containing these elements in the study area during recent years (Anon., 2005; Nziguheba and Smolders, 2008). As mentioned before, a significant positive correlation was also found between these two elements.

Figs. 3, 4 and 5 show the dendrograms for qanats, streams and wells, respectively. In terms of qanats, considerable similarities could be observed between the dendrograms of Ni and Cr, because in both cases if an arbitrary dashed line crosses the horizontal lines, at a distance of about 4, two distinct clusters can be observed: {3, 16} and {1, 48}. Some similarities were also observed between Mn and Zn.

In terms of streams, if an arbitrary line drawn at a distance of about 5 on the dendrograms of Cr, Mn and V, the related grid cells can be divided into two general groups, including 9, 11 and 21 in one group and the grid cell 3 in another group.

In terms of wells, some similarities can be observed between the dendrograms of Ni and Mn as well as Cr and Zn. For Ni and Mn the grid cells 2, 3, 4, 7 and 46 can be clustered into one group (at a distance of about 4). In both cases the major differences (maximum distance) are in clustering of the cell 19 and the other cells (at a distance of about 8). Meanwhile for Cr and Zn, at a distance of about 3 the grid cells 2, 7 and 8 can be clustered into one group and the second group consists of the grid cells 29 and 46.

Following a case by case comparison of the soil and water dendrograms (Figs. 2 to 5), some similarities between Mn dendrogram for soil with that of qanats and streams could be found, because from one side comparison between the soil and qanats dendrograms shows that in both cases at a distance about 8, the grids 1 and 3 can be grouped in one cluster and the grids 16 and 48 in segregated ones. On the other side, comparison between the soil and streams dendrograms indicates that in both cases at the same distance the grids 9, 11 and 21 can be classified in one cluster. Moreover, some similarities between Pb dendrogram for soil with that of qanats and streams could be observed. Hence, generally it can be concluded that the major sources of the Mn and Pb distribution in soil of the study area are most likely irrigation with water from the mentioned resources (especially in the case of those grid cells where the irrigation water resources located within them). However, as mentioned before, with respect to the considerable temporal and spatial variations of trace metal concentrations in the irrigation water, in order to provide a more comprehensive view of the metals distribution in the study area, further studies need to be conducted.

Following the conduction of a one-way ANOVA (testing the null hypothesis that there were no significant differences among concentration of heavy metals in soil samples from the grid cells)(F= 534.173, Pd" 0.0001) and a Duncan's new multiple range test, the pattern of the metal levels in the soil samples can be written in descending order as follows:

Mn> Zn > Cr > V > Ni > Pb

Table 2 presents a general view on results of several studies regarding the order of heavy metals concentration in agricultural soil from various parts of the world. The obtained pattern in this study is in general agreement with those reported by other researchers as well as is mostly in accordance with the order of elements concentration in natural and normal uncontaminated soils (Table 2). From the literature it is clear that among the selected metals in this study the highest and lowest levels were found for Mn and Pb, respectively (except for a few cases).

The high level of Mn in the soil samples from the study area could probably be attributed to both the
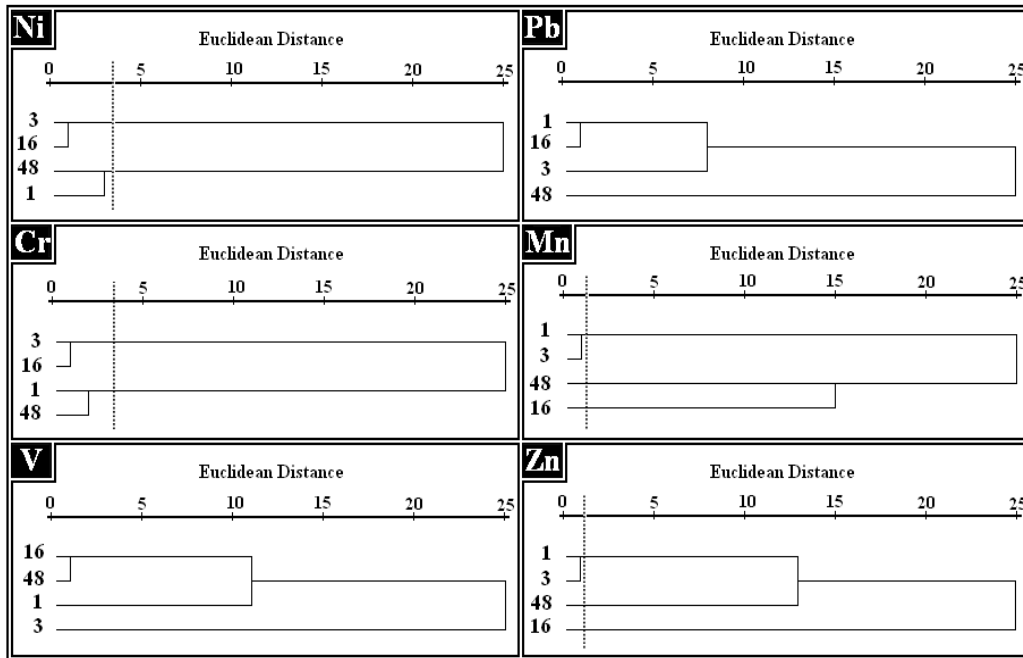
Fig. 3. The dendrograms for hierarchical cluster analysis of the grid cells (derived by average linkage clustering), based on the heavy metal levels in water samples from the qanats

Fig. 4. The dendrograms for hierarchical cluster analysis of the grid cells (derived by average linkage clustering), based on the heavy metal levels in water samples from the streams
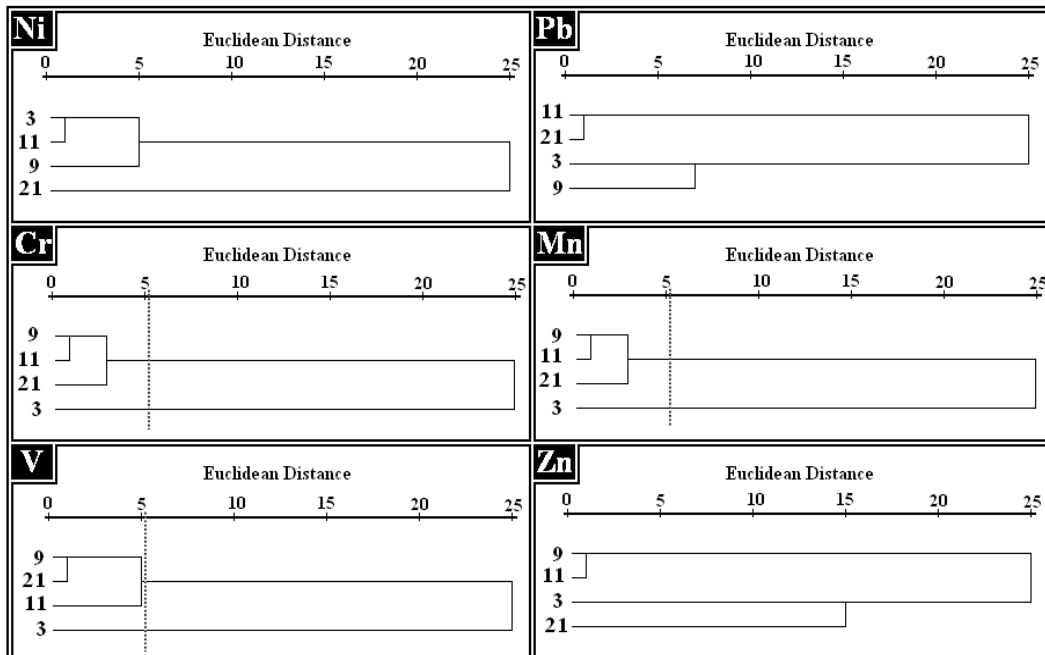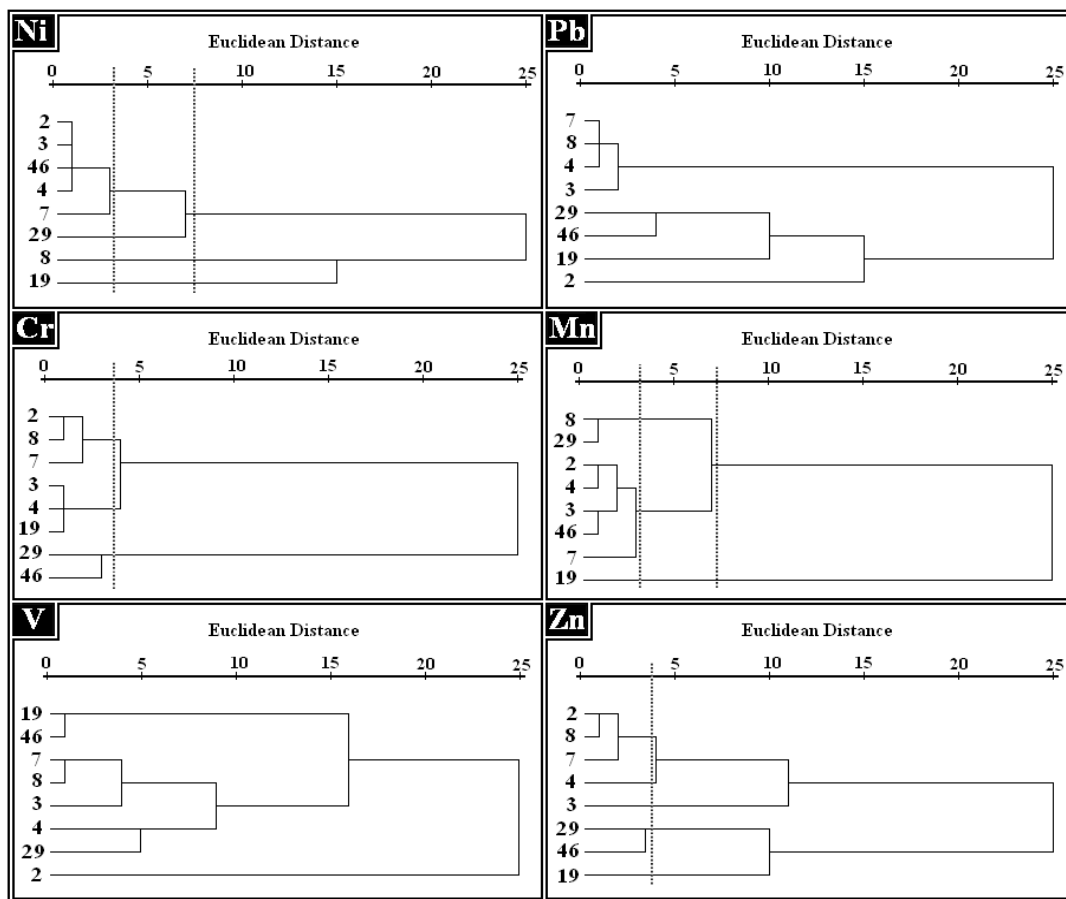
Fig. 5. The dendrograms for hierarchical cluster analysis of the grid cells (derived by average linkage clustering), based on the heavy metal levels in water samples from the wells

natural soil composition as well as the application of agrochemical products: Because from one side, Mn is the eighth most abundant element in the earth's crust and is widely distributed in soils (Housecroft and Sharpe, 2007) and from the other side, it has been reported that some phosphate fertilizers and pesticides, which contain high levels of Mn, have been used in the area during recent years (Anon., 2005; Khairiah *et al.,* 2009).

The low level of Pb in the soil samples from the studied region, which is comparable to other world areas, may be mainly due to the natural soil composition of the area.

With regards to the patterns from the literature (Table 2), the observed variations in the order of some elements (especially for Zn, Ni and Cr) in agricultural soil could be attributed to many factors, in which the differences in application of chemical fertilizers containing these elements as well as use of contaminated water for irrigation of crops have been reported by some other researchers (Smith *et al.,* 1996; Nziguheba and Smolders, 2008, Scott *et al.,* 2008).

With regards to Table 1, the mean values of the metal concentration in water samples from the wells and streams followed the sequence:
Wells: Pb, Ni, Mn > Zn, V, Cr
Streams: Ni, Pb > Cr, V > Mn, Zn

In both cases, Ni and Pb were the most abundant and Zn was the least abundant elements. No significant differences could be observed in concentrations of the metals in water samples from the qanats (Table 1).

Table 3 summarizes the overall results from several studies regarding the order of heavy metals concentration in agricultural irrigation water from various parts of the world. No clear similarity can be detected between the patterns. The observed differences in the patterns might be ascribed to the spatial and temporal variations of heavy metal sources and the quantity of heavy metals discharged through the effluents and sewage in irrigating water (Ahmad

Table 1. Results of 3 one-way ANOVAs testing the null hypothesis that there were no significant differences among the levels of heavy metals in groundwater and wastewater samples from the study area. The metals, which have a common letter are not significantly different from one another
(Duncan's new multiple range test) (P< 0.05)

	F-ratio	DF	P-value	Metals					
				Mn	Zn	Cr	V	Ni	Pb
Qanats	0.488	5	0.781						
Wells	3.588	5	0.009	a b	b	b	b	a	a
Streams	36.311	5	≤0.0001	c	c	b	b	a	a

DF: Degrees of Freedom

Table 2. Patterns of heavy metals occurrence in agricultural soil from various parts of the world. The orders are not based on statistical analyses

Sampling region/ Guidelines	Order	Reference
East and south of Tehran oil refinery, Iran	Mn > Zn > Cr > V > Ni > Pb	Present study
Normal uncontaminated soils	Mn > Cr > Zn > Ni > Pb	Pais and Jones, 1997
Average Soil	Mn > Zn , V > Cr > Ni > Pb	Bowen, 1979
Around the Tehran oil refinery (near the Firoozabad Stream), Iran	Mn > Zn > Cr > Pb > Ni	Bigdeli and Seilsepour, 2008
Segura River Valley (Alicante, Spain)	Mn > Zn > Cr > Ni > Pb	Micó et al., 2006
Lower Vinalopó region (SE Spain)	Mn > Zn > Pb > Cr > Ni	Micó et al., 2008
Pearl River Delta, South China	Zn > Cr > Pb > Ni	Wong et al., 2002
Mangalpur, West Bengal, India	Cr > Mn > Zn	Gupta et al., 2008
Dongguan City, Guangdong, China	Zn > Pb > Cr > Ni	Lei et al., 2008
Musi river bank of Hyderabad, India	Zn > Pb > Mn > Cr > Ni	Adinarayana et al., 2006
Jiangsu Province, China	Zn > Cr > Ni > Pb	Huang and Jin, 2008
western-central part of Addis Ababa, Ethiopia	Mn > Cr > Zn > Ni > Pb	Melaku et al., 2005
Ohio, USA	Zn > Ni > Cr > Pb	Neupane and Roberts, 2008
Beijing, China	Mn > Zn > Cr > Pb > Ni	Wang and Tao, 1998
Kanpur, India	Ni > Zn > Cr > Pb	Sanghi and Sasi, 2001
Central Greece	Zn > Pb > Cr > Ni	Golia et al., 2008
Cameron Highland, Malaysia	Mn > Zn > Cr > Pb	Khairiah et al., 2006
Castellón province, east of Spain	Mn > Zn > Pb > Cr > Ni	Peris et al., 2008
Inner Mongolia	Mn > Zn > V > Cr > Ni > Pb	Xu and Tao, 2004
Bursa city, Turkey	Mn > Zn > Ni > Cr > Pb	Aydinalp and Marinova, 2003
Jundiaí, São Paulo state, Brazil	Mn > Zn > Pb > Ni > Cr	Valladares et al., 2009

Table 3. Patterns of heavy metals occurrence in groundwater and surface water (used for agricultural irrigation) from various parts of the world. The orders are not based on statistical analyses

Sampling region	Source type	Order	Reference
East and south of Tehran oil refinery, Iran	GW	Pb, Ni , Mn > Zn , V , Cr	Present study
East and south of Tehran oil refinery, Iran	SW	Ni, Pb > Cr, V > Mn, Zn	Present study
Around the Tehran oil refinery (near the Firoozabad), Iran	SW	Ni > Mn > Zn > Pb > Cr	Bigdeli and Seilsepour, 2008
Assam, India	GW	Zn > Mn > Cr > Ni	Buragohain et al., 2009
Bara River, Akbarpura, Pakistan	SW	Mn > Ni > Pb > Cr > Zn	Nazif et al., 2006
Delhi, India	GW	Cr > Ni > Zn > Pb	Kaur and Rani, 2006
Guadalquivir marshlands, Spain	GW	Zn > Mn > Ni > Pb	Santos et al., 2002
Thessaloniki, northern Greece	SW	Zn > Ni > Mn > Pb > Cr	Karvelas et al., 2003
Lich and Kim Nguu Rivers, Hanoi City, Vietnam	SW	Cr > Pb > Zn > Ni	Huong et al., 2008

GW: Groundwater, SW: Surface water

and Goni, 2009).

Possible associations among the elements in soil from the study area were assessed by Pearson's correlation coefficient. With respect to the results, significant positive correlations were found between Zn and Ni (r = 0.592, P≤0.0001), Zn and Cr (r = 0.713, P≤0.0001), Ni and Cr (r = 0.570, P=0.001), Mn and Zn (r = 0.632, P≤0.0001), Pb and Zn (r = 0.882, P≤0.0001), and Ni and V (r = 0.414, P=0.032).

Generally, the relationships of soil heavy metals are influenced by many natural and anthropogenic factors such as parent material, climate, vegetation, land use, fertilizer application and so on (Xu and Tao, 2004). The significant positive correlations among some heavy metals, shows that they are derived mainly from the same contaminating sources (Li *et al.,* 2009).

In the present study, the observed significant positive correlations among Zn, Cr and Ni may be attributable to application of chemical fertilizers containing these elements (Nziguheba and Smolders, 2008). According to Gimeno-Garcia et al. (1996) the significant correlation between Mn and Zn might be due to use of some herbicides which contain high amounts of these elements. Since Ni and V are environmental indicators for petroleum sources and keep relatively constant mutual proportions (Ganor et al., 1988; Bairwise, 1990), the significant correlation between them in the present study suggests a common origin, which would be associated with contamination of the area soil by oil spills from Tehran oil refinery and leakages of the underground storage tanks. On the other side, the significant relationship between Pb and Zn may be arose from their similar chemical behaviour as they form the group of calcophile elements according to the Goldschmidt classification (Peris *et al.,* 2008).

An analysis of correlation coefficient between element concentration pairs in the surface water and groundwater samples revealed that in the case of qanats, Cr was negatively and significantly correlated with Ni (r = - 0.981, P≤0.019), in the case of Wells, Mn was positively and significantly correlated with Ni (r = 0.849, P=0.008), while Cr was negatively and significantly correlated with Zn (r = - 0.828, P=0.011). In the case of streams, Cr showed a significant positive correlation with Mn (r = 0.985, P=0.015).

In terms of the inter-metal correlations in the water samples, it should be noted that the large city of Tehran produces a large amount of wastewater with residential, commercial and industrial sources (containing highly variable concentrations of metals). Growing volume of the wastewater is currently being discharged directly or indirectly into surface water (streams) and groundwater (wells and qanats) sources in the plains south of Tehran (including the study area) (Behbahaninia and Mirbagheri, 2008). On the other side, several reports on pollution of the area's water sources caused by oil leakage from the pipelines and underground storage tanks have also been published As mentioned before, with respect to considerable temporal and spatial variations in heavy metal contamination of the water sources (that seems to be a common problem in many developing countries, Drechsel *et al.,* 2010), identification of the main pollution sources at the time of sampling was actually impossible. Thus, interpretation of the observed inter-elemental relationships in water samples is very difficult.

Comparison of the gained data from this study with several guidelines and standards (Table 4) shows that our results are considerably higher than normal uncontaminated soils (except for V which no guideline value is recommended for that). In the case of Cr, Zn and V, our obtained results exceeded the soil critical range, however, in most cases are below the maximum allowable limits of different countries. On the other hand, Fig. 6 shows that concentrations of V and Zn in soil samples from all the grid cells are higher than the soil critical range.

From the literature (Table 4) it is clear that the widest and narrowest range of variations can be observed in the case of Mn and Cr, respectively. These data indicate that metal contents in soil from the studied region are comparable to other world areas. It can be seen that in all cases the levels of all the metals in this investigation fell within the range for other areas. However, it should be noted that some of the values mentioned in the Table correspond to relatively polluted areas.

According to Figs. 1 and 6, it can be seen that in some grid cells, where Firoozabad stream flowing through them (i.e. 3, 4, 9, 10, 11, 14 and 20), Cr, Pb and Ni levels are markedly higher than the uncontaminated soil values. Hence, it can be concluded that the main possible source of the relatively high concentration of these elements could be irrigation of agricultural soils in the mentioned grids with the wastewater containing the elements.

Comparison between the mean concentrations of the six elements in the surface and groundwater from the study area and existing guidelines and limits (Table 5) clearly indicates that, in all the cases, the concentrations are considerably below the limits. However, the highest mean concentrations of Cr and V were found in the wells, where as Ni and Pb were maximum in the qanats and the streams showed the highest mean levels of Mn and Zn.
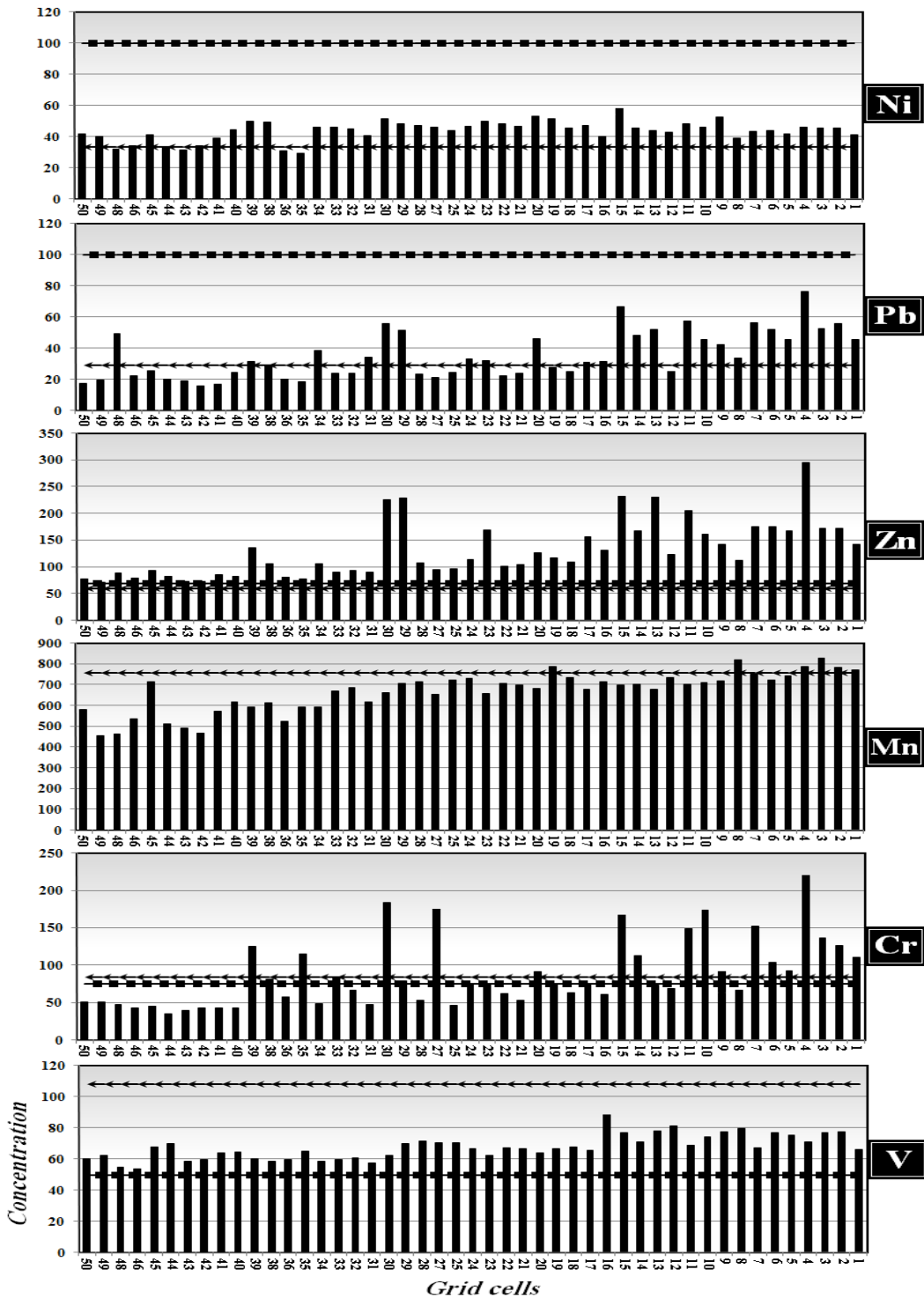
Fig.6. Mean heavy metal concentrations (mg/kg) in soil samples from the grid cells compared to two related standards (as presented in Table 4). The concentrations are means of analysis of three composite samples collected from each cell.

◄—◄—: uncontaminated soils; ◄■–■►: soil critical range

Table 4. Comparison of mean heavy metal concentrations (mg/kg) in agricultural soil from different areas of the world as well as the related standards and guidelines. The cases which are below the present study values are denoted with asterisk

Geographical area/ Standards	Cr	Mn	Ni	Pb	Zn	V	Reference
East and south of Tehran oil refinery, Iran [a]	87.15	665.06	43.60	35.08	130.36	67.14	Present study
Normal, uncontaminated soils	65*	550*	20*	10*	50*	-	Pais and Jones, 1997
Uncontaminated soils	84*	760	33.7*	29.2*	59.8*	108	Ure and Berrow, 1982
Earth's crust	100	950	80	14*	75*	160	Alloway, 1995
Average soil	70*	1000	50	35*	90*	90	Bowen, 1979
USEPA 503 standards [b]	1500	-	260	150	1400	-	USEPA, 1993
The Netherlands MAL	-	-	-	85	140	-	Adriano et al., 1997
Austria MAL	100	-	100	100	300	-	Kabata-Pendias, 1995
Canada MAL	75*	-	100	200	400	-	Kabata-Pendias, 1995
Poland MAL	100	-	100	100	300	-	Kabata-Pendias, 1995
Japan MAL	-	-	100	400	250	-	Kabata-Pendias, 1995
UK MAL	50*	-	50	100	300	-	Kabata-Pendias, 1995
Germany MAL	200	-	100	500	300	-	Kabata-Pendias, 1995
Italy MAL	150	-	120	100	150	-	Brunetti et al., 2009
Threshold of natural background in China	90	-	40*	35*	100*	-	Wong et al., 2002
Spain national regulations	-	-	-	50	150	-	Adriano et al., 1997
Reference values for horticultural soils in Huerta of Murica	73*	-	43*	30*	192	-	Pérez et al., 2002
Guideline values for application of sewage sludge on agricultural soils	150	-	75	300	300	-	CEC, 1986
Soil critical range [c]	75*	-	100	100	70*	50*	Kabata-Pendias and Pendias, 2001
86/278/EEC Directive [d]	-	-	75	300	300	-	CEC, 1986
Around the Tehran oil refinery (near the Firoozabad Stream), Iran	70*	870	32	60	190	-	Bigdeli and Seilsepour, 2008
Khoshk River Banks, Shiraz, Iran	124.5	-	171.4	254.6	117.0*	-	Qishlaqi and Moore, 2007
Castellón province, east of Spain	33.3*	385*	19.3*	55.8	78.5*	-	Peris et al., 2008
Kanpur, India	19.34*	-	80.6	15.11*	28.42*	-	Sanghi and Sasi, 2001
Beijing, China	62.42*	484.0*	29.9*	31.7*	124.2*	-	Wang and Tao, 1998
Jiangsu Province, China	78.8*	-	-	27.7*	56.6*	-	Huang and Jin, 2008
Dongguan City, Guangdong, China	-	-	-	69.4	158.6	-	Lei et al., 2008
Chongming Island, Shanghai City, China	69.4	-	-	21.6	-	-	Chao et al., 2010
Dongguan, Guangdong Province, China	43.01	-	20.52	65.38	66.15	-	Limei et al., 2010

[a] The average total elemental concentration in normal, uncontaminated soils, [b] Cumulative loading rates based on the final concentration in soil in upper 15 cm of soil, [c] Maximum permissible agricultural soil concentration in some European countries, [d] Guidelines values for agricultural soils with a pH > 7, MAL: Maximum Allowable Limit, —: not determined.

Table 5. Comparison of mean heavy metal concentrations (mg/l) in the water samples from the study area with the related guidelines and standards

Standards	Cr	Mn	Ni	Pb	Zn	V	Reference
Present study (wells)	0.018	0.003	0.001	0.001	0.032	0.010	
Present study (qanats)	0.007	0.010	0.008	0.011	0.019	0.006	
Present study (streams)	0.010	0.072	0.002	0.003	0.082	0.009	
FAO and WHO guidelines	0.1	0.2	0.2	5	2	-	WHO, 1989; Pescod, 1992
Malaysia, national quality water standards, irrigation water	0.1	0.2	0.2	5	2	-	Malaysia DOE, 2006
ANZECC, LTV in irrigation water	0.1	0.2	0.2	2	2	0.1	ANZECC, 2000
ANZECC, STV in irrigation water	1	10	2	5	5	0.5	ANZECC, 2000
Iranian standard for effluent discharge-irrigation	1	1	2	1	2	0.1	Iran DOE, 2003
EPA recommended limits for constituents in reclaimed water for irrigation, long-term use	0.1	0.2	0.2	5	2	0.1	Rowe and Abdel-Magid, 1995
EPA recommended limits for constituents in reclaimed water for irrigation, short-term use	1	10	2	10	10	1	Rowe and Abdel-Magid, 1995
Long-term irrigation water	0.1	0.2	0.2	2	2	0.1	Australia DOE, 2003

LTV: long-term trigger value, STV: Short-term trigger value, ANZECC: Australian and New Zealand Environment and Conservation Council, —: not determined.

CONCLUSION

In general, comparison of the obtained results from this study with the relevant guidelines and standards indicates that the mean concentrations of the heavy metals in the soil are markedly higher than normal contaminated soils. Hence, with respect to the contamination of soil in the study area, it is recommended that the heavy metal accumulator edible plants should not be cultivated in the region. Moreover, a great deal of attention should be paid to apply appropriate environment friendly technologies for remediation of the contaminated soil and water resources, and simultaneously long-monitoring programs should be initiated in the region.

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