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Changes in soil properties and the availability of soil micronutrients after 18 years of cropping and fertilization

Xiaorong Wei [a,b,*], Mingde Hao [a], Mingan Shao [c,a], William J. Gale [d]

[a] *State Key Laboratory of Soil Erosion and Dryland Farming on the Loess Plateau, Institute of Soil and Water Conservation, CAS and MWR, Yangling, Shaanxi Province 712100, PR China*

[b] *Graduate School of CAS, Beijing 100039, PR China*

[c] *Institute of Geographical Science and Natural Resources Research, CAS, Beijing 100101, PR China*

[d] *Northwest Sci-Tech. University of Agriculture & Forestry, College of Natural Resources and the Environment, Yangling, Shaanxi Province 712100, PR China*

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Abstract

Micronutrient deficiencies are common in many parts of China's Loess Plateau. The objective of this experiment was to study the effects of long-term cropping and fertilization practices on soil properties and micronutrient availability in this region. The field plot experiment began in 1984. It included five cropping systems and four fertilizer treatments. In September 2002, soil samples were collected and soil pH, organic matter content, available P, and $CaCO_3$ were measured. Total and available Zn, Cu, Mn, and Fe were also determined. The relationship between soil properties and available micronutrients was determined by correlation and path analysis. After 18 years, soil pH and $CaCO_3$ levels were lower in the cropped and fertilized treatments compared to the fallow treatment. In contrast, soil organic matter and available P levels were higher in cropped compared to fallow treatments. A comparison of unfertilized treatments indicated that available Zn and Cu levels in cropped treatments were lower compared to the fallow treatment, probably due to the removal of these micronutrients from the system through crop uptake and harvest. In contrast, available Mn and Fe levels were higher in cropped treatments compared to the fallow treatment. The impacts of fertilization on available micronutrients varied with cropping systems. Generally, available Zn and Fe were higher in fertilized compared to unfertilized treatments, but available Cu was not significantly influenced by fertilization. Fertilization tended to increase available Mn in continuous wheat and maize, but reduced available Mn in continuous clover and the crop–legume rotation. The total (plant available + unavailable) micronutrient contents were lower in the four cropped-treatments compared to the fallow treatment. The addition of manure or P fertilizer increased total Zn, Fe, and Mn, but had no significant effect on total Cu. The results of correlation analysis and path analysis indicated that soil organic matter exerts a significant and direct effect on the availability of Zn, Mn, and Fe, but has little influence on available Cu. The effects of available P, $CaCO_3$, and pH on micronutrient availability were indirect, passing through soil organic matter. The results of this study suggest that long-term cropping and fertilization altered several important soil properties and increased the plant available micronutrient content of this loess-derived soil.

Keywords: Cropping; Fertilization; Soil properties; Micronutrients; Availability

1. Introduction

Soil provides the micronutrients that are needed by plants in order to complete their life cycle. Previous studies have shown that the availability of soil

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* Corresponding author.
E-mail address: xrwei78@163.com (X. Wei).

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micronutrients is largely influenced by the soil microenvironment as well as soil properties, such as pH, $CaCO_3$, organic matter, and available P (Christensen et al., 1951; Jenne, 1968; Lutz et al., 1972; Olomu et al., 1973; Yuan, 1983; Shuman, 1988a,b). Cropping systems and fertilization practices also influence micronutrient availability. Liu et al. (2002) studied the effects of rice-based cropping on Mn distribution in a paddy soil profile derived from red earth and found that a rice-upland crop rotation prompted the reduction of Mn in the surface soil and accelerated the oxidation and accumulation of Mn in the subsoil, especially when large amounts of manure were applied to the soil. Gao et al. (2000) conducted a 9 years fertilization study on a purple paddy soil in southwest China and found that manure was a better source of available Fe, Mn, and Zn compared to synthetic fertilizers, but manure accelerated the depletion of available Cu.

Soils in the Loess Plateau of China are calcareous with a low organic matter content. Soil pH values range from 7.6 to 8.7. $CaCO_3$ content varies from 1 to 300 g kg^{-1}. Under these conditions, soil micronutrients are often in forms that are unavailable to the plant. This leads to nutrient deficiencies and reductions in crop yield. Although micronutrient deficiencies have often been observed in the Loess Plateau, little is known about the long-term effect of cropping systems and fertilization practices on micronutrient availability in the region.

In this paper, we report results from an 18 years experiment conducted in the southern part of the Loess Plateau. The objective of this research was to study the effect of cropping systems and fertilization practices on soil properties and micronutrient availability.

2. Materials and methods

2.1. Experimental site and soil characterization

The long-term field experiment was initiated in September 1984 at the Agro-ecological Experiment Station of the Chinese Academy of Science, Changwu County, Shaanxi Province, China (35°12′N, 107°40′E). Average annual temperature is 9.1 °C and annual precipitation is 585 mm. In China, the soil is referred to as a Heilu soil, which corresponds to a Calcarid Regosol according to the FAO/UNESCO classification system (FAO/Unesco, 1988). Its properties are shown in Table 1. Soil loss due to water and wind erosion is very low.

Table 1
Chemical properties of the soil at the start of the experiment in 1984

Chemical property	Content
Organic matter (g kg^{-1})	10.5
Total nitrogen (g kg^{-1})	0.8
Available nitrogen (mg kg^{-1})	37.0
Total phosphorous (mg kg^{-1})	0.7
Olsen phosphorous (mg kg^{-1})	3.0
Available potassium (mg kg^{-1})	129.3
DTPA extractable Zn (mg kg^{-1})	0.8
DTPA extractable Cu (mg kg^{-1})	1.1
DTPA extractable Mn (mg kg^{-1})	9.4
DTPA extractable Fe (mg kg^{-1})	5.9
$CaCO_3$ (g kg^{-1})	108.4

2.2. Experiment design and management

The experimental design was a randomized complete block in a split-plot arrangement. Cropping system was the main plot treatment and fertilizer was the split-plot treatment. The cropping systems were long-term fallow, continuously cropped clover (*Trifolium repens* L.), continuously cropped maize (*Zea mays* L.), continuously cropped winter wheat (*Triticum aestivum* L.), and pea (*Pisum sativum* L.)–winter wheat–winter wheat–millet (*Panicum miliaceum* L.) as a crop–legume rotation system. The fertilizer treatments were unfertilized control (CK), nitrogen (N), phosphorus (P), nitrogen + phosphorus (NP), and nitrogen + phosphorus + manure (NPM). Fertilizer treatments differed according to the cropping systems. Continuously cropped clover received the CK, P, and NPM treatments. Continuously cropped maize received the NP and NPM treatments. Continuously cropped wheat received the CK, N, P, and NPM treatments. The crop–legume rotation system received the CK, P, NP, and NPM treatments.

Urea and superphosphate were used as the source of N and P. Manure came from cattle. In all the fertilizer treatments, the N rate was 120 kg ha^{-1}, the P rate was 26 kg ha^{-1}, and the M rate was 75 t ha^{-1}. Total N content of the manure was 1.97 g kg^{-1} and available N was 91 mg kg^{-1}. Total P content of the manure was 0.97 g kg^{-1} and available P was 115 mg kg^{-1}. The Zn, Cu, Mn, and Fe contents of the P fertilizer were 70, 9, 332, and 408 mg kg^{-1}, respectively, and of the manure were 65, 19, 24, and 50 mg kg^{-1}, respectively.

The experiment was replicated three times. Each plot was 10.3 m × 6.5 m. Crop varieties, seeding rates, and sowing and harvest times are shown in Table 2. Routine crop management practices for this region were used. Prior to seeding, fertilizers were broadcast on the soil surface, and then the land was plowed two times with a

Table 2
Crop varieties, seeding rates, seeding, and harvest times in the experiment

Crop	Varieties	Seeding rate (kg ha^{-1})	Seeding period	Harvest period
Clover	Native varieties	7.5		Early June or Mid-August
Maize	Zhongdan #2 or Danyu #13	15.0	Mid-April	Mid-September
Winter wheat	Qinmai #4 (1984–1985), Changwu #131 (1986–1995), Changwu #134 (1996–2002)	187.5	Mid-September	Late June
Pea	White pea	187.5	Mid-March	Early July
Millet	Native varieties	62.5	Early July	Early October

cattle-drawn moldboard to a depth of about 20 cm. Wheat and pea were sown in rows 25 cm apart. After seeding, the soil was raked to cover the seed. Maize was sown in rows 60 cm apart. Clover and millet were broadcast-sown.

The legume crop was cut twice each year for hay. When the other crops reached maturity, they were harvested at ground-level, the straw and grain were removed, and then the soil was plowed two times to a depth of about 20 cm with a moldboard. No crop was planted in the fallow treatment and no fertilizer was applied either. The fallow plots were plowed twice in June and twice in September of each year. Weeds were removed by hand in all cropping systems, including the fallow treatment.

2.3. Soil sampling

Soil samples were collected on 23 September 2002. Five random cores were taken from the plow layer (0–15 cm) and plow sole (20–32 cm) of each plot with a 5 cm diameter tube auger. Large pieces of organic matter were removed by hand. Moist subsamples were brought to the laboratory, air dried, and ground to pass through 1 and 0.25 mm nylon screens.

2.4. Laboratory analysis

Soil pH was measured in a 1:2 soil:water suspension with a glass electrode. Organic matter was determined by the titration method (Walkley and Black, 1934). Available P was determined by the Olsen method (Olsen et al., 1954). $CaCO_3$ was tested by manometry (Agrochemistry Commission, Soil Science Society of China, 1983).

Because the soil was calcareous, available Zn, Cu, Mn, and Fe were extracted by the DTPA procedure developed for calcareous soils (Lindsay and Norvell, 1978). Twenty milliliters of 0.005 mol L^{-1} DTPA (diethylene thiamine pentacetic acid) + 0.1 mol L^{-1} TEA (trietanolamine) + 0.01 mol L^{-1} $CaCl_2$ (pH 7.30) were added to 10 g soil (<1 mm). The solutions were shaken for 2 h at 25 °C, centrifuged, and filtered through no. 5 Whatman filter paper. Aliquots were analyzed by atomic absorption spectrophotometry to determine the amount of available Zn, Cu, Mn, and Fe.

Total amounts of Zn, Cu, Mn, and Fe were determined by a tri-acid digestion method (Shuman, 1985). A 0.5000 g sample of soil (<0.25 mm) was put into a Teflon beaker, placed on a hot plate, and digested with a mixture of HNO_3–$HClO_4$–HF. After digestion, the solution was transferred into a 100 mL flask and analyzed by atomic absorption spectrophotometry to determine the total amount of each micronutrient.

All laboratory glassware was pre-soaked in 14% HNO_3 (v/v) and rinsed with deionized water. Chemical reagents used in this study were analytical grade.

2.5. Statistical analysis

Variance analysis, correlation analysis, and path analysis were conducted using SAS software (SAS Institute, 1989). Path analysis is a statistical technique that partitions correlations into direct and indirect effects, and attempts to differentiate between correlation and causation. This technique also features multiple linear regressions and generates standardized partial regression coefficients (path coefficients) (Wright, 1934).

3. Results and discussion

3.1. Soil properties

The effects of the cropping systems and fertilizer practices on soil pH, organic matter, available P, and $CaCO_3$ are shown in Table 3.

Soil pH values were lower in the cropped treatments compared to the fallow treatment (Table 3). Soil pH values for both the plow layer and plow sole were lowest in the continuous clover treatment followed by the continuous wheat and crop–legume rotation

Table 3
Soil pH, organic matter, available P, and $CaCO_3$ 18 years after the start of the experiment

Cropping system	Fertilizer treatment	Depth (cm)	pH	Organic matter (g kg^{-1})	Available P (mg kg^{-1})	$CaCO_3$ (g kg^{-1})
FW		0–15	8.62 a	10.7 jk	5.1 jlk	100 ced
		20–32	8.66 a	8.8 o	1.5 on	75 kji
CC	CK	0–15	8.50 a	21.6 c	3.0 mn	91 fged
		20–32	8.57 a	10.1 l	0.9 on	43 m
	P	0–15	8.50 a	24.5 a	18.5 e	82 jgih
		20–32	8.57 a	10.4 lk	5.6 jk	88 fgeh
	NPM	0–15	8.47 a	23.3 b	22.0 d	90 fged
		20–32	8.53 a	11.6 h	6.6 ji	96 fed
MC	NP	0–15	8.49 a	12.8 g	15.9 f	97 fed
		20–32	8.55 a	9.6 m	4.8 mlk	78 kjih
	NPM	0–15	8.44 a	17.7 d	24.7 c	112 b
		20–32	8.53 a	10.7 jk	7.4 i	95 fed
WC	CK	0–15	8.55 a	11.8 h	1.7 on	101 cbd
		20–32	8.59 a	9.5 nm	0.5 o	80 kjgih
	P	0–15	8.52 a	11.8 h	20.5 d	101 cbd
		20–32	8.62 a	8.2 p	6.1 jih	70 kl
	N	0–15	8.43 a	11.6 h	1.9 on	97 fed
		20–32	8.55 a	8.5 po	0.6 o	95 fed
	NPM	0–15	8.28 a	17.4 e	42.0 a	126 a
		20–32	8.36 a	9.2 n	12.6 g	91 fged
CLR	CK	0–15	8.59 a	11.0 ji	3.7 ml	89 fgeh
		20–32	8.62 a	8.4 p	1.1 o	79 kjgih
	P	0–15	8.49 a	11.6 h	31.0 b	86 fgih
		20–32	8.55 a	8.4 p	9.3 h	62 l
	NP	0–15	8.23 a	13.7 f	15.8 f	87 fgh
		20–32	8.34 a	9.8 m	4.8 mlk	73 kjl
	NPM	0–15	8.37 a	17.6 ed	42.6 a	110 cb
		20–32	8.45 a	11.2 i	12.8 g	87 fgh

FW, long-term fallow; CC, continuously cropped clover; MC, continuously cropped maize; WC, continuously cropped winter wheat; CLR, crop–legume rotation system; CK, unfertilized control; N, nitrogen; P, phosphorus; NP, nitrogen + phosphorus; NPM, nitrogen + phosphorus + manure. Values with the same letter are not significantly different at $p < 0.05$.

treatments. This was probably related to crop root activity in the soil (Haynes, 1983).

A comparison of fertilizer treatments within each cropping system indicated that the long-term application of manure and N fertilizer also led to a decrease in soil pH (Table 3). The reduction in pH varied with cropping system and ranged from 0.03 to 0.27 units in the plow layer and 0.04–0.23 units in the plow sole. Conyers et al. (1996) reported a reduction of 0.4 pH units in the top 10 cm of soil due to the addition of 100 kg N ha^{-1} as urea. The decrease in soil pH in the NPM treatments might have resulted from the release of organic acids and CO_2 into the soil during the decomposition of the manure. The decrease in the pH of the N fertilized treatments may have been due to nitrification of NH_4^+. The uptake of N as NH_4^+ by the crops could have also contributed to this effect.

Soil organic matter levels were higher in the cropped treatments compared to the fallow treatment (Table 3). This was expected since organic matter was continually being added to the soil from plant roots in the cropped treatments, but there were no organic inputs in the fallow treatment. Organic matter levels were generally higher in the plow layer compared to the plow sole. For example, soil organic matter levels in continuous clover were 103% higher in the plow layer and 15% higher in the plow sole compared to the fallow treatment. In continuous wheat, soil organic matter levels were 10% higher in the plow layer and 8% higher in the plow sole compared to the same depth in the fallow treatment. In contrast, the organic matter content in the crop–legume rotation was nearly the same or slightly lower than in the fallow treatment. These results indicate that under the soil and climatic conditions in the southern part of the Loess Plateau, continuous clover can increase soil organic matter levels, continuous wheat can maintain organic matter levels, but crop–legume rotations result in a slight decrease in soil organic matter levels.

A comparison of treatments within each cropping system indicated that fertilizer had a larger effect on soil organic matter (Table 3). For example, in the continuous clover treatment, soil organic matter in P fertilized plots was 13% higher in the plow layer and 3% higher in the plow sole compared to unfertilized plots. In NPM plots, organic matter was 8 and 15% higher in the plow layer and plow sole. In the crop–legume rotation, soil organic matter in the NP treatment was 25% higher in the plow layer and 16% higher in the plow sole. Also in the crop–legume rotation, organic matter in the NPM treatment was 61% and 33% higher in the plow layer and plow sole, respectively.

Some researchers have also found that long-term cropping can increase soil organic matter content. Bronick and Lal (2005) reported that crop rotation and manure application enhanced soil organic C. Diekow et al. (2005) reported that higher residue input associated with legume-based cropping systems increased soil organic C significantly. Mitchell and Entry (1998) found that long-term planting of legumes as a winter cover crop resulted in higher soil organic C levels (9.5 g C kg^{-1}) in the plow layer (0–20 cm depth) compared with treatments that did not include a winter cover crop (4.2 g C kg^{-1}).

Available P in the unfertilized treatment of each cropping system was significantly lower than in the fallow system (Table 3). This was due to the fact that in the cropped treatments, P was removed from the soil by plant uptake and subsequent harvest. The amount of available P in the plow layer and plow sole decreased in the following order: crop–legume rotation > continu-continuous clover > continuous wheat. Adding P (either P fertilizer or manure) greatly increased available P in both the plow layer and plow sole for all cropping systems.

Soil $CaCO_3$ in continuous clover decreased by 9% in the plow layer and 43% in the plow sole compared to the fallow treatment. Similarly, $CaCO_3$ in continuous wheat decreased by 1.5% in the plow layer and 7.6% in the plow sole. Within the same cropping system, synthetic fertilizers led to a slight reduction in the $CaCO_3$ content of the soil compared to the unfertilized treatment, but manure resulted in an increase in the $CaCO_3$ content. This was probably due to manure being treated with $CaCO_3$ in order to kill harmful microorganisms.

3.2. Available micronutrients

3.2.1. Available zinc

Available Zn in the unfertilized treatment of each cropping system was lower than in the fallow system (Table 4). Furthermore, available Zn levels in the unfertilized treatments were lower than 0.50 mg kg^{-1} (DTPA extractable Zn), the critical value for Zn deficiency that has been adopted by Peng et al. (1980) for this area. Available Zn varied with cropping systems. Lowest available Zn occurred in the continuous wheat treatment (41% reduction in the plow layer and 52% reduction in the plow sole compared to the same layers in the fallow treatment). Available Zn in the continuous clover treatment was similar in amount to that in the crop–legume rotation treatment. Low available Zn can be attributed to the removal of Zn from the cropped treatments due to harvest. On the other hand, crop root activity was reduced in the unfertilized treatments. This could have affected the release of non-available Zn from soil.

Available Zn was higher in the P fertilizer treatments compared to the unfertilized treatments. This was because the superphosphate fertilizer supplied Zn to the soil and offset the loss of Zn from the plots due to crop harvest. One interesting observation was that in the crop–legume rotation, available Zn was lower in the NP fertilizer treatment compared to the P treatment. One possible explanation for this could be that NP fertilizer promoted crop growth more than P fertilizer, resulting in an increase in plant uptake and subsequent removal of Zn at harvest from the NP fertilized plots. In this study, average pea yield was 11% higher in the NP compared to P treatment. Millet and wheat yields were more than 110% higher in the NP compared to P treatment.

Manure not only supplies large amounts of Zn to the soil, but also promotes biological and chemical reactions that result in the dissolution of non-available Zn. Consequently, available Zn in the NPM treatments was significantly higher than in the CK, P, or NP treatments, and this effect was greater in the plow layer than in the plow sole.

3.2.2. Available copper

Available Cu was lower in the cropped treatments compared to the fallow treatment (Table 4). The amount of available Cu in unfertilized treatments decreased

Table 4
Soil available Zn, Cu, Mn, and Fe 18 years after the start of the experiment

Cropping system	Fertilizer treatment	Depth (cm)	Available zinc (mg kg^{-1})	Available copper (mg kg^{-1})	Available manganese (mg kg^{-1})	Available iron (mg kg^{-1})
FW		0–15	0.60 c	0.84 c	7.4 h	3.2 n
		20–32	0.51 dfce	0.98 a	4.7 qp	3.2 nm
CC	CK	0–15	0.49 fge	0.72 ed	11.7 a	4.9 b
		20–32	0.26 lnom	0.95 ba	5.8 lnm	3.4 nlmk
	P	0–15	0.60 dc	0.73 d	11.2 a	5.5 a
		20–32	0.33 ljkm	0.86 c	6.8 ihj	3.6 hjik
	NPM	0–15	0.84 ba	0.70 edf	9.9 cd	4.9 b
		20–32	0.58 dce	0.89 bc	6.0 lkm	3.5 jlmk
MC	NP	0–15	0.34 lhjkim	0.60 ijh	8.2 g	3.7 hgif
		20–32	0.35 lhjki	0.61 ijh	4.9 op	3.8 hegf
	NPM	0–15	0.75 b	0.63 ijgh	10.4 cb	4.1 d
		20–32	0.22 no	0.59 ij	5.4 on	3.9 egdf
WC	CK	0–15	0.36 hjki	0.66 ieghf	6.9 ih	3.1 n
		20–32	0.25 nom	0.74 d	4.7 qp	4.0 ed
	P	0–15	0.43 hfg	0.63 ijgh	6.7 ij	3.3 nlm
		20–32	0.19 o	0.70 edf	4.1 q	3.8 hgf
	N	0–15	0.41 lhikm	0.61 ijghf	6.7 ef	4.0 jlk
		20–32	0.26 lnkom	0.70 d	4.9 lnm	3.7 edf
	NPM	0–15	0.75 b	0.69 egdf	8.9 f	5.3 a
		20–32	0.33 ljkim	0.66 eghf	7.4 h	3.7 hjgif
CLR	CK	0–15	0.47 fg	0.70 edf	10.6 b	3.5 jlik
		20–32	0.29 lnkm	0.73 d	6.5 ikj	3.9 hegdf
	P	0–15	0.51 dfe	0.64 ijgh	8.3 g	3.7 hjgi
		20–32	0.36 hjki	0.69 d	6.3 lkj	3.9 egdf
	NP	0–15	0.39 hjgi	0.57 j	9.5 ed	3.9 egdf
		20–32	0.26 lnom	0.65 ieghf	5.8 lnm	3.8 hgf
	NPM	0–15	0.93 a	0.61 ijgh	8.2 g	4.5 c
		20–32	0.42 hfgi	0.65 ieghf	5.6 nm	4.6 c

FW, long-term fallow; CC, continuously cropped clover; MC, continuously cropped maize; WC, continuously cropped winter wheat; CLR, crop–legume rotation system; CK, unfertilized control; N, nitrogen; P, phosphorus; NP, nitrogen + phosphorus; NPM, nitrogen + phosphorus + manure. Values with the same letter are not significantly different at $p < 0.05$.

in the order: continuous clover > crop–legume rotation > continuous wheat. Differences among cropping systems can probably be attributed to differences in the Cu uptake capacity of each crop.

Fertilization did not have a significant effect on available Cu. One reason for this might have been that the fertilizers used in this experiment contained very little Cu. A second reason might have been that the application of manure increased the amount of chelating agents in soil. In this case, Cu could be bound with organic matter and relatively unavailable to plants.

3.2.3. Available manganese

The amount of available Mn in the unfertilized treatments declined in the order: continuous clover > crop–legume rotation > long-term fallow > continuous wheat. In the P-fertilized treatments, available Mn decreased in the following order: continuous clover > crop–legume rotation > continuous wheat. These data indicate that the long-term planting of leguminous crops led to a large increase in available Mn. This increase might have been related to changes in the soil microenvironment by leguminous crops that resulted in the release of plant available Mn (Williams and David, 1976). For example, in the continuous clover treatment, soil pH was lower and organic matter levels were higher compared to the fallow treatment. The lower pH may have resulted in the release of previously non-available Mn from soil minerals. In addition, the decomposition of organic matter would have provided protons to the soil solution and also decreased soil Eh values. These changes could have resulted in the dissolution and reduction of Mn, thus increasing its availability.

The influence of fertilizer on available Mn differed between cropping systems (Table 4). In continuous wheat, available Mn was significantly higher in the NPM treatment compared to the unfertilized treatment, but the NP and P treatments had no significant effect on available Mn. In continuous maize, available Mn was also higher in NPM than in NP. In comparison, available Mn was lower in the fertilized compared to unfertilized treatments with continuous clover and crop–legume rotation.

3.2.4. Available iron

Changes in available Fe content in each cropping system were similar to those described above for available Mn. Compared to the fallow treatment, long-term continuous planting of clover increased available Fe by 54% in the plow layer and 5% in the plow sole (Table 4). The amount of available Fe in the crop–legume rotation treatment was 12% higher in the plow layer and 20% higher in the plow sole compared to the fallow treatment. This suggests that legume-based cropping systems can increase available Fe and improve the Fe nutrient status of crops.

Long-term fertilization also increased plant available Fe compared to the unfertilized treatment (Table 4). The effect of long-term fertilization varied among cropping systems. In continuous clover, available Fe was highest in the P and NPM treatments. In fertilized treatments of continuous wheat and crop–legume rotation, available Fe decreased in the order: NPM > NP > P.

3.3. Total micronutrients

Due to crop uptake and removal through harvest, total Zn, Cu, Mn, and Fe contents of unfertilized treatments in all four cropping systems were lower than in fallow. Total micronutrient content of the soil varied depending on the crop (Table 5). Total Cu, Mn, and Fe amounts were generally lowest in continuous wheat, while total Zn was lowest in the crop–legume rotation. Changes in available and total micronutrient contents were somewhat different. Total nutrient content was affected mainly by crop uptake, and therefore the magnitude of the decrease depended on crop type and uptake intensity. However, changes in available nutrient content were governed by root uptake and the release of non-available forms into soil solution. The impact of cropping on available nutrients was the result of an equilibrium between the two processes. So the influence of cropping on available nutrients was more complex than on total nutrient content.

Within the same cropping system, the total Zn, Fe, and Mn contents generally declined in the order: NPM > P > NP > CK > N. This pattern was different than the pattern that we observed for available micronutrients. Fertilization had little effect on the total Cu content of the soil.

3.4. Relationship between soil properties and available micronutrients

3.4.1. Zinc

Correlation analysis showed that available Zn was positively correlated with soil organic matter, available P, and $CaCO_3$ (Table 6). The coefficients were all significant at levels of $p < 0.01$. In contrast, there tended to be a negative relationship between available Zn and soil pH, but the correlation was not significant ($p > 0.05$).

Path analysis was used to partition the relationship between DTPA extractable micronutrients and soil properties into direct and indirect effects. Direct path coefficients measure the direct effect of a soil property on micronutrient availability, while indirect path coefficients specify the effect of a soil property passed through other properties. A high path coefficient indicates a strong effect on micronutrient availability.

Path analysis showed that direct path coefficients between available Zn and soil organic matter and available P were greater than the direct path coefficients between available Zn and $CaCO_3$ and soil pH (Table 6). The largest indirect path coefficient for available Zn was found when $CaCO_3$ passed through soil organic matter and available P. Although the direct path coefficient between soil pH and available Zn was positive, the indirect path coefficients for soil pH that passed through organic matter and available P were negative and larger than the direct path coefficient. This resulted in a negative correlation between available Zn and pH values. The results in Table 6 show that the interactive effect between soil properties on micronutrient availability was greater than the effect of any single soil property.

3.4.2. Copper

Available Cu was negatively correlated with soil available P and $CaCO_3$. Due to the narrow range of pH values used in the correlation analysis, a positive correlation between pH and available Cu was obtained, but this may not explain the relationship between pH and available Cu completely. In contrast to available Zn,

Table 5
Soil total Zn, Cu, Mn, and Fe 18 years after the start of the experiment

Cropping system	Fertilizer treatment	Depth (cm)	Total zinc (mg kg^{-1})	Total copper (mg kg^{-1})	Total manganese (mg kg^{-1})	Total iron (g kg^{-1})
FW		0–15	63 ml	24 f	646 s	34 m
		20–32	64 j	24 e	662 r	37 e
CC	CK	0–15	61 q	20 lk	633 x	33 p
		20–32	62 on	17 p	642 t	35 l
	P	0–15	66 g	23 hg	678 n	34 m
		20–32	65 i	15 s	673 p	34 o
	NPM	0–15	68 e	24 d	704 d	36 f
		20–32	67 f	17 o	682 l	35 l
MC	NP	0–15	63 l	19 m	680 m	34 n
		20–32	62 o	18 n	685 k	35 k
	NPM	0–15	78 a	22 i	686 j	35 j
		20–32	66 h	20 l	700 e	35 k
WC	CK	0–15	62 p	20 l	629 y	32 r
		20–32	63 k	15 r	638 v	34 n
	P	0–15	68 d	20 l	671 q	36 g
		20–32	67 f	21 j	675 o	36 f
	N	0–15	60 r	16 q	626 z	31 s
		20–32	61 q	15 r	636 w	33 q
	NPM	0–15	75 b	27 b	678 n	36 g
		20–32	67 fe	22 i	689 I	40 d
CLR	CK	0–15	61 q	22 i	632 x	34 on
		20–32	63 m	23 g	641 u	36 i
	P	0–15	64 j	25 c	718 b	35 i
		20–32	64 j	17 o	693 h	40 c
	NP	0–15	64 k	22 h	695 g	36 c
		20–32	62 n	20 k	707 c	43 b
	NPM	0–15	70 c	28 a	737 a	36 h
		20–32	66 hg	22 i	697 f	44 a

FW, long-term fallow; CC, continuously cropped clover; MC, continuously cropped maize; WC, continuously cropped winter wheat; CLR, crop–legume rotation system; CK, unfertilized control; N, nitrogen; P, phosphorus; NP, nitrogen + phosphorus; NPM, nitrogen + phosphorus + manure. Values with the same letter are not significantly different at $p < 0.05$.

path analysis indicated that soil pH and $CaCO_3$ influenced the availability of Cu directly, but organic matter and available P influenced Cu indirectly. Mehra and Jackson (1960) reported that Cu in calcareous soils appeared to precipitate as carbonate of hydroxides. Furthermore, Cu^{2+} is known to form strong bonds with soil organic matter (Hodgson et al., 1966; Stevenson and Arda Kani, 1972). These reasons may explain the results from our study.

3.4.3. *Manganese*

Available Mn was positively correlated with organic matter. The correlation coefficient was significant at a level of $p < 0.01$. Shuman (1988a) reported that adding organic matter can increase plant available Mn. Mandal and Mitra (1982) found that the application of organic matter brought an increase in water soluble and exchangeable Mn in soils. The formation of stable organic–Mn complexes can compete with precipitation as the mechanism controlling Mn availability (Ellis and Knezek, 1972). Besides complexation, organic matter degradation can supply electrons for the reduction of Mn oxides. This would increase the amount of Mn ions in the soil solution and increase Mn availability.

Available Mn was also positively correlated with available P and $CaCO_3$ at $p < 0.05$, but negatively correlated with soil pH. These findings are in agreement with Christensen et al. (1951) who reported that an

Table 6
Path coefficients and correlation coefficient of soil properties for available Zn, Cu, Mn, and Fe

		Direct path coefficient	Indirect path coefficients				r
			Via organic matter	Via available P	Via $CaCO_3$	Via pH	
Zn	Organic matter → Zn	0.435*		0.298	0.086	−0.089	0.75**
	Available P → Zn	0.519**	0.261		0.108	−0.140	0.75**
	$CaCO_3$ → Zn	0.185	0.210	0.303		−0.091	0.61**
	pH → Zn	0.241	−0.168	−0.301	−0.070		−0.30
Cu	Organic matter → Cu	0.157		−0.028	−0.103	−0.187	−0.16
	Available P → Cu	−0.048	0.090		−0.130	−0.292	−0.38*
	$CaCO_3$ → Cu	−0.222	0.072	−0.028		−0.191	−0.37*
	pH → Cu	0.504**	−0.058	0.028	0.084		0.56**
Mn	Organic matter → Mn	0.780**		−0.035	0.025	0.044	0.81**
	Available P → Mn	−0.061	0.448*		0.032	0.069	0.49**
	$CaCO_3$ → Mn	0.054	0.360	−0.035		0.045	0.42*
	pH → Mn	−0.119	−0.290	0.035	−0.021		−0.39*
Fe	Organic matter → Fe	0.722**		0.077	−0.073	0.041	0.77**
	Available P → Fe	0.134	0.415*		−0.092	0.064	0.52**
	$CaCO_3$ → Fe	−0.158	0.334	0.078		0.042	0.30
	pH → Fe	−0.111	−0.269	−0.078	0.060		−0.40*

Indirect path coefficients means the path coefficients of soil properties to soil micronutrients via certain soil properties and r is the correlation coefficient between soil properties and micronutrients.

* Values were significant at $p < 0.05$.

** Values were significant at $p < 0.01$.

increase in soil pH from 4.6 to 6.5 by liming reduced the concentration of exchangeable Mn between 20 and 50 times. The authors concluded that plant available Mn was influenced mainly by pH.

The direct path coefficient of available Mn with organic matter was larger than the other direct path coefficients, which explains the significant correlation between available Mn and organic matter. The indirect path coefficients of available P, $CaCO_3$, and pH that passed through organic matter were larger than the other indirect path coefficients.

3.4.4. *Iron*

Available Fe was positively correlated with organic matter and available P ($p < 0.01$) and negatively correlated with soil pH ($p < 0.05$). The correlation between available Fe and $CaCO_3$ was not significant. Moslehuddin et al. (1999) also reported a significant correlation between DTPA-Fe and soil organic C content in a Bangladesh paddy soil in a floodplain area. The direct path coefficient of available Fe with organic matter was larger than the coefficients for other soil properties, indicating that organic matter affected available Fe directly. The indirect path coefficients that passed through organic matter were greater than the coefficients that passed through the other soil properties. These relationships were similar to our observations for available Mn.

The statistical analyses described above indicated that organic matter had a large influence on available Zn, Mn, and Fe. Organic matter has a strong ability to dissolve and complex with non-available micronutrients. As a result, available Zn, Mn, and Fe usually increase as the amount of soil organic matter increases. In addition, soil processes such as organic matter transformations, soil microbial activities, and crop root activities release organic acids into the soil. This leads to a decline in the soil pH and accelerates the dissolution of non-available micronutrients. Therefore, organic matter plays an important role in enhancing the availability of these elements.

The relationship between organic matter and available Cu is variable. In soils with low amounts of organic matter, including normal mineral soils, available Cu increases as organic matter increases. In contrast, in soils with high amounts of organic matter, the amount of available Cu is often reduced due to the formation of complexes between organic matter and Cu.

The effect of P on micronutrient availability is a complex process that depends on several soil properties and varies among the elements. Zhang et al. (2001) reported a positive correlation between available P and Zn, which also agrees with our findings. Phosphate can cause micronutrient cations to precipitate out of the soil solution, thus decreasing their availability. Cations from the exchange sites may move into the soil solution in order to maintain equilibrium, but these cations are also subject to precipitation by phosphate (Shuman, 1988b). The cation associated with phosphate may also affect the exchange of elements and make them susceptible to precipitation by phosphate (Sample et al., 1979). Copper and Zn phosphates are unstable and will eventually dissolve (Lindsay, 1979). The Mn phosphates are very stable at certain pH and Eh values (Boyle and Lindsay, 1986). The solubility of Mn and Fe oxides controls the solubility of Mn and Fe phosphates (Lindsay, 1979). These findings may explain the relationship between available P and micronutrient availability in our study.

Our results also show that the effect of available P may be directly or indirectly influenced by long-term fertilization and crop root activities. Long-term cropping and fertilization can affect the amount and form of available P in the soil solution. Interaction between the different forms of available P and micronutrients in the soil solution can alter micronutrient availability.

Changes in soil pH can result in the transformation of micronutrients from non-available to available forms (Neilsen et al., 1986). A number of studies have shown that the availability of micronutrients to plants depends on soil pH (Lutz et al., 1972; Olomu et al., 1973; Loneragan, 1975). Our results showed that the effects of pH varied among micronutrients and depended on the interaction with other soil properties (Table 6). The $CaCO_3$ content of the soil used in our study was high and the pH > 8. Under these conditions, the change in soil pH due to crop root activities and fertilizer application was in the range of 0.3 pH units. This is a relatively small change and would have had little direct influence on the availability of soil micronutrients. However, our results indicated that the interaction between pH and other soil properties such as organic matter and available P could influence micronutrient availability greatly (Table 6).

$CaCO_3$ often adsorbs or precipitates micronutrient ions in soil solution during the formation of carbonate, thus reducing their availability. The effect of $CaCO_3$ on micronutrients, therefore, depends on the release or desorption characteristics of adsorbed elements and the solubility of carbonate. The above processes are largely governed by pH, organic matter, and available P contents of soil. This may partly explain the indirect effects of $CaCO_3$ on micronutrient availability.

4. Conclusions

Cropping systems and fertilizer treatments had significant effects on soil pH, organic matter, available P, and $CaCO_3$. Long-term cropping increased soil organic matter and generally decreased soil pH, available P, and $CaCO_3$. Fertilization increased soil organic matter and available P but decreased soil pH. Available Zn, Mn, and Fe were positively correlated with soil organic matter and available P. There was a positive correlation between $CaCO_3$ and available Zn and Mn, but a negative correlation between $CaCO_3$ and Fe. Available Cu was negatively correlated with available P and $CaCO_3$. Path analysis indicated that organic matter directly influenced the availability of micronutrients while the effect of soil available P, $CaCO_3$, and pH mainly passed through their interaction with organic matter. These results emphasize the important influence of organic matter on micronutrient availability and suggest new explanations about the relationship between soil properties and available micronutrients. The results also indicate that legume-based cropping systems and the application of manure fertilizer can help overcome the problem of micronutrient deficiency that is commonly reported in the Loess Plateau.

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