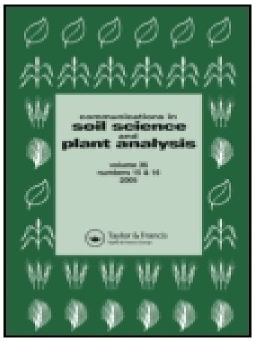

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Effects of Long-Term Inorganic and Organic Fertilization on Soil Micronutrient Status

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Soil micronutrients were studied on loess soil with an 18-year long-term experiment. The results indicated that total soil iron and copper contents were similar under all treatments, but total soil manganese and zinc contents were significantly greater at the surface soil in the fertilized plots than in the controls, and total manganese contents were significantly greater in the whole soil profile under manure plus inorganic fertilizers than under controls. Generally, application of inorganic fertilizers had no effects on available soil micronutrient contents. The straw plus inorganic fertilizers significantly increased available manganese content at surface soil and available iron in subsurface soils. However, manure plus inorganic fertilizers significantly augmented soil-available iron contents throughout the profile, and raised available manganese, copper, and zinc contents, respectively, at surface soil relative to controls. The results suggest that long-term input of organic amendments alter the properties of soil and increase its plant-available micronutrient contents.

Keywords Copper, crop straw, dairy manure, iron, manganese, zinc

Introduction

Micronutrients are essential for the growth of plants and animals. Micronutrient deficiencies in soil not only limit the crop production but also have negative effects on human nutrition and health (Govindaraj, Kannan, and Arunachalam 2011). Similarly, excessive agroecosystem inputs of micronutrients such as iron (Fe), manganese (Mn), copper (Cu), and zinc (Zn), which are heavy metals, can possibly lead to toxicity in plants and animals and consequently pose a threat to human health through the food chain (Westfall et al. 2005; Soriano-Disla et al. 2010). The original geological substrate and subsequent geochemical and pedogenic regimes determine total levels of micronutrients in soils, but their total contents are rarely indicative of plant availability, which is also influenced by soil pH, organic-matter content, adsorptive surfaces, and other physical, chemical, and biological factors in the rhizosphere. The availability of micronutrients in a given soil can also be strongly affected by fertilization practices. For example, long-term applications of

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inorganic nitrogen (N) and phosphorus (P) fertilizers reportedly result in depletion of soil-available Zn, Mn, and Cu in the plow layer, while incorporation of organic manure significantly increases contents of Zn, Mn, and Cu in soils of the Loess Plateau, China (Li et al. 1994). However, Wei et al. (2006) found that available Zn and Fe were greater under treatments with nitrogen, phosphorus, and potassium (NPK) (at various rates) and organic fertilizer than under control treatments, while available copper (Cu) was not significantly influenced by fertilization under a monoculture system on calcareous soil in the Loess Plateau. Gao et al. (2000) found that manure is a better source of available Fe, Mn, and Zn than synthetic fertilizers, but manure applications accelerated the depletion of available Cu on a purple paddy soil in southwestern China after 9 years of fertilization. In contrast, in northern Italy, high liquid manure inputs reportedly increase risks of copper contamination on silty clay loam soils (Mantovi1 et al. 2003).

Winter wheat–summer maize rotation is the principal agricultural production system in northern China; an area of ca. 16 million ha is cultivated in this fashion, accounting for about a quarter of total national food production. Since the late 1970s, rapid increases in the use of inorganic fertilizers and the introduction of high-yielding varieties have resulted in substantial increases in yields per hectare. However, these positive results have been accompanied by greater depletion of micronutrient reserves in the soil, accentuating widespread deficiencies of micronutrients. Soils covering 48.6 and 20.3 M ha are reportedly deficient in Zn and Mn, respectively, in China, mainly calcareous soils in the northern part of the country (Zou et al. 2008). Iron deficiency (diethylene triamine pentaacetic acid (DTPA)–extractable Fe < 4.5 mg kg^{-1}) is also widespread in these calcareous soils (Zou et al. 2008). Several surveys have shown that, until recently at least, most farmers only applied N and P inorganic fertilizers in the winter wheat–summer maize rotation, with no organic manure or micronutrient input (Tong et al. 2004; Niu and Zhang 2010). However, in recent years farmers have started to incorporate crop straw into the soil after harvest (Tong 2010; Kong and Zhao 2011).

Clearly, there are urgent needs to understand the effects of current practices on micronutrients in key agricultural regions such as the Loess Plateau and to identify the most efficient practices for managing them. Previously, nearly all studies have focused on micronutrient status in the soil plow layer (e.g., Prasad and Sinha 1982; Wei et al. 2006; Li et al. 2007). Therefore, the study presented here evaluated effects of long-term applications of crop residue incorporation and organic manure amendment on total and available micronutrients (Fe, Mn, Cu, and Zn) through the profile of soil at a site in the Loess Plateau.

Materials and Methods

Study Site and Experimental Design

A long-term winter wheat–summer maize rotation experiment was established in October 1990 at the Chinese National Soil Fertility and Fertilizer Efficiency Monitoring Base of Loess Soil (N 34° 17′ 51″, E 108° 00′ 48″, altitude 524.7 m above sea level), at a site located on leveled land of the third terrace of the Weihe River, a tributary of the Yellow River, Yangling, Shaanxi, China. According to the USDA texture classification system, the soil at the site is a silt clay loam (clay 32 percent, silt 52 percent, and sand 16 percent; Eumorthic Anthrosol, FAO) derived from loess materials. On average, at the time of establishment the soil at the site contained 7.44 g kg^{-1} organic C, 1.69 g kg^{-1} labile organic carbon (C), 0.93 g kg^{-1} total N, 9.57 mg kg^{-1} Olsen P, 191 mg kg^{-1} exchangeable

K, 92.5 g kg^{-1} calcium carbonate ($CaCO_3$), 27.7 g kg^{-1} total Fe, 665 mg kg^{-1} total Mn, 24.1 mg kg^{-1} total Cu, 65.8 mg kg^{-1} total Zn, 6.51 mg kg^{-1} DTPA-Fe, 4.08 mg kg^{-1} DTPA-Mn, 1.88 mg kg^{-1} DTPA-Cu, and 1.35 mg kg^{-1} DTPA-Zn and had a mean pH of 8.62 across all plots. The details of the experimental site and design have been previously described by Yang et al. (2012).

In this study four nutrient-management regimes were evaluated: (1) no added fertilizer or manure (the control treatment, henceforth CK), (2) combination applications of inorganic NPK fertilizers, (3) NPK plus wheat or maize straw (SNPK), and (4) NPK plus dairy manure (MNPK). For winter wheat, the inorganic N, P, and K application rates were 165, 57.6, and 68.5 kg ha^{-1} a^{-1}, respectively, in the NPK and SNPK treatments. In the MNPK treatment, in which 70 percent N was supplied by dairy manure and the remaining 30 percent N by inorganic fertilizer, application rates of total N and inorganic P and K were 1.5-fold greater than in the NPK treatment. In addition, the dairy manure supplied 159 and 209 kg ha^{-1} a^{-1} P and K, respectively. For summer maize, the same amounts of inorganic N, P, and K were applied in each of the fertilizer (NPK, SNPK, and MNPK) treatments: 187.5, 24.6, and 77.8 kg ha^{-1} a^{-1}, respectively. The SNPK plots also received 4500 kg (air-dried) wheat straw ha^{-1} annually between 1990 and 1998, and then from 1999 until the end of the experiment they received the aboveground parts of the maize straw harvested in the preceding season (mean weight 4392 kg ha^{-1}, ranging from 2630 to 5990 kg ha^{-1}). The added straw was manually chopped into small pieces ca. 3 cm long and incorporated into the soil in autumn, before the winter wheat was sown. Similarly, dairy manure with a mean dry weight of 20.0 t ha^{-1} was added once per year, immediately before the sowing of the wheat. All inorganic fertilizers and organic materials applied were incorporated into the soil to plowing depth (ca. 20 cm) before the winter wheat was sown and in the interrow areas about a month after maize was planted. The N-containing inorganic fertilizer used in the experiment was urea, P was added as single superphosphate, and K was potassium sulfate. The Fe, Mn, Cu, and Zn contents of the P fertilizer were 6078, 913, 20, and 157 mg kg^{-1}, respectively. The micronutrient contents of the K fertilizer, manure, wheat straw, and maize straw were 84, 0, 0, and 0 mg kg^{-1} (Fe), 6247, 586, 37, and 170 mg kg^{-1} (Mn); 286, 31, 1.2, and 5.9 mg kg^{-1} (Cu); and 474, 44, 7.8, and 18.8 mg kg^{-1} (Zn), respectively. Winter wheat was sown in October and harvested in the following June; summer maize was planted and harvested about 3 months later, at the end of September or in early October. The plots were irrigated with ground water once or twice during the winter wheat season and between zero and three times during the summer maize season, as required, applying approximately 90 mm of water on each occasion. All aboveground crop residues were removed after harvesting unless otherwise specified. The fields were conventionally tilled with a rototiller.

Soil Sampling and Analyses

Soil samples were collected after winter wheat harvest in June 2008 from depths of 0–10, 10–20, 20–30, 30–40, and 40–60 cm, using a stainless steel auger with an internal diameter of 2.0 cm. Each treatment took three replicates, and each replicate was a composite of eight soil cores. Soil samples were air-dried, and ground to pass through a 1-mm sieve for analyses of soil pH, labile organic carbon (LOC), and DTPA-extractable Cu, Zn, Fe, and Mn contents. Part of each soil sample was ground to pass through a 100-mesh sieve for the analysis of soil total Cu, Zn, Fe, and Mn concentrations and soil organic carbon (SOC).

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Soil pH was determined with a pH electrode at a soil-to-water ratio of 1:2.5. The SOC was analyzed using the Walkley–Black method (Walkley and Black 1934). The LOC was determined as described by Blair, Lefroy, and Lisle (1995). DTPA-extractable soil Cu, Zn, Fe, and Mn (DTPA-Cu, -Zn, -Fe, and Mn hereafter) were obtained by extracting 10 g soil with 20 mL 0.005 M DTPA + 0.01 M calcium chloride ($CaCl_2$) + 0.1 M TEA (triethanolamine) solution (Lindsay and Norvell 1978). After 2 h continuous shaking at room temperature, the soil suspension was centrifuged and filtered through a 0.45-mm micropore filter. Copper, Zn, Fe, and Mn in the extract were then analyzed with an atomic absorption spectrometer (AAS). Soil total Cu, Zn, Fe, and Mn contents were also analyzed by atomic absorption spectrometry, after digesting 0.1 g samples with perchloric acid–nitric acid–hydrogen fluoride ($HClO_4$-HNO_3-HF) (Emteryd 2002).

Statistical Analyses

One-way analysis of variance was used to analyze differences in tested parameters among the treatments. The least significant difference (LSD) test was used to test the significance (at the 5 percent probability level) of differences between treatment means. Correlations between soil parameters were evaluated by calculating simple linear correlation coefficients (deeming results to be very significant and significant at $P < 0.01$ and $P < 0.05$, respectively). All statistical analyses were performed using the SPSS (v16.0) software package.

Results

Soil pH, SOC, and LOC

After 18 years of treatment, soil pH was significantly affected by the fertilization regimes (Table 1). In the 0- to 10-cm soil layer, pH was 0.28 units lower in the MNPK treatment and 0.15 units lower in the SNPK treatment compared with the CK treatment, but was not significantly affected in the NPK treatment. For the other soil layers, there were no significant differences in soil pH between CK, NPK, and MNPK treatments, except that it was significantly lower in the 30- to 40-cm layer of SNPK treatment than in CK treatment (Table 1).

SOC contents were significantly influenced by the fertilization regimes in the soil profile (Table 1). The SOC values in MNPK soils were significantly greater than in CK, NPK, and SNPK soils in all tested layers except at 30–40 cm deep, where SOC contents were similar between MPNK treatment and NPK or SNPK treatment. The SNPK treatment showed SOC contents similar to the NPK treatment in the whole soil profile, but enhanced SOC contents in the top soil layers over the CK treatment. The NPK treatment presented the only significantly greater SOC content in the surface 10-cm depth relative to the CK treatment. In the 0- to 10-cm soil layer, SOC contents ranged from 8.6 to 21.37 g kg^{-1} and were 148, 90, and 72 percent greater in the MNPK treatment relative to CK, NPK, and SNPK treatments, respectively. In the 10- to 20-cm soil layer, SOC contents ranged from 6.6 to 10.2 g kg^{-1}, and again were significantly greater under MNPK than under the other treatments (55 percent greater than under CK), whereas under NPK the SOC content did not significantly differ from the control. In the other soil layers, SOC contents were relatively within a narrow range (5.2–7.5 g kg^{-1}), and still were 20 percent greater under MNPK than under CK.

The LOC contents were also affected by the fertilization regimes (Table 1). In the soil layers 0–10 and 10–20 cm deep, LOC contents under the SNPK treatment were similar to

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Table 1

Soil pH, organic carbon (SOC), and labile organic carbon (LOC) contents (g kg^{-1}) under four long-term soil fertilization treatments [CK, control; NPK, inorganic fertilizer (N, P, and K) application; SNPK, straw plus NPK; and MNPK, manure plus NPK]

		Soil depth (cm)				
Soil variable	Treatment	0–10	10–20	20–30	30–40	40–60
pH	CK	8.34 C a	8.36 BC	8.37 ABC a	8.42 AB a	8.44 A
	NPK	8.30 a	8.36	8.34 a	8.34 b	8.36
	SNPK	8.19 b	8.30	8.26 b	8.26 c	8.33
	MNPK	8.06 C c	8.25 B	8.33 AB a	8.35 A ab	8.37 A
SOC	CK	8.60 A c	6.61 B c	6.10 BC b	5.48 CD b	5.24 D b
	NPK	11.25 A b	7.13 B bc	6.15 C b	6.15 C ab	5.29 D b
	SNPK	12.40 A b	8.22 B b	6.37 C b	6.14 C ab	5.36 C b
	MNPK	21.37 A a	10.23 B a	7.51 C a	6.72 C a	6.70 C a
LOC	CK	1.60 A c	1.18 A b	1.15 A b	1.24 A ab	0.56 B b
	NPK	2.20 bc	0.99 b	0.92 b	1.02 b	1.23 ab
	SNPK	3.70 A b	1.89 B ab	1.20 B b	0.94 B b	0.94 B b
	MNPK	5.73 A a	3.02 B a	1.95 B a	1.55 B a	1.53 B a

Notes. Different uppercase letters indicate significant ($P < 0.05$) differences between depths within each treatment, while different lowercase letters indicate significant differences between treatments at the same depth, and no letters indicate no significant differences among depths or among treatments.

those under the other treatments, but they were significantly greater under MNPK than under NPK and CK. In the 20- to 30-cm layer, the LOC content was significantly greater under MNPK than under the other treatments, and there were no significant differences in this respect among the other three treatments.

Soil Total Micronutrients

The concentrations and distributions of soil micronutrients under the four long-term fertilization management regimes, which differed in some respects but not others, are shown in Table 2. The total Fe concentration ranged from 3.5 to 3.7 percent; Fe was distributed evenly through the soil profile and did not significantly differ among the four treatments. Similarly, the total Mn concentration was evenly distributed through the soil profile. However, total Mn concentrations were significantly influenced by the nutrient-management treatments. Significantly greater concentrations of soil total Mn than those under CK were observed in the layers 0–10 cm and 40–60 cm deep under NPK, the layer 0–10 cm deep under SNPK, and all five soil layers under the MNPK treatment. In addition, the MNPK-treated soil had significantly greater concentrations of total Mn than NPK- and SNPK-treated soils in the 20- to 30-cm and 30- to 40-cm layers.

Like total Fe contents, the total Cu content was also distributed evenly in the soil profile, and the nutrient-management treatments had no pronounced effects on its concentration (Table 2). However, the distribution of total Zn in the soil profile was significantly changed by application of straw and/or manure, which resulted in greater total Zn concentrations in the surface 10-cm soil layer compared with other soil layers. In

Table 2

Total micronutrient concentrations of soils (mg kg^{-1}) under four long-term soil fertilization treatments [CK, control; NPK, inorganic fertilizer (N, P, and K) application; SNPK, straw plus NPK; MNPK, manure plus NPK]

		Soil depth (cm)				
Micronutrient	Treatment	0–10	10–20	20–30	30–40	40–60
Fe	CK	35156	35576	36163	34704	35099
	NPK	36274	36320	34602	36083	35788
	SNPK	34712	37304	35096	35477	36400
	MNPK	34827	36700	36678	36782	35714
Mn	CK	686 b	694 b	694 b	696 b	684 b
	NPK	729 a	731 ab	713 b	693 b	725 a
	SNPK	732 a	725 ab	694 b	677 b	705 ab
	MNPK	744 a	748 a	757 a	732 a	726 a
Cu	CK	28.4	27.9	27.2	26.2	27.0
	NPK	28.2	28.1	27.6	27.9	29.7
	SNPK	31.0	30.6	30.4	28.6	29.3
	MNPK	27.9	27.8	28.5	28.6	27.4
Zn	CK	77.9 b	83.8	81.6	81.7	88.7
	NPK	93.7 a	89.3	86.5	87.6	85.5
	SNPK	95.8 A a	83.0 B	79.1 B	84.0 B	79.2 B
	MNPK	101.3 A a	82.4 B	87.5 B	89.6 B	81.6 B

Notes. Different uppercase letters indicate significant ($P < 0.05$) differences between depths within each treatment, while different lowercase letters indicate significant differences between treatments at the same depth, and no letters indicate no significant differences among depths or among treatments.

addition, relative to the control, all nutrient-management treatments significantly increased total Zn concentrations in the top 10-cm soil layer.

DTPA-Extractable Micronutrients

The available Fe content significantly decreased, from 8.4 mg kg^{-1} at 0- to 10-cm deep to 5.5 mg kg^{-1} at 40- to 60-cm deep, under the MNPK treatment (Figure 1). However, under the CK, NPK, and SNPK treatments, available Fe was lowest at 0–10 cm deep, greater and relatively constant from 10–20 cm down to 30–40 cm deep, and then declined at 40–60 cm deep. Available Fe contents in all layers, except 0–10 cm, of MNPK-treated soil were similar to those in SNPK-treated soil, and significantly greater than in both CK-treated soil (except at 20–30 cm deep) and NPK-treated soils (except at 20–30 cm and 30–40 cm deep). Available Fe contents in the soil profile under SNPK were also significantly greater than those under CK, except at 0–10 cm and 20–30 cm deep. Available Fe contents were comparable between SNPK and NPK treatments, and between NPK and CK treatments for all soil layers except 40–60 cm. Overall, available Fe contents decreased between the treatments for all soil layers in the following order: MNPK > SNPK > NPK > CK.

The available Mn content generally decreased with increasing soil depth (Figure 2). Input of organic materials significantly increased available Mn contents in the 0- to 10-cm soil layer, from 8.3 mg kg^{-1} under CK to 12.6 and 13.8 mg kg^{-1} under the MNPK and

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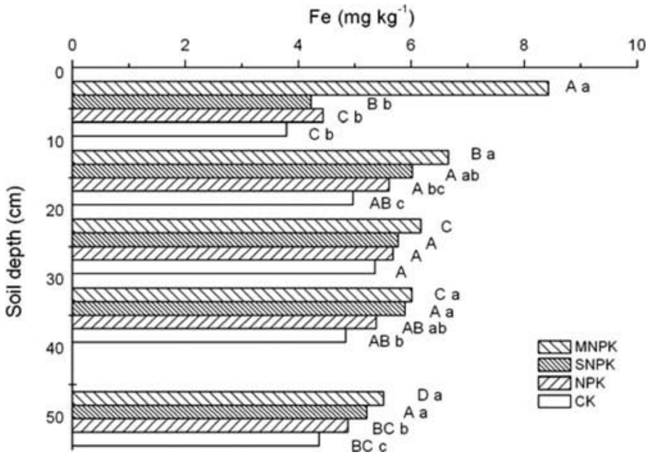

Figure 1. DTPA-Fe concentrations (mg kg^{-1}) in soil under the four treatments (CK, control; NPK, inorganic N, P, and K fertilizer application; SNPK, inorganic fertilizers plus straw; MNPK, inorganic fertilizers plus manure). Different uppercase letters indicate significant differences at $P < 0.05$ by depth within a treatment, while different lowercase letters denote significant differences between treatments at the same depth, and no letters indicate no significant differences among depths within a treatment or among treatments at the same depth.

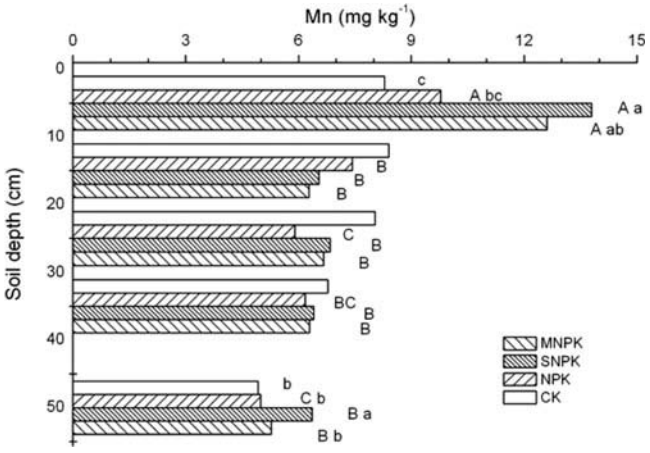

Figure 2. DTPA-Mn concentrations (mg kg^{-1}) in soil under the four treatments (CK, control; NPK, inorganic N, P, and K fertilizer application; SNPK, inorganic fertilizers plus straw; MNPK, inorganic fertilizers plus manure). Different uppercase letters indicate significant differences at $P < 0.05$ by depth within a treatment, while different lowercase letters denote significant differences between treatments at the same depth, and no letters indicate no significant differences among depths within a treatment or among treatments at the same depth.

SNPK treatments, respectively. In addition, they were significantly greater under SNPK in the 40- to 60-cm soil layer than under the other treatments. The available Mn concentrations were similar under all treatments from 10 cm down to 40 cm deep.

The available Cu content remained relatively constant in the soil profile (Figure 3). The fertilization regimes only influenced it in the 0- to 10-cm soil layer, in which it was greatest under

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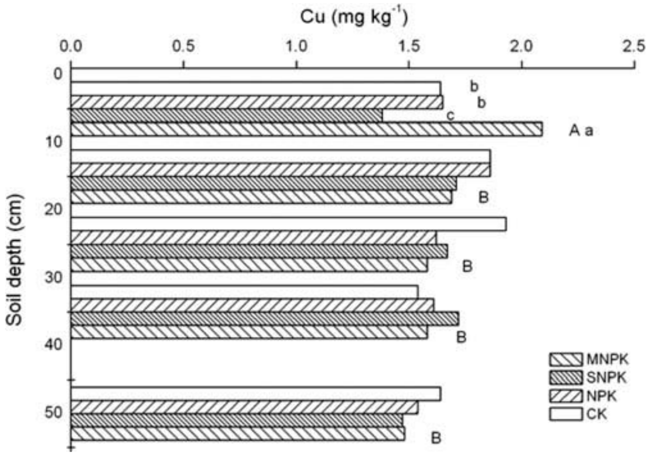

Figure 3. DTPA-Cu concentrations (mg kg^{-1}) in soil under the four treatments (CK, control; NPK, inorganic N, P, and K fertilizer application; SNPK, inorganic fertilizers plus straw; MNPK, inorganic fertilizers plus manure). Different capital letters indicate significant differences at $P < 0.05$ by depth within a treatment, while different lowercase letters denote significant differences between treatments at the same depth, and no letters indicate no significant differences among depths within a treatment or among treatments at the same depth.

MNPK (2.1 mg kg^{-1}), followed by NPK (1.65 mg kg^{-1}), CK (1.64 mg kg^{-1}), and SNPK (1.38 mg kg^{-1}).

The distribution of available Zn in the soil profile was similar to that of available Mn, being greatest in the surface soil layer and lowest in the bottom layer (Figure 4). Available Zn contents were significantly greater under MNPK in the 0- to 10-cm layer than under the

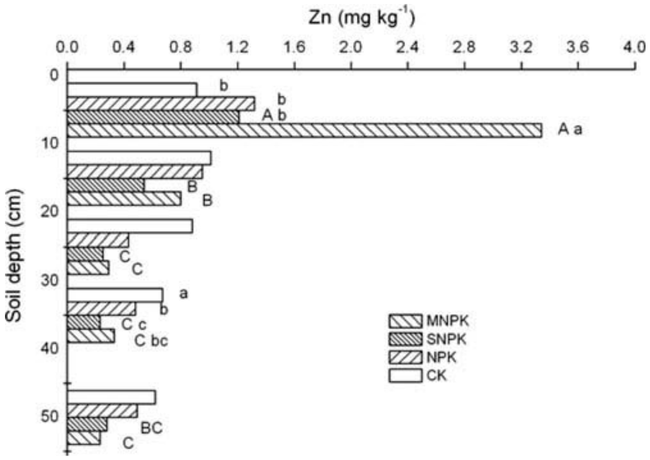

Figure 4. DTPA-Zn concentrations (mg kg^{-1}) in soil under the four treatments (CK, control; NPK, inorganic N, P, and K fertilizer application; SNPK, inorganic fertilizers plus straw; MNPK, inorganic fertilizers plus manure). Different capital letters indicate significant differences at $P < 0.05$ by depth within a treatment, while different lowercase letters denote significant differences between treatments at the same depth, and no letters indicate no significant differences among depths within a treatment or among treatments at the same depth.

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Table 3

Pearson correlation coefficients between soil properties for all soil layers under the four treatments in the long-term loess soil management experiment (1990–2008)

	DTPA				Total			
	Fe	Mn	Cu	Zn	Fe	Mn	Cu	Zn
DTPA Mn	0.089							
DTPA Cu	0.547*	0.257						
DTPA Zn	0.419	0.766**	0.623**					
Total Fe	0.192	−0.320	0.024	−0.291				
Total Mn	0.486*	0.259	−0.018	0.301	0.392			
Total Cu	−0.044	0.258	−0.283	−0.109	0.185	0.196		
Total Zn	0.321	0.636**	0.244	0.697**	−0.161	0.494*	0.043	
pH	−0.605**	−0.708**	−0.329	−0.678**	0.154	−0.404	−0.416	−0.544*
SOC	0.525*	0.793**	0.434	0.910**	−0.178	0.506*	0.111	0.715**
LOC	0.540*	0.763**	0.290	0.820**	−0.128	0.602**	0.182	0.659**

*Correlation significant at the $P < 0.05$ level.

**Correlation significant at the $P < 0.01$ level.

other treatments, but similar under SNPK and NPK to CK contents. For other soil layers, MNPK, SNPK, and NPK treatments had no marked effects on available Zn content compared with CK, except the 30- to 40-cm layer, where the CK treatment resulted in significantly greater available Zn content than the fertilization treatments.

Relationships between Available Micronutrients and Total Micronutrients, Ph, SOC, and LOC

The linear correlation analysis showed there were no significant correlations between available Fe and total Fe, available Mn and total Mn, or available Cu and total Cu (Table 3). However, available Zn content was strongly positively correlated with total Zn content. Among the available micronutrients, Fe, Mn, and Zn contents were negatively correlated (but available Cu was not significantly correlated) with soil pH. In addition, soil-available Fe, Mn, and Zn contents were positively correlated with SOC and LOC contents. Soil total Mn and total Zn were also both significantly correlated with soil SOC and LOC contents.

Discussion

Total Micronutrients

The effects of fertilization on total micronutrient contents in soils heavily depend on crop removal rates and both the quantities and forms (inorganic and organic) of nutrient inputs. The total soil Fe concentrations between the fertilization and control treatments were similar (Table 2), although Fe had been supplied to the soil for 18 years in the NPK, SNPK, and MNPK applications. However, yields were up to three-fold greater, and thus more Fe may have been removed from the soil under the fertilized treatments than under CK (data not shown), offsetting the Fe gained from fertilizer inputs. Furthermore, the amount of Fe added through inorganic and organic fertilizers was low compared with the

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high background total soil Fe content. Similarly, Li et al. (2007) found that total soil Fe content in the plow layer was not affected by straw incorporation or manure addition after 16 years under the same cropping system. However, both Wei et al. (2006) and Li et al. (2010) found that addition of P (superphosphate), alone or combined with organic materials, increased total Fe under both single and double cropping systems. Differences between these results and ours may be related to differences in inputs and outputs of total Fe in the system linked to variations in the fertilizer sources and/or quantities of fertilizer/manure used and crop yields. Furthermore, we found no significant correlations between total Fe contents and soil pH, SOC, and LOC contents (Table 3), in agreement with a previous analysis of fertilization effects on Inceptisols (Sharma et al. 2004), suggesting that total soil Fe content was still dominated by parent materials.

The total Mn contents were significantly greater under the fertilized treatments than under CK in the 0- to 10-cm soil layer (Table 2), presumably due to Mn inputs through the fertilizers, mainly the superphosphate, straw, and manure (Li et al. 2010). Furthermore, the total Mn content was significantly augmented, and uniformly distributed, throughout the soil profile in MNPK plots, reflecting the leaching of Mn compounds. Wei et al. (2006) also found that total Mn contents were significantly enhanced, in the 0- to 15-cm and 20- to 32-cm soil layers, by addition of manure and N + P. Unlike total Fe, the total soil Mn content was significantly affected by variations in soil properties, such as soil SOC and LOC (Table 3). Hence, sound fertilizer management could help to improve total Mn content in the soil.

Like total Fe, neither the distribution nor content of total Cu in the soil profile was affected by the fertilization treatments, indicating that Cu inputs through fertilizers were balanced by crop removal. In contrast, Wei et al. (2007) reported that application of copper (15 kg ha^{-1} $CuSO_4 \cdot 5H_2O$) for 17 years significantly increased total Cu content in the surface to 15-cm layer of a dryland calcareous soil under a single cropping system on the Loess Plateau, although the copper input rate was lower than in the MNPK treatment applied in our study. The difference in results may be related to the lower yields (and hence probably lower crop removal rates), under the single cropping system than under the double cropping system in the present study.

The total soil Zn content was significantly greater under the NPK, SNPK, and MNPK treatments than under the CK treatment in the surface soil layer. This may have been due to Zn inputs (albeit small) through the inorganic and organic fertilizer applications, and/or to certain soil properties (e.g., alkaline pH, and high $CaCO_3$ contents) enhancing the retention and reducing the mobility of Zn.

DTPA-Extractable Micronutrients

Changes in available micronutrient contents were somewhat different from total contents. After 18 years soil DTPA-Fe contents ranged from 3.79 to 8.43 mg kg^{-1}, overlapping the marginal values of 2.5–4.5 mg kg^{-1}, below which plants are likely to suffer from Fe deficiency in the studied soil (Yu et al. 1984). DTPA-Fe was within the marginal range in the 0- to 10-cm layer of the CK-, NPK-, and SNPK-treated soils, whereas in other layers it was still adequate after 18 years of the field experiment. It was also significantly greater under the MNPK and SNPK treatments than under both the CK and NPK treatments, presumably partly due to the direct input of Fe through straw or manure. The lower soil pH and greater SOC and LOC contents under MNPK and SNPK (Table 1) also presumably contributed to this, because the solubility of micronutrients generally increases with reductions in soil pH, including iron, because pH is closely correlated to the proportions of iron in ferrous and much less soluble ferric oxidation states (Prasad and Sinha 1982).

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The results of continuous application of manure in conjunction with inorganic fertilizers indicate that microbial decomposition of organic matter released these elements, as well as complexing agents, such as organic acids and humic substances, that facilitated the movement of micronutrients from the solid phase into solution. These results are consistent with findings of Wei et al. (2006) and Li et al. (2007), but while these authors, and Fan et al. (2012), have found that NPK applications increased DTPA-Fe contents, relative to CK treatments, in the present study NPK application resulted in similar DTPA-Fe contents to those in control plots. This difference might be related to variations in soil type, crop yields / removal rates, and sources of fertilizer used. There was no correlation between total Fe and DTPA-Fe concentrations, which explains why widespread Fe deficiency can occur despite high total Fe contents in soils (Brown 1977).

The available Mn content ranged from 4.92 to 13.79 mg kg^{-1} after the 18-year experiment. In comparison with the marginal crop growth values of 7–9 mg kg^{-1} (Yu et al. 1984), the DTPA-Mn content was sufficient in the 0- to 10-cm soil layer under NPK, SNPK, and MNPK treatments, but marginal under CK and in deeper soil layers. It was also significantly greater in the 0- to 10-cm soil layer under the SNPK and MNPK treatments than under CK, presumably due to the same factors related to soil pH and organic carbon as mentioned for iron above. In addition, the decomposition of added organic matter would have provided protons to the soil solution and decreased soil Eh values (as well as pH), thereby enhancing the dissolution and reduction of Mn, and hence increasing its availability. Application of NPK resulted in similar DTPA-Mn contents to the control, in accordance with earlier findings (Wei et al. 2006; Li et al. 2007). The minor effects on DTPA-Mn in subsurface layers of the SNPK- and MNPK-treated soil indicate that Mn inputs were still very limited under these treatments. The survey data showed that most farmers only applied N and P inorganic fertilizers in the winter wheat–summer maize rotation system, without organic manure or micronutrient inputs (Tong et al. 2004; Niu and Zhang 2010). Farmers have recently started to incorporate crop straw into soil after harvest (Tong 2010; Kong and Zhao 2011), which might improve the status of soil available Mn, but our findings indicate that further measures may be required.

The available Cu content ranged from 1.38 to 2.09 mg kg^{-1}. In comparison with the marginal crop growth values of 0.5–1.0 mg kg^{-1} (Yu et al. 1984), the DTPA-Cu content was still adequate after 18 years of the treatments. Similarly to the DTPA-Mn content, no significant effect of fertilization on DTPA-Cu content was observed except in the 0- to 10-cm soil layer. In contrast, Sistani, Sikora, and Rasnake (2008) found that three consecutive annual applications of poultry litter significantly increased Mehlich-3 Cu contents down to 45 cm or 60 cm deep in a silt loam soil under a single-cropping system, possibly because the poultry litter had greater Cu contents than the dairy manure used in our study, and/or rates of Cu removal by the crop were lower.

The DTPA-Zn content was only adequate in the 0- to 10-cm layers of NPK-, SNPK-, and MNPK-treated soils. It was deficient or within the marginal range (0.5–1.0 mg kg^{-1}; Yu et al. 1984) in deeper soil layers and throughout the whole soil profile of CK-treated soils. It was significantly greater in the 0- to 10-cm soil layer under MNPK than under the control treatment, presumably due to the direct input of Zn in the manure, in conjunction with the lower soil pH and greater SOC and LOC contents under MNPK (Table 1). The pH is one of numerous soil properties that influence the plant availability of Zn in soils (Anderson and Christensen 1988), which generally increases with reductions in soil pH (Alloway 2008). In addition, soil organic-matter content can affect the availability of Zn in soils in several ways (Moody, Yo, and Aitken 1997); notably increased concentrations of organic matter can increase exchangeable and organic fractions of Zn and decrease oxide-bound fractions, by

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changing redox states. In contrast to the patterns for the other three micronutrients, DTPA-Zn content was significantly lower under the fertilized treatments than under the control treatment in the 30- to 40-cm soil layer. Furthermore, there were sharp declines in DTPA-Zn contents in the subsurface horizon, especially under the SNPK and MNPK treatments, indicating that this element was mined by the crops and redeposited on the surface with organic matter, thus maintaining the Zn status of the topsoil (Rengel 2007). Thus, although farmers have started to incorporate crop straw into soil after harvest in recent years (Tong 2010; Kong and Zhao 2011), the soil may still not supply sufficient Zn to crops.

Conclusions

Total soil concentrations of Mn and Zn in the soil profiles were significantly impacted by the 18 years of contrasting fertilization regimes. DTPA-extractable Fe and Zn contents were more strongly affected by fertilization than DTPA-extractable Cu and Mn contents. Apart from DTPA-Cu, the other three elements, especially Mn and Zn, were deficient or within the marginal crop growth ranges in either surface or subsurface soil layers. The MNPK treatment improved DTPA-Fe status and maintained adequate Fe levels throughout the soil profile, but in manner similar to the NPK and SNPK treatments, it only maintained sufficient DTPA-Mn and DTPA-Zn concentrations in the top 10-cm soil layer. Hence, to sustain crop production and quality, the application of fertilizers containing Zn and Mn may be needed to maintain or increase soil available Zn and Mn contents.

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