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RESEARCH ARTICLE

Heavy metal accumulation and source analysis in greenhouse soils of Wuwei District, Gansu Province, China

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Abstract Greenhouse soils and arable (wheat field) soil samples were collected to identify the effects of greenhouse cultivation on the accumulation of six heavy metals (Cd, Cu, Zn, Pb, Cr, and Ni) and to evaluate the likely sources responsible for heavy metal accumulation in the irrigated desert soils of Wuwei District, China. The results indicated that the mean concentrations of Cd, Cu, Zn, Pb, Cr, and Ni were 0.421, 33.85, 85.31, 20.76, 53.12, and 28.59 mg kg^{-1}, respectively. The concentrations of Cd, Cu, and Zn in greenhouse soils were 60, 23, and 14 % higher than those in arable soils and 263, 40, and 25 % higher than background concentrations of natural soils in the study area, respectively. These results indicated that Cd, Cu, and Zn accumulation occurred in the greenhouse soils, and Cd was the most problematically accumulated heavy metal, followed by Cu and Zn. There was a significant positive correlation between the concentrations of Cd, Cu, and Zn in greenhouse soils and the number of years under cultivation ($P<0.05$). Greenhouse cultivation had little impact on the accumulation of Cr, Ni, or Pb. Correlation analysis and principal component analysis suggested that the accumulation of Cd, Cu, and Zn in greenhouse soils resulted mainly from fertilizer applications. Our results indicated that the excessive and long-term use of fertilizers and livestock manures with high heavy metal levels leads to the accumulation of heavy metals in soils. Therefore, rational fertilization programs and reductions in the concentrations of heavy metals in both fertilizers and manure must be recommended to maintain a safe concentration of heavy metals in greenhouse soils.

Keywords Greenhouse soil · Heavy metals · Principal component analysis · Fertilization · Source

Introduction

Greenhouse cultivation plays an important role in the off-season and cross-regional production of vegetables and other important economic crops throughout China. In 1999, greenhouses occupied 1.395 million hm^2; by the end of 2008, greenhouses used for growing vegetables occupied more than 3.3 million hm^2 (Zhang et al. 2011). Greenhouse cultivation is also widely applied in other Asian countries, such as India, Japan, and South Korea. In addition, it is also distributed in Europe and the Mediterranean countries (Serra et al. 1994). Compared with open-field cultivation, productivity in the greenhouse is maintained through chronic intensive agriculture, a high multi-cropping index, and excessive use of fertilizer. These characteristics of greenhouse culture and management of water and fertilizer lead to a series of problems and obstacles to continuous cropping, such as soil secondary salinization, nutrient imbalance, soil acidification, nitrate accumulation, and heavy metal accumulation (Li et al. 2001, Yao et al. 2006, Yu et al. 2010, Liu et al. 2008). Because the concentrations of heavy metals in soil have a direct influence on human health via food production, the problem of heavy metal accumulation in greenhouse soils is increasingly attracting attention (Gao et al. 2007, Rodríguez Martín et al. 2013).

Reducing heavy metal inputs to soil is a strategic aim of soil protection policies in China. However, information on the significance and extent of soil contaminated with heavy metals from different sources is required so that appropriate

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actions can be effectively targeted to reduce the heavy metal inputs to soil. Correlation analysis and principal component analysis (PCA) are widely used to measure the degree of correlation among heavy metal concentrations and to provide suggestive information on heavy metal sources (Romic and Romic 2003, Facchinelli et al. 2001, Rodríguez Martín et al. 2013; Loska and Wiechuła 2003; Martínez et al. 2008).

The irrigated desert soil, a typically cultivated soil of arid inland regions, is distributed in inland river basin and the Yellow River Basin of the desert border region and occupies more than 20 % of the total land area in China (Li et al. 2009). The land area used for greenhouse cultivation in regions with the irrigated desert soils has increased rapidly in recent times due to the conditions of abundant light and heat which are suitable for photosynthesis and nutrient accumulation. Wuwei District represents a typical irrigated desert soil region in China with an area of greenhouse cultivation exceeding 8,000 hm^2 in 2013. Therefore, it is necessary to identify the accumulation status of heavy metals and the key factors that cause heavy metal accumulation in irrigated desert soils in greenhouse cultivation systems. However, research analyzing the source(s) of heavy metal accumulation in greenhouse cultivation has not been widely performed for Gansu Province, China.

The purpose of this study was to evaluate three factors in greenhouse soils from an irrigated desert soils district: first, the accumulation status of heavy metals; second, the relationship between heavy metal concentrations and the number of years under cultivation; and third, the sources responsible for heavy metal accumulation. The results of this study are important for improving the quality of greenhouse soil for ensuring produce meets health and safety guidelines, and for increasing the sustainability of greenhouse cultivation practices.

Materials and methods

Description of the study area

Wuwei District is located between latitudes 37° 23′ and 38° 12′ N and longitudes 101° 59′ and 103° 23′ E in the northwest of Gansu Province, and it is also the east end of the Hexi Corridor and in the north of the Qilian Mountains. The total land area is 5.08×10^5 hm^2 with 1.28×10^5 hm^2 of arable land. The Gansu soil in this study is a calcareous desert soil (sandy clay loam, Typic Anthrosol), which is classified as an “irrigated desert soil” in accordance with the Chinese Soil Classification System (Gansu Provincial Soil Survey Staff 1992) and which approximates to an Anthropic Camborthid soil according to “Keys to Soil Taxonomy” (Soil Survey Staff 1998). Carbonate contents in soils range from 4.5 to 14.6 % in the study area. The parent material consists of alluvial deposits, pedogenic rock including carbonatite, metamorphic fine rocks, and marine volcanic rocks.

Sampling and pretreating

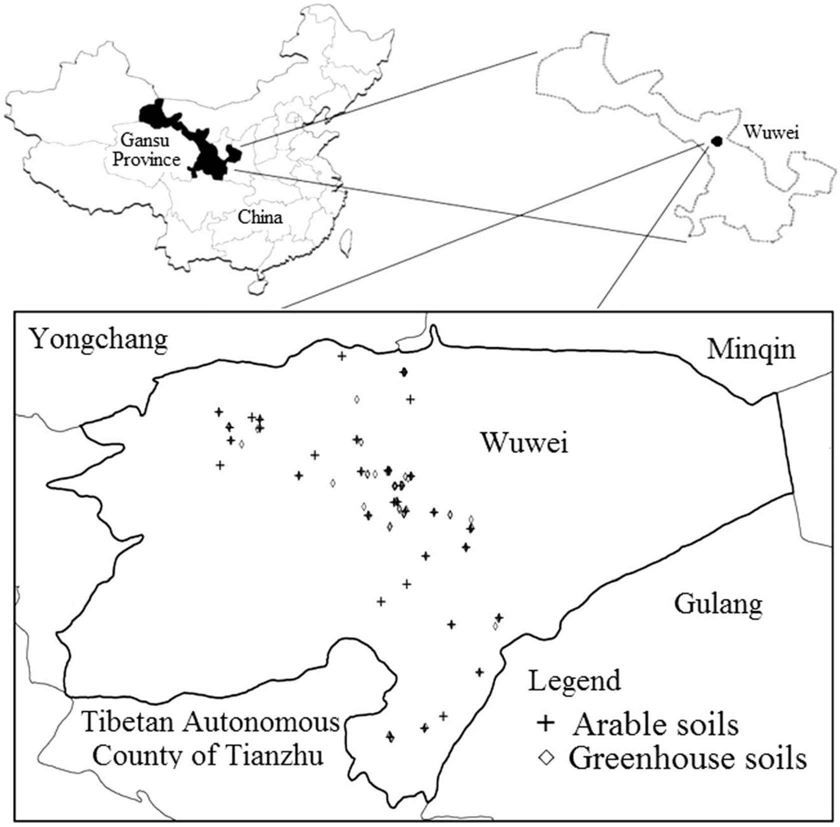
Ninety-seven greenhouses in the study area were selected for sampling. The selected greenhouses were 50–90-m long and 7–7.5-m wide and had been producing vegetables between 1 to 14 years. Surface soil horizons (0–20 cm) were collected from the 97 selected greenhouses (Fig. 1), and 35 samples (0–20 cm) of soil were collected from arable land (wheat field) near the greenhouse (as greenhouse cultivation reference samples) in July 2011 (Fig. 1). Five soil subsamples were taken from each plot using a stainless steel tool and mixed to form one composite sample (approximately 1 kg) for the measurement of Cd, Cu, Zn, Pb, Cr, Ni, and basic edaphic parameters. In addition, four greenhouses that had been used for different numbers of planting years were selected for soil profile sampling to determine the distribution of heavy metal concentrations in profiles of greenhouse soil. For each of these four plots, five subsamples were taken at five different depths (0–20, 20–40, 40–60, 60–80, and 80–100 cm) using an auger and mixed to provide five composite samples. Samples were put in clean polyethylene bags for transporting to the laboratory. All soil samples were air-dried at ambient temperature for about 1 week; large debris, stones, and pebbles were removed, and the samples were sieved through a 2-mm polyethylene sieve. About 200 g of sample was ground into fine particles (<0.074 mm) in an agate mortar awaiting analysis.

To evaluate the heavy metal content in fertilizer and manure applied to greenhouse soil in Wuwei District, 85 samples of common inorganic fertilizers and livestock manures were collected in the study area. These included 53 samples of complex P fertilizers, 4 samples of potassic fertilizer, 9 samples of nitrogenous fertilizer, 13 samples of pig manure, and 6 samples of cattle and sheep manure. Inorganic fertilizer samples were ground into fine particles (<0.074 mm) in an agate mortar. The livestock manure samples were air-dried and milled into fine particles (<1 mm) with stainless steel grinder mill awaiting analysis.

Chemical analysis

A 0.5 g sample of soil, livestock manure, or inorganic fertilizer was digested in 10 ml of ultrapure concentrated nitric acid (HNO_3) and 15–20 ml of hydrogen peroxide (H_2O_2), according to the USEPA 3050B method (EPA, 1994). The concentrations of total Cd, Cu, Zn, Pb, Cr, and Ni in the digested solutions were determined by inductively coupled plasma mass spectrometry (ICP-MS PQ-ExCell, TJA Solutions, USA). Detection limits for Cd, Zn, Cu, Pb, Cr, and Ni were 2, 15, 4, 3, 5, and 2 ng g^{-1}, respectively. The total Al and K concentrations in the soil samples were determined by digesting 0.25 g subsamples with four kinds of acid (HCl, HNO_3, $HClO_4$, and HF) and analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Optima

Fig. 1 Distribution of sampling sites



5300DV, PerkinElmer, USA). Total phosphorus content was determined by colorimetry with a molybdenum blue reagent after extraction with NaOH. Soil organic matter (SOM) was determined using the potassium dichromate volumetric method. Soil pH was measured in a soil-to-water suspension (1:2.5, *w*/*v*) using a pH meter (Bao 2007). Ultrapure grade acids were used for digestion, and the other reagents used were of analytical grade. All glassware and plastic ware used were soaked overnight in a 10 % HNO_3 solution (*v*/*v*) and then rinsed three times with ultrapure water prior to use. Soil standard reference materials GSS-1, GSS-4 obtained from the Center of National Standard Reference Material of China (QA/QC), and reagent blanks were prepared and analyzed with the same procedure and reagents for assessing the quality of the applied methodology. Two replicates were analyzed per sample to evaluate the precision of the results. Recovery percentages of the analytes were as follows: Cd (95–105 %), Cu (93–102 %), Zn (95–104), Pb (88–93 %), Cr (87–94 %), and Ni (90–95 %); these values were within the acceptable range specified for the USEPA 3050B method. The concentrations of heavy metals Cd, Cu, Zn, Pb, Cr, and Ni were present as milligrams per kilogram dry matter.

Data analysis

Data analysis was performed by using Microsoft Office Excel 2003 and SPSS 16.0 statistical software. The sampling map was charted by ArcGIS 9.0 software. Correlation analysis was used to determine the relationships among different heavy metals in this study. The relationships between concentrations of the investigated heavy metals and selected basic edaphic parameters such as SOM, total phosphorus (P), total potassium (K), and aluminum (Al_2O_3, main constituents of geogenic and pedogenic material) were examined. PCA also was used with the aim of identifying associations and common origins among metals in this study. PCA was performed with varimax rotation, a procedure that facilitates the interpretation of the results by minimizing the number of variables with a high loading on each component. Variables were considered to identify source categories only if their factor loadings were >0.5 (absolute value). Results from PCA were interpreted according to the hypothetical sources of chemical elements (Peris et al., 2008, Zhou et al. 2014, Kelepertzis 2014; Lu et al., 2012)

Results and discussion

Heavy metal concentrations in greenhouse soils

Table 1 presents descriptive statistics of the heavy metal concentrations in greenhouse soils and arable soils of Wuwei District. The mean concentrations of Cd, Cu, Zn, Pb, Cr, and Ni in the greenhouse soils were 0.421, 33.85, 85.31, 20.76, 53.12, and 28.59 mg kg^{-1}, respectively. Compared with open-field cultivation (arable soils: Cd, 0.261; Cu, 27.36; Zn, 74.23; Pb, 20.48; Cr, 54.18; and Ni, 30.50 mg kg^{-1}), the concentrations of Cd, Cu, and Zn in the greenhouse soils were 60, 23, and 14 %, respectively, higher than those in arable soils. The concentrations of Pb, Cr, and Ni in the greenhouse soils did not exceed the concentrations of arable soils. Compared with corresponding natural background concentration of heavy metals in Gansu (Cd, 0.116; Cu, 24.10; Zn, 68.50; Pb, 18.80; Cr, 70.20; and Ni, 35.20 mg kg^{-1}; China National Environmental Monitoring Centre, 1990), the concentrations of Cd, Cu, Zn, and Pb in the greenhouse soils increased by 263, 40, 25, and 10 %, respectively. The concentrations of Cr and Ni in the greenhouse soils did not exceed the concentrations in the background soils. These results indicated that greenhouse cultivation had a significant effect on the concentrations of Cd, Cu, and Zn in irrigated desert soil of China, while having no significant impact on the accumulation of Cr, Ni, or Pb. Compared with the Chinese Soil Quality Criterion (threshold values for agricultural soil) established by the State Environmental Protection Administration of China (GB 15618-1995, Table 1), the mean concentrations of heavy metals in greenhouse soils were lower than the threshold values for agricultural soil. However, the concentration of Cd in 15 greenhouse soil samples were higher than threshold values of 0.6 mg kg^{-1} (soil pH>7.5), which accounted for nearly 15 % of all greenhouse samples. No arable soil sample had Cd concentrations that exceeded the GB 15618-1995 threshold values. For the heavy metals other than Cd, none of the greenhouse soil samples had concentrations that exceeded GB 15618-1995 threshold values. These results led us to conclude that researchers, producers, and regulators need to pay more attention on Cd accumulation in greenhouse soils.

Compared with prevision studies conducted in Spain (Table 2), the mean concentrations of Cd, Zn, Pb, and Ni in the greenhouse soils from Wuwei were much lower than those in Spain. While Cu and Cr were higher than the corresponding values determined in previous studies (Rodríguez Martín et al. 2013, Gil et al. 2004). However, there are rather few data sets of heavy metal content in greenhouse soil that can be used for comparison among countries. Compared with prevision studies in China (Table 2), the mean Cd concentration was similar to values measured in Siping and Yunnan, but was higher than values measured in Lanzhou, Shandong, and Jiangsu (Shi and Zhang 2010, Bai et al. 2010, Qin et al. 2013, Yang et al. 2014, Liu et al. 2008). The mean concentration of Cu in the Wuwei greenhouse soils was lower than values measured in Siping, Yunnan, and Jiangsu, but higher than those in Shandong. The mean Wuwei Zn concentration was found to be lower than that of other Chinese areas, with the exception of Yunnan. The different heavy metal concentrations of the greenhouse soils in the above study area might be due to spatial heterogeneity (i.e., a diversity of soil types in separate greenhouses), but all studies showed that greenhouse culture undoubtedly accelerated heavy metal accumulation in soils as compared to traditional agriculture, a finding that should motivate constant attention from producers and regulatory agencies.

Soil properties have a large influence on the distribution and the environmental chemistry properties of heavy metals (Ramos-Miras et al. 2011, Zhou et al. 2014). Significant differences in the concentrations SOM and P were detected between greenhouse and arable soil samples of Wuwei. The SOM content (mean of 2.97 g kg^{-1}) in greenhouse soil was 1.5 times higher than that of the arable soil (1.99 g kg^{-1}). P content in greenhouse soil (2.25 g kg^{-1}) was nearly two times higher than that found in arable soil (1.16 g kg^{-1}). Given the large amounts of livestock manure and phosphorus fertilizers that are used in the production of greenhouse vegetables in Wuwei, the increased SOM and P values are not surprising. The pH (7.86) of greenhouse soil was 0.43 lower than that of arable soil (8.29), which may affect the values of available heavy metals in soils (Ramos-Miras et al. 2011); this lower pH might result from the massive application of physiological acid fertilizer. However, no significant differences in K or Al_2O_3 concentrations were observed between greenhouse and arable soils.

The relationship between heavy metal concentration and the number of years under cultivation of greenhouse soil

The effect of the number of years under cultivation on heavy metal concentrations in greenhouse soils was studied with correlation analysis. There was a significant positive correlation between concentrations of Cd, Cu, and Zn in greenhouse soils and the number of years under cultivation, with linear correlations of $y_{Cd}=0.021x+0.273$ ($r=0.361, p<0.01, n=97$), $y_{Cu}=0.649x+29.232$ ($r=0.308$, $p<0.01$, $n=97$), and $y_{Zn}=1.378x+75.535$ ($r=0.327, p<0.01, n=97$) respectively. These equations indicated that the annual average accumulation rates for Cd, Cu, and Zn were 0.021, 0.649, 1.378 mg kg^{-1}, respectively. Similar results were observed in Shandong and Beijing (China) by other researchers (Li et al. 2005, Zhang et al. 2011). No significant correlations were found between the concentrations of Pb, Cr, and Ni in greenhouse soils and the number of years under cultivation. Significant positive linear correlations were found between SOM and P contents and the number of years under cultivation, $y=0.656x+25.013$ ($r=0.290$, $p<0.01$, $n=97$) for SOM and $y=0.027x+0.322$ ($r=0.599$, $p<0.01$, $n=97$) for P. The SOM and P content increased with the number of years of greenhouse cultivation due to long-term overfertilization with manure and phosphorus fertilizers. Meanwhile, Cd, Cu, and Zn in manure and phosphorus fertilizers might be put into soils with fertilization. No significant correlations were found between the concentrations of K or Al_2O_3 in greenhouse soils and the number of years under cultivation.

Table 1 Statistic values of total elemental contents of some heavy metal and basic edaphic parameters in the surface horizon of greenhouse soil and arable soil

Item	Number	Mean	Median	Min	Max	SD	CV	Background value[a]	Threshold values[b]
Greenhouse soil									
Cd (mg kg^{-1})	97	0.421a	0.346	0.097	1.531	0.22	53.27	0.116	0.6
Cu (mg kg^{-1})	97	33.85a	32.51	21.99	61.30	8.16	24.11	24.1	100
Zn (mg kg^{-1})	97	85.31a	81.91	55.38	139.00	16.36	19.17	68.5	300
Pb (mg kg^{-1})	97	20.76a	20.51	15.33	27.89	3.11	14.99	18.8	350
Cr (mg kg^{-1})	97	53.12a	53.30	40.08	60.48	4.08	7.68	70.2	250
Ni (mg kg^{-1})	97	28.59a	28.66	23.24	39.50	2.54	8.88	35.2	60
P (g kg^{-1})	97	2.25a	2.18	0.87	4.10	0.76	33.78	–	–
K (g kg^{-1})	97	22.31a	22.41	18.59	26.07	1.45	6.50	–	–
SOM (%)	97	2.97a	2.98	1.04	5.23	0.87	29.41	–	–
pH	97	7.86a	7.87	7.44	8.34	0.37	4.69	–	–
Al$_2$O$_3$ (%)	97	12.16a	12.17	10.23	13.76	0.67	5.48	–	–
Arable soil									
Cd (mg kg^{-1})	35	0.261b	0.231	0.149	0.558	0.09	35.00	0.116	0.6
Cu (mg kg^{-1})	35	27.36b	26.70	20.11	34.43	3.36	12.28	24.1	100
Zn (mg kg^{-1})	35	74.23b	72.94	53.08	130.10	13.33	17.95	68.5	300
Pb (mg kg^{-1})	35	20.48a	19.44	13.35	35.44	4.02	19.62	18.8	350
Cr (mg kg^{-1})	35	54.18a	54.93	44.00	61.62	4.04	7.45	70.2	250
Ni (mg kg^{-1})	35	30.50a	30.87	24.13	33.21	1.90	6.22	35.2	60
P (g kg^{-1})	35	1.16b	1.13	0.74	1.92	0.25	21.55	–	–
K (g kg^{-1})	35	21.95a	21.91	18.51	24.65	1.43	6.51	–	–
SOM (%)	35	1.99b	1.99	1.22	2.96	0.32	15.91	–	–
pH	35	8.29b	8.30	8.01	8.62	0.24	2.90	–	–
Al$_2$O$_3$ (%)	35	12.51a	12.67	10.74	13.66	0.72	5.72	–	–

Different letters mean significant difference at $P<0.01$ between greenhouse soil and arable soil

SOM Soil organic matter (%), *SD* standard deviation, *CV* coefficient of variation (in %)

[a] Soil background values for heavy metals in Wuwei, Gansu Province

[b] Chinese environmental quality standard for agricultural soils (grade II pH<7.5; GB15618-1995) (Liu 2001)

To determine the distribution of heavy metals in soil profiles of greenhouse soil, four greenhouses soil profiles with different numbers of planting years were analyzed (Fig. 2). It can be seen in Fig. 2 that the concentrations of Cd, Zn, and Cu in 0–40 cm soils profiles were higher than those in 40–100 cm soils profiles, and the concentrations of Cd, Cu, and Zn in greenhouse soil profiles increased as the number of years under cultivation increased. Accumulation of Cd, Zn, and Cu in greenhouse soils occurred mainly in the 0–40 cm of surface soil, which might indicate that Cd, Zn, and Cu were derived mainly from human activities rather than from geological factors.

Identification of the main sources causing heavy metal accumulation

Heavy metals in soil can originate from natural soil, forming parent materials and can be enriched by human activities (Rodríguez Martín et al. 2006, Luo et al. 2009). As heavy metals accumulate slowly in soil profiles over long periods of time, soils can act as long-term sinks for potentially toxic heavy metals. The major sources of heavy metals to agricultural soils include sewage sludge, livestock manures, inorganic fertilizers and lime, agrochemicals, irrigation water, industrial by-products such as wastes and composts, and atmospheric deposition. It is important to understand the sources of heavy metals when land managers attempt to reduce toxic element accumulation in agricultural soils.

Correlation analysis is one of the commonly used methods for analyzing similarities between paired data; it is widely used in trace metal database analyses (Gil et al. 2004). In order to ascertain the sources of heavy metals in greenhouse soils in Wuwei, the heavy metal concentrations in soils and selected soil property parameters were analyzed with correlation analysis (Table 3). There were significant positive correlations ($p<0.01$) between Cd and Cu ($r=0.460$), Cd and Zn ($r=0.480$), Cu and Zn ($r=0.675$), and Cr and Ni ($r=0.544$). Significant positive correlations of Cd, Cu, and Zn, with SOM

Table 2 Comparison of average concentrations of heavy metals in greenhouse soil and arable soils from Spain and China/mg kg^{-1}

Study area	Soil	Concentrations						Reference
		Cd	Cu	Zn	Pb	Cr	Ni	
Andalusian, Spain	Greenhouse	1.1	30.2	133	68.9	50.3	36.0	Martin et al. 2013
	Arable	0.4	25.7	65.7	25.6	29.6	26.9	
Almeria Spain	Greenhouse	1.2	–[a]	–[a]	69.9	–[a]	38.0	Gil et al. 2004
	Arable	0.6	–[a]	–[a]	46.2	–[a]	23.4	
Jiangsu, China	Greenhouse	0.21	35.9	96.0	34.5	–[a]	–[a]	Yang et al. 2014
	Arable	0.17	32.1	80.2	32.5	–[a]	–[a]	
Yunnan, China	Greenhouse	0.40	46.6	48.6	19.8	89.9	18.3	Shi and Zhang 2010
	Arable	0.35	35.9	46.9	26.1	88.3	13.6	
Lanzhou, China	Greenhouse	0.26	–[a]	–[a]	23.9	65.5	12.3	Qin et al. 2013
	Arable	0.14	–[a]	–[a]	22.0	63.9	11.1	
Siping, China	Greenhouse	0.47	37.0	87.7	18.0	67.5	25.2	Bai et al. 2011
	Arable	0.11	16.8	49.1	15.7	46.5	21.8	
Shandong, China	Greenhouse	0.22	28.6	102	30.7	–[a]	–[a]	Li et al. 2005
	Arable	0.10	21.4	77.0	26.0	–[a]	–[a]	
Shandong, China	Greenhouse	0.20	29.9	91.9	14.6	38.8	28.7	Liu et al. 2008
	Arable	0.11	24.1	56.7	13.2	29.8	22.2	
Shandong, China	Greenhouse	0.44	32.9	106	20.7	–[a]	–[a]	Yang et al. 2014
	Arable	0.12	23.5	64.1	21.8	–[a]	–[a]	
Wuwei, China	Greenhouse	0.42	33.9	85.3	20.8	67.9	28.6	This study
	Arable	0.26	27.5	74.7	20.6	70.3	30.4	

[a] Not available

and P were also found, with correlation coefficients of 0.265 (Cd–SOM, n=97), 0.473 (Cd–P, n=97), 0.202 (Cu–SOM, n=97), 0.490 (Cu–P, n=97), 0.307 (Zn–SOM, n=97), and 0.604 (Zn–P, n=97). Similar results have been reported previously (Gjoka et al. 2011, Lu et al. 2012, Zhang et al. 2011). Significant positive correlation between Cr and Ni and Al_2O_3 were observed, with correlation coefficients of 0.522 for Cr and 0.439 for Ni. No significant correlation was found between Pb and the other heavy metals, likely indicating a specific source for Pb. However, there was significant correlation between Pb and Al_2O_3 (0.264). The putative source of Pb may be geochemical or atmospheric deposition (Luo et al. 2009). Positive correlations among heavy metals may suggest that they share a similar origin (Gil et al. 2004). However, a single correlation analysis may not be enough for source identification of heavy metals and it should be combined with other analytical procedures (Zhou et al. 2014).

The individual associations of elements as distributed in greenhouse soil and arable soil were further determined by the PCA method. Factor loadings for heavy metal values in greenhouse soils and arable soil varimax rotations are shown in Table 4. Based on eigenvalues (eigenvalue >1), two principal components (PC1 and PC2) cumulatively explained 62.851 and 71.655 % of the total variance in greenhouse soil and arable soils, respectively. In greenhouse soils, PC1 explained 35.517 % of total variance and was strongly and positively related to Cd, Cu, and Zn (0.710–0.882); PC2 explained 27.334 % of total variance and showed high positive factor loadings for Cr and Ni (0.832–0.867). Pb did not present a clear separation in greenhouse soils, but showed partial loading for PC1 and PC2 (Fig. 3). In arable soils, PC1 explained 39.427 % of total variance and was strongly and positively related to Cd, Cu, Zn, and Pb (0.752–0.779); PC2 explained 32.228 % of total variance and showed high

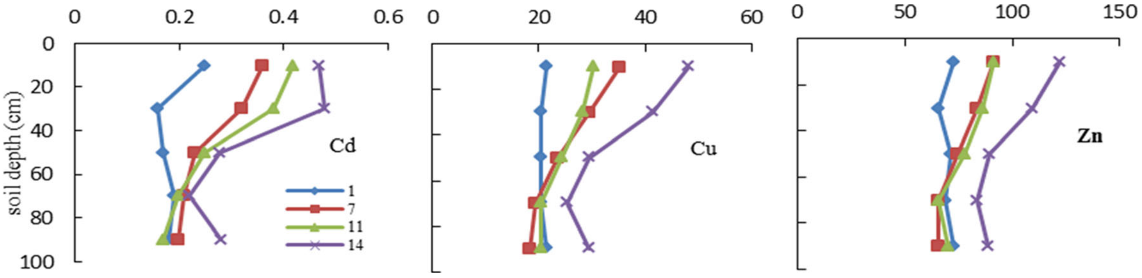


Fig. 2 Distribution of heavy metal concentrations (mg kg^{-1}) in profiles of greenhouse soil with different planting years (1–14 years)

Table 3 Correlation coefficient (*r*) among total content of heavy metal and soil property parameters in greenhouse soils (n=97)

Item	Cd	Cu	Zn	Pb	Cr	Ni	K	P	SOM	Al2O$_3$
Cd	1									
Cu	0.460[a]	1								
Zn	0.480[a]	0.675[a]	1							
Pb	0.127	0.094	0.179	1						
Cr	−0.163	−0.143	−0.159	0.126	1					
Ni	−0.332[a]	−0.151	0.071	0.023	0.544[a]	1				
K	−0.132	0.112	0.239[b]	0.513[a]	0.188	0.246[b]	1			
P	0.473[a]	0.490[a]	0.604[a]	0.178	−0.029	−0.187	0.087	1		
SOM	0.265[a]	0.202[b]	0.307[a]	0.101	0.002	−0.149	−0.037	0.623[a]	1	
Al2O$_3$	−0.253[b]	−0.031	0.093	0.264[a]	0.439[a]	0.522[a]	0.744[a]	−0.127	−0.216[b]	1

[a] Correlation is significant at the 0.01 level

[b] Correlation is significant at the 0.05 level

positive factor loadings on Cr and Ni (0.923–0.949) (Fig. 3). This high positive factor loading is strongly suggestive of common source for these metals.

PC1 can be considered to represent anthropogenic input since the mean concentrations of Cd, Cu, and Zn in greenhouse soils were higher than the natural background values; these concentrations were, respectively, 263, 40, and 25 % higher than the background values. The mean concentrations of these four elements (Cd, Cu, Zn, and Pb) in arable soils were also higher than the natural background values by 125, 14, 8, and 9 %, respectively. The anthropogenic inputs of these metals likely include irrigation, fertilization, pesticide application, and atmospheric deposition resulting from industrialized activities (Luo et al. 2009, Ahmad and Goni 2010). In our study area, irrigation water was mainly snow water from the Qilian Mountains, the heavy metal concentrations in this water are lower than the Chinese national water standard. This region is an important national commodity grain production base and is the fruit and vegetables production base of Gansu Province. As a result of its importance in agricultural production, the application of sludge is not allowed here, meaning that the accumulation of organic matter and phosphorus in the soils results mainly from the application of manure and phosphate fertilizer. Based on the significant positive correlation of Cd, Cu, and Zn with SOM and P, livestock manures and phosphate fertilizers were one of the main sources for Cd, Cu, and Zn accumulation in Wuwei soils. Luo et al. (2009) reported a similar result, showing that livestock manures accounted for approximately 55, 69, and 51 %, respectively, of the total Cd, Cu, and Zn accumulation in agricultural soils in China. Numerous other studies have been conducted and show similar sources of accumulated heavy metals in soils. For example, Cd in Zlatibor soil was identified to derive from fertilization (Dragović et al. 2008), and Cd and Pb accumulation in British soil was present as a consequence of fertilization (Spurgeon et al. 2008). Nicholson et al. (2003) reported livestock manures and inorganic fertilizers as responsible for an estimated 42, 43, and 41 % of total

Table 4 Matrix of principal component analysis for heavy metals concentrations of greenhouse soils and arable soils in Wuwei distract

Element	Rotated component matrix (greenhouse soils)		Rotated component matrix (arable soils)	
	PC1	PC2	PC1	PC2
Cd	*0.710*	−0.300	*0.779*	−0.199
Cu	*0.839*	−0.106	*0.752*	0.259
Zn	*0.882*	0.055	*0.757*	0.110
Pb	0.355	0.303	*0.762*	0247
Cr	−0.107	*0.832*	0.198	*0.923*
Ni	−0.078	*0.867*	0.030	*0.949*
Eigenvalue	2.131	1.640	2.366	1.934
% of Variance	35.517	27.334	39.427	32.228
Cumulative %	35.517	62.851	39.427	71.655

Significant loading factors are marked in italics

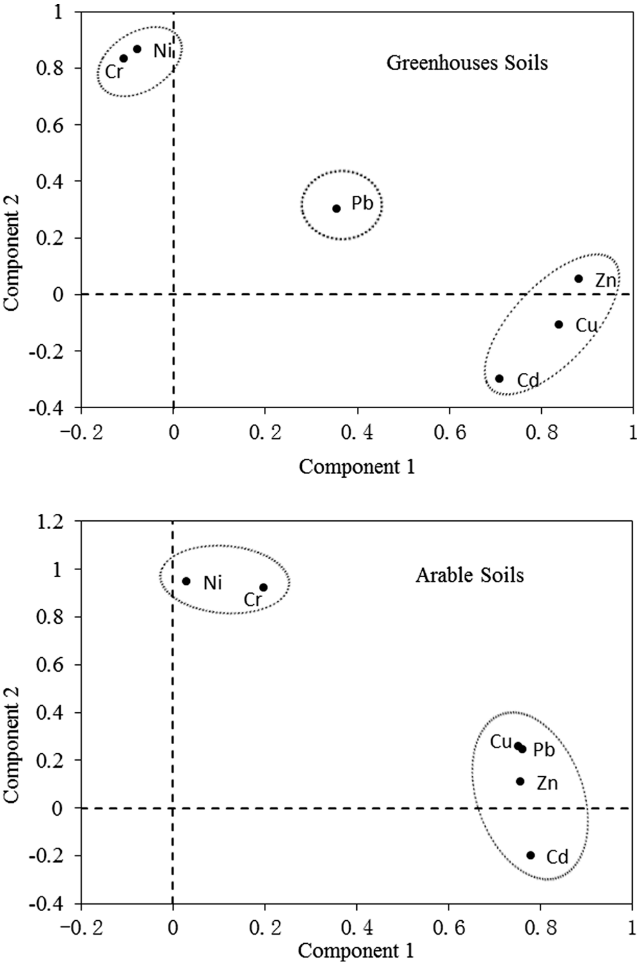


Fig. 3 Loading plots of the first two soil dominant components in greenhouse soils and arable soils

Zn, Cu, and Cd inputs to agricultural land in England and Wales, respectively. Our inventory of the heavy metal concentrations of manure and inorganic fertilizers typically used in the study area also identified a similar trend (Table 5). Atmospheric deposition is one of the most important sources for the input of heave metals (especially Pb) to agricultural soils. Atmospheric deposition accounted for approximately 78, 53, 39, and 49 % of the total input of Pb, Cd, Cu, and Zn to agricultural land in England and Wales, respectively (Nicholson et al. 2003). A previous study in China showed that atmospheric deposition accounted for approximately 85, 34, 18, and 42 % of the total input of Pb, Cd, Cu, and Zn in soil, respectively (Luo et al. 2009). However, in greenhouse soils, it is possible that the input of heavy metals from atmospheric deposition might be minimized by the use of protective plastic mulch.

PC2 can be considered to represent geogenic and pedogenic contributions as the likely primary sources of Cr and Ni since the mean concentrations of Cr and Ni (53.12 and 28.59 mg/kg) in greenhouse soils and (54.16 and 30.50 mg/kg) in arable soils did not exceed the background values. Based on correlation analyses (Table 3), there were significant correlations of Cr and Ni with Al_2O_3, but no significant correlations were found among Cr or Ni with SOM or P. The significant correlations of Cr and Ni with Al_2O_3 further support the supposition that the parent material was the main source of Cr and Ni, as Al_2O_3 is one of the main constituents of geogenic and pedogenic material. Several authors' reports presented the same result, showing that Ni and Cr status in soils was highly dependent on the Ni and Cr content in parent rocks (Facchinelli et al. 2001, Brūmelis et al., 2002, Nanos and Rodríguez Martín, 2012); our PCA analysis demonstrated this relationship clearly, as Cr and Ni were grouped in the same component.

The effect of fertilization on heavy metal concentrations in greenhouse soils

Based on principal component analysis and correlation analyses, anthropogenic influences were clearly observed in the Cd, Cu, and Zn concentrations in greenhouse soils in Wuwei District. Livestock manures and phosphate fertilizer might be the main sources of Cd, Cu, and Zn accumulation in greenhouse soils. This suggestion was supported by our findings for the higher concentrations of heavy metals of manure and inorganic fertilizers sampled in our study area (Table 5) and the organic matter and phosphate levels in these soils (Table 1). The mean concentrations of Cd, Cu, and Zn in pig manure were 0.707, 328.85, and 597.88 mg kg^{-1}, respectively, and the maximum concentrations of Cd, Cu, and Zn were 2.927, 1007.84, and 1068.22 mg kg^{-1}, respectively, higher than those in cattle and sheep manure. The Cd, Cu, and Zn concentrations were relatively high in complex phosphorous fertilizers; the maximum concentrations of Cd, Cu, and Zn were 37.69, 303.81, and 4463.67 mg kg^{-1}, respectively, and the mean concentrations of Cd, Cu, and Zn were 2.41, 14.31, and 175.91 mg kg^{-1}. Heavy metal concentrations were relatively lower in Potash and Urea. Numerous studies have reported that livestock manures contain high concentrations of heavy metals (Nicholson et al. 1999, Cang et al. 2004; Bolan et al. 2004; Lindén et al. 2001). In England and Wales, typical concentrations in poultry manures were 400 mg Zn kg^{-1} dm and 80 mg Cu kg^{-1} dm (Nicholson et al. 1999). In Jiangsu, China, the mean concentrations of Cu, Zn, and Cd in pig manure were 399.0, 505.9, and 0.80 mg kg^{-1} dm, respectively (Cang et al. 2004). The most widely recognized phosphorous fertilizer is an ubiquitous source of Cd contamination in agricultural soils throughout the world (McLaughlin and Singh 1999, Taylor 1997, Kongshaug et al. 1992). Phosphorous fertilizers can contain up to 300 mg Cd kg^{-1} (Fergusson 1990). It is estimated that phosphorous fertilizers contribute 334 t Cd $year^{-1}$, more than 50 % of the total Cd input into soils in countries of the European Union (McLaughlin and Singh 1999).

Table 5 Contents of heavy metal in fertilizer and manure in Wuwei (mg kg^{-1})

Element	Fertilizer	Mix	Max	Mean	SD	Element	Fertilizer	Mix	Max	Mean	SD
Cd	Complex phosphate[a]	ND	37.69	2.409	8.059	Cu	Complex phosphate	0.87	303.81	14.31	42.50
	Potash	ND	0.029	0.016	0.012		Potash	0.25	1.99	1.46	0.82
	Nitrogen	ND	0.01	0.002	0.003		Nitrogen	ND	1.67	0.74	0.69
	pig manure	0.221	2.927	0.707	0.714		pig manure	35.26	1007.84	328.85	289.21
	Cattle/sheep manure	0.158	0.801	0.367	0.256		Cattle/sheep manure	21.65	94.52	37.93	27.98
Zn	Complex phosphate	0.99	4463.7	175.91	620.29	Pb	Complex phosphate	0.02	127.40	8.26	21.79
	Potash	ND	0.26	7.25	4.90		Potash	0.62	1.57	1.25	0.43
	Nitrogen	ND	4.96	1.95	1.80		Nitrogen	ND	0.62	0.34	0.17
	Pig manure	187.94	1068.22	597.88	318.44		Pig manure	4.82	28.96	11.25	7.27
	Cattle/sheep manure	72.15	33.93	102.47	20.09		Cattle/sheep manure	3.92	16.10	9.11	4.69
Cr	Complex phosphate[a]	0.07	380.88	31.71	76.38	Ni	Complex phosphate	ND	28.32	10.34	14.73
	Potash	0.03	0.58	0.32	0.24		Potash	0.87	4.06	2.13	1.50
	Nitrogen	ND	0.76	0.17	0.27		Nitrogen	ND	1.33	0.42	0.51
	Pig manure	7.82	39.37	21.76	11.68		Pig manure	8.18	25.80	14.83	5.31
	Cattle/sheep manure	5.80	44.52	19.85	14.55		Cattle/sheep manure	5.10	21.69	12.18	6.55

[a] Complex phosphate fertilizers mean contain P and N or K nutrients; compound phosphate fertilizers $n=53$, potash $n=4$, nitrogen $n=9$, pig manure $n=13$, cattle/sheep manure $n=6$

In Greenhouse cultivation, fertilizers are frequently overused and misused to achieve high multi-cropping indexes and economic gains. In Wuwei District, the amount of livestock manure (dry weight) and complex phosphorus fertilizers applied to soil is approximately 22.50 and 2.25 t hm^{-2} year^{-1}, respectively. Our results indicated that greenhouse cultivation had a significant effect on the accumulation of Cd, Cu, and Zn in soils. Cd content in greenhouse soil (0.421 mg/kg) was more than 1.5 times higher than that found in arable soil (0.261 mg/kg), mainly due to applications of organic and complex fertilizers. Similar results have been reported by other authors (Huang et al. 2007, Atafar et al. 2010, Arvas et al. 2013, Fekri and Kaveh 2013). The long-term application of animal manure containing high concentrations of heavy metals increases the risk of ecological and environmental contamination (Eneji et al. 2001; Bolan et al. 2003). Field experiments in northeast China conducted over 17 years showed that applications of pig manure and inorganic fertilizers increased concentrations of Cd in the topsoil by 17.0- to 18.9-fold (Wu et al. 2012). Fan et al. (2013) reported that application of both inorganic fertilizer and manure significantly stimulated Zn accumulation and that horse manure application increased Cu, Pb, and Cr concentrations in bulk soils compared to controls. Moreno-Caselles et al. (2005) deemed that repeated applications of pig manure would lead to accumulation of heavy metals, especially Zn and Cu.

In general, the continuous excessive application of inorganic fertilizers and livestock manures with high concentrations of heavy metals will lead to a continual enrichment of heavy metals in greenhouse soils. The results of our study will assist producers, land managers, and regulators in developing strategies for reducing heavy metal inputs to agricultural land and aid in the evaluation of the efficacy of policies seeking to protect soils from long-term heavy metal accumulation.

Conclusion

We evaluated the heavy metal concentrations in greenhouse soils and arable soils in Wuwei District; we also investigated the relationships between heavy metal concentrations in these soils and the length of time under cultivation. Our results indicated that greenhouse cultivation increased the accumulation rates of Cd, Cu, and Zn in soil and that some of the greenhouse soils tested had cadmium concentrations high enough to pose potential ecological and health risks.

Anthropogenic influences were clearly observed in the Cd, Cu, and Zn concentrations in greenhouse soils in Wuwei District. We conclude that the higher Cd, Cu, and Zn content in greenhouse soils resulted from many years of uncontrolled application of fertilizers and livestock manures; this conclusion was supported by our findings for the organic matter and phosphate levels in these soils.

Our results indicated that the excessive and long-term use of fertilizers and livestock manure that contain high heavy metal levels leads to the accumulation of heavy metals in soils. Therefore, rational fertilization programs and reductions in the concentrations of heavy metals in both fertilizers and manure must be recommended to maintain a safe concentration of heavy metals in greenhouse soils.

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