Managing Manganese Toxicity in Former Sugarcane Soils on Oahu

Use of agricultural land is changing on Oahu

The closing of sugarcane production on Oahu has opened up nearly 15,000 acres of land on the North Shore and in central Oahu (Fig. 1) for other uses, mainly the production of diversified crops such as bush bean, seed corn, and watermelon. Most soils in these areas are high in manganese (Mn); levels of 1 to 4% total Mn are not uncommon (Fig. 2). For comparison, most soils on the Big Island contain less than 0.2% total Mn. This publication discusses the potential for Mn toxicity, its causes, and how to identify and manage it.

Manganese Mn

- a metallic element found worldwide
- Mn is essential for plant growth but is present in plants in very small amounts as a “micro-” or “trace” element
- some soils of Oahu are rich in Mn
- Mn availability in soils increases as soil pH decreases
- Mn is toxic to plants when too much is taken up

*References are given on p. 7.
Manganese: a nutrient or a toxicant?
Manganese can be either. At low levels, usually present as Mn\(^{2+}\) in the soil solution, Mn is a nutrient essential to all crops, but it is a toxicant when in excess. However, “low” and “excess” are relative terms. Different plant species or even varieties within a species have different degrees of tolerance of Mn toxicity. For example, beans, lettuce, potato, and roses are considered sensitive (less tolerant of Mn); carnation, cucumber, and watermelon are moderate; and field corn, rice, sugarcane, and tomato are tolerant, which explains why sugarcane had no toxicity problem when grown on these high-Mn soils. The adaptation of many other crops has yet to be tested.

Soils on Oahu after sugarcane
On the North Shore, soils classified as Oxisols of the Lahaina and Wahiawa series are intermingled at higher elevations (above 600–700 ft) with Ultisols of the Leilehua and Paaloa series (Fig. 3). The Oxisols have high Mn reserves, although the Lahaina soil, being close to the coast where rainfall is low, has a pH near neutral (pH 6.0–7.0), and Mn toxicity is not usually a problem in this soil. In contrast, the Wahiawa soil, found at higher elevations where rainfall is higher, is acidic (pH 5.0 or lower), and its potential for Mn toxicity is great (Table 1). After many years of sugarcane cultivation, both the Lahaina and Wahiawa soils are also low in calcium (Ca) and, to a lesser extent, magnesium (Mg).

In central Oahu, the soils are classified as the Molokai series (an Oxisol) or the Ewa and Waialua series (Mollisols). These soils have relatively high Mn reserves, as indicated by the levels of Mehlich 3-extractable Mn in Table 1. Again, when the pH values are relatively high, as with the Molokai series (pH 6.0) and the Ewa series (pH 7.0), the potential for Mn toxicity is not great, despite the high Mn reserves, because most of the Mn remains insoluble at those pH levels.

It is on the Wahiawa soil that Mn toxicity is likely to occur if the soil is not properly managed. In fact, you can easily see black Mn oxide nodules of 1–5 mm size in this reddish-brown soil. You can also observe violent effervescence when wetting the material with a few drops of 5–10% hydrogen peroxide (H\(_2\)O\(_2\)). (The H\(_2\)O\(_2\) test should be interpreted with caution, because H\(_2\)O\(_2\) also reacts with organic matter in the soil to give off gases, although at a lesser intensity.)

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Table 1. Soil pH and extractable manganese and aluminum in selected soils from former sugarcane land on Oahu.

<table>
<thead>
<tr>
<th>Soil series</th>
<th>Soil order</th>
<th>Soil pH (1:1 water)</th>
<th>Mehlich-3 extractable Mn (mg / kg)</th>
<th>KCl-extractable Al (mg / kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>North Shore</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lahaina</td>
<td>Oxisol</td>
<td>6.5</td>
<td>350</td>
<td>0</td>
</tr>
<tr>
<td>Leilehua</td>
<td>Ultisol</td>
<td>5.2</td>
<td>11</td>
<td>90</td>
</tr>
<tr>
<td>Paaloa</td>
<td>Ultisol</td>
<td>4.5</td>
<td>7</td>
<td>180</td>
</tr>
<tr>
<td>Wahiawa</td>
<td>Oxisol</td>
<td>4.6</td>
<td>460</td>
<td>9</td>
</tr>
<tr>
<td><strong>Central Oahu</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ewa</td>
<td>Mollisol</td>
<td>6.8</td>
<td>435</td>
<td>0</td>
</tr>
<tr>
<td>Molokai</td>
<td>Oxisol</td>
<td>6.0</td>
<td>690</td>
<td>4</td>
</tr>
<tr>
<td>Waialua</td>
<td>Mollisol</td>
<td>6.6</td>
<td>150</td>
<td>0</td>
</tr>
</tbody>
</table>
Causes of Mn toxicity

Soil acidity, or low soil pH as indicated by an abundance of hydrogen ions (H\(^+\)), can cause mineral Mn oxides to dissolve and release enough manganese ions (Mn\(^{2+}\)) into the soil solution to make the soil toxic to many plants. This is illustrated by the following chemical reaction.

\[
\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}
\]

(soluble Mn, readily available for plant uptake)

In this reaction, soluble Mn is controlled by more factors than just soil pH, but soil pH is nevertheless the major indicator of Mn availability and toxicity. In reality, each unit decrease in pH results in a 10-fold to 100-fold increase in soluble Mn, as data for the Wahiawa soil indicate (Fig. 4).

The abundance of electrons (e\(^-\)) in acidic soils also makes Mn more soluble and potentially more toxic to crops. Electrons are often provided directly by organic amendments such as animal manures, crop residues, and composts.\(^1\) Instances of Mn toxicity to lettuce and beans grown on high-Mn soils amended with animal manures have been observed even at pH 7.0.\(^3\) Electrons also can indirectly be made more available to react with Mn oxides by depriving the soil of oxygen (O\(_2\)), which is the most common and effective e\(^-\) acceptor. Oxygen deprivation occurs when the soil is flooded or becomes poorly drained. Thus, high-Mn soils should be kept well aerated to provide adequate O\(_2\), otherwise Mn toxicity may occur.

If Mn levels in the soil solution exceed the range of 0.1–0.5 mg/L, then Mn is usually harmful to most crops, except the most tolerant ones.\(^4\) In watermelon, the toxicity is so dramatic that we named it the “sudden crash” syndrome. As this name implies, the crop looks quite healthy and grows rapidly from transplanting (or seeding) to flowering, or sometimes to the early fruit-filling stage, and then the older leaves suddenly wilt, dry up, and drop in a matter of days (see p. 4). Loss of leaves reduces the plant’s ability to absorb sunlight for photosynthesis, resulting in reduced fruit set, fruit size, and quality (not sweet enough by commercial standards). See p. 6 for Mn toxicity symptoms in other crops.
Managing Mn toxicity

Liming soil to pH 5.8–6.2
We can decrease the amount of soluble Mn by increasing soil pH with lime. Adding lime as Ca(OH)₂ (hydrated lime) or CaCO₃ (finely ground limestone) to an acidic soil produces the following reactions:

\[
\text{Ca(OH)}_2 \rightarrow \text{Ca}^{2+} + 2\text{OH}^- \quad \text{in the presence of water}
\]

or

\[
\text{CaCO}_3 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{OH}^- + \text{CO}_2 \quad \text{over time}
\]

The OH⁻ produced by lime will neutralize H⁺ in the soil to form water:

\[
\text{OH}^- + \text{H}^+ \rightarrow \text{H}_2\text{O} \quad \text{water}
\]

We recommend that you lime the acidic soil to a pH level between 5.8 and 6.2 so that soluble Mn is reduced to below 0.1 mg/L in the extract of a saturated soil paste.

Lime titration curves (Fig. 5) have been constructed specifically for the Wahiawa soil using both a local lime source (Grace Pacific lime) and pure CaCO₃ (100% agricultural lime). As the two reaction equations above indicate, moisture and time are required for the correction of soil acidity. Over-liming (raising soil pH above 7.0) should be avoided because other nutrients, particularly Fe and Zn, may become less available or even deficient at high soil pH. For more information about liming acid soils of Hawaii, refer to CTAHR publication AS-1.⁵

In general, for soils high in Mn and regardless of soil pH, avoid applying organic soil amendments, practices leading to poor soil drainage, and water management that leads to flooding.

Providing adequate calcium and magnesium to the soil
Not only does lime provide OH⁻, which neutralizes H⁺ in acid soils, but it also provides Ca²⁺, as well as Mg²⁺ if dolomitic lime is used. These are essential for plant growth and can reduce Mn toxicity by competing with Mn²⁺ for plant uptake. Our research on watermelon and corn has shown that Mn toxicity is better predicted with the Mn/Ca ratio than with the absolute Mn level in leaves (see Fig. 6).⁶,⁷

The “sudden crash” syndrome
Watermelon before the appearance of the “sudden crash” syndrome.

Watermelon about five weeks after transplanting, after the “crash” caused by Mn toxicity.
Where soil pH is between 6.0 and 7.0 but soil Ca is low, a situation often encountered in the Lahaina, Molokai, and Waialua soils, we recommend that you use gypsum (CaSO$_4$·2H$_2$O) to bring the soil-test Ca level to at least 2000 mg Ca per kg soil (2000 ppm). Have the soil tested by the Agricultural Diagnostic Service Center (ADSC) at the University of Hawaii, or another laboratory, to decide what actions should be taken to correct fertility or acidity problems. For information on the recommended levels of various nutrients in soils of Hawaii and on how to take a representative soil sample, consult CTAHR publications AS-3 and AS-4.8,9

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Figure 5. Lime titration curves for the Wahiawa soil show how soil pH changes with increasing lime application, either as pure calcium carbonate or a commercial product.

Figure 6. The number of fruits per watermelon plant decreases as the amount of manganese increases relative to calcium in the leaf tissue.

\[ Y = \frac{2.135}{(1 + 0.33\times10^{-6}\exp(0.02X + 0.8\times10^{-5}X^2))} \]

\[ r^2 = 0.77 \]
Manganese in the soil solution, present mainly as manganese ions (Mn²⁺), is readily taken up by roots and transported to shoots. This ease of movement from roots to shoots explains why Mn is less toxic to roots compared with other metals present in soils, such as aluminum, which tend to concentrate in root tissues. It also explains why Mn toxicity symptoms first occur in the above-ground parts of plants, particularly in older leaves.

Mn toxicity symptoms vary with plant species and among plant tissue organs. On older leaves, Mn toxicity symptoms generally appear as small, distinct, dark-brown spots, necrotic lesions, and chlorosis of leaf edges and tips. In a typical sequence of symptom development,

- chlorotic (yellowed) areas appear on the leaves
- the areas subsequently change to dark brown spots
- the leaves desiccate (dry), and
- the leaves fall.

The small, dark brown spots are believed to contain Mn oxides and polyphenols.⁷

On young, expanding leaves, Mn toxicity symptoms are commonly known as “crinkle leaf”: the leaf cups upward, crinkles, is smaller than normal, and has chlorotic edges. The symptoms resemble those of Ca deficiency—in fact, there is evidence that “crinkle leaf” is due to Mn-induced Ca deficiency.⁷
References

*References 5, 8, and 9 can be obtained from the CTAHR website <www.ctahr.hawaii.edu/publications>, or by calling 808-956-7046, or by email to ctahrpub@hawaii.edu.

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