CHAPTER TWO

ADJUVANT EFFECTS and GOOSEGRASS: STAGE OF GROWTH RESPONSE TO QUINCLORAC

ABSTRACT

Several commercial and experimental adjuvants were evaluated for selectivity and effectiveness in enhancing activity of quinclorac in canola (*Brassica napus* L.) and turfgrass. Weed species investigated included cleavers (*Galium aparine* L.), annual sowthistle (*Sonchus oleraceus* L.), large crabgrass (*Digitaria sanguinalis* L. [Scop.]), and goosegrass (*Eleusine indica* L. [Gaertn.]). Weed species were selected for their importance in canola (cleavers and annual sowthistle) and turfgrass (large crabgrass and goosegrass). Canola cultivars evaluated for selectivity included "Garrison" and "Goldrush". Turfgrass species evaluated included Kentucky bluegrass (*Poa pratensis* L.), perennial ryegrass (*Lolium perenne* L.), tall fescue (*Festuca arundinacea* L. [Schreb.]), and creeping bentgrass (*Agrostis palustris* L. [Huds.]. Adjuvants were selected to give a representative sample across adjuvant types such as methylated seed oil ("Sunit II"), petroleum based crop oil concentrate, silicone based ("Sylgard 309"), cationic surfactant ("Frigate" [fatty amine ethoxylate]), and modified crop oils ("Dash" and "Merge").

Effectiveness of adjuvants was evaluated for cleavers, annual sowthistle, and large crabgrass by calculating quinclorac GR_{50} (herbicide rate required to reduce plant growth 50%) values based on applied at rates of 0, 15.6, 31.2, 62.5, and 125 g ai ha^{-1}. For goosegrass, quinclorac rates evaluated were increased to 250, 500, 1000, and 2000 g ai ha^{-1}. Treatments also included quinclorac applied with no adjuvant at each rate.

Applications were made at the three to five-whorl stage for cleavers, four to six-leaf stage for annual sowthistle and the one to two-tiller stage for large crabgrass and goosegrass. Root uptake was minimized by the use of a vermiculite soil barrier. Shoot fresh weight data were recorded 14 days after treatment.

Adjuvant selectivity in canola and turfgrass was evaluated by applying the adjuvants alone with no added quinclorac. Applications were made at the six to eight-leaf stage for canola. Turfgrass species were maintained and treated at a clipped height of 6.25 cm. Crop selectivity was evaluated by rating visual injury 7 days after application.

All evaluated adjuvants provided similar enhancement of control for cleavers and annual sowthistle. Sylgard 309 was the only adjuvant that did not enhance control of large crabgrass. Goosegrass was tolerant to quinclorac across the evaluated rate range regardless of adjuvant, and therefore, GR_{50} values could not be determined. None of the adjuvants caused phytotoxicity to canola or any turfgrass species.

Goosegrass, at several stages of growth studies was treated with quinclorac at 0, 1, 2, 4, 8, and 16 kg ha^{-1} applied with 1% v/v of "Merge" spray adjuvant. The growth stages included preemergence, one to two true leaf, four to five true leaf and one to two-tiller. The effects of root uptake were also tested by evaluating treatments with and without a vermiculite soil barrier. Results showed differences in calculated GR_{50} values and improved control as a result of root absorption. The lowest GR_{50} value was 2.7 kg ha^{-1} for the one to two-leaf stage with no soil barrier. However, this value is approximately 3.5 times higher than the maximum labeled rate for turfgrass.

INTRODUCTION

An adjuvant can be defined as "any substance in a herbicide formulation or added to the spray tank to improve herbicidal activity or application characteristics" (12). The primary function of an adjuvant is to decrease the surface tension of the spray droplets, which results in more uniform spreading over the leaf surface (1,8). An effective adjuvant may also enhance the penetration of the herbicide through the major barriers to cell entry. An adjuvant must also be nonphytotoxic to the crop or desirable species. Efficacy of postemergence herbicides usually requires the addition of adjuvants (1,8,11). Work conducted with quinclorac has shown that a proper adjuvant is vital to enhance the postemergence activity (2,7).

Plant leaves are the main point of entry for foliar applied herbicides. However, entry can also occur via the stems and buds (1). Once the herbicide is delivered to the leaf surface, several factors can effect its fate. Environmental factors such as light, temperature, humidity, rainfall and wind can effect resultant absorption (1). The degree of pubescence or makeup of the cuticular waxes on the leaf surface can also affect absorption. For foliar applied herbicides to be effective, the herbicide molecule must be delivered to the site of action.

Foliar applied herbicides face three main barriers of entry into plant cells via the leaves. The barriers include the leaf cuticle, the cell wall and the plasmalemma. (1,11). The cuticle consists of waxes, pectin, cutin and cellulosic material (11). The structure has been likened to a sponge in which the framework is of spongy cutin and the holes are filled with waxes (1).

The movement of herbicides across the cuticle is by simple diffusion (9). There are three main pathways along which the herbicides may diffuse: 1). penetration via intermolecular spaces; 2). for water-soluble material, via water-filled and swollen pectin corridors between lipid platelets; and 3). for oil-soluble materials, directly through the waxy portions of the cuticle (1). The cell wall is composed of a dense network of cellulose and hemicellulose microfibrils with interfibrillar spaces that are commonly filled with water (3). The cell wall is known to offer little resistance to herbicide penetration (1,11). The main process for movement through this barrier is diffusion. The final barrier to herbicide movement is the plasmalemma ,which is a semipermeable, bimolecular membrane composed of tightly packed, globular lipoprotein molecules. (1). The penetration of herbicides through this barrier may require energy and a carrier (1,11).

The stage of growth of weeds at the time of application can affect resultant control. In general with postemergence herbicides, weeds tend to be more readily controlled in the early seedling stages than in advanced growth stages (1). Chism *et al.* (6) demonstrated differences in sensitivity of southern crabgrass (*Digitaria ciliaris* [Retz.]) to applied quinclorac when applied at different growth stages. He found that flowering crabgrass plants had a higher GR_{50} value than preemergence, three to five true leaf or two to four tiller stages.

The first objective of these studies was to investigate selected commercial and experimental adjuvants for their selectivity and effectiveness in enhancing quinclorac activity on important weed species in canola and turfgrass. A wide range of adjuvant types were evaluated including a series of experimental adjuvants from BASF. Adjuvants were selected to give a representative sample across adjuvant types such as methylated seed oil ("Sunit II"), petroleum based crop oil concentrate ("Herbimax"), silicone based ("Sylgard 309"), cationic surfactant ("Frigate" [fatty amine ethoxylate]), and modified crop oils ("Dash" and "Merge"). Cleavers and annual sowthistle represent important broadleaf weeds in canola production in Canada. Large crabgrass and goosegrass are major grassy weed problems in both cool and warm season turfgrass(4,5).

Adjuvant selectivity was evaluated in canola (*Brassica napus* L.) and several cool season turfgrass species including Kentucky bluegrass (*Poa pratensis* L.), perennial ryegrass (*Lolium perenne* L.), tall fescue (*Festuca arundinacea* L. [Schreb.]), and creeping bentgrass (*Agrostis palustris* L. [Huds.]. Canola was selected for evaluation based on the plans of BASF to pursue a future registration for the use of quinclorac. The second objective of these studies was to evaluate the effectiveness of quinclorac in controlling goosegrass at different stages of plant growth including preemergence, one to two true-leaf, four to five true-leaf and one to two-tiller. As part of this second objective, the role of root absorption of quinclorac was also investigated.

METHODS AND MATERIALS

Adjuvant Studies :

Cleavers (*Galium aparine* L.), annual sowthistle (*Sonchus oleraceus* L.), large crabgrass (*Digitaria sanguinalis* L. [Scop.]), and goosegrass (*Eleusine indica* L. [Gaertn.]) were seeded in Metro Mix 360[1] greenhouse potting soil in 946 ml plastic pots. The pots received an application of OSMOCOTE [2] fertilizer (10-10-10) at planting and were maintained with daily overhead irrigation. Greenhouse conditions were maintained at approximate day/night temperatures of 30 $^{\circ}$ /20 $^{\circ}$ C. Plants were grown in a 16 hour photoperiod and consisted of natural light supplemented with metal halide light at 600 uE m^{-2} s^{-1} photosynthetic photon flux density (PPFD). After emergence, plants were thinned to one per pot.

Quinclorac was applied at rates of 0, 15.6, 31.2, 62.5, and 125 g ai ha^{-1} to all species except goosegrass. For goosegrass, quinclorac rates used were 0, 250, 500, 1000, and 2000 g ai ha^{-1}. Adjuvants were applied at a rate of 1% (v/v) except for Sylgard 309 (0.125% (v/v)), and Frigate 0.5% (v/v). A description of the adjuvants used is presented in Table 1. Separate experiments were conducted with annual sowthistle and large crabgrass to determine GR_{50} values with quinclorac applied without an adjuvant.

A rate range of 0, 250, 500, 1000, and 2000 g ai ha^{-1} was used for annual sowthistle. For large crabgrass evaluated rates were 0, 1, 2, 4, 8, and 16 kg ha^{-1}.

Treatments were applied when the weed species were in the following growth stages : Cleavers (three to five-whorl), annual sowthistle (four to six leaf), large crabgrass and goosegrass (one to two-tiller). For cleavers and sowthistle, spray applications were made with an overhead track sprayer set to deliver 187 l ha^{-1} at an operating pressure of 275 kPa using an 8001 even flat fan nozzle [3]. For large crabgrass and goosegrass, applications were made at 748 l ha^{-1} at 275 kPa using an 8004 even flat fan nozzle. The spray volumes were selected to approximate those used under field conditions. Root uptake of quinclorac was prevented by covering the soil with a one cm layer of vermiculite before spraying. The vermiculite was removed after the spray had dried. Pots were watered by subsurface irrigation after treatments were applied. At 14 days after treatment, weeds were harvested at soil level and fresh weights recorded.

For the crop selectivity evaluations, canola cultivars "Garrison" and "Goldrush" were seeded in Metro Mix 360 greenhouse potting soil and maintained as discussed with the evaluated weed species. After emergence, pots were thinned to one plant per pot. Applications were timed when the plants reached the six to eight-leaf stage.

Spray parameters were the same as discussed for cleavers and annual sowthistle.

Evaluated turfgrass species, Kentucky bluegrass (*Poa pratensis* L.), perennial ryegrass (*Lolium perenne* L.), tall fescue (*Festuca arundinacea* L. [Schreb.]), and creeping bentgrass (*Agrostis palustris* L. [Huds.]. were broadcast seeded into pots containing Metro Mix 360 greenhouse potting soil and maintained at a clipped height of 6.25 cm. Applications were made after the grasses were well established and clipped several times. Turfgrass growth was supplemented with periodic applications of liquid fertilizer solution on an as needed basis. Adjuvants were applied alone (with no herbicide) at the rates discussed with the evaluated weed species. Spray parameters for the turfgrass species were the same as discussed for large crabgrass and goosegrass.

[1] Metro Mix 360, Scotts-Sierra Horticultural Products Company , Marysville, OH 43041.

[2] OSOMOCOTE Fertilizer, Scotts Company, Marysville, OH 43041.

[3] Flat fan Nozzle, Spraying Systems Co., Wheaton, IL 60188.

Table 1. Adjuvant description and source.

Name	Description	Address
Sylgard 309	Organosilicone mixture: the active ingredient 2 -(3-hydroxypropyl)-heptamethyl-trisiloxane,ethoxylated acetate	Dow Corning Corp. Midland,MI 48686
Herbimax	83% Petroleum hydrocarbons,17% surfactant (mono and diesters of omega hydroxypoly oxyethylene)	Loveland Indust. P.O. Box 1289 Greeley,CO 80632
Sunit II	Methylated seed oil	AGSCO, Inc., Fargo,ND,58105
Dash	45% petroleum hydrocarbons, 5% naphthalene, 1.5% phosphoric acid, and 48.5% mixture of alkyl esters and anionic surfactant	BASF Corp., RTP, NC 27709
Frigate	Mixture of ethoxlated long -chain fatty amines	ISK Biosciences Corp., Mentor,OH 44061
Merge	Proprietary Adjuvant	BASF Canada,Inc., Toronto, Ont M9W 6N9
Exp 1,2, 3,& 4	Proprietary Adjuvants	BASF Corp.,RTP,NC 27709

Goosegrass Stage of Growth Studies:

Goosegrass plants were grown and spray applications made as previously described in the adjuvant studies except that an actual field soil was used in place of a potting mix. The soil used for these studies was characterized as a silt loam with 3.8 % organic matter, a cation exchange capacity of 21.5 meq/100 grams and a pH of 6.6. Quinclorac was applied at rates of 0, 1, 2, 4, 8, and 16 kg ai ha^{-1} with "Merge" adjuvant at 1% v/v. Treatments were applied as preemergence (i.e. applied immediately after seeding), one to two-leaf, four to five-leaf and one to two-tiller stage of goosegrass. Each treatment was applied with and without a vermiculite soil barrier. The method used for the vermiculite barrier was the same as outlined in the adjuvant studies. Immediately after the spray solution had dried on the leaf surface, the "without vermiculite" treatments were surface irrigated with enough water to approximate a 1.25 cm depth applied per pot. Care was taken not to allow any water to come in contact with the treated leaves. The vermiculite barrier was removed for those specific treatments as well after the spray solution had dried on the leaf surface. Pots were subsequently subsurface irrigated daily. At 14 days after treatment, weeds were harvested at soil level and fresh weights recorded.

Data Analysis :

All experiments were conducted in completely randomized designs. For the adjuvant studies, treatments were arranged as a two factor (herbicide rate by adjuvant) factorial. For the goosegrass stage of growth studies, treatments were arranged as a three factor (growth stage by herbicide rate by soil barrier) factorial. Each treatment was replicated four times (one plant per replication) and each experiment was repeated once. Each weed species was evaluated as a separate experiment. Linear regression was conducted for the fresh weight data for each replication across the range of evaluated rates and GR_{50} values were calculated. Data were subjected to Analysis of Variance (ANOVA). No interactions were present between experiments; therefore, data were combined over time. Means were separated by Fisher's Protected LSD at $\alpha = 0.05$ (10).

RESULTS AND DISCUSSION

Adjuvant studies :

Results are presented in Fig. 1. The calculated GR_{50} values across both selected commercial and experimental adjuvants were equivalent in providing control on cleavers. All adjuvants combined with quinclorac provided significantly greater control than quinclorac without an adjuvant.

Results obtained from the annual sowthistle study followed a similar trend to that observed on cleavers (Fig. 2). All evaluated adjuvants provided greater control of annual sowthistle compared to the use of no adjuvant. However, there was no statistical difference observed among adjuvants. Quinclorac applied without adjuvant failed to provide adequate control of sowthistle within the evaluated rate range (i.e. 0 to 125 g ha^{-1}). The calculated GR_{50} value from the separate experiments for quinclorac on sowthistle without the use of an adjuvant was 0.98 kg ha^{-1}. These results suggested that there may be major differences in the cuticular makeup of the leaf surfaces of these two species that affects the absorption of formulated quinclorac (12); however, these differences are virtually overcome with the use of adjuvants.

Adjuvant effects on quinclorac activity on large crabgrass are presented in Fig. 3. All adjuvants increased quinclorac activity except for Sylgard 309. This suggested that a silicone based adjuvant that does exhibit excellent spreadibility and leaf coverage (8), may not be as effective in aiding quinclorac to penetration of the leaf cuticle in the case of large crabgrass.

As observed with annual sowthistle, the calculated GR_{50} for quinclorac used alone was greater than the scope of evaluated rates (i.e. > 125 grams ha $^{-1}$). The calculated GR_{50} value from the separate experiments for quinclorac on large crabgrass without the use of an adjuvant was 12.9 kg ha^{-1}.A separate experiment was conducted to determine the GR_{50} value for quinclorac without an adjuvant for large crabgrass and was determine to be 12.9 kg ha $^{-1}$.

An initial study was conducted with goosegrass across the same evaluated rate range and cultural conditions as used for the other weed species (i.e. 0 to 125 g ha $^{-1}$). However, no growth suppression was observed with quinclorac applied with any adjuvant at even 125 g ha $^{-1}$. An additional study was conducted to evaluate effects at 0, 250, 500, 1000, and 2,000 g ha $^{-1}$. The only noted growth suppression observed with quinclorac applied with adjuvants occurred at a rate of 2000 g ha $^{-1}$ as presented in Fig. 4. The 2000 g ha $^{-1}$ rate represents about a 2.5X rate over the projected maximum use rate in turfgrass for quinclorac (0.84 kg ha $^{-1}$).

Only three of the adjuvants, "Merge" and two experimentals coded #1 and #2, enhanced quinclorac activity to provide significant growth suppression of goosegrass in comparison to the untreated control.

A follow-up study was initiated to determine a GR_{50} value for the control of one to two-tiller goosegrass with quinclorac without an adjuvant. A rate titration of quinclorac up to 16 kg ha^{-1} was evaluated. Results showed that the calculated GR_{50} was greater than the evaluated 16 kg ha^{-1}.

The GR_{50} results presented in Fig. 5 are an overview of the values determined for each species to quinclorac applied without the use of an adjuvant. Values ranged from 0.052 kg ha^{-1} for cleavers to greater than 16 kg ha^{-1} for goosegrass. These comparisons suggested that there may be major differences in the cuticular makeup of the leaf surfaces of these species that affects the absorption of formulated quinclorac (8,11). However, these studies showed that control with quinclorac can be markedly increased with the use of effective adjuvants. Since it was difficult to induce significant growth suppression in goosegrass with several adjuvant types, tolerance may involve other mechanisms.

In addition to effects on quinclorac efficacy, the adjuvants were evaluated for crop safety in canola and several turfgrass species. Canola varieties evaluated included "Garrison" and "Goldrush". Turfgrass included Kentucky bluegrass (*Poa pratensis* L.), tall fescue (*Festuca arundinacea* L. [Schreb.]), perennial ryegrass (*Lolium perenne* L.), and creeping bentgrass (*Agrostis palustris* L. [Huds.]). No injury was observed at 7 days after treatment with any adjuvant in either canola or turfgrass species.

Goosegrass studies :

Based on the results of the adjuvant studies, studies were conducted with goosegrass to investigate the effects of growth stage and the role of both foliage and roots on quinclorac uptake. Results presented in Fig. 6 summarize the sensitivity of goosegrass to quinclorac applied at several growth stages with and without a vermiculite soil barrier. Calculated GR_{50} values ranged from 2.7 kg ha $^{-1}$ to greater than 16 kg ha $^{-1}$. Quinclorac applied as a preemergence treatment had a measured GR_{50} value of 3.4 kg ha $^{-1}$. At the one to two-leaf stage, the GR_{50} value was similar for both the with and without vermiculite treatments 2.7 and 3.1 kg ha $^{-1}$, respectively. At the four to five-leaf stage, however, there was a large difference between the GR_{50} values for the with (4.3 kg ha $^{-1}$) and without (> 16 kg ha $^{-1}$) vermiculite treatments. Once the goosegrass reached the one to two-tiller stage, the calculated GR_{50} values for the presence or absence of vermiculite were above the scope of inference for the experiment (i.e., greater than 16 kg ha $^{-1}$). Mean separations were made among the GR_{50} values for the preemergence, the one to two-leaf and four to five-leaf stages without vermiculite treatments (3.4, 2.7 and 4.3 kg ha $^{-1}$, respectively). Among these three means, there was a significant difference between the one to two, and four to five-leaf stage.

These results suggested that quinclorac did exhibit preemergence activity on goosegrass although only at very high rates that were beyond the scope of the suggested labeled rates in turfgrass. Postemergence results demonstrated that, at the one to two and four to five-leaf stages, root uptake enhanced resultant control. The difference was markedly pronounced at the four to five-leaf stage where the no vermiculite treatment had a measured GR_{50} value of 4.3 kg ha $^{-1}$ vs. the vermiculite treatment of > 16.0 kg ha $^{-1}$. These data suggested that root uptake can be an important factor in resultant weed control with quinclorac. However, in the case of goosegrass (even at the more "sensitive" stage of one to two-leaf, it is not enough to increase control to within labeled rates.

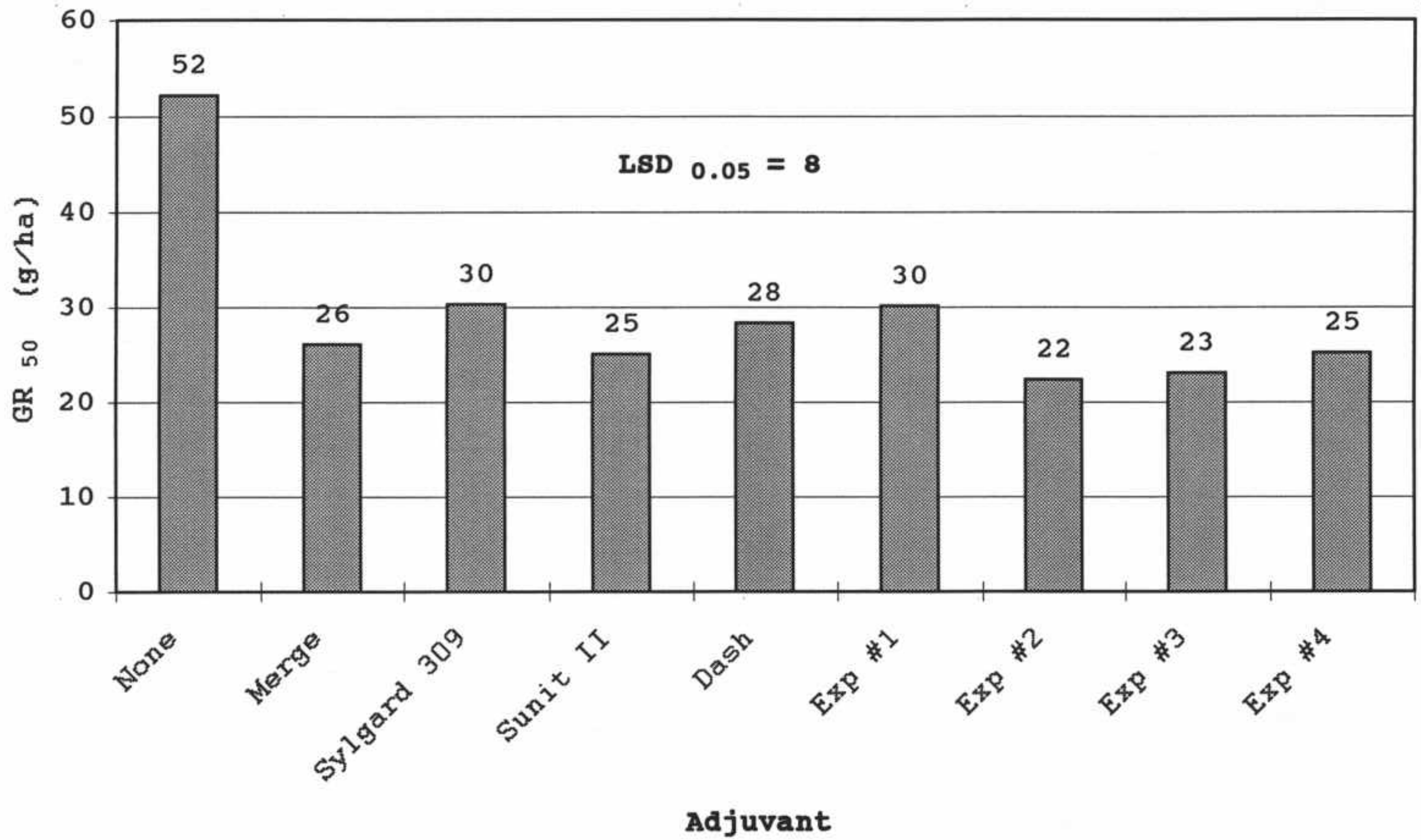

Figure 1. Calculated GR_{50} values for cleavers treated with quinclorac using several adjuvants.

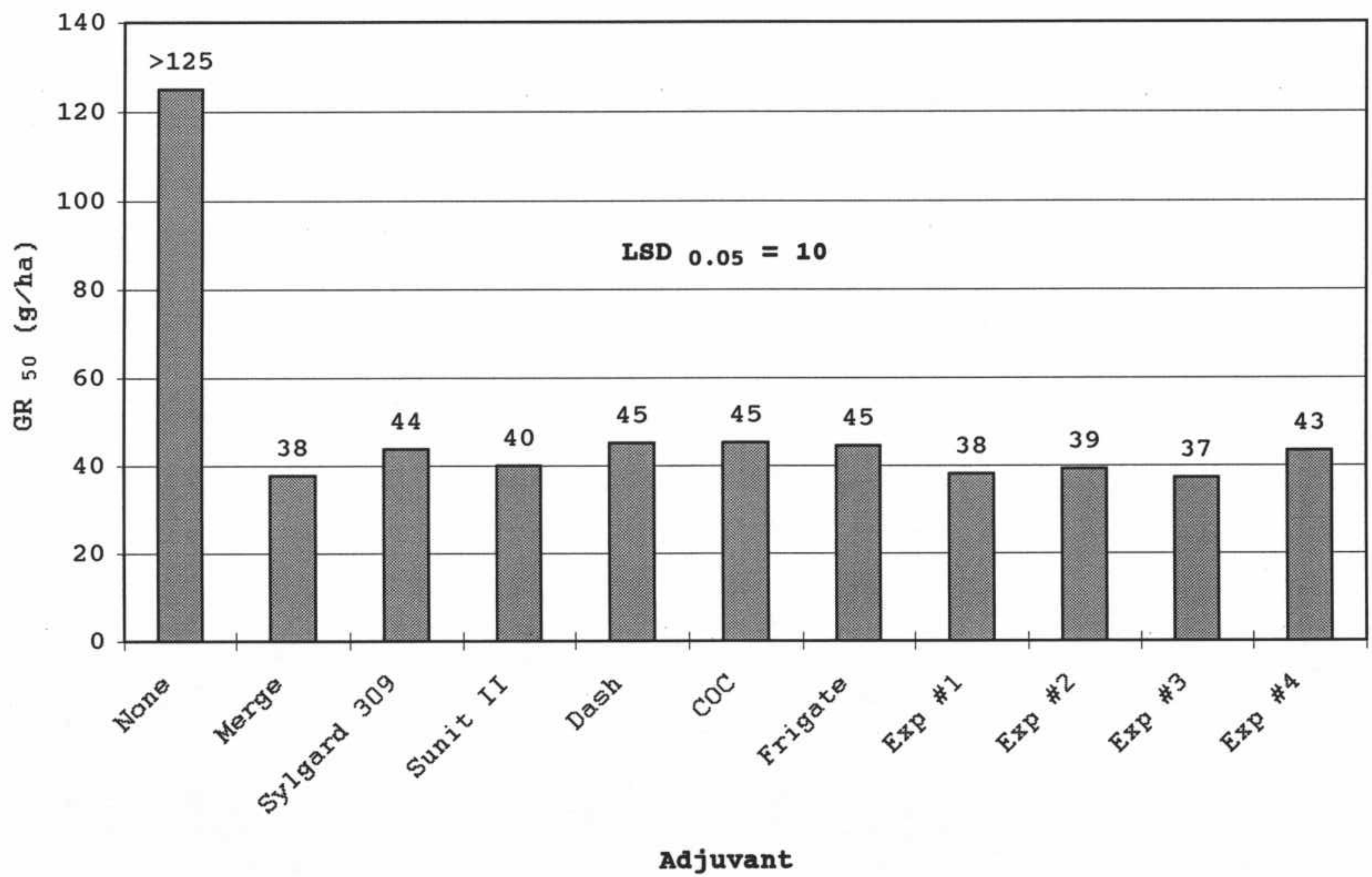

Figure 2. Calculated GR_{50} values for annual sowthistle treated with quinclorac using several adjuvants.

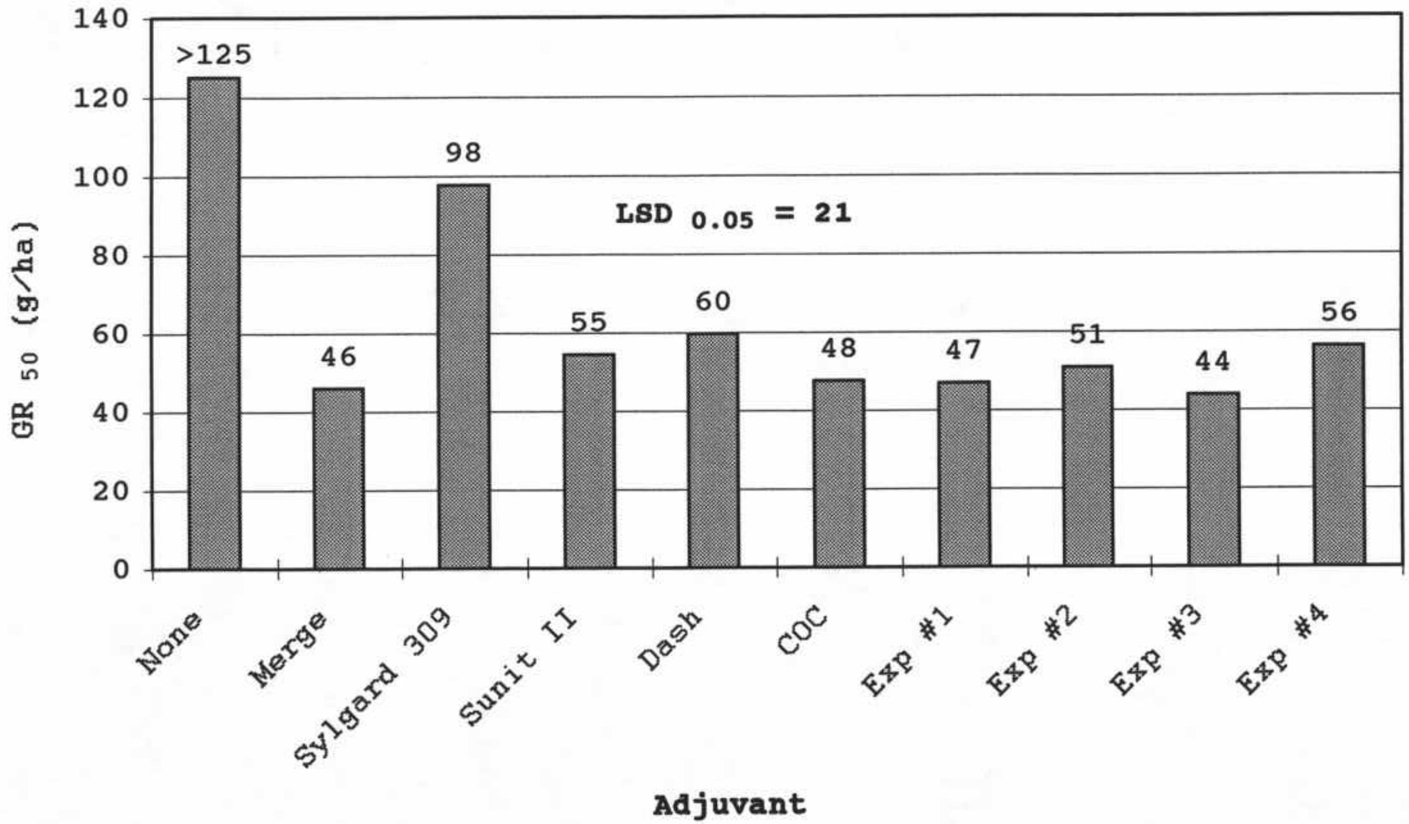

Figure 3. Calculated GR_{50} values for large crabgrass treated with quinclorac using several adjuvants.

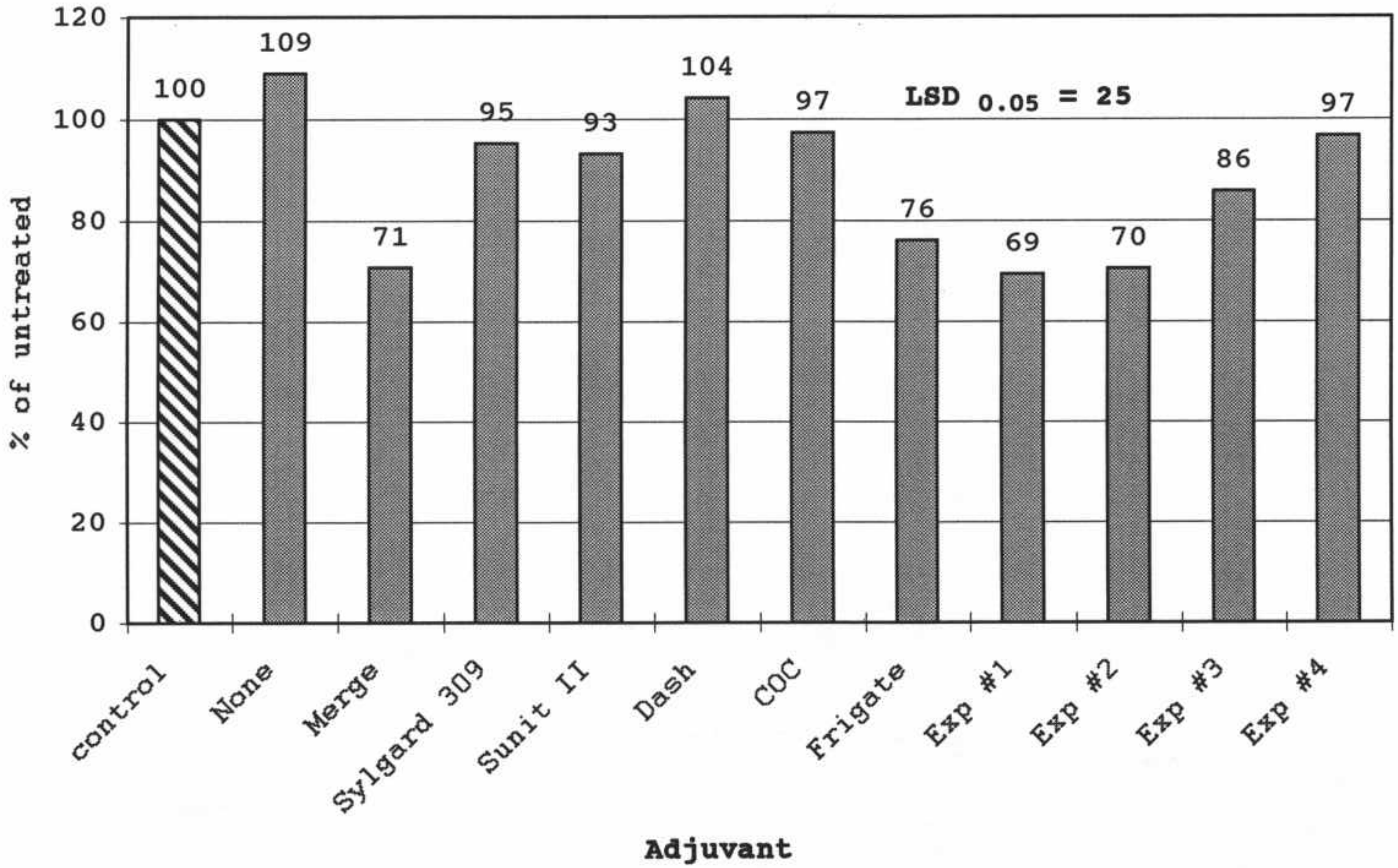

Figure 4. Influence of 2.0 kg ha^{-1} quinclorac applied at the 1 to 2 tiller stage on fresh weight values of treated goosegrass using several adjuvants.

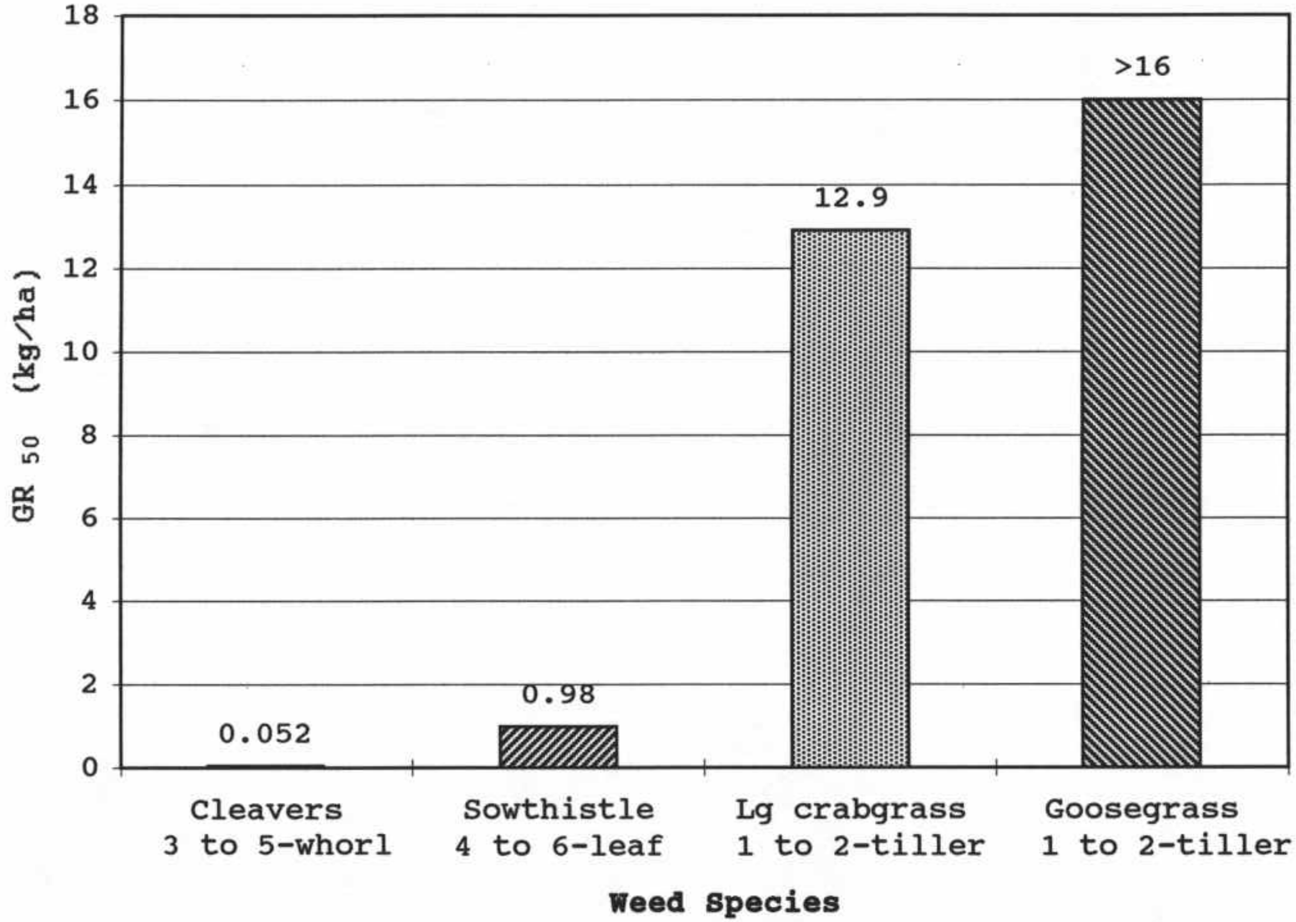

Figure 5. Comparative GR $_{50}$ values for cleavers, annual sowthistle ,large crabgrass and goosegrass treated with quinclorac without adjuvants.

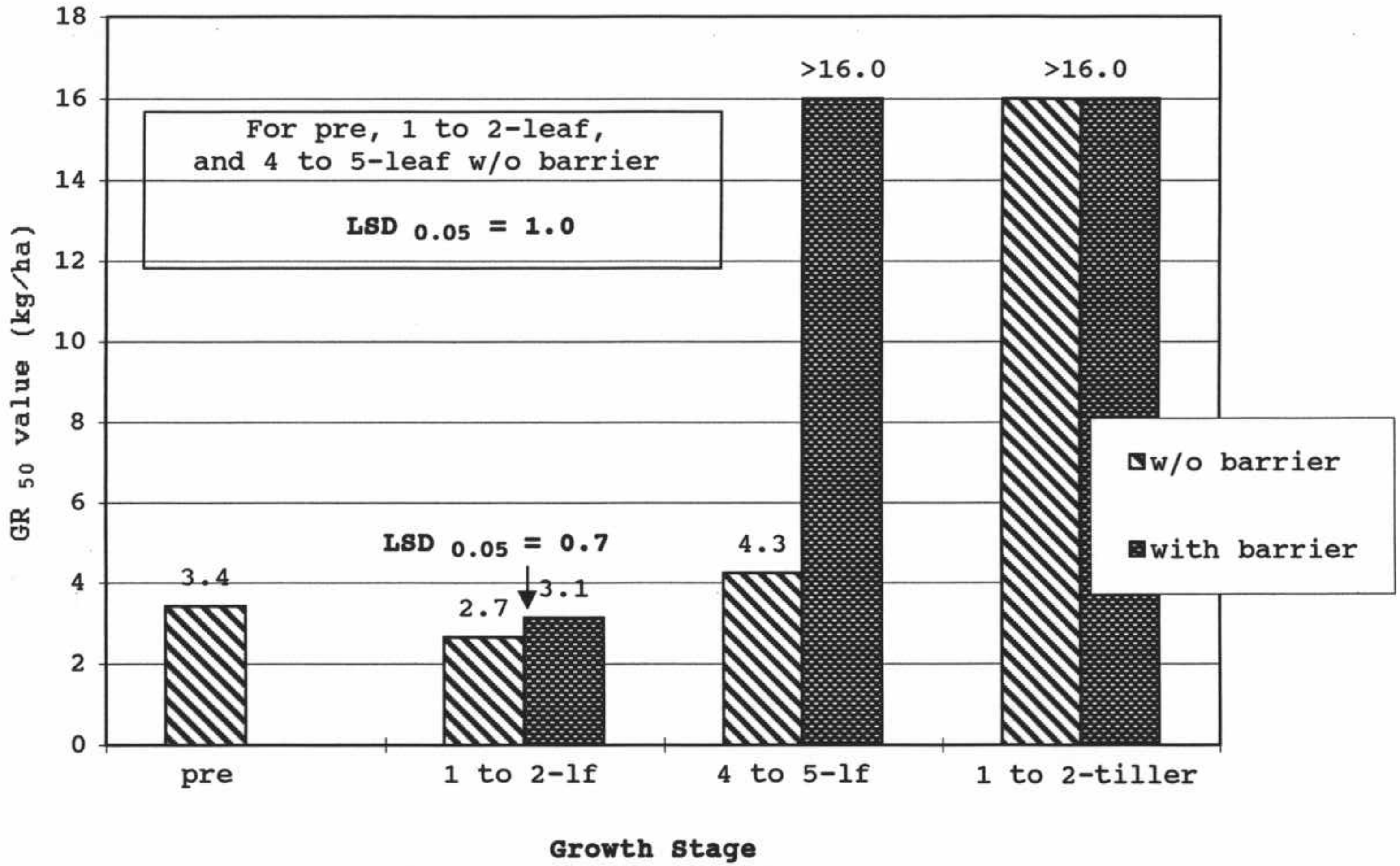

Figure 6. Calculated GR $_{50}$ values for quinclorac as affected by goosegrass growth stage and presence of vermiculite soil barrier.

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