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# Effects of tilling no-till soil on losses of atrazine and glyphosate to runoff water under variable intensity simulated rainfall

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## Abstract

Herbicides released through agricultural activities to surface waters and drinking water systems represent a risk to human and environmental health, as well as a cost to municipalities for removal. This study focuses on the viability of glyphosate tolerant cropping systems as an alternative to atrazine-based systems, and the impact of tilling historically no-till ground on the runoff pollution potential of these systems. Variable intensity field rainfall simulations were performed on 2 m long × 1 m wide plots within a field in first-year disk and harrow following no-till (CT), and within a long-term no-tilled (NT) field, both treated with atrazine and glyphosate according to label. Rainfall sequence was: 50 mm $h^{-1}$ for 50 min followed by 75 mm $h^{-1}$ for 15 min, 25 mm $h^{-1}$ for 15 min, and 100 mm $h^{-1}$ for 15 min. Runoff was collected at regular time intervals during two simulated rainfall events and analyzed for herbicide concentration, sediment content, and volume. Maximum glyphosate concentration in runoff was 233 $\mu g\ L^{-1}$ for NT and 180 $\mu g\ L^{-1}$ for CT (approximately 33% and 26% of the maximum contaminant limit (MCL) for glyphosate (700 $\mu g\ L^{-1}$), respectively, while maximum atrazine concentrations in runoff was 303 $\mu g\ L^{-1}$ for NT and 79 $\mu g\ L^{-1}$ for CT (approximately 100 times and 26 times the atrazine MCL (3 $\mu g\ L^{-1}$)). Atrazine concentration and loading were significantly higher in runoff from NT plots than from CT plots, whereas glyphosate concentration and loading were impacted by tillage treatment to a much lesser degree. Results suggest that glyphosate-based weed management may represent a lower drinking water risk than atrazine-based weed management, especially in NT systems.

*Keywords:* Glyphosate; Atrazine; Tillage effects; Water quality

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## 1. Introduction

Atrazine [2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine], which is used to control annual broad leaf and grass weeds in corn (*Zea mays*), sorghum (*Sorghum species*), sugarcane (*Saccharum officinarum*), and other crops, is among the most widely used herbicides in the US (NASS, 1995). Atrazine that is transported off-site, primarily with direct surface runoff, may pose a risk to ecological and human health. Exposure to atrazine has both acute and chronic toxic effects to humans. Therefore, levels in municipal drinking water must not exceed the Environmental Protection Agency (EPA)-established maximum contaminant level (MCL) of 3 $\mu g\ L^{-1}$, determined by quarterly monitoring. Atrazine is frequently detected in surface waters in regions where it is used (Kalkhoff et al., 2003), with levels sometimes significantly higher than its MCL (Shipitalo et al., 1997; Johnson and Baker, 1982, 1984; USGS, 1993). Because of this, some

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municipalities have been forced to adopt more rigorous and more expensive filtration techniques to meet atrazine drinking water standards.

The development of glyphosate [*N*-(phosphonomethyl)glycine]-tolerant crops, such as corn, has created a new alternative to atrazine-based weed management. Glyphosate has been linked to several health effects in humans, but exhibits lower toxicity than atrazine, as is reflected by its drinking water MCL of 700 $\mu g\ L^{-1}$. Management factors influencing the environmental fate of glyphosate are not well understood, and the increasingly widespread use of glyphosate has raised some concern regarding its pollution potential. Model predictions have indicated that replacement of triazine-based corn weed management, such as atrazine, with post-emergent herbicide-based weed management, such as glyphosate, in conjunction with herbicide tolerant crops, would dramatically reduce herbicide concentrations in vulnerable watersheds (Wauchope et al., 2002). Since glyphosate is also less toxic than atrazine, this could represent a significantly lower risk to humans through drinking water. Comprehensive field research is necessary to validate these predictions.

Herbicide losses with surface runoff may be further minimized with optimum tillage management, but diverse opinions exist regarding which tillage practice is most likely to minimize herbicide runoff. Some studies have shown significant reductions in herbicide loss under no-tillage (NT) compared to conventional tillage (CT) practices (Hall et al., 1984; Kenimer et al., 1987), while others have observed higher herbicide concentrations in runoff from NT than CT (Baker and Johnson, 1978; Gaynor et al., 1995; Smith et al., 1995). Additionally, increased surface crop residues associated with NT may reduce runoff of herbicides by reducing surface sealing and maintaining higher infiltration rates, but also may lead to increased herbicide wash-off during early rainfall events following herbicide application. Residue cover may additionally affect other important herbicide fate and transport factors such as soil pH, pesticide adsorption, and microbial activity.

While many benefits of long-term NT are documented, producers may choose to periodically till NT fields, especially where soils are cooler or poorly drained. Perceived benefits of such periodic tillage include temporary alleviation of soil compaction, gulley formation, and some moisture-related and/or residue-hosted crop diseases. It is important to also consider water quality impacts of periodic tillage of NT fields. Few studies have examined the impacts of tilling long-term NT ground, especially in comparing and the atrazine-based versus glyphosate-based weed management. This study is part of an ongoing effort to evaluate the herbicide impacts of tillage practices as they become established over time. The objective of the study was to evaluate the first-year impacts of tilling land previously in long-term NT management on glyphosate and atrazine transport to surface runoff under variable intensity rainfall.

## 2. Materials and methods

### 2.1. Location characteristics

The study plots were located within a NT field and a proximal CT field in DeKalb County, IN within St. Joseph River Watershed, which drains 280,852 ha of land in northeast Indiana, northwest Ohio, and south central Michigan. The watershed is primarily agriculture, approximately 79%, while 10% is woodlands or wetlands, and 11% consists of urban, residential, and other land uses. The St. Joseph River serves as the drinking-water supply for over 200,000 residents of Fort Wayne, IN. Fort Wayne's Three Rivers Filtration Plant processes 129 million L of water daily from the St. Joseph River. This water supply has a history of excessive atrazine contamination, and requires extensive treatment in order to meet the safe drinking water standard set forth by the EPA. The area receives 94 cm of annual precipitation and has average daily temperatures ranging from −1 °C to 28 °C.

The predominant soil at the study sites was an eroded Glynwood loam (fine, illitic, mesic, Aquic Hapludalf) (USDA-SCS, 1980), having clay loam texture and properties given in Table 1. Initial surface soil moisture (0–10 cm) was determined by time domain reflectometry (TDR). Initial soil moisture in NT plots averaged 31.5% and 30% for the first and second rainfall events, respectively, while initial soil moisture in CT plots averaged 19% and 21% for the first and second rainfall events. The line transect method described by Hanna et al. (1995) was used to determine the percentage of residue cover. Average residue cover for NT and CT before raining were 53% and 28%, respectively. Soil hydraulic and physical properties were also determined from 3-cm diameter cores taken from three locations at the experimental site at depths of 0–15 cm and 15–30 cm. Bulk density (BD) was measured by the core method and saturated hydraulic conductivity ($K_{sat}$) was measured by falling head method (Dane and Topp, 2002).

### 2.2. Plot preparation

The experimental design was a randomized complete block. Each block contained three plots, 2 m long and

Table 1
Organic matter content (OM), cation exchange capacity (CEC), pH, bulk density (BD), saturated hydraulic conductivity ($K_{sat}$), and particle size distribution of soils at the study sites

| Site | Soil type | Taxonomic classification | Depth (cm) | OM (%) | CEC (meq 100 $g^{-1}$) | pH | BD (g $(cm^3)^{-1}$) | $K_{sat}$ (cm $h^{-1}$) | Particle size distribution | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Sand (%) | Silt (%) | Clay (%) |
| NT | Glynwood | Aquic Hapludalf | 0–15 | 3 | 13 | 7.5 | 1.5 | 1.2 | 43 | 25 | 32 |
| | | | 15–30 | 2 | 24 | 7.9 | 1.6 | 0.8 | 39 | 25 | 36 |
| CT | Glynwood | Aquic Hapludalf | 0–15 | 3 | 11 | 6.7 | 1.3 | 1.6 | 43 | 27 | 30 |
| | | | 15–30 | 3 | 11 | 6.8 | 1.6 | 0.7 | 39 | 27 | 34 |

1 m wide, representing three replications of CT and NT treatments. Plots were defined by differential leveling and taping, and then isolated to a depth of 8 cm with metal borders. Plots had a mean slope of 5.5%. A runoff collection trough was installed at the down slope end of each plot. Prior to the study, the entire research site had been in long-term NT for 14 years, and cropped to annual corn and soybean (*Glycine max*) rotation, with historic use of glyphosate, atrazine, and metolachlor. Approximately 2 weeks before planting, CT plots were tilled using a Krause TL6200 Landsman tillage system. All plots were planted in glyphosate-tolerant corn, in annual rotation with soybeans. Plots received very only trace precipitation between cultivation and herbicide application. To remove effects of significant canopy variability, above-ground plant mass was removed from plots. This simulates normal conditions for atrazine application, but not for post-emergent glyphosate application, which would normally occur in the presence of some degree of canopy. Herbicides were applied by a certified pesticide applicator to all plots 24 h prior to the first rainfall event according to label: Bicep II Magnum (33% atrazine) at a rate 1621 g atrazine $ha^{-1}$ and Roundup Ultra Max (41% glyphosate) at a rate of 709 g glyphosate $ha^{-1}$. Immediately before herbicide application and immediately prior to the rainfall, soil was sampled and analyzed for herbicide levels to establish initial soil concentrations and confirm uniform and precise application.

### 2.3. Rainfall simulation methods

A programmable, variable intensity rainfall simulator with eight oscillating nozzle type rainfall simulation troughs were used. Troughs each had 5 VeeJet 80100 nozzles spaced 1 m apart, and were mounted 2.5 m above the plot surface on an aluminum frame. Two rainfall events were performed on each plot, at 1 day and 8 days after herbicide application. Rainfall sequence was: 50 mm $h^{-1}$ for 50 min followed by 75 mm $h^{-1}$ for 15 min, 25 mm $h^{-1}$ for 15 min, and 100 mm $h^{-1}$ for 15 min. The sequence of rain intensities was designed to allow steady state of runoff to be achieved at several runoff rates, and represents a 200-year return period storm for the region. Deionized water was used as source water in the simulations, and source water samples were collected at the end of each simulation to verify quality.

### 2.4. Sampling and analytical methods

Runoff samples were collected at 5 min intervals from the onset of runoff to 50 min and 3 min intervals from 53 min to 95 min. During each sampling period, a 1-L timed sample for runoff and sediment rate determination, and a 40-mL glass vial for herbicide analysis were collected. Gravimetric analysis was performed on timed runoff samples in order to determine rates of sediment and runoff losses. Runoff herbicide samples were filtered and frozen on site until analyzed. Runoff samples were analyzed for glyphosate by liquid chromatography methods, using post-column reaction coupled with a fluorescence detector according to EPA Drinking Water Method for Chemical Contaminants #547. No preconcentration step was necessary for glyphosate determination (detection limit = 2 $\mu g\ L^{-1}$). Atrazine levels in runoff water were determined by gas chromatography/mass spectrometry coupled with automated solid-phase microextraction (SPME) according to a modified EPA method 525.2 described by Tugulea et al. (1998) (detection limit = 2 $\mu g\ L^{-1}$). Prior to analysis, samples were saturated with NaCl and then concentrated by SPME.

Before pesticide application, prior to rainfall, and after rainfall, composite soil samples were taken from the 0–2 cm depth immediately outside the plot borders using a clean trowel, and then analyzed for glyphosate (method: Monsanto RES-014-91) and atrazine (method: FAO PAM 302/SPE/NPD).

Statistical analyses were performed using SAS 9.1 (SAS Institute Inc., Cary, NC), and SigmaPlot V. 6.0 (SPSS Inc., Chicago, IL). Non-normally distributed data were log-transformed according to Neter et al. (1996). The effects of tillage method on runoff volumes, and concentrations and mass losses of sediment, glyphosate, and atrazine were determined using PROC GLM with $P \leq 0.05$. Since replicate plots were placed within 10 m of one another in the same field, the authors recognize that this pseudo-replication negates some of the randomness inherently assumed by analysis of variance. Regression analyses were performed using linear and logarithmic functions in SigmaPlot V. 6.0.

## 3. Results and discussion

### 3.1. Runoff and sediment losses

Average runoff rates are presented in Fig. 1. In all cases, time to runoff was greater in NT than in CT plots. This was expected due to the crop residue effects and presence of intact macropores associated with NT systems. Runoff rates corresponded with rainfall intensity as expected. Average maximum runoff rates in NT were 85.2 mm $h^{-1}$ and 79.4 mm $h^{-1}$ for events 1 and 2, respectively, while average maximum runoff rates in CT were 63.0 mm $h^{-1}$ and 61.9 mm $h^{-1}$ for events 1 and 2, respectively. Tillage had a significant effect on the rate of runoff for both events, with CT having approximately 50% lower steady state runoff rates than NT treatments. This result can be explained by the difference in mean saturated hydraulic conductivity ($K_{sat}$), which ranged 0.07–1.61 cm $h^{-1}$ for NT and 0.52–2.30 cm $h^{-1}$ for CT. In the top 5 cm of the plots, NT $K_{sat}$ was greater than CT $K_{sat}$, while in the 10–30 cm depth range, the reverse was true. This may further explain the greater time to runoff initiation observed in NT plots, followed by higher runoff rates in NT than CT plots. Cumulative runoff volumes were also found to be higher in NT than CT plots during both events. Because the CT plots in this experiment were in their first year of tillage following long-term NT management, differences in runoff volume between tillage treatments do not represent those where both tillage practices are well established, but are applicable to infrequent tillage of long-term NT soil. Differences in water runoff volumes from plots under different tillage treatment tend to become more pronounced with the length of time the land is under a specific tillage system (Baker, 1983). During the first year of tillage, infiltration problems may be temporarily relieved, while after subsequent years of tillage, these problems may well become more evident. However, some previous research indicates that long-term NT can lead to compaction and reduced infiltration (Voorhees and Lindstrom, 1983). This would be especially likely on poorly drained fine-textured soils.

Differences in sediment loss rates between tillage treatment were moderated by lower runoff quantities from CT plots, and these differences were not significant. However, sediment mass loss rates were slightly greater for CT than NT (Fig. 2). Similarly to runoff rates, sediment loss rates closely followed the trend of rainfall intensity.

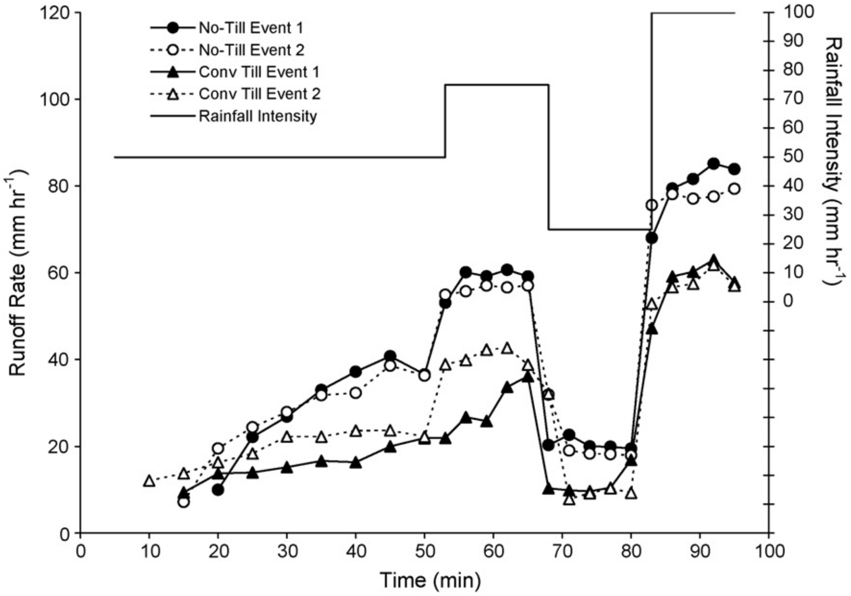

Fig. 1. Average runoff rates for NT and CT plots during rainfall events 1 and 2.

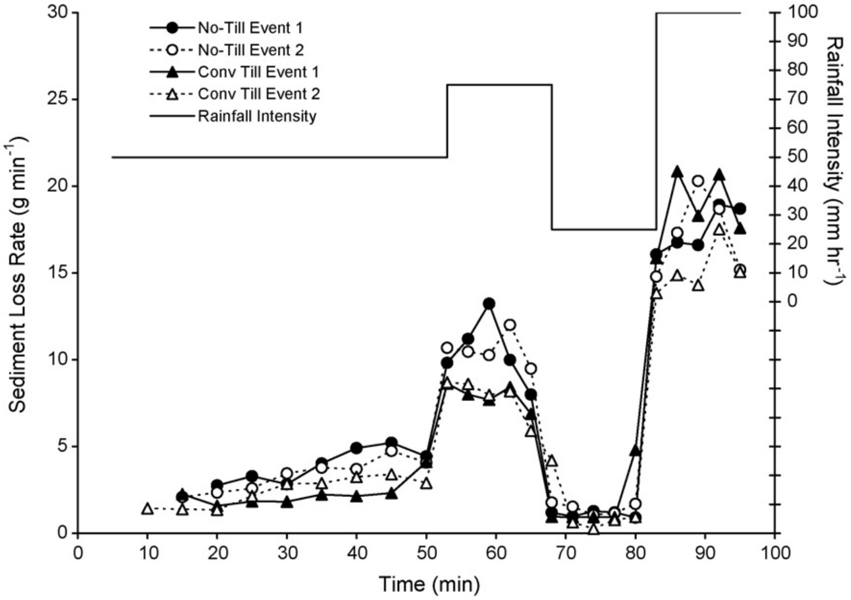

Fig. 2. Average sediment loss rates for nt and ct plots during rainfall events 1 and 2.

### 3.2. Herbicide losses

Runoff herbicide concentrations are given as a function of time in Figs. 3 and 4. Herbicide concentrations from both tillage treatments decreased with time, with the highest average concentrations (>300 μg L$^{-1}$ atrazine, >200 μg L$^{-1}$ glyphosate) usually occurring in the first or second runoff samples after runoff initiation. This may be partly attributed to the shift in dominant transport process from initial movement of soil solution herbicide into surface runoff to desorption of herbicide from soil particles. Herbicide concentrations were also generally much higher for the first runoff event than in the second event. In the 7 days between the first and second runoff events, herbicide available for transport decreased due to loss into soil and from dissipation processes, such a degradation, volatilization, sorption, and photolysis. Leonard (1990) predicted that total

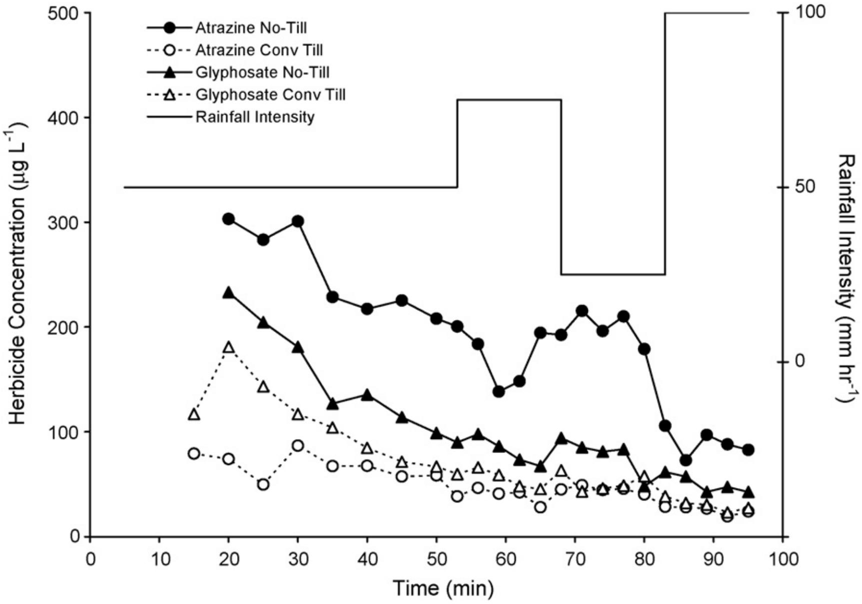

Fig. 3. Average runoff herbicide concentrations during rainfall event 1.

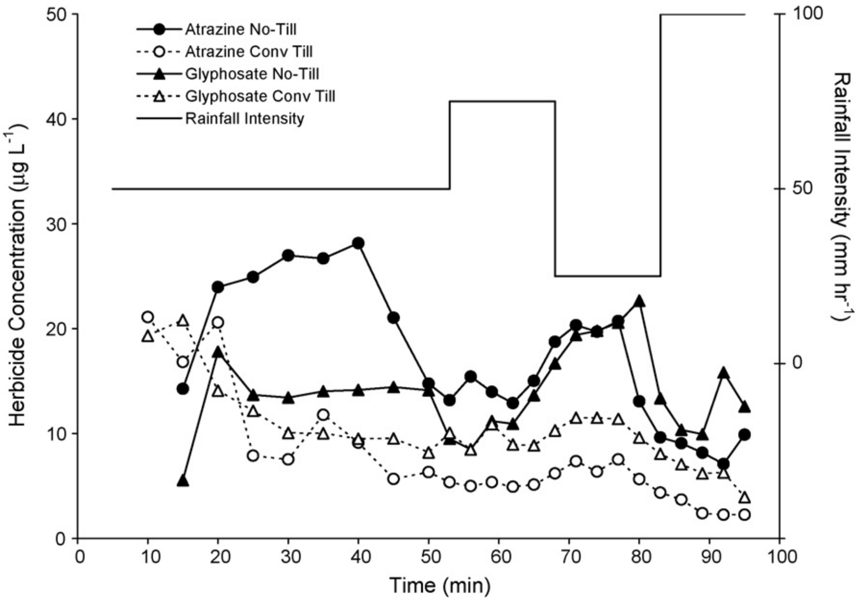

Fig. 4. Average runoff herbicide concentrations during rainfall event 2.

runoff losses of pesticides (such as herbicides) would decline exponentially with time in each runoff event. Mean glyphosate concentration in runoff was about 20% of the glyphosate MCL of 700 μg $L^{-1}$, while atrazine consistently exceeded its MCL of 3 μg $L^{-1}$. This suggests that glyphosate-based weed management may be a viable alternative to atrazine to help protect receiving drinking water supplies from excess herbicide loading.

During both events, runoff herbicide concentrations were significantly greater from NT than from CT plots. Previous studies also observed or predicted higher concentrations of herbicide in runoff from NT than CT (Baker and Johnson, 1978; Gaynor et al., 1995; Smith

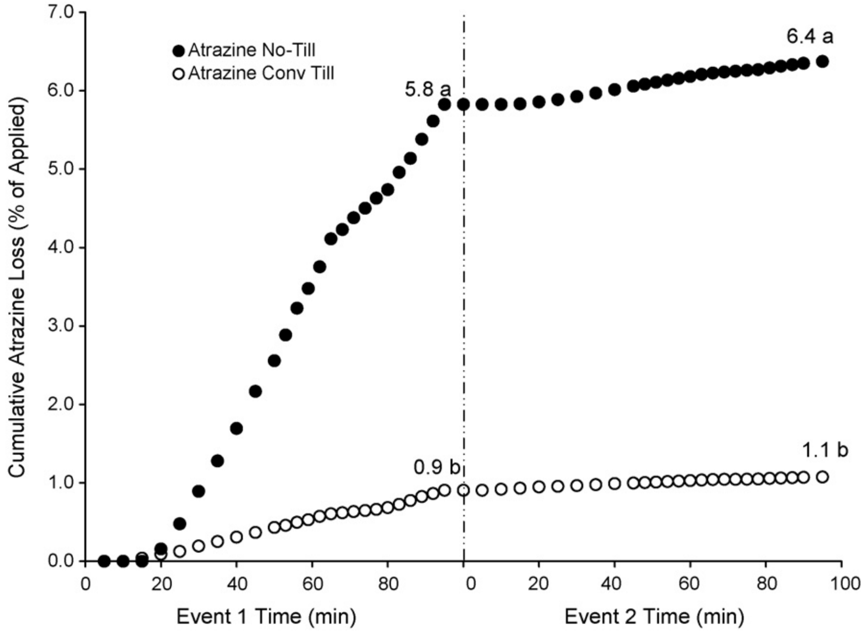

Fig. 5. Cumulative atrazine mass loss as a percentage of total applied during rainfall events 1 and 2. Values having the same lower-case letter designation within the same event are not significantly different, $\alpha = 0.05$.

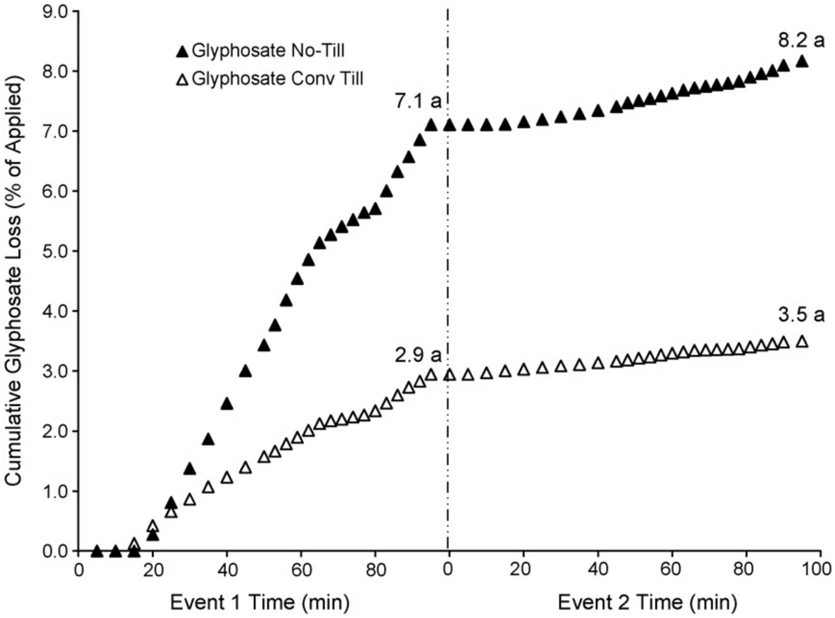

Fig. 6. Cumulative glyphosate mass loss as a percentage of total applied during rainfall events 1 and 2. Values having the same lower-case letter designation within the same event are not significantly different, $\alpha = 0.05$.

et al., 1995). This may be partly attributed to crop residue effects, as higher amounts of crop residue have been shown to increase the concentrations of herbicides in runoff water (Baker and Johnson, 1978; Sauer and Daniel, 1987).

Herbicide mass losses, represented as percentage of mass applied, were also greater from NT treatment than CT treatment during both events, due to higher concentrations and runoff volumes observed from NT plots as compared to CT plots (Figs. 5 and 6). For atrazine, differences in mass losses between tillage treatments were significant with $\alpha = 0.05$, where replicate plots were located within the same field. Glyphosate mass losses were influenced by tillage treatment to a lesser degree than atrazine losses, and in fact differences in glyphosate mass losses between tillage treatments were not significant. Since runoff water rates were impacted by tillage treatment, and atrazine has lower sorptivity as compared to glyphosate with consequent higher propensity to be transported with runoff water, it was expected that atrazine mass losses would be more strongly influenced by tillage treatment than glyphosate mass losses. Average atrazine mass losses were greater during the first event (5.8% of applied and 0.9% of applied for NT and CT, respectively), than during the second event (0.6% and 0.2%), and a similar trend was observed for glyphosate. This can be attributed to dissipation and degradation processes occurring during the 7 days between events 1 and 2, as well as the loss of the readily transported fraction of herbicides with runoff and into the soil during event 1.

## 4. Conclusions

During the first year of tillage following long-term NT management, levels of atrazine and glyphosate in runoff generated by simulated rainfall on small plots were higher from NT plots than from CT plots. This effect was greater for atrazine than for glyphosate. Average atrazine concentrations in runoff water from both tillage treatments consistently exceeded the atrazine MCL of 3 $\mu g\ L^{-1}$, whereas average glyphosate levels represented only 20% of the glyphosate MCL of 700 $\mu g\ L^{-1}$. Data from this study indicate that tillage of historically no-till ground may lead to decreased herbicide runoff loading potential during the first year of tillage. Additionally, conversion from atrazine-based to glyphosate-based weed management may represent a potential improvement in herbicide runoff water quality, especially in NT systems.

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