Manganese Toxicity in Watermelon as Affected by Lime and Compost Amended to a Hawaiian Acid Oxisol

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Abstract. Manganese (Mn) toxicity in crops is a serious problem in Hawaii, especially Kauai and Oahu, where most soils are highly weathered. To devise a management strategy to control Mn toxicity, a greenhouse experiment was conducted on an acid (pH 4.4) Oxisol (Wahiawa series) having 15 g·kg–1 total Mn. Factorial combinations of lime (0, 2, 4, and 4.0 g·kg–1 CaCO3) and two composts (made from chicken manure and from sewage sludge at 0, 5, and 10 g·kg–1) were applied to the soil, which was subsequently planted to watermelon (Citrullus lanatus Thunb. ‘Crimson Sweet’). Our preliminary results showed that: 1) liming reduced Mn extractability and phytoavailability, but the reduction in Mn per unit increase in pH was much less than predicted by theory; 2) for good watermelon growth, soluble Mn, as extracted by the saturated paste method, should be <2.0 mg·L–1 corresponding to a soil pH >5.7; 3) unlike the saturated-paste extractable Mn, the Mehlich3-extractable Mn varied less with pH in a given soil series than between soil series; 4) effects of composts on Mn toxicity varied with compost properties, especially their Ca content and pH altering capacity; and 5) the diagnostic criteria for Mn toxicity in watermelon are tentatively proposed as: leaf Mn >1000 mg·kg–1 and leaf Ca/Mn ratio (g·g–1) <25.

Manganese (Mn) is an essential plant nutrient at low levels, but is toxic when in excess (Marschner, 1995). In fact, Mn toxicity is often more common than Mn deficiency in some regions, such as the humid tropics, where most soils are highly weathered and acidic (Hue et al., 2001). This is because the solubility and availability/toxicity of soil Mn are increased many fold by low pH, and the abundance of electrons (e–) as shown below (Adams, 1981; Sparrow and Uren, 1987):

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

Acid soils with high Mn content have been found in many parts of the Hawaiian Islands, particularly on Kauai and Oahu, the two geographically oldest islands in the state. A major portion of agricultural land on Oahu consists of soils, mostly Oxisols of basaltic origin, with 10–40 g·kg–1 total Mn concentration (Fujimoto and Sherman, 1948). Such Mn concentrations are ~10× greater than the average soil Mn concentration worldwide (Kabata-Pendias and Adrian, 1995). Total soil Mn, however, only indicates the potential toxicity. Actual Mn toxicity is associated with forms that are either water soluble or easily reducible. Adams (1984) suggested a reducible (presumably NH4OH-HCl extractable) Mn range of 50–100 mg·kg–1 in soil, above which Mn toxicity would occur. To avoid Mn toxicity to soybean (Glycine max ‘Kahalii’), Hue et al. (2001) proposed to keep Mn concentrations in the saturated paste extract below 0.5 mg·L–1, which corresponds to a soil pH of 5.6 or higher. The authors also reported that some low-molecular-weight organic compounds, green manure, and biosolids added to a high-Mn soil increased Mn phytotoxicity.

Different plant species or even varieties within a species have different degrees of tolerance to Mn (El-Jaoual and Cox, 1998; Foy et al., 1988). For example, adverse effects were observed when leaf Mn (in mg·kg–1) exceeded 150 in bean (Phaseolus vulgaris), 650 in clover (Trifolium subterraneum), and 5000 in lowland rice (Oryza sativa) (Hannam and Ohki, 1988). Elamin and Wilcox (1986) reported that watermelon (Citrullus lanatus Thunb. ‘Sugar Baby’) developed Mn toxicity symptoms when leaf Mn exceeded 1300 mg·kg–1; watermelon seemed to be more tolerant of Mn toxicity than was muskmelon (Cucumis melo) (Simon et al., 1986). Also, Mn toxicity was alleviated by high levels of other nutrients, particularly Ca (Horst, 1988; Hue et al., 2001), Mg (Elamin and Wilcox, 1986; Goss et al., 1991; Lohnis, 1960), and Si (Horst and Marschner, 1978).

The objective of this study was to determine how lime and organic materials (i.e., composts) used to amend a high-Mn, acid Oxisol affect soil Mn solubility/availability and watermelon growth, which was severely damaged when planted in the unamended soil. Our preliminary goal was to find a proper management between lime and organic amendments that would increase soil productivity and vegetable production, especially watermelon. (Given the Hawaii’s remote location from other U.S. states and nations, fresh local vegetables are always important.)

Materials and Methods

Soil and amendment properties, and treatments. An acid soil with high Mn content (clayey kaolinitic isohyperthermic, Rhodic Eutrustox, Wahiawa series) was selected for the study for the following reasons: 1) the soil represents a large agricultural area in central Oahu, Hawaii, which was recently converted from sugarcane (Saccharum officinarum) to vegetables and other crops, such as coffee (Coffea arabica) and papaya (Carica papaya); and 2) several watermelon crops grown in this soil had consistently shed leaves at or just a few days after flowering, thereby yielding few and low-quality fruit (Hue et al., 1998).

In the unamended state, the soil had a pH of 4.4, 15 g·kg–1 total Mn, and 550 mg·kg–1 Mn as extracted by the Mehlich3 solution. However, the soil’s AL, as extracted by 1:1 KCl, was only 10 mg·kg–1. The X-ray diffraction data of the soil’s clay fraction showed kaolinite and...
gibbsite as the major mineral phases, and δ-MnO₂ (either vernadite or birnessite) was the predominant Mn oxide mineral. The lime titration curve (Fig. 1) of the soil showed that 2.0 and 4.0 g·kg⁻¹ CaCO₃ were required to raise the soil pH to 5.5 and 6.5, respectively.

The lime (CaCO₃) used was of reagent grade having particle size <0.1 mm in diameter (from Fisher Scientific Co., Calif.). The organic amendments consisted of a chicken manure-based (CM) compost and a sewage sludge-based (SS) compost, which were ground and screened to pass a 2-mm sieve before use. Nutrient contents of the composts are listed in Table 1.

The CaCO₃ powder applied at 0, 2.0, and 4.0 g·kg⁻¹ was thoroughly mixed with the dry soil, then deionized water was added to bring the soil to the field water holding capacity (≈280 g·kg⁻¹ H₂O). The treated soil was air dried on a lab bench for 1 week, then crushed, re-wetted, and re-incubated (until dried) for another week. Two weeks after liming, composts were applied to the soil—limed and unlimed—at 0.5, and 10 g·kg⁻¹ by mixing the screened compost with the soil and subjecting the compost-amended soils to 2 wetting-drying cycles as previously described.

The treatments were a factorial combination of lime (three rates) and two composts at three rates each. There were 15 treatments, each replicated three times, and arranged in a completely randomized design in a greenhouse (Fig. 2). Each pot (replication) contained ≈2.0 kg dry soil and received (throughly mixed with the soil) a basal fertilizer containing (in mg·kg⁻¹) 140 N as urea, 130 K and 103 P as KH₂PO₄, 48 Mg as MgSO₄, 5 Cu and 5 Zn as their sulfate salts, 1 B and 0.5 Mo.

One week after the basal fertilizer application, ≈100 g of soil was sampled from each pot for chemical analysis. Then one 2-week-old watermelon seedling, ‘Crimson Sweet’, was transplanted in each pot, and grown for 4 w until the early flowering stage.

The aboveground biomass was harvested, dried in a forced-air oven at 70 °C for 48 h, and dry weight was recorded. The dried leaf tissue was ground to pass a 0.42-mm (60 mesh) sieve for nutrient analysis.

Chemical and statistical analyses

Soil samples. Soil pH was determined by equilibrating 20 g of soil with 20 mL of deionized water and measuring with a pH meter equipped with a pair of glass/calomel electrodes. Saturated paste extracts were obtained by equilibrating 50 g of soil with enough deionized water to form a paste for 30 min, then applying a vacuum suction to collect the liquid. Calcium, Mn, and other nutrients (e.g., P, K, Mg, Zn) in the saturated paste extract were measured with an inductively coupled plasma (ICP) spectrometer. However, only Ca and Mn are reported here. Mehlich-3 extractable Mn was obtained by shaking 2.0 g soil with 25 mL of the Mehlich-3 solution (Mehlich, 1984) for 5 min and filtering through Whatmann No. 65 filter paper. Calcium and Mn were measured with the ICP as previously described.

Plant tissues. Finely ground leaf tissues (0.20 g of the 4th and 5th leaves from the growing point) were dry ashed at 500 °C for ≈4 h until the ash turned whitish gray. The residue was mixed with 5 mL of 1 M HNO₃, and heated slowly at 120 °C until dryness (this step was taken to ensure a complete dissolution of Mn oxides). The residue was subsequently re-dissolved in 20 mL of 0.1 M HCl and filtered through Whatmann No. 2 filter paper before nutrient analysis (Ca, K, Mg, Mn, P, Zn) with the ICP.

Statistics. Effects of lime and compost on soil properties and watermelon growth were
analyzed with the analysis of variance (ANOVA) and least significant difference (LSD) mean comparisons, using the SAS® software (SAS Inst., Cary, N.C.). Regression analysis (linear and nonlinear) was performed with the PLOTIT® software (Scientific Programming Enterprises, Haslett, Mich.).

Results and Discussion

Soil Mn and related properties as affected by lime and compost amendments. Soil pH increased by ≈1 unit for each 2 g kg⁻¹ CaCO₃ addition (Fig. 2A). The increase agreed well with the lime titration curve (Fig. 1). More interestingly, at each lime level, the CM compost raised soil pH ≈0.2–0.4 units whereas the SS compost slightly lowered soil pH (Fig. 2A). The differential effect on soil pH of the composts was likely a result of the higher liming potential of the CM compost than the SS compost as reflected by the former’s higher total Ca content (Table 1) and high Ca concentration in the saturated paste extract (Fig. 2B).

Soluble Mn clearly decreased with increasing pH (Fig. 2C). The decrease, however, was not as fast as would be predicted by theory. In theory (Havlin et al., 1999; Hue et al., 2001), if the soil system is poised (i.e., pH + pe = constant), then solution Mn should decrease by 100-fold for each unit pH increase as illustrated below:

\[ \text{Mn}^{2+} + 4 \text{OH}^- \rightleftharpoons \text{MnO}_2 \text{(solid)} + 2\text{H}^+ + 2\text{H}_2\text{O} \]

Equilibrium constant \( (K_{eq}) \) of reaction [2] can be expressed as

\[ K_{eq} = \frac{([e^-]^2 \cdot \text{H}^+)^2}{[\text{Mn}^{2+}] [\text{OH}^-]^4} \]

where \( K_w \) is the dissolution constant of water, which is \( 10^{-14} \) at 25 °C.

Thus,

\[ \log K_{eq} = 2 \log (e^-) + 4 \log (\text{H}^+) - \log (\text{Mn}^{2+}) - 4 \log K_w \]

Rearranging yields

\[ \log (\text{Mn}^{2+}) = -4 \log K_w - \log K_{eq} + 2 \log (e^-) + \log (\text{H}^+) + 2 \log (\text{H}^+) \]

or

\[ \log (\text{Mn}^{2+}) = K' - 2 \text{pH} \]

where \( K' = -4 \log K_w - \log K_{eq} + 2 \log (\text{e}^-) + \log (\text{H}^+) \)

\[ = -4 \log K_w - \log K_{eq} - 2 (\text{pe} + \text{pH}) = \text{constant} \]

Our data, however, showed that solution Mn was decreased by only ≈10 fold for each unit increase in pH (Fig. 3). This is probably because the composts would produce organic substances capable of dissolving solid Mn and keeping it in solution (chelation) regardless of pH. For example, catechol can dissolve solid Mn, then chelate soluble Mn as suggested as shown above.

Also, it should be noted that the ICP-measured Mn represents total soluble Mn, not Mn²⁺.

Although Mn concentration (and activity) in the saturated paste extract responded sensitively to soil pH changes, as illustrated by the 10- to 100-fold decrease in Mn for each pH unit increase, this parameter may not be suitable for soil testing purposes because considerable time, effort, and perhaps skills are required in its determination. Thus, an attempt was made to see if the Mehlich-3
Table 2. Mehlich3 extractable Ca and Mn (mg·kg⁻¹) and soil pH of selected Hawaiian soils as affected by the addition of 2.0 g·kg⁻¹CaCO₃.

<table>
<thead>
<tr>
<th>Soil series/order</th>
<th>pH</th>
<th>Ca (mg·kg⁻¹)</th>
<th>Mn (mg·kg⁻¹)</th>
<th>pH</th>
<th>Ca (mg·kg⁻¹)</th>
<th>Mn (mg·kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Halii/Oxisol</td>
<td>6.2</td>
<td>1710</td>
<td>4</td>
<td>7.1</td>
<td>1775</td>
<td>5</td>
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<td>2. Lahaina/Oxisol</td>
<td>6.5</td>
<td>1440</td>
<td>350</td>
<td>7.8</td>
<td>1900</td>
<td>340</td>
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<td>3. Leiluhia/Ultisol</td>
<td>5.1</td>
<td>1180</td>
<td>11</td>
<td>6.3</td>
<td>1275</td>
<td>10</td>
</tr>
<tr>
<td>4. Laualualei/Vertisol</td>
<td>7.3</td>
<td>5560</td>
<td>225</td>
<td>8.0</td>
<td>5600</td>
<td>220</td>
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<td>5. Makawii/Mollisol</td>
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<td>8.0</td>
<td>1720</td>
<td>290</td>
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<td>6. Manana/Ultisol</td>
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<td>200</td>
<td>4</td>
<td>5.5</td>
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<td>7. Molokai/Oxisol</td>
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<td>695</td>
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<td>1660</td>
<td>605</td>
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<td>8. Paola/Ultisol</td>
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<td>6.3</td>
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<td>11. Waimea/Andisol</td>
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<td>4200</td>
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<td>6.2</td>
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</table>

Fig. 5. Effects of lime and composts on dry-matter yield of (A) watermelon, (B) leaf Ca, and (C) leaf Mn. CM = chicken manure-based compost; SS = sewage sludge-based compost. Vertical T's are standard errors of the means. LSD = least significant difference.

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extract (Mehlich, 1984), which is a common extractant used by several soil testing labs to measure availability/toxicity of many plant nutrients including Mn, could detect changes in Mn with pH. The results were not encouraging, however. Although Mehlich-3-extractable Mn decreased slightly with increasing soil pH, its values varied greatly and independently of pH (Fig. 4). Soil pH only accounted for 21% of the variation in extractable Mn. To further confirm that the Mehlich-3 procedure did not extract Mn in proportion to the Mn solubility with respect to soil pH, a side experiment was conducted. The Mehlich-3 extractable Mn was measured in samples from 10 additional soil series from five different soil orders with and without 2.0 g·kg⁻¹ wired to the Mn solubility with respect to soil pH, a side experiment was conducted. The Mehlich-3 extractable Mn was measured in samples from 10 additional soil series from five different soil orders with and without 2.0 g·kg⁻¹ CaCO₃.
Watermelon dry biomass and Ca, Mn concentrations in leaves as affected by lime and compost amendments. As expected, liming improved watermelon growth significantly: from <0.5 g per pot in the unamended control to ~8.0 g per pot in the 2.0 g·kg⁻¹ CaCO₃ treatment (Fig. 5A). Liming above this rate (i.e., at 4.0 g·kg⁻¹ CaCO₃), however, did not increase the dry biomass. If leaf area and/or biomass is an early requirement for fruit weight and quality (the saleable product) then liming the unamended control, and no lime, but amended with 2 composts at 3 application rates and with lime (CaCO₃) at 3 rates, in the treatments factorially arranged. The results showed that: 1) adequate lime to raise soil pH to 5.7 or above, resulting in soluble (paste extracted) Mn <2.0 mg·L⁻¹ is essential for normal watermelon growth; 2) Mehlich 3 extracting solution is not sensitive to soluble/available Mn in a given soil at different pH levels; 3) reduced growth is expected if leaf Mn exceeds 1000 mg·kg⁻¹ in watermelon; and 4) leaf Ca/Mn ratio should be used in predicting Mn toxicity.

Although our results were preliminary, it is recommended that when watermelons are grown on high-Mn soils, lime be applied enough to attain pH >5.7, so Mn in the soil can be reduced. The use of composts on such soils is more complex: compost properties must be identified. This is because some are beneficial while others may be detrimental to the plant yield.

**Literature Cited**


