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HERBICIDE TRANSPORT IN GOODWATER CREEK EXPERIMENTAL WATERSHED: II. LONG-TERM RESEARCH ON ACETOCHLOR, ALACHLOR, METOLACHLOR, AND METRIBUZIN[1]

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ABSTRACT: Farmers in the Midwestern United States continue to be reliant on soil-applied herbicides for weed control in crop production, and herbicide contamination of streams remains an environmental problem. The main objective of this study was to analyze trends in concentration and load of acetochlor, alachlor, metolachlor, and metribuzin in Goodwater Creek Experimental Watershed (GCEW) from 1992 to 2006. A secondary objective was to document the effects of best management practices (BMPs) implemented within GCEW on herbicide transport trends. Median relative herbicide loads, as a percent of applied, were 3.7% for metolachlor, 1.3% for metribuzin, 0.36% for acetochlor, and 0.18% for alachlor. The major decrease in alachlor use and increase in acetochlor use caused shifts in flow-weighted concentrations that were observed over the entire concentration range. The smaller decrease in metolachlor use led to a consistent decreasing time trend only for the upper end of the concentration distribution. Metribuzin also showed moderate decreases in concentration with time since 1998. Annual loads were generally correlated to second quarter discharge. Despite extensive education efforts in the watershed, conservation BMPs within GCEW were mainly implemented to control erosion, and therefore had no discernable impact on reducing herbicide transport. Overall, changes in herbicide use and second quarter discharge had the greatest effect on trends in flow-weighted concentration and annual load.

(KEY TERMS: best management practices; correlation analysis; cumulative frequency distributions; herbicide transport; regression analysis; watershed regression for pesticides models.)

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INTRODUCTION

The acetanilide herbicides have been among the most commonly used soil-applied herbicides for row-crop production in the United States (U.S.) and Missouri (USDA-NASS, 1992-2006; Scribner *et al.*, 2000; Lerch and Blanchard, 2003; Battaglin *et al.*, 2005). Alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxy-methyl)acetamide] and metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide] were commonly used on corn (*Zea mays*) and soybean (*Glycine max*) through the mid-1990s. Since then, alachlor use has substantially

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declined due to the introduction of acetochlor [2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl) acetamide] and new classes of soybean herbicides (e.g., imidiazolinones, sulfonylureas), and more recently, due to the availability of herbicide-resistant soybean varieties. Metolachlor use has also declined because it is now rarely used on soybean, and the introduction of *S*-metolachlor reduced application rates on corn. Since its introduction in 1995, acetochlor has become the second most commonly used (based on mass applied) corn herbicide in the U.S. and Missouri (USDA-NASS, 1992-2006). Metribuzin, a triazinone herbicide [4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazin-5(4*H*)-one] has not been as widely used as the acetanilides, but it has traditionally been used on about 10 to 20% of the planted soybean area, and more recently, has been used on about 4 to 5% of the planted corn area in Missouri (USDA-NASS, 1992-2006). Within Goodwater Creek Experimental Watershed (GCEW), trends in herbicide use have reflected these state and national trends (see below).

Like atrazine, the acetanilides and metribuzin are usually pre-plant soil-applied herbicides, and therefore, exhibit similar seasonality in their hydrologic transport (Lerch and Blanchard, 2003; Lerch *et al.*, this issue). Concentrations and loads of these herbicides have been reported to be highest during post-application runoff events in the spring (Thurman *et al.*, 1992; Ng and Clegg, 1997; Lerch and Blanchard, 2003; Ghidey *et al.*, 2005). Lerch and Blanchard (2003) reported that the median relative loads (as a percent of applied) of metribuzin and three acetanilide herbicides for 20 watersheds in northern Missouri and southern Iowa were: metribuzin, 2.1%; metolachlor, 2.0%; acetochlor, 0.50%; and alachlor, 0.33%. In this same study, median relative atrazine losses were 3.9% of applied (Lerch and Blanchard, 2003). Thus, metribuzin and metolachlor loads were comparable to atrazine, but acetochlor and alachlor loads were considerably lower. These relative loads did not include metabolites, and therefore, they largely reflect the stability of the parent compounds rather than any inherent differences in vulnerability to hydrologic transport. For instance, compared to atrazine, the acetanilides and metribuzin have similar soil sorption intensity, but they are typically less stable in soil (Montgomery, 1993; Vencill, 2002). Furthermore, the contribution of metabolites to relative losses of the acetanilides would be expected to be much greater than that of atrazine since the acetanilide herbicides form stable and mobile metabolites that have been documented to be present in surface waters at concentrations greater than that of the parent compound (Kalkhoff *et al.*, 1998; Phillips *et al.*, 1999; Battaglin *et al.*, 2003; Rebich *et al.*, 2004).

Management practices designed to reduce the transport of soil-applied herbicides include soil incorporation, vegetative buffer strips, split applications, decreased application rates, and post-emergence application. Ghidey *et al.* (2005) examined the effectiveness of soil incorporation on atrazine and metolachlor transport from a Missouri claypan soil. Soil incorporation decreased losses by 39 to 55% compared to the unincorporated treatments. These findings create a dilemma for the development of cropping systems that can control both soil erosion and herbicide transport for these high runoff potential claypan soils. As incorporation requires additional tillage and results in less crop residue cover, soil erosion would be increased to achieve reductions in herbicide transport. Conversely, no-till and minimum-till cropping systems that do not employ herbicide incorporation would reduce soil erosion but increase herbicide transport. Thus, the challenge for claypan soils is to develop cropping systems that can optimize this tradeoff (Lerch *et al.*, 2008).

Potential negative impacts to human health and aquatic ecosystems by the acetanilides and metribuzin remain a concern because of their continued contamination of water resources in areas such as the Midwestern U.S., where these herbicides are most heavily used (Battaglin *et al.*, 2003; Lerch and Blanchard, 2003; Gilliom *et al.*, 2006). The United States Environmental Protection Agency (USEPA) has established maximum contaminant (MCL) or health advisory levels (HAL) for alachlor (MCL = 2 μg/l), acetochlor (MCL = 2 μg/l), metolachlor (HAL = 100 μg/l), and metribuzin (HAL = 200 μg/l) in finished drinking water (USEPA, 1996). These standards were chosen to minimize the occurrence of cancer in persons chronically exposed to these herbicides via drinking water. With respect to aquatic ecosystems, toxic concentrations of the acetanilides and metribuzin to photosynthetic species have been established (Fairchild *et al.*, 1998; Junghans *et al.*, 2003). The concentration that creates 50% of the maximum effect or inhibition (EC_{50}) in these studies ranged from 10 μg/l to >3,000 μg/l, depending upon the test species and endpoint measured. Hackett *et al.* (2005) examined the human health and aquatic ecosystem impacts of acetochlor and its ethane sulfonic acid and oxanilic acid metabolites in corn-producing areas of the Eastern and Midwestern U.S. Their results from 175 community water supplies (raw and finished water) showed that the acetochlor MCL was not exceeded, based on annual mean concentrations, and that the observed levels of acetochlor and its metabolites posed no significant risk to human health or aquatic ecosystems. However, mixtures of eight acetanilides were reported to be much more toxic to green algae than the individual components, and the concentration addition model best explained the results (Junghans *et al.*, 2003).

Long-term trends in contamination of Midwestern U.S. streams by acetanilides and metribuzin reflect their changes in use (Battaglin and Goolsby, 1999; Scribner *et al.*, 2000). From 1989 to 1998, median stream concentrations of alachlor, metolachlor, and metribuzin decreased by 42 to 97%, whereas median concentrations of acetochlor increased from 0.05 μg/l in 1994 to 0.72 μg/l in 1998 (Scribner *et al.*, 2000). Like the companion article on trends in atrazine transport (Lerch *et al.*, this issue), the primary objective of this study was to analyze trends in concentration and load of acetochlor, alachlor, metolachlor, and metribuzin in GCEW from 1992 to 2006. A secondary objective was to document the effects of best management practices (BMPs) implemented within GCEW over the last 15 years on trends in herbicide transport.

MATERIALS AND METHODS

Details related to the physical description, location, land and herbicide use, instrumentation, water quality monitoring protocols, precipitation data, and stream discharge data for GCEW were reported in the companion article (Lerch *et al.*, this issue).

Herbicide Analysis

Sample handling, solid-phase extraction, and other analytical details were the same as those described for analysis of atrazine in water (Lerch *et al.*, this issue). From 1992 to 1997, limits of detection for alachlor, metolachlor, and metribuzin using gas chromatography with an N-P detector varied from 0.10 to 0.29 μg/l (Lerch and Blanchard, 2003), with the acetanilide herbicides having the highest detection limits because they have only one nitrogen atom in their molecular structures. Analysis of acetochlor was added in 1998, and from 1998 to 2006, herbicide concentrations were determined by gas chromatography/mass spectrometry (GC/MS) using a Saturn 2000 ion-trap mass selective detector (Varian, Harbor City, CA) (Lerch and Blanchard, 2003). Limits of detection varied from 0.002 to 0.008 μg/l (Lerch and Blanchard, 2003).

Computations and Statistics

Cumulative frequency distributions (CFDs) were developed for daily flow-weighted herbicide concentrations as described by Lerch *et al.* (this issue). For the purpose of computing flow-weighted concentrations, samples in which the herbicide concentrations were below the detection limit were considered to be zero. The occurrence of flow-weighted concentrations below the detection limit resulted from interpolation between a sample with a low herbicide concentration and a sample with a nondetectable concentration (recorded as zero) or by a nondetection followed by a low concentration sample. Because of this, interpolated concentrations <0.001 μg/l were censored for all compounds and years. The censored level was an arbitrary cut-off made necessary by the linear interpolation methodology used for computing flow-weighted concentrations on un-sampled days. For the CFDs, all data below the censored level were assigned a value of zero, resulting in zero percent rank.

Linear regression analysis was performed to discern temporal trends in selected percentile concentrations, load, and use on an annual basis, with time in years as the independent variable. Visual inspection of the data did not suggest the presence of nonlinear trends, hence nonlinear regression was not pursued as part of the trend analysis. Regression analyses were not conducted for acetochlor, alachlor, and metribuzin for the minimum, 10th, and 25th percentiles as concentrations for all or most years were <0.001 μg/l. In addition, censored flow-weighted concentrations were not included in any of the linear regression analyses. Correlation analyses were also performed to determine if a relationship existed between second quarter discharge and relative or absolute annual loads. The *a priori* level of significance for linear regression or correlation analyses was chosen to be $\alpha = 0.10$ because of the highly variable annual data and the limited number of observations for the regression and correlation analyses. Autocorrelation among years was assessed for all linear regression analyses using first-order autocorrelation, and the *a priori* level of significance for the Durbin-Watson statistic was $\alpha = 0.05$. Both positive and negative autocorrelations were tested. If the Durbin-Watson statistic was significant, then autoregression analysis was performed using the maximum likelihood estimation of the AR(1) generalized linear model, and these regression statistics were then reported. The Watershed Regression for Pesticides (WARP) models for percentile concentrations greater than the censored level were used to generate estimates of metolachlor and alachlor concentrations for comparison against the observed GCEW data (Larson and Gilliom, 2001; Larson *et al.*, 2004). Input parameters for the WARP model were as described by Lerch *et al.* (this issue), and 15-year average herbicide use intensities were based on the data in Figure 1.

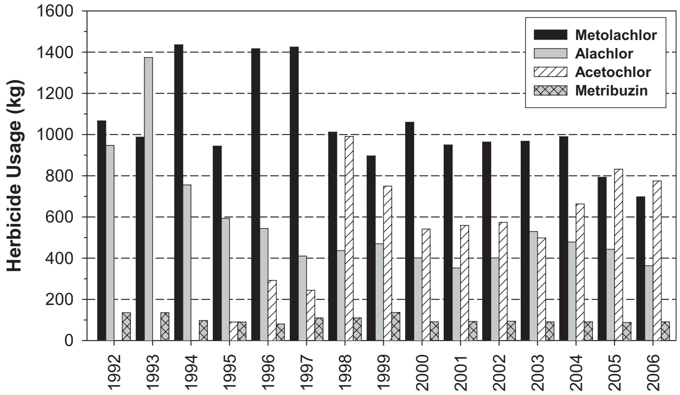

FIGURE 1. Estimated Usage of Metolachlor, Alachlor, Acetochlor, and Metribuzin in Goodwater Creek Experimental Watershed From 1992 to 2006.

Implementation of Best Management Practices in GCEW

Soil conservationists with the USDA-Natural Resources Conservation Service (USDA-NRCS) from Audrain and Boone Counties of Missouri provided information on the implementation of cost-shared BMPs within GCEW. Using a large aerial photograph of the watershed, the conservationists identified the type of practice, the area it protected, and the implementation year. However, there was only one practice listed for each field. For example, if a grassed waterway was implemented on a field, and the field was also enrolled in the Conservation Reserve Program (CRP), the field was characterized as only having a grassed waterway or only being in CRP, but not both.

Comparisons of Herbicide Transport in GCEW to Local and Regional Studies

In an effort to provide context for the herbicide transport data from GCEW for this and the companion investigation (Lerch *et al.*, this issue), comparisons were made to a study conducted at the field scale within GCEW (Ghidey *et al.*, 2002; Lerch *et al.*, 2005) and a regional-scale study of 20 watersheds in northern Missouri and southern Iowa (Lerch and Blanchard, 2003). For all comparisons, herbicide loss data were expressed as areal loss on a treated area basis (in g/ha). This approach to normalize the data allows for comparisons across all scales. Two sets of comparisons were made: (1) field (35 ha) to watershed, and (2) watershed to watershed (21,280 to 1,796,150 ha). Comparisons of the watershed-scale herbicide transport to the field study conducted within GCEW were made only for atrazine and metolachlor as these were the only herbicides studied at the field scale. Comparisons between watersheds were made for all five parent herbicides reported here and in Lerch *et al.* (this issue).

The field study evaluated herbicide losses from 1993 to 2001 using two cropping systems as treatments (Ghidey *et al.*, 2002; Lerch *et al.*, 2005). Cropping system one (CS1) was a minimum-till, corn-soybean rotation in which atrazine and metolachlor were applied pre-plant and incorporated, and cropping system two (CS2) was a no-till, corn-soybean rotation in which the same two herbicides were not incorporated. Atrazine was applied to corn in both cropping systems every other year beginning in 1993 for CS1 and 1995 for CS2, and metolachlor was applied to corn and soybean in both cropping systems beginning in 1996. Thus, the average areal losses of atrazine were computed for the odd years from 1993 to 2001 for CS1 and 1995 to 2001 for CS2, and average areal losses of metolachlor were computed for every year from 1996 to 2001. For comparison to the field-scale study, areal losses at the watershed scale represented the average loss from 1993 to 2001 for atrazine and from 1996 to 2001 for metolachlor. The regional-scale study of herbicide transport (Lerch and Blanchard, 2003) was conducted from 1997 to 1999. Watershed-scale herbicide transport in this study was computed for the critical transport period of April 15 through June 30 of each year. Therefore, the areal loss rates for GCEW were recomputed for this same period to facilitate comparisons across watersheds.

RESULTS AND DISCUSSION

Herbicide Use

Metolachlor was the second most commonly used herbicide compared to atrazine over the 15-year record, but its use varied considerably (Figure 1). From 1992 to 1997, metolachlor use exceeded 1,000 kg/year in four of six years, including peak usage of about 1,400 kg/year in 1994, 1996, and 1997. From 1998 to 2006, metolachlor use was generally <1,000 kg/year, but the introduction of the *S*-metolachlor formulation in 1999 had little effect on use. Compared to its peak use in 1994, metolachlor use decreased 51% by 2006. Alachlor use decreased more than any of the other soil-applied herbicides, primarily due to the introduction of acetochlor in 1995. Alachlor use peaked at nearly 1,400 kg in 1993, steadily decreased to about 400 kg/year by 1997, and remained at about 400 to 500 kg/year thereafter, for a decrease of 74% from 1993 to 2006. Acetochlor use in the watershed began in 1995, when 90 kg were reportedly used. The maximum reported use was about 1,000 kg in 1998, with use decreasing to about 500 kg/year from 2000 to 2003, then increasing to about 700 to 800 kg/year from 2004 to 2006. Metribuzin was the least used of the soil-applied herbicides, with average use of about 100 kg/year. The highest reported use of metribuzin was 136 kg in 1999, decreasing to about 90 kg from 2000 to 2006. From 1992 to 1999, metribuzin was used only on soybean, but beginning in 2000 it was also used on about 5% of the planted corn area.

Concentration Trends

Flow-weighted concentrations of metolachlor, alachlor, metribuzin, and acetochlor for selected percentiles by year are given in Tables 1 and 2. Metolachlor concentrations in GCEW were the second highest overall compared to atrazine (Table 1, Lerch *et al.*, this issue). Minimum and 10th percentile concentrations were usually below the censored level before 1998. From 1998 to 2006, these percentiles were always greater than the censored level because of the substantial improvement in detection limits using

TABLE 1. Flow-Weighted Metolachlor and Alachlor Concentrations for Selected Percentiles.

	Metolachlor (μg/l)							Alachlor (μg/l)						
Year	Min	10th	25th	Median	75th	90th	Max	Min	10th	25th	Median	75th	90th	Max
All data	<0.001	0.093	0.234	0.460	0.964	3.03	90.1	<0.001	<0.001	<0.001	0.003	0.018	0.095	4.97
1992	<0.001	<0.001	<0.001	0.259	6.29	17.0	33.5	<0.001	<0.001	0.007	0.096	0.512	0.758	2.21
1993	<0.001	<0.001	0.052	0.198	0.491	5.91	37.6	<0.001	<0.001	<0.001	<0.001	<0.001	0.378	2.87
1994	<0.001	0.040	0.143	0.506	1.19	2.95	8.21	<0.001	<0.001	<0.001	<0.001	<0.001	0.066	1.42
1995	<0.001	<0.001	0.200	0.651	1.07	3.00	26.7	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	2.18
1996	<0.001	0.229	0.398	0.574	1.54	5.22	73.3	<0.001	<0.001	<0.001	<0.001	<0.001	0.071	0.354
1997	<0.001	<0.001	0.314	0.576	1.07	2.87	23.5	<0.001	<0.001	<0.001	<0.001	0.180	0.292	0.491
1998	0.027	0.098	0.155	0.394	0.822	1.94	13.8	<0.001	<0.001	0.006	0.021	0.032	0.051	0.092
1999	0.082	0.150	0.314	0.633	1.71	3.53	6.84	<0.001	0.001	0.006	0.012	0.020	0.028	0.061
2000	0.176	0.272	0.336	0.447	0.626	1.63	90.1	<0.001	<0.001	0.002	0.009	0.018	0.050	0.219
2001	0.200	0.277	0.400	0.528	1.13	2.76	11.3	<0.001	<0.001	<0.001	0.001	0.007	0.012	0.043
2002	0.110	0.156	0.222	0.468	0.848	4.39	13.7	<0.001	<0.001	<0.001	0.006	0.012	0.028	2.48
2003	0.068	0.199	0.294	0.555	0.969	2.00	4.50	<0.001	<0.001	0.001	0.010	0.018	0.023	0.698
2004	0.189	0.257	0.315	0.416	0.625	2.45	6.12	<0.001	<0.001	<0.001	0.004	0.011	0.023	0.295
2005	0.016	0.091	0.246	0.462	0.964	1.56	6.72	<0.001	<0.001	0.002	0.007	0.021	0.059	4.97
2006	0.055	0.094	0.151	0.271	0.534	1.09	2.86	<0.001	<0.001	<0.001	0.002	0.009	0.028	1.59
Median	0.027	0.098	0.246	0.468	0.969	2.87	13.7	<0.001	<0.001	<0.001	0.004	0.012	0.050	0.698

TABLE 2. Flow-Weighted Metribuzin and Acetochlor Concentrations for Selected Percentiles.

	Metribuzin (μg/l)							Acetochlor (μg/l)						
Year	Min	10th	25th	Median	75th	90th	Max	Min	10th	25th	Median	75th	90th	Max
All data	<0.001	<0.001	<0.001	0.017	0.051	0.110	5.92	<0.001	<0.001	0.001	0.021	0.072	0.266	3.50
1992	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	-[1]	-	-	-	-	-	-
1993	<0.001	<0.001	<0.001	<0.001	<0.001	0.074	0.691	-	-	-	-	-	-	-
1994	<0.001	<0.001	<0.001	<0.001	0.0393	0.123	5.92	-	-	-	-	-	-	-
1995	<0.001	<0.001	<0.001	<0.001	<0.001	0.005	0.375	-	-	-	-	-	-	-
1996	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.160	-	-	-	-	-	-	-
1997	<0.001	<0.001	<0.001	<0.001	0.045	0.149	0.816	-	-	-	-	-	-	-
1998	<0.001	<0.001	0.013	0.054	0.076	0.157	0.452	<0.001	<0.001	<0.001	0.001	0.013	0.030	0.088
1999	<0.001	0.024	0.035	0.056	0.118	0.180	0.596	<0.001	<0.001	<0.001	0.002	0.011	0.017	0.055
2000	<0.001	<0.001	0.009	0.039	0.069	0.147	0.524	<0.001	<0.001	<0.001	<0.001	0.011	0.024	0.134
2001	<0.001	<0.001	0.005	0.038	0.099	0.372	0.625	<0.001	<0.001	<0.001	0.011	0.050	0.117	3.50
2002	<0.001	<0.001	<0.001	0.035	0.057	0.782	2.72	<0.001	<0.001	<0.001	0.020	0.186	0.543	2.56
2003	<0.001	0.006	0.026	0.041	0.059	0.090	0.261	0.007	0.021	0.031	0.054	0.153	0.299	1.25
2004	<0.001	<0.001	0.020	0.033	0.053	0.073	0.145	0.001	0.016	0.023	0.048	0.078	0.162	1.22
2005	<0.001	0.011	0.018	0.031	0.049	0.064	0.299	<0.001	0.011	0.024	0.060	0.276	0.614	2.10
2006	<0.001	0.002	0.010	0.020	0.031	0.050	0.569	<0.001	0.007	0.025	0.057	0.226	0.475	2.69
Median	<0.001	<0.001	0.005	0.031	0.049	0.090	0.524	<0.001	<0.001	<0.001	0.020	0.078	0.162	1.25

[1]Acetochlor was not determined from 1992 to 1997.

TABLE 3. Linear Regression Analysis to Assess Trends in Herbicide Concentration and Load From 1992 to 2006.[1]

Dependent Variable	Acetochlor				Alachlor				Metolachlor				Metribuzin			
	r^2	p-Value	Slope	d.f.	r^2	p-Value	Slope	d.f.	r^2	p-Value	Slope	d.f.	r^2	p-Value	Slope	d.f.
Minimum[2]	-[3]	-	-	-	-	-	-	-	0.02	0.75	−0.003	8	-	-	-	-
10th percentile[2]	-	-	-	-	-	-	-	-	0.01	0.72	0.003	10	-	-	-	-
25th percentile[2]	-	-	-	-	-	-	-	-	0.13	0.46	0.007	13	-	-	-	-
Median[2]	**0.88**	**<0.01**	**0.009**	7	**0.92**	**≤0.01**	**−0.007**	**9**	0.08	0.90	0.002	14	**0.82**	**<0.01**	**−0.004**	**8**
75th percentile[2]	**0.72**	**<0.01**	**0.031**	**8**	**0.89**	**≤0.01**	**−0.036**	**10**	**0.23**	**0.07**	**−0.153**	**14**	0.09	0.83	−0.001	10
90th percentile[2]	**0.60**	**0.01**	**0.067**	**8**	**0.50**	**0.04**	**−0.036**	**13**	**0.41**	**0.04**	**−0.675**	**14**	0.05	0.46	0.009	13
Maximum[2]	**0.35**	**0.10**	**0.274**	**8**	<0.01	0.92	0.008	14	0.15	0.16	−2.23	14	0.05	0.43	−0.074	14
Absolute load[2]	0.22	0.21	0.647	8	0.13	0.19	−0.124	14	**0.30**	**0.03**	**−3.44**	**14**	<0.01	0.83	0.027	14
Relative load[2]	0.13	0.34	0.089	8	<0.01	0.93	−0.001	14	**0.23**	**0.07**	**−0.282**	**14**	0.01	0.73	0.042	14

Notes: r^2 is the coefficient of determination; p-value is the probability of observing a more extreme value for the F statistic; slope units are μg/l/year for concentrations, kg/yr for absolute load, and %/yr for relative load; d.f. is the total degrees of freedom for the regression sum of squares.

[1]Bold type indicates statistically significant linear trends for the regression or autoregression analyses (α = 0.10). Underlined text indicates statistics for those linear trends in which autoregression among years was significant.

[2]Independent variable is time, in years.

[3]Concentrations were less than the detection limit for more than half the years and regression analyses were not performed.

GC/MS, resulting in detectable levels of metolachlor for all samples collected during this period. Linear regression analyses of metolachlor concentrations showed that the 75th and 90th percentiles significantly decreased with time, but none of the lower percentile concentrations showed significant trends (Tables 1 and 3). Maximum metolachlor concentrations ranged from 2.86 μg/l in 2006 to 90.1 μg/l in 2000.

Trends in metolachlor concentration based on the three-year CFDs (Figure 2) showed only moderate changes in flow-weighted concentration despite a 51% decrease in use from 1994 to 2006 (Figure 1). At concentrations of 0.10 μg/l or less, the greater cumulative frequencies observed in the first six years

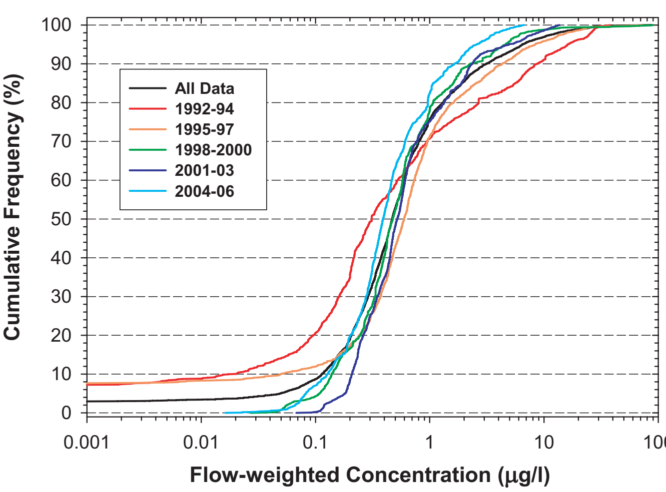

FIGURE 2. Cumulative Frequency Distributions of Daily Flow-Weighted Metolachlor Concentrations in Goodwater Creek Experimental Watershed.

compared to the latter nine years was a result of the improved detection limit. At concentrations >1.0 μg/l, a consistent trend of increasing cumulative frequency (i.e., decreasing occurrence of high concentrations) with time was evident in the metolachlor CFDs (Figure 2), and the impact of decreased metolachlor use within GCEW was most apparent in the upper range of the concentration distribution. This was supported by the significant decrease in metolachlor concentrations observed for the 75th and 90th percentiles (Table 3). Median concentrations (i.e., concentration equal to 50% cumulative frequency) also showed a steady decline from 0.60 μg/l in 1995 to 1997 to 0.39 μg/l in 2004 to 2006 (Figure 2), but linear regression of median concentration over all years showed no significant trend in median metolachlor concentrations (Table 3).

Alachlor concentrations by year showed that it had the overall lowest concentrations of the herbicides studied (Tables 1 and 2). Maximum alachlor concentrations varied over two orders of magnitude, ranging from 0.0433 μg/l in 2001 to 4.97 μg/l in 2005. Minimum, 10th, and 25th percentile alachlor concentrations were generally less than the censored level and always <0.01 μg/l (Table 1). Median concentrations were <0.001 μg/l in five of the first six years, and the overall median alachlor concentration was 0.0028 μg/l. The median, 75th, and 90th percentile concentrations all showed significant decreasing trends over years, which was consistent with the major decrease in alachlor use during the study (Table 3).

For the alachlor CFDs (Figure 3), the substantial improvement in detection limit combined with its generally low concentrations make comparisons of

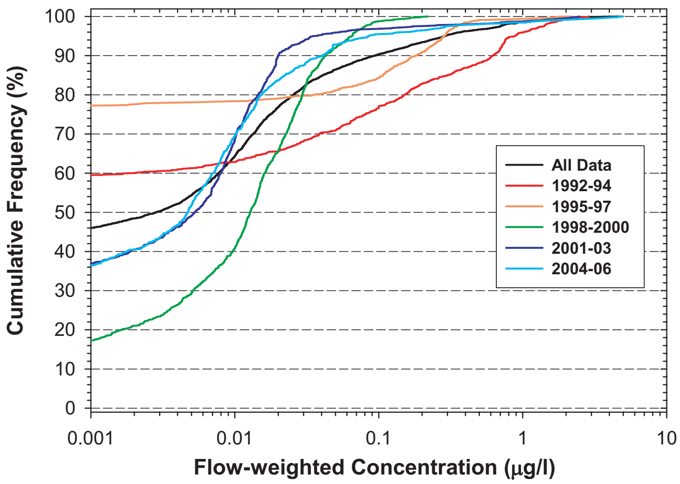

FIGURE 3. Cumulative Frequency Distributions of Daily Flow-Weighted Alachlor Concentrations in Goodwater Creek Experimental Watershed.

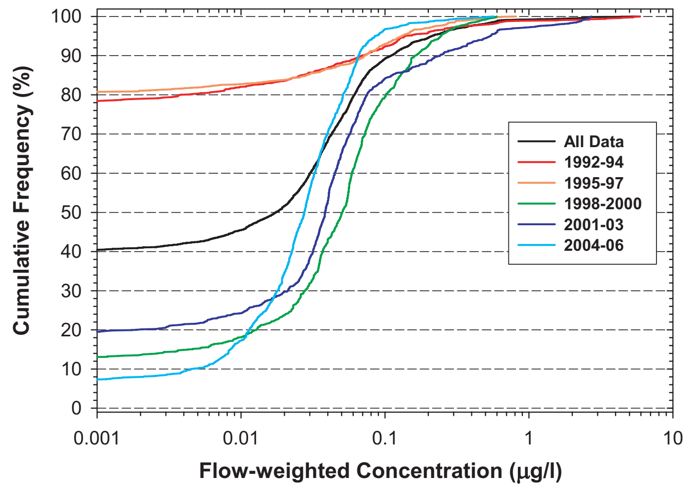

FIGURE 4. Cumulative Frequency Distributions of Daily Flow-Weighted Metribuzin Concentrations in Goodwater Creek Experimental Watershed.

the first six years to the last nine years invalid for concentrations <0.01 µg/l. At the low end of the concentration distribution (i.e., <0.005 µg/l), cumulative frequencies from 1998 to 2000 were consistently lower than those for 2001 to 2003 and 2004 to 2006 (Figure 3). The trend of lower cumulative frequencies from 1998 to 2000 compared to the last six years was consistent for concentrations up to about 0.02 µg/l. Thus, at the low end of the distribution, alachlor concentrations from 1998 to 2000 were consistently higher than for the last six years. At alachlor concentrations of 0.02 to 0.20 µg/l, the 1992 to 1994 and 1995 to 1997 periods had lower cumulative frequencies than any of the three-year periods from 1998 to 2006, indicating a consistent decrease in alachlor concentrations over time at the higher end of the concentration distribution. This was further supported by the significant decrease in 75th and 90th percentile alachlor concentrations (Table 3).

Metribuzin concentrations by year showed that its concentrations were generally quite low across all percentiles (Table 2). Maximum concentrations ranged from <0.001 µg/l in 1992 to 5.92 µg/l in 1994. Minimum and 10th percentile concentrations were <0.001 µg/l in most years, and 25th, median, and 75th percentiles were generally <0.001 µg/l from 1992 to 1997. From 1998 to 2006, median metribuzin concentration showed a significant decrease with time, but the 75th, 90th, and maximum metribuzin concentrations showed no significant trends over time (Table 3).

Similar to alachlor, the metribuzin CFDs for 1992 to 1994 and 1995 to 1997 cannot be validly compared to the latter nine years for concentrations <0.05 µg/l (Figure 4). At concentrations <0.01 µg/l, cumulative frequencies increased in the order: 2004 to 2006 < 1998 to 2000 < 2001 to 2003 (Figure 4). This indicated that more low-level detections occurred in the 2004 to 2006 period. From 0.02 µg/l to 0.05 µg/l, there was a consistent increase in cumulative frequency with time, and median concentrations decreased from 0.05 µg/l in 1998 to 2000 to 0.03 µg/l in 2004 to 2006. This was consistent with the significant decrease in median metribuzin concentration from 1998 to 2006 (Table 3). Within the concentration range of 0.05 to 0.14 µg/l, the two three-year periods from 1998 to 2003 had the lowest cumulative frequencies, while the 1992 to 1997 and 2004 to 2006 three-year periods had cumulative frequencies of 92% or greater. At concentrations of 0.14 to 2.0 µg/l, the 2001 to 2003 period had the lowest cumulative frequencies, indicating that the greatest percentage of high concentration samples occurred during this three-year period.

Acetochlor concentrations for selected percentiles over all years showed that its concentrations were similar to, but consistently greater than, metribuzin (Tables 1 and 2). Overall acetochlor concentrations were the third highest of the herbicides studied, but its concentrations were well below that of metolachlor (Table 1) or atrazine (Table 1, Lerch *et al.*, this issue). Maximum acetochlor concentrations ranged from 0.055 µg/l in 1999 to 3.50 µg/l in 2001. Minimum acetochlor concentrations were below the detection limit in seven of nine years, and the 10th and 25th percentile concentrations were below the detection limit from 1998 to 2002. In contrast, the median, 75th, 90th, and maximum concentrations all showed significant increasing trends from 1998 to 2006 (Table 3).

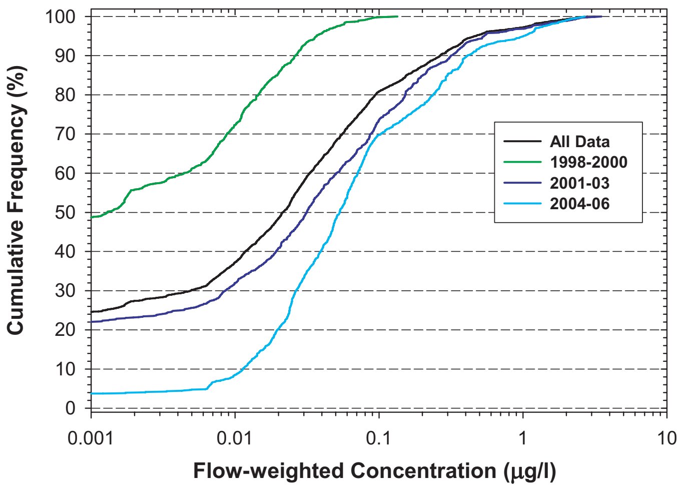

FIGURE 5. Cumulative Frequency Distributions of Daily Flow-Weighted Acetochlor Concentrations in Goodwater Creek Experimental Watershed.

The acetochlor CFDs showed evident increases in concentration over time (Figure 5). For concentrations of 1.0 μg/l or less, cumulative frequencies increased in the order: 2004 to 2006 < 2001 to 2003 < 1998 to 2000. The spread in the data were greatest for concentrations <0.01 μg/l. For example, at 0.005 μg/l, the cumulative frequency decreased from 61.2% in 1998 to 2000 to 4.7% in 2004 to 2006 (Figure 5); thus, 95.3% of the days with measurable streamflow were >0.005 μg/l in 2004 to 2006 compared to only 38.8% from 1998 to 2000. In addition, median concentrations increased 50-fold from 0.001 μg/l in 1998 to 2000 to 0.05 μg/l in 2004 to 2006. Based on the observed concentration data (Table 2; Figure 5), it appears that acetochlor use was overreported for 1998 and 1999 (Figure 1), as flow-weighted concentrations from 1998 to 2000 were much lower than for 2001 to 2003 and 2004 to 2006 periods, when similar or lower use was reported. This conclusion was further supported by the acetochlor load data (Table 4) in which the loads for 1998 and 1999 were much lower than the median acetochlor loads over the study, while load data for the other herbicides were generally greater than the median loads for these years. Furthermore, the stream discharge data (Lerch *et al.*, this issue) showed that 1998 and 1999 were not atypical years. These two years were the 5th and 6th wettest years, respectively, and they also had near median second quarter discharge. Therefore, based on the stream discharge, load, and concentration data, the acetochlor use for 1998 and 1999 were evidently overreported.

Changes in herbicide use had the greatest effect on trends in flow-weighted concentration. Since 1998, the major decrease in alachlor use and increase in acetochlor use caused shifts in flow-weighted concentrations that were observed over the entire concentration range (Figures 3 and 5). In contrast, the smaller decrease in metolachlor use led to a consistent decreasing time trend only for the upper end of the concentration distribution (Table 3; Figure 2). Metribuzin also showed moderate decreases in concentration with time, especially since 1998. This was consistent with the 33% decrease in metribuzin use since 1999. The range of herbicide concentrations reported in this

TABLE 4. Annual Herbicide Loads on an Absolute and Relative Basis.

	Acetochlor		Alachlor		Metolachlor		Metribuzin	
Year	Absolute (kg)	Relative (% of applied)	Absolute (kg)	Relative (% of applied)	Absolute (kg)	Relative (% of applied)	Absolute (kg)	Relative (% of applied)
1992	-[1]	-	0.74	0.08	12	1.8	0.00	0.00
1993	-	-	4.5	0.33	65	6.6	0.56	0.42
1994	-	-	3.2	0.42	31	2.2	4.8	5.0
1995	-	-	4.7	0.80	101	10.7	0.57	0.64
1996	-	-	0.29	0.05	96	6.7	0.01	0.02
1997	-	-	0.62	0.15	37	2.6	1.4	1.3
1998	0.25	0.02	0.93	0.21	51	5.1	3.8	3.5
1999	0.47	0.06	0.57	0.12	46	5.1	4.8	3.5
2000	0.08	0.02	0.14	0.04	31	2.9	0.46	0.51
2001	2.5	0.45	0.37	0.11	40	4.2	5.9	6.3
2002	12	2.1	1.1	0.28	36	3.8	2.2	2.4
2003	5.5	1.1	3.1	0.58	36	3.7	2.5	2.7
2004	2.3	0.35	0.36	0.07	17	1.7	1.7	1.9
2005	3.0	0.36	0.81	0.18	8.3	1.1	0.70	0.79
2006	6.2	0.80	1.7	0.47	4.8	0.69	0.32	0.35
Median	2.5	0.36	0.81	0.18	36	3.7	1.4	1.3

[1]Acetochlor was not determined from 1992 to 1997.

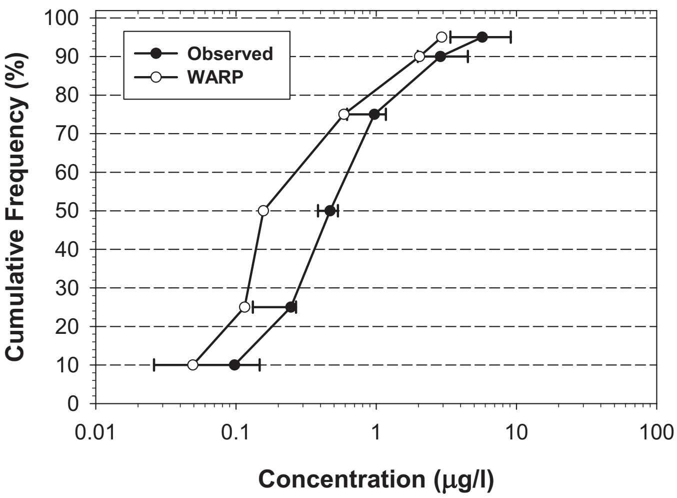

FIGURE 6. Cumulative Frequency Distributions Comparing Metolachlor Concentrations Predicted by the Watershed Regression for Pesticides (WARP) Model Against the Observed Metolachlor Concentrations for Goodwater Creek Experimental Watershed. Error bars for the observed median concentrations represent distribution-free 95% confidence intervals.

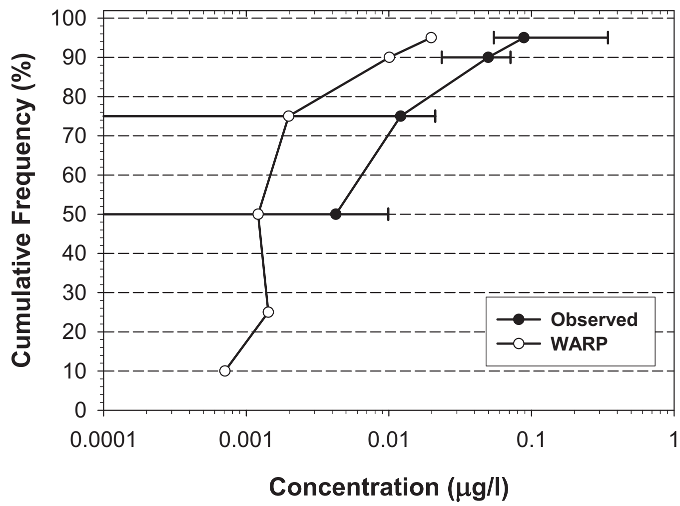

FIGURE 7. Cumulative Frequency Distributions Comparing Alachlor Concentrations Predicted by the Watershed Regression for Pesticides (WARP) Model Against the Observed Alachlor Concentrations for Goodwater Creek Experimental Watershed. Error bars for the observed median concentrations represent distribution-free 95% confidence intervals.

study fell within the range reported for other streams throughout the Midwestern U.S. (Scribner *et al.*, 2000; Battaglin *et al.*, 2003; Lerch and Blanchard, 2003). However, comparison of median concentrations with these studies was not valid since their sampling schemes focused on the second and third quarters of the year, rather than the year-round data reported in this study. Therefore, the WARP models developed for metolachlor and alachlor (Larson and Gilliom, 2001) were used to compare observed concentrations in GCEW to that predicted by WARP. No WARP models have been developed for acetochlor or metribuzin.

Watershed Regression for Pesticides concentration predictions showed consistent underestimation of metolachlor and alachlor concentrations over all percentiles for which the observed concentrations were greater than the censored level (Figures 6 and 7). At the 10th and 90th percentiles, the metolachlor concentrations predicted by WARP were within the 95% confidence interval of the observed metolachlor concentrations, and overall, WARP predictions for metolachlor fit the observed data better than alachlor (Figure 7) and atrazine (Figure 8, Lerch *et al.*, this issue). For alachlor, all WARP predictions for concentrations greater than the censored level (i.e., 50th through 95th percentiles) were underestimated by a factor of 3.5 to 6.1 compared to the observed concentrations. The median and 75th percentile WARP predictions were within the 95% confidence interval of the observed concentrations as the lower confidence interval was zero, but the 90th and 95th percentile concentrations predicted by WARP were below the 95% confidence intervals for the observed data (Figure 7). WARP overestimated the lower percentile alachlor concentrations with predictions of 0.0014 μg/l and 0.0007 μg/l for the 25th and 10th percentiles, respectively. The observed 10th and 25th percentile concentrations for alachlor were <0.001 μg/l. Also, WARP estimated a greater alachlor concentration for the 25th percentile than the 50th percentile.

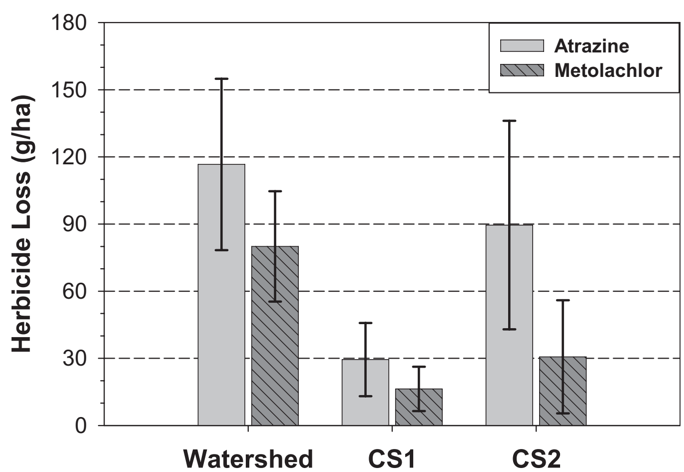

FIGURE 8. Areal Loss Rates (on a treated area basis) for Atrazine (1993-2001) and Metolachlor (1996-2001) for Goodwater Creek Experimental Watershed (GCEW) and Two Research Fields Located Within GCEW. CS1 was a minimum-till system in which herbicides were pre-plant incorporated. CS2 was a no-till system in which herbicides were not incorporated. Error bars indicate 95% confidence interval.

Analysis of the data used to develop the WARP models was conducted to further compare herbicide concentrations in GCEW to that of a national database (available at: http://infotrek.er.usgs.gov/nawqa_queries/swmaster/). The WARP data from the National Water-Quality Assessment Program (NAWQA) sites were assigned specific land uses (agricultural, cropland, pasture, mixed, and urban) while the large scale National Stream Quality Accounting Network (NASQAN) sites are designated as "other" since they integrate all these land uses.

Metolachlor concentrations in GCEW were greater at all percentiles than any of the land uses, including those designated as cropland or NASQAN sites, which had the highest concentrations of the four herbicides. Further analysis of the metolachlor data for the 17 cropland sites showed 4 sites had greater 90th and 95th percentile concentrations and 2 sites had greater concentrations at all percentiles than GCEW. For alachlor, the 50th to 95th percentile concentrations in GCEW were nearly equal to those for all the WARP data (i.e., data pooled across all the land uses) and much less than those for watersheds designated as agricultural, cropland, mixed land use, and NASQAN sites. This is consistent with the overall low alachlor usage within GCEW, but it is surprising that alachlor WARP models would so significantly underestimate alachlor concentrations for GCEW. Acetochlor concentrations in GCEW were generally greater than the WARP sites, regardless of land use, for the median and 75th percentiles, but the cropland, NASQAN, and mixed land use watersheds generally had greater 90th and 95th percentile concentrations than GCEW. Metribuzin concentrations in GCEW were greater than all WARP sites when the data were pooled by land use. Within the cropland sites, 7 sites had at least one percentile concentration greater than GCEW and 4 of these sites had greater concentrations over the entire frequency distribution than GCEW. Overall, these results support the conclusion that concentrations of metolachlor and metribuzin in GCEW were greater than most other cropland watersheds in the U.S.

Load Trends

Annual metolachlor loads, on an absolute or relative basis, were generally much greater than the other three herbicides (Table 4) over the 15-year record. Absolute metolachlor loads ranged from 4.8 kg in 2006 to 100 kg in 1995, with a median load of 36 kg. Five years had loads >40 kg (1993, 1995, 1996, 1998, and 1999), and four years had loads <20 kg (1992, 2004, 2005, and 2006). The highest loads occurred from 1993 to 1999, and after 1999 annual loads did not exceed 40 kg (Table 4). Relative metolachlor loads ranged from 0.69% in 2006 to 10.7% in 1995, with a median of 3.7% (Table 4). Among the herbicides included in this and the companion study, metolachlor was the only herbicide with absolute or relative loads similar in magnitude to that of atrazine, particularly before 1999. However, because of the decrease in metolachlor use in GCEW, loads remained consistently low after 1999, while atrazine loads exceeded 100 kg four times from 2000 to 2006 (Lerch *et al.*, this issue). Regression analyses showed that metolachlor loads, absolute and relative, have significantly decreased over years (Table 3). Furthermore, second quarter stream discharge was shown to be significantly correlated to metolachlor loads, but loads were not significantly correlated to annual use (Table 5). These findings suggested that annual variation in metolachlor transport was even more affected by variation in precipitation than changes in use.

TABLE 5. Correlation Analyses of Absolute and Relative Load to Second Quarter Discharge and Annual Use.

	Second Quarter Discharge		Annual Use	
Herbicide	**Absolute Load**	**Relative Load**	**Absolute Load**	**Relative Load**
Acetochlor	**0.58**[1] (0.10)	**0.58** (0.10)	−0.34 (0.37)	−0.44 (0.24)
Alachlor	**0.53** (0.04)	**0.61** (0.02)	**0.58** (0.02)	0.13 (0.65)
Metolachlor	**0.50** (0.06)	**0.61** (0.02)	0.34 (0.22)	0.09 (0.75)
Metribuzin	0.34 (0.22)	0.35 (0.21)	0.10 (0.72)	−0.02 (0.93)

[1]Correlation coefficient, *r*; d.f. = 14, except acetochlor, d.f. = 8; bold type indicates statistically significant correlation coefficients (α = 0.10); numbers in parentheses are *p*-values.

Despite very different mass input within GCEW, absolute annual loads of acetochlor, alachlor, and metribuzin were very low over the 15-year period of record (Table 4). Absolute loads of these three herbicides ranged from 0.00 to 12 kg, with median loads of 0.81 kg for alachlor, 1.4 kg for metribuzin, and 2.5 kg for acetochlor. Relative loads of acetochlor and alachlor were very comparable, ranging from 0.02 to 2.1% of applied, and median relative loads were <0.40% of applied for both herbicides (Table 4). Metribuzin relative loads ranged from 0.00 to 6.3% of applied with a median of 1.3%. Metribuzin relative loads were usually greater than acetochlor and alachlor, and in several years were similar to or greater than metolachlor. Correlation analyses showed that acetochlor and alachlor loads, absolute or relative, were significantly correlated to second quarter discharge, and absolute alachlor loads were also significantly correlated to annual use (Table 5). In the case of alachlor, the 74% decrease in its use resulted in the significant correlation between annual use and load. However, the major increase in acetochlor use did not result in a significant relationship between use and load because annual variation in load was primarily a function of variation in precipitation and second quarter stream discharge rather than use. Even when the questionable usage estimates for 1998 and 1999 were excluded, there was no significant relationship between acetochlor loads and use. Metribuzin was the only herbicide that did not show a significant relationship to second quarter stream discharge (Table 5), and metribuzin loads, relative or absolute, showed no significant trend over years (Table 3). The pattern of metribuzin loads did not coincide with the other herbicides. For example, the highest absolute and relative metribuzin loads occurred in 1994 and 2001, but the other herbicides, including atrazine (Figure 10, Lerch *et al.*, this issue), had loads that were near their median values for these same two years. Only in 1999, when the metribuzin load was much greater than the median load, did metolachlor and atrazine also have loads considerably greater than their median values. Because metribuzin was used on a much smaller proportion of the watershed than the other herbicides, the temporal and spatial distribution of metribuzin-treated fields was apparently different than that of the other widely used herbicides. This, in turn, created a distribution of fields whose vulnerability to metribuzin transport was different than that of the other herbicides. In addition, metribuzin was primarily used on soybean, and therefore, it was applied later in the growing season than the corn herbicides, further reducing its vulnerability to transport as runoff-generating precipitation events are less probable as the growing season proceeds.

The much greater loads of metolachlor and atrazine compared to alachlor, acetochlor, and metribuzin reflected their greater stability in the soil environment and more extensive use within GCEW. As discussed above, alachlor and acetochlor have much shorter dissipation half-lives in soil than atrazine, metolachlor, and metribuzin, and they form stable and mobile metabolites. Because of this, metabolite transport would be expected to account for a higher proportion of the total alachlor and acetochlor loads (i.e., parent plus metabolites) in surface waters than atrazine, metolachlor, and metribuzin. The environmental fate of these five herbicides is mainly controlled by sorption and microbial degradation, and other loss pathways, such as photolysis and volatilization, are not appreciable under normal field conditions (Vencill, 2002). Therefore, the median relative load over the last 15 years (Table 4 and Figure 10, Lerch *et al.*, this issue) was a useful indicator of overall herbicide stability within GCEW. On this basis, the stability of the herbicides was: atrazine > metolachlor > metribuzin > acetochlor > alachlor.

The relative loads of acetochlor, alachlor, and metribuzin in 20 northern Missouri/southern Iowa streams reported by Lerch and Blanchard (2003) were slightly greater than those reported for GCEW, while metolachlor relative loads in GCEW were 85% higher than in streams of the northern Missouri/southern Iowa region. Relative metolachlor and metribuzin loads for GCEW were much greater than those reported for numerous studies conducted at watershed scales from 100 to 10,000,000 ha (Capel *et al.*, 2001). Depending upon the scale, median relative loads reported by Capel *et al.* (2001) were 0.25 to 0.80% of applied for metolachlor and 0.05 to 0.28% of applied for metribuzin. Median relative alachlor loads in GCEW (0.18% of applied) were very similar to those reported by Capel *et al.* (2001) (0.12 to 0.13% of applied). As discussed in the companion article, GCEW is extremely vulnerable to herbicide transport due to the predominance of high runoff potential soils in this watershed. The high relative loads of metolachlor and metribuzin in GCEW compared to other midwestern watersheds provide further evidence that watersheds with high runoff potential soils should be targeted for reductions in the use of soil-applied herbicides and/or implementation of BMPs specifically designed to reduce herbicide transport.

Areal Loss Rates

Comparison of field- and watershed-scale areal losses showed that losses were considerably greater at the watershed scale for both atrazine and metolachlor from 1993 to 2001 (Figure 8). Average areal loss of atrazine for the watershed was 117 g/ha compared to 29 g/ha for CS1 (herbicides incorporated) and 90 g/ha for CS2 (herbicides not incorporated). Metolachlor losses were 80 g/ha at the watershed scale and 16 g/ha for CS1 and 31 g/ha for CS2. These data strongly suggest that most farmers within GCEW did not incorporate atrazine or metolachlor. Incorporation decreased herbicide transport from CS1 compared to CS2 by 61 g/ha for atrazine and by 15 g/ha for metolachlor (Figure 8). These substantial reductions showed that herbicide incorporation is an effective BMP for reducing herbicide transport in surface runoff. This finding is consistent with other studies that reported major reductions in transport when herbicides were incorporated (Capel *et al.*, 2001; Ghidey *et al.*, 2005). Furthermore, the differences observed between the watershed scale and the field scale for CS2 reflected sources of variation not present at the field scale. These include transport from multiple treated fields, spatial variation in treated fields, spatial variation in precipitation, timing of application relative to runoff-generating rainfall events, flow

TABLE 6. Comparison of Herbicide Transport in Goodwater Creek Experimental Watershed (GCEW) to Other Watersheds in the Northern Missouri/ Southern Iowa Region.

Watershed	Watershed Area (ha)[1]	Row-Crop Intensity (% of watershed)[2]	Areal Herbicide Loss (g/ha)[3]	General Location
GCEW	7,250	58.5	140	Salt River Basin
North Fork Salt River	119,290	33.0	160	Salt River Basin
Crooked Creek	21,280	47.2	95	Salt River Basin
Middle Fork Salt River	86,560	32.1	81	Salt River Basin
Elk Fork Salt River	67,490	45.1	95	Salt River Basin
Long Branch Creek	47,130	59.2	150	Salt River Basin
South Fork Salt River	59,050	46.4	120	Salt River Basin
Lick Creek	26,940	69.0	94	Salt River Basin
Cuivre River	240,570	50.2	66	Southeast
Fox River	102,980	28.9	150	Northeast
Wyaconda River	103,230	37.3	230	Northeast
North Fabius River	115,530	30.7	190	Northeast
Middle Fabius River	100,150	22.6	210	Northeast
South Fabius River	156,560	32.9	240	Northeast
North River	92,130	35.4	110	Northeast
Nishnabotna River	730,160	76.8	58	Northwest
Nodaway River	393,200	57.0	72	Northwest
Platte River	454,440	51.2	110	Northwest
Grand River	1,796,150	30.1	180	North-central
Chariton River	489,170	22.1	72	North-central
Blackwater River	289,740	34.4	210	North-central
Median	103,230	37.3	120	

[1]Monitored watershed area.
[2]Percent of watershed area in soybean, corn, and sorghum; average for 1997 to 1999 (Lerch and Blanchard, 2003).
[3]Sum of acetochlor, alachlor, atrazine, metolachlor, and metribuzin loads on a treated area basis for April 15 to June 30; average from 1997 to 1999 (Lerch and Blanchard, 2003).

routing, and field-scale differences in soils and topography.

Areal losses of atrazine, alachlor, acetochlor, metolachlor, and metribuzin from GCEW were slightly greater than the median areal losses for 20 other streams in the region (Table 6). Areal losses from GCEW were very similar to Long Branch Creek, which includes GCEW as one of its subwatersheds. Compared to other watersheds in the Salt River Basin, areal losses from GCEW were the third highest, and it also had the third highest row-crop intensity in the basin. Lick Creek had the highest row-crop intensity of the Salt River Basin watersheds, but it had much lower areal losses than GCEW. On a regional basis, GCEW had greater herbicide losses than all of the northwestern Missouri watersheds, despite similar or lower row-crop intensity, but generally lower losses than watersheds in the north-central or northeastern part of the region, despite much greater row-crop intensity. Within this region, land use (i.e., row-crop intensity) has been shown to be a less important factor to herbicide transport than the runoff potential of the soils within a watershed (Lerch and Blanchard, 2003). Watersheds in the north-central and northeastern part of the region are largely dominated by high runoff potential soils combined with more sloping topography than watersheds within the Salt River Basin, which resulted in greater areal herbicide losses.

BMP Implementation

By the end of 2006, USDA-NRCS records indicated that 15% of the watershed (based on monitored area) was protected by some type of conservation practice (Table 7). Grassed waterways were by far the most commonly employed conservation practice in GCEW, accounting for 720 of the 1,063 ha protected. Terraces, with or without underground outlets, were the second most common conservation practice implemented, accounting for 221 ha. Land enrolled in the CRP was the third most common conservation practice, with 110 ha removed from crop production. Continuous CRP (does not require bidding process and enrollment of eligible land is guaranteed) and vegetative buffers accounted for the remainder of the conservation practices utilized in GCEW. Other cost-shared practices in the watershed were diversion structures, lagoons, managed grazing systems, and a sedimentation basin. In addition, a survey of 18 of the 30 farmers in the watershed indicated that most farmers implement some BMPs without cost-share, so the data reported in Table 7 are likely underestimates of

TABLE 7. Total Area Protected Each Year by Selected Cost-Shared Practices in Goodwater Creek Experimental Watershed (GCEW) (source: USDA-Natural Resources Conservation Service).

Year	Buffer (ha)	CRP (ha)	Continuous CRP (ha)	Grassed Waterways (ha)	Terraces (ha)	Total (ha)
1990	-[1]	5.9	-	56.3	17.4	79.6
1991	-	-	-	97.2	27.7	124.9
1992	-	24.6	-	70.9	53.5	149.0
1993	-	-	-	0.04	6.5	6.54
1994	-	-	-	-	-	0.0
1995	-	-	-	15.4	43.3	58.7
1996	-	-	-	-	8.9	8.9
1997	-	47.9	-	-	19.9	67.8
1998	-	25.6	-	-	5.3	30.9
1999	3.2	-	-	47.0	2.4	52.6
2000	-	4.1	8.1	-	-	12.2
2001	-	-	-	-	11.3	11.3
2002	-	-	-	186	10.1	196
2003	-	-	-	127	4.1	131
2004	-	-	-	20.3	-	20.3
2005	0.9	1.7	-	93.2	2.8	98.6
2006	-	-	-	6.9	7.7	14.6
Total	4.1	110	8.1	720	221	1,063

Note: CRP, Conservation Reserve Program.
[1]Conservation practice not implemented for the year indicated.

the actual area being protected by conservation practices.

From the type of BMPs implemented in GCEW, it was apparent that erosion control was the primary conservation problem being addressed, and BMPs specifically designed to reduce herbicide transport were generally not considered. However, some of the BMPs, such as grassed waterways and buffers, could reduce herbicide transport via sediment trapping and increased infiltration of runoff water (Krutz *et al.*, 2004; Lin *et al.*, 2007). Land enrolled in CRP and continuous CRP would also reduce herbicide inputs to the watershed, but the area protected by CRP represented only 2.2% of the row-crop area within the watershed. In prior work, the Soil and Water Assessment Tool (SWAT) model was used to estimate the impact of grassed waterways on atrazine transport in GCEW (Lerch *et al.*, 2008). Results of SWAT simulations comparing atrazine transport with and without grassed waterways showed a 13% reduction in median atrazine concentrations. However, no significant trends in atrazine concentration were found from 1992 to 2006 (Lerch *et al.*, this issue), in spite of continual implementation of grassed waterways over this time (Table 7). The simulated reduction in median atrazine concentrations by the SWAT model were also much less than the variation observed among three-year periods, which ranged from 0.51 to 0.98 μg/l and showed no time trends (Figure 7, Lerch *et al.*, this issue).

The BMPs implemented in GCEW may be typical of most midwestern watersheds given the historic emphasis of the USDA-NRCS on implementing BMPs for erosion control. However, GCEW was specifically targeted in the 1990s by the Management Systems Evaluation Areas (Ward *et al.*, 1994) and the Agricultural Systems for Environmental Quality programs to conduct research, education, and outreach efforts regarding the vulnerability of this claypan watershed to herbicide transport. As part of these projects, extension publications (e.g., Smith *et al.*, 1999), field days, and grower meetings were developed to specifically educate farmers about the nature and extent of herbicide contamination in Goodwater Creek. Furthermore, specific recommendations for herbicide BMPs were developed (Smith *et al.*, 1999), including incorporation of soil-applied herbicides, post-emergence atrazine application to reduce atrazine rates, use of integrated pest management strategies, planting of conservation buffers, avoiding spraying when rain is predicted, and avoiding spraying near streams, lakes, ponds, and wells. Despite the major effort to educate farmers in GCEW about practices they could employ to reduce herbicide transport, the herbicide concentration and load trends discussed above and in Lerch *et al.* (this issue) showed that changes in herbicide use and annual variation in second quarter stream discharge remain the primary factors affecting trends in GCEW. Therefore, the type of BMPs implemented and the area protected by these BMPs were apparently either ineffective, because they were not designed for reducing herbicide transport, and/or insufficient in their areal extent to achieve meaningful reductions in herbicide transport.

SUMMARY AND CONCLUSIONS

This long-term study showed that trends in concentration and load of acetochlor, alachlor, metolachlor, and metribuzin in GCEW were mainly a function of changes in use and annual variation in second quarter stream discharge. In contrast to the small changes in atrazine use that did not impact trends in concentration or load (Lerch *et al.*, this issue), there were major changes in use of these herbicides, with the exception of metribuzin. The major decrease in alachlor use and increase in acetochlor use caused shifts in flow-weighted concentrations over the entire range of observed concentrations. The smaller decrease in metolachlor use led to a consistent decreasing time trend only for the upper end of the concentration distribution. Metribuzin showed moderate decreases in concentration that were consistent with its decreased use since 1999. Acetochlor, alachlor, and metolachlor loads were all significantly correlated to second quarter discharge, further demonstrating that the timing of runoff events critically affected annual loads for these herbicides. Metolachlor loads were also shown to be significantly decreasing over time.

Comparison of areal loss rates between watershed and field scales indicated that farmers in GCEW apparently did not incorporate soil-applied herbicides as losses at the watershed scale were greater than from a no-till field in which herbicides were not incorporated. Comparisons of areal transport between GCEW and other watersheds showed that GCEW had near median areal losses for the region, but higher loss rates than most other Salt River Basin watersheds. In spite of extensive education and outreach efforts regarding BMPs to reduce herbicide transport, conservation BMPs implemented within GCEW primarily targeted erosion control, and herbicide BMPs were generally not considered. Based on the data presented, these BMPs had negligible impact on reducing herbicide transport in GCEW.

DISCLAIMER

Mention of specific companies, products, or trade names is made only to provide information to the reader and does not constitute endorsement by the USDA-Agricultural Research Service.

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