JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

ARTICLE

pubs.acs.org/JAFC

Tillage, Cover-Crop Residue Management, and Irrigation Incorporation Impact on Fomesafen Runoff

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ABSTRACT: Intensive glyphosate use has contributed to the evolution and occurrence of glyphosate-resistant weeds that threaten production of many crops. Sustained use of this highly valued herbicide requires rotation and/or substitution of herbicides with different modes of action. Cotton growers have shown considerable interest in the protoporphyrinogen oxidase inhibitor, fomesafen. Following registration for cotton in 2008, use has increased rapidly. Environmental fate data in major use areas are needed to appropriately evaluate risks. Field-based rainfall simulation was used to evaluate fomesafen runoff potential with and without irrigation incorporation in a conventional tillage system (CT) and when conservation tillage (CsT) was practiced with and without cover crop residue rolling. Without irrigation incorporation, relatively high runoff, about 5% of applied, was measured from the CT system, indicating that this compound may present a runoff risk. Runoff was reduced by >50% when the herbicide was irrigation incorporated after application or when used with a CsT system. Data indicate that these practices should be implemented whenever possible to reduce fomesafen runoff risk. Results also raised concerns about leaching and potential groundwater contamination and crop injury due to rapid washoff from cover crop residues in CsT systems. Further work is needed to address these concerns.

KEYWORDS: herbicide, cotton, glyphosate, resistance, strip-tillage, roller

INTRODUCTION

The herbicide glyphosate [*N*-(phosphonomethyl)glycine] is the most widely used agricultural pesticide in the United States, accounting for >35% of total conventional pesticides applied to farm fields annually.[1] Intensive use of this product is linked to widespread planting of glyphosate-tolerant cultivars (GTCs) of cotton (*Gossypium hirsutum*), soybean (*Glycine max*), and corn (*Zea mays*) and glyphosate for both preplant (replacing tillage) and postemergence weed control. Current estimates indicate that GTCs are grown on >80% of the acreage of these crops.[2]

In the southeastern United States, glyphosate efficacy loss and a changing weed spectrum are a direct consequence of widespread cotton GTC adoption and use.[3] Most troubling is the emergence of highly glyphosate resistant Palmer amaranth (*Amaranthus palmeri*).[4,5] This weedy plant threatens the economic health of cotton producers throughout the region.[3]

Current recommendations for sustainable GTC and glyphosate use in North American cotton cropping systems include rotation and/or direct substitution of active ingredients (AI) with alternate modes of action.[5,6] An AI that has received considerable attention is the diphenyl ether fomesafen (Figure 1). It is labeled for both soybean and cotton and is recommended for preemergence applications in cotton due to high efficacy on Palmer amaranth.[5−8] Products containing this AI became available to southeastern cotton growers in the 2009 growing season.

Although fomesafen-containing herbicides are currently labeled for cotton and other crops, there are continuing concerns about the potential for persistence in soil and aquatic environments, negative impacts on surface and groundwater quality through runoff and leaching, and threats to endangered species.[9] Simulation modeling has indicated that the compound is mobile in the environment;[9] however, there are few published studies that have evaluated fomesafen environmental fate and transport. To our knowledge, none have examined surface runoff potential and how the magnitude of runoff losses may be controlled by management practices, in particular, postapplication irrigation incorporation and conservation tillage (CsT). Data are needed to effectively assess risks associated with fomesafen use.

The current study focused on cotton cropping systems in the Atlantic Coastal Plain region of the southeastern United States. Field-based rainfall simulations were conducted to assess impacts on fomesafen runoff loss due to (1) postapplication irrigation under conventional tillage (CT), (2) implementation of a common CsT practice, strip tillage (ST), and (3) cover crop residue rolling prior to ST and fomesafen application. Residue rolling was included as a variable because use among growers practicing CsT is increasing. Rolling is done to terminate cover crops, increase ground coverage by cover crop mulch, and improve weed control.[10,11] During simulations, the rate of fomesafen washoff from treated cover crop residue was also examined to more fully assess fomesafen performance in CsT systems.

MATERIALS AND METHODS

Study Site, Management, and Rainfall Simulations. Site conditions, management, and rainfall simulation procedures were described in the same prior publications.[12,13] The current study was conducted in May 2009 1 ha field located in Tift County, GA, that was equally divided between CT and ST. Practices were implemented in 1999 and maintained continuously. Soil was classed at the series level as Tifton loamy sand (fine-loamy, kaolinitic, thermic, Plinthic Kanidudult). Since tillage practice establishment, cotton and peanut (*Arachis hypogaea* L.) were produced

Received: May 2, 2011
Revised: June 20, 2011
Accepted: June 21, 2011
Published: June 21, 2011

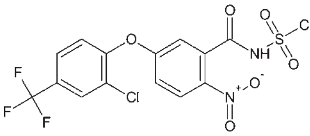

Figure 1. Fomesafen structure.

rotationally with a rye (*Secale cearale* L.) cover crop planted after crop harvest each autumn. Each spring, a burndown glyphosate application was made to the cover crop about 1 month prior to planting into 15 cm strips tilled into the cover crop mulch (ST) or after inversion plowing and bedding (CT). When the current study was conducted (spring 2009), about half of the residue in the ST area was rolled with a tractor-mounted cylindrical steel roller (1.8 m long by 0.32 m diameter) prior to ST. The roller was filled with water and weighed about 200 kg. Rolling was done 3 weeks after the burndown herbicide application.

Rainfall simulation plots, 2 m × 3 m, were established by pushing steel frames into the soil to a depth of 5 cm. The frame width spanned a wheel track and two crop rows on either side. In each tillage system, CT and ST, there were six of these plots. Among the ST plots, three were in the area where cover crop residue was rolled and three in the area that was not. Within 2 h after herbicide application on all ST plots and on three CT plots, 12.5 mm of simulated irrigation was applied in 0.5 h with the rainfall simulator. Simulations were conducted the following day with water obtained from a deep-irrigation well drawing from the Floridian aquifer system. Water was applied though oscillating 80150 Veejet nozzles for 70 min in a variable-intensity pattern that mirrored characteristics of convective thunderstorms that commonly occur in the region.[12] Rainfall rates and amounts were measured using a tipping bucket rain gage (Global Water Instrumentation, Gold View, CA) and 15 cm diameter collection cans ($n = 5$) that were deployed beneath the simulator but outside the plot frame. The average ± standard deviation of total rainfall for the 12 simulations was 55 ± 1.5 mm.

Runoff was collected from aluminum troughs installed at the downslope end of each frame and 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 simulations were completed. The remaining water in buckets (if any) was poured into 1 L polyethylene bottles. These bottles were weighed, and weights were summed to determine the total runoff volume for each time increment. Sediment mass was determined gravimetrically after acid flocculation and oven-drying at 105 °C. This material was termed the bulk sediment. Sediment recovered from the 500 mL bottle after oven-drying was termed “filtered sediment”. 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 (AWC).

Crop Residue Washoff. Crop residue for washoff studies was obtained from a sprayed area about 20 m from simulator plots. Soil in the area was completely covered by the residue. Subsamples were cut with a box cutter using a 20 cm diameter aluminum pie plate as a template. They were wrapped in aluminum foil, avoiding disturbance of the crop residue arrangement. After they were weighed, samples were stored in a laboratory refrigerator overnight. Prior to four of the simulations, the crop residue was transferred, sprayed surface up, to a second plate perforated with 0.3 cm diameter holes. During simulations, this plate was placed in a 25 cm diameter glass funnel mounted on a wooden stand positioned under the simulator. The leachate was collected directly into 250 mL glass bottles in 5 min time steps.

Herbicide Formulation and Application. Fomesafen was applied to plots or crop residue 24 h prior to rainfall simulation at a target rate of 0.75 kg ha^{-1} using the commercial formulation Reflex.[14] This was two times the maximum label rate for a single application. The emulsifiable concentrate was mixed with water and applied using a CO_2-pressurized backpack sprayer equipped with flat-fan nozzles (TeeJet XR 11002 nozzles; Spraying Systems Co., Wheaton, IL) 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 2 m × 3 m frame and three on the surface of the cover crop residue prior to spray application. Targets were analyzed to measure application rate. The average measured rate ± standard deviation across all applications was 0.71 ± 0.04 kg ha^{-1} fomesafen. Among spray targets within plots, the average ± standard deviation of the relative standard deviation was 18 ± 7%, indicating that application was uniform.

Soil and Water Sample Preparation, Analysis, and Quality Control. Washoff and runoff samples collected for fomesafen analysis were glass fiber filtered (Whatman GFF; 0.7 μm nominal pore size). Runoff sample filters and sediment were wrapped in aluminum foil and frozen. The filtrate was analyzed after fortification with the internal standard, 4-nitrophenol at 1 μg mL^{-1}, by direct aqueous injection high-performance liquid chromatography−electrospray ionization−tandem mass spectrometry (HPLC-ESI-MS-MS) using a Thermoquest Finnigan LCQ Deca HPLC-MS System (ThermoFinnigan, San Jose, CA). Separations were on a 2.1 mm × 50 mm, 5 μm, Zorbax SB-C8 column (Agilent, San Jose, CA) using two mobile phases, 0.1% (v/v) formic acid in both water (A) and acetonitrile (B). Initial conditions of 90% A/10% B were increased linearly to 10% A/90% B in 4 min and held isocratic for 2 min. The combined flow rate was 0.6 mL min^{-1}. The negative ion m/z^- 316 produced by collision-induced dissociation (CID) of the ionized parent, m/z^- 437, was used for quantitation. The instrument was optimized for m/z 437 and 316 sequentially prior to each analysis by flow injection of an aqueous fomesafen solution into the ESI source. The method limit of detection (MDL) based on the lowest concentration standard used for calibration was 5 μg L^{-1}. A field blank and matrix spike were included with each rainfall simulation sample set ($n = 12$). Fomesafen was not detected in any of the blanks. The average ± standard deviation recovery of fomesafen spikes at 50 μg L^{-1} was 108 ± 20%.

After they were thawed, filters and sediment were sequentially extracted (three times) with methanol by shaking on a rotating bed shaker. The methanol was recovered by glass fiber filtration and concentrated to 10 mL under a stream of N_2 gas. The sediment recovered on filters was oven-dried and weighed. Fomesafen recovery from soil/sediment matrix was evaluated by extraction of fomesafen-fortified Tifton soil (0.4 μg g^{-1}). The average ± standard deviation percent recovery was 91 ± 4%.

Sediment from other portions of runoff samples recovered by oven-drying (filtered sediment) or by acid flocculation and oven-drying (bulk sediment) 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).

Data Analysis. Bulk sediment was not analyzed for fomesafen. Its concentration in this material was estimated by multiplying the measured filtered sediment fomesafen concentration times the ratio of OC in bulk sediment and filtered sediment. Linear equilibrium partitioning of the herbicides between sediment OC and water was assumed. Washoff and runoff data were evaluated by multiplying the total concentration 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 or the cover crop residue. Four treatment groups are described in the text as ST-I, ST-R-I, CT-I, and CT-NI: ST = strip tillage, CT = conventional tillage, I = irrigation incorporated, NI = not-irrigation incorporated, and R = rolled cover crop residue. Means between groups were compared pairwise using t tests and slopes of regression lines relating cumulative losses by analysis of covariance with Graphpad version 5.0 (Graphpad Software, San Diego, CA). Significance was assigned at $p < 0.05$.

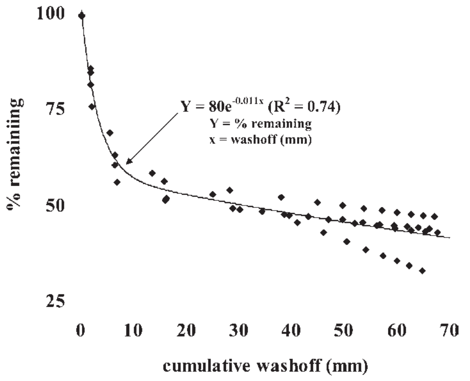

Figure 2. Fomesafen washoff from cover crop mulch during rainfall simulations.

RESULTS

Fomesafen Washoff. Washoff data were fit to eq 1 using Sigma Plot 11.0 (Systat Software, San Jose, CA).

$$Y = F_{\mathrm{wo}}\, \mathrm{e}^{-(P_{\mathrm{wo}} x)} \qquad (1)$$

The R^2, 0.74, indicated a reasonable data fit (Figure 2). P_{wo} and F_{wo} are fitted parameters termed the "washoff coefficient" and "available washoff fraction", respectively. Y is the percent of herbicide remaining on the residue, and x is the cumulative washoff (mm). The equation is a form of a commonly used pesticide washoff equation that is incorporated in pesticide fate simulation models.[15,16] As indicated by the exponential decay relationship, studies have shown that a large fraction of the pesticide that is washed off is recovered in the first few millimeters of rainfall or irrigation.[13,15,16]

P_{wo} is effectively the washoff rate constant, and as the value increases, the washoff rate increases. Fomesafen's fitted value, 0.011 mm^{-1}, was indicative of relatively rapid washoff (Figure 2). Fomesafen's P_{wo} was about 2 times greater than the P_{wo} for metolachlor and 30 times greater than the P_{wo} for pendimethalin obtained using the same experimental conditions.[13] Relative differences in washoff rates of these compounds are reflected in differences in their water solubility. Fomesafen's water solubility was reported as 1200 mg L^{-1},[9] metolachlor's as 500 mg L^{-1}, and pendimethalin's as 0.3 mg L^{-1}.[17] An increase in washoff rate with increasing water solubility was also reported in insecticide washoff studies from cotton foliage with the washoff coefficient, P_{wo}, increasing 2−3-fold with a 10-fold increase in water solubility.[15]

The fomesafen value for the other parameter in this equation, F_{wo} (available washoff fraction), was 80 (Figure 2). This indicated that 80% of the fomesafen deposited on the dry crop residue was available for washoff. In prior investigations, corresponding values obtained for metolachlor and pendimethalin were 96 and 100.[13]

Combined results indicated an inverse trend with water solubility for this parameter. In fomesafen's case, the compound's relatively high water solubility likely contributed to greater penetration into the dry crop residue as it took up water from the spray mixture. In turn, physical entrapment within the residue likely reduced the amount available for washoff. Pendimethalin's very low water solubility and F_{wo} value, 100, indicted that the compound remained on the residue surface, where it was available for washoff. Metolachlor's water solubility is relatively high, about 2 times less than that of fomesafen and 1000 times greater than that of pendimethalin. Nevertheless, the magnitude of metolachlor's F_{wo}, 96, suggested that most of the compound remained on the residue surface and available for washoff. A possible explanation is specific bonding to the crop residue surface. Metolachlor was reported to form stronger bonds with wheat straw than two other acetanilide herbicides, acetochlor and alachlor.[18] The water solubility of both compounds is about half metolachlor's value.[17]

Table 1. Average (Standard Deviation) Soil AWC, Simulated Rainfall Applied, Runoff Volume, Sediment Load, and Fomesafen Loss as a Percent of Applied (n = 3 per Treatment Group)

	treatment group[a,b]			
parameter	ST-I	ST-R-I	CT-I	CT-NI
AWC (%)[c]				
0−2 cm	13 (3) a	15 (1) b	8 (3) abc	1.3 (1.0) abc
0−15 cm	11 (0.2) a	11 (0.4) b	11 (0.6) c	9.6 (0.6) abc
rain (mm)	59 (1.6) a	58 (1.6) b	56 (2.1)	55 (0.8) ab
runoff (% of rain applied)	20 (2.8) a	25 (0.9) ab	67 (2.7) abc	50 (0.9) abc
sediment (Mg ha^{-1})	0.2 (0.1) a	0.8 (0.1) ab	2.3 (0.5) ab	2.6 (0.6) ab
fomesafen event total				
% of applied	1.6 (0.7) a	2.1 (0.2) b	2.2 (0.5) c	4.9 (0.6) abc
concentration (μg L^{-1})[d]	86 (33)	93 (25) b	43 (9) bc	142 (22) c
% dissolved[e]	98 (3.6)	98 (3.6)	95 (4)	98 (1.9)

[a] ST-I, a; ST-R-I, b; and CT-I, c: means significantly different from other similarly labeled treatment group means (P = 0.05). [b] R, rolled cover crop residue; I, irrigation-incorporated; NI, not irrigation incorporated; R, cover residue rolled. [c] AWC, antecedent soil−water content. [d] Total mass loss divided by total runoff volume. [e] Percent of fomesafen "dissolved" (GFF filtrate).

Fitted fomesafen P_{wo} and F_{wo} values were used in eq 1 to estimate the impact of the postapplication irrigation, 12.5 mm, on transfer of fomesafen intercepted by cover crop residue to the soil surface. Results indicated 45% washoff. Similar calculations for metolachlor and pendimethalin indicated that metolachlor washoff would be 13% and pendimethalin washoff 0.6%.[13] Fomesafen's relatively high washoff rate suggests that it may provide superior performance when used preemergence in CsT systems when compared to metolachlor and pendimethalin and other herbicides that wash off cover crop residue at lower rates.

The herbicide's high washoff rate also indicates that lower application rates may be used without compromising weed control efficacy. A companion benefit is that reduced rates may limit cotton injury potential. Emerged cotton is susceptible to fomesafen injury;[14] thus, depending on the timing and amount of postapplication rainfall and irrigation, washoff of fomesafen intercepted by cover crop residue could affect cotton growth. We are not aware of any reports in this regard. Further work is needed to evaluate the potential impacts. There is considerable interest in fomesafen use in CsT cotton production.[8]

Another possible negative consequence of rapid fomesafen washoff from cover crop residues in CsT systems is increased runoff. Studies with other herbicides have shown that washoff can substantially increase herbicide runoff concentrations.[12,13] Residue cover of soil in our ST system is typically about 50%; thus,

Table 2. Slopes and R^2 Values for Stepwise Linear Regression between Cumulative Simulated Rainfall and Cumulative Runoff, Sediment Loss, and Fomesafen Runoff

	treatment group[a,b]			
parameter	ST-I	ST-R-I	CT-I	CT-NI
fomesafen runoff (% of applied mm^{-1})				
slope	0.03 a	0.04 ab	0.04 ac	0.09 abc
R^2	0.976	0.977	0.997	0.983
sediment ($\text{Mg ha}^{-1}\ \text{mm}^{-1}$)				
slope	0.004 a	0.015 ab	0.04 abc	0.05 abc
R^2	0.986	0.979	0.985	0.986
runoff (mm mm^{-1})				
slope	0.23 a	0.28 ab	0.69 abc	0.51 abc
R^2	0.989	0.991	0.992	0.974

[a] The first appearance of a letter indicates a significant difference in the slope of regression line to the slopes shown in successive columns by ANCOVA ($P < 0.05$). [b] R, rolled cover crop residue; I, irrigation-incorporated; NI, not irrigation incorporated; and R, cover residue rolled.

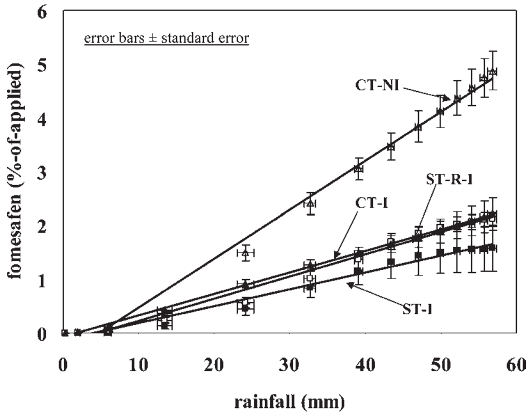

Figure 3. Cumulative fomesafen runoff (percent of applied) versus simulated rainfall.

about 50% of herbicides that are broadcast applied are intercepted. Given washoff estimates, postapplication irrigation or rainfall washoff would substantially increase the fomesafen load in the runoff zone at the soil surface and increase potential fomesafen runoff. The connection between washoff and runoff is being evaluated with an event-based simulation model and will be reported at a later date.

Fomesafen Runoff Loss. Trends in both total fomesafen runoff for the rainfall simulations (Table 1) and the runoff rate evaluated by linear regression of cumulative rainfall and loss expressed as percent of applied fomesafen (Table 2 and Figure 3) were CT-NI > CT-I ≈ ST-R-I > ST-I. When compared to values compiled from other rainfall simulation based pesticide runoff studies, the mean CT-NI fomesafen loss, 4.9% of applied, was relatively high. The value was in the 85th percentile of a comprehensive assessment of published field studies.[19] This result suggests that fomesafen is prone to runoff when applied to CT soil without irrigation incorporation. The compound has relatively high water solubility, 1200 mg L^{-1}, and low K_{oc}, 50 mL g^{-1}; thus, soil binding is weak, and there is a strong tendency to dissolve in runoff.[9]

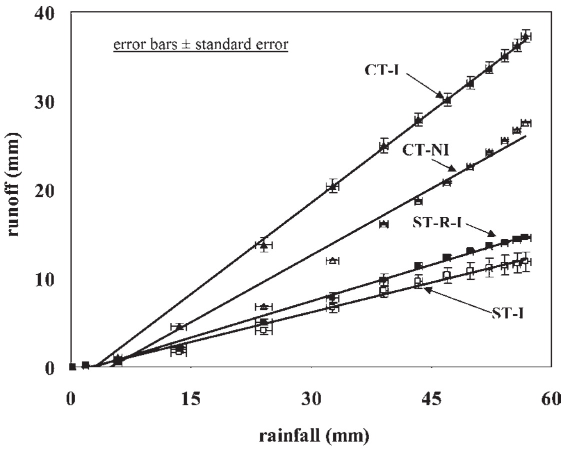

Figure 4. Cumulative runoff versus simulated rainfall.

Notably, irrigation incorporation after fomesafen application to CT soil (CT-I) reduced the total fomesafen loss and relative loss rate evaluated by comparing slopes of linear regression lines comparing cumulative runoff loss and rainfall by >2-fold. Values were significantly lower than corresponding CT-NI treatment results (Tables 1 and 2). The reduction was observed even though CT-I mean runoff and runoff rate were significantly greater (Tables 1 and 2 and Figure 4). Higher CT-I runoff was directly linked to significantly greater soil AWC at the soil surface and to the bottom of the plow layer (Table 1). AWC was higher due to the irrigation. Results followed a widely reported trend that increases in AWC increase runoff.[20]

An evaluation of irrigation incorporation impact on metolachlor runoff at the same study site produced similar results, that is, that 12.5 mm irrigation after herbicide application increased runoff but reduced CT metolachlor runoff by a factor of 2.[13] Our explanation was that metolachlor leaching with infiltrating irrigation water carried the compound into the soil, where it was less available for runoff. Calculations combining a plug-flow model to calculate depth of metolachlor penetration into the soil and a widely used exponential decay equation relating soil depth to runoff availability indicated that 12.5 mm of irrigation reduced metolachlor availability for runoff by 63% for the CT system.[13] This was in reasonable agreement with measured runoff loss reduction due to irrigation incorporation, 50%.

Irrigation incorporation impact on fomesafen runoff was likely explained by the same process. Comparison of the compounds' water solubilities, 1200 mg L^{-1} for fomesafen and 512 mg L^{-1} metolachlor, and K_{oc} values, 200 mL g^{-1} for metolachlor and 50 mL g^{-1} fomesafen, indicated that fomesafen leaching may be somewhat greater.[9,17] This could contribute to greater runoff reduction due to deeper fomesafen movement into the soil, where runoff availability is reduced. A concern raised by these observations is that fomesafen may leach rapidly and contaminate shallow groundwater and/or be transported down hillslopes in regions with lateral subsurface flow.

Differences in total fomesafen runoff means among the CT-I, ST-R-I, and ST-I treatment groups were relatively small and not significant (Table 1). Findings highlighted the large impact irrigation incorporation had on reducing fomesafen availability for runoff from CT soil. CT-I runoff and sediment mean loss and rates of loss were significantly greater than from the two ST treatment groups (Tables 1 and 2 and Figures 3 and 4).

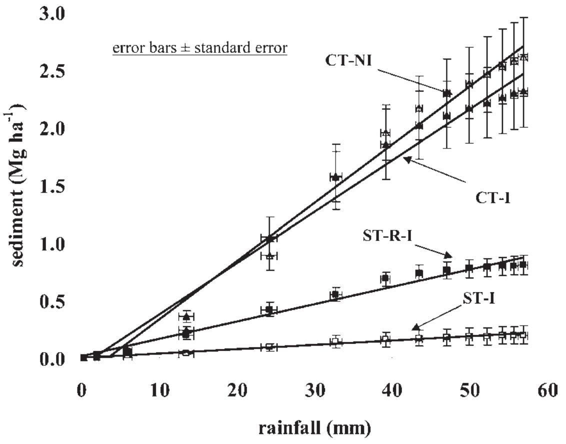

Figure 5. Cumulative sediment loss versus simulated rainfall.

The magnitudes of differences were large, 2−3 times for runoff and 3−10 times for sediment. These large differences, especially for runoff, indicated relatively low fomesafen availability for runoff from the CT-I treatment. In this case, differences in runoff are emphasized because computations showed that on an event basis only, 2−5% of the fomesafen lost in runoff was bound to sediment. Across all treatment groups, >95% of fomesafen in runoff was functionally defined (by filtration) as dissolved, and small differences in mean percent dissolved values were not significant (Table 1).

Whereas runoff volume had little impact on fomesafen mass loss among treatments that were irrigated after herbicide application, there was a large impact when fomesafen runoff response was evaluated on the basis of volume-weighted fomesafen concentration (VWC) for the event. VWC magnitude may play a role in risk assessments that involve herbicide exposures in runoff that accumulates at the edge of farm fields. In our study, the ST-I and ST-R-I values were both about 2 times greater than the CT-I value, and means were significantly different (Table 1). It should also be noted that runoff from CT soil that was not irrigated, the CT-NI treatment, had the highest overall mean VWC.

Finally, comparison of results from the two ST treatments, ST-I and ST-R-I, that is, with and without rolling of cover crop residue, did not indicate a large impact of this practice. Differences in fomesafen VWC and total runoff means were small and not significantly different. Some impact was indicated when rates of loss were compared using slopes of linear regression lines relating cumulative loss and cumulative rainfall (Table 2 and Figure 3). There was a greater rate of loss when the cover crop residue was rolled. This followed trends in runoff volume and sediment loss (Tables 1 and 2 and Figure 5). The ST-R-I treatment had 1.2-fold greater runoff and 4-fold greater sediment loss than the ST-I treatment. A possible explanation is soil compaction due to rolling and reduced infiltration into surface soil. Further work is needed to clarify this point. A study conducted in the Tennessee valley region of Alabama quantified changes in soil cone penetrator index (CPI) before and after rolling to terminate cover crops.[20] CPI is used as a compaction indicator. In one season, CPI decreased after rolling, and in a second, CPI increased. Their findings suggest the potential for complex interactions between compaction, rolling, soil water content, residue cover, and soil type.

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■ ACKNOWLEDGMENT

We give special thanks to U.S. Department of Agriculture Agricultural Research Service employees Sally Belflower, Margie Whittle, Lorine Lewis, Rickey Fletcher, and Anthony Camp. The University of Georgia Coastal Plain Experiment Station donated use of the land and irrigation for crop production.

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