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Hero T Gollany

`hero.gollany@usda.gov`

USDA-ARS: USDA Agricultural Research Service <https://orcid.org/0000-0002-6095-3618>

Thomas E. Schumacher

Paul E. Fixen

Research Article

Keywords: Calcareous soils, CaCO₃, Fe, Mn, Zn, rhizotron

Posted Date: October 30th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-11228440/v1>

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**II. Micronutrients, pH, and Eh variations in the rhizosphere of two
maize genotypes**

H.T. Gollany¹, T.E. Schumacher²

¹USDA-ARS, Columbia Plateau Conservation Research Center, 48037 Tubbs Ranch
Road, Adams, OR 97810, USA. ORCHID 0000-0002-6095-3618.

²Department of Agronomy, Horticulture, and Plant Science, South Dakota State
University, Brookings, SD 57007, USA; ORCHID ID 0000-0002-7508-2804.

⁴Corresponding author* (hero.gollany@usda.gov; Telephone 541-215-5227).

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ABSTRACT

Soil-root interface (rhizosphere) is the unavoidable link in the transfer of nutrients from soil to plant. Field measurements of two maize genotypes (*Zea mays* L., cv. Pioneer-3732 and -3737) have shown differences in plant nutrient uptake which appeared to be accentuated in eroded calcareous soils. Rhizotron studies were conducted to: (1) determine the effect of soil CaCO_3 on plant micronutrients (Cu, Fe, Mn, and Zn) availability in the rhizosphere; and (2) characterize the rhizosphere properties of these two maize genotypes. Maize seedlings were transferred to rhizotrons containing the Ap horizon of clay loam soils with low (5 g kg^{-1}) or high (204 g kg^{-1}) levels of CaCO_3 . Rhizosphere pH, Eh, and CO_2 were monitored with pH-glass, platinum, and pCO_2 microelectrodes. At the six-leaf stage, the soil was thin-sectioned at 1-, 2-, and 3-mm distances from the root. The soluble soil ions and plant nutrient uptakes were determined. Higher Mn^{2+} and Fe^{2+} concentrations were found in the rhizosphere of P-3737 relative to P-3732. Higher Mn^{2+} , Cu^{2+} , and Zn^{2+} uptake for Pioneer-3737 were observed in the high CaCO_3 soil relative to Pioneer-3732. The plant shoot/root ratio was reduced by 21.4% for P-3732 while increased by 15.7% for P-3737 in the calcareous soil compared to those in the non-calcareous soil. The rhizosphere pH, Eh and pCO_2 differences correlated to nutrient uptake and were dependent on plant genotype in addition to bulk soil concentration. As rhizosphere physicochemical properties differ from bulk soil, bulk soil micronutrients values do not reliably indicate plant nutrient availability. 248 words

Key words: Calcareous soils, CaCO_3 , Fe, Mn, Zn, rhizotron

Abbreviations: P-3732, Pioneer-3732; P-3737, Pioneer-3737; p_e , denotes $-\log$ of the activity of electrons (e^-); $p_e + pH$, denotes the redox status of soil.

INTRODUCTION

Calcareous soils cover almost one-third of the world's surface area and are widely spread in arid, semi-arid, semi-humid, and humid regions (Bolan et al., 2023). On heavy glacial till soils, minerals of intermediate solubility such as calcium carbonate (CaCO_3) are commonly present in the rooting zone due to soil losses from erosion in these soils, resulting in reduced depth to pedogenic CaCO_3 and incorporation of calcareous materials in the topsoil (Halverson et al., 2025). In some soils the free CaCO_3 can form hard layers, known as 'caliche', that are impermeable to water infiltration and plant root penetration. Although calcareous soils may be dominated by CaCO_3 , they may also contain significant amounts of iron (Fe), aluminum (Al), and manganese (Mn). These can be complexed with soil organic matter (SOM) or as discrete and mixed minerals, coatings on clay, sand, and silt (Bolan et al., 2023). The bio-availabilities of many plant nutrients including major nutrients and trace elements are reduced in calcareous soils (McLaughlin et al., 1981; Kaiser, 2018; Bolan et al., 2023; Najafi-Ghiri et al., 2025).

The living plant is the driving force controlling nutrient mobility in the rhizosphere (Jungk and Claassen, 1986). The rhizosphere is the unavoidable link in the transfer of nutrients from soil to plant. Form modification of plant nutrients is likely to occur during the passage through this interface. The rhizosphere properties differ in many respects from those in the soil distanced away from the root (bulk soil). The plant root induces changes in the rhizosphere through (i) the consumption of O_2 and the subsequent release of CO_2 which may alter the redox potential (Eh) and the pH; (ii) the preferential uptake of specific cations and anions which may produce a depletion or accumulation of ions; (iii) the release of H^+ or HCO_3^- which changes pH; and (iv) the release of

phytosiderophores and exudates (organic solutes, mucilage, sloughed cells) which provides the energy for microbial activity and may mobilize mineral nutrients (Darrah, 1993; Jones and Darrah, 1994; Hinsinger, 2001; Marschner et al., 2006; Tang et al., 2004). Molina and coworkers (2001) estimated that 2.5 to 6 times the amount of C incorporated into root biomass was accounted for as rhizodeposition (e.g. mucilage, sloughed cells, and root exudates).

Several studies have confirmed the significance of the rhizosphere chemical composition in nutrient availability (Sarkar and Wyn Jones, 1982a; Jungk and Claassen, 1986; Gijsman, 1990). Linehan et al. (1985) reported substantial solubilization of Zn, Cu, and Mn during the early stages of barley rhizosphere development. Rhizosphere soil solution concentrations increased ten-fold for Mn and three-fold for Cu and Zn (Linehan et al., 1985). A study by Merckx and co-workers (1986) revealed that compared to the fallow soil, extracts from wheat and maize rhizospheres complexed 5- and 30- times more Mn, respectively, along with an 8-fold Zn increase for both crops. The authors concluded that the physicochemical status of transition metals in the rhizosphere is entirely different from that in the bulk soil. These differences depend on plant species, genotypes within species, soil properties, nutrient supply, and the nutritional status of the plant (Marschner and Römheld, 1983; Hoffland et al., 1989).

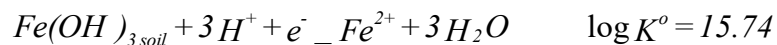
Landsberg (1981) showed that monocots (barley, oats, millet) did not acidify the nutrient solution under Fe stress when NO_3^- was the only form of N supply, while dicots (pea, sugar beet, beans) did acidify the nutrient solution. There was also a substantial increase in organic acids (citrate and malate) in the roots of dicots during the acidification. The author postulated that organic acids may be the source of the H^+ excreted by the root. The occurrence of iron chlorosis on calcareous soil also has been closely related to the form of nitrogen supply (Wallace, 1982). Brown and Olsen (1980) also found that monocots are generally less efficient in Fe uptake than dicots.

As early as 1956, Brown had shown that varieties of the same plant species differed in ability to utilize Fe from soils of low iron availability. Clark and Brown (1974) reported that two maize genotypes (WF9, YS₁/YS₁), with wide differences in Fe uptake and utilization, differed in their susceptibility to Fe deficiency. Iron-stressed WF9 produced higher amounts of H⁺ and "reductants" in nutrient solutions and reduced more Fe at the root surface than the YS₁/YS₁ cultivar (Clark and Brown, 1974). They concluded that Fe-efficiency in these two cultivars was controlled inside the root. A decade later, with the aid of antimony microelectrodes, Römheld and Marschner (1984) studied the pH changes in the rhizosphere of intact root systems of WF9 and YS₁/YS₁ and with two soybean cultivars (PI-54169 and Hawkeye). They found that the rhizosphere pH was higher in "Fe-inefficient" cultivars (YS₁/YS₁; PI-54169) compared to the "Fe-efficient" cultivars. The rhizosphere pH in the basal zones of YS₁/YS₁ and PI-54169 increased to 6.8 and 7.5 units, respectively, compared to the bulk soil (pH 6.0). The pH values for WF9 and Hawkeye were 5.6 and 6.8, respectively. The rhizosphere pH of the basal zones was always more than one pH unit higher than the apical zones within the same root system (Römheld and Marschner, 1984).

Camp et al. (1987) reported that Fe-efficient tomato (cv., T3238FER) and soybean (cv., A7) responded to Fe-stress by increasing reduction of Fe³⁺ to Fe²⁺ in the root, in addition to the excretion of H⁺ and reductants concurrently. Marschner and coworkers (Römheld and Marschner, 1984; Marschner et al., 1986) described two distinct strategies for Fe uptake in soils with limited Fe availability. Strategy I involves three steps of Fe stress response mechanisms: (i) increase in net H⁺ excretion (acidification) in the apical root zones of most plant species; (ii) release of reductants (phenolic compounds) which enhance the solubility of Fe (Olsen et al., 1981) or maintain a favorable environment for Fe²⁺ inside the root (Sijmons and Bienfait, 1983; 1984); and (iii) reduction of Fe³⁺ by the roots (Marschner et al., 1986; Camp et al., 1987). Tomato (cv., T3238FER) and soybean (CV., A7) responded to Fe deficiency by increasing

reduction of Fe^{3+} to Fe^{2+} by the roots (in addition to H^+ and reductants release) (Camp et al., 1987). Römheld and Marschner (1983) suggested that a plasmalemma bound enzyme to be the site of Fe^{3+} reduction. In laboratory and greenhouse studies, Fe-reduction and methanogenesis have been observed at higher rates in rhizosphere than bulk soils (Praeg et al., 2020; Veelen et al., 2020).

These three mechanisms work together to aid in the absorption and transport of Fe in the plant (Clark and Brown, 1974; Jolley and Brown, 1987). Iron-efficient genotypes release hydrogen (Marschner et al., 1986) into the rhizosphere which in turn affects the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio (Lindsay, 1979) as follows:



Strategy II is characterized by excretion of phytosiderophores - iron chelators (Römheld and Marschner, 1986). The chelated Fe^{3+} (Ferrated phytosiderophores) then pass through the plasmalemma directly.

Acidification due to organic acid excretion seems to be negligible, but such excretion may be most important for the heavy metal chelation and subsequent increase in micronutrient availability. The root responses to nutrient deficiency (Fe or P) enhance mobilization and uptake of other nutrients. This was demonstrated by Marschner et al., (1982). Enhanced MnO_2 reduction to Mn^{2+} was observed around the apical zones of Fe-deficient sunflower roots. Bromfield (1958a, 1958b) showed the dissolution of $\gamma\text{-MnO}_2$ by root washings of vetch and oats in both aseptic and unsterilized cultures. Godo and Reisenauer (1980) demonstrated that $\gamma\text{-MnO}_2$ was more soluble in the rhizosphere than in bulk soil. The authors attributed the increased manganese availability to pH, reducing effects and chelation. They collected root exudates from three-week-old wheat seedlings. After adding the exudate to $\gamma\text{-MnO}_2$, they demonstrated the dissolution of $\gamma\text{-MnO}_2$ over a period of 24 to 72 hours.

Some dissolution of MnO_2 has been shown to occur in a narrow zone (< 2 mm) around the root of lupin (Gardner et al., 1982). However, the zone of dissolution extended up to 3 cm around proetids and tap roots of lupin. The authors postulated that MnO_2 dissolution was caused by reduction of Mn^{4+} to Mn^{2+} in the rhizosphere. Warden (1991) showed higher 'readily soluble', 'weakly adsorbed' 'carbonate bound', and 'specifically adsorbed' Mn in the rhizosphere samples, but lower 'oxide-Mn' than in bulk soil.

Substantial mobilization of Mn, Zn, and Cu occurred in the rhizosphere of barley during the growing season (Linehan et al., 1985). The mobilization was attributed to the secretion and exudation of low molecular weight organic ligands. An accumulation of root-derived organic material from wheat and maize was reported within 4 weeks (Merckx et al., 1986b). Also, a parallel shift from ionic metal to higher molecular weight form was observed. Extracts from fallow soil as well as maize and wheat rhizosphere soil were analyzed for metal complexes. The results revealed that minor amounts of added tracers (1.9 and 0.2% of ^{65}Zn and ^{54}Mn , respectively) were complexed in the fallow soil extract. In comparison, the wheat rhizosphere extracts complexed 15% and 1% of Zn and Mn respectively, while the maize rhizosphere extracts complexed 16% and 6%, respectively (Merckx et al., 1986b). In pot experiments, Sarkar and Wyn Jones (1982) found significant decreases in rhizosphere pH of dwarf French beans with application of ammonium phosphates and an increase with calcium nitrate application. The shoot Fe, Mn, and Zn content were significantly correlated with the extractable rhizosphere Fe, Mn, and Zn and inversely proportional to rhizosphere pH (Sarkar and Wyn Jones, 1982).

Hydroponic experiments have been used for studying micronutrients in the rhizosphere. However, results from hydroponic studies cannot be extrapolated directly to soil (Wouterlood et al., 2004). Progress in this field is restricted by a lack of convenient methods to examine this opaque and structurally complex medium without disturbing the soil-root interface. There are no published studies of rhizosphere micronutrient availability for maize genotypes on undisturbed calcareous soil. We describe here a

nondestructive method which preserved the spatial arrangement of soil and rhizosphere and allowed simultaneous pH, and Eh measurements with high resolution and accuracy. The objectives of this study were to: (1) characterize the rhizosphere properties of these two maize genotypes, and (2) determine the effect of bulk soil CaCO_3 level on micronutrient availability in the rhizosphere and uptake.

MATERIALS AND METHODS

Rhizotron preparation

Rhizotrons (Fig. 1) were made of plexiglass-lined wooden boxes (45 x 13 x 2.5 cm) having a sliding door (45 x 13 cm) on one side. The soil used (Table 1) was the Ap horizon of a Beadle clay loam (fine, montmorillonitic, mesic Typic Argiustoll) with low (5 g kg^{-1}) and high (204 g kg^{-1}) levels of CaCO_3 (Gollany et al., 1992). The soils were thoroughly mixed with urea [$\text{CO}(\text{NH}_2)_2$] and DAP [$\text{Ca}_2(\text{NH}_4)_2(\text{HPO}_4)_3\text{H}_2\text{O}$] fertilizers. The fertilizer application rates were based on South Dakota State University soil-test recommendations for a yield goal of 10 Mg ha^{-1} (Gerwing et al., 1982). Urea was added at a rate of 0.246 and 0.258 g kg^{-1} to the low and high CaCO_3 soils, respectively. DAP was added at a rate of 0.046 and 0.220 g kg^{-1} to the low and high CaCO_3 soils, respectively. The rhizotrons were filled with the soil and fertilizer mixture at a soil density of 1.3 Mg m^{-3} .

Table 1. Selected soil properties of the soil used in the rhizotrons.

Soil	CaCO_3	Organic C	AWHC ^a	Clay	Silt	Sand	pH (1:1)	Bulk density
			g kg^{-1}					Mg m^{-3}
Low CaCO_3	5	30	187	303	533	164	7.0	1.17
High CaCO_3	204	13	132	316	621	63	7.6	1.42

^aAWHC = Available Water Holding Capacity

Plants and Growth Conditions

Seeds of selected genotypes of maize (*Zea mays* L., cv., Pioneer-3732 and Pioneer-3737)¹ were surface-sterilized in 10% NaOCl, sown on wet germination paper towels, and then wrapped and placed in a plastic bag allowing germinated seedlings to emerge in a moist environment. The bags containing the seeds were placed in plastic beakers in an incubator at 25°C and 8 hours light. Four days after germination, seedlings were transferred to a growth chamber (model CMP 3023, Controlled Environment Products of America, Pembina, ND)¹.



Fig.1. Corn grown in the rhizotrons positioned at a 45° angle on a stand and kept hydrated at the rhizotron capacity using trickle irrigation system.

¹ Mention of trade names or commercial products in this manuscript is solely for the purpose of providing specific information and does not imply recommendation or endorsement by USDA.

One maize seedling was planted per rhizotron. The rhizotrons were positioned at a 45° angle on a stand and kept moist at the rhizotron capacity ($\approx 90\%$ of field capacity) with a trickle irrigation system. Leachate was collected in Erlenmeyer flasks and was recycled every second day. The seedlings were kept on a day/night regime of 8/16 hours, 18-25°C, relative humidity 65 - 75 %, and light intensity of $460 \mu\text{mol m}^{-2} \text{s}^{-1}$. Two rhizotrons without plants were maintained at the same conditions to serve as controls. Experiments were carried out twice independently with two replicates. The two growth cycles produced similar results. The results presented are from the second growth cycle, because this data was the most complete.

A chamber was constructed from a wooden frame and covered with saran wrap. The sliding door of the rhizotron was removed carefully to expose the growing root at the soil interface for measurements.

Microelectrodes

Platinum microelectrodes were used to measure redox potential (Eh). The microelectrodes were prepared by fusing a 1-cm length of 24-gauge (0.5 mm) Pt wire (Aldrich Chemical Company, Inc., Milwaukee, WI)¹ to one end of a 2.5-cm length of 24 gauge (0.508 mm) solid copper wire at 1083°C. After cooling, each microelectrode was electrolytically cleaned in 0.1 N HCl solution and platinized (Willard et al., 1965). Microelectrodes were then standardized using a standard 0.1 M ferric-ferrous ammonium sulfate solution (Light, 1972). Electrodes that were not read within ± 10 mV at 25°C of the standard value were discarded. After standardization, a 2-cm piece of heat-sensitive teflon tubing (24 gauge) was slid over the Cu wire and worked down so that about 5 mm of the Pt wire was covered, to ensure that only the Pt wire encountered the soil. The tubing was heated gently until it shrank, leaving 5 mm of the Pt wire at one end and 5 mm of the Cu wire at the other end exposed. Epoxy glue was mixed and applied with a toothpick to the Cu end of the microelectrode. The Cu wire was then inserted into a

microelectrode holder (MEH3SFW, WPI)¹ which was attached directly to the pre-amplifier of the electrometer (FD-223, WPI)¹.

A chamber was constructed from a wooden frame and covered with saran wrap. The sliding door of the rhizotron was removed carefully to expose the growing root at the soil interface for measurements.

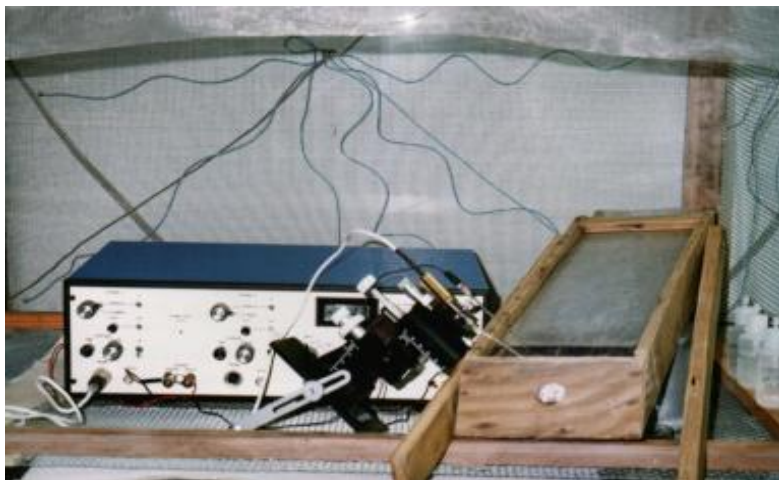


Fig. 2. Measurements of pH, Eh, and pCO₂ taken at 1-, 2-, and 3-mm distances from the maize root surface and 0.5 mm above root tips in a rhizotron. Microelectrodes were connected to input terminal of the electrometer (FD-223) and mounted on a micromanipulator in a Faraday cage.

Periodic pH monitoring was carried out with a pH-glass microelectrode and micro-manipulator (model M3301, WPI)¹. The pH-glass microelectrodes were fabricated as described by Conkling and Blanchar (1989). Rhizosphere Eh was monitored with a platinum microelectrode. All microelectrodes were standardized and rechecked before and after taking measurements on each plant. Buffer solutions of pH 4, 7, and 10 were used for pH calibration, while a ferric-ferrous sulfate ammonium sulfate solution was used for Eh microelectrode calibration. The Eh measured with microelectrode was then converted to pe as follows:

$$pe = \frac{Eh (mV)}{59.2}$$

Eh measurements with the platinum microelectrode were made with the soil atmosphere replaced by N₂ gas. The N₂ gas continuously flushed the system while the readings were taken.

Measurements of pH and Eh were taken at 1-, 2-, and 3-mm distances from the root surfaces. Measurements of pCO₂ were carried out first by piercing the saran wrap with the microelectrode mounted on a micromanipulator. All microelectrodes were standardized and rechecked before and after taking measurements on each plant. Buffer solutions of pH 4, 7, and 10 were used for pH calibration. Measurements of pH and Eh were taken at 1-, 2-, and 3-mm distances from the root surfaces.

Rhizosphere aqueous extraction and plant analysis

Roots and shoots were separated and rinsed with deionized water. After 24 hours drying in a forced-air oven at 67° C, the samples were weighed, and the shoot/root ratios were determined. Samples were prepared for cation and anion determination and analyzed by atomic absorption spectroscopy, flame emission spectroscopy, and colorimetric analysis. Total cation uptake was calculated as $\Sigma (\text{Ca}^{2+}, \text{Mg}^{2+}, \text{K}^{+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Mn}^{2+}, \text{Fe}^{2+}) \text{ g}^{-1} \text{ plant dry weight}$.

The rhizosphere soil was thin-sectioned at 1-, 2-, and 3-mm from the root axis immediately after removing them from the growth chamber at the six-leaf stage. Soil water was extracted at the rhizotron capacity by a fluorocarbon (FC70, 3M Company, St. Paul, MN)¹ as a modification of the immiscible displacement by centrifugation methods (Gollany et al., 1997). A sample of thin-sectioned moist rhizosphere soil (6 g) was placed in a centrifuge filter equipped with a one μm polytetrafluoroethylene (PIFE) membrane (Fisher Scientific)¹ and fitted on a collection tube. Two ml of FC70 was added to the moist soil and mixed with a small spatula. The filter units were tightly capped and placed in a 25 ml rubber centrifuge tube adapter. Samples were centrifuged at 14,500 g for one

hour. The displaced aqueous solution was acidified with 0.1 M HCl and analyzed by inductively coupled plasma optical emission spectrometry (ICP).

RESULTS AND DISCUSSION

pe + pH

The redox status across the rhizosphere of the two maize cultivars is illustrated in Figure 3. The graph shows that the rhizosphere of Pioneer-3737, in the low CaCO_3 soil, was the most reduced relative to the other treatments. The lower redox status for this cultivar in this soil can be attributed to the high pCO_2 (Gollany et al., 2026 in review).

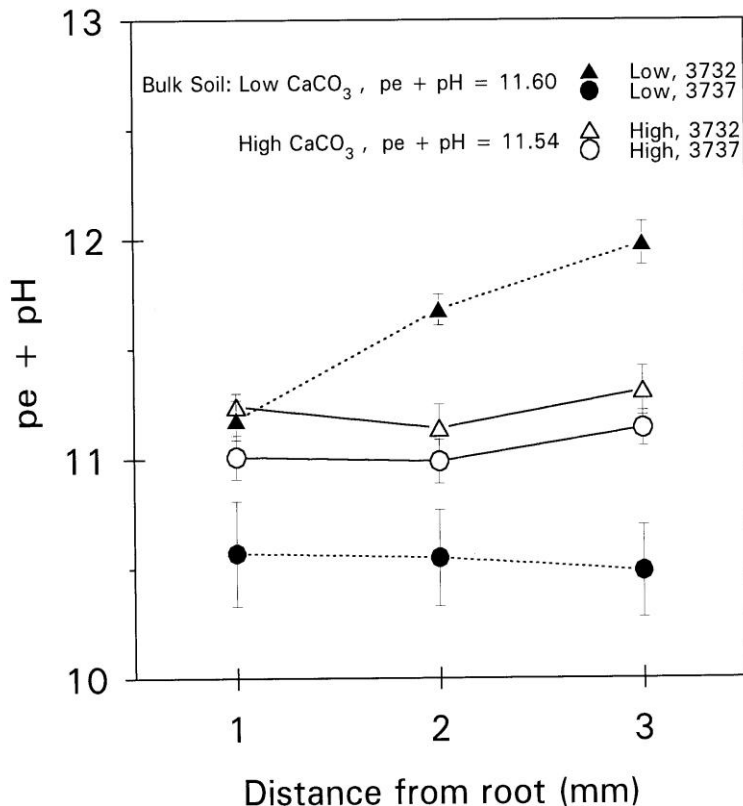


Fig. 3. Mean redox relationship changes ($\pm$ standard error) across the rhizosphere of the two maize genotypes, Pioneer-3732 and Pioneer-3737, in soils with low (5 g kg^{-1}) and high (204 g kg^{-1}) CaCO_3 levels.

Our results indicated that the rhizosphere soils were more reduced than bulk soil (distances greater than 3.0 mm from the root surface) especially for the Pioneer-3732 cultivar in the low CaCO_3 soil. These changes in rhizosphere redox status could be of

considerable importance in mobilization of Fe, Zn, and Mn (Gardner et al., 1982; Marschner et al., 1982; Sarkar and Wyn Jones, 1982a).

Micronutrients in the Rhizosphere

More available manganese (Mn) was found in the rhizoplane relative to the rest of the rhizosphere (Fig. 4). Increased available Mn in the rhizoplane for Pioneer-3737 was more pronounced on both soils. This may be due partly to the lower pH and a greater reducing microenvironment at the rhizoplane of Pioneer-3737 due to higher CO₂ (Gollany et al. 2026 in review). Merckx and co-workers (1986) reported that extracts from maize rhizospheres complexed 30- times Mn compared to the fallow soil. Manganese availability depends on pH, redox potential, and chelator availability. Increased manganese availability in the rhizosphere has been demonstrated previously (Godo and Reisenauer, 1980; Gardner et al., 1982; Linehan et al., 1985). Godo and Reisenauer (1980) attributed the increase in Mn availability in the rhizosphere to pH, reducing effects, and chelators released by the growing roots.

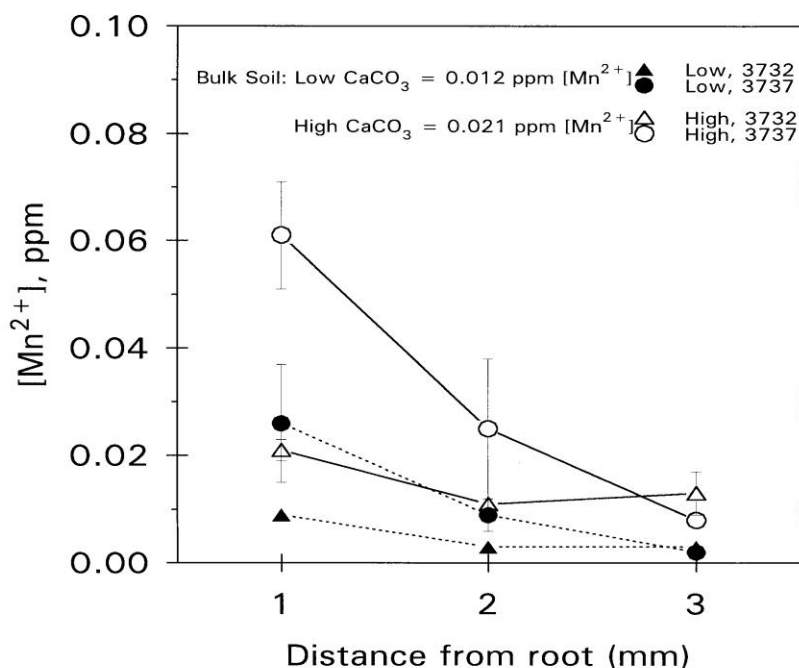


Fig. 4. Mean manganese ($\pm$ standard error) across the rhizosphere of the two maize genotypes, Pioneer-3732 and Pioneer-3737, in soil with low (5 g kg⁻¹) and high (204 g kg⁻¹) $CaCO_3$ levels.

The available zinc (Zn) content was slightly increased at the rhizoplane relative to the soil further away from the root surface (Fig. 5). Sarong et al. (1989) observed that the Zn concentration in rhizosphere soil-water extracts of oats and rice varied inversely with the rhizosphere pH. The authors indicated that the rhizosphere pH, however, did not always explain the observed differences in the extractable Zn. Organic ligand secretion could possibly explain these results. Linehan et al. (1985) reported that rhizosphere extracts of wheat and maize complexed 15% and 16% of the Zn, respectively, compared to only 1.9% for the fallow soil extract. In another study by Merckx and co-workers (1986), the extract from maize rhizospheres complexed an 8-fold Zn compared to the fallow soil.

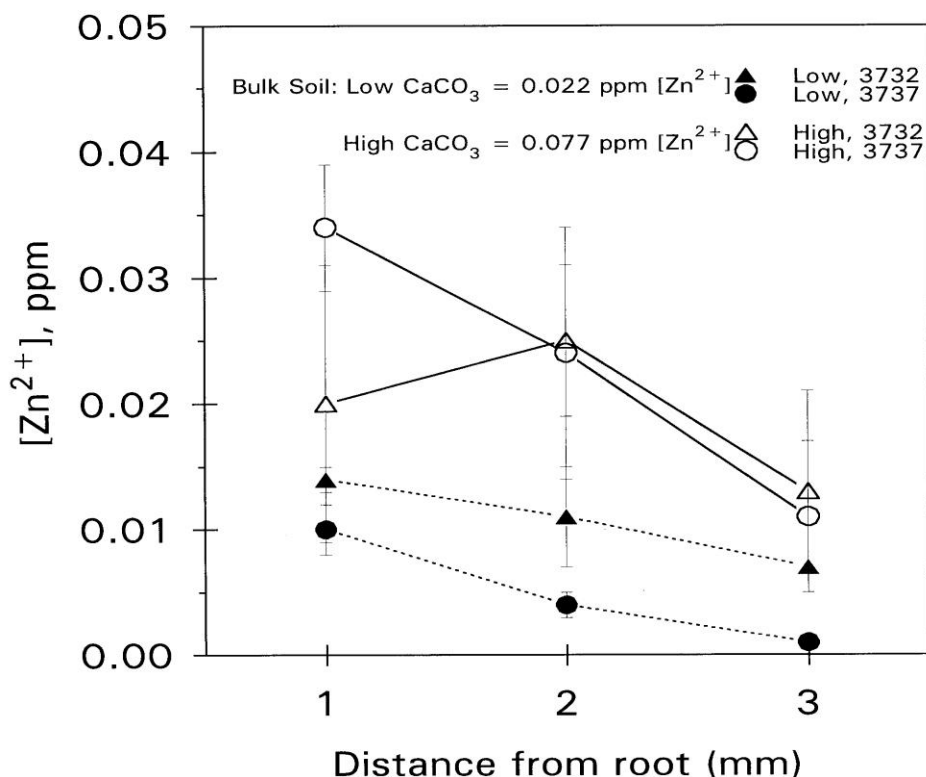


Fig. 5. Mean soluble zinc ($\pm$ standard error) across the rhizosphere of the two maize genotypes, Pioneer-3732 and Pioneer-3737, in soils with low (5 g kg^{-1}) and high (204 g kg^{-1}) CaCO_3 levels.

Iron: Iron depletion at the rhizoplane was found for both cultivars in both soils (Fig. 6). The depletion zone was broader for Pioneer-3737 in the low CaCO_3 soils than for Pioneer-3732 in the low CaCO_3 soil and extended to 3-mm. Rhizosphere acidification under Fe stress has been shown for soybean (Brown et al., 1961), sugar beet (Nagaraja and Ulrich, 1966), tomato (Brown et al., 1971), and sunflower (Oertli and Jacobson, 1960; Römheld et al., 1984). As shown by Marschner (1978), the rate of iron uptake increases markedly within days when the stress-response mechanism was actively functioning. Furthermore, Olsen et al. (1981) observed that the stress effects were temporary, and the plant responds if the nutritional disorder exists.

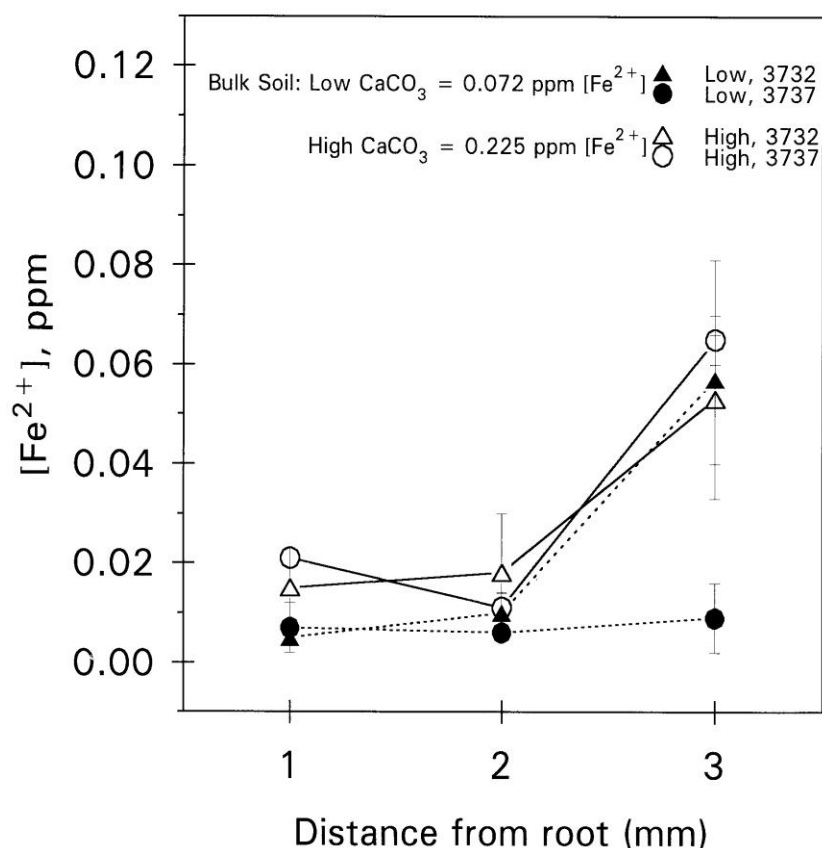


Fig. 5. Mean soluble iron ($\pm$ standard error) across the rhizosphere of the two maize genotypes, Pioneer-3732 and Pioneer-3737 in soils with low (5 g kg⁻¹) and high (204 g kg⁻¹) CaCO_3 levels.

Cation Uptake and Shoot to Root Ratios:

Cation uptake was higher for P-3737 than for P-3732 in the low CaCO₃ soil (Table 2). There were no differences in the plant Cu and Zn contents, while Fe and Mn were higher in P-3737 shoots and shoot to root ratio decreased in the low CaCO₃ soil. However, shoot to root ratio for the Pioneer-3737 increased in high CaCO₃ soil. The sum of the cations in the low CaCO₃ soil was higher in P-3737, though P-3732 was higher in high CaCO₃ soil and both greater compared to the low CaCO₃ soil sums. More available Mn was found in the rhizoplane for Pioneer-3737 on both soils. Depletions of Fe, S, and K were observed for all treatments, yet Pioneer-3737 had more available P and K especially in the high CaCO₃ soil.

Table 2. Mean micronutrient content and shoot/root ratio of Pioneer-3732 and Pioneer-3737 genotypes at the 6-leaf stage.

Treatment	Shoot/root	Cu	Fe	Zn	Mn	Σ (cations) ^a
μmole / g dry matter						
Low, P-3732	1.54 ^b (0.08) ^c	0.4 (0.04)	7.1 (0.04)	0.5 (0.01)	5.2 (0.18)	2388.4
Low, P-3737	1.31 (0.08)	0.5 (0.04)	8.0 (0.20)	0.6 (0.06)	6.2 (0.44)	2678.6
High, P-3732	1.21 (0.13)	0.4 (0.03)	7.9 (0.27)	0.5 (0.04)	6.5 (0.59)	3128.8
High, P-3737	1.40 (0.22)	0.5 (0.02)	7.1 (0.37)	0.6 (0.02)	5.5 (0.18)	2869.4

^aSum of K, Ca, Mg, Cu, Fe, Zn and Mn.

^bMean value calculated for the duplicate rhizotrons.

^cStandard error calculated for the duplicate rhizotrons.

There were no differences in the plant Cu content, while Fe and Mn concentrations were slightly higher in the shoots of Pioneer-3732 compared to the Pioneer-3737, and the shoot to root ratio for Pioneer-3732 decreased in the high CaCO₃ soil compared to the low CaCO₃ soil. However, shoot to root ratio for the Pioneer-3737 increased in high CaCO₃ soil. More available Mn was found in the rhizoplane for Pioneer-3737 low CaCO₃ soils.

Cation-anion uptake imbalance

Changes in the rhizosphere pH due to imbalance in cation-anion uptake are well documented. The theory of contact exchange (Jenny and Overstreet, 1939) proposed that a root absorbs cations from soil colloids by exchanging them at its surface for H^+ . This is true only if cation uptake exceeds anion uptake or during nutrient deficiency.

Certain plants are equipped with the capability of sensing nutrient stress and have fine-tuned 'biofeedback mechanisms' at the molecular level for alleviating this stress (Olsen et al., 1981). They respond to their nutritional disorders by altering only their rhizosphere properties with high efficiency. Progress in rhizosphere studies requires convenient methods for rhizosphere soil-water extraction and accurate knowledge of the physicochemical properties of the rhizosphere. Inferences about the importance of physicochemical rhizosphere properties on plant nutrients are mostly based on indirect evidence (Jungk and Claassen, 1986; Merckx et al., 1986) and theoretical calculations (Nye, 1981). These genotypic differences in the rhizosphere physicochemical properties could be critical for the mobilization and uptake of nutrients. The root-induced pH changes also could affect pathogens and microbial activity in the vicinity of the root.

Results from relatively limited pioneering research on differences in rhizosphere properties among species are very promising. Perhaps the most important areas for further investigation are: i) the new techniques and concepts that are still needed for *in situ* measurements of rhizosphere properties and plant nutrients, ii) understanding the mechanism of "biofeedback control" with which some species or genotypes are equipped for alleviating stress under adverse soil conditions, and iii) pursuing the tremendous potential expected from selecting genotypes with desirable genetic characteristics and matching these genotypes to the particular soil under management.

CONCLUSIONS

Characterizing and quantifying the processes that determine the availability of plant nutrients at the soil-root interface is essential for environmentally sound

management of our resources and obtaining the productive potential of each soil type under specific crop production.

The genotype of maize played a significant role in altering plant nutrient availability in the rhizosphere. The results indicate that the rhizosphere is a very heterogeneous system and its physicochemical properties are different from those of the bulk soil. The roots of the two maize genotypes altered the nutrient composition within the rhizosphere and responded differently to the CaCO_3 content of the bulk soil. Higher Mn^{2+} and Fe^{2+} concentrations were found in the rhizosphere of Pioneer-3737 relative to Pioneer-3732 variety. Higher Mn^{2+} , Cu^{2+} and Zn^{2+} uptake for P-3737 corn were observed in the high calcium carbonate soil relative to P-3732 corn variety. The plant shoot/root ratio was reduced by 21.4% for corn P-3732 while increased by 15.7% for corn P-3737 in the calcareous soil. Bulk soil extraction methods ignore rhizosphere effects on nutrient availability. Caution should therefore be used when average bulk soil values are used in making predictions of mineral nutrient availability and root uptake, particularly under adverse soil conditions. These genotypic differences in the rhizosphere physicochemical properties could be critical for the mobilization and uptake of nutrients, however, have not received adequate attention. The principal limitation to progress in this field is the need to develop new methods and techniques to examine an opaque and structurally complex medium without disturbing the soil-root interface.

Declaration of competing interest:

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

REFERENCES

- Bekele T, Cino BJ, Ehlert PAI, Van der Maas AA, Van Diest A (1983) An evaluation of plant-borne factors promoting the solubilization of alkaline rock phosphates. *Plant and Soil* 75: 361-378
- Bolan N, Prashant S, Cherukumalli SR, Satyanaraya PV, Anderson GC, Bolana S, Nortje GP, Kronenberg R, Bardhan S, Abbotta LK, Zhao H, Mehra P, Satyanarayana SV, Khan N, Wangl H, Rinklebe J, Siddiquea KHM, Kirkham MB (2023). Distribution, characteristics and management of calcareous soils. *Advances in Agronomy* 182: 81-130
- Bromfield SM (1958a) The properties of a biologically formed manganese oxide, its availability to oats and its solution by root washings. *Plant and Soil* 9: 325-337
- Bromfield SM (1958b) The solution of γ -MnO₂ by substances released from soil and from the roots of oats and vetch in relation to manganese availability. *Plant and Soil* 10: 147-160
- Brown JC (1956) Iron chlorosis. *Ann Rev Plant Physiol* 7: 171-190
- Brown JC, Chaney RL, Ambler JE (1971) A new tomato mutant inefficient in the transport of iron. *Physiol Plant* 25, 48-53
- Brown JC, Holmes RS, Tiffin LO (1961) Chlorosis in soybeans as related to the genotype of rootstalk: 3. Chlorosis susceptibility and reductive capacity at the root. *Soil Sci* 91: 127-132
- Brown JC, Olsen RA (1980) Factors related to iron uptake by dicotyledonous and monocotyledonous plants: III. Competition between root and external factors for Fe. *J Plant Nutr* 2: 661-682
- Camp SD, Jolley VD, Brown JC (1987) Comparative evaluation of factors involved in Fe stress response in tomato and soybean. *J Plant Nutr* 10: 423-442
- Claassen N, Hendriks L, Jungk A (1981a) Erfassung der Mineralstoffverteilung im wurzelnahen Boden durch Autoradiographie. *Z Pflanzenernähr Bodenk* 144: 306-316
- Claassen N, Hendriks L, Jungk A (1981b) Rubidium-Verarmung des wurzelnahen Boden durch Maispflanzen. *Z Pflanzenernähr Bodenk* 144: 553-545
- Claassen N, Jungk A, (1982) Kaliumdynamik im wurzelnahen Boden in Beziehung zur Kaliumaufnahme Maispflanzen. *Z Pflanzenernähr Bodenk* 145: 513-525
- Clark FE (1949) Soil microorganisms and plant roots. *Adv Agron* 1: 241-288

- Clark RB, Brown JC (1974) Internal root control of iron uptake and utilization in maize genotypes. *Plant Soil* 40: 669-677
- Conkling BL, Blanchar RW (1989) Glass microelectrode techniques for *in situ* pH measurements. *Soil Sci Soc Am J* 53: 58-62
- Cunningham RK (1964) Cation-anion relationships in crop nutrition: III. Relationships between the ratios of sum of the cations: sum of the anions and nitrogen concentrations in several plant species. *J Agric Sci* 63: 109-111
- Curl EA, Truelove B (1985) *The Rhizosphere*. Springer-Verlag, New Yor, p 281
- Doner HE, Pratt PF (1969) Solubility of calcium carbonate precipitated in aqueous solutions of magnesium and sulfate salts. *Soil Sci Soc Amer Proc* 33: 690-693
- Egmond F van, Aktas M (1977) Iron-nutritional aspects of the ionic balance of plants. *Plant Soil* 48: 685-703\
- Enoch H, Dasberg S (1971) The occurrence of high CO₂ concentrations in soil air. *Geoderma* 6: 17-21
- Gardner WK, Barber DA, Parbery DG (1983) The acquisition of phosphorus by *Lupinus albus* L.: III. The probable mechanism by which phosphorus movement in the soil/root interface is enhanced. *Plant and Soil* 70: 107-124
- Gardner WK, Parbery DG, Barber DA (1982) The acquisition of phosphorus by *Lupinus albus* L.: I. Some characteristics of the soil/root interface. *Plant and Soil* 68: 19-32
- Gardner WK, Parbery DG, Barber DA (1981) Proteoid root morphology and function in *Lupinus albus*. *Plant and Soil* 60: 143-147
- Gijsman AJ (1990a) Nitrogen nutrition of Douglas-fir (*Pseudotsuga menziesii*) on strongly acid sandy soil: II. Proton excretion and rhizosphere pH. *Plant and Soil* 126: 63-70
- Gijsman AJ (1990b) Nitrogen nutrition of Douglas-fir (*Pseudotsuga menziesii*) on strongly acid sandy soil: I. Growth, nutrient uptake and ionic balance. *Plant and Soil* 126: 53-61
- Gijsman AJ (1990c) Rhizosphere pH along different root zones of Douglas-fir (*Pseudotsuga menziesii*), as affected by source of nitrogen. *Plant and Soil* 124: 161-167
- Godo GH, Reisenauer HM (1980) Plant effects on soil manganese availability. *Soil Sci Soc Am Proc* 44: 993-995

- Graham JH, Leonard RT, Menge JA (1981) Membrane-mediated decrease in root exudation responsible for phosphorus inhibition of vesicular-arbuscular mycorrhiza formation. *Plant Physiol* 68: 548-552
- Grinsted MJ, Hedley MJ, White RE, Nye PH (1982) Plant-induced changes in the rhizosphere of rape (*Brassica Napus* var. *Emerald*) seedlings: I. pH change and the increase in P concentration in the soil solution. *New Phytol* 91: 19-29
- Halverson E, Malo D, Osterloh K (2025). Century-long soil profile truncation in easter. South Dakota. *Geoderma* 460: 227399.
<https://doi.org/10.1016/j.geoderma.2025.117399>.
- Hedley MJ, Nye PH, and White RE (1982) Plant-induced changes in the rhizosphere of rape (*Brassica Napus* var. *Emerald*) seedlings: II. Origin of the pH change. *New Phytol* 91: 31-44
- Hedley MJ, Nye PH and White RE (1983) Plant-induced changes in the rhizosphere of rape (*Brassica Napus* var. *Emerald*) seedlings: IV. The effect of rhizosphere phosphorus status on the pH, phosphatase activity and depletion of soil phosphorus fractions in the rhizosphere and on the cation-anion balance in plants. *New Phytol* 95: 69-82
- Hoffland E, Findenegg GR, Nelemans JA (1989) Solubilization of rock phosphate by rape: II. Local root exudation of organic acids as a response to P-starvation. *Plant and Soil* 113: 161-165
- Jenny H, Overstreet R (1939) Cation interchange between plant roots and soil colloids. *Soil Sci* 47: 257-272
- Jolley VD, Brown JC (1987) Soybean response to iron-deficiency stress as related to iron supply in the growth medium. *Anal Plant Nutr* 10, 637-651
- Jungk A, Claassen N (1986) Availability of phosphate and potassium as the result of interactions between root and soil in the rhizosphere. *Z Pflanzenernähr Bodenk* 149: 411-427
- Landsberg EC (1981) Organic acid synthesis and release of hydrogen ions in response to Fe-deficiency stress of mono- and dicotyledonous plant species. *J Plant Nutr* 3: 579-591
- Light TS (1972) Standard solution for redox potential measurements. *Anal Chem* 44: 1038-1039
- Lindsay WL (1979) *Chemical Equilibria in Soils*. Wiley Interscience. New York.

- Linehan DJ, Sinclair AH, Mitchell MC (1985) Mobilisation of Cu, Mn and Zn in the soil solutions of barley rhizospheres. *Plant and Soil* 86: 147-149
- Lipton GS, Blanchar RW, Blevins DG (1987) Citrate, malate and succinate concentration in exudates from P-sufficient and P-stressed *Medicago sativa* L. seedlings. *Plant Physiol* 85: 315-317
- Marschner H (1978) Role of the rhizosphere in iron nutrition of plants. *Iran J Agric Res* 6: 69-80
- Marschner H, Römheld V, Ossenberger-Neuhaus H (1982) Rapid method for measuring changes in pH and reducing processes along roots of intact plants. *Z Pflanzenphysiol Bodenkd* 105: 407-416
- Marschner H, Römheld V (1983) In vivo measurement of root-induced pH changes at the soil-root interface: Effect of plant species and nitrogen source. *Z Pflanzenphysiol* 111: 241-251
- Marschner H, Römheld V, Horst WJ, Martin P (1986) Root-induced changes in the rhizosphere: Importance for the mineral nutrition of plants. *Z Pflanzenernähr Bodenkd* 149: 441-456
- Mengel K, Kirkby EA (1978) Principles of Plant Nutrition. International Potash Institute, Worblau-Bern, Switzerland.
- Merckx R, van Ginkel JH, Sinnaeve J, Cremers A (1986a) Plant-induced changes in the rhizosphere of maize and wheat: I. Production and turnover of root-derived material in the rhizosphere of maize and wheat. *Plant and Soil* 96: 85-93
- Merckx R, van Ginkel JH, Sinnaeve J, Cremers A (1986b) Plant-induced changes in the rhizosphere of maize and wheat: II. Complexation of cobalt, zinc and manganese in the rhizosphere of maize and wheat. *Plant and Soil* 96: 95-107
- Metzger WH (1928) The effect of growing plants on solubility of soil nutrients. *Soil Sci* 25: 273-280
- Miller RD, Johnson DD (1964) The effect of soil moisture tension on carbon dioxide evolution, nitrification, and nitrogen mineralization. *Soil Sci Soc Am Proc* 28: 644-647
- Miller MH, Mamaril CP, Blair GJ (1970) Ammonium effects on phosphorus absorption through pH changes and phosphorus precipitated at the soil-root interface. *Agron J* 62: 524-527
- Moorby H, White RE, Nye PH (1988) The influence of phosphate nutrition on H ion efflux from the roots of young rape plants. *Plant and Soil* 105: 247-256

- 599
600 Mortland MM, Lawton K, Vehara G (1956) Alteration of biotite to vermiculite by plant
601 growth. *Soil Sci* 82: 477-481
602
- 603 Mubarak A, Olsen RA (1976) Immiscible displacement of the soil solution by
604 centrifugation. *Soil Sci Soc Am J* 40: 329-331
605
- 606 Nagaraja S, Ulrich A (1966) Fe-nutrition of sugarbeet plant in relation to growth, mineral
607 balance and riboflavin formation. *Soil Sci* 102: 399-407
608
- 609 Nakayama FS (1968) Calcium activity, complex and ion-pair in saturated CaCO_3
610 solutions. *Soil Sci* 106: 429-434
611
- 612 Nakayama FS (1970) Hydrolysis of CaCO_3 , NaCO_3 and NaHCO_3 and their combinations
613 in the presence and absence of external CO_2 source. *Soil Sci* 109: 391-398
614
- 615 Nilovskaya NT, Kovalenko VK, Laptev VV (1970) Uptake and liberation of carbon
616 dioxide by plants under artificial environment conditions. *Soviet Pl Physiol* 17:
617 567
618
- 619 Nyatsanga T, Pierre WH (1973) Effect of nitrogen fixation by legumes on soil acidity.
620 *Agron J* 65: 936-940
621
- 622 Nye PH (1968) Processes in the root environment. *J Soil Sci* 19: 205-215
623
- 624 Nye PH (1981) Changes of pH across the rhizosphere induced by roots. *Plant and Soil*
625 61: 7-26
626
- 627 Olsen SR, Watanabe FS (1959) Solubility of calcium carbonate in calcareous soils. *Soil*
628 *Sci* 88: 123-129
629
- 630 Olsen RA (1968) The driving force on an ion in the absorption process. *Soil Sci Soc Am*
631 *Proc* 32: 660-664
632
- 633 Olsen RA, Clark RB, Bennett JH (1981) The enhancement of soil fertility by plant roots.
634 *Am Scientist* 69: 378-384
635
- 636 Olsthoorn AFM, Keltjens WG, Van Baren B, Hopman MCG (1991) Influence of
637 ammonium on fine root development and rhizosphere pH of Douglas-fir seedlings
638 in sand. *Plant and Soil* 133: 75-81
639
- 640 Oertli JJ, Jacobson L (1960) Some quantitative considerations in iron nutrition of higher
641 plants. *Plant Physiol* 35: 683-688
642
- 643 Peterson W, Böttger M (1991) Contribution of organic acids to the acidification of the
644 rhizosphere of maize seedlings. *Plant and Soil* 132: 159-163

- Riley D, Barber SA (1969) Bicarbonate accumulation and pH changes at soybean (Glycine max (L.) Merr.) root-soil interface. *Soil Sci Soc Am Proc* 33: 905-908
- Riley D, Barber SA (1971) Effect of ammonium and nitrate fertilization on phosphorus uptake as related to root-induced pH changes at the root-soil interface. *Soil Sci Soc Am Proc* 35: 301-306
- Robbins CW (1985) The CaCO_3 - CO_2 - H_2O system in soils. *J Agron Educ* 14: 3-7
- Robbins CW (1986a) Carbon dioxide partial pressure in lysimeter soils. *Agron J* 78: 151-158
- Robbins CW (1986b) Sodic calcareous soil reclamation as affected by different amendments and crops. *Agron J* 78: 916-920
- Römheld V, Marschner H (1983) Mechanism of iron uptake by peanut plants: I. Fe III reduction, chelate splitting release of phenolics. *Plant Physiol* 72: 949-954
- Römheld V, Marschner H (1984) Plant-induced pH changes in the rhizosphere of "Fe-efficient" and "Fe-inefficient" soybean and corn cultivars. *J Plant Nutr* 7: 623-630
- Römheld V, Müller C, Marschner H (1984) Localization and capacity of proton pumps in roots of intact sunflower plants. *Plant Physiol* 76: 603-606
- Römheld V, Marschner H (1986) Evidence for a specific uptake system for iron phytosiderophores in root of grasses. *Plant Physiol* 80: 175-180
- Rovira AD (1956) Plant root excretions in relation to the rhizosphere effect. I. The nature of root exudate from oats and peas. *Plant and Soil* 7: 178-194
- Rovira AD (1959) Root excretions in relation to the rhizosphere effect. IV. Influence of plant species, age of plant, light, temperature, and calcium nutrition on exudation. *Plant and Soil* 11: 53-64
- Sarong LQ, Bouldin DR, Reid WS (1989) Total and labile zinc concentrations in water extracts of rhizosphere and bulk soils of oats and rice. *Commun in Soil Sci Plant Anal* 20: 271-289
- Sarkar AN, Jenkins DA, Wyn Jones RG (1978) Modifications to mechanical and mineralogical composition of soil within the rhizosphere. *In* Soil-Root Interface. Eds. Harley J L and Russell R S. 403 p. Academic Press. London, U. K.
- Sarkar AN, Wyn Jones RG (1982) Effect of rhizosphere pH on the availability and uptake of Fe, Mn, and Zn. *Plant and Soil* 66: 361-372

- Schaller G, Fischer WR (1981) Die Verwendung von Antimon-Elektroden zur pH-Messung in Böden. *Z Pflanzenernähr Bodenk* 144: 197-204
- Schaller G, Fischer WR (1985) pH-Änderungen in der Rhizosphäre von Mais- und Erdnußwurzeln. *Z Pflanzenernähr Bodenk* 148: 306-320
- Sijmons PC, Bienfait JF (1983) Source of electrons for extracellular Fe III reduction in iron-deficient bean roots. *Physiol Plant* 59: 409-415
- Sijmons PC, Bienfait JF (1984) Mechanism of iron reduction by roots of *Phaseolus vulgaris* L. *J Plant Nutr* 7: 678-693
- So HB (1978) Water potential gradients and resistances of a soil-root system measured with the root and soil psychrometer. *In Soil-Root Interface*. Eds. Harley J I and Russell R S. 430 p. Academic Press, London, U.K.
- Soulides DA, Allison FE (1961) Effect of drying and freezing soils on carbon dioxide production, available mineral nutrients, aggregation, and bacterial population. *Soil Sci* 91: 291-298
- Tanji KK, Doneen LD (1966) A computer technique for prediction of CaCO_3 precipitation in HCO_3 salt solutions. *Soil Sci Soc Am Proc* 30: 53-56
- Turner RC, Clark JS (1956) The pH of calcareous soils. *Soil Sci* 82: 337-341
- Turner RC (1958) A theoretical treatment of the pH of calcareous soils. *Soil Sci* 86: 32-34
- Vancura V (1964) Root exudates of Plants. I. Analysis of root exudates of barley and wheat in their initial phases of growth. *Plant and Soil* 21: 231-248
- Vancura V, Hanzlikova A (1972) Root exudates of plants. IV. Differences in chemical composition of seed and seedling exudates. *Plant Soil* 36: 271-282
- Wallace A (1982) Effect of nitrogen fertilizer and nodulation on lime-induced chlorosis in soybeans. *J Plant Nutr* 5: 363-368
- Warden BT (1991) Manganese extracted from different chemical fractions of bulk and rhizosphere soil as affected by method of sample preparation. *Commun Soil Sci Anal* 22: 169-176
- Willard HH, Merritt LL and Dean JA (1965) The measurement of pH. *In Instrumental Methods of Analysis*. pp 582-613. Van Nostrand, New York, USA.
- Whitney RS, Gardner R (1943) The effect of carbon dioxide on soil reaction. *Soil Sci* 55: 127-141

- 736 Wouterlood M, Cawthray G R, Turner S, Lambers H, Veneklaas EJ (2004) Rhizosphere
737 carboxylate concentrations of chickpea are affected by genotype and soil type.
738 Plant and Soil (261): 1-10
739
- 740 Yamaguchi M, Flocker WJ, Howard FD, 1967 Soil atmosphere as influenced by
741 temperature and moisture. Soil Sci Soc Am Proc 31: 164-167
742
- 743 Youssef RA, Chino M (1987) Studies on the behavior of nutrients in the rhizosphere: I.
744 Establishment of a New rhizobox system to study nutrient status in the
745 rhizosphere. J Plant Nutr 10: 1185-1195
746

FIGURES

Figure 1. Corn grown in the rhizotrons positioned at a 45° angle on a stand and kept hydrated at the rhizotron capacity using trickle irrigation system.

Figure 2. Measurements of pH, Eh, and pCO₂ taken at 1-, 2-, and 3-mm distances from the maize root surface and 0.5 mm above root tips in a rhizotron. Microelectrodes were connected to input terminal of the electrometer (FD-223) and mounted on a micromanipulator in a Faraday cage.

Figure 3, Mean redox relationship changes ($\pm$ standard error) across the rhizosphere of the two maize genotypes, Pioneer-3732 and Pioneer-3737, in soils with low (5 g kg⁻¹) and high (204 g kg⁻¹) CaCO₃ levels.

Figure 4. Fig. 4. Mean manganese ($\pm$ standard error) across the rhizosphere of the two maize genotypes, Pioneer-3732 and Pioneer-3737, in soil with low (5 g kg⁻¹) and high (204 g kg⁻¹) CaCO₃ levels.

Figure. 5. Mean soluble zinc ($\pm$ standard error) across the rhizosphere of the two maize genotypes, Pioneer-3732 and Pioneer-3737, in soils with low (5 g kg⁻¹) and high (204 g kg⁻¹) CaCO₃ levels.

Figure 6. Mean soluble iron ($\pm$ standard error) across the rhizosphere of the two maize genotypes, Pioneer-3732 and Pioneer-3737 in soils with low with low (5 g kg⁻¹) and high (204 g kg⁻¹) CaCO₃ levels.