Acidification of Calcareous Soils Improves Zinc Absorption of Pecan Trees

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Abstract. Acidification of < 1% of the effective root zone of a mature pecan tree (Carya illinoinensis (Wanghnh.) C. Koch) significantly increased uptake of Zn into the tree and maintained elevated Zn in leaves for 9 years. Sulfuric acid and ZnSO₄ applied in a shallow trench, lowered soil pH to a depth of 60 cm and increased volubility of Zn in the acid band. Large concentrations of CaSO₄ were formed. Laboratory tests confirmed the movement and volubility of Zn in soils under conditions similar to those in the field. Tree roots did not grow into the acidified band, presumably due to high salinity, but proliferated extensively at the interface of the acidified band and calcareous soil.

Micronutrient deficiencies commonly are found in plants on calcareous soils and usually are corrected by foliar applications. Zinc deficiency of pecan is common in the southwestern United States, and foliar application of Zn to large trees requires expensive equipment and is labor-intensive.

It is difficult to correct Zn shortages with soil fertilization because Zn precipitates rapidly in calcareous soils (Sharpless et al., 1969; Stewart and Leonard, 1963; Shuman, 1975). Zinc is more available to plants and readily absorbed from acidic soils (Miyamoto et al., 1975; Wallace and Mueller, 1978; Melton et al., 1973; Stewart and Leonard, 1963).

It is neither physically nor economically feasible to acidify an entire soil profile. Because plants require low micronutrient concentrations, an increased availability in a small soil zone can often satisfy the plant’s need (Miyamoto et al., 1975; Wallace and Mueller, 1978). A small band of H₂SO₄ applied near the roots of an annual crop growing in a calcareous soil has eliminated micronutrient deficiencies (Lindsay and Norvell, 1978; Wallace and Mueller, 1978). Acids or acid-forming materials, such as elemental S (Miyamoto et al., 1975), are often used to reduce soil pH because they are inexpensive and abundant. Sulfuric acid is more effective, but transport costs and hazards limit its widespread popularity. Yearly applications of acid are required in annual crops because the acidified band is destroyed by tillage. However, under minimum or no-tillage situations, such as found in orchards, a long-term benefit might be achieved from a single application.

There is little information on the efficacy of a single application of acid to increase micronutrient availability over several years under low-tillage orchard conditions. It is possible that infrequent small booster applications of acid might be required to maintain the desired effect. The objectives of this study were to determine 1) the chemical changes in a calcareous soil treated with H₂SO₄, 2) the mobility of Zn in calcareous and acidified soil, 3) the persistence of pH change in small bands, and 4) whether increased availability of Zn in a small root area is sufficient to increase the Zn concentration in the tree.

Materials and Methods

Laboratory experiments. Laboratory tests were run to determine the nature of Zn movement in calcareous and acids soils, and to determine the best application methods under field conditions. The effect of soil pH on soluble, exchangeable, and precipitated Zn was determined by establishing pH regimes at 4, 5, 6, 7, and 8. Duplicate Harkey silty clay loam (coarse, silty, mixed (calcareous), thermic, Typic Torrifuvents) samples were developed by adding H₂SO₄ until the pH of soil solution stabilized for 2 hr. Zinc was mixed with the soils (1000 μg Zn/g of soil) of each pH regime, and all treatments were replicated four times. Samples were shaken for 2 hr, then one sample was extracted with water, the other with DTPA (extracts freely soluble, exchangeable, and some precipitated Zn) (Lindsay and Newell, 1978; Black et al., 1965). Zinc extraction with DTPA correlates well with plant root extractions. Both extracts were filtered and Zn determined by atomic absorption spectrophotometry.

A second study was designed to determine Zn volubility and mobility in a calcareous (pH 7.7) or acidified soil (pH 5.0). Harkey samples of either 1000 or 2000 g of soil (10 or 20 cm deep, respectively) were placed in 10-cm-diameter plexiglass columns on top of 2.5 cm of coarse sand. Several treatments, replicated four times in a randomized complete block design, were established as outlined in Table 1. Each column was leached 10 times, each time with 500 ml of deionized water, or until no Zn was detected in the leachate. For treatment 7 only, a concentrated solution of CaCl₂ (36 g, a quantity equal to four times the cation exchange capacity of the Harkey soil) was added to the column surface after seven leachings and subsequently leached five more times with water. The CaCl₂ was added to remove

| Treatment | Quantity (g) | Zn application method | Zn recovered in leachate (%) |
|-----------|-------------|-----------------------|-----------------------------|
| 1         | 4           | 2000(–)               | Surface                      |
| 2         | 20          | 1000(–)               | Surface                      |
| 3         | 20          | 1000(–)               | Mixture                      |
| 4         | 20          | 1000(+ )              | Surface                      |
| 5         | 20          | 1000(+ )              | Mixture                      |
| 6         | 20          | 750(+)                | Mixture                      |
| 7         | 20          | 2000(–)               | Surface                      |

(1) Native calcareous soil, pH 7.7. (2) Native calcareous soil adjusted to pH 5.4 with H₂SO₄.
(1) All Zn broadcast on surface or homogeneously mixed with soil.
(1) Mean separation by Duncan’s multiple range test, P = 0.01.
(1) Zinc mixed with 750 g acidified soil placed on top of 250 g untreated calcareous soil.
(1) After seven leachings, CaCl₂, applied to surface and leached seven more times with deionized water.
all Zn from the exchange sites. Leachates were analyzed for Zn using atomic absorption spectrophotometry. Data were analyzed using analysis of variance (ANOVA), Duncan’s multiple range test, and regression analysis.

Field experiments. We established plots in 1979 in a 15-year-old commercial pecan orchard (‘Western’ on ‘Riverside’ rootstock), planted on Harkey soil (same as the laboratory experiments), in the lower El Paso Valley, Texas. The trees, spaced 10 x 10 m, were irrigated eight times per season with 150 mm of water at each irrigation. Water was from the Rio Grande river [600 mg liter\(^{-1}\) total salt (1.0 dS m\(^{-1}\))]. Nitrogen (11 g m\(^{-2}\)) was added annually at budbreak. The trees had been sprayed using atomic absorption spectrophotometry. Data were analyzed of water at each irrigation. Water was from the Rio Grande river

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Two-tree plots (bordered by at least one tree in all directions) were treated as follows: 1) a one-time soil application of ZnSO\(_4\) (9 kg/tree) uniformly applied in V-shaped trenches 15 cm deep, 15 cm wide at the top, and 7 m long on two sides of the tree and 3 m from the tree trunk; 2) a one-time soil application of ZnSO\(_4\), (9 kg/tree, as in treatment 1) plus 113 liter H\(_2\)SO\(_4\) (36 %) uniformly applied in the trenches; and 3) control, no soil Zn treatments (Fig. 1). None of the treatments received foliar applications of Zn. Each treatment was replicated five times in a randomized complete block and data were analyzed by ANOVA and means separated using Duncan’s multiple range test.

Soil samples were taken each of the four years after treatment. Soil increments were taken in 15-cm depth layers to a depth of 60 cm (Fig. 1). They were sampled identically the second year, except to a depth of 120 cm. An undisturbed part of the treatment trench at 15-cm increments, two on each side of a center point in the trench. Samples from all field sampling sites were analyzed selectively for pH (1 soil : 1 water), DTPA-extractable Zn (Lindsay and Norvell, 1978), total (per-

Fig. 1. Design used to apply treatments and take soil samples in the orchard.

1955). DTPA extracted 80% of the applied Zn at pH 4, and 97% at pH 7. Most of the added Zn was in water-soluble, lightly precipitated, or exchangeable forms, except at pH 4, where 20% was not extractable.

Only a small amount of Zn was leached from the soil when Zn was broadcast on the surface of a calcareous soil (Table 1). There was more recovery (23%) when Zn (20 g) moved through a 1000-g (10-cm) soil than when 4 g moved through 2000 g (20 cm) (0.8%). Leachate from a calcareous soil to which Zn had been uniformly mixed (treatment 3) contained nearly twice as much of the applied Zn as when Zn had been applied to the surface (treatment 2) (Table 1). About two-thirds of the Zn was extracted from an acidified soil where it had been placed on the surface compared to the one-third where it had been uniformly mixed. Significant amounts of CaSO\(_4\) (> 3%) were formed when H\(_2\)SO\(_4\) was added to the calcareous soil.

Little Zn was found in the first seven leachings with water when 20 g of Zn was applied to the soil surface (Table 3). Further leaching, after CaCl\(_2\) was added, removed more Zn, but recovery remained low. About 97% of the applied Zn was in the precipitated form.

Table 2. Effect of pH on availability of water- and DTPA-extractable Zn. Zinc was added at 1000 µg Zn/g of soil.

| pH | Water-extractable Zn | DTPA-extractable Zn |
|----|----------------------|---------------------|
|    | µg Zn/g soil         | µg Zn/g soil        |
| 4  | 394                  | 796                 |
| 5  | 231                  | 941                 |
| 6  | 162                  | 959                 |
| 7  | 81                   | 975                 |
| 8  | 12                   | 903                 |

*Mean separation by linear regression analysis, significant at P = 0.01.

*Mean separation by quadratic regression analysis, significant at P = 0.01.

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Table 3. Water-soluble and exchangeable Zn leached from soil of treatment 7 where 20 g of Zn was applied.

| Leaching number | Leached with | Zn in leachate (mg) | Percent of total Zn |
|-----------------|--------------|---------------------|---------------------|
| 1               | Water        | 0                   | 0.00                |
| 2               | Water        | 0.5                 | 0.00                |
| 3               | Water        | 0.8                 | 0.04                |
| 4               | Water        | 8.6                 | 0.04                |
| 5               | Water        | 8.6                 | 0.04                |
| 6               | Water        | 10.6                | 0.05                |
| 7               | Water        | 8.1                 | 0.04                |
| Total           |              |                     | 37.2               |

Fig. 2. Distribution of DTPA-extractable Zn in increments of soil to a depth of 120 cm for Zn alone, Zn plus acid, and control treatments 2 years after application.

Table 4. Analysis of variance for distribution of DTPA-extractable Zn in increments of soil to a depth of 120 cm for Zn alone, Zn plus acid, and control treatments 2 years after application.

| Source                        | df | Sum of squares | Mean squares | F test |
|-------------------------------|----|----------------|--------------|--------|
| Total                         | 120| 211,868        | 1,084        |        |
| Replication                   | 4  | 4,337          | 1,084        |        |
| Zinc treatment (A)            | 2  | 35,517         | 17,758       | 27.0** |
| Error (a)                     | 8  | 5262           | 658          |        |
| Soil depth (B)                | 7  | 45,993         | 6,570        | 6.8**  |
| A x B                         | 14 | 40,069         | 2,862        | 3.0**  |
| Error (b)                     | 84 | 80,691         | 961          |        |

Table 5. Distribution of DTPA-extractable Zn in and around the field treatment band the 4th year following treatment. Each value is a mean of five replications.

| Treatment | Horizontal distance from treatment band (cm) | Zinc (mg·g\(^{-1}\) soil) |
|-----------|-----------------------------------------------|---------------------------|
| 3-4-3     | 30-15                                        | 29 b                      |
|           | 15-0                                          | 214 a                     |
|           | 0-15                                          | 227 a                     |
|           | 15-30                                         | 42 a                      |
|           | Sum                                           | 512 a                     |
|           | Zn plus H\(_2\)SO\(_4\)                     | 62 a                      |
|           |                                               | 47 b                      |
|           |                                               | 39 b                      |
|           |                                               | 77 a                      |
|           |                                               | 225 b                     |
|            | Control                                       | 5 b                       |
|            |                                               | 5 b                       |
|            |                                               | 5 b                       |
|            |                                               | 20 c                      |

Table 6. Concentration of Zn in leaves of pecan trees from samples taken in mid-July at time intervals after treatment.

| Years after treatment | Treatment | Zinc (mg·g\(^{-1}\) dry wt) |
|-----------------------|-----------|-----------------------------|
| 3                     | Control   | 74 a                        |
|                       | Zinc      | 95 a                        |
|                       | Zinc plus acid | 101 a                  |
| 4                     | Control   | 39 b                        |
|                       | Zinc      | 39 b                        |
|                       | Zinc plus acid | 54 a                  |
| 9                     | Control   | 45 c                        |
|                       | Zinc      | 56 b                        |
|                       | Zinc plus acid | 68 a                  |

Leaf Zn concentration of the Zn plus acid treatment was significantly higher in the 4th and 9th years compared to no Zn application or Zn only (Table 6). Root growth proliferated at the interface of the acid band and the calcareous soil. This proliferation was not visible until the 3rd year after treatment, but was still observed 9 years after treatment. Nut yield and weight and percentage kernel were unaffected by treatment.

Discussion

The laboratory tests showed that a larger amount of Zn moved through the profile with leachate when mixed with a calcareous soil than when broadcast on the surface (Table 1). Zinc sulfate at high concentration has a pH of 5.3 and is water-soluble (Table 2). However, as the ZnSO\(_4\) migrates through the soil and the concentration decreases, pH of the environment increases and Zn precipitates. This relationship explains why a much greater percentage of Zn was recovered when it was applied in high concentration (Table 1). The precipitation is the primary reason for the immobility and unavailability of exogenous ZnSO\(_4\) in a calcareous soil.

The chemical fate of Zn in an acid soil is quite different. Here it is more water-soluble and the mobility depends on how it was applied. Zinc applied on the surface was more mobile than when mixed in an acid soil (Table 1). The Zn broadcast on the surface...
probably moved through the profile in mass flow down macro pores (Fenn and Escarzaga, 1977; Priebe and Blackmer, 1989). The Zn mixed with the soil was forced into micropores, where it maintained a closer contact with soil colloids and, therefore, was more susceptible to attachment or precipitation.

The Zn moved more rapidly and completely in the acid soil than in the calcareous soil, but the difference was not as great as one might expect (Table 1). Zinc sulfate (pH 5.3) reacts with CaCO₃ and the soil silicates to form ZnCO₃–ZnSiO₃ precipitates that are highly insoluble (Elgabaly, 1950, Lindsay, 1979). Highly insoluble precipitates form in calcareous soils, but this may take longer than the 2-hr duration of the laboratory pH experiments. Had the time interval been several days, the amount of Zn recovered would have been lower.

Precipitates in the acid soil environment also affect the rate of Zn movement. Sulfuric acid reacts with the calcareous soil to form CaSO₄ in our experiments. Calcium sulfate is more soluble than CaCO₃, and the higher available amounts probably competed with Zn for cation exchange sites on the soil colloids. Much of the nonexchangeable Zn probably precipitated or was leached. This may have been an additional reason why there was greater Zn movement when it was applied to the surface (less potential exchange and precipitation) than when mixed into an acid soil.

The DPTA-extractable Zn was greater than water extractable Zn (Table 2). Movement of soluble Zn in an acid soil will cause redistribution into a larger soil volume, where it will contact more soil colloids and roots. Plants can absorb soluble, exchangeable, and precipitated forms of Zn, depending on the proximity to roots (Stewart and Leonard, 1963). Roots in contact with precipitated Zn can shift the equilibrium toward dissociation because of acidity produced by uptake.

Based on the laboratory results, we chose the best method of Zn application in the field. We placed the Zn in high concentration cm top of the acid placement site (Table 1) and in close proximity to the roots (15 cm deep). The Zn in acid soil moved farther both vertically (Table 4) and horizontally (Table 5). The pH of the calcareous soil to which Zn alone was added did not change, despite the low pH of ZnSO₄. The relative soil volume where Zn was more available in the acid environment was much greater than in the calcareous soil.

Roots were destroyed in the immediate proximity of the acid application. They grew back in 2 years and proliferated profusely at the interface of the acidified/calcareous zone. They did not reenter the acid zone, probably due to the salinity generated by the reactions. The high concentration of CaSO₄ produced by H₂SO₄ was probably deleterious. We believe that the root proliferation near the acid band favored significant uptake of Zn (Table 6).

Neither fruit yield per tree nor nut quality were changed by increased Zn uptake. The Zn concentration in the untreated trees must have been above the threshold deficiency level, which is postulated to be 40 ppm or lower (Worley et al., 1972; Sparks and Payne, 1982). Although pecan trees in calcareous soils of the southwestern United States can suffer from severe Zn deficiency, we postulate that the repeated annual foliar applications created accumulation in storage organs that provided reserves for several years.

Zonal acidification in a calcareous soil increased leaf Zn concentration of pecan trees for up to 9 years. The treatment mechanism is relatively simple and sulfuric acid is relatively inexpensive. If convenient means of hauling and applying the acid are available, this offers a considerable cost savings to the pecan growers accustomed to several foliar applications each year.

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