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Original Research

Temporal Distribution Characteristic and Risk Analysis of Heavy Metals in Greenhouse Vegetable Soils

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Abstract

The aim of this study was to explore the distribution characteristics, sources, ecological risks and health indexes of heavy metals in greenhouse vegetable soils (GVS) of vicennial cultivation. Concentrations of chromium (Cr), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd), and lead (Pb) were detected, and principle component analysis and cluster analysis were conducted. The potential ecological risk index and health index of the metals were also calculated to evaluate their multi-effects. Concentrations of Ni, Cu, Zn, Cd, and Pb reached peaks in GVS duration of 6-10 or 11-15 years, representing the high metal accumulation. Additionally, concentrations of Cr were significantly higher during the first decade than the second decade of GVS duration, which may be related to its bio-accumulation and leaching. Metals in soil depths of 20-40 cm showed a trend of intensive accumulation, especially in the second decade of duration. Cluster analysis revealed that Cr, Ni, and Zn were mostly from similar anthropogenic activities, and significantly high Cd in the studied area indicated the excessive human input. Furthermore, risk index demonstrated that GVS duration of 6-10 years was in moderate ecological risk and GVS duration of the second decade had a high health index.

Keywords: farming duration, greenhouse vegetable soils, heavy metals, potential ecological risk, health index

Introduction

Heavy metal contamination in soils has been focused over centuries around the world [1]. Due to the emphasis on food safety, metal accumulation in farming soils is also widely studied, and particularly greenhouse vegetable soils (GVS) have higher metal concentrations than open field vegetable soils, which would bring about a greater threat to the ecological environment and human health by food chain and human exposure [2, 3]. Two opinions were offered on metal accumulation and GVS duration. One view is that metal concentrations are increasing by perennial sowing, pesticide spraying

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and fertilization application, which dominated metal accumulation [4, 5]. For example, concentrations of chromium (Cr), lead (Pb), zinc (Zn), and copper (Cu) were significantly correlated and increased with cultivating years in farming soils [6, 7]. Another view is that metals have different distribution characteristics with the increase in cultivation ages. For example, no significant difference was observed in available contents of cadmium (Cd) and Zn between four-year and 17-year-cultivation in GVS of eastern China [8]. In addition, concentrations of nickel (Ni) and Pb also had no significant difference along with GVS duration [9].

Studies on temporal and vertical distribution of heavy metals in GVS were previously involved. Liu et al. (2011) argued that concentrations of Cd, Cu, and Cr had increasing trends during the process of vegetable growth in GVS, indicating metal accumulation with the cultivation years [10], while Zn and Cr had no significant difference and Cd significantly increased with the increase in GVS duration in southwestern China [11]. Previous studies showed that temporal distribution of every metal in GVS had considerable divergence, suggesting that the relevant research was limited and that further specialized studies were needed. Published data showed that metal concentration decreased with the increase in soil depths in agriculture [11, 12]. However, the vertical distribution pattern in the soil profile of GVS has been not particularly clear until now.

Metal accumulation in soils brought about a great deal of contamination to surroundings and threatened human health. Many models were discussed and calculated to evaluate the potential risk of heavy metals [13]. Based on the background values and toxic-response factors of metals, the potential ecological risk index (RI) of heavy metals were explored to evaluate the contamination level to the environment [14, 15]. Metals in soils can also be absorbed into human organs by routes of incidental ingestion, dermal contact, and inhalation of soils, which further bring about health risks [16]. Thus, health index (HI) was also previously analyzed and modeled by combining the metal daily intake, exposure time, etc. [17].

The GVS of vicennial duration and three soil depths (0-20, 20-40, and 40-60 cm) were collected and Cr, Ni, Cu, Zn, Cd, and Pb were detected as the research issues in this study. The temporal and vertical distribution of heavy metals in different GVS durations were analyzed, and the sources of heavy metals in GVS were explored by cluster analysis and principle correlation analysis. Furthermore, the potential ecological risk and health risk of heavy metals in the GVS were assessed by calculating the RI and HI.

Material and Methods

Study Areas and Sample Collection

Samples were collected from GVS in Lanling, Linyi of Shandong Province, China, in December 2017. Three sites were collected from greenhouses during the cultivation ages of 1, 3, 5, 8, 9, 10, 12, 13, 15, 18, and 20 years, respectively. As a reference, three sites were also selected and collected in open-field vegetable soils around the greenhouse area. For each sampling site, soils were collected at three depths (0-20, 20-40, and 40-60 cm) and by five-point sampling method in 1 m^2 [18]. Thus, 108 soil samples were collected in this study. Due to the vegetable types in GVS varying from season to season per year, metal bio-accumulation was considered as uniform in this study. The sampling positions are described in Fig. 1.

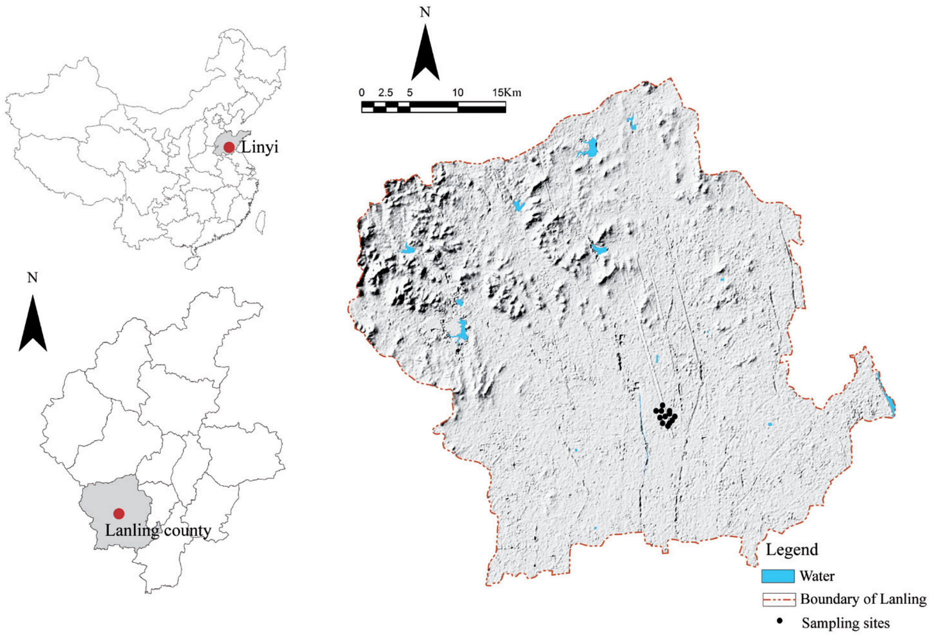

Fig. 1. Studied areas and sampling sites.

Sample Treatments

Dried at 20ºC, soil samples were ground and then sifted through a 0.8-mm nylon sieve for analysis of soil pH and cation exchange capacity (CEC). Then concentrations of heavy metals were determined after sifted through a 0.149-mm nylon sieve. In detail, 0.2000 g of each sample was weighed and digested in the polytetrafluoroethylene crucibles with a mixture of 10 ml HNO_3, 5 ml HF, and 2 ml $HClO_4$. Covering up for 12 hours at 130ºC, the temperature was then increased to 180ºC, and the lids were taken off until residues were less than 1 ml. The final residues were dissolved in 1 ml HNO_3 (50%) and diluted to a volumetric flask of 25 ml [19]. All glassware used were cleaned by soaking in 10% dilute nitric acid for at least 24 h and rinsed abundantly in deionized water before use during the digestion of heavy metals.

The concentrations of Cr, Cu, Ni, and Zn were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES; IRIS Advantage OPTIMA 7000DV, THERMO, America) with a detection wavelength of 170-850 nm. Soil samples were analyzed for Cd and Pb by using graphite furnace atomic absorption spectrometry (GFAAS; PE800, American PE Company, America) with a detection limit of 10-13 g·mL^{-1}. Jiangsu Province and Shandong Province have the largest vegetable production and greenhouse vegetable bases in China, which mostly centered on the cities of Shouguang, Nanjing, Linyi, and Dongtai [20, 21]. Thus, the relevant literatures were retrieved and metal concentrations in GVS were compared in this study.

For the determination of pH, 10 g of soils and 25 g of distilled water were thoroughly mixed, stirred, and determined by using a pH meter (Rex PHS-3E; Shanghai INESE Scientific Instrument Co., Ltd). Soil samples (2.00 g) were mixed with CH_3COONH_4 and then C_2H_5OH solution, then they were distilled and titrated by solution of HCl, and concentrations of CEC were calculated by recording the volume of hydrochloric acid in titration. The detailed methodology to determine CEC was previously reported by Shiri et al. [22].

Potential Ecological Risk Index (RI)

Risk index (RI) was introduced to assess the potential ecological risk of contamination in soils and sediments, and its calculation was listed as follows [15, 23]:

$$RI = \sum_{i=1}^{n} E_r^i = \sum_{i=1}^{n} T_r^i * C_f^i$$

$$C_f^i = \frac{c_n^i}{c_0^i}$$

…where c_n^i is the concentration of any metal in samples, and c_0^i is the corresponding background value of metal, which are 66.6, 29.6, 22.1, 71.1, 0.103, and 21.9 mg·kg^{-1} for Cr, Ni, Cu, Zn, Cd, and Pb, respectively referring to the background value of yellow fluvo-aquic soils in Shandong Province in this study [24]. E^i_r is the monomial potential ecological risk factor, and T^i_r is the toxic-response factor, which for Cr, Ni, Cu, Zn, Cd, and Pb are 2, 5, 5, 1, 30, and 5, respectively [25]. The risk rank and evaluation classification are listed in Table 1 [23].

Health Index (HI)

Humans are vulnerable to heavy metals during agricultural activities in greenhouse vegetable, and incidental ingestion is a major route of exposure to metals for human beings [16]. A model of the human health index (HI) is determined by calculating the chemical daily intake (CDI) through incidental ingestion, summing hazard quotient (HQ) for non-carcinogenic chemicals, and evaluating carcinogenic risk (CR) for carcinogenic chemicals [26, 27]. Metal of Cd has strong carcinogenic capability as the classification for carcinogenicity of heavy metals [26], thus carcinogenic risk for Cd is conducted in this study. The health risk of children is not calculated in this study as children rarely appear in greenhouses.

The CDI of metals through incidental ingestion is calculated as the following formula:

$$CDI_{\text{ingestion}} = CS \times IR \times \frac{EF \times ED}{BW \times AT} \times 10^{-6}$$

In this study, $CDI_{\text{ingestion}}$ is the daily take of metals (mg·kg^{-1} day^{-1}) through incidental ingestion; CS is the concentrations of metals in soils (mg·kg^{-1}); and IR is the ingestion rate: 100 mg·day^{-1} for adults [28]. EF is the exposure frequency, understood as 365 d·yr^{-1}; ED is the

Table 1. Risk rank and evaluation classificationsof E_i and RI [23].

The risk rank of C_f^i		Risk rank of E_i		Risk rank of RI	
C_f^i<1	Low contamination	E_i<40	Low risk	RI<150	Low risk
1≤C_f^i<3	Moderate contamination	40≤E_i<80	Moderate risk	150≤RI<300	Moderate risk
3≤C_f^i<6	Considerable contamination	80 ≤E_i<160	Considerable risk	300≤RI<600	Considerable risk
C_f^i≥6	Very high contamination	320>E_i>160	Great risk	RI>600	Very great risk

Table 2. Concentrations of heavy metals in soils of typical greenhouse bases of China ($mg \cdot kg^{-1}$).

Study area	N*	Cr	Ni	Cu	Zn	Cd	Pb	References
Linyi, Shandong Province	108	88.23	39.00	37.62	111.35	0.52	29.87	This study
Shouguang, Shandong Province	59	67.13	28.93	27.86	115.79	0.196	20.06	[21]
Shouguang, Shandong Province	65	—	—	32.9	106	0.44	20.7	[8]
Shouguang, Shandong Province	69	41.34	28.02	28.43	90.76	0.21	15.32	[29]
Dongtai, Jiangsu Province	108	49.33	21.3	14.87	56.63	0.16	17.58	[19]
Nanjing, Jiangsu Province	112	—	—	52.17	117.4	0.15	53	[27]
Nanjing, Jiangsu Province	85	—	—	36.4	95.56	0.23	32.19	[20]
Nanjing, Jiangsu Province	320	—	—	37.68	98.01	0.21	37.3	[8]

*: the numbers of samples.

exposure duration (ED) and the body weight (BW) are 30 years and 70 kg for adults [26]. AT is averaging time (for non-carcinogens, TA = ED × 365; for carcinogens, TA = 70×365).

HQ for non-carcinogenic metals and the CR for carcinogenic Cd were calculated as the following formulas:

$$HI = \sum_{i=1}^{6} HQ = \sum_{i=1}^{6} \frac{CDI}{RfD}$$

$$CR = CDI \times SF$$

HI is the sum of HQ for the six metals in this study. As the oral reference dose (RfD), RfD of Cr, Ni, Cu, Zn, Cd, and Pb are 0.003, 0.02, 0.037, 0.3, 0.001 and 0.0035 $mg \cdot kg^{-1}d^{-1}$ respectively for non-carcinogenic metals ($mg \cdot kg^{-1}\ d^{-1}$). SF is the slope factor of carcinogenic chemicals and SF of Cd is 0.38 $kg \cdot d \cdot mg^{-1}$ [26]. The acceptable CR is between 1×10^{-6} and 1×10^{-4}. The risk of non-carcinogenic metals is low when the HQ<1, and this risk exists when HQ>1.

Results

Temporal and Vertical Distribution Characteristics of Heavy Metals

The average concentrations of the studied metals were 88.23 $mg \cdot kg^{-1}$ for Cr, 39.00 $mg \cdot kg^{-1}$ for Ni, 37.62 $mg \cdot kg^{-1}$ for Cu, 111.35 $mg \cdot kg^{-1}$ for Zn, 0.52 $mg \cdot kg^{-1}$ for Cd and 29.87 $mg \cdot kg^{-1}$ for Pb, respectively, which exceeded the background values (Fig. 2). Specifically, Cd was significantly higher in GVS (0.55 $mg \cdot kg^{-1}$) than in open field (0.19 $mg \cdot kg^{-1}$), indicating the high accumulation of Cd in GVS.

Comparison analysis of heavy metals in GVS according to literature retrieval were listed in Table 2. GVS of Lanling, Linyi in this study had the highest Cr, Ni, and Cd, whereas concentrations of Cu and Pb in Nanjing were relatively high, reflecting that accumulation levels of heavy metals were greatly distinguished from different areas.

The metals had different distribution patterns among cultivation ages of every five-year period in this study. The Cr and Ni showed a decreased trend with significantly higher concentrations in the first decade of duration than the second decade duration of GVS. The result indicated an export trend of Cr and Ni with the increase in cultivation ages, dominance of which can be plant bio-accumulation (Table 3). Metal of Cu reached a peak in GVS duration of 6-10 years, revealing that the accumulation of Cu was not consistent with the increase in GVS duration (Fig. 2). Concentration of Cd was significantly lower in GVS duration of 1-5 years and open field, while accumulating the most in duration of 6-10 years (0.70 $mg \cdot kg^{-1}$; $P<0.05$). Metals of Zn and Pb showed no significant distribution difference among the GVS duration. The highest standard deviation of Zn and Pb in duration of 1-5 years suggested that this duration period of GVS was vulnerable to Zn and Pb contamination.

Characteristics of metal leaching in the soil profile can be indicated by evaluating the differences of metal concentrations among the three soil depths (0-20 cm, 20-40 cm, and 40-60 cm) in this study. The subtracted concentrations of Cr, Ni, and Cu from soil depth of 20-40 cm to that of 0-20 cm or 40-60 cm were mostly positive values (Fig. 3) – especially in the second decade duration of GVS. The finding revealed the intensive metal accumulation in soil depth of 20-40 cm and may be caused by agriculture activities, metal accumulation in roots, and root decomposition. The pH was higher in open field and GVS duration of 1-5 years than in other cultivation ages, representing soil acidification with the increase in GVS duration. The CEC was the highest in open field (45.8) and lowest in GVS of the second decade duration (23.6), exhibiting a decreasing absorption on cation with the increase in GVS duration.

Previous studies indicated that coefficient of variation (CV) of heavy metals would exceed 20% when suffering from anthropogenic activities [4]. The CV of Cd and

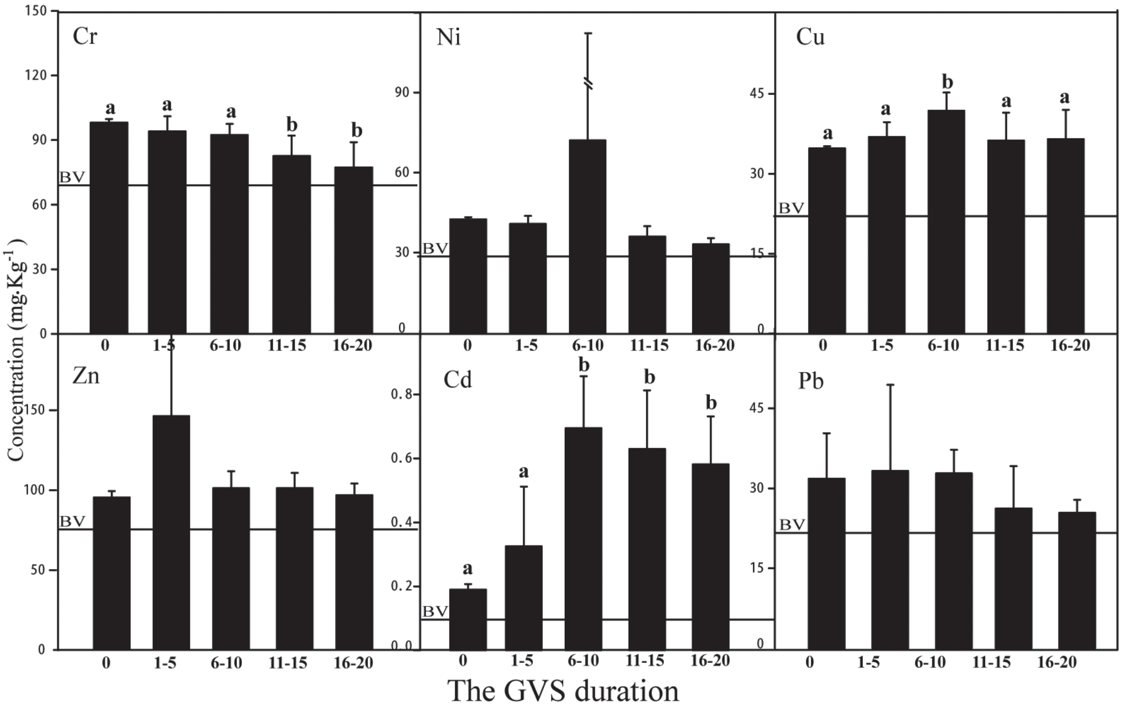

Fig. 2. Distribution patterns of heavy metals in GVS duration of 20 years; BV: background values of the metals; bars sharing the same lowercase letter (a or b) are not significant at α = 0.05 (Duncan test).

Pb were 40.3% and 34.1% in this study, indicating the human effect (Table 3). The significantly higher CV of Zn (61.3%), Cd (57.3%), and Pb (48.6%) in GVS duration of 1-5 years revealed the prominent anthropogenic input during cultivation. Metal concentrations and CV had no remarkable difference or significant trend among the soil profile in this study, a finding that may be related to soil plowing and turning up and further reflects that metal accumulation in subsurface soils can also be directly affected by human activities. With notably higher CV of the metals in GVS than those in open field, the CV decreased with the order: Zn (44.4%) > Cd (40.3%) > Pb (34.1%) > Ni (13.4%) > Cu (12.4%) > Cr (12.0%).

The principal component analysis (PCA) and factor analysis were conducted and three primary factors were extracted by factor analysis on the metals pH and CEC (Fig. 4). Results showed that factor 1 was dominated by Cr, Ni, Cu, Pb, and CEC, and explained 37.8% of the total variances. With the contribution of 11.6% and 13.4% to the variances, factor 2 and factor 3 were mainly dominated by Cd and Zn, respectively. The PCA showed that most samples were concentrated near the coordinates, and principal component 1 and principal component 2 explained 94.1% of the total variances. Cluster analysis on the six metals according to correlation analysis showed that Cu, Ni, and Cr were

Table 3. Concentrations of heavy metals in GVS duration (mg·kg^{-1}).

GVS duration (year)		Cr**	Ni	Cu	Zn	Cd	Pb*	CEC**
Open field	Mean (SD)	98.1 (1.7)	42.5 (0.8)	34.8 (0.4)	95.4 (4)	0.19 (0.02)	31.8 (8.5)	45.8 (3.2)
	Range	96.8-100	41.9-43.4	34.4-35.2	90.9-97.7	0.17-0.2	23.5-40.5	43.2-49.4
	CV (%)	1.7	1.9	1.2	4.2	9.1	26.8	7
1-10	Mean (SD)	93.3 (6)	42.3 (3.6)	39.2 (3.9)	123.8 (66.2)	0.5 (0.26)	33 (11.8)	31.3 (4.4)
	Range	81.8-106.3	36.1-49.1	33.9-47.8	78.5-300.9	0.2-0.9	18.3-73.9	23.2-38.8
	CV (%)	6.5	8.6	10	53.5	51.1	35.7	14.2
11-20	Mean (SD)	80.5 (10.4)	34.8 (3.5)	36.4 (5.1)	99.6 (8.7)	0.61 (0.17)	25.9 (6.2)	23.8 (2.2)
	Range	58.5-103.9	30-43.3	28.2-44.5	87.7-111.3	0.35-0.9	12.5-39.1	20.2-27.7
	CV (%)	12.9	10.2	14.1	8.7	27.3	23.9	9.3

*: $P<0.05$ in concentrations of metals; **: $P<0.01$ in concentrations of metals. SD: standard deviation; CV: coefficient of variation.

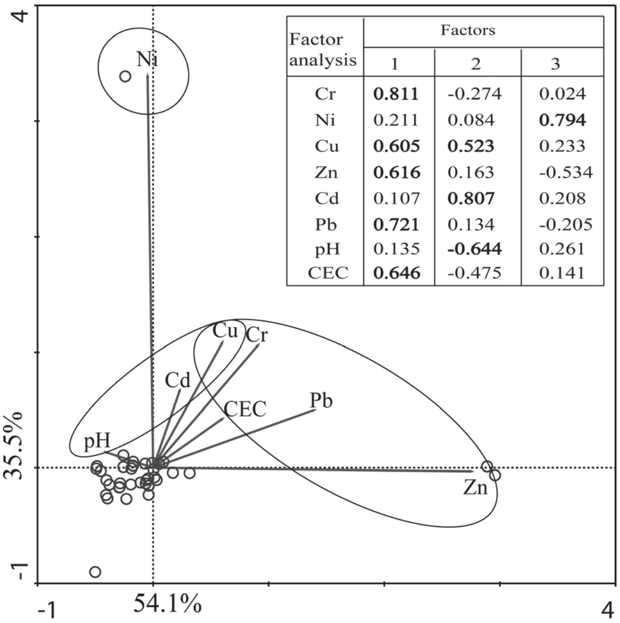

Fig. 3. Cluster analysis and comparison analysis of heavy metals (mg·kg^{-1}; metals 1, 2 and 3 refer to metal concentrations in soil depth of 0-20 cm, 20-40 cm, and 40-60 cm).

significantly and positively clustered, and then gathered the cluster of Pb and Zn (Fig. 3).

Potential Ecological Risk Index (RI) and Human Health Risk Index (HI)

The E_i and R revealed the damaging degree of potential pollution to the terrestrial soils or sediments (Table 4). E_i of the six metals suggested that contamination by Cr, Ni, Cu, Zn, and Pb in two decades of GVS duration were at low risk. But for the E_i of Cd, it showed low ecological risk in open field, moderate risk in GVS duration of 1-5 years, and considerable risk in GVS of other cultivation duration (Table 4), which indicated the potential harm to ecological environment and further to human health. R of the six metals revealed that GVS duration of 1-5 years was in moderate risk, whereas other GVS durations were in low risk. Moreover, R in GVS duration of the first decade was significantly lower than that in GVS duration of the second decade (Fig. 5). The non-significant difference of RI among the soil depths indicated that potential ecological risk polluted by the metals cannot be avoided in deep soils.

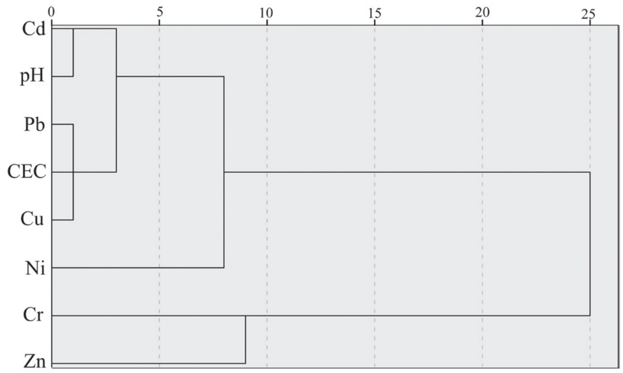

Fig. 4. Factor analysis and principal component analysis (PCA) on metals, pH, and CEC of GVS (CEC: cation exchange capacity).

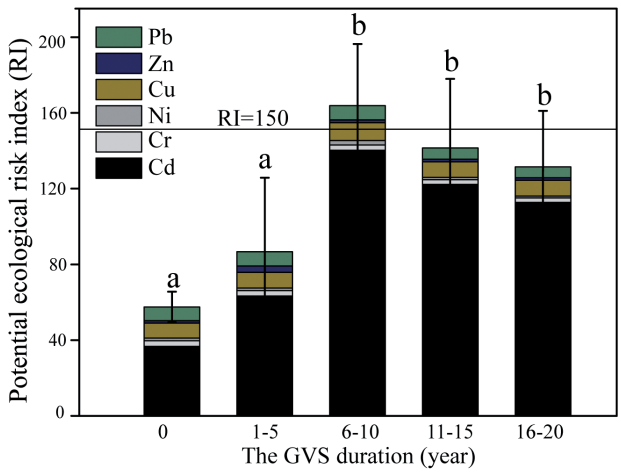

Fig. 5. Potential ecological risk index (R) of metals at different GVS durations; bars sharing the same lowercase letter (a or b) are not significant at α = 0.05 (Duncan test).

Table 4. Potential ecological risk index (R) of heavy metals at different GVS durations.

GVS duration (year)	E_i (Cr)	E_i (Ni)	E_i (Cu)	E_i (Zn)	E_i (Cd)	E_i (Pb)	RI
Open field	2.95 a	1.44	7.86 a	1.36	36.67 a	7.26	57.54
1-5	2.83 a	1.38	8.35 ab	3.31	63.29 a	7.59	86.74
6-10	2.79 a	2.33	9.42 b	1.45	140.31 b	7.60	163.89
11-15	2.48 b	1.22	8.20 a	1.39	122.26 b	5.98	141.53
16-20	2.32 b	1.12	8.26 a	1.29	112.73 b	5.80	131.52
Mean values	2.66	1.54	8.53	1.87	103.31	6.86	124.76

E_i (Cr): The potential ecological risk index of monomial metal. The different letters (a or b) in each column indicate the significant differences at α = 0.05 (Duncan test).

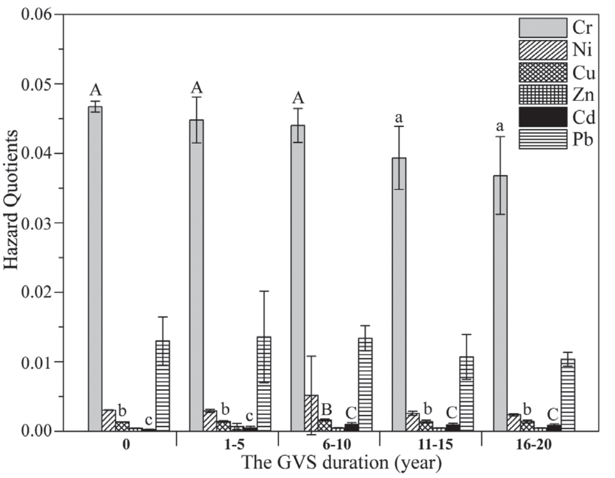

Fig. 6. Hazard quotients of the six metals in different GVS durations; bars sharing the same capital letter or the same lowercase letter are not significant at α = 0.05 (Duncan test).

The $CDI_{ingestion}$ of Cr and Cd were 0.13 and 0.16 ug·day^{-1} respectively. With a mean value of 0.04, Cr had the highest HQ in this study, followed by HQ of Pb (0.012). HQ of Cr was significantly higher in GVS duration of the first decade (0.045) than that of the second decade duration (0.038), leading to the same trend in the HI (Fig. 6). The HQ was far less than one, which indicated a low health risk. Moreover, the carcinogenic risk of Cd also showed significantly lower than the threshold value (1×10^{-6} ~1×10^{-4}), suggesting little carcinogenic risk.

Discussion

Concentration and Distribution of Heavy Metals

The decreased trend of Cr with the increase in GVS duration in this study was not consistent with the trend in the reports of Fang et al. (2011), who revealed the increasing accumulation of Cr as cultivation time increased [29]. Previous reports showed that Cr had no significant difference between GVS and open fields, and the concentration of Cr in vegetables was higher than other metals [30, 31]. Thus, the decreased Cr in this study may suggest that Cr is easily transferred from soils to vegetables with the increase in GVS duration, and the transfer of Cr may also be related with the change of soil structure [32]. Peaks are shown in the distribution of Cu, Zn, Cd, and Pb with the increase in GVS duration, which coincide with the distribution of Cu, Pb, and Zn in the report of Zhang et al. [11]. Concentrations of $CaCl_2$-extractable Cd and Cu in GVS duration of 6-10 years are the highest with the increase in GVS duration, and Ni, Cu, and Cd reach the highest values in GVS duration of 6-10 years [8]. Thus, this finding indicates that this cultivation duration is vulnerable to the metal accumulation, and it may also be associated with the organic matter in soils [32]. Metal of Pb is significantly higher in the first decade duration than the second decade duration of GVS, whereas Cd has a reverse trend. The finding may be associated to the input of fertilizer and their existing forms, as both extractable fractions of Cd and residual fraction of Pb dominate the soils [33, 34].

Previous reports showed that contents of Ni, Pb, Cu, Cd, Cr, and Zn had a decreased trend with the sampling depths in sediments of the Pearl River estuary [12, 33]. Whereas Li et al. (2009) showed the heavy metals in soils of 0-20 cm and 20-40 cm followed the exponential regression equations and the linear equations respectively in a historical sewage farm during 105 years, revealing that the distribution pattern of heavy metals in soil profile is related with historical land use [35]. The trend of intensive metal accumulation in soil depths of 20-40 cm may be related to the soil plowing and turning up, whereas the relative low concentrations of the metals in surface soils may be associated with metal activation and plant bio-accumulation, which can be further confirmed by the significantly low pH and surface soil acidification. For example, Schneider et al. (2017) showed that metal contamination in soil profile was related to the soil digging and ploughing, which can increase soil quality and crop yield [36]. The significantly lower pH in top-soils than deep-soils may increase the available contents of certain metals in surface soils [37].

Source Identification

The higher concentrations of Cr, Ni, Cu, Zn, Cd, and Pb in GVS than the background values indicate anthropogenic effects [38], a finding that is in accordance with the significantly high CV of Zn, Cd, and Pb – especially in the first lustrum duration of GVS, which demonstrate that GVS is prone to metal accumulation and can be affected by farming activities in this cultivation stage. Factor analysis, principle component analysis and cluster analysis were also used to explore the sources of heavy metals in soils and sediments in previous studies [12, 39, 40]. The cluster of Cr, Cu, and Ni indicated their similar human inputs, and so was the cluster of Pb and Zn. Qiutong and Mingkui (2017) reported that the contamination of Cd mainly resulted from the amendment of chemical fertilizer, and the contamination of Cu, Zn and Pb were most from the input of organic manure [21, 31, 34]. Therefore, the Pb and Zn are mainly from the application of organic manure in this study. Long-term use of pesticides and chemical fertilizers could highly elevate the concentrations of Cd [41], and many common pesticides had significantly higher concentrations of Cd [42]. Thus, the significantly higher Cd in this study than in GVS of other provinces may suggest the excessive input of chemical fertilizer and pesticides.

Risk Evaluation

The potential ecological risk assessment indicated the risk index of the six metals to the ecological environment, as well as the metal contamination levels [12]. Metals of Cr and Cu are at low ecological risk, though they have significant differences among the GVS duration. The significantly higher Cd in GVS duration of six to 20 years than in duration of 1-5 years indicates the moderate ecological risk. Thus, the metal accumulation and potential risk of Cd should be paid great attention. Qiutong and Mingkui (2017) showed that the concentration of Cd was the highest in soils amended by inorganic fertilizer, followed by soil amended by organic manure and compound fertilizer; thus the components of fertilizer should be optimized [34]. Guo et al. (2018) showed that the excessive input of organic manure cannot be utilized absolutely to elevate vegetable production, so the fertilization frequency should be reasonable [43].

Health index (HI) of adults by incidental ingestion in this study indicates the health risk when people farm. HQ of Cr and Pb dominate the HI and the values in this study below the threshold, which reveal little health risk. The carcinogenic risk of Cd in this study is also below the threshold, suggesting little carcinogenic possibility through the ingestion of GVS.

Conclusions

This study expounded the temporal and vertical distribution pattern of Cr, Ni, Cu, Zn, Cd, and Pb, identified the sources, and assessed the potential ecological risk and health risk in GVS duration of the last 20 years. The results presented support the following conclusions:

(1) The six metals had various distribution characteristic in GVS of two-decade duration.
(2) Elements of Cr, Ni, Cu, and Pb are mostly from anthropogenic activities, and the high content of Cd indicates excessive human activities.
(3) GVS with duration of 6-10 years is in moderate ecological risk, and GVS has little non-carcinogenic risk or carcinogenic risk in this study.

The distribution and risk assessment of heavy metals in this study provide the theoretical basis for standardizing vegetable planting systems in GVS.

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Conflict of Interest

The authors declare no conflict of interest.

References

1. ZHANG J., YU F., PANG S., YU Y. Spatial Distribution and Pollution Assessment of Potentially Toxic Elements in Urban Forest Soil of Nanjing, China. Pol. J. Environ. Stud. **28**, 3015, **2019**.
2. BIAN B., LIN C., LV L. Health risk assessment of heavy metals in soil-plant system amended with biogas slurry in Taihu Basin, China. Environ. Sci. Pollut. Res. Int. **23**, 16955, **2016**.
3. FAN Y., LI H., XUE Z., ZHANG Q., CHENG F. Accumulation characteristics and potential risk of heavy metals in soil-vegetable system under greenhouse cultivation condition in Northern China. Ecol. Eng. **102**, 367, **2017**.
4. CAI L., XU Z., BAO P., HE M., DOU L., CHEN L., ZHOU Y., ZHU Y. Multivariate and geostatistical analyses of the spatial distribution and source of arsenic and heavy metals in the agricultural soils in Shunde, Southeast China. J. Geochem. Explor. **148**, 189, **2015**.
5. JANKIEWICZ B., ADAMCZYK D. Assessing heavy metal content in soils surrounding a power plant. Pol. J. Environ. Stud. **19**, 849, **2010**.
6. BERGHOFER R., WILCKE W., VLADIMIR L., NESTROV O., ZECH W. Changes of Al and heavy metal concentrations in slovak soils during the last 25 years. J. Plant. Nutr. Soil. Sc. **160**, 469, **2010**.
7. CHEN B., YANG H., ZHOU J., REN X., MA J., SUN L., LI X. Effect of cultivating years of vegetable field on soil heavy metal content and enzyme activity in plastic shed. Trans. Chin. Soc. Agr. Eng. **28**, 213, **2012**.
8. YANG L., HUANG B., HU W., CHEN Y., MAO M., YAO L. The impact of greenhouse vegetable farming duration and soil types on phytoavailability of heavy metals and their health risk in Eastern China. Chemosphere, **103**, 121, **2014**.
9. PING L., LI Y., SHU-FANG Y.U., LIU Z.H., WEI J.L., WANG X.J. Evaluation on environmental quality of heavy metal contents in soils of vegetable greenhouses in Shouguang city. Res. Environ. Sci. **21**, 66, **2008**.
10. LIU J., HUANG B., SUN W.X., ZONG L.G. Spatial-temporal distribution and prediction of heavy metals under different soil use patterns in an economically developed area. Soils. **43**, 210, **2011**.
11. ZHANG H., HUANG B., DONG L., HU W., AKHTAR M.S., QU M. Accumulation, sources and health risks of trace metals in elevated geochemical background soils used for greenhouse vegetable production in southwestern China. Ecotox. Environ. Safe. **137**, 233, **2017**.
12. KONG X., CAO J., TANG R., ZHANG S., DONG F. Pollution of intensively managed greenhouse soils by nutrients and heavy metals in the yellow river irrigation region, Northwest China. Environ. Monit. Assess. **186**, 7719, **2014**.
13. SUN Y. Ecological risk evaluation of heavy metal pollution in soil in Yanggu. Pol. J. Environ. Stud. **26**, 1, **2017**.
14. LUO C., LIU C., WANG Y., LIU X., LI F., ZHANG G., LI X. Heavy metal contamination in soils and vegetables near

an e-waste processing site, South China. J. Hazard. Mater. **186**, 481, **2011**.
15. SZYMAN SKACHABOWSKA A., BECK A., POREBA R., ANDRZEJAK R., ANTONOWICZJUCHNIEWICA J. Evaluation of DNA damage in people occupationally exposed to arsenic and some heavy metals. Pol. J. Environ. Stud. 1, **2009**.
16. FALLAHZADEH R.A., GHANEIAN M.T., MIRI M., DASHTI M.M. Spatial analysis and health risk assessment of heavy metals concentration in drinking water resources. Environ. Sci. Pollut. Res. **24**, 1, **2017**.
17. MA W., DING X., LONG J., WANG L., LIU H., LIU S., DAI J. Source analysis and risk assessment of polycyclic aromatic hydrocarbons (PAHs) in paddy soils. Soil. Sediment. Contam. **26**, 1, **2017**.
18. LU R. Agricultural chemical analysis method of soil. China Agricultural Science and Technology Press. **2000**.
19. SONG H., SUN Z. Temporal variations and bioaccumulation of heavy metals in different suaeda salsa, marshes of the yellow river estuary, China. Environ. Sci. Pollut. Res. **21**, 14174, **2014**.
20. CHEN Y., HUANG B., HU W., WEINDORF D.C., LIU X., YANG L. Accumulation and ecological effects of soil heavy metals in conventional and organic greenhouse vegetable production systems in Nanjing, China. Environ. Earth. Sci. **71**, 3605, **2014**.
21. TIAN K., HU W., XING Z., HUANG B., JIA M., WAN M. Determination and evaluation of heavy metals in soils under two different greenhouse vegetable production systems in eastern China. Chemosphere. **165**, 555, **2016**.
22. SHIRI J., KESHAVARZI A., KISI O., ITURRANRAN-VIVEROS U., BAGHERZADEH A., MOUSAVI R., KARIMIA S. Modeling soil cation exchange capacity using soil parameters: assessing the heuristic models. Comput. Electron. Agr. **135**, 242, **2017**.
23. HAKANSON L. An ecological risk index for aquatic pollution control. A sedimentological approach. Water. Res. **14**, 975, **1980**.
24. NATIONAL BUREAU OF STATISTICS OF CHINA. China Statistical Yearbook (in Chinese). China Statistics Press, Beijing. **2015**.
25. STATE ENVIRONMENTAL PROTECTION BUREAU, STATE BUREAU OF TECHNICAL SUPERVISION. National environmental soil quality standard (GB15618-1995). China Standard Press, Beijing. **1997**.
26. ENVIRONMENTAL PROTECTION AGENCY (EPA). Final draft bat guidance note on best available techniques for the initial melting and production of iron & steel sector. **2011**.
27. HU W., CHEN Y., HUANG B., NIEDERMANN S. Health risk assessment of heavy metals in soils and vegetables from a typical greenhouse vegetable production system in China. Human. Ecol. Risk. Assess. **20**, 1264, **2014**.
28. USDOE N.E., SERVICES E. Technical data to justify full burnup credit in criticality safety licensing analysis. Office of Scientific & Technical Information Technical Reports, **2011**.
29. FANG S.B., HU H., SUN W.C., PAN J.J. Spatial variations of heavy metals in the soils of vegetable-growing land along urban-rural gradient of Nanjing, China. Int. J. Environ. Res. Public. Health. **8**, 1805, **2011**.
30. PING L., ZHAO H.J., WANG L.L., LIU Z.H., WEI J.L., WANG Y.Q., JIANG L.H., DONG L., ZHANG Y.F. Analysis of heavy metal sources for vegetable soils from Shandong Province, China. J. Integr. Agr. **10**, 109, **2011**.
31. XU L., LU A., WANG J., MA Z., PAN L., FENG X., LUAN Y. Accumulation status, sources and phytoavailability of metals in greenhouse vegetable production systems in Beijing, China. Ecotox. Environ. Safe. **122**, 214, **2015**.
32. BAREEN B., RAFIQ K., SHAFIQ M., NAZIR A. Uptake and Leaching of Cu, Cd, and Cr after EDTA Application in Sand Columns Using Sorghum and Pearl Millet. Pol. J. Environ. Stud. **28**, 2065, **2019**.
33. LIU B., WU F., DAI X., LIU F., MI B. Variations of cadmium accumulation and translocation in different pakchoi cultivars and screening for Cd-pollution-safe cultivars using cluster analysis. Pol. J. Environ. Stud. **28**, 2215, **2019**.
34. QIUTONG X., MINGKUI Z. Source identification and exchangeability of heavy metals accumulated in vegetable soils in the coastal plain of eastern Zhejiang Province, China. Ecotox. Environ. Safe. **142**, 410. **2017**.
35. LI P.J., STAGNITTI F., XIONG X., PETERSON J. Temporal and spatial distribution patterns of heavy metals in soil at a long-standing sewage farm. Environ. Monitor. Assess. **149**, 275, **2009**.
36. SCHNEIDER F., DON A., HENNINGS I., SCHMITTMANN O., SEIDEL S.J. The effect of deep tillage on crop yield – what do we really know? Soil. Till. Res. **174**, 193, **2017**.
37. SINGH R.P., AGRAWAL M. Effects of sewage sludge amendment on heavy metal accumulation and consequent responses of beta vulgaris plants. Chemosphere. **67**, 2229, **2007**.
38. LI Q., GAO Y. Remediation of Cd-, Pb- and Cu-Contaminated Agricultural Soils by Phosphate Fertilization and Applying Biochar. Pol. J. Environ. Stud. **28**, 2697, **2019**.
39. CAO Q., SONG Y., ZHANG Y., WANG R., LIU J. Risk analysis on heavy metal contamination in sediments of rivers flowing into Nansi Lake. Environ. Sci. Pollut. Res. **24**, 1, **2015**.
40. GAN Y., MIAO Y., WANG L., LI Y., WANG W., DAI J. Source contribution analysis and collaborative assessment of heavy metals in vegetable-growing soils. J. Agric. Food. Chem. **66**, 10943, **2018**.
41. BAHMAN Y., SONA A. Long-term effects of pesticides and chemical fertilizers usage on some soil properties and accumulation of heavy metals in the soil (case study of Moghan plain's (Iran) irrigation and drainage network) Intl. J. Agri. Crop. Sci. **7**, 518, **2014**.
42. GIMENO-GARCIA E., ANDREU V., BOLUDA R. Incidence of heavy metals in the application of inorganic fertilizers to rice farming soils (Valencia, Spain). Fertilizer. Environ. **66**, 491, **1996**.
43. GUO T., LOU C., ZHAI W., TANG X., HASHMI M.Z., MURTAZA R., LI Y., LIU X., XU J. Increased occurrence of heavy metals, antibiotics and resistance genes in surface soil after long-term application of manure. Sci. Total. Environ. **635**, 995, **2018**.