

## Formulation and Adjuvant Effects on Uptake and Translocation of Clethodim in Bermudagrass (*Cynodon dactylon*)

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The effect of formulation and adjuvants on absorption and translocation of  $^{14}\text{C}$ -clethodim was determined at 1, 4, 12, 24, 48, and 72 h after treatment (HAT) in bermudagrass under greenhouse conditions. Absorption of  $^{14}\text{C}$ -clethodim with the  $0.12\text{ kg L}^{-1}$  (15 to 85%) formulation was higher than with the  $0.24\text{ kg L}^{-1}$  (5 to 40%) formulation, regardless of presence or absence of adjuvant. There was considerable variation in the effect of adjuvant on  $^{14}\text{C}$ -clethodim absorption. When either ammonium sulfate (AMS) or AMS plus crop oil concentrate (COC) was added to the  $0.12\text{ kg L}^{-1}$  formulation,  $^{14}\text{C}$ -clethodim absorption increased significantly at all harvest times except at 12 HAT compared with  $0.12\text{ kg L}^{-1}$  formulation alone, whereas,  $^{14}\text{C}$ -clethodim absorption after addition of COC to the  $0.12\text{ kg L}^{-1}$  formulation was similar to the  $0.12\text{ kg L}^{-1}$  formulation alone up to 24 HAT. Conversely, COC enhanced  $^{14}\text{C}$ -absorption at all harvest times when added to  $0.24\text{ kg L}^{-1}$  formulation. Most of  $^{14}\text{C}$ -clethodim (79 to 100% of absorbed) remained in the treated leaf, independent of formulation or adjuvant. Formulation did not have an impact on distribution of absorbed  $^{14}\text{C}$ -clethodim; however, presence of an adjuvant increased movement of  $^{14}\text{C}$ -clethodim out of treated leaf. Of the absorbed  $^{14}\text{C}$ -label, most remained in the treated leaf.  $^{14}\text{C}$ -clethodim that translocated out of the treated leaf remained in the shoot, and negligible amount of  $^{14}\text{C}$ -clethodim translocated to roots. These results demonstrated improved absorption of clethodim with formulations containing half the active ingredient ( $0.12\text{ kg L}^{-1}$ ) and inclusion of both AMS and COC.

**Nomenclature:** Clethodim; bermudagrass, *Cynodon dactylon* (L.) Pers. CYNDA.

**Key words:** Absorption; adjuvant; autoradiography; distribution.

Growers in the United States have rapidly adopted herbicide-resistant crops, especially glyphosate-resistant (GR) crops, and have planted about 87% of soybean [*Glycine max* (L.) Merr.], 61% of cotton [*Gossypium hirsutum* L.], and 26% of corn [*Zea mays* L.] hectares to GR varieties in 2005 (USDA 2005). Volunteer grass crops, especially volunteer GR corn, pose real management challenges (in soybean and cotton). Traditionally, volunteer grass crops and grass weeds, for example, bermudagrass, have been controlled by POST graminicides, such as clethodim. Bermudagrass is considered a menace in 40 crops, spread over 80 countries (Holm et al. 1979). Bermudagrass was first introduced into the United States in 1751 (Callahan and Engel 1965). It has been used as a forage crop, soil erosion barrier, and a turfgrass because of its hardy growth habit and ability to survive in conditions not suitable for other weeds. Bermudagrass has eventually developed into a troublesome weed across the southern United States (Webster and Coble 1997). For example, it has reduced sugar yields by 8 to 13% in sugarcane (*Saccharum officinarum* L.) (Richard and Dalley 2005).

Clethodim is registered in cotton, peanut (*Arachis hypogaea* L.), soybean, and various other broadleaf crops (Anonymous 2005a). It belongs to the cyclohexanedione chemical family of herbicides, which are potent inhibitors of the enzyme acetyl-coenzyme A carboxylase (ACCase, EC 6.4.1.2) (Burton et al. 1987). Clethodim is commercially available as a  $0.24\text{ kg ai L}^{-1}$  emulsifiable concentrate formulation. The composition of this formulation comprises of clethodim (25 to 27%), naphthalene (5 to 7%), trimethylbenzene (2 to 3%), total hydrocarbons (65 to 71%), and other ingredients (1 to 10%), all percentages on the basis of weight (Anonymous 2005b). A newer formulation of clethodim with half the active in-

gredient ( $0.12\text{ kg L}^{-1}$ ) will be commercialized soon for control of grasses and volunteer grass crops including glyphosate-resistant corn (J. Smith, personal communication). Differences in composition of the  $0.12\text{ kg L}^{-1}$  formulation and the  $0.24\text{ kg L}^{-1}$  formulation are not limited to the amount of active ingredient clethodim. The  $0.12\text{ kg L}^{-1}$  formulation consists of clethodim (12 to 14%), naphthalene (<5%), total hydrocarbons (45 to 48%), and other ingredients (39 to 42%), all percentages on the basis of weight (J. Smith, personal communication). A pending patent on the new formulation limits further description of its composition.

Clethodim is generally applied with an adjuvant, crop oil concentrate (COC), alone or in combination with a nitrogen source (e.g., ammonium sulfate [AMS]), for maximum efficacy (Anonymous 2005a). Potentially, the  $0.12\text{ kg L}^{-1}$  formulation will be tank-mixed with glyphosate in the near future, and glyphosate ( $660\text{ g L}^{-1}$  formulation, Monsanto Co.) cannot be mixed with a formulation requiring COC. AMS improved control of selected annual grasses by clethodim, despite presence of broadleaf- and sedge-controlling herbicide treatments (Burke et al. 2004), which have been shown to antagonize graminicidal activity of clethodim (Burke and Wilcut 2003). Adjuvants improve herbicide efficacy (Hatzios and Penner 1985; Wanamarta and Penner 1989a) by increasing herbicide absorption (Hull et al. 1982; Wanamarta and Penner 1989b). The performance of adjuvants is influenced by the herbicide with which it is used as well as the weed species, water quality, and prevailing weather conditions (Hatzios and Penner 1985; Hull et al. 1982; McWhorter 1982). Ahrens (1994) noted that ultraviolet light degrades clethodim. Therefore, the addition of adjuvants to clethodim potentially increase herbicide efficacy by decreasing exposure of clethodim to ultraviolet light and preventing its breakdown to nonphytotoxic forms.

Characterization of clethodim formulation efficacy and the influence of formulation and adjuvants on  $^{14}\text{C}$ -clethodim absorption would lead to better understanding and efficient use of clethodim in grass weed management. The objectives of

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this research were (1) to determine efficacy of two formulations of clethodim, 0.12 kg L<sup>-1</sup> and 0.24 kg L<sup>-1</sup>, on bermudagrass and (2) to determine effect of formulation and adjuvants on absorption and translocation of clethodim in bermudagrass. Commercial formulations of clethodim were used in the efficacy studies, and <sup>14</sup>C-clethodim was used in the absorption and translocation studies.

## Materials and Methods

**Plant Materials.** Seeds of bermudagrass<sup>1</sup> were planted in 10-cm-diam by 10-cm-deep plastic pots<sup>2</sup> containing a mixture of soil<sup>3</sup> (Bosket sandy loam, fine-loamy, mixed, thermic Mollic Hapludalfs) and potting soil<sup>4</sup> (1 : 1 v/v). Plants were subirrigated as needed. After emergence, seedlings were thinned to one plant per pot. At 2 wk after emergence, plants were fertilized with a nutrient solution<sup>5</sup> containing 200 mg L<sup>-1</sup> each of N, P<sub>2</sub>O<sub>5</sub>, and K<sub>2</sub>O. Plants were grown outdoors during September to October 2004 at the Southern Weed Science Research Unit, U.S. Department of Agriculture, Stoneville, MS. Outdoor conditions were 27/16 ± 4 C day/night temperatures, with a natural light photoperiod of 12 to 13 h. For absorption, translocation, and autoradiography experiments, uniform plants with 15-cm lateral shoot growth were transferred from outdoors to a greenhouse 2 d before <sup>14</sup>C-clethodim application for acclimatization. The greenhouse was maintained at 25/20 ± 3 C day/night temperatures, with natural light supplemented by sodium vapor lamps to provide a 13-h photoperiod (300 μmol m<sup>-2</sup> s<sup>-1</sup>) from the time of <sup>14</sup>C-clethodim-based treatments until harvest.

**Herbicide Efficacy.** Herbicide solutions were prepared using commercial formulations. All treatments were applied with a handheld, backpack boom sprayer, equipped with 8002E flat-fan nozzles,<sup>6</sup> delivering a spray volume of 140 L ha<sup>-1</sup> at 140 kPa. Bermudagrass (15-cm lateral shoot growth, 42 d after planting) plants were treated with both formulations, 0.12 kg L<sup>-1</sup>-clethodim<sup>7</sup> and 0.24 kg L<sup>-1</sup>-clethodim,<sup>7</sup> at 0.11 and 0.14 kg ha<sup>-1</sup>. A nonionic surfactant (NIS)<sup>8</sup> at 0.25% (v/v) was added to the 0.12 kg L<sup>-1</sup> formulation, and a COC<sup>9</sup> at 1% (v/v) was added to the 0.24 kg L<sup>-1</sup> clethodim treatments. Treatments containing 0.12 kg L<sup>-1</sup> clethodim with COC were not included. The 0.12 kg L<sup>-1</sup> formulation will potentially be tank-mixed with glyphosate in the near future, and glyphosate cannot be mixed with a formulation requiring COC. All treatments included 2.8 kg ha<sup>-1</sup> AMS.<sup>10</sup>

Nontreated bermudagrass plants were used as the controls. Aboveground shoot dry weight was measured 3 wk after treatment (WAT). Dry weight measurements are expressed as a percentage of the nontreated control. The experiment was conducted twice using eight replications per treatment.

**Absorption and Translocation.** <sup>14</sup>C-clethodim<sup>11</sup> (<sup>14</sup>C-label on the four and six positions of the cyclohexane ring, 98% purity, specific activity 2.12 GBq mmol<sup>-1</sup>) in acetonitrile was mixed with either the commercial 0.12 kg L<sup>-1</sup> formulation or the 0.24 kg L<sup>-1</sup> formulation of clethodim and selected additives to create the treatment solutions. The <sup>14</sup>C-clethodim treatment solution was prepared by diluting <sup>14</sup>C-clethodim in commercial formulations of clethodim with and without adjuvants to give a final concentration of 0.0053 g ml<sup>-1</sup> at an

application rate of 0.11 kg ha<sup>-1</sup> in 190 L of water. Bermudagrass plants were treated with the 0.12 kg L<sup>-1</sup> formulation of clethodim at 0.1 kg, alone, and in combination with AMS (2.8 kg ha<sup>-1</sup>), COC (1% v/v), and COC (1% v/v) plus AMS (2.8 kg ha<sup>-1</sup>), and treated with the 0.24 kg L<sup>-1</sup> formulation of clethodim at 0.1 kg, alone and in combination with COC (1% v/v). Each plant received 6.7 kBq of <sup>14</sup>C-clethodim in a total volume of 10 μL. Treatment solutions were applied with a microsyringe<sup>12</sup> to the adaxial leaf surface of lateral or secondary shoot growth of 6-wk-old bermudagrass as four 2.5-μl droplets.

Plants were harvested 1, 4, 12, 24, 48, and 72 h after treatment (HAT) and divided into treated leaf, shoot, and root. Treated leaves were excised and washed by gentle shaking for 20 s in 5 ml of 50% aqueous methanol to remove nonabsorbed <sup>14</sup>C-clethodim remaining on the leaf surface. The harvested parts were each wrapped in a single layer of tissue paper,<sup>13</sup> placed in a glass vial, and oven-dried at 60 C for 48 h. Oven-dried plant samples were combusted in a biological oxidizer,<sup>14</sup> and the evolved <sup>14</sup>CO<sub>2</sub> was trapped in 10 ml of Carbosorb E<sup>15</sup> and 12 ml of Permaflour E<sup>+</sup>.<sup>16</sup> Two 1-ml aliquots of each leaf wash were mixed with 10 ml of scintillation cocktail.<sup>17</sup> Radioactivity from leaf washes and oxidations was quantified using liquid scintillation spectrometry.<sup>18</sup> Recovery of <sup>14</sup>C was 94%. The experiment was conducted twice using three replications per treatment.

**Autoradiography.** Six-week-old bermudagrass plants were treated with 13.4 kBq of <sup>14</sup>C-clethodim in a total volume of 10 μl, as described in the absorption and translocation experiments. After harvest, plants were mounted on white, glossy paper (avoiding contact of the treated leaf with other parts of the plant), pressed, and dried at 60 C for 48 h. The order of the material stacked in the press from bottom to top was metal plate, mounted plant, piece of foam rubber, wire screen, and second metal plate. The press was held together by large, metal binder clips on all four sides. X-ray film<sup>19</sup> was exposed to dried plants for 4 wk. After exposure, the film was developed<sup>20</sup> and fixed.<sup>21</sup> The experiment was conducted once using two replications per treatment. Plants not treated with <sup>14</sup>C-clethodim were used as the control.

**Statistical Analyses.** Data from all experiments, except autoradiography, were analyzed by ANOVA. The data represent the average of the repeated experiments because there was a nonsignificant experiment-by-treatment interaction. Fisher's Protected LSD (P = 0.05) was used to compare treatment means in the herbicide efficacy experiments. Data from absorption and translocation experiments was subjected to regression analysis.

## Results and Discussion

**Herbicide Efficacy.** Control of 6-wk-old bermudagrass plants was 100% (with 0 indicating no injury, and 100% indicating complete plant death) averaged across all herbicide treatments, regardless of the formulation or adjuvant used (data not shown). Injury symptoms were similar between the formulations, with complete leaf necrosis and disintegration of the growing point. The percentage of reduction in shoot dry weight, compared with nontreated control, tended to be higher with the 0.12 kg L<sup>-1</sup> formulation (80 to 84%) than

Table 1. Effect of 0.12 kg L<sup>-1</sup> and 0.24 kg L<sup>-1</sup> formulations of clethodim on 6-wk-old bermudagrass 3 wk after treatment.

Treatment	Rate	Shoot dry weight
	kg ha <sup>-1</sup>	% of nontreated control
0.12 kg L <sup>-1</sup> clethodim + NIS <sup>ca</sup> + AMS <sup>cb</sup>	0.11	20
0.12 kg L <sup>-1</sup> clethodim + NIS + AMS	0.14	16
0.24 kg L <sup>-1</sup> clethodim + COC <sup>ca</sup> + AMS	0.11	31
0.24 kg L <sup>-1</sup> clethodim + COC + AMS	0.14	24
LSD (0.05)		6

<sup>a</sup> Abbreviations: AMS, ammonium sulfate; COC, crop oil concentrate; NIS, nonionic surfactant.

<sup>b</sup> NIS applied at 0.25% v/v, AMS at 28 kg ha<sup>-1</sup>, and COC at 1% v/v.

with the 0.24 kg L<sup>-1</sup> formulation (69 to 76%) (Table 1). Clethodim rate had a significant impact on the growth reduction of bermudagrass with the 0.24 kg L<sup>-1</sup> formulation but not with the 0.12 kg L<sup>-1</sup> formulation. This suggests that a lethal dose of clethodim was being translocated more often in plants treated with the 0.12 kg L<sup>-1</sup> formulation than in plants treated with the 0.24 kg L<sup>-1</sup> formulation. The practical implications of a quicker plant death with the 0.12 kg L<sup>-1</sup> formulation could be a narrower window between application and planting, when bermudagrass is a problem or when a shorter period of crop competition is important, as in the case of volunteer GR corn in broadleaf crops. Of course, the latter case would require further investigation to determine whether GR corn is also more effectively killed with the 0.12 g L<sup>-1</sup> formulation.

**Absorption and Translocation.** <sup>14</sup>C-clethodim absorption pattern over time could best be described by an equation, fitted to the raw data, in the form:  $y = a / \{1 + \exp[-(x - x_0) / b]\}$ , where  $y$  is the amount of <sup>14</sup>C as a percentage of that applied,  $a$  is the difference between the upper and lower response limits (asymptotes),  $x_0$  is the time after treatment for a given measure of  $y$ ,  $b$  is the slope of the curve around  $x_0$ , and  $x$  is the time after treatment (Figure 1). The type of clethodim formulation clearly affected absorption of <sup>14</sup>C-clethodim in 6-

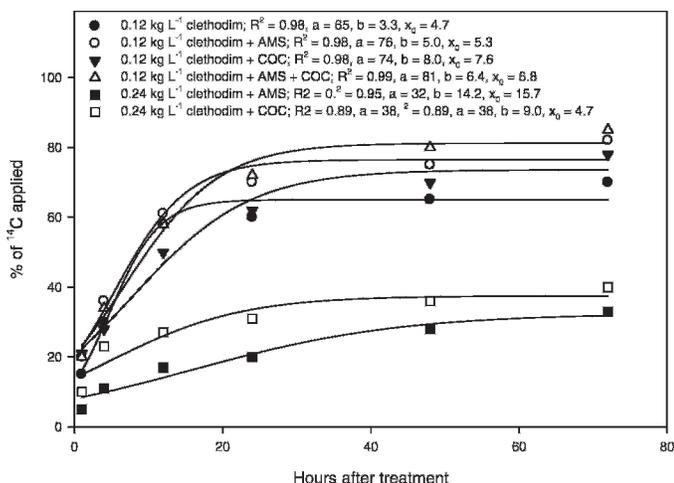


Figure 1. Absorption of <sup>14</sup>C-clethodim applied to 6-wk-old bermudagrass. Abbreviations: AMS, ammonium sulfate; COC, crop oil concentrate. AMS applied at 2.8 kg ha<sup>-1</sup> and COC at 1% v/v. Plants were grown outdoors and then transferred to a greenhouse 2 d before <sup>14</sup>C-clethodim application for acclimatization. The greenhouse was maintained at 25/20 ± 3 C day/night temperatures, with natural light supplemented by sodium vapor lamps to provide a 13-h photoperiod (300 μmol m<sup>-2</sup> s<sup>-1</sup>) from the time of <sup>14</sup>C-clethodim-based treatments until harvest.

wk-old bermudagrass, especially at 12 HAT and beyond. Absorption was greater with the 0.12 kg L<sup>-1</sup> formulation at 72 HAT (70%) than with the 0.24 kg L<sup>-1</sup> formulation (33%). By 24 HAT, <sup>14</sup>C-clethodim absorption in bermudagrass treated with the 0.12 kg L<sup>-1</sup> formulation with COC, AMS or COC + AMS was at least 62% of applied. In general, clethodim and other cyclohexanedione herbicides are rapidly absorbed (Culpepper et al. 1999; Wanamarta and Penner 1989a). For example, <sup>14</sup>C-clethodim absorption in goosegrass [*Eleusine indica* (L.) Gaertn.] increased from 36% of applied at 0.5 HAT to 89% of applied at 96 h (Burke and Wilcut 2003). There was variation in the effects of adjuvants on <sup>14</sup>C-clethodim absorption. However, there were few apparent trends. The addition of COC to the 0.12 kg L<sup>-1</sup> formulation did not cause an increase in <sup>14</sup>C-absorption compared with the 0.12 kg L<sup>-1</sup> formulation alone. In fact, absorption was 8 percentage points less at 12 HAT with the addition of COC to the 0.12 kg L<sup>-1</sup> formulation. When either AMS or AMS plus COC was added to the 0.12 kg L<sup>-1</sup> formulation, <sup>14</sup>C-clethodim absorption increased significantly at all harvest times except at 12 HAT compared with the 0.12 kg L<sup>-1</sup> formulation alone. Jordan et al. (1990) reported increased rates of sethoxydim absorption when applied with COC and AMS in large crabgrass (*Digitaria sanguinalis* (L.) Scop.) rather than COC alone. COC enhanced <sup>14</sup>C-absorption at all harvest intervals when applied in mixture with the 0.24 kg L<sup>-1</sup> formulation. Culpepper et al. (1999) reported that COC caused more <sup>14</sup>C-clethodim to be absorbed than NIS in barnyardgrass [*Echinochloa crus-galli* (L.) Beauv.].

<sup>14</sup>C-clethodim remaining in the treated leaf over time could best be described by an equation of the form:  $y = y_0 + ax$ , where  $y$  is amount of <sup>14</sup>C as the percentage of that absorbed,  $y_0$  is the intercept,  $a$  is the slope, and  $x$  is the time after treatment (Figure 2). The majority (79 to 100%) of absorbed <sup>14</sup>C-clethodim remained in the treated leaf. Cyclohexanedione herbicides typically are very rapidly absorbed, but very little <sup>14</sup>C is actually translocated out of the treated leaf (Campbell and Penner 1987; Culpepper et al. 1999). There were no clear differences in <sup>14</sup>C-clethodim accumulation in the treated leaf between the 0.12 kg L<sup>-1</sup> and 0.24 kg L<sup>-1</sup> formulations, except, as harvest time increased from 1 to 72 HAT, more <sup>14</sup>C-clethodim moved out of the treated leaf. Variation was observed on the influence of adjuvants on <sup>14</sup>C-clethodim distribution. Addition of COC plus AMS in mixture with the 0.12 kg L<sup>-1</sup> formulation resulted in greater movement of <sup>14</sup>C-clethodim (1 to 14%) from the treated leaf at all harvest times except 1 HAT compared with all the other formulation and adjuvant combinations. Neither COC or AMS added to the 0.12 kg L<sup>-1</sup> formulation nor COC added to 0.24 kg L<sup>-1</sup> formulation caused consistent movement of <sup>14</sup>C-clethodim out of the treated leaf.

<sup>14</sup>C-clethodim translocation to the shoot over time could best be described by an equation of the form:  $y = y_0 + ax$  (Figure 3). Parameters of the equation have been explained earlier. The rate of translocation of <sup>14</sup>C-clethodim in the shoot was nearly doubled (1.6-fold) from the 0.24 kg L<sup>-1</sup> formulation to the 0.12 kg L<sup>-1</sup> formulation at 72 HAT without any adjuvants. The amount of <sup>14</sup>C-clethodim (percentage absorbed) that moved in to the shoot per unit time was 0.17, 0.14, 0.15, 0.14, and 0.13 with the 0.12 kg L<sup>-1</sup> formulation and 0.15, 0.13, 0.11, 0.12, and 0.8 with the 0.24 kg L<sup>-1</sup> formulation at 4, 12, 24, 28, and 72 HAT,

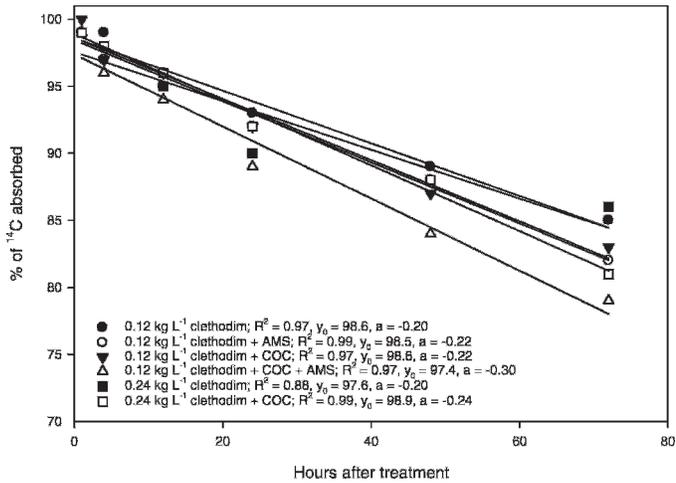


Figure 2. Amount of absorbed  $^{14}\text{C}$ -clethodim remaining in the treated leaf of 6-wk-old bermudagrass. Abbreviations: AMS, ammonium sulfate; COC, crop oil concentrate. AMS applied at  $2.8 \text{ kg ha}^{-1}$  and COC at 1% v/v. Plants were grown outdoors and then transferred to a greenhouse 2 d before  $^{14}\text{C}$ -clethodim application for acclimatization. The greenhouse was maintained at  $25/20 \pm 3 \text{ C}$  day/night temperatures, with natural light supplemented by sodium vapor lamps to provide a 13-h photoperiod ( $300 \mu\text{mol m}^{-2} \text{ s}^{-1}$ ) from the time of  $^{14}\text{C}$ -clethodim-based treatments until harvest.

respectively. This increase in translocation of clethodim with the  $0.12 \text{ kg L}^{-1}$  formulation over the  $0.24 \text{ kg L}^{-1}$  formulation may explain the observed efficacy results. Addition of adjuvant in mixture with the  $0.12 \text{ kg L}^{-1}$  formulation did not cause any increase in accumulation of  $^{14}\text{C}$ -clethodim in the shoot. In contrast, accumulation of  $^{14}\text{C}$ -clethodim was greater when COC was applied in mixture with the  $0.24 \text{ kg L}^{-1}$  formulation than when the  $0.24 \text{ kg L}^{-1}$  formulation was applied alone. By 72 HAT,  $^{14}\text{C}$ -label movement to the shoot at 24 to 72 HAT ranged from 3 to 14% of absorbed, irrespective of formulation or adjuvant. Translocation of  $^{14}\text{C}$ -clethodim in goosegrass was 8.3% of applied  $^{14}\text{C}$  into the shoot portion at 96 HAT (Burke and Wilcut 2003).

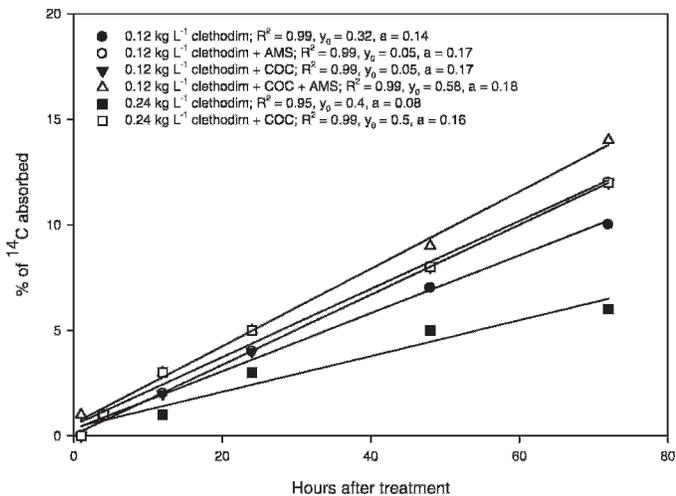


Figure 3. Amount of absorbed  $^{14}\text{C}$ -clethodim in the shoot of 6-wk-old bermudagrass. Abbreviations: AMS, ammonium sulfate; COC, crop oil concentrate. AMS applied at  $2.8 \text{ kg ha}^{-1}$  and COC at 1% v/v. Plants were grown outdoors and then transferred to a greenhouse 2 d before  $^{14}\text{C}$ -clethodim application for acclimatization. The greenhouse was maintained at  $25/20 \pm 3 \text{ C}$  day/night temperatures, with natural light supplemented by sodium vapor lamps to provide a 13-h photoperiod ( $300 \mu\text{mol m}^{-2} \text{ s}^{-1}$ ) from the time of  $^{14}\text{C}$ -clethodim-based treatments until harvest.

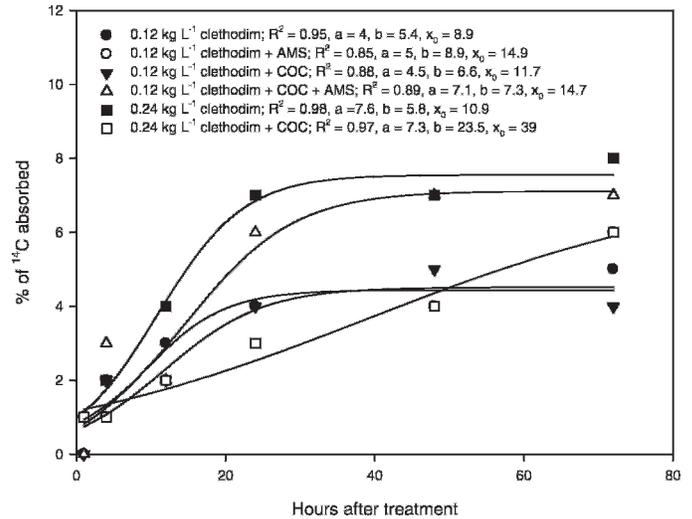


Figure 4. Amount of absorbed  $^{14}\text{C}$ -clethodim in the roots of 6-wk-old bermudagrass. Abbreviations: AMS, ammonium sulfate; COC, crop oil concentrate. AMS applied at  $2.8 \text{ kg ha}^{-1}$  and COC at 1% v/v. Plants were grown outdoors and then transferred to a greenhouse 2 d before  $^{14}\text{C}$ -clethodim application for acclimatization. The greenhouse was maintained at  $25/20 \pm 3 \text{ C}$  day/night temperatures, with natural light supplemented by sodium vapor lamps to provide a 13-h photoperiod ( $300 \mu\text{mol m}^{-2} \text{ s}^{-1}$ ) from the time of  $^{14}\text{C}$ -clethodim-based treatments until harvest.

$^{14}\text{C}$ -clethodim translocation to the root over time could best be described by an equation of the form:  $y = a\{1 + \exp[-(x - x_0)/b]\}$  (Figure 4). Parameters of the equation have been explained earlier. A significant interaction between formulation and adjuvant occurred for translocation of the radiolabel to the root. When applied without adjuvant, greater  $^{14}\text{C}$ -clethodim levels accumulated in the root with the  $0.24 \text{ kg L}^{-1}$  formulation (1 to 8%) compared with the  $0.12 \text{ kg L}^{-1}$  formulation (1 to 5%) up to 24 HAT (Table 3). No trend was evident in the translocation of  $^{14}\text{C}$ -label to the roots with the addition of the adjuvants, AMS, COC, or COC plus AMS, to the  $0.12 \text{ kg L}^{-1}$  formulation, whereas COC caused a decrease in  $^{14}\text{C}$ -label accumulation with the  $0.24 \text{ kg L}^{-1}$  formulation (1 to 6%) compared with  $0.24 \text{ kg L}^{-1}$  formulation alone (1 to 8%). This is reflected in the increased accumulation of  $^{14}\text{C}$ -clethodim in the rest of the shoot on addition of adjuvant at 12 HAT and beyond.

**Autoradiography.** X-ray autoradiograms of bermudagrass are represented in Figure 5. Numbers represent  $^{14}\text{C}$ -clethodim applied as (1)  $0.12 \text{ kg L}^{-1}$ , (2)  $0.12 \text{ kg L}^{-1} + \text{AMS}$ , (3)  $0.12 \text{ kg L}^{-1} + \text{COC}$ , (4)  $0.12 \text{ kg L}^{-1} + \text{AMS}$  plus COC, (5)  $0.24 \text{ kg L}^{-1}$ , and (6)  $0.24 \text{ kg L}^{-1} + \text{COC}$ , respectively. Panels A to H and A' to H' represent bermudagrass plant specimens and autoradiograms, respectively. The first and second rows of panels correspond to 24 HAT, and the third and fourth rows of panels correspond to 72 HAT. The arrow indicates the treated leaf.  $^{14}\text{C}$ -clethodim applied to the third true leaf of 20-cm-tall bermudagrass plants did not translocate appreciably to all parts of the plant. Of the absorbed  $^{14}\text{C}$ -label, most remained in the treated leaf as evidenced by the intense image of treated leaf in all treatments at both 24 and 72 HAT (Figures 5A', B', C', E', F', G'). The same was also ascertained by quantization in the translocation study (Figures 2–4). Distribution of  $^{14}\text{C}$ -label that translocated out of the treated leaf was restricted to the shoot, and only

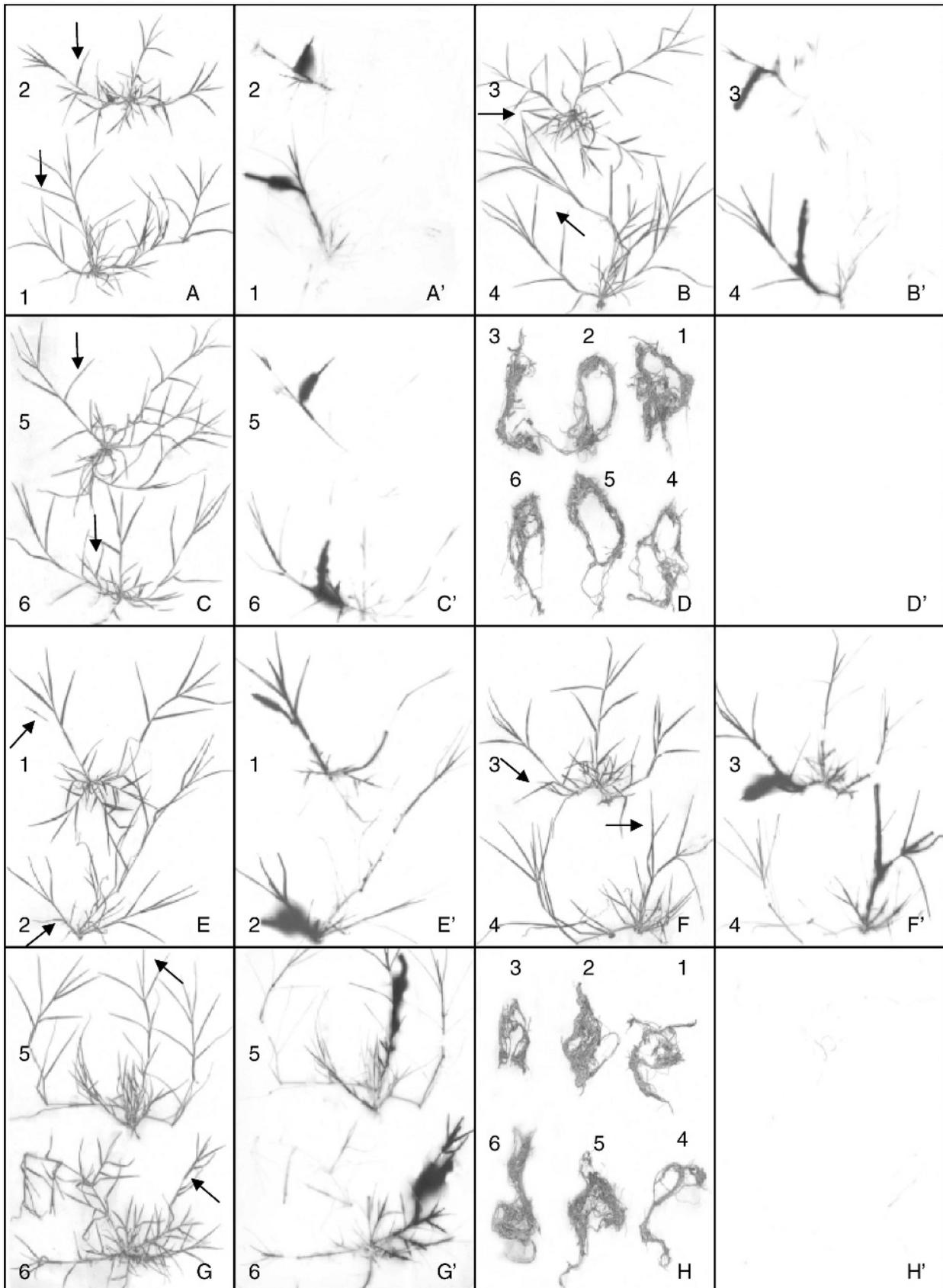


Figure 5. Autoradiograms representing translocation and distribution of  $^{14}\text{C}$ -clethodim applied in a solution of  $0.12 \text{ kg L}^{-1}$  formulation or  $0.24 \text{ kg L}^{-1}$  formulation in 6-wk-old bermudagrass at 24 h (first and second rows) and 72 h (third and fourth rows). Arrow indicates the treated leaf. Panels A to H and A' to H' represent bermudagrass plant specimens and corresponding autoradiograms, respectively. Numbers represent  $^{14}\text{C}$ -clethodim applied as (1)  $0.12 \text{ kg L}^{-1}$ , (2)  $0.12 \text{ kg L}^{-1}$  + ammonium sulfate (AMS), (3)  $0.12 \text{ kg L}^{-1}$  + crop oil concentrate (COC), (4)  $0.12 \text{ kg L}^{-1}$  + AMS plus COC, (5)  $0.24 \text{ kg L}^{-1}$ , and (6)  $0.24 \text{ kg L}^{-1}$  + COC, respectively.

a negligible quantity of  $^{14}\text{C}$ -label translocated to roots (Figures 5D', H'). Increase in intensity of the image in the autoradiograms indicated that  $^{14}\text{C}$ -clethodim accumulations increased in the shoot from 24 to 72 HAT (Figure 5A' vs. E', B' vs. F', C' vs. G') with only a faint increase in the image intensity of the roots from 24 HAT to 72 HAT (Figure 5D' vs. H'). The addition of adjuvant to either clethodim formulation caused an increase in absorption of  $^{14}\text{C}$ -clethodim (Figure 1) compared with  $^{14}\text{C}$ -label absorption when clethodim formulation was applied alone to bermudagrass plants. The enhanced absorption in the presence of an adjuvant directly contributed to increased translocation of  $^{14}\text{C}$ -label in the shoot compared with that with formulation alone, visibly more evident at 72 HAT (Figure 5E'–G').

In summary, the  $0.12\text{ kg L}^{-1}$  formulation of clethodim, with half the active ingredient concentration, was absorbed to a greater extent than the  $0.24\text{ kg L}^{-1}$  formulation, when applied at the same rate. The addition of an adjuvant can appreciably increase absorption of the  $0.12\text{ kg L}^{-1}$  formulation, thereby resulting in enhanced efficacy of clethodim on the targeted weeds. Future research should address, simultaneously, the effect of the presence and absence of COC on absorption and translocation of the  $0.12\text{ kg L}^{-1}$  clethodim formulation to verify the premise that it can be an effective tank-mix partner of glyphosate.

### Sources of Materials

<sup>1</sup> Bermudagrass, Valent USA Corporation, Walnut Creek, CA 94596.

<sup>2</sup> National Polymers Inc., Lakeville, MN 55044.

<sup>3</sup> Research farm, Delta Research and Extension Center, Mississippi State University, Stoneville, MS 38776.

<sup>4</sup> Jiffy Mix, Jiffy Products of America Inc., Batavia, IL 60510.

<sup>5</sup> Peters Fertilizer Products, W. R. Grace and Co., Fogelsville, PA 18051.

<sup>6</sup> Teejet 8002E nozzle, Spraying Systems Company, Wheaton, IL 60118.

<sup>7</sup> Clethodim commercial formulations, Valent USA Corporation, Walnut Creek, CA 94596.

<sup>8</sup> Nonionic surfactant, X-77<sup>®</sup>, Loveland Industries Inc., Greeley, CO 80632.

<sup>9</sup> Crop oil concentrate, Methylated Spray Oil, Helena Chemical Co., Collierville, TN 38017.

<sup>10</sup> Ammonium sulfate, Platte Chemical Co., Fremont, NE 68025.

<sup>11</sup>  $^{14}\text{C}$ -clethodim, Valent USA Corporation, Walnut Creek, CA 94596.

<sup>12</sup> Hamilton syringe, Hamilton Company, Reno, NV 89520.

<sup>13</sup> Kimwipes EX-L, Kimberly-Clark Corporation, Roswell, GA 30076.

<sup>14</sup> Packard oxidizer 306, Packard Instruments Co., Dowers Grove, IL 60515.

<sup>15</sup> Carbosorb E, Packard Instruments Co., Meridian, CT 06450.

<sup>16</sup> Permafluor E<sup>+</sup>, Packard Instrument Co., Meridian, CT 06450.

<sup>17</sup> EcoLume, ICN, Costa Mesa, CA 92626.

<sup>18</sup> Minaxi $\beta$  Tri-carb 4000 series liquid scintillation counter, Packard Instruments Co., Dowers Grove, IL 60515.

<sup>19</sup> X-ray film, X-Omat<sup>®</sup> AR 5, Eastman Kodak Co., Rochester, NY 14650.

<sup>20</sup> GBX Developer, Eastman Kodak Co., Rochester, NY 14650.

<sup>21</sup> GBX Fixer, Eastman Kodak Co., Rochester, NY 14650.

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