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ARTICLE

Fate and Efficacy of Metolachlor Granular and Emulsifiable Concentrate Formulations in a Conservation Tillage System

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Use of genetically modified cultivars resistant to the herbicide glyphosate (*N*-phosphonomethylglycine) is strongly associated with conservation-tillage (CsT) management for maize (*Zea mays* L.), soybean (*Glycine max* L.), and cotton (*Gossypium hirsutum* L.) cultivation. Due to the emergence of glyphosate-resistant weed biotypes, alternate weed management practices are needed to sustain CsT use. This work focused on metolachlor use (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide) in a CsT system. The fate and efficacy of granular and emulsifiable concentrate (EC) formulations or an EC surrogate were compared for CsT cotton production in the Atlantic Coastal Plain region of southern Georgia (USA). The granular formulation, a clay−alginate polymer, was produced in the authors' laboratory; EC was a commercial product. In field and laboratory dissipations the granular metolachlor exhibited 8-fold greater soil persistence. Rainfall simulation runoff assessments indicated that use of the granular formulation in a common CsT system, strip-tillage (ST), may reduce metolachlor runoff loss when compared to conventional tillage (CT) management or when EC formulations are used in the ST system. Metolachlor leaching assessments using field-deployed lysimeters showed some tillage (ST > CT) and formulation (EC > granular) differences. Overall leaching was generally small when compared to runoff loss. Finally, greenhouse bioassays showed control of two weed species with the granular was greater than or equal to that of the EC formulation; however, the granular formulation suppressed cotton growth to a greater extent. In sum, this metolachlor granular formulation has advantages for CsT cotton production; however, additional research is needed to assess impacts on crop injury.

KEYWORDS: Herbicide; cotton; glyphosate; resistance; strip-tillage

INTRODUCTION

Over the past three decades conservation tillage (CsT) management for large-scale maize, soybean, and cotton cultivation has steadily increased worldwide (*1*). For cotton there is a strong association with CsT and use of herbicide-tolerant varieties produced by genetic modification (*2*). These varieties facilitate weed control by allowing both pre- and postemegence application of nonselective herbicides such as glyphosate (*3*). A troubling development is emergence of glyphosate-resistant weed biotypes. One of the most problematic is a 16-fold glyphosate-resistant Palmer amaranth (*Amaranthus palmeri*), initially identifed in a cotton field in south-central Georgia (USA) (*4*). The weed is rapidly spreading and unless controlled may cause significant economic or total crop loss (*5*).

The current recommendation for CsT cotton production in the region is to increase use of soil residual herbicides (*6*). Typically, they are broadcast spray applied at planting. CsT systems by definition have >30% of the soil surface covered by prior crop residue at planting (*7*). The residue mulch intercepts a portion of herbicide spray approximatley equal to the soil surface coverage. This may reduce weed control efficacy, especially with herbicides that bind strongly to crop residues (*8*−*11*). Additionally, several studies have indicated that mulch interception and subsequent washoff of active ingredients that are weakly to moderately sorbed may increase herbcide runoff loss even though total runoff volumes are decreased (*10*−*12*).

Use of dry granular herbicide formulations in CsT systems may offer a solution by reducing mulch interception and increasing delivery to soil during application. For example, a granular alachlor (2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide) formulation contributed 2−3 times more of the active ingredient to soil surfaces covered by corn stover residues when compared to alachlor EC applied in water and provided better control of common lambsquarters (*Chenopodium album* L.), giant foxtail (*Setaria faberi*), and green foxtail (*Seteria vividis*) in a no-till corn system (*13*).

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These data suggest that granular herbicide formulations have the potential to improve weed management options for CsT cropping systems while reducing off-site water quality impacts. However, studies that report granular herbicide performance in CsT systems are rare and have focused almost entirely on no-till corn production systems (*13*−*16*).

Data needs for cropping systems used for cotton production in the Atantic Coastal Plain region of the southeastern United States prompted the current study. The performance of clay−alginate encapsulated granular (hereafter referred to as "granular") and emulsifiable concentrate (EC) metolachlor formulations when applied in either a strip-till (ST) CsT system or a "conventional tillage system" (CT) were compared. In field-based lysimeter leaching studies and laboratory dissipation assessments, technical grade metolachlor coated on fine sand was used as a surrogate for the EC formulation when applied to soil. This approach improved application precision for these small-scale experiments. CT management involved turning cover crop residue into soil prior to planting. Metolachlor was chosen for study because herbicides containing this active ingredient are widely used by cotton and peanut (*Arachis hypogaea*) growers in the region. The herbicide provides effective control of many problematic weedy plants including those that have become resistant to glyphosate (*6*). Metolachlor also has properties that may contrubute to leaching and runoff, and its use has the potential to negatively affect surface and groundwater quality (*17*).

MATERIALS AND METHODS

Study Site and Management. A gently sloping (3−4%) 0.4 ha field in Tift County, Georgia (USA), was the focus of investigations. Soil is classified as Tifton loamy sand (fine-loamy, kaolinitic, thermic, Plinthic Kaniudult). Soil properties and management were described in prior publications (*10*, *11*). The field was equally divided across the slope into the two tillage blocks (ST and CT). Tillage practices were established in 1999 and maintained annually. Since establishment, cotton and peanut were produced rotationally in the field with a rye (*Secale cearale* L.) cover crop planted after crop harvest each autumn. A burn-down application of glyphosate was made about 1 month prior to planting in each of the following springs. With the ST system, crops were planted in 15 cm strips tilled into the cover crop residue. At planting, the average (standard deviation) of ST soil coverage by residue was 52 (11)% (Dana Sullivan, personal communication). In the CT area, crops were planted into beds of freshly tilled soil free of surface residue. Tillage was accomplished with a chisel plow followed by disking and bedding. Planting dates and crop management followed University of Georgia recommended practices.

Herbicide Formulations. Metolachlor emulsifiable concentrate was the commercial product Stalwart (Sipcam Agro USA, Raleigh, NC; 86.4% ai). The EC surrogate used in small-scale lysimeter and laboratory dissipation studies was prepared by mixing an acetone solution of technical grade metolachlor (Drexel Inc., Memphis, TN; 96% ai) with fine sand, passing a 60-mesh stainless steel sieve and allowing the acetone to evaporate in a fume hood. After drying to constant weight, the sand was mixed and stored in a sealed glass container. The granular formulation was prepared by dropwise addition of an aqueous suspension of the technical metolachlor, sodium bentonite, and sodium alginate to 0.5 M $CaCl_2$ (*18*). The suspension was prepared by stirring metolachlor (0.4 g) and 3 g each of the bentonite and alginate overnight in 100 mL of deionized water. A peristaltic pump operated at 1.3 mL min^{-1} delivered the suspension to the $CaCl_2$ solution through a 26-guage flat-tip stainless steel syringe needle. After the entire volume of the suspension was added, beads were allowed to settle for an additional 5−10 min. They were recovered by vacuum filtration followed by rinsing with 10 mL of 40% (v/v) isopropanol in water. Beads were then air-dried in a fume hood to constant weight (≈48 h). Unless specified, chemicals and supplies were purchased from Sigma-Aldrich (St. Louis, MO).

Granular Formulation Characterization. Metolachlor content of 3 lots of 10 granules was determined by crushing in a mortar pestle, suspension of the residue in methanol, and sonication for 10 min in a water bath in a Branson model 5200 Ultrasonic Cleaner (Branson Ultrasonics Inc., Danbury, CT), followed by syringe filtration (0.45 u Teflon FEP membrane) and HPLC-MS analysis. Granules were also analyzed by shaking for 3 h in 0.1 M sodium citrate, suspension in water, sequential extraction with methylene chloride, solvent exchange in methanol, and analysis by HPLC-MS. Granule volume was determined by measuring water displacement in calibrated 1 mL flasks with measurements on 6 lots of 10 granules each. Density and diameters were computed by dividing the mass by volume with diameter computed assuming spherical geometry. Metolachlor release into water was evaluated by shaking granules (100 mg) on a rotary bed shaker operating at 180 oscillations per minute with 250 mL of deionized water in screw-cap Erlenmeyer flask for 96 h at ambient temperature, 25 ± 2 °C. One milliliter samples were taken from each flask at 0.5, 1, 2, 4, 7, 24, 48, 72, and 96 h and analyzed for metolachlor by direct aqueous injection HPLC-MS.

Rainfall Simulations. Procedures and equipment were reported in prior investigations (*10*, *11*). In the current study, simulations were conducted on eight 2 × 3 m plots (four within each tillage (ST or CT) block) in May 2008. Plots were defined by pushing steel frames into the soil to a depth of 5 cm with frames spanning a wheel track and two crop rows. CT and ST plots, two each, were treated with either the EC or granular formulations. The EC was applied using a CO_2-pressurized backpack sprayer equipped with flat-fan nozzles calibrated to deliver 140 L ha^{-1} at 4.8 km h^{-1}. Four spray-targets (7 cm diameter cellulose Whatman no. 1 filter paper) were placed on the soil surface within each frame prior to spray application. Targets were analyzed to measure application rate. The measured rate (standard deviation) across all plots was 1.0 (0.5) kg ha^{-1} metolachlor. The granular formulation was applied uniformly across the plots by hand shaking from a glass bottle at 2.2 kg ha^{-1} metolachlor. The 2-fold greater metolachlor application rate with the granular product was due to a calculation error. Simulations were conducted 24 h after herbicides were applied with water obtained from a irrigation well drawing from the Floridian aquifer system. During simulations, rainfall rates and amounts were measured using a tipping bucket rain gage (Global Water Instrumentation, Gold View, CA) and 15 cm diameter collection cans (n = 3). All runoff was collected from an aluminum trough installed at the down-slope end of each frame. Runoff was composited in 5 min intervals in 12 L stainless steel buckets. Bucket contents were mixed prior to collection of two subsamples: one by filling a 1 L glass bottle and the second a 500 mL glass bottle. Bottles were sealed with Teflon-lined screw caps and placed in a 4 °C laboratory refrigerator after each simulation was completed. The remaining water in buckets (if any) was poured into 1 L polyethylene bottles. All bottles were weighed, and weights were summed to determine the total runoff volume for each time increment. Sediment mass was determined after acid flocculation and oven-drying. One hour prior to simulations composite soil samples were collected at four depths, 0−2, 2−8, 8−15, and 15−30 cm, in the area adjacent to frames to measure antecedent water content.

Field Dissipation. Sixteen gravity drainage core lysimeters, constructed from schedule-80 polyvinyl chloride (PVC) pipe (**Figure 1**), were installed in the field 2 weeks after planting. At each location (eight each in ST and CT areas), holes for the lysimeters were excavated using a posthole digger. The soil was added to the lysimeters according to position within the soil profile. Final packing density was 1.35 g cm^{-3}, the average bulk density of the surface soil. Metolachlor was added to each lysimeter surface either as the granular formulation or as technical grade coated on sand. Metolachlor application rates were 1.1 kg ha^{-1} for the latter material and 2.1 kg ha^{-1} with the granular formulation. As noted, the difference in rates was due to a computation error. Lysimeter tops were covered with nylon mesh (1 mm diameter square openings) secured with a plastic zip tie. Each core was reinserted into the same field position where soil originated. A 13 cm diameter square polyethylene tray, with the center removed, was inverted and inserted over the top of each core and placed at the soil surface to redirect rain and irrigation away from the core outer sides. Lysimeters were hand irrigated with 150 mL of deionized water on 15 occasions at weekly intervals. This was equivalent to 3.3 cm sprinkler irrigation per week. During field-wide irrigation events (six during the growing season), lysimeters were covered with polystyrene Petri dish lids; otherwise, they were left open to the atmosphere. Water samples were extracted from lysimeters by applying a vacuum to a side arm flask at 12, 21, 28, 32, 54, 67, 89, 95, and 102 days after installation. Not all lysimeters had recoverable

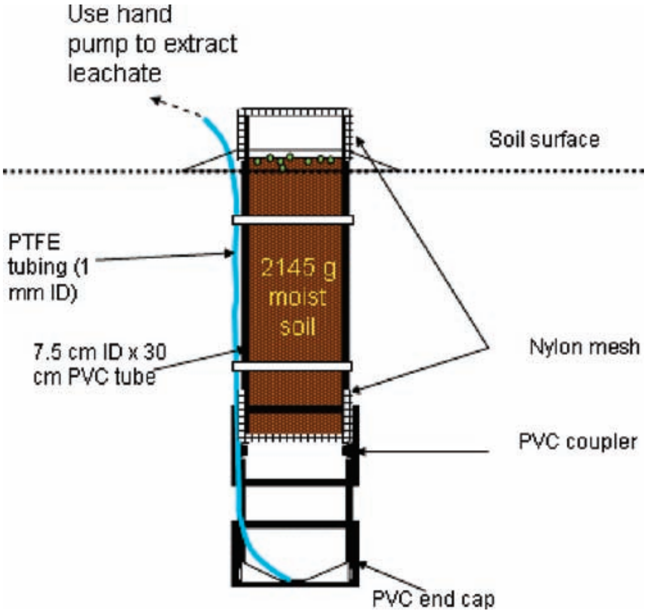

Figure 1. Lysimeter schematic.

sample at each sample time. Germinating weeds were removed by hand from lysimeter surfaces. At 110 days after installation, soil was removed in layers by depth increments corresponding to 0−2.5, 2.5−5, 5−7.5, 7.5−10, 10−15, 15−20, and 20−30 cm from one lysimeter from each treatment group. Each sample was homogenized. A 50 g subsample (wet weight) was placed in a 250 mL French-square glass bottle followed by 50 mL of methanol. Bottles were capped with Teflon-lined screw caps and stored at −20 °C.

Laboratory Soil Dissipation. A composite surface (0−2 cm) soil sample collected from the ST area of the field was sieved (10 mesh) and field-moist 50 g subsamples placed in 250 mL French-square glass bottles. The granular formulation or technical grade metolachlor coated on sand was added to 24 bottles each. The target soil metolachlor concentration, 5 μg g^{-1}, was equivalent to an application rate of 1.3 kg ha^{-1} assuming incorporation to 2 cm and soil bulk density of 1.35 g cm^{-3}. Deionized water was added to adjust gravimetric soil−water content to 0.06 g of H_2O g^{-1} of dry soil. The water content was equal to the mean for field capacity reported in USDA-NRCS SSURGO database for Tifton loamy sands in Tift county, Georgia. Fifty milliliters of methanol was added to three bottles from each treatment group. Bottles were capped with Teflon-lined screw caps and stored at −20 °C. All remaining bottles were similarly capped, shaken, and placed in a dark laboratory incubator held at 25 ± 1 °C. At 3, 7, 14, 21, 28, 42, 56, and 105 days after treatment (DAT) 50 mL of methanol was added to three bottles from each treatment group. After recapping, these bottles were placed in a −20 °C freezer.

Soil and Water Sample Preparation, Analysis, and Quality Control. Runoff samples collected for metolachlor analysis were glass fiber filtered (Whatman GFF; 0.7 μm nominal pore size). Filters and sediment were wrapped in aluminum foil and frozen. Duplicate portions (1 g) of the filtrate were placed in 2 mL autosampler vials and fortified with 5 μg of 2-chlorolepidine (internal standard), and analyzed by APCI-HPLC-MS (*11*). A field blank and matrix spike were included with each rainfall simulation sample set (n = 8). Metolachlor was not detected (MDL < 1.0 μg L^{-1}) in any of the blanks. The average (standard deviation) recovery of metolachlor spikes (50 μg L^{-1}) was 108 (22)%.

After GFF filtration, water samples collected from core lysimeters were analyzed similarly with the exception that the HPLC-MS mass filter was operated in the selected ion monitoring mode targeting the metolachlor base peak and its chlorine isotope, m/z^+ 284 and 286, respectively. The detection limit was 0.1 μg L^{-1}.

After thawing, filters and sediment from granular metolachlor treated plot samples were visually inspected under a magnifying glass. Intact granules were recovered with stainless steel tweezers and afterwards combined by plot, wrapped in foil, and stored in a −20 °C freezer. Each set of granules corresponding to 5 min increments during the simulation were tested for metolachlor by crushing, methanol extraction, and HPLC-MS as described under formulation characterization above.

The remaining sediment and filters and all other filtered sediment samples were sequentially extracted (three times) with methanol by shaking on a rotating bed shaker. The methanol was recovered by glass fiber filtration. The sediment recovered on filters was oven-dried and weighed. Soil samples from laboratory and field dissipations were extracted similarly. Bottles were brought to room temperature and shaken, and the methanol was recovered by glass fiber filtration. This was repeated with two additional 50 mL methanol aliquots. Soil and sediment extracts were concentrated to 10 mL under a stream of N_2 gas. Prior work with this compound in fortified soil and sediment indicated that recoveries were quantitative and reproducible (*11*).

Sediment from other portions of runoff samples recovered by acid flocculation and oven-drying was pulverized with a roller mill and tested for organic carbon (OC) by dry combustion using a Carlo-Erba model NA1500 II CN analyzer (CE Elantech, Inc., Lakewood, NJ). Soil OC was analyzed similarly.

Greenhouse Efficacy Assessment. The EC and granular formulations were evaluated against Palmer amaranth (a common weed species), cereal rye (a grass weed surrogate), and cotton. The herbicides were applied at 1.0 kg ha^{-1} to 10 cm square plastic pots (n = 4 per plant and treatment) filled with a standard potting mix. The EC rate was verified to be within ±10% of the target rate by analysis of filter paper (7 cm diameter) spray targets deployed within the sprayed area. Treatments included a no-herbicide control, bare soil, soil completely covered with desiccated rye mulch, and 50% of the soil surface covered with the mulch. The mulch was collected from a farm field 30 days after the rye was killed with glyphosate. Plant growth, emergence and height, were evaluated 28 days after planting.

Data Analysis. Metolachlor dissolution into water from the granular formulation was evaluated by fitting data to eq 1 (*19*).

$$M_t/M_0 = Kt^n \tag{1}$$

where M_t is mass dissolved at time t, M_0 is mass dissolved at t = infinity, n is a dimensionless diffusional parameter, and K is a dimensionless diffusional network parameter. Laboratory soil dissipation kinetics were natural log-transformed and evaluated as the percent remaining using a linear first-order rate model with data fit and evaluated statistically using Graphpad 7.0 (Graphpad Software Inc., La Jolla, CA). In runoff samples, metolachlor concentration in bulk sediment was estimated by multiplying the measured sediment metolachlor concentration times the ratio of OC in the bulk sediment and the filtered sediment. This was done to reduce runoff subsampling bias due to different settling rates of sediment fractions in runoff samples. In computations linear equilibrium partitioning of the herbicides between sediment OC and water was assumed. Herbicide runoff and leaching data were evaluated by multiplying the total concentration (dissolved and sediment-bound) by the volume of runoff measured in each time step and summing over the duration of each simulation to determine total mass loss. Values were divided by the computed mass applied to rainfall simulator plots (average of spray target measurements) or lysimeters to determine percent loss of applied. Runoff means were compared by tillage and formulation pairwise using t tests assuming equal variance. Lysimeter study medians were evaluated similarly using the Mann−Whitney rank sum test. Comparisons were made by pooling data by treatment group. This test was used because the data set had a relatively large number of nondetects (50%). This occurred when the metolachlor concentration was less than the analytical detection limit or lysimeters did not yield a sample. All test statistics were computed using SigmaStat 3.1 (SYSTAT Software Inc., Point Richmond, CA) with significance assigned at p < 0.05. Plant growth data were evaluated using the PROC MIXED procedure in SAS for a factorial arrangement of treatment (SAS, Cary, NC).

RESULTS

Granular Formulation Characterization. Granules were generally spherical with computed diameter and density 1.4 mm and 1.95 g cm^{-3}, respectively. Metolachlor concentration was 1.3 ± 0.2% (**Table 1**). During shaking in deionized water approximately 50% of the metolachlor dissolved in 12 h, 75% in 24 h, and 100% in 96 h (**Figure 2**). The diffusional parameter n determined by fitting data for the initial 60% release of metolachlor to eq 1 was

Table 1. Mean (Standard Deviation) of Clay−Alginate Granule Properties[a]

property	value
volume (mm^3)	1.43 (0.30)
diameter (mm)	1.40 (0.09)
density (g cm^{-3})	1.95 (0.38)
metolachlor (% wt)	1.34 (0.14)[b]
	1.30 (0.20)[c]

[a] Measurements made on 10 granule lots (3 each). [b] Crushed granules and dissolved metolachlor in methanol. [c] Dissolved in sodium citrate and back extracted into methylene chloride.

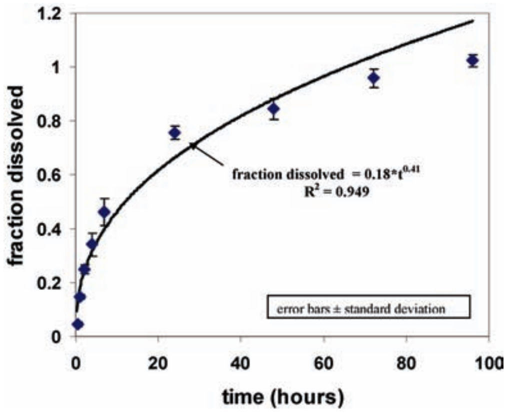

Figure 2. Metolachlor dissolution from clay−alginate granules.

Table 2. Average (Standard Deviation) Soil Antecedent Water Content, Simulated Rainfall Applied, Runoff Volume and Sediment Load, and Metolachlor Loss as a Percent of Applied[a]

	ST		CT	
	granular	EC	granular	EC
AWC (%)	6.6 (0.1)	7.1 (0.1)	7.3 (0.4)	5.6 (0.8)
rain (mm)	63 (1.9)	65 (1.0)	63 (2.2)	64 (0.8)
runoff (% of rain applied)	13 (2.2)	12 (0.6)	11 (1.6)	10 (2.1)
sediment (mg ha^{-1})	0.89 (0.17)	0.47 (0.02)	1.4 (0.13)	1.6 (0.33)
metolachlor (% of applied)				
total	1.0 (0.1)	1.8 (0.8)	1.7 (0.4)	1.1 (0.3)
dissolved	0.4 (0.1)	1.6 (0.6)	0.7 (0.2)	1.0 (0.2)
sediment-bound	0.1 (0.03)	0.2 (0.1)	0.3 (0.2)	0.1 (0.1)
granules	0.5 (0.03)		0.8 (0.5)	

[a] ST, strip tillage; CT, conventional tillage; AWC, antecedent soil−water content; EC, emulsifiable concentrate.

approximately 0.41. The R^2, 0.949, indicated a good fit to the model. Values of the diffusional parameter in the same range were obtained with carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate) and alachlor clay−alginate granules prepared similarly (*20*, *21*). Data were consistent with dissolution controlled by diffusion of the solute within a monolithic sphere (*19*).

Runoff Assessment. Soil at the start of simulations was dry. The depth integrated (0−30 cm) mean (standard deviation) of gravimetric antecedent water content (AWC) was 0.067 (0.008) g of H_2O g^{-1} of soil. Both tillage treatments yielded about 12% of the simulated rainfall in runoff (**Table 2**). In prior studies CT-plot runoff was approximately 2-fold greater than ST-plot runoff, ranging from 25 to 50% of simulated rainfall applied to plots. The lower AWC prior to the current study likely explained the 2−3-fold lower runoff volume when compared to previously published investigations (*10*, *11*) and why no difference in ST and CT system runoff was observed.

Although runoff volumes were nearly equal when CT and ST system plots were compared, the CT plots had significantly greater (2.3-fold) sediment loss when data were combined across formulation by tillage, ST or CT (**Table 2**). The higher CT sediment loss resulted in higher loss of metolachlor-containing granules from plots that received this formulation. As noted above, granules were recovered with tweezers from filtered sediment during visual inspection, and granules recovered in each 5 min runoff increment were crushed and analyzed for metolachlor. The amount in granules recovered from CT plot sediment averaged 0.8% and that from ST plots, 0.5% of applied (**Table 2**).

For corresponding plots, total metolachlor loss, the sum of metolachlor dissolved in runoff, bound to suspended sediment, and incorporated in granules recovered in sediment was 1.7% for CT plots and 1.0% for the ST plots (**Table 2**). The dissolved fraction and material recovered in intact granules were the predominant metolachlor forms in runoff. The relative mass loss in each fraction was approximately equal, accounting for 80−90% of total metolachlor loss for both tillage treatments. Statistical analysis did not identify significant differences in means for total and or the three metolachlor forms (dissolved, sediment-bound, or incorporated in granules) in runoff when the ST and CT treatments were compared. This was due in part to the low power of the statistical tests with only two replicates (n = 2). However, the nearly 1.7-fold difference in means suggests that ST management may substantially reduce metolachlor runoff loss when applied as a dry granular formulation. A primary reason is reduction in sediment loss with ST and a reduction in the loss of metolachlor-containing granules entrained in sediment.

When total metolachlor loss from plots treated with the granular formulation was compared to plots treated with the EC, opposite trends were noted for the CT and ST system treatment groups. With CT, the granular-treated plots yielded about 2-fold more metolachlor (**Table 2**). The difference was due primarily to the amount lost on granules entrained in sediment. With ST system plots, the EC treatment yielded 1.8% of metolachlor applied versus 1.0% for the granular formulation. The trend to higher EC formulation metolachlor loss, numerically the highest among all treatments, was consistent with other tillage-based investigations of metolachlor runoff at the site (*11*). We hypothesized that washoff of herbicide intercepted by cover crop residue contributed to increased metolachlor runoff loss when compared to CT management. Similar observations have been made in other cropping systems with no-till management (*12*).

Findings were in general agreement with published investigations; that is, granular pesticide application can result in relatively large runoff losses when CT is practiced (*14*). There have been few studies examining granular product behavior in ST systems. Our results indicate that herbicide runoff with a granular product will be less likely to occur, and if it does occur, will be substantially reduced relative to EC formulations used in ST systems on southern Atlantic Coastal Plain soils.

Field and Laboratory Dissipation. Field dissipation studies had two components: (1) assessment of metolachlor leaching potential as a function of formulation and tillage using soil core lysimeters deployed in the field and (2) evaluation of total metolachlor loss during a field season (110 days) by comparing the amount recovered in soil removed from lysimeter soil to the amount applied. In these studies technical grade metolachlor was used as a surrogate for scenarios where EC is sprayed on soil surfaces.

Combined metolachlor leachate loss for the nine sample collection dates was 0.06−0.23% of applied with ST−technical > ST−granular > CT−granular ≫ CT−technical (**Table 3**). Treatment group medians are shown by days after treatment (DAT) that samples were collected in **Figure 3**. Comparison of medians

Table 3. Total Leachate Volume, Leachate as Percent of Total Rainfall and Irrigation Applied to Lysimeters, and Percent Metolachlor Applied in Leachate and in Lysimeter Soil 116 Days after Metolachlor Application[a]

	granular		technical	
tillage formulation	ST	CT	ST	CT
leachate (cm)	14	5	25	4
leachate (% of total irrigation and rainfall)	13	5	23	3
% of metolachlor applied in leachate	0.20	0.15	0.23	0.06
% of metolachlor applied detected in lysimeter soil (study end, day 110)	26	27	3.0	5.1

[a] ST, strip tillage; CT, conventional tillage; EC, emulsifiable concentrate.

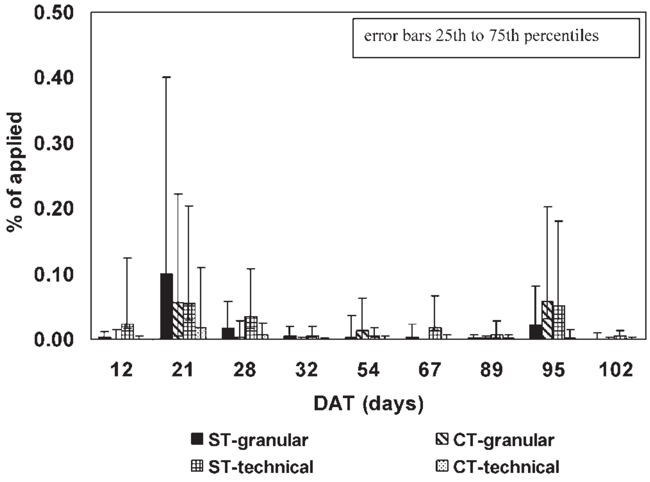

Figure 3. Median metolachlor loss expressed as percent of applied from lysimeters by tillage-formulation treatment groups. ST, strip tillage; CT, conventional tillage; tech, technical grade coated on sand.

Table 4. Average (Standard) of Soil Organic Carbon Content in Soil Cores ($n = 12$)[a]

	% soil organic carbon	
depth increment (cm)	ST	CT
0−2	1.3 (0.32)[b]	0.9 (0.08)[b]
2−8	0.89 (0.14)	0.84 (0.25)
8−15	0.70 (0.12)	0.63 (0.19)
15−30	0.72 (0.25)	0.59 (0.10)

[a] ST, strip tillage; CT, conventional. [b] Means within corresponding depth increments significantly different.

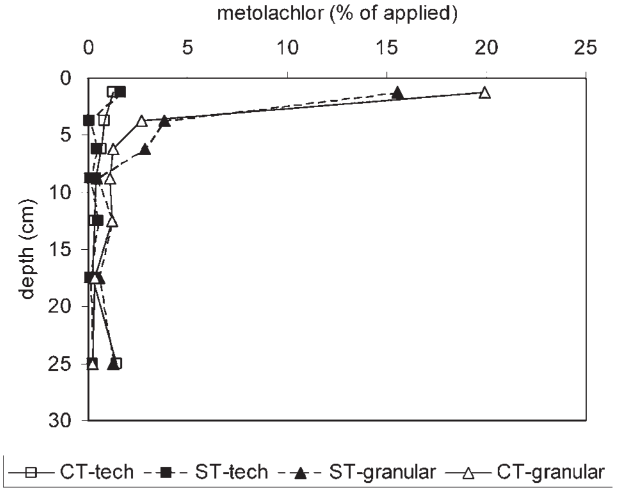

Figure 4. Percent of metolachlor applied by depth in lysimeter soil 110 days after application. ST, strip tillage; CT, conventional tillage; tech, technical grade coated on sand.

computed by combining data by tillage and formulation across all samples showed that significantly more metolachlor was lost with the technical versus granular formulation with the ST- but not the CT-soil-filled lysimeters. ST results were in agreement with the behavior of several other pesticides when encapsulated in calcium−alginate granules (*18*, *20*, *24*−*27*). CT results were inconclusive because medians computed by formulation were not significantly different. Contributing factors were relatively low leaching rates and higher variability when compared to corresponding ST treatment groups.

Lower loss rate for the CT−technical and CT−granular formulations was linked to much lower total leachate volume, 4−5 cm for the CT system versus 14−25 cm for the ST system soil (**Table 3**). Statistical comparisons across sample dates on the basis of tillage showed a significant tillage impact with ST > CT for lysimeters treated with the technical formulation. The same trend was observed with the granular formulation treatments; however, the difference in medians was not significant ($p = 0.14$).

We have no direct explanation of why 3−5-fold more leachate was obtained when ST soil was placed in the lysimeters. A factor that likely contributed was greater ST soil OC. Results obtained from 12 soil cores collected in the same field 1 year prior to the study show that the mean surface soil (0−2 cm) OC in the ST system portion of the field was significantly greater than in the area where CT was practiced (**Table 4**). At other depth increments mean ST soil OC was greater but the differences were not significant.

Generally increased soil OC contributes to formation of stable soil aggregates and is frequently associated with higher soil−water infiltration rate and greater water-holding capacity. For example, a 3-fold higher infiltration rate was observed in soil cores taken from a field in long-term no-tillage management when compared to cores from a nearby field in long-term CT management (*22*). In a companion greenhouse study using topsoil (0− 3 cm) from the no-till and CT field, the CT field soil was found have 2 times less soil-water after drying in a greenhouse at ambient temperature for 2 weeks (*22*). This trend was in agreement with many published studies that reported higher herbicide leaching rates when conservation practices such as no-tillage were applied (*23*).

Results from the analysis of soil from one randomly selected lysimeter from each treatment 110 days after placement in the field are shown in **Table 3** and **Figure 4**. ST and CT soil recoveries expressed as a percent of metolachlor applied were 26−27% for the granular and 3−5% for the technical metolachlor coated on sand (**Table 3**). A large fraction (50−70%) of the metolachlor was found in the top 2.5 cm of soil (**Figure 4**), indicating that translocation of metolachlor downward within the soil column was relatively small. Although small, in all cases, data suggest that metolachlor movement with infiltrating water was greatest with the granular formulation (**Figure 4**). This was presumably because metolachlor was available for leaching over a longer time period.

Companion laboratory incubations with metolachlor-fortified ST soil showed significantly greater soil metolachlor persistence with the granular formulation when compared to the technical grade on sand. The difference in pseudo-first-order dissipation rate constants was nearly 8 times (**Table 5**). The slower metolachlor dissipation rate when applied in granules was likely linked to relatively slow metolachlor release into soil solution in the field-moist soil and as a result relatively low bioavailability. Dissolution kinetics experiments showed that > 96 h of vigorous shaking was required to release all metolachlor in granules to water (**Figure 2**). Nasser et al. (*21*) reported that the release rate of a closely related compound, alachlor, from alginate beads in soil was inversely correlated to soil-water content.

Soil half-lives ($t_{1/2}$) estimated from rate constants were 27 and 204 days for the technical grade on sand and granular metolachlor, respectively (**Table 5**). The value for the technical grade on sand was in the typical range reported for aerobic metolachlor soil dissipation, 15−90 days (*28*). It was also in very close agreement with the field dissipation $t_{1/2}$ estimate, 22−25 days, based on lysimeter soil analysis and the assumption of linear first-order kinetics in calculations. For granular metolachlor field dissipation $t_{1/2}$ estimated similarly was 56−58 days. The nearly 4 times lower soil persistence estimated from field data was likely linked to water relations. When water was added to lysimeters with granules at the soil surface, metolachlor was leached from them as water infiltrated. Additionally, after water had infiltrated, metolachlor continued to be released to soil solution as granules remained in contact with moist soil. The two processes likely resulted in a higher rate of release of metolachlor to soil solution, where it was available for microbial degradation when compared to the laboratory incubation. In this case, diffusional gradients were likely the primary process controlling metolachlor release.

Table 5. Parameters for Metolachlor Laboratory Dissipation in ST Soil When Data Were Fit to a First-Order Decay Model[a]

	technical	granular
k (days^{-1})	−0.026[b]	−0.0034[b]
R^2	0.955	0.889
$t_{1/2}$ (days)	27	204

[a] k, rate constant; R^2, goodness of fit; $t_{1/2}$, soil half-life. [b] Slopes of regression lines significantly different ($p < 0.05$) based on analysis of covariance.

Efficacy Assessment. On the basis of emergence, the granular formulation was more effective (98% suppression) than the EC formulation (55% suppression) in controlling both Palmer amaranth and the surrogate grass weed, cereal rye (**Table 6**). In terms of total plant height, the granular and EC formulations were equally effective in suppressing Palmer amaranth and rye growth in the no-mulch and 50% mulch coverage treatments (**Table 6**). However, in the 100% mulch treatment, total plant height was greater in the EC compared to the granular formulation. With this case, mulch interception of the sprayed formulation may have reduced the amount of metolachlor reaching the soil and hindered its impact on plant growth. Despite the mulch, the granular formulation was capable of suppressing Palmer amaranth and rye emergence.

There were significant effects of herbicide formulation on cotton emergence and biomass (**Table 7**). Cotton emergence was suppressed 21% by the granular formulation relative to the EC formulation (**Table 7**). A similar trend was observed for cotton biomass. The granular formulation also appeared to have a suppressive effect on cotton growth. Cotton plant heights were lower in the granular formulation treatments compared to the EC formulation when there was 50 and 100% mulch cover. There were no differences in cotton plant height between formulations in the absence of rye mulch.

Overall study findings have indicated that use of a metolachlor granular formulation may have substantial benefit in ST system management for cotton production under Atlantic Coastal Plain conditions in the southeastern United States. Products will likely enhance weed control options, but there is potential for cotton crop injury due to increased metolachlor soil persistence. Season-long field studies are needed to assess impacts.

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Table 6. Effect of Herbicide Formulation on Reduction in Plant Emergence, Mean Plant Height of Emerged Palmer Amaranth and Rye Plants after 21 Days, and Plant Dry Biomass[a]

		weed plant height (cm)			weed biomass (g)		
herbicide	reduction in emergence (%)	0% mulch	50% mulch	100% mulch	0% mulch	50% mulch	100% mulch
control	0 A	6.9 B	6.4 BC	12.3 A	0.57 A	0.10 BC	0.33 AB
granular	98 C	1.1 D	0 D	0 D	0.01 C	0 C	0 C
EC	55 B	1.9 D	0 D	5.1 B	0.07 BC	0 C	0.11 BC

[a] Due to similarities in response, rye and Palmer amaranth were combined for analysis. Treatment means were separated using Fisher's protected $\text{LSD}_{0.05}$; treatment means with different letters within a measurement are significantly different. EC, emulsifiable concentrate.

Table 7. Effect of Herbicide Formulation on Reduction in Cotton Plant Emergence, Mean Plant Height of Emerged Cotton Plants after 21 Days, and Plant Dry Biomass[a]

		plant height (cm)			
herbicide	reduction in emergence (%)	0% mulch	50% mulch	100% mulch	biomass (g)
control	13 AB	13.3 F	18.8 BC	20.1 A	2.38 BC
granular	21 B	14.6 EF	5.6 G	17.7 BD	1.97 C
EC	0 A	15.5 DF	16.6 CE	21.4 A	2.74 AB

[a] Treatment means were separated using Fisher's Pprotected $\text{LSD}_{0.05}$; treatment means with different letters within a measurement are significantly different. EC, emulsifiable concentrate.

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LITERATURE CITED

(1) Derpsch, R.; Friedrich, T. *Global overview of conservation agriculture adoption*. Congress on Conservation Agriculture, New Delhi, India, 2009; 2010; pp 429−438; available at http://www.rolf-derpsch.com/globaloverview.pdf.

(2) Dill, G. M.; CaJacob, C. A.; Padgette, S. R. Glyphosate resistant crops: adoption, use, and future considerations. *Pest. Manage. Sci.* **2008**, *64*, 326−331.

(3) Fawcett, R. D. Towery. *Conservation Tillage and Plant Biotechnology: How New Technolgies Can Improve the Environment by Reducing the Need to Plow*. Conservation Technology Information Center: West Lafayette, IN, 2002.

(4) Culpepper, A. S.; Grey, T. L.; Vencil, W. K.; Kichler, J. M.; Webster, T. M.; Brown, S. M.; York, A. C.; Davis, J. W.; Hanna, W. W. Glyphosate-resistant Palmer amaranth (*Amaranthus palmeri*) confirmed in Georgia. *Weed Sci.* **2006**, *54*, 620−626.

(5) Ervin, D. E.; Carriere, Y.; Cox, W. J.; Fernandez-Cornejo, J.; Jussarme, R. A.; Marra, M.; Raven, P. H.; Wolfenburger, L. L.; Zilberman, D. *Impact of Genetically Engineered Crops on Farm Sustainability in the United States*; National Academy of Sciences, Washington, DC, 2010; available at http://www.nap.edu/catalog/12804.html.

(6) Culpepper, A. S.; York, A. C.; Kichler, J. *University of Georgia Herbicide Programs for Controlling Glyphosate-Resistant Palmer Amaranth in 2008 Cotton*, 2008; available at http://mulch.cropsoil.uga.edu/weedsci/HomepageFiles/Palmer2008.pdf.

(7) CTIC. Conservation Tillage. Conservation Technology Information Center, 2009; available at http://www.ctic.purdue.edu/Core4/CT/CT.html.

(8) Gaston, L. A.; Boquet, D. J.; Bosch, M. A. Fluometuron wash-off from cover crop residues and fate in a loessial soil. *Soil Sci.* **2001**, *166*, 681−690.

(9) Gaston, L. A.; Boquet, D. J.; Bosch, M. A. Pendimethalin wash-off from cover crop residues and degradation in loessial soil. *Commun. Soil Sci. Plant Anal.* **2003**, *34*, 2515−2527.

(10) Potter, T. L.; Truman, C. C.; Strickland, T. C.; Bosch, D. D.; Webster, T. M.; Franklin, D. H.; Bednarz, C. W. Combined effects of constant versus variable intensity simulated rainfall and reduced tillage management on cotton preemergence herbicide runoff. *J. Environ. Qual.* **2006**, *35*, 1894−1902.

(11) Potter, T. L.; Truman, C. C.; Strickland, T. C.; Bosch, D. D.; Webster, T. M. Herbicide incorporation by irrigation and tillage impact on runoff loss. *J. Environ. Qual.* **2008**, *37*, 839−847.

(12) Baker, J. L.; Mickelson, S. K. Application technology and best management practices for minimizing herbicide runoff. *Weed Technol.* **1994**, *8*, 862−869.

(13) Johnson, M. D.; Wyse, D. L.; Lueschen, W. E. The influence of herbicide formulation on weed control in four tillage systems. *Weed Sci.* **1989**, *37*, 239−249.

(14) Kenimer, A. L.; Mitchell, J. K.; Felsot, A. S.; Hirschi, M. C. Pesticide formulation and application technique effects on surface pesticide losses. *Trans. ASAE* **1997**, *40*, 1617−1622.

(15) Gish, T. J.; Shirmohammadi, A.; Weinhold, B. J. Field-scale mobility and persistence of commercial and starch-encapsulated atrazine and alachlor. *J. Environ. Qual.* **1994**, *23*, 355−359.

(16) Smith, S.; Johnson, R. M.; Pepperman, A. B. Formulation and tillage effects on atrazine and alachlor in shallow ground water in upland corn production. *Bull. Environ. Contam. Toxicol.* **2001**, *67*, 1132−121.

(17) Gilliom, R. J. Pesticides in the nation's streams and ground water. *Environ. Sci. Technol.* **2007**, *41*, 3408−3414.

(18) Gerstl, Z.; Nasser, A.; Mingelgrin, U. Controlled release of pesticide into water for clay−polymer formulations. *J. Agric. Food Chem.* **1998**, *46*, 3803−3809.

(19) Ritger, P. L.; Peppas, N. A. A simple equation for description of solute release I. Fickian and anomalous release from non-swellable devices in the form of slabs, spheres, cylinders, or discs. *J. Controlled Release* **1987**, *5*, 23−36.

(20) Fernandez-Perez, M.; Villafranca-Sanchez, M.; Gonzalez-Pradas, E.; Martinez-Lopez, F.; Flores-Cespedes, F. Controlled release of carbofuran from an aliginate-bentonite formulation: water release kinetics and soil mobility. *J. Agric. Food Chem.* **2000**, *48*, 938−943.

(21) Nasser, A.; Mingelgrin, U.; Gerstl, Z. Effect of soil moisture on the release of alachlor from alginate-based controlled-release formulations. *J. Agric. Food Chem.* **2008**, *56*, 1322−1327.

(22) Franzleubbers, A. Water infiltration and soil structure related to organic matter and it stratification with depth. *Soil Tillage Res.* **2002**, *6*, 197−205.

(23) Malone, R.; Logsdon, S.; Shipitalo, M. J.; Weatherington-Rice, J.; Ahuja, L.; Ma, L. Tillage effect on macroporosity and herbicide transport in percolate. *Geoderma* **2003**, *115*, 191−215.

(24) Johnson, R. M.; Pepperman, A. B. Leaching of alachlor from alginate-encapsulated controlled-release formulations. *Pestic. Sci.* **1996**, *48*, 157−164.

(25) Johnson, R. M.; Pepperman, A. B. Mobility of atrazine from alginate-controlled release formulations. *J. Environ. Sci. Health, B* **1996**, *30*, 27−47.

(26) Johnson, R. M.; Pepperman, A. B.; Selim, H. M. Field mobility of alginate controlled release formulations of atrazine. *Soil Sci.* **1998**, *163*, 46−52.

(27) Selim, H. M.; McGowen, S. L.; Johnson, R. M.; Pepperman, A. B. Fate of metribuzin from alginate controlled release formulations in a Sharkey soil: 2. Transport. *Soil Sci.* **1998**, *163*, 535−543.

(28) Footprint. The FOOTPRINT Pesticide Properties DataBase, database collated by the University of Hertfordshire as part of the EU-funded FOOTPRINT project (FP6-SSP-022704), 2009; available online at http://www.eu-footprint.org/ppdb.html.

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