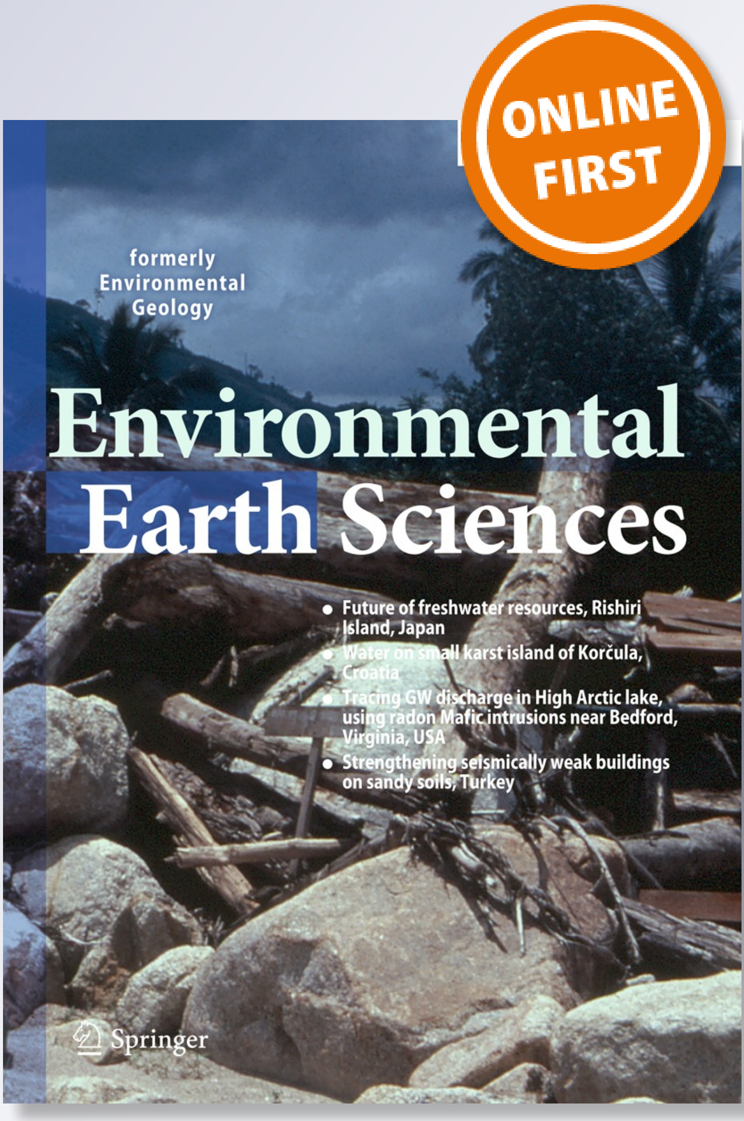
The effects of agricultural practice and land-use on the distribution and origin of some potentially toxic metals in the soils of Golestan province, Iran

Naser Hafezi Moghaddas, Hadi Hajizadeh Namaghi, Hadi Ghorbani & Behnaz Dahrazma

Environmental Earth Sciences

ISSN 1866-6280

Environ Earth Sci
DOI 10.1007/s12665-012-1753-5



Springer

Your article is protected by copyright and all rights are held exclusively by Springer-Verlag. This e-offprint is for personal use only and shall not be self-archived in electronic repositories. If you wish to self-archive your work, please use the accepted author's version for posting to your own website or your institution's repository. You may further deposit the accepted author's version on a funder's repository at a funder's request, provided it is not made publicly available until 12 months after publication.

Author's personal copy

Environ Earth Sci
DOI 10.1007/s12665-012-1753-5

ORIGINAL ARTICLE

The effects of agricultural practice and land-use on the distribution and origin of some potentially toxic metals in the soils of Golestan province, Iran

Naser Hafezi Moghaddas · Hadi Hajizadeh Namaghi · Hadi Ghorbani · Behnaz Dahrazma

Received: 6 April 2011 / Accepted: 28 May 2012
© Springer-Verlag 2012

Abstract Soil samples were collected from the agricultural lands of Golestan province, north of Iran and analyzed for 24 elements including eight toxic metals of As, Cd, Co, Cr, Cu, Pb, Se and Zn. Electrical conductivity, pH, organic matter, soil texture, calcium carbonate content as well as soil cation exchange capacity were also determined. The possible sources of metals are identified with multivariate analysis such as correlation analysis, principal component analysis (PCA), and cluster analysis. In addition, enrichment factors were used to quantitatively evaluate the influences of agricultural practice on metal loads to the surface soils. The PCA and cluster analysis studies revealed that natural geochemical background are the main source of most elements including Al, Co, Cr, Cs, Cu, Fe, K, Li, Ni, Pb, V and Zn in the arable soils of the province (more than 90 %), however, those soils which have been developed on the mafic and metamorphic rocks were considerably contributed on metal concentration (43 %). Calcium and Sr were constituents of calcareous rocks and Na and S were mainly controlled by saline soils in the north of the province. Loess deposits was also accounting for high levels of selenium concentration. Phosphorous was mostly related to application of P-fertilizers and organophosphate pesticides. The comparison of metal load and enrichment factor for dry and irrigated farmlands showed that Cd, Co, Pb, Se and Zn had higher concentrations in the irrigated lands where considerable amounts of agrochemicals had been applied. However, it also found that proximity of arable lands to urban and industrial areas resulted in higher Pb and Cd values in the irrigated agricultural sources relative to dry ones.

Keywords Toxic metals · Distribution · Land-use · Golestan · Iran

Introduction

Trace elements are accumulated locally in soils due to weathering of rock minerals. Since trace elements are essential for plants, animals, and human, the adequate level of these elements would be necessary in all agricultural products. Apart from trace elements originating in parent materials and entering the soil through chemical weathering processes, soil toxic trace elements have also many anthropogenic sources (Mitsios and Danalatos 2006). The natural input of several heavy metals to soils due to pedogenic processes has been exceeded in some local areas by human input, even on a regional scale. In particular, agricultural soils can be a long-term sink for heavy metals (Mico et al. 2006). Because some soils can have fertility levels that are out of balance, animal manures have historically been applied to soils as a fertilizer and to improve the soil's physicochemical properties (Sistani and Novak 2006). However, agricultural activities and especially application of sewage sludge, manure, mineral fertilizers and pesticides also significantly contribute to the trace metal status of agroecosystems (Kabata-Pendias and Mukherjee 2007).

N. Hafezi Moghaddas (✉) · B. Dahrazma
Faculty of Earth Sciences, Shahrood University of Technology, Shahrood, Iran
e-mail: nhafezi@shahroodut.ac.ir

H. Hajizadeh Namaghi
School of Mining, Liaoning Technical University, Fuxin, China

H. Ghorbani
Department of Soil Sciences, Faculty of Agriculture, Shahrood University of Technology, Shahrood, Iran

Published online: 18 July 2012

Author's personal copy

The ever-growing world population requires intensive land use for the production of food, which includes repeated and heavy input of fertilizers, pesticides, and soil amendments (Bradl 2005). A quantitative inventory of heavy metals input to agricultural soils is necessary to determine the scale and relative importance of different sources of metals, either deposited from the atmosphere or applied to farmlands (Nicholson et al. 2003). Because trace metal accumulation in soils will probably have a long residence time, it is important to understand reasons for the accumulation and to determine soil factors controlling their mobility in the soil and more importantly their bioavailability to the plants. An understanding of these factors is critical for the development of physical or chemical remediation strategies or adjustments in manure management practice to reduce trace metal accumulation (Sistani and Novak 2006).

The behavior of heavy metals in soil can be different due to the variation in both physicochemical properties of the soil and the activities of soil organisms associated with land-use change (Bradl 2004). The comparison of metal levels has been studied in a wide range of land types in/and agricultural lands (Luo et al. 2007; Huang and Jin 2008; Anguelov and Anguelova 2009; Marzaioli et al. 2010; Bai et al. 2010; Acosta et al. 2011).

The present paper is trying to highlight the role and contribution of long-term agricultural practice on heavy metals distribution across the arable lands. Due to the presence of large arable lands, considerable amounts of fertilizers as well as pesticides are being used in the studied area, which could contain high amounts of potentially toxic elements. The objective of this work was to investigate the source of 24 elements emphasizing eight toxic metals, namely, As, Cd, Co, Cr, Cu, Pb, Se and Zn in agricultural soils of Golestan province. The physicochemical characteristics of soil were also examined in relation to the heavy metal concentrations. A final objective of this study was to determine if the concentration of selected metals has changed with land types to evaluate the effects of land-use in the irrigated and dry farmlands.

Materials and methods

Study area description

The province of Golestan is located in the north of Iran and south of Caspian Sea. The surface area is over 20,000 km^2 (approximately 1.3 % of the total area of Iran). The climate of province is variable; the southern part has a typical mountainous climate, the central and southwestern regions have a temperate Mediterranean climate, and the northern part is semiarid or arid. The absolute minimum daily temperature is −1.4 °C and the maximum 46.5 °C. Annual rainfall ranges from 250 to 700 mm. The suitable climate, supply adequate amounts of water and therefore, appropriate fertile lands results to extension of agricultural activities in the Golestan province (Fig. 1). The total area under cultivation within the province is estimated at 730 thousands hectares from which about 33.4 % is irrigated and remaining 65.6 is dry lands. Wheat, cotton and summer crops are the main products in Golestan and the area is one of the most important parts of the country due to extensive agricultural activities. Industries are also young and since soils are fertile in central parts of region, population has evenly distributed. This study has focused on arable lands in central parts of province where agricultural activities are dense. Other types of farming in other parts (north and south) are local and spars and have no any considerable affect on regional soil pollution of study area. The soil quality in central parts is influenced by geological materials from mountainous regions in south and vast eolian dry lands (loess deposits) in north. The main lithologic units in southern regions are igneous and metamorphic rocks while northern parts composed of vast thick loess deposits. Therefore, groundwater availability is restricted in northern dry lands. Rainfall and groundwater irrigation is much higher in southern and central parts of the province.

Soil sampling

Soil samples were collected from arable lands. A total of 198 agricultural soil samples were collected at the depth of 0–30 cm and 18 soil samples were also taken from the depth of 100 cm at the same time. The physicochemical parameters such as electrical conductivity (EC), pH, organic matter (OC) and soil texture were measured at Zaravand Lab Company, Mashhad, Iran. Among the surface soil samples, 74 samples were chosen from irrigated farmlands and 46 samples were selected from dry arable lands. The irrigated farmlands in this area usually are cultivated more than one times, then it is expected that irrigated farmlands have more contaminant bearing potential than dry lands due to higher applications of different agrochemicals such as fertilizers and pesticides. It is also given higher priority to the areas with higher organic matter and clay contents as these two parameters serve as a sink to heavy metals. Therefore, more samples were chosen from these areas. Geographical positions of the selected agricultural samples are shown in Fig. 2. Most of arable lands and irrigated agricultural soil samples are located in southern parts of the province while most dry ones have occurred in northern parts of the area.

The selected samples were air-dried and sieved through a 2-mm polyethylene sieve and ground to fine powder. Then heavy and trace metals in soils from 138 sampling

Author's personal copy

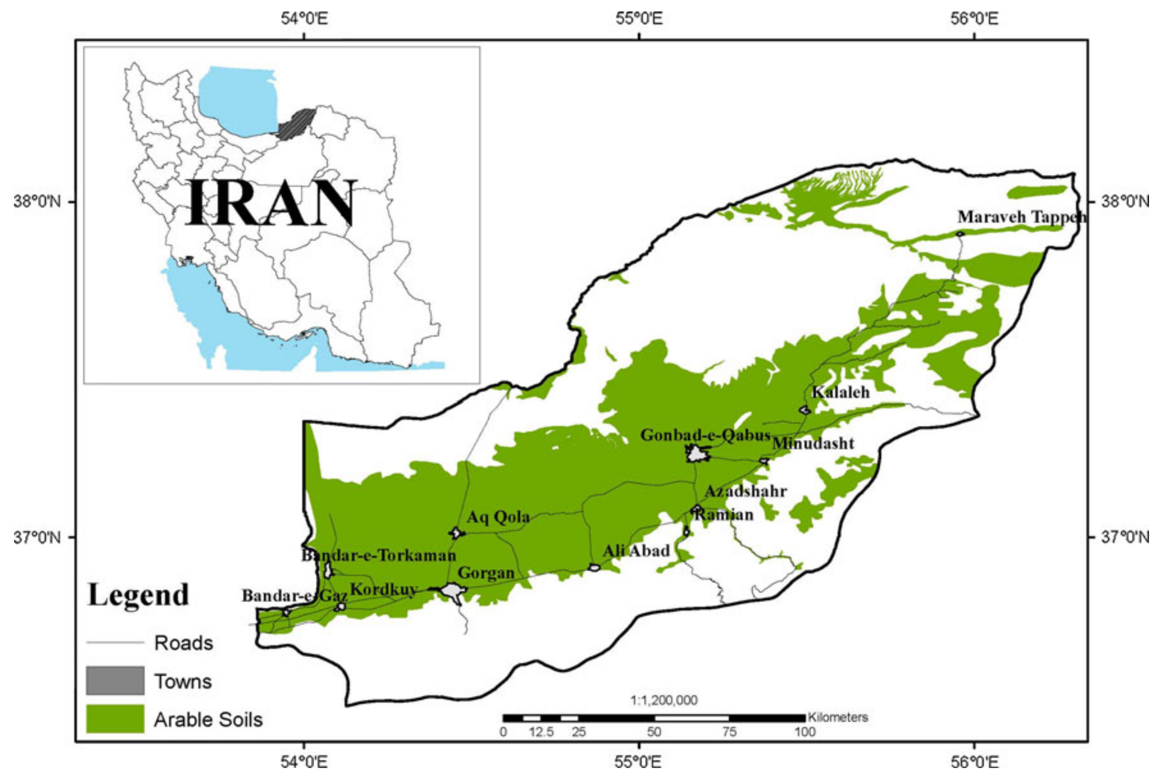


Fig. 1 The map of Golestan province showing arable lands

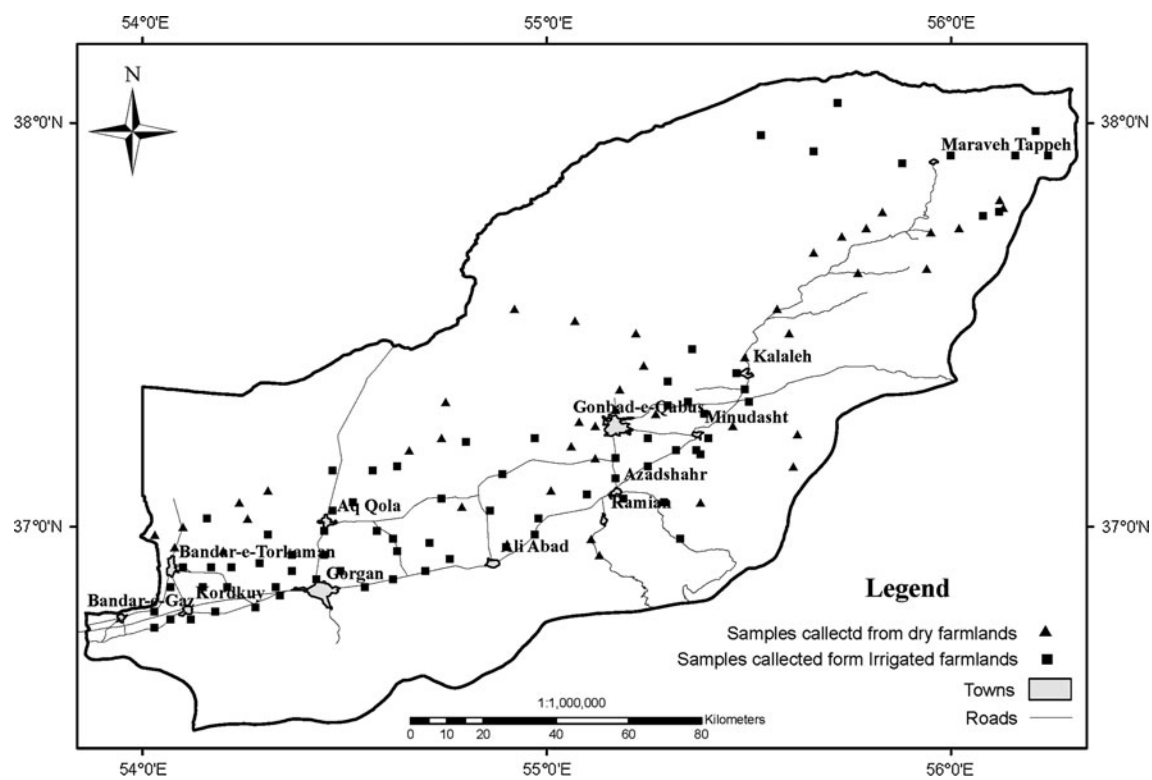


Fig. 2 Geographical position of sampling points

Author's personal copy

points (120 samples from 0 to 30 cm and 18 samples from 1 m depth) were analyzed using ICP method at LabWest Minerals Analysis Pty Ltd (an accredited Australian laboratory).

Statistical analysis

The relationships of different heavy metals were determined by calculating the correlation coefficients of all possible non-reciprocal metal pairs (28 pairs), principal component analysis (PCA) and by the cluster analysis. The correlations between physicochemical properties and heavy and trace metals were carried out to determine the influence of physicochemical parameters in terms of heavy metal distribution. Non-zero correlation coefficient with accompanying $p \leq 0.05$ is considered statistically significant at the 95 % confidence limit. PCA is used to reduce data and to extract a small number of latent factors for analyzing relationships among the elements (Wang et al. 2009). Prior to the PCA analysis, heavy metal concentrations were log-transferred to minimize the influence of high values. PCA was conducted using factor extraction with an eigenvalue >1 after Varimax rotation using SPSS 16.0 version for Windows. The presence of outliers in the dataset was determined using the Tukey (1977) box plot method.

Results and discussion

Descriptive statistics

Brief descriptive statistical data of measured soil parameters in the studied area are shown in Table 1. Soil pH range is limited and varies from 6.9 to 8.5 with a mean value of 7.9 ± 0.2. The agricultural soils in the west part of the province near coastal plains of Caspian Sea had slightly higher pH values. Such neutral soil reaction would limit metal mobility in soils. In general, organic matter contents are low in all soils and range from 0.34 to 2.89 % with a mean value of 1.13 ± 0.55 %. OC in eastern parts of the study area has lower values (<1 %) compared to central and western parts. Soil textures of the agricultural samples are mostly classified as clay, clay loam and silty clay loam (Fig. 3). Electrical conductivity ranges from 0.36 dSm^{-1} to 47.7 dSm^{-1} and have arithmetical mean of 3.69 ± 5.8 dSm^{-1}. However, EC was low in most of the samples and only few higher values have measured in some samples in the north of study area. Cation exchange capacity (CEC) is varied and ranged from 6.12 Cmol(+) kg^{-1} to 54.3 Cmol(+) kg^{-1} with a mean value of 22.13 ± 9.78 Cmol(+) kg^{-1}. Central parts of the study area have greater CEC values. $CaCO_3$ is low in most of the samples and are ranged from 1.76 to 36.4 % with a mean value of 16.73 ± 7.2 %.The greater $CaCO_3$ values have measured in some parts of the northern study area.

Multivariate analysis approaches

Correlation matrix

Some of heavy metals are significantly correlated with each other and with soil physicochemical properties. The degree of correlation for all possible non-reciprocal element pairs (28 pairs) and their correlation coefficients were calculated after excluding statistically identified outliers and the results are presented in Table 2. Cobalt is significantly and positively correlated with Cr ($r = 0.87$), Cu ($r = 0.85$) and Zn ($r = 75$) with $p \leq 0.01$. Chromium is significantly and positively correlated with Cu ($r = 0.88$) and Zn ($r = 70$) with $p \leq 0.01$. Cupper is also significantly and positively correlated with Zn ($r = 0.80$) with $p \leq 0.01$. The relationships of As and Cd with Se is shown to be insignificant.

The correlations ($p \leq 0.01$) of selected metals with organic matter and fine fractions are rather more considerable than other parameters. The relationships of metals with other soil parameters are very poor or negatively correlated indicating respective role of soil organic carbons and clay contents in the distribution of toxic metals. Lack of correlation of CEC with most metals is possibly due to the absence of metals in the soil exchangeable phases. On the other hands, since the concentrations of major cations in the soils are normally much greater than heavy metals, then it seems that CEC tends to be more affected by those metals than potentially toxic metals.

Principal component analysis

Principal component analysis (PCA) is a dimension reduction technique that takes correlated attributes, or variables, and identifies orthogonal linear recombinations (PCs) of the attributes that summarize the principal sources of variability in the data (Officer et al. 2004). PCA was used to quantify elements sources in agricultural soil samples. The obtained factors were rotated using a Varimax-normalized algorithm, which allows an easier interpretation of the principal component loadings and maximization of the variance explained by the extracted factors. Table 3 displays the factor loadings with a Varimax rotation, as well as the eigenvalues. Six principal components were extracted from the available dataset that explained a total variance of approximately 82.3 %.

Factor 1 is dominated by Al, Co, Cr, Cs, Cu, Fe, K, Li, Ni, Pb, V and Zn and accounts for 42.9 % of total variance. The distribution of these elements is mainly controlled by

Author's personal copy

Table 1 Brief statistical data of soil metal concentrations and properties (metals in ppm)

Soil parameters	Minimum	Maximum	Mean	SD	Skewness	Kurtosis
As	3.50	15.57	9.52	2.02	−0.24	0.87
Cd	0.025	0.28	0.067	0.056	1.37	1.37
Co	7.20	25.50	13.22	3.20	1.25	2.58
Cr	38.00	110.0	61.53	12.22	1.15	2.80
Cu	11.50	52.90	23.62	6.58	1.40	3.67
Pb	7.30	21.80	13.16	3.21	0.73	0.04
Se	0.17	1.23	0.55	0.22	0.88	0.408
Zn	41.90	125.00	70.63	16.26	0.573	0.264
pH	6.9	8.5	7.9	0.22	−1.31	3.85
EC (dSm^{-1})	0.36	47.70	3.69	5.82	4.39	28.29
OC (%)	0.34	2.89	1.13	0.55	1.07	1.25
Clay (%)	12.00	64.00	37.08	10.725	0.12	−0.256
CEC (Cmol(+) kg^{-1})	6.12	54.30	22.13	9.78	0.78	0.519
$CaCO_3$ (%)	1.76	36.40	16.73	7.20	0.12	−0.025

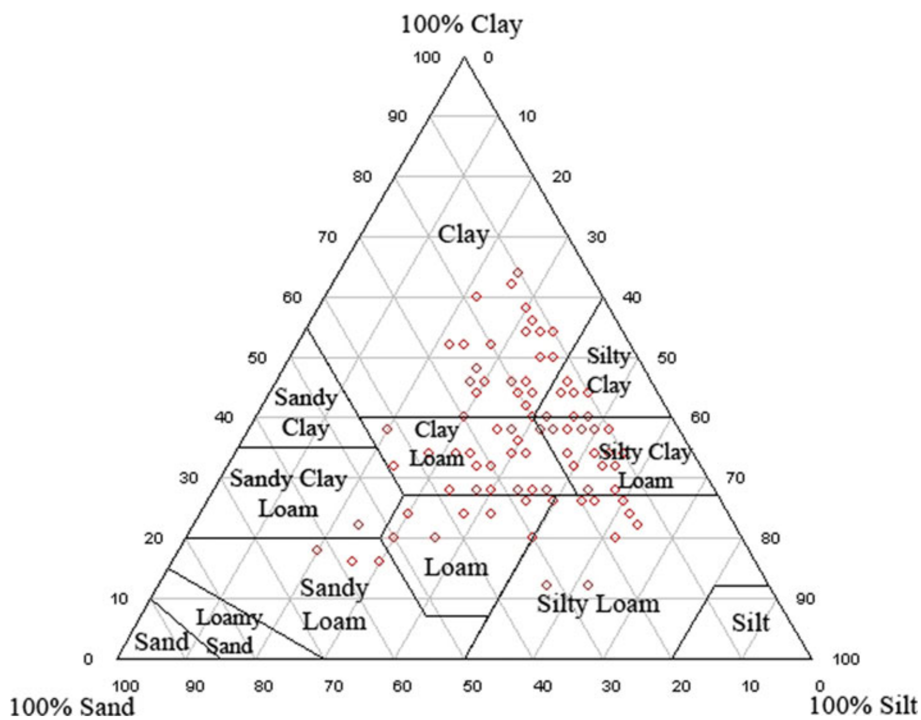


Fig. 3 Soil samples textural classification

natural parent materials. The higher loadings related to mafic and metamorphic rocks, which are dominant in the southern parts of the province and agricultural soils are directly affected by pedological processes of such rocks. Mico et al. (2006) is also believe that lithogenic factors are most important component in metal loads of agricultural soils of Alicante province in Spain.

Factor 2 is strongly associated with only Ca and Sr (10 % of total variance). Both geochemical and biochemical characteristics of Sr are similar to those of Ca and geological occurrence of it, is associated mainly with calcareous rocks (Kabata-Pendias and Mukherjee 2007). There are substantial carbonate rocks sources in the southern parts of the region. Therefore factor 2 explains another natural source in the studied soils.

Factor 3 is responsible for 9.2 % of the total element variables and indicated great correlation with Na and S. This factor is related to saline soils in the north of the area. The northern parts of Golestan province are extensively covered by old coastal plains composing silt and clay where agricultural practices are being performed in forms of dry farming.

In general, PC1, PC2, and PC3 in the rotated component matrix of the agricultural soils depicted the natural

Author's personal copy

Table 2 Correlation of soil metals and soil physicochemical properties

	As	Cd	Co	Cr	Cu	Pb	Se	Zn	pH	EC	OC	Clay	CEC	$CaCO_3$
As	1													
Cd	0.30**	1												
Co	0.27**	0.38**	1											
Cr	0.39**	0.50**	**0.87****	1										
Cu	0.33**	0.51**	**0.85****	**0.88****	1									
Pb	0.39**	0.48**	0.53**	**0.64****	**0.62****	1								
Se	0.12	0.13	0.32**	0.31**	0.27**	0.24*	1							
Zn	0.26**	0.56**	**0.75****	**0.70****	**0.80****	**0.67****	0.39**	1						
pH	−0.10	−0.06	−0.20*	−0.30**	−0.21*	−0.25**	0.005	−0.04	1					
EC	−0.07	−0.16	−0.14	−0.11	−0.11	−0.21*	0.11	−0.09	0.08	1				
OC	0.30**	0.29**	0.39**	0.43**	0.37**	0.39**	0.56**	0.42**	−0.16	−0.17	1			
Clay	0.31**	0.37**	0.58**	**0.70****	0.47**	0.57**	0.34**	0.57**	−0.08	−0.15	0.42**	1		
CEC	−0.15	0.15	0.01	0.06	0.08	0.33**	0.06	0.06	−0.16	−0.25**	0.19*	0.12	1	
$CaCO_3$	0.08	−0.03	−0.07	−0.04	−0.09	−0.18	0.23*	0.04	0.19*	0.07	0.17	0.02	−0.44**	1

Bold values are statistically significant

* Correlation is significant at 0.05 confidence limit

** Correlation is significant at 0.01 confidence limit

geochemical associations of elements in soils derived from their parental materials.

Factor 4 is correlated very strongly with P and somehow to Se and explains 6.9 % of the total variance. The higher loadings of phosphorus indicate increased elemental concentration due to application of phosphorus fertilizers as well as organophosphate pesticides in the agricultural soils of Golestan province. Selenium is probably originated by loess deposits in the area, which naturally has high concentration in soils of Golestan province (Hafezi Moghaddas et al. 2010; Semnani et al. 2010).

Factor 5 is loaded with As and Mo and account for 6.8 %. This factor source may be explained by contribution of many sources but the probability of anthropogenic sources is more likely.

Except for Ti and to less extent for Mg, no significant loading value was obtained for any variable of *Factor 6*, which is responsible for 6.5 % of total variance. These two elements are indicative of erosion in some resistant igneous rocks, which exist in the southern parts of the province.

Factor loadings are represented in binary diagrams (PC1 vs. PC2, PC1 vs. PC3 and PC1 vs. PC4) in Fig. 4. It can be seen from these diagrams that most of the elements are related to parent materials like mafic and metamorphic rocks, sandstone and shales. Magnesium in the first and second components and Se in the third one are showing mixed sources.

Cluster analysis

In order to discriminate distinct groups of studied elements as tracers of natural or anthropogenic source, a hierarchical cluster analysis was performed on the 24 elements of interest (Fig. 5). The distance cluster represents the degree of association between elements. The lower value on the distance cluster is showing more significant for the association.

A cluster analysis was applied to reorganize the datasets (samples) into homogenous groups based on their geochemical properties (Salonen and Korkka-Niemi 2007). Cluster tree of all element variables in soil was produced by the Pearson's correlation coefficient and the Ward method (Fig. 5). The method of Ward is the best performing hierarchical clustering method, and even performs well for observation clustering (Templ et al. 2008). The produced cluster analysis is rather in good agreement with principal component analysis results. The following three groups can be identified:

Group 1 consisted of Al, V, K, Cs, Co, Fe, Zn, Li, Cr, Ni, Cu, Pb, Cd and Mn. The relationships within this group are very strong, and they are mainly controlled by geology. However, some subgroups of Al, V, K and Cs (felsic rocks), Co, Fe, Zn and Li (intermediate rocks), Cr, Ni, Cu

Author's personal copy

Table 3 Values of the six extracted factor loadings for 24 elements

Elements	PC1	PC2	PC3	PC4	PC5	PC6
Al	**0.962**	0.027	0.04	0.023	0.082	−0.105
As	0.477	−0.098	−0.152	−0.026	**0.687**	0.136
Ca	−0.325	**0.861**	−0.045	0.056	−0.096	−0.083
Cd	0.582	0.105	−0.247	0.177	0.095	0.082
Co	**0.848**	−0.219	−0.022	0.283	0.202	0.016
Cr	**0.934**	−0.199	0.044	0.037	0.15	0.091
Cs	**0.837**	−0.085	0.157	−0.307	−0.152	0.168
Cu	**0.834**	−0.344	0.045	0.21	0.16	0.017
Fe	**0.836**	−0.123	−0.078	0.23	0.266	−0.005
K	**0.888**	0.038	0.125	−0.021	−0.107	0.068
Li	**0.865**	0.164	0.148	0.07	0.11	−0.182
Mg	0.355	0.342	0.509	−0.104	−0.089	**0.507**
Mn	0.424	−0.445	0.004	0.26	−0.092	0.347
Mo	0.075	−0.109	0.163	0.07	**0.886**	0.067
Na	0.036	0.036	**0.91**	−0.026	0.071	0.049
Ni	**0.896**	−0.247	−0.005	0.141	0.153	0.08
P	0.172	0.101	−0.035	**0.865**	0.043	0.176
Pb	**0.708**	−0.37	−0.222	0.142	−0.014	−0.216
S	−0.047	0.082	**0.893**	0.046	0.018	−0.104
Se	0.402	0.102	0.141	**0.508**	0.04	−0.485
Sr	0.055	**0.879**	0.239	0.164	−0.14	−0.077
Ti	−0.027	−0.206	−0.042	0.188	0.235	**0.850**
V	**0.95**	−0.014	0.052	0.006	0.133	0.149
Zn	**0.867**	−0.093	−0.012	0.387	0.023	−0.117
Eigenvalue	11.03	2.82	2.01	1.54	1.28	1.08
Variation (%)	42.9	10	9.2	6.9	6.8	6.5

Bold values are statistically significant

Extraction method: PCA, Rotation method: Varimax with Kaiser normalization

and Pb (mafic rocks) and Cd and Mn (probably sandstone and shale interbedded with coal) could also be identified. The effects of anthropogenic sources for this group are poor.

Group 2 comprised As, Mo, Ti, P and Se. These elements have both natural and anthropogenic sources. This group is in close relationship with group 1. Phosphorous is mostly originated from application of chemical fertilizers, pesticides or manure while other metals of this group (except Ti) are enriched by both sources.

Group 3 consisted of Ca, Sr, Mg, Na and S. These elements are mainly enriched in saline soils in the north or limestone rocks in the south of the studied area.

Effects of land-use in metal concentrations

Box plots were used to describe the difference between metal content of different groups. Box plots illustrating distributions of metals among samples collected from irrigated farmlands and dry farmlands are shown in Fig. 6. It seems that the concentrations of two sample types are similar in two groups. Statistical analyses were carried out to see if there were differences in concentrations of heavy metals due to land-use type. A two-sample t test was conducted using the SPSS 16.0 Statistical Software to determine whether the difference between two datasets is statistically significant or not (Neupane and Roberts 2009). This test compares mean and variance of the two datasets to determine a p value. Smaller p values indicate the greater probability of difference in mean and variance of the two datasets. In general, $p \leq 0.05$ is considered statistically significant at the 95 % confidence limit. The two datasets of concentration of a heavy metal measured in different land-use were used to test whether the concentration of that particular metal is significantly different. The t test results for two groups are given in Table 4.

Co, Se and Zn are shown statistically different concentrations in samples which were collected from irrigated farmlands and dry farmlands. All of them are enriched in the irrigated farmlands. The concentrations of other studied

Author's personal copy

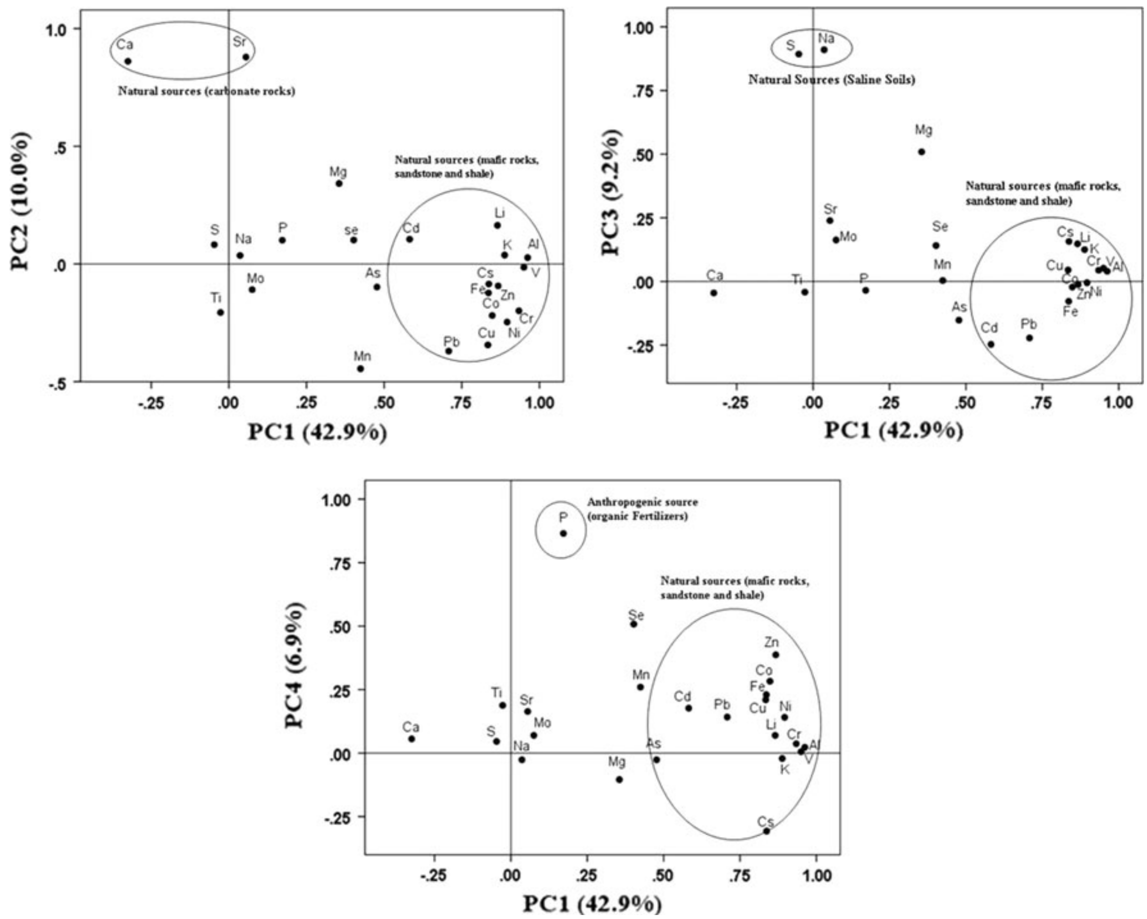


Fig. 4 Loading plots of elements in agricultural soils (PC1 vs. PC2, PC3 and PC4)

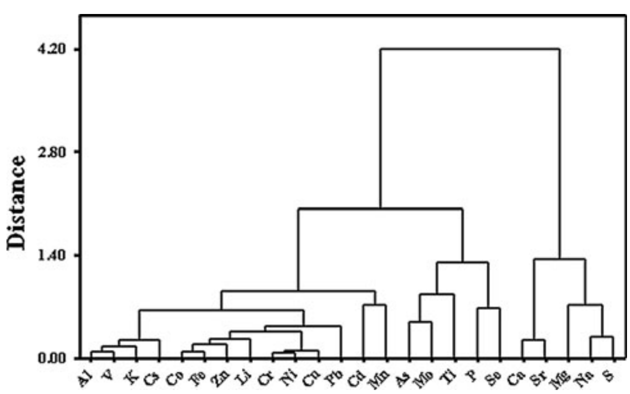


Fig. 5 Cluster tree of variables for agricultural soils (measure: pearson's correlation coefficient; linkage method: ward)

metals (As, Cd, Co, Cr, Cu and Pb) are not statistically different. The significantly higher Co, Se and Zn contents in the samples of irrigated farmlands compared to the dry farmlands requires either a secondary anthropogenic source in the former or a depletion of naturally occurring of mentioned metals in the latter. Studying applied agro-chemicals in the region is showed that pesticides and manures are not enriched with Co, Se and Zn. Therefore, geochemical background is the main source of difference in soil metal concentrations between two agricultural land types. Mafic rocks in the southern parts of the study area which most fertile soils are formed near them are seems to be a possible sources of Co and Zn and loess deposits which consists most arable lands of the study area, is accounted for higher values of Se. However, Yu et al. (2008) found that the main factor of accumulation of the heavy metal is lithological factor in arid agricultural areas while anthropogenic factors has major contribution in chemical properties of irrigated soils in central Gansu province, China.

Enrichment factor (EF)

The enrichment factor is the relative abundance of a chemical element in a soil compared to the reference matter. EFs are calculated based on different reference materials such as earth crust (Krishna and Govil 2008l; Kim and Kim 1998), local soil geochemical background (Acosta et al. 2009; Yu et al. 2008; Salvagio et al. 2002 etc.), etc. Useful environmental information that affects the

Author's personal copy

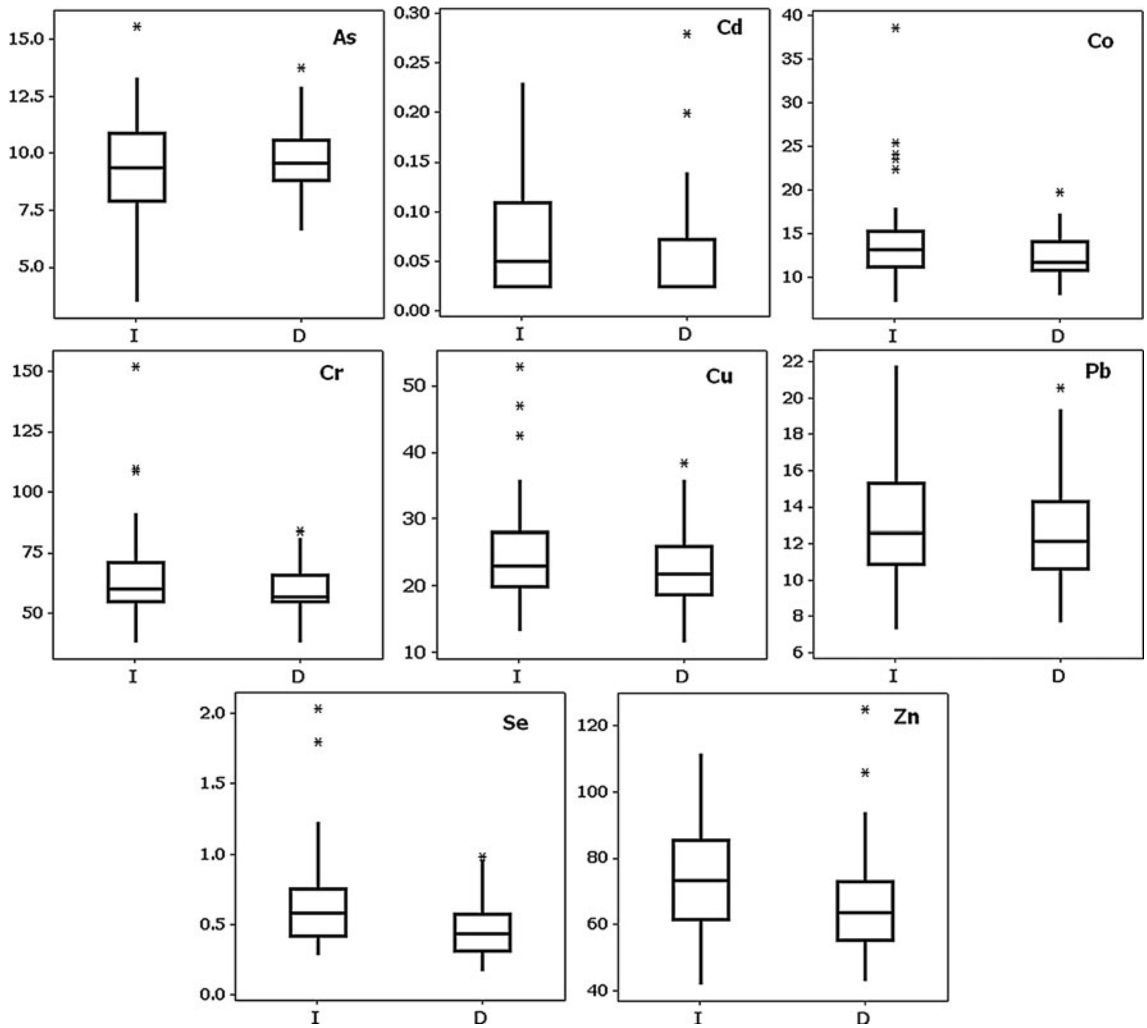


Fig. 6 Box plots depicting distributions of toxic metals between two agricultural land-uses

soil ecosystem owing to human activity can be extracted by studying and examining the relevant elemental concentrations and their changes from top-soil and sub-soil at each site (Liao et al. 2007). The enrichment factor is defined as the concentration ratio of a given element and the normalizing element in the given sample divided by the same ratio in reference material as follows:

$$EF = \frac{(M/Al)_{sample}}{(M/Al)_{reference}}$$

where EF is Enrichment factor, $(M/Al)_{sample}$ is the metal to Al ratio in the sample of interest; $(M/Al)_{reference}$ is the reference value of metal to Al ratio. References materials are related to average concentration of 18 samples collected from 1 m depth of arable lands. Aluminum has been used as normalizing element. Metal concentrations can be normalized to other factors, which are measured in the same sample (Cooke and Drury 1998). Deeper horizon samples are close to natural background and parent material characteristic in the region and any exceeding values in the surface could be considered as a sign of anthropogenic contamination, mainly resulted from agricultural practices. Box plot diagrams (Fig. 7) were used to show general assessment of samples from surface enrichment point of view and also in comparison EF values between samples collected from irrigated and dry farmlands (Fig 7). The comparison of these two types of samples can clarify if application of agrochemicals and soil amendment can affect metal concentrations in the surface soils of the study area. EF values greater than one indicates some enrichment corresponding mainly to anthropogenic effects; whereas an EF value less than one means depletion. Figure 7 shows that EF values for Cd, Pb and Se in most of the samples are higher than other metals whereas EF for Co is least among the studied metals. Although natural background of study area has high levels of Cd and Pb, however, high EF values for these two metals relative to deeper horizons could be due to addition of such metals

Author's personal copy

Table 4 Two-sample *t* test result showing significant variation in concentration at $p < 0.05$

Metal	Type	Mean	SD	*p* value
As	I	9.34	2.26	0.186
	D	9.81	1.56	
Cd	I	0.071	0.05	0.315
	D	0.061	0.06	
Co	I	14.03	4.54	**0.035**
	D	12.47	2.53	
Cr	I	63.65	17.04	0.198
	D	60.09	9.63	
Cu	I	24.23	7.14	0.201
	D	22.64	5.49	
Pb	I	13.35	3.22	0.414
	D	12.85	3.21	
Se	I	0.64	0.31	**0.001**
	D	0.47	0.19	
Zn	I	73.60	15.80	**0.011**
	D	65.86	16.02	

Bold values are statistically significant

I irrigated farmland

D dry farmland

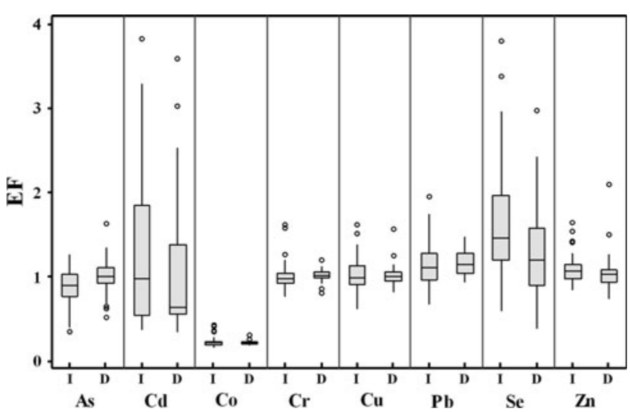


Fig. 7 Enrichment factors (EFs) of samples collected from irrigated farmlands (I) and dry farmlands (D) of agricultural soils in Golestan province

from anthropogenic sources such as fertilizers and pesticides. The major sources of Cd pollution are atmospheric deposition and P-fertilizers (Kabata-Pendias and Mukherjee 2007). Wei and Yang (2009) also believe that Cd in agricultural soils of China is mainly originated from fertilizers and pesticides. Phosphorous fertilizers are applied more to the irrigated farmlands. The close proximity of arable lands to urban and industrial areas could account for higher Pb and Cd values in the irrigated agricultural sources particularly for farmlands. Elevated EF values for Se are probably due to flux from natural sources in the region. As mentioned before, high levels of Se have been observed in loess deposits of Golestan province, which have close associations with arable lands in the studied area. However, samples of irrigated soils were slightly more enriched than dry ones. The lower values for Co are also related to their natural sources. Mafic and metamorphic rocks in the southern parts of the province are considerably enriched with Co. Therefore, its concentration is less in surface horizons compared to deeper samples. EF values for As, Cr, Cu and Zn are near to 1 indicating natural enrichment for these metals in the agricultural soils of Golestan province. There is also no significant difference for EF values mentioned metals between samples collected from irrigated and dry farmland indicating dominance of natural background of studied soils for these metals.

Conclusion

This study also elucidated heavy metal contents and their possible sources in the agricultural soils of Golestan province. The results from this study indicate that, concentrations of heavy metals in agricultural soils are mostly comparable with natural geochemical background of the study area, especially for Al, Ca, Co, Cr, Cs, Cu, Fe, K, Li, Ni, S, Sr, V and Zn while concentration of As, Cd, Mo, P, Pb and Se is controlled both by pedogenic as well as agricultural factors. It is also found that Cd, Pb and Se in most of the samples are more enriched in the surface soils. This study suggested that Cd, Pb and Se are more likely to accumulate in the surface horizons by anthropogenic sources mainly atmospheric deposition near urban areas. Selenium is extensively derived from loess deposits of Golestan province so natural background in the top layers is the main source to supply Se. The results demonstrated that among toxic metals, concentration of Co, Se and Zn in the soil samples collected from irrigated farmland is statistically higher than samples collected from dry farming areas. But such increase is not completely related to agrochemicals and soil amendments which are typically used more in irrigated farmlands. Geochemical background of most fertile soils has occurred in areas with higher natural concentrations of the mentioned elements.

Acknowledgments This work is part of the comprehensive project entitled 'Soil Contamination Atlas of Golestan province', which is funded by the Iran Department of Environment. The authors are thankful for the financial support to this project.

References

Acosta JA, Faz Cano A, Arocena JM, Debela F, Martínez-Martínez S (2009) Distribution of metals in soil particle size fractions and its implication to risk assessment of playgrounds in Murcia City (Spain). Geoderma 149:101–109

Author's personal copy

Acosta JA, Fazb A, Martinez-Martínezb S, Arocena JM (2011) Enrichment of metals in soils subjected to different land uses in a typical Mediterranean environment (Murcia City, southeast Spain. Appl Geochem 26(3):405–414

Anguelov G, Anguelova I (2009) Assessment of land-use effect on trace elements concentrations in soil solution from Ultisols in North Florida. Agric Ecosyst Environ 130(1–2):59–66

Bai L, Zeng X, Li L, Pen C, Li S (2010) Effects of land use on heavy metal accumulation in soils and sources analysis. Agric Sci China 9(11):1650–1658

Bradl HB (2004) Adsorption of heavy metal ions on soils and soils constituents. J Colloid Interface Sci 277:1–18. doi:10.1016/j.jcis.2004.04.005

Bradl HB (2005) Heavy metals in the environment volume 6. Elsevier, Amsterdam

Cooke TD, Drury DD (1998) Calabazas creek pilot sediment sampling study. In: Proceedings of NWQMC National Monitoring Conference. Monitoring: Critical Foundations to Protect our Waters. Reno, Nevada, July 7–9

Hafezi Moghaddas N, Ghorbani H, Dahrazma B, Hajizadeh Namaghi H, Ramezani Omali R (2010) Soil atlas of Golestan province. Investigation report. Department of environment, water and soil pollution Bureau

Huang S, Jin J (2008) Status of heavy metals in agricultural soils as affected by different patterns of land use. Environmental monitoring and assessment Volume 139. Numbers 1–3:317–327

Kabata-Pendias A, Mukherjee AB (2007) Trace elements from soil to human. Springer, Berlin

Kim K, Kim S (1998) Heavy metal pollution of agricultural soils in central regions of Korea. Water Air Soil Pollut 111:109–122

Krishna AK, Govil PK (2008) Assessment of heavy metal contamination in soils around Manali industrial area, Chennai, Southern India. Environ Geol 54:1465–1472

Liao Q, Evans LJ, Gu X, Fan D, Jin Y, Wang H (2007) A regional geochemical survey of soils in Jiangsu province, China: preliminary assessment of soil fertility and soil contamination. Geoderma 142:18–28

Luo W, Lu Y, Giesy JP, Wang T, Shi Y, Wang G, Xing Y (2007) Effects of land use on concentrations of metals in surface soils and ecological risk around Guanting reservoir, China. Environ Geochem Health 29(6):459–471

Marzaioli R, D'Ascoli R, De Pascalea RA, Rutigliano FA (2010) Soil quality in a Mediterranean area of southern Italy as related to different land use types. Appl Soil Ecol 44(3):205–212

Mico C, Recatala L, Peris M, Sanchez J (2006) Assessing heavy metal sources in agricultural soils of an European Mediterranean area by multivariate analysis. Chemosphere 65:863–872

Mitsios LK, Danalatos NG (2006) Bioavailability of trace elements in relation to root modification in the rhizosphere. In: Prasad MNV, Sajwan KS, Naidu R (eds) Trace elements in the environment: biogeochemistry, biotechnology, and bioremediation. Taylor and Francis Group, London

Neupane G, Roberts SJ (2009) Quantitative comparison of heavy metals and as accumulation in agricultural and forest soils near bowling green, Ohio. Water Air Soil Pollut 197:289–301

Nicholson FA, Smith SR, Alloway BJ, Carlton-Smith C, Chambers BJ (2003) An inventory of heavy metals inputs to agricultural soils in England and Wales. Sci Total Environ 311:205–219

Officer SJ, Kravchenko A, Bollero GA, Sudduth KA, Kitchen NR, Wiebold WJ, Palm HL, Bullock DG (2004) Relationships between soil bulk electrical conductivity and the principal component analysis of topography and soil fertility values. Plant Soil 258:269–280

Salonen V, Korkka-Niemi K (2007) Influence of parent sediments on the concentration of heavy metals in urban and suburban soils in Turku, Finland. Appl Geochem 22:906–918

Salvagio Manta D, Angelone M, Bellanca A, Neri R, Sprovieri M (2002) Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. Sci Total Environ 300:229–243

Semnani S, Roshandel G, Zendehbad A, Keshtkar A, Rahimzadeh H, Abdolahi N, Besharat S, Moradi A, Mirkarimi H, Hasheminasab S (2010) Soils selenium level and esophageal cancer: an ecological study in a high risk area for esophageal cancer. J Trace Elem Med Biol 24(3):174–177

Sistani KR, Novak JM (2006) Trace metal accumulation, movement, and remediation in soils receiving animal manure. In: Prasad MNV, Sajwan KS, Naidu R (eds) Trace elements in the environment: biogeochemistry, biotechnology, and bioremediation. Taylor and Francis Group, London

Templ M, Filzmoser P, Reimann C (2008) Cluster analysis applied to regional geochemical data: problems and possibilities. Appl Geochem 23(8):2198–2213

Tukey JW (1977) Exploratory data analysis, reading7. Addison-Wesley, Reading

Wang X, Cheng G, Zhong X, Li M (2009) Trace elements in sub-alpine forest soils on the eastern edge of the Tibetan Plateau. China Environ Geol 58:635–643

Wei B, Yang L (2009) A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. Microchem J. doi:10.1016/j.microc.2009.09.014

Yu L, Xin G, Gang W, Zhang Q, Qiong S, Guoju X (2008) Heavy metal contamination and source in arid agricultural soil in central Gansu province, China. J Environ Sci 20:607–612