Variation in available micronutrients in black soil after 30-year fertilization treatment

Y.G. Zhang[1,2], Y.Y. Zhang[1], J.P. Cai[1], P. Zhu[3], H.J. Gao[3], Y. Jiang[1]

[1]*State Key Laboratory of Forest and Soil Ecology, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang, P.R. China*
[2]*College of Environmental Engineering, Shenyang University, Shenyang, P.R. China*
[3]*Agricultural Environment and Resources Research Center, Jilin Academy of Agricultural Sciences, Changchun, P.R. China*

ABSTRACT

To assess the effects of long-term fertilization on soil available micronutrients in farmland, this study examined diethylenetriaminepentaacetic acid (DTPA) extractable iron (Fe), manganese (Mn), copper (Cu), and zinc (Zn) in surface soil with monoculture of corn (*Zea mays* L.) with a 30-year filed fertilization experiment established in Northeast China. Treatments included no fertilization (CK); nitrogen only (N); nitrogen and phosphorus only (NP); NP and potassium (NPK); NPK plus cornstalk (SNPK), and NPK plus farmyard manure (MNPK). Results showed that DTPA-Fe and Mn were significantly increased with chemical N application, and DTPA-Cu and Zn were significantly increased with farmyard manure amendment, while micronutrients were not significantly different between treatment SNPK and CK. DTPA-Fe and Mn were about twice to threefold in treatments N, NP, and NPK as much as in treatments SNPK, MNPK and CK. DTPA-Cu and Zn in treatment MNPK were about 3.9 and 6.5 times as much as in CK. DTPA-Fe and Mn decreased with the increasing of soil pH and cation exchange capacity, while DTPA-Cu and Zn increased with the increase of soil organic carbon and electrical conductivity.

Keywords: cornstalk; farmyard manure; long-term fertilization; nutrient cycling; soil fertility

Micronutrient deficiency is widespread all over the world because of the generally low levels of available micronutrients in agricultural soils, and also because of increased nutrient demands from intensive cropping practices (Alloway 2008). Human activities such as tillage, crop residue recycling, fertilization, pesticide application, and waste disposal affect soil physiochemical properties, and will lead to changes of micronutrients in soils (Jiang et al. 2005, 2009).

Organic manures are significant sources of micronutrients in agroecosystems (Uprety et al. 2009, Xu et al. 2013). Long-term application of pig slurry (Nikoli and Matsi 2011), poultry litter (Pederson et al. 2002), or cattle manure (Benke et al. 2008, Abu-Zahra et al. 2010) have been corroborated to increase Cu and Zn contents substantially in the upper soil layer. Manure amendment increased soil DTPA-extractable Cu, Zn, Fe, and Mn, but did not significantly affect the total contents of micronutrients, after 19 years of cropping and fertilization in an Aquic Inceptisol in middle China (Li et al. 2010).

Many mineral P fertilizers possess considerable amounts of micronutrients, thus they may also be significant sources of micronutrients in agroecosystems (Uprety et al. 2009). Chemical N fertilizer application and balanced application of NPK could increase (Li et al. 2007), or decrease (Rengel 2007), or have no significant effect (Behera and Singh 2009) on DTPA-extractable micronutrients in soils. Increased yields achieved by mineral

Supported by the National Basic Research Program of China, Project No. 2013CB100504, and by the National Key Technology R&D Program of China, Project No. 2012BAD14B04.

NPK application may accelerate micronutrient removal from agroecosystems, causing imbalance in nutrient cycling, and hence, the variation in soil available micronutrient with different fertilization regimes was dependent on fertilizer varieties, soil physiochemical properties, crop absorptions, and recycling rates (Caliskan et al. 2008).

Many researches involving long-term fertilization focused on soil productivity, carbon and macronutrients, relative to micronutrients (Edmeades 2003, Yan and Gong 2010). From the early 1980's, many long-term fertilization experiments were established in China's farmlands, but little information is available relating to long-term fertilization on plant available soil micronutrients. Black soils in Northeast China (43'50°N, 124'127°E) are fertile and productive, accounting for one-third of China's total corn yield, thus, measures and studies related to the maintainability of soil fertility are of critical importance. It is basically clear that soil organic C, macronutrients, soil pH and oxidation-reduction conditions, water-holding capacity, soil fauna, microbes and enzyme change a lot under different fertilization regimes (Zhu et al. 2007, Li et al. 2009), and our hypothesis was that, with different fertilizer application, soil extractable micronutrients would change along with soil physicochemical and biological properties mentioned above, and hence, the objectives were to examine the variation in soil DTPA-extractable micronutrients under chemical fertilizer application, cornstalk addition and farmyard manure amendment in a long-term field experiment with monoculture of corn, and to identify factors contributing to the variation in soil micronutrients.

MATERIAL AND METHODS

Site description. The study was conducted at an ongoing National Long-term Experimental Station for Soil Fertility Monitoring in Black Soil, located at Gongzhuling, China (43°30'N, 124°48'E). It is located in a continental temperate monsoon zone. The annual temperature ranges 4.0–5.0°C, annual precipitation ranges 500–650 mm, and annual non-frost period ranges 125–140 days. The soil is classified as Halpic Phaeozem (FAO 1988).

A long-term fertilization experiment with monoculture corn was established in 1980, including six treatments: (1) CK – no fertilizer; (2) N only; (3) NP only; (4) NPK; (5) NPK plus cornstalk (SNPK), and (6) NPK plus farmyard manure (MNPK). Nutrient input was 165 kg N/ha, 36 kg P/ha, and 68.5 kg K/ha, with urea, $(NH_4)_2HPO_4$, and KCl, and 7500 kg/ha/year air-dried cornstalk in SNPK, and 30 t/ha/year farmyard manure (a mixture of swine manure, plant residue and soil) in MNPK, respectively. The total amount of N, P and K input in the last three treatments was the same. The treatments were allocated in 100 m^2 plots, replicated thrice. Before the experiment was established, the soil properties in 0–20 cm soil layer were as follows, soil organic matter 23.3 g/kg, total N 1.40 g/kg, total P 0.39 g/kg, total K 22.1 g/kg; soil pH 7.3; the soil texture is loamy clay with particle size distribution 2.0–0.2 mm 5.50%; 0.2–0.02 mm 32.81%; 0.02–0.002 mm 29.87%, and < 0.002 mm 31.05%; the bulk density was 1.19 g/cm^3, the total porosity was 53.91%. Except for the SNPK treatment, all the aboveground crop residues were removed after harvest. All plots were ploughed to a depth of 15–20 cm in autumn, and the field was disked and ridged in spring before sowing. The average corn yield during 2003 to 2010 was about 3490 and 10 560 kg/ha for CK and MNPK treatments, respectively, while the other four treatments harvested about 8500–9800 kg/ha corn per year.

Sampling and soil analyses. In October 2010, after harvesting, mixed soil samples were collected from the treatment plots at the depth of 0–20 cm. Soil samples were air-dried and ground to pass through 2-mm and 0.149-mm sieves. Soil micronutrients were extracted with 0.005 mol/L DTPA, 0.01 mol/L $CaCl_2$, and 0.1 mol/L TEA at pH 7.3, the total contents were digested with 48% HF and concentrated HNO_3. Both total and DTPA-Fe, Mn, Cu, and Zn were analyzed by atomic absorption spectrophotometer (AAS, Shimadzu, Japan). Soil pH and electrical conductivity (EC) were measured with electrodes in a 1:2.5 soil:water suspension. Exchangeable Ca, Mg, K and Na were determined by AAS. Soil organic C and total N were determined by using a Vario ELIII elemental analyzer (Elementar, Germany). Soil total P was determined with spectrophotometer at 410-nm wavelength, and K was measured by using flame photometer; ammoniac N and NO_3^--N were extracted with 2 mol/L KCl and determined using magnesium oxide-devarda alloy method (Page 1982). China's national standard soil reference materials for black soil (GBW07424 and GBW07458) were adopted through the digestion, extraction and analysis procedures as a part of the QA/QC protocol.

Statistical analysis. The obtained data were analyzed with the SPSS (SPSS Inc., Chicago, USA) Version 11.5 for Windows, using one-way ANOVA and the Duncan's pairwise comparison for means separation, and a significance level of $P < 0.05$ was chosen for detecting significant differences.

RESULTS AND DISCUSSION

Chemical N application significantly increased DTPA-extractable Fe and Mn in soils. Between groups ANOVA showed that DTPA-Fe was significantly greater in treatments NP and NPK than in the other treatments, and it was greater in N treatment than in SNPK treatment and CK. DTPA-Mn was significantly greater in treatments NP, NPK, and N than in the other three treatments (Figure 1). The variation in DTPA-Fe and Mn among different fertilization treatments was highly dependent on soil pH (Figure 2). The average soil pH values in treatments N, NP, and NPK were 6.72, 6.26, and 6.22, respectively, which were lower relative to those in treatments SNPK, MNPK and CK (7.29, 6.84 and 7.10, respectively). The initial soil pH at the beginning of the experiment was 7.3 in 1980, while it was 7.1 in the CK while sampling in 2010, and this reduction may be due to the atmospheric deposition of N in this region.

For one unit decrease of soil pH, DTPA-Fe or Mn was observed to increase about threefold. As cation exchange capacity (CEC) was increased along with increasing soil pH, it was negatively correlated ($P < 0.01$) with DTPA-Fe or Mn could also be expressed with linear regression equations (Figure 2).

For each soil pH unit increase, Fe^{2+}, Fe^{3+}, and Mn^{2+} decrease hundred to thousand fold. Thus, Fe and/or Mn deficiency is most often observed on high-pH and calcareous soils in arid regions (Havlin et al. 2004), and also in north China's farmlands (Alloway 2008). Iron and Mn are soluble in the reduced state but readily oxidized in high pH soils, and so rendered highly unavailable in such soils (Alloway 2008). It was well documented that plant available Fe and Mn in soils decrease with increasing pH (Sharma et al. 2000). Darusman et al. (1991) reported that N fertilization for 20 years caused a significant increase in available Fe and Mn, and a decrease in soil pH (5.2 vs. 6.2) in surface soil. Thus, chemical N fertilizer induced pH reduction was considered as the leading factor that increases DTPA-Fe and Mn in soils.

Most animal waste and crop residues contain small quantity of plant available Fe and Mn (Havlin

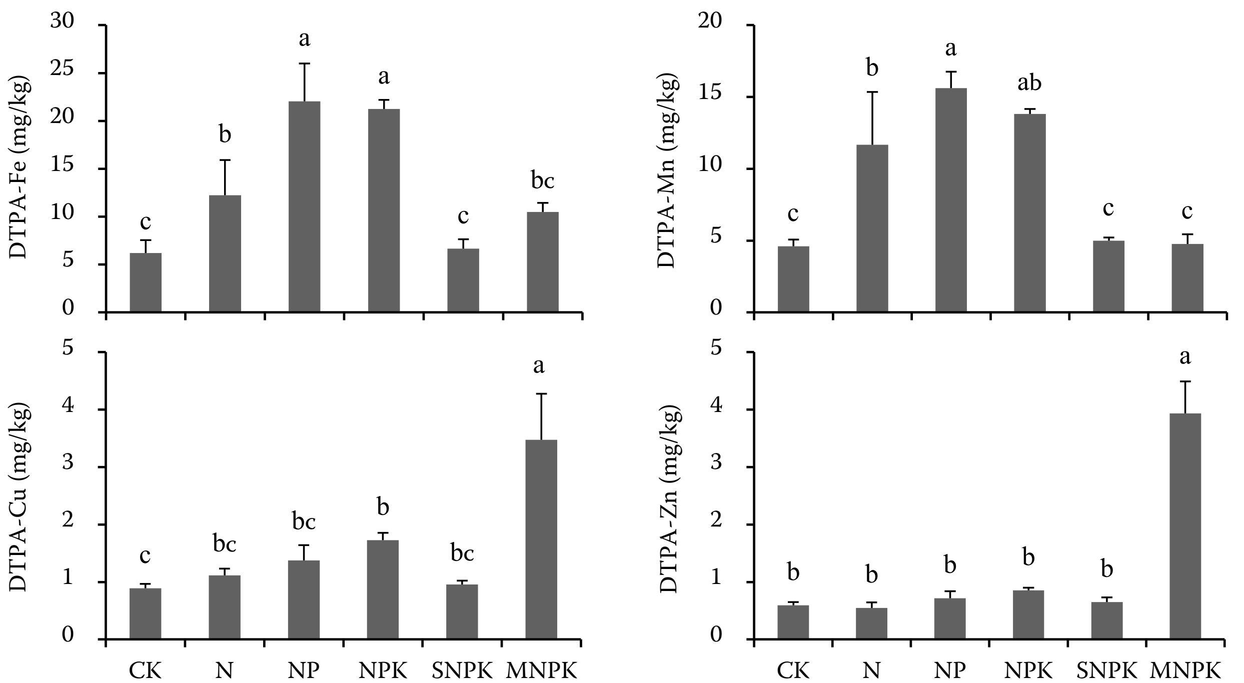

Figure 1. DTPA-extractable micronutrient concentrations under different fertilization treatments. CK – no fertilization; N, P and K – 165 kg N/ha, 36 kg P/ha and 68.5 kg K/ha input; S – 7500 kg/ha cornstalk input; M – 30 t/ha farmyard manure input. Values above the column of a single figure followed by different letters are significantly different at $P < 0.05$ according to the Duncan's multiple range test

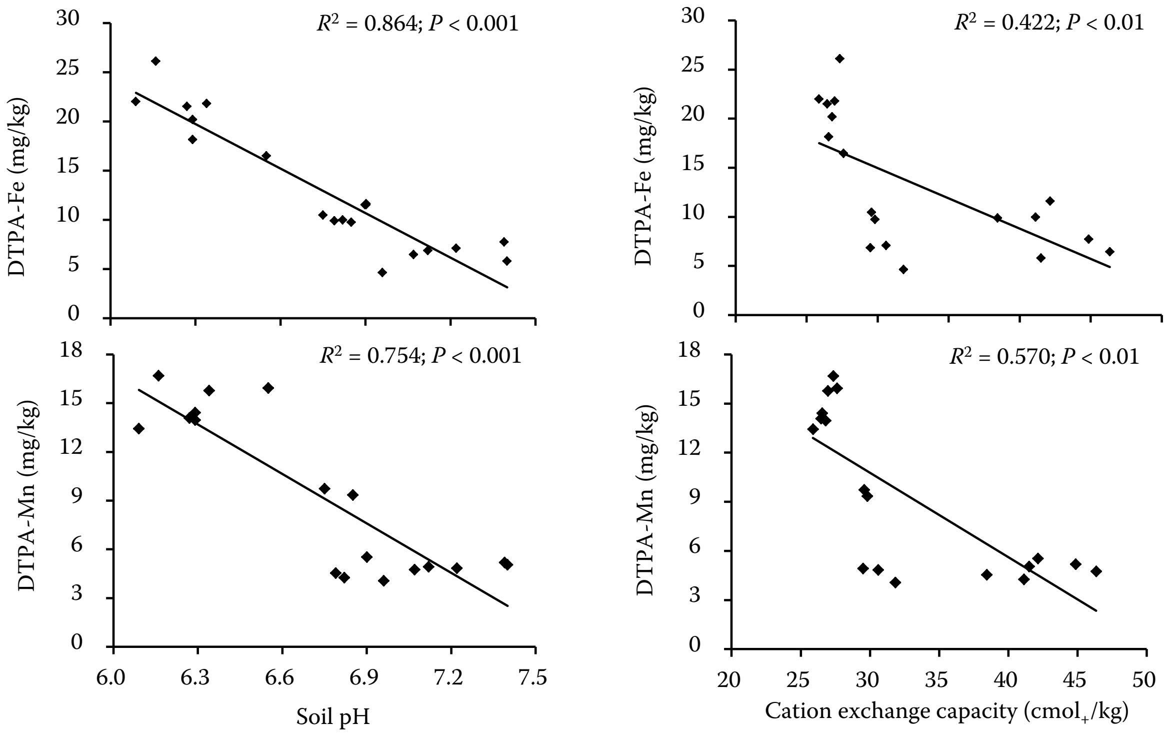

Figure 2. Linear regression of DTPA-Fe and Mn with soil pH and cation exchange capacity

et al. 2004). Although farmyard manure amendment and cornstalk addition may increase Fe and Mn solubility through chelation reactions, the increased soil pH in treatments SNPK and MNPK decreased concentrations of DTPA-Fe and Mn in soil, relative to chemical N fertilization treatments (Figure 1). However, a 19-year experiment in middle China showed that cornstalk incorporated with mineral NPK (pH 8.0) did not significantly affect DTPA-Fe and Mn, as compared with mineral fertilization (pH 8.06–8.54) and no fertilizer (pH 8.58) treatments (Li et al. 2010). Our results may be different due to the different soil pH and other physicochemical conditions in the two regions.

Farmyard manure amendment significantly increased DTPA-extractable Cu and Zn in soils. DTPA-Cu and Zn were significantly increased in MNPK treatment, while NPK treatment had more DTPA-Cu than in SNPK treatment and CK. Concentrations of DTPA-Cu were about 4 times higher in MNPK treatment than in CK or SNPK treatment, while DTPA-Zn was about 4.8–6.5 times higher in MNPK treatment than in the other treatments (Figure 1). The variations of DTPA-Cu and Zn mainly occurred as farmyard manure amendment induced changes in chemical properties, such as soil organic carbon (SOC), exchangeable cations and EC in soils. DTPA-Cu and Zn were significantly and positively correlated with SOC and EC (Figure 3). A case study with 98 soil samples in India also showed that DTPA-Cu and Zn were positively correlated with soil SOC and EC (Vijaynkumar et al. 2011).

Organic amendments are often used for organic matter replenishment and to avoid application of high levels of chemical fertilizers. Although most animal wastes contain small quantity of plant available Cu and Zn, animals require metals as a part of their diet, so micronutrients like Cu and Zn are added to feedstuffs as growth promoters or diarrhea preventers (Carlson et al. 2008). Thus, long-term farmyard manure amendment tended to increase Cu and Zn in soils. A six year study showed that compost amendment resulted in an increase in all extractable micronutrients, as compared with soil with mineral fertilization (Herencia et al. 2008). Relative to mineral fertilizer inputs, farmyard manure applied at 35 t/ha significantly increased soil levels of Cu and Zn, using the data from the Rothamsted experiments (Johnston 1997). Consequently, long-term application of farmyard manure significantly increased DTPA-Cu and Zn in soil in this study.

Cornstalk incorporated with mineral NPK did not significantly affect DTPA-Cu and Zn, as compared with CK, which was in accordance with a similar

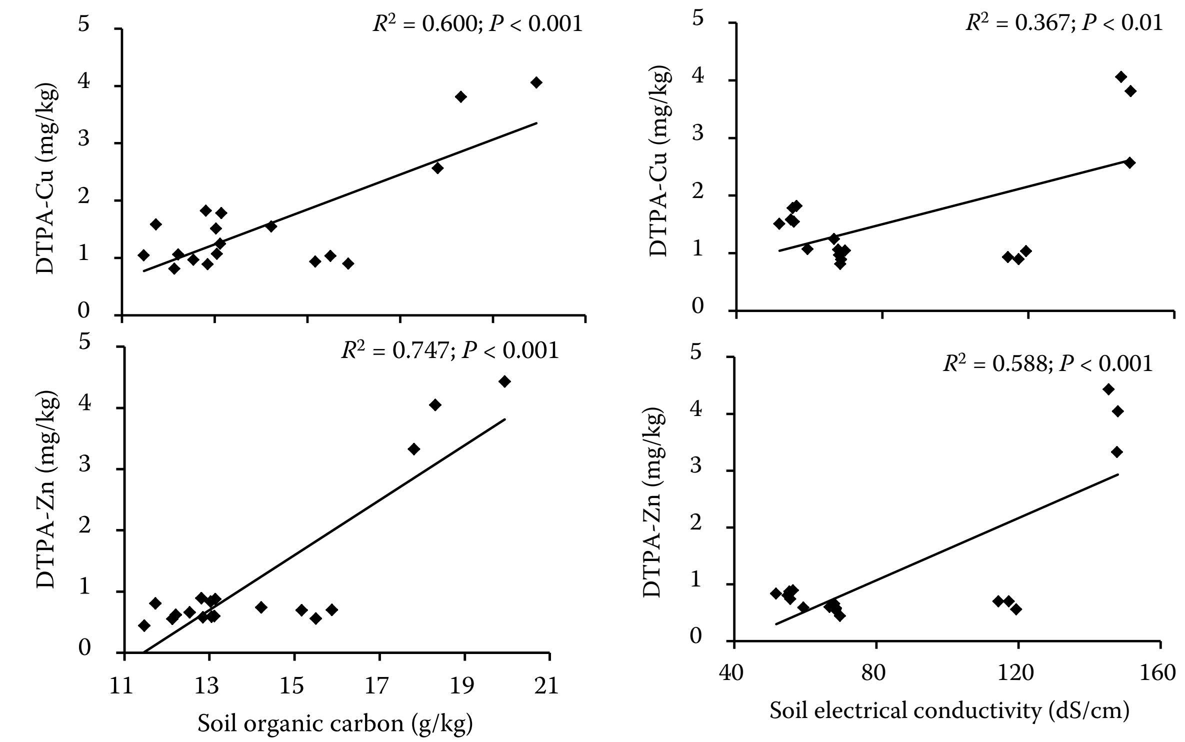

Figure 3. Linear regression of DTPA-Cu and Zn with soil organic carbon and electrical conductivity

study conducted in an Aquic Inceptisol for 19 years in middle China (Li et al. 2010). The main reasons for lower DTPA-Cu and Zn in SNPK treatment were deduced as follows, (i) comparatively lower total Cu and Zn in soil because of the small quantity of micronutrients in cornstalk (Figure 4), and (ii) comparatively higher soil pH (7.29) decreased the availability of soil micronutrients.

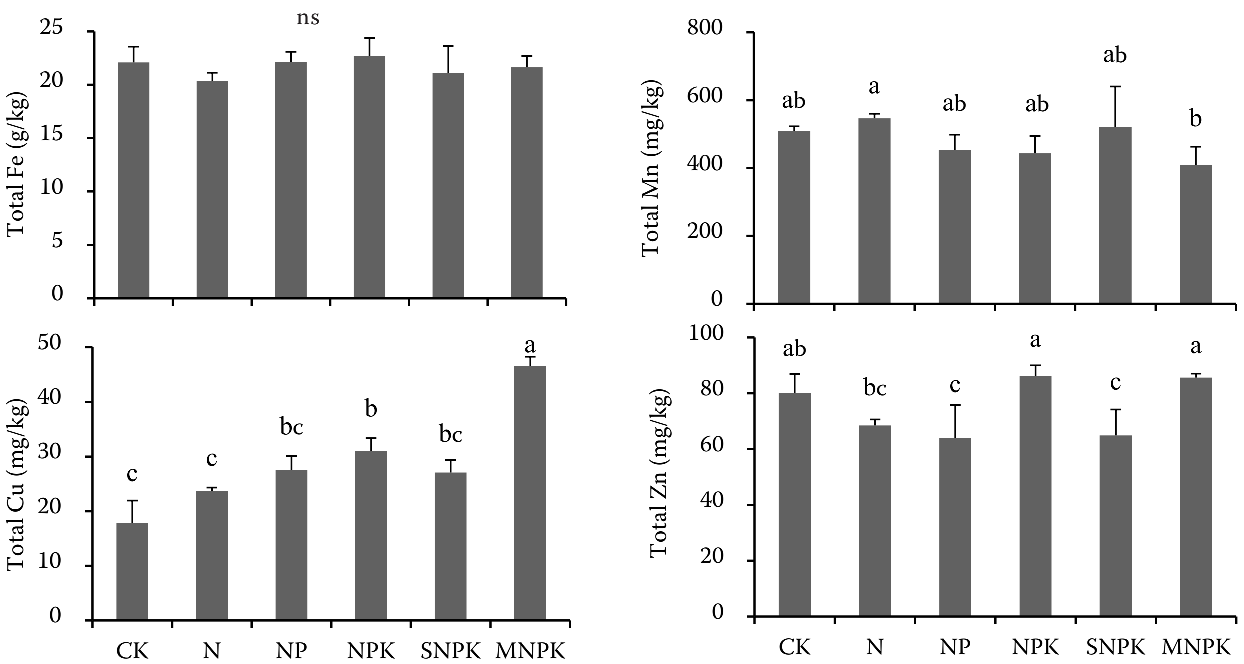

Figure 4. Total micronutrient concentrations under different fertilization treatments. CK – no fertilization; N, P and K – 165 kg N/ha, 36 kg P/ha and 68.5 kg K/ha input; S – 7500 kg/ha cornstalk input; M – 30 t/ha farmyard manure input. Values above the column of a single figure followed by different letters are significantly different at $P < 0.05$ according to the Duncan's multiple range test

Table 1. Pearson correlation coefficients of DTPA-extractable micronutrients with related soil chemical properties (n = 18)

	DTPA-Fe	DTPA-Mn	DTPA-Cu	DTPA-Zn
Total Cu	–	–	0.893**	–
Electrical conductivity	–0.540*	–0.708**	0.606**	0.767**
Soil pH	–0.929**	–0.868**	–0.167	0.053
Soil organic carbon	–0.242	–0.479*	0.774**	0.864**
Total nitrogen	–0.106	–0.382	0.890**	0.930**
Total phosphorus	–0.155	–0.278	0.223	0.320
Total potassium	–0.065	–0.131	–0.121	–0.110
Ammonia nitrogen (NH_4^+-N)	0.651**	0.461	0.445	0.298
Nitrate nitrogen (NO_3^--N)	0.361	0.224	0.633**	0.604**
Exchangeable calcium	–0.713**	–0.786**	0.158	0.350
Exchangeable magnesium	0.634**	0.398	0.802**	0.670**
Exchangeable potassium	–0.455	–0.604**	0.608**	0.747**
Exchangeable sodium	–0.042	–0.340	0.897**	0.921**
Cation exchange capacity	–0.650**	–0.755**	0.268	0.448

*P < 0.05; **P < 0.01

It was well reported that soil available Cu and Zn would be increased with application of mineral P fertilizers (e.g. Li et al. 2007), but a case study showed that continuous application of inorganic NPK fertilizers in cassava production resulted in a decrease of available Zn and Cu in soil (Rengel 2007). However, no significant difference was observed in DTPA-Cu and Zn among chemical fertilization treatments, and SNPK (Figure 1).

Relationships of DTPA-extractable micronutrients with other soil chemical properties. The concentration of DTPA-Cu was highly correlated with total Cu (Table 1), while DTPA-extractable Fe, Mn or Zn were not significantly correlated with their total contents. No significant difference was observed for total Fe among treatments, while total Mn was only significantly greater in N treatment than in MNPK treatment. Total Cu contents in treatments were sequenced from high to low as MNPK, NPK, NP, SNPK, N, and CK. Total Zn content was significantly lower in treatments NP and SNPK than in the other treatments (Figure 4).

Soil EC was positively correlated with DTPA-Fe and Mn, as opposed to negatively with Cu and Zn. Soil pH was only significantly and negatively correlated with Fe and Mn. Soil organic C and total N were positively correlated with Cu and Zn, but nitrite N that correlated negatively with them; neither total P nor total K was significantly correlated with any of the micronutrients. Ammonia N was the only one to correlate with Fe, exchangeable Ca and CEC correlated negatively with Fe and Mn, while exchangeable Mg, K and Na positively with Cu and Zn (Table 1).

In conclusion, long-term chemical N application significantly increased DTPA-extractable Fe and Mn in soils, while the farmyard manure amendment significantly increased DTPA-extractable Cu and Zn in soils. DTPA-Fe and Mn increased significantly with the decrease of soil pH and CEC, while DTPA-Cu and Zn increased significantly with increasing SOC and EC. Although cornstalk addition significantly increased SOC, low contents of total micronutrients in cornstalk and the comparatively higher soil pH decreased the availability of soil micronutrients. The research implicates that farmyard manure amendment is for beneficial enhancing of soil Cu and Zn fertility, while micronutrients should be added to meet crop requirements in cornstalk addition practices in the black soil farmlands of Northeast China.

REFERENCES

Abu-Zahra T.R., Abubaker S.M., Tahboub A.B., Al-Abbadi A.A. (2010): Effect of organic matter sources on micronutrients and heavy metals accumulation in soil. Food, Agriculture and Environment, *8*: 1199–1202.

Alloway B.J. (2008): Micronutrient Deficiencies in Global Crop Production. Springer-Verlag, Berlin, Heidelberg.

Behera S.K., Singh D. (2009): Effect of 31 years of continuous cropping and fertilizer use on soil properties and uptake of micronutrients by maize (*Zea mays*)-wheat (*Triticum aestivum*) system. Indian Journal of Agricultural Sciences, *79*: 264–267.

Benke M.B., Indraratne S.P., Hao X.Y., Chang C., Goh T.B. (2008): Trace element changes in soil after long-term cattle manure applications. Journal of Environmental Quality, *37*: 798–807.

Caliskan S., Ozkaya I., Caliskan M.E., Arslan M. (2008): The effects of nitrogen and iron fertilization on growth, yield and fertilizer use efficiency of soybean in a Mediterranean-type soil. Field Crops Research, *108*: 126–132.

Carlson D., Sehested J., Feng Z., Poulsen H.D. (2008): Serosal zinc attenuate serotonin and vasoactive intestinal peptide induced secretion in piglet small intestinal epithelium *in vitro*. Comparative Biochemistry and Physiology. Part A, Molecular and Integrative Physiology, *149*: 51–58.

Darusman, Stone L.R., Whitney D.A., Janssen K.A., Long J.H. (1991): Soil properties after twenty years of fertilization with different nitrogen sources. Soil Science Society of America Journal, *55*: 1097–1100.

Edmeades D.C. (2003): The long-term effects of manures and fertilisers on soil productivity and quality: A review. Nutrient Cycling in Agroecosystems, *66*: 165–180.

FAO (1988): FAO-UNESCO Soil Maps of the World, Revised Legend. World Soil Resources Reports 60, FAO, Rome.

Havlin J.H., Tisdale S.L., Nelson W.L., Beaton J.D. (2004): Soil Fertility and Fertilizers: An Introduction to Nutrient Management. 7th Edition. Pearson Education, Prentice Hall.

Herencia J.F., Ruiz J.C., Morillo E., Melero S., Villaverde J., Maqueda C. (2008): The effect of organic and mineral fertilization on micronutrient availability in soil. Soil Science, *173*: 69–80.

Jiang Y., Liang W.J., Wen D.Z., Zhang Y.G., Chen W.B. (2005): Spatial heterogeneity of DTPA-extractable zinc in cultivated soils induced by city pollution and land use. Science in China Series C Life Sciences, *48*: 82–91.

Jiang Y., Zhang Y.G., Zhou D., Qin Y., Liang W.J. (2009): Profile distribution of micronutrients in an aquic brown soil as affected by land use. Plant, Soil and Environment, *55*: 468–476.

Johnston A.E. (1997): The value of long-term field experiments in agricultural, ecological, and environmental research. Advances in Agronomy, *59*: 291–333.

Li B.Y., Zhou D.M., Cang L., Zhang H.L., Fan X.H., Qin S.W. (2007): Soil micronutrient availability to crops as affected by long-term inorganic and organic fertilizer applications. Soil and Tillage Research, *96*: 166–173.

Li B.Y., Huang S.M., Wei M.B., Zhang H.L., Shen A.L., Xu J.M., Ruan X.L. (2010): Dynamics of soil and grain micronutrients as affected by long-term fertilization in an Aquic Inceptisol. Pedosphere, *20*: 725–735.

Li Q., Jiang Y., Liang W.J., Wang H., Jiang S.W. (2009): Nematode diversity in phaeozem agroecosystems of Northeast China. Pedosphere, *19*: 597–605.

Nikoli T., Matsi T. (2011): Influence of liquid cattle manure on micronutrients content and uptake by corn and their availability in a calcareous soil. Agronomy Journal, *103*: 113–118.

Page A.L. (1982): Methods of Soil Analysis. Agronomy Monograph 9, Part 2: Chemical and Mineralogical Properties. 2nd Edition. American Society of Agronomy, Madison.

Pederson G.A., Brink G.E., Fairbrother T.E. (2002): Nutrient uptake in plant parts of sixteen forages fertilized with poultry litter: Nitrogen, phosphorus, potassium, copper, and zinc. Agronomy Journal, *94*: 895–904.

Rengel Z. (2007): Cycling of micronutrients in terrestrial ecosystems. In: Marschner P., Rengel Z. (eds.): Nutrient Cycling in Terrestrial Ecosystems. Springer-Verlag, Berlin, Heidelberg, 93–121.

Sharma B.D., Mukhopadhyay S.S., Sidhu P.S., Katyal J.C. (2000): Pedospheric attributes in distribution of total and DTPA-extractable Zn, Cu, Mn and Fe in Indo-Gangetic plains. Geoderma, *96*: 131–151.

Uprety D., Hejcman M., Száková J., Kunzová E., Tlustoš P. (2009): Concentration of trace elements in arable soil after long-term application of organic and inorganic fertilizers. Nutrient Cycling in Agroecosystems, *85*: 241–252.

Vijaynkumar R., Arokiaraj A., Prasath M.D.P. (2011): Macronutrient and micronutrient status and their relationship with soil properties of natural disaster prone coastal soils. Research Journal of Chemistry and Environment, *15*: 415–418.

Yan X., Gong W. (2010): The role of chemical and organic fertilizers on yield, yield variability and carbon sequestration – results of a 19-year experiment. Plant and Soil, *331*: 471–480.

Xu Y., Yu W., Ma Q., Zhou H. (2013): Accumulation of copper and zinc in soil and plant within ten-year application of different pig manure rates. Plant, Soil and Environment, *59*: 492–499.

Zhu P., Ren J., Wang L.C., Zhang X.P., Yang X.M., Don MacTavish (2007): Long-term fertilization impacts on corn yields and soil organic matter on a clay-loam soil in Northeast China. Journal of Plant Nutrition and Soil Science, *170*: 219–223.

Received on January 22, 2014
Accepted on July 21, 2014

Corresponding author:

Prof. Dr. Yong Jiang, Chinese Academy of Sciences, Institute of Applied Ecology, State Key Laboratory of Forest and Soil Ecology, Shenyang 110164, P.R. China
phone: + 86 24 8397 0902, fax: + 86 24 8397 0300, e-mail: jiangyong@iae.ac.cn