The Soil Heavy Metal Information Accurate Collection and Evaluation about Lycium Barbarum Cultivation in Western China

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Abstract: We selected two small sections of *Lycium Barbarum* cropland at Nuomuhong Farm in the Qaidam basin, western China: one had been farmed for only one year (original land), and the other had been farmed for many years (farm land). We tested surface soil samples for their content and distribution of six heavy metals (Cd, Zn, Pb, Cu, As, and Cr). All six heavy metals appeared at medium levels in samples from both sections of cropland. We conducted an interpolation analysis and drew a spatial distribution map based on the inverse distance weight (IDW) method. The distribution graph revealed a relatively consistent distribution of the six heavy metals in soil samples, a different gradation in the original land, and areas of higher values in the farm land. These findings suggest that the soil had been polluted. According to the Pollution-Free Food Standard and the Green Food Standard, we calculated the integrate pollution index using the Nemerow index method to check whether the levels met Pollution-Free food Standard and Green Food Standards. The values were 0.5 and 0.7 (defined as 'clean') in samples from the original land, but were 0.6 and 0.9 in samples from the farm land, which may be considered excessive.

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Key words: assessment; heavy metal pollution; standard; *Lycium barbarum*; Qaidam

1 Introduction

Under heavy metal pollution, crop soils may exhibit latency, chronicity, irreversibility, and have strong toxic properties and abiotic degradation. This is an important challenge for producers of high-quality agricultural products and researchers in the fields such as edaphology, resource environmental protection, and agricultural product quality safety. Investigations of spatial variations in heavy metals, which are important to evaluating soil environmental quality and heavy metal pollution, involve analyzing spatial features including the content of heavy metals, along with any changes, trends, and spatial variation in those metals[1]. Recently, researchers have combined geographic statistics with geographic information system (GIS) data to analyze regional environmental processes. Mingkai Qu, Weidong Li and Chuanrong Zhang has assessed the spatial distribution and uncertainty of the potential ecological risks of heavy metals in soil using sequential Gaussian simulation (SGS) and the Hakanson potential ecological risk index (PERI) in Wuhan, China. Results show that the potential ecological risks of Cr, Cu, Pb, and Zn are relatively low in the study area, but Cd indeed reaches a serious level that deserves much attention and essential treatment[2]. Linsen Zhang, Jun Liang, Chunlin Wu *et al*. evaluated the contents of As Pb Cr Cd and Cu in an apple-planting region in Shanxi province using a method that incorporated a single pollution index and a comprehensive pollution index according the Green Food Standard, show that the heavy metals were not accumulated gradually in old apple orchards and all meet the standards[3]. Gailin Wu, like li, Mingde Hao *et al*. on the basis of the integrate pollution index of heavy metal research proposed fertilizer application should pay attention to the content of heavy metals in fertilizer, a reasonable choice, in order to avoid the contamination of the soil environment[4]. Xia Huang, Tingxuan Li and Haiying Yu. used a signal pollution index and the Nemerow composite index to evaluate the heavy metals risk, and the results show that there was Cd contamination in greenhouse topsoils in Shouang Shandong Province[5].

The Qaidam basin, located on the Tibetan Plateau, is a closed region and few studies have assessed environmental effects in the area of reclamation. No studies have investigated the spatial variation in heavy metals or their potential pollution risk in soils in the planting region of *Lycium barbarum* (common names: goqi berry, wolfberry, medlar).

2 Experiments and Methods

2.1 Experimental Samples

2.1.1 Study area overview

The Qaidam Basin is located on the edge of the Tibetan Plateau, surrounded by the Kunlun, Qilian, and Altun Mountains. Nuomuhong Farm is located southeast of the basin at altitudes ranging from 2700～3000 m. It is irrigated by snow waters from the Kunlun Mountains, which enables oasis farming. The area is cold and dry with little rainfall, abundant sunlight, and large differences between daytime and nighttime temperatures. Soil in the area has PH values ranging from 7.8～8.2. Because the area is mostly sandy loam and has few plant diseases and insect pests, it is suitable for growing *L. barbarum*, and the *L. barbarum* produced in this area is famous for its quality and is quite valuable [6].

2.1.2 Soil sample collection, tests, and data processing

Sample collection： Samples were collected based on the following guiding principles: Select cultivated farmland in flat areas (avoid depressions or mounds).Try to avoid non-representative areas, e.g., those that have been altered by human activity or where soil has greatly eroded. Do not collect samples from areas currently being fertilized. Try to collect samples 30 days before or after fertilization.

The farm land field was a rectangular area of 660 m × 510 m, and the original land was a rectangular area of 400 m × 330 m. We adopted the grid soil sampling method and selected samples at 100 m × 50 m intervals. A dot in each interval served as a center point; we randomly selected five points, each with a 3 m radius. We then took a 20 cm × 20 cm × 20 cm cube of soil from each point. From these samples, we took 1 kg from each and created a mixed sample by equally mixing the 1 kg samples from all the sites.

The samples were taken to our lab for analysis. We recorded the fixed position sampling point coordinates using GPS. In order to prevent sample contamination, we did not let the samples touch metal containers during sample collection, preservation, and processing.

Sample testing:Stones, grass roots, and other plant residues were removed from the samples, which were left to dry in a ventilated room. Samples were then filtered using a 100 mesh sieve (150 um mesh size). A MILESTONE brand microwave digestion instrument was used, along with an inductively coupled plasma emission spectrometer. The testing method involved using 7 ml (top grade and pure) concentrated nitric acid, 2 ml (top grade and pure) hydrogen peroxide, and 2 ml (top grade and pure) hydrofluoric acid. Standard substances of these chemicals were purchased from the National Standard Substance Center; for the standard curve, we used three density gradients of 0, 0.5, and 1 and a unit of mg/l.

2.2.3 Data processing

The data were entered into Excel and subjected to the inverse distance weighting (IDW) method. A spatial analysis was conducted and the results were presented using ARCGIS9.3.

2.2.4 Heavy metal soil pollution assessment method

Single pollution index evaluation: For the evaluation, $P_i=C_i/S_i$, where P_i is the i single pollution index of a pollutant, C_i is the i actual measurement, and S_i is the evaluation standard for the pollutant. The evaluation standard was calculated separately in accordance with the industrial standards of “Pollution-Free Food standard” (NY/T 5249-2004) [7] (**Table 1**), and “Green Food Standard” (NY/T 391-2000) [8] (**Table 2**). Values of $P_i<1$ for As, Hg, Cd, Cr, and Pb indicate that the soil is not polluted, and the sample meets environmental standards. If one or more elements has a value of $P_i>1$, the soil is polluted and does not meet environmental standard.

Table 1. Pollution-Free Food standard (NY/T 5249-2004). Heavy metals: mg/kg

Item	Grade level

	Grade I	Grade II		
	Background	＜6.5	6.5～7.5	＞7.5
Cd≤	0.20	0.30	0.30	0.60
Hg≤	0.15	0.30	0.50	1.0
As≤	15	40	30	25
Cu≤	/	150	200	200
Pb≤	35	250	300	350
Cr≤	90	150	200	250
Zn≤	100	200	250	300

Table 2. Green Food Standard (NY/T 391-2000). Heavy metals: mg/kg

Farming condition	Dry field			Paddy field		
PH	＜6.5	6.5-7.5	＞7.5	＜6.5	6.5-7.5	＞7.5
Cd≤	0.30	0.30	0.40	0.30	0.30	0.40
Hg≤	0.25	0.30	0.35	0.30	0.40	0.40
As≤	25	20	20	20	20	15
Pb≤	50	50	50	50	50	50
Cr≤	120	120	120	120	120	120
Cu≤	50	60	60	50	60	60

Nemerow pollution index evaluation: In $P_N=((P_i^2+P_0^2)/2)^{1/2}$, P_N is the Nemerow composite index, Pi is the average pollution index for the soil, and P_0 is the maximum pollution index of the soil. As shown in (**Table 3**), soil quality is determined by changes in the P_N value and crops are affected by the degree and accumulation of pollutants.

Table 3. Nemerow composite index as evaluation standard

Degree	index	Pollution status	Pollution level
I	$P_N \le 0.7$	safe	clean
II	$0.7<P_N \le 1.0$	caution	potentially unclean
III	$1.0<P_N \le 2.0$	mild contamination	pollution over limit
IV	$2.0<P_N \le 3.0$	mid-level pollution	soil, crops subject to severe pollution
V	$P_N>3.0$	heavy pollution	soil, crops subject to heavy pollution

3 Results and discussion

3.1Analysis of heavy metal content in samples

Table 4 lists the heavy metal contents in 22 surface soil samples taken from original cropland. The variable coefficient reflects the average variable degree of sampling points in the total sample. Generally, 10%～100% exhibited medium variation: the variable coefficient for Cu in samples from original land reached a maximum of 61.48%, and the variable coefficient for As reached a minimum of 8.45%. The heavy metals can be arranged from maximum to minimum degree of variation as follows: Cd, Zn, Pb, Cu, As, and Cr.

Table 4. Descriptive statistics for heavy metal contents from original land

Element	Min (mg/kg)	Max (mg/kg)	Mean (mg/kg)	SD	CV(%)	Skew-ness	Kurtosis
As	0	26.40	15.47	8.45	8.45	-0.318	-0.689
Cd	0.14	0.42	0.30	0.077	25.49	-0.847	0.095
Cr	18.24	56.34	48.16	8.19	17.01	-2.507	8.265
Cu	13.44	90.12	28.16	17.66	61.48	2.447	6.572
Pb	5.76	28.49	13.38	4.92	36.80	1.380	3.287
Zn	30.08	61.90	44.84	9.28	20.70	0.471	-0.767

Table 5 lists the heavy metal contents in 50 surface soil samples taken from farm land. The variable coefficient reflects the average variable degree of sampling points in the total sample. The variable coefficient for Cd reached a maximum of 34.74%, and the variable coefficient for Cr reached a minimum of 6.15%. The heavy metals can be arranged from maximum to minimum degree of variation as follows: Cd, Zn, Pb, Cu, As, and Cr. Comparison between the two kinds of farmland reveals that the variable coefficients of Cr, Cu, Pb, and Zn decrease over time, but the variable coefficient of Cd increases significantly after years of farming.

Table 5. Descriptive statistics for heavy metal contents from farm land.

Element	Min	Max	Mean	SD	CV(%)	Skew-	Kurtosis

	(mg/kg)	(mg/kg)	(mg/kg)			ness	
As	11.53	18.34	14.50	1.45	10.13	0.235	0.064
Cd	0.19	1.23	0.43	0.15	35.09	3.165	16.817
Cr	41.78	58.12	47.13	2.90	6.21	0.896	2.709
Cu	19.97	34.20	25.51	2.59	10.26	0.893	2.839
Pb	18.19	34.18	22.17	2.28	10.39	2.775	14.466
Zn	56.58	108.29	69.18	8.47	12.37	2.194	8.012

3.2 Spatial distribution features of heavy metals in soil

We used the inverse distance weighting (IDW) method to conduct an interpolation analysis and examine spatial variation in the soil pollutants. As shown in **Fig. 1**, As content in original soil was greater in the west than in the east, and As content in the southwest region is greater than the natural background value. Few regions reached the level II standard. Cd content in original soil was clearly greater in the southeast and northeast than in other regions. In most areas, Cd content in soil was greater than the natural background value: in some areas values were greater than 0.40 and reached the level II standard. Cr content in original soil was less than the natural background value, with considerable spatial variation in the north and southwest regions. Cu content in original soil was highest in most north and northeast areas and the highest point was 90.12 mg/kg, but far lower than the level II standard and did not exceed the natural background value. Spatial variation in Pb content in original land tended to be greater in the north than in the south, and tended to change gradually. Zn content was less than the natural background value, and spatial variations revealed that content tended to be higher in the west than in the east. Zn content was very high in some northeast areas.

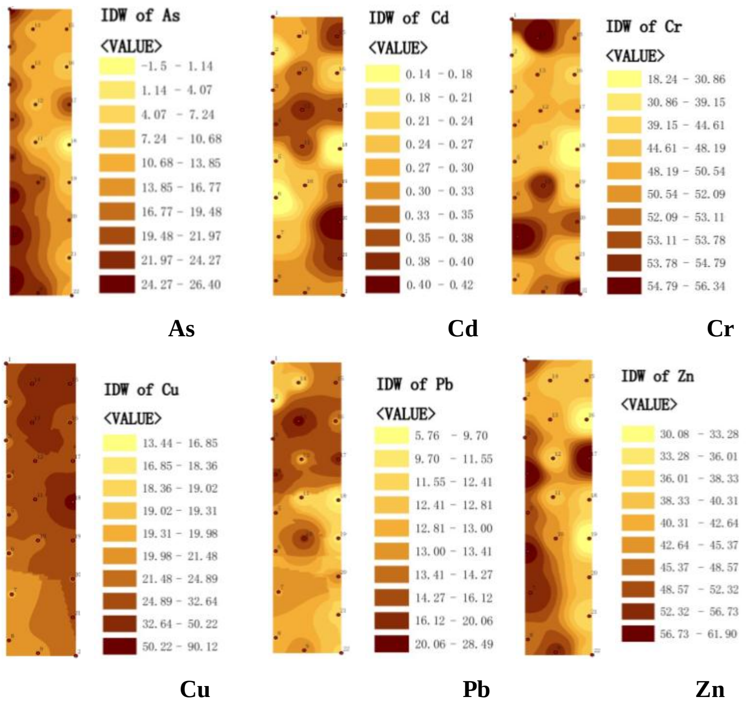


Fig.1 The heavy metals content in soil and spatial variation in original land

Fig. 2 shows that As content in farm land was lower than the natural background value; only a few southwest and northwest regions reached the level II standard. Overall Cd content was greater than the natural background value, with most regions reaching the level II standard. The contents of Cr, Cu, and Zn in farm land exhibited a scattered spatial distribution. Generally, the comparisons revealed that in original land, spatial variation was very similar for all heavy metals, gradation levels differed, and the natural status of soil was relative stable. In farm land, heavy metal content exceeded the standard and differed greatly in quantity: Cr, As, Zn, Pb, and Cu contents were all more than 1.2～1.7 times higher than normal, and Cd content was nearly 5 times the normal value. These findings indicate that farm land has been polluted.

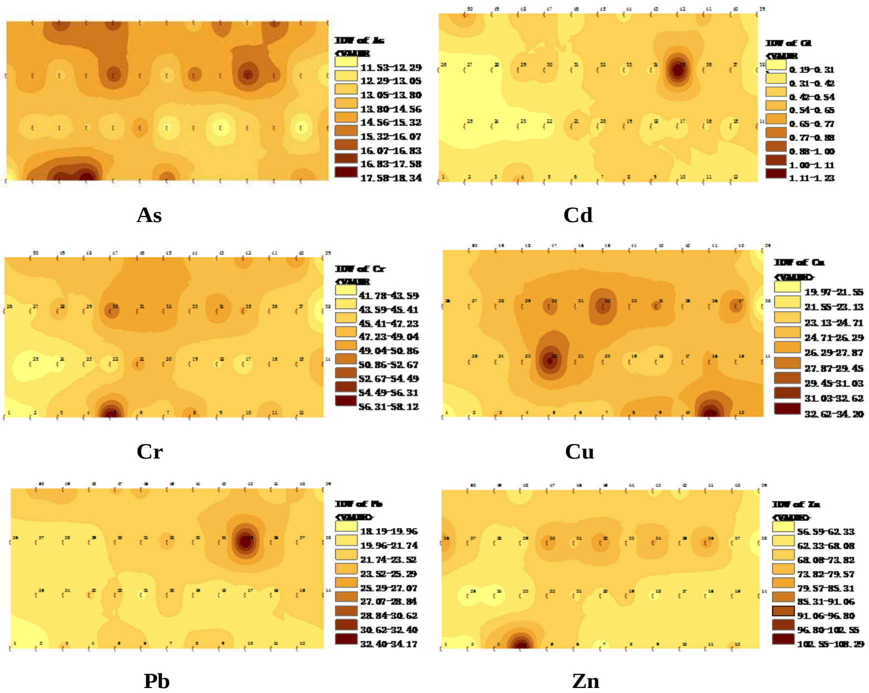


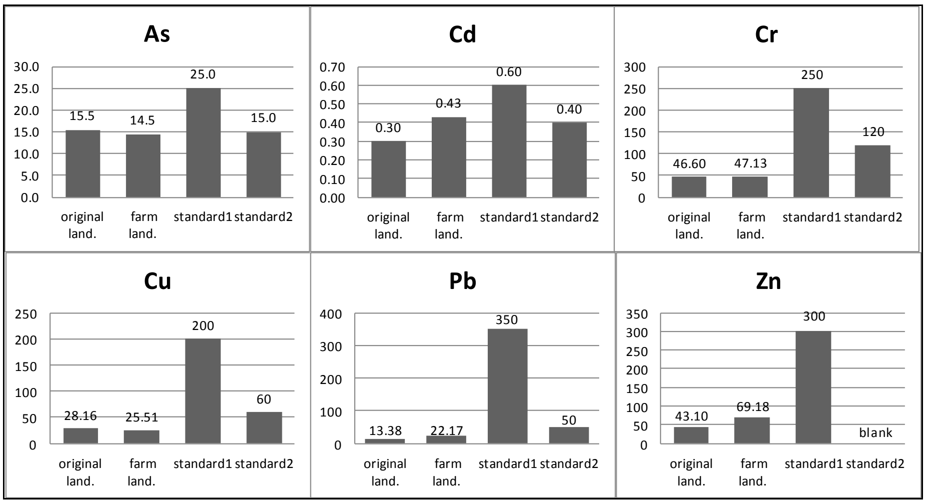
Fig.2 The heavy metals content in soil and spatial variation in farm land

3.3 Soil heavy metal pollution assessment

3.3.1 Soil heavy metal contents compared with the standards

The As from the original land and farm land are both meet to the Green Food standard, but more less than the Pollution-Free Food standard; the Cr、Cu、Pb and Zn, from the original land and farm land are all far less than the Pollution-Free Food standard, and less than the Green Food standard (there is not Limited value for the Zn in the Green Food standard); the Cd is only 0.30 mg/kg in original land, both less than the two standards, but it rise to 0.43 mg/kg in farm land, increased 43%, over the Green Food standard, show that there is accumulation of Cd in farm land(see **Fig.3**).

Unit:mg/kg



(Standard1= Pollution-Free Food standard, standard2= Green Food standard)

Fig. 3 Comparison of soil heavy metals contents according to different standards

3.3.2 The superscalar rate of soil heavy metal according different standards

In original land 4 samples exceed the Pollution-free Food Standard and 18 samples exceed Green Food Standard of As, the rate were 10% and 45% (**Table 6**). In farm land 31 samples exceed Green Food Standard of Cd, the rate is 62% (**Table 7**), show that there is accumulation of Cd in farm land.

Table 6. The superscalar rate of soil heavy metal in original land

heavy meatal	samples	Pollution-free Food Standard		Green Food Standard	
		Superscalar	Superscalar rate(%)	Superscalar	Superscalar rate(%)
As	22	4	18	10	45
Cd	22	0	0	1	5
Cr	22	0	0	0	0
Cu	22	0	0	1	5
Pb	22	0	0	0	0
Zn	22	0	0	/	/

Table 7. The superscalar rate of soil heavy metal in farm land

heavy meatal	samples	Pollution-free Food Standard		Green Food Standard	
		Superscalar	Superscalar rate(%)	Superscalar	Superscalar rate(%)
As	50	0	0	0	0
Cd	50	2	4	31	62
Cr	50	0	0	0	0
Cu	50	0	0	0	0
Pb	50	0	0	0	0
Zn	50	0	0	/	/

3.3.3 Single pollution index evaluation

With regard to upper limits for elements in the Pollution-Free Food Standard and the Green Food Standard, separate environmental evaluation criteria were used to calculate and analyze factors in the pollution index of heavy metals for soil samples taken from the two study areas. With regard to Pollution-Free Food Standard requirements, the pollution index was less than 1 in all samples from original land. This means that this area meets the Pollution-Free food standard for the six heavy metals investigated. With regard to the Green Food Standard, all pollution indices were also less than 1, indicating that this area also qualifies for the Green Food Standard (see **Table 8**).

Table 8. Single pollution index evaluation of soil heavy metal in original land

Heavy metal	Mean (mg/kg)	Pollution-Free food standards pollution index	Green Food Standard pollution index
As	15.47	0.62	0.77
Cd	0.30	0.50	0.75
Cr	46.60	0.19	0.39
Cu	28.16	0.14	0.47
Pb	13.38	0.04	0.27
Zn	43.10	0.14	/

With regard to upper limits for elements in the Pollution-Free Food Standard and the Green Food Standard, separate environmental evaluation criteria were again used to calculate and study analyze factors in the pollution index of heavy metals in 50 surface soil samples taken from farm land. With regard to the Pollution-Free Food Standard requirements, the maximum pollution index was 0.71 and the minimum was 0.06; because these values were less than 1 for all six heavy metals, this area meets Pollution-Free Food Standards. With regard to the Green Food Standard, five heavy metals had a pollution index less than 1, but the index for Cd was greater than 1, meaning that the soil is polluted and this area does not meet the Green Food Standards (see **Table 9**).

Table 9. Single pollution index evaluation of soil heavy metal in farm land

Heavy metal	Mean (mg/kg)	Pollution-Free food standards pollution index	Green Food Standard pollution index
As	14.50	0.58	0.72
Cd	0.43	0.71	1.06
Cr	47.13	0.19	0.39
Cu	25.51	0.13	0.43
Pb	22.17	0.06	0.44
Zn	69.18	0.23	/

3.3.3 Composite pollution index evaluation

Composite Index is calculated based on Nemerow index method, and the Pollution-Free Food and the Green Food standards. According to the Pollution-Free Food and the Green Food standards the original land soil index were 0.5, 0.7 , both in the "clean" level; the farm land were 0.6, 0.9, in the "clean" level according the Pollution-Free Food standard , in the "potentially unclean" leave according to the Green Food standard. (see **Table 10**).

Table 10. Nemerow index depend on different Standards (mg/kg).

	As	Cd	Cr	Cu	Pb	Zn	Mean	Max	Nemerow index

Pollution-free	Original land	0.62	0.5	0.19	0.14	0.04	0.14	0.27	0.62	0.5
food standard	Farm land	0.58	0.71	0.19	0.13	0.06	0.23	0.32	0.71	0.6
Green food	Original land	0.77	0.75	0.39	0.47	0.27	/	0.53	0.77	0.7
standard	Original land	0.72	1.06	0.39	0.43	0.44	/	0.61	1.06	0.9

4 Conclusions

We analyzed data about six heavy metals (Cd, Zn, Pb, Cu, As, and Cr) and found that the Nuomuhong farm original land soil is pure and can comply with the Pollution-Free Food Standard and the Green Food Standard, but the farmland were subject to pollution during many years of farming, which resulted in heavy metal pollution, especially Cd pollution. Further research will be required to clarify the process of pollution.

We analyzed soil from two different areas of Nuomuhong Farm: original land and farm land, in terms of their heavy metal (Cd, Zn, Pb, Cu, As, and Cr) content. We used the Nemerow composite index to analyze and evaluate data. According to the Pollution-Free Food Standards, the soils in Nuomuhong Farm are all near or below excessive levels, and according to the Green Food Standard, original soil is all considered clean, whereas the farm land is at a borderline excessive level.

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