Comparative Losses of Glyphosate and Selected Residual Herbicides in Surface Runoff from Conservation-tilled Watersheds Planted with Corn or Soybean

Martin J. Shipitalo* and Lloyd B. Owens

Residual herbicides regularly used in conjuction with conservation tillage to produce corn (Zea mays L.) and soybean (Glycine max (L.) Merr) are often detected in surface water at concentrations that exceed their U.S. maximum contaminant levels (MCL) and ecological standards. These risks might be reduced by planting glyphosate-tolerant varieties of these crops and totally or partially replacing the residual herbicides alachlor, atrazine, linuron, and metribuzin with glyphosate, a contact herbicide that has a short half-life and is strongly sorbed to soil. Therefore, we applied both herbicide types at typical rates and times to two chisel-plowed and two no-till watersheds in a 2-yr corn/soybean rotation and at half rates to three disked watersheds in a 3-yr corn/soybean/wheat–red clover (Triticum aestivum L.–Trifolium pratense L.) rotation and monitored herbicide losses in surface runoff for three crop years. Average dissolved glyphosate loss for all tillage practices, as a percentage of the amount applied, was significantly less (P ≤ 0.05) than the losses of atrazine (21.4x), alachlor (3.5x), and linuron (8.7x) in corn-crop years. Annual, flow-weighted, concentration of atrazine was as high as 41.3 μg L⁻¹, much greater than its 3 μg L⁻¹ MCL. Likewise, annual, flow-weighted alachlor concentration (MCL = 2 μg L⁻¹) was as high as 11.2 and 4.9 μg L⁻¹ in corn- and soybean-crop years, respectively. In only one runoff event during the 18 watershed-years it was applied did glyphosate concentration exceed its 700 μg L⁻¹ MCL and the highest, annual, flow-weighted concentration was 3.9 μg L⁻¹. Planting glyphosate-tolerant corn and soybean and using glyphosate in lieu of some residual herbicides should reduce the impact of the production of these crops on surface water quality.

Glyphosate [N-(phosphonomethyl)glycine] has been described as one of the most effective herbicides ever discovered (Dewar, 2009) and a once-in-a-century, virtually ideal herbicide (Duke and Powles, 2008). These accolades are attributable to the fact that it is highly effective on a wide range of weed species, has limited persistence and volatility, and is of low toxicity (Duke and Powles, 2008). In fact, the toxicity of the adjuvants used to formulate the commercial products is often greater than that of glyphosate (Struger et al., 2008; Battaglin et al., 2009).

Although glyphosate has been commercially available in the United States since 1974, its widespread and expanding use is linked to the introduction of glyphosate-tolerant, transgenic crops in 1996 (Duke and Powles, 2008; CTIC, 2010). Within the United States, this technology has been rapidly adopted. And by 2010, an estimated 93% of the soybean and 70% of the corn crop planted was herbicide tolerant with the majority of these plantings resistant to glyphosate (Fernandez-Cornejo, 2010). Worldwide adoption has proceeded at a slower pace, but by 2008, annual planting of herbicide-tolerant crops was up to 79 million ha (ISAAA, 2008). This has contributed to glyphosate becoming the most widely used herbicide in the world (Duke and Powles, 2008).

The advent of glyphosate-tolerant crops has also made it easier and less risky to implement no-till and other conservation tillage practices. This has led to increased land areas farmed using these methods with presumed positive effects on soil and water quality (Cerdeira and Duke, 2006; Locke et al., 2008; Givens et al., 2009; Krutz et al., 2009; CTIC, 2010). These effects include increased soil organic carbon and reduced runoff and erosion (Givens et al., 2009; CTIC, 2010). In addition, the switch to glyphosate-tolerant crops has resulted in the substitution of glyphosate for more toxic and persistent herbicides. In 1998, an estimated 2.5 million kg of active ingredient glyphosate were applied to herbicide-tolerant soybean as an alternative to 3.3 million kg of active ingredient of other, more traditional herbicides (Heimlich et al., 2000). Moreover, the herbicides that were replaced by glyphosate were more toxic (3.4–16.8 times) and had longer half-lives (60–90 d), compared with 47 d for glyphosate (Heimlich et al., 2000). By 2006, the estimated reduction
in herbicide use attributable to glyphosate-tolerant soybean was 10.5 million kg (a.i.) (Johnson et al., 2007). Devos et al. (2008) calculated that using glyphosate alone to control weeds in corn would reduce the pesticide occupational and environmental risk exceedance factor by 1/6, compared with other herbicide-based weed management regimes.

This substitution of glyphosate for other herbicides has probably contributed to declines in concentration of these herbicides in surface bodies of water in the United States. In a long-term investigation, Sullivan et al. (2009) noted downward trends in flow-adjusted atrazine [6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine], alachlor [2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide], and metribuzin [4-amino-6-(1,1-dimethylylethyl)-3-(methylythio)-1,2,4-triazin-5(4H)-one] concentrations in most of the 31 sites monitored in Corn Belt streams. They correlated these declines in concentration to reduced use of these products and, in the case of alachlor and metribuzin, they attributed reduced use to the planting of glyphosate-tolerant soybean.

Despite its relatively short half-life and strong sorption, glyphosate and one of its degradation products—aminomethylphosphonic acid (AMPA)—have been widely detected in surface bodies of water (Battaglin et al., 2005, 2009; Zablotowicz et al., 2006; Borggaard and Gimsing, 2008; Struger et al., 2008; Dewar, 2009). For the most part, these detections have been much less than the U.S. maximum contaminant level (MCL) for drinking water (MCL = 700 μg L⁻¹) and aquatic life standards (65 μg L⁻¹). In Europe, where a drinking water standard of 0.1 μg L⁻¹ applies to all pesticides, glyphosate and AMPA have been frequently detected at levels more than this limit (Dewar, 2009). In addition, glyphosate has been identified as one of only four herbicides that are European-selected stormwater priority pollutants (Eriksson et al., 2007). In boreal climates, glyphosate degradation can be slowed considerably and Laitinen et al. (2009) noted detectable concentrations (>0.10 μg L⁻¹) in surface runoff 20 mo after a fall application to residue-covered plots in Finland.

Unfortunately, there have been few studies of glyphosate losses in surface runoff when applied under conditions that typify use on glyphosate-tolerant crops (Borggaard and Gimsing, 2008; Locke et al., 2008). In earlier work, we compared glyphosate application to herbicide-tolerant soybean with more traditional residual herbicides by monitoring their concentrations in surface runoff from small watersheds (Shipitalo et al., 2008). In this 4-yr investigation, we noted that glyphosate losses were ~1/7 that of metribuzin and ~1/2 that of alachlor—two residual herbicides it can replace. In our current research, we used these same watersheds to investigate glyphosate application to herbicide-tolerant corn, as well as herbicide-tolerant soybean. Previous research has shown that crop residues and living vegetation can intercept a significant proportion of herbicide application and that washoff and subsequent potential for loss in surface runoff can be greatly affected by the amount and composition of these materials (Isensee et al., 1998; Mickelson et al., 2001; Matocha et al., 2006). This suggests that the runoff losses of glyphosate might be different among these two crops. Therefore, our primary objective was to determine if the use of glyphosate in lieu of some of the residual herbicides typically used in corn production would also result in reduced losses of herbicide in surface runoff. Since there is little available information on the interactions between glyphosate-tolerant crops and conservation tillage practices (Locke et al., 2008), three tillage systems—no-till, chiseled, and disked—were investigated.

Materials and Methods

Watershed Characteristics and Crop Management

Losses of glyphosate in surface runoff were compared with losses of commonly used residual herbicides for three crop years (2002–2004), using seven small (0.45–0.79 ha; 6–13% average slope) watersheds used to grow glyphosate-tolerant corn and soybean. From 1998 to 2001, these same watersheds were used to investigate losses of glufosinate [2-amino-4-(hydroxymethylphosphinyl)butanoic acid] applied to glufosinate-tolerant corn and glyphosate applied to glyphosate-tolerant soybean (Shipitalo et al., 2008). General characteristics of watersheds are provided in that report and are detailed in the soil survey by Kelley et al. (1975).

The tillage treatments assigned to the watersheds were identical to those reported in the previous study. Briefly, two watersheds (WS 113 and WS 118) were in 2-yr, no-till corn/soybean rotation and two watersheds (WS 109 and WS 123) were in the same rotation but were chisel plowed before planting (Table 1). Cereal rye (Secale cereale L.) was drilled into these watersheds following soybean harvest and served as a cover crop. Three watersheds (WS 111, WS 115, and WS 127) were in a 3-yr, corn/soybean/wheat—clover rotation and were disked in the spring just before corn and soybean planting (Table 1). Winter wheat was drilled into these watersheds after soybean harvest and red clover was broadcast into the standing wheat the following March or April. The red clover was disked into the soil the following spring to provide some of the nitrogen requirement of the corn crop. Within each tillage treatment, one watershed was planted to each crop each year.

In years they were planted to corn, the watersheds were treated within a few days of planting with 3.36 kg ha⁻¹ alachlor, 2.24 kg ha⁻¹ atrazine, and 1.12 kg ha⁻¹ linuron [N-(3,4-dichlorophenyl)-N-methoxy-N-methylurea]. In 2002, the soybean watersheds were treated with 3.36 kg ha⁻¹ alachlor and 0.38 kg ha⁻¹ metribuzin, and in 2003 they received only alachlor (Table 1). These application rates were equivalent to the maximum label rates. Due to a sprayer malfunction, only a partial application of alachlor and metribuzin was made to WS 127 in 2004 and no residual herbicides were applied to the other soybean watersheds (Table 1). Half rates of herbicides were used on the disked watersheds and they were usually cultivated between the rows twice during the corn- and soybean-crop years. In corn- and soybean-crop years, two 1.12 kg ha⁻¹ applications of a 2-propanamine formulation of glyphosate (equivalent to 0.84 kg ha⁻¹ of glyphosate acid per application) were applied to the no-till and chiseled watersheds on the dates indicated in Table 1. Glyphosate applications to the disked watersheds were at half this rate (i.e., 0.56 kg ha⁻¹). In 2002, weather unsuitable for herbicide application combined with rapid growth of the corn prevented the second application of glyphosate to all watersheds planted to corn.
Runoff Measurement and Sampling Procedures

Runoff volumes were measured and samples collected using the procedures detailed in Shipitalo et al. (2008). Each watershed was equipped with an H flume (Brakensiek et al., 1979), data logger to record the hydrograph, and ISCO samplers (Teledyne ISCO, Lincoln, NE). These were used to collect approximately 300-mL discrete samples for each event every 10 min for the first 100 min, every 20 min for the next 200 min, and then every 60 min until all bottles were full or runoff ended. When high concentrations of herbicide were expected shortly after application, all samples were analyzed, but this was reduced to samples collected at the beginning, peak, and end of the runoff later in the crop year. The concentrations in individual samples were used to calculate flow-weighted average concentrations for each runoff event and annual flow-weighted concentrations. Flow-proportional samples collected using Coshocton Wheels (Brakensiek et al., 1979) were used for analysis in instances when the ISCO samplers failed and during the winter and early spring when runoff events sometimes spanned several days. Precipitation amounts and intensities were measured using recording rain gages positioned near each watershed.

Herbicide Analysis

Detailed descriptions of the procedures used to determine herbicide concentrations in the runoff samples are provided in Shipitalo et al. (2008). Briefly, solid-phase extraction of unfiltered samples was used to concentrate alachlor, linuron, metribuzin, and atrazine and its metabolites deethylatrazine (DEA) (6-chloro-N-(1-methylethyl)-1,3,5-triazine-2,4-diamine) and deisopropylatrazine (DIA) (6-chloro-N-ethyl-1,3,5-triazine-2,4-diamine). Concentrations of these substances in the extracts were determined using capillary gas chromatography with nitrogen phosphorus detection with hypochlorite, derivatization with o-phthalaldehyde and Thiofluor (Pickering Laboratories, Mountain View, CA), and fluorescent detection. Minimum detection limit for both compounds was 1.0 μg L⁻¹. Soil losses from these watersheds were minimal (Shipitalo and Edwards, 1998); consequently, losses of glyphosate attached to the sediment were not assessed.

Data Analysis

Samples with herbicide concentrations less than the detection limits were assigned a value of zero when calculating flow-weighted average concentrations and transport amounts. One-sided, paired t tests with $P \leq 0.05$ selected as the minimum level for significance were used to test the hypothesis that annual losses of glyphosate in runoff would be less than that of the residual herbicides. Since the watersheds are not replicates and tillage treatments were not assigned by randomization, no statistical comparisons of tillage treatments were made. The effect of time on herbicide concentration in surface runoff was determined by regressing ln days after application (DAA) against ln concentration for those events with concentrations among the detection limits. Previous research has shown that herbicide concentrations in surface runoff typically decline exponentially with time (Ghidey et al., 2010). Measured herbicide concentrations are compared with their associated drinking water standards (MCLs) with the realization that these standards are not applicable to edge-of-field losses and that several processes (i.e., dilution, degradation, sorption) are likely to reduce these concentrations before and after surface runoff enters permanent bodies of water.

Table 1. Dates of planting and herbicide application for corn and soybean in 2002, 2003, and 2004.

<table>
<thead>
<tr>
<th>Crop year</th>
<th>Watershed and tillage treatment</th>
<th>Planted</th>
<th>Residual herbicides</th>
<th>Glyphosate</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002 Corn</td>
<td>WS 109 Chiseled</td>
<td>22 May</td>
<td>24 May</td>
<td>25 June</td>
</tr>
<tr>
<td></td>
<td>WS 113 No-till</td>
<td>22 May</td>
<td>24 May</td>
<td>25 June</td>
</tr>
<tr>
<td></td>
<td>WS 111 Disked</td>
<td>23 May</td>
<td>24 May</td>
<td>25 June</td>
</tr>
<tr>
<td>2002 Soybean</td>
<td>WS 123 Chiseled</td>
<td>5 June</td>
<td>10 June</td>
<td>1 July, 15 July</td>
</tr>
<tr>
<td></td>
<td>WS 118 No-till</td>
<td>5 June</td>
<td>10 June</td>
<td>1 July, 15 July</td>
</tr>
<tr>
<td></td>
<td>WS 115 Disked</td>
<td>5 June</td>
<td>5 June</td>
<td>2 July, 15 July</td>
</tr>
<tr>
<td>2003 Corn</td>
<td>WS 123 Chiseled</td>
<td>28 Apr.</td>
<td>30 Apr.</td>
<td>10 June, 23 June</td>
</tr>
<tr>
<td></td>
<td>WS 118 No-till</td>
<td>28 Apr.</td>
<td>30 Apr.</td>
<td>10 June, 23 June</td>
</tr>
<tr>
<td></td>
<td>WS 127 Disked</td>
<td>28 Apr.</td>
<td>30 Apr.</td>
<td>10 June, 23 June</td>
</tr>
<tr>
<td></td>
<td>WS 113 No-till</td>
<td>20 May</td>
<td>28 May</td>
<td>17 July, 31 July</td>
</tr>
<tr>
<td></td>
<td>WS 111 Disked</td>
<td>29 May</td>
<td>29 May</td>
<td>17 July, 31 July</td>
</tr>
<tr>
<td>2004 Corn</td>
<td>WS 109 Chiseled</td>
<td>10 May</td>
<td>11 May</td>
<td>4 June, 21 June</td>
</tr>
<tr>
<td></td>
<td>WS 113 No-till</td>
<td>10 May</td>
<td>11 May</td>
<td>4 June, 21 June</td>
</tr>
<tr>
<td></td>
<td>WS 115 Disked</td>
<td>12 May</td>
<td>13 May</td>
<td>4 June, 21 June</td>
</tr>
<tr>
<td>2004 Soybean</td>
<td>WS 123 Chiseled</td>
<td>14 May</td>
<td>not applied</td>
<td>4 June, 21 June</td>
</tr>
<tr>
<td></td>
<td>WS 118 No-till</td>
<td>14 May</td>
<td>not applied</td>
<td>4 June, 21 June</td>
</tr>
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<td></td>
<td>WS 127 Disked</td>
<td>4 June</td>
<td>partial application‡</td>
<td>21 June, 4 Aug.</td>
</tr>
</tbody>
</table>

† Watershed.
‡ The sprayer malfunctioned during application to this watershed. Therefore, residual herbicides were not analyzed in runoff from WS 127 in 2004.
Results and Discussion

Rainfall and Runoff Variability

Decisions on when to till, plant, and apply herbicides were based on the weather and crop conditions. Therefore, the date of residual herbicide application was used to define the start of a crop year that ended with residual herbicide application in the subsequent year. In years when no residual herbicides were applied, 1 June was selected as the beginning of the crop year. This variation in crop-year beginning and ending dates, as well as slight variation in measured precipitation among locations, contributed to differences in annual rainfall among watersheds within years (Table 2).

Nevertheless, for all three tillage treatments, annual precipitation for the 2002 crop year was substantially less than the North Appalachian Experimental Watershed (NAEW) long-term (1937–2009) average of 962 mm yr\(^{-1}\). Although this did not adversely impact crop growth, the fewest number of runoff events and runoff as a percentage of rainfall were less in 2002 than in the other crop years (Table 2). In contrast, crop years 2003 and 2004 were much wetter than average with calendar year 2004 being the wettest year in the 72-yr record with greater-than-average rainfall every month.

A combined total of 1015 runoff events were sampled for the seven watersheds during the 3-yr period. The arithmetic mean amount of runoff as a percentage of precipitation was the same for the chiseled and no-till watersheds (14.9% yr\(^{-1}\)), and slightly higher for the disked watersheds (18.0% yr\(^{-1}\)). The amount of surface runoff alone, however, was not a good predictor of herbicide loss as average transport of all herbicides, except metribuzin, was lowest for the chiseled watersheds (Table 2). The mean runoff during the corn crop years for all watersheds (14.9%) was slightly less than that noted for the soybean crop years (17.3%).

<table>
<thead>
<tr>
<th>Crop year</th>
<th>Crop</th>
<th>Rainfall</th>
<th>No. of events</th>
<th>% of rainfall</th>
<th>Runoff Percentage of applied</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Alachlor</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>2002</td>
<td>Corn</td>
<td>880</td>
<td>12</td>
<td>3.6</td>
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<td>1159</td>
<td>35</td>
<td>6.5</td>
<td>0.0295</td>
</tr>
<tr>
<td>2004</td>
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<td>1483</td>
<td>68</td>
<td>6.6</td>
<td>0.0110</td>
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<td></td>
<td>Soybean</td>
<td>1537</td>
<td>49</td>
<td>34.0</td>
<td>0.0234/na</td>
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<tr>
<td>Mean chiseled†</td>
<td></td>
<td>1187</td>
<td>39</td>
<td>14.9</td>
<td>0.090</td>
</tr>
<tr>
<td>2002</td>
<td>Corn</td>
<td>909</td>
<td>15</td>
<td>7.6</td>
<td>0.1809</td>
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<tr>
<td>2003</td>
<td>Soybean</td>
<td>1160</td>
<td>55</td>
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<td>2004</td>
<td>Corn</td>
<td>1526</td>
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<td>22.2</td>
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<td>Mean no-till §</td>
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<td>1201</td>
<td>58</td>
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<td>2002</td>
<td>Corn</td>
<td>909</td>
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<td>11.4</td>
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<td>Soybean</td>
<td>1323</td>
<td>61</td>
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<td>2004</td>
<td>Wheat</td>
<td>1328</td>
<td>46</td>
<td>27.8</td>
<td>0.0149/na</td>
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<tr>
<td>Mean disked‡</td>
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<td>1224</td>
<td>49</td>
<td>18.0</td>
<td>0.34</td>
</tr>
<tr>
<td>2002</td>
<td>Soybean</td>
<td>916</td>
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<td>Wheat</td>
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<td>1224</td>
<td>49</td>
<td>18.0</td>
<td>0.34</td>
</tr>
</tbody>
</table>

† Losses of herbicide degradation products are expressed as the equivalent amount of the parent compound.
‡ na = not applied; nd = not detected; tr = trace <0.0001%. Losses in crop years when the herbicide was detected, but not applied, are based on the rates in the previous year of application.
§ Tillage treatment means for percent herbicide loss are the means of the amount applied, thus are not numerical averages of the yearly losses.
Glyphosate is generally considered to be more strongly sorbed to soils and degrade more rapidly than alachlor, atrazine, and linuron (Wauchope et al., 2002; Battaglin et al., 2005; Screpanti et al., 2005; Vereecken, 2005). Therefore, glyphosate losses in surface runoff should be less than that of these three residual herbicides. Based on modeling using PRZM-EXAMS, Wauchope et al. (2002) noted that glyphosate loads in surface runoff should be 10 to 20% of those for atrazine and alachlor. Runoff events shortly after application, however, tend to dominate herbicide transport (Shipitalo and Owens, 2006; Zablhotowicz et al., 2006; Ghidiey et al., 2010). Since there were two applications of glyphosate each corn-crop year, except 2002, but only a single application of the residual herbicides each year, the potential for loss in runoff was increased. In fact, glyphosate concentrations in surface runoff peaked shortly after each application. Therefore, for comparison purposes, herbicide concentration was plotted as a function of days after the most recent application. In addition, the residual herbicides were applied pre-emergence, which increased the likelihood that they would contact the soil and be subject to sorption. In contrast, glyphosate was applied to standing corn and was subject to foliar washoff (Isensee et al., 1998; Michelson et al., 2001; Matocha et al., 2006).

The concentrations in surface runoff of all four herbicides applied to the corn crop declined rapidly with DAA. In all cases, highly significant relationships ($P < 0.0001$) between ln concentration and ln DAA were noted with each tillage treatment exhibiting a similar response except for linuron (Fig. 1–4). In the case of linuron, a homogeneity-of-slopes test indicated a significant difference ($P < 0.05$) in the relationships among tillage treatments with a steeper slope noted for no-till than for the other tillage treatments (Fig. 3). For all tillage treatments, atrazine was the most frequently detected herbicide. Atrazine is also the most frequently detected pesticide in surface water and groundwater in North America (Solomon et al., 1996), and has been banned in the European Union since 2003, mainly based on detections in groundwater (Dewar, 2009). Generally, only runoff events that occurred during the winter and that were a result of melting snow or rain on frozen soil did not have detectable concentrations of atrazine. The relationship depicted in Fig. 1 ends with the beginning of the next crop year, but atrazine was detected in all crop years, including wheat years on the disked watersheds more than 2 yr after atrazine application (Table 2). The maximum flow-weighted atrazine concentration observed for a single event was $198 \mu g L^{-1}$ when runoff occurred 6 DAA to the chiseled WS 109 in 2004. The last regular detection greater than its $2 \mu g L^{-1}$ MCL occurred 80 DAA to the no-till WS 113 in 2002—the same event that produced the last detection of atrazine greater than its MCL. There were, however, two instances of alachlor greater than its MCL just before planting, which may have been a result of spray drift or atmospheric deposition (Goolsby et al., 1997). There is no MCL for linuron and the maximum concentration ($189 \mu g L^{-1}$) observed was in 2004 when runoff occurred 6 DAA to the no-till WS 113. Unlike atrazine and alachlor, there were only sporadic detections of linuron beyond approximately 80 DAA and the detections near the end of the crop years may have been related to atmospheric deposition or tillage (Fig. 3).

In contrast to atrazine and alachlor applied to the corn crop, no glyphosate concentrations greater than its $700 \mu g L^{-1}$ MCL were noted and the last detection was 79 DAA to the no-till WS 113 in 2004 (Fig. 4). The highest concentration ($286 \mu g L^{-1}$) was the result of runoff 1 DAA to the disked WS 127 in 2003. This was similar to the highest glyphosate concentration ($233 \mu g L^{-1}$) noted by Warnemuende et al. (2007) when they applied a 200-yr return period, simulated rainfall to vegetation-free, no-till plots 24 h after herbicide application. While
the lack of glyphosate detection later in the crop year compared with atrazine and alachlor is partially attributable to differences in analysis methodologies, our glyphosate detection limit was 700 times less than its MCL. In contrast, our detection limit for alachlor was 15 times less than its MCL and that for atrazine was 100 times less than its MCL.

The relationship of glyphosate concentration to DAA was similar for all tillage treatments (Fig. 4). Tillage practice reportedly has little effect on glyphosate degradation or sorption since it is controlled by the mineral faction rather than soil organic matter (Zabloto-wicz et al., 2009). Nevertheless, in their simulated rainfall study, Warnemuende et al. (2007) noted greater losses of glyphosate from no-till plots than from conventional-tilled plots, which was partially attributable to a greater volume of runoff from the no-till plots. Similarly, we noted that average glyphosate loss in the corn years was greater from the no-till watersheds (0.25%) than from the chiseled (0.08%) and disked watersheds (0.01%). The higher losses of glyphosate from the no-till watersheds may be a consequence of greater residue cover than in the other tillage treatments, resulting in decreasing contact with the soil and less sorption (Accinelli et al., 2005; Krutz et al., 2009).

Probably due to a lag in its formation from its parent compound, AMPA concentrations in surface runoff were proportionally lower when high glyphosate concentrations were observed shortly after application than when glyphosate concentrations declined with time. Their concentrations, however, were strongly correlated as described by the relationship ln [AMPA] = 0.47 + 0.54 ln [glyphosate] (r = 0.87, P = 0.0001, n = 75). In most instances, AMPA losses, expressed as the equivalent amount of glyphosate (Table 2), were similar to those of the parent compound and there was no significant difference (P = 0.05), based on a paired t test, in mean loss of AMPA (0.09%) compared with glyphosate (0.11%). This suggested that losses of AMPA should be considered to fully assess the impact of glyphosate use. Similarly, based on the results of a modeling study, Mamy et al. (2010) concluded that it is critical that the fate of AMPA be considered when assessing the environmental impact of glyphosate-tolerant crops.

Because of less-than-normal rainfall in crop year 2002 and few runoff-producing rainfall events in the first few months immediately after herbicide application, net losses of all materials tended to be lower than in subsequent crop years (Table 2). In the cases of the chiseled WS 109 and disked WS 111, the first runoff after glyphosate application did not occur until 10 Nov. 2002, 138 d after glyphosate was applied. Similarly, the first runoff from the no-till WS 113 did not occur until 48 d after glyphosate application. Consequently, no glyphosate losses were detected for this crop year. In the other crop years that were wetter than average, runoff occurred as soon as 1 d after glyphosate application (Fig. 4).

In the corn years, average annual loss of glyphosate (0.11%) was significantly less than that of atrazine (2.35%, P = 0.01), alachlor (0.39%, P = 0.01), and linuron (0.96%, P = 0.02), based on one-sided paired t tests. These differences in transport were still significant (P = 0.05) when the contribution of AMPA, equivalent to an average of 0.09% of the applied glyphosate, was added to the total (Table 2). Only in crop year 2004 for the chiseled WS 109 did the percentage loss of applied glyphosate exceed the percentage losses of the other herbicides. Most of the glyphosate loss that year (67%) was the result of a relatively large runoff event that accounted for 14% of the annual runoff and occurred 19 DAA. For all other corn-crop years, atrazine losses as a percentage applied exceeded that of the other herbicides. When its two metabolites were added to the total, average loss increased to 2.81% (Table 2). The greatest loss for any herbicide occurred from the disked WS 127 in crop year 2003 when 6.76% of the applied atrazine was lost in surface runoff. Most of this loss (68%) was the result of a relatively small runoff event that accounted for 3.5% of the yearly runoff but occurred 9 DAA. These observations reinforce the contention that timing of runoff relative to...
application, rather than event size, is the dominant factor affecting herbicide transport (Shipitalo and Owens, 2006).

Thus, the transport data (Table 2) supported our hypothesis that glyphosate loss would be less than the losses of the residual herbicides. Moreover, the annual, average, flow-weighted concentrations of atrazine and alachlor exceeded their MCLs for all three corn-crop years for the no-till watershed and 1 of the 3 yr for the chiseled watersheds. Even with half-rate applications to the disked watersheds, MCLs for these herbicides were exceeded each year (Fig. 5). The highest annual, flow-weighted concentration was 41.3 μg L⁻¹ for atrazine and 11.3 μg L⁻¹ for alachlor, both of which occurred for no-till WS 113 in 2004 and were much greater than their respective MCLs of 3 and 2 μg L⁻¹. In contrast, the maximum observed for glyphosate was 3.9 μg L⁻¹ for the chiseled WS 109 in 2004, much less than its 700 μg L⁻¹ MCL (Fig. 5). According to Wauchope et al. (2002), annual, average concentrations of alachlor, atrazine, and glyphosate are the most toxicological-relevant endpoint for these herbicides.

Herbicide Losses in Soybean Years

Since the residual herbicides alachlor and metribuzin were both applied to soybean only in 2002 when rainfall was less than average and there were few runoff-producing events, there was insufficient data on which to base statistical comparisons with losses of glyphosate. Average loss of applied glyphosate for the three tillage treatments for all soybean-crop years, however, was 0.11% (Table 2). This is identical to the average loss measured with the corn crop for these years. Although the dates of glyphosate application were not identical for the two crops (Table 1), hence the timing of runoff relative to DAA varied, this observation suggested that composition of the crop had a minimal effect on the amount of glyphosate lost in runoff. In the earlier 4-yr study (Shipitalo et al., 2008) in which rainfall and runoff were generally lower than observed during the current study, glyphosate losses during soybean-crop years averaged 0.07% of the amount applied.

The greatest loss of glyphosate observed during the 3-yr period for either crop was noted in 2004 for the disked WS 127 when the loss was equivalent to 1.09% of the amount applied (Table 2). Most of this loss (93%) was attributable to a relatively small runoff event that accounted for only 0.2% of the runoff for the crop year. This event occurred on 4 Aug. 2004, the day of the second application to soybean (Table 1) and was the only instance when glyphosate concentration (887 μg L⁻¹) exceeded the MCL for this herbicide (Fig. 4 and 6). This suggested that only in extreme circumstances (i.e., runoff within 1 or 2 d of application) is the 700 μg L⁻¹ MCL likely to be exceeded.

Average glyphosate loss in the soybean years was greater from the no-till (0.13%) than from the chiseled watersheds (0.05%), once again suggesting that the greater residue cover in the no-till watersheds may have decreased contact with the soil and reduced sorption. As opposed to the no-till and chiseled watersheds that received glyphosate application each year on the same day, the glyphosate applications to the disked watersheds followed a different schedule (Table 1). The average glyphosate loss from disked watersheds for the 3-yr period (0.36%) was greater than that from the no-till and chiseled watersheds, but this comparison was skewed by the losses in 2004 attributable to the runoff event that occurred on the day of application as no glyphosate was lost in 2002 and only a trace amount was recorded in 2003 for these watersheds.

![Flow-Weighted Herbicide Concentrations (Corn 2002-2004)](chart)

Fig. 5. Flow-weighted yearly average concentrations for atrazine, alachlor, linuron, and glyphosate (and aminomethylphosphonic acid [APMA], a degradation product of glyphosate) applied during the three corn-crop years to no-till (NT), chiseled (CH), and disked (DS) watersheds. The average concentration is the arithmetic mean of the yearly flow-weighted averages for all tillage treatments.
As was observed during the corn years, average AMPA loss (0.10%) was not significantly different \((P = 0.05)\) from that for glyphosate (0.18%), its parent compound (Table 2). In addition, their concentrations were strongly correlated as described by the relationship \(\ln \text{[AMPA]} = 0.39 + 0.75 \ln \text{[glyphosate]}\) \((r = 0.83, P < 0.0001, n = 60)\). This further supports our contention that losses of this glyphosate degradation product should be considered when assessing the impact of growing glyphosate-tolerant crops on water quality.

The annual, flow-weighted concentration for alachlor was greater than its 2 \(\mu g\) L\(^{-1}\) MCL in 2002 for the disked WS 115 (6.1 \(\mu g\) L\(^{-1}\)) and in 2003 for the no-till WS 113 (4.9 \(\mu g\) L\(^{-1}\)), indicating a potential concern with the use of this herbicide. Only applied in 2002, metribuzin never exceeded its 200 \(\mu g\) L\(^{-1}\) health advisory level and highest concentration noted for a single event was 98 \(\mu g\) L\(^{-1}\) when runoff occurred 1 DAA to the disked WS 115. In our previous study using these watersheds, the highest concentration of metribuzin noted was 562 \(\mu g\) L\(^{-1}\) when runoff occurred 1 DAA to the no-till WS 118 (Shipitalo et al., 2008). Thus, concentrations of this herbicide can be problematic under some circumstances. In contrast, the highest annual, flow-weighted concentration for glyphosate was 1.9 \(\mu g\) L\(^{-1}\) for the disked WS 127 in 2004.

### Summary and Conclusions

In corn-crop years, losses of dissolved glyphosate, as a percentage of the amount applied, were significantly lower \((P \leq 0.05)\) than that of the residual herbicides atrazine, alachlor, and linuron. Glyphosate losses in soybean-crop years were similar to the losses in corn years, suggesting that, in this instance, crop type had a minimal effect on glyphosate losses in runoff. Losses of glyphosate tended to be higher in runoff from the no-till watersheds than from the other tillage practices, despite similar amounts of total runoff. This suggested that leaving the crop residue on the soil surface may have reduced glyphosate sorption. Losses of the glyphosate metabolite AMPA were of similar magnitude to that of its parent compound. Thus, this should be considered when evaluating the impact of glyphosate-tolerant crops on surface water quality. Annual, flow-weighted concentrations of atrazine and alachlor in corn years, and alachlor in soybean years, frequently exceeded their U.S. drinking water standards. In contrast, annual, flow-weighted glyphosate concentrations were much less than its drinking water standard in each of the 18 watershed years it was applied (33 total applications), despite the fact that the study included the wettest year in the 72-yr history of NAEW. Only when runoff occurred on the day of application was the glyphosate MCL exceeded, whereas the atrazine and alachlor concentrations typically exceeded their water quality standards for up to 80 d after they were applied. Growing transgenic corn and soybean, and partially or totally replacing these residual herbicides with glyphosate should reduce the impact of the production of these crops on surface water quality. It is critical, however, to maintain a diversity of weed management practices in the face of the evolution of glyphosate-resistant weeds (Duke and Powles, 2008; Krutz et al., 2009).

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### References


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**Fig. 6. Relationship of glyphosate concentration to days after application to soybean for all three tillage treatments. No comparisons of slope among tillage treatments were made due to the limited number of observations.**


