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Use of magnetic susceptibility to assess metals concentration in soils developed on a range of parent materials

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ABSTRACT

This research was conducted to evaluate the utilization of magnetic susceptibility measurements in the assessment of metal concentrations in soils developed on a range of parent materials in northwestern Iran. Eighty surface soil samples were collected from eight parent rocks including ultrabasic rocks, basalt, andesite, granite, marl, limestone, Qom formation, and shale. The collected samples were assessed to determine magnetic susceptibility at low frequency (χlf) and concentrations of some metals comprising chromium (Cr), iron (Fe), copper (Cu), nickel (Ni), zinc (Zn), cobalt (Co), and manganese (Mn). The results showed that the highest levels of metals and χlf were observed in basic and ultrabasic soils. Strong positive correlations ($P < 0.01$) detected between χlf and Fe (0.87), Mn (0.78), Zn (0.74), Ni (0.90), Co (0.78), and Cr (0.90) in all samples indicated a potential for using magnetic susceptibility in semi-quantitative estimation of metal concentrations in soils of natural ecosystems. Multiple linear regression between metal contents and χ_{lf} showed that Ni, Zn, Mn, and Co could explain 77% of the total variance in χ_{lf} in the study area. K-means cluster analysis categorized the studied soils into three groups based on metals and χ_{lf} variability. Clustering of soils based on their parent rocks and use of further magnetic measures, i.e., saturation isothermal remanent magnetization (SIRM), isothermal remanent magnetization (IRM100mT) and natural remanent magnetization (NRM) are expected to improve the accuracy of metal concentration predictions in natural soils of the study area.

1. Introduction

Numerous harmful contaminants like as heavy metals are detected in soils and sediments of natural ecosystems. These contaminants are transported by soil erosion and water drainage into reservoirs and cause potential health risks to humans (Erenturk et al., 2014; Szarlowicz et al., 2013; Acosta et al., 2015; Trujillo-González et al., 2016). Due to their non-biodegradable nature, heavy metals, which are precipitated on or adsorbed by particulate matter and accumulated in sediments, may influence the environment over a course of few decades or even centuries (Doichinova et al., 2014; Peng et al., 2017).

Human activities, including vehicle traffic and industrial, agricultural, and mining activities can cause obvious increases in the metal contents of sediments (Jordanova et al., 2013; Dankoub et al., 2012; Taghipour et al., 2011). Meanwhile, in some regions, natural sources, especially igneous and some sedimentary rocks, largely contribute to the release of metals to sediments and their subsequent transfer to reservoirs (Ayoubi et al., 2014).

Lithology is one of the main factors with major effects on soil characteristics. Therefore, characterization of soils developed on various parent materials in arid and semiarid regions is vital (Lu, 2000; Rahardjo et al., 2004; Hanesch et al., 2007). One of the most important soil properties influenced by parent material is magnetic susceptibility. Magnetic susceptibility is greatly affected by natural and anthropogenic factors and various rocks show significant variability in magnetic susceptibility depending on their ferrimagnetic mineral content (Mullis, 1977; Magiera et al., 2006). The presence of ferrimagnetic minerals in soil profiles resulted on highly magnetic parent rocks, e.g. ultrabasic rocks and basalts, indicate high magnetic susceptibility in the surface horizon (Magiera et al., 2006).

Magnetic susceptibility measurements have several applications including the explanation of soil development (Singer et al., 1996), parent rocks and lithology effects (Lu, 2000; Karimi et al., 2017), determination of sedimentation processes (Caitcheon, 1993) and soil drainage circumstances (Mathé and Lévêque, 2003; Asgari et al., 2018), investigation of hydrocarbon (Morris et al., 1994), and heavy metal pollution of the soil (Karimi et al., 2011; Dankoub et al., 2012; Bourliva et al., 2018), soil survey and differentiation of soil boundaries (Grimley

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et al., 2004), soil degradation (Mokhtari Karchegani et al., 2011; Ayoubi et al., 2012; Rahimi et al., 2013), soil moisture regimes discrimination (Valaee et al., 2016), and soil-paleosol studies (Karimi et al., 2013).

Many attempts have been made to monitor of metals in soils and sediments (e.g. Erenturk et al., 2014; Jordanova et al., 2013; Ayoubi et al., 2018a). Geochemical approaches are generally used to monitor the presence of metals in sediments (Jordanova et al., 2013). Considering the need for sampling procedures before analysis, the whole process is typically expensive and time consuming. Therefore, geophysical technologies, which are usually time- and cost-effective, have been proposed to identify the presence and sources of metals and to estimate their risks in soils and sediments (Hay et al., 1997; Lu et al., 2007; Karimi et al., 2011; Naimi and Ayoubi, 2013, Lu et al., 2016; Ayoubi et al., 2018b). These methods commonly use magnetic susceptibility, as an easy-to-measure and concentration-dependent geophysical parameter, to estimate metal contamination.

Up to date, in prediction metals using magnetic susceptibility and other soil properties mainly correlation analysis, multiple linear regression, principal component analysis and cluster analysis have been employed (Taghipour et al., 2011; Dankoub et al., 2012; Shi and Zeng, 2014). It seems that applying using intelligent system such as artificial neural network (Zolfaghari et al., 2015), genetic algorithm (Besalatpour et al., 2014), CHILD algorithm (Abbaszadeh Afshar et al., 2016) should be used by researchers in new future.

Grouping and clustering for soil pollution studies have been successfully in several studies (e.g. Taghipour et al., 2011; Shi and Zeng, 2014). Among the clustering formulation that are based on minimizing a formal objectives function, perhaps the most widely used and studied is K-means clustering. Clustering based on K-means is closely related to a number of other clustering and location problems. These include the Euclidean k-means in which the objective is to minimize the sum of distances to the nearest center, and the geometric K-center problem (Pollard, 1982).

Although many investigations in various countries including Iran have assessed the use of magnetic measures for the evaluation of heavy metals in industrial sites (Ayoubi et al., 2014; Naimi and Ayoubi, 2013; Karimi et al., 2011; Dankoub et al., 2012), limited attempts have been made to determine the effectiveness of magnetic susceptibility measurement for estimating metals in natural ecosystems with various parent materials. The leading objectives of this study were thus i) to determine the variability of magnetic susceptibility and some metals (Fe, Zn, Cu, Mn, Fe, Ni, Cr, and Co) in soils developed on various parent materials and ii) to examine the utilization of magnetic susceptibility measurements for estimating metal concentrations in studied soils in a semiarid region, northwestern Iran.

2. Methods and materials

2.1. Description of the study area

The study area was located in Makoo region, western Azerbaijan Province, northwestern Iran (~39.21° N 45.5° E; Fig. 1). The mean annual precipitation, annual temperature, and elevation of the selected area are 270 mm, 10 °C, and 1634 m above sea level, respectively. Irrigated wheat cropping, dryland farming, and pastures are the main land uses in this area. The major parent materials in the studied area include Permian (limestone), Ordovician (metamorphic rocks), and Cretaceous sedimentary rocks and Eocene igneous rocks. Soil moisture regime is Xeric and soil temperature regime is Mesic in the studied area (Soil Survey Staff, 2006).

2.2. Soil sampling

To examine the hypothesis of this study, eight parent materials, including sedimentary rocks and deposits (limestone, Qom formation, shale, and marl) and igneous rocks (ultrabasic rocks, basalt, andesite, and granite), were selected in the study area. Qom formation consisted of evaporative materials including gypsum, calcite, halite, and fine materials which slightly consolidated. Fig. 1 shows the spatial distributions of the studied rocks. Locations of the studied samples were similar in nature and environmental features (i.e. slope gradient, aspect, vegetation cover, and land uses). All samples were collected from pasture lands on the eastern slopes with 10–20% gradient. Ten soil samples were collected from soils developed on each of the eight parent materials (total number of samples = 80). In each site, three soil samples from 0 to 10 cm were collected and then composited for laboratory analyses. The studied soils were belonged to Entisols and Inceptisols orders according to Soil Taxonomy (Soil Survey Staff, 2010).

2.3. Laboratory analysis

The collected soil samples were air dried, crushed, and passed through a 2-mm sieve for laboratory analyses. Soil pH and electrical conductivity (EC) of saturated soil paste were determined by a pH-meter and EC-meter, respectively (Rhoades, 1982). Pipette approach was applied for particle size distribution analysis (Gee and Bauder, 1986). Soil organic carbon (OC) and calcium carbonate equivalent (CCE) were determined by wet oxidation (Nelson and Sommers, 1986), and back titration (Black, 1965), respectively.

After crushing, a Bartington MS2 dual frequency sensor was applied for measurements of soil magnetic susceptibility (χ) at low (0.47 kHz; χ_{lf}) and high frequency (4.7 kHz, χ_{hf}) using about 10 g of soil held in a plastic vial with 2.3 cm diameter. The dependent frequency (χfd) was calculated using the following equation (Dearing et al., 1996):

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

0.2 g of each soil sample was weighted for metal analysis. A 5 mol L^{-1} HNO_3 solution was used to digest soil samples (Ajayi and Kamson, 1983). Pseudo total content of Cu, Zn, Fe, Cr, Co, Mn and Ni were determined by using an atomic absorption spectrophotometer (AAS). A certified reference material San Joaquin #2709 was analyzed for checking of the precision of the procedure. The detection limits of AAS were 0.015, 0.05, 0.016, 0.05, 0.015, 0.042, 0.1 and 0.035 mg/L, for Zn, Co, Cu, Ni, Cr, Fe, and Mn, respectively.

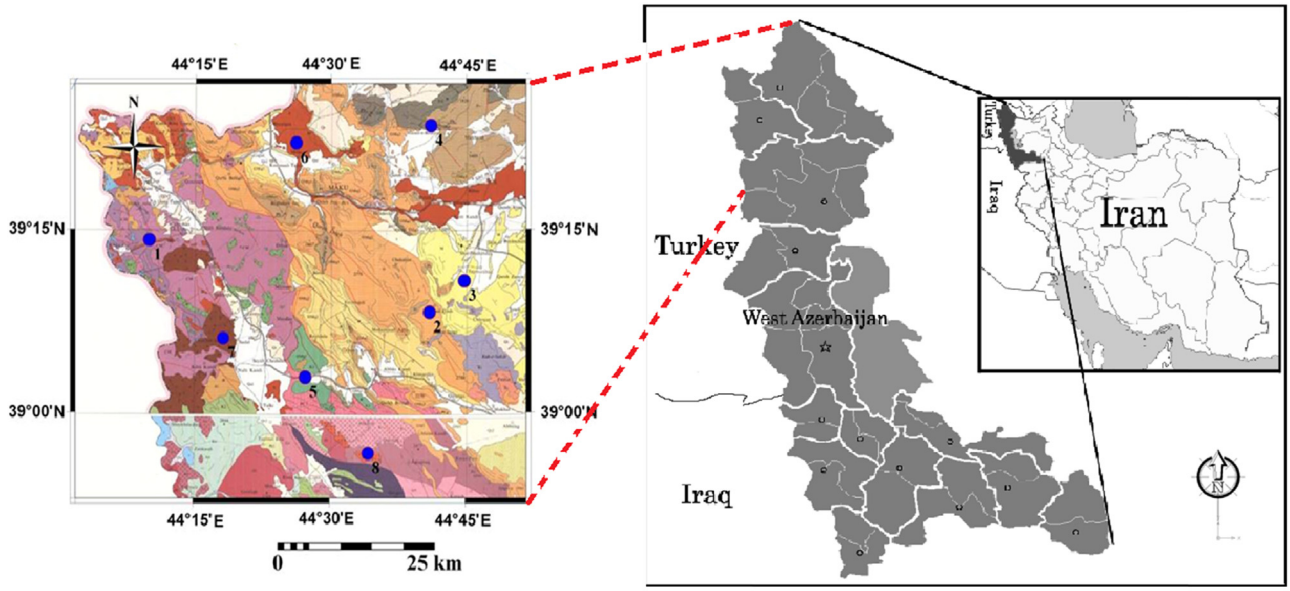
2.4. Statistical analysis

SPSS 19.0 was used for descriptive statistics and determination of correlations between soil magnetic measurements, metals, and soil properties (Swan and Sandilands, 1995). A stepwise regression model was developed to relate magnetic susceptibility to metal concentrations. The factors were included in the model based upon probability ≤ 0.05 according to Freund and Littell (2000). R^2 coefficients were calculated to determine the most accurate predictive model. A K-mean clustering was applied for plausible grouping of the soils based on their parent materials using metals and magnetic susceptibility. R statistical software package was used for this purpose (R Development Core Team, 2013).

3. Results and discussion

3.1. Variability of magnetic measures and soil properties

Table 1 presents soil properties including magnetic susceptibility and metal contents. As seen, soils developed on ultrabasic rocks had the highest χ_{lf} (1274×10^{-8} m^3/kg). The lowest χ_{lf} belonged to soils developed on limestone rocks (71.09×10^{-8} m^3/kg). The mean magnetic susceptibility of dependent frequency (χ_{fd}) was higher than 4% in soils developed on sedimentary rocks. Therefore, the predominant magnetic minerals in these soils were superparamagnetic and the obtained χ_{fd}



Number of location	Sybmbol	GPS	Lithology
1		39° 12 ´E, 44° 9 ´N	Ultrabasic rocks
2		39° 19 ´E, 44° 21 ´N	Qom formation
3		39° 12 ´E, 44° 50 ´N	Marl
4		39° 24 ´E, 44° 38´N	Shale
5		39° 02´E, 44° 26 ´N	Limestone
6		39° 22 ´E, 44° 23 ´N	Basalt
7		39° 12 ´E, 44° 15 ´N	Andesite
8		38° 59 ´E, 44° 37 ´N	Granite

Fig. 1. Location of the studied area in north-western Iran, Azerbaijan province, Maku district, and locations of studied sites in various parent materials.

Table 1
Description statistics of heavy metals (mg kg^{-1}), magnetic susceptibility at low frequency ($\times 10^{-8}$ m^3 kg^{-3}) and frequency dependent (%) and some soil properties in studied rocks.

Lithology	Statistics	Fe	Mn	Cu	Zn	Ni	Co	Cr	χfd	χlf	EC	Clay	SOM	CCE	pH	Sand
Ultrabasic (*N* = 10)	Mean	22,062	1122	22	43.5	1667	94	304	1.47	1274	0.23	12.01	3.44	5.01	7.09	68.9
	CV %	12.03	34.01	11.2	9.80	11.32	12.12	23.90	35.3	23.38	11.23	17.8	11.2	9.80	11.32	21.0
	Skewness	0.01	−0.12	0.23	−0.20	0.11	0.23	0.12	1.10	0.49	0.10	0.23	0.23	−0.2	0.11	0.23
Basalt (*N* = 10)	Mean	18,460	890	41.5	43.4	91.3	20.8	131.4	2.66	1201	0.17	30.01	3.78	4.3	7.21	28.9
	CV %	11.2	12.3	8.5	14.8	19.2	21.4	14.9	13.72	16.811	9.89	12.21	18.21	23.1	24.9	19.0
	Skewness	0.01	−0.12	0.23	−0.2	0.11	0.23	0.12	0.99	0.08	0.11	0.23	0.13	−0.12	0.23	0.09
Andesite (*N* = 10)	Mean	12,096	742	53	57	322	35	140	1.67	404	0.13	31.01	4.22	4.6	7.01	26.7
	CV %	14.56	27.02	18.09	11.20	17	12.0	23.10	23.46	21.49	11.23	18.9	17.9	21.3	22.3	23.0
	Skewness	0.22	0.01	0.89	−0.01	0.32	0.34	0.77	−0.21	−0.01	0.23	0.34	0.89	1.01	0.89	1.0
Granite (*N* = 10)	Mean	15,395	947	27	68	42	21	52	1.45	376	0.23	5.8	4.21	4.5	7.22	80.21
	CV %	23.1	24.1	11.1	13.2	15.9	21.1	11.0	46.6	10.1	12.34	18.4	13.1	15.2	15.9	19.0
	Skewness	0.01	−0.99	0.01	0.12	0.23	1.01	−0.23	0.11	0.90	0.99	0.44	0.01	0.12	0.23	0.23
Malr (N = 10)	Mean	8367	392	43	37	106	19.9	62.8	4.56	264	0.17	27.8	3.99	7.0	7.23	49.2
	CV %	32.1	18.21	23.1	24.9	22.1	17.8	9.7	45.99	21.66	14.5	19.32	11.1	13.2	19.9	25.0
	Skewness	0.21	0.13	− 0.12	0.23	−0.20	0.11	0.23	1.01	−0.10	0.34	0.21	0.01	0.12	0.23	0.23
Limestone (N = 10)	Mean	11,906	475	29	46.9	72	18.7	56.5	5.01	71.09	0.23	32.9	3.21	28.0	7.5	40.2
	CV %	12.03	34.01	11.2	9.80	11.32	12.12	23.90	67.89	33.21	16.78	7.9	18.21	23.1	24.9	17.9
	Skewness	0.34	0.01	1.10	1.10	0.99	0.09	0.01	1.10	0.40	0.32	0.32	0.13	−0.12	0.23	0.33
Qom formation (N = 10)	Mean	6885	308	33.1	37.3	94.8	18.8	56.8	5.02	90.71	0.22	33.8	3.89	32.0	7.4	29.1
	CV %	12.56	17.8	13.44	21.45	23.67	12.1	12.09	78.09	36.08	20.1	9.8	11.32	12.12	23.90	19.01
	Skewness	0.09	−0.99	1.10	1.10	0.90	0.43	0.12	0.09	0.76	0.45	1.01	0.99	0.09	0.01	0.12
Shale (N = 10)	Mean	7815	712	31.1	58.4	66.9	18.9	48.1	4.84	138	0.09	35.8	4.01	8.0	7.6	38.9
	CV %	17.9	21.3	22.3	34.11	12.4	12.7	24.1	52.33	31.79	18.9	11.1	17.9	21.3	22.3	18.9
	Skewness	0.89	1.01	0.89	1.01	0.12	0.34	0.47	−0.89	0.64	0.01	1.01	0.89	1.01	0.89	0.21

values reflected their control of the magnetic signal (Dearing, 1996; Jordanova et al., 2003). A strong positive correlation was observed between χ_{lf} and χ_{fd} in sedimentary rocks ($r = 0.85$; $P < 0.01$) and confirmed that χ_{lf} was increased by pedogenic processes throughout an increasing content in superparamagnetic particles (Hu et al., 2007). Moreover, soil developed on sedimentary rocks (marl, limestone, Qom formation, and shale) showed lower χ_{lf} than soils developed on igneous rocks. This finding can mainly be attributed to the larger amounts of ferrimagnetic minerals in their parent materials. Sedimentary rocks with high amount of diamagnetic (calcite, gypsum, and halite) and paramagnetic minerals (e.g. aluminosilicate clays) had low magnetic susceptibility as already reported by de Jong et al. (1999), and Karimi et al. (2017).

Soils developed on igneous rocks had low χ_{fd} values (1.45–2.66%)

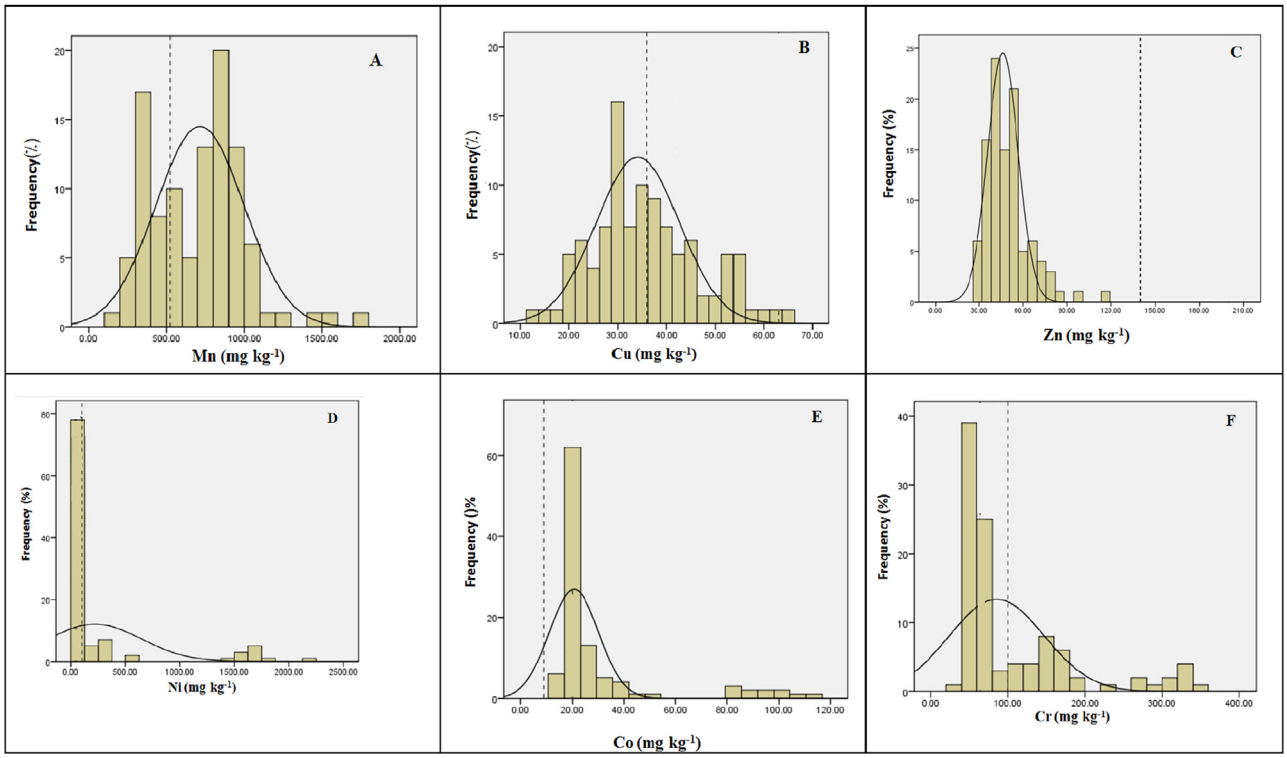


Fig. 2. Plot frequency distributions of metal concentrations (mg kg^{-1}) measured for the whole data as compared to the Netherlands soil guideline values.

Table 2
Correlations between soil properties with magnetic susceptibility and heavy metals concentration (N = 80).

	χlf	χfd	Fe	Mn	Cu	Zn	Ni	Co	Cr
Clay	**−0.44****	0.66**	−0.25*	−0.27*	0.59**	−0.17	0.31**	−0.014	0.22*
Sand	**0.38****	−0.76**	0.32**	0.21*	−0.64**	0.11	−0.29**	0.068	−0.23*
SOM	**−0.54****	**0.5****	**0.34****	**0.67****	**0.78****	**0.59****	**0.81****	**0.38****	**0.39****
CCE	**−0.70****	0.13	**−0.66****	**−0.71****	−0.18	**−0.33****	−0.13	**−0.44****	**−0.53****
EC	**−0.43****	0.46**	−0.50**	−0.31**	0.42**	−0.12	0.22*	−0.08	0.11
pH	−0.38**	−0.003	−0.35**	−0.61**	−0.01	−0.44**	0.28**	−0.24*	−0.075

*, ** significant at 0.05 and 0.01 probability level.

and the absence of significant correlations between χ_{lf} and χ_{fd} (r = 0.05; P > 0.05) indicated that a dominant portion of ferrimagnetic minerals in soils developed on ultrabasic, basalt, granite, and andesite rocks originated from their parent rocks, but the dilution effects of soil development decreased χ_{lf} in soils compared to their parent materials.

According to Table 1, the studied soils were alkaline (pH > 7) and non-saline (EC < 1 dS/m). Soil organic matter (SOM) varied from 3.21% to 4.22% and (CCE) ranged from 4.3% in basaltic soils to 32% in soils developed on Qom formation. Particle size distribution also had a high variability within the studied soils. The heaviest soils were those developed on basalt and some sedimentary rocks (limestone and Qom formation). The lightest soils were those developed on granite and had about 80% sand content. These findings are in accordance with previous literature (Yousefifrad et al., 2012).

3.2. Variability of metals

Table 1 summarizes the concentrations of the studied metals. The highest and lowest Fe contents were observed in soils developed on basic and ultrabasic rocks (22,062 mg/kg) and Qom formation (6885 mg/kg), respectively. Similar findings were recorded in cases of Mn, Ni, Co, and Cr. However, the highest Cu and Zn levels were present in soils developed on basalt and granite, respectively. These results are in line with the findings of Alloway (1990), Fergusson (1990), Galan et al. (2008), and Mico et al. (2006) who reported higher contributions of basic rocks to the release of these elements to soil compared to acidic rocks. According to Fergusson (1990), shale deposits may be rich in some metals including Zn, V, Mo, Hg, As, Ag, and Pb. Meanwhile, other elements, e.g. Cu, Cr, Co, and Ni have higher concentrations in basic igneous rocks. Igneous rocks and especially basic and ultrabasic have generally higher concentrations of metals rather than acidic and sedimentary rocks (Galan, 2008); moreover, they are more sensitive to physical and chemical weathering (Yousefifrad et al., 2012); and consequently release more elements in associated soils.

For the assessment of soil contamination status, the Netherlands Guideline was employed. According to Swartjes, (1999), the Netherlands target values determine concentrations which fully recover the functional properties of the soil for animals, plants, and humans. The frequency distributions of the measured metals are presented in Fig. 2 and showed that several of the metal contents exceeded the Netherlands Guideline. Co levels were higher than the Netherlands target value in all studied sites. Mn, Cu, Ni, and Cr concentrations exceeded the Netherlands Guidelines in 64.0%, 43.7%, 36.9%, and 34.0% of the studied soils, respectively. Zn and Fe levels were within the allowed range in all sites (Fig. 2). As the studied area was located far from the urban and industrial sites, lithology had the main contribution to the metal contents of soils. Likewise, studies in Alicante Province, Spain

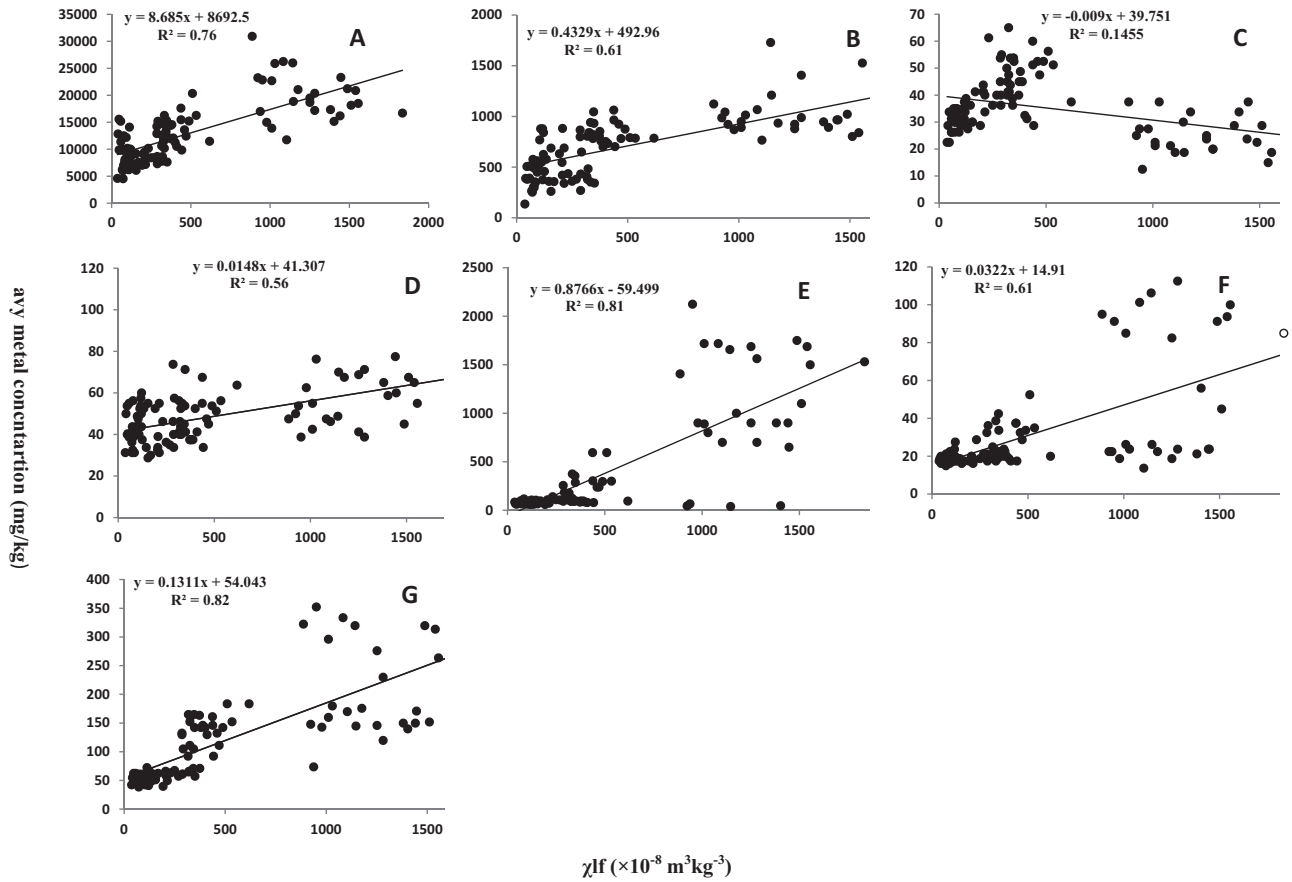


Fig. 3. Relationships between heavy metals concentration (mg/kg), and magnetic susceptibility in all studied soils. A) Fe, B) Mn, C) Cu, D) Zn; E) Ni: F) Co; G) Cr.

Table 3
Pearson correlation coefficients among metals of the studied soils in the study area ($N = 80$).

Metals	Fe	Mn	Cu	Zn	Ni	Co	Cr
Fe	1						
Mn	0.81**	1					
Cu	−0.11	−0.14	1				
Zn	0.50**	0.57**	0.025	1			
Ni	0.17	0.05	0.41**	−0.30**	1		
Co	0.70**	0.64**	0.14	0.25*	0.56**	1	
Cr	0.50**	0.38**	0.36**	−0.08	0.80**	0.65**	1

Table 4
Multiple regression analysis results between magnetic susceptibility as dependent variable and heavy metal concentrations as independent variables in the study area.

Model	*Unstandardized coefficients*		*Standardized coefficients*	
	B	Std. Error	Beta	Sig.
(Constant)	−341.920	105.511		0.001
Ni	0.687	0.093	0.759	0.0001
Zn	8.499	2.171	0.228	0.0001
Mn	0.431	0.112	0.269	0.0001
Co	4.559	2.075	0.230	0.03
R^2	0.77			

(Mico et al., 2006) and Piemonte, Italy (Facchinelli et al., 2001) used multivariate analysis and showed that Co, Cr, and Ni were mainly controlled by lithology.

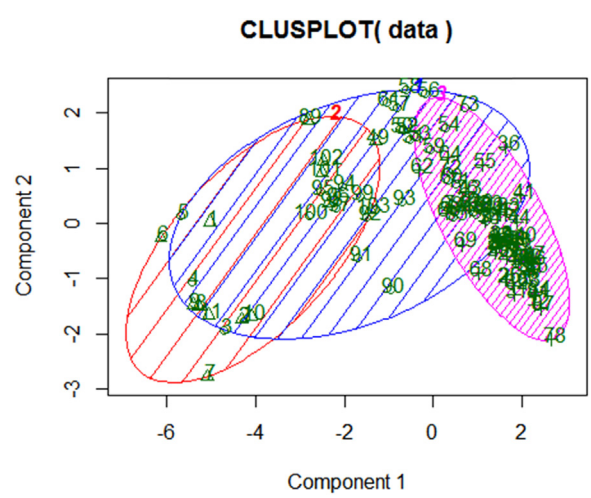


Fig. 4. K-means cluster analysis of all sampling sites (N = 81) based on the variables of magnetic susceptibility, heavy metals. The sites were classified into three groups, showing group 1 (△), group 2 (×) and group 3(+).

3.3. Correlation analysis

Correlation analysis was done to explore the linear relationships between magnetic susceptibility (χlf), metals and selected soil properties (Table 2). Soil organic matter (SOM) was positively related to content of Fe ($r = 0.34$; $P < 0.01$), Mn ($r = 0.67$; $P < 0.01$), Cu ($r = 0.78$; $P < 0{:}01$), Zn ($r = 0.59$; $P < 0.01$), Co ($r = 0.38$; $P < 0.01$), and Cr ($r = 0.39$; $P < 0.01$). Rodriguez Martin et al. (2006) stated that cation exchange capacity (CEC) of organic matter led to high sorption of metals in soils. These positive and significant

Table 5
Loadings in components 1 and 2 for studied variables extracted from k-means clustering for grouping soils.

Variable	Components		Communalities
	1	2	
χ_{lf}	0.89	−0.006	0.79
Fe	0.88	0.21	0.83
Mn	0.81	0.28	0.75
Cu	−0.33	0.76	0.68
Zn	0.52	0.53	0.57
Ni	0.91	−0.26	0.90
Co	0.84	−0.21	0.76
Cr	0.93	−0.03	0.87

correlations implied that the tendency of metals to organic matter to make stable organic complexes (Rustullet, 1996; Qishlagi and Moor, 2007).

The analysis of correlations between magnetic susceptibility and soil properties showed that χ_{lf} had a significant positive correlation with sand content ($r = 0.38$, $P < 0.01$). This positive relationship emphasized that ferrimagnetic minerals remained in sand fraction (especially in igneous rocks) and semiarid conditions of the studied area were not sufficient to release Fe-bearing minerals to clay fraction. Significant negative correlations were observed between χ_{lf} and SOM ($r = -0.54$; $P < 0.01$), EC ($r = -0.43$; $P < 0.01$), and CCE ($r = -0.70$; $P < 0.01$). These negative correlations confirmed that diamagnetic minerals including organic particles, halite and calcium carbonates reduced magnetic susceptibility. These results are in accord with the findings of Marwick (2005), Dankoub et al. (2012) and Naimi any Ayoubi (2013).

Fig. 3 presents linear relationships between metal concentrations and magnetic susceptibility at low frequency for all studied soils. As seen, significant positive linear coefficients ($P < 0.01$) were found between χ_{lf} and Cr, Zn, Mn, Co, Ni, and Fe. No significant relationship was found between Cu and magnetic susceptibility. The association between metals and magnetic minerals indicated that higher metal contents improved magnetic susceptibility. The developed linear equations could explain about 82%, 81%, 76%, 61%, 61%, and 56% of the variability in Cr, Ni, Fe, Mn, Co, and Zn in all studied soils, respectively. Although several studies have reported significant relationships among magnetic susceptibility and heavy metals in industrial and urban sites (i.e. Marwick, 2005; Rodriguez Martin et al., 2006; Canbay et al., 2010; Ayoubi et al., 2018a,b), there has been little evidence regarding natural ecosystems such as that studied in the present research. Overall, our findings suggested that the developed linear equations for Cr, Mn, Co, Zn, Fe, and Cu are reliable and reasonable for the prediction of metals in soils developed on various parent rocks in reconnaissance surveys where preliminary information is required at the large scale. It seems that the clustering of soils in the region based on their parent materials would improve coefficients of determination for developed linear models. Moreover, it is speculated that applying non-linear modeling and intelligent systems (artificial neural network, genetic algorithm, and so on) may improve the results of metal prediction using magnetic measurement.

The correlation coefficients among different metals are given in Table 3. The high correlations among metals suggest similar underlying factors regarding their sources and releasing in soils. The correlation coefficients among Mn, Fe indicated the same sources and similar pathways to be release in soils (Li et al., 2001; Dankoub et al., 2012). On the other hand, a high and positive significant correlation was found between Cr and Ni ($r = 0.80$ $P < 0.01$). Some researchers attributed such auto-correlations to various sources including natural or anthropogenic sources (Dankoub et al., 2012), but in our study area far away the anthropogenic sources, these correlations mainly attributed to variability in parent material.

3.4. Multivariate analysis

The results of MLR modeling between χ_{lf} and metal concentrations are given in Table 4. Stepwise regression modeling was employed to ascertain the priority of metals in the model. The results showed that Ni, Zn, Mn, and Co explained the variance in χ_{lf} in all studied soils. According to the obtained correlations, about 77% of the variance in magnetic susceptibility was explained by Ni, Zn, Mn, and Co concentrations, which had the highest correlation coefficients (Table 2). Despite their strong correlations with χ_{lf} (Table 2), Fe and Cr were not entered in the stepwise regression model (Table 4). This was due to the collinearity among metals in the study area. The standardized coefficients provided in Table 3 imply that Ni accounted for the major proportion of variance in χ_{lf} (standardized coefficient of 0.759 compared to 0.228, 0.269, and 0.230 for Zn, Mn, and Co, respectively). Previous studies have identified different metals to explain magnetic susceptibility depending on local conditions, land use, climate, and lithology. In Isfahan, Iran (an area highly affected by urbanization), Karimi et al. (2011) reported Pb, V, and Cu explained 54% of the variance in χ_{lf}. Ayoubi et al. (2018b) studied an industrial site around Isfahan and concluded that Fe, Pb, and Cu were the main metals controlling the variance in χ_{lf} (coefficient of determination = 0.65).

To explore the contributions of different parent materials to the variance in metals and magnetic susceptibility in the studied area, K-means cluster analysis was carried out based on the variables of magnetic susceptibility and metals. As seen in Fig. 4, the soils in the study area were divided into three groups based on magnetic susceptibility and the concentrations of metals. Group 1 consisted mainly of soil samples developed on ultrabasic and basic rocks and group 3 predominantly consisted of soil samples developed on sedimentary rocks such as marl, limestone, shale, and Qom formation. The second group, i.e. the intermediate cluster, comprised soil samples of acidic igneous rocks. The loadings of two first components are presented in Table 5. As seen in this table, at the first components most of variables including magnetic susceptibility (loading factor (LF) = 0.89) and metals of Fe (LF = 0.88), Mn (LF = 0.81), Ni (LF = 0.91), Co (LF = 0.84), and Cr (LF = 0.93) had major contributions. As well, only Cu (LF = 0.76) and partially Zn (LF = 0.53) showed high contributions in component 2. While some features of this group, like magnetic susceptibility, were almost similar to those of basic rocks, they resembled sedimentary rocks, e.g. shale, in some other features, such as the concentration of elements. Soil grouping based on these clusters seems to facilitate the development of more powerful predictive models.

4. Conclusion

This study investigated the relationships between the content of metals (Fe, Mn, Cu, Zn, Ni, Co, and Cr) and magnetic susceptibility in soils developed on a range of parent rocks, ranging from sedimentary to basic igneous rocks, in a semiarid area in northwestern Iran. The highest magnetic susceptibility and greatest concentrations of some metals were observed in soils developed on ultrabasic rocks. The association between metals and ferrimagnetic metals enables us to predict metal concentrations in soils using magnetic susceptibility as a geophysical approach. Our results showed that magnetic susceptibility could successfully predict the concentrations of Co, Cr, Mn, Fe, Zn, and Ni with coefficients of determination equal to 0.61, 0.82, 0.61, 0.76, 0.56, and 0.81, respectively. These coefficients are acceptable and reliable (considering that magnetic measures are cost-effective and fast) in reconnaissance studies where general information about metal pollution in natural ecosystems is required. The inclusion of other magnetic measures, such as saturation isothermal remanent magnetization (SIRM), natural remanent magnetization (NRM), isothermal remanent magnetization at the field of 100 mT (IRM100mT) and the backfield of 100 mT (IRM-100mT), is expected to improve the accuracy of metal predictions and can thus be applied as a fast and cost-effective

alternative for geochemical analyses.

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