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Mapping and risk assessment of heavy metals in agricultural soils of the Siakh Darengoun Region, Shiraz, Iran

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Abstract

Four heavy metals were measured in forty-nine topsoil samples collected from agricultural areas in Siakh-Darengoun, Iran. The goals were to investigate soil spatial distribution patterns of metals; their potential ecological risk; and sources. The Hakanson potential ecological risk index and index of geo-accumulation (Igeo) were used for evaluating the condition of soil heavy metal enrichment and the extent of potential ecological risk. Results demonstrated that the mean concentrations in the agricultural soils were 2.23 mg/kg for Cd, 5.3 mg/kg for Cu, 38.002 mg/kg for Pb, and 13.84 mg/kg for Zn. The average concentrations of Cd and Pb in the agricultural soils were higher than average worldwide soils and for Cu and Zn, values were lower than average worldwide soils. The spatial mapping of the distribution of heavy metals produced by kriging interpolation showed similar patterns for all heavy metals, and higher concentrations of all heavy metals were observed in the western and southern parts of the study area. Our findings demonstrated that in the Siakh-Darengoun plain, natural sources affect the levels of Cu and Zn, however, anthropogenic sources such as chemical fertilizers, especially phosphate fertilizers could be the major sources of Cd and Pb. Hossain Abad agro industry in the west of the study area can be considered as one of the most important heavy metal sources. The geo-accumulation index classified Cu and Zn into no pollution levels, Cd and Pb into unpolluted to moderately polluted level. Cd produced serious ecological risk in agricultural soils and was the main pollutant, while the Cu, Pb and Zn had low ecological risk. Comprehensive potential ecological risk indexes of all metals showed that the soils in Siakh Darengoun were suffering from high level of ecological risk.

Keywords: Spatial Distribution, Geostatistics, Ecological Risk, Heavy Metals, Chemical Fertilizers.

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Introduction

Soil is an important sink for heavy metals released into the environment because of natural and anthropogenic activities (Bednářová et al., 2016). Heavy metal inputs from anthropogenic origins to the soil are much greater than metals from natural sources (Teng et al., 2014). Natural accumulation of heavy metals in the soil is caused by weathering from parent materials (bedrock) and pedogenic processes (Mentese and Tagil, 2016). Other natural factors like water regime and atmospheric transmission could contribute to different heavy metal accumulation in soils (Zhang et al., 2015). In addition, heavy metals in soil may originate from anthropogenic sources such as mining and smelting, atmospheric deposition, fossil fuel combustion, waste incineration, chemical industry, and agricultural activities (Kelepertzis, 2014). The presence of heavy metals in agricultural soils is of increasing concern due to their potential to accumulate in less soluble forms, their transfer into soil solution and finally leading to deterioration of groundwater and crop quality (Marrugo-Negrete et al., 2017). However, conventional farming practices can commonly cause heavy metal enrichment in the soil. Excessive accumulation of heavy metals in the soil are closely related to intensive agricultural practices such as application of commercial fertilizers, pesticides and sewage sludge, which generally contain varying amounts of heavy metals as impurities (Cai et al., 2014). The agricultural activities like sewage sludge or fertilizer spreading are the main sources of heavy metals, particularly for cadmium (Cd), copper (Cu) and zinc (Zn) (Maas et al., 2010). Although fertilizers provide adequate amounts of nutrients to crop plants and produce high harvests, long-term use of inorganic fertilizers, metal-containing pesticides, and organic waste can gradually add elevated concentrations of heavy metals in agricultural soils. The soil enrichment with heavy metals (Cu, Zn and Cd) is the most discernible result characterizing districts that have undergone a long history of intensive agrochemical application (Kelepertzis, 2014). Regardless of the origin or contamination source, heavy metals enter in crops and reach humans through the food chain and are therefore health hazards (Mirzaei et al., 2014). Adverse effects of heavy metals in common plants include weak plant growth, dark green leaves, chlorosis, and stunted foliage. The common human health effects include nephrotoxicity, cardiovascular toxicity, carcinogenicity, allergy, neuro-developmental disorders, and damage to the reproductive system Thus, assessment of heavy metal contamination and spatial distribution in agricultural soils and its consequences for food production and quality is of special concern (Bednářová et al., 2016). Studying spatial distribution patterns of important heavy metals is necessary to evaluate their effects on soils and for delineating soil contamination zones (Omran et al., 2012). Geographical information systems (GIS) and geo-statistical methods provide useful tools to evaluate the distribution of soil variables (Delavar and Safari, 2016). Kriging is a geo-statistical technique, which was originally developed by D.J. Krige and H.S. Sichel in mining in the 1950s and 1960s and was further extended by Matheron (1963) as a fully-fledged scientific theory. Kriging provides unbiased estimation of variable values at un-sampled locations and it is a minimum-mean-square-error method of spatial estimation (Wang et al., 2012). The geo-statistical methods apply the stochastic theory of spatial autocorrelation for both interpolation and for apportioning uncertainty. The theory of a regionalized variable is the base of geo-statistics that uses variogram to measure the spatial variability of a regionalized variable and provides the input parameters for the kriging method of spatial interpolation (Yang et al., 2014). In recent years, numerous studies have focused on the concentration, spatial distribution, and sources of heavy metals in agricultural soils (Nicholson et al., 2003; Xia et al., 2004; Rodríguez Martín et al., 2007; Dou et al., 2008; Lei et al., 2009; Maas et al., 2010; Lu et al., 2012; Sun et al., 2013; Liu et al., 2013; Khan et al., 2013; Cai et al., 2014; Kelepertzis, 2014; Xu et al., 2014;

Bednářová et al., 2016; Tóth et al., 2016; Mohammadpour et al., 2016; Liu et al., 2016; Marrugo-Negrete et al., 2017; Baran et al., 2017). Because agricultural soils are the basis for food production and their role in transfer of pollutants to other ecosystem components and humans, therefore, it is essential to monitor heavy metals concentrations, spatial distributions and sources in agricultural soils. Siakh Darengoun is located in the southwest of Shiraz County, Fars Province Iran. Siakh Darengoun is one of the main poles of crops and agricultural production in this area. However, no literature exists about the heavy metal pollution in agricultural soils of the area. The aim of this research was to investigate and study spatial distribution of heavy metals in Siakh Darengoun soils using geo-statistics techniques. Another objective of this work was to estimate the potential ecological risk of heavy metals in soils.

Materials and Methods

Study area

The case study of Siakh Darengoun (29° 13' - 29° 36' N, 52° 14' to 53° 35' E), with an elevation of 1700 m above sea level, is part of the large area of Ghareh Aghaj river basin (Figure 1). The annual average precipitation in the region is 320 mm with a mean annual temperature of 14 °C. The total area of the study area is about 120 km^2. Approximate area under cultivation is 12000 ha with annual production of about 11000 tons. The soil in the area is mainly silty-clay with medium to fine soil particle-size. The dominant crops in this area are wheat, barley, alfalfa, corn, tomatoes, rapeseed and potatoes.

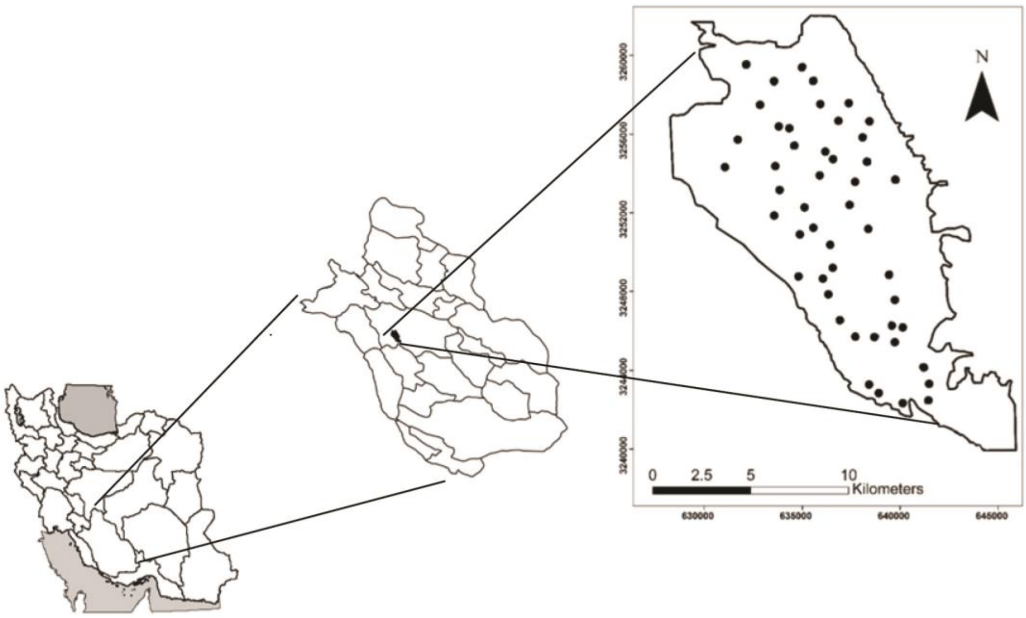

Figure 1. Study area and the distribution of sampling points.

Soil sampling and chemical analysis

The survey area was divided into 49 cells of 1.5 km × 1.5 km in size and 49 topsoil samples (0-20 cm depth) were collected from the center of each cell. At each sampling point, 4 to 5 subsamples were collected and mixed to obtain a composite sample. All soil samples were stored in polyethylene bags, and were air-dried, then sieved through a 2.0-mm mesh sieve to remove debris, stones, and coarse materials. Soil samples were then ground until fine particles (<150 μm) were obtained. Digestion of milled soil samples were carried out by HNO_3, $HCLO_4$ and HCl. Concentrations of Cd, Cu, Pb and Zn were determined by atomic absorption spectrometry (Analytik Jena ContrAA 700). Cu, and Zn were measured by flame atomic absorption spectrometry (F-AAS), while Pb, and Cd were measured by Graphite furnace atomic absorption spectroscopy (GF-AAS). The values of LODs were 1.062 mg/kg, 0.24 mg/kg, 1.008µg/kg, 0, and 1.126 µg/kg for Zn, Cu, Pb, and Cd respectively. Also, the limit of quantification (LOQ) of the metals were 3.92 mg/kg, 0.90 mg/kg, 3.79 µg/kg, and 3.89 µg/kg for Zn, Cu, Pb, and Cd respectively. Each soil sample was measured in three replicates. The blank samples (sample with all reagents except the soil sample) underwent the same applications as for soil samples. The precision was expressed by the %RSD (percent relative standard deviation). The %RSD values of heavy metals ranged from 2.9-6.5.

Statistical analysis

SPSS version 20 and MS-Excel 2007 were used for all statistical analysis. The Kolmogorov–Smirnov test was applied to check for the normality of the each heavy metal. Pearson’s correlation analysis was used to evaluate the relationship between soil properties (pH and EC) and heavy metals concentrations.

Heavy metals risk assessment: Geo-accumulation Index (I_{geo}) and Assessment of potential ecological risk

In this study, different indexes such as Geo-accumulation Index (I_{geo}) and Ecological risk index were used for risk assessment of heavy metals pollution in agricultural soils.

Geo-accumulation index (Igeo) for the heavy metals in agricultural soils in the study area was evaluated using equation 1 (Muller, 1979). This method determines the pollution levels in sediments or soils with respect to the toxic metals by comparing present soil concentrations of heavy metals with past concentrations (Giri et al., 2017). As describe by Müller [21], the geo-accumulation index is a quantitative measure of metal pollution in sediments and soils (Jiang et al., 2013).

$$I_{geo} = \log_2\left(\frac{c_n}{1.5B_n}\right) \quad (1)$$

Where C_n is the concentration of metals measured in soil samples, and B_n is the geochemical background or pristine concentration of the metals. The factor 1.5 in the equation is the background matrix correction factor due to the natural changes that may have occurred throughout the years in the environment (Christophoridis et al., 2009). Seven classes of pollution from uncontaminated (Igeo ≤ 0) to extremely contaminated (Igeo ≥ 5) are considered for the quality of soils or sediments according to values of Igeo.

Potential ecological risk index (RI) has been widely used to assess the degree of heavy metal pollution in soil based on Eqs. (3)-(5) (Yan et al., 2017; Hakanson, 1980) which has been initially used by Hakanson (1980), according to the toxicity of heavy metals and the response of the environment (Sun et al., 2010).

$$RI = \Sigma E_i \quad (2)$$

$$E_i = T_i f_i \quad (3)$$

$$f_i = \frac{c_i}{B_i} \quad (4)$$

where RI is the sum of all risk factors for heavy metals in soils, Eri is the potential ecological risk index value of each heavy metal, T_i is the toxic response factor of heavy metal, f_i is the contamination factor, C_i is the measured concentration in the soil, and Bi is the background value for metals. The toxic coefficient of heavy metals (toxic-response factors) for Cd, Cu, Pb, and Zn are 30, 5, 5, and 1, respectively (Yangchun et al., 2017).

Based on Hakanson (1980), the following classifications are proposed for the Er and RI values: The Er (potential ecological risk coefficient) is categorized into five classes: Er <40, low ecological risk; 40 < Er ≤80, moderate ecological risk; 80 < Er ≤160, appreciable ecological risk; 160 < Er ≤320, high ecological risk; and >320, serious ecological risk; and the RI is classified into four classes: RI <150, low ecological risk;

150 < RI <300, moderate ecological risk; 300 < RI <600, high ecological risk; and RI ≥ 600, very high ecological risk (Ranjbar Jafarabadi et al., 2017).

Geo-statistical analysis

Interpolation methods for spatial interpolation is extensively applied when data are collected at separate points (e.g. soil profiles) for creating continuous information (Ali and Moghanm, 2013). The geo-statistical interpolation techniques such as kriging use the semivariograms to explain the spatial dependence of regionalized variables and provide basis of spatial interpolation. Ordinary kriging (OK) is one of the most commonly applied interpolation methods of analyzing spatial distribution variability of heavy metals in soil (Yan et al., 2015). GS+ software was used to carry out the geo-statistical analysis. The semivariograms function is expressed as:

$$\gamma(h)=\frac{1}{2\mathrm{n}(\mathrm{h})}\sum_{i=1}^{n(h)}\left[Z(xi)-Z(xi+h)\right]^2 \quad (5)$$

where $\gamma(h)$ is the semivariance, h is the lag distance, n(h) is the number of data pairs separated by h, e Z(xi) is the measured value for soil heavy metal at location xi, and $Z(xi + h)$ is soil heavy metal value at location (xi + h).

Experimental semivariograms were obtained by computing variogram at various lags. Therefore, the variogram plot was fitted with a theoretical model like spherical, Gaussian, and exponential models. The fitted model provides data on the spatial structure as well as the input parameters such as range, nugget, and sill for kriging interpolation. The obtained information from semivariogram was applied to calculate sample-weighing factors for spatial interpolation by a kriging method with the nearest 16 sampling points and a maximum searching distance equal to the range distance of the variable (Lark and Ferguson, 2004). The OK estimator is expressed as (Webster and Oliver, 2001):

$$Z^*(x_0)=\sum_{i=1}^{n}\lambda_i z(x_i) \quad (6)$$

where Z(xi) is the value measured in location xi, Z*(xo) is the interpolated value of variable Z at location xo, n is the number of neighboring observation used in kriging, and λ_i is an unknown weighting of the measured value in location *i*.

The variography, fitting of models, and kriging were performed using the software package GS+ (Gamma Design Software 2004), while mapping was conducted using ArcGIS 9.0.

Results and Discussion

Concentration of heavy metals in agricultural soils of Siakh Darengoun area

Table 1 presents the descriptive statistics for the studied heavy metal concentrations in the agricultural soils of Siakh Darengoun. Application of the K-S test indicated that Cd, Cu, Pb, and Zn data are all normally distributed, and the EC and pH do not conform to a normal distribution. The mean concentrations of heavy metals in agricultural soils follow a decreasing order as: Pb > Zn > Cu > Cd. The mean level of Cd, Cu, Pb, and Zn in the study area was 2.23, 5.3, 38.002 and 13.84 mg/kg, respectively. Also the heavy metals concentrations (mg/kg) in agricultural soils ranged as follows: Cd 1.3–3.08), Pb 10.3–95.83, Cu 1.2–9.75, and Zn 0.73–43.04 mg/kg. The average concentrations of Cd and Pb in the agricultural soils were higher than average worldwide soils (Cd= 0.41, Pb= 27 mg/kg) (Table 1), and for Cu and Zn, values were lower than average worldwide soils (Cu= 38.9, Zn= 70 mg/kg) (Kabata-Pendias (2011). These results indicate that agricultural soils of the study area are contaminated with cadmium and lead due to excess application of agricultural inputs such as fertilizers and pesticides in agricultural activities to enhance productivity. Use of several phosphate fertilizers unintentionally adds Cd and other heavy metals to the soil such as F, Hg, and Pb (Raven et al., 1998). Gimeno-García (1993) stated that Cd content of soils was increased due to the excessive use of phosphatic fertilizers and other agrochemicals used on vegetable crops, which have a Cd content of 2-156 mg/kg. In addition, Gimeno-García (1993) reported a little increase in Pb content of soil because of urea and superphosphate fertilizers addition in cultivated soils of Valencia.

Table 1. Statistical summary of heavy metal concentrations in topsoil and some soil properties.

	Minimum	Maximum	Mean	Median	S.d	Cv%	Var	Skewness	kurtosis	$K–S_p$
Cd	1.31	3.08	2.23	2.21	0.37	16%	0.138	0.052	-0.271	0.8
Pb	10.3	95.83	38.002	34.85	20.24	53.2%	409.8	1.35	1.61	0.4
Cu	1.2	9.75	5.3	5.31	1.73	32.6%	3.011	0.198	0.473	0.6
Zn	0.73	43.04	13.84	10.45	11.04	79.7%	120.7	1.078	0.172	0.2
pH	6.88	8.96	8.25	8.33	0.46	5.5%	121.93	1.079	0.199	0.06
EC	0.14	0.72	0.23	0.18	0.118	51.3%	0.014	2.21	5.58	0.006

$K–S_P$ is the p-value of Kolmogorov Smirnov test for normal distribution.

The heavy metal levels measured in this research were compared with those of other studies around the world (Romic and Romic, 2003; Huang et al., 2007; Li et al., 2009; Hani and Pazira, 2011; Tume et al., 2011; Salazar et al., 2012; Lu et al., 2012; Antibachi et al., 2012; Rodríguez Martín et al., 2013; Mileusni´c et al., 2014; Kelepertzis, 2014; Mirzaei et al., 2015; Dartan et al., 2015; Yong et al., 2015; Ma et al., 2015; Rodríguez Martín et al., 2006; Mungai et al., 2016; Giri et al., 2017; Liang et al., 2017) in Table 2. According to this table, the comparison of the findings of this research with other studies indicated that the Cd content in the study area was higher than the concentrations of Cd in other studies except for Cd in Argentina (Salazar et al., 2012) and Turkey (Dartan et al., 2015). The high levels of cadmium, may be related to the anthropogenic sources, such as phosphate fertilizers in the study area. The comparison of Cu and Zn levels with other regions show that their concentrations are lowest. The mean concentration of the Pb was generally higher than or close to those obtained in several other studies in the world and lower than that in Argentina, Guangzhou, Chenzhou, Singhbhum, and Kombat.

Table 2. Comparison of the mean concentration of heavy metals (mg/kg) in agricultural soils of the study area with other studies around the world.

Country	Cd	Pb	Cu	Zn	reference
Argentina	3	375	-	600	Salazar et al., 2012
Spain	0.32	20.3	24	72.2	Tume et al., 2011
Taiyuan, China	0.25	27.87	32.11	90.76	Yong et al., 2015
Zagreb, Croatia	0.66	25.9	20.8	77.9	Romic and Romic, 2003
Beijing, China	0.14	20.40	22.40	69.80	Lu et al., 2012
Guangzhou, China	0.28	58.00	24.00	162.60	Li et al., 2009
Almería (Spain)	0.4	25.6	25.7	65.7	Rodríguez Martín et al., 2013
Jiangsu (China)	0.3	35.7	33.9	98.1	Huang et al., 2007
Thiva (Greece)	-	24	32	67	Antibachi et al., 2012
Argolida basin (Greece)	0.54	19.74	74.68	74.88	Kelepertzis, 2014
Ebro basin (Spain)	0.42	17.54	17.33	57.53	Rodríguez Martín et al., 2006
Bandırma, Turkey	39	36	71	114	Dartan et al., 2015
Chenzhou,China	2.14	204	36.0	244	Ma et al., 2015
Tehran, Iran	0.77	16.46	36.09	217.99	Hani and Pazira, 2011
Kenya, Eastern Africa	0.23	6.09	5.05	34.71	Mungai et al., 2016
Singhbhum, India	0.34	47.0	218.0	210.6	Giri et al., 2017
Lianyuan, China	0.59	37.82	33.26	107.24	Liang et al., 2017
Shahroud (Iran)	0.3	18.1	24.3	80.4	Mirzaei et al., 2015
Kombat (Namibia)	-	119	108	45	Mileusni´c et al., 2014
Siakh Darengoun area	2.23	38.002	5.3	13.58	Our study

Correlation between heavy metals and soil properties

Pearson's correlation was used to characterize the relationships between the heavy metal concentrations and soil properties and the findings are shown in Table 3. The very positive correlations between metals may suggest that these metals have common origins (Lv et al., 2015). The correlation coefficient between Cd and Pb was 0.35, which shows linear correlation at 0.01 significance level suggesting a common source of these heavy metals. In addition, significant correlation is also observed between Pb and Cu. There was positive correlation between Cu and Zn with a correlation coefficient of 0.45, indicating they probably were derived from similar sources. In agreement with finding of this study, Romic and Romic (2003) found a significant correlation between Cd and Pb (r=0.65), Cu and Pb (r=0.65) and Cu and Zn (r=0.73). Also Marrugo-Negrete et al. (2017), Esmaeili et al. (2014), and Shang et al. (2016) obtained similar results. A significant negative correlation was found between EC of soil and Cd. There was no significant correlation between concentrations of metals with pH. Lack of significant relationship between pH of agricultural soils and heavy metals may be related to variations in soil type, cultivation system within the sampling area, fertilizer use, and pollution sources (Ma et al., 2015; Bortey-Sam et al., 2015; Zhou et al., 2014; Lu et al., 2012).

Table 3. Pearson's correlation matrix between heavy metals and soils properties in Siakh Darengoun.

	Cd	Pb	Cu	Zn	pH	EC
Cd	1					
Pb	0.35*	1				
Cu	0.08	0.4**	1			
Zn	0.16	0.22	0.45**	1		
pH	0.04	0.03	0.07	-0.02	1	
EC	-0.35*	0.11	0.07	-0.002	-0.07	1

**Correlation is significant at the 0.01 level. *Correlation is significant at the 0.05 level.

Spatial structure and spatial distribution

The semivariogram parameters including nugget value (C0), sill (C0 + C), range (R) and coefficients of determination (R^2) for each heavy metal and soil properties are given in Table 4. The Cd, Cu and Pb in agricultural soils were best fitted with spherical models. The Zn and EC were determined by the exponential model and the pH was fitted by the Gaussian model. The ranges of the semivariograms for the studied heavy metals varied from 6330 to 12620 m. Range (r) is the distance where data are spatially autocorrelated. As presented in Table 5, the range for soil Zn was the largest and for soil Pb was the smallest. The rank of the ranges for the four heavy metals was in the order of Zn > Cu>Cd > Pb. The values of R^2 indicated that the semivariogram models gave good descriptions of spatial structure of heavy metals in the soil. The nugget/sill ratios for Cd, Cu, Pb, Zn, pH and EC in agricultural soils were 33%, 29.6%, 9.52%, 31.8%, 49.7%, 42.1% and 6.1%, respectively. The ratio of nugget to sill (RNS=C0)/(C0 + C) indicates the spatial autocorrelation of soil properties. According to the classification used by Cambardella et al. (1994), a low RNS (<25%) demonstrates strong spatial dependence of soil variables, RNS between 25-75% indicates moderate spatial dependence and in RNS> 75% variable has weak spatial dependence. Strong spatial dependence was found for Pb, and EC, while Cd, Cu, Zn and pH indicated moderate spatial dependency. Usually, strong spatial autocorrelation may be related to intrinsic factors, moderate spatial dependency can be brought about both by intrinsic and extrinsic agents and weak spatial autocorrelation can be associated with extrinsic factors (Gu et al., 2014). This moderate spatial autocorrelation illustrates that anthropogenic sources like fertilizers and pesticides have altered spatial dependency and distribution of heavy metals in the study area. Also Table 4 indicates the estimated RMSE (Root Mean Square Error), MAE(Mean Absolute Error), and MBE (Mean Bias Error) values by kriging method interpolations. To evaluate the kriging method, statistical indices of RMSE MAE and MBE were applied.

The spatial distribution maps of the heavy metals created from their semivariograms are provided in Figure 2. The spatial distribution map of Cd indicates that Cd has relatively high concentrations in the western and southern parts of the study area. In fact, there is an increasing trend of Cd from north to south and east to west. With regard to rainfed agriculture in the northern and northwest parts is practiced; chemical fertilizers are less used and therefore low concentrations of Cd was observed in soils. The rest of the area is cultivated through irrigated agriculture, so uses large amounts of chemical fertilizer. On the other hand, the presence and activity of the Hossain Abad Agro Industry in the west of the study area can be a factor that increases Cd concentration. Therefore, we suggest cadmium in the agricultural soils of Siakh Darengoun have anthropogenic source. As seen from the spatial distribution map of Pb, there is an increasing trend from all directions to the west. Lu et al. (2012) stated that fertilizer and manure is the main source of Cd, Cu and Zn entering the agricultural soil.

Table 4. Summary of variogram parameters and best fitted models for heavy metals and soil properties.

	Model	Co	Co+C	Co/Co+C	R^2	RSS	Effective range (m)	MBE	MAE	RMSE
Cd	Spherical	0.05	0.16	33%	0.87	1.27	9690	0.0005	0.25	1.12
Pb	Spherical	47	493.4	9.52%	0.84	32203	6330	-0.33	11.87	2.28
Cu	spherical	1.24	3.89	31.8%	0.92	0.474	12620	0.003	1.171	0.02
Zn	exponential	105.9	211.9	49.7%	0.70	317	93310	0.17	8.72	1.18
pH	Gaussian	0.20	0.46	42.1%	0.54	2.072	55044	-0.003	0.35	0.027
EC	exponential	0.00001	0.02	6.1%	0.63	4.79	3180	0.008	0.09	0.06

Table 5. The results of Geo-accumulation index (I_{geo}) and potential ecological risk.

Heavy metals	Potential ecological risk index Er			RI			Igeo		
	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Cd	197.17	461.25	335.09	212.46	504.24	355.54	2.13	3.36	2.88
Pb	4.2917	78.34	18.10				-0.80	3.38	0.99
Cu	0.36	10.73	2.01				-4.38	0.52	-2.20
Zn	0.007	1.10	0.34				-7.61	-0.44	-2.72

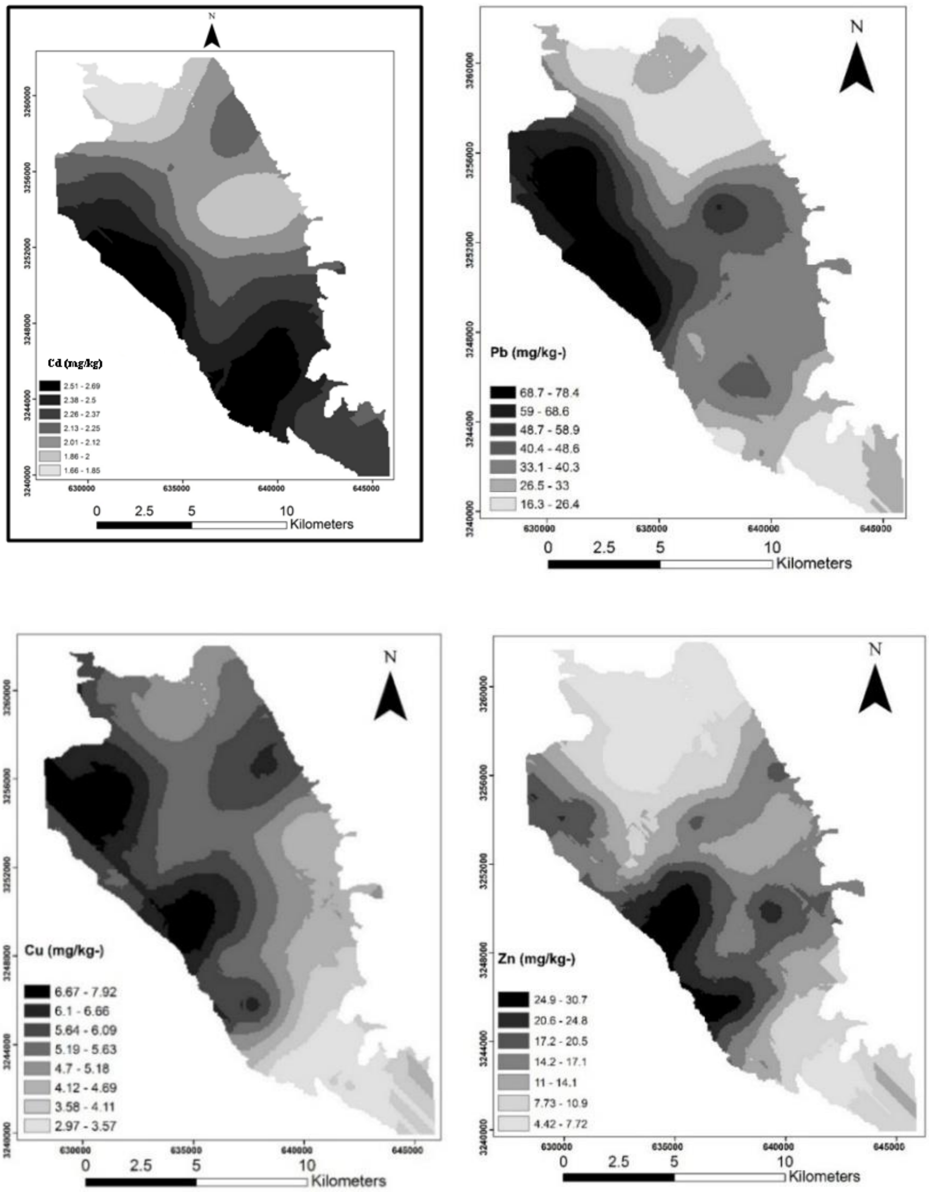

Figure 2. Map of the spatial distribution of heavy metals in agricultural soils of Siakh Darengoun.

Geo-accumulation index (I_{geo}) and potential ecological risk index

The results of Igeo in agricultural soils of the Siakh Darengoun District are presented in Table 5. The average values of Igeo decreased in the order of Cd>Pb> Cu>Zn. The mean Igeo for Cd, Cu, Pb and Zn were 2.88, -2.20, 0.99, and -2.72. The mean Igeo of Cu and Zn indicated the soil were in the unpolluted class, while the average Igeo for Pb, showed levels of unpolluted to moderately polluted and for Cd indicated moderately polluted soil. In general, enrichment of heavy metals in agricultural soils is mainly due to application of fertilizers and pesticides used in agricultural activities.

The obtained values of the Er and RI for Cd, Cu, Pb and Zn are summarized in Table 5. The order of mean potential ecological risk coefficient (Er) of the four metals in soils of the Siakh Darengoun was Cd > Pb > Cu > Zn. The findings of Er of metals indicated that Pb, Cu and Zn caused a low potential ecological risk to environment while Cd had a serious potential ecological risk. Altogether, the value of RI ranged from 212.46 to 504.24, and generated an average value of 355.54, suggesting high ecological risk from these metals in the Siakh Darengoun area.

Conclusion

This research was designed to determine accumulation and spatial distribution of heavy metals (Cd, Cu, Pb and Zn) in agricultural soils of Siakh Darengoun, the main poles of crops and agricultural production in Fars Province, Iran. The average concentrations of Cd and Pb in the agricultural soils were higher than average worldwide soils and for Cu and Zn, values were lower than average worldwide soils. Comparison of the findings of this research with other studies indicated that the Cd content in the study area was higher than the other studies. The spatial distribution maps of metals were produced by ordinary kriging. The result of semivariogram analysis indicated that the Cd, Cu and Pb in agricultural soils were best fitted with spherical models. The Zn and EC were determined by the exponential model and the pH was fitted by the Gaussian model. The highest levels of Cd, Cu, Pb, and Zn in the studied soil samples were observed in the western and southern parts of the study area. Based on the results of geo-statistic analyses, sampling method in this research (regular grid cell size 1.5 km×1.5 km) was sufficient to characterize spatial patterns. The results of RI and Igeo indicated that Pb, Cu and Zn imposed low risk to the environment while Cd generated a serious potential risk. So, Cd was the most important pollutant of the Siakh Darengoun area. Among the studied metals, Cd was the main metal pollutant, and the average concentration of Cd was higher than most other studies. Agricultural soil Cd might be mostly originated from the uncontrolled application of fertilizers. Hossain Abad agro industry in the west of the study area can be considered as one of the most important sources of metal contamination leading to higher concentrations of heavy metals in surface soils.

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