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Level, pattern, and risk assessment of the selected soil trace metals in the calcareous-cultivated Vertisols

Salar Rezapour^{a*}, P. Kouhinezhad^a, A. Samadi^a and M. Rezapour^b

^aSoil Science Department, Urmia University, P.O. Box 165, Urmia 57134, Islamic Republic of Iran;

^bAdministration of Education Kermanshah, Regional 3, Kermanshah, Islamic Republic of Iran

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Dynamics and distribution pattern of trace metals in agricultural lands are an increasing concern due to potential risks to the environment and human health. To ascertain more knowledge of this aspect, the fractions of total and available Fe, Mn, Zn, Cu, and Cd belonging to Vertisols under intensive cultivation and adjoining uncultivated soils were investigated. The order of abundance of metals in both cultivated and uncultivated soils was Fe > Mn > Cu > Zn > Cd and Fe > Mn > Zn > Cu > Cd for both available and total fraction, respectively. A relative enrichment was observed in the value of diethylene-triamine pentaacetic acid-extractable Fe (1.2–201%), Mn (2–31%), Cu (1–40%), and Cd (21–45%) as well as total fraction of Zn (3–17%), Cu (12–32%), and Cd (42–108%) after intensive cropping, which can be contributed to repeated application of agrochemical inputs and manure over long time. The values of RI (potential ecological risk) showed that cultivation caused a low potential ecological risk (33.3% of the soil samples) to moderate potential ecological risk (66.7% of the soil samples) in the study region and that cadmium made up 88%, on average, of the RI value.

Keywords: cultivated soil; long-term cultivation; trace metal; total fraction; DTPA-extractable

1. Introduction

The term ‘trace elements’ refers to the element that occur in the Earth’s crust in amounts less than 0.1% (1000 mg kg⁻¹). Most of the trace metals are essential for normal growth of both plants and animals within the acceptable level; however, when these metals are present in bioavailable forms and at excessive levels, they have the potential to become toxic to living organisms. Some trace elements, such as iron (Fe), manganese (Mn), copper (Cu), and zinc (Zn), are essential to the growth and health of animals and human beings, and lead (Pb), cadmium (Cd), chromium, Cu, Zn, and Mn are the most environmentally concerning elements that have been often reported to cause contamination of soil, water, and food chains.[1] Soils act as long-term sinks for adsorbing and retaining trace metals. Nevertheless, the capacity of soil to retain the metals could be declined due to continuous loading trace metals from different sources, leading to the release of the metals into soil solution and/or groundwater.[2] Consistent with this toxic condition, the

*Corresponding author. Emails: s.rezapour@urmia.ac.ir; s_rezapour2000@yahoo.com

metals (irrespective of their source) can and does reach the soil, where they become part of the food chain: Soil–Plant–Animal–Human. The greatest problems mostly involve Cd, Pb, As, F, Ni, Cu, Zn, Cr, Mn, and Se. To a greater or lesser degree, all of these metals are toxic to humans and other animals. Cadmium and arsenic are extremely poisonous; Pb, F, and Ni are moderately so; Cu, Zn, and Mn are relatively lower in mammalian toxicity.[3] Trace metal pollution can occur in the soil from both natural and anthropogenic sources. Soil directly inherits trace metals from the lithosphere or parent rock. In contrast, anthropogenic metals are directly or indirectly related to human activities, mainly both industrial and agricultural operations.[4–6]

Nowadays, long-term intensive agricultural activities with frequent application of agrichemicals are one of the major causes of accumulation of trace metals (such as Cu, Mn, Zn, and Cd) in soil. Agricultural activities such as the use of the chemical and organic fertilisers (mainly phosphate fertilisers), which are added to soil to improve plant growth and yield, contribute considerable amounts of trace metals to agricultural soils, depending on the rates and types of fertilisers applied.[7] In the countries of the European Union, total Cd inputs to soils through fertilisers have been estimated to be around 334 t yr⁻¹. [8] In California vegetable croplands, Chen et al. [9] observed significant correlations between Cd and soil phosphorus, indicating that the application of P-fertilisers contributes significantly to the accumulation of Cd in soils. Others, particularly metal-enriched chemicals (such as fungicides) and manure, have variable levels of Cd, Cr, Ni, Pb, and Zn, depending on the rate of application of the contributors with its elemental concentration and soil characteristics to which it is applied.[10,11] Some soils in Florida (old citrus groves) contain Cu as high as 4200 mg kg⁻¹ due to fungicide sprays (Mehlich III). A similar pattern was found for Zn and Mn.[1,12]

Generally, the Vertisols of Iran are mostly developed from limestone and other parent rocks rich in calcium and magnesium, which have high potential for agricultural productions. Although substantial data are documented on properties of Vertisols, few studies are available to assess the effects of long-term continuous cultivation on the level and pattern of trace metals of the soils mainly in calcareous environments. The specific aims of this research were: (1) to determine the diethylene-triamine pentaacetic acid (DTPA)-extractable and total concentration of Fe, Mn, Zn, Cu, and Cd in the cultivated and the adjoining uncultivated soils; (2) to investigate the impact of long-term continuous cropping on the level and pattern of the metals; and (3) to assess the degree of possible contamination of the cultivated soil by Mn, Zn, Cu, and Cd using some pollution indices and potential ecological risk.

2. Material and methods

2.1. Site characterisation

This study was conducted in the Pasvah area (36°46' to 36°50' N and 45°09' to 45°50' E, 1500 m above sea level) Western-Azarbaijan province, in the north-west of Iran (Figure 1). The climate of the region is a Mediterranean type with an average of 650 mm annual precipitation as both rain and snow. Mean daily temperature maximum and minimum was 32 and – 5.2°C, respectively, and annual mean temperature was about 12.2°C. The native vegetation was composed of various grasses such as *Altheea officinalis*, *Astragalus officinalis*, *Alhagi camelorum*, *Carthamus oxyacantha*, and *Achillea millefolium*. The soil moisture regime is xeric and the temperature regime is mesic. The area has been continuously cultivated by sugar beet in rotation with wheat, barley, and pea (without any fallow), irrigated through rainfall, ground water, and/or seasonal river's water. The history of intensive farming goes back to over five decades. Currently, anthropogenic processes occur during land preparation, planting, cultural practices, and harvest operations, linked with the presence of livestock after harvest.

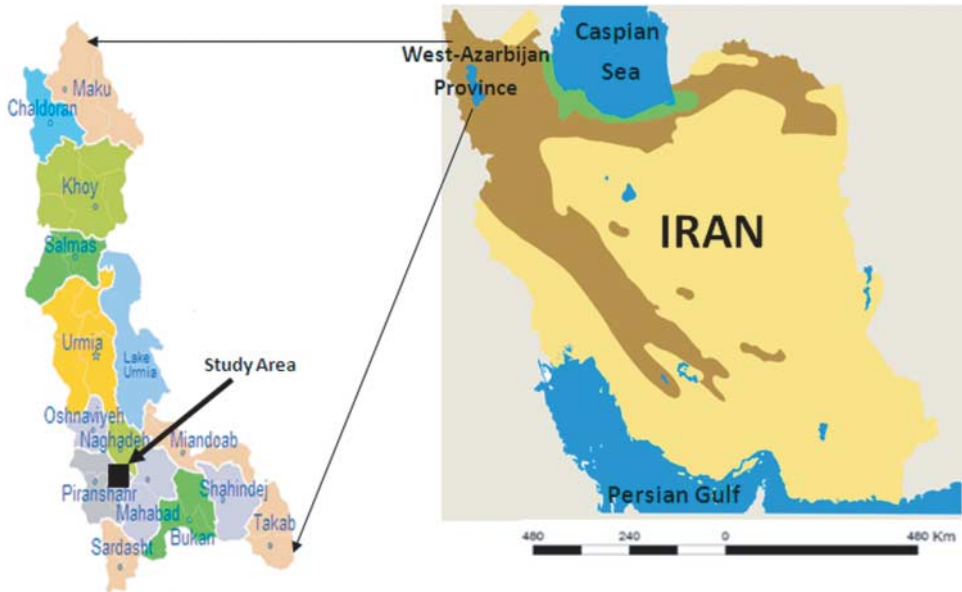


Figure 1. Location map of study region.

The sampling sites were selected from previous regional soil surveys. A total of 36 composite soil samples (0–30 cm deep) belonging to six soil pedons and three subgroups of the Vertisols order (Chromic Calcixererts, Typic Haploxererts, and Typic Calcixererts) were described [13] and sampled from the main sugar beet growing soils (after the harvest in September–October 2013) and similar soils from the nearby uncultivated region as grassland. The uncultivated soil is referred to as the control. At each sampling point, four individual sub-samples were collected (using a stainless steel spade) within a radius of 5 m of a central point and mixed to achieve a composite soil sample. In each soil pedon, the paired sites (cultivated soil and adjacent uncultivated soil) were selected in similar slope, topography aspect, drainage condition, and parent materials. Soil samples were air-dried and passed through a 2-mm mesh sieve before the analysis.

2.2. Physical and chemical characteristics

The amounts of clay, silt, and sand were estimated by the Bouyoucos methods.[14] The saturation extract and 0.01 M CaCl_2 suspension were used for determination of electrical conductivity (EC) and soil pH, respectively. The standard methods were applied for measuring of organic carbon,[15] calcium carbonate equivalent (CCE),[16] and cation exchange capacity (CEC).[17] Free Fe oxides (Fe_d) were extracted with citrate-dithionite-bicarbonate [18] and amorphous Fe oxides (Fe_o) with ammonium oxalate at a pH of 3.[19]

2.3. Trace metals analysis

The DTPA-fraction of Fe, Mn, Zn, Cu, and Cd were extracted from 10 g soil with 20 mL of DTPA extractant.[20] The extracted Fe_d and Fe_o were then determined using atomic absorption spectrometry. For total elemental analysis, 2 g dry soil + 10 mL of HNO_3 (1:1) was heated for 15 min at 95°C on a heating block after addition of 2 mL deionised water and 3 mL of

30% H₂O₂. [21] The concentrations of Mn, Zn, Cu, and Cd were determined using an atomic absorption spectrophotometer (Shimadzu AA-6300).

2.4. Soil pollution indexes

The following formula was applied for the calculation of the availability fraction percentage (AP) [22]:

$$AP = \left(\frac{C_{ia}}{C_{it}} \right) \times 100,$$

where C_{ia} denotes the available metal concentration in the i th sampling sites and C_{it} , the total metal concentration in the i th sampling sites. This index is applied to provide a basis to compare the potential trace metal mobility and toxicity in soils. [23]

Single-factor pollution index (PI) was calculated as the ratio between the amount of metals in each soil and its control value (uncultivated soil).

Nemerow pollution index (PIN) or comprehensive PI was evaluated for Mn, Cu, Zn, and Cd by the following relation [24]:

$$PIN = \sqrt{\frac{\left((1/n) \sum_{i=1}^n PI_i \right)^2 + [\max(PI)]^2}{2}},$$

where $\max(PI)$ represents the maximum value of the single-factor PI, n number of study metals, and i i th metals. The following categories were applied to describe the Nemerow pollution index: $PIN \leq 0.7$ = clean; $0.7 < PIN \leq 1$ = low pollution; $1 < PIN \leq 2$ = slight pollution; $2 < PIN \leq 3$ = moderate pollution; $PIN > 3$ = high pollution.

Potential ecological risk index (RI) was determined as the sum of the risk factor of the Zn, Cu, and Cd using the following equations:

$$f_i = \frac{C_i}{B_i} \quad f_{deg} = \sum f_i,$$

$$E_i = T_i f_i \quad RI = \sum E_i,$$

where f_i is the concentration ratio of the metal in soil (C_i) and reference (B_i). f_{deg} shows the integrated pollution level of soil, defined as the sum of f_i for the analysed metals. E_i is the single-factor PI for the metals and T_i is the metal toxic factor. Based on Hakanson, [25] the T_i values for Zn, Cu, and Cd are 1, 5, and 30, respectively. The following terminologies were applied to describe the Potential ecological RI: $RI \leq 50$ = low potential ecological risk; $50 < RI \leq 100$ = moderate potential ecological risk; $100 < RI \leq 200$ = Considerable potential ecological risk; $RI > 200$ = high potential ecological risk.

The degree of soil contamination (C_d) was calculated by the following relation [26]:

$$C_d = \frac{\sum_{i=1}^{i=n} C_F}{n},$$

where C_F denotes concentration factor, n number of the studied metals, and i the i th metals.

Concentration factor (CF) calculated as the concentration of each metal in the soil divided by concentration of soil reference metal.

The mean values of both total and DTPA-fraction of the metals in the cultivated soils and the adjoining uncultivated soils were compared with a paired t -test using the SPSS software.

3. Results and discussion

3.1. General soil properties

Intensive cultivation resulted in remarkable changes in the selected soil attributes, as shown in Table 1. On average, the amount of clay increased by cultivation in Typic Calcixererts and mainly Chromic Calcixererts (a rise of 2–60% with EF of 1.02 and 1.6), which could be attributed to the alteration accelerated during farming practices. Surely, the cultivated soils must be wetter for a longer period of time relative to the uncultivated land, which can lead to increased mineral

Table 1. Comparison of the mean \pm standard deviation values of the examined soil characteristics for the cultivated and adjacent uncultivated soils.

Characteristics	Chromic calcixererts			
	Cultivated soil	Uncultivated soil	Change (%)	DF or EF
Sand (g kg ⁻¹)	201 \pm 17.10	260 \pm 73.0	- 22.7*	0.77
Silt (g kg ⁻¹)	325 \pm 17.3	286 \pm 52.9	13.6	1.14
Clay (g kg ⁻¹)	474 \pm 26.3	354 \pm 25.8	33.9*	1.34
pH	7.1 \pm 0.08	7.2 \pm 0.10	- 1.4	0.99
EC (dS m ⁻¹)	0.52 \pm 0.09	0.62 \pm 0.13	- 16.1	0.84
OC (g kg ⁻¹)	5.22 \pm 2.30	14.5 \pm 2.80	- 64**	0.36
CCE (g kg ⁻¹)	159 \pm 47.3	211 \pm 34.9	- 24.6	0.75
CEC (cmolc kg ⁻¹)	39.0 \pm 3.90	33.20 \pm 2.90	17.5	1.17
Fe _d (g kg ⁻¹)	3.4 \pm 1.11	1.28 \pm 0.73	165.6***	2.66
Fe _o (g kg ⁻¹)	1.10 \pm 0.43	0.90 \pm 0.12	22.2	1.22
Characteristics	Typic haploxererts			
	Cultivated soil	Uncultivated soil	Change (%)	DF or EF
Sand (g kg ⁻¹)	260 \pm 35.7	212 \pm 71.8	22.6	1.23
Silt (g kg ⁻¹)	325 \pm 30.8	292 \pm 9.6	11.3	1.11
Clay (g kg ⁻¹)	416 \pm 35.1	495 \pm 77.2	- 15.9	0.84
pH	6.98 \pm 0.14	7.2 \pm 0.04	- 3.0	0.97
EC (dS m ⁻¹)	0.58 \pm 0.24	0.66 \pm 0.06	- 12.1	0.88
OC (g kg ⁻¹)	6.0 \pm 1.3	7.8 \pm 2.8	- 23.0*	0.77
CCE (g kg ⁻¹)	38.7 \pm 18	80.0 \pm 26.7	- 51.6**	0.48
CEC (cmolc kg ⁻¹)	32.5 \pm 2.7	35.2 \pm 1.6	- 7.7	0.92
Fe _d (g kg ⁻¹)	2.9 \pm 0.91	2.73 \pm 0.84	6.23	1.06
Fe _o (g kg ⁻¹)	1.18 \pm 0.41	1.12 \pm 0.36	5.34	1.05
Characteristics	Typic calcixererts			
	Cultivated soil	Uncultivated soil	Change (%)	DF or EF
Sand (g kg ⁻¹)	124 \pm 28.3	169 \pm 34.1	- 26.6	0.73
Silt (g kg ⁻¹)	391 \pm 50.0	356 \pm 32.6	9.8	1.1
Clay (g kg ⁻¹)	485 \pm 77.2	475 \pm 41.2	2.1	1.02
pH	7.25 \pm 0.27	7.4 \pm 0.48	- 2.0	0.98
EC (dS m ⁻¹)	1.9 \pm 1.7	2.3 \pm 1.9	- 17.4	0.83
OC (g kg ⁻¹)	5.0 \pm 3.9	6.8 \pm 3.9	- 26.5*	0.73
CCE (g kg ⁻¹)	196 \pm 41.1	154 \pm 47.3	27.0*	1.27
CEC (cmolc kg ⁻¹)	31.6 \pm 4.2	30.4 \pm 4.3	3.9	1.04
Fe _d (g kg ⁻¹)	1.95 \pm 0.61	1.7 \pm 0.59	14.7	1.15
Fe _o (g kg ⁻¹)	1.31 \pm 0.56	1.22 \pm 0.58	7.38	1.07

Notes: EC, electrical conductivity; OC, organic carbon; CCE, calcium carbonate equivalent; CEC, cation exchangeable capacity. DF, depletion factor; EF, enrichment factor that was calculated as the value of each property in the cultivated soil divided by the value of that property in the adjoining uncultivated soil.

* $P < .05$.

** $P < .01$.

*** $P < .001$ based on paired t -test results.

weathering.[27] In contrast to that, clay content was decreased by 16% (a DF of 0.85) in Typic Haploxererts after cropping mainly due to clay depletion resulted from runoff or erosion.[28] The pH values of both the cultivated and uncultivated soils (min = 6.9, max = 7.4, min = 7.2) were classified into neutral category. The soil pH was somewhat lower in the cultivated soil (a drop of 1–3%) compared to the control (adjacent uncultivated soil), which may be due to the movement of salts into and out of different soil zones as soil moisture moves up and down through the soil profiles following irrigation practices. For different great groups of Vertisol, the values of soil organic carbon were dropped in the order of Chromic Calcixererts (a loss of 64% with depletion factor (DF) of 0.36) > Typic Calcixererts (a loss of 26% with DF of 0.73) > Typic Haploxererts (a loss of 23% with DF of 0.77) by cultivation, which is in agreement with past works.[27–29] Such trends can be contributed to increased removal of biomass, well soil mixing, and an enhanced decomposition rate resulting from well contact between crop residues and the soil, higher aeration, and greater soil temperature.[5,28] The average CCE from Chromic Calcixererts and Typic Haploxererts had 25% (DF of 0.75) and 52% (DF of 0.48) loss, respectively, with cultivation. The possible explanation might be attributed to the dissolution and translocation of carbonates under the influence of ambient moisture and amplified CO₂ levels related to root respiration and organic matter oxidation.[5] In contrast, soils from Typic Calcixererts had 27% more CCE after cultivation than soils from the adjacent uncultivated area due to the mixing of topsoil to subsoil by tillage operation.[27] Intensive cropping led to a decreasing pattern in the values of EC (a drop of 12–17%), reflecting a positive change in the soil quality after cultivation. After long-term cultivation, the mean values of CEC increased up to 4% (EF of 1.04) and 18% (EF of 1.18) for Typic Calcixererts and Chromic Calcixererts while a drop of 8% (DF of 0.92) observed in Typic Haploxererts. Sharply, this pattern was in matching to the distributive trend of clay fraction, suggesting the significant contribution of clay to CEC. The impact of long-term cultivation improved 6% (with an EF of 1.06) to 166% (with an EF of 2.66) and 5% (with an EF of 1.05) to 22% (with an EF of 1.22) the amount of Fe_d (free iron oxides) and Fe_o (amorphous Fe), respectively, (Table 1). This might be associated with the accelerated weathering of Fe-bearing minerals (e.g. chlorite and illite) resulted from the higher temperature condition and the number of wetting-drying cycles during farming practices.[30]

3.2. Trace metals

There was a remarkable build-up in both DTPA-extractable and total trace metals (Fe, Mn, Zn, Cu, and Cd) with cultivation in the majority of soil types, as illustrated in Table 2. The values of DTPA-Fe in the cultivated (min = 6, max = 9.8, mean = 8.2 mg kg⁻¹) and uncultivated soils (min = 2.9, max = 6.5, mean = 5.1 mg kg⁻¹) were within the maximum permissible limits of 2.5–20 mg kg⁻¹ [31] and 0–25 mg kg⁻¹. [32] Long-term cropping produced a considerable increase in available Fe, with cultivation ranging from 1.2% (Typic Haploxererts) to 201% (Chromic Calcixererts). A similar pattern was observed for Fe_o (amorphous Fe) (Table 1). This explains that the precipitation of amorphous Fe compounds under the influence of cultivation probably enhanced Fe solubility as reflected in a positive correlation between them ($r = 0.63$, $P \leq .05$). Similar results were reported by Santiago and Delgado [33] who found that amorphous Fe can be controlled solubility and availability of Fe. For both cultivated (min = 9, max = 15, mean = 11.3 mg kg⁻¹) and uncultivated (min = 8, max = 14, mean = 10.5 mg kg⁻¹) soils, the values of DTPA-Mn were well within the maximum permissible limits of 0–30 mg kg⁻¹. [32] Compared to the uncultivated soils, long-term cropping increased DTPA-Mn by 2% (Typic Haploxererts) to 13% (Typic Calcixererts). The susceptibility of Mn to change from an oxidised to a reduced state caused by irrigation practices and vice versa with soil moisture [34]

Table 2. Comparison of the mean \pm standard deviation values of the trace metals in the cultivated and uncultivated soils.

Trace metal	Chromic calcixererts			
	Cultivated soil	Uncultivated soil	Change (%)	DF or EF
DTPA-Fe (mg kg ⁻¹)	8.92 \pm 1.35	2.96 \pm 0.23	201.4***	3.01
DTPA-Mn (mg kg ⁻¹)	10.09 \pm 1.23	8.95 \pm 0.35	12.7	1.13
DTPA-Zn (mg kg ⁻¹)	1.43 \pm 0.38	1.66 \pm 0.04	- 13.8	0.86
DTPA-Cu (mg kg ⁻¹)	2.14 \pm 0.21	2.92 \pm 0.37	- 26.7	0.73
DTPA-Cd (mg kg ⁻¹)	0.70 \pm 0.03	0.49 \pm 0.10	42.9*	1.43
Total-Fe (g kg ⁻¹)	21.168 \pm 0.02	21.270 \pm 0.01	- 0.48	0.99
Total-Mn (mg kg ⁻¹)	802.50 \pm 102.5	815.0 \pm 91.9	- 1.53	0.98
Total-Zn (mg kg ⁻¹)	68.18 \pm 0.10	58.50 \pm 0.71	16.55	1.16
Total-Cu (mg kg ⁻¹)	26.99 \pm 0.40	23.13 \pm 1.24	16.69	1.17
Total-Cd (mg kg ⁻¹)	3.34 \pm 0.18	1.6 \pm 0.23	108.75***	2.09
Trace metal	Typic haploxererts			
	Cultivated soil	Uncultivated soil	Change (%)	DF or EF
DTPA-Fe (mg kg ⁻¹)	6.1 \pm 0.81	6.03 \pm 1.8	1.2	1.01
DTPA-Mn (mg kg ⁻¹)	14.62 \pm 0.47	14.31 \pm 5.52	2.2	1.02
DTPA-Zn (mg kg ⁻¹)	1.98 \pm 1.06	0.97 \pm 0.15	104.1***	2.04
DTPA-Cu (mg kg ⁻¹)	3.08 \pm .83	2.2 \pm 0.42	40*	1.4
DTPA-Cd (mg kg ⁻¹)	0.55 \pm 0.02	0.45 \pm 0.01	22.2	1.22
Total-Fe (g kg ⁻¹)	22.768 \pm 2.68	26.820 \pm 2.46	- 15.1	0.85
Total-Mn (mg kg ⁻¹)	871.25 \pm 30.05	958.5 \pm 72.83	- 9.1	0.91
Total-Zn (mg kg ⁻¹)	76.5 \pm 0.71	74.5 \pm 0.72	2.68	1.03
Total-Cu (mg kg ⁻¹)	37.18 \pm 0.11	28.08 \pm 0.25	32.4*	1.32
Total-Cd (mg kg ⁻¹)	3.05 \pm 0.05	1.93 \pm 0.2	58.03*	1.58
Trace metal	Typic calcixererts			
	Cultivated soil	Uncultivated soil	Change (%)	DF or EF
DTPA-Fe (mg kg ⁻¹)	9.64 \pm 0.93	6.48 \pm 0.25	48.8*	1.49
DTPA-Mn (mg kg ⁻¹)	9.21 \pm 0.75	8.13 \pm 1.94	13.3	1.13
DTPA-Zn (mg kg ⁻¹)	1.04 \pm 0.23	1.28 \pm 0.35	- 18.8	0.81
DTPA-Cu (mg kg ⁻¹)	2.91 \pm 0.35	2.87 \pm 0.42	1.4	1.01
DTPA-Cd (mg kg ⁻¹)	0.52 \pm 0.03	0.43 \pm 0.02	20.9	1.21
Total-Fe (g kg ⁻¹)	22.586 \pm 2.68	22.649 \pm 0.019	- 0.28	1.0
Total-Mn (mg kg ⁻¹)	804.75 \pm 10.25	872.4 \pm 90.51	- 7.75	0.92
Total-Zn (mg kg ⁻¹)	77.5 \pm 0.71	74.88 \pm 2.64	3.5	1.03
Total-Cu (mg kg ⁻¹)	39.0 \pm 0.71	34.75 \pm 0.35	12.23	1.12
Total-Cd (mg kg ⁻¹)	3.13 \pm 0.08	2.2 \pm 0.18	42.3*	1.42

Notes: * $P < .05$.*** $P < .001$ based on paired t -test results.

can explain the increasing trend of DTPA-Mn in the cultivated soils. Chromic Calcixererts and Typic Calcixererts appeared a depletion aspect (a drop of 13–22%) and Typic Haploxererts had an enrichment pattern (a rise of 200–210%) in the DTPA-Zn with cultivation. Nevertheless, the amounts of available Zn in both cultivated (min = 1, max = 2.2, mean = 1.5 mg kg⁻¹) and uncultivated (min = 0.92, max = 1.8, mean = 1.4 mg kg⁻¹) soils were well within the maximum permissible limits of 0.6–10 mg kg⁻¹ [31] and 0–6 mg kg⁻¹. [32] Plant uptake, soil sheet erosion, and Zn movement to subsoil by flooding irrigation may be the most important factors responsible for the decreasing trend of DTPA-Zn in the cultivated soils. [3] In contrast, extraction of Zn by roots at greater depths, translocation into plant issue and re-entry into the soil after the decomposition of crop residues [28] along with the repeated use of organic compounds (e.g. manures and compost) to soil can be explained by the observed

increase in DTPA-Zn after cultivation. Ramos and Lopea-Acevedo [35] reported that the application of composting cattle manure increased the Ethylene diamine tetraacetic acid (EDTA)- and DTPA-extractable Zn in alkaline soils (pH of 7.8–8.9) from the North Eastern Spain regions. The Cu concentrations in the soils do not, in principle, pose any risk. The values of DTPA-Cu in both cultivated (min = 2.1, max = 3.2, mean = 2.8 mg kg⁻¹) and uncultivated (min = 2.2, max = 2.9, mean = 2.7 mg kg⁻¹) soils were found to be within the permissible limits of 0.2–5 mg kg⁻¹. [31] On average, the content of DTPA-Cu increased by 1–40% after cultivation in the majority of the study soils, mainly due to the breakdown of organic plant residues by agricultural practices and reduced conditions, generated by heavy irrigation. The mean values of DTPA-Cd were above the permissible limits of 0.01–0.5 mg kg⁻¹ [31] in the cultivated soils (min = 0.51, max = 0.72, mean = 0.6 mg kg⁻¹), whereas it was within the permitted limits in the uncultivated soils [(min = 0.42, max = 0.49, mean = 0.46 mg kg⁻¹). Compared to the adjoining uncultivated soils, intensive cultivation produced a remarkable increase in the mean values of DTPA-Cd, ranging from 21% (Typic Calcixererts) to 45% (Chromic Calcixererts). Such patterns imply that DTPA-Cd was enriched by agricultural practices, particularly through the uncontrolled application rates of Cd-enriched chemicals (e.g. both inorganic P fertilisers and organic P sources), which are in agreement with the finding of other authors. [23]

Intensive cropping resulted in a narrow change in total Fe (a drop of 0.3–18%) and total Mn (a drop of 1.5–9%) compared with the adjoining uncultivated soils. This can be ascribed to the depletion of Fe and Mn by sheet erosion and leaching processes during long-term irrigation and tillage. [27] Typic Haploxererts indicated the highest drop of total Fe and Mn where the greatest depletion of clay was observed (Table 2), suggesting that the loss of Fe and Mn were occurred in parallel to clay depletion.

Long-term cultivation resulted in a narrow increase in the amount of total Zn from 3% (with an EF of 1.03, Typic Haploxererts) to 16.5% (with an EF of 1.16, Chromic Calcixererts) than those of uncultivated soils. Such findings have been reported elsewhere. [36] However, the total Zn values of the cultivated soils (min = 67, max = 78, and mean = 74 mg kg⁻¹) and the uncultivated soils (min = 58, max = 75, and mean = 69 mg kg⁻¹) were far below its maximum permissible level [(< 300 mg kg⁻¹. [7] The values of total Cu in both cultivated (min = 26, max = 40, mean = 34 mg kg⁻¹) and uncultivated soils (min = 23, max = 35, mean = 29 mg kg⁻¹) were far below its maximum permissible level (< 100 mg kg⁻¹). [7] Similar to total Zn pattern, there was an increase in the values of total Cu with cultivation ranging from 12% (with an EF of 1.12, Typic Calcixererts) to 32% (with an EF of 1.32, Typic Haploxererts). The major sources of Cu and Zn in agricultural soils, like the studied region, are the application of various agrochemicals [7] (e.g. pesticides, herbicides and fungicides, and manure). In the study area, compounds such as Bordeaux mixture, Bordeaux fix, and Mancozeb were used largely to control plant pests and fungi that Cu and Zn were applied predominantly in formulations of the compounds. Similar findings have been reported elsewhere. [37,38] Also, Cu and Zn are present in animal wastes and manure (used largely in the examined soils), which could contribute to their concentration in soils. [38] Nicholson et al. [39] found that livestock manure contributes to 37–40% of total Zn inputs in the agricultural soils of England and Wales.

Cadmium is a toxic metal that exhibited higher values in the agricultural soils (min = 3, max = 3.4, mean = 3.17 mg kg⁻¹), ranging from 42% (with an EF of 1.42, Typic Calcixererts) to 108% (with an EF of 2.09, Chromic Calcixererts) compared to the uncultivated soils (min = 1.6, max = 2.2, mean = 1.91 mg kg⁻¹), which suggests that Cd is enriched by agricultural practices. However, the values of total Cd were below its maximum permissible level (< 5 mg kg⁻¹). [7]

The presence of high rates of Cd in the cultivated soils could be attributed to many years of uncontrolled application rates of chemical fertilisers and Organic materials. In the study area,

farmers apply many chemical fertilisers (mainly phosphate fertilisers) and manure to the soils to obtain high crop production. The Cd was found predominantly in phosphate fertilisers because Cd is commonly present as an impurity in phosphate rocks.[40,41] Long-term investigations worldwide have shown that application of phosphate fertilisers has resulted in soil enrichment with Cd in the range of 0.3–4.4 g ha⁻¹ yr⁻¹, depending on the rates and types of fertilisers applied.[40] In agricultural soils of New Zealand, Gray et al. [42] also found a high significant correlation between total concentrations of Cd and phosphorus following long-term application of phosphate fertilisers. On the other hand, organic fertilisers – mainly manure, which was used largely in the region – have variable levels of Cd depending on their source;[1] therefore, they may also be a possible source of Cd to soil. Consistent with this, an important percentage of Cd contained in agricultural soils of England was reported by manure application.[39] Domestic and industrial that sometimes were used for irrigation in the region may be another source of Cd to soil.[2]

3.3. Assessment of soil pollution indices

3.3.1. Availability fraction percentage

The availability fraction percentage (AP) is identified as a suitable index to compare the potential trace metal mobility and their toxicity in soils by some authors.[23,43] The values of this index are presented in Table 3. The levels of AP in both cultivated and uncultivated soils showed the following order: Cd > Cu > Zn > Mn > Fe, which differs from the order established for

Table 3. Comparison of the mean values of available fraction percentage (Ap) values in the cultivated and adjacent uncultivated soils.

Trace metal	Chromic calcixererts	
	Cultivated soil	Uncultivated soil
Fe	0.042***	0.014
Mn	1.26	1.10
Zn	2.10	2.84
Cu	7.93*	12.62
Cd	19.1*	29.6
Trace metal	Typic haploxererts	
	Cultivated soil	Uncultivated soil
Fe	0.023	0.026
Mn	1.68	1.49
Zn	2.59	2.95
Cu	8.28	7.83
Cd	18.0*	23.3
Trace metal	Typic calcixererts	
	Cultivated soil	Uncultivated soil
Fe	0.043*	0.029
Mn	1.14	1.03
Zn	1.34	1.71
Cu	7.46	8.26
Cd	16.6	19.5

Note: * $P < .05$.

*** $P < .001$ based on paired t -test results.

the available concentration. This pattern shows that Cd is the most mobile and toxic element, as well documented elsewhere.[23] There was also a significant drop in the AP values of Cd in the cultivated soils compared to the corresponding uncultivated soils probably due to Cd movement within soil profiles caused by agricultural practices (such as moldboard tillage and strong flooding irrigation).

3.3.2. Nemerow pollution index

The values of the single-factor PI and comprehensive pollution index or PIN were calculated using the concentration of Mn, Zn, Cu, and Cd for all the soil types to highlight the relative magnitudes of soil pollution (Table 4). Consistent with this, the order of mean value PI is: Cd > Cu > Zn > Mn in the different soil types, in which some differs from the order established for the PIN (Cd > Zn > Cu > Mn). Similar patterns were reported by other authors.[44,45] Following long-term cultivation, the values of PI were ranged as 0.91–0.98, 1.03–1.52, 1.12–1.32, and 1.42–2.1 for Mn, Zn, Cu, and Cd, respectively, indicting the categories of cleans to moderate pollution. In this context, 100%, 100%, 100%, and 67% of the total soils were classified as ‘clean to low contamination’ by Mn, Zn, Cu, and Cd, respectively. In contrast, only 33% of the total soils were classified as ‘moderate contamination’ by the Cd. Considering the PIN values, ranging from 1 to 1.9 with the a mean value of 1.5, the cultivated soils were in low pollution (Figure 2).

3.3.3. Potential ecological risk

The contamination factor values (f_i) are in the range of 1.03–2.1 and are ranked in the order of Cd > Cu > Zn, suggesting the low level of contamination for the metals in all of the soil types (Figure 3). The range of f_{deg} (integrated pollution level) was from 3.5 to 4.85, with a mean value of 4.13, reflecting a low pollution for all the soils (Table 5). For different soil types, the f_{deg} levels showed the following order: Chromic Calcixererts > Typic Haploxererts > Typic Calcixererts, which is similar to the order established for the f_i values. This pattern suggests that the Chromic Calcixererts have a high tend to the load rate of the trace metals compared to other soil types. The values of single risk factor level (E_i) were in the range of 1.03–63, with a mean value of 51.2 for Cd, which is significantly higher than the values of Zn (min = 1, max = 1.55, mean = 1.19) and Cu (min = 5.2, max = 6.8, mean = 6.02). This implies that, of the total agricultural soils, Cd falls into moderate ecological risk ($40 < E_i \leq 80$) (Figure 4), whereas Zn and Cu fall into low ecological risk ($E_i \leq 40$). Considering the potential ecological risk (RI) assessment of the cultivated soils (min = 47, max = 72, mean = 58.4), 33.3% of the samples are categorised as

Table 4. Description of the soil pollution indices.

Soil type	Single-factor pollution index (PI) ^a				Comprehensive pollution index (PIN)
	Mn	Zn	Cu	Cd	
Chromic calcixererts	0.98 (Clean)	1.52 (Low pollution)	1.17 (Low pollution)	2.1 (Moderate pollution)	1.8
Typic Haploxererts	0.91 (Clean)	1.03 (Low pollution)	1.32 (Low pollution)	1.60 (Low pollution)	1.42
Typic Calcixererts	0.92 (Clean)	1.03 (Low pollution)	1.12 (Low pollution)	1.42 (Low pollution)	1.29

Note: ^aClean = $PL \leq 1$; Low pollution = $1 < PL \leq 2$; Moderate pollution = $2 < PL \leq 3$.

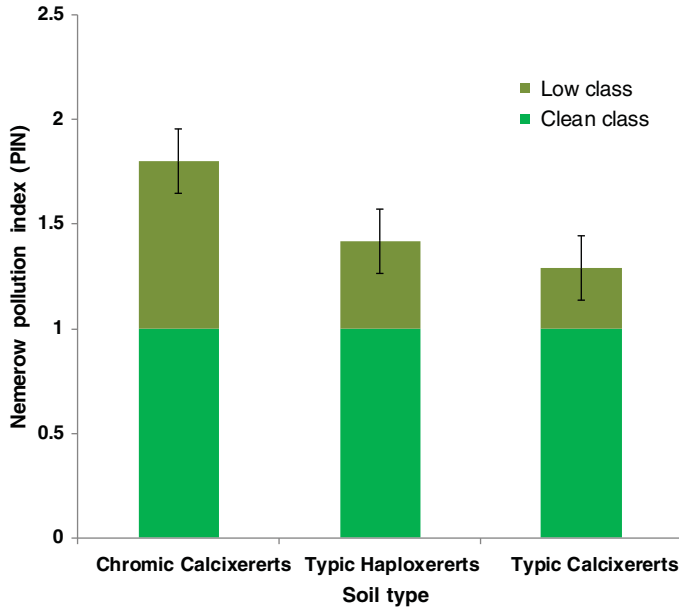


Figure 2. Histogram of the PIN or comprehensive PI in the different soil types. The contrasting colours show two class 1 (low pollution) and class 2 (slight pollution).

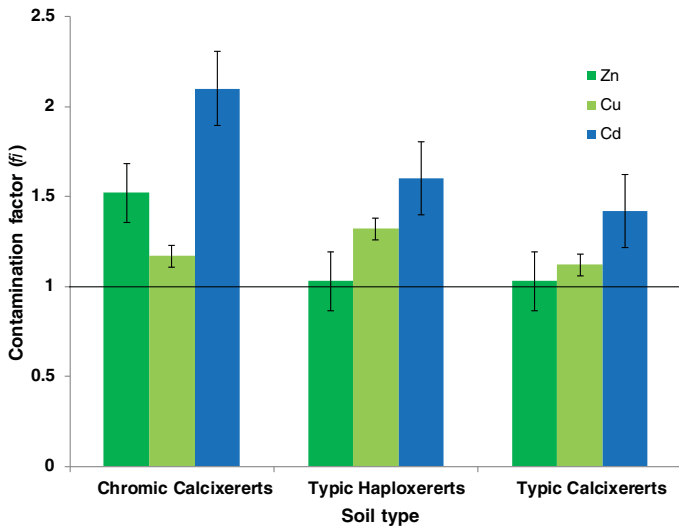


Figure 3. Histogram of the contamination factor (f_i) for Zn, Cu, and Cd in the different soil types. The horizontal line shows boundaries between clean class ($f_i \leq 1$) and low pollution ($1 < f_i \leq 3$).

low potential ecological risk ($RI \leq 50$) and 66.7% is also considered as moderate potential ecological risk [$50 < RI \leq 100$] (Figure 5). In the light of this, Cd was known to be the main factor causing the RI values, accounting in the range of 86–90% (an average of 88%), followed by Cu and Zn, which accounted in the range of 8–12% (an average of 10%) and 2–2.5% (an average of 1.9%), respectively, of the RI values. Such results are comparable with the finding of Zhou et al. [46]. Compared to other soil types, potential ecological risk was relatively more serious in the

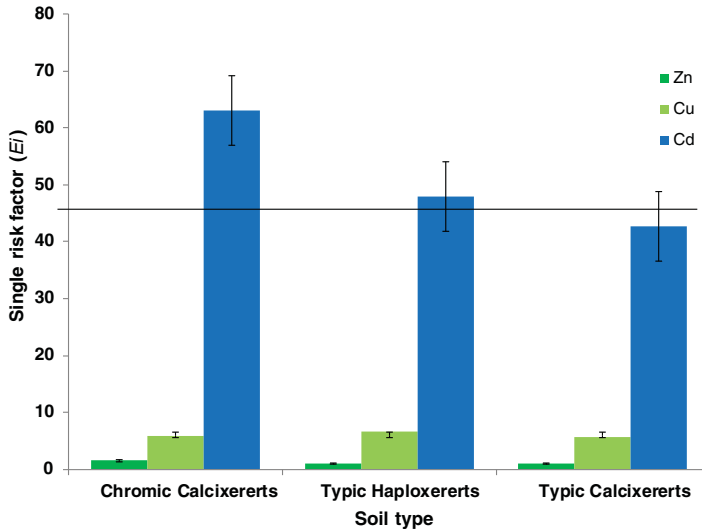


Figure 4. Histogram of the single risk factor (E_i) for Zn, Cu, and Cd in the different soil types. The horizontal line shows boundaries between low ($E_i \leq 40$) and moderate risk ($40 < E_i \leq 80$).

Table 5. Description of the potential ecological risk.

Soil type	Integrated pollution level (f_{deg})	Single risk factor (E_i)			Potential ecological risk (RI)
		Zn	Cu	Cd	
Chromic calcixererts	4.8 (1)	1.52 ^a	5.85 ^a	63.0 ^b	70.27
Typic haploxererts	3.95 (1)	1.03 ^a	6.6 ^a	48.0 ^b	55.63
Typic calcixererts	3.65 (1)	1.03 ^a	5.6 ^a	42.6 ^b	49.23

Notes: 1, Class 1 ($f_{deg} < 5$).

^aLow risk ($E_i \leq 40$).

^bModerate risk ($40 < E_i \leq 80$).

Chromic Calcixererts, where high rates of clay, CEC, iron oxides, expandable clay minerals (e.g. smectite) were found to occur (the data not shown for clay minerals). Clay minerals found in our soils were predominantly smectite and illite, which could be sinking of trace metals. Consequently, the presence of the greatest clay content, iron oxides, smectite, and a corresponding high surface area and CEC in Chromic Calcixererts probably contributed to a significant accumulation of the trace metals in the soil than those in other soil types.[2]

CF and degree of soil contamination (C_d) for the metals (total Zn, Cu, and Cd) were in the range of 1.03–2.1 and 1.2–1.6, respectively (Table 6). Consistent with this, the CF values for three metals were between 1 and 3 ($1 < CF < 3$), suggesting a low contaminated level. Based on C_d values, the soils were categorised as class 0 (nil to very low degree of contamination, $C_d < 1.5$) to class 1 (low degree of contamination, $1.5 < C_d < 2$). Indeed, the values of C_d led to 73% of the soils to class 0 and 17% to class 1, indicating that crop produced in the region will be safe for human consumption regarding the three analysed metals. Similarly with RI, the CF, $\sum CF$, and C_d rates of the metals were found to increase markedly in Chromic Calcixererts compared to other soil types (Table 6). As has been discussed before, the possible explanation might be attributed to the presence of more clay fraction, CEC and smectite as the major contributors in retaining the metals [27] in this soil type.

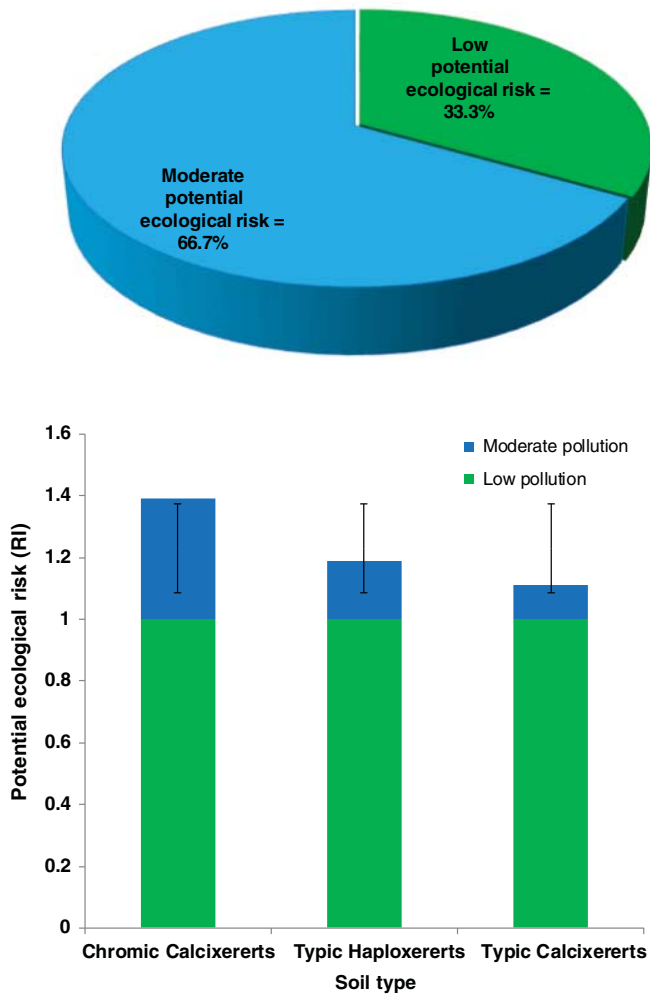


Figure 5. Histogram of the potential ecological risk (RI) in the different soil types. The contrasting colours show two classes' low potential ecological risk (LPER) and moderate potential ecological risk (MPER).

Table 6. Contamination factor (CF) and degree of contamination (C_d) for total trace metal in the examined soils.

Soil type	CF			ΣCF	CD
	Zn	Cu	Cd		
Chromic calcixererts	1.52	1.17	2.1	4.79	1.60 (1)
Typic haploxererts	1.03	1.32	1.60	3.95	1.32 (0)
Typic calcixererts	1.03	1.12	1.42	3.65	1.22 (0)

Note: Class 0 = Nil to very low degree of contamination, Class 1 = Low degree of contamination.

4. Conclusions

The values of DTPA-extractable Fe (2.5–10 mg kg⁻¹), Mn (8–15 mg kg⁻¹), Zn (1–2 mg kg⁻¹), Cu (2–3.5 mg kg⁻¹), and Cd (0.45–0.75 mg kg⁻¹) and total fraction of the metals (Fe: 21–23 g kg⁻¹, Mn: 800–960 mg kg⁻¹, Zn: 57–78 mg kg⁻¹, Cu: 23–40 mg kg⁻¹, and Cd: 1.5–3.5 mg kg⁻¹) were in low-to-medium levels when compared with the values in the literature.

Following long-term intensive cropping (over five decades), an increasing pattern in the concentration of DTPA-extractable Fe, Mn, Cu, and that in Cd and total Zn, Cu, and Cu were observed mainly due to the uncontrolled application rates of various agrochemicals (e.g. fertilisers, and pesticides–herbicides–fungicides) during many years. However, the values of both available and total fractions of the metals were below their maximum permissible limits in cultivated and uncultivated soils except DTPA-extractable Cd. Considering the assessment of PI and PIN values, the soils are classified into clean to low pollution after intensive cultivation and most of the study soils are at moderate potential ecological risk. Finally, the cadmium pollution was known to be more serious than other metals.

Disclosure statement

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