

The manganese fertilizer antagonism of glyphosate story for 2002

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Abstract

Michigan soybean producers have observed antagonism of glyphosate efficacy when it is tank-mixed with foliar manganese (Mn) fertilizers. The objectives of this study were to 1) document the basis for the observed antagonism of glyphosate activity when applied with Mn micronutrient solutions, 2) determine why the antagonism occurs, and 3) develop recommendations for growers to effectively use foliar applied Mn with glyphosate in their soybean production systems.

In 2000 and 2001 greenhouse bioassays and field trials showed that three manganese fertilizer formulations significantly antagonized glyphosate efficacy (Mn-ethylaminoacetate, Mn-lignin sulfonate, and $\text{MnSO}_4 \cdot \text{monohydrate}$), and one did not (Mn-EDTA). The adjuvants diammonium sulfate (AMS), EDTA, and citric acid each reduced, but did not eliminate, the antagonism in tank-mixtures. The extent to which the antagonism was overcome depended upon the specific combination of Mn and adjuvant. In greenhouse studies, Mn-ethylaminoacetate sprayed 3 days before glyphosate antagonized glyphosate efficacy on velvetleaf but not giant foxtail. The degree of antagonism increased as the interval between applications decreased. However, Mn sprayed 1 day after glyphosate application had no effect on glyphosate efficacy. There was no antagonism on species present in field trials when Mn was sprayed prior to glyphosate.

To understand why the antagonism occurs, we conducted greenhouse bioassays using ^{14}C labeled glyphosate to measure velvetleaf absorption of glyphosate mixed with four Mn fertilizers. The studies showed that Mn-lignin sulfonate (Mn-LS) and $\text{MnSO}_4 \cdot \text{monohydrate}$ (MnSO_4) reduced glyphosate absorption, but that glyphosate uptake increased when AMS was added to the treatment solutions. Glyphosate absorption was not altered by Mn-EDTA. Mn-ethylaminoacetate (Mn-EAA) caused an increase in the rate, but not quantity, of glyphosate absorbed. Thus, reduced absorption of glyphosate is responsible for some of the antagonism, but does not explain the effect of Mn-EAA.

Field studies were conducted in three locations in 2002: East Lansing, Washtenaw Co. (Don Korte, cooperator) and Saginaw Co. (Randy Rupp, cooperator). Weed pressure was so light in Washtenaw and Saginaw counties and we were unable to obtain useful weed control data. Common lambsquarters data in the East Lansing experiment confirmed results of previous years: Mn-EAA and MnSO_4 caused significant antagonisms in solutions with and without AMS; Mn-EDTA caused no antagonism; and the antagonism caused by Mn-LS was overcome by adding AMS to the spray solution. There was again no evidence of a timing antagonism when Mn-EAA was sprayed before glyphosate.

Because concerns were raised about the "high" rates of manganese fertilizer used in our studies, we compared velvetleaf control using all the combinations of 6 rates of Mn-EAA (0.00 - 1.6 lb/ac) and 6 rates of glyphosate (0.00 - 2.96 lb a.e./ac), both with and without AMS. All rates of Mn greater than 0.1 lb Mn/ac caused an antagonism. The degree of antagonism increased as the Mn rate increased, and the antagonism intensified as the rate of glyphosate was reduced.

Introduction

Mn deficiency is the most common micronutrient problem in Michigan. The plant availability of Manganese (Mn) generally decreases with increasing soil pH levels. Soybeans grown in the calcareous soils of Michigan's Thumb area and in the lake-bed soils of Michigan's lower peninsula have historically been found to be deficient in Manganese (Mn). Producers in these prominent soybean growing areas have applied Mn micronutrient solutions as tank-mixes with foliar applied herbicides. Greater than 70% of Michigan's soybean acres are planted in glyphosate resistant species. Glyphosate efficacy has been observed to be antagonized when tank-mixed with Mn micronutrient solutions.

Previous studies have shown glyphosate efficacy to be antagonized by hard water ions such as calcium and iron. The glyphosate molecule acts as a chelator; in neutral water (pH 7) it is a divalent or trivalent anion and complexes with cations in solution. Mixing glyphosate with stronger chelates (like EDTA), adding an excess of cations that are not antagonistic when complexed to glyphosate (like AMS), or acidifying the spray solution (with sulfuric acid) are techniques that have used to overcome the antagonism. Glyphosate may also be antagonized by ions on the plant surface, such as ions found in soil or calcium ions that are excreted by the plant.

The objectives of this study were to 1) document the basis for the observed antagonism of glyphosate activity when applied with Mn micronutrient solutions, and 2) determine why the antagonism occurs, and 3) develop recommendations for growers to effectively use foliar applied Mn with glyphosate in their soybean production systems.

Materials and Methods

In greenhouse bioassays velvetleaf and giant foxtail plants were grown in deep 4"-plastic pots in the greenhouse. Prior to treatment they were thinned to 1 velvetleaf plant per pot and 3 giant foxtail plants per pot. Pots were randomly assigned to treatments and were sprayed at the 4-5 leaf stage on a track sprayer. Plants were rated for control 7 and 14 days after treatment on a scale of 0 (no control) to 10 (dead plant). For the ¹⁴C-glyphosate studies plants were moved into growth chambers prior to treatment. At the 4 leaf stage, the second leaf was treated with 1µL drops of treatment solution. Plants were randomly selected for leaf rinsing and harvest at 4, 24, and 48 hours following treatment. The rinsate was analyzed on a liquid scintillation counter to determine percent absorption.

Field trials were conducted at three locations. In East Lansing the dominant weed species was common lambsquarters. In Washtenaw and Saginaw Co. weed pressure was very light, but included common lambsquarters, smartweed sp., giant foxtail, and fall panicum. Plots were treated when weeds were 6-8" tall, and were evaluated for control 14, 28, and 100+ days after treatment.

Three formulations of glyphosate (Roundup Ultra, Roundup UltraMAX, and MON 007), four formulations of manganese fertilizer (Traco – Mn-EDTA; Tecmangam – MnSO₄ monohydrate powder;

Post-Man – MnSO₄ with ethylaminoacetate as a chelating agent; and Meta-gro – MnSO₄ with lignin sulfonate), and 2 adjuvants (AMS and citric acid) were used in these experiments.

Data was analyzed using proc glm and proc mixed of SAS.

Results and Discussion

One possible explanation for the cause of the Mn fertilizer antagonism of glyphosate activity is that it interferes with glyphosate absorption. Using ¹⁴C-glyphosate, we showed that the rate and quantity velvetleaf absorption of glyphosate was reduced by Mn-LS and MnSO₄ (Fig. 1). Glyphosate absorption was not affected when tankmixed with Mn-EDTA. However, Mn-EAA substantially increased the rate of glyphosate absorption, although the total amount absorbed at 48 h was statistically equivalent to the glyphosate check. This was puzzling because Mn-EAA frequently caused the most severe antagonisms observed in bioassays.

Glyphosate activity is enhanced by including AMS in the spray solution. Part of this positive effect is increased glyphosate absorption (Fig. 1). In our bioassays AMS reduced the degree of antagonism caused by Mn-EAA, MnSO₄, and Mn-LS. Although AMS did not alter glyphosate absorption from solutions containing Mn-EAA or Mn-EDTA, it did increase absorption from solutions containing MnSO₄ and Mn-LS. This parallels the large activity response of Mn-LS tankmix solutions to AMS, and the moderate response of MnSO₄ (Fig. 3). It also parallels the limited activity response of Mn-EDTA to the addition of AMS (Fig. 3).

Thelen et al. (1995) demonstrated that glyphosate ions complex with hard water cations (Ca²⁺) in spray solutions, thereby reducing glyphosate absorption and activity. We hypothesized that a similar interaction occurs between Mn and glyphosate. After initiating work using NMR technology to confirm this hypothesis, we learned that Mn is attracted to magnetic charges, and when it is included in solutions to be analyzed in the NMR, it is impossible to detect changes in the structure of the glyphosate molecule. Consequently, that option for answering why Mn-EAA causes its negative effect is not available.

In field studies we repeated treatments conducted in greenhouse bioassays. Mn-EAA, Mn-LS and MnSO₄ all antagonized glyphosate efficacy relative to the glyphosate check, but Mn-EDTA did not (Fig. 3). AMS and citric acid improved weed control in combination with Mn-LS and MnSO₄; only AMS improved control in combination with Mn-EAA. It is important to note that a significant antagonism persisted even after AMS was added to solutions with Mn-EAA and MnSO₄. Control was not significantly changed when AMS or citric acid were added to solutions with Mn-EDTA. Once again, we were unable to detect any antagonism caused by spraying Mn-EAA before glyphosate, even at an interval as short as 1 h.

We received communications voicing concern over our use of unlabeled rates of Mn-EAA. We have been applying it at 4 qt/ac, twice the labeled rate of 1-2 qt/ac. Reducing the rate of Mn-EAA from 4 qt/ac to 1 qt/ac improved control of velvetleaf significantly but not practically (Fig. 4). Reducing the rates of the other three fertilizers did not significantly affect control (Fig. 4). We also thought it valuable to

determine the importance of glyphosate rate on the antagonism since all our studies were treated using low rates of glyphosate. The data in Figs. 5 and 6 were obtained using 6 rates of Mn-EAA and 6 rates of glyphosate (Roundup UltraMAX). The lines each represent a level of Mn fertilizer and show three important trends. First, efficacy increases dramatically as glyphosate rate increases, but only reaches acceptable levels of velvetleaf control when the full labeled rate of glyphosate was used (1.48 lb a.e./ac). Second, each increase in Mn-EAA concentration decreased velvetleaf control. Third, adding AMS (Fig. 6) improved glyphosate efficacy, enabling greater control to be reached at lower rates of herbicide.

In anticipation of the upcoming release of MON 007 (Roundup WEATHERMAX), we thought it prudent to test it in tankmixes with Mn fertilizers. Earlier studies showed that Roundup Ultra and Roundup UltraMAX were equally affected by Mn. Unlike UltraMAX, MON 007 activity on velvetleaf was antagonized by Mn-EDTA (Fig. 7), indicating that each glyphosate formulation has the potential to interact differently with Mn, and generally gave poorer velvetleaf control.

Conclusions

Some Mn fertilizers antagonized glyphosate efficacy. Using fertilizer formulations with strong chelating agents like EDTA may minimize or eliminate any antagonism. However, the most severe antagonism come from 'chelated' Mn like Mn-EAA and Mn-glucoheptonate (Bailey et al., 2002), so growers should be cautious about which 'chelated' Mn they choose to apply. The glyphosate formulation may also impact the degree of antagonism. One explanation for Mn antagonism of glyphosate is that it blocks absorption of the glyphosate, but this does not accurately describe the effect of Mn-EAA. Depending upon the species and the Mn fertilizer formulation used, there may be an antagonism if Mn is applied a few days or hours before glyphosate, although we failed to demonstrate this in the field. If foliar Mn fertilizer and glyphosate are applied separately, glyphosate should be sprayed first. AMS should always be included in tankmixes of glyphosate and Mn, along with full labeled rates of glyphosate. Reducing the Mn concentration reduces the antagonism, but never eliminated it.

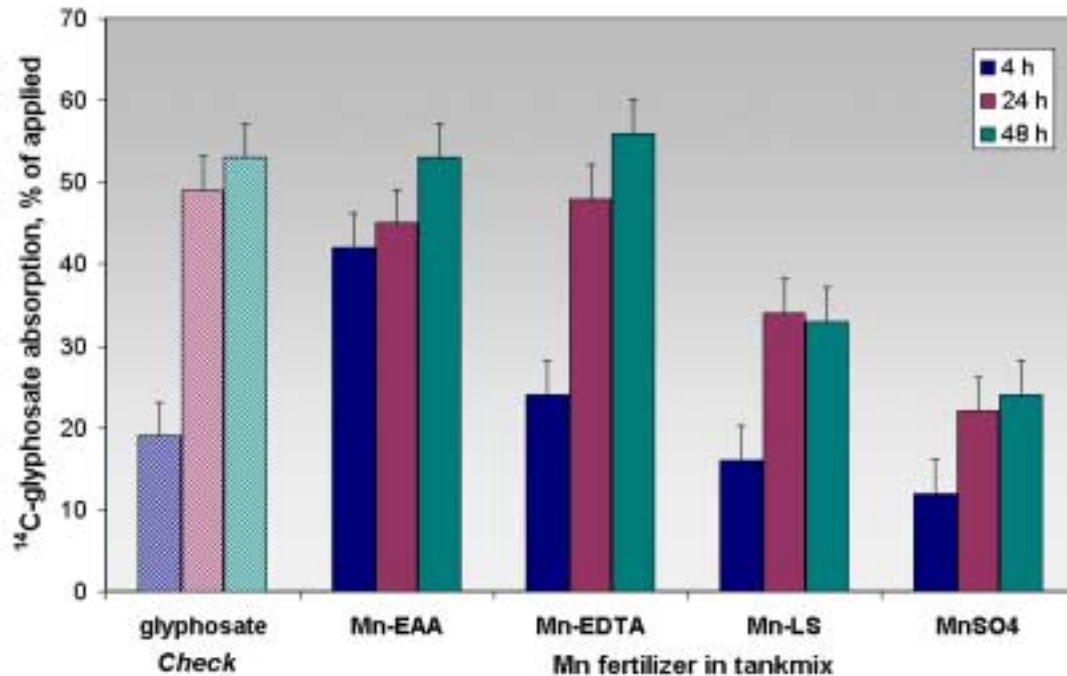


Figure 1. Velvetleaf absorption of ¹⁴C-labeled glyphosate in glyphosate-Mn fertilizer tankmixes at 4, 24, and 48 h. Data represent the average of with and without AMS treatments. Error bars represent the standard error, p = 0.05.

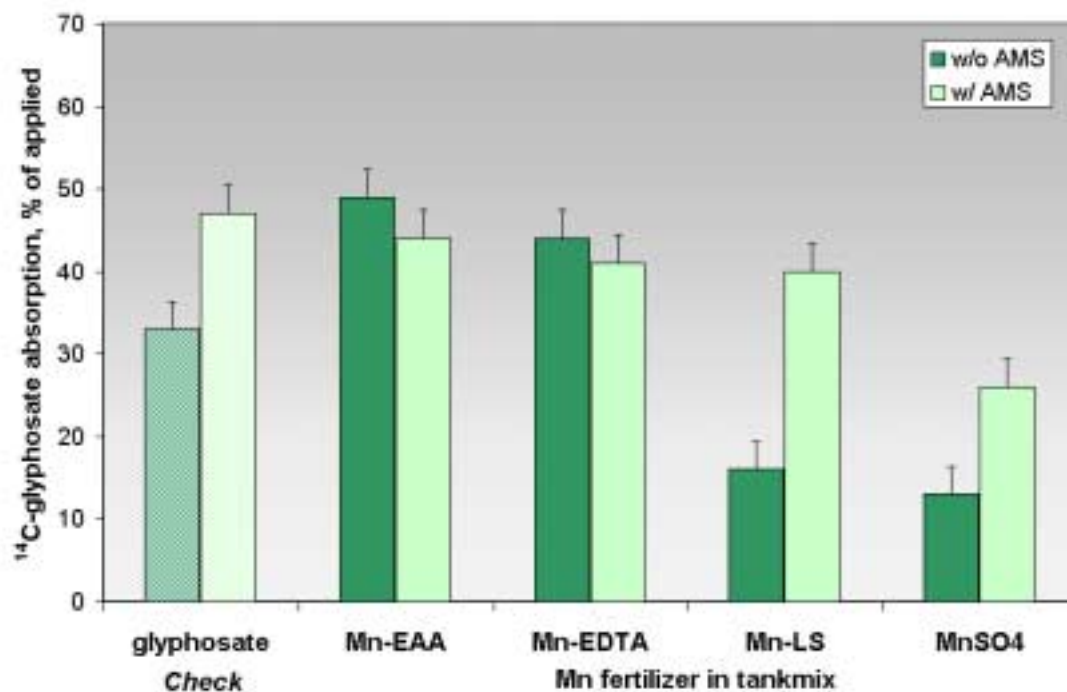


Figure 2. Velvetleaf absorption of ¹⁴C-labeled glyphosate from glyphosate-Mn fertilizer tank mix solutions, either with or without AMS. Data represent the average of three rinses (4, 24, and 48 h after treatment). Error bars represent the standard error, p = 0.05.

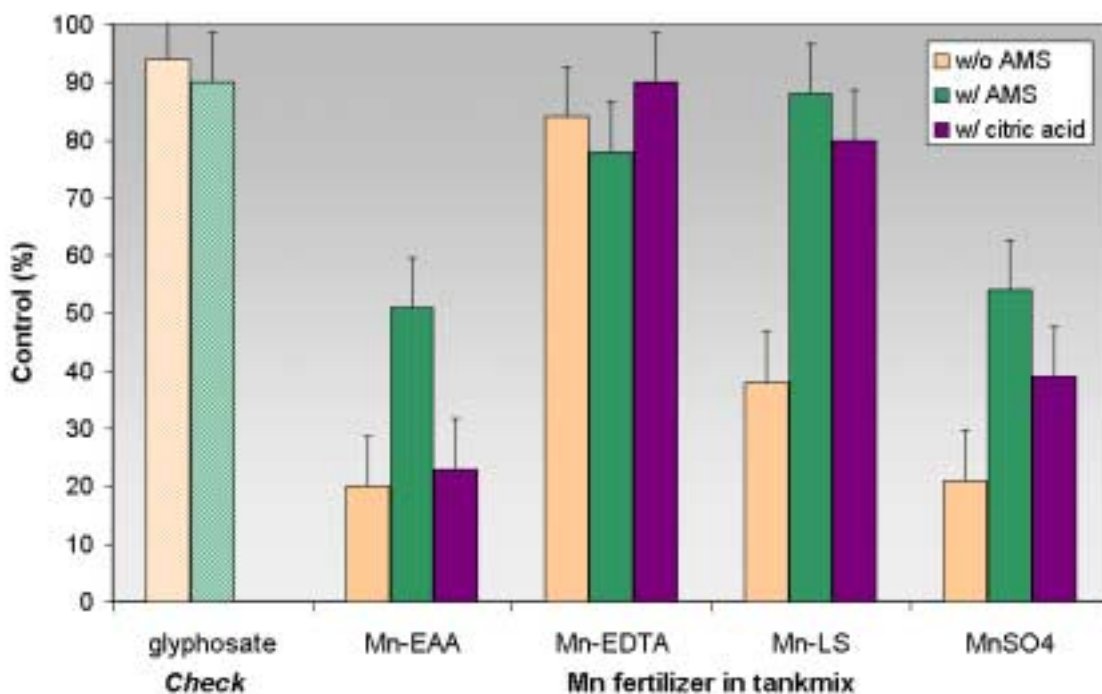


Figure 3. Control of common lambsquarters 45 days after treatment with glyphosate-Mn fertilizer tankmixes in a soybean field. Three adjuvant treatments, - AMS, + AMS, and + citric acid, were used. Error bars represent standard error, $p=0.05$.

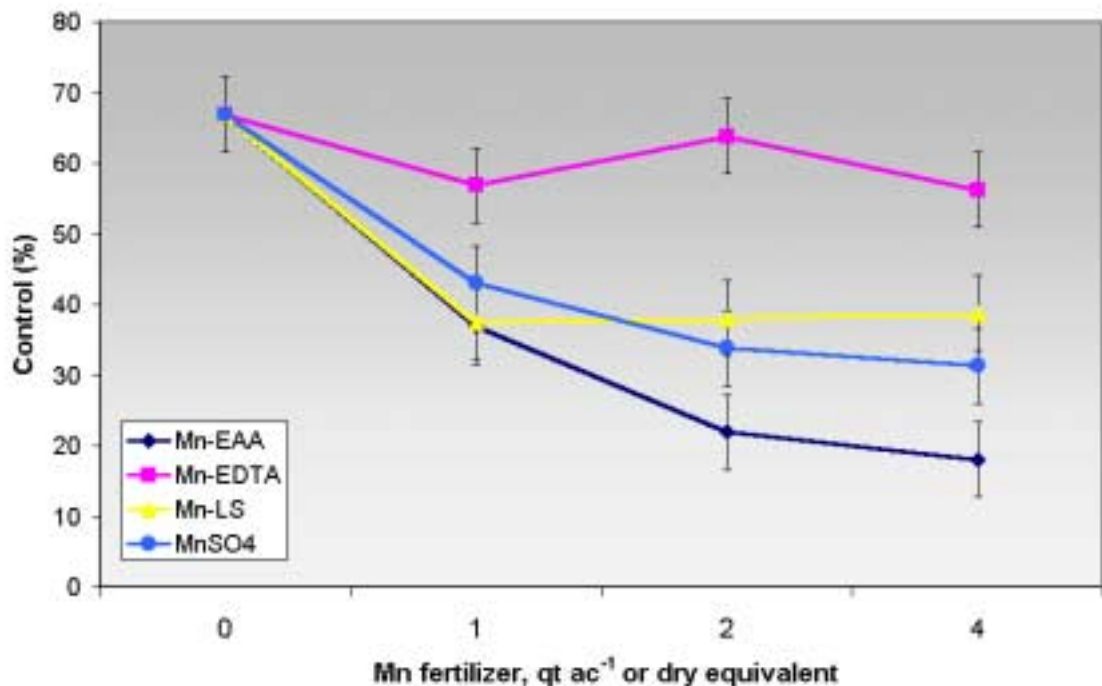


Figure 4. Velvetleaf control 14 days after treatment with glyphosate-Mn fertilizer tankmixes at three Mn fertilizer concentrations. "0" is efficacy of glyphosate without Mn. Data represent the averages of +/- AMS treatments. Error bars represent the standard error, $p=0.05$.

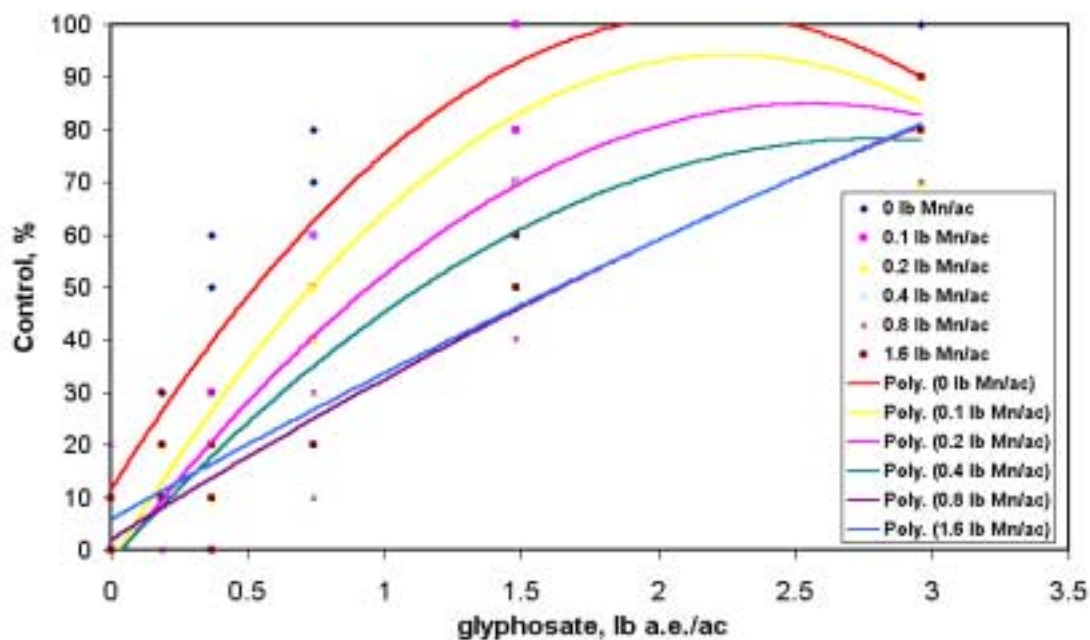


Figure 5. Velvetleaf control 7 days after treatment with factorial combinations of 6 levels of Mn-EAA and 6 levels of glyphosate (Roundup UltraMAX). No AMS was included. Lines fitted to the data were obtained using Microsoft Excel and a 2 variable polynomial equation.

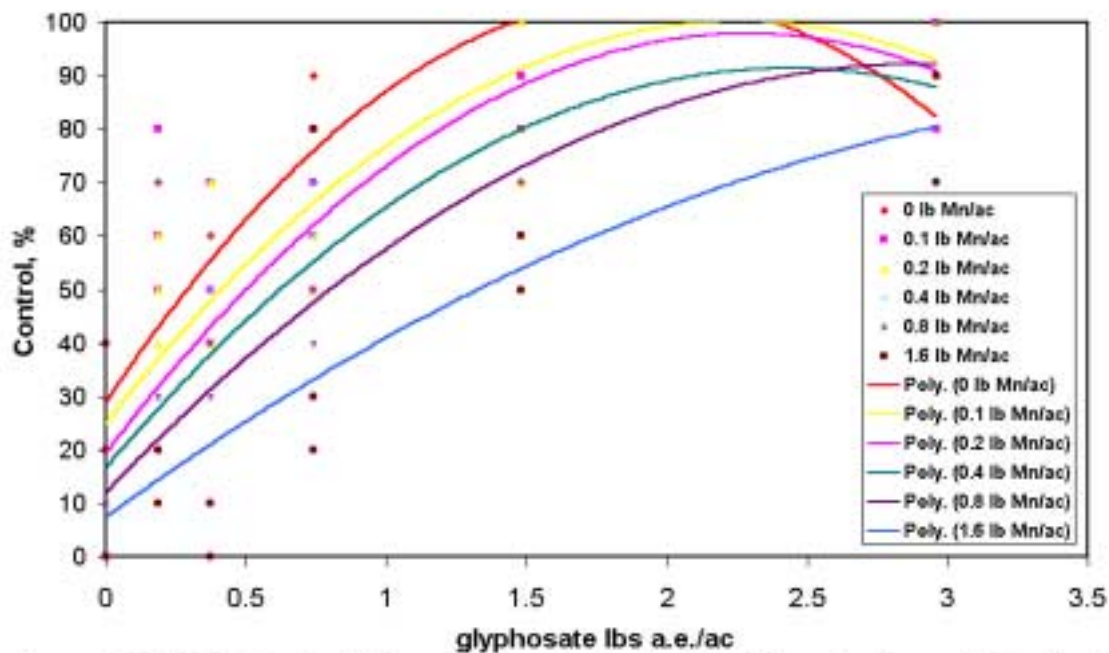


Figure 6. Velvetleaf control 7 days after treatment with factorial combinations of 6 levels of Mn-EAA and 6 levels of glyphosate (Roundup UltraMAX). AMS was included. Lines fitted to the data were obtained using Microsoft Excel and a 2 variable polynomial equation.

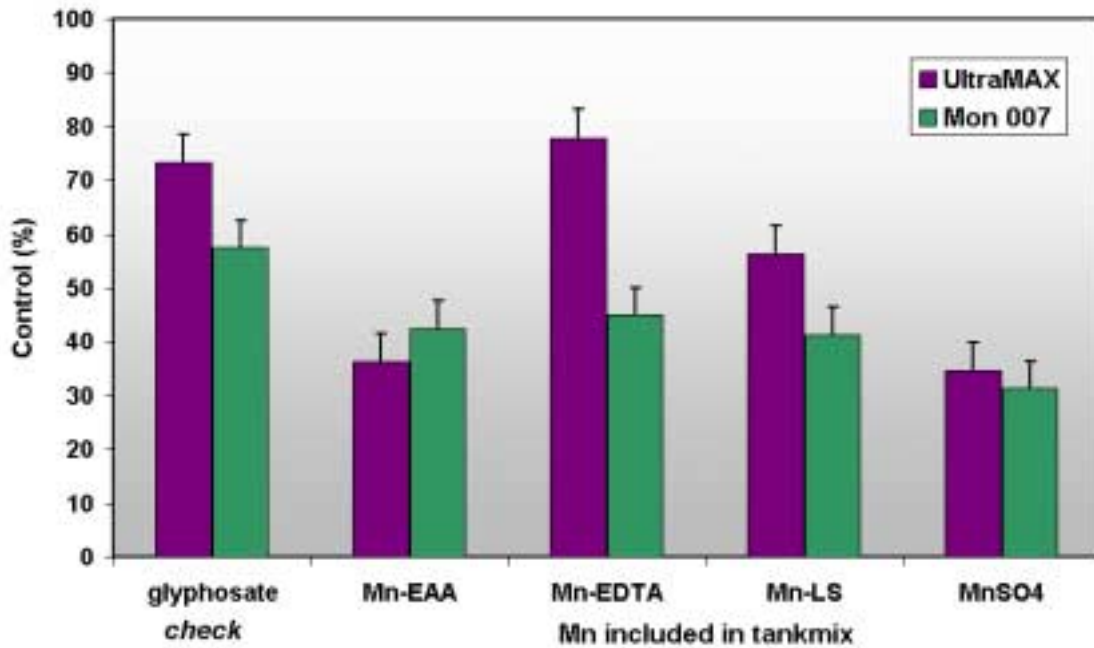


Figure 7. Velvetleaf control 14 d after treatment with 2 formulations of glyphosate tankmixed with 4 manganese fertilizer. Data represent averages of + and - AMS treatments. Error bars represent standard error, $p=0.05$.