

Organic Acid Effect on Calcium Uptake by the Wheat Roots

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ABSTRACT

This work evaluated the effect of the natural organic acids on the uptake of Ca by the wheat roots in a hydroponic solution. The following organic acids were evaluated: citric, oxalic, tartaric, malic, malonic, maleic, DL-malic, p-hydroxybenzoic, aconitic, and salicylic. The organic acids neither enhanced the root growth nor increased Ca uptake. The salicylic and malic acids were highly toxic and decreased the root growth. The citric, tartaric, maleic, aconitic, and salicylic decreased the Ca uptake by the roots due to their higher capacity to form the stable complexes with Ca in solution at pH 6.0. Decreasing the Ca valence from Ca^{++} to CaL^+ or CaL_2^0 through the organic ligand complexation reactions decreased the Ca uptake. The results suggested that the wheat roots do not absorb Ca-organic complexes.

Key words: Nutrient uptake, metal-organic complex, organic ligand, organic molecule

INTRODUCTION

Considerable attention has been dedicated on calcium (Ca) research in acid soils due to its relation with the crop productivity (Malavolta et al., 1979), root growth and water stress (Ritchey et al., 1980), fruit quality (Shear, 1975; Pavan et al., 1987; Fidalski et al., 1999), and plant vascular diseases (Cardoso et al., 1985). The Ca deficiency in the acid soil can be corrected with the lime application. The major limitation of the lime is its low efficiency to neutralize the subsoil acidity and to introduce the Ca deep in the soil profile. Consequently, strategies must be developed to move the alkalinity from the topsoil lime into the subsoil profile. Recent findings have reported that the plant residues left as mulch on the soil surface release a large number of organic compounds with low molecular weight, such as citric, acetic, oxalic, succinic, etc. Although these organic acids are considered to be short-lived in the soils, their

continual production under the conservation agricultural systems makes their anions important in the acid soil chemistry and Ca transport into the soil profile (Ziglio et al., 1999; Franchini et al., 2001a; Miyazawa et al., 2002). These authors showed that due to the presence of the atomic groups in the organic molecules that posse the acidic properties, such as $-COOH$, $-OH$, $=NOH$, $=NH$, $-NH_2$, SO_3H , etc., the H^+ atoms may under certain circumstances (pH, ionic strength, oxy-reduction potential, etc.) be displaced by the Ca^{++} ions, which forms strong binding with the uncharged organic ligand (CaL_2^0) or mono positively charged (CaL^+) (where L = organic ligand). Franchini et al. (2001a) showed that the Ca organic ligand complexes are mobile in the soil profile. Chaves et al. (1991) reported that the presence of ion pair between the Ca and inorganic anions, such as $CaSO_4^0$, $CaNO_3^+$, and $CaCl^+$, decreased the uptake of the Ca by coffee roots. They also found that the coffee roots absorbed preferentially free Ca^{++} ions in solution. Thus, the question is: although the ion pair of Ca^{++} with the

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organic anions is possible to form in the soil can the roots absorb it? Thus, the objective was to evaluate the effect of the natural organic acids on Ca uptake by the wheat roots.

MATERIALS AND METHODS

Organic acid stock solutions

Solution concentrations of $1.25 \times 10^{-1} \text{ mol L}^{-1}$ were prepared for the following organic acids: citric ($\text{C}_6\text{H}_5\text{O}_7$), oxalic ($\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), tartaric ($\text{C}_4\text{H}_6\text{O}_6$), malic ($\text{C}_4\text{H}_6\text{O}_5$), malonic ($\text{C}_3\text{H}_4\text{O}_4$), maleic ($\text{C}_4\text{H}_2\text{O}_4\text{Na}_2$), DL= malic ($\text{C}_4\text{H}_6\text{O}_5$), salicylic ($\text{C}_7\text{H}_6\text{O}_3$), p-hydroxybenzoic ($\text{C}_7\text{H}_6\text{O}_3$), and aconitic ($\text{C}_6\text{H}_6\text{O}_6$).

Organic acid work solutions

Volumes of 0.0, 0.5, 1.0, 1.5, and $2.0 \times 10^{-4} \text{ mol L}^{-1}$ of each organic acid stock solution were transferred to a 250 ml plastic beaker containing a diluted nutrient solution. The pH was adjusted to 6.0 with $0.01 \text{ mol L}^{-1} \text{ HCl}$ or $0.01 \text{ mol L}^{-1} \text{ NaOH}$. The solutions were sterilized in autoclave.

Nutrient solutions

The following salt concentrations were prepared for the nutrient solutions: $1.0 \times 10^{-4} \text{ mol L}^{-1} \text{ KH}_2\text{PO}_4$, $5.0 \times 10^{-4} \text{ mol L}^{-1} \text{ KNO}_3$, $2.0 \times 10^{-4} \text{ mol L}^{-1} \text{ MgSO}_4$, and $5.0 \times 10^{-4} \text{ mol L}^{-1} \text{ Ca}(\text{NO}_3)_2$.

Experimental procedures

A nylon screen was placed on the top of each beaker just in contact with the nutrient solution. Three pre-germinated wheat seedlings (*Triticum aestivum*, cultivar Anahuac) were placed on the nylon screen. Anahuac cultivar was used because of its high Ca requirement. During the experimental work, the solutions were kept aerated and the evaporated water was replaced daily. After five days from the beginning of the experiment, the wheat seedlings were collected and the root elongation was measured. Then, the plant materials were dried at 65°C for 48h, digested in $1 \text{ mol L}^{-1} \text{ HCl}$ solution and the Ca was determined by the Inductively Coupled Plasma (ICP). The eleven treatments were replicated four times in a completely randomized block design. All the Ca determinations were made in duplicate.

RESULTS AND DISCUSSION

Table 1 shows the effect of the organic acids on the means of the root length with the respective standard error. All the organic acids did not enhance the root growth. Increasing the concentrations of the salicylic and malic acids decreased drastically the root elongation in the solution. The toxic effect of the salicylic acid on the root growth was also reported by Hue et al. (1986). They also found that the salicylic acid was not able to alleviate the Al toxicity in the acid subsoil. Fig. 1 illustrates the effect of the organic acids on Ca uptake by the wheat roots. Ca uptake was not increased by the organic acids. The citric, tartaric, maleic, aconitic, and salicylic acids decreased the Ca uptake. The organic acids have the capacity to complex the metal ions in the solution which degree depends on the particular organic acid, the concentration and the type of metal, and pH (Jones, 1998). The solution pH was adjusted to 6.0 in order to increase both the Ca^{++} activity and the dissociation of the organic acids (Halvorson & Lindsay, 1972; Lide, 1991-1992; Parker et al., 1995). Thus, it was expected that at pH 6.0 the Ca^{++} ions can not replace H^+ in the acid groups to form coordinated bonds with the organic molecules. The decrease in the Ca uptake in the presence of the citric, tartaric, maleic, aconitic, and salicylic acids was probably due to the higher stability constant values of their anions with the Ca ions (Martell & Smith, 1976-1989; Lide, 1991-1992). It is well known that the efficiency of the organic compounds to form the complexes with the metals depends on the stability constant of the ligand (Halvorson & Lindsay, 1972). Thus, as expected, the citrate was the most effective in decreasing the Ca uptake by the wheat roots due to its higher affinity for Ca^{++} at pH 6.0. However, the efficiency for the organic metal complexation depends on pH. For example, Parker et al. (1995) using a speciation program GEOCHEM-PC, estimated that the Ca-citrate complex was higher at pH near the neutrality and decreased as the solution acidification increased. It was also unlikely that the organic acids formed precipitated in the presence of Ca at pH 6.0.

Decreasing Ca valence in the solution by the organic ligand complexation might influence the Ca uptake by the wheat roots. The effect of the ion

valence on the Ca uptake has been demonstrated for coffee roots in an inorganic system by Chaves et al. (1991) who reported that decreasing the valence from Ca^{++} to CaNO_3^+ , CaCl^+ , and CaSO_4^0 decreased the Ca uptake by the coffee roots. For the organic system used in the present study, the Ca uptake was also affected by varying the Ca

valence in the solution. The Ca uptake decreased with decreasing the valence from Ca^{++} (control) to CaL^+ or CaL_2^0 (where L = organic ligand) in the presence of thecitric, tartaric, and salicilic acids. The importance of the valence ion on absorption by roots was suggested by Dekock & Mitchell (1957).

Table 1 - Effect of organic acids on wheat root growth.

Organic acids	Concentration $\times 10^{-4}$ mol L ⁻¹				
	0.0	0.5	1.0	1.5	2.0
Citric	7.8 ± 2.7	8.3 ± 0.9	8.2 ± 2.4	8.9 ± 1.7	8.7 ± 1.7
Oxalic	10.5 ± 1.3	10.4 ± 2.4	10.9 ± 1.6	10.3 ± 0.6	10.4 ± 0.7
Tartaric	10.7 ± 1.0	10.5 ± 0.3	10.5 ± 2.6	10.0 ± 1.3	9.8 ± 1.9
Malic	8.9 ± 1.9	8.9 ± 2.1	10.1 ± 0.8	9.5 ± 1.8	9.5 ± 2.8
Malonic	10.1 ± 0.9	10.7 ± 0.9	10.6 ± 0.8	10.5 ± 1.3	10.5 ± 1.2
Maleic	10.6 ± 1.5	8.6 ± 1.2	7.8 ± 1.5	7.4 ± 0.8	6.6 ± 1.0
DL-Malic	9.8 ± 0.9	10.2 ± 1.7	9.9 ± 1.5	10.0 ± 1.2	9.8 ± 1.2
p-hydroxyb.	10.9 ± 2.6	10.8 ± 2.5	11.1 ± 1.6	11.0 ± 1.4	10.8 ± 0.7
Aconitic	10.8 ± 1.1	10.9 ± 1.8	11.0 ± 1.8	11.0 ± 2.1	11.1 ± 1.7
Salicilic	10.0 ± 1.2	3.0 ± 0.5	2.8 ± 0.6	2.6 ± 0.3	2.5 ± 0.3

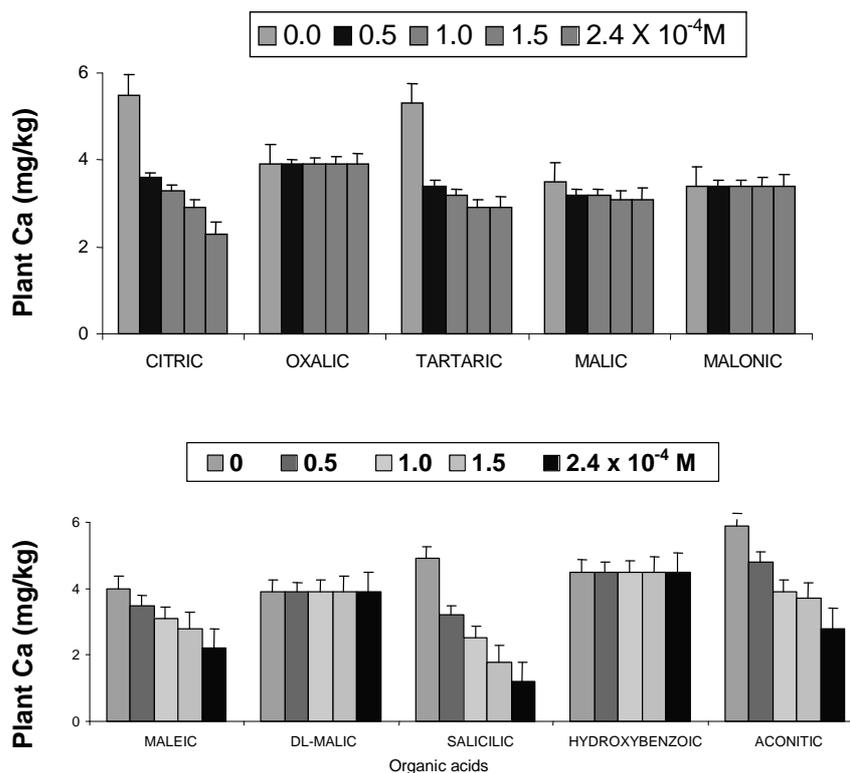


Figure 1 - Effect of organic acids on Ca uptake by wheat roots. Means of four replicates; vertical lines indicate mean standard error.

Franchini et al. (2001a) reported that the organic compounds released by the plant residues are of short chain and form complexes with the Ca, increasing the Ca transport into the subsoil profile. Although the complex reaction enhances the Ca transport in the soil as demonstrated by Franchini et al. (2001a), it is unlikely that the roots absorb the Ca-organic complex. However, Franchini et al. (2001b) showed that the plant residues increased not only the Ca transport into the soil profile but also the root elongation and Ca uptake. It seemed that in Franchini's study the Ca organic complex was formed in the alkalized topsoil layers and then moved down into the subsoil profile. In the acid subsoil layers, the H^+ ion displaced the Ca^{++} from the organic complex increasing the concentration of the soluble free Ca^{++} in the solution and consequently enhanced the Ca^{++} uptake. The Ca^{++} uptake can not continue as long as the subsoil pH was acidic. As the alkalinity increases in the subsoil, the stability of the Ca-organic complex was increased and the Ca uptake by the roots should decrease.

RESUMO

Ácidos orgânicos possuem grupos funcionais com cargas negativas que complexam íons metálicos em solução. Este trabalho avaliou o efeito de ácidos orgânicos naturais na absorção de Ca pelas raízes de trigo. Foram avaliados os seguintes ácidos orgânicos: cítrico, oxálico, tartárico, málico, malônico, maleico, DL-málico, p-hidroxibenzoico, aconítico e salicílico. Os ácidos orgânicos não estimularam o crescimento das raízes e não aumentaram a absorção de Ca. Os ácidos salicílico e maleico diminuíram drasticamente o crescimento radicular. Os ácidos cítrico, tartárico, maleico, aconítico e salicílico diminuíram a absorção de Ca pelas raízes devido à maior capacidade de formar complexos estáveis com Ca em solução no pH 6,0. A redução da valência de Ca^{++} para CaL^+ e CaL_2^0 , através das reações de complexação, diminuiu a absorção de Ca pelas raízes. Os resultados sugerem que os complexos de Ca-orgânico não são absorvidos pelas raízes de trigo.

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