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ORIGINAL PAPER

Spatial distribution of soil heavy metals in different land uses of an industrial area of Tehran (Iran)

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Abstract Vegetation and different land uses may affect the spatial distribution of heavy metals in soils. The objective of the current article was to study the impact of industrial activities and land use type on the distribution of heavy metals in soils of Chitgar Forrest Park, located in industrial zone in the west of Tehran City. The soil samples were taken from 116 sites in a regular sampling grid (250 × 250 m) at a depth of 0–20 cm, including three different land uses, needle leaf forests, broadleaf forests and rangeland. Nitric acid-extractable form of seven metals, Cu, Cd, Fe, Mn, Ni, Pb and Zn, and DTPA-extractable form of Cu, Fe, Mn and Zn were measured. Soil texture, pH, organic carbon, carbon-to-nitrogen ratio, percentage of calcium carbonate and electrical conductivity (EC) were also determined. According to the maps and background amounts, heavy metals were affected by industrial activities and road traffic. Proximity to heavy traffic highway of Tehran–Karaj and large autoindustry plants can be considered for increasing metal concentrations. Results of statistical methods (coefficient variation and cluster analysis), besides geostatistical analysis (variogram and map), showed that total concentrations of heavy metals are controlled by intrinsic and extrinsic factors in the studied area. Although land use type did not affect the alteration in the distribution of total concentrations of heavy metals, it changed the distribution of DTPA form of heavy metals in the soils through affecting the soil organic matter.

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Introduction

Many studies have shown increasing concentrations of heavy metals in soils of industrial and urban areas due to industrial activities and use of fossil fuels (Wu et al. 2011; Yaylal and Yaylalı-Abanuz 2011; Xia et al. 2011; Li et al. 2013; Szolnoki et al. 2013; Karim et al. 2014). Soils contaminated with heavy metals pose serious health risks to inhabitants, especially in urban soils, which can easily enter their body through ingestion, inhalation or dermal routes (Xia et al. 2011). In addition, several researchers have also described the potential risks of heavy metals entering into human bodies through edible plants grown in contaminated soils (Bai et al. 2010a; Dumat et al. 2006; Notten et al. 2005). Whereas total heavy metal concentrations and the concentrations of extractable heavy metals can be used to assess the level of contamination (Zhao et al. 2012), the available soil metal concentrations predict metal transfer from soil to crops better than total metal concentrations (Amini et al. 2005). Zhao et al. (2012) showed that the areas with the highest human health risks do not directly coincide with the areas of highest heavy metal concentrations, but do coincide with the areas of lower soil pH. They also mentioned that contamination with high concentrations of heavy metals provides the risk source, but the combination of high heavy metal concentrations, low pH and agricultural or residential land use is required for human health risks to be present.

On one hand, many studies have reported the significant effects of land use on chemical and physical properties of soil and so, indirectly, on the environment (Busse et al.

2009; Shi et al. 2011; Li et al. 2014; Traoré et al. 2015; Xinjiang 2015). For example, it is indicated that land use information is significantly related to the spatial pattern of soil properties (Hu et al. 2007; Başaran et al. 2008; Shi et al. 2011). On the other hand, accumulation and retention of metals in soil are strongly dependent on soil properties (En-qing et al. 2015). Physical and chemical properties of the soil have a fundamental role on the spatial distribution of heavy metals. Zhao et al. (2010) illustrated that enrichment index of some heavy metals was significantly correlated with most soil properties and the spatial distribution of enrichment index for Cd, Ni and Zn was similar to the spatial structures of pH, OM, sand and clay. Increase in soil pH, organic matter, cation exchange capacity and the amount of iron and manganese oxides can lead to an increase in metal accumulation (Lake et al. 1984). You et al. (2011) indicated that land use is one of the most important factors affecting the heavy metals. Bai et al. (2010a) showed that the average total concentrations of As, Cd, Cu, Pb and Zn were generally higher in wetland soils and abandoned tilled soils than in conventionally tilled soil.

It seems that information about the effects of changing land use on contamination levels of heavy metals is not completely clear. The objectives of this study were to evaluate the extent and level of heavy metal contamination in topsoil of an industrial zone of Tehran (Chitgar) and to investigate the effects of land use type and industrial activities on the accumulation and distribution of total and available form of heavy metals in soil. Chitgar forest park, which comprises three different land uses (needle leaf forest—NF, broadleaf forests—BF and rangeland—RL) and located near Iran's largest industrial center in the west of Tehran City, was selected as the study area. All land uses were rangeland before 1966, and our research was conducted 45 years after changing of rangeland into broadleaf and needle leaf forests in 2011.

Materials and methods

Study area

The study area covers western section of Chitgar forest park besides its adjacent rangeland which is located in the west of Tehran city and near the Tehran-Karaj highway and Chitgar industrial area, between 35°43′14.17″N to 35°44′51.71″N and 51°11′30.07″E to 51°13′9.34″E, encompasses about 665 ha (Fig. 1).

Elevation varies between 1225 and 1313 m a.s.l. The average annual precipitation was 267 mm, and average annual temperature was 17.2 °C (these data were calculated by statistical analysis of Chitgar meteorological synoptic station database from 1996 to 2011).

Three land uses were selected: needle leaf forest, broadleaf forest and rangeland vegetation cover. Needle leaf trees are *Eldarica pinus*, broadleaf trees are mainly black locust (*Robinia pseudoacacia*) and desert ash (*Fraxinus rotundifolia*), and rangeland vegetation includes camelthorn (*Alhagi maurorum*), mouse barley (*Hordeum murinum*) and some other grass species.

Sampling soil and experimental methods

In order to identify sampling sites, stratified grid sampling method was used: 116 samples were collected in a regular sampling grid (250 × 250 m) at a depth of 0–20 cm. Moreover, for evaluation of heavy metals in natural local background (NLB) soil, 12 samples randomly distributed on the entire grid were collected at a depth of 1 m.

Soil samples were air-dried, homogenized, sieved through 2-mm mesh and stored in polyethylene bags at ambient temperature.

Nitric acid-extractable form of Pb, Cd, Ni, Zn, Cu, Mn and Fe was determined after extraction with 4 M HNO3 (1:8 mass ratio of soil to final mixture) at 80 °C for 16 h. After cooling, samples were filtered through coarse acid-washed cellulose filters (Richards et al. 1998).

For measuring Cu, Mn, Ni and Zn DTPA form, soil (10 g) was extracted with 20 ml of 0.005 M DTPA + 0.01 M TEA + 0.01 M $CaCl_2$, adjusted to pH 7.3 and shaken for 2 h (Lindsay and Norvell 1978).

In both cases, metal concentrations were determined using atomic absorption system (Shimadzu model AA.670). Soil particle size was measured by using the hydrometer method, soil organic carbon by the wet oxidation method of Walkley and Black and soil nitrogen by Kjeldahl method. Electrical conductivity was measured in saturation extract of soils using an EC meter; soil reaction (pH) was determined in 1:1 water-to-soil extract; $CaCO_3$ was measured through volumetric measurements method by calcimetry (Pansu and Gautheyrou 2006).

Data analysis

Descriptive statistical parameters were calculated using SPSS16.0 package, and the correlations between heavy metals were assessed by using Pearson correlation coefficient. The land-utilization effects on the amount of nitric acid-extractable form and DTPA-extractable form of heavy metals were investigated using one-way ANOVA, and comparison of means was conducted by Duncan multiple-range tests.

GS+ (5.1) and ARC GIS version 9.3 software were used for spatial data analysis. Variogram was the first step in examining the spatial patterns estimated by following equation (Goovaerts 1998):

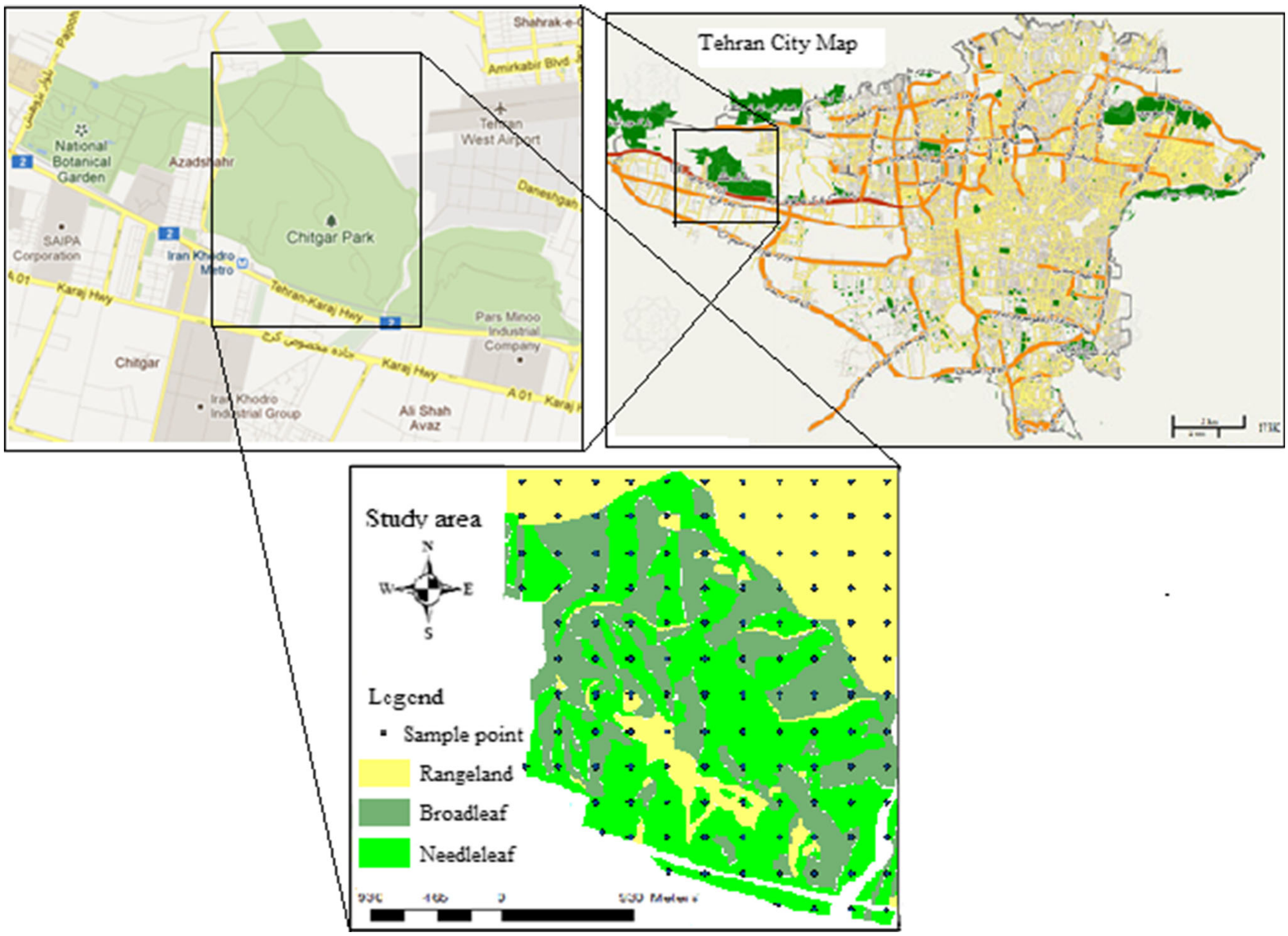

Fig. 1 Location and land use type of the study area and sampling pattern

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} \{Z(x_i) - Z(x_i + h)\}^2 \quad (1)$$

where $\gamma(h)$ is semivariogram, $N(h)$ is the couple number of sampling points, $Z(x_i)$ is the observed value of the variable x at location i and $Z(x_i + h)$ is the observed value of variable x at distance h. Next step is to fit the best theoretical model to empirical variogram. The ideal model provides information about the spatial structure as well as the input parameters such as nugget, sill and range for kriging interpolation.

In order to evaluate and compare interpolation methods, cross-validation was conducted and parameters such as root mean square error (RMSE), mean absolute error (MAE) and mean bias error (MBE) were used. By getting further from zero value, these above-mentioned parameters show the accuracy reduction or increase in deviation (Wackernagel 2003). Therefore, based on the results obtained, kriging was chosen as the best estimator of interpolation in the current study. Kriging method, which can be called the best non-diagonal linear estimator with the least variance, operates based on weighted moving average.

Results and discussion

Descriptive statistics

To evaluate the raw data, the descriptive statistical parameters of soil heavy metals are presented in Table 1. The results of Kolmogorov–Smirnov normality test ($p < 0.05$) showed that Zn, Mn, Pb, Fe and Cd did not have a normal distribution, while nitric Ni and Cu followed the normal distribution. For stabilizing variances in all subsequent statistical analysis, logarithmic transformation of the data was performed. The mean concentrations of Zn, Pb, Fe, Ni, Mn, Cu and Cd were 76.54, 21.33, 25558.04, 21.2, 905.43, 34.52 and 0.13 mg/kg, respectively. Based on the comparison between heavy metal mean values and their background contents (Table 1), there is a marked difference

Table 1 Descriptive statistics parameters of soil nitric acid-extractable form for 116 sample points (mg/kg)

Variable	Background mean	Mean	Minimum	Maximum	SD	Skewness	Kurtosis	CV%
Zn	65.17	76.54	45.25	120.00	17.37	0.87	0.55	22.69
Pb	7.52	21.33	11.50	39.80	5.48	1.18	1.96	25.68
Fe	24,492.97	25,558.04	17,800.00	31,925.00	3668.06	−0.41	−0.48	14.35
Ni	15.37	21.20	4.69	37.42	7.32	0.02	−0.30	34.55
Mn	792.92	905.43	631.25	1273.75	139.50	0.73	0.29	15.41
Cu	27.18	34.52	22.80	43.00	4.52	−0.45	−0.29	13.10
Cd	0.09	0.13	0.03	0.30	0.07	0.53	−0.75	53.31

between mean concentrations of Pb and Cd and their background levels, while the average concentrations of Pb and Cd are approximately three times and 1.5 times as large as their backgrounds. Moreover, other elements also showed higher mean levels than their backgrounds levels. The mean comparison analysis (Table 3) showed that all heavy metal concentrations in surface soil, except for Fe, have increased compared to the background values ($p < 0.05$). This obviously indicates that the anthropogenic activities have enriched the amount of these elements in the topsoil. On the other hand, in comparison with Fe background levels, the increase in Fe concentration caused by anthropogenic activities in surface soil was insignificant, suggesting that Fe concentration is mostly affected by parent materials and soil intrinsic properties.

The coefficient of variation (CV) values of seven heavy metals in the study area (Table 1) ranged from 13.1 to 53.1 %, indicating moderate variations of these metals in the region. Among all seven metals, Cd showed the highest CV value of 53.1 %, suggesting that it has the greatest variation among the soil samples and thus would have the highest probability of being influenced by the extrinsic factors including industrial activities (Chen et al. 2008). Cai et al. (2015) also found the most remarkable CV for Cd among the studied elements in Shunde City, China. Cu, Fe and Mn showed the lowest CV values, 13.1, 14.35 and 15.41 %, respectively, showing that these three elements have weak variations and their concentrations are almost constant across the area. It can be a logical explanation that these elements are less affected by the external factors such as human activities. CV values of Zn, Pb and Ni were 22.69, 25.68 and 34.55, respectively. According to Luo et al. (2007), this means that human activities have moderate effects on the concentrations of heavy metals in soils around the region.

Correlation values among heavy metals

Correlation analyses have been widely applied in environmental studies. They provide an effective way to show the relationships between multiple variables and thus have been helpful for understanding the influencing factors as well as the sources of chemical components. There are usually complicated relationships among heavy metals in soil (Li et al. 2013). Correlation matrix in Table 2 reveals that most of the elements are correlated with each other. For example, Zn is correlated with all metals ($p < 0.05$); however, correlation with Pb was the highest. Fe showed a remarkable correlation with Cu (0.643) followed by Mn (0.393). The high correlations between heavy metals in soil may reflect that the accumulated concentrations of these heavy metals result from similar pollution sources (Li et al. 2013).

Cluster analysis (CA)

Cluster analysis can be used to identify contamination sources (Lee et al. 2006; Zheng et al. 2008; Xia et al. 2011). Therefore, cluster analysis was conducted on element concentrations in soils, using the furthest neighbor linkage method based on correlation coefficients (the Pearson coefficient). The results of CA are illustrated in the dendrogram (Fig. 2). The distance cluster shows the degree of association between elements. The smaller the value on the distance cluster, the more significant the association (Luo et al. 2007). Three distinct clusters can be identified. Cluster I contained Fe and Cu; the long distance between this cluster and others suggests the same source in the soils for these two elements. Regarding their background level which is almost near to soil surface amount, it can be inferred that concentrations of these two elements in topsoils are mainly originated from soil intrinsic attributes. Mn indexed in cluster II, which was the nearest cluster to cluster I, indicating that Mn concentration is affected by cluster I and cluster II sources. With respect to Mn CV percentage (Table 1), correlation value between Mn and Fe (Table 2) and mean comparisons (Table 3), it seems that Mn was not affected substantially by industrial activities. Mean comparison (Table 3) illustrates that there is no difference between broadleaf forest's Mn value and Mn background level. Regarding significant correlation between Mn and soil clay content, it can be suggested that

Table 2 Pearson correlation coefficient among the nitric acid-extractable form, DTPA-extractable form of different heavy metals and soil factors ($N = 116$)

	pH	$CaCO_3$	Clay	OC	C/N	Zn	Pb	Fe	Ni	Mn	Cu	Cd	Zn DTPA	Cu DTPA	Mn DTPA	Fe DTPA
pH	1															
$CaCO_3$	0.184 ns	1														
Clay	0.117 ns	−0.049 ns	1													
OC	0.063 ns	0.232*	−0.195*	1												
C/N	0.127 ns	0.239*	−0.223*	0.762**	1											
Zn	0.312**	−0.219*	0.132 ns	0.219*	0.119 ns	1										
Pb	0.072 ns	−0.145 ns	0.044 ns	0.229*	0.188*	0.397**	1									
Fe	0.184 ns	−0.641**	0.112 ns	−0.375**	−0.337**	0.276**	0.061 ns	1								
Ni	0.1 ns	−0.297**	0.510**	−0.03 ns	−0.03 ns	0.204*	0.272**	0.069 ns	1							
Mn	0.122 ns	−0.441**	0.545**	−0.350**	−0.213*	0.254**	0.144 ns	0.398**	0.300**	1						
Cu	0.149 ns	−0.469**	0.031 ns	−0.03 ns	−0.1 ns	0.378**	0.269**	0.643**	0.06 ns	0.137 ns	1					
Cd	0.102 ns	−0.095 ns	0.258**	0.083 ns	0.069 ns	0.290**	0.214*	0.033 ns	0.301**	0.12 ns	0.203*	1				
Zn DTPA	−0.004 ns	0.197*	−0.251**	0.762**	0.611**	0.404**	0.439**	−0.370**	0.105	−0.354**	0.051 ns	0.051 ns	1			
Cu DTPA	0.227*	−0.316**	0.494**	0.087 ns	−0.031	0.529**	0.352**	0.204*	0.425**	0.492**	0.412**	0.325**	0.197*	1		
Mn DTPA	0.111 ns	−0.215*	0.452**	0.206*	0.126 ns	0.247*	0.305**	0.034 ns	0.473**	0.443**	0.1 ns	0.07 ns	0.307**	0.560**	1	
Fe DTPA	0.099 ns	−0.275**	0.026 ns	0.218*	0.14 ns	0.352**	0.294**	0.072 ns	0.214*	0.129	0.246**	0.071 ns	0.394**	0.345**	0.496**	1

ns nonsignificant

** Significant at 0.01 level, * significant at 0.05 level higher Mn concentration in surface soils is due to higher clay particles rather than industrial activities. Cluster III contains Zn and Pb in addition to Cd and Ni (Fig. 2). Based on the CV value and correlation coefficient between the elements, the source of these elements is the same, and these elements are influenced by anthropogenic sources as well as natural sources. However, according to Cd and Ni CV values (Table 1), which were the greatest among all elements, anthropogenic sources have more effects on Ni and Cd concentrations, thus leading to a big distance in dendrogram to cluster I with natural sources.

Comparison of nitric acid form of heavy metals in three types of land uses

Based on the results of ANOVA of metal concentrations in soils of different land uses, apart from Mn which showed significant differences ($p < 0.05$), there were no significant differences between nitric acid-extractable forms of Cu, Cd, Fe, Pb, Ni and Zn in three different types of land use (Table 3). As shown in Table 2, the highest correlation coefficient, 0.545, was observed between Mn concentrations and soil factors, especially clay. Due to the considerably higher quantity of clay in RL and NF in BF and also lower tendency of course-textured soils to adsorb heavy metals in comparison with fine-textured ones (Bradl 2004), it can be deduced that greater values of Mn concentration are related to the higher amount of clay in RL and NL. Soto-Jiménez and Páez-Osuna (2001) and (Wang and Wu 2008) also found a positive correlation between Mn and clay contents. Since soil texture is one of the constant properties of soil, clay content is not affected by land use type. Therefore, land uses had no effect on accumulation of Mn in the region, and it is the intrinsic characteristics of soil such as soil texture that determine Mn content in the study area. This is also in agreement with the CV value and CA mentioned in the above sections. Our results are in contrast to the results of Bai et al. (2010b), which is conducted in different land uses in Siping area of Jilin Province. Their results showed that there was a rather large difference in the effects of Cr, Ni, Cu, As, Cd and Zn accumulation in soils under greenhouse field, uncovered vegetable field, maize field and forest field land uses. In contrast to that study, in Chitgar Park, fertilizers have not been applied. In addition, human practice for all land uses was nearly similar; therefore, no significant difference can be observed. Nevertheless, Pouyat et al. (2007) demonstrated that heavy metal concentrations were not affected by land use and cover, suggesting that these elements are more related to other factors.

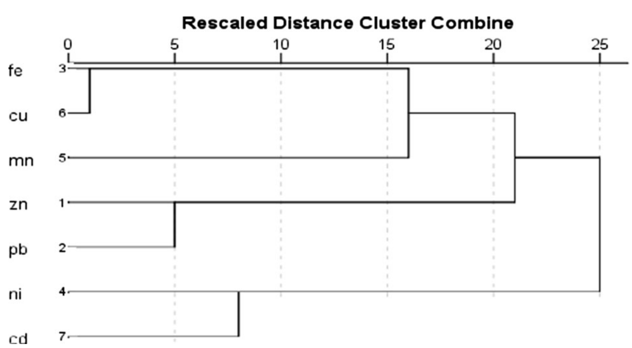

Fig. 2 Dendrogram for seven heavy metals obtained by furthest neighbor method

Spatial structure of nitric acid-extractable form of heavy metals

Semivariogram calculation was carried out, and the experimental semivariogram of soil heavy metal concentrations could be fitted with a spherical model for Zn, Fe, Pb, Cd and Cu and exponential model for Ni and Mn (Table 4). Spatial dependency degree can be calculated by dividing nugget effect (C0) by the total variance (sill) (C0/C0 + C). The ratios lower than 0.25, in the range of 0.25–0.75 and higher than 0.75 represent strong, moderate and weak spatial dependency of variable, respectively (Zhao et al.

Table 3 Mean comparison of nitric acid form of heavy metals in three types of land uses (mean ± SD, mg/kg)

	Land use			
	Rangeland (RL) (*N* = 32)	Needle leaf forest (NL) (*N* = 55)	Broadleaf forest (BF) (*N* = 29)	Background value (BG) (*N* = 12)
Cd	0.15a ± 0.07	0.12a ± 0.06	0.13a ± 0.08	0.09b ± 0.03
Cu	34.08a ± 5.57	34.78a ± 3.93	34.51a ± 4.41	27.18b ± 5.3
Fe	26,758.33a ± 148	25,264.35a ± 3833.36	24,838.39a	24,492.97a
Mn	**1028.17a** ± 219.05	**874.29b** ± 118.22	**839.26bc** ± 81.5	792.92c ± 98.34
Ni	22.37a ± 7.51	21.25ab ± 8.00	19.76a ± 5.46	15.37b ± 3.85
Pb	20.53a ± 3.42	22.87a ± 6.78	19.32a ± 3.49	7.52b ± 2.70
Zn	76.73a ± 17.69	76.65a ± 17.59	76.14a ± 17.23	65.17b ± 8.00

Different letters in each column of the table indicate significant differences at $p < 0.05$ (based on Duncan test) between land use types

2010; Li et al. 2013; Dragović et al. 2014). Moreover, a strong spatial dependency can be attributed to the intrinsic properties of the soil, whereas a weak spatial dependency can be due to significant influence of external factors (Rodríguez Martín et al. 2006; Yang et al. 2009; Dragović et al. 2014). In our study, the nugget/sill ratios of all the investigated heavy metals ranged from 0.34 to 0.71 for Ni and Cd, respectively (Table 4), which represents a moderate degree of spatial dependency for all metals. This moderate spatial dependency demonstrates that anthropogenic factors such as industrial activities and traffic factor have changed spatial dependency and distribution of heavy metals in the studied area. Yang et al. (2009) also reported that the anthropogenic factors changed spatial correlation of heavy metals through industrial productions, fertilization and other soil management practices in their study area. Based on variogram analysis, we can see that Cd showed the highest nugget/sill ratios, which verified that this element has been affected by human activities in the region. Although nugget/sill ratio of Ni was smaller than others, this ratio represents moderate spatial dependency. Moreover, with regard to the result of mean comparison of Ni with background level as well as positive marked correlation ($p < 0.05$) with Cd and CA, we can infer that Ni source is likely the same as Cd. Nugget/sill ratios for remaining elements were approximately similar to each other, revealing a moderate spatial dependency of these variables.

Investigation of spatial distribution of nitric acid-extractable form of heavy metals

After the interpolation of all variables using three interpolation methods, ordinary kriging as the most accurate method was used for mapping of heavy metals and soil properties. The accuracy of the kriging was verified by the standard errors of estimated kriged value calculated by the cross-validation results, and it showed that the accuracy of using kriging method was acceptable. Figures 3 and 4 show the mapping of soil properties and heavy metals using the kriging method. As can be seen, there are high amounts of Cu and Fe in northeastern regions (Figs. 3b, 4a). With respect to Fe, Cu and $CaCO_3$ maps, spatial distribution of these two metals was in contrast to the distribution of $CaCO_3$ percentage which was in agreement with correlation matrix (Table 2), in which Fe and Cu indicated significant negative correlation with $CaCO_3$ percentage ($p < 0.01$). However, in south-eastern parts which become closer to industrial factories, neither Cu nor Fe increases can be seen, indicating that Fe and Cu are mainly under the influence of natural sources which control the distribution of these metals. Lv et al. (2014) also stated that human activities in urban area did not change the spatial variation of heavy metals in soils. The results are in accord with the results of CV and CA. Nonetheless, based on semivariogram analysis and mean comparison results, concentration of Cu was more affected by anthropogenic activities in the region compared to Fe.

Mn kriging map (Fig. 4g) seems to follow clay map, and, the high values of Mn were mainly in the areas with high percentage of clay and low amount of $CaCO_3$ (Fig. 3a, b). These areas are located in the northeastern and southern regions. Mn distribution represents that Mn concentration is mainly controlled by soil intrinsic factors, including clay and $CaCO_3$ percentage. Korte et al. (1976) and Qishlaqi et al. (2009) also found an association between clay and heavy metals such as Mn.

Cd, Ni, Pb and Zn also show nearly the same distribution which verified the same source in the region for these elements as CA results represented. As shown in CV analysis and mean comparison, these elements are affected by industrial activities or natural sources in topsoils, a fact that is confirmed by continued maps. The lowest concentrations of Cd, Ni, Pb and Zn were observed in the central part of the forest (Fig. 3). This could be due to the maximum distance from the highway near the park. Another possible reason according to Wilcke and Kaupenjohann (1994), Wenzel et al. (1996) and Yongfeng et al. (2008) can be the role of forest's function as a filter for atmospheric and airborne pollutants, which prevents the transition of metals in central areas. However, according to the

Table 4 Variogram analysis for the parameters studied

Parameter	Model	Nugget effect (C0)	Sill (C0 + C)	Range (A)	Proportion C0/(C0+C)	R2	RSS
Zn	Spherical	0.03	0.052	1350	0.57	0.90	2.6E−05
Fe	Spherical	0.014	0.028	2638	0.5	0.94	1.01E−05
Ni	Exponential	21.1	62.3	2247	0.34	0.97	25.6
Mn	Exponential	1.3	2.96	2553	0.43	0.96	0.34
Pb	Spherical	0.027	0.057	775	0.47	0.94	1.66E−5
Cu	Spherical	13	21	1200	0.62	0.92	2.63
Cd	Spherical	3.7E−03	5.2E−03	1100	0.71	0.71	3.8E−07

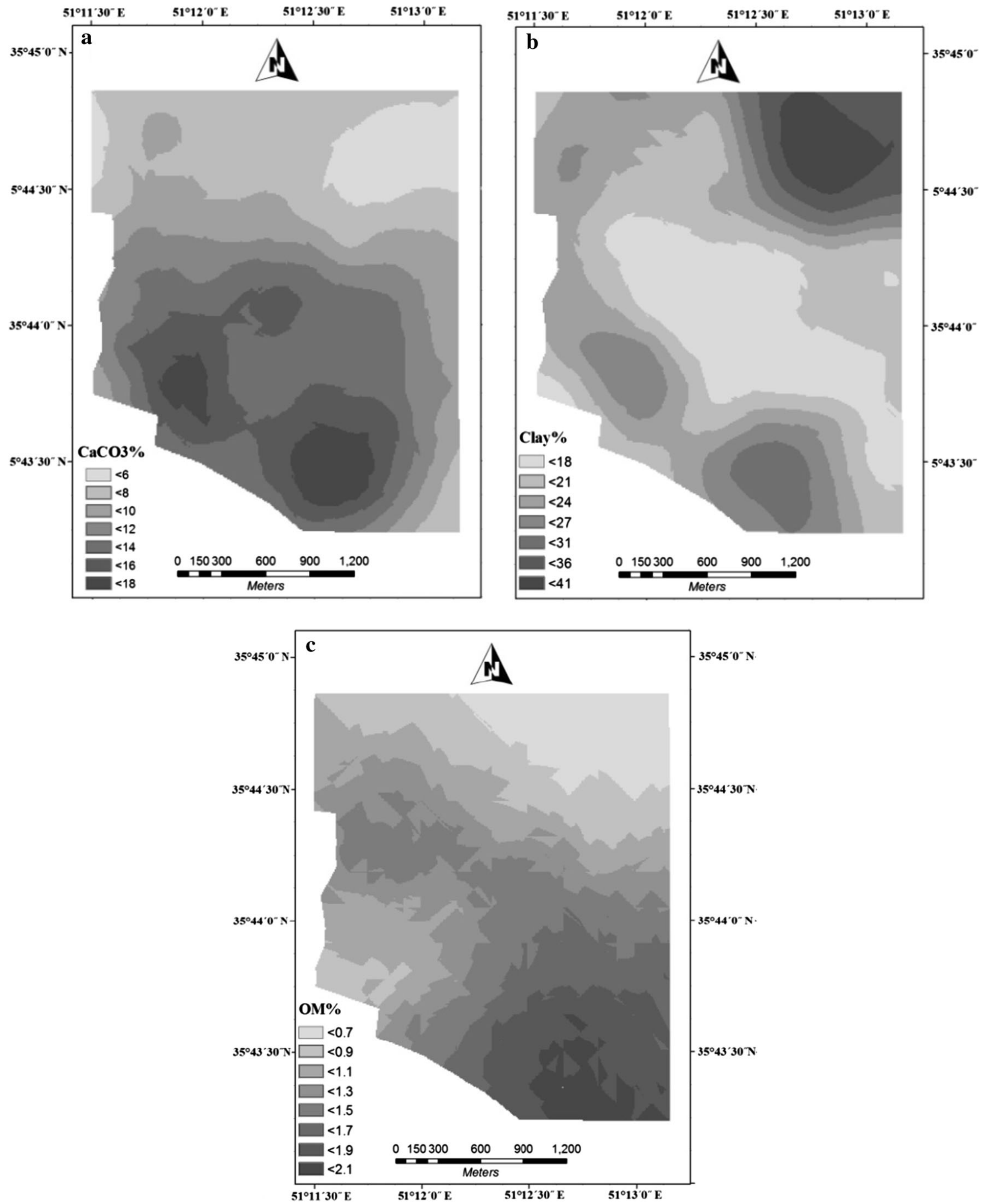

Fig. 3 Spatial distribution maps of soil parameters; the percentage of $CaCO_3$ (**a**), clay (**b**) and organic carbon (**c**)

obtained map and area location study, these metals showed high concentrations in the southern region, which can be explained by closeness of the area to highway Tehran–Karaj, with a high volume of traffic and atmospheric pollution, and large industrial plants in Iran Khodro and Saipa. It was stated that extensive anthropogenic activities related to vehicle emissions and traffic can lead to the increases in heavy metal concentrations in urban soils (Kamruzzaman 2014). It should be noted that approximately uniform distribution pattern of these metals as well as positive correlations between these elements can be resulted from the same source, which is consistent with the researches of Madrid et al. (2006), Wu et al. (2011), Sun et al. (2010) and many other studies.

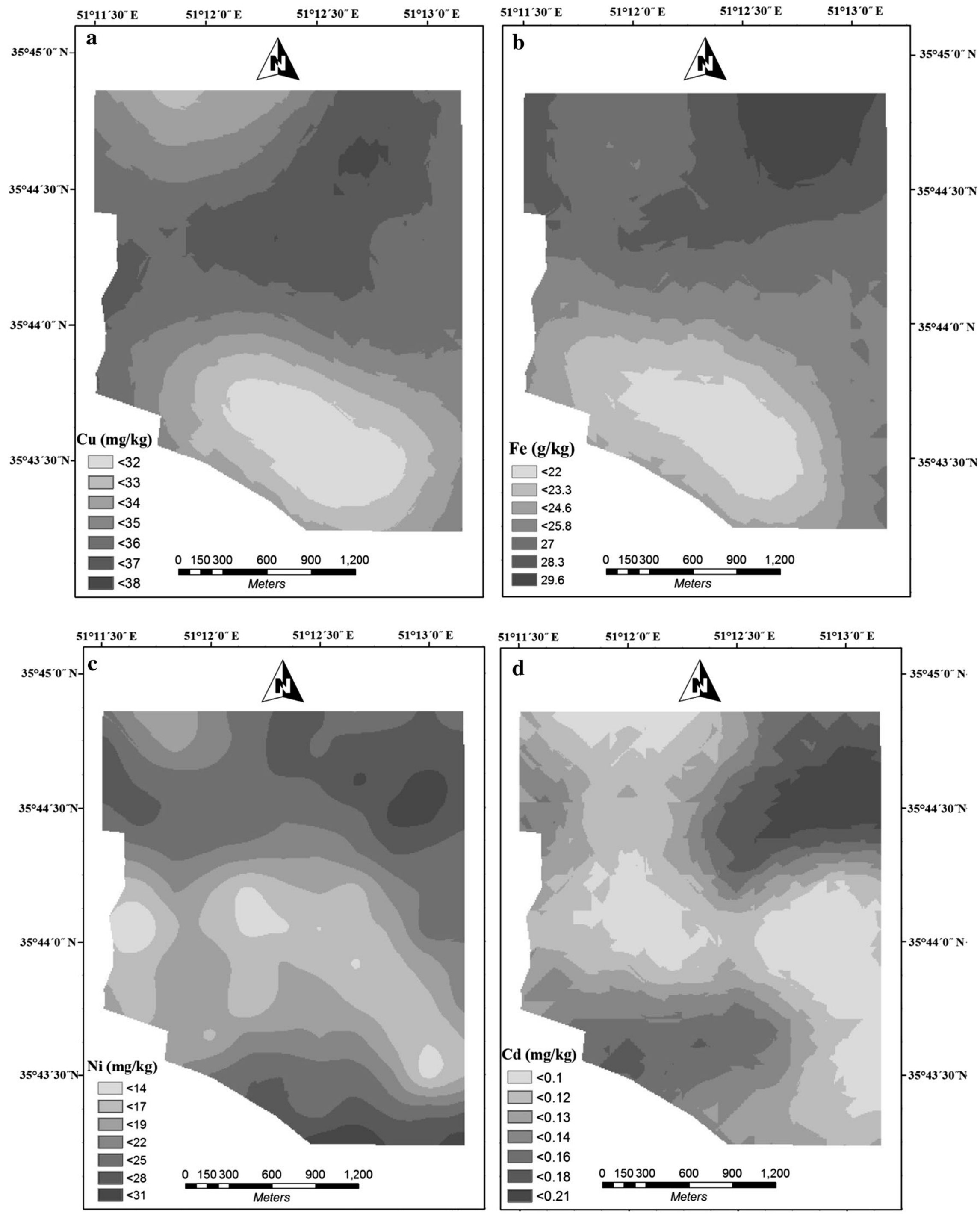

Fig. 4 Spatial distribution maps of nitric acid form of Cu (**a**), Fe (**b**), Ni (**c**), Cd (**d**), Pb (**e**), Zn (**f**) and Mn (**g**)

DTPA-extractable form of heavy metals

The results of Kolmogorov–Smirnov normality test ($p < 0.05$) showed that the DTPA form of Fe, Zn and Cu did not have a normal distribution, whereas Cu followed the normal distribution (Table 5). According to Cai et al. (2015), Fe, Cu and Mn CV values with the percentages of 28.07, 32.65 and 34.3, respectively, showed moderate variation, revealing that the effects of human activities were moderate. On the other hand, CV value of Zn was approximately two-fold as high as other DTPA forms of heavy metals (63.63), which demonstrates the major impact of extrinsic factors.

Based on the results of ANOVA, DTPA-extractable form of Zn, Cu and Mn showed that there are significant

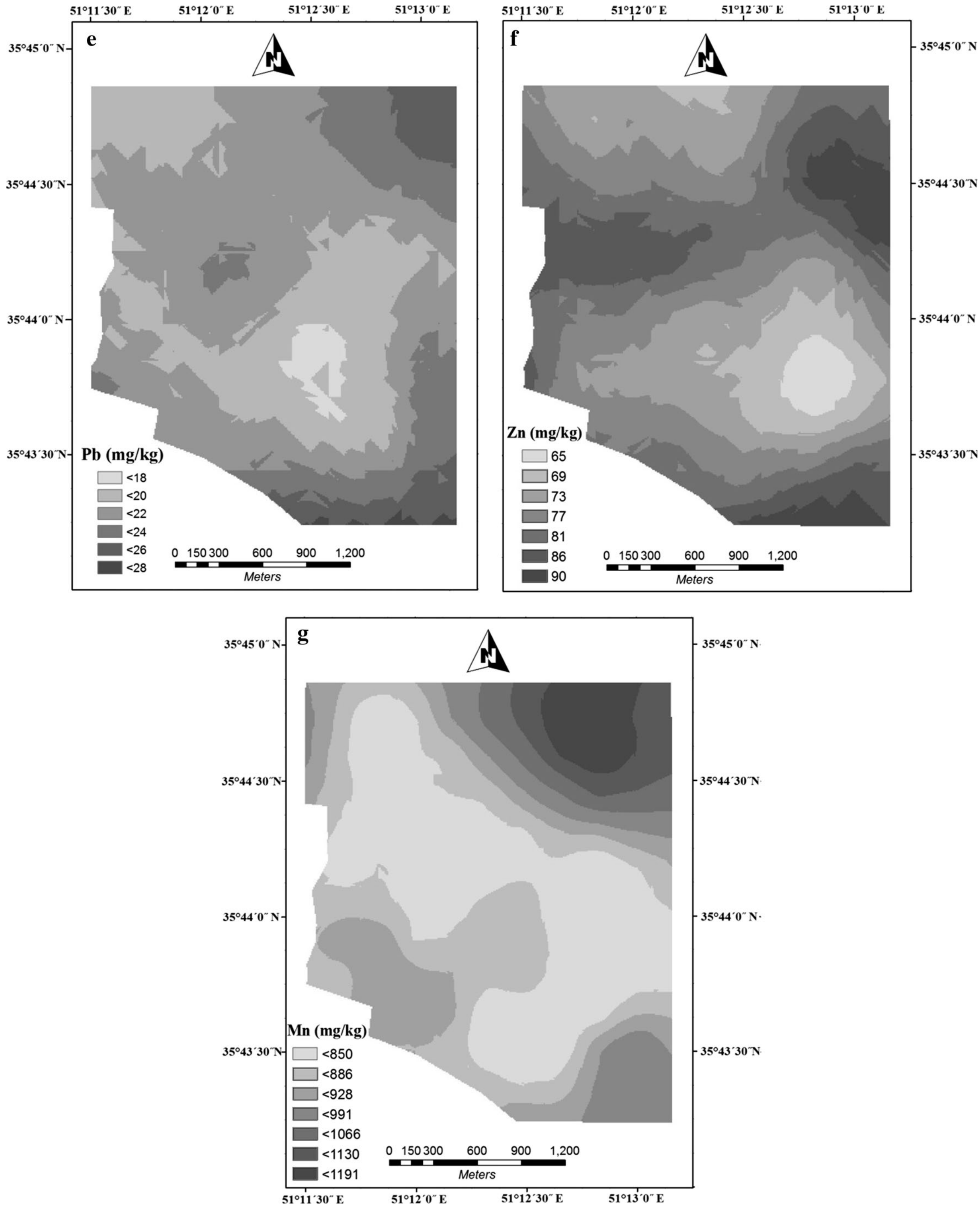

Fig. 4 continued

differences between land use types ($p < 0.05$). For Mn and Cu, comparison mean values (Table 6) showed that maximum concentrations of Mn and Cu were in the rangeland, while Zn content was higher in broadleaf and needle leaf forests ($p < 0.05$).

Mean comparison results (Table 6) demonstrated that Mn DTPA concentration in RL was significantly higher than in NF, whereas there was no significant difference between RL and BF. Regarding Pearson correlation coefficient (Table 2), which showed a significant correlation between DTPA form and nitric acid form of Mn, Mn DTPA form followed the total form of Mn. However, CV value for DTPA form was greater than that of total form of Mn; therefore, land use type and external factors have more

Table 5 Descriptive statistics parameters of DTPA form of heavy metal for 116 sample points (mg/kg)

Variable	Mean	Minimum	Maximum	SD	Skewness	Kurtosis	CV%
Zn	3.33	0.4	7.8	2.12	0.42	−1.24	63.63
Cu	0.87	0.42	1.6	0.28	0.7	−0.12	32.65
Mn	16.47	5.7	31.92	5.65	0.5	−0.17	34.3
Fe	4	1.6	6.53	1.12	−0.14	−0.84	28.07

Table 6 Mean comparison of DTPA form of heavy metals and soil properties in three types of land uses (mean ± SD, mg/kg)

	Land use		
	Rangeland (RL) ($N = 32$)	Needle leaf forest (NL) ($N = 55$)	Broadleaf forest (BF) ($N = 29$)
Cu	1.03a ± 0.28	0.79b ± 0.22	0.83b ± 0.32
Fe	4.00a ± 1.08	4.18a ± 1.16	3.65a ± 1.05
Mn	18.69a ± 5.91	15.1b ± 5.3	16.62ab ± 5.37
Zn	1.71a ± 1.39	3.68b ± 2.04	4.44b ± 1.91
OM	0.53c ± 0.40	1.05b ± 0.77	1.9a ± 1.31
clay	28.41a ± 9.13	19.42b ± 4.80	19.91b ± 5.82
$CaCO_3$	8.13b ± 5.18	10.80a ± 5.5	11.71a ± 4.48
pH	8.42a ± 0.23	8.30a ± 0.24	8.40a ± 0.25

Different letters in each column of the table indicate significant differences at $p < 0.05$ (based on Duncan test) between land use types

impacts on this form of Mn. Many studies showed the effect of total amount of heavy metals on their available form (McBride et al. 1997; Sauvé et al. 1997; Peijnenburg et al. 2000). As discussed earlier, the total concentration of Mn was mostly controlled by clay content; thus, significant correlation between Mn DTPA and clay can also be attributed to high concentration of Mn in clay minerals. Mean comparison of nitric acid form (Table 3) showed a significant difference between RL and BF, while there was no significant difference between DTPA form of Mn in RL and BF land uses (Table 6). Since the amount of organic matter in BF is almost three times more than in RL (Table 6), it can be inferred that organic matter caused an increase in the available form of Mn. While there was a positive correlation between Mn available form and organic carbon (Table 2), it seems that $CaCO_3$ decreases the impact of organic matter. Bradl 2004 reported that Mn chemical adsorption by $CaCO_3$ surface, which in turn results in the sedimentation of $MnCO_3$, may play a pivotal role in the reduction of available form of Mn. Chelating agents existing in soil cannot form stable complexes with Mn; thus, replacement of Mn by Ca and Fe may occur (Bradl 2004). However, it should be mentioned that the competition between organic matter and $CaCO_3$ led to decrease in Mn DTPA and $CaCO_3$ (−0.215) correlation rather than Mn nitric acid form and $CaCO_3$ (−0.441).

Cu DTPA also showed the highest concentration in RL; however, it was insignificant with BF ($p < 0.05$) and NF (Table 6). The bioavailability of Cu in the soil is controlled by the total concentration of Cu as well as clay and $CaCO_3$ percentage with regard to correlation coefficients, which were 0.412, 0.492 and −0.316, respectively. Renella et al. (2004) showed that carbonate amount had a remarkable impact on bioavailability of heavy metals through exchange processes, as did clay content reported by Yong (2002) and Kabata-Pendias (2011). Sorption isotherms indicate preferential adsorption of Cu onto soil organic matter associated with the clay fraction of the soil (Wu et al. 1999; Bradl 2004). Bradl (2004) investigated the adsorption of Cu onto various soil constituents and reported that at pH greater than six, the share of montmorillonite and Fe oxide was the most significant. RL with the highest percentage of clay maintains more available Cu on their adsorption exchange sites. Negative correlation between $CaCO_3$ and Cu may be originated from precipitation process and mostly Cu carbonate as Renella et al. (2004) and Amini et al. (2005) reported. Therefore, although there was no significant difference between total Cu in three land uses, it seems that different land uses resulted in significant differences in Cu DTPA forms through higher amounts of clay content and lower percentages of $CaCO_3$.

According to mean comparison (Table 6), the highest concentrations of Zn were observed in broadleaf forests which were nonsignificantly different from those of needle leaf forests, while Zn concentrations in rangeland were approximately half of those in two mentioned land uses and the differences were significant too (Table 6). There was a significant positive correlation between the percentage of

Table 7 Variogram analysis for DTPA form of heavy metals

Parameter	Model	Nugget effect (C0)	Range (A)	Sill (C0 + C)	Proportion (C0/(C0 + C	R2	RSS
Zn DTPA	Exponential	0.3	0.63	3300	0.46	0.95	1.92E−03
Mn DTPA	Spherical	13.6	37.4	20.17	0.36	0.98	5.83
Cu DTPA	Spherical	0.05	0.012	1983	0.42	0.97	1.40E−04
Fe DTPA	Spherical	0.87	1.32	800	0.66	0.82	0.01

soil organic carbon and DTPA-extractable Zn according to Pearson correlation coefficient (Table 2). Bradl (2004) reported that organic chelate agents have a tremendous effect on Zn bioavailability. Thus, higher concentrations of Zn available form is attributed to higher amount of organic matter in BF and NF. Therefore, land use types determine Zn concentrations around the region through impacting on organic matter value. Liu et al. (2006) and Hu et al. (2007) have shown that the spatial distribution pattern of soil organic matter is approximately consistent with land use types. This is completely in agreement with CV value of Zn, which was twice as high as the other elements. The effect of organic matter on heavy metals may be different. Adsorption is one of the most important processes determining Zn concentration in soils, which depends on pH, clay minerals, CEC, soil organic matter and soil type (Bradl 2004). Udo et al. (1970) stated that the strong bond between metal and low-weight organic matter like fulvic acid results in rising availability of metals.

The effect of land use on DTPA-extractable form of Fe was insignificant, although Fe concentration was higher in needle leaf forest in comparison with other land uses. Based on Pearson correlation coefficients (Table 2), DTPA-extractable Fe showed a significant correlation ($p < 0.05$) with calcium carbonate and soil organic matter, but these factors did not bring about significant differences between land uses (Table 6).

Geostatistical study of variables

Spherical model was determined as the best model for estimation of DTPA-extractable form of Fe, Mn and Cu, while exponential model fitted as the best model for estimation of Zn (Table 7). The lowest nugget/sill ratio was due to Fe (0.61), followed by Zn, Cu and Mn with the figures of 0.46, 0.42 and 0.36, respectively (Table 7). DTPA forms of all heavy metals demonstrated a moderate degree of spatial dependency (nugget/sill ratio = 0.25–0.75), which can be due to both intrinsic and extrinsic factors determining the availability of these metals. With respect to the value of correlation coefficient (Table 2) and mean comparison results (Table 6), it seems that land use type as an extrinsic factor and total concentration of heavy metals as an intrinsic factor control spatial distribution of DTPA-extractable form of heavy metals in the studied area. This is in agreement with CV value which shows a moderate variation.

Investigation of spatial distribution of DTPA-extractable form of Mn, Zn, Cu and Fe

According to Mn map (Fig. 5a), the highest values of Mn were observed in the north and southeast parts, but the central part showed lower levels. As shown by Pearson correlation (Table 2), DTPA-extractable Mn showed a strong positive correlation with the nitric acid-extractable form of Mn so that higher concentration of this element in the northern regions can be due to high amounts of total Mn in these parts. The nitric acid-extractable form of Mn and the DTPA-extractable Mn had almost similar distribution in the area (Figs. 4g, 5a). Nevertheless, in some parts, land use changed the pattern through rising organic matter. For instance, the higher amount of organic matter in southeastern parts has impact on the Mn DTPA distribution which increases the concentration of available Mn in southwestern parts.

The highest and the lowest Zn concentrations were due to the southeastern and the northeastern regions, respectively (Fig. 5b). Moreover, based on the mean comparison table (Table 6), the highest and the lowest concentrations of Zn were seen in rangeland and broadleaf land uses. In other parts, this element exhibited small variations owing to the insignificant difference between needle leaf and broadleaf land uses. Concentrations of Zn have increased in southern and southeastern parts, so that southeastern parts showed the highest value. Among the factors assessed, Zn showed the highest correlation with organic carbon amount, which can be explained by the important role chelating agents have to play in solubility of Zn in the soil (Bradl 2004). Indeed, formation of stable complex between organic acids and Zn in soil solution results in the reduction of Zn binding on adsorption sites of soil, and thus, concentration of DTPA-extractable form of Zn increases. On the other hand, clay content of soils showed negative correlation with the studied metals. The ability of clay minerals to create a bond with the metal ions is associated with cation exchange capacity (Korte et al. 1976). Clay surface charges affect Zn adsorption and thus reduce the

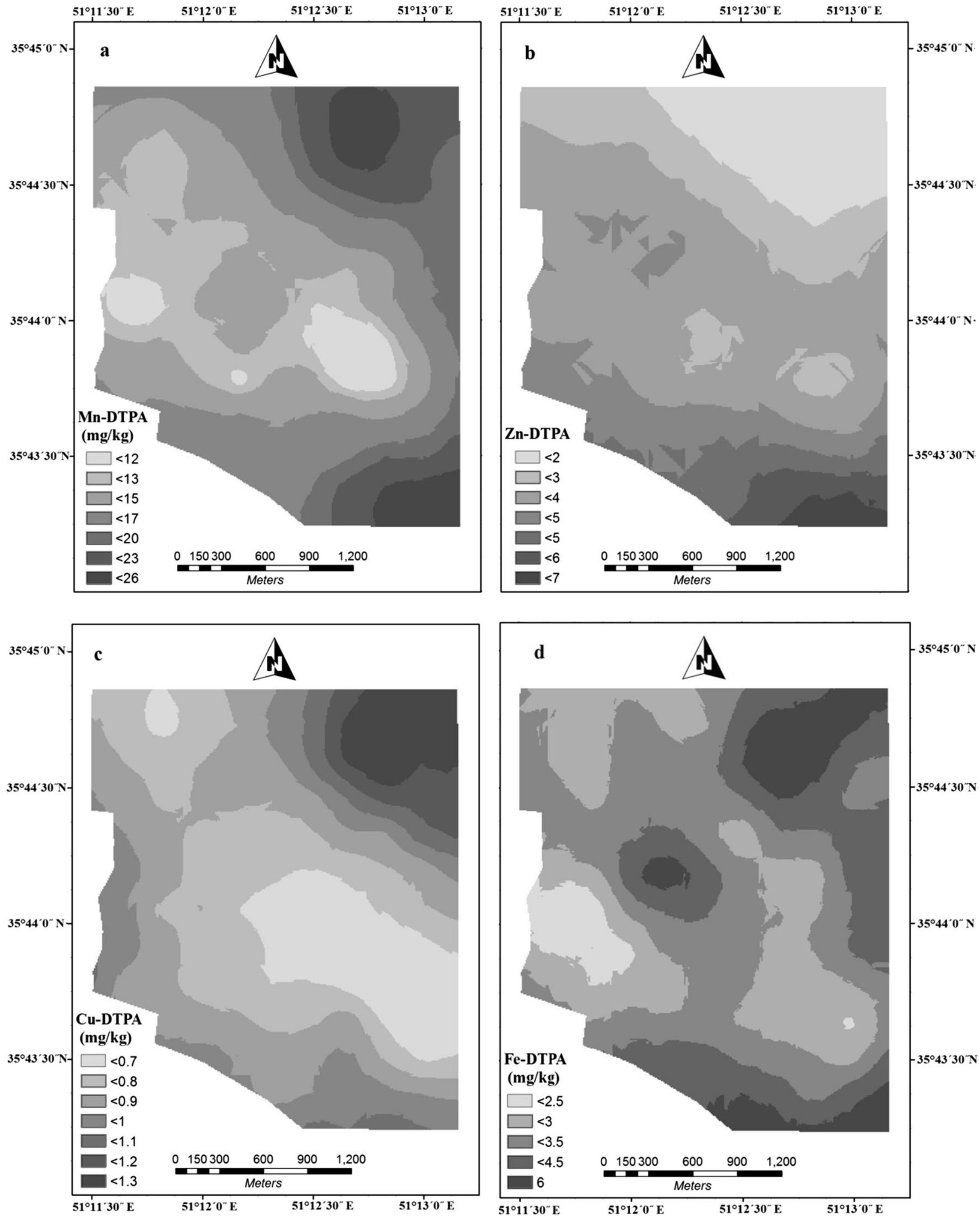

Fig. 5 Spatial distribution maps of Mn (**a**), Zn (**b**), Cu (**c**) and Fe (**d**) DTPA-extractable form

bioavailability of this element in soil solution. Thus, lower concentrations of Zn in the northern area in rangeland can be attributed to the presence of low organic matter amount and high clay content in the mentioned area (Fig. 3b, c).

The lowest amount of calcium carbonate and significant contents of clay existed in the RL (Fig. 3a, b), which led to the highest concentrations of Cu DTPA in northeastern area (Fig. 5c). Naidu et al. (2003) showed that chemical adsorption of some heavy metals by calcium carbonate can have a vital role in the reduction of their soluble forms to play. The amount of DTPA Cu showed a high correlation with Cu nitric acid-extractable form. In southern region, clay content mostly determined availability of Cu. Regarding marked correlation between total and DTPA form of Cu (Table 2), it seems that DTPA form of Cu is influenced by total concentration of Cu. Therefore, spatial distribution of available form of Cu was determined by total form of Cu along with clay content and $CaCO_3$ around the study area.

Spatial distribution showed high Fe variability in the area (Fig. 5d). Based on Pearson correlation (Table 2), Fe showed positive and negative correlations with organic carbon and calcium carbonate factors, respectively. On the one hand, the positive correlation with organic carbon led to an increase in the availability of Fe in the southern and central parts of the map. On the other hand, increasing Fe availability in the northeast region was due to its negative correlation with calcium carbonate. Emmerich et al. (1982) also showed that calcium carbonate can absorb and retain heavy metals and thus reduce the activity of soluble forms of these elements.

Conclusion

We attempted to investigate the spatial distribution of soil heavy metals in topsoils of an industrial region in different land uses. Like many other studies, this study showed an increase in concentrations of heavy metals in soils owing to industrial and urban activities. The data analysis of nitric acid-extractable form of heavy metals showed that concentrations of all heavy metals in surface soil, except for Fe, have increased compared to the background values ($p < 0.05$), indicating the anthropogenic contribution in increasing the amount of these elements in the area. Tehran–Karaj highway as well as industrial plants in the Chitgar area can be mentioned as one of the most important resources of contamination that resulted in the increase in total concentrations of heavy metals in surface soils. Geostatistical analysis demonstrates that spatial dependency of seven metals was moderate and concentrations of heavy metals were determined by intrinsic and extrinsic factors. This is verified by CV and CA. Except for Mn, there was no significant difference in nitric acid-extractable form of heavy metals among different land use types. Higher concentrations of nitric acid-extractable Mn in rangeland soils can be attributed to the higher clay contents in this land use. By contrast, DTPA-extractable amounts of Zn, Cu and Mn showed that there are significant differences between the three types of land use owing to different impacts of land use types on soil properties that affect the solubility of these elements. Among the soil factors, soil organic matter was greatly influenced by the land use type. It was also observed that there is a positive correlation, especially about Zn DTPA, between DTPA-extractable form of heavy metals and organic matter. Results of geostatistical analysis were in agreement with statistical analyses such as mean comparison analysis and correlation matrix. Spatial distribution of Cu and Mn DTPA forms in the region was almost similar. Availability of these two elements was affected by the amount of calcium carbonate and their total amount in the region. By contrast, Zn showed a different spatial distribution and its availability was under the influence of soil organic matter. Furthermore, Fe was determined by the amount of calcium carbonate and soil organic matter.

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