Journal of Geochemical Exploration 197 (2019) 212–219

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/gexplo

Pedotransfer functions for predicting heavy metals in natural soils using magnetic measures and soil properties

Shamsollah Ayoubi*, Mostafa Karami

Department of Soil Sciences, College of Agriculture, Isfahan University of Technology, Isfahan 84156-83111, Iran

ARTICLE INFO

Keywords:
Multiple linear regression
Soil pollution
Ferrimagnetic minerals
Soil properties
Natural ecosystems

ABSTRACT

In this study, pedotransfer functions were developed using magnetic measures and soil properties to evaluate the concentrations of some heavy metals (Cr, Co, Fe, Cu, Ni, Mn, and Zn) in soils developed on some igneous rocks (gabbro, diorite-gabbro, gabbro-diorite, monzodiorite, spilite basalt, granite, and porphyritic-granite) in Kurdistan province, western Iran. A total number of 105 samples from both rocks and the associated surface soils were taken; magnetic susceptibility at two frequencies, concentrations of selected metals, and physcio-chemical properties of soils were then measured. The highest concentrations of metals were obtained for Co, Ni, Fe, Mn, and Cu in soils developed on gabbro and for Zn and Cr in soils developed on porphyritic-granite and spilite basalt, respectively. Magnetic measurements in soils and associated rocks could explain 78, 74, 77, 72, 75, 68, and 69% of the total variability of Zn, Cu, Ni, Fe, Mn, Co, and Cr concentrations in the studied soils. Inclusion of soil physcio-chemical properties did not significantly improve the prediction. Therefore, it seems that magnetic measurements, as fast, non-destructive, and cost-effective tools, could solely be used to successfully predict heavy metals in natural ecosystems, especially in reconnaissance scale studies.

1. Introduction

As harmful contaminants, heavy metals detected in soils and sediment of natural ecosystems, transported by soil loss and water discharge into reservoirs, account for potential human health risks (Erenturk et al., 2014; Szarlowicz et al., 2013; Acosta et al., 2015; Trujillo-González et al., 2016). Heavy metals, as non-biodegradable contaminants, are adsorbed by particulate materials or are precipitated and accumulated in sediments and may affect environment during the next few decades (Doichinova et al., 2014; Peng et al., 2017).

Two major sources have been identified for enrichment of heavy metals in soils and sediments, including lithogenic and anthropogenic sources (Lu, 2000; Li et al., 2014; Karimi et al., 2017). Human activities cause obvious enrichment of heavy metals in the sediments mainly through the vehicle traffic, industrial and agricultural activities, and mining activities (Jordanova et al., 2013; Dankoub et al., 2012; Taghipour et al., 2011). In arid and semiarid regions covered by igneous rocks, lithology has a significant contribution to enrichment of heavy metals in soils and sediments (Ayoubi et al., 2014).

Geochemical techniques are commonly employed to monitor the occurrence of heavy metals in soils and sediments (Jordanova et al., 2013). Considering the sampling procedures before analysis, the whole process is commonly destructive, laborious, time-consuming, and expensive. Therefore, in recent years, finding fast and cost-effective approaches for the determination of metals in soils have impressively attracted the attention of researchers. Geophysical techniques have been identified to determine the occurrence of these heavy metals together with their sources, and estimate their potential risks in soils and sediments (Hay et al., 1997; Lu et al., 2008; Karimi et al., 2011, Naimi and Ayoubi, 2013, Lu et al., 2016; Ayoubi et al., 2018b). Among the geophysical techniques, magnetic susceptibility has widely been employed for approximation of heavy metal contamination because it is an easily measurable and concentration-dependent geophysical parameters.

One of the most important geophysical attributes of soils and sediments is magnetic susceptibility, which is influenced by the parent material. Accordingly, various parent rocks show significant variability in magnetic susceptibility depending on the existence of ferrimagnetic minerals (Mullins, 1977; Magiera et al., 2006). Therefore, it is speculated that in various parent rocks with various potential of magnetic susceptibility, there will be different magnetic susceptibility values. Magnetic susceptibility has widely and successfully been used in investigating the lithological influences as well as the effects of parent material (Lu, 2000; Karimi et al., 2017), in explaining sedimentation processes (Caitcheon, 1993), and in examining soil pollution by hydrocarbon and heavy metals (Morris et al., 1994; Zhang et al., 2012;

* Corresponding author.
E-mail address: ayoubi@cc.iut.ac.ir (S. Ayoubi).

https://doi.org/10.1016/j.gexplo.2018.12.006
Received 2 July 2018; Received in revised form 24 November 2018; Accepted 9 December 2018
Available online 12 December 2018

Dankoub et al., 2012; Karimi et al., 2011; Bourliva et al., 2018).

Several studies have been conducted throughout the world as well as in Iran regarding the use of magnetic measures for predicting heavy metals in urbanized and industrial sites (Ayoubi et al., 2014; Naimi and Ayoubi, 2013; Ayoubi et al., 2018a). However, few studies have been conducted to explore the variability of heavy metals in natural ecosystems in Iran and to examine their associations with magnetic susceptibility. Also, few attempts have been made to develop pedotransfer functions to estimate heavy metals concentration using magnetic susceptibility and soil properties as covariates, especially in natural ecosystems. Therefore, we selected a natural ecosystem that had not been affected by human activities or natural circumstances in western Iran. Thus, the main objectives of this research were i) to characterize variations of heavy metals, magnetic susceptibility, and some heavy metals (Fe, Zn, Cu, Mn, Ni, Cr, and Co) in soils developed on various igneous rocks and ii) to develop pedotransfer functions for predicting heavy metals concentration using magnetic susceptibly and soil characteristics in a semiarid region, west of Iran.

2. Methods and materials

2.1. Description of the study area and sampling

The study area is located in south of Ghorveh district, Kurdistan province, west of Iran (Fig. 1). The average elevation of this mountainous area is 2200 m a.s.l. The average annual rainfall and temperature are 480 mm and 14.5 °C, respectively. The dominant geological formations of the studied region included igneous and metamorphic rocks of Tertiary and Jurassic epochs. To examine the hypothesis of this investigation, seven dominant bedrocks, including Gabbro, Diorite-gabbro, Gabbro-diorite, Monzodiorite; Spilite basalt, Granite, and Porphyritic granite were selected. In each rock, 15 sites were selected, which were similar in terms of slope gradient, aspect and vegetation among the studied rocks. Soil samples were gathered from the uppermost horizon (0–10 cm) and intact rocks of each site; totally 105 soil samples and 105 rock samples were collected.

2.2. Laboratory analyses

Collected soil samples were air-dried, crushed, and passed through a 2-mm sieve for laboratory analyses. Soil pH and electrical conductivity (EC) were measured by a pH-meter and EC-meter in saturated soil paste, respectively (Rhoades, 1982). Particle size distribution analysis was done using the Pipette method (Gee and Bauder, 1986). Wet-oxidation method was used for measuring soil organic carbon (SOC) (Nelson and Sommers, 1982). Calcium carbonate equivalent (CCE) was determined using the back titration method (Black, 1965). For magnetic measurements in all soil and rock samples, after crushing, a Bartington MS2 dual frequency sensor was employed to measure magnetic susceptibility (χ) at low (0.47 kHz; χ_{lf}) and high frequencies (4.7 kHz, χ_{hf}) using roughly 10 g of the soil or crushed rock held in a four-dram clear plastic vial (2.3 cm diameter) (Dearing et al., 1996). The dependent frequency (χ_{fd}) was computed as follows:

$$\chi_{fd}\,(\%) = [(\chi_{lf} - \chi_{hf})/\chi_{lf}] \times 100 \tag{1}$$

According to the method proposed by Ajayi and Kamson (1983), a subsample (0.2 g) of each collected soil was exploited for the heavy metal analysis, and then the sample was digested in a 5 mol L^{-1} HNO_3 solution. An atomic absorption spectrophotometer (AAS) was used to measure the total content of nickel (Ni), chromium (Cr), cobalt (Co), zinc (Zn), copper (Cu), manganese (Mn), and iron (Fe). San Joaquin #2709, a certified reference material, was analyzed to evaluate the precision of the procedure. The detection limits of AAS for Zn, Cu, Ni, Co, Cr, Fe, and Mn were 0.016, 0.015, 0.05, 0.05, 0.015, 0.042, 0.10, and 0.0.035 mg L^{-1}, respectively.

2.3. Statistical analysis

Descriptive statistics were obtained using SPSS software (V. 19.0). Also, SPSS was used to calculate the correlation coefficients among magnetic measurements, heavy metals, and soil properties (Swan and Sandilands, 1995).

Multiple-linear regression (MLR) in SPSS Ver. 19 was employed to predict the concentrations of heavy metals using two groups of input variables: i) magnetic measurements, including χ_{lf} and χ_{fd} of soils and their associated parent rocks (symbolized as MS dataset, i.e. scenario I) and ii) inclusion of previous data set and some soil properties (symbolized as MSS dataset, i.e. scenario II). Soil organic matter (SOM), calcium carbonate equivalent (CCE), and electrical conductivity (EC) were the soil properties which were considered as predictors in MLR analysis. MLR modeling was done employing the initial variables (x) and transformed variables [x, x^{-1}, x^2, log(x), ln(x), exp(x) and $x^{0.5}$] as predictors. The factors included in the qualified model were selected based on probability ≤ 0.05 according to Freund and Littell (2000). The dataset was divided into two parts: i) 80 samples for MLR modeling and ii) 25 samples to validate the data set for evaluation of models.

Primarily, Kolmogorov − Smirnov test using SPSS was employed to evaluate the normality conditions for input and target variables. Then, logarithmic transformations were performed for non-normal variables before further statistical analyses. Derived pedotransfer functions (PTFs) were evaluated by the coefficient of determination (R^2), and the root mean square errors (RMSE) were computed as follows:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N} (Y_i - \hat{Y}_i)^2}{N}} \tag{2}$$

where Yi and Ŷi were the observed and predicted values of heavy metals concentration, respectively, and N is the number of observations (= 25). Model validation was done using a dataset of 25 samples which were stratified randomly selected. The Akaike Information Criterion (AIC) was also employed to judge the efficacy of the developed functions in two datasets (Akaike, 1974) as follows:

$$AIC = 2K + N\ln\left(\frac{\mathrm{SSE}}{\mathrm{N}}\right) \tag{3}$$

where K is the number of regression coefficients in the PTFs, N is the number of observations and SSE is the sum squares of errors. Corrected AIC (AIC_c) was computed as a version of Eq. (3), due to the relatively small number of N in our investigation as follows:

$$AIC_c = AIC + \frac{2K(K+1)}{N-K+1} \tag{4}$$

Since the absolute AIC_c values were subject to the sample size and units of model variables and subsequently not interpretable, the difference (Δ) between AIC_c values of two models was considered independent of the sample size and units. The model rendered more accurate when the lower values were achieved forAIC or AIC_c (Burnham and Anderson, 2004).

3. Results and discussion

3.1. Variability of soil properties

Soil pH varied from 7.03 to 7.80 and electrical conductivity (EC) varied from 0.11 to 0.59 dS m^{-1}. According to these results, soils of the studied area were slightly alkaline and non-saline. pH and EC showed 2.30 and 38.8% of coefficient of variability (CV), respectively. The lowest CV was found for pH, similar to the results reported by Nourozi et al. (2009), Ayoubi and Sahrawat (2011) and Ayoubi et al. (2009) in arid and semiarid regions. Calcium carbonate equivalent (CCE) varied from 1.0 to 36% with a mean of 8.74%. This average was relatively lower than that in other soils of Iran (Shahriari et al., 2011; Jafari et al.,

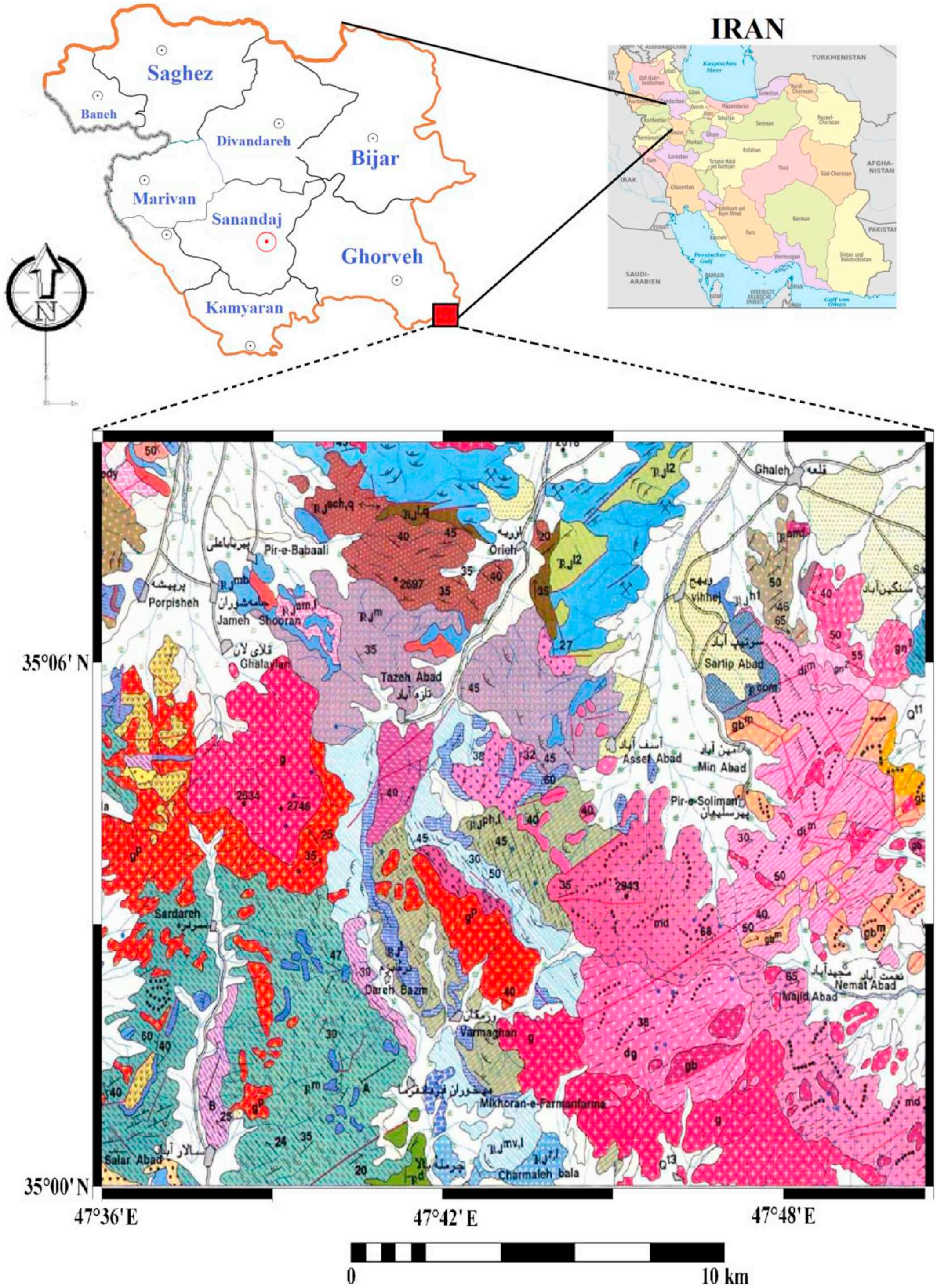

Fig. 1. Location of the studied area in Kurdistan province, western Iran.

2013), mainly attributed to the composition of parent materials forming the igneous rocks. Soil organic matter (SOM) ranged from 0.42 to 4.33% with a high CV (85.1%), which might be attributed to i) high variability in the soil texture (see CV value of clay in Table 1), ii) great variability in the vegetation species and the organic particulates returned to soils and iii) soil erosion and redistribution influences. Among the studied soil properties, CCE and EC showed non-normal distribution according to K-S test and Skewness values ($> +1$, Table 1); therefore, in the MLR modeling, transformed values of these variables were included.

3.2. Variability of heavy metals and magnetic susceptibility

A summary of statistics of heavy metals and magnetic susceptibility are given in Table 2. According to this table, the highest ($834 \times 10^{-8}\,m^3\,kg^{-1}$) and lowest ($206 \times 10^{-8}\,m^3\,kg^{-1}$) χlf in the studied rocks were observed for Gabbro and Granite, respectively. The results of magnetic susceptibility of soils developed on studied rocks, also showed that the highest susceptibility was observed in Gabbro and the lowest in Granite (Table 2). These results were in line with those revealed by Adman (2014) who reported that basalt and ultrabasic rocks had the

Table 1
Summary statistics of selected soil physical and chemical properties, heavy metals, and magnetic parameters in the study area ($N = 105$).

Variable	Unit	Min	Max	Mean	CV	Skewness	Kurtosis
pH	− log [H+]	7.03	7.8	7.46	2.30	−0.33	1.34
EC	dS/m	0.11	0.59	0.20	38.80	2.20	2.89
CCE	%	1.0	36.0	8.74	45.90	2.38	1.89
Sand	%	30.0	90.0	56.4	25.43	0.21	1.43
Clay	%	1.0	24.0	9.85	61.6	0.41	1.01
SOM	%	0.42	4.33	1.91	85.1	0.87	2.12

Min: Minimum, Max: Maximum, CV: Coefficient of Variation, EC: Electrical conductivity, CCE: calcium carbonate equivalent, SOM: Soil organic matter.

highest concentrations of the total iron in western Iran because of the presence of higher ferrimagnetic minerals. Comparing some igneous rocks, Mooney and Bleifuss (1953) also showed that the basalt ($1260 \times 10^{-8}\,m^3\,kg^{-1}$) and granite ($220 \times 10^{-8}\,m^3\,kg^{-1}$) had the highest and the lowest magnetic susceptibility, respectively.

Comparison of magnetic susceptibility observed in soils with the associated parent rocks showed that χlf decreased in all soils compared to the parent rocks. Negative changes seen in χlf in soils developed on the studied rocks compared to the parent materials confirmed dilution effects of pedogenic processes for ferrimagnetic minerals (Lu et al., 2008). It was speculated that during soil-forming processes, formation of some diamagnetic minerals, such as calcite, and transformation of ferrimagnetic minerals to other forms (i.e. paramagnetic minerals) could be the major causes of χ_{lf} reduction in soils.

The mean magnetic susceptibility of the dependent frequency (χ_{fd}) was lower than 4% (see Table 2). It was predominantly attributed to higher existence of ferrimagnetic minerals in the parent materials. The fact that no significant correlations were found between χ_{lf} and χ_{fd} ($r = -0.10$, Not significant, $P < 0.05$, Table 3) confirmed that a dominant portion of ferrimagnetic minerals in studied soils originated from the parent rocks. Because of dilution effects as a consequence of soil development, χ_{lf}, however, declined compared to the parent materials.

3.3. Variability of heavy metals

A summary of descriptive statistics of studied heavy metals are given Table 2. According to the results presented in this table, the highest concentration of Fe was observed in soils developed on Gabbro rocks, while the least was observed in Granite as an acidic rock. Similar trends were obtained for Mn, Cu, Ni, and Co. These results were in line with findings obtained by Alloway (1990), Fergusson (1990), Galan et al. (2008), and Mico et al. (2006) who reported that, compared to acidic rocks, basic rocks contributed more in releasing these elements to soils. The highest value of Zn was observed in porphyritic granite and the greatest Cr value was seen in spilite basaltic soils.

The Netherland permissible values indicate the concentrations of heavy metals that should be attained to fully recover the functional properties of the soil for plants, animals, and humans (Swartjes, 1999). Frequency distributions of the contents of the measured heavy metals showed that some of the observations surpassed the Netherland permissible values (Fig. 2). Ni had the highest number of observations which exceeded the Netherlands permissible value by 96.8%. Similarly, the concentrations of Mn, Cu, Zn, Co, and Cr in the studied sites, i.e. 90, 23.1, 4.6, 95.4 and 12.5, surpassed the Netherlands permissible values, respectively (Fig. 2). Refereed to the Netherlands permissible values, none of the sites indicated the potential public health risk due to Fe in the studied area. As the studied area was located far away from the urban and industrial sites, lithology had almost the chief contribution to the existence of heavy metals in soils. Using multivariate analysis, Mico et al. (2006), and Facchinelli et al. (2001) showed that Co, Cr, Ni were mainly controlled by lithology in Alicante province (Spain) and Piemonte (Italy), respectively. The concentration of metals for the test data set predicted by MLR models compared with measured values are given in Fig. 3.

Table 2
Statistics of heavy metals in soils and magnetic measures in studied rocks and associated soils in the study area.

Variable	Unit	Gab-Di	Di-Gab	Monz	Spl-Ba	Grant	Por-Gran	Gab
Cu	$mg\,kg^{-1}$	31.2^{ab}	33.4^{ab}	27.8^{ab}	32.1^{ab}	24.1^{b}	25.8^{b}	37.6^{a}
Zn	$mg\,kg^{-1}$	65.0^{b}	65.6^{b}	79.2^{b}	83.0^{b}	61.1^{b}	119.5^{a}	86.7^{b}
Ni	$mg\,kg^{-1}$	78.7^{abc}	69.0^{c}	78.9^{abc}	91.2^{ab}	73.2^{bc}	78.0^{abc}	98.0^{a}
Co	$mg\,kg^{-1}$	25.9^{ab}	31.2^{ab}	30.0^{ab}	33.8^{ab}	22.6^{b}	27.1^{ab}	38.86^{a}
Cr	$mg\,kg^{-1}$	67.8^{b}	65.4^{b}	75.9^{b}	114.1^{a}	57.5^{b}	76.4^{b}	78.3^{b}
Fe	$mg\,kg^{-1}$	16300^{ab}	17500^{ab}	19000^{ab}	21800^{a}	12000^{ab}	15000^{ab}	22500^{a}
Mn	$mg\,kg^{-1}$	493.7^{d}	732.3^{bc}	678.1^{bc}	836.0^{b}	621.8^{cd}	716.1^{bc}	1019.8^{a}
$\chi_{lf\ (r)}$	$\times 10^{-8}\,m^3\,kg^{-1}$	456^{c}	366^{d}	314^{d}	546^{b}	206^{d}	305^{d}	834^{a}
$\chi_{fd(r)}$	%	1.22^{c}	1.34^{c}	1.44^{c}	2.33^{b}	2.43^{a}	1.98^{b}	2.30^{b}
$\chi_{lf(s)}$	$\times 10^{-8}\,m^3\,kg^{-1}$	291.7^{b}	165.4^{c}	185.9^{c}	264.1^{b}	105.2^{c}	165.4^{c}	372.6^{a}
$\chi_{fd(s)}$	%	1.6^{c}	1.57^{c}	1.6^{c}	1.57^{c}	2.4^{b}	0.86^{d}	3.02^{a}

Gab: Gabbro, Di-Gab: Diorite-gabbro, Gab-Di: Gabbro-diorite, Mon: Monzodiorite; Spl-Ba: Spilite Basalt, Gran: Granite; Por-Gran: Porphyritic Granite.
a, b, c … different letters in a specified row has different significant at $P < 0.05$.

Table 3
Correlation coefficients among heavy metals, magnetic measures, and soil properties in studied soils ($N = 105$).

	Fe	Mn	Zn	Cu	Co	Cr	Ni	χlf	χfd
χlf	0.81**	0.80**	0.67**	0.76**	0.78**	0.79**	0.75**	1	−0.10
χfd	−0.45**	−0.57**	−0.67**	−0.39**	−0.45**	−0.65**	−0.28*	−0.10	1
Clay	0.17	0.05	−0.03	0.12	0.12	0.03	−0.01	0.18	0.01
Silt	0.14	0.03	−0.01	0.15	0.15	0.13	0.02	−0.02	0.01
Sand	0.56**	0.58**	0.47**	0.14	0.67**	0.71**	0.59**	0.44**	0.13
SOM	0.34**	0.30**	0.27*	0.45**	0.34**	0.38**	0.28*	0.36**	0.12
EC	−0.27*	0.03	−0.34**	0.19	0.17	−0.29*	−0.13	−0.66**	0.09
CCE	−0.29**	−0.29**	0.12	−0.21*	−0.27*	0.12	0.21	−0.49**	0.12

* Significant at the 5% probability level.
** Significant at the 1% probability level.

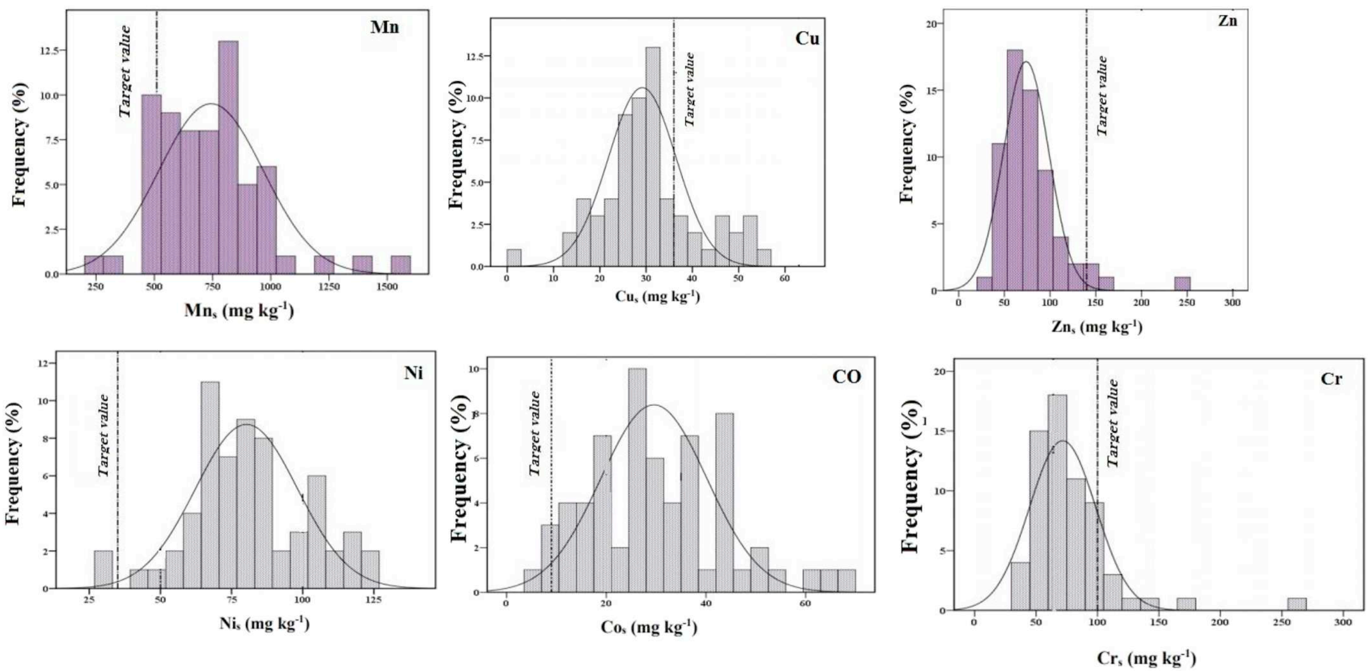

Fig. 2. Plot frequency distributions of metal concentrations (mg kg^{-1}) measured for the whole data as compared to the Netherlands soil guideline values.

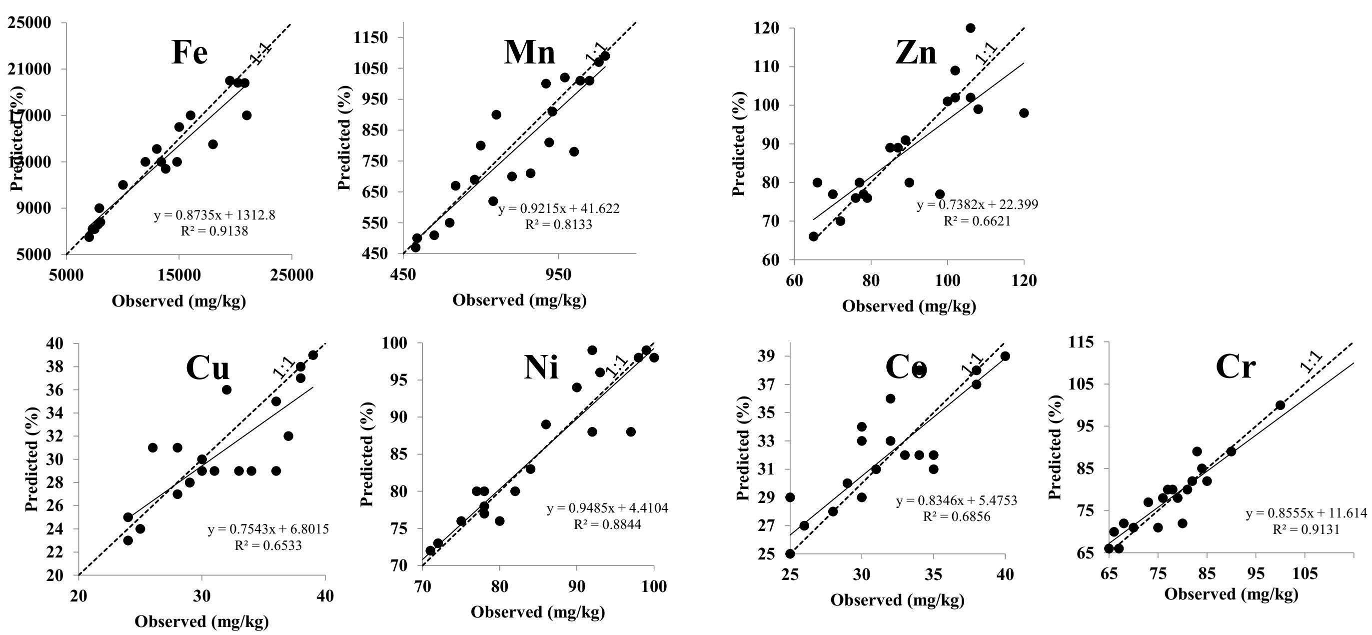

Fig. 3. Scatter plots between measured and predicted concentration of heavy metals by the MLR models using the first dataset (i.e. solely magnetic measures).

3.4. Correlation analysis

Correlation coefficients among magnetic susceptibility measurements, heavy metals, and the selected soil properties were computed to understand the impacts of the soil properties on the variability of heavy metals and magnetic susceptibility (Table 3). Soil organic matter (SOM) was positively correlated with the concentrations of Fe ($r = 0.34$, $P < 0.01$), Mn ($r = 0.30$, $P < 0.01$), Cu ($r = 0.45$, $P < 0{:}01$), Zn ($r = 0.27$, $P < 0.01$), Co ($r = 0.34$, $P < 0.01$), and Cr ($r = 0.38$, $P < 0.01$). Rodriguez Martin et al. (2006) stated that soil organic matter was also found to influence absorption of heavy metals in soils; this effect was presumably because of the existence of cation exchange capacity in organic material. These correlations confirmed the tendency of organic matter to adsorb heavy metals in order to fabricate stable organic complexes (Rustullet, 1996; Qishlaqi and Moore, 2007).

Correlation analysis between χ_{lf} and soil properties showed that χ_{lf} had a positive and significant correlation with sand content ($r = 0.44$, $P < 0.01$). This positive relationship confirmed that ferrimagnetic minerals remained in sand fractions (especially in igneous rocks), and semiarid conditions of the studied area were not sufficient to release Fe-bearing minerals to clay fractions. Negative and significant correlations were obtained between χ_{lf} and SOM ($r = -0.36$, $P < 0.01$), electrical conductivity (EC) ($r = -0.66$, $P < 0.01$), and calcium carbonate equivalent (CCE) ($r = -0.49$, $P < 0.01$). These negative correlations confirmed the presence of diamagnetic minerals, decreasing χ_{lf} forming organic particles, halite and calcium carbonates, respectively. These

Table 4
Developed Pedotrnasfer functions (PTFs) for estimation of heavy metals ($mg\,kg^{-1}$) in the studies soils.

Metal	Dataset	PTFs	R^2	Adj. R^2	RMSE	ΔR^2	AICc
Fe	MS	$Y = 8600 + 19.80\chi_{lf\,(s)} + 0.12\frac{\chi_{lf\,(s)}}{\chi_{fd\,(s)}} + 0.04\chi_{lf\,(r)}$	0.78	0.79	21.34	0.01^{ns}	381.2
	MSS	$Y = 7500 + 17.50\chi_{lf(s)} + 0.12\ \chi_{lf(s)} + 0.01\chi lf(r) + 0.13\ Sand - 0.013 LogCCE$	0.79	0.82	19.32		380.8
Mn	MS	$Y = 670 + 23.30\chi_{lf\,(s)} + 0.05\frac{\chi_{lf\,(s)}}{\chi_{fd\,(s)}} - 1.21\chi_{fd\,(s)}$	0.74	0.78	1.23	0.04^{ns}	−421.6
	MSS	$Y = 630 + 19.80\chi_{lf\,(s)} + 0.07\frac{\chi_{lf\,(s)}}{\chi_{fd\,(s)}} - 0.12\chi_{fd\,(s)} + 0.58\ Sand - 0.031 LnCCE$	0.78	0.80	1.19		−423.8
Zn	MS	$Y = 77 + 1.2\chi_{lf\,(s)} + 0.34\frac{\chi_{lf\,(s)}}{\chi_{fd\,(s)}} - 2.133\chi_{fd\,(s)}$	0.77	0.76	0.124	0.01^{ns}	−220.8
	MSS	$Y = 65 + 2.3\chi_{lf\,(s)} + 0.67\frac{\chi_{lf\,(s)}}{\chi_{fd\,(s)}} - 1.45\chi_{fd\,(s)} + 0.12Sand - 0.011LnEC$	0.78	0.77	0.099		−222.8
Ni	MS	$Y = 72 + 0.66\chi_{lf\,(s)} + 1.10\frac{\chi_{lf\,(s)}}{\chi_{fd\,(s)}} + 1.90\chi_{lf\,(r)}$	0.72	0.73	0.021	0.05^{ns}	−44.4
	MSS	$Y = 69 + 0.89\chi_{lf\,(s)} + 1.89\frac{\chi_{lf\,(s)}}{\chi_{fd\,(s)}} + 2.1\chi_{lf\,(r)} + 1.89Sand - 0.03\ CCE$	0.77	0.79	0.019		−48.3
Cu	MS	$Y = 33 + 1.29\chi_{lf\,(s)} + 1.32\frac{\chi_{lf\,(s)}}{\chi_{fd\,(s)}} + 2.19\chi_{lf\,(r)}$	0.75	0.76	0.09	0.04^{ns}	457.6
	MSS	$Y = 30 + 1.09\chi_{lf\,(s)} + 1.77\frac{\chi_{lf\,(s)}}{\chi_{fd\,(s)}} + 1.02\chi_{lf\,(r)} + 2.98Log\ SOM - 0.7\ LnCCE$	0.79	0.81	0.08		459.5
Co	MS	$Y = 32 + 1.43\chi_{lf\,(s)} + 0.22\frac{\chi_{lf\,(s)}}{\chi_{fd\,(s)}} - 0.22\chi_{fd\,(s)} + 0.21\chi_{lf\,(r)}$	0.68	0.69	0.001	0.05^{ns}	−434.2
	MSS	$Y = 85 + 1.43\chi_{lf\,(s)} + 0.17\frac{\chi_{lf\,(s)}}{\chi_{fd\,(s)}} - 0.33Log\chi_{fd\,(s)} + 2.10SOM - 1.12\ LnCCE$	0.73	0.74	0.001		−436.5
Cr	MS	$Y = 81 + 0.17\chi_{lf\,(s)} + 0.08\frac{\chi_{lf\,(s)}}{\chi_{fd\,(s)}} + 1.09\chi_{lf\,(r)}$	0.69	0.71	0.09	0.02^{ns}	−492.6
	MSS	$Y = 79 + 0.23\chi_{lf\,(s)} + 0.23\frac{\chi_{lf\,(s)}}{\chi_{fd\,(s)}} + 1.11\chi_{lf\,(r)} + 2.13\sqrt{SOM} - 0.89LOgEC$	0.71	0.72	0.08		−493.5

PTF: Pedotrnasfer function, R2: Coefficient of determination; Adj. R^2: Adjusted coefficient of determination; RMSE: Root mean square error; ΔR^2: Difference in coefficient of determination; MS; magnetic susceptibility data; MSS: magnetic susceptibility and soil properties data. χlf(s): Magnetic susceptibility of soil; χlf(r): Magnetic susceptibility of rocks; χfd(s): Dependent magnetic susceptibility of soils. CCE: Calcium carbonate equivalent; EC: Electrical conductivity; SOM: soil organic matter.

results were in line with the findings revealed by Naimi and Ayoubi (2013), Dankoub et al. (2012), and Marwick (2005).

The results showed that significant coefficients were found between χ_{lf} and Fe ($r = 0.89$, $P < 0.01$), Mn ($r = 0.80$, $P < 0.01$), Zn ($r = 0.67$, $P < 0.01$), Ni ($r = 0.75$, $P < 0.01$), Co ($r = 0.78$, $P < 0.01$), and Cr ($r = 0.79$, $P < 0.01$). Association of selected metals with magnetic minerals led to enhancing the magnetic susceptibility together with an increase in heavy metals.

3.5. Pedotrnasfer functions (PTFs)

Many studies have successfully found significant relationships between heavy metals and magnetic susceptibility in urban and industrial sites (i.e. Marwick (2005), Rodriguez Martin et al., 2006; Canbay et al., 2010; Ayoubi et al., 2018a), while there have been few reports regarding natural ecosystems similar to our study area.

The PTFs for predicting the concentrations of heavy metals were derived from two scenarios (I) using magnetic susceptibility measurements of soils and rock samples and (II) using magnetic measures and some soil physico-chemical properties. The results of multiple linear regression, using two datasets, are presented in Table 4. Stepwise regression analysis was used to discover the priority of the heavy metals in the models. In the first dataset (only magnetic measures), for predicting the Fe content in soils, χlf in soils, χlf in rocks, and the ratio of $\frac{\chi_{lf}}{\chi_{fd}}$ in soils were included; these parameters could explain 78% of the total variability of Fe in the studied soils. Likewise, for the prediction of Mn, Zn, Cu, Ni, Co, and Cr, the above-mentioned variables were included in the MLR models together with various standardized coefficients. These parameters accounted for 74, 77, 72, 75, 68, and 69% of the variability of Mn, Zn, Ni, Cu, Co, and Cr, respectively, in the studied area (Table 4).

In the second dataset (MSS), some soil properties, including SOM, EC, CCE, Clay, and Sand were included in the MLR models. The results showed that inclusion of Sand (with positive contribution) and CCE (with negative contribution) improved the perdition of Fe concentrations in soils, while R^2 improved from 0.88 in the MS dataset to 0.91 in the MSS dataset, and RMSE reduced from 21.34 to 19.32 correspondingly. Moreover, the inclusion of these two soil properties as well as other features (SOM, EC) improved the perdition of Mn, Zn, Ni, Cu, Co, and Cr based on an increase in R^2 and a decrease in RMSE (Table 4). The inserted variables were in line with the results of correlation analysis (Table 3) in that they had the high and significant correlation coefficients. In overall, the scenario (II), for all given metals, led to better prediction (higher R^2, lower AIC_c value, and smaller RMSE).

The models developed by two datasets were compared using ΔR^2. For all selected heavy metals, the results of ΔR^2 (Table 4) showed that R^2 values could only be improved by 0.01, 0.04, 0.01, 0.05, 0.04, 0.05, and 0.02 in Fe, Mn, Zn, Ni, Cu, Co, and Cr, respectively. ΔR^2 test indicated that these differences were not significant at $P < 0.05$ probability level. Moreover, the calculated AIC_c were used to compare the results of two scenarios. The differences between AIC_c (ΔAIC_c) of two scenarios (MS and MSS) were calculated to evaluate the degree of support between two models as follows: $\Delta AICc < 2$, substantial support; ΔAIC_c between 2 and 4, less support; $\Delta AICc$ between 4 and 7, considerably less support; $\Delta AICc > 7$, no support (Burnham and Anderson, 2004). It was revealed that, for predicting Fe, Zn, Cu, and Cr, scenario (I) had substantial support with ΔAIC_c values of 0.4, 2, 1.9, and 0.9 compared to the best models (i.e. MSS, scenario II). Moreover, for predicting Mn, Ni, and Co, MS scenario had less support with ΔAIC_c values of 2.2, 3.9, and 2.3 compared to the best models (i.e. MSS, scenario II). In conclusion, it seems that readily available auxiliary variables, such as magnetic measurements in soils and rocks, could be used as powerful predictors of heavy metals in the studied soils developed on igneous rocks.

Although the use of soil characteristic data as the auxiliary predictors led to improvement in the prediction of the concentrations of heavy metals, this enhancement was not significant according to the statistics (ΔR^2 and $\Delta AICc$). On the other hand, measuring the soil physical and chemical properties was time-consuming and costly, and the use of them as the auxiliary variables was not logically and reasonably suggested. Therefore, the use of auxiliary magnetic data could solely justify a large part of the variations observed in the heavy elements in our study area. The accuracy and reliability of these PTFs were sufficient for the prediction of heavy metals in soils developed on various parent rocks in reconnaissance surveys, where preliminary information is required at a large scale. It seems that soil clustering in the region based on the parent materials could improve the coefficients of determination for developed linear models.

4. Conclusion

Pedotrnasfer functions were developed for estimating some heavy metals (Fe, Mn, Cu, Zn, Ni, Co and Cr) concentration using two scenarios (magnetic measures, and combination of magnetic measures and soil physical and chemical properties) in soils developed on a range of igneous rocks in western Iran. Association of metals with ferrimagnetic metals enabled us to predict the concentrations of heavy metals in soils using magnetic susceptibility as a geophysical approach. Comparing two scenarios in this study showed that magnetic susceptibility could solely explain a comprehensive variability of metals in the studied area. Our results showed that magnetic susceptibility measurements in soils and their associated rocks could successfully develop multiple linear models to predict some heavy metals concentration in these soils. The developed models were statistically reliable and reasonable (considering that magnetic measures are cost-effective and fast) for estimating the concentrations of heavy metals in reconnaissance studies, where general information about the pollution as a result of heavy metals is required in natural ecosystems.

Acknowledgements

We would like to thank Isfahan University of Technology for the financial support of the study.

References

Acosta, J.A., Gabarrón, M., Faz, A., Martínez-Martínez, S., Zornoza, R., Arocena, J.M., 2015. Influence of population density on the concentration and speciation of metals in the soil and street dust from urban areas. Chemosphere 134, 328–337.
Adman, V., 2014. Variability of heavy metals and magnetic susceptibility in soils developed in the range of parent material, from sedimentary to ultrabasic (western Iran, Msc Thesis). IUT press, Isfahan University of Technology, Isfahan, Iran.
Ajayi, A., Kamson, O.F., 1983. Determination of lead in roadside dust in Lagos City by atomic absorption spectrophotometry. Environ. Int. 9, 397–400.
Akaike, H., 1974. A new look at the statistical model identification. IEEE Trans. Autom. Control 19, 716–723.
Alloway, B.J., 1990. Heavy Metals in Soil. Blackie and Son, Glasgrow and London, pp. 339.
Ayoubi, S., Sahrawat, K.L., 2011. Comparing multivariate regression and artificial neural network to predict barley production from soil characteristics in northern Iran. Arch. Agron. Soil Sci. 57, 549–565.
Ayoubi, S., Khormali, F., Sahrawat, K.L., 2009. Relationships of barley biomass and grain yields to soil properties within a field in the arid region: use of factor analysis. Acta Agric. Scand. Sect. B Soil Plant Sci. 59, 107–117.
Ayoubi, S., Amiri, S., Tajik, S., 2014. Lithogenic and anthropogenic impacts on soil surface magnetic susceptibility in an arid region of central Iran. Arch. Agron. Soil Sci. 60, 1467–1483.
Ayoubi, S., Jababri, M., Khademi, H., 2018a. Multiple linear modeling between soil properties, magnetic susceptibility and heavy metals in various land uses. Model. Earth Syst. Environ. 4, 579–589.
Ayoubi, S., Soltani, Z., Khademi, H., 2018b. Particle size distribution of heavy metals and magnetic susceptibility in an industrial site. Bull. Environ. Contam. Toxicol. 100, 708–714.
Black, C.A., 1965. Methods of soil analysis. Am. Soc. Agronomy, Mono. 2 (9) (Madison, Wise, 1572 pp).
Bourliva, A., Kantiranis, N., Papadopoulou, L., Aidona, E., Christophoridis, C., Kollias, P., Evgenakis, M., Fytianos, K., 2018. Seasonal and spatial variations of magnetic susceptibility and potentially toxic elements (PTEs) in road dusts of Thessaloniki city, Greece: a one-year monitoring period. Sci. Total Environ. 639, 417–427.
Burnham, K.P., Anderson, D.R., 2004. Multimodel inference: understanding AIC and BIC in model selection. Sociol. Methods Res. 33, 261–304.
Caitcheon, G., 1993. Sediment source tracing using environmental magnetism: a new approach with examples from Australia. Hydrol. Process. 7, 349–358.
Canbay, M., Aydin, A., Kurtulus, C., 2010. Magnetic susceptibility and heavy-metal contamination in top- soils along the Izmit Gulf coastal area and IZAYTAS (Turkey). J. Appl. Geophys. 70, 46–57.
Dankoub, Z., Ayoubi, S., Khademi, H., Lu, S.G., 2012. Spatial distribution of magnetic properties and selected heavy metals as affected by land use in calcareous soils of the Isfahan region, central Iran. Pedosphere 22, 33–47.
Dearing, J.A., Hay, K.L., Balsan, S.M.J., Huddleston, A.S., Wellington, E.M.H., Loveland, P.J., 1996. Magnetic susceptibility of soil: an evaluation of contributing theories using a national data set. J. Geophys. J. Int. 127, 728–734.
Doichinova, V., Zhiyanski, M., Hursthouse, A., Bech, J., 2014. Study on the mobility and bioavailability of PTEs in soils from Urban Forest Parks in Sofia, Bulgaria. J. Geochem. Explor. 147, 222–228.
Erenturk, S., Yusan, S., Turkozu, D.A., Camtakan, Z., Olgen, M.K., Aslani, M.A.A., Aytas, S., Isik, M.A., 2014. Spatial distribution and risk assessment of radioactivity and heavy metal levels of sediment, surface water and fish samples from Lake Van, Turkey. J. Radioanal. Nucl. Chem. 300, 919–931.
Facchinelli, A., Sacchi, E., Mallen, L., 2001. Multivariate statistical and GIS-based approach to identify heavy metal sources in soils. Environ. Pollut. 114, 313–324.
Fergusson, J.E., 1990. Heavy Elements: Chemistry, Environmental Impact and Health Effects. Pergamon, Oxford (614 P).
Freund, R.J., Littell, R.C., 2000. SAS System for Regression. SAS Inst, Cary (NC).
Galan, E., Fernandez-Caliani, J.C., Gonzalez, I., Aparicio, P., Romero, A., 2008. Influence of geological setting on geochemical baselines of trace elements in soils. Application to soils of South-West Spain. J. Geochem. Explor. 98, 89–106.
Gee, G.W., Bauder, J.W., 1986. Particle size analysis. In: Klute, A. (Ed.), Methods of Soil Analysis: Part 1. In: Agronomy Handbook No 9. American Society of Agronomy and Soil Science Society of America, Madison, WI, pp. 383–411.
Hay, K.L., Dearing, J.A., Baban, S.M.J., Loveland, P., 1997. A preliminary attempt to identify atmospherically-derived pollution particles in English topsoils from magnetic susceptibility measurements. Phys. Chem. Earth 22, 207–210.
Jafari, A., Ayoubi, S., Khademi, H., Finke, p., Toomanian, T., 2013. Selection of a taxonomic level for soil mapping using diversity and map purity indices: a case study from an Iranian arid region. Geomorphology 201, 86–97.
Jordanova, D., Goddu, S.R., Kotsev, T., Jordanova, N., 2013. Industrial contamination of alluvial soils near Fe–Pb mining site revealed by 441 magnetic and geochemical studies. Geoderma 192, 237–248.
Karimi, R., Ayoubi, S., Jalalian, A., Sheikh-Hosseini, A.R., Afyuni, M., 2011. Relationships between magnetic susceptibility and heavy metals in urban topsoils in the arid region of Isfahan, central Iran. J. Appl. Geophys. 74, 1–7.
Karimi, A., Haghnia, G.H., Ayoubi, S., Safari, T., 2017. Impacts of geology and land use on magnetic susceptibility and selected heavy metals in surface soils of Mashhad plain, northeastern Iran. J. Appl. Geophys. 138, 127–134.
Li, Y., Zuo, R., Bai, Y., Yang, M., 2014. The relationships between magnetic susceptibility and elemental variations for mineralized rocks. J. Geochem. Explor. 146, 17–26.
Lu, S.G., 2000. Lithological factors affecting magnetic susceptibility of subtropical soils, Zhejiang Province, China. Catena 40, 359–373.
Lu, S.G., Xue, Q.F., Zhu, L., Yu, J.Y., 2008. Mineral magnetic properties of weathering sequence of soil derived from basalt in Eastern China. Catena 73, 23–33.
Lu, S.G., Yu, X., Chen, Y., 2016. Magnetic properties, microstructure and mineralogical phases of technogenic magnetic particles (TMPs) in urban soils: their source identification and environmental implications. Sci. Total Environ. 543, 239–247.
Magiera, T., Strzyszcz, Z., Kapicka, A., Petrovsky, E., 2006. Discrimination of lithogenic and anthropogenic influences on topsoil magnetic susceptibility in central Europe. Geoderma 130, 299–311.
Marwick, B., 2005. Element concentrations and magnetic susceptibility of anthrosols: indicators of prehistoric human occupation in the inland Pilbara, Western Australia. J. Archeol. Sci. 32, 1357–1368.
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.
Mooney, H.M., Bleifuss, R., 1953. Magnetic susceptibility measurements in Minnesota. Part 11: analysis of field results. Ibid 18, 383–394.
Morris, W.A., Versteeg, J.K., Marvin, C.H., McCarry, B.E., Rukavina, N.A., 1994. Preliminary comparisons between magnetic susceptibility and polycyclic aromatic hydrocarbon content in sediments from Hamilton Harbour, western Lake Ontario. Sci. Total Environ. 152, 153–160.
Mullins, C.E., 1977. Magnetic susceptibility of the soil and its significance in soil science a review. J. Soil Sci. 28, 223–246.
Naimi, S., Ayoubi, S., 2013. Vertical and horizontal distribution of magnetic susceptibility and metal contents in an industrial district of central Iran. J. Appl. Geophys. 96, 55–66.
Nelson, D.W., Sommers, L.P., 1982. Total carbon, organic carbon and organic matter. In: Page, A.L. (Ed.), Methods of Soil Analysis: Part 2: Chemical and Microbiological Properties. Agronomy Handbook No 9. American Society of Agronomy and Soil Science Society of America, Madison, WI, pp. 539–579.
Nourozi, M., Ayoubi, S., Jalalian, A., Khademi, H., Dehghani, A.A., 2009. Predicting rainfed wheat quality and quantity by artificial neural network using terrain and Soil Characteristics. Acta Agri. Scand. Soil Plant Sci. 60, 241–352.
Peng, X., Shi, G., Liu, G., Xu, J., Tian, Y., Zhang, Y., Feng, Y., Russell, A.G., 2017. Source apportionment and heavy metal health risk (HMHR) quantification from sources in a southern city in China, using an ME2-HMHR model. Environ. Pollut. 221, 335–342.
Qishlaqi, A., Moore, F., 2007. Statistical analysis of accumulation and sources of heavy metals occurrence in agricultural soils of Khoshk River banks, Shiraz, Iran. Am. Eurasian J. Agric. Environ. Sci. 2, 565–573.
Rhoades, J.D., 1982. Cation Exchange Capacity. In: Page, A.L. (Ed.), Methods of Soil

Analysis. Part 2. Chemical and Microbiological Properties. American Society of Agronomy, Madison, WI, pp. 49–158.

Rodriguez Martin, J.A., Lopez Arias, M., Grau Corb, J.M., 2006. Heavy metals contents in agricultural top- soils in the Ebro basin (Spain). Application of the multivariate geostatistical methods to study spatial variations. Environ. Pollut. 144, 1001–1012.

Rustullet, J., del Masss del Garraf, Vora N.E., 1996. Estudi de sols fersial. Litics de la serralada litoral catalana. University of Barcelona (Ph.D. Dissertation, Alloway, B. J. 1990. Heavy metals in soil. Blackie and Son, Glasgrow and London, Pp.339).

Shahriari, A., Khormali, F., Kehl, M., Ayoubi, S., Welp, G., 2011. Effect of long-term cultivation and crop rotation on organic carbon in loess soils of Golestan Province, northern Iran. Int. J. Plant Prod. 5 (2), 147–152.

Swan, A.R.H., Sandilands, M., 1995. Introduction to Geological Data Analysis. Blackwell Science, Cambridge (MA).

Swartjes, F.A., 1999. Risk-based assessment of soil and groundwater quality in the Netherlands: Standards and remediation urgency. Risk Anal. 19, 1235–1249.

Szarlowicz, K., Reczynski, W., Misiak, R., Kubica, B., 2013. Radionuclides and heavy metal concentrations as complementary tools for studying the impact of industrialization on the environment. J. Radioanal. Nucl. Chem. 298, 1323–1333.

Taghipour, M., Ayoubi, S., Khadmei, H., 2011. Contribution of lithologic and anthropogenic factors to surface soil heavy metals in western Iran using multivariate geostatistical analyses. Soil Sediment Contam. 28, 921–937.

Trujillo-González, J.M., Torres-Mora, M.A., Keesstra, S., Brevik, E.C., Jiménez-Ballesta, R., 2016. Heavy metal accumulation related to population density in road dust samples taken from urban sites under different land uses. Sci. Total Environ. 553, 636–642.

Zhang, C., Qiao, Q., Appel, E., Huang, B., 2012. Discriminating sources of anthropogenic heavy metals in urban street dusts using magnetic and chemical methods. J. Geochem. Explor. 119-120, 60–75.