

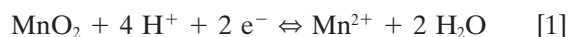
Manganese Toxicity in a Hawaiian Oxisol Affected by Soil pH and Organic Amendments

Nguyen V. Hue,* Silvio Vega, and James A. Silva

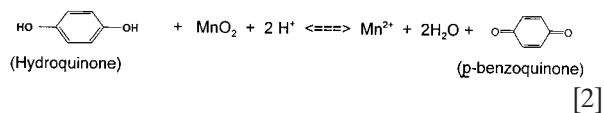
ABSTRACT

Manganese toxicity is a serious constraint to many crops grown on acid soils in Hawaii. To develop management strategies to deal with the Mn problem, four experiments were conducted. First, to study soil pH effect, a pH gradient from 4.7 (unamended) to 6.0 was established in a high-Mn Oxisol (Wahiawa series), using combinations of Ca(OH)₂ (lime) and CaSO₄ · 2H₂O (gypsum); soybean [*Glycine max* (L.) Merr. cv. Kahala] was grown as a test crop. Second, effects of Ca, and particularly SO₄, on ameliorating Mn toxicity to soybean were subsequently evaluated. Third, soil Mn solubility by organic molecules was studied in the laboratory as a function of chemical structure, pH, and equilibration time. Fourth, soybean responses to green manure and biosolids applied at 5 and 10 g kg⁻¹ to the Wahiawa soil were compared with those of the unamended control and CaCO₃ treatments. Manganese concentration in the saturated paste extract of the first experiment increased 100-fold for each pH unit decrease. A combination of gypsum and lime was more effective in correcting Mn toxicity than either amendment alone. Soybean growth was better correlated with leaf Ca/Mn ratio than with leaf Mn concentration. Increased SO₄ concentration alleviated Mn toxicity. Organic molecules or ions containing OH-OH in the ortho position or SH groups, such as catechol, tannic acid, and cysteine, were more effective in dissolving soil Mn than molecules or ions not containing these functional groups. Application of green manure and biosolids generally increased Mn toxicity.

MANGANESE (usually present as Mn²⁺ in the soil solution) is an essential nutrient that can be toxic to crops when occurring in excess (Marschner, 1995). Levels of Mn in the soil solution are controlled mainly by a soil's Mn reserve, pH, and the availability of electrons (e⁻) as illustrated by the following reaction (Adams, 1981; Sparrow and Uren, 1987).



Thus, soils with high Mn reserves may be Mn toxic when soil pH is below 6.0, a pH level at which soil Al remains virtually insoluble (Hue et al., 1987). In an electron-rich environment (reducing conditions) caused by overwatering, poor drainage, or heavy applications of organic materials, Mn toxicity can occur even at alkaline pH (Hue, 1988). Several organic molecules can dissolve solid Mn oxides via e⁻ transfer (reductive processes) (Stone and Morgan, 1984; Laha and Luthy, 1990). For example, hydroquinone can dissolve solid Mn as follows (Stone and Ulrich, 1989):



Although less widespread than Al-toxic acid soils, Mn-toxic acid soils do exist in Hawaii (Hue et al., 1998a), Brazil (R.S. Yost, personal communication, 1999), and the Philippines (Hue, 1999). For example, a major portion of agricultural land on Oahu, Hawaii, consists of soils with 10 to 40 g kg⁻¹ total Mn concentration (Fujimoto and Sherman, 1948). These soils, mostly Oxisols of basaltic origin, are often located in areas of low to moderate elevations (70–250 m above sea level) and with moderate annual rainfall (50–150 cm) (Swindale and Uehara, 1966). The total Mn contents of these Hawaii Oxisols are about 10 times greater than the average soil Mn content worldwide (Kabata-Pendias and Adriano, 1995). However, total soil Mn 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 Mn range of 50 to 100 mg kg⁻¹, above which Mn toxicity would occur. To avoid Mn toxicity, Hue et al. (1998b) proposed to keep Mn concentrations in the saturated paste extract below 0.5 mg L⁻¹. This value agrees well with the critical toxic levels of 5 to 10 μM Mn (0.27–0.55 mg L⁻¹) in nutrient solutions that contained some Si (0.75–40 mg Si L⁻¹) (Horst and Marschner, 1978). The same authors reported that Mn toxicity in bean (*Phaseolus vulgaris* L.) was observed at 0.5 μM when the nutrient solution was free of Si.

Different plant species or even varieties within a species have different degrees of tolerance to Mn (Foy et al., 1988). For example, adverse effects were observed when leaf Mn (in mg kg⁻¹) exceeded 150 in bean, 650 in clover (*Trifolium subterraneum* L.), and 5000 in lowland rice (*Oryza sativa* L.) (Hannam and Ohki, 1988). Also, Mn toxicity was alleviated by high levels of other nutrients, such as Ca (Horst, 1988), Mg (Lohnis, 1960; Goss et al., 1991), and Si (Horst and Marschner, 1978).

The objective of this study was to determine the extent to which Mn solubility and toxicity in a high-Mn Oxisol was affected by soil pH, Ca, and SO₄ sources, and by organic molecules and amendments, so that proper management strategies can be developed.

MATERIALS AND METHODS

A high-Mn soil (Wahiawa series [clayey Kaolinitic Isohyperthermic, Rhodic Eustrustox]) from central Oahu, HI, was selected for this study because several watermelon [*Citrullus lanatus* (Thunb.) Matsum. & Nakai var. *lanatus*] crops grown on this soil had failed due to severe Mn toxicity (Hue et al., 1998a). In the unamended state, the soil had a pH of 4.7, 17 g kg⁻¹ total Mn, and 540 mg kg⁻¹ Mn as extracted by the Mehlich-3 solution. Its KCl-extractable Al was only 10 mg kg⁻¹,

Abbreviations: AA, atomic absorption; EDDHA, ethylenediaminedi(*o*-hydroxy phenylacetic) acid; EDTA, ethylenediaminetetraacetic acid; ICP, inductively coupled plasma; UV, ultraviolet light.

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Table 1. Quantities of lime and gypsum added to the Wahiawa Oxisol to attain certain pH levels.

Treatment	Soil pH		Total Ca added cmol _c kg ⁻¹	Fraction of Ca from	
	Target	Measured		Ca(OH) ₂	CaSO ₄
1	4.7	4.72	0	0	0
2	4.7	4.70	0.67	0	1/3 (of #4)
3	4.7	4.69	1.33	0	2/3 (of #4)
4	5.2	5.19	2.0	3/3	0
5	4.7-5.2	5.07	2.0	2/3	1/3
6	4.7-5.2	4.85	2.0	1/3	2/3
7	≤4.7	4.66	2.0	0	3/3
8	6.0	5.96	4.0	3/3	0
9	5.2-6.0	5.48	4.0	2/3	1/3
10	5.0	5.09	4.0	1/3	2/3
11	≤4.7	4.60	4.0	0	3/3

and its zero point of net charge was pH 3.6 (Vega, 1993). The x-ray diffraction data of its clay fraction showed kaolinite and gibbsite as the major mineral phases, and δ -MnO₂ was apparently the predominant Mn oxide mineral. The lime titration curve of the soil (Hue et al., 1998a) showed that 1.0 and 2.0 g CaCO₃ kg⁻¹, which are equivalent to 2 and 4 cmol_c kg⁻¹ as Ca²⁺, were required to raise the soil pH to 5.2 and 6.0, respectively.

Experiment on Manganese Toxicity as Affected by Soil pH without Organic Inputs

Effects of Calcium Sources

Hydrated lime [Ca(OH)₂] and gypsum [CaSO₄ · 2H₂O] were added and thoroughly mixed with the soil, in various combinations, to establish the 11 treatments listed in Table 1. The experiment had three replications and was arranged in a randomized complete block design. Basal fertilizers included (in mg kg⁻¹) 140 N as urea, 130 K as KH₂PO₄, 48 Mg as MgSO₄, 5 Cu and 5 Zn as their sulfate salts, 2 B, and 0.5 Mo. After 2 wk of moist incubation, the treatments were sampled for pH and Mn determinations. Soil pH was measured in water at 1:1 soil/water ratio by weight. Soil Mn was extracted from a paste saturated for 30 min with deionized water, and measured by atomic absorption (AA) spectrophotometry. Six seeds of soybean cv. Kahala were planted to each pot of 2.0 kg soil and were thinned to three plants 1 wk later. Plants were harvested 5 wk after seeding. Dry weights of the aboveground portions were recorded, and leaves (0.250 g) were dry-ashed at 500°C for nutrient determination. Five milliliters of 1 M HNO₃ were added to the ash and heated at 120°C for ≈2 h to dryness. The residue was then dissolved in 20 mL of 0.1 M HCl and filtered through Whatman no. 42 paper. Nine plant nutrients (B, Ca, Cu, K, Mg, Mn, P, S, and Zn) in the solution were measured with an inductively coupled plasma (ICP) spectrophotometer (Thermo-Jarell Ash Atom Scan 16, Waltham, MA). However, only Ca and Mn are reported here.

Effects of Anion Sources, Especially Sulfate

Gypsum, CaCl₂, MgCl₂, and MgSO₄ · 7H₂O were added at 4 cmol_c kg⁻¹ to the acid Wahiawa soil in powder form and mixed thoroughly under dry conditions. The treated soil was wetted to the field water holding capacity (≈300 g water kg⁻¹ soil) with deionized water. The unamended soil and a limed soil treatment [4 cmol_c kg⁻¹ Ca(OH)₂] served as controls. Basal fertilizers (in mg kg⁻¹) were 140 N as urea and 130 K as KH₂PO₄. Kahala soybean was grown as a test crop at two plants per pot of 2.0 kg soil. The plants were harvested 5 wk after seeding. The experiment had three replications and was arranged in a completely randomized design.

Experiment on Manganese Toxicity as Affected by Organic Amendments

Dissolution of Soil Manganese by Selected Organic Molecules

Sixteen low-molecular-weight organic molecules (Fig. 1), referred to as organics hereafter, were evaluated for their ability to dissolve soil Mn at pH 4.5 in 0.1 M KCl solution. The soil/solution ratio was 1:100 (by weight), concentrations of the organics were 0, 25, 50, and 100 μM, and equilibration time consisted of shaking at 60 cycles min⁻¹ for 2 h. The experiment was repeated at pH 5.5 and 7.0 for catechol, citric acid, *l*-cysteine, and gallic and tannic acids only at 100 μM. Solutions of 1.0 M KOH or HCl were used to adjust the pH of the organics containing KCl solutions before the soil was added. Effect of equilibration time (0.5, 1, 2, 4, 8, 16, and 24 h) on Mn solubility by 100 μM of catechol, citric acid, *l*-cysteine, and gallic and tannic acids was also evaluated. The studied solutions were centrifuged at 12 000 g for 10 min, then the supernatants were filtered through a 0.45-μm membrane, and soluble Mn was determined with an AA spectrophotometer. Ultraviolet (UV) spectra of selected organics after reaction with soil Mn for a specified time were obtained by scanning the filtered solutions from 200 to 400 nm at 2-nm increments, using an Hewlett-Packard 8452A UV spectrophotometer (Hewlett-Packard Analytical, Palo Alto, CA) equipped with a diode array detector.

Effects of Organic Manure Additions on Manganese Phytotoxicity

Ground cowpea (*Vigna unguiculata* L.) leaves and an anaerobically digested sewage sludge (biosolids) were added to the Wahiawa soil at 5 and 10 g kg⁻¹. The cowpea green manure contained (in g kg⁻¹) 36 N, 4 P, 35 K, 15 Ca, and 4 Mg, and 63 mg Mn kg⁻¹; the sewage sludge contained (in g kg⁻¹) 53 N, 8 P, 0.1 K, 4 Ca, and 4 Mg, and 120 mg Mn kg⁻¹. Treatments with no lime (pH 4.7) or 2 g CaCO₃ kg⁻¹ (pH 6.0) served as controls. All treatments received (in mg kg⁻¹) 140 N, 200 Ca, 48 Mg, 160 S, 5 Cu, 5 Zn, 2 B, and 0.5 Mo (basal fertilizers). After 2 wk of moist (≈30 kPa tension) incubation, Kahala soybean was planted as a test crop with one plant per pot of 1.5 kg soil. Shoot dry weights were recorded 5 wk after planting. Leaf Mn, Ca, and other nutrients were measured with an ICP spectrophotometer as previously described.

Regression analysis (linear and nonlinear) was performed with the PLOTIT software (Scientific Programming Enterprises, Haslett, MI). Analysis of variance and least significant difference mean comparisons were obtained with the SAS program (SAS Institute, Cary, NC).

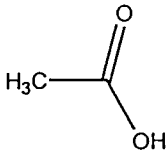
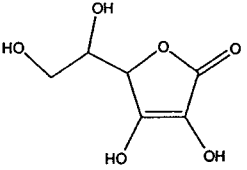
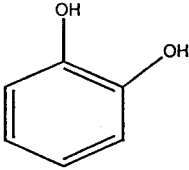
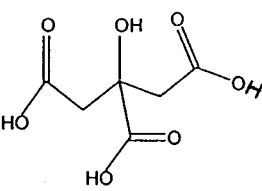
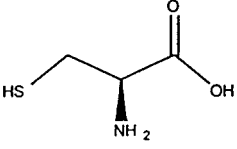
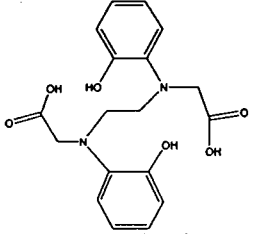
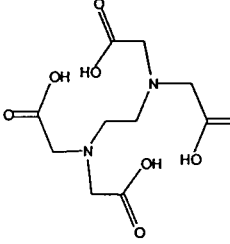
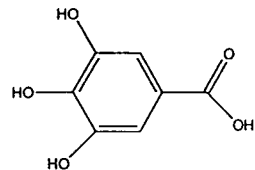
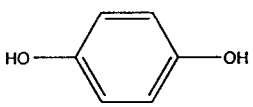
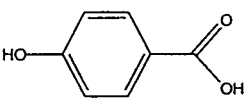
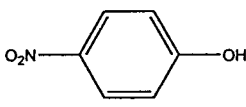
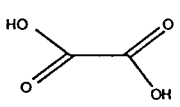
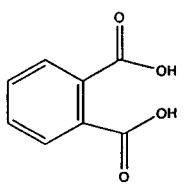
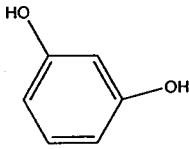
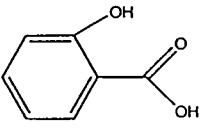
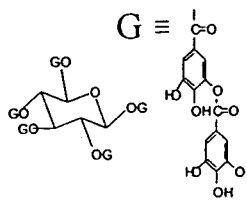
			
acetic acid	ascorbic acid	catechol	citric acid
			
l-cysteine	Ethylenediamine di(o-hydroxy phenyl)acetic acid (EDDHA)	Ethylenediamine tetraacetic acid (EDTA)	gallic acid
			
hydroquinone	p-hydroxy benzoic acid	p-nitrophenol	oxalic acid
			
phthalic acid	resorcinol	salicylic acid	tannic acid

Fig. 1. Chemical structure and common names of the 16 organic compounds used in the soil Mn dissolution study.

RESULTS AND DISCUSSION

Manganese Toxicity as Affected by Soil pH and Calcium Sources

Liming increased soil pH and decreased soluble Mn significantly. In general, each pH unit increase lowered Mn concentration in the saturated paste extract by 100-fold (Fig. 2). The result could be explained by the following expressions.



At equilibrium:

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

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

or

$$\begin{aligned} \log(\text{Mn}^{2+}) &= \log K_{\text{eq}} - 4\text{pH} - 2\text{pe} \\ &= \log K_{\text{eq}} - 2(\text{pH} + \text{pe}) - 2\text{pH} \end{aligned}$$

where K represents the reaction constant and pe is $-\log(\text{e}^-)$.

Since most soil systems are poised, that is $\text{pH} + \text{pe}$ remains constant (Bartlett, 1988; Norvell, 1988; Lindsay

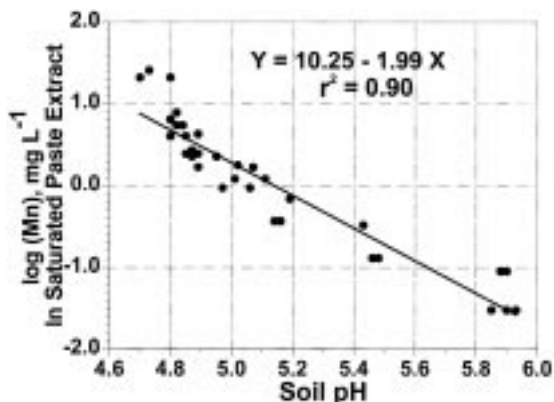


Fig. 2. Concentration of Mn in the saturated paste extract as a function of soil pH in the Wahiawa Oxisol.

and Catlett, 1998), activity (and concentration) of Mn²⁺ can be expressed as follows.

$$\log(\text{Mn}^{2+}) = \text{constant} - 2\text{pH} \quad [4]$$

More interesting, however, was the effect of gypsum, which did not change soil pH more than 0.2 unit, yet gypsum detoxified Mn effectively as demonstrated by the dry matter yields of soybean (Fig. 3). Treatments receiving a combination of 1.33 cmol_c kg⁻¹ as gypsum and 0.67 cmol_c kg⁻¹ as Ca(OH)₂ yielded as much dry matter as those receiving 4 cmol_c kg⁻¹ of gypsum or lime. There are at least three possible explanations for this effect. First, Ca²⁺ competes with Mn²⁺ for uptake, so higher Ca reduces Mn uptake. Second, high plant Ca increases plant tolerance of Mn. In fact, soybean dry weights were better correlated with leaf Ca/Mn ratio than with concentrations of Mn, and normal growth of soybean requires a Ca/Mn ratio of 50:1 or greater (Fig. 4a, 4b). Horst (1988) reported that Ca alleviates Mn toxicities in many crops. Third, sulfate reacts with Mn²⁺ to form MnSO₄⁰ ion pairs, which may not be as toxic as

Table 2. Selected chemical composition of saturated paste extracts as affected by Ca(OH)₂, CaCl₂, CaSO₄, MgCl₂, and MgSO₄ additions to the Wahiawa Oxisol.

Treatment	pH	Chemical composition					Mn ²⁺ (free)‡
		EC†	Ca	Mg	SO ₄ -S	Mn	
Control	4.41	1.8	20	10	3	33	97
Ca(OH) ₂	5.82	2.5	60	7	16	0.2	90
CaCl ₂	4.18	8.0	180	20	15	70	93
CaSO ₄	4.50	4.5	115	13	420	29	69
MgCl ₂	4.25	15.7	60	250	14	72	93
MgSO ₄	4.70	4.8	30	80	540	25	69

† EC is electrical conductivity.

‡ Estimated by the SOILSOLN program (Wolt, 1987).

Mn²⁺ (analogous to the differential toxicities of AlSO₄⁺ vs. Al³⁺) as estimated in Table 2 and reflected by increased soybean growth in the SO₄²⁻ treatments (Fig. 5). In contrast, plants in the Cl⁻ treatments were either severely stunted or died because of high soluble Mn and high salinities (Table 2).

Dissolution of Soil Manganese by Organic Molecules

Among the 16 organics studied, tannic acid, gallic acid, and catechol were most effective in dissolving soil Mn at pH 4.5 in 0.1 M KCl (Fig. 6). Hydroquinone, resorcinol, ascorbic acid, and *l*-cysteine were intermediate. Acetic, oxalic, *p*-hydroxy benzoic acid, *p*-nitrophenol, and phthalic acid dissolved less Mn than KCl alone, whereas ethylenediaminetetraacetic acid (EDTA), ethylenediaminedi(*o*-hydroxy phenylacetic) acid (ED-DHA), citric and salicylic acids dissolved slightly more Mn than KCl. Our results agree well with the relative dissolution rates of synthetic Mn oxides by 27 aromatic and nonaromatic compounds measured by Stone and Morgan (1984).

Definitive processes by which soil Mn oxidizes or-

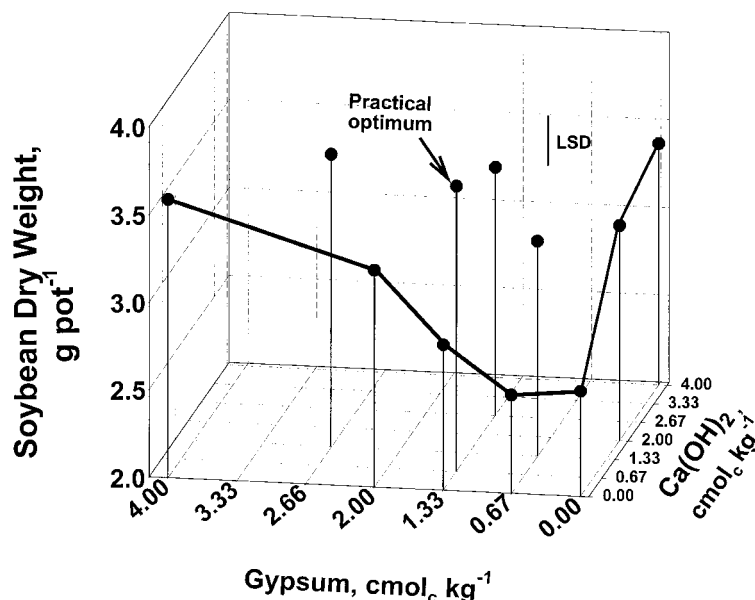


Fig. 3. Soybean cv. Kahala response to lime and gypsum applied to the Wahiawa Oxisol. LSD is the least significant difference at 0.95 probability level.

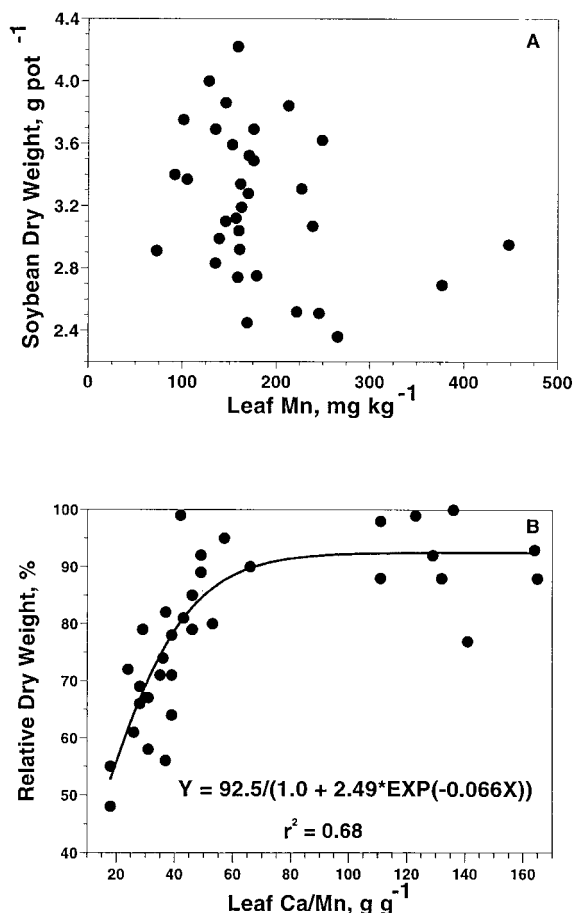


Fig. 4. Soybean shoot dry weight as a function of (A) leaf Mn and (B) leaf Ca/Mn ratio grown on the Wahiawa Oxisol.

ganic compounds, especially polyphenols, are difficult to assess. McBride (1987) cited several reasons, including (i) Fe oxides and layer silicates can also react with the organics; (ii) adsorption of H⁺ ions generated by oxidation of the organics (for example, oxidation of hydroquinone to *p*-benzoquinone produces 2 H⁺ and 2 e⁻); and (iii) preferential adsorption of the oxidation product relative to the unoxidized organic. For these reasons, pure and synthetic Mn oxides have often been

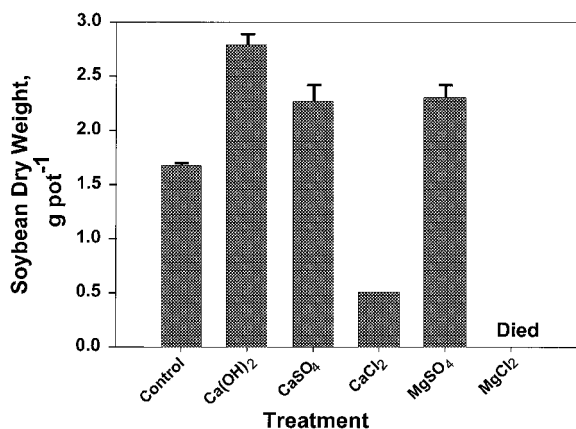


Fig. 5. Soybean response to different Ca and Mg salts (anion effects) added to the acid Wahiawa Oxisol. Standard errors of the mean are drawn on the top of bars.

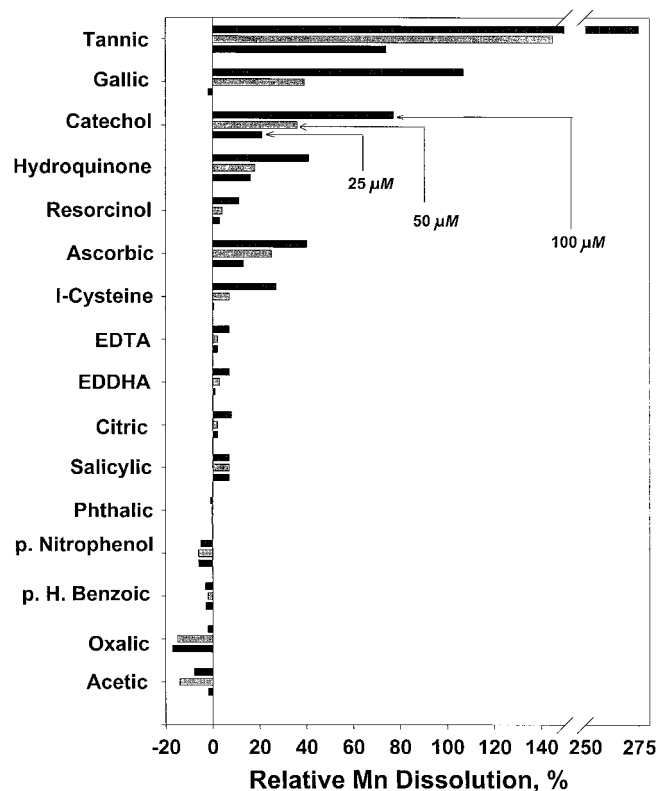


Fig. 6. Soil Mn dissolution as affected by 16 organic compounds (organics). Relative Mn dissolution = 100[(organics-extractable Mn - KCl-extractable Mn)/KCl-extractable Mn]. Experimental conditions: initial pH 4.5 in 0.1 M KCl, 2-h shaking, 80 mg Mn kg⁻¹ soil was extracted by KCl alone.

used in dissolution mechanism studies (Stone and Morgan, 1984; McBride, 1987). The proposed processes from these studies, however, are helpful in interpreting our results. According to Stone and coworkers (Stone, 1987; Stone and Morgan, 1987; Stone and Ulrich, 1989), the reductive dissolution of metal (hydr) oxide minerals involves the following steps, using Mn (III, IV) oxides (>Mn^{III}) and substituted phenols (ArOH) as an example.

- Step 1: Precursor complex formation
 $>\text{Mn}^{\text{III}} + \text{ArOH} \rightleftharpoons (>\text{Mn}^{\text{III}}, \text{ArOH})$
- Step 2: Electron transfer
 $(>\text{Mn}^{\text{III}}, \text{ArOH}) \rightleftharpoons (>\text{Mn}^{\text{II}}, \text{ArO}^{\cdot}) + \text{H}^+$
- Step 3: (a) Release of oxidized organic product (phenoxy radical)
 $(>\text{Mn}^{\text{II}}, \text{ArO}^{\cdot}) \rightleftharpoons >\text{Mn}^{\text{II}} + \text{ArO}^{\cdot}$
 (b) Coupling and further oxidation
 $\text{ArO}^{\cdot} + \text{ArO}^{\cdot} \Rightarrow \text{quinones, dimers, and polymeric oxidation products}$
- Step 4: Release of reduced metal ion (>Mn^{II})
 $>\text{Mn}^{\text{II}} \rightleftharpoons \text{Mn}^{2+} + >\text{Mn}^{\text{III}}$

The precursor complex may be an inner-sphere complex (direct binding of the incoming phenols to surface metal center) or an outer-sphere complex, which contains a layer of coordinated OH⁻ or H₂O separating phenols from surface metal centers (Stone and Morgan, 1987). The surface complexes, in turn, can affect the e⁻ transfer, which depends on the concentration of reduc-

tant molecules in the aqueous phase, the density of receptor sites on the solid surface, and on the activation energy that must be exceeded before e^- can be transferred (Morrison, 1980). Steps 1 and/or 2 are deemed reaction-rate limiting (Stone and Morgan, 1987), and the existence of organic radicals has been confirmed by electron-spin resonance spectrometry (McBride, 1987). In our results, catechol and its derivatives (gallic and tannic acids) were the strongest Mn solubilizers, probably because each has at least two OH functional groups in the ortho position that can form strong surface complexes with soil Mn and/or can transfer e^- to the metal effectively. On the other hand, phenols substituted with e^- withdrawing groups (*p*-nitrophenol and *p*-hydroxy benzoic acid) cannot transfer e^- to Mn oxides easily, making them ineffective in dissolving soil Mn. Similarly, oxalic and citric acids (at pH 4.5, they are actually oxalate and citrates) are known to be adsorbed by the surfaces of Mn oxides (Stone and Morgan, 1984; McBride, 1987), but cannot transfer e^- easily to the oxides. The ineffectiveness of EDTA and EDDHA in dissolving soil Mn is not clear to us, but perhaps it is because they tend to react with Fe oxides first. Secondly, EDTA and EDDHA carry negative charge at pH 4.5 (similar to acetate, citrate, oxalate, and *p*-benzoate anions) and are rather bulky; thus, it is hard for them to approach soil Mn, mainly δ -MnO₂, which is also negatively charged at pH 4.5 (Balistreri and Murray, 1982). *L*-Cysteine, in contrast, carries a net positive charge at pH 4.5, so it can readily approach the soil particle and δ -MnO₂, which has a zero point of net charge around pH 2.0 (Balistreri and Murray, 1982). Secondly, S (a softer Lewis base than O) of the SH functional group has a stronger affinity for Mn (a relatively soft Lewis acid) than does O. These factors helped make cysteine an average Mn solubilizer among the 16 organics studied.

Depending on the relative concentrations of organics and soil Mn, during the dissolution reactions the organics themselves were also partially or completely transformed to other compounds, which was the case for hydroquinone (Stone and Morgan, 1984) and aniline (Laha and Luthy, 1990) or were polymerized/adsorbed, as for catechol (Stone and Morgan, 1984). More specifically, Fig. 7A shows the UV spectra of hydroquinone in the process of being transformed to *p*-benzoquinone by soil Mn; the two organic species coexisted in the aqueous phase as indicated by the isobestic point at 266 nm. An identical result was obtained by Stone and Morgan (1984) using synthetic Mn oxides, suggesting that their laboratory-made Mn oxides behaved not much differently from our soil Mn minerals. This agreement supports the use of their proposed dissolution processes in explaining our experimental findings. Figure 7B shows UV spectra of tannic acid, which progressively decreased in absorbance intensity as the reaction time with soil Mn increased, an indication of polymerization or adsorption (Stone and Morgan, 1984). The reactivity of these products with Mn was not investigated in this study. However, it is not unreasonable to speculate that these organics may form stable complexes with Mn²⁺ (Reed, 1986; Norvell, 1988).

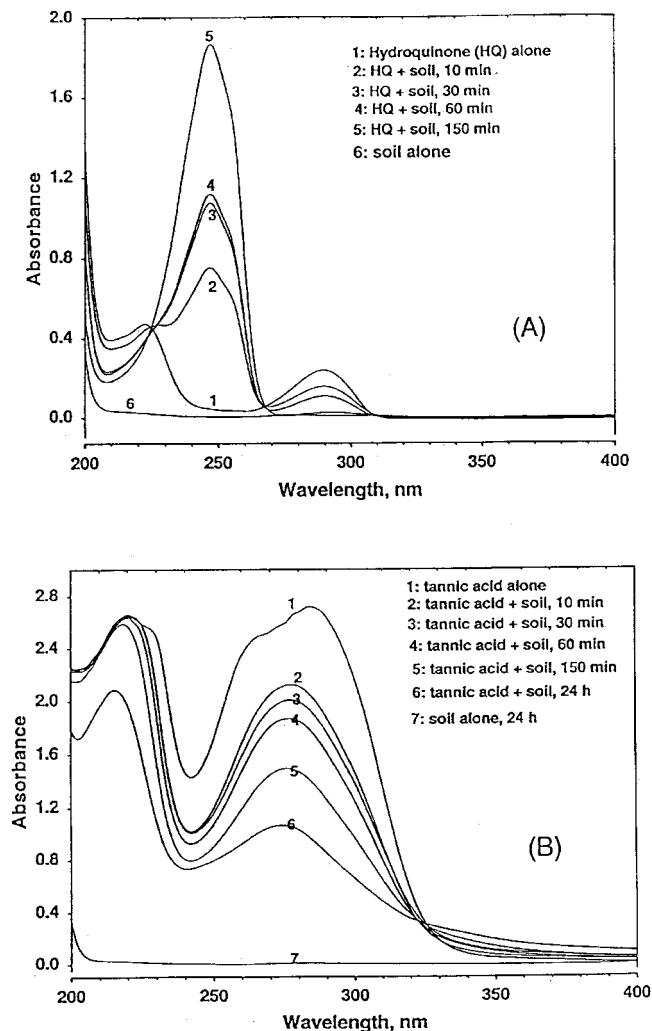


Fig. 7. Ultraviolet spectra of (A) 100 μ M hydroquinone in 0.1 M KCl, pH 5.0 with and without 1.00 g Wahiawa soil after different equilibration time intervals and filtration. Note the change from hydroquinone (curve 1) to *p*-benzoquinone (curves 2-5). In contrast, UV spectra of (B) 50 μ M tannic acid in 0.1 M KCl, pH 5.0 with and without 1.00 g Wahiawa soil showed little change in shape but a sharp decrease in absorbance intensity (an indication of polymerization or adsorption) with the reaction time.

The Mn dissolving capacities of catechol, gallic acids, and tannic acids became stronger (relative to KCl) as solution pH increased from 4.5 to 5.5 and remained constant between pH 5.5 and 7.0 (Fig. 8). Following the dissolution of solid soil Mn, these molecules apparently can maintain Mn²⁺ in solution at high pH by chelation (Pohlman and McColl, 1986; Reed, 1986). In contrast, *L*-cysteine dissolved most soil Mn at pH 5.5 relative to KCl. A similar maximum at pH 4.5 was observed for the reductive dissolution of magnetite (Fe₃O₄) by thioglycolic acid (HSCH₂COOH) (Baumgartner et al., 1982). It is thought that protonated surface sites and deprotonated thioglycolate anion form the precursor complex. The concentration of thioglycolate anion increases with increasing pH ($pK_a = 3.5$) while the concentration of protonated Fe(III) surface groups ($>Fe^{III}OH_2^+$) decreases with increasing pH. The product $[HSCH_2COO^-][>Fe^{III}OH_2^+]$ reaches a maximum value at pH

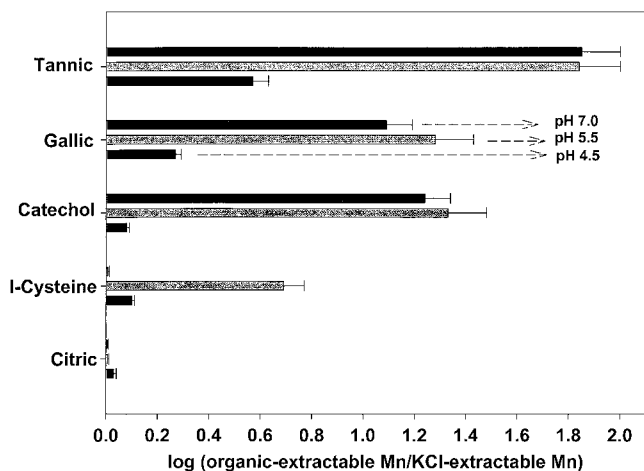


Fig. 8. Effect of five organic compounds ($100 \mu\text{M}$) on soil Mn dissolution at different initial pH. Supporting electrolyte: 0.1 M KCl , soil/solution ratio: 1:100, equilibration time: 2 h. Standard errors of the mean are drawn on the top of bars.

4.5, explaining the observed pH dependence (Baumgartner et al., 1982; Stone, 1987). By analogy, it is believed that the concentration of positively charged cysteine ions is decreasing with increasing pH from 4.5 to 5.15 (the first zero point of charge of cysteine), whereas the negative charge on $\delta\text{-MnO}_2$ is increasing with increasing pH, and the product (cysteine $\times \text{MnO}_2$) of the precursor complex reaches a maximum at pH 5.0 to 5.5.

The dissolution of soil Mn at pH 6.0 increased with increasing equilibration time for tannic acid and *l*-cysteine, whereas the Mn dissolving power of catechol and gallic acid seemed to reach a plateau at or before 16 h (Fig. 9). In contrast, equilibration time had little effect on the Mn dissolving power of citric acid. The results suggested that catechol and gallic acid, with two and three OHs, respectively, in the ortho position on the benzene ring had been completely oxidized by the soil (Mn oxides and perhaps other oxides such as Fe oxides) within 16 h. Tannic acid, with 10 times more OH-OH pairs than catechol on a molar basis, was probably still being oxidized by the soil after 24 h of equilibration. Cysteine, being a moderate MnO_2 solubilizer, may require more time to dissolve (reduce) MnO_2 , and likely transforms itself into cystine (Clark, 1960). As for citric acid, the activation energy required for e^- transfer from citrate to Mn oxides might be too high, making equilibration time unrelated to Mn dissolution.

Manganese Phytotoxicity as Affected by Organic Amendments

Soybean growth was significantly decreased by additions of both cowpea green manure and biosolids relative to the control (Fig. 10). The higher the amendment rate, the poorer the growth. In contrast, the lime treatment doubled the dry-matter yield and lowered leaf Mn concentration nearly 10-fold (Fig. 10). It is likely that organic amendments created a strong reducing environment by (i) depleting O_2 supply through intense microbial activities and (ii) producing organics that can dissolve and maintain a high level of Mn in solution (Hue,

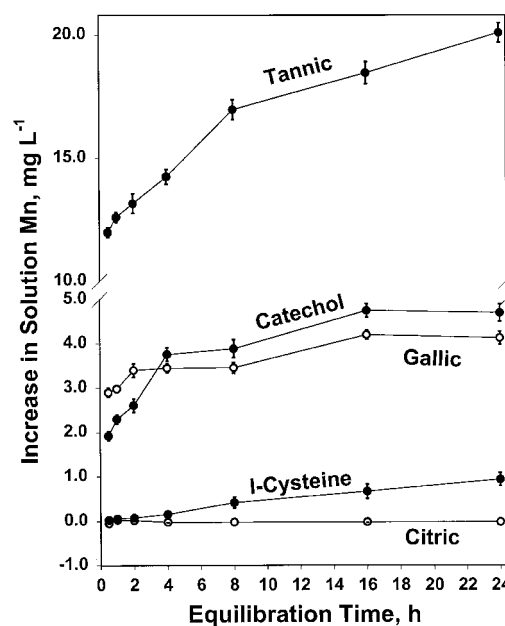


Fig. 9. Soil Mn dissolution by five organic compounds ($100 \mu\text{M}$) as a function of equilibration time. Supporting electrolyte: 0.1 M KCl , initial pH 6.0, 1:100 soil/solution ratio. Standard errors of the mean are drawn as vertical bars.

1988). These results agree with those reported by Sherman and Fujimoto (1946) and Hue and coworkers (Hue, 1988; Vega et al., 1992; Hue and Ranjith, 1994).

SUMMARY AND CONCLUSIONS

Manganese toxicity is a problem in many acid soils of Hawaii. The problem is intensified by low soil pH (<5.6), low available Ca, and organic amendments. Specifically, Mn activity (and concentration) in solution was increased 100-fold for each pH unit decrease, and a combination of gypsum and lime was more effective (in terms of total Ca added) in correcting Mn toxicity than either amendment alone. Manganese toxicity was better correlated with leaf Ca/Mn ratio than with leaf Mn con-

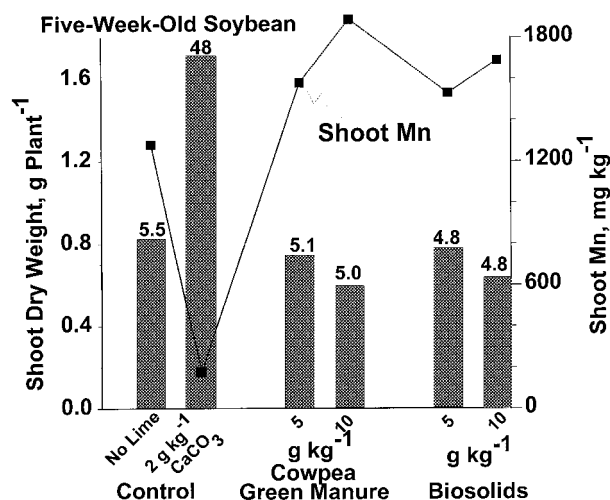


Fig. 10. Soybean shoot dry weight and shoot Mn contents as affected by CaCO_3 , cowpea green manure, and biosolid additions. Numbers on the top of bars are leaf Ca/Mn ratios.

centration. Catechol and its derivatives, such as gallic and tannic acids, and SH-containing organics were quite effective in dissolving soil Mn and in keeping Mn in solution, particularly at near neutral pH. Organic manures aggravated Mn toxicity, presumably by increasing Mn in solution via dissolution and chelation.

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