Occlusive effect of soil aggregates on increased soil DTPA-extractable zinc under low soil pH caused by long-term fertilization

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ABSTRACT

To investigate the effect of low soil pH caused by fertilization on soil available zinc in calcareous soil, this study was conducted based on a long-term experiment consisting of: (a) no fertilization (CT); (b) mineral fertilizer application coupled with 7500 kg/ha of wheat straw (WS-NPK); (c) mineral fertilizer application coupled with 3750 kg/ha of wheat straw (1/2WS-NPK); (d) mineral fertilizer application alone (NPK). Long-term fertilization results in a significant increase in soil DTPA-extractable zinc. However, the increased soil DTPA-extractable zinc is unavailable to crops and mainly confined to 0.25 mm > and 0.25 mm to 1 mm aggregates. Compared to CT, soil DTPA-extractable zinc under fertilization is more than 9.67% and 122.36% higher in 0.25 mm > and 0.25 mm to 1 mm aggregates, respectively. Furthermore, plant-available zinc in the 0–15 cm soil layer and wheat grain zinc are both significantly positive related to soil DTPA-extractable zinc in > 2 mm aggregates. Therefore, plant-available zinc in the 0–15 cm layer is closely associated with DTPA-extractable zinc in > 2 mm aggregates, and the low soil pH caused by long-term fertilization could not enhance plant-available zinc in the surface soil layer nor elevate wheat grain zinc concentration because of the occlusive effect of soil aggregates.

Keywords: soil total zinc; soil organic carbon; wheat straw; grain zinc concentrations

Zinc is directly related to the physical growth, immune competence, reproductive function, and neuron-behavioral development of humans (Gibson 2006). However, approximately 50% of soils suffer from zinc deficiency globally, and some diseases caused by zinc deficiency, such as diarrhea and pneumonia in children, consequently occur widely in developing countries. During agricultural production, crops grown in zinc-deficient soils not only exhibit low grain zinc concentration but are also highly sensitive to biotic and abiotic stress (Obata et al. 1999). Moreover, zinc-deficient soils perform worse in terms of seed germination, seedling health, crop growth, and yield compared with soils with high zinc availability (Cakmak et al. 1996).

In the Northern region of China, wheat is one of the most important staple food crops and supplies more than 20% of dietary zinc intake (Ma et al. 2008). However, the low grain zinc concentration caused the daily zinc intake of the local population to be insufficient to meet daily human requirements. Consequently, approximately 100 million people in China have suffered from zinc deficiency, especially children living in rural re-

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gions (Ma et al. 2008). To enhance wheat grain, zinc concentration, zinc fertilization including foliar zinc application alone or coupled with soil zinc application was recommended (Zhang et al. 2012, Zou et al. 2012). Further studies suggest that increasing the nitrogen fertilizer application rate coupled with zinc fertilizer application maximizes grain zinc concentration (Xue et al. 2012). However, determining the optimum rates of zinc or nitrogen fertilizer for different crops is difficult and complicated, and excessive zinc and nitrogen fertilization in intensive agricultural areas generally result in serious environmental problems such as heavy metal pollution, soil acidification, greenhouse gas emissions, and eutrophication (Zheng et al. 2004, Guo et al. 2010, Le et al. 2010).

Moreover, a large proportion of zinc fertilizer applied to soil is lost because of sorption or depletion (Sinha et al. 1977, Cakmak 2008). To enhance the uptake of soil zinc, releasing the zinc sorbed on soil particle surfaces, dissolving zinc-containing minerals, and zinc fertilizer application become necessary for crops (Uygur and Rimmer 2000). Zinc sorption and desorption is generally linked to soil pH. Under low pH, sorbed zinc can be desorbed back into the soil solution, thus enhancing the availability of soil zinc (Singh et al. 2008). Long-term fertilization results in a decrease in soil pH, whether soil zinc availability increases or not (Guo et al. 2010, Guo and Wang 2013). Therefore, this study was undertaken to explore the effect of long-term fertilization on soil zinc availability and to determine the factors affecting soil zinc availability.

MATERIAL AND METHODS

Description of the experimental site and experimental design. This research was conducted based on the experiment on a field in the MengChen County of Anhui province, Central China, which has undergone long-term fertilization; detailed information on the experimental site was described in our previous study (Guo and Wang 2013). The long-term field experiment ranged from 1984 to 2011 and consisted of four treatments: (1) no fertilization (CT); (2) mineral fertilizer application coupled with 7500 kg/ha of wheat straw (WS-NPK); (3) mineral fertilizer application coupled with 3750 kg/ha of wheat straw (1/2WS-NPK); (4) mineral fertilizer application alone (NPK). The number of chemical fertilizers applied in the experiment was 180 kg N/ha, 39.6 kg P/ha and 112 kg K/ha. In this trial, a randomized block design with four replicates was used. The area of each experimental plot was 66.6 m^2 (15.0 m × 4.44 m), separated by a ridge 0.3 m high and 0.5 m wide. Prior to the experiment, winter wheat was planted for several decades. From 1982 to 2011 except the period of 1993–1997 when wheat-corn were used, the rotational crops were wheat-soybean.

Samplings and measurements. Plant samples consisting of wheat straw and wheat grain were taken after wheat harvest in July 2011. Specifically, plant samples with three replicates were randomly taken in each plot with at least 0.5 m from the edge to avoid an edge effect. Wheat straw refers to wheat shoots excluding the grains. All plant samples were dried at 105°C for 1 h and then at 70°C for a minimum of 72 h.

Soil samples at the 0 cm to 15 cm layer were collected in each plot thrice after wheat harvest. Subsequently, the collected samples were air-dried and divided into two groups. The first group was for soil organic carbon and zinc content analysis, and the second group was analyzed for soil organic carbon and DTPA-extractable zinc content in different size classes of soil aggregates using dry sieving, as described by Lyles et al. (1970). In the dry-sieving method, 200 g air-dried soil sample was divided into four different classes using a stack of three 15 cm diameter sieves with screen openings of 2, 1, and 0.25 mm. The aggregate fractions were: (i) > 2 mm; (ii) 1 mm to 2 mm; (iii) 0.25 mm to 1 mm, and (iv) 0.25 mm >.

After digestion in a nitric and perchloric acid mixture, the wheat straw and grain zinc concentrations were determined using atomic absorption spectrometry (AAS, Perkin Elmer; Model- AAanalyst 100) (Johnson and Ulrich 1959). Total soil and available Zn were obtained by microwave-assisted digestion with an acid mixture (V:HNO_3:H_2O_2:HF = 3:2:1) and DTPA solution (5 mmol/L diethylene triamine pentaacetic acid, 0.108 mol/L triethanolamine, 10 mmol/L $CaCl_2$, pH 7.3), and then determined by AAS (Perkin Elmer 3110, PerkinElmer Inc., Waltham, USA). The soil organic carbon was determined by the Walkley-Black dichromate oxidation method (Nelson and Sommers 1982).

Statistical analysis. Statistical analyses in the research were all conducted using SAS 9.1.3 (SAS Institute Inc., Cary, USA), and graphs were plotted by SigmaPlot 10.0 (Systat Software Inc., San Jose, USA).

RESULTS AND DISCUSSION

Fertilization and soil available zinc. Soil DTPA-extractable zinc and the ratio of DTPA/total zinc are generally used to evaluate the availability of zinc in soils (Dabkowska-Naskret 2003). The results of this experiment indicate that long-term mineral fertilizer application, alone or in combination with wheat straw returning into croplands, which results in a reduction in soil zinc availability in the 0 cm to 15 cm layer even under lower soil pH caused by long-term fertilization (Figure 1b) (Guo and Wang 2013). However, significantly higher soil total zinc concentrations in the 0 cm to 15 cm layer were observed in both 1/2WS-NPK and NPK treatments (Figure 1a). Compared with the CT treatment, soil total zinc content was higher by 62.63% and 55.60% in the 1/2WS-NPK and NPK treatments, respectively, whereas available zinc concentration was lower by 17.24% and 15.28%, respectively. When the amount of wheat straw returning into cropland increased from 3750 kg/ha to 7500 kg/ha, soil total zinc decreased by 35.07%, which may be attributed to the annual soil zinc output through higher wheat yield (Cakmak 2008, Guo and Wang 2013). Furthermore, fertilization results in lower soil DTPA/total zinc ratio. Specifically, compared with CT with 3.95% of DTPA/total zinc, the DTPA/total zinc ratio was lower by 3.24% in WS-NPK, 2.00% in 1/2WS-NPK, and 2.16% in NPK, respectively. These results indicate that low soil pH caused by long-term fertilization does not result in high soil zinc availability for crops, which is in strong disagreement with Delorme et al. (2001), who reported that soil acidification would increase the availability of soil zinc. In this study, the lower availability of soil zinc in all fertilized treatments may be attributed to the occlusive effect of soil aggregates on increased soil DTPA-extractable zinc caused by low soil pH.

Figure 1c shows the distribution of DTPA-extractable zinc in different classes of soil aggre-

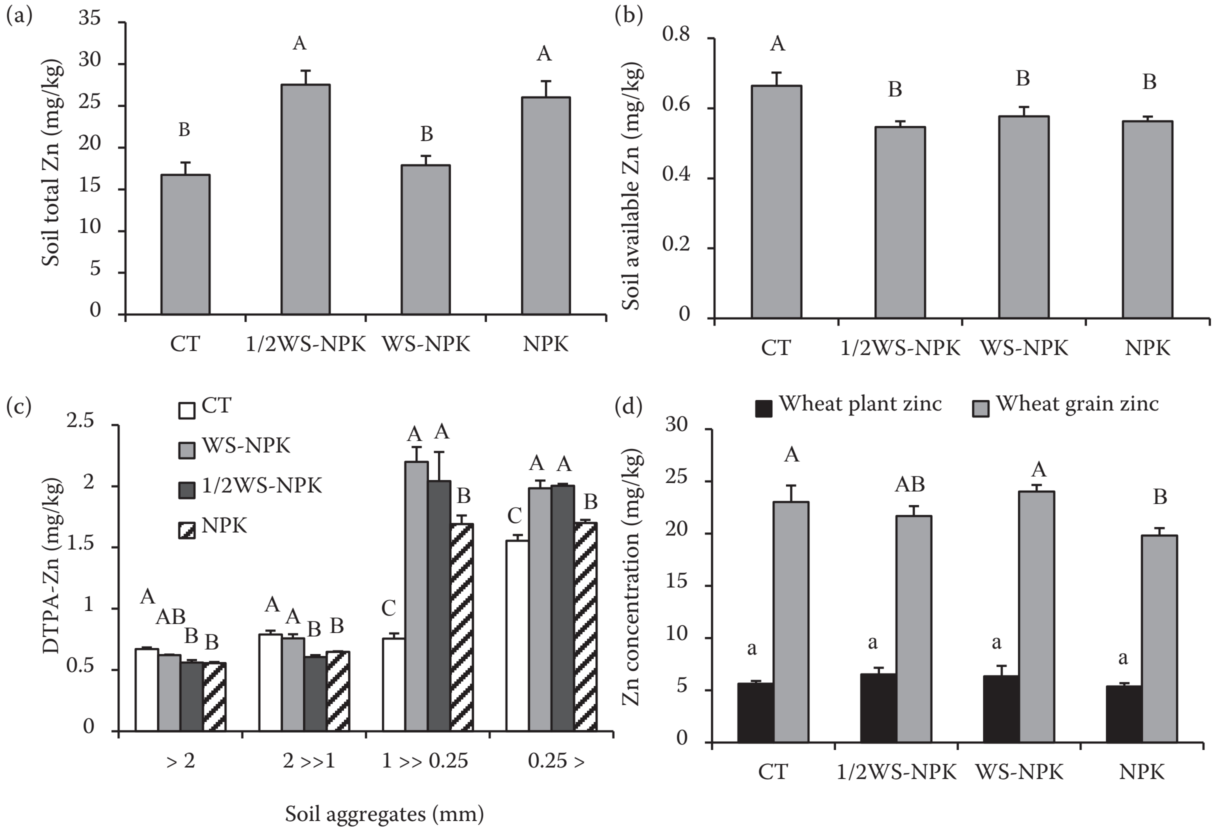

Figure 1. Soil total and available zinc in the 0 cm to 15 cm layer (a, b); DTPA-extractable zinc in different classes of soil aggregates (c), and wheat plant and grain zinc concentrations (d) in CT, WS-NPK, 1/2WS-NPK and NPK treatments. The bars represent the standard error of the mean (n = 4). Columns with different letters indicate significant difference at $P < 0.05$. CT – no fertilization; WS-NPK – mineral fertilizer application coupled with 7500 kg/ha of wheat straw; 1/2WS-NPK – mineral fertilizer application coupled with 3750 kg/ha of wheat straw; NPK – mineral fertilizer application alone

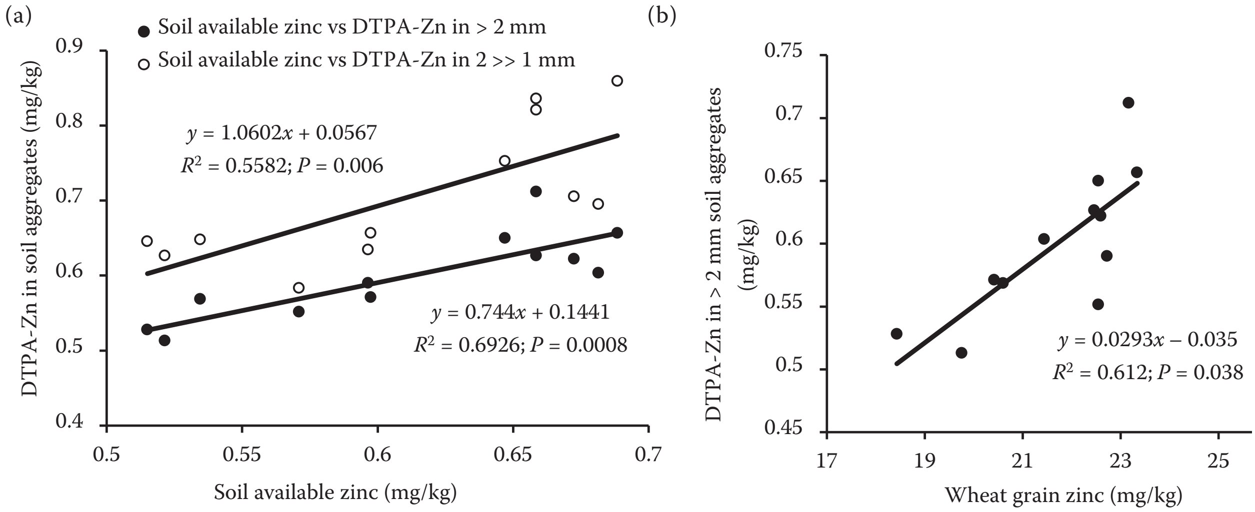

Figure 2. (a) Relationships between soil DTPA-extractable zinc in the 0 cm to 15 cm layer and DTPA-extractable zinc in the > 2 mm and 1 mm to 2 mm aggregates and (b) between wheat grain zinc concentration and DTPA-extractable zinc in the > 2 mm aggregates in the experiment

gates. In all fertilized treatments, no statistically significant differences were found in soil DTPA-extractable zinc between 0.25 mm > and 0.25 mm to 1 mm aggregates and between > 2 mm and 1 mm to 2 mm aggregates. However, the soil DTPA-extractable zinc in 0.25 mm > and 0.25 mm to 1 mm aggregates under fertilization was significantly higher compared with CT treatment but progressively lower in > 2 mm and 1 mm to 2 mm aggregates. Moreover, when the size class of soil aggregates ranged from 0.25–1 mm to 1–2 mm, the soil DTPA-extractable zinc concentration significantly decreased in all fertilized treatments, whereas no significant differences were observed in CT. In contrast to 0.25 mm to 1 mm aggregates, DTPA-extractable zinc in 1 mm to 2 mm aggregates decreased by 65.56% in WS-NPK, 70.31% in 1/2WS-NPK, and 61.63% in NPK. However, when the size class of soil aggregates ranged from 1–2 mm to > 2 mm, no significant differences in soil DTPA-extractable zinc were observed in all fertilized treatments. Thus, the improvement in soil DTPA-extractable zinc by low soil pH was mainly confined to the 0.25 mm > and 0.25 mm to 1 mm aggregates, which is further supported by the positive relationships that exist between soil DTPA-extractable zinc in the 0 cm to 15 cm layer and soil DTPA-extractable zinc in > 2 mm and 1 mm to 2 mm aggregates (Figure 2a).

Soil DTPA-extractable zinc and wheat grain and straw zinc concentrations. High soil zinc availability generally contributes to high accumulation of wheat straw and grain zinc (Xue et al. 2012). In this research, wheat grain zinc concentration in all treatments responded significantly to soil DTPA-extractable zinc concentration in the 0 cm to 15 cm layer. Figure 1d shows wheat straw and grain zinc concentrations in CT, WS-NPK, 1/2WS-NPK, and NPK treatments. For wheat straw zinc, no statistically significant differences were found among all treatments, whereas NPK and 1/2WS-NPK treatments resulted in a reduction in wheat grain zinc concentration. In contrast to

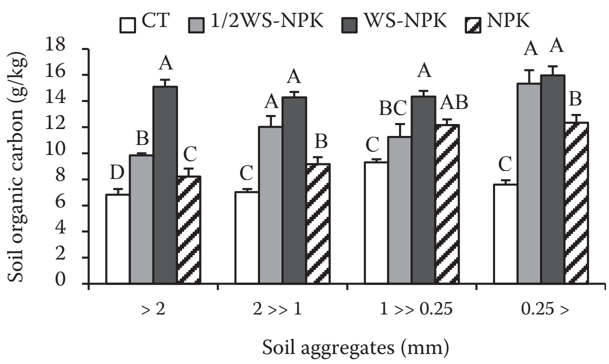

Figure 3. Distribution of soil organic carbon in CT, WS-NPK, 1/2WS-NPK and NPK treatments. The bars represent the standard error of the mean ($n = 4$). Columns with different letters indicate significant difference at $P < 0.05$. CT – no fertilization; WS-NPK – mineral fertilizer application coupled with 7500 kg/ha of wheat straw; 1/2WS-NPK – mineral fertilizer application coupled with 3750 kg/ha of wheat straw; NPK – mineral fertilizer application alone

Table 1. Correlation coefficients (*R*) between soil DTPA-extractable zinc (SDE-Zn) in aggregates and soil organic carbon in aggregates in 0–20 cm depth layer

	Aggregates	Soil organic carbon (g/kg)			
		> 2 mm	2 mm >> 1 mm	1 mm >> 0.25 mm	0.25 mm>
SDE-Zn (mg/kg)	> 2 mm	–0.031	–0.245	–0.419	–0.620
	2 mm >> 1 mm	0.051	–0.217	–0.129	–0.555
	1 mm >> 0.25 mm	0.766**	0.780**	0.779**	0.935***
	0.25 mm >	0.730**	0.808**	0.584*	0.842***

*$P \leq 0.05$; **$P \leq 0.01$; ***$P \leq 0.001$

CT, wheat grain zinc concentration was by 5.82% and 13.90% lower with 1/2WS-NPK and NPK treatments, respectively. However, increasing the amount of wheat straw returning into cropland contributed to a progressive increase in wheat grain zinc concentration. When the amount of wheat straw returning into cropland doubled, an approximately 10.81% increase in wheat grain zinc concentration was observed (Figure 1d), which can be attributed to two aspects. (a) More plant-available zinc is released during the decomposition of wheat straw. In WS-NPK treatment, the annual zinc input into soil is approximately 47.55 g/ha according to the level of wheat straw zinc shown in Figure 1d, which is twofold higher compared with 1/2WS-NPK treatment. (b) Increasing rate of organic amendment results in an increase in DTPA-extractable zinc (Karaca 2004, Reyhanitabar and Gilkes 2010). In this experiment, soil organic carbon increased significantly as the number of wheat straw returning into cropland increases (Figure 3). Moreover, a significantly positive relationship was observed between DTPA-extractable zinc and soil organic carbon (Table 1).

A significantly positive relationship was also found between wheat grain zinc concentration and DTPA-extractable zinc in the > 2 mm aggregates (Figure 2b), which indicates that wheat grain zinc is significantly affected by the DTPA-extractable zinc in > 2 mm aggregates in the 0 cm to 15 cm layer. This relationship indirectly supports the occlusive effect of soil aggregates on increased soil DTPA-extractable zinc under low soil pH.

In conclusion, the results provide evidence that low soil pH caused by long-term fertilization helps to improve soil DTPA-extractable zinc. However, the increased soil DTPA-extractable zinc is unavailable for plant growth because of an occlusive effect of soil aggregates and is thus mainly confined to 0.25 mm > and 0.25 mm to 1 mm aggregates. Moreover, soil available zinc in the 0 cm to 15 cm layer and wheat grain zinc concentration were both positively related to soil DTPA-extractable zinc in > 2 mm aggregates. Therefore, to improve wheat grain zinc concentration during agricultural production, enhanced soil DTPA-extractable zinc in > 2 mm aggregates is important, even under low soil pH.

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