Extraction methods and availability of micronutrients for wheat under a no-till system with a surface application of lime

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ABSTRACT: Micronutrient availability can be affected by the increase of the soil pH due to surface liming. A field trial was carried out on a loamy, kaolinitic, thermic Typic Hapludox at Ponta Grossa, Paraná State, Brazil. The main objective was to evaluate the effects of surface liming and re-liming on the availability of micronutrients [copper (Cu), iron (Fe), manganese (Mn), and zinc (Zn)] for wheat (Triticum aestivum L.) cropped under a no-till system. A randomized complete block design was used in a split-plot arrangement. The main plots received surface lime applications (2, 4, and 6 Mg ha⁻¹) in July 1993. In the subplots, surface lime (3 Mg ha⁻¹) was applied again in June 2000. In 2003, before the wheat sowing, soil samples were taken at 0-5, 5-10, and 10-20 cm layers. Soil cationic micronutrients concentrations using different extractants (DTPA-TEA, Mehlich-1, HCl, and Mehlich-3) and solution/soil ratios were determined. Application of lime increased soil pH at 0-5, 5-10, and 10-20 cm. The increase in soil pH by liming did not affect soil organic carbon content. The Mehlich-3 solution had a greater capacity in extracting soil micronutrients. Increasing solution/soil ratio of the DTPA-TEA, Mehlich-1, and HCl solutions generally increased the extraction of Cu, Fe, Mn, and Zn. Liming and re-liming caused a decrease in Mn concentration in the wheat leaves. Leaf concentrations of Cu, Fe and Zn were not affected by liming treatments. The solutions of DTPA-TEA, Mehlich-1, HCl, and Mehlich-3 were ineffective to predict the soil cationic micronutrients availability for a wheat crop after surface application of lime. Key words: Triticum aestivum L., soil acidity, dolomitic lime, multinutrient extractants, soil with variable charge

Métodos de extração e disponibilidade de micronutrientes para o trigo cultivado em plantio direto com calagem na superfície

RESUMO: A disponibilidade de micronutrientes pode ser alterada pelo aumento no pH do solo proporcionado pela calagem superficial. Os efeitos da calagem e da reaplicação de cálcio na superfície sobre a disponibilidade de micronutrientes [cobre (Cu), ferro (Fe), manganes (Mn) e zinco (Zn)] para o trigo (Triticum aestivum L.) foram estudados em um Latossolo Vermelho textura média sob plantio direto, em Ponta Grossa (PR). O delineamento experimental empregado foi o de blocos completos ao acaso com parcelas subdivididas. As parcelas receberam calagem superficial (2, 4 e 6 Mg ha⁻¹) em julho de 1993. O cálcio (3 Mg ha⁻¹) foi reaplicado nas subparcelas em junho de 2000. Antes da semeadura do trigo em 2003, retiraram-se amostras de solo nas camadas de 0-5, 5-10 e 10-20 cm e determinaram-se os micronutrientes catiônicos com diferentes extratores (DTPA-TEA, Mehlich-1, HCl e Mehlich-3) e relações solução/solo. A calagem aumentou o pH do solo nas camadas de 0-5, 5-10 e 10-20 cm, mas não alterou o carbono orgânico. O extrator Mehlich-3 apresentou maior capacidade de extração de micronutrientes catiônicos. O aumento da relação solução/solo dos extratores DTPA-TEA, Mehlich-1 e HCl geralmente aumentou a extração de Cu, Fe, Mn e Zn. A calagem e a reaplicação do cálcio diminuíram a concentração de Mn nas folhas de trigo. Os teores foliares de Cu, Fe e Zn não foram alterados pela calagem. As soluções de DTPA-TEA, Mehlich-1, HCl e Mehlich-3 foram ineficazes para prever a disponibilidade de micronutrientes catiônicos para o trigo, após aplicação superficial de cálcio. Palavras-chave: Triticum aestivum L., acidez do solo, cálcio dolomítico, extratores multinutrientes, solo com carga variável

Introduction

Surface application of lime without incorporation has been the usual practice to control soil acidity in no-till (NT) systems (Caires et al., 2005). However, surface liming can decrease the cationic micronutrients availability as a consequence of increasing soil pH at the most superficial layers of the soil (Caires & Da Fonseca, 2000; Godsey et al., 2007). Studies related to bioavailability of cationic micro-nutrients in Brazilian soils have been carried out in pots under greenhouse conditions or in field trials under conventional tillage systems (Camargo et al., 1982; Bataglia & Raij, 1989; Abreu et al., 1994, 1996, 1998, 2002; Rodrigues et al. 2001; Nascimento et al., 2006). In no-till systems, soil organic matter and cationic micronutrients concentrations have been higher up to 10 cm depth (Zanão Júnior et al., 2007). Because the surface-applied
Micronutrients for wheat under a no-till system

The experimental area has been fertilized with N, P, and K, without addition of cationic micronutrients. Soybean [Glycine max (L.) Merr.] or corn (Zea mays L.) in the spring-summer season, and wheat or triticale (× Triticosecale) or black oat (Avena strigosa Schreb.) in the autumn-winter season has been cultivated. More details about the historic of cropping and fertilization and the effects of surface application of lime in the soil-plant system was reported elsewhere (Caires et al. 2005).

Wheat, cv. CD 104 (moderately susceptible to the soil exchangeable Al^{3+}) was sown in June 2003, with 17 cm between rows and 140 kg of seed per hectare, for a population between 250 and 300 plants m^{-2}. Fertilizers were applied by top dressing at the rates of 80 kg ha^{-1} N and 35 kg ha^{-1} K, as ammonium nitrate and potassium chloride, respectively.

Wheat plants flowered fully 84 days after emergence, and the crop maturation occurred 126 days after emergence. Air temperature was adequate for wheat growing and rainfall was on a considerable amount before sowing (55 mm) and before the plant flowering stage (56 mm). However, there was an extended water deficit during the vegetative development stage. Rainfall was 434 mm during the wheat crop cycle. More details about the wheat crop management are in Caires et al. (2006b).

During the flowering period of the wheat crop, leaves were sampled from 30 plants (flag leaf standard) of each subplot (Bataglia et al., 1978). These samples were washed in de-ionized water, dried in a forced-air oven at 60ºC until constant mass was achieved, and ground in a Wiley type mill to pass a 0.75 mm screen. After nitric-perchloric acid digestion of the plant tissues, Cu, Fe, Mn, and Zn concentrations were determined by atomic absorption spectrophotometry, according to Malavolta et al. (1997).

In May 2003, before wheat sowing – ten years after surface liming and three years after surface re-liming – soil samples were taken at 0-5, 5-10, and 10-20 cm layers. Twelve soil core samples per subplot were taken with a soil probe sampler and mixed to obtain a composite sample, which was air dried, and crushed to pass a 2-mm sieve. Soil pH and SOC were determined according to procedures suggested by Pavan et al. (1992). Soil available contents of Cu, Fe, Mn and Zn were extracted using the following procedures:

a) Method-1 [DTPA-TEA solution (2:1)]: Ten cm^{3} of air dried soil + 20 mL of extracting solution were shaken during 2 h. Soil extracts (2:1 extractant/soil ratio) were obtained with DTPA-TEA (0.005 mol L^{-1} diethylenetriaminepentaacetic acid + 0.1 mol L^{-1} triethanolamine + 0.01 mol L^{-1} CaCl_{2}) solution at pH 7.3 as described by Lindsay & Norvell (1978). This is the method used by some Brazilian laboratories, adopting the "IAC System of Soil Analysis" (Abreu et al., 1998). The experimental area area has been fertilized with N, P, and K, without addition of cationic micronutrients. Soybean [Glycine max (L.) Merr.] or corn (Zea mays L.) in the spring-summer season, and wheat or triticale (× Triticosecale) or black oat (Avena strigosa Schreb.) in the autumn-winter season has been cultivated. More details about the historic of cropping and fertilization and the effects of surface application of lime in the soil-plant system was reported elsewhere (Caires et al. 2005).

b) Method-2 [DTPA-TEA solution (5:1)]: Ten cm^{3} of air dried soil + 50 mL of extracting solution were shaken for 2 h. Soil extracts (5:1 extractant/soil ratio, ac-
c) Method-3 [Mehlich-1 solution (5:1)]: Five cm³ of air dried soil + 25 mL of extracting solution were shaken for 5 min. Soil extracts (5:1 extractant/soil ratio) were obtained with Mehlich-1 \( (0.05 \text{ mol L}^{-1} \text{ hydrochloric acid (HCl)} + 0.0125 \text{ mol L}^{-1} \text{ sulfuric acid (H}_2\text{SO}_4)) \) solution. This procedure is widely used by many laboratories in Brazil for determination of micronutrients (Bernardi et al., 2002).

d) Method-4 [Mehlich-1 solution (10:1)]: Two and one-half cm³ of air dried soil + 25 mL of extracting solution were shaken for 5 min. Soil extracts (10:1 extractant/soil ratio) were obtained with Mehlich-1 solution. This procedure is widely used by many laboratories in Brazil as a multinutrient extractant (Abreu et al., 1998).

e) Method-5 [HCl solution (5:1)]: Five cm³ of air dried soil + 25 mL of extracting solution were shaken for 30 min. Soil extracts (5:1 extractant/soil ratio) were obtained with 0.1 mol L⁻¹ HCl solution as described by Osiname et al. (1973).

f) Method-6 [HCl solution (10:1)]: Two and one-half cm³ of air dried soil + 25 mL of extracting solution were shaken for 30 min. Soil extracts (10:1 extractant/soil ratio) were obtained with 0.1 mol L⁻¹ HCl solution as described by Osiname et al. (1973).

g) Method-7 [Mehlich-3 solution]: Two and one-half cm³ of air dried soil + 25 mL of extracting solution were shaken for 5 min. Soil extracts (10:1 extractant/soil ratio) were obtained with Mehlich-3 \( (0.2 \text{ mol L}^{-1} \text{ acetic acid (CH}_3\text{COOH)} + 0.25 \text{ mol L}^{-1} \text{ NH}_4\text{NO}_3 + 0.015 \text{ mol L}^{-1} \text{ ammonium fluoride (NH}_4\text{F)} + 0.013 \text{ mol L}^{-1} \text{ nitric acid (HNO}_3) + 0.001 \text{ mol L}^{-1} \text{ ethylenediaminetetraacetic acid (EDTA)) \) solution at pH 2.5 as described by Mehlich (1984).

All soil extracting solution suspensions were shaken on a horizontal-circular shaking machine at 220 rpm. After this step, all suspensions were filtered through Whatman #42 filter paper and the concentration of micronutrients were measured using a PerkinElmer Optima 3000 XL simultaneous inductively coupled plasma optical emission spectrometry (ICP-OES), under routine operating conditions, at the 324.754 nm, 259.940 nm, 188.223 nm, 213.856 nm atomic lines for Cu, Fe, Mn, and Zn, respectively.

Soil and plant data were submitted to variance and regression analyses. Regression equations were adjusted to the obtained data according to lime rates (0, 2, 4, and 6 Mg ha⁻¹), adopting the magnitude of coefficients of determination \( (p < 0.05) \) as the criteria of choice. The effects of re-liming at 0 and 3 Mg ha⁻¹ were compared by the Tukey test \( (p = 0.05) \). When a no significant interaction of the liming versus the re-liming treatment was observed, the effects of treatments were compared by using their means. Simple linear correlation analyses (Pearson correlation, \( p < 0.05 \)) were obtained for soil pH and cationic micronutrients extracted by different procedures. All statistical analyses were performed using the SAS program, version 8.02 (SAS Institute, 1999).

**Results and Discussion**

**Soil organic carbon and soil reaction**

No interactions were observed between the surface liming rates (0, 2, 4, and 6 Mg ha⁻¹) and surface re-liming (0 and 3 Mg ha⁻¹) for SOC and soil pH. Surface liming and re-liming did not cause changes in the SOC concentrations. The mean concentrations of SOC at 0-5, 5-10 and 10-20 cm layers were 25.1, 19.2 and 17.7 g dm⁻³, respectively. Caires et al. (2006a) reported similar results for other Oxisol (clayey, kaolinitic, thermic Rhodic Hapludox) under a NT system.

Soil pH \( (\bar{p}) \) increased linearly with increasing surface liming rate \( (x, \text{ in Mg ha}^{-1}) \) in the following layers: 0-5 cm \( (\bar{p} = 4.85 + 0.14x, R^2 = 0.98) \), 5-10 cm \( (\bar{p} = 4.31 + 0.13x, R^2 = 0.99) \) and 10-20 cm \( (\bar{p} = 4.32 + 0.07x, R^2 = 0.97) \). Surface re-liming increased significantly soil pH from 4.9 to 5.7, 4.6 to 4.8, and 4.5 to 4.6 at the 0-5, 5-10 and 10-20 cm layers, respectively. More details about the effects of surface liming on the soil chemical attributes are related elsewhere (Caires et al., 2006b).

The availability of micronutrients to the crops is controlled by many soil factors such as pH, soil organic matter, temperature, and moisture (Fageria et al., 2002). In this study, because the wheat crop presented adequate growth and yield (Caires et al., 2006b) and SOC concentrations were unchanged due to liming treatments, soil pH was assumed to be the major factor on determining the bioavailability of Cu, Fe, Mn, and Zn.

**Extractable cationic micronutrients**

Soil extractable Cu, for all extraction methods, was not influenced by the interaction between lime rates (0, 2, 4, and 6 Mg ha⁻¹) and re-liming (0 and 3 Mg ha⁻¹). Copper concentrations decreased linearly with increasing lime application rates for DTPA-TEA solution (5:1), Mehlich-1 solution (5:1 and 10:1) and HCl solution (5:1 and 10:1) at 0-5 cm layer; and also by 0.1 mol L⁻¹ HCl solution (5:1) at 5-10 cm layer (Figure 1). Negative correlations were observed between concentrations of extractable Cu and soil pH, mainly, at 0-5 cm layer (Table 1). Solubility of Cu is soil pH dependent and decreases 100-fold for each unit increase in pH (Fageria et al., 2002). Moreover, these authors also state that increases in soil pH above 6.0 induces hydrolysis of hydrated Cu which can lead to a stronger Cu adsorption by the clay minerals and organic matter.

Unusual effects were also observed and associated with lime; e.g. quadratic increase of the Cu concentrations extracted by DTPA-TEA solution (5:1) at 0-5 cm layer; by DTPA-TEA solution (2:1 and 5:1), Mehlich-1 solution (5:1 and 10:1) and Mehlich-3 solution at 5-10 cm layer; and, by 0.1 mol L⁻¹ HCl solution (10:1) at 10-20 cm layer (Figure 1). A possible explanation for these ef-
effects is that an increase in soil pH as a consequence of liming can have enhanced microbial activity, increasing dissolved organic matter (Filep et al., 2003) and, consequently, improving solubility of Cu bounded to the low molecular-weight organic compounds.

Soil extractable Fe by DTPA-TEA solution at pH 7.3 (2:1 extractant/soil ratio), (2)Method-2: extraction by DTPA-TEA solution at pH 7.3 (5:1 extractant/soil ratio), (3)Method-3: extraction by Mehlich-1 solution (5:1 extractant/soil ratio), (4)Method-4: extraction by Mehlich-1 solution (10:1 extractant/soil ratio), (5)Method-5: extraction by 0.1 mol L–1 HCl solution (5:1 extractant/soil ratio), (6)Method-6: extraction by 0.1 mol L–1 HCl solution (10:1 extractant/soil ratio), (7)Method-7: extraction by Mehlich-3 solution (10:1 extractant/soil ratio). NS: not significant, *p < 0.05, and **p < 0.01.

<table>
<thead>
<tr>
<th>Method</th>
<th>Copper (Cu)</th>
<th>Iron (Fe)</th>
<th>Manganese (Mn)</th>
<th>Zinc (Zn)</th>
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<td>-0.91**</td>
<td>-0.35NS</td>
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<td>0.24NS</td>
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<td>-0.85**</td>
<td>-0.29NS</td>
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</tr>
<tr>
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<td>-0.89**</td>
<td>0.04NS</td>
<td>0.27SN</td>
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<td>0.85**</td>
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<td>0.21NS</td>
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<td>-0.83**</td>
<td>0.30NS</td>
<td>0.28NS</td>
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<td>-0.41*</td>
<td>0.52**</td>
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(1)Method-1: extraction by DTPA-TEA solution at pH 7.3 (2:1 extractant/soil ratio). (2)Method-2: extraction by DTPA-TEA solution at pH 7.3 (5:1 extractant/soil ratio). (3)Method-3: extraction by Mehlich-1 solution (5:1 extractant/soil ratio). (4)Method-4: extraction by Mehlich-1 solution (10:1 extractant/soil ratio). (5)Method-5: extraction by 0.1 mol L–1 HCl solution (5:1 extractant/soil ratio). (6)Method-6: extraction by 0.1 mol L–1 HCl solution (10:1 extractant/soil ratio). (7)Method-7: extraction by Mehlich-3 solution (10:1 extractant/soil ratio). NS: not significant, *p < 0.05, and **p < 0.01.
ods, no reductions in extractable Mn at the soil surface layer (0-5 cm) were detected from surface application of lime. However, increasing surface lime rate decreased linearly Mn concentration extracted by DTPA-TEA solution (5:1) at 5-10 cm layer, and by DTPA-TEA solution (2:1 and 5:1), 0.1 mol L\(^{-1}\) HCl solution (5:1 and 10:1) and Mehlich-3 solution at 10-20 cm layer. In these cases, negative correlations were generally observed between concentrations of extractable Mn and soil pH, mainly, below the 5 cm depth (Table 1). According to Fageria et al. (2002), the main ionic Mn species in a soil solution is Mn\(^{2+}\), and its concentrations decrease 100-fold for each unit increase in soil pH.

The various soil extractable Zn concentrations (Method-1 to Method-7) were not influenced by the interaction between lime rates (0, 2, 4, and 6 Mg ha\(^{-1}\)) and re-liming (0 and 3 Mg ha\(^{-1}\)) (Figure 4). Increasing surface lime rate increased linearly Zn concentrations extracted by DTPA-TEA solution (5:1) at 5-10 cm layer. This can be interpreted as a direct effect of the high chelation capacity as proportioned by 5:1 solution/soil ratio used in Method-2. Norvell (1984) proposed to use a greater solution/soil ratio to compensate the limitations of extractants, mainly of their chelation capacity in soil at low pH. For the other depths and procedures, changes on extractable Zn concentrations after liming treatments were not observed. Acid extractants have normally not been efficient to detect slight changes in extractable Zn as a consequence of liming, becoming a hard task to select an adequate extractant for this micronutrient (Abreu et al., 2007).

Figure 1 - Soil copper (Cu) concentrations extracted by different procedures as affected by surface-applied lime rates, without (●) and with (○) surface re-liming at the rate of 3 Mg ha\(^{-1}\). *\(p < 0.05\) and **\(p < 0.01\).

- **Method-1:** extraction by DTPA-TEA solution at pH 7.3 (2:1 extractant/soil ratio)
  - \(y = 0.289 + 0.068x - 0.011x^2\) \(R^2 = 0.99^*\)
  - \(y = 0.914 - 0.042x\) \(R^2 = 0.64^{**}\)
- **Method-2:** extraction by DTPA-TEA solution at pH 7.3 (5:1 extractant/soil ratio)
  - \(y = 1.403 - 0.039x\) \(R^2 = 0.73^*\)
  - \(y = 1.515 + 0.221x - 0.040x^2\) \(R^2 = 0.96^{**}\)
- **Method-3:** extraction by Mehlich-1 solution (5:1 extractant/soil ratio)
  - \(y = 0.914 - 0.042x\) \(R^2 = 0.64^{**}\)
  - \(y = 1.214 + 0.113x - 0.022x^2\) \(R^2 = 0.83^{**}\)
- **Method-4:** extraction by Mehlich-1 solution (10:1 extractant/soil ratio)
  - \(y = 0.865 - 0.039x\) \(R^2 = 0.91^{**}\)
  - \(y = 1.088 + 0.122x - 0.022x^2\) \(R^2 = 0.84^{**}\)
- **Method-5:** extraction by 0.1 mol L\(^{-1}\) HCl solution (5:1 extractant/soil ratio)
  - \(y = 0.312 - 0.036x\) \(R^2 = 0.82^{**}\)
  - \(y = 0.657 - 0.038x\) \(R^2 = 0.81^{**}\)
- **Method-6:** extraction by 0.1 mol L\(^{-1}\) HCl solution (10:1 extractant/soil ratio)
  - \(y = 0.688 - 0.043x\) \(R^2 = 0.87^{**}\)
  - \(y = 1.001\)
- **Method-7:** extraction by Mehlich-3 solution (10:1 extractant/soil ratio)
  - \(y = 1.380 + 0.189x - 0.030x^2\) \(R^2 = 0.75^{**}\)
  - \(y = 2.047\)
The mean capacity of the evaluated solutions to extract soil Cu followed this order at 0-5 cm layer (Table 2): Mehlich-3 solution > DTPA-TEA solution (5:1) > Mehlich-1 solution (5:1) > 0.1 mol L⁻¹ HCl solution (10:1) > DTPA-TEA solution (2:1) > 0.1 mol L⁻¹ HCl solution (5:1). At 5-10 and 10-20 cm layers this order was similar; only the 0.1 mol L⁻¹ HCl solution (5:1) extracted more Cu than the DTPA-TEA solution (2:1). The Mehlich-3 solution demonstrated a greater capacity of extraction in comparison to the other extractants, which is in agreement with Abreu et al. (1996). Because of the acid reagents and chelates, such as EDTA, it is expected higher amounts of micronutrients when they are extracted by the Mehlich-3 solution than by the DTPA-TEA (Vidal-Vázquez et al., 2005) and by diluted acids (e.g. Mehlich-1 and HCl) (Abreu et al., 2002). Diluted acid solutions may only partially solubilize soil’s Cu, while chelating agents such as DTPA or EDTA reduce the Cu activity in solution by complexation, causing the dissolution of the labile forms of Cu in soils (Abreu et al., 1998). Also, a greater solution/soil ratio induces an increase in extraction capacity, except for Mehlich-1 solution (Table 2).

Soil Fe concentrations occurred in the following order at 0-5 and 5-10 cm layers, considering the extraction mean capacity of various solutions (Table 2): Mehlich-3 solution > Mehlich-1 solution (10:1) > DTPA-TEA solution (5:1) > Mehlich-1 solution (5:1) > DTPA-TEA solution (2:1) > 0.1 mol L⁻¹ HCl solution (10:1) > 0.1 mol L⁻¹ HCl solution (5:1). At the layer of 10-20 cm this order occurred in the following order: Mehlich-3 solution > Mehlich-1 solution (10:1) > DTPA-TEA solution (5:1) > Mehlich-1 solution (5:1) > DTPA-TEA solution (2:1) > 0.1 mol L⁻¹ HCl solution (10:1) > 0.1 mol L⁻¹ HCl solution (5:1).

Figure 2 - Soil iron (Fe) concentrations extracted by different procedures as affected by surface-applied lime rates, without (●) and with (○) surface re-liming at the rate of 3 Mg ha⁻¹. *p < 0.05 and **p < 0.01.
was similar; only the 0.1 mol L\(^{-1}\) HCl solution (10:1) extracted slightly more Fe than the DTPA-TEA solution (2:1). Abreu et al. (2004) verified that extracting the Fe followed this order: Mehlich-3 > Mehlich-1 (5:1 extractant/soil ratio) > DTPA-TEA (2:1 extractant/soil ratio). Similar results were also observed by Rodrigues et al. (2001).

The order of the Mn extraction, according to the mean capacity of the various solutions and to the 0-5, 5-10, and 10-20 cm layers was the following (Table 2): Mehlich-1 solution (10:1) > Mehlich-1 solution (5:1) > 0.1 mol L\(^{-1}\) HCl solution (10:1) ≅ Mehlich-3 solution ≅ 0.1 mol L\(^{-1}\) HCl solution (5:1) ≅ DTPA-TEA solution (2:1). Abreu et al. (2004) also observed that Mehlich-1 (5:1 extractant/soil ratio) solution extracted more Mn than Mehlich-3 solution. On the other hand, Rodrigues et al. (2001) found that the Mehlich-3 solution have a higher Mn extraction capacity than the DTPA-TEA (2:1 extractant/soil ratio) solution and Mehlich-1 (5:1 extractant/soil ratio) solution.

The mean capacity of the evaluated solutions when extracting the Zn from the soil followed this order at 0-5 cm layer: DTPA-TEA solution (5:1) ≅ Mehlich-1 solution (5:1) > Mehlich-3 solution (10:1) > 0.1 mol L\(^{-1}\) HCl solution (5:1) > 0.1 mol L\(^{-1}\) HCl solution (10:1) > DTPA-TEA solution (2:1). At the layer of 5-10 cm this order was: DTPA-TEA solution (5:1) ≅ Mehlich-1 solution (5:1) > Mehlich-3 solution (5:1) > 0.1 mol L\(^{-1}\) HCl solution (5:1) ≅ Mehlich-1 solution (10:1) ≅ Mehlich-3 solution ≅ 0.1 mol L\(^{-1}\) HCl solution (10:1) > DTPA-TEA solution (2:1). At the layer of 10-20 cm this order was: Mehlich-1 solution (5:1) > Mehlich-3 solution (5:1) > Mehlich-3 solution (10:1) > 0.1 mol L\(^{-1}\) HCl solution (5:1) > DTPA-TEA solution (5:1) > DTPA-TEA solution (2:1). The order of the Mn extraction, according to the mean capacity of the various solutions and to the 0-5, 5-10, and 10-20 cm layers was the following (Table 2): Mehlich-1 solution (10:1) > Mehlich-1 solution (5:1) > 0.1 mol L\(^{-1}\) HCl solution (10:1) ≅ Mehlich-3 solution ≅ 0.1 mol L\(^{-1}\) HCl solution (5:1) ≅ DTPA-TEA solution (2:1). Abreu et al. (2004) also observed that Mehlich-1 (5:1 extractant/soil ratio) solution extracted more Mn than Mehlich-3 solution. On the other hand, Rodrigues et al. (2001) found that the Mehlich-3 solution have a higher Mn extraction capacity than the DTPA-TEA (2:1 extractant/soil ratio) solution and Mehlich-1 (5:1 extractant/soil ratio) solution.
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Wang et al. (2004) also observed that Mehlich-3 solution extracted more Zn than DTPA-TEA (2:1 solution/soil ratio). Abreu et al. (2002) also verified that extracting the Zn followed this order: Mehlich-1 (5:1 extractant/soil ratio) > Mehlich-3 > DTPA-TEA (2:1 extractant/soil ratio). Diluted strong acids (as with Mehlich-1 and Mehlich-3 solutions) apparently dissolved partially the Zn contained in the soil solid phase (Abreu et al., 2002). Moreover, HCl solution may preferentially remove Zn from mineral surfaces while EDTA and DTPA may remove Zn preferentially from the soil organic matter (Haynes, 1997).

Figure 4 - Soil zinc (Zn) concentrations extracted by different procedures as affected by surface-applied lime rates, without (●) and with (○) surface re-liming at the rate of 3 Mg ha⁻¹. *p < 0.05.

Micronutrients in the wheat leaves

The 1993 liming and the 2000 re-liming treatments did not affect the Cu, Fe and Zn concentrations in the wheat leaves in 2003 (Figure 5). However, Mn concentration in the leaves was influenced by the interaction between lime rates (0, 2, 4, and 6 Mg ha⁻¹) and re-liming (0 and 3 Mg ha⁻¹). Increasing the surface liming rate decreased linearly Mn concentration in the wheat leaves both in the plots with or without re-liming. Surface re-liming caused a decrease in Mn concentration in the wheat leaves, mainly in the plots not limed in 1993. However, these observed Mn concentrations were adequate for wheat, according to Malavolta et al. (1997).

Surface liming application under NT systems has been shown to decrease the plant’s Mn uptake (Caires
Figure 5 - Copper (Cu), iron (Fe), manganese (Mn), and zinc (Zn) concentrations in wheat leaves as affected by surface-applied lime rates, without (●) and with (Ο) surface re-liming at the rate of 3 Mg ha⁻¹. **p < 0.01.

Table 2 - Minimal (Min), maximum (Max) and mean of cationic micronutrients concentrations in soil considering all treatments, in different layers, after liming and re-liming according to extraction methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>Copper (Cu)</th>
<th>Iron (Fe)</th>
<th>Manganese (Mn)</th>
<th>Zinc (Zn)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min (mg dm⁻³)</td>
<td>Max (mg dm⁻³)</td>
<td>Mean (mg dm⁻³)</td>
<td>Min (mg dm⁻³)</td>
</tr>
<tr>
<td>0-5 cm layer</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Method-1</td>
<td>0.20</td>
<td>0.38</td>
<td>0.28</td>
<td>6.11</td>
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<tr>
<td>Method-2</td>
<td>1.02</td>
<td>1.67</td>
<td>1.29</td>
<td>26.86</td>
</tr>
<tr>
<td>Method-3</td>
<td>0.49</td>
<td>1.11</td>
<td>0.79</td>
<td>13.38</td>
</tr>
<tr>
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<td>1.13</td>
<td>0.75</td>
<td>43.66</td>
</tr>
<tr>
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<td>0.66</td>
<td>0.20</td>
<td>0.55</td>
</tr>
<tr>
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<td>0.89</td>
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<td>1.73</td>
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<tr>
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<td>2.74</td>
<td>1.90</td>
<td>88.74</td>
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<tr>
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<tr>
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<td>1.24</td>
<td>32.33</td>
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<td>0.77</td>
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<td>1.61</td>
<td>2.48</td>
<td>2.05</td>
<td>101.03</td>
</tr>
</tbody>
</table>

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& Da Fonseca, 2000; Godsey et al., 2007; Caires et al., 2008). This may be due to a decrease its concentration due to a decrease on the bioavailable form in the soil solution due to a soil pH increase. In all studied methods, no decreases were detected in extractable Mn at the 0-5 cm soil layer due to an increase in soil pH as a consequence of a surface liming (Figure 3). Increasing surface lime rate only decreased Mn concentration extracted by DTPA-TEA solution (5:1) at 5-10 cm layer, and by DTPA-TEA solution (2:1 and 5:1). 0.1 mol L⁻¹ HCl solution (5:1 and 10:1) and Mehlich-3 solution at 10-20 cm layer. So, the solutions of DTPA-TEA, Mehlich-1, Mehlich-3, and HCl were ineffective to detect important decreases in soil Mn availability pursuant to the surface-applied lime.

Changes in cationic micronutrients availability at the soil most superficial layers after liming affect the mineral nutrition of plants, mainly under NT systems (Caires & Da Fonseca, 2000; Godsey et al., 2007; Caires et al., 2008). However, the cationic micronutrients concentrations extracted by the DTPA-TEA, Mehlich-1, Mehlich-3, and HCl solutions after the surface lime application under a NT system cannot represent the available amount to the crops. Our study highlight the difficulty of selecting a procedure for the extraction of these micronutrients that would be more appropriated to predict their cationic micronutrients bioavailability. This is in agreement with the results obtained in other studies in Brazilian soils (Vidal-Vázquez et al., 2005; Nascimento et al., 2006; Abreu et al., 2007).

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References


