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Impact of agricultural activities on accumulation of Cadmium, Cobalt, Chromium, Copper, Nickel and Lead in soil of Hamedan province

A. Shahbazi[1], A.R. Soffianian[2], N. Mirghaffari[2], H. Rezaei[3*]

[1]Lecturer of Dept. of Natural Resources, Baharan Institute of Higher Education, Gorgan, Iran

[2]Associate Prof. of Environmental Science, Dept. of Natural Resources, Isfahan University of Technology, Isfahan.

[3]Assistant Prof. Dept. of Environmental Sciences, Gorgan University of Agricultural Sciences and Natural Resources, Gorgan, Iran

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Abstract

Use of chemical fertilizers, pesticides and sewage sludge in agriculture lands have increased soils trace metals concentration in many parts of the world. In This article we report the results of a study on impacts of agricultural activities on soil accumulation of Cadmium, Cobalt, Chromium, Copper, Nickel and Lead and risk of metal contamination in Hamedan Province using contamination factor. The soil samples were collected systematically from agriculture fields with cultivation period of 65, 35 and 20 years. The results showed the mean concentration of Cd, Co, Cr, Cu, Ni and Pb in the soils was increased with the cultivation period and a significant difference was seen between the concentrations of metals, except for Pb, in the soil under different cultivation periods. The trend of soils trace metal accumulation of Cd, Co, Cr and Cu was exponential, whereas for Ni and Pb, it was quadratic and linear, respectively. Also, based on the calculated contamination factors, the soils classified as none and none to medium class pollution were generally found in lands with more length of cultivation. The increase of trace metals concentration in the soil followed the increase in the use of fertilizers in the region. The cultivated soils thus provide a way for entrance of trace elements in the human's food chain. Therefore, monitoring contaminated soils is necessary to control and prevent the risks from contaminated soils.

Keywords: Accumulation trend, Agricultural activities, Contamination factor, Traces metal

*Corresponding author; hassanrezaei@gau.ac.ir

Introduction

The most important soil contaminants are trace metals, acid precipitation and organic materials. In recent years, soil pollution by trace metals has received much attention due to their properties (Yalcin *et al.*, 2007). Spatial variations of trace metals contents in agricultural topsoil may be affected by soil parent material and anthropogenic sources (De Temmerman *et al.*, 2003). Agricultural activities cause enrichment of elements in agricultural ecosystems. Trace metals can enter soil due to the use of solid and liquid inorganic and organic fertilizers (Kashem and Singh, 2001; Mantovi *et al.,* 2003). The application of fertilizers is an important source of trace metals especially Cd, Cu and Zn (Nicholson *et al.,* 2003) and causes the accumulation of these metals in soil (Yalcin *et al.,* 2007). Application of phosphate fertilizers in agricultural soils can lead to increase in the levels of cadmium, arsenic, chromium and lead in soil and decreas in soil pH, and consequently the mobility of trace metals from the soil matrix (Alloway, 1995). Alloway (1990) reported that soil contamination by trace metals resulting from application of phosphate fertilizers is a cause for concern in some countries.

Nowadays, due to limited access to fresh water for irrigation, wastewater especially sewage water is being used for irrigation of agricultural lands and several researches have confirmed that the use of sewage water for agricultural irrigation can be useful (Mehrdadi *et al.,* 2008; Palese *et al.,* 2009). Application of sewage water leads to improvement of the physico-chemical properties and nutrient status of the soil and increase in crop production (Panicker, 1995). On the other hand, the use of sewage water in agriculture is associated with some risks, because it increases the presence of disease microorganisms (Toze, 2006), metal contaminations such as copper, nickel, cadmium, chromium, zinc (Misra and Mani, 1991) and poly-chlorides (Bansal, 1998). McGrath *et al.,* (1995) declared that after 25 years, more than 80 percent of the added toxic metals to the surface layer of soil was due to application of sewage sludge.

Agricultural soils, both directly and indirectly, affect public health by food production; therefore, conservating this source and ensuring its constancy could be very important. Rapid industrial developing and high release of chemical materials used in agriculture cause concerns about accumulation of trace metals in agricultural soils (Alloway, 1990; Wong *et al.,* 2002). Trace metals can accumulate in crops or plants and cause the damage and changes in humans and animals' physiological functions through the food chain (Dudka *et al.,* 1994; Otte, *et al.,* 1993). Previous studies have shown human exposure to the risk of accumulation of trace metals and their accumulation in the fatty tissues of the human body. Trace metals may impact the central nervous system or can be settled in circulatory system and disrupt the normal function of internal organs (Bocca *et al.,* 2004; Waisberg *et al.,* 2003).

Cuihua *et al.,* (2007) studied spatial-temporal variations of trace metals contamination of sediments using GIS 3D spatial analysis methods in Dexing mines, Jiangxi Province, China. The geo-accumulation index (Igeo) was used to assess the environmental quality. Spatial-temporal contrast was performed using GIS 3D spatial analysis from original testing data and geo-accumulation index. The results of the maximum increases in As, Hg, Cd, Cr, Zn, Cu and Pb concentration in 2004 and in sediments were up to 9, 4, 4.6, 1.5, 5.9, 6.3 and 5.6 times higher than those in 1989, respectively. All the contrast results indicated that the extent and scope of trace metals contamination of sediments in 2004 were higher than those in 1989.

Overuse of chemical fertilizers in Iran (placed among the first 12 countries of the world's fertilizer consumers until 2006 (Khodakarami, 2009)), its rapid growing consumption (21.5% increase in fertilizer consumption in 2003 compared to 2002 (Motasadi Zarandi and Babran, 2009)), the direct use of wastewater for agricultural purposes due to lack of irrigation water (Motasadi Zarandi and Babran, 2009) and lack of sewage treatment systems in many cities (Motasadi Zarandi and Babran, 2009), have caused the transfer of trace metals to agricultural soils. Due to concerns about the effects of trace metals in soil fertility and their potential transfer to the human's diets, we need to quantify the metal inputs to agricultural soils and evaluate the soil contamination. The accumulation of trace metals in agricultural soils has been investigated in few studies in Iran (Amini *et al.,* 2007). The aim of this study was to determine the impact of agriculture activities on the accumulation of Cadmium, Cobalt, Chromium, Copper, Nickel and Lead in the soil under different cultivation conditions and the risk of metal contamination in soil using contamination factor.

Materials and methods

Study area

Hamedan Province is one of the western provinces of Iran with a population of 1700000 and area of 19547 KM^2. It is located between 33˚58′ and 35˚44′ northern latitudes and 47˚48′ and 49˚28′ eastern longitudes (Figure 1). Dominant geological formations are alluvial fans from quaternary, orbitolina limestone, shale and marl from Cretacea, catabolized sandstone from Jurassic, and andesite lava, limestone from early Neocene & late Paleocene. Soil depth is shallow to semi deep, gravelly, with light to medium texture and lime accumulated layer. Soil texture is clay-loam and loam (Khodakarami, 2009). Total agricultural lands are 1,005,000 hectares in area with 719,000 hectares being under cultivation and the rest is fallow. Around 43.3% of cultivated lands are irrigated and the rest are dry farms, gardens and nurseries (Khodakarami, 2009). The major crops include wheat, barley, alfalfa, potato & maize (Khodakarami, 2009).

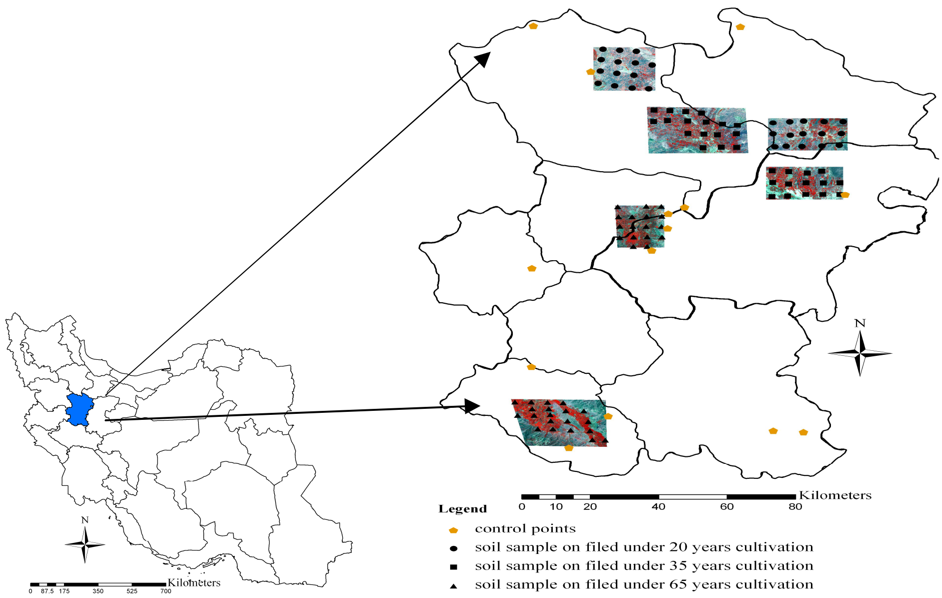

Figure 1. Location of sampling sites in agricultural land in Hamedan Province of Iran

Soil sampling and chemical analysis

The satellite images of different years were used to determine the cultivated lands having a cultivation period. Referring to selected sites and a questionnaire, the cultivation period at each site was determined. Soil sampling was done in six sites having a cultivation duration of 65 (37 samples), 35 (31 samples) and 20 (29 samples) years as well as 12 samples from non-agriculture lands as control points. The surface soil samples (0–20 cm) were collected by systematic methods in late September after crop harvesting. All sites were located in the same bedrocks (alluvial) (Figure 1).

Soil samples were air dried, ground and sieved. Solution of aqua regia (HNO_3, HCL, H_2O_2) was used for digestion of soil samples. The concentration of Co, Cr, Cu, Ni and Pb were determined using atomic absorption spectrophotometer (Model AAnalyst 700 Perkian Elmer). HNO_3 and H_2O_2 were used for digestion of Cd because HCl interferes with the analysis of Cd by graphite furnace (McGrath and Cunliffe, 1985).

Descriptive statistical analysis and trace metal accumulation trend

The normality of data was verified by Kolmogorov-Smirnov test. ANOVA was used to compare the concentration of trace metals. To determine trends in the metals concentration, Kendall and Spearman tests were used. The statistic analysis was performed using SPSS 15.0 software and Minitab 15.

Soil contamination factor

The soil contamination risk was evaluated by contamination factor (Equation 1) (Abrahim and Parker, 2008). According to this factor, soil contamination was classified in seven classes (Table1).

CF= [C] (trace metal/ [C] background (1)

Table 1. Classification levels of contamination factor (Bhuiyan *et al.,* 2010)

Pollution	Contamination Factor
None	0
none to medium	1
Moderate	2
moderately to strong	3
strongly polluted	4
strong to very strong	5
very strong	6

Results and discussion

Descriptive statistic

Descriptive statistics are shown in Table 2. The concentration of Cd, Co, Cr, Cu, Ni and Pb in the agricultural soils were more than control points. In general, the mean concentration of trace metals in the soils was increased in the cultivation period. The concentration of all elements in the soil had normal distribution. However, due to non homogeneity of variance for Cd, Cr and Ni, a logarithmic transformation was used for Cr and Ni, and Box-Cox transformation for Cd. However, there were variations between the elements. For Cd, Co, Cr, Cu and Ni, the mean concentration in the soil under 65 years-cultivation was significantly higher than control points. Whereas for Pb, there was no significant difference between the mean concentration in the soil (Table 3). This indicates the effect of cultivation length on the trace metals accumulation in the soils. The presence of these metals in chemical fertilizers and sewage samples used in the study area can be the reason for their increase in the soil (Khodakarami, 2009).

Probably, increased concentration of trace metals in agricultural soils can be a result of presence of trace metals in irrigation sewage (Al-Nakshabandi *et al.,* 1997) as well as the use of chemical/organic fertilizers (Huang and Jin, 2008). Khodakarami (2009) investigated the concentration of 14 trace metals in different land uses in a part of Hamedan Province. He showed that the main factor controlling the concentration of Cd, Co, Cr, Cu, Ni and Pb in the study area was geological formation, but excessive use of chemical fertilizers can contribute to increasing concentration of these trace metals in soil.

Table 2. Descriptive statistics of trace metals concentration (mg/kg) in agricultural soils

Site		Cd	Co	Cr	Cu	Ni	Pb	pH	EC	OM
Control points	Mean	0.13	16.22	49.95	23.94	60.1	20.7	7.47	1.38	0.4
	Min	0.04	10	20	14.98	29	10.62	7.23	0.91	0.06
	Max	0.34	20	110	33.16	82	23	7.93	1.79	0.86
	Median	0.09	17	32.17	14.15	65.06	22	7.39	1.46	0.38
	Std. Error	0.02	0.94	9.77	1.51	5.06	1.56	0.08	0.11	0.08
	K-S test	0.11	0.84	0.16	0.99	0.71	0.84	0.61	0.90	0.99
20 years	Mean	0.14	17.94	58.89	27.53	61.93	23.97	8.1	0.86	0.7
	Min	0.09	8.10	24.08	15	26	12.21	7.23	0.12	0.07
	Max	0.33	26.54	110	41	102.01	52.43	8.77	3.12	1.62
	Median	0.11	17.6	60	29.3	54	22.4	8.28	0.73	0.59
	Std. Error	0.01	0.81	3.85	1.18	3.74	1.52	0.08	0.12	0.07
	K-S test	0.07	0.96	0.99	0.64	0.27	0.28	0.28	0.21	0.17
35 years	Mean	0.16	18.05	72.99	23.94	61.63	25.41	7.99	1.97	0.84
	Min	0.09	8.90	28.49	19.75	27	15.10	7.44	0.41	0.14
	Max	0.33	22	110	47	88	50.18	8.81	9.65	1.9
	Median	0.14	18	75	30.5	62	24	7.87	1.54	0.82
	Std. Error	0.01	0.46	4.45	1.36	2.36	1.24	0.07	0.31	0.07
	K-S test	0.11	0.33	0.52	0.83	0.97	0.61	0.10	0.02	0.27
65 years	Mean	0.19	20.79	88.09	34.96	73.85	26.13	7.8	1.83	1.22
	Min	0.09	11	43.64	19	39	14.78	6.7	0.63	0.31
	Max	0.51	32.05	160	52	122.28	81.14	8.61	4.26	2.38
	Median	0.17	20	78	34.5	73	24	7.78	1.32	1.18
	Std. Error	0.01	0.70	4.40	1.36	3.64	1.77	0.07	0.17	0.08
	K-S test	0.19	0.66	0.29	0.90	0.80	0.17	0.72	0.10	0.99

K-S: Kolmogorov-Smirnov

Table 3. ANOVA test results in agricultural regions

	Cd	Co	Cr	Cu	Ni	Pb
65 years	0.19^{a}	20.79^{a}	88.09^{a}	34.96^{a}	73.85^{a}	26.13^{a}
35 years	0.16^{ab}	18.05^{b}	72.99^{b}	31.98^{a}	61.63^{b}	25.41^{a}
20 years	0.14^{b}	17.94^{b}	58.89^{c}	27.53^{b}	61.93^{b}	23.97^{a}
Control point	0.13^{b}	16.22^{b}	49.95^{c}	23.94^{b}	60.10^{b}	20.70^{a}

(Different letters in each column indicate significant differences using LSD in mean level of 0.05)

Trace metal accumulation trend

The results of Kendall and Spearman tests showed a trend in the concentrations of all metals. To understand trace metals accumulation trend in 65 year old fields, it was necessary to have information about the concentration variations of trace metals in the soil. The current metal concentration in the soils of 35 and 20 year cultivation period can be simulated as the reference concentration in the soils of 65 year old fields. As there is a similarity between the lands both geologically and in terms of farming management, the curve of trace metal accumulation trend in the soil under 65 year cultivation was drawn using the current concentration of metals (Figure 2).

Trace metals accumulation trend in 65 year old field soils is shown in Figure 2 and Table 4. The trace metal accumulation trend of Cd, Co, Cr and Cu was exponential, but this pattern was quadratic for Ni and linear for Pb.

Li *et al.,* (2009) studied three regions irrigated with sewage in different temporal periods. In their study, 41 soil samples were taken from 0-20 and 20-40 cm of soil depth, 17 samples in regions irrigated with sewage since 1893 (LFA_{1893}), 10 samples from regions irrigated with sewage since 1920 (LFA_{1920}), 8 samples in regions irrigated with sewage since 1944 (LFA_{1944}) and 6 samples in regions not irrigated with sewage, as control points. The results showed that trace metals concentration in LFA_{1893} was more than LFA_{1920}, that of LFA_{1920} was more than LFA_{1944} and those of all three regions were more than control points. Moreover, in order to understand temporal accumulation pattern in LFA_{1893} region, the current trace metal concentration in LFA_{1920} and LFA_{1944} was used in the absence of archive data. The results showed that distribution pattern of trace metals were exponential in 0-20 cm depth and linear in 20-40 cm depth.

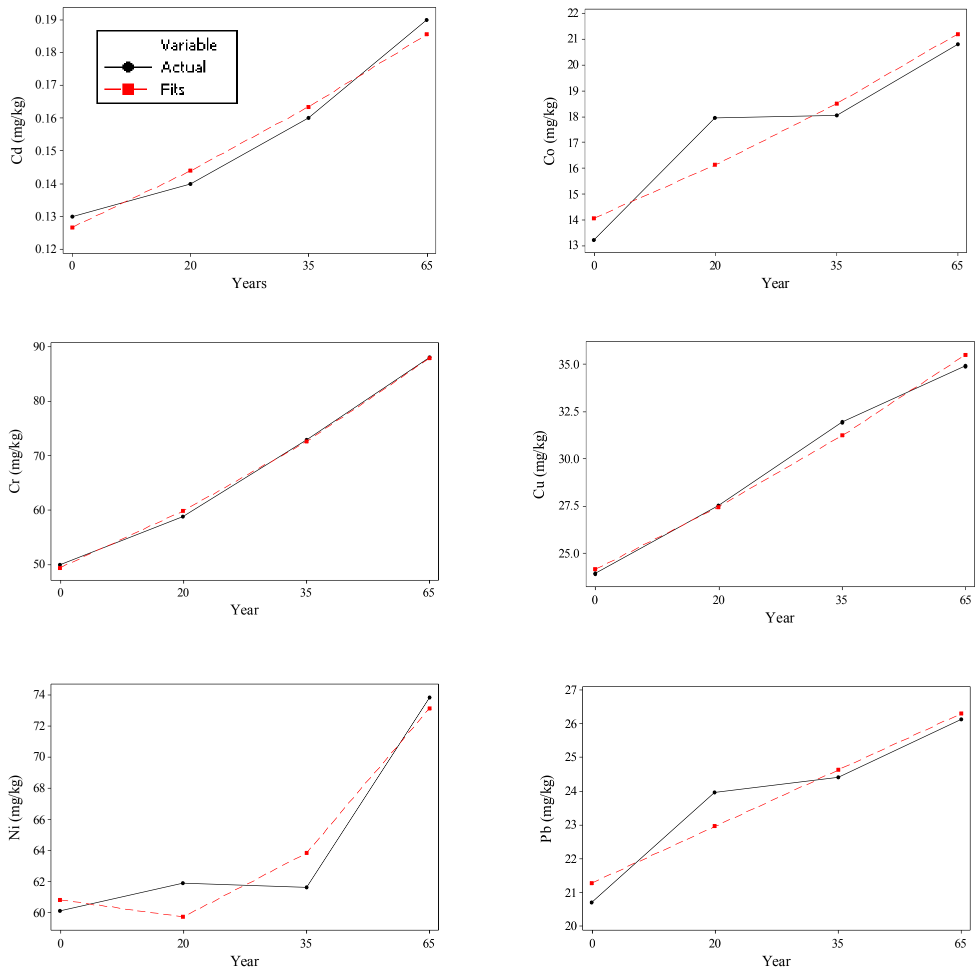

Figure 2. The trace metals accumulation trend in the soil under 65 year cultivation

Table 4. Equations for accumulation trend of trace metal in the soil under 65 year cultivation

Metal		R^2
Cd	$y=0.13e^{0.005x}$	0.98
Co	$y=16.29e^{0.003x}$	0.96
Cr	$y=50.44e^{0.008x}$	0.97
Cu	$y=24.53e^{0.005x}$	0.94
Ni	$y=0.004x^2-0.09x+60.52$	0.82
Pb	$y=0.08x+21.64$	0.83

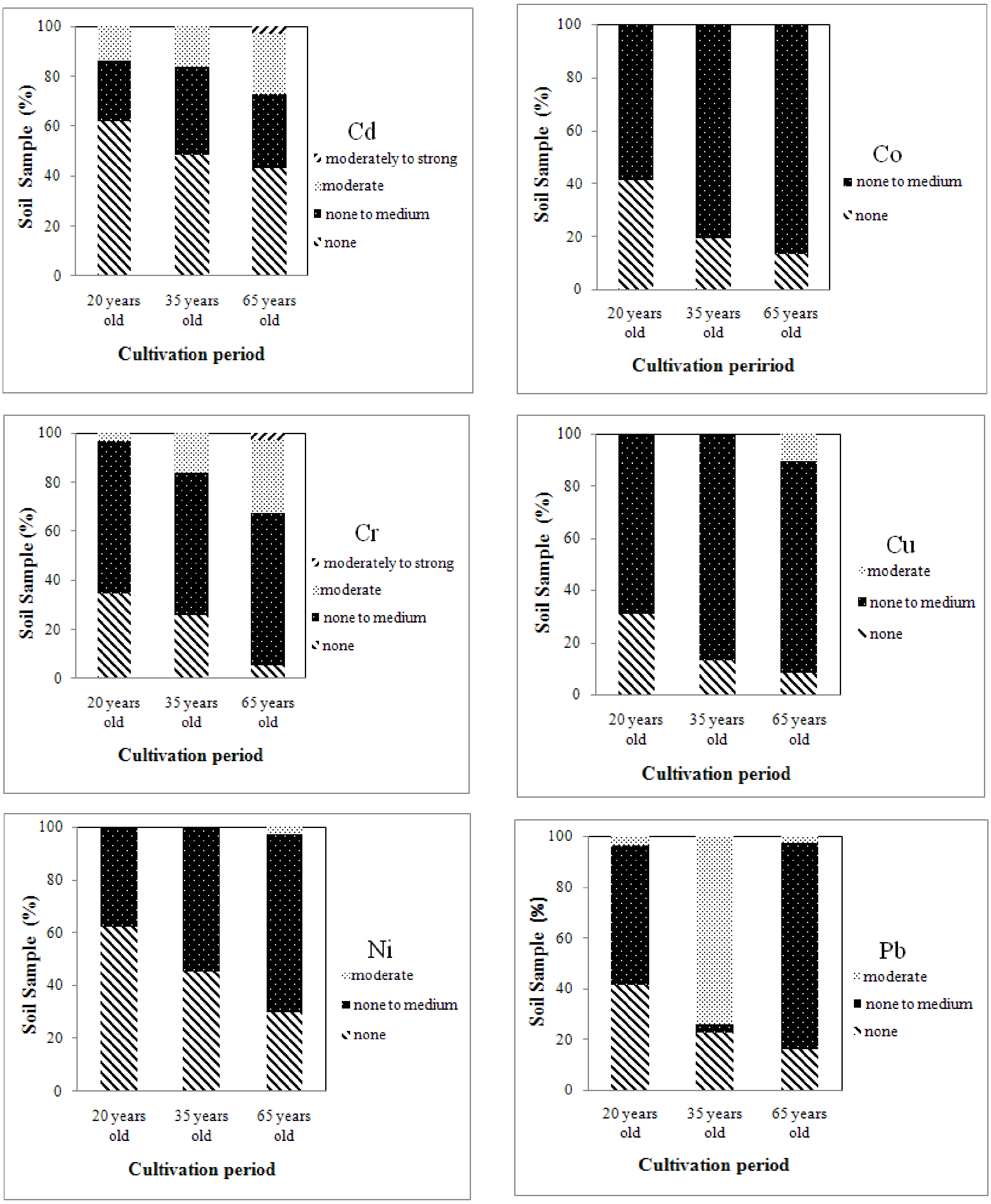

Figure 3. Contamination factor for trace metals in agricultural lands

Soil contamination factor

To calculate background concentration, the mean concentration of 12 soil samples from uncultivated lands on alluvial bed was used. The "Geochemical background" can be described as normal abundance of an element in an empty and barren land. In other words, it is the supply of rare elements which are in soil without human activities (McGrath *et al.,* 1995). The results of calculated contamination factor show that the majority of samples can be classified as none polluted and none to medium polluted classes (Figure 3). For Cd and Cr, an amount of 2.7 percent of the samples cultivated in 65 year were classified as moderate to strong contamination class, 24.3 and 29.7 percent of samples as moderate contamination class, respectively. For Cu and Ni, 10.8 and 2.1 percent of the samples in 65 year cultivated lands fell in moderate contamination class, respectively. Co had the lowest contamination factor. The soil contamination index in 65 year cultivated land was more than 20 & 35 year cultivated lands (Figure 3).

Liu *et al.,* (2005) studied the effects of irrigation with sewage on pollution and trace metals distribution in Beijing, and the change in Cd, Cr, Cu, Zn and Pb concentration in three kinds of soils including cultivated soil, industrial park and a region not irrigated with sewage. They also calculated the amount of pollution load index (PLI), enrichment factor (EF) and contamination factor (CF). The results of EF indicated that the concentration of each metal in soil has an increasing trend (EF was more than 1). The contamination factor (CF) as well as pollution load index (PLI) values indicated the accumulation of these metals during the past 20 years.

Conclusion

The results indicated that the mean concentration of trace metals in the fields with 65 year cultivation period has a significant difference from background concentration. The increasing trend of the metal concentration with the cultivation duration was obvious. The soil contamination factor in the lands under 65 years of cultivation was maximum. The increase of trace metals concentration in the soil followed the increase in the use of fertilizers in the region. The cultivated soils are important ways for entrance of trace elements in the human's food chain. Therefore, monitoring contaminated soils is necessary to control and prevent the risks from these soils.

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