



EFFECT OF SOIL CHARACTERISTICS ON SPATIAL DISTRIBUTION OF CADMIUM IN CALCAREOUS PADDIES

ALI CHAMANNEJADIAN*¹, ABDOL AMIR MOEZZI², GHOLAMABBAS SAYYAD³,
ALIREZA JAHANGIRI⁴, ALIREZA JAFARNEJADI⁵

1-Department of Soil Science, Faculty of Agriculture, Shahid Chamran University of Ahvaz, Ahvaz, Khuzestan province, Iran. Post code: 6135783151.

2-Department of Soil Science, Faculty of Agriculture, Shahid Chamran University, Ahvaz, Iran.

3-Department of Soil Science, Faculty of Agriculture, Shahid Chamran University, Ahvaz, Iran.

4-Nanotechnology Research Center and Department of Medicinal Chemistry, School of Pharmacy, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran.

5-Soil and Water Department, Khuzestan Agricultural and Natural Research Resource Center.

*Corresponding Author Email: Chamannejadian@gmail.com

ABSTRACT: In this research, soil samples of different places of Khuzestan province were sampled. The sampling position was registered and determined through GPS. The geostatistics and Geographic Information System (GIS) techniques were applied, and the lognormal kriging were used to map the spatial patterns of the cadmium. Cd_{DTPA} was fitted to the spherical model with a range of 105 km, and Cd in rice seeds was fitted to the Gaussian model with a range of 100 km. The extractable soil cadmium and plant cadmium in total places were 273.56 and 81.42 µg/kg respectively. Both Cd_{DTPA} and Cd 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 cadmium spread in paddies done through SPSS statistical software (v17). The results showed that existed close relationships between Cd in seed with OM ($r = 0.376^{**}$), Cd_{DTPA} ($r = 0.271^*$), pH ($r = 0.280^*$) and between Cd_{DTPA} with TNV ($r = 0.277^{**}$), Cd in seed with ($r = 0.376^{**}$) and Ece ($r = 0.435^{**}$). The geostatistical analyses and the probability calculation were carried out with GS+ software.

Key words: Cadmium, Geostatistics, Rice, Spatial variability, Soil Characteristics

INTRODUCTION

Heavy metals due to poisonous, accumulating traits and long longevity in organism's body are considerably important. Soil and water resources in many countries have been affected by heavy metal contamination (Smith et al., 1998). Among them, Cadmium (Cd) is very important due to its more mobility and persistency in soil-plant system which can endanger food chain more than other metals. FAO organization and World Health Organization (WHO) mentioned the acceptable rate of cadmium entering to an adult human of 420 mg week⁻¹ (JECFA, 1989). So, even the low

amount of cadmium in meal materials can causes negative effects on human being health in long time (Reilly et al., 2003). Cadmium can enter in soil and water resources through different ways especially human activity. For example fertilizer application especially phosphate fertilizers, which have Cd in the form of impurities, can contaminate agricultural soils (Duruibe et al., 2007 and Yu-sheng et al., 2010).

Plants are the main way of Cd transfer from contaminated soils to humans. In a Cd contaminated soil, plants can uptake more Cd and accumulate it in different organs especially edible parts (McBride, 1995). Soil factors affecting Cd

absorption rate by plants and its entering into food chain, include redox potential, soil pH, organic matter, clay percent, electrical conductivity (EC), and the amounts of chloride, carbonate calcium, and Phosphate (Chaney et al., 1987; Appel et al., 2002; Yu-sheng et al., 2010; Wei et al., 2009 and Ghafoor et al., 2008). Also different plants have various ability in Cd uptake from soil (Alloway, 1995).

One of the plants that grow in both reduced (i.e. water logging soils) and oxidized condition (i.e. after drainage and the drying of paddies) is rice. Rice is the dominant staple food crop in developing countries, particularly in the humid tropics across the globe (Hossain, 2004). Almost 96% of the world's rice is produced and consumed in developing countries (Hossain, 2004), making up over 70% of the daily energy intake (Phuong et al., 1999). The protein component in rice (7–9% by weight) is relatively low (Font et al., 2005), but it forms a major source of protein (50%) in these countries (Phuong et al., 1999). With food that is consumed in such large amounts it is crucial to have information about its toxic trace levels so that potential effects on human health can be established. In water logging soils, redox decrease. In this condition, Cd availability decrease due to solid cadmium-sulphate formation. After soil drainage and with increasing redox potential, cadmium-sulphate oxidizes and changes to cadmium (II) which increases its availability in soil (McLaughlin et al., 1999). Therefore, Cd uptake by rice plants may be increased.

In the mentioned large-scale studies again both the number of samples and studied area were restricted, and the results cannot be generalized to wider regions. Also, more studies were conducted in wet lands where the soil and plant situations were completely different from arid and semi-arid regions. In addition, there are few large-scale studies in which Cd uptake by rice seed and its relationships with soil properties was evaluated. In this study, a large-scale investigation was conducted, using paired soil and rice seed samples ($n = 70$). These samples were taken from a large number of field sites located in 300 km² with different soil types of calcareous soils in arid regions of Iran. The aim of the present work was to elucidate the spatial distribution of heavy metals in soils of Khuzestan province. Our specific objectives were (i) to examine the spatial dependency of Cd in soils and rice seed, (ii) to map the spatial distribution of Cd in soils and rice seed.

MATERIALS AND METHODS

Study area

The research focused on the paddy fields of Khuzestan province, Southwest Iran (Fig. 1). The study region consists of five sub regions including Dashtazadegan, Ahvaz, Shushtar, Ramhormoz, and Baghmalek. In total 70 paddy farms was randomly selected in study region and soil and rice seed samples were taken from each farm.



Figure 1. Distribution of sampling locations

Oryza sativa L. rice farms are mainly located at dry land farms, while bread wheat farms are distributed in irrigated farms. Three permanent main rivers (Karoon, Karkheh and Dez) are supplying agricultural water that flows from north to the south. There are different land uses including agricultural, industrial, urban, and bare lands. Agricultural activities are mostly distributed around the rivers, except in some southern parts of the province that were covered by saline and marshy lands. The local farmers usually overuse nitrogen and phosphate fertilizers to produce mainly wheat, barley, rice, corn, canola, and vegetables (Jafarnejadi et al., 2011). The soils are highly calcareous with more than 40 percent lime content in most parts. The dominant soil orders are Entisols (including Fluvent, Psamment and Orthent groups), Aridisols (including Haplosalids, Haplogypsis, Haplocambids groups), and Inceptisols (including Calcicustochrepts group). The mean annual precipitation, temperature and evaporation are 240 mm, 22 C, and 3000 mm (Farshi et al., 1997), respectively.

Soil and seed sampling and analysis

A total of 70 compound soil samples (0–15 cm) were collected from paddy fields in summery 2010 (Fig. 1). When sampling, in each site (i.e. paddy farm), topsoil samples were collected using a plastic spade (to avoid any heavy metal contamination) from 6–8 points and then fully mixed, and finally a 1–2 kg of soil was taken for analysis. The coordinates of sample sites were recorded using a hand-held Global Position System (GPS) instrument.

All soil samples were air-dried and passed through a 2-mm stainless steel sieve. Available cadmium concentration (Cd_{DTPA}) was extracted by 0.05 M Diethylene Triamine Penta Acetic Acid (DTPA) (Lindsay and Norvell, 1978) and measured by graphite furnace atomic absorption spectrometry (Rayleigh model W X F - 210). Soil pH was measured in saturated paste using a pH-meter (Model Metrohm 644), electrical conductivity (EC) in saturated paste extract by EC-meter (Model Metrohm 691), and lime content as the total neutralizing value (TNV) by titration with NaOH. Cation exchange capacity (CEC) was determined by the CH_3COONa method (Sumner and Miller, 1996), organic carbon (OC) by the wet oxidation method (Walkley and Black, 1934), and soil texture by the hydrometer method (Gee and

Bauder, 1986). Sub-samples of 0.2 g rice seeds were digested in 6 mL of 65% HNO_3 , 2 mL of 2% H_2O_2 and 2 mL of distilled water, and heated at 100 C for 25 minutes. The solution was then filtered using Whatman No. 42 filter paper and analyzed by graphite furnace atomic absorption spectrometry (Rayleigh model W X F - 210). Quality control samples included Standard Reference International Soil Analytical Exchange report 2000, number 981 sandy soils from The Netherlands. Good agreements were achieved between the obtained data and the certified values. The Cd concentrations in rice seeds were compared with the guide values suggested by the Iranian Ministry of Health ($150 \mu g kg^{-1}$ for Cd).

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 variograms (or semivariogram) 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). The semivariogram function is expressed as:

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

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

Since the probability distributions of the metal concentration data were skewed, the experimental semivariogram were developed using transformed data to stabilize variance (Goovaerts, 1999). Logarithmic transformation was used in this study.

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 one 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 Cd 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 the ratio between 0.25 and 0.75 is moderately spatial dependent; whereas the variable with the ratio greater than 0.75 is only weakly spatial dependent (Jiachun et al., 2007).

Thereafter Cd 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 is done base on the flowing equation:

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

In which λ_i equals variable weight in the measured points and $Z(x_i)$ equals variable amount in measured points.

Data analysis

Data sets were analyzed with different software packages. Statistical analysis was

conducted with SPSS software version 17 (2009). Descriptive statistics variables such as mean, variance, maximum, minimum, Skewness and kurtosis of Cd concentrations in soil and wheat grain and measured soil parameters were calculated. The correlation analysis was used to evaluate the relationship between soil properties and seed Cd concentrations. Spatial analyses were carried out using GS+ software package version 5.1 for windows, Gamma Design Software.

RESULTS AND DISCUSSION

Descriptive parameters and probability distribution of the raw data set

The descriptive statistics of studied variable are presented in Table 1. The average of extractable soil cadmium and plant cadmium in total points (areas) are 42.81 and 56.273 µg/kg respectively, that this numbers regarding cadmium in rice plant and extractable cadmium of soil that their numbers respectively are 2.0 and 3-8 mg/kg are lower than the permissible amount and doesn't make any concern now (Oustan, S et al., 2011; Afyoni et al., 2007 and Alloway, 1995). But by separating areas from each other, we noticed that in Baghmalek area the amount of this element in some points of plant inside is exceeded a bit from its permissible rate that needs to be taken into consideration (Table 2).

Table 1. Statistical summary of soil characteristics in and cadmium contents in the topsoil collected from the study area

Soil attributes	N	Min	Max	Mean	SD	CV (%)	Skewness	Kurtosis
pH	70	6.8	7.7	7.22	0.220	3.03	0.43	-0.64
ECe (dSm ⁻¹)	70	1.2	40.5	7.63	6.761	8.86	0.47	1.45
Clay (%)	70	16	52	33.41	9.035	2.70	-0.02	-0.89
TNV	70	22.4	49.91	48.45	3.552	7.33	-1.03	0.31
OM (%)	70	0.28	1.69	0.81	0.250	3.08	1.08	1.21
Cd _{seed} (µg/kg)	70	8.9	266.24	81.43	53.69	65.94	1.05	0.89
Cd _{DTPA} (µg/kg)	70	63.3	521	273.56	111.75	40.85	0.34	-0.56

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

Table 2. Comparison of mean soil characteristics and cadmium in between different regions

	pH	ECe (dSm ⁻¹)	TNV	Clay%	OM%	Cd _{DTPA}	Cd _{seed}
z Ahv	7.05 ^c	6.90 ^b	48.99 ^{ab}	36.3 ^b	0.86 ^b	270.0 ^b	73.10 ^c
Baghmalek	7.40 ^a	2.40 ^d	45.90 ^c	30.4 ^a	1.05 ^a	296.7 ^a	155.13 ^a
Dashtazadegan	7.23 ^b	12.70 ^a	48.43 ^b	33.1 ^c	0.72 ^c	274.5 ^b	96.21 ^d
Ramhurmoz	7.20 ^b	5.20 ^c	48.85 ^{ab}	36.8 ^b	0.89 ^b	249.62 ^c	85.00 ^b
Shushtar	7.24 ^b	5.00 ^c	49.17 ^a	32.5 ^c	0.77 ^c	269.64 ^b	74.62 ^c

Geostatistical analysis

Cross validation showed that Gaussian model provided the best fit to the experimental variograms (Cd_{DTPA} in soil and Cd in seed) for kriging method with the lowest RSS and highest r² (Table 4 , Fig.2- A, C). At the end of the kriging,

the resulting grid values were back-transformed to create interpolated cadmium distribution cadmium maps of soil and seed rice of paddies in Khuzestan province (Fig.2- B, D).

	ECe	Clay	pH	TNV	OM	Cd _{seed}	Cd _{DTPA}
ECe	1						
Clay	0.127	1					
pH	-0.183	-0.056	1				
TNV	0.090	0.013	-0.137	1			
OM	-0.139	0.375 ^{**}	-0.084	0.012	1		
Cd _{seed}	-0.435 ^{**}	-0.138	-0.009	-0.277 [*]	0.111	1	
Cd _{DTPA}	0.032	-0.141	0.280 [*]	0.091	-0.376 ^{**}	0.271 [*]	1

*p<0.05, **p< 0.01, OM organic matter, TNV Total neutralizing value, Cd_{DTPA} extractable soil cadmium, Cd_{seed} cadmium in rice seed.

Table 4. Best-fitted semivariogram models of heavy metals and their parameters

Soil attributes	Model	C ₀	$\frac{C}{C_0} + C_0$	C ₀ /C + C ₀	Range (km)	R ²	RSS
Cd _{DTPA}	Spherical	0.0007	0.002	0.65	105	0.525	5.497E-07
Cd _{seed}	Gaussian	0.0900	0.175	0.503	100	0.470	1.08E-03

C₀ nugget variance, C structural variance, C + C₀ sill variance

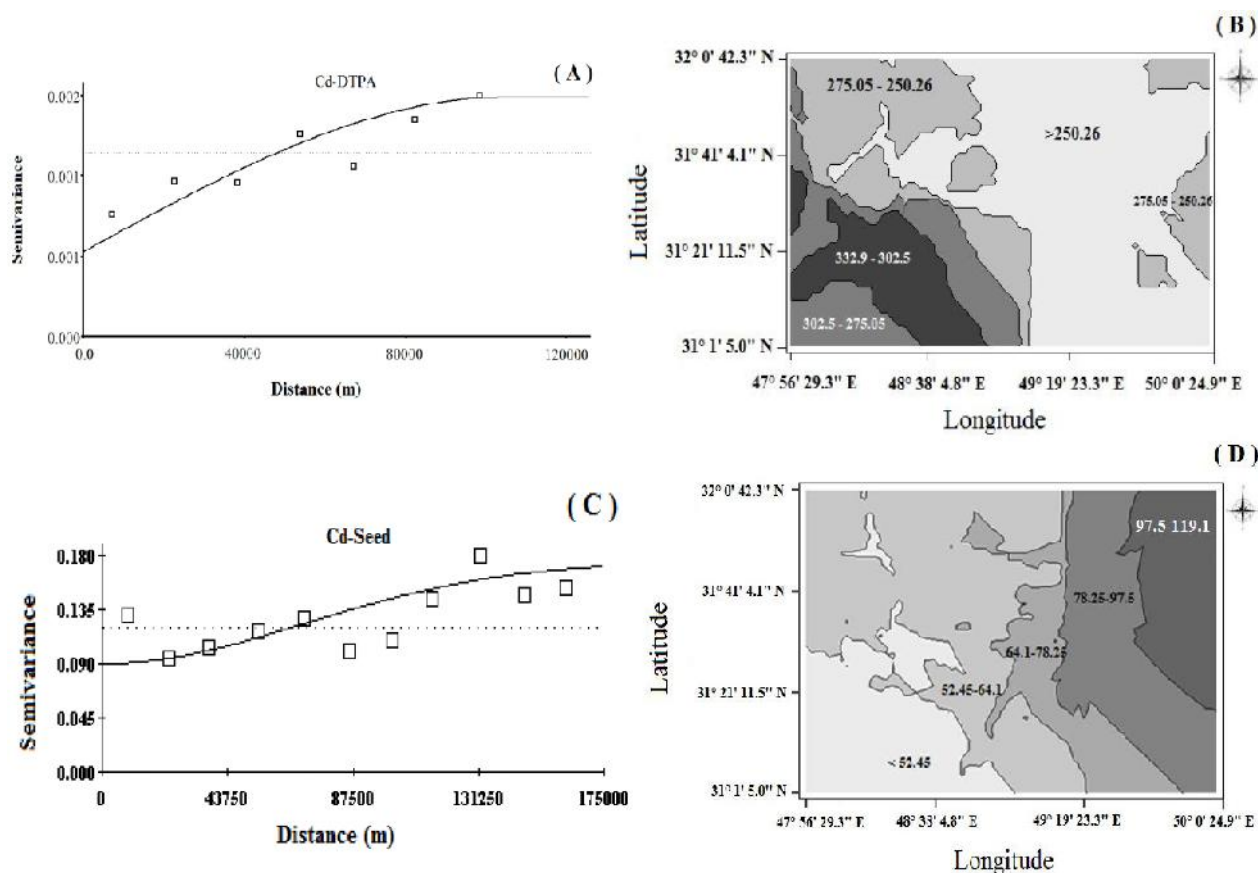


Figure 2. Experimental semivariograms with fitted model of soil Cd-DTPA (A), Cd-Seed (B), and related kriging maps (C and D) ($\mu\text{g}/\text{kg}$).

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 regions 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 ($150 \mu\text{g}/\text{kg}$ for Cd). Figure 3 presents the spatial patterns of the Cd_{DTPA} and Cd in rice seeds in paddy soils of Khuzestan province generated from their semivariogram.

The direct relationship between DTPA-extractable Cd and the accumulated Cadmium by plants is shown in Table 3. In conveying the relationships between soil and cadmium distribution in soil and plant, the achieved results were so that the extractable cadmium amount through DTPA of soil has a direct relationship with pH number, EC and lime number in total

surveyed points and had an indirect relationship with clay and organic matter amount factor that both are important regarding the active topsoil, and the plant cadmium had direct relationship with organic matter and the extractable cadmium amount through DTPA and but had an indirect relation with pH, EC and soil lime. By noticing Table 3 one can notice that these relationships aren't in this way in all areas that can be due to different reasons. For example, researchers discussed that the heavy metals absorbable concentration specially cadmium is relate to both amount and type of organic matter existed in soil so that the analysis of organic heavy metals type cause to these elements release in the form of accessible bio-available from that these forms may be poisonous for agricultural crops (Jing et al., 1992 and McBride, 1995). Del Castilho et al (1997) mentioned that the absorption and solution increasing reasons are decreasing soil pH due to nitrification, ion power

increase and solvable organic matters. The cadmium formability complex is associated with cholera, the increase of chloride cadmium complex in soil is effective in decreasing the cadmium absorption by soil colloids resulted from its extractability increase (Smolders et al., 1998 and Yin-Ming, 1994). And of course, concerning this point that the present research is done in paddies and these areas leaching is high, can emphasized the gained results of this research that express the indirect relationship between plant cadmium amount and saltiness. Because in one hand due to complex formation causes to cadmium extraction power increase in soil and in another hand by preventing cadmium from being placed over active levels leads in cadmium leaching increase. In a research administered about the effect if liming on the cadmium, lead and zinc absorption amount, it was showed that the high amount of liming leads in these elements absorption uptake within wheat culm and seed (Tlustoš et al., 2006). And naturally this causes the cadmium amount within soil that is as much as the amount of liming increases due to pH increasing and insolvable cadmium and the high competition of calcium with cadmium in calcareous soils, the cadmium transported to the plant is lower and stages more in the soil. That this issue emphasizes the indirect relationship between the cadmium existed in plant and the liming amount within soil and the direct relationship between extractable cadmium rate

Conclusions

Detailed geostatistical analysis on Cd distributions will help to gather more information variability of Cd concentrations in soil and rice seeds in this region. Sixty-one rice seed samples in area have Cd concentrations higher than $150 \mu\text{g kg}^{-1}$. Cd concentrations in soil and rice seed samples were moderate spatial dependence. Cd D_{DTPA} was fitted to the spherical model with a range of 105 km, and Cd in rice seeds was fitted to the Gaussian model with a range of 100 km. lognormal ordinary kriging methods achieved the best result of Cd estimation regarding the lowest statistical measures. Over the long history of land utilization, the spatial variability of investigated elements was influenced by both natural and anthropogenic factors. Cd in rice seed and Cd extractable by DTPA had low risks for environmental pollution and human health. Both natural and anthropogenic

and oil liming amount. As much as the heavy metals concentration of soil increases their accessibility for plant will be raised (De Temmerman, 1984). As it is determined in the figure according to geographical length and width, the western areas of Khuzestan province which are related to Dasht-e Azadegan, include high level of extractable cadmium in soil. It may be expected that within plant amount has the same plot, but as it is shown in the Fig. 3, in the eastern areas, the existed cadmium in the plant is higher and although in the western areas the increasing procedure of cadmium amount follow its increasing procedure in the soil, but this matter is of lower intensity rather than eastern areas. So many reasons can be existed as it is mentioned previously, that the environment factors effect in plant absorption is very influential. The more percentage of organic matter in Baghmalek area rather than western areas is shown and this procedure can be observed from west to east in general (Table 2). Another reason can be liming percentage and the soil saltiness rate. Regarding to this matter that previously between liming and soil saltiness with plant cadmium rate there was a negative relationship (Table 2) and also concerning this Table it can be seen that the average of liming and soil saltiness in western areas in Khuzestan province (Dasht-e Azadegan) in comparison to eastern areas (Baghmalek) is bigger and it disturbs the cadmium release, its more solution and finally its absorption by plant. factors had contributed to the genesis of pollution process. The association of the higher soil heavy metal concentrations with soil texture and soil organic matter was because of 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 and decision support. Although the characterization of a complex relationship between soil contamination and soil properties requires more comprehensive studies, the results of this preliminary study can serve as a basis for supplementary (more detailed) studies in which soil attributes, including all regulated heavy metals, are analyzed with the help of GIS methodologies for accurately assessing the environmental quality.

Acknowledgment

We gratefully acknowledge the support of this work by the Shahid Chamran University of Ahvaz.

REFERENCES

- Afyoni M, Khoshgoftarmanesh AH, Dorostkar V, Moshiri R (2007) Zinc and Cadmium content in fertilizers commonly used in Iran. International Conference of Zinc-Crops. May 24–28, Istanbul, Turkey.
- Alloway B (1995) Heavy metal in soils, 2nd edn, Blackie and Academic and professional, Glasgow, UK.
- Appel C, Ma L (2002) Concentration, pH and surface charge effects on cadmium and lead sorption in three tropical soils. *J Environ Qual.* 31: 581-589.
- Chaney R L, Hornick SB (1978) Accumulation and effects of cadmium on crops Cadmium 77. Proc 1st Int Cadmium Conf, San Francisco. London: Metal Bulletin. 125-40.
- De Temmerman LO, Hoening H, Scokart PO (1984) Determination of normal levels and upper limit values of trace elements in soils. *Z.Pflanzen. Bodenk.* 147: 687-694.
- Del Castilho P, Chardon WJ, Salomons W (1993) Influence Of cattle-manure slurry application on Solubility of Cd, Cu and Zn in a manured acidic soil, loamy-sand soil. *J. Environ. Qua.l.* 22: 689-697.
- Duruibe JO, Ogwuegbu MO C, Egwurugwu JN (2007) Heavy metal pollution and human biotoxic effects. *International Journal of Physical Sciences.* 2 (5): 112-118.
- Farshi AA, Shariati M, Jaroliahai R, Ghaemi MR, Shahabifar M, Tavallaei MM (1997) An Estimate of Water Requirement of Main Field Crops and Orchards in Iran, Agricultural Education Publisher, Tehran, Iran, p. 900.
- Font R, Ve'lez D, Del Rí'o-Celestino M, De Haro-Bailo A, Montoro R (2005) Screening Inorganic Arsenic in Rice by Visible and Near-Infrared Spectroscopy. *Microchim Acta* 151: 231–239
- Fox MRS, Tao SH, Stone CL, Fry BE (1984) Effect of zinc, iron and copper deficiencies on cadmium in tissues of Japanese Quail. *Nviron. Health Perspect.* 54: 57-65.
- Gee GW, Bauder JW (1986) Particle size analysis. In: Klute, A., ed., *Methods of Soil Analysis.* Part 1, 2nd edn, American Society of Agronomy, Madison, WI, pp. 383–411.
- Ghafoor A, Zia-ur-raman M, Ghafoor A, Murtaza G, Sabir M (2008) Fractionation and availability of cadmium to wheat as affected by inorganic amendments. *Int. J. Agri. Biol.* 10: 469-474.
- Goovaerts P (1999) Geostatistics in soil science: state-of-the art and perspectives. *Geoderma.* 89, 1–45.
- Hossain M (2004) Long-term prospects for the global rice economy, FAO Rice Conference. Rome, Italy, 12–13 February.
- Jafarnejadi A, Homae M, Sayyad Gh, Bybordi M (2011) Large Scale Spatial Variability of Accumulated Cadmium in the Wheat Farm Grains. *Soil and Sediment Contamination: An International Journal.* 20: 98–113.
- Jiachun Shi, Haizhen W , Jianming Xu, Jianjun Wu, Xingmei Liu, Haiping Zhu, Chunlan, Yu (2007) Spatial distribution of heavy metals in soils: a case study of Changxing, China. *Environ Geol.* 52:1–10.
- Jing J, Logan TJ (1992) Effects of sewage sludge cadmium concentration on chemical extractability and plant uptake. *J. Environ. Qual.* 21:73-81.
- Kara Y, Kara I (2005) Removal of cadmium from water using duckweed (*Lemna trisulca* L.). *Int. J. Agri. Biol.* 7: 660-662.
- Lindsay WL, Norvell WA (1978) Development of a DTPA soil test for zinc, iron, manganese, and copper. *Soil Sci. Soc. Am. J.* 42: 421–428
- Loganathan P, Hedley MJ, Grace ND, Lee J, Cronin SJ, Bolan, NS, Zanders JM (2003) Fertilizer contaminants in New Zealand grazed pasture with special reference to cadmium and fluorine: a review, *Australian Journal soil Research.* 41: 501-532
- Matheron G (1963) Principles of geostatistics. *Econ Geol.* 58:1246–1266.
- McBride MB (1995) Toxic metal accumulation from agricultural use of sludge: Are USEPA regulations Protective. *J. Environ. Qual.* 24: 5-18.
- McGrath D, Zhang C, Carton, OT (2004) Geostatistical analyses and hazard assessment on soil lead in Silvermines Area, Ireland. *Environmental Pollution.* 127: 239–248.
- McLaughlin MJ, Tiller KG, Sing BR (1999) Cadmium in soils and plants. Kluwer

- Academic Publishers, Dordrecht, the Netherlands.
- Oustan S, Heidari S, Neyshabouri MR, Reyhanitabar A, Bybordi A (2011) Removal of heavy metals from a contaminated calcareous soil using oxalic and acetic acids as chelating agents. IPCBEE, vol.8
- Phuong TD, Chuong PV, Khiem DT, Kokot S (1999) *Analyst*. 124: 553
- Reilly C, Bphil BS, Faifst PD (2002) *Metal Contamination of Food, its Significance for Food Quality and Human Health*. 3rd ed., Blackwell Science Ltd., Osney Mead, Oxford, UK.
- Simmons RW, Pongsakul P, Saiyasitpanich D, Klinphoklap S (2005) Elevated levels of cadmium and zinc in paddy soils and elevated levels of cadmium in rice grain downstream of a zinc mineralized area in Thailand: Implications for public health. *Env Geochem Health*. 27: 501–11
- Smith E, Naidu R, Alston AM (1998) Arsenic in the soil environment: A Review. *Adv. Agron*. 64:149-195
- Sumner ME, Miller WP (1996) Cation exchange capacity and exchange coefficients. In: Sparks, D. L. ed., and *Methods of Soil Analysis*. Part 2. America Society of Agronomy, Madison, WI, pp. 1201–1229.
- Taylor MD, Percival HJ (2001) Cadmium in soil solutions from a transect of soil away from a fertilizer bin. *Environ Pollut*. 113: 35-40
- Tlustoš P, Száková J, Kořínek K, Pavlíková D, Han A, Balík J (2006) The effect of liming on cadmium, lead and zinc uptake reduction by spring wheat grown in contaminated soil. *Plant Soil Environ*. 52: 16–24.
- Walkley A, Black IA (1934) An examination of the Degtjareff for determining soil organic matter and a proposed modification of the chromic acid titration method, *Soil Science*. 37, 29–38.
- Webster R, Oliver MA (2001) *Geostatistics for environmental scientists*. Wiley, Chichester, 89–96.
- Wei WY, Wei ZG, Zhao HY, Li HX, Hu F (2009) Roles of Organic Acids and Nitrate in the Long-Distance Transport of Cobalt in Xylem Saps of *Alyssum murale* and *Trifolium subterraneum*. *Biological Trace Element Research*. 131: 165-176
- Yin-Ming Li, Chaney RL, Schneiter AA (1994) Effect of Soil Chloride Level on Cd Concentration in Sunflower Kernels. *Plant and Soil*. 167: 275-280
- Yu-sheng Q, Zheng-yin W, La-tie J, Shi-hua T (2010) Cadmium Uptake by Paddy Rice and Soil Available Cd under Water Flooding as Affected by Nitrogen Fertilizer. ICBBE, 4th International Conference on.
- Zhang XY, Lin FF, Wong MTF, Feng XL, Wang K (2009) Identification of soil heavy metal sources from anthropogenic activities and pollution assessment of Fuyang County, China. *Environmental Monitoring and Assessment*. 154: 439–449.
- Zimdahl RL, Skogerboe RK (1997) Behavior of lead in soil. *Environ. Sci. Technol*. 11: 1202–1207.