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Effects of nitrogen fertilization of grapefruit trees on soil acidification and nutrient availability in a Riviera fine sand

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Abstract

Nitrogen (N) fertilizer applied in the NH_4^+ form results in some degree of soil acidification, which could influence nutrient availability to plants and nutrient losses through leaching. Effects of various N rates (0 – 168 kg N ha^{-1} yr^{-1}) on soil acidification and nutrient availability were investigated in a Riviera fine sand with 26-year-old white Marsh grapefruit (*Citrus paradisi* MacFadyen) trees. Soil pH significantly decreased with increasing NH_4–N rates. Application of 112 kg N ha^{-1} yr^{-1} for four years decreased the pH by 0.7 to 1.7 unit. Soil acidification was greater when the NH_4^+ form of N fertilizer was applied as dry soluble granular material compared to fertigation or controlled release forms. The marked effect of NH_4–N fertilization on the pH of the Riviera fine sand was due to its low buffering capacity. Soil acidification increased the concentration of extractable Fe and P but decreased that of K, Zn and Mn. Soil pH was positively correlated with concentration of Ca, but negatively with concentrations of Fe, Mn and Zn in six-month-old spring flush leaves of the grapefruit trees. Leaf P concentrations, however, were poorly correlated with soil pH. This study also demonstrated an increase in leaching of P and K below the grapefruit trees rootzone with a decrease in soil pH.

Introduction

Soil acidification caused by routine fertilization practices for crop production has been reported in different parts of the world (Wallace, 1994). Improved management of nitrogen (N) has received considerable attention due to its effects on soil sustainability and its potential for nitrate (NO_3^-) contamination of groundwater (Alva and Paramasivam, 1998; Alva et al., 1998; Dasberg, 1987; Ramos, 1996). Application of acid-forming N fertilizers such as NH_4 NO_3, $(NH_4)_2S0_4$, and NH_2–CO–NH_2 has been reported to decrease soil pH (Bouman et al., 1995; Neilsen et al., 1994; Parachomchuk et al., 1993). Surface layer acidification was observed to develop within 6–10 weeks following urea-N application (Black, 1992). Soil acidity was increased with increasing application of N fertilizer (Bouman et al., 1995) and application of nitrogen fertilizers at high rates could result in a soil pH (H_20) as low as 2.9, as was detected in a green tea field by Tachibana et al. (1995). The major mechanism of soil acidification by nitrogen fertilization is related to H^+ ion release through nitrification of NH_4^+ and the subsequent leaching of $N0_3^-$ (Bouman et al., 1995; Neilsen et al., 1994; Parachomchuk et al., 1993). The most important consequence of soil acidification was the depletion of exchangeable Ca, Mg and K and an increase in Mn solubility (Bouman et al., 1995; Neilsen et al., 1994; Tachibana et al., 1995). However, no systematic study was done on the quantitative relationship of soil acidification to N rates and the effect of soil acidification on leaching and availability of soil nutrients.

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Nitrogen fertilization and irrigation are crucial for sustainable citrus production (Davies, 1997). Many soils under citrus production, in Florida, are light-textured with low nutrient-holding capacity. Therefore, there is increasing concern about NO_3 leaching in this area, especially along the ridge in Central Florida. Soil acidification effects as a result of N fertilization in a citrus production region were reported in the 60's (Calvert et al., 1962), but received very little attention. They observed that the pH of two sandy soils decreased by 1.5 unit following 12-years' application of ammonium sulfate or urea to Valencia orange trees on sour orange rootstock. Fruit yield and quality of citrus are affected by both macro- and micro-nutrient status (Calvert, 1970; Calvert and Reitz, 1963; Koo and Reese, 1977; Tao, 1993; Tucker et al., 1995). Soil pH influences the amount and plant availability of various macro- and micro- nutrients (Alva, 1992; Alva and Chen, 1995; Alva et al., 1995). Soil acidification affects the transformation and availability of macro- and micro-nutrients which, in turn, could affect the fruit yield, quality and leaching loss of nutrients. For instance, there was some indication of reduction in brix/acid ratio in low pH soils (Calvert et al., 1962). More information is needed to address the effects of soil acidification on nutrient leaching and availability, and on fruit yield and quality of citrus. Development of best management practices (BMPs) for fertilization and irrigation of grapefruit is in progress to improve fruit yield and quality, while minimizing various losses of N (Alva, 1998, unpublished data). This study was conducted in a Riviera fine sand with various rates and sources of N under two different irrigation regimes. The objective of this paper was to examine the long-term effects of N fertilization on the soil pH and nutrient availability and/or leaching.

Materials and methods

The field experiment was conducted in a commercial grove with 26-year-old white Marsh grapefruit (*Citrus paradisi* MacFadyen) trees on sour orange (*Citrus aurantium* Lush) rootstock in Martin County, FL. The experiment occupied an area of approximately 8 ha on a Riviera fine sand (Loamy, siliceous, hyperthermic Arenic Glossaqualfs). Some basic properties of the soil are shown in Table 1. Each plot consisted of five uniform trees planted at a 6×6 m spacing (269 trees/ha). The trees were irrigated using under the tree microirrigation, with one emitter per tree at a delivery rate of 3.78×10^{-2} m^3 h^{-1}. The experimental plots were laid out on a factorial split plot design with 2 irrigation treatments as the main plots and different fertilizer sources and rates as the subplots with 4 replications. The experiment was started in 1994. Two irrigation treatments were; (i) irrigation at low soil moisture tension, i.e., scheduled when the tensiometer (at 15 cm depth) readings attained 15 cbar, equivalent to 25% depletion of available soil moisture content, and (ii) irrigation at high soil moisture tension, i.e., scheduled when the tensiometer readings attained 30 cbar; equivalent to 40% depletion of available soil moisture content. Percent depletion of available soil moisture was calculated using soil moisture characteristic curves developed from undisturbed soil core samples taken from 8 locations within the experimental area. Subtreatments consisted of 56, 112 and 168 kg N ha^{-1} yr^{-1} as either broadcast application of dry soluble granular form (3 appl. yr^{-1}) or as liquid form applied through the irrigation system; i.e., fertigation (15 appl. yr^{-1}) and 28, 56 and 112 kg N ha^{-1} yr^{-1} of controlled release fertilizers (CRF; appl. yr^{-1}). The CRF rates were raised the same as those for the other sources after three years. The N:P:K ratio of the fertilizers was at 1:0.17:1.02 regardless of sources for all the years to meet the nutritional demand of the grapefruit trees. An unfertilized treatment was also maintained as a control.

Four years after the above treatments were in place (July, 1997), soil was sampled from selected plots at 0–15 and 15–30 cm depth. The soil samples were air-dried, ground and passed through a 2-mm sieve. Olsen-P (Olsen and Sommers, 1982), pH, and Mehlich 3 (Mehlich, 1984) extractable nutrients were analyzed. Soil pH was measured in water and 1 *M* KCl solution at a soil:solution ratio of 1:1, using a pH/ion/conductivity meter (ACCUMET, Denver Instrument Inc., Norfolk, PE). Organic matter content of the surface soil (0–30 cm) was determined using an elemental analyzer (NA 1500, Fisons Scientific Company). Olsen-P was extracted with 0.5 *M* $NaHCO_3$. The air-dried surface soil samples were weighed out (2.5 g) into 50 mL polystyrene centrifuge tubes and 25 mL Mehlich 3 extractant was added. The suspension was shaken for 5 min, and filtered through Whatman 42 filter paper. Concentrations of P, K, Mg, Zn, Mn and Fe in the extract were measured using Inductively Coupled Plasma Emission Spectroscopy (ICPES, Plasma 40, Perkin Elmer Inc., Norwalk, CT).

The soil buffering curve for H^+ or OH^- was determined by adding increments of 0.1 *M* HCl or 0.1

Table 1. Basic properties of a Riviera fine sand under white Marsh grapefruit production

Depth (cm)	Organic matter	pH (H_20)	Olsen-P (mg kg^{-1})	Soil texture (g kg^{-1})		
				Clay	Sand	Silt
	(g kg^{-1})					
0–15	17.3	7.50	6.42	14	958	28
15–30	13.1	7.59	4.12	14	958	28
30–60	11.1	7.48	10.00	4	986	10
60–90	7.3	7.36	11.50	15	980	5
90–120	7.5	7.50	5.35	220	766	14
120–150	5.0	7.52	6.27	179	818	3
150–180	3.8	7.57	4.05	nd	nd	nd[a]
180–210	3.8	7.71	nd	nd	nd	nd

[a] nd, not determined.

M NaOH to the soil suspension at a soil:water ratio of 1:1. After each addition of HCl or NaOH, the suspension was shaken for 30 min and the pH was measured. This measurement was made on the assumption that an equilibrium was attained during this period for this sandy soil.

Soil solution samples were collected from suction lysimeters installed at the 120 cm depth. Nutrients at this depth are considered unavailable to the tree roots, as this depth is well below the root zone of grapefruit trees in this soil (Zhang et al., 1996). The suction lysimeters were constructed using 0.1 MPa, high-flow porous ceramic cylinders (Soil Moisture Equipment Company, Santa Barbara, CA). A 2-inch soil auger was used to drill a hole in the ground under the canopy to the required depth. The installation was done along the tree line 120 cm from the trunk under the canopy. The suction lysimeter was lowered into the hole. The hole was back-filled using the respective depth soil along with an abundance of water so that the soil was packed around the ceramic cup in order to maintain a good contact between the porous cup and the soil. Suction was applied using a vacuum pump (ROA Manufacturing Corporation, Benton Harbor, MI) operated by a generator (EMI 1800, Honda Motor Co., Japan) as a power source. The vacuum pump was used to extract the leachate collected in the suction lysimeter. The leachate sample was stored in a cooler with dry ice and transported to the laboratory. The concentrations of $P0_4$–P, K and Ca in the leachate were measured within 24 h of sample collection (U.S. EPA, Method 300.OA) using an Ion Chromatograph (DX 500; Dionex Corporation Sunnyvale, CA). Collection of soil leachates from the lysimeters began on July 27, 1995 and continued at 2-week intervals.

Six-month-old spring flush leaves were sampled for mineral analysis in July 1997. Twenty leaves per tree were collected from non-fruiting branches around the tree from each of the middle 3 trees within a plot. The leaf samples were washed in detergent, rinsed several times in tap water, soaked in 5% HCl for 20 s and rinsed in distilled water. The leaves were dried at 70°C for 48 h, ground using a Wiley Mill and passed through a 0.4-mm sieve. Half a gram of the ground leaf tissue was dry-ashed at 550°C for 5 h. The ash was cooled and 20 mL of 1 *M* HC1 was added. The concentrations of P, K, Ca, Mg, Na, Zn, Mn, Fe and Al were determined using the ICPES. The concentration of N in the leaves was analyzed by the Kjeldahl method. The correlations between nutrient concentration in soil, citrus leaf, or soil solution and soil pH were conducted using the correlation procedure of SAS (SAS Institute, 1996). The regressions of soil pH vs. nitrogen fertilizer rate, and of nutrient concentration in either soil, citrus leaf or soil solution vs. soil pH were analyzed with the linear regression procedure (SAS Institute, 1996).

Results and discussion

Effects on soil pH

The Riviera fine sand was developed on unconsolidated, marine sandy and loamy materials. It had a relatively uniform surface and subsurface layer (0–90 cm), which contained more than 96–98% sand. The

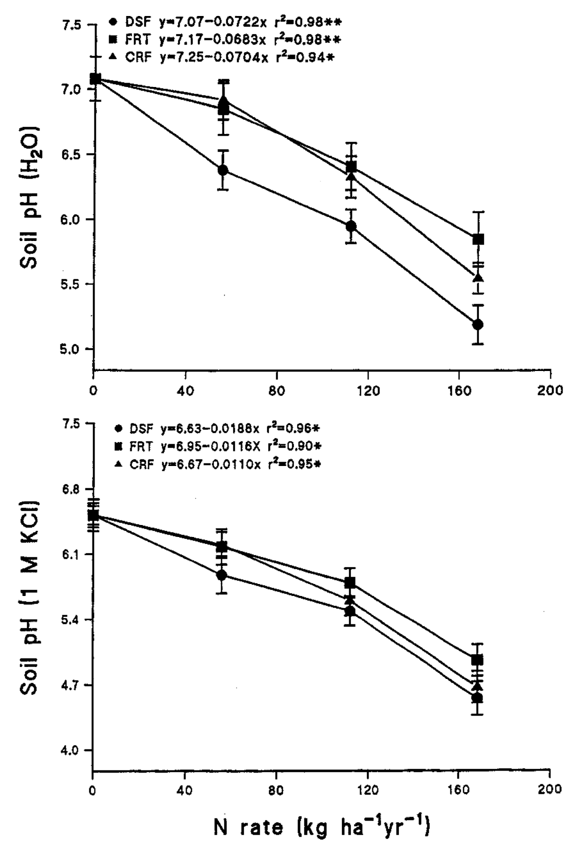

Figure 1. Changes in soil pH of a Riviera fine sand under white Marsh grapefruit after four years of N fertilization at various rates as either dry soluble fertilizer (DSF), fertigation (FRT) or controlled release fertilizer (CRF).

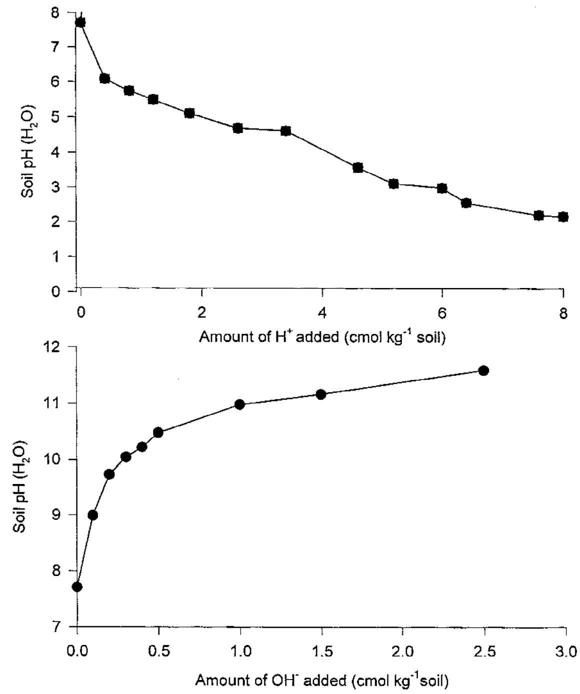

Figure 2. Buffering curves for a Riviera fine sand (0 – 30 cm depth only) to acidity and alkalinity.

clay content was greater below 90 cm than at the 0–90 cm depth (Table 1). Being affected by underlying alkaline materials, the pH of the soil varied from 7.4 to 7.7 (Table 1). After four years of different treatments, the pH of the surface soil (0–30 cm) was influenced by N sources and rates (Figure 1). The irrigation effects on soil pH and/or nutrient availability were not significant. Therefore, the results are discussed in reference to N rates and sources only. Soil pH significantly decreased with increasing N rates for all N sources. There was a significant negative relationship between soil pH and N rates (Figure 1). Soil pH was lower by 0.7 to 1.69 units (0.67 to 1.88 pH in 1 *M* KCl) for the 112 kg N ha^{-1} yr^{-1} as compared to the control (no fertilizer) after four years. The decrease in soil pH was greater with dry fertilizer application than with fertigation or controlled release N source (Figure 1).

The marked acidifying effect of N fertilization on the Riviera fine sand can probably be attributed to the low buffering capacity of the soil (Figure 2). Based on the buffering curve, the soil had low buffering capacity within the pH range studied. Addition of a small amount of H^+ (0.8 cmol kg^{-1} soil) decreased the soil pH to around 6, and further decreased to 5 and 4, with addition of 2 and 4 cmol H^+ kg^{-1} soil, respectively.

The process of nitrification converts NH_4^+ to NO_3^- form by the following reaction:

$$NH_4^+ + 20_2 \xrightarrow{microbes} NO_3^- + H_20 + 2H^+$$

Two moles of H^+ are produced when 1 mole of NH_4^+ is converted to NO_3^-. The application of 100 kg N ha^{-1} yr^{-1} in the form of NH_4–N could potentially produce 0.71 cmol H^+ kg^{-1} soil in a year or 2.9 cmol H^+ kg^{-1} soil in four years. This magnitude of acidity could theoretically decrease soil pH to below 5.0.

Extractable nutrients in relation to soil pH

Soil pH significantly influenced the concentration of various nutrients in the soil (Figure 3). Significant positive relationships were found between soil pH and concentrations of Zn, Mn and K (Figure 3 and Table 2). Based on simple regression analysis, a decrease in soil pH by one unit could decrease the extractable Zn,

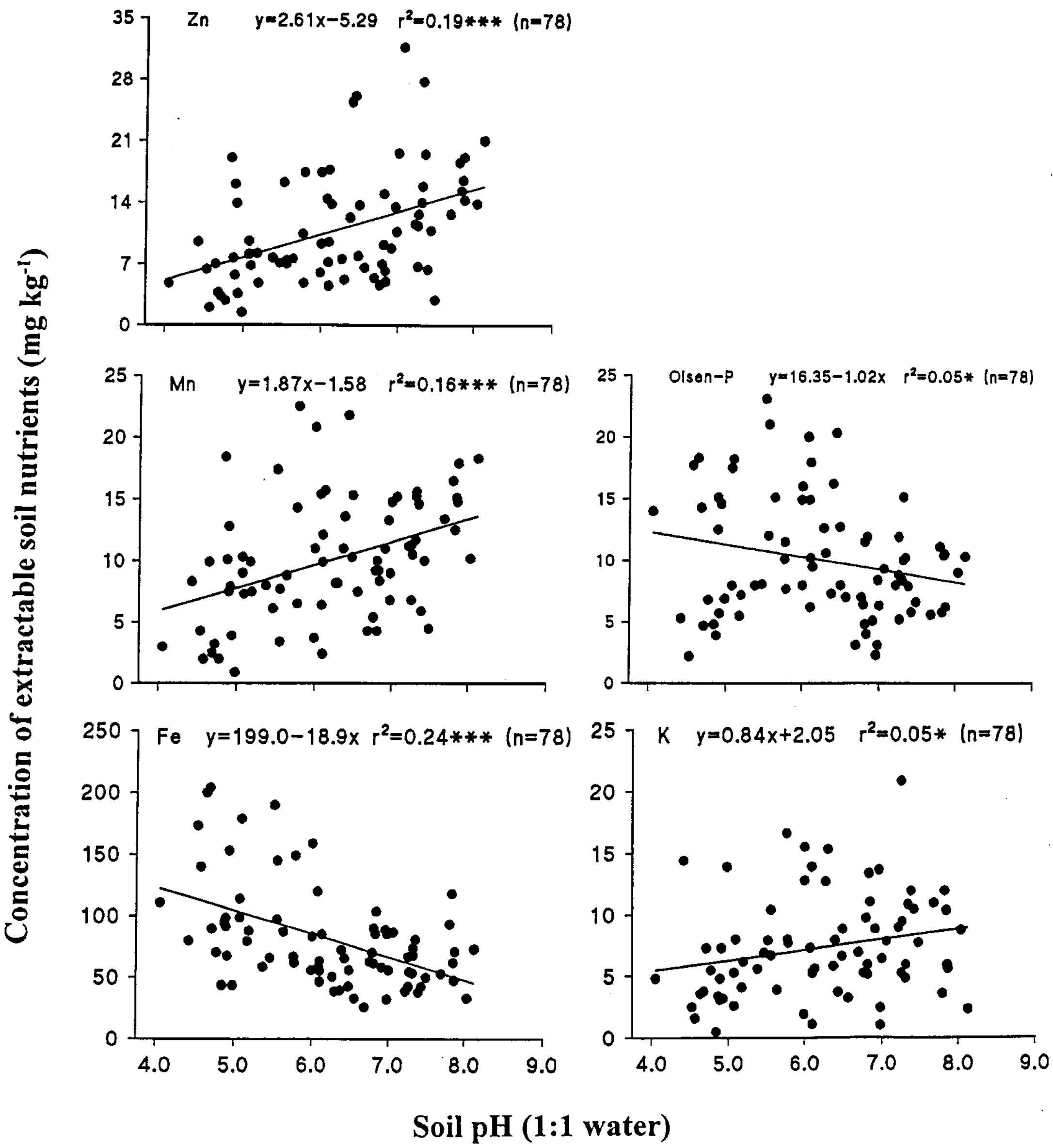

Figure 3. Effects of soil pH on extractable P, K, Fe, Zn and Mn in a Riviera fine sand under grapefruit production with various rates and sources of N fertilization.

Mn and K by 2.6, 1.87, and 0.8 mg kg^{-1}, respectively (Figure 3). In contrast, the concentration of P and Fe increased with a decrease in soil pH (Figure 3 and Table 2). The effect of soil pH on Mehlich 3 extractable Fe was the most marked among the nutrients studied, i.e., an increase of 18.9 mg Fe kg^{-1} soil for each unit decrease in soil pH (Figure 3). The fertilizer application was made using a N:P:K blend, therefore, an increase in rate of N application also resulted in an increase in P and K rates. Increases in N rate tended to lower soil pH. Therefore observed increases in the concentration of extactable P are attributable to reduced pH as well as higher rate of P application.

Concentration of mineral elements in grapefruit leaf in relation to soil pH

Leaf-tissue testing is routinely used to evaluate the nutritional status of grapefruit and orange trees (Tucker

Table 2. Correlation coefficients (*r*) between the soil pH vs. either plant nutrients in soil, in soil solution at 120 cm depth or in 6-month-old spring flush leaves of white Marsh grapefruit trees

Elements or pH[a]	Soil (n = 78)	Grapefruit leaf (n = 78)	Soil solution (n = 78)
pH(S)	0.9771 (***)[b]		0.9797 (***)
P	−0.0267 (NS)	0.2837 (*)	−0.3315 (**)
K	0.1880 (NS)	0.0692 (NS)	−0.3438 (**)
Ca		0.3930 (***)	0.4017 (***)
NO_3^- N			−0.2906 (**)
Cu	0.2351 (*)	0.2592 (*)	
Fe	−0.4926 (***)	−0.4627 (***)	
Zn	0.4393 (***)	−0.2849 (*)	
Mn	0.3756 (***)	−0.6965 (***)	
Olsen-P	−0.3283 (**)		
Mg		−0.1225 (NS)	
Na		0.2009 (NS)	
Al		−0.1883 (NS)	

[a] P, Cu, Zn, Mn and Fe in soil were extracted by Mehlich 3 method, K by 1 *M* ammonium acetate, and Olsen-P by 0.5 *M* $NaHCO_3$, pH(s) is pH measured in 1 *M* KCl. [b] Values in parentheses are probability (p) of statistical significance: $p < 0.05$, $p < 0.01$ and $p < 0.001$ represent significant, very significant and extremely significant level, respectively.

et al., 1995). Leaf P and Ca concentrations decreased by 0.03 and 2.78 g kg^{-1}, respectively, for each unit decrease in soil pH (Figure 4). The results indicate that the availability of P and Ca decreased with decreasing soil pH (Figure 4). The decrease in Ca availability at lower soil pH could be due to enhanced leaching of Ca from the soil as was reported by Bouman et al. (1995). The decrease in P availability with decreasing soil pH could be due to increased precipitation of P with Fe or Al. Leaf N, Mn and Zn concentrations were negatively ($p < 0.01$, < 0.001 and < 0.05, respectively) correlated with soil pH (Table 2). A significant negative relationship between leaf Fe concentration and soil pH ($r = -0.46$, $p < 0.001$) is in good agreement with the Mehlich 3 extractable soil Fe vs. soil pH relationship (Figures 3 and 4).

Leaching of $P0_4$–P, K and Ca in relation to soil pH

Mean concentrations of $N0_3$–N, P, K and Ca in soil solution sampled at 120 cm depth were significantly related to soil pH (Figure 5). The concentrations of $N0_3$–N, P and K in soil solution at the 120 cm depth increased by 0.67, 0.55 and 2.53 mg L^{-1} per each unit decrease in soil pH (Figure 5). The results indicate that leaching of N, P and K below the root zone was greater at lower soil pH. The decrease in soil pH was due to increased rates of N application which was also accompanied by increased rates of P and K since N application was made using N:P:K blend. Therefore, increased leaching of N, P and K, along with a decrease in soil pH, was in part, due to an increase in application of each of the nutrients. Inorganic P in the soil was mainly associated with Ca, as this soil contained a high amount of Ca in the form of exchangeable and free $CaCO_3$. With decreasing pH, less Ca was available to hold $P0_4$–P in soil and therefore, $P0_4$–P leaching was enhanced. The increased leaching of K at lower pH was probably due to the fact that H^+ is stronger than Ca^{2+} in replacing K^+ on the soil exchanger. In addition, this soil had a very low P adsorption capacity (He et al., 1998 unpublished data), and thus, increasing P rates could result in an increased P leaching below the root zone. The Ca concentration in the soil solution at the 120 cm depth was positively related to soil pH and it decreased by 20 mg L^{-1} for each unit decrease in soil pH (Figure 5 and Table 2).

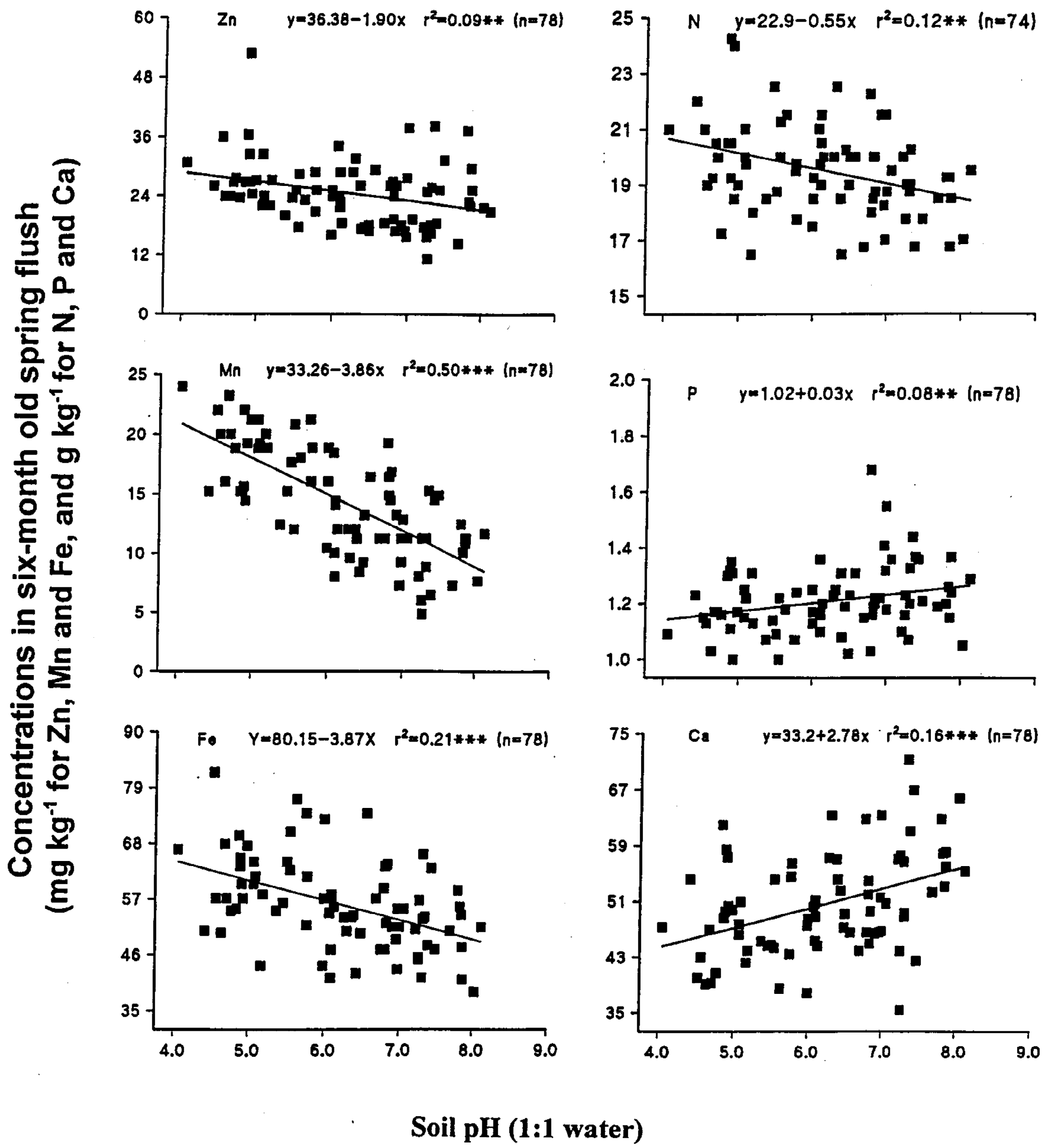

Figure 4. Effects of soil pH on concentrations of N, P, Ca, Fe, Zn and Mn in 6-month-old spring flush leaves of white Marsh grapefruit trees with various rates and sources of N fertilization.

Conclusions

Continuous application of acid-forming N fertilizer influences the soil pH, and plant availability and leaching loss of nutrients in sandy soils. In this study, soil acidification appeared to enhance the leaching of P, K and Ca. Soil acidification increased the availability of Fe and Zn to plants. This may be beneficial to citrus growth since Fe and Zn deficiencies are common problems in citrus production.

Acknowledgments

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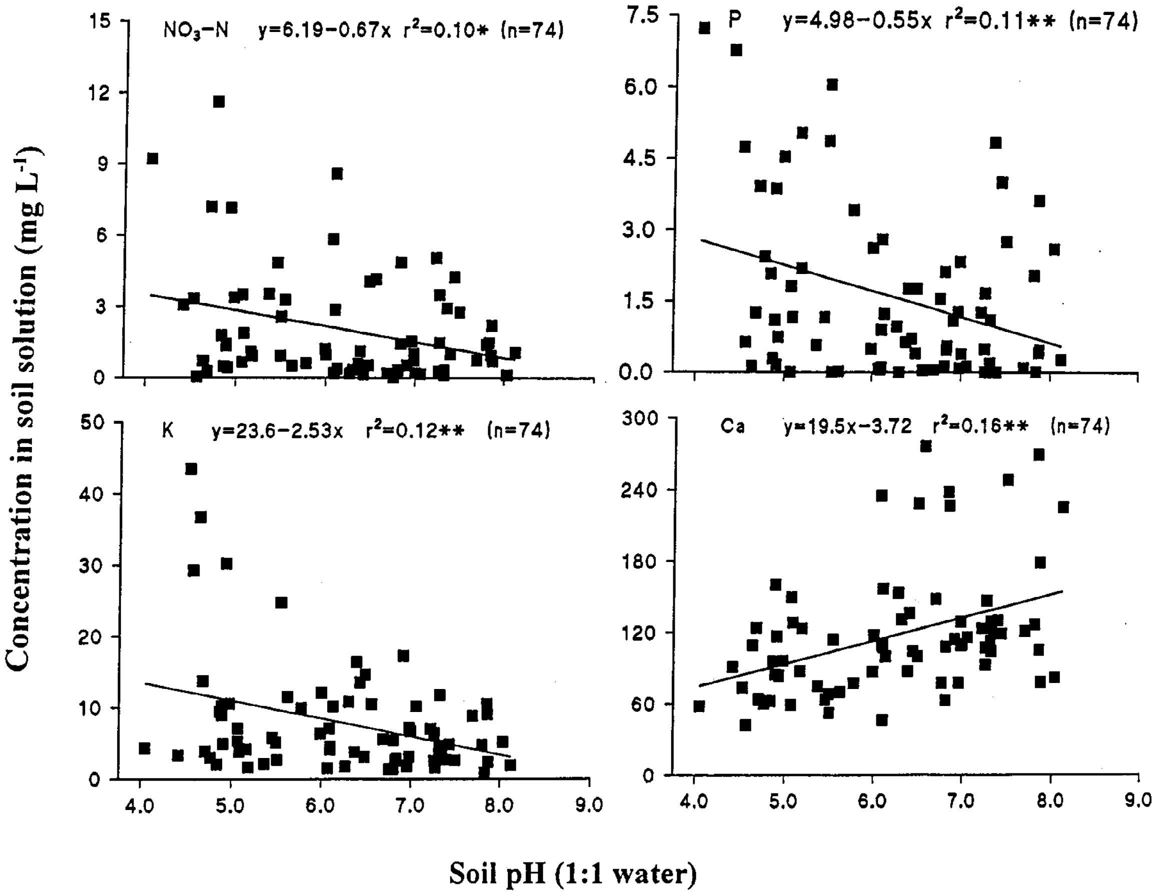

Figure 5. Effects of soil pH on NO_3–N, P, K and Ca concentration in soil solution sampled from suction lysimeters at 120 cm depth in a Riviera fine sand under white Marsh grapefruit production with various rates and sources of N fertilization.

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References

Alva A K 1992 Micronutrients status of Florida soils under citrus production. Commun. Soil Sci. Plant Anal. 23, 2493–2510.

Alva A K and Chen E Q 1995 Hydrogen ion inhibition of copper uptake by citrus seedlings. *In* Plant Soil Interactions at Low pH. Ed. R A Date. pp 631–634. Kluwer Academic Publishers, The Netherlands.

Alva A K, Graham J H and Anderson C A 1995 Soil pH and copper effects on young 'Hamlin' orange trees. Soil Sci. Soc. Am. J. 59, 481–487.

Alva A K and Paramasivam S 1998 Nitrogen management for high yield and quality of citrus in andy soils. Soil Sci. Soc. Am. J. 62, 1335–1342.

Alva A K, Paramasivam S and Graham W D 1998 Impact of different nitrogen management practice on leaf nutritional status and yield of Valencia orange trees and groundwater nitrate in a sandy Entisol. J. Environ. Qual. 27, 904–910.

Black A S 1992 Soil acidification in urine-affected and urea-affected soil. Aust. J. Soil Res. 30, 989–999.

Bouman O T, Curtin D, Campbell C A, Biederbeck V O and Ukrainetz H 1995 Soil acidification from long-term use of anhydrous ammonia and urea. Soil Sci. Soc. Am. J. 59, 1488–1494.

Calvert D V 1970 Response of 'Temple' oranges to varying rates of nitrogen, potassium, and magnesium. Proc. Fla. State Hort. Soc. 83, 10–15.

Calvert D V and Reitz H J 1963 A fertilizer rate study with Valencia oranges in the Indian River area. Proc. Fla. State Hort. Soc. 76, 13–17.

Calvert D V, Hunziker R R and Reitz H J 1962 A nitrogen source experiment with Valencia oranges on two soil types in the Indian River area. Proc. Fla. State Hort. Soc. 75, 75–82.

Dasberg S 1987 Nitrogen fertilization in citrus orchards. Plant Soil 100, 1–9.

Davies F S 1997 Literature review of research related to citrus nitrogen nutrition, fertilization, and potential groundwater pollution of citrus. A report prepared for Florida Dept. Agric. Consumer Services: Nitrogen BMP Technical Group.

Koo R C J and Reese R L 1977 Influence of nitrogen, potassium, and irrigation on citrus fruit quality. Proc. Int. Soc. Citriculture 1, 34–38.

Mehlich A 1984 Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. Commun. Soil Sci. Plant Anal. 15, 1409–1416.

Neilsen G H, Parachomchuk P, Hogue E J, Wolk W D and Lau O L 1994 Response of apple-trees to fertigation-induced soil acidification. Can. J. Plant Sci. 74, 347–351.

Olsen S R and Sommers L E 1982 Phosphorus. *In* Methods of Soil Analysis, Part 2, 2nd ed Eds. A L Page, R H Miller and D R Keeney. pp 403–430. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Parachomchuk P, Neilsen G H and Hogue E J 1993 Effect of drip fertigation of NH_4^-N and P on soil pH and cation leaching. Can. J. Soil Sci. 73, 157–164.

Ramos C 1996 Effect of agricultural practices on the nitrogen losses to the environment. Fert. Res. 43, 183–189.

SAS Institute Inc. 1996 The SAS System–Release 6.12. Cary, NC.

Tachibana N, Yoshikawa S and Ikeda K 1995 Influences of heavy application of nitrogen on soil acidification and root growth in tea fields. Japanese J. Crop Sci. 64, 5 16–522.

Tao O 1993 Soil micronutrients and citrus growth. Pedosphere 3, 341–347.

Tucker D P H, Alva A K, Jackson L K and Wheaton T A 1995 Nutrition of Florida Citrus Trees. Extension Bulletin SP 169, p 41. Univ. of Florida, Coop. Ext. Service, Gainesville, FL.

Wallace A 1994 Soil acidification from use of too much fertilizer. Commun. Soil Sci. Plant Anal. 25, 87–92.

Zhang M, Alva A K, Li Y C and Calvert D V 1996 Root distribution of grapefruit trees under dry granular broadcast vs. fertigation method. Plant Soil 183, 79–84.

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