Accumulation and Partitioning of Phosphorus and Heavy Metals in a Sandy Soil Under Long-Term Vegetable Crop Production

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ABSTRACT

Increased inputs of phosphorus (P) and heavy metals to agricultural soils have caused considerable concern. Information on accumulation and chemical forms of the elements in soils is needed as a guide for the judicious application of agricultural chemicals and organic manures. The focus of this study was to assess accumulation of P and heavy metals among various fractions of a sandy soil with a 25 year history of vegetable crop production and primarily inorganic fertilization. The results demonstrated that long-term vegetable production practices changed concentrations and partitioning of P and heavy metals in the soil. Phosphorus, Cu, Zn, and Mn were significantly accumulated and moved downward along the soil profile. Most of the total Cr in the vegetable soil accumulated in the upper 0–15 cm. However, there was no

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significant accumulation and transport of Cd, Co, Mo, Ni, and Pb in the vegetable soil. Major P fractions in the vegetable soil were $NaHCO_3$-P, followed by HCl-P and residual P. Copper, Zn, and Mn accumulated predominantly in the $CaCO_3$ fraction or oxide fraction, whereas Cr accumulated mainly in the organically bound fraction, indicating that P, Cu, Zn, and Mn in the vegetable soil have greater mobility potential. Compared with adjacent forest soil, the vegetable soil had a lower percentage of P, Cu, Zn, and Mn in the residual fractions, and a higher percentage of P, Cu, Zn, and Mn in the $CaCO_3$ fractions or organically bound fraction.

Key Words: Accumulation; Fractionation; Heavy metals; Phosphorus; Vegetable soil.

INTRODUCTION

Increased inputs of phosphorus (P) and heavy metals in agricultural soils have caused considerable concern over potential contamination of surface and ground-water through runoff and leaching.[1–5] Repeated applications of chemical fertilizer, organic manures, municipal waste, fungicides, and pesticides to soils are likely to result in phosphorus (P) and heavy metal accumulation in soils.[3,6–10] Studying accumulation and chemical forms of the elements in soils can provide information in decision making for judicious application of agricultural chemicals and organic amendments.

Phosphorus and heavy metals accumulate in soils in water-soluble, exchangeable, carbonate associated, Fe and Al oxide associated, organic associated and residual.[11] Several chemical selective extraction techniques have been employed to fractionate P and heavy metals.[11–18] Distributions of P and heavy metals in various forms depend on soil chemical and mineral environments.[19–21] Phosphorus and heavy metals present in these forms have different remobilization potential under fluctuating environmental conditions.[3,22–24] Water-soluble and exchangeable fractions are readily bioavailable, whereas residual fraction is relatively stable under natural conditions.

More than 122,000 ha of vegetable crops are grown on various soil types throughout Florida.[25] These soil types include sandy soils, sandy loam soils, Histosols (organic muck), and calcareous marl soils. Sandy soils make up the dominant soil type for vegetable production in Florida.[25] Sandy soils have the advantage of ease tillage and they can produce the earliest vegetable crops in a particular region. Sandy soils, however, have low nutrient holding capacities, and lack of nutrients and very low in organic matter. Therefore, it is standard practice in Florida vegetable production system to routinely apply macro- and micro-nutrients.[25] The fertilizer application is essential to sustain high yields for vegetable crops. However, there is a lack of soil-test calibrations to guide judicious application of fertilizers. Compounding the problem has been the use of micronutrient-containing pesticides for disease control.[25] Therefore, these elements may have accumulated in the soils. Recently, studies have been conducted on forms of P and heavy metals in sandy soils under citrus production.[21,26–28] However, minimal information is available on accumulation

and distribution of P and heavy metals in sandy soil under long-term commercial vegetable crop production in Florida. The objective of this study was to quantify the accumulation and partitioning of P and heavy metals among the various solid-component fractions in the profile of sandy soils that received mainly inorganic fertilizers for the last decade under long-term commercial vegetable crop production.

MATERIALS AND METHODS

Soils

This study was conducted on a commercial vegetable farm located near Fort Pierce, FL. The major vegetable crops grown on this farm are tomatoes (*Lycopersicon esculentum*) and peppers (*Capsicum annuum*) with records on previous cropping history going back 25 years. The farm was irrigated by sub-irrigation and the groundwater level was controlled within 30–50 cm below the surface throughout the year. Commercial inorganic fertilizers were the main source of plant nutrients. An estimated 290 and 90 kg of N and P, respectively, were annually applied per hectare. Both vegetable crop soil and adjacent noncultivated forest soil (control site) were collected in April 2001. The control site had a native population of sand pine (*Pinus clausa* [Chapm] *vasey*) and was used to determine a baseline of soil P and heavy metal levels. The soils were Wabasso (sandy, siliceous, hyperthermic Alfic Haplaquods). Sixteen surface soil samples (0–15 cm depth) were collected from the vegetable farm and eight from the noncultivated forestland. In addition, eight soil profiles from the vegetable farm and four from the forestland were also collected at 0–15, 15–30, 30–60, and 60–90 cm depths. Soil samples were air-dried, and ground to pass a 2-mm sieve. These samples were directly used for measurement of pH. Subsamples of the air-dried soils were further ground to pass a 0.15-mm sieve and analyzed for organic carbon (C), P, zinc (Zn), copper (Cu), manganese (Mn), cadmium (Cd), cobalt (Co), chromium (Cr), lead (Pb), molybdenum (Mo), and nickel (Ni). Soil pH was measured both in water at a soil:deionized water ratio of 1:1 using a pH/ion/conductivity meter (Accumet Model 50, Fisher Scientific, Norcross, GA). Soil Olsen-P was extracted using both $0.5 \, mol \, L^{-1}$ $NaHCO_3$ (pH 8.5) and P concentration in the extract was determined by the molybdenum-blue method.[29] Soil particle composition was determined using a micro-pipette method.[30] Organic carbon (C) was determined using a CNS Analyzer (NA 1500, Fisons Instruments Inc., Dearborn, MI). Selected properties of the soils are presented in Table 1. The pH was higher in the vegetable soil than in the forest soil. However, there were no statistical differences in organic C and particle composition between the vegetable soil and the forest soil.

Fractionation of Phosphorus

A modified method of Hedley et al. (1982)[14] was selected to determine soil P fractions in this study. Soil samples (each 1.00 g) were placed in 50-mL centrifuge tubes and were sequentially extracted with 30-mL of deionized water, $0.5 \, mol \, L^{-1}$ $NaHCO_3$ (pH = 8.2), $0.1 \, mol \, L^{-1}$ NaOH, and $1 \, mol \, L^{-1}$ HCl. Each extraction lasted for 16 h on

Table 1. Selected properties of the surface soils.

Property	Vegetable crop Mean (SD)[†]	Forest Mean (SD)
pH	7.3 (0.1)	5.5 (0.4)
Organic C ($g\,kg^{-1}$)	5.4 (0.5)	5.9 (0.5)
Sand ($g\,kg^{-1}$)	920 (19)	907 (27)
Silt ($g\,kg^{-1}$)	32 (19)	43 (15)
Clay ($g\,kg^{-1}$)	48 (3)	50 (5)

[†]SD: standard deviation.

an end-to-end shaker (180 cycles/min). After each extraction, the tubes were centrifuged at $7500 \times g$ (relative centrifugal force) for 30 min. The supernatant was then passed through a Whatman 42 filter paper. The P concentrations in the filtrates from the deionized water and HCl extracts were colorimetrically determined using the molybdenum-blue method.[29] Phosphorus concentrations in the bicarbonate and hydroxide extracts were also determined with the molybdenum-blue method after digestion with acidified ammonium persulfate.[31] The perchloric acid digestion method was used to determine total P.[29] Residual-P was calculated by subtracting the sum of the above four types of extractable P from the total P content in the soil. The residual P was also measured separately to evaluate the P budget. The total P contents calculated by summation of all fractions were consistent with the measured total P concentration (Table 2). Based on the sequence of extractions, soil P fractions were referred to as water soluble P (H_2O-P), bioavailable P ($NaHCO_3$-P), potentially bioavailable (NaOH-P), acid soluble P (Ca-bound P/HCl-P), and residual P.

Soil Phosphorus Saturation

The degree of phosphorus saturation (DPS), expressed as a percent, was calculated by dividing the oxalate-extractable P ($mmol\,kg^{-1}$) by the sum of oxalate-extractable Fe and Al ($mmol\,kg^{-1}$).[32] Phosphorus, Fe, and Al were extracted by shaking 1.00 g soil with an extractant of $0.1\,mol\,L^{-1}$ oxalic acid $+ 0.175\,mol\,L^{-1}$ ammonium oxalate (pH 3.0) in the dark for 2 h [33] and P, Fe, and Al concentrations in the extracts were determined using an Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, Ultima, JY Horiba Inc. Edison, N.J.).

Fractionation of Heavy Metals

A modified procedure of Amacher (1996)[12] was employed to fractionate heavy metals in the soils. This method is based on both solubility of individual solid-phase components and on selectivity and specificity of chemical reagents. The procedure provides a gradient for the physico-chemical association strength between heavy metals and solid components rather than for actual speciation. Therefore, the terms of the fractions are more operationally than chemically defined. Heavy metals in the

Table 2. Recovery of phosphorus and heavy metals extracted by sequential fractionation.

Elements	Recovery[†] (%)	
	Range	Mean
P	96.5–108	102
Cu	99.9–107	103
Zn	89.8–107	102
Mn	98.3–108	104
Cr	91.5–107	104
Cd	100–109	106
Co	104–112	108
Mo	94.1–131	107
Ni	101–118	106
Pb	97.9–121	106

[†]Relative percentages of cumulative element concentrations (from summation of all fractions as determined by the sequential extraction procedure) in the measured total concentrations.

soil were sequentially fractionated into: (i) exchangeable metals (including water soluble) extracted with $0.1 \, mol \, L^{-1} \, Mg(NO_3)_2$ (shaking 2 h at 80 cycles/min); (ii) carbonate associated metals extracted with $1 \, mol \, L^{-1}$ sodium acetate at pH 5 (shaking 5 h at 80 cycles/min); (iii) oxide associated metals extracted with $0.2 \, mol \, L^{-1}$ ammonium oxalate $+ \, 0.2 \, mol \, L^{-1}$ oxalic acid $+ \, 0.1 \, mol \, L^{-1}$ ascorbic acid at pH 3.3 (in a boiling water bath for 30 min); (iv) organically bound associated metals extracted with 30% H_2O_2 at pH 2 (in a boiling water bath for 30 min); and (v) the residual metals extracted by digestion with nitric acid and perchloric acid. Five grams of each soil were sequentially extracted. After each successive extraction, the supernatant solution was separated by centrifuging the suspension at $7500 \times g$ for 30 min and filtered through a Whatman 42 filter paper. The concentrations of Cd, Co, Cr, Co, Ni, Pb, Zn, Mn, and Mo in the solutions were determined using the ICP-AES. Total Cd, Co, Cr, Co, Ni, Pb, Zn, Mn, and Mo concentrations in the soils were determined by the ICP-AES after digestion with nitric acid and perchloric acid.[12] The detection limits of the ICP-AES are 0.22, 0.52, 0.42, 2.50, 0.61, 1.96, 0.60, 0.11, and 0.81 µg L^{-1}, respectively for Cd, Co, Cr, Cu, Ni, Pb, Zn, Mn, and Mo. The mean recoveries of extracted heavy metals, relative percentages of cumulative element concentrations (from summation of all fractions as determined by the sequential extraction procedure), in the measured total concentrations were 102–108% (Table 2).

RESULTS AND DISCUSSION

Accumulation and Partitioning of Phosphorus in the Soils

Total P, Olsen-P, and all P fractions significantly accumulated in the surface layer of the vegetable crop soil (Table 3). Phosphorus concentrations were higher in

Table 3. Mean concentrations of P fractions, total P, and Olsen-P in surface soils (0–15 cm).

Location	P fractions ($mg\,kg^{-1}$)					Total P ($g\,kg^{-1}$)	Olsen-P ($mg\,kg^{-1}$)
	H_2O-P	$NaHCO_3$-P	NaOH-P	HCl-P	Residual-P		
Vegetable crop ($n = 16$)	35.3a[†]	120.8a	46.6a	81.5a	51.3a	0.34a	52.9a
Forest ($n = 8$)	1.6b	1.4b	2.7b	2.3b	7.5b	0.02b	2.9b

[†]Means followed by the same letter within a column are not significant different at 5% probability level based on Fisher' LSD test.

Table 4. Distribution of P fractions, total P, and Olsen-P in the soil profiles.

Location	Depth (cm)	P fractions					Total P	Olsen-P
		H_2O-P	$NaHCO_3$-P	NaOH-P	HCl-P	Residual-P		
		($mg\,kg^{-1}$)						
Vegetable crop ($n = 8$)	0–15	35.2a[†]	121.1a	47.1a	81.3a	69.3a	0.35a	51.2a
	15–30	23.2a	68.9a	22.8a	32.5a	32.9a	0.18a	28.4a
	30–60	14.6a	24.7a	22.4a	7.8a	29.0a	0.10a	14.8a
	60–90	9.2a	20.6a	22.2a	7.2a	29.2a	0.09a	12.5a
Forest ($n = 4$)	0–15	1.2b	1.9b	3.2b	3.0b	9.8b	0.02b	4.5b
	15–30	1.5b	1.7b	2.8b	3.0b	21.6a	0.03b	2.8b
	30–60	1.9b	2.8b	5.9b	3.4b	30.7a	0.04b	4.5b
	60–90	1.3b	1.1b	4.6b	2.3b	25.9a	0.04b	2.9b

[†]Means followed by the same letter for the same depth in a column are not significantly different at 5% probability level based on Fisher' LSD test.

the vegetable soil than the forest soil. The concentrations of total P, Olsen-P, H_2O-P, $NaHCO_3$-P, NaOH-P, HCl-P, and residual P in surface layer from the vegetable soil were 21, 18, 22, 89, 17, 36, and 7 fold of those from the forest soil. The $NaHCO_3$-P and HCl-P accumulations in the surface layer from the vegetable soil were most dramatic whereas the residual P was the least accumulated, as compared with the forest soil. There was a significant difference in P distribution in the profiles between the vegetable and the forest soil (Table 4). For the forest soil, the total P, H_2O-P, and residual P were lower in the surface than in subsoil. This may be caused by plant uptake or leaching of P without replenishment from the surface layer. Phosphorus in the forest soil mostly appeared in the residual fraction, which accounted for 52–73% of the total P. For the vegetable soil, phosphorus accumulated mainly in the upper 0–15 cm and, to a lesser extent, in the 15–90 cm depth (Table 4). Major P fractions at the 0–30 cm depth in the vegetable soil were $NaHCO_3$-P, followed by HCl-P and residual P. However, the concentrations of total P, Olsen-P, and all P fractions at all the depths except for residual P at depths of
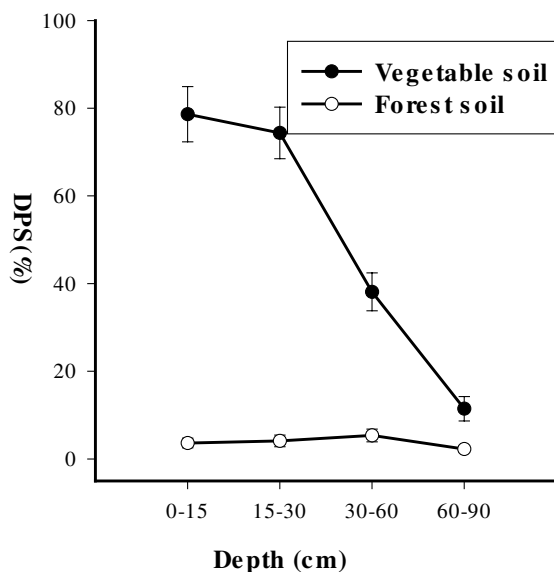
Figure 1. The degree of phosphorus saturation (DPS) for the vegetable and forest soils. Error bars represent SD.

15–90 cm in the vegetable soil were significantly higher than those in the forest soil, indicating that there was a remarkable P mobility in the vegetable soil profile. Most of P in the vegetable soil was extractable, and the residual P fraction was as low as 18–33% of the total P. High concentrations of labile P (H_2O-P and $NaHCO_3$-P) in the vegetable soil suggest that the soil has a high P mobility.

The vegetable soil had higher DPS values compared to the forest soil throughout the soil profile (Fig. 1). A high degree of soil DPS may lead to significant P loss to shallow ground water and surface waters. Values for DPS of above 25% are commonly associated with the strongly increased risk of P loss in leaching or runoff and thus nonpoint-source pollution.[34] The vegetable soils had surface horizon DPS about 78% which could be considered as a risk of P loss in leaching.

Heavy Metal Accumulation in Soils

Total concentrations of selected heavy metals (Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, and Zn) in the surface samples of both vegetable and forest soils are presented in Table 5. Copper, Zn, Mn, and Cr accumulated considerably in the surface layer of the vegetable soil. Concentrations of Cu, Zn, Mn, and Cr in the surface layer were significantly higher in the vegetable soil than in the forest soil. Mean total Cu concentration in the surface layer of forest soil averaged $4.1\,mg\,kg^{-1}$, whereas that in the vegetable soil was $53.6\,mg\,kg^{-1}$. Mean total Zn concentration in the forest soil was $6.6\,mg\,kg^{-1}$ but was about four times higher ($26.8\,mg\,kg^{-1}$) in the vegetable soil. Mean total Mn and Cr concentrations in the surface layer of vegetable soil were

Table 5. Total Concentrations of heavy metals in surface soils.

Location	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Zn
	(mg kg^{-1})								
Vegetable Crop (n = 16)	0.2a[†]	0.3a	8.0a	53.6a	63.9a	0.2a	0.8a	4.1a	26.8a
Forest (n = 8)	0.2a	0.3a	1.8b	4.1b	4.7b	0.2a	0.7a	4.5a	6.6b

[†]Means followed by the same letter within a column are not significantly different at 5% probability level based on Fisher' LSD test.

Table 6. Distribution of total heavy metals in soil profiles.

Location	Depth (cm)	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Zn
		(mg kg^{-1})								
Vegetable Crop (n = 8)	0–15	0.1a[†]	0.3a	7.7a	66.1a	62.9a	0.3a	0.7a	3.4a	28.9a
	15–30	0.1a	0.2a	3.7a	43.7a	20.2a	0.3a	0.6a	2.1a	17.3a
	30–60	0.1a	0.2a	1.6a	26.8a	6.5a	0.3a	0.4a	1.5a	10.7a
	60–90	0.1a	0.3a	3.1a	28.1a	4.3a	0.4a	1.0a	2.4a	8.3a
Forest (n = 4)	0–15	0.1a	0.2a	2.3b	5.8b	6.8b	0.2a	0.6a	2.8a	6.3b
	15–30	0.1a	0.3a	3.9a	4.1b	11.3b	0.4a	0.9a	2.6a	7.0b
	30–60	0.1a	0.2a	2.7a	1.0b	7.4a	0.4a	0.9a	1.5a	6.2b
	60–90	0.1a	0.4a	3.9a	0.6b	3.5a	0.4a	1.0a	2.1a	3.7b

[†]Means followed by the same letter for the same depth in a column are not significantly different at 5% probability level based on Fisher' LSD test.

about 14 and 4 fold of those in the forest soil. But there were no significant differences in Cd, Co, Mo, Ni, and Pb concentrations between the two soils.

There were distinctly different distributions among heavy metals in the vegetable soil (Table 6). Most of the total Cr in the vegetable soil accumulated in the upper 0–15 cm. Total Cr at depths of 15–90 cm were similar between the vegetable soil and the forest soil. Copper and Zn concentrations at all depths were higher in the vegetable than the forest soil. Total Mn concentration at the depth 0–30 cm in the vegetable soil was significantly higher than that in the forest soil. However, no Mn accumulation was found at the depth 30–90 cm in the vegetable soil. There was an abrupt change in Mn concentration at the depth of 30 cm in the profile. This probably attributed to Mn reduction caused by high groundwater level (generally 30–50 cm below the surface) in the vegetable soil. The high groundwater level probably resulted in rapid reduction of Mn. As a result, Mn was removed from the subsoil where the groundwater fluctuated. There was no evidence of a significant accumulation and transport of Cd, Co, Mo, Ni, and Pb in the vegetable soil. No

significant differences were found in vertical distributions of Cd, Co, Mo, Ni, and Pb between the vegetable and the forest soil (Table 6).

Partitioning of Heavy Metals in the Soil Profiles

The partitioning of Cu, Zn, Mn, and Cr in various solid components with depth in the soil profiles of both vegetable and forest is presented in Table 7. Copper concentrations in all fractions except for residual fraction at the depth of 15–60 cm in the vegetable soil were significantly higher than those in the forest soil. Zinc concentrations in all fractions except for residual fraction at the depth of 15–90 cm and oxide fraction at the depth of 30–90 cm in vegetable soil were significantly higher than those in the forest soil. Manganese concentrations in all fractions except for $CaCO_3$ fraction at the depth of 30–90 cm and oxide fraction at the depth of 15–90 cm in vegetable soil were significantly greater than those in forest soil. Chromium concentrations in all fractions except for exchangeable fraction at the surface layer in vegetable soil were higher than those in the forest soil. However, for subsoil (15–90 cm), there was significant difference between the vegetable soil and the forest soil only for organically bound fraction of Cr. Cadmium, Co, Ni, Mo, and Pb concentrations in all fractions at all depths in vegetable soil were very low. Similar to their total concentrations, the differences in concentrations of all fractions of these elements (Cd, Co, Ni, Mo, and Pb) between the vegetable soil and forest soil were generally not significant with a few exceptions (Table 8). In the vegetable soil, Cu accumulated predominantly in the oxide fraction, followed by the $CaCO_3$ fraction, the organically bound fraction and the exchangeable fraction. Zinc accumulated mainly in the $CaCO_3$ fraction, followed by the oxide, exchangeable and organically bound fractions. Manganese accumulated mainly in the $CaCO_3$ fraction, followed by organically bound, exchangeable and oxide fractions. Chromium accumulated mainly in the organically bound fraction. Compared with the forest soil, the vegetable soil had lower percentages of residual fractions except for Ni, higher percentages of $CaCO_3$ fractions, and lower percentages of exchangeable fractions except for Ni and Mo (Table 9). Percentages of Mn, Cr, Cd, Co, Mo, and Pb in the organically bound fraction were higher in the vegetable soil than in forest soil, and percentages of Cu, Mn, Cr, Cd, Co, and Pb in the oxide fraction were higher in the vegetable soil than in the forest soil.

Mobility of Heavy Metals in the Soil Profile

The vegetable soil had higher proportions of Cu, Zn, Mn in the $CaCO_3$ and oxide fractions, which may have greater mobility (Table 7). The Cu, Zn, and Mn in the $CaCO_3$ and oxide fractions may be solubilized and released into the soil solution during periods of soil water saturation and/or water ponding of the soil surface, or when acidic fertilizer is applied. The greater mobility of Cu, Zn, and Mn in the soil increased downward movement of these elements in the profile, which was consistent with the accumulation of the elements in the profile. Chromium in the organically bound fraction may also be somewhat subject to transport in the soil profile, which

Table 7. Distribution of Cu, Zn, Mn, and Cr in the solid-phase fractions in the soil profiles.

Depth (cm)	Exchangeable Vegetable†	Exchangeable Forest‡	CaCO₃ Vegetable	CaCO₃ Forest	Organically bound Vegetable	Organically bound Forest	Oxide Vegetable	Oxide Forest	Residual Vegetable	Residual Forest
					$Cu\ (mg\ kg^{-1})$					
0–15	2.1a§	0.3b	14.2a	0.9b	10.2a	1.8b	36.7a	2.0b	2.7a	1.0b
15–30	1.8a	0.1b	13.2a	0.6b	7.7a	0.4b	19.9a	1.6b	1.8a	1.7a
30–60	2.0a	0.0b	9.8a	0.0b	6.2a	0.1b	9.8a	0.2b	0.9a	0.7a
60–90	2.9a	0.0b	7.5a	0.0b	4.4a	0.1b	12.0a	0.1b	2.9a	0.5b
					$Zn\ (mg\ kg^{-1})$					
0–15	3.0a	1.0b	15.1a	1.3b	3.0a	0.8b	5.4a	1.5b	4.3a	2.2b
15–30	3.0a	0.01b	7.2a	1.6b	1.7a	0.8b	2.6a	1.5b	3.8a	3.1a
30–60	2.0a	0.00b	2.8a	0.6b	1.0a	0.4b	1.5a	1.1a	3.7a	3.5a
60–90	2.2a	0.00b	1.6a	0.7b	0.8a	0.4b	1.6a	0.9a	1.9a	2.0a
					$Mn\ (mg\ kg^{-1})$					
0–15	12.0a	1.5b	23.6a	2.4b	13.5a	1.3b	12.2a	0.9b	4.3a	0.8b
15–30	7.6a	1.3b	8.2a	4.3b	2.4a	1.3b	1.9a	2.4a	1.2b	2.6a
30–60	2.6a	0.3b	1.8a	1.9a	1.0a	0.6b	0.9a	0.8a	0.8b	3.8a
60–90	1.3a	0.1b	0.8a	0.2a	0.8a	0.4b	0.3a	0.5a	1.2b	2.3a
					$Cr\ (mg\ kg^{-1})$					
0–15	0.1a	0.1a	0.2a	0.02b	5.0a	1.1b	0.9a	0.2b	1.9a	0.9b
15–30	0.1a	0.1a	0.1a	0.1a	2.5a	0.7b	0.4a	0.4a	0.8b	2.9a
30–60	0.1a	0.1a	0.03a	0.01a	1.0a	0.6b	0.2a	0.3a	0.4b	1.5a
60–90	0.1a	0.1a	0.02a	0.01a	1.0a	0.6b	0.3a	0.3a	2.0a	3.0a

†n = 8.
‡n = 4.
§Means followed by the same letter within a row for each fraction are not significant different at 5% probability level based on Fisher' LSD test.

Table 8. Distribution of Cd, Co, Mo, Ni, and Pb in the solid-phase fractions in the soil profiles.

Depth (cm)	Exchangeable Vegetable[†]	Exchangeable Forest[‡]	CaCO$_3$ Vegetable	CaCO$_3$ Forest	Organically bound Vegetable	Organically bound Forest	Oxide Vegetable	Oxide Forest	Residual Vegetable	Residual Forest
					Cd (mg kg^{-1})					
0–15	0.01a[§]	0.01a	0.03a	0.02b	0.04a	0.03b	0.03a	0.00b	0.04a	0.06a
15–30	0.02a	0.00b	0.01a	0.01a	0.03a	0.02a	0.02a	0.01a	0.02b	0.09a
30–60	0.02a	0.00b	0.01a	0.00a	0.03a	0.01b	0.00a	0.00a	0.06b	0.1a
60–90	0.02a	0.00b	0.00a	0.00a	0.04a	0.01b	0.00a	0.00a	0.09a	0.1a
					Co (mg kg^{-1})					
0–15	0.05a	0.05a	0.01a	0.00a	0.09a	0.06a	0.03a	0.01a	0.1a	0.1a
15–30	0.06a	0.04a	0.01a	0.04a	0.07a	0.06a	0.01a	0.01a	0.06b	0.1a
30–60	0.06a	0.04a	0.00a	0.02a	0.08a	0.07a	0.00b	0.05a	0.05a	0.08a
60–90	0.08a	0.04a	0.00a	0.01a	0.08a	0.06a	0.01a	0.02a	0.2a	0.3a
					Mo (mg kg^{-1})					
0–15	0.07a	0.03a	0.02a	0.00a	0.08a	0.00b	0.01a	0.01a	0.2a	0.1a
15–30	0.08a	0.01a	0.00a	0.1a	0.04a	0.00b	0.01a	0.02a	0.2a	0.2a
30–60	0.05a	0.00a	0.00a	0.01a	0.04a	0.01a	0.1a	0.2a	0.1b	0.4a
60–90	0.05a	0.02a	0.00a	0.01a	0.09a	0.08a	0.01a	0.05a	0.3a	0.3a
					Ni (mg kg^{-1})					
0–15	0.1a	0.08a	0.06a	0.04a	0.1a	0.2a	0.1a	0.1a	0.3a	0.2a
15–30	0.1a	0.07a	0.03a	0.05a	0.1a	0.2a	0.08a	0.04a	0.3b	0.6a
30–60	0.1a	0.08a	0.01a	0.02a	0.2a	0.2a	0.04a	0.08a	0.09b	0.7a
60–90	0.2a	0.10a	0.00a	0.02a	0.2a	0.2a	0.04a	0.04a	0.6a	0.7a
					Pb (mg kg^{-1})					
0–15	0.2a	0.3a	0.20a	0.1a	0.2a	0.04a	2.3a	1.4b	0.7b	0.9a
15–30	0.2a	0.2a	0.20a	0.4a	0.1a	0.08a	1.2a	1.3a	0.4b	0.8a
30–60	0.3a	0.1a	0.10a	0.3a	0.2a	0.01a	0.6b	1.2a	0.3a	0.2a
60–90	0.3a	0.2a	0.03a	0.4a	0.2a	0.03a	0.6a	0.8a	1.4a	0.9a

[†]$n = 8$
[‡]$n = 4$
[§]Means followed by the same letter within a row for each fraction are not significant different at 5% probability level based on Fisher' LSD test.

Table 9. Mean proportions of various heavy metal fractions in the surface soils (0–15 cm).

Element	Location	Exchangeable	CaCO$_3$	Organically bound	Oxide	Residual
				(%)		
Cu	Vegetable[†]	3	22	15	56	4
	Forest[‡]	5	15	30	33	17
Zn	Vegetable	10	49	10	17	14
	Forest	15	20	12	22	32
Mn	Vegetable	18	36	21	19	7
	Forest	22	35	18	13	12
Cr	Vegetable	1	2	61	12	24
	Forest	3	1	45	10	40
Cd	Vegetable	7	20	27	20	27
	Forest	8	17	25	0	50
Co	Vegetable	18	4	32	11	36
	Forest	21	0	25	4	50
Ni	Vegetable	17	8	19	18	38
	Forest	12	6	24	20	38
Mo	Vegetable	20	6	23	3	49
	Forest	19	0	0	6	75
Pb	Vegetable	6	5	4	66	19
	Forest	12	4	1	51	32

[†]$n = 8$.
[‡]$n = 4$.

would result in higher concentration of organically bound Cr at all depths in the vegetable soil than the forest soil (Table 7). Cadmium, Co, Ni, Mo, and Pb, however, exhibited limited accumulation and mobility in the soil profile.

CONCLUSIONS

Long-term vegetable production practices resulted in considerable accumulation of P, Cu, Zn, and Mn in the soil. Cadmium, Co, Mo, Ni, and Pb were not enriched in the soil. Chromium in the vegetable soil accumulated mainly in the upper 0–15 cm. Enrichment of P, Cu, Zn, and Mn at all depths of the soil profile suggests that these elements were leached from the surface. The major contribution of P, Cu, Zn, Mn, and Cr in the sandy soil may be from repeated application of fertilizer and fungicides. Major P fractions in the vegetable soil were NaHCO$_3$-P, followed by HCl-P and residual P. The dominant fractions of Cu in the vegetable soil were the oxide and CaCO$_3$ fractions, and those of Zn were the CaCO$_3$ and oxide fractions. Manganese accumulated mainly in the CaCO$_3$ fraction, followed by the organically bound, exchangeable, and oxide fractions. Chromium accumulated mainly in the organically bound fraction. Higher percentages of Cu, Zn, and Mn in the CaCO$_3$ or oxide fractions indicated that Cu, Zn, and Mn in the soil have greater release potential and may pose environmental risk to the surface and groundwater. Compared with

the forest soil, the vegetable soil had lower percentages of residual fractions, and higher percentages of the $CaCO_3$ or organic fractions of P, Cu, Zn, and Mn.

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