The Role of Chelated Nutrients in Pecan Production

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Soil pH

Arid region soils have high pH’s

Soil pH is low in high rainfall areas

- pH < 5.0
- 5.0 to 5.5
- 5.5 to 6.0
- 6.0 to 6.5
- 6.5 to 7.0
- 7.0 to 7.5
- 7.5 to 8.0
- > 8.0
The metal micronutrients (Cu, Fe, Mn, Ni, Zn) are most available in low pH soils, least available in alkaline soils.

This is a log scale. Each unit represents a 10-fold change of availability.
These nutrients can pair with CHELATES.
What is a Chelate?

- Cage-like chelate molecules bind metal ions and protect them from fixation by carbonates and other soil minerals.
- The only plant nutrients that can combine with chelates are: calcium, copper, iron, magnesium, manganese, nickel, and zinc.
- Chelation increases soil solution metal concentrations and therefore plant availability.

Metal ion + Chelate = Chelate-metal complex
The metal-chelate complex is soluble, can move to the root, and release the metal ion for root uptake.

The chelate can be re-used, but other soil cations (like calcium) can also compete for chelates.
## Synthetic chelates used in agriculture

<table>
<thead>
<tr>
<th>Chelate</th>
<th>Chemical Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTPA</td>
<td>Diethylenetriaminepentaacetic acid</td>
</tr>
<tr>
<td>EDDHA</td>
<td>Ethylenediamine-$N,N'$-bis(2-hydroxyphenylacetic acid)</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic acid</td>
</tr>
<tr>
<td>HBED</td>
<td>$N, N$-bis (2-hydroxybenzyl) ethylenediamine-$N,N$-diacetic acid</td>
</tr>
<tr>
<td>HEDTA</td>
<td>Hydroxyethylethyleneiminetriacetic acid</td>
</tr>
</tbody>
</table>

![Chemical structures](image-url)
Some other important chelates

Hemoglobin

Chlorophyll
Natural iron chelates

- Bacteria and fungi can produce Fe chelates (siderophores)
- When iron stressed, grasses can produce Fe chelates (phytosiderophores)
In alkaline soils, chelated micronutrient fertilizers can greatly increase nutrient availability and uptake relative to un-chelated sources.

Iron uptake in plants fertilized with un-chelated FeSO₄ versus chelated FeEDDHA
• Trees were treated with Zn-EDTA or ZnSO₄ once at the beginning of the study
• Zn-EDTA elevated leaf zinc; ZnSO₄ did not
• Effect of Zn-EDTA was gone in the second year
Some chelates are more effective than others.

Effectiveness depends on:

- Characteristics of the chelate
- Stability of the metal ion-chelate complex
- Soil pH
We can measure stability of chelate-metal complexes. This table shows chelate-metal ion formation constants (units are log K). A higher formation constant relates to greater chelate-metal stability.

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>Citric acid</th>
<th>DTPA</th>
<th>EDDHA</th>
<th>EDTA</th>
<th>HBED</th>
<th>HEDTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$</td>
<td>3.5</td>
<td>6.1</td>
<td>0.2</td>
<td>10.7</td>
<td>0.9</td>
<td>5.4</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>6.1</td>
<td>17.0</td>
<td>15.8</td>
<td>18.8</td>
<td>14.2</td>
<td>14.7</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>3.2</td>
<td>11.5</td>
<td>5.3</td>
<td>14.3</td>
<td></td>
<td>9.5</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>11.9</td>
<td>23.3</td>
<td>24.9</td>
<td>25.1</td>
<td>28.6</td>
<td>20.3</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>3.2</td>
<td></td>
<td></td>
<td>14.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>4.8</td>
<td></td>
<td></td>
<td>18.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>4.5</td>
<td>14.8</td>
<td>8.4</td>
<td>16.5</td>
<td>9.6</td>
<td>11.9</td>
</tr>
</tbody>
</table>

*Formation constant* = \[
\frac{(\text{chelate} - \text{metal complex concentration})}{(\text{metal ion concentration}) \times (\text{chelate concentration})}
\]
Effect of natural organic chelates on zinc availability

- The strength of the chelate-metal bond is too weak to maintain a metal-chelate combination in soil conditions
- Naturally-formed chelates are generally not effective as soil-applied micronutrient fertilizers in alkaline soils
Chelate effectiveness is pH-dependent

- Stability of chelate complexes changes with soil pH
- Chelates tend to be most effective in low and medium pH soils
- Some metal-chelate complexes are less affected by pH than others
- Select stable metal-chelates based on soil conditions
Only a few iron chelates are effective in alkaline soils. The most widely-used is Fe-EDDHA. Fe-HBED is relatively new on the market, and has not been well-tested in our soils.
EDTA is the preferred chelate for the other micronutrients (Cu, Mn, Zn) for soil application.

### pH stabilities of non-iron EDTA chelates in practical conditions

<table>
<thead>
<tr>
<th>Chelates</th>
<th>Acidity</th>
<th>Alkalinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn- EDTA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn-EDTA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu-EDTA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca-EDTA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg-EDTA*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

pH

- 1
- 2
- 3
- 4
- 5
- 6
- 7
- 8
- 9
- 10
Zinc chelates: EDTA vs HBED

Effects of soil applied Zn-EDTA and Zn-HBED on pecans in Artesia, NM

from Dr. Robert Flynn and Dr. Richard Heerema
**Soil vs Foliar** application of metal micronutrients

**Soil**
- Must use more expensive chelated forms
- Synthetic chelates are not certified for ‘organic’ use
- Soil applications last much longer than foliar application
- Number of applications per year can be reduced

**Foliar**
- A ‘Quick Fix’ – plants respond immediately
- Foliar sprays must be repeated frequently
- Can use inexpensive inorganic nutrient salts (sulfates, nitrates, etc.)
- Inorganic micronutrient salts can be used in ‘organic’ production
- Foliar sprays affect only foliage directly hit with droplets and must be repeated in rapidly growing plants

- Soil applied chelated zinc fertilizes all parts of the tree

Autoradiographs of $^{65}\text{Zn}$ in 12 week old pecan one day after application of a drop of ZnSO$_4$.

Autoradiograph of $^{65}\text{Zn}$ in 8 week old pecan after root placement for 96 hrs in $\frac{1}{2}$ strength Hoagland’s solution containing ZnSO$_4$. 
Foliar zinc concentrations in young pecans fertigated with Zn-EDTA

Leaf Zinc Concentration (mg/kg)

Amount of Zn-EDTA applied

- 0 lb/ac
- 2 lb/ac
- 4 lb/ac

<table>
<thead>
<tr>
<th>Year</th>
<th>0 lb/ac</th>
<th>2 lb/ac</th>
<th>4 lb/ac</th>
</tr>
</thead>
<tbody>
<tr>
<td>2011</td>
<td>14</td>
<td>18</td>
<td>22</td>
</tr>
<tr>
<td>2012</td>
<td>11</td>
<td>20</td>
<td>27</td>
</tr>
<tr>
<td>2013</td>
<td>7</td>
<td>16</td>
<td>26</td>
</tr>
<tr>
<td>2014</td>
<td>11</td>
<td>23</td>
<td>35</td>
</tr>
<tr>
<td>2015</td>
<td>9</td>
<td>17</td>
<td>24</td>
</tr>
<tr>
<td>2016</td>
<td>8</td>
<td>16</td>
<td>22</td>
</tr>
</tbody>
</table>
Zinc Concentration in Other Organs

Plant tissue zinc concentration (ppm)

- Shoot
- Root
- Kernel

- No Zinc
- 2 lb/ac zinc
- 4 lb/ac zinc
Micronutrient Fertilizers

<table>
<thead>
<tr>
<th>Micronutrient</th>
<th>Chelates</th>
<th>Sulfates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Fe-EDDHA, Fe-DTPA</td>
<td>FeSO₄, Fe₂(SO₄)₃</td>
</tr>
<tr>
<td>Manganese</td>
<td>Mn-EDTA</td>
<td>MnSO₄</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu-EDTA</td>
<td>CuSO₄</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn-EDTA, Zn-HBED</td>
<td>ZnSO₄</td>
</tr>
<tr>
<td>Appropriate use</td>
<td>Soil or foliar application</td>
<td>Only foliar application</td>
</tr>
</tbody>
</table>
Read the label to identify specific chelate used

Derived from calcium ethylenediaminetetraacetate

Derived from ferric ethylenediamine di-(o-hydroxyphenylacetate)
(FeEDDHA)

Derived from zinc ethylenediaminetetraacetate
(Zn(NH₄)₂EDTA)
Summary

• Alkaline soil conditions in southern Arizona limit availability of metal micronutrients: copper, iron, manganese, nickel, zinc

• Soil applied inorganic salts of the metal micronutrients are not very effective in alkaline soils

• Chelates protect metal micronutrients from soil reactions

• Select the proper chelate-metal combination for your conditions
  • Cu-EDTA
  • Fe-EDDHA, Fe-HBED
  • Mn-EDTA
  • Zn-EDTA, Zn-HBED
  • Organic or natural chelates will probably not be effective in our soils