Herbicide Contamination and Transport in Northern Missouri and Southern Iowa Streams

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Abstract

Herbicide contamination of streams has been well documented, but little is currently known about the specific factors affecting watershed vulnerability to herbicide transport. The primary objectives of this study were: 1) to document herbicide occurrence and transport from watersheds in the northern Missouri/ southern Iowa region in an effort to quantify watershed vulnerability to herbicide transport; and 2) to compute the contribution of this region to the herbicide load of the Missouri and Mississippi Rivers. Grab samples were collected under baseflow and runoff conditions at 21 hydrologic monitoring stations between April 15 and July 15 from 1996 to 1999. Samples were analyzed for commonly used soil-applied herbicides (atrazine, cyanazine, acetochlor, alachlor, metolachlor, and metribuzin) and four triazine metabolites. Estimates of herbicide load and relative losses were computed for each watershed. Median parent herbicide losses, as a percentage of applied, ranged from 0.33 to 3.9%; loss rates that were considerably higher than other areas of the United States. Watershed vulnerability to herbicide transport, measured as herbicide load per treated area, showed that the runoff potential of soils was a critical factor affecting herbicide transport. Herbicide transport from these watersheds contributed a disproportionately high amount of the herbicide load to both the Missouri and Mississippi Rivers. Based on these results, this region of the Corn Belt is highly vulnerable to hydrologic transport of herbicides from fields to streams, and it should be targeted for implementation of management practices designed to reduce herbicide losses in surface runoff.

Keywords: herbicide transport, watershed vulnerability, hydrologic soil group, corn and soybean herbicides

Introduction

In the Corn Belt region of the United States, herbicide contamination of streams is widely recognized as one of the major environmental impacts of row crop production. Field runoff represents the primary hydrologic mechanism responsible for herbicide transport from agricultural fields to streams (Wauchope 1978, Leonard 1988). Over the last decade, several studies have overwhelmingly demonstrated that row crop production leads to frequent detections and potentially harmful levels of commonly used corn and soybean herbicides and their metabolites in stream water (Thurman et al. 1992, Richards et al. 1993, Lerch et al. 1998, Blanchard and Lerch 2000). Maximum herbicide concentrations and frequency of detections follow herbicide application to fields in the spring (Thurman et al. 1992, Blanchard and Lerch 2000). The inopportune coincidence of herbicide application with intense spring rainfall events creates a critical herbicide loss period during the second and third quarters of each year (Richards et al. 1993, Clark et al. 1999).

There are many factors affecting herbicide transport to streams, and they can be organized into four general categories: 1) intrinsic factors - soil and hydrologic properties and geomorphologic characteristics of the watershed; 2) anthropogenic factors - land-use and herbicide management; 3) climate factors - particularly precipitation and temperature; and 4) herbicide factors - chemical and physical properties and formulation.

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One of the most important intrinsic watershed characteristics affecting herbicide transport is the runoff potential of its soils, which is primarily determined by soil particle size distribution (i.e., soil texture) and topography. Hydrologic soil group (HSG) categories represent one way to rank runoff potential of soils, and they have been shown to be valid indicators of regional hydrology and watershed vulnerability to herbicide transport (Blanchard and Lerch 2000). Soil texture directly affects water infiltration rate and, therefore, it largely determines the dominant hydrologic pathway of the watershed. Watersheds dominated by clayey soils, or those with prominent argillic horizons, will typically have low infiltration rates, high surface runoff volume, and will be vulnerable to surface transport of herbicides. Those watersheds with a predominance of silty or sandy soils will have high infiltration and percolation rates, low surface runoff volume, low vulnerability to surface transport of herbicides, but high vulnerability to nitrate leaching.

Studies conducted by the U.S. Geological Survey (USGS) National Stream Quality Accounting Network (NASQAN) have been used to estimate the herbicide load of the largest sub-basins to the Mississippi River (Clark et al. 1999). While the NASQAN data has provided useful information about herbicide transport in these large sub-basins, there remains a gap in our knowledge regarding the herbicide contribution of smaller sub-basins within the Missouri and Mississippi Rivers. This information would contribute to a more detailed understanding of which areas transport the greatest herbicide load to the large river systems, and it will provide a basis for prioritizing implementation of best management practices (BMPs) to the most vulnerable watersheds.

The primary objectives of this study were to document herbicide occurrence and to estimate herbicide transport from 21 watersheds encompassing the northern Missouri/ southern Iowa region (Figure 1) in an effort to quantify watershed vulnerability to herbicide transport. An additional objective was to compute the contribution of northern Missouri and southern Iowa streams to the herbicide load of the Missouri and Mississippi Rivers.

Methods

Stream sampling

The study area included 21 sites, 20 streams and one reservoir outlet, draining approximately 56,700 km^2 in northern Missouri and southern Iowa (Figure 1 and Table 1). Stream samples represented watershed areas ranging from 21,276 to 1,796,154 ha, with a median area of 115,500 ha (Table 1). Grab samples were collected at USGS hydrologic monitoring stations (Figure 1 and Table 1) between April 15 and July 15 from 1996 to 1999. Samples were collected under baseflow and runoff conditions. A single sample was collected from the main flow paths for the smallest streams, and for the larger streams, sub-samples were collected at two or three locations in a transect across the stream. All samples were transported to the lab on ice and filtered through 0.45 μm nylon filters within 48 hours of collection. For the larger streams, all sub-samples were mixed to create a single composite sample just before filtration. The fewest number of samples collected at any site was five and the most was 11, with an average of eight samples per site per year. Only seven sites were sampled in 1996 (Table 1), and data from these sites were only used for computing annual herbicide loss as a percent of applied.

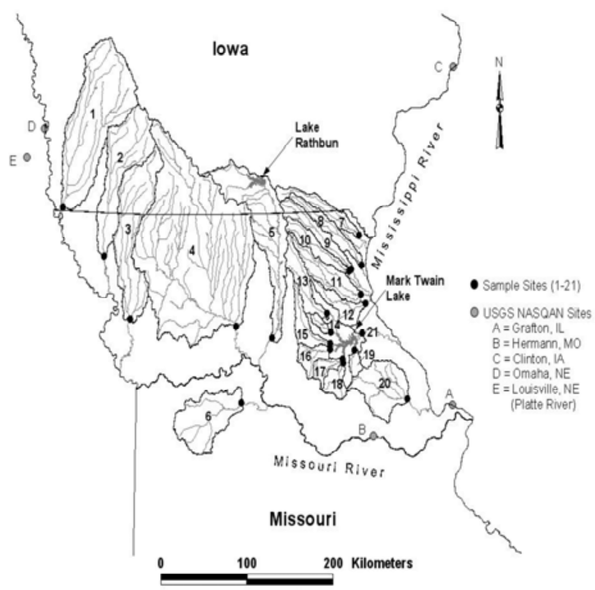

Figure 1. Watersheds of included in this study. Entire area encompasses ~56,700 km^2. See Table 1 for list of watershed names.

Table 1. Sampled watersheds and watershed drainage areas.

Watershed	Site Number	Years Sampled	Watershed Area (ha)
Nishnabotna River	1	1997-1999	730,161
Nodaway River	2	1997-1999	393,200
Platte River	3	1997-1999	454,439
Grand River	4	1997-1999	1,796,154
Chariton River	5	1997-1999	489,167
Blackwater River	6	1997-1999	289,744
Fox River	7	1997-1999	102,980
Wyaconda River	8	1997-1999	103,230
North Fabius River	9	1997-1999	115,526
Middle Fabius River	10	1997-1999	100,152
South Fabius River	11	1996-1999	156,558
North River	12	1996-1999	92,130
North Fk Salt River¶	13	1996-1999	119,286
Crooked Creek¶	14	1996-1999	21,276
Middle Fk Salt River¶	15	1996-1999	86,556
Elk Fk Salt River¶	16	1997-1999	67,488
Long Branch Creek¶	17	1997-1999	47,129
South Fk Salt River¶	18	1996-1999	59,050
Lick Creek¶	19	1996-1999	26,943
Cuivre River	20	1997-1999	240,570
Salt River§	21	1997-1999	608,650

¶ Sub-basins of the Salt River.
§ Salt River site was only used for computing herbicide load to Mississippi River.

Chemical analyses

Samples were analyzed for the following commonly used corn and soybean herbicides and selected triazine metabolites: acetochlor, alachlor, atrazine, cyanazine, cyanazine amide, deethylatrazine, deisopropylatrazine, hydroxyatrazine, metolachlor, and metribuzin. For all analytes, terbutylazine was added as a surrogate to 100 or 200 mL samples which were then concentrated using 500 mg C_{18} solid-phase extraction cartridges. Herbicide concentrations were then determined by gas chromatography (GC) with N-P or mass spectral (MS) detection or high performance liquid chromatography (HPLC) with UV detection. Only hydroxyatrazine and cyanazine amide were analyzed by HPLC. Detection limits, using GC/MS or HPLC/UV, and frequencies of detection are given in Table 2.

Table 2. Detection limits and frequency of herbicide detection (average of 1998 and 1999).

Herbicide or Metabolite	Detection Limit	Frequency of Detection
	ng L^{-1}	%
Atrazine	3	100
Deethylatrazine	4	99
Deisopropylatrazi	8	95
Hydroxyatrazine	50	99
Cyanazine	9	89
Cyanazine Amide	20	85
Acetochlor	6	91
Alachlor	3	92
Metolachlor	2	99
Metribuzin	8	87

Land and herbicide use estimates

Land use was based on land cover data produced from 30 meter resolution Landsat Thematic Mapper spectral data. Both the Iowa and the Missouri data sets were developed using nominal 1992 data. Planted row crop acreage was estimated for each watershed by combining the land cover data with county-level row crop data from the USDA-National Agricultural Statistics Service (USDA-NASS 1997-2000). The key assumption in this approach is that the distribution of row crops was uniform within a county. The suite of herbicides analyzed in this study pertained only to corn, soybeans, and sorghum. Therefore, herbicide use estimates were computed for each watershed by using the estimated acreage of these crops within each watershed combined with state level annual reports of agricultural chemical usage (USDA-NASS 1997-2000) for each relevant crop. These reports include planted crop acres, the percentage of crop acres treated by a given herbicide, and its average annual use rate for each state.

Load calculations

Herbicide loads for all sampled watersheds, and the NASQAN sites (Figure 1), were computed on a daily basis for the critical loss period of April 15 to June 30 of each year. Herbicide concentrations for non-sampled days were estimated by linear interpolation between measured concentrations (Clark et al. 1999). In addition, boundary conditions were assumed for extrapolating herbicide concentrations to the beginning and ending of the critical loss period. All herbicide and metabolite concentrations were assumed to be zero on April 1 and July 31. Since the NASQAN project performs year-round monitoring, no assumptions were required with respect to beginning or ending concentrations. Measured or estimated concentrations were multiplied by the average daily stream discharge to estimate daily load.

Results

Study area characteristics

Land-use within the study area is predominantly agricultural, with an average of 96% of the watershed areas in row crop or forage production. Corn and soybeans account for about 80% of the row crop production. Sorghum is a significant crop only in the eastern portion of the study area within Missouri. Row cropping intensity ranged from 22% to 77% of the watershed area. In general, row cropping intensity is high in the western watersheds (sites 1-3), low in the central watersheds (sites 4-6), and intermediate in the eastern watersheds.

The HSG represent four general soil categories (A to D), with HSGA having the lowest and HSGD the highest runoff potential. Since runoff potential is critical to surface transport of herbicides, it follows that watersheds dominated by HSGC and D would be the most vulnerable to herbicide transport and subsequent stream contamination. Within the study area, the runoff potential of soils increases from west to east (Figure 2). Sites 1-3 represent watersheds with low runoff potential soils mainly within HSGA or B. Sites 4-6 represent a transition in which the soils become progressively higher in runoff potential from west to east. Sites 7-21 represent watersheds with the highest proportion of soils within the HSGC and D categories. These watersheds have >75% of their terrace and upland areas within the two highest runoff potential categories.

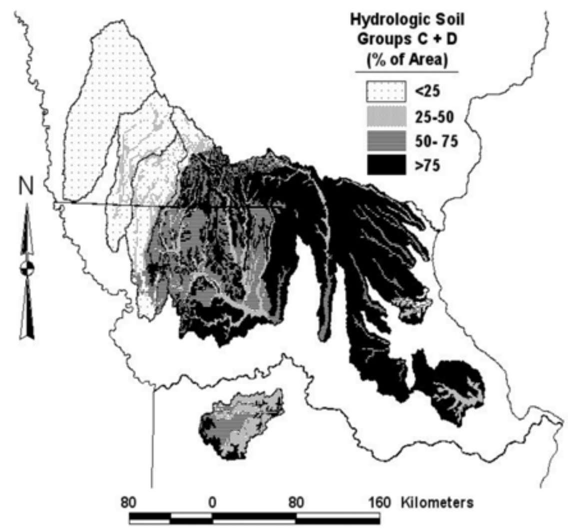

Figure 2. Percentage of watershed area in Hydrologic Soil Groups C and D.

Relative herbicide losses

Relative herbicide losses were computed as a percent of the herbicide applied within the watershed. This approach removes the dominant influence that watershed size and herbicide usage have on absolute loads, but it relies on herbicide usage estimates of unknown accuracy (USDA-NASS 1997-2000). Relative herbicide loss estimates for 1996-1999 showed that the triazine herbicides had the highest losses, with peak atrazine or cyanazine losses exceeding 10% of applied in five watersheds (sites 11-15) in 1996 (Figure 3). Median herbicide losses were: 3.9% for atrazine, 2.3% for cyanazine, 2.1% for metribuzin, 2.0% for metolachlor, 0.50% for acetochlor, and 0.33% for alachlor (Figure 3). These median losses were 2.8 to 40 times higher than median herbicide losses reported by Capel et al. (2001) for 43 USGS

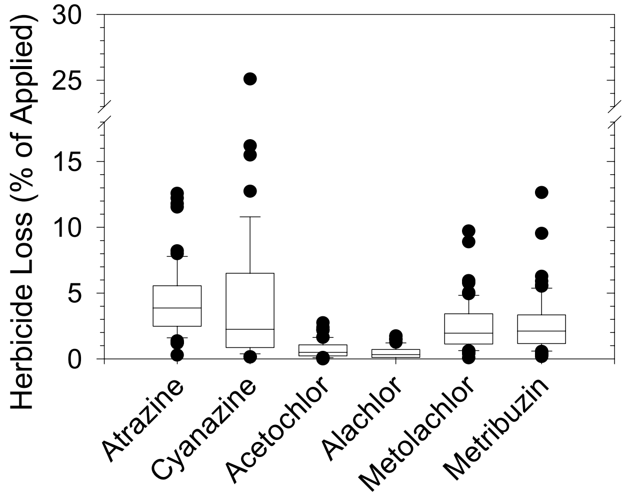

Figure 3. Relative herbicide loss, expressed as percent of applied, for 1996-1999.

National Water-Quality Assessment Program sites and their review of several hundred studies published in the international literature.

The relative herbicide losses reported in Figure 3 represent conservative estimates of actual herbicide loss for three reasons: 1) metabolites were not included (when atrazine metabolites were included median losses increased from 3.9% to 4.5% of applied); 2) loss was computed for three months of the year; and 3) the assumed boundary conditions for extrapolation were conservative, particularly for the triazine herbicides.

Areal herbicide losses and watershed vulnerability

Areal herbicide loss, expressed as the sum of all herbicide and metabolite losses on a treated area basis, provides a direct measure of watershed vulnerability to herbicide transport (Figure 4). This approach to calculating relative herbicide losses, like loss as a percent of applied, also removes the influence of watershed size and herbicide usage, but it has the additional advantage of using land-use data that has been verified for accuracy. Herbicide transport from treated fields occurred at the lowest rates in the northwestern (sites 1-3) and southeastern (sites 18-20) watersheds, and the highest loss rates occurred in several of the northeastern watersheds (sites 7-9, 11, 13, and 15) and in site 6 (Figure 4). The areal loss rates generally follow the pattern of HSGC and D soils (Figure 2), in which herbicide loss rates tend to increase with increasing runoff potential of soils (Figure 2). Of the seven watersheds in which areal loss rates were 350 g/ha or greater, six of them (Sites 7-9, 11, 13, and 15) have >75% of their area comprised of high runoff potential soils within HSGC and D categories. Soils within these most vulnerable watersheds have claypans or pronounced argillic horizons that restrict water percolation and increase surface runoff.

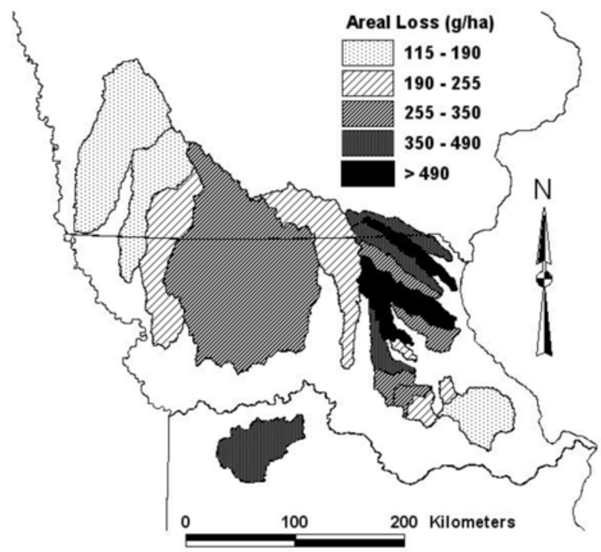

Figure 4. Watershed vulnerability to herbicide transport, expressed as the sum of all herbicide and metabolite losses on a treated area basis.

Contribution to the herbicide load in the Missouri and Mississippi Rivers

Herbicide transport from the six Missouri River tributaries (sites 1-6) contributed a disproportionately high amount of the herbicide load to the Missouri River at Hermann, MO (site B) from 1997 to 1999 (Figure 1 and Table 3). These six tributaries account for only 3.1% of the drainage area and an average of 14% of the stream discharge within the Missouri River basin. Averaged over the three years, this region of the Missouri River basin contributed just over three-fourths of the metribuzin load, approximately one-third of the atrazine, cyanazine, and acetochlor loads, and about one-fifth of the metolachlor load. The small area of the Missouri River basin monitored in this study was obviously a major contributor to the herbicide load within the entire basin. This indicated that the

Table 3. Contribution of Missouri and Mississippi River tributaries to the herbicide load at Hermann, MO (Site B) and Grafton, IL (Site A).*

Watershed	Area	Discharge	Atrazine	Cyanazine	Aceto-chlor	Alachlor	Metol-achlor	Metribuzin
	------------------------------- % of Missouri River at Hermann, MO-----------------------------------							
MO River Tributaries†	3.1	14	38	37	30	12	21	78
	------------------------------- % of Mississippi River at Grafton, IL------------------------------------							
MS River Tributaries‡	3.4	3.2	7.4	9.1	2.3	7.5	5.4	31

* Average of 1997-1999.

† Missouri River tributaries represent the sum of Sites 1-6.

‡ Mississippi River tributaries represent the sum of Sites 7-12 and 21.

combination of high herbicide inputs and moderate to high runoff potential of the soils resulted in the disproportionately greater herbicide loss rates of these six watersheds compared to other intensive cropping regions within the lower Missouri River basin.

The Mississippi River tributaries (sites 7-12 and 21) also contributed a disproportionately high amount of the herbicide load to the upper Mississippi River at Grafton, IL (site A) (Figure 1 and Table 3). These seven watersheds represent 3.4% of the drainage area, and an average of 3.2% of the stream discharge within the upper Mississippi River basin (Table 3). Metribuzin transport was the most highly disproportionate of the herbicides measured, accounting for an average of 31% of the load at Grafton, IL. Atrazine, cyanazine, alachlor, and metolachlor transport were also disproportionately high from this region, but much less so than metribuzin. Acetochlor transport was disproportionately low relative to stream discharge when averaged over the three years. Because of the greater similarity in land-use of these watersheds to the upper Mississippi River basin, the contribution was generally not as disproportionate as that computed for the Missouri River basin.

Conclusions

Relative herbicide loss, as a percentage of applied, was considerably higher within the northern Missouri/ southern Iowa region compared to other areas of the U.S. or Corn Belt. The computation of areal herbicide loss rates, on a treated area basis, provided a direct measure of watershed vulnerability to transport. Areal loss rates were strongly correlated to soil runoff potential. The most vulnerable watersheds are dominated by claypan soils or soils with pronounced argillic horizons that increase surface runoff. Herbicide transport from the northern MO/southern IA region contributed a disproportionately high amount of the herbicide load to the MO and MS Rivers from 1997 to 1999. Atrazine, cyanazine, metolachlor, and metribuzin transport were disproportionately high from both the MO and MS tributaries. This region of the Corn Belt is highly vulnerable to herbicide transport, and many of these watersheds should be targeted for BMP implementation to reduce herbicide loading to streams.

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