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Spatial Distribution of Lead in Calcareous Soils and Rice Seeds of Khuzestan, Iran

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ABSTRACT

In this study, soil samples of different places of Khuzestan province were sampled. The sampling positions were registered and determined through GPS. The geostatistics and Geographic Information System (GIS) techniques were applied, and lognormal kriging were used to map the spatial patterns of Pb. Both soil extractable Pb by diethylene triamine penta-acetic acid (Pb-DTPA) and Pb in rice seed were fitted to the Gaussian model with a range of 85 and 89.5 km, respectively. The mean content of extractable soil lead and plant lead in all the sites investigated were 702.88 and 121.82 µg kg^{-1}, respectively. Both Pb-DTPA and Pb in rice seeds had moderate spatial dependence due to the effects of natural factors including parent material, topography and soil type. The statistical survey to determine the possible correlation between some soils characteristics with lead distribution in rice seeds was done through SPSS statistical software. The results showed that close relationships existed between Pb-DTPA with organic matter (OM) (r = 0.376**), Pb in rice seed (r = 0. 68**), calcium carbonate equivalent (CCE) (r = 0.084*) and between Pb in rice seed with CCE (r = -0.716**), Pb-DTPA (r = 0. 68**) and pH (r = 0.263*).

Key Words: Geostatistics, lead, calcareous soil, anaerobic rice, spatial variability

INTRODUCTION

Soils, the most endangered component of the terrestrial ecosystem, is habitat for a great number of organisms and open to influences from a variety of pollutants arising from human activities. In this respect, heavy metals are among the serious pollutants in soil due to their toxicity, persistence, and bio-accumulation (Morton-Bermea *et al.* 2002). Heavy metals are of considerable importance due to their toxicity, accumulating traits and longevity in an organism's body. Many

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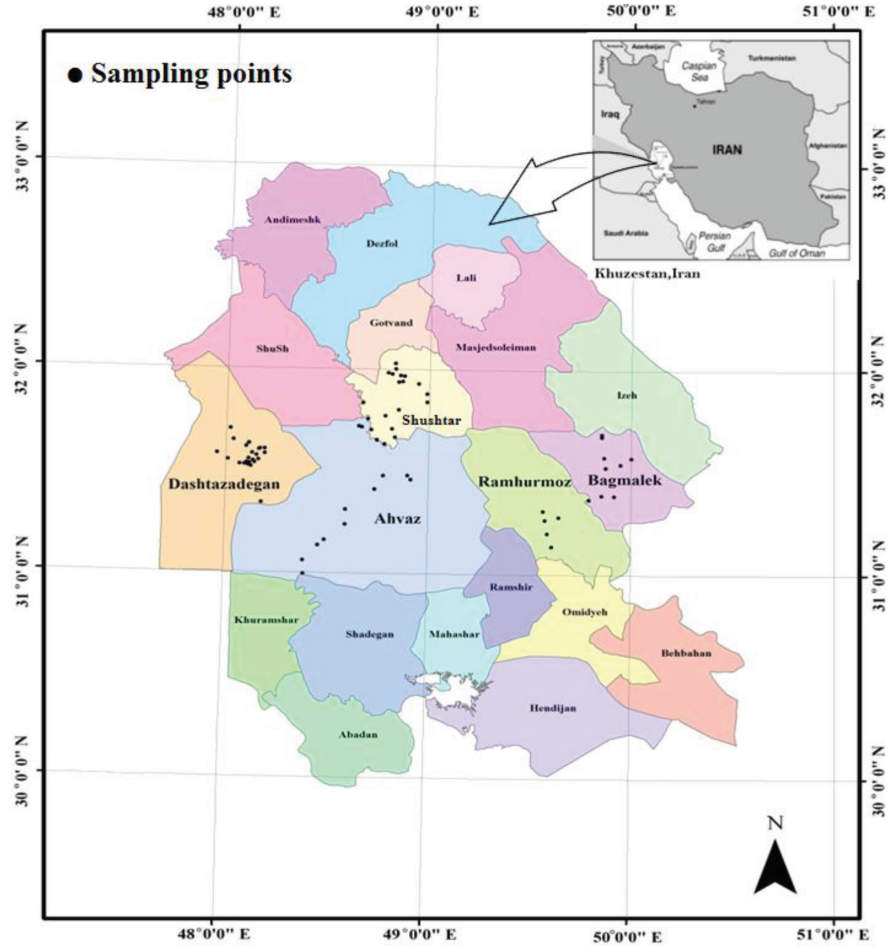
countries have been affected by water and soil pollution crisis due to heavy metals contamination (Smith *et al.* 1998). Human beings are usually the cause of these types of pollution through different actions, for example, application of metal-contaminated sewage sludge, fertilizers, and animal manure on plants. All these actions can result in high concentrations of heavy metals in agricultural soils (Wu *et al.* 2009). As these practices continue, soil heavy metal accumulation especially in agricultural lands has led to soil degradation and environmental pollution, subsequently endangering the health of the food chain. Lead (Pb) occurs 'naturally' in all soils, in concentrations ranging from 1 to 200 mg kg^{-1}, with a mean of 15 mg kg^{-1} (Zimdahl and Skogerboe 1997). The adverse health effects caused by low-level exposure to Pb have been extensively documented. Such health effects include neurological impairment and deficits in the functioning of the central nervous system (Needleman 1983; Needleman *et al.* 1990). Notably, the Pb and Cd contents in rice samples of North Iran were found to be higher than the FAO/WHO Guidelines (Khaniki and Zazoli 2005). Lead absorption rate by plant and its entry into the food chain is mainly dependent on the absorption of this element from the soil (Alloway 1995). The first source of heavy metals uptake by plants is the solution the plant roots are in contact with. In general, the more soil heavy metal concentration, the more it is accessible to the plant (McBride 1995). In addition, Pb absorbability by plants from the soil is dependent on its characteristics such as soil pH, organic matter, clay content, soil salt concentration, chloride concentration, carbonate and lime as well as the plant species (Chaney and Hornick 1987; Appel and Ma 2002; Yu-sheng *et al.* 2010; Wei *et al.* 2009 and Ghafoor *et al*. 2008). Geostatistics provide an advanced methodology which facilitates spatial interpolation and quantification of spatial temporal variability in soil variables and has become a useful tool for the study of spatial uncertainty and hazard assessment (McGrath *et al*. 2004; Robinson and Metternicht 2006). The geostatistical approach is a popular application to analyze spatial structure and spatial distribution of soil heavy metals (Imperato *et al.* 2003; Liu *et al.* 2006; Ahsan *et al*. 2009; Zhang *et al.* 2009 and Wu *et al*. 2009). Kriging is a precise estimator for spatial data analysis as it is unbiased and minimizes total uncertainty (Isaaks and Srivastava 1989). Although Khuzestan is one of the most important agricultural and industrial areas of Iran, the spatial distribution of soil heavy metal concentrations is still largely unknown. The aim of the present work was to elucidate the spatial distribution of heavy metals in soils of Khuzestan province. The specific objectives of the study were (1) to examine the spatial dependency of Pb in soils and rice seeds and (2) to map the spatial distribution of Pb in soils and rice seeds.

MATERIALS AND METHODS

Study Area

This study focuses on the cultivated land of Khuzestan Province which is located in Western Iran. The study region consists of five regions: Dashtazadegan, Ahvaz, Shoushtar, Ramhurmoz and Baghmalek *(Fig. 1)*. In total, 70 farms were randomly selected in the study region and soil and anaerobic rice seed samples were taken.



Projected Coordinate System: WGS 1984 UTM Zone 39N

Fig. 1: Distribution of sampling locations

Soil Sampling and Analysis

A total of 70 soil samples (0 - 15 cm) were collected from the drained paddy fields in the summer of 2010, taking into consideration soil types and land use uniformity to ensure all samples were located in paddy fields and a soil sample was collected from each soil type *(Fig. 1)*. When sampling, soils in top layer from 6 to 8 points in each site of an area were collected and then fully mixed, and finally divided into parts of 1 to 2 kg each. All sample sites were recorded using a hand-held Global Position System (GPS). The samples were obtained using a plastic spade to avoid any heavy metal contamination. Gravels and coarse organic matter or plant root residues were removed, soil samples were air dried and passed through a 2-mm sieve. The particle-size distribution was analyzed using the pipette-method. Calcium Carbonate Equivalent (CCE) content was determined by titration method (Oustan *et al*. 2011). A total of 70 seed samples were digested in 2:1 v/v HNO_3:$HClO_4$ using an open tube digestion technique. Lead availability in soil was attained by the diethylenetriamene pentaacetate acid (DTPA) extraction procedure (Simmons *et al.* 2005; Matheron 1963; Webster and Oliver 2001). Lead concentrations in plant and soil samples were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Electrical conductivity and pH were measured on fresh soil samples in deionized water (soil-solution, 1:2.5). Organic Matter (OM) was determined by potassium dichromate wet combustion procedure. Lead concentrations in rice seeds were compared with the guide values suggested by the Iranian Ministry of Health (150 $\mu g\ kg^{-1}$ for Pb) (Janati *et al.* 2011).

Geostatistical methods

Geostatistics is based on the theory of a regionalized variable (Matheron 1963), which is distributed in space (with spatial coordinates) and shows spatial auto correlation such that samples close together in space are more alike than those that are further apart. Geostatistics uses the technique of variogram (or semi-variogram) to measure the spatial variability of a regionalized variable, and provides the input parameters for the spatial interpolation of kriging (Jiachun *et al.* 2007; Webster and Oliver 2001). Since the probability distributions of the metal concentration data were skewed, the experimental semivariograms were developed using transformed data to stabilize variance (Goovaerts 1999). Logarithmic transformations data was used in the study. The semi-variogram function is expressed as:

$$y(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [Z(xi) - Z(xi+h)]^2$$

where Z(xi) is the value of the variable Z at location of xi, and N(h) is the number of pairs of sample points separated by the lag distance h (Jiachun *et al.* 2007).

Experimental variograms were fitted with the five models, i.e. exponential, linear, spherical, Gaussian and linear to sill models, using statistical indices (i.e. correlation coefficients (r^2) and residual sum of squares (RSS)). Cross validation was done to validate the accuracy of the fitted different models for prediction and the models were compared using correlation coefficients (r^2) and residual sum of squares (RSS) and the best fit was selected for kriging phase. The model with the highest r^2 and the lowest RSS values was selected. Before kriging, the spatial dependency of Pb in soil and rice seed was evaluated using Nugget/Sill ratio. In theory, the Nugget/Sill ratio in the geostatistics can be regarded as a criterion to classify the spatial dependence of soil attributes. The ratio of 0.25 and 0.75 are two thresholds for the relative strength index of spatial correlations. The variable with a ratio of less than 0.25 is strongly spatial dependent; the variable with a ratio between 0.25 and 0.75 is moderately spatial dependent; whereas the variable with a ratio greater than 0.75 is only weakly spatial dependent (Jiachun *et al.* 2007). Thereafter, Pb concentrations in soil and rice seeds were estimated for unsampled locations using lognormal ordinary kriging method.

The most important trait of kriging that separates it from other estimators is minimizing the error variance. The kriging action takes place through the 2nd equation:

$$\bar{Z}(x) = \sum_{i=1}^{n} \lambda_i \times Z(x_i)$$

where λi equals variable weight in the measured points and Z(xi) equals variable amounts in measured points.

The kriging plots and the error estimation plots are measured and calculated using calculating system of GS+ software.

Data analysis

Data sets were analyzed with different software packages. The descriptive statistical parameters were calculated with statistical software. Maps were produced with arcGIS software and its extension of Spatial Analyst. The geostatistical analyses and the probability calculation were carried out with GS+ software package.

RESULTS

Descriptive Parameters and Probability Distribution of the Raw Data Set

The descriptive statistics of studied variable are given in Table 1. In this study, the direct relationship between extractable lead by DTPA and the absorbed lead amount by plant is shown in Table 2.

Cross validation showed that the Gaussian model provided the best fit to the experimental variograms (Pb-DTPA in soil and Pb in seed) for the kriging method with the lowest RSS and highest r^2 *(Table 3 , Fig. 2a and 2b).* At the end of the kriging process, the resulting grid values were back-transformed to create interpolated lead distribution maps of soils and rice seeds in Khuzestan province *(Fig. 2c and 2d).*

Geostatistical analysis

The effective ranges of semi-variograms for Pb-DTPA (soil) and Pb (rice seeds) were 85 and 89.5 km, respectively (Table 3). Capitalizing on the spatial correlation between the available data, ordinary lognormal kriging techniques were used here to predict attribute values at unsampled points of cultivated land. The experimental semi-variograms of Pb-DTPA and Pb in rice seeds with the fitted models are presented in Figure 3. The results showed that Pb-DTPA and Pb in rice seeds data fitted with the Gaussian model. The attributes of the semi-variograms for Pb-DTPA and Pb in rice seeds are summarized in Table 3. The Nugget/Sill ratios for Pb-DTPA and Pb in rice seeds were less than 0.75.

TABLE 1
Statistical summary of heavy metal contents in the topsoil collected from the study area

Soil attributes	N	Min	Max	Mean	SD	CV (%)	Skewness	Kurtosi
pH	70	6.8	7.7	7.22	0.22	3.03	0.43	-0.64
ECe (dS m^{-1})	70	1.2	40.5	7.63	6.76	8.86	3.47	1. 45
Clay (%)	70	16	52	33.41	9.04	2. 70	-0.02	-0.89
CCE	70	22.4	49.91	48.45	3.55	7.33	-6.03	4.31
OM (%)	70	0.28	1.69	0.81	0.25	3.08	1.08	2.21
Pb-seed (μg kg^{-1})	70	100	219	122	15.18	12.46	3.89	2. 38
Pb-DTPA (μg kg^{-1})	70	199	1450	703	250	3.55	0.71	-0.60

Min - minimum, Max- maximum, SD - standard deviation, CV - coefficient of variation

TABLE 2
The correlation coefficients between heavy metals and soil attributes

	ECe	Clay	pH	CCE	OM	Pb-Seed	Pb-DTPA
ECe	1						
Clay	0.127	1					
pH	-0.183	-0.056	1				
CCE	0.090	0.013	-0.137	1			
OM	-0.139	0.375**	-0.084	0.012	1		
Pb-Seed	-0.035	-0.048	0.263*	-0.716**	-0.061	1	
Pb-DTPA	0.032	0.046	0.149	0.084	0.376**	0. 68**	1

*p<0.05, **p< 0.01, OM - organic matter, CCE - Calcium carbonate equivalent ,
Pb-DTPA extractable soil lead, Pb-Seed lead in rice seed.

TABLE 3
Best-fitted semi-variogram models of heavy metals and their parameters

Soil attributes	Model	C_0	$C + C_0$	$C_0/C + C_0$	Effective ranges (km)	R^2	RSS
Pb-DTPA	Gaussian	0.0407	0.07	0.419	85	0.505	0.001076
Pb-Seed	Gaussian	0.0419	0.081	0.483	89.5	0.513	0.00166

C_0 nugget variance, C structural variance, $C + C_0$ sill variance

Spatial Distributions and Risk Assessment

Mapping metal contents is often a preliminary step towards decision making, such as delineation of polluted areas or identification of zones that are suitable for crop growth. For soil pollution, a straightforward approach is to delineate all contaminated locations where the estimated pollutant content exceeds the guide value (150 μg kg^{-1} for Pb). Figure 3 presents the spatial patterns of the Pb-DTPA and Pb in rice seeds in paddy soils of Khuzestan province generated from their semi-variograms.

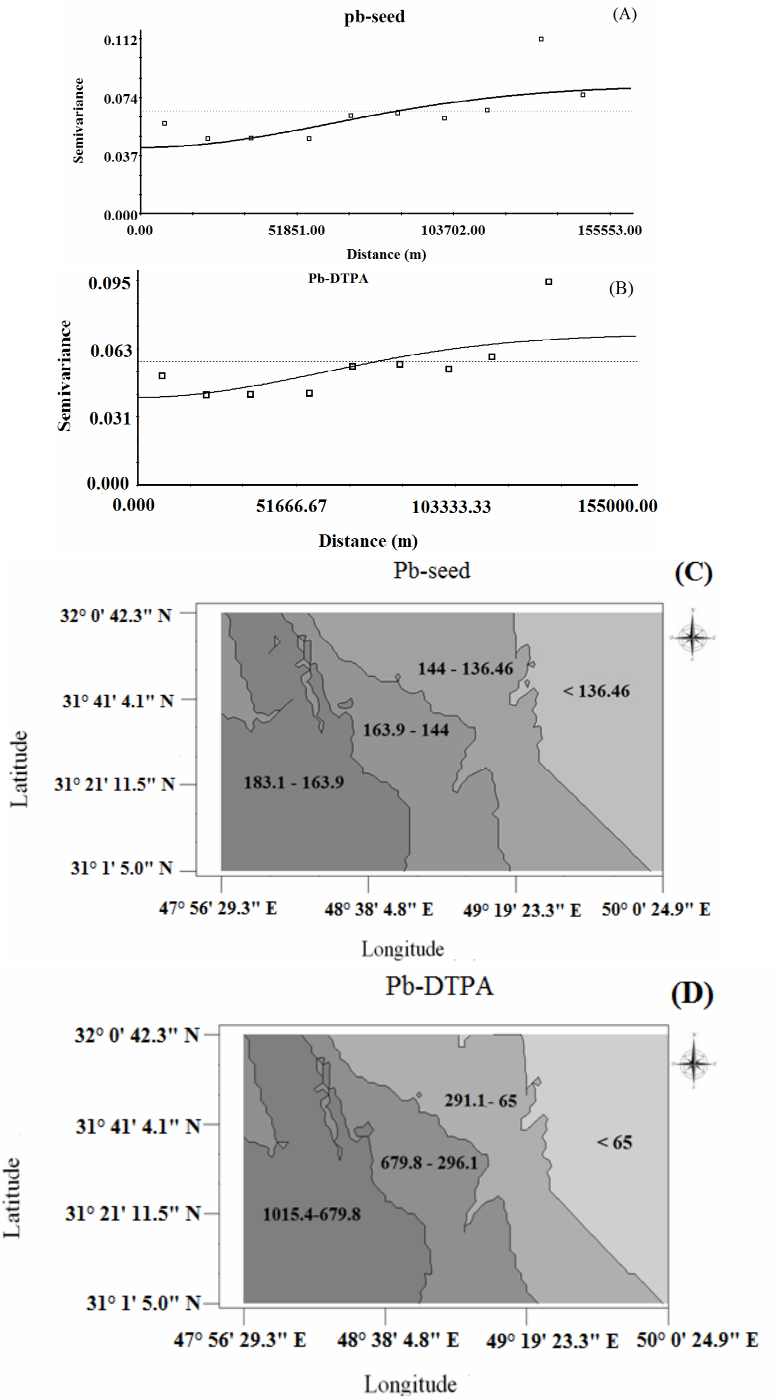


Fig. 2. Experimental semi-variograms with fitted model of soil Pb-seed (a), Pb-DTPA (b), and related kriging maps (c and d) (µg kg^{-1}).

DISCUSSION

The spatial variability of soil attributes can be affected by both soil pedogenic factors (such as parent materials) and human activities (such as industrial and agricultural production). As shown in Table 3, the Nugget/Sill ratios of both Pb-DTPA and Pb-seed were between 0.25 and 0.75, showing moderately spatial dependence, revealing that the anthropogenic factors such as industrial production, fertilization and other soil management practices can change their spatial correlation after a long process of utilization (Khaniki and Zazoli 2005). To further discriminate the natural and anthropogenic contributions, the correlations between Pb-DTPA and Pb in rice seeds and soil properties (OM, Clay, CCE, ECe and pH) were performed (Table 2). There existed significant linear relationships between Pb-DTPA with several soil characteristics including organic matter ($r = 0.376^{**}$). Also, Pb in rice seed significantly correlated with CCE ($r = -0.716^{**}$), Pb-DTPA ($r = 0.68^{**}$), and pH ($r = 0.263^{*}$). Therefore, these results show the significant effects of other soil properties on soil and rice seed Pb. Hence, different anthropogenic activities can have an affect on soil and seed variability by affecting other soil properties.

Researchers reported that the heavy metals absorbable concentrations especially lead, is related to both amount and type of organic matter which exists in soil. Therefore, the analysis of organic heavy metals type, which results in the release of these elements in the bioavailable form, which might be toxic for agricultural crops, needs to be carried out (Jing *at el.* 1992 and McBride 1995). Del Castilho *et al.* (1993) stated that the absorption and increasing solution concentration might be due to decreasing soil pH due to nitrification, solution ionic strength increase and soluble organic matters. In a research conducted on the effect of liming on lead uptake by wheat, it was concluded that the high amount of liming can decrease metal uptake by wheat. The absorbed lead accumulated more in the stem and seed (Tlustoš *et al.* 2006). The lead amount which was retained in the soil increases as the amount of liming increases due to pH increase, and also, because of competition between calcium with lead in calcareous soils, the lead transported to the plant is lower. The same phenomenon could have occurred in the calcareous soils in this study. This emphasizes the indirect relationship between plant lead and the liming amount within soil, and, the direct relationship between extractable lead rate and soil liming amount. Thus, as the heavy metals concentration of soil increases, their accessibility to plant will increase (De Temmerman 1984).

The mean and maximum contents of Pb in rice seed are shown in Table 1. Lead concentrations in rice seed samples were lower compared to the guide value of 150 $\mu g\ kg^{-1}$ Pb suggested by the Iranian Ministry of Health (Janati *et al.* 2011). In most places, there is no Pb health problem resulting from Khuzestan rice consumption. Thus, Pb in this paddy ecosystem is unlikely to exhibit a risk of environmental pollution or threat to human health. However, there were sixteen samples that had Pb contents which exceeded the guide value. Most of these sites are located in central and western parts of Khuzestan province *(Fig. 2c)*, suggesting that some cultivated lands in Khuzestan province need to be monitored.

CONCLUSIONS

Detailed geostatistical analysis on lead distributions will help to gather more information on the variability of Pb concentrations in soil and rice seeds in this region. Sixteen rice seed samples in the area have Pb concentrations higher than 150 µg kg^{-1}. Lead concentrations in soil and rice seed samples show moderate spatial dependence. The Gaussian model was the model that best fitted the experimental variogram (Pb-DTPA in soil and Pb in seed). Lognormal ordinary kriging methods provide the best results of Pb estimation with regard to the lowest statistical measures. Over the long history of land utilization, the spatial variability of Pb was influenced by both natural and anthropogenic factors. Lead in rice seed and Pb extracted by DTPA indicated low risks for environmental pollution and human health. Both natural and anthropogenic factors have contributed to the genesis of the pollution process. The association of the higher soil heavy metal concentrations with soil texture and soil organic matter is largely attributed to to the higher metal-holding capacity of clay and SOM when compared with sand. The probability map produced based on kriging provides useful information for hazard assessment in the decision-making process.

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