Accumulation, risk assessment and source apportionment of heavy metals in protected cultivation soil, China

Weihong Lu[1], Juan Liu[1], Naiming Zhang[1], Kangwei Hao[2], Hong Yu[2], Jiaqi Li[2], Chang Yu[2], and Kelin Hu[3]

[1]Yunnan Agricultural University
[2]Yunnan Province Soil Fertilization and Pollution Remediation Engineering Laboratory
[3]China Agricultural University

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Abstract

The problem of soil heavy metals (HMs) accumulation from protected cultivation (PC) needs an urgent solution. 132 soil samples from typically high-density PC areas were analyzed for accumulation, risk, and sources of 8 HMs in 16 cities of 8 provinces, China. The soil HMs accumulation characteristics were prominent; Cu, Zn, Pb, Cd, As over-standard (GB 15618-2016) rates reached 15.2, 4.5, 3.0, 27.3, and 2.3%, respectively. The single-factor pollution index indicates that Cd reached slightly contaminated levels in the whole area, while Cu was at a slightly contaminated level only in Yunnan Province. The Nemeiro comprehensive pollution index and the comprehensive quality index suggested that HMs accumulation were at the slightly contaminated levels, with Yunnan province being the most affected and Henan followed. Cu and Zn accumulations are mainly related to frequent input of organic fertilizer, especially livestock manure's direct return to the field. Therefore, Cu and Zn showed a strong correlation (P¡0.01) with soil organic material (SOM), and their available amounts linearly correlated with the extension of planting years in PC. On the contrary, Pb and Cd amounts are only related (P¡0.01) to soil texture, and their main sources are related to the parent material of soil formation. Moreover, their available amounts did not correlate with the planting years. Our results suggest that long-term and unreasonable PC may lead to soil HMs accumulation. Therefore, appropriate agricultural materials, planting systems, and fertilization methods must be used to effectively avoid the risk of excessive HMs accumulation in the PC soils.

Highlight:

(1) Protected cultivation (PC) soil HMs over-standard rates are prominent in China.

(2) Overall PC area is slightly contaminated, Yunnan and Henan are more harshly affected.

(3) Cu and Zn accumulation is derived from anthropogenic agricultural activities.

(4) Pb, Cd, and As accumulation is derived from the soil parent material.

(5) Available Cu, Zn, As amounts showed a linear correlation with planting years.

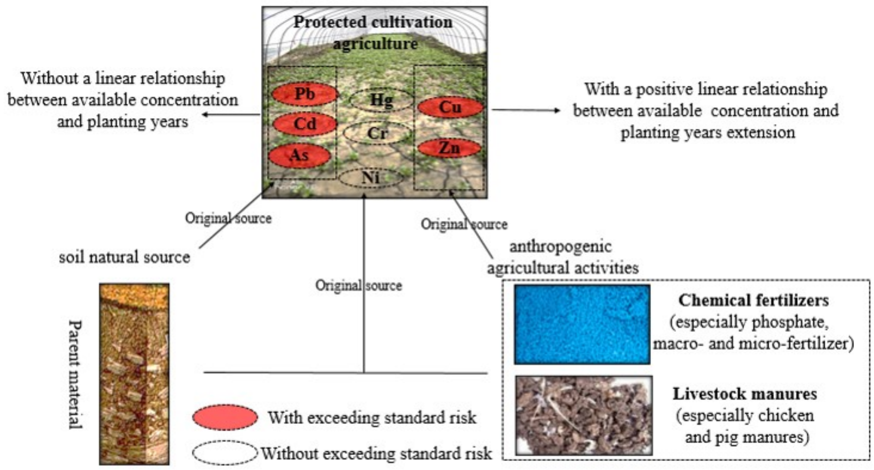

Fig. Graphical abstract

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Weihong Lu [a, b, 1], Juan Liu [a, b, 1], Naiming Zhang [b, c, *], Kangwei Hao[b, c], Hong Yu [b, c], Jiaqi Li[b,c], Chang Yu [b, c], Kelin Hu[d]

[a] College of Plant Protection, Yunnan Agricultural University, Kunming 650201, China

[b] Yunnan Province Soil Fertilization and Pollution Remediation Engineering Laboratory, Kunming 650201, China

[c] College of Resource and Environment, Yunnan Agricultural University, Kunming 650201, China

[d] College of Soil and Water Sciences, China Agricultural University, Beijing, 100193, China

[1] Weihong Lu and Juan Liu as Co-first author

[*] Corresponding author: Naiming Zhang

Correspondence address: College of Resource and Environment Science, Yunnan Agricultural University, Kunming 650201, China

Tel: +86-871-65229840

E-mail: soilenvironment@163.com

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On the contrary, Pb and Cd amounts are only related (P¡0.01) to soil texture, and their main sources are related to the parent material of soil formation. Moreover, their available amounts did not correlate with the planting years. Our results suggest that long-term and unreasonable PC may lead to soil HMs accumulation. Therefore, appropriate agricultural materials, planting systems, and fertilization methods must be used to effectively avoid the risk of excessive HMs accumulation in the PC soils.

Key words: Protected cultivation soil; Heavy metals; Accumulation characteristics; Risk assessment; Planting years

1 Introduction

Protected cultivation (PC), a symbol of agricultural modernization, is the future direction for agricultural development (Balliu et al., 2016; Guo et al., 2012). To ensure healthy and sustainable development, soil quality is an important requirement for PC. In the past few decades, several developed countries, including the United States, Netherlands, Israel, and Japan, have taken a large lead in PC (Sun et al., 2019). This involved constructing large-scale multi-span greenhouses and advanced soilless cultivation techniques such as hydroponic cultivation, rock wool cultivation, and substrate cultivation (Katsoulas et al., 2007). Since the 1980s, PC is also rapidly growing in China with an increasing cultivated area of $4.0\times10^{6}hm^{2}$ (Jensen et al., 2002; Lu et al., 2020). Moreover, China has emerged as the world's largest producer, consumer, and exporter of vegetables with an export trade of 1.55×10^{10} dollars in 2017 (Xu et al., 2019). However, PC in China mainly relies on arable land soil transformed from the extensive field planting pattern lacking precise experience. To pursue high yields, over-applying pesticides, chemical, and organic (especially livestock and poultry manures) fertilizers has become common agricultural intensification activity (Verma, 2015). Moreover, long-term continuous cropping of single crops and high multiple cropping index are reducing soil quality in PC, such as acidification (Guo et al., 2010), salinization, nutrient imbalance, pollutants accumulation, and soil-borne diseases (Tang et al., 2021). These may also cause agricultural non-point source pollution (Huang et al., 2021), which may severely restrict the sustainable development of PC in China, especially in HMs (heavy metals) accumulation regions (Li et al., 2021; Gil et al., 2018).

Anthropogenic activities can severely impede PC. Studies showed that the risk of soil HMs enrichment is higher in PC than that in the open-air cultivation fields (Ramos-Miras et al., 2011; Tian et al., 2016). Apart from high water, fertilizer, and pesticide inputs, PC has the characteristics of high rotation frequency and surface evaporation. In PC, the soil and certain crops are more likely to accumulate HMs than the traditional fields, which may pose a higher risk to the ecological environment and human health (Hu et al., 2017). Studies showed that PC soils are relatively more enriched in copper (Cu), zinc (Zn), lead (Pb), cadmium (Cd), arsenic (As), mercury (Hg), nickel (Ni), and chromium (Cr); and, the trend aggravates with the extension of planting years (Jia et al., 2020). For instance, PC soil samples of Wuhan showed a higher enrichment of As, Cd, Ni, and Pb with the increasing planting years; after 10-15 planting years, Cd, Cr, Cu, Pb, and Zn reached the highest amounts (Wang et al., 2020). Organic fertilizer, especially the livestock and poultry manure, is one of the main inputs in PC; the required amount can reach up to 75000 $kg\cdot ha^{-1}$(air-dried weight). , the total annual production of livestock manure in China exceeded 2.235×10^{9} t in 2010 (Geng et al., 2013). In poultry/livestock breeding, feed additives containing Cu, Zn, and other elements are widely used for disease resistance and/or growth stimulation (Sager, 2007). In Huanghuaihai, the middle and lower reaches of the Yangtze River and the south region mainly use pig and livestock manures for PC with a field return rate of ˜50% (Liu et al., 2018). A survey of commercial organic fertilizers and livestock manures (Huang et al., 2017) showed that commercial chicken manures exceeded the standard (NY 525-2012) for Cd, Pb, and Cr by 10.3, 17.2, and 17.2%; the commercial pig manure exceeded the standard for Cd and As by 20.0 and 6.7%; the chicken and pig manures exceeded the standard for As by 7.1 and 15.4%, respectively. In the 1990s, most chicken and pig manures exceeded Cu and Zn by 1.5-16.2 and 1.3-4.7 times respectively. Cu and Zn concentrations reached up to 208.6 and 776.8 $mg\cdot kg^{-1}$ in the chicken manure, and 140.8 and 592.8 $mg\cdot kg^{-1}$ in the pig manure, respectively.

In China, extensive management has advanced PC exponentially, which has certainly raised alarms for soil quality degradation. Therefore, for risk assessment, it is critical to examine the HMs accumulation in the

PC soils. Regrettably, most previous studies only focused on field cultivation rather than on PC or the local area rather than the overall situation. This study systematically surveyed the soils in 16 cities of 8 provinces in China for the accumulation of Cu, Zn, Pb, Cd, As, Hg, Cr, and Ni in the largest PC area. Apart from risk characteristics and sources, we also evaluated the relationship between HMs accumulation and the planting years of PC. This study can provide scientific insights for harmless PC.

2 Materials and method

2.1 Soil sample collection and preparation

In China, the main PC area includes the northeast temperate zone (~4.0%), northwest temperate arid and Qinghai-Tibet alpine zones (~10.7%), Huanghuaihai and Bohai Rim warm temperature zones (~50.7%), and subtropical rainy area in Yangtze River Basin (~23.6%). Covering the four major PC areas in China, from May to November 2019, we collected 132 soil samples from Liaoning province (including Tieling city, Shenyang city, and Jinzhou city), Shaanxi province (including Yan/an city and Xianyang city), Ningxia Autonomous Region (including Yinchuan city and Wuzhong city), Hebei province (including Cangzhou city and Baoding city), Shandong province (including Liaocheng city and Weifang city), Henan province (including Xinxiang city), Jiangsu province (including Nantong city), and Yunnan province (including Kunming city, Honghe prefecture and Chuxiong prefecture), respectively. The specific sampling area information is shown in Fig. 1.

The soil samples were collected from a depth of 0-20 cm in the greenhouses of 0 (open-air cultivation), 1-5, 6-10, and >10 years of PC using the S-shaped 5-point sampling method. The soil samples were evenly mixed and then packed in marked kraft bags to transport to the Yunnan Soil Fertilization and Pollution Remediation Engineering Laboratory in Yunnan Agricultural University. The samples were freed from impurities, naturally air-dried, ground, and passed through 2.0, 1.0, and 0.149-mm nylon sieves. The final samples were tested following the 4-point method.

2.2 Soil analysis

To estimate soil HMs concentration, the soil samples were digested with concentrated nitric acid-hydrochloric acid (1:1, v/v) according to the National Standards GB/T 22105.1-2008 and GB/T 2205.2-2008 (General Administration of Quality Inspection and Quarantine Supervision of the People's Republic of China, et al., 2008a, 2008b) and Industry Standards NY/T 1613-2008 (Ministry of Agriculture of the People's Republic of China, 2008) of the People's Republic of China. Cu, Zn, Ni, and Cr amounts were determined by flame atomic absorption spectroscopy (FAAS, PerkinElmer 900H, PerkinElmer, Akron, OH, U.S.A.); Pb and Cd amounts were estimated by graphite furnace atomic absorption spectroscopy (GFAAS, PerkinElmer 900H, PerkinElmer, Akron, OH, U.S.A.); As and Hg amounts were determined by atomic fluorescence spectroscopy (AFS-933, Titan Instrument, Beijing, China). The bioavailable Cu, Zn, Pb, and Cd, extracted with Diethylenetriaminepentaacetic acid (DTPA) buffered solution, were determined by Inductively coupled plasma optical emission spectrometry (ICP-OES iCAP7400) according to National Environmental Protection Standards of the People's Republic of China (State Environmental Protection Administration, 2016). The bioavailable As, extracted with sodium dihydrogen phosphate-buffered solution, was determined by atomic fluorescence spectroscopy. Two certified reference soils (GBW07413a and GBW07451) from the National Research Center for Certified Reference Materials of China were used for quality control. Concentrations of reference materials were within the certified ranges, and the average recoveries for soil Cu, Zn, Pb, Cd, As, Hg, Cr, and Ni were 94.6, 103, 98.2, 93.5, 90.5, 95.7, 108, and 93.5%, respectively.

The main soil physicochemical indicators such as texture (including sand, clay, powder), pH, organic matter (SOM), and cation exchange capacity (CEC) were determined. The particle size distribution of the soil was determined by a laser particle size analyzer (BT-9300HT, Dandong Bettersize Instruments Ltd., China) using water as the medium. Soil pH was measured by a glass electrode (PHSJ-3F, Shanghai Instrument Instruments Co. Ltd., China) in a 1:2.5 soil/water (w/v) suspension. SOM was determined using the $K_2Cr_2O_7$-H_2SO_4oxidation method (Bao, 2000). Extracted CEC was determined using the ammonium acetate method (Lu, 2000).

2.3 Risk assessment of soil HMs accumulation

1) Single-factor pollution index (SFPI)

The SFPI signifies the cumulative risk characteristics of soil elements (Cheng et al., 2007; Yu et al., 2016). It is the ratio of the determined concentration of soil HMs to the corresponding limit in the standard GB 15618-2018 (Ministry of Ecology and Environment of China, 2019). This can be calculated as follows:

$$P_i = \frac{C_{si}}{C_{st}}$$

(1)

where P_i is the SFPI of a certain HM;C_{si} is the determined concentration of the respective HM, mg·kg^{-1}; C_{st} is the permitted limit of the respective HM in the soil, mg·kg^{-1}.

2) Nemeiro comprehensive pollution index (NCPI)

The NCPI considers the average and the highest value of the SFPI to highlight the impact (pollution risk rate) of the highest contributing pollutant on the environmental quality of farmland soil (Duan et al., 2021). It can be calculated as follows:

$$P_{nc} = \sqrt{\frac{\left(\frac{1}{n}\sum_{i=1}^{n} P_i\right)^2 + \left(P_{i,max}\right)^2}{2}}$$

(2)

where P_{nc} is the NCPI of soil HMs;$P_{i,\ max}$ is the maximum SFPI of certain HM in the soil; n is the number of soil HMs determined; evaluation: the standard classification of P_{nc} is the same as the SFPI.

3) Impact index of comprehensive quality (*IICQ*)

The *IICQ* takes into account multiple evaluation indicators such as "soil geological background value", "pollutant limit value", "HM ion impulse-valence effect" and other evaluation indicators, eliminating the defects of the traditional "soil standard management method" (Wilson et al., 2010; Wang et al., 2016). It is more objective to evaluate the cumulative risk of HMs in farmland soil, which can be calculated as follows:

$$RIE = \frac{\left[\sum_{i=1}^{n} (P_i)^{\frac{1}{m}}\right]}{n}$$

(3)

$$DDDB = \frac{\left[\sum_{i=1}^{n} (P_{bi})^{\frac{1}{m}}\right]}{n} = \frac{\left[\sum_{i=1}^{n} \left(\frac{C_i}{C_{bi}}\right)^{\frac{1}{m}}\right]}{n}$$

(4)

$$DDTB = \sum_{i=1}^{n} \left(\frac{C_{st}}{C_{bi}}\right)^{\frac{1}{m}}$$

(5)

In formula (2) (3) (4), RIE is the relative impact equivalent of soil; m is the stable oxidation value of element i (Cu: 2; Zn: 2; Pb 2; Cd: 2; As: 5; Hg: 2; Cr: 3, and Ni: 2) (Wang et al., 2016);$DDDB$ is the deviation degree between the detected and background values; P_{bi} is the determined concentration of element i that exceeds the geological background concentration in the soil; C_{bi} is the geological background concentration of element i .

2.4 Data and statistical analysis

The normal distribution of the HMs concentrations in soils was examined by the one-sample Kolmogorov-Smirnov test. Data were processed with Microsoft Excel 2016. Principal component factor and Pearson correlation analysis were performed with SPSS 18.0 software. One-way variance and least significant difference (LSD) were employed to find data significance. Linear correlation results were plotted with Origin Pro 9.1 (64 Bit) program.

3 Results and discussion

3.1 Soil HMs contents

The respective HM (Cu, Zn, Pb, Cd, As, Hg, Cr, and Ni) concentration in PC topsoil (0-20 cm) is presented in Table 1. Compared with the soil environmental background values in various provinces and the national standard, the amounts of 8 HMs were increased to varying degrees; the increase was more prominent for

Cu, Zn, Pb, Cd, and Hg. In the whole area, soil amounts of Cu, Zn, Pb, and Cd were 2.09, 1.56, 1.21, 4.70, and 1.06 times higher than the national background value, respectively. Cr and Ni were 1.13 and 1.15 times higher, respectively. The corresponding soil samples in provinces showed a similar trend. In Liaoning province, the greenhouse soil concentration of Cu, Zn, Pb, Cd, and Hg reached up to 1.87, 1.77, 1.10, 1.82, and 1.65 times the background value, respectively. Likewise, compared to the background value, in Hebei province, Cu, Zn, Pb, Cd, and Hg were higher by 1.07, 1.40, 1.03, 2.44, and 0.89 times; in Shandong province, the increase was 1.18, 1.95, 0.76, 3.38, and 2.10 times; In Henan province, the increase was 3.33, 2.78, 1.26, 8.28, and 1.82 times; in Shaanxi province, the increase was 1.24, 1.26, 1.04, 1.69, and 6.92 times; in Ningxia Autonomous Region, the increase was 1.14, 1.39, 0.84, 1.55, and 1.57 times; in Jiangsu province, the increase was 0.77, 1.26, 0.76, 0.92, and 1.85 times, and in Yunnan Province, the increase was 2.30, 1.57, 1.73, 5.82, 2.16 times, respectively.

Based on GB15618-2018 standard and the distribution point exceeding the rate of soil HMs, Cd (27.3%) was critically above the over-standard rate, followed by Cu (15.2%), Zn (4.5%), Pb (3.0%), and As (2.3%), while Hg and Cr were within the over-standard rates. The over-standard rate of the 8 HMs in greenhouse soil from respective provinces also showed higher levels of Cd. Yunnan province was most significantly affected (84.0%) followed by Henan (50.0%), Liaoning (16.7%), Shandong (11.8%), and Hebei (6.7%) provinces, respectively. Shaanxi province, Ningxia Autonomous Region, and Jiangsu province had Cd within the standard range. In general, Yunnan province was most significantly affected; apart from Cd, the over-standard rates of Cu, Zn, Pb, As and Ni reached 64.0, 4.0, 16.0, 12.0, and 8.0%, respectively. Next was Henan province with 25.0% over-standard rates for Cu and Zn. Studies showed that HMs enrichment occurs under low pH conditions, mobility, and biological activity (Lu et al., 2020). Notably, PC soil pH and in general soil pH of the whole area was 0.8 units higher than the average background value in China. This can be attributed to soil conditioners or remediation agents used in PC (Hamid et al., 2019; Lebrun et al., 2020; Wu et al., 2016). However, some areas, such as Liaoning, Henan, and Jiangsu, showed acidification characteristics, which could promote soil HMs exposure to the food chain causing health risks.

3.2 Risk assessment of soil HMs

Next, we calculated the SFPI, NCPI (P_{nc}), and soil comprehensive quality index (IICQ) to evaluate the cumulative risk of HMs in PC soil in the whole area. The results are shown in Figure 1. We found that the whole area average P_{nc} and IICQ reached up to 1.03 and 1.71, suggesting a slightly contaminated level. Cd contributed the largest; the average P_{Cd} was 1.25 at a slightly contaminated level. The remaining 7 HMs were within the safe limits.

Among the different test regions, the pollution risks are more serious in Henan and Yunnan provinces. Yunnan province is at the highest cumulative risk with the NCPI (P_{nc} average 2.92) reaching to moderately contaminated level and$IICQ_s$ (average 6.04) reaching the extremely contaminated level. Cd (P_{Cd} average 3.71) and Cu (P_{Cu} average 1.52) contributed most with the average SFPI (P_i) at the heavily and slightly contaminated levels, respectively. The average NCPI (P_{nc} 1.23) and $\mathrm{IICQ_s}$ (2.10) respectively suggested that Henan Province is at slightly and moderately contaminated levels. Here too, Cd contributed the highest with the SFPI (P_{Cd} 1.60) at a slightly contaminated level. Meanwhile, the PC soils in the remaining 6 provinces are at the uncontaminated or safe level.

Excessive soil HMs accumulation, with concerns of phytotoxicity and risk to human health via the food chain, has become one of the prime environmental issues worldwide (Ye et al., 2020; Corguinha et al., 2015; Zhang et al., 2018). Cd is considered redundant for metabolism and other biological function and has been listed in the top 20 hazardous substances by the United States Environmental Protection Agency and the Agency for Toxic Substances and Disease Registry (ATSDR) (Rai et al., 2019; Khalid et al., 2017). On the contrary, although Cu is relatively low-toxic, excessive Cu concentrations may pose a serious health risk, such as liver and kidney damage.

3.3 Sources of soil HMs

Principal component analysis (PCA), a classic multivariate statistical method is popularly used to identify the natural and anthropogenic sources of soil HMs (Chen et al., 2019). Kaiser-Meyer-Olkin (KMO) and Bartlett tests were performed to analyze the concentration data of HMs. The KMO value at 0.76 >0.5 (P <0.05) suggested that the data was suitable for PCA analysis. Based on the principal component analysis, Kaiser standardized orthogonal rotation method, and the maximum variance method, the factor loading matrix was orthogonally rotated. The cumulative contribution rate (76.78%) of the variance of the soil HMs concentration eigenvalues, principal factor 1 (PF1), and principal factor 2 (PF2) with eigenvalues >1 explain the sources of HMs in the PC soil (Table 2). The variance contribution rate of PF1 was 44.35%, and the PF1 factor loadings for Pb, Cd, and As were 0.894, 0.840, and 0.924, respectively. The variance contribution rate of PF2 was 32.43%, and the factor loadings for Cu and Zn were 0.930 and 0.713, respectively. The other three elements, Hg, Cr, and Ni were mainly affected by PF1 and PF2, with factor loadings for Hg reaching 0.756 and 0.433, Cr 0.417 and 0.625, and Ni 0.626 and 0.656, respectively.

Next, we analyzed the Pearson correlation (Table 3) between the HMs concentration and physiochemical indicators (the proportion of sand, powder, clay, soil pH, SOM, and CEC). We found that Cu and Zn showed a significant correlation (R =0.547, P ¡0.05) with 6 soil physiochemical indices (P ¡0.01). The correlation coefficient (R -value) between Cu concentration and soil organic matter (SOM) reached 0.482, and between Zn concentration and SOM reached 0.453, respectively. These indicated that soil Cu and Zn concentrations were strongly correlated to SOM. Notably, SOM in the PC soil mainly originates from the return of crop residues and organic fertilizer. Furthermore, PF1 can be attributed to chemical fertilizer, organic fertilizer, and other anthropogenic activities (Geng W et al., 2013; Sager, 2007; Liu et al., 2018; Huang et al., 2017). Soil Pb, Cd, and As exhibited a very significant correlation with soil physical indicators (the proportion of sand, powder, and clay) (P <0.01), but not with soil chemical indicators (pH, SOM, CEC) (P>0.05). This suggests that Pb, Cd, and As are mainly from soil geological backgrounds, such as soil parent material and the PF2 can be attributed to soil parent material and other natural factors (Yang et al., 2020). Some studies showed that livestock manure and chemical fertilizers (especially phosphate fertilizers) can be a source of Pb, Cd, and As (Luo et al., 2009); however, compared with the geological background source factor, the contribution of fertilization was found minimal for Pb, Cd, and As soil contamination in PC. Moreover, Hg, Cr, and Ni contents in PC soils were found affected by anthropogenic agricultural activities and natural factors such as soil parent material.

3.4 Relationship between the soil HMs contents and planting year

HMs have an obvious cumulative effect in the PC soil; the over-standard GB15618-2018 rates of Cu, Zn, Pb, Cd, and As exceeded 2%. Specifically, in the study area, the accumulation of Cu and Cd is at serious environmental risk. Several studies suggest that the available soil concentration is the bioavailable part of the total HMs concentration (Fang et al., 2018; Xia et al., 2016; Wang et al., 2020). Excessive bioavailable HMs in the soil get easily absorbed into the food chain (crops) or leached by irrigation water as agricultural non-point source pollution (Natasha et al., 2021). To further understand the relationship between the available concentration of five HMs (Cu, Zn, Pb, Cd, and As) and the planting years in PC, we did a correlation analysis (Fig. 2). We found that the available Cu (Fig. 2 a), Zn (Fig. 2 b), and As (Fig. 2 e) exhibited a significant (P <0.05) linear correlation with the planting years, while the available Cd (Fig. 2 c) and Pb (Fig. 2 d) did not (P >0.05). This further indicates that Cu and Zn are mainly derived from frequent anthropogenic agricultural activities, and the cumulative effect and potential cumulative risk increase with the extension of planting years in PC. Likewise, available As showed a significant linear relationship (Fig. 2 e) with the planting years; however, the main source of As is the soil parent material. This suggests that frequent anthropogenic agricultural activities in the PC can increase total As conversion into available As (Antoniadis et al., 2019). Available Pb and Cd did not correlate with the extension of planting years, indicating a minor contribution of anthropogenic agricultural activities compared to soil geological background value.

4 Conclusion

We systematically examined the accumulation, risk, source, and the relationship between available concentration and planting year of 8 HMs in typical PC soils from 16 cities of 8 provinces, China. In the current PC soils, HMs showed different degrees of accumulation characteristics, especially Cu, Zn, Pb, Cd, As exceeding rate reached 15.2, 4.5, 3.0, 27.3, and 2.3%, respectively. The SFPI of Cd suggested slight Cd contamination in the whole area, while Cu reached the slightly contaminated level only in Yunnan Province. Both the NCPI and IICQ indicated that PC soil was slightly contaminated in the whole area, while Yunnan and Henan provinces were severely affected. Cu and Zn accumulation was mainly related to frequent anthropogenic agricultural activities and showed a strong correlation with SOM. Also, available Cu and Zn showed a significant linear correlation with the planting years in PC. However, Pb and Cd were only significantly related to soil texture that could be the main source of soil-forming parent material, while their available state did not correlate with the planting years. We suggest that reasonable selection of agricultural materials and scientific planting systems in PC can be effective strategies to avoid the risk of excessive soil HMs accumulation, delay soil quality degradation, and reduce agricultural non-point source pollution to ensure healthy and efficient PC for sustained development.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Table 1. Accumulation characteristics of HMs in PC soils in various regions (Unit: mg*kg^{-1})

Area	Item	Cu	Zn	Pb	Cd	As	Hg	Cr	Ni
Liaoning province (n=12)	Average	37.1	112.6	23.6	0.20	6.8	0.061	51.9	21.7
	Maximum	68.6	190.4	31.6	0.42	9.3	0.145	74.3	27.4
	Minimum	13.6	48.5	17.9	0.08	3.5	0.018	40.0	12.9
	Background	19.8	63.5	21.4	0.11	8.8	0.037	57.9	25.6
Hebei province (n=15)	Average	23.4	110.0	22.1	0.22	9.5	0.032	62.5	26.3
	Maximum	32.1	152.2	27.1	0.35	13.8	0.055	85.6	33.4
	Minimum	16.4	60.5	17.8	0.11	6.3	0.016	49.3	19.4
	Background	21.8	78.4	21.5	0.09	13.6	0.036	68.3	30.8
Shandong province (n=17)	Average	28.4	123.9	19.6	0.27	7.5	0.040	67.3	30.7
	Maximum	57.8	272.4	23.9	0.57	10.2	0.070	134.2	47.8
	Minimum	17.8	60.1	16.8	0.18	4.4	0.020	47.8	23.1
	Background	24.0	63.5	25.8	0.08	9.3	0.019	66.0	25.8
Henan province (n=16)	Average	65.6	167.3	24.6	0.58	11.1	0.062	54.3	25.9
	Maximum	128.1	273.8	32.2	1.22	14.9	0.143	66.6	32.8
	Minimum	16.6	65.0	17.6	0.21	9.2	0.017	47.0	21.1
	Background	19.7	60.1	19.6	0.07	11.4	0.034	63.8	26.7
Shaanxi province (n=18)	Average	26.6	87.4	22.2	0.22	12.6	0.090	76.5	30.1
	Maximum	50.6	119.8	32.6	0.48	16.2	0.267	291.5	54.9
	Minimum	16.8	61.2	17.6	0.13	9.6	0.013	51.6	24.3
	Background	21.4	69.4	21.4	0.09	11.1	0.030	62.5	28.8
Ningxia Autonomous Region (n=11)	Average	25.2	81.7	17.4	0.17	9.4	0.033	46.2	22.2

Area	Item	Cu	Zn	Pb	Cd	As	Hg	Cr	Ni
	Maximum	53.1	169.0	21.5	0.49	14.9	0.179	55.6	27.6
	Minimum	13.8	45.1	14.1	0.08	4.8	0.007	30.6	14.6
	Background	22.1	58.8	20.6	0.11	11.9	0.021	60.0	36.5
Jiangsu province (n=12)	Average	17.2	78.7	19.9	0.12	7.1	0.050	61.7	26.4
	Maximum	21.5	100.7	22.3	0.20	8.9	0.085	71.6	31.5
	Minimum	14.1	70.1	18.2	0.08	5.2	0.027	55.1	21.8
	Background	22.3	62.5	26.2	0.13	10.0	0.029	77.8	26.7
Yunnan province (n=25)	Average	106.6	140.5	70.2	1.28	10.7	0.125	98.3	48.2
	Maximum	202.2	250.8	322.1	6.67	45.6	0.376	163.9	101.1
	Minimum	26.4	70.0	18.6	0.31	1.7	0.019	52.2	22.9
	Background	46.3	89.7	40.6	0.22	18.4	0.058	65.2	42.5
Whole area (n=132)	Average	47.2	115.6	31.4	0.47	9.6	0.069	68.9	31.0
	Maximum	202.2	273.8	322.1	6.67	45.6	0.376	291.5	101.1
	Minimum	13.6	45.1	14.1	0.08	1.65	0.007	30.6	12.9
	National background value	22.6	74.2	26.0	0.10	11.2	0.065	61.0	26.9
Over standard rate (%)[a]	/	15.2	4.5	3.0	27.3	2.3	0.0	0.0	1.5

Table 2. Orthogonal rotation factor load of MHs in PC soil, China

HMs	PC1	PC2
Cu	0.088	0.930
Zn	0.209	0.713
Pb	0.894	0.327
Cd	0.840	0.322
As	0.924	0.036
Hg	0.756	0.433
Cr	0.417	0.625
Ni	0.626	0.656
Original eigenvalue	4.96	1.19
Variance contribution rate	44.35	32.43
Cumulative contribution rate	44.35	76.78

Table 3 Pearson correlation between HMs concentration and physiochemical indexes in PC soils, China

	Cu	Zn	Pb	Cd	As	Hg	Cr	Ni	pH	SOM	CEC	sandy
Cu	1	0.547*	0.436**	0.453*	0.124	0.442**	0.530**	0.712**	-0.477**	0.482**	0.751**	-0.46
Zn		1	0.563**	0.525**	0.408**	0.527**	0.409**	0.571**	-0.388**	0.453**	0.655**	-0.40
Pb			1	0.883**	0.828**	0.775**	0.503**	0.803**	-0.262**	0.180	0.518**	-0.41
Cd				1	0.768**	0.721**	0.425**	0.688**	-0.108	0.141	0.462**	-0.32
As					1	0.726**	0.394**	0.599**	0.082	0.028	0.291**	-0.40
Hg						1	0.632**	0.701**	-0.217*	0.290**	0.494**	-0.52
Cr							1	0.756**	-0.164	0.195*	0.464**	-0.45
Ni								1	-0.248*	0.253**	0.706**	-0.53
pH									1	-0.511**	-0.446**	0.088
SOM										1	0.681**	-0.21
CEC											1	-0.47
sandy												1
powder												
clay												

Note: *Correlation is significant at P <0.05; ** Correlation is significant at P < 0.01.

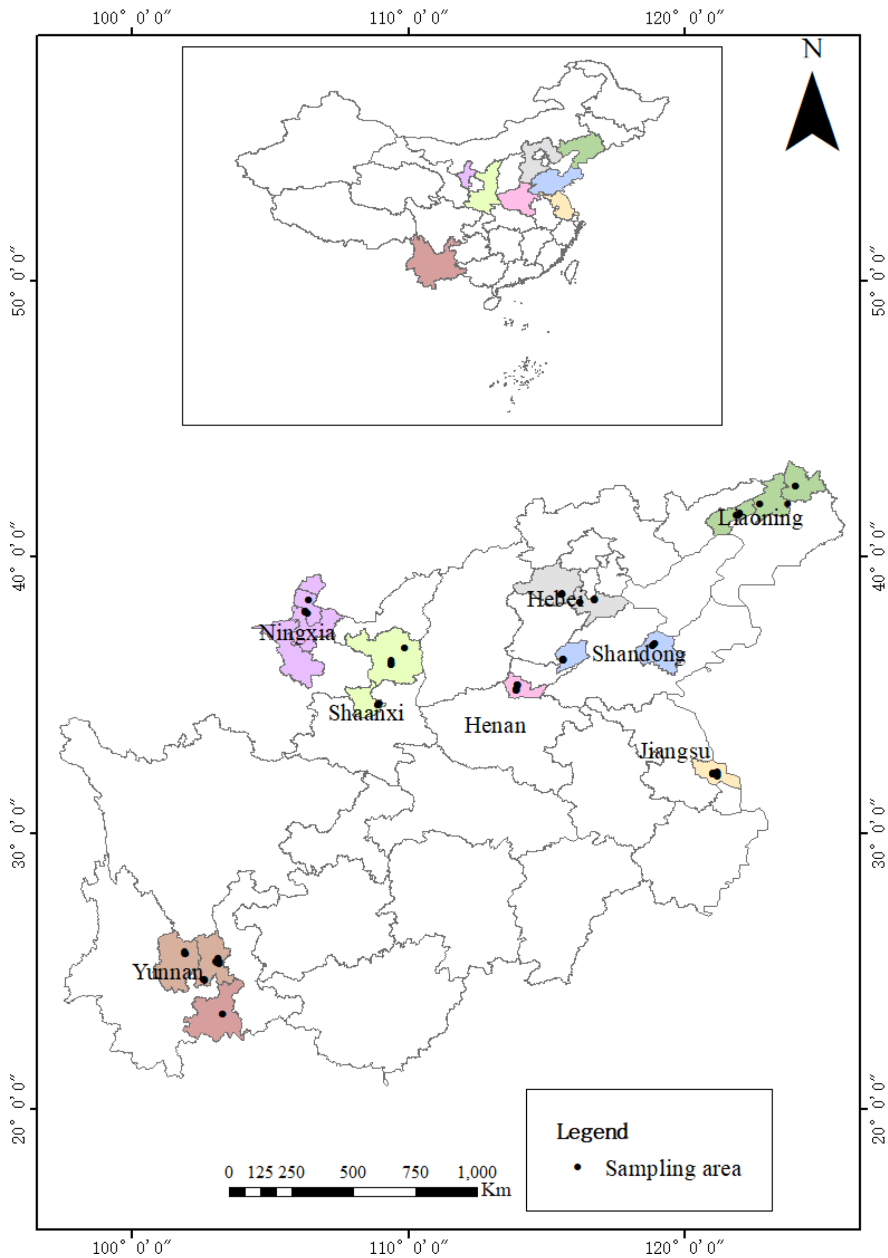

Fig. 1 Map of soil samples collected from protected cultivation areas in China

Fig. 2 Soil HMs contaminated risk characteristics under two different assessment methods

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Fig. 3 Linear relationship between soil available HM concentrations and planting years

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