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Cultivation Ages Effect on Soil Physicochemical Properties and Heavy Metal Accumulation in Greenhouse Soils

WANG Jun, MI Wenkui, SONG Peipei, XIE Hui, ZHU Lusheng, WANG Jinhua

(*College of Resources and Environment*, *Key Laboratory of Agricultural Environment in Universities of Shandong*, *Shandong Agricultural University*, *Taian* 271018, *China*)

Abstract: The intensive management practices in greenhouse production may alter the soil physicochemical properties and contribute to the accumulation of heavy metals (HMs). To determine the HM concentrations in vegetable soil in relation to soil physicochemical properties and cultivation age, we conducted a soil survey for typical greenhouse soils in Shouguang, China. The results indicated that Cd is a major HM pollutant in the tested soils, as the only HM element exceeding the allowed limit for vegetable soil. The surveyed data was analyzed with regression analysis, correlation analysis and canonical correspondence analysis (CCA). A positive correlation is observed between HM pollution level and cultivation age. CCA results suggest that the HM pollution level and distribution in soil are significantly affected by soil physicochemical properties, which was a function of years of cultivation as revealed by regression analysis. In summary, cultivation age is an important factor to affect soil physicochemical properties (organic matter and inorganic nutrients) as well as HM contamination.

Keywords: heavy metal; greenhouse soil; cultivation age; physicochemical property; canonical correspondence analysis (CCA)

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1 Introduction

Heavy metals (HMs) in soil can be dissolved in soil solution and immobilized by solid phase of soil. The easily bioavailable fractions of HMs can be uptaken by plant roots, and transported via leaching and surface water runoff (Sastre et al., 2007; Zeng et al., 2008; Bai et al., 2010; Wang et al., 2011; Cambier et al., 2014; Georgiev et al., 2014; Xia et al., 2014; Xiao et al., 2017). The HMs in undisturbed soil are largely inherited from parent materials, which tend to maintain at a stable level (Rodríguez Martín et al., 2013; Lv et al., 2014). However, anthropogenic activities such as industrial activities, application of pesticides and chemical fertilizers, wastewater irrigation, sewage sludge application and vehicle exhaust contribute to elevated levels of HMs in urban and rural soils (Cao et al., 2010; Khan et al., 2013; Gu et al., 2014; Kelepertzis, 2014; Guo et al., 2017). This is especially true of greenhouse soils due to frequent applications of large amounts of pesticides and fertilizers.

Greenhouse industry adopts management-intensive agricultural production technologies, contributing to large production of agricultural crops. In China, the greenhouse cultivation has increased by almost 4.67 × 10^6 hr from 1983 to 2010 (Yang et al., 2013). However, highly intensive cultivation and multiple cropping lead to declines in soil quality, e.g., soil nutrient imbalances, soil salinization, soil acidification, and excessive HMs accu-

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Corresponding author: ZHU Lusheng. E-mail: lushzhu@sdau.edu.cn

mulation. It is found that the contents of cadmium (Cd), copper (Cu), zinc (Zn) and lead (Pb) in greenhouse vegetable soils can be nearly twice the background values, which threaten food security and human health (Zhang et al., 2011; Khan et al., 2013; Werkenthin et al., 2014). Thus, it is of practical significance to understand the characteristics of HM pollution in vegetable soils.

Shouguang City of Shandong Province is the largest base for greenhouse vegetable production in China, with annual vegetable production of 4 × 10^6 t (Liu et al., 2011). Intensive management practices of greenhouse industry for more than three decades in this region are causing excessive accumulation of HMs in soils. For example, Gu et al. (2014) studied HMs accumulation and spatial distribution patterns in soil at different scales, and concluded that Cd, Cr, and Cu concentrations in soil were above the background values due to application of chemical fertilziers. The multivariate geostatistical analyses of HMs on non-greenhouse land in Wulian County (adjacent to Shouguang City), Shandong Province at both regional and local scale (Lv et al., 2014) suggested that human activities and agricultural practices explain the spatial variation of Cd, Cu, Pb and Zn at local scale. These findings suggest that agricultural practices, e.g. application of chemical fertilizers and other human activities, contribute to high HMs concentrations in soil. Thus, it is expected that anthropogenic sources may be the main contributor for HMs accumulation in greenhouse soil, which is characterized with even more intensive fertilizer application and human activities. A comprehensive study of HMs profile in Shouguang area indicated that the soils were polluted by arsenic (As), Cu, Zn, and Pb, and to larger extent by Cd and Hg (Yang et al., 2013). The source identification reveals that Cd, Zn, Cu and mercury (Hg) accumulation largely result from anthropogenic activities, i.e., manure and pesticide applications. However, little work has been conducted to investigate the effects of cultivation years on HMs pollution in greenhouse soils.

To find out the characteristics of HMs pollution in greenhouse soil in relation to cultivation ages and soil properties, a field survey was implemented to reveal the correlation of HMs with different soil properties and cultivation years. The objectives of this work were to: 1) analyze the physicochemical properties and heavy metal pollution status in greenhouse soils; 2) find out the relationships between the cultivation age and soil properties as well as HM concentrations; and 3) determine the association of HMs with soil physicochemical properties.

2 Materials and Methods

2.1 Study sites

Soil samples were collected from the Shouguang area, with geographic coordinates from 118°32'E–119°10'E and 36°41'N–37°19'N in the northern part of Shandong Peninsula, China. This region has a typical continental monsoon climate with hot and humid summers and generally cold, windy and dry winters. The average annual temperature is 12.4°C, and the mean annual precipitation is 608.2 mm. The soil-forming parent materials are mainly derived from alluvial deposits of the Mi River in the Shouguang area.

A survey of agricultural production activities in this area was conducted with the methods of documentary and fact finding in May 2016, including vegetable planting, field management, fertilizer application and pesticide utilization. The main vegetables species in study aerea include *Cucurbita maxima*, *Lycopersicon esculentum*, *Lycium chinense* and *Solanum melongena*, with high cropping index values and annual cropping frequency of 2–3 times. The cultivation years of studied soil range from 1 to 19 years. The major organic fertilizers consist of chicken manure, pig manure and soybean pulp. The maximum application rates on fresh mass basis are 347.23 t/(hr·yr) for chicken manure, 192.33 t/(hr·yr) for pig manure, and 18.36 t/(hr·yr) for soybean pulp. Pesticide (fungicides and nematicides) application rates and frequency followed the requirements of the National Green Food Production Technology of China. Groundwater and surface water are supplied with drip and furrow irrigation systems to water plants.

2.2 Soil sampling and preparation

A total of 19 sites were selected representing different physicochemical soil properties and cultivation ages (Fig.1). The cultivation age of the 19 sampling sites ranged from 2 to 19 years. The latitude and longitude as well as cultivation age of sampling sites were displayed in Table 1. Surface soil samples (0–20 cm) were collected in accordance with the diagonal sampling method. To avoid exogenous metal contamination during sampling, nonmetallic sampling tools was used to

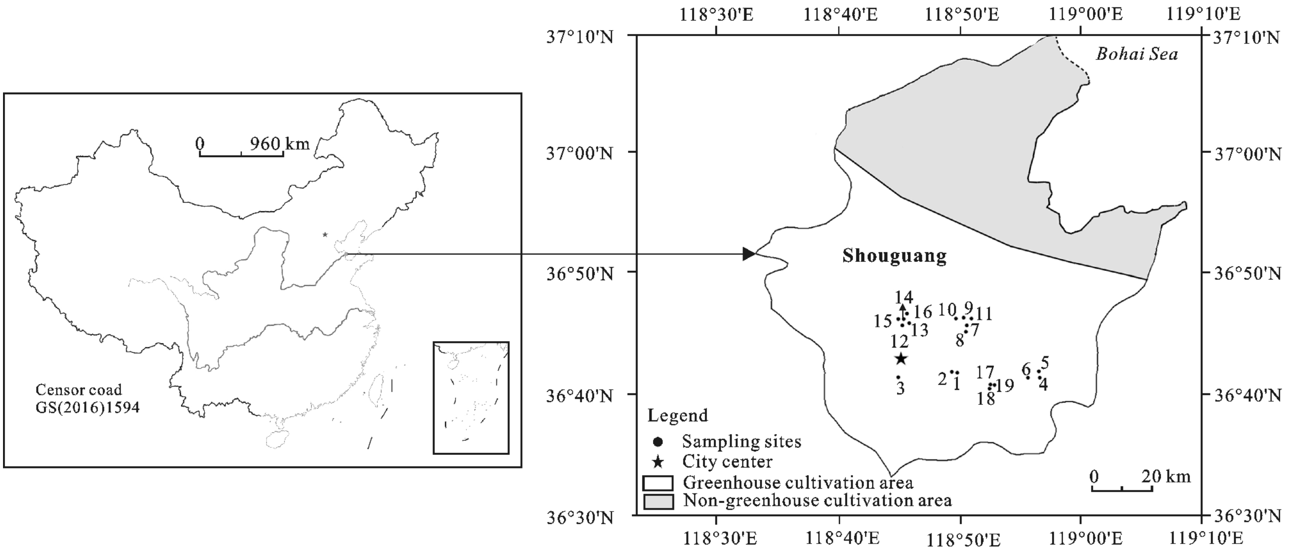

Fig. 1 Sampling sites of soils taken from 19 greenhouses in Shouguang City of China

collect soil samples. Three representative soil samples were collected for each sampling site. The soil samples were homogenized and subsamples were placed in labeled polyethylene bags. All soil samples were air dried, ground, and passed through a 2-mm nylon sieve. The screened samples were stored in sealed polyethylene containers before analysis.

Table 1 The latitude and longitude as well as cultivation age of sampling sites.

No.	Sites (latitude and longitude)	Cultivation age (yr)
1	36°51.557′N, 118°48.773′E	4
2	36°51.568′N, 118°48.685′E	11
3	36°51.168′N, 118°44.110′E	12
4	36°51.134′N, 118°55.738′E	7
5	36°51.646′N, 118°55.648′E	2
6	36°51.132′N, 118°54.773′E	6
7	36°55.669′N, 118°49.599′E	3
8	36°55.257′N, 118°49.405′E	17
9	36°55.803′N, 118°49.467′E	4
10	36°55.808′N, 118°49.410′E	7
11	36°55.793′N, 118°49.545′E	10
12	36°55.924′N, 118°44.533′E	9
13	36°55.925′N, 118°44.547′E	3
14	36°55.964′N, 118°44.549′E	12
15	36°55.958′N, 118°44.541′E	12
16	36°55.972′N, 118°44.551′E	4
17	36°50.541′N, 118°51.808′E	3
18	36°50.528′N, 118°51.806′E	19
19	36°50.536′N, 118°51.929′E	2

2.3 Chemical analyses

All chemicals used in this work were analytical grade and were dissolved in Milli-Q water (18.2 MΩ). The pH values, organic matter (OM), total nitrogen (TN), available nitrogen (AN), available phosphorus (AP), available potassium (AK) and microbial biomass carbon (Bc) were measured using the electrode method (PHSJ-3E meter, Shanghai Leici, China), the potassium dichromate volumetric method, persulphate oxidation method, alkaline hydrolysis diffusion method, the Olsen method, ammonium acetate extraction method, and the chloroform fumigation-extraction method, respectively. To determine the concentrations of Cu, Zn, Pb, Cd, chromium (Cr) and nickel (Ni) in the soil samples, 0.5–1.0 g of representative soil samples were digested using a mixture of hydrochloric acid, hydrofluoric acid, nitric acid and perchloric acid ($HCl/HF/HNO_3/HClO_4$) on hot plates at ambient atmospheric pressure. The concentrations of Cu, Zn, Cr, and Ni were measured using flame atomic absorption spectrophotometry (Thermo M939QZ/989QZ). The concentrations of Pb and Cd were measured using graphite furnace atomic absorption spectrophotometry (AAS5EA, Analytik Jena AG). The soil samples were digested with aqua regia and perchloric acid, and contents of Hg and As were analyzed by an atomic fluorescence spectrophotometry (AF-640A, Beijing Beifen-Ruili Analytical Instrumental Co., China). To guarantee the accuracy of analysis, the national standard soil samples (GSS-1 and GSS-4) were used as spikes for quality control. All measurements were run in duplicate.

2.4 Statistical analysis

Regression analysis were carried out using the statistical software package SPSS (Statistical Program for the Social Sciences, release 20.0). CANOCO software package for Windows 4.5 was used to obtain the canonical correspondence analysis (CCA) to find out the contribution of physicochemical properties of soil samples on HM accumulation in soil samples (Jin et al., 2014).

2.5 Contamination assessment method

To assess the heavy metal pollution at the 19 sites, the single-factor pollution index (SPI) and the Nemerow multi-factor pollution index (NPI) were used for classification and evaluation (Wang et al., 2011).

The SPI is a widely used method for evaluating the degree of heavy metal pollution in soils. The formula is,

$$P_i = C_i/S_i \tag{1}$$

where P_i is pollution index of heavy metal i; C_i is measured concentration of heavy metal i; S_i is standard concentration of heavy metal i according to the Greenhouse Vegetable Production and Environmental Quality Standards (HJ333-2006, State Environmental Protection Administration, People's Republic of China, 2006); $P_i \leq 1.0$, means the soil is not polluted by heavy metal i; $P_i > 1.0$, means the soil is polluted by heavy metal i.

The NPI reflects the effects of each pollutant on soils. It highlights the influence of HM levels on soil environmental quality. The NPI was computed as:

$$P_N = \sqrt{\frac{P_{im}^{\ 2} + P_{ia}^{\ 2}}{2}} \tag{2}$$

where P_N is the Nemerow multi-factor pollution index; P_{im} is the maximum of the single pollution index values; P_{ia} is the average of the single pollution index values.

As shown in Table 2, the soil evaluation standard based on the Nemerow pollution index is divided into five levels (HJ166-2004, State Environmental Protection Administration, People's Republic of China, 2004).

Table 2 The soil pollution evaluation standard based on the Nemerow pollution index

Classification	Nemerow pollution index	Pollution level
I	$P_N \leq 0.7$	Safety
II	$0.7 < P_N \leq 1.0$	Slight safety
III	$1.0 < P_N \leq 2.0$	Slight pollution
IV	$2.0 < P_N \leq 3.0$	Moderate pollution
V	$P_N \geq 3.0$	High pollution

3 Results

3.1 Soil physicochemical properties

The physicochemical properties of the soil samples including soil OM, pH, Bc, and nutrient concentrations are presented in Table 3. The soil pH are between 6.68 and 6.90.

The regression analysis was performed and significant regression equations were obtained between soil nutrient concentrations and cultivation age (Table 4). The relationships between independent variable (cultivation age) and dependent variables (soil OM, TN, AN, AK, and AP concentrations) conform to quadratic polynomials. The parabola-shaped curves suggest that optimal nutrient concentrations and OM content could be found after 8–12 years of cultivation under current management practices.

Correlation analysis was performed to quantify the association between various variables (soil properties and cultivation age) (Table 5). The results indicated different degrees of correlation existed between tested variables. For example, soil OM, TN, AN and AP are significantly correlated with each other. The close association between OM and inorganic nutrients may result from simultaneous application of compound and organic fertilizers. These observations agree with the investigation by Guo in 2010 (Guo et al., 2010).

3.2 HM concentrations in greenhouse soils

The mean Cd content exceeded the limit of Environmental Quality Evaluation Standard for Farmland of Greenhouse Vegetables Production (HJ333-2006, State Environmental Protection Administration, People's Republic of China, 2006), while Hg, Cr, Pb, Cu, Ni, As and Zn concentrations were below the limits (Table 6). Specifically, 36.84% of soil samples exceeded GVPESS limit for Cd content, while 10.53% exceeded the HJ333-2006 limit for Ni content. The HM concentrations were also compared with their corresponding background values (http://lib.sdsqw.cn/bin/mse.exe?seachword=&K=a&A=45&rec=41&run=13). The mean concentrations of Hg, Cr, and Pb were below their background values. Instead, the mean contents of Cd, Cu, Zn and Ni were 4.13, 1.21, 1.89 and 1.34 times the background values, respectively.

3.3 Soil pollution level assessment

To further evaluate HM pollution status at the 19 sites,

Table 3 Physical-chemical properties of soil samples in study area

No.	pH	OM (g/kg)	TN(g/kg)	AN (mg/kg)	AP(mg/kg)	AK(mg/kg)	Bc(mg/kg)
1	6.81±0.04	15.19±2.37	0.96±0.15	59.03±6.55	182.08±24.33	371.25±56.74	172.49±27.85
2	6.87±0.01	34.57±4.42	1.51±0.17	100.52±14.33	313.45±47.85	315.67±63.23	310.32±76.46
3	6.78±0.03	26.32±3.85	2.35±0.33	130.97±23.52	468.64±50.16	589.44±117.27	253.94±33.87
4	6.90±0.01	20.60±1.15	1.22±0.24	78.17±3.78	238.10±42.11	448.35±93.24	706.03±195.31
5	6.81±0.04	9.30±0.83	0.65±0.11	37.25±10.76	167.47±46.32	223.16±34.58	181.73±54.77
6	6.70±0.02	14.42±2.27	1.21±0.19	64.75±8.75	202.50±22.65	473.72±102.35	297.14±26.96
7	6.81±0.05	30.73±4.45	1.55±0.25	96.06±12.31	303.96±28.74	471.34±67.55	310.15±87.35
8	6.73±0.05	23.49±3.21	1.46±0.27	90.86±12.45	465.89±87.43	566.27±144.20	396.97±67.45
9	6.72±0.06	23.99±2.83	1.55±0.09	90.96±17.58	432.97±92.64	468.78±27.85	354.28±48.93
10	6.69±0.04	18.39±1.17	1.32±0.13	75.60±5.57	255.26±72.32	556.20±86.72	335.10±73.23
11	6.67±0.02	30.89±5.45	1.87±0.28	104.28±10.65	515.87±62.17	764.67±202.33	337.75±44.15
12	6.77±0.05	19.78±3.23	1.21±0.21	74.23±11.82	293.59±38.38	348.10±65.37	214.03±64.37
13	6.68±0.03	16.59±1.94	1.13±0.19	68.87±8.46	294.01±47.57	351.12±45.64	206.21±67.19
14	6.76±0.04	17.46±2.26	1.09±0.17	70.58±13.71	239.41±21.03	446.15±98.75	380.44±84.14
15	6.72±0.05	20.77±1.17	1.36±0.34	38.32±4.54	388.04±24.56	497.94±124.51	266.57±43.35
16	6.80±0.06	10.76±1.45	0.76±0.12	38.12±7.27	166.46±18.79	189.21±69.15	284.00±76.38
17	6.78±0.04	24.03±2.96	1.40±0.29	81.35±5.32	233.10±42.36	573.38±34.76	749.65±102.27
18	6.69±0.03	25.50±3.56	1.59±0.35	113.09±11.32	253.59±23.44	481.70±87.92	933.16±195.34
19	6.75±0.04	22.77±2.71	1.31±0.22	75.14±14.54	215.78±27.92	454.87±77.31	474.69±45.23
Mean value	6.76	21.34	1.34	78.32	296.32	452.17	277.09
Standard deviation	0.064	6.71	0.38	25.20	108.02	134.78	205.10

Notes: OM, Organic Matter; TN, Total Nitrogen; AN, Available Nitrogen; AP, Available Phosphorus ; AK, Available Potassium; Bc, Biocarbon

Table 4 Regression analysis between soil nutrient concentrations and cultivation age

	Regression equation	Correlation coefficient(r)
OM	$y = -0.0944x^2+2.346x+11.421$	0.5012
TN	$y = -0.05x^2+0.1114x+0.9102$	0.5029
AN	$y = -0.2394x^2+5.5803x+56.364$	0.4058
AP	$y = -1.3168x^2+31.184x+165.31$	0.5079
AK	$y = -1.5719x^2+31.549x+339.2$	0.3362

Notes: OM, Organic Matter; TN, Total Nitrogen; AN, Available Nitrogen; AP, Available Phosphorus; AK, Available Potassium; Bc, Biocarbon

both SPI and NPI were calculated (Table 7). Most of the soil samples were sorted out as ‘safety’ or ‘slight safety’, five of which were slightly or moderately polluted (Table 7). Generally, the sites with longer cultivation age tended to have higher pollution levels. Among excessive pollution factors, Cd is the dominant pollution factor, and further studies are needed to investigate the potential impact of Cd pollution.

Table 5 Correlation matrix between soil properties and cultivation age

	Age	OM	TN	AN	AP	AK	Bc	pH
Age	1							
OM	0.235	1						
TN	0.100	0.789^{**}	1					
AN	0.037	0.797^{**}	0.880^{**}	1				
AP	0.193	0.624^{**}	0.778^{**}	0.584^{**}	1			
AK	0.025	0.554^{**}	0.748^{**}	0.593^{**}	0.666^{**}	1		
Bc	–0.297	0.286	0.197	0.360	–0.113	0.301	1	
pH	0.067	0.041	–0.218	–0.086	–0.342	-0.471^{*}	0.020	1

Notes: * $P < 0.05$; ** $P < 0.01$

Table 6 Heavy metal concentrations in soil samples of different cultivation ages (mg/kg)

Site	Pb	Cd	Cu	Zn	Cr	Ni	Hg	As
1	22.07±4.31	0.132±0.044	22.42±4.12	133.11±21.13	27.92±3.13	45.20±3.54	0.0086±0.0017	14.20±2.18
2	21.63±5.75	0.239±0.065	35.72±10.30	148.34±18.27	42.08±2.87	39.44±2.83	0.0144±0.0028	11.04±1.21
3	23.54±2.14	0.560±0.125	35.04±6.22	130.66±6.65	156.63±12.36	42.35±1.99	0.0108±0.0019	8.02±1.17
4	18.77±3.72	0.124±0.046	20.01±2.74	124.72±22.26	73.57±3.85	55.34±4.35	0.0244±0.0046	7.44±0.53
5	16.45±2.93	0.071±0.021	23.34±2.12	79.31±8.71	60.61±4.77	60.11±9.86	0.0054±0.0016	8.74±0.87
6	14.78±2.84	0.142±0.017	16.41±3.63	68.19±11.85	77.39±8.94	50.02±11.23	0.0071±0.0018	7.64±1.27
7	18.23±3.26	0.316±0.095	43.78±9.76	177.12±23.63	58.54±2.73	30.56±7.36	0.0176±0.0021	9.76±0.65
8	22.55±4.12	1.188±0.207	19.34±3.57	127.97±11.95	74.46±7.87	29.67±1.43	0.0106±0.0023	9.96±0.78
9	17.05±1.27	0.194±0.019	34.74±4.61	138.03±14.76	69.24±4.17	35.02±4.37	0.0156±0.0031	9.00±1.65
10	15.95±1.93	0.162±0.022	26.05±2.42	104.37±17.68	85.07±6.33	29.12±3.23	0.0164±0.0042	9.60±1.72
11	15.51±4.31	0.435±0.040	62.15±8.68	156.23±18.54	18.32±2.45	25.13±2.15	0.0164±0.0040	11.56±2.33
12	18.79±2.35	0.330±0.029	31.17±8.75	96.78±20.42	45.89±4.54	35.41±1.78	0.0154±0.0015	12.56±0.96
13	17.43±3.26	0.263±0.049	29.56±10.13	90.72±10.64	59.33±10.71	31.35±6.35	0.0174±0.0022	11.94±0.84
14	17.67±2.17	0.256±0.041	20.40±6.13	91.17±5.45	27.45±5.43	34.72±3.45	0.0264±0.0031	10.87±1.53
15	21.66±5.18	0.223±0.024	25.23±2.15	92.63±18.36	31.01±2.72	35.45±5.18	0.0268±00033	11.68±1.41
16	16.74±4.33	0.087±0.028	21.03±1.83	91.4±11.93	23.39±2.35	30.03±2.78	0.0078±0.0019	10.26±0.75
17	25.07±5.57	0.680±0.157	22.81±8.76	115.32±16.81	49.82±4.63	39.67±4.45	0.0141±0.0027	10.42±0.48
18	22.01±1.41	1.005±0.138	25.89±4.23	151.22±25.74	70.51±3.77	38.89±5.64	0.0128±0.0014	10.52±0.93
19	16.82±6.24	0.149±0.053	26.00±2.84	194.89±17.66	22.32±2.38	39.10±3.71	0.0114±0.0013	11.64±1.37
Average value	19.08	0.345	28.48	121.69	56.51	38.25	0.0147	10.36
Standard deviation	3.01	0.31	10.69	34.17	32.22	9.19	0.0061	1.74
Limited value	50	0.30	100	250	200	50	0.30	25
Standard background value*	25.98	0.08	23.58	64.49	66.02	28.58	0.02	10.49

Note: *, data from Element Background Values in Soil (A layer) of Shandong Province, http://lib.sdsqw.cn/bin/mse.exe?seachword=&K=a&A=45&rec=41&run=13

Table 7 Single pollution index values and Nemerow pollution index values of heavy metals

Site No.	P_{Pb}	P_{Cd}	P_{Cu}	P_{Zn}	P_{Cr}	P_{Ni}	P_{Hg}	P_{As}	$\overline{P_i}$	P_N	Pollution Level
1	0.44	0.44	0.22	0.53	0.14	0.90	0.029	0.57	0.41	0.70	Slight safety
2	0.43	0.80	0.36	0.59	0.21	0.79	0.048	0.44	0.46	0.65	Safety
3	0.47	1.88	0.35	0.52	0.78	0.85	0.036	0.32	0.65	1.40	Slight pollution
4	0.37	0.41	0.20	0.50	0.37	1.11	0.081	0.30	0.42	0.84	Slight safety
5	0.33	0.24	0.23	0.32	0.30	1.20	0.018	0.35	0.37	0.89	Slight safety
6	0.30	0.47	0.16	0.27	0.39	1.00	0.024	0.31	0.37	0.75	Slight safety
7	0.37	1.05	0.44	0.71	0.29	0.61	0.059	0.39	0.49	0.82	Slight safety
8	0.45	3.96	0.19	0.51	0.37	0.59	0.035	0.40	0.81	2.86	Moderate pollution
9	0.34	0.65	0.35	0.55	0.35	0.70	0.052	0.36	0.42	0.58	Safety
10	0.32	0.54	0.26	0.42	0.47	0.58	0.055	0.38	0.37	0.49	Safety
11	0.31	1.45	0.62	0.62	0.09	0.50	0.055	0.46	0.52	1.09	Slight pollution
12	0.38	1.10	0.31	0.39	0.23	0.71	0.051	0.50	0.46	0.84	Slight safety
13	0.35	0.88	0.30	0.36	0.30	0.63	0.058	0.48	0.42	0.69	Safety
14	0.35	0.85	0.20	0.36	0.14	0.69	0.088	0.44	0.39	0.66	Safety
15	0.43	0.74	0.25	0.37	0.16	0.71	0.089	0.47	0.40	0.60	Safety
16	0.34	0.29	0.21	0.37	0.12	0.60	0.026	0.41	0.29	0.47	Safety
17	0.50	2.27	0.23	0.46	0.25	0.79	0.047	0.42	0.62	1.66	Slight pollution
18	0.44	3.35	0.26	0.61	0.35	0.78	0.043	0.42	0.78	2.43	Moderate pollution
19	0.34	0.50	0.26	0.78	0.11	0.78	0.038	0.47	0.41	0.62	Safety

Notes: P_i is pollution index of heavy metal i; $\overline{P_i}$ is the average value of the pollution indexs

3.4 CCA analysis of soil physicochemical properties and HM contents

CCA is a powerful tool to find out the correlation between elemental concentration and environmental variables (Shahriary et al., 2012; Jin et al., 2014; Srinivasan et al., 2015). CCA analysis result shows that the eigenvalues of the first three ordination axes are 0.523, 0.158, and 0.125, and the correlation coefficients with HMs content axis are 0.857, 0.923 and 0.895, respectively (data not shown). These results indicate that the ordination axes can significantly reflect the relationships between soil properties and HMs concentrations in soils. Thus, CCA biplots can be able to present the relationship between the environmental variables (soil properties) and target HMs concentrations in soil.

To manipulate CCA, ordination diagram was plotted, in which points and arrows represent scores associated with HMs concentrations and soil physicochemical properties, respectively (Fig. 2). The angles between arrows (vectors) characterize correlations between soil physicochemical properties, which indicated that Bc, TN and AN on one hand, and AK, AP and OM on the other hand, are well correlated. As shown in Fig. 2, CCA sorted the HMs into four categories, located in four quadrants. For the HMs in quadrant Ⅰ, Cr, Pb, Cd concentrations are positively related to Bc, AN, TN, but negatively with cultivation age. pH is also positively correlated with Cr concentration but negatively with Pb and Cd. In quadrant Ⅱ, Ni concentration is positively correlated with pH but negatively with all other attributes. In quadrant Ⅲ, As concentration is positively related with age; pH, AK, AP and OM are negatively with Bc, AN and TN. In quadrant Ⅳ, Hg, Cu, Zn concentrations are positively related with AK, AP, OM, Bc, AN, TN and age, but negatively with pH. The soil HMs concentrations are related to soil physicochemical properties.

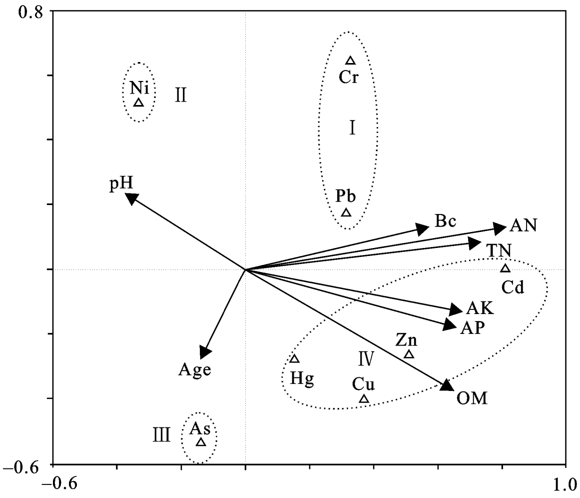

Fig. 2 The results of canonical correspondence analysis (CCA) between the heavy metal contents and the physicochemical properties of the soil samples

4 Discussion

4.1 Correlations among soil properties

Soil physicochemical properties, especially soil nutrient concentrations, may be correlated with each other. The association among soil properties were analyzed with CCA and correlation analysis. Based on CCA analysis in this study, the soil properties can be categorized into four groups. First, AN, TN and Bc are mostly related, as indicated by the small angles between vectors on Fig. 2. The AN can be derived from dissolution and conversion of TN, which is confirmed by significantly high correlation coeffcient between TN and AN (Table 4). Besides, Bc facilitates decomposition and mineralization of organic N to AN (Baaru et al., 2007). This suggested the abundance of Bc may well represent the production of inorganic N from organic N. Second, the variables AK, AP and OM were confined in fourth quadrant. The small angles between these nutrient attributes indicate close relationships among each other. The CCA results was also supported by correlation analysis, which showed that OM, AP and AK were significantly closely related (Table 2). This has been proved by previous work, suggesting application of organic fertilizer or organic matter to soil could improve retention of P and K in soil (Wang and Huang, 2001; Yu et al., 2013). Thus, OM attribute may represent the soil properties in this quadrant.

4.2 HM contamination status in soil

A precise evaluation of HM levels in soils is of great significance for pollution control. Our results showed that mean concentrations of Cd, Cu, Zn and Ni are above the background values, while Cd is the only element exceeding the HJ333-2006 limit. Occurrence of HM contamination was repeatedly reported in China, for example, Lv et al. (2014) observed that Cd, Cu, Pb and Zn concentrations were higher than background values in a county of Shandong Province.

4.3 Relationship among cultivation ages, soil nutrients and HM concentrations

This work indicated soil nutrients were well correlated with cultivation ages (Table 3). Previous work also showed that long-term application of manure and chemical fertilizers leads to the accumulation of organic carbon, N and P in greenhouse soils (Bai et al., 2010; Cristaldi et al., 2017). It was found that OM, TN, TP, AN, AK and AP in greenhouse soils increased with cultivation age (Li and Feng, 2012). However, few works have been documented to quantify the soil physicochemical properties (especially nutrient) as a function of cultivation age. In this work, the regression analysis results showed the relationship can be described with quadratic equations (Table 4). The maximal nutrient concentrations in soil can be achieved between 8–12 years of cultivation for OM, AN, AP and AK.

Because of close relationship between soil nutrients and HMs concentrations in soil (Fig. 2), higher HM concentrations could be expected as a result of intensive use of fertilizers. To confirm association between HM concentration and years of cultivation, the regression analysis were performed between age and Cd which is the only HM exceedling the HJ333-2006 limit. The regression results suggested that Cd concentration increased with years of cultivation (the slope of the equation is 0.0486), with $R^2 = 0.6463$ (by excluding one extra value). This consolidates HM concentration in soil may change with years of cultivation.

4.4 Correlation between soil properties and HMs

The effects of cultivation ages on soil properties and HM concentration may suggest potential association between them. Previous work revealed that HM concentrations and bioavailability are closely related to soil physicochemical properties, e.g., OM contents (Luo et al., 2017), pH (Jackson et al., 1993; Liu et al., 2013) and nutrient concentrations. The effect of soil properties on HM concentrations in soil could result from the biogeochemical processess in soil including adsorption, precipitation and complexation reaction with soil components (Wang et al., 2015a; 2015b; 2017). In this study, the correlation between soil physcochemical properties and HM concentrations were suggested in CCA results (Fig. 2). AN and OM with longest arrows in quadrants Ⅰ and Ⅳ were expected to have greater influence on HMs. Firstly, OM plays very important roles in Zn, Cu, Hg, Pb, Cd and Cr fixation in soil, which may ascribe to complexation of abundant functional groups of OM with HMs. The interaction between OM and HMs, i.e., Cu (Ho and Mauk, 1996; Karlsson et al., 2006), Zn (Shukla, 1971), Hg (Ravichandran, 2004), Pb (Sinwar et al., 2011), Cd (Diagboya et al., 2015) and Cr (Banks et al., 2006) can affect the speciation, solubility and mobility in soil (Kaiser and Zech, 1997). That is, higher OM content could promote complexation with HMs. Soil P may also precipitate with these HMs, reducing the leaching potential of these HMs. It was found that Cd is also positively related with AP, and Cd can be immobolized by P fertilizers in different soil conditions (Seshadri et al., 2016). Besides, soil AN, mainly as ammonium and nitrate N, may also enhance the sorption of these HMs to soil colloids. The soil colloids with good cation and anion exchange capacity can well retain ammonium and nitrate N, and can thus adsorb HMs via ion exchang mechanisms (Bradl, 2004). The close relationship between N and Cd collaborated the previous finding (Wångstrand et al., 2007). Conversely, pH is generally negatively related to all HMs except Ni. Lower pH encourages the dissolution of HMs (Chuan et al., 1996) and thus increases HM concentration in soil.

Since HMs are well correlated with soil physicochemical properties, the change in pH, OM content, and nutrient concentrations may alter HMs concentration in soil. This change can be ascribed to altered geochemical reactions as well as introduction of HMs along with fertilizer application. For example, higher Cd, Cr and Cu in soil were ascribed to application of chemical fertilzers (Gu et al., 2014). P fertilizers, animal manure and sewage sludge usually come with Cd and other HMs (As, Pb, Hg, Cr, Ni), and thus may elevate HM concentrations in soil (Mortvedt, 1995). Moreover, improper application of fertilizers can cause soil acidity, which elevates HM mobility in soil. This suggest more intensive anthropogenic activities and increased fertilizer application may aggravate HMs contamination in greenhouse soil (Cristaldi et al., 2017).

5 Conclusions

A soil survey was conducted to investigate the effects of cultivation age on HMs concentration in greenhouse soil and soil properties. The relationship between soil nutrient concentration and years of cultivation can be fitted with quadrant equations, and regression analysis indicated optimal nutrient status is obtained between 8–12 years of cultivation. The survey data showed that Cd is the major HM in surveyed greenhouse soil which exceeded GVPESS limit. Regression analysis also indicates Cd concentration increased linearly with cultivation ages. Thus, cultivation age is an important factor which influences soil properties and HMs accumulation in greenhouse soil. Considering the close association between some soil properties and HM concentrations in soil as revealed by the CCA analysis, a better management practice in terms of efficient use of fertilizers is necessary to restrain the HM levels in greenhouse soils.

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