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Heavy Metals Contamination in Greenhouse Soils and Vegetables in Guanzhong, China

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Abstract

This study used a flame atomic absorption spectrometer (FAAS) and atomic fluorescence spectrophotometer (AFS) to detect the concentrations of chromium (Cr), cadmium (Cd), lead (Pb), hydrargyrum (Hg) and arsenic (As) in soils and three genotypes of vegetables in greenhouse, as well as analyzed the physical and chemical properties of soils, including soil pH, soil organic matter (OM), basic nutrients, electrical conductivity (EC) and cation exchange capacity (CEC) in Guanzhong areas, Shaanxi province, China. The results showed that comparing to subsoil, the sampled topsoil is enriched in Cr, Cd, Pb, As and Hg. Cd (0.83 - 3.17 mg·kg^{-1}) and Hg (0.40 - 1.44 mg·kg^{-1}) are exceeding the limited value stated in "the 2006 Greenhouse Vegetable Producing Environmental Quality Evaluation Standards" of 0.40 mg·kg^{-1} and 0.35 mg·kg^{-1} respectively. However, Nanzhuang greenhouse soil is within the limits. The heavy metal pollution index (HPI) of soil in Sanyuan (8.10) is the highest and in Dongzhang (4.23) is the lowest. The contents of Pb (0.201 - 0.376 mg·kg^{-1}) were exceeding the limited value (0.20 mg·kg^{-1}) in vegetables species, and Cd (0.0363 - 0.0572 mg·kg^{-1}) in some place were also exceeding the limited value (0.05 mg·kg^{-1}). Greenhouse soils were becoming acidified year after year; the ratios of N, P and K in soil were seriously imbalanced. According to the impacting factors, OM, pH, available P, EC and CEC have obviously effected the accumulation of Cr and Hg. However, there was not enough evidence for the effects of available nitrogen and available potassium.

Keywords

Heavy Metals, Soils, Vegetables, Greenhouse

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1. Introduction

Heavy metals are toxic to animals and human through the food chain. Metal pollution of agricultural soils is a major environmental problem that can affect plant productivity, food quality and human health [1]-[3]. Elevated levels of metals in agricultural soils were the results of atmospheric deposition, wastewater irrigation, sludge amendment, and fertilizer application, as well as industrial activities, in particularly the metallurgical industries [4] [5]. The uptake and bioaccumulation of heavy metals in vegetables are influenced by a number of factors such as climate, atmospheric depositions, the concentrations of heavy metals in soil, the nature of soil on which the vegetables are grown and the degree of maturity of the plants at the time of harvest [6] [7]. Furthermore, it is a direct basis for rational fertilization. Many phosphate rocks contain heavy metals such as Pb and Cd and high application rates of phosphorus (P) fertilizer may not only increase soil P but also lead to accumulation of the metals above the maximum limited values [8]-[10]. Jinadasa *et al*. [11] found that Cd concentrations in vegetables could exceed the limited value if the soil Cd concentration reached 0.3 mg·kg^{-1} Cd.

Guanzhong plain lies in the middle of Shaanxi province of China, where the land is fertile with plenty agriculture products, and is one of the principal birthplaces of Chinese Yellow River Valley civilization. The agricultural history is long with well developed irrigation farming, concentrating 52% of cultivated land and 75% of effective irrigated areas of Shaanxi [12] [13], and serving also as the main provincial base for suburban vegetable plot in Qin River. However, most farmers apply a large number of organic fertilizers and mineral manures in greenhouse, leading to heavy metals accumulation in soil and vegetables, increasing potential health risks. At present, as the worldwide food pollution problem becomes more and more serious and the environmental consciousness improves continuously, the limiting measures to the agricultural products, fruits and vegetables markets are becoming gradually complete, and there are many studies about greenhouse soil acidification, nutrient accumulation, salinization, biotic population and enzymatic activity at home and abroad [14]. To our knowledge, there are few systematic published studies on metal contamination in Chinese vegetable-growing regions, particularly in greenhouse. In recent years, with the development of establishment agriculture, areas with greenhouses rapidly increased in Shannxi province of China. However up to now, heavy metal contents of agricultural soil in Guanzhong and its pollution problem have been studied very little [15], especially there is no systematical investigation for heavy metals in greenhouse soil and vegetables, as well as soil nutrition status in Shaanxi Guanzhong district. For heavy metals in soil which have a long residence time and are potentially dangerous, it is very important to study the condition of heavy metals accumulation in soil and the heavy metal pollution index (HPI) in greenhouse soil. It is also vital to pay attention to food safety, which will bring up potential adverse effects to us through vegetables polluted by heavy metals. In recent years, with the development of establishment agriculture, the areas of greenhouses rapidly increased in Shannxi province of China. At present, our study focused on the contents of heavy metals in the greenhouse soils and the main plant species of vegetables in Guanzhong district, Shannxi province. However, the content of heavy metals in greenhouse soils and vegetables in other districts in Shannxi province, as well as other species of vegetables should be tested in order to ensure safe production of establishment agriculture.

In this study, field survey method includes sampling and analysis, the system investigated on greenhouse heavy metals, including Cd, Pb, Cr, Hg and As in soil and vegetables, as well as soil nutrition status in Guanzhong district of Shaanxi province. The aims of this study: 1) to detect the concentrations of five metals in greenhouse soil and three main species of greenhouse vegetables, and to examine the relationship between them; 2) to assess environmental risks of heavy metals pollution in the greenhouse soils and vegetables by using pollution index; 3) and to research the contents of basic nutrients, as well as the relationships between basic nutrient and metal concentrations in greenhouse soils so that it can provide a scientific basis for harmless cultivation.

2. Materials and Methods

2.1. Site Description

The study area is located in Shaanxi province, including Xi'an city, Xianyang, Yangling and Baoji, these districts is called Guanzhong areas. We choose seven greenhouses as our main study places which were built 10 - 12 years ago in Guanzhong areas. Xi'an is the capital city of Shaanxi province in central China, we selected Xiwang and Wenchang village in Xi'an as the sampling places. The last three cities are located at the suburb of Xi'an city. Baoji is the second largest city of Shaanxi province, is situated at the western end of the Guanzhong

(Wei River) valley about 150 km west of the provincial capital city Xi'an, we selected village Dongbai as the sampling place. Sanyuan, Fanyao and Dongzhang were also chosen as the sampling place in Xianyang city, as well as Nanzhuang village in Yangling district. Detailed locations of the sampling sites are shown in **Figure 1**. A total of 7 topsoil (0 - 20 cm) samples, 7 subsoil (20 - 40 cm) samples, and 21 vegetable samples, including tomato (*Lycopersicum esculentum* Mill), cucumber (*Cucumis sativus* L.) and celery (*Apium graveolens*) were collected from the study areas. Topsoil, subsoil and vegetable samples were taken from the same sites.

2.2. Soil and Vegetable Sampling

From each plot topsoil and subsoil samples were collected with a stainless steel shovel. Five random samples from each soil plot were taken and bulked together as one composite sample, approximately 200 g in total weight. At the same time, vegetable samples were collected on the plot where soil sample was taken. Samples of soil and vegetables were stored in polyethylene bags in the field, and were transferred to the laboratory within three hours for sample processing. The soil samples were air-dried at room temperature, and mechanically ground using a wood roller to pass through a 100-mesh sieve. This fine material was used to determine the total metal contents. Vegetables were washed and the inedible parts were removed immediately. The edible parts of the vegetables were washed with deionized water, blotted dry with tissue paper and weighed. All the vegetable samples were then dried in an oven at 70˚C - 80˚C for 24 h to constant weight, weighed again, and ground using a smash instrument and a homogenizer [16].

2.3. Sample Analysis

A 2.0 g sample of soil was digested with perchloric acid and nitric acid (1:4) solution, and taken to 25 ml with distilled water for metals determination. A 0.5 g sample of plant powder was also digested with perchloric acid and nitric acid (1:4) medium, and taken to 10 ml with distilled water for metals determination. Three replicates of Soil and plant for each sample. Concentrations of Cd, Cr and Pb in all samples were determined by a atomic absorption spectrometer (Perkin-Elmer AA800) with an autosampler (combined with flame atomic absorption spectrometer (FAAS). And the before concentrations of Hg and As were determined by atomic fluorescence spectrophotometry (AF-640A) (AFS) according to standard analytical procedures. Samples of soil and plant with certified concentration of metals (GSS-15, GSD-8 and GSV-2, respectively, China National Center for Standard Materials) were included for quality assurance.

2.4. The Basic Nutrient in Soil

Prior to total elemental analysis, soils were air dried (25˚C, 14 d) and mechanically ground using a wood roller to pass through a 100-mesh sieve. The basic nutrients of soil were determined by the Bao's method [17].

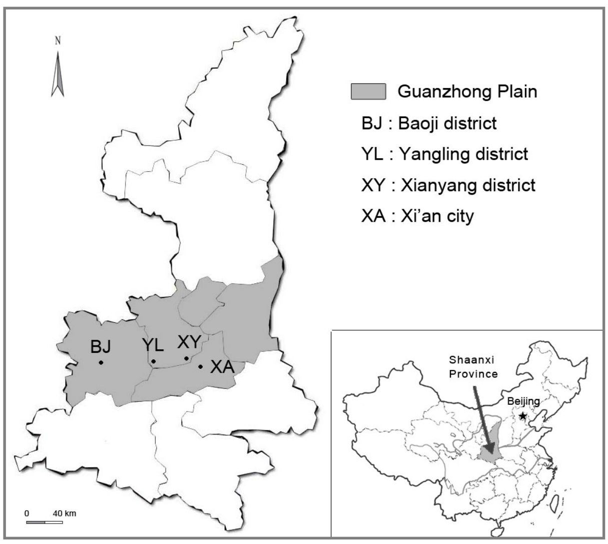

Figure 1. The locations of the greenhouse and sampling sites.

The soil pH (209 pH meter, Hanna Instruments) and electrical conductivity (EC) (4010 EC meter, Jenway) were measured by a glass electrode in a 1:2.5 soil/water suspension. The organic matter in soil was determined by the $K_2Cr_2O_7$-H_2SO_4 oxidation method, the 0.3 g soil sample was acceded to 10 ml of 1.0 mol·L^{-1} $K_2Cr_2O_7$-H_2SO_4 solution, entering a 170˚C - 180˚C paraffin oil bath pot for 5 min. After cooling, affiliating with 2 - 3 drops of ferrous indicator, using standard $FeSO_4$ titration. Soil NH_4^+-N was extracted from 1:5 (w/v) dry soil samples with 20% NaCl solution, shaken for 1 h on a reciprocating shaker at 250 rev·min^{-1}, acceded to 1.0 ml sodium tartrate solution, and determined at 390 nm by a spectrometer. Soil NO^{-3}-N was extracted from fresh soil samples with 0.5 mol·L^{-1} $CaSO_4 \cdot 2H_2O$ solution, added 0.05 g $CaCO_3$, 2.0 ml phenol disulfonic acid solution and 1:1 NH_4OH, and determined at 420 nm by a spectrometer. Olsen P was extracted by 0.5 mol·L^{-1} $NaHCO_3$ and a ratio of 1:20 (w/v) fresh sample extractant and shaken for 1 h on a reciprocating shaker at 250 rev·min^{-1} and then determined colourimetrically. Soil available potassium was extracted by 1:5 (w/v) sample extractant ratio of 1.0 mol·L^{-1} NH_4OAc, buffered to pH 7.0, shaken for 30 min on a reciprocating shaker at 250 rev·min^{-1} and was then analysed by flame spectrophotometer. Cation exchange capacity (CEC) was extracted by CH_3COONa, 4.0 g soil sample was added to 33 ml of 1.0 mol·L^{-1} (pH 8.2) CH_3COONa; after shaking 5 min, the solution was discarded and repeated distilling for 4 times, alcohol was used in washing the sample 3 times in the same way, and using 1.0 mol·L^{-1} CH_3COONH_4 washed twice, collected the solution for 100 ml, determined Na^+ concentration by a flame spectrophotometer.

2.5. Statistical Analysis

To compare the total heavy metal load through soils and vegetables at different sampling locations, heavy metal pollution index (HPI) was calculated using the equation given by Usero *et al.* [18].

$$HPI = (Cf_1 \times Cf_2 \times Cf_3 \times \cdots \times Cf_n)^{1/n}$$

where Cf is the concentration of n heavy metals in soil samples or vegetable samples. Original data was processed and correlation analysis was done in Excel 2003 and SPSS 16.0. The results are the means ± SD of the three replicates.

3. Result and Discussion

3.1. The Concentration of Heavy Metals in Topsoil and Subsoil

The total concentrations of metals (Cr, Cd, Pb, As, Hg) in greenhouse topsoil and subsoil and the limited values for metals are presented in **Table 1**. The results indicated that the total concentrations of metals were elevated in surface layers for all samples relative to the underlying subsoil. It demonstrated that the contents of metals in the order: topsoil (0 - 20 cm) > subsoil (20 - 40 cm), but it was not significant. The concentrations of Cd were exceeding the limits in soils of 7 districts. Furthermore, Cd contents (2.9 - 3.2 mg·kg^{-1}) in Dongbai soil samples were 7 to 8 times higher than the limited level (0.4 mg·kg^{-1}), other districts' Cd contents (0.83 - 2.13 mg·kg^{-1}) were 2 to 5 times higher than the limited level. Except in Nanzhuang, Yangling district, the Hg concentration was exceeding the limit in soil of 7 districts. Hg content (1.44 mg·kg^{-1}) in Xiwang was significantly higher than others, and 3 to 5 times higher than the limited level. Meanwhile, Cr, Pb and As contents in all soil samples were not exceeding the limits. According to seven villages in Guanzhong district, HPI in the soil samples were all up by 1.0, the total heavy metal load in Sanyuan was the highest. Cd and Hg caused the most heavy metal pollutions in greenhouse soils in Guanzhong districts.

Greenhouse arable soil layer is generally 0 - 40 cm; artificial disturbance frequency, may be the main reasons for the small difference in heavy metal contents between the 0 - 20 cm and 20 - 40 cm layers. Heavy metal accumulation in soil is generally caused by elevated fertilization, pesticides, sewage irrigation and agricultural residues, such as thin-film. At present, the study areas are using groundwater irrigation, except for Xiwang, and have a history of sewage irrigation in Xi'an city. And there are certain restrictions on pesticides, therefore, irrigation and pesticides in greenhouse were not the main reasons for heavy metal accumulation in soil. Study found that in recent years, some feeds contained large amounts of heavy metals; therefore, the defecation of livestock that ingest these feeds is another source of heavy metal pollution in vegetable field [19]. Fertilization led to the occurrence of a large number of heavy metal accumulation in soil throughout the world [20]. Application of large number of poultry droppings, such as chicken defecates, and calcium magnesium phosphate fertilizer,

Table 1. The total concentrations and heavy metal pollution index (HPI) in the soil samples.

Sample sites	Soil layers	Heavy metals (mg·kg^{-1})					HPI
		Cr	Cd	Pb	As	Hg	
Xiwang	T	27.92 ± 0.56	1.08 ± 0.29	29.38 ± 2.61	9.78 ± 0.18	1.44 ± 0.05	6.60
	S	21.08 ± 0.95	0.83 ± 0.36	26.67 ± 0.19	8.90 ± 0.51	1.26 ± 0.03	5.55
Wenchang	T	34.21 ± 0.52	1.17 ± 0.14	17.08 ± 1.72	10.24 ± 0.91	0.48 ± 0.02	5.07
	S	31.38 ± 2.10	0.91 ± 0.40	13.58 ± 3.22	9.37 ± 0.50	0.45 ± 0.01	4.39
Fanyao	T	32.13 ± 1.63	1.13 ± 0.33	23.63 ± 1.44	16.52 ± 0.72	0.44 ± 0.02	5.74
	S	28.17 ± 1.86	0.63 ± 0.45	20.29 ± 4.84	15.07 ± 0.43	0.40 ± 0.02	4.65
Sanyuan	T	42.17 ± 0.52	2.13 ± 0.63	20.42 ± 3.21	13.48 ± 0.41	1.41 ± 0.79	8.10
	S	31.50 ± 1.02	1.42 ± 0.44	18.33 ± 1.87	12.34 ± 0.36	1.10 ± 0.06	6.45
Dongzhang	T	26.38 ± 0.78	0.83 ± 0.40	21.58 ± 2.80	11.98 ± 0.62	0.53 ± 0.01	4.96
	S	20.21 ± 1.92	0.71 ± 0.36	18.71 ± 2.42	9.91 ± 1.07	0.51 ± 0.01	4.23
Nanzhuang	T	30.42 ± 1.99	2.08 ± 0.51	22.04 ± 6.47	15.92 ± 0.90	0.34 ± 0.02	5.96
	S	22.21 ± 1.23	0.83 ± 0.07	20.37 ± 2.28	13.88 ± 1.21	0.28 ± 0.02	4.29
Dongbai	T	36.29 ± 2.37	3.17 ± 0.26	19.38 ± 2.55	12.79 ± 0.84	0.67 ± 0.04	7.18
	S	29.13 ± 0.45	2.88 ± 0.13	19.04 ± 2.60	11.12 ± 0.43	0.61 ± 0.02	6.41
Limit (pH > 7.5)		250	0.40	50	20	0.35	

Note: T-topsoil (0 - 20 cm), S-subsoil (20 - 40 cm). Limit: limit values in soil (HJ333-2006); HPI: heavy metal pollution index. The content of heavy metals in the table is based on dry weight of soil, values are means ± SD (n = 3); Limit: the limit values for metals set by the State Environmental Protection Administration of China (GVPEQES, 2006).

which contains a certain amount of heavy metals, may be the main sources of heavy metal accumulated in greenhouse soils, in Guanzhong districts. Compared with the vegetable field in Guanzhong district, heavy metals contents in greenhouse soils had been increasing with farming year after year. So people should pay more attention to it.

3.2. The Concentrations of Heavy Metals in Vegetables

The total heavy metal concentrations and the limited values in the vegetables are presented in **Table 2**. The concentrations of heavy metals in three species of vegetables are in the following order: celery > tomato > cucumber. The contents of Pb (0.201 - 0.376 mg·kg^{-1}) in three species of vegetables were exceeding the limited values (0.20 mg·kg^{-1}) according to the 7 districts in Guanzhong. And the contents of Cd were exceeding the limited values in 4 districts, including Xiwang, Sanyuan, Nanzhuang and Dongbai. In addition, Cd found in celery was only exceeding in Xiwang and Nanzhuang. The other three metals were not exceeding the limited values in three species of greenhouse vegetables. However, they have a high metal content when compared to field vegetables. HPI is the highest in cucumber and tomato in Sanyuan, as well as in Xiwang's celery. Meanwhile, HPI is the lowest in tomato and celery in Dongzhang, as well as in Wenchang's cucumber.

In recent years, celery, tomato and cucumber are the main cultural greenhouse vegetables in Guanzhong district, in Shannxi province, having high numbers of growing areas and the higher yields. Previous studies showed that leafy vegetables have a stronger absorptive capacity for heavy metals in soil, atmosphere and water, which are easily polluted, followed by root vegetables, and fruits vegetables has less absorptive capacity of heavy metals [21]. In our study, we only detected the heavy metals in root vegetables and fruit vegetables, the result showed that celery has the highest concentrations of metals, because celery has the enrichment ability to heavy metals [22]. It is indicated that in the vegetables, Xiwang and Sanyuan have higher metal concentrations, because Xiwang has the waste-water irrigation history, and Sanyuan has a large number of fertilization. Although the source of heavy metals contamination of vegetables were more complex, according to the previous studies, heavy metal pollution in greenhouse vegetables in Guangzhong district was caused by heavy metals polluting

Table 2. The total concentrations and heavy metal pollution index (HPI) in vegetables.

Sample sites	Vegetable samples	Heavy metals ($mg \cdot kg^{-1}$)					
		Cr	Cd	Pb	As	Hg	HPI
Xiwang	Cucumber	0.359 ± 0.56	0.0477 ± 0.21	0.219 ± 1.11	0.178 ± 0.18	0.0066 ± 0.02	0.085
	Tomato	0.41 ± 0.52	0.0489 ± 0.14	0.234 ± 1.32	0.185 ± 0.45	0.0078 ± 0.03	0.092
	Celery	0.517 ± 0.95	0.0517 ± 0.27	0.376 ± 1.29	0.196 ± 0.51	0.0153 ± 0.01	0.125
Wenchang	Cucumber	0.224 ± 0.34	0.0421 ± 0.33	0.204 ± 1.55	0.146 ± 0.32	0.0058 ± 0.01	0.070
	Tomato	0.278 ± 0.41	0.0437 ± 0.19	0.212 ± 1.60	0.159 ± 0.34	0.0067 ± 0.02	0.077
	Celery	0.359 ± 0.33	0.0481 ± 0.27	0.227 ± 1.34	0.164 ± 0.41	0.0073 ± 0.02	0.086
Fanyao	Cucumber	0.298 ± 0.71	0.0363 ± 0.12	0.203 ± 1.28	0.165 ± 0.47	0.0057 ± 0.01	0.073
	Tomato	0.301 ± 0.58	0.0387 ± 0.34	0.217 ± 1.62	0.177 ± 0.45	0.0062 ± 0.04	0.077
	Celery	0.379 ± 0.28	0.0419 ± 0.33	0.241 ± 0.98	0.182 ± 0.23	0.0071 ± 0.03	0.087
Sanyuan	Cucumber	0.455 ± 0.72	0.0503 ± 0.17	0.227 ± 0.69	0.196 ± 0.31	0.0084 ± 0.03	0.097
	Tomato	0.482 ± 0.43	0.0512 ± 0.28	0.249 ± 1.32	0.159 ± 0.45	0.0089 ± 0.04	0.097
	Celery	0.522 ± 0.55	0.0545 ± 0.55	0.325 ± 1.01	0.168 ± 0.65	0.0091 ± 0.01	0.107
Dongzhang	Cucumber	0.221 ± 0.51	0.0363 ± 0.78	0.201 ± 1.43	0.199 ± 0.55	0.0063 ± 0.01	0.073
	Tomato	0.247 ± 0.39	0.0379 ± 0.69	0.217 ± 1.71	0.117 ± 0.71	0.0072 ± 0.03	0.070
	Celery	0.298 ± 0.44	0.0434 ± 0.17	0.233 ± 1.82	0.154 ± 0.91	0.0081 ± 0.02	0.082
Nanzhuang	Cucumber	0.376 ± 0.83	0.0467 ± 0.49	0.209 ± 2.02	0.154 ± 0.74	0.0043 ± 0.03	0.075
	Tomato	0.399 ± 0.73	0.0479 ± 0.81	0.211 ± 1.62	0.161 ± 0.32	0.0055 ± 0.02	0.081
	Celery	0.432 ± 1.21	0.0509 ± 0.23	0.224 ± 1.23	0.173 ± 0.52	0.0067 ± 0.01	0.089
Dongbai	Cucumber	0.401 ± 0.99	0.0536 ± 0.71	0.218 ± 1.37	0.171 ± 0.43	0.0058 ± 0.02	0.085
	Tomato	0.437 ± 0.87	0.0554 ± 0.32	0.244 ± 1.24	0.187 ± 0.59	0.0066 ± 0.02	0.094
	Celery	0.475 ± 0.79	0.0572 ± 0.92	0.293 ± 1.44	0.199 ± 0.71	0.0078 ± 0.01	0.104
Safe limit		0.50	0.05	0.20	0.50	0.01	

Note: HPI: heavy metal pollution index. The content of heavy metals in the table is based on dry weight of vegetables, values are means ± SD (n = 3).

agricultural soil [21]. Our studies showed that greenhouse soils were mainly polluted by Cd and Hg in Guanzhong district, but greenhouse vegetables were polluted by Pb and Cd, this is because Pb and Cd element have the ability of enrichment in vegetables [23]. Farming measures, using many fertilizers and pesticides will cause heavy metal residues in vegetables.

3.3. The Basic Nutrition, pH and Organic Matter (OM) in Greenhouse Soil

The basic nutrients, pH and OM in the greenhouse soils are given in **Table 3**, respectively. Basic nutrients, pH and OM in the greenhouse soils is in the following order: topsoil (0 - 20 cm) > subsoil (20 - 40 cm). The pH of the upper soil layer was always higher than the bottom layer. The pH (7.0 - 7.7) of greenhouse soils was lower than the normal value of the general field soil (7.9 - 8.3), and with the years passing by the soil became acidified, especially in the topsoil (0 - 20 cm). Soil pH can directly affect metals activity, thereby impacting on metals transfer and accumulate in soil. Usually, the soil pH is much lower, and the metal is easier to transfer. However, when the soil pH is litmus or alkalescent, metal is easy to accumulate in soil. OM in topsoil is the highest in Xiwang, and is the lowest in Fanyao. Commonly, with the growing stage increased, the OM contents in soil declined. However, the content of OM in greenhouse soil was higher than that of growing crops field, because of the usage of chicken defecates. In addition, soil organic matters provided nutrients such as carbon, N, P and K to support plant growth and reduced the metal toxicity to plants. The topsoil contents of basic nutrient, including available soil potassium, available phosphorus, available nitrogen, soil EC and CEC were the highest in Sanyuan.

Table 3. Basic nutritions ,pH and soil organic matter (OM) in the greenhouse soils.

Sample sites	Soil layers	pH	OM (%)	NO_3^--N ($mg \cdot kg^{-1}$)	NH_4^+-N ($mg \cdot kg^{-1}$)	NH_4Ac-K ($mg \cdot kg^{-1}$)	Olsen-P ($mg \cdot kg^{-1}$)	EC ($mS \cdot cm^{-1}$)	CEC Me/100g
Xiwang	T	7.04	3.14	59.80	65.8	292.8	91.8	65.5	30.7
	S	7.13	1.28	52.10	58.8	264.1	69.2	61.0	24.2
Wenchang	T	7.42	2.34	690.7	102.0	260.0	92.9	63.9	26.6
	S	7.55	1.50	541.9	90.2	197.6	87.2	60.5	15.9
Fanyao	T	7.32	1.51	783.2	47.5	191.2	78.1	58.4	25.6
	S	7.36	1.24	731.1	44.8	166.2	50.8	56.6	15.7
Sanyuan	T	7.02	2.90	787.3	280.2	465.8	134.2	99.5	34.7
	S	7.19	1.89	738.6	163.6	399.3	109.7	86.5	24.9
Dongzhang	T	7.35	1.58	199.5	191.1	394.7	62.8	57.9	26.5
	S	7.56	1.34	154.9	153.3	232.2	29.8	52.6	21.5
Nanzhuang	T	7.39	2.08	138.2	111.8	185.8	82.5	52.8	27.9
	S	7.59	1.35	97.9	103.1	112.5	53.6	47.2	22.9
Dongbai	T	7.11	2.80	331.9	118.3	332.4	120.5	93.9	30.9
	S	7.38	2.18	249.1	79.91	281.4	115.3	89.4	26.79

Note: T-topsoil (0 - 20 cm), S-subsoil (20 - 40 cm). The content of NO_3^--N in the table was based on fresh weight of soil, others were based on dry weight of soils, values are means ± SD (n = 3).

This high level of soluble nutrients in soil can be attributed to high levels of EC in the soil. Most of greenhouse soil Olsen-P are more than 60 $mg \cdot kg^{-1}$, especially in Sanyuan and Dongbai. In general, vegetables need about 60 - 90 $mg \cdot kg^{-1}$ [19] of P. However, the available P were exceeding the limit by 1 - 2 times in Guanzhong district, it was far beyond the necessity for vegetables. Although P has little mobility in soil profile, when plowed, soil P content is higher than 60 $mg \cdot kg^{-1}$, it may pollute the environment. Applying large amounts of organic fertilizer in the soil may lead to P downward migration to soil profile, thus creating a potential pollution of groundwater [24]. Greenhouse soil nitrate and ammonium nitrogen contents are higher than average vegetable content, especially the soil nitrate content found in Sanyuan. With the greenhouse shedage increasing, available K content increased, but the increasing amount of the content was limited This indicated that the fertilization of greenhouse vegetable production was imbalanced in Guanzhong district where input of fertilizer N and P is too much while fertilizer K is relatively small. The imbalanced fertilization not only lead to wasting many fertilizers, but also result in secondary environment pollution, and nitrate content increasing, finally the quality of vegetables declining. Therefore, people should pay attention to the rational application of fertilizer K in greenhouse soil, in order to keep fertilizer balanced. The level of soil salinity can be measured by soil EC and CEC, which were rising in study areas, this mainly due to a large number of fertilizers in soil.

3.4. Relationships between Basic Nutrients and Metal Concentrations in Soil

According to these impacting factors, OM, pH, available soil phosphorus, EC and CEC have a great impact on heavy metal contents (**Table 4**). Soil pH and the contents of heavy metals (Cr, Cd, Pb, Hg) were negative correlation coefficients, except for As, and it had a great impact on the Hg, achieving a very significant level ($p < 0.01$). Soil Olsen-P had a great impact on the Cr, by a very significant level ($p < 0.01$). It maybe because the elements can combine with soil P and form phosphate, accumulating with the increasing of available soil phosphorus contents. EC and Cr had a positive correlation of a significant level ($p < 0.05$). CEC and Hg had a positive correlation of a significant level ($p < 0.05$). Available soil nitrogen and available soil potassium were not significant to correlation coefficients of heavy metals. The significant differences between greenhouse soil and growing crop field are the large accumulation of OM and high available nutrient contents. From different view of the impacting factors, correlation analysis showed that the OM, pH, available P, EC and CEC have more influence on the heavy metals Cr and Hg in soil.

4. Conclusions

1) Major survey of the seven regions in Shaanxi Province greenhouse soil for heavy metals showed that the contents of Cd and Hg were exceeding the limited value stated in "the Greenhouse Vegetable Producing Environmental Quality Evaluation Standards". The contents of As, Pb and Cr were not exceeding the limited value. The

Table 4. Correlation coefficients of heavy metal contents with properties of greenhouse soils.

Soil property	Cr	Cd	Pb	As	Hg
pH	−0.432	−0.395	−0.394	0.244	−0.895**
OM	0.327	0.118	0.320	−0.546	0.860*
Olsen-P	0.898**	0.724	−0.271	−0.076	0.573
NH_4 Ac-K	0.415	0.157	−0.176	−0.375	0.596
NO_3^--N	0.718	0.015	−0.314	0.367	0.144
NH_4^+-N	0.522	0.221	−0.376	−0.040	0.481
EC	0.834*	0.689	−0.292	−0.117	0.565
CEC	0.659	0.556	0.079	−0.178	0.823*

Note: *indicated that the correlation between the two factor to achieve $p < 0.05$ significant level; **indicated that the correlation between the two factor to achieve $p < 0.01$ significant level.

HPI in Sanyuan is the highest, and in Dongzhang is the lowest. The heavy metal contents were increasing in greenhouse soils in Guanzhong districts; maybe it is related to the use of large amounts of the chemical and organic fertilizers and pesticides.

2) The heavy metals for the seven regions of Shaanxi greenhouse vegetables are in the following order: celery > tomato > cucumber. The content of metals in rooted vegetables is higher than that in eggplant vegetables. The contents of Pb were exceeding the limited value in three species of vegetables. Cd in tomato and cucumber were exceeding the limited value in Sanyuan and Dongbai. Cr, Pb and Hg were not exceeding the limited value in three species of vegetables.

3) The contents of soil pH, OM, soil available nitrogen, Olsen-P, available potassium, CEC and EC were higher than common vegetable contents in field. Moreover, the contents of available nitrogen and Olsen-P were the highest and the ratio of N, P and K in soil was seriously imbalanced.

4) Using the correlation analysis, according to these impacting factors, OM, pH, Olsen-P, EC and CEC have obvious effect on Cr and Hg. However, the effects of available nitrogen and available potassium were not evidence.

At present, our study focused on the contents of heavy metals in the greenhouse soils and the main plant species of vegetables in Guanzhong district, Shannxi province. However, the contents of heavy metals in greenhouse soils and vegetables in other districts in Shannxi province, as well as other species of vegetables should be tested in upcoming years, in order to ensure the safety production of establishment agriculture.

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