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Chemical forms in soil and availability of manganese and zinc to soybean in soil under different tillage systems

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ABSTRACT

Chemical forms of Mn and Zn in the soil and its availability to soybeans grown in a Latosol for 12 years under different tillage systems were studied. The effects of these systems on Mn complexation by soil humic acid (HA) were also evaluated. The field experiment was carried out in a randomized block (three blocks) split-plot experimental design. The main treatments consisted of four tillage systems and the secondary, of three soil sampling depths (0.00–0.05 m, 0.05–0.10 m and 0.10–0.20 m). The tillage systems were no tillage (NT), conventional tillage (CT), minimum tillage (MT) and NT with scarification, every three years. The results presented refers to the last 2 years of the experiment, 2000 and 2001. In average numbers, the Zn content of the 0.00–0.05 m layer was lower in soil under CT (2 mg kg^{-1}), compared to the other tillage systems (NT and NT with scarification = 2.7 and MT = 2.8 mg kg^{-1}). In general, Zn percentages in exchangeable, organic, oxides and residual forms were not modified by the tillage systems. In turn, the Mn content of the soil surface layer under the NT was higher than in the soil under CT. Mn contents extracted with DTPA were 11 and 5.2 mg kg^{-1} in the soil under NT and CT, respectively. The Mn contents extracted with Mehlich I, Mehlich III and HCl in the soil under CT were 20.8, 8.7 and 16.8 mg kg^{-1}, respectively. In the soil under NT, the contents extracted with the same extractors were 27.9, 15 and 29.2 mg kg^{-1}. In the surface layer, higher Mn percentages in the organic fraction were found in the soil under NT (19.2%) and NT with scarification (15.9%) than in soil under CT (11.8%). The Mn content of this layer was also positively correlated with the soil organic matter, but none of the extractors used (DTPA-TEA pH 7.3, HCl 0.1 mol L^{-1}, Mehlich I and III) properly assessed the levels of Mn and Zn available to plants, suggesting the need for further studies. It was not observed presence of Mn in the HA samples by electron paramagnetic resonance (EPR). Since the digestion by nitro-perchloric acid of the HA samples showed the presence of Mn in these samples, it strengthens the hypothesis that Mn was bound to the HA in the form of stable complexes (covalent bonds), since this form of Mn cannot be detected by EPR. During soybean cultivation, Mn concentrations in the leaves did not vary with the tillage methods and were near or below the range considered adequate for the crop. Furthermore, visual symptoms of Mn deficiency in the leaves were observed in the initial stages of plant development, regardless of treatment. This suggests the need for new correlation and calibration studies for micronutrients in Brazil, especially for soils cultivated under the NT.

1. Introduction

The availability of micronutrients to plants is affected by several soil properties, especially the pH and the organic matter (OM) levels. In soils under NT, long-term experiments conducted in

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different locations have shown increases of OM content in the surface layer (0.00–0.05 m) (Bayer et al., 2002; Teixeira et al., 2003; Thomas et al., 2007; Santiago et al., 2008; Aziz et al., 2013; Motschenbacher et al., 2014; Vukasinovic et al., 2015) and an increase in pH values, mainly due to surface liming (Caires et al., 2003, 2008; Teixeira et al., 2003; Fonseca et al., 2010).

In many cases higher Mn and Zn levels in topsoil, determined by official analysis methods, have been reported (Moreira et al., 2006; Martin-Rueda et al., 2007; Santiago et al., 2008). However, correlations of soil micronutrient content with leaf content and/or amount accumulated in plant have not been observed (Moreira et al., 2006; Santiago et al., 2008; Fonseca et al., 2010). This demonstrates that the current extractors used may not properly be assessing the availability of Mn and Zn in soils cultivated under NT.

In locations under NT there are some reports of "patches" of Mn deficiency caused by poor distribution of lime applied on the surface, due to the sharp increase in the pH, in a localized manner. However, these explanations do not always hold true for many soils under NT, which have been presenting Mn deficiencies in soybean *Glycine max* (L.) Merr. and Zn in maize (Pauletti., 1999; Moreira et al., 2006) and feature soil content considered suitable according to official analysis methodology.

The tendency of "exchangeable" Mn and Zn contents being higher in NT soils in relation to CT, can not be explained only by means of the soil pH. In NT, the surface lime application results in higher surface pH values (Caires et al., 2003, 2008; Fonseca et al., 2010), which, as a result, should decrease and not increase availability of these nutrients in the soil. Several authors have attributed the higher amounts of "exchangeable" Mn and Zn in the NT to the higher OM levels in soils subjected to this cultivation system (Moreira et al., 2006; Martin-Rueda et al., 2007; Santiago et al., 2008; Vukasinovic et al., 2015).

Although the effects of these systems on the OM and micronutrient levels are well documented (Bayer et al., 2002; Teixeira et al., 2003; Thomas et al., 2007; Santiago et al., 2008; Aziz et al., 2013; Motschenbacher et al., 2014; Vukasinovic et al., 2015) the effect of tillage systems on the humification degree of humic substances (HS) and the way in which the micronutrients are complexed by OM is still little known. Using electron paramagnetic resonance (EPR) it is possible to characterize the degree of humification of HS and, in some cases, to study the way some metals are organically complexed. With the aid of EPR, Moreira et al. (2006) showed that in soils under NT much of the Mn applied can be held more strongly in the soil organic fraction and has limited availability.

The chemical fractionation or sequential extraction of micronutrients (soluble + exchangeable, organic, oxides and residual forms), and further study of the correlation between micronutrient contents distributed in these forms and the amount absorbed by the plant, can help in the study of the selection of more suitable chemical extractors for assessing micronutrient availability.

The objective of this work was to study the effect of different tillage systems on Mn and Zn availability to soybean, evaluated by various chemical extractors; on the forms of these elements in the soil, obtained by sequential extraction; and on the Mn complexation by HS, via EPR.

The first hypothesis is that the Mn and Zn levels in soils under NT, in humid subtropical conditions in southern Brazil, tend to be higher than in soils cultivated under CT. The other hypothesis is that stable bonds between Mn and OM in NT are responsible for the contradiction, observed under field conditions, between high Mn and Zn levels revealed by soil analysis and the deficiency of this element in the soybean plants.

Table 1
Chemical properties of the diastrophic Red Latosol at different depths, in 1989, after liming (prior to experiment installation).

Depth m	pH ($CaCl_2$)	P mg dm^{-3}	OM g dm^{-3}	K mmol$_c$ dm^{-3}	Ca	Mg	V %
0.00–0.10	5.6	6	35	3.7	37.5	29.6	59.6
0.10–0.20	4.5	3	30	1.3	13.5	9.4	28.3
0.20–0.30	4.3	0	23	0.8	6.5	4.9	16.6

2. Material and methods

The experiment site belongs to the ABC Foundation and is located in the city of Ponta Grossa, State of Paraná, southern Brazil, on a very clayey dystrophic typic Red Latosol in the Brazilian Classification System (EMBRAPA, 2013a) or Rhodic Ferralsol in FAO classification system (FAO, 1998). The climate is mesothermal humid subtropical (cfb), with fresh summer and severe and frequent frosts in winter. The average temperature of the hottest month is 22 °C, and of the coldest, 18 °C, with no dry season. The altitude varies between 840 and 980 m.

At the experiment site the surface is flat and the soil was previously cultivated for many years with soybean under CT. In the winter of 1988 soil correction was accomplished with the application of 7.300 kg ha^{-1} of limestone incorporated 0.35 m deep with a moldboard plow. Two other surface limestone application of 2000 kg ha^{-1} each were carried out before the winter crops of 1992 and 1994. The chemical and physical characteristics of soil samples collected in 1989, after the liming of 1988, can be seen in Tables 1 and 2.

The field experiment was carried out in the summer of 1990 with a randomized block (three blocks) experimental design, with split plots. The size of the plots was 8.3 m × 25.0 m (207.5 m^2). Each plot consisted of about 20 soybean (BRS 133) rows, spaced 0.40 m, with a central area of 10 rows 4 m long.

The main treatments consisted of four tillage systems and the secondary, three sampling depths (0.00–0.05 m, 0.05–0.10 m and 0.10–0.20 m). Tillage systems were: NT – No tillage; CT – conventional tillage, consisting of one plowing with a "Jan" conventional, reversible disc plow, with three 36-inch discs (at ≅0.20 m) and a harrowing with a "Tatu" leveling harrow with 32 20-inch discs (at ≅0.10 m), before the summer and winter crops of each year; MT – minimum tillage, consisting of one harrowing with a "Massey Ferguson" harrow with 16 32-inch discs (at ≅0.17 m) and two with a "Tatu" leveling harrow with 32 20-inch discs (at ≅0.10 m), before the summer crops and winter of each year; NT/preparation – scarification with a "Max, 855 model" subsoiler, cruiser type, with 5 stems and working depth up to 40 cm (at ≅0.30 m), every three years in winter. Scarification was accomplished in 1990, 1992, 1995, 1999 and 2002.

The summary of the cultivation and fertilization history of the experimental area from 1988 to 2002 is shown in Table 3. The present study refers only to the cropping years of 2000/2001 and 2001/2002, i.e, 12 years after installation of the first experiments in the area.

Table 2
Total sand, silt and clay content of the distrophyc Red Latosol at different depths.

Depth m	Sand g kg^{-1}	Silt	Clay	Textural classification
0.00–0.10	300	70	630	very clayey
0.10–0.20	340	20	640	very clayey
0.20–0.30	300	70	630	very clayey