

Herbicide Distribution and Variability Across Goodwater Creek Watershed in North Central Missouri

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ABSTRACT

One objective of the Missouri Management Systems Evaluation Area was to monitor and assess surface water quality, including spatial and temporal variability in herbicide concentrations within the 7250 ha Goodwater Creek Watershed. Stream water was sampled at all stream-road intersections across the watershed on 10 occasions in 1993 and 1994. Maps of herbicide distribution established that widespread, seasonal contamination of streams in Goodwater Creek Watershed was due to nonpoint sources (e.g., widespread, but normal farm use) rather than from point sources. Box plots documented concentration variability over time. Concentrations of atrazine [2-chloro-4-ethylamino-6-isopropylamino-s-triazine], deethylatrazine [2,4-diamino-6-chloro-N-(1-methylethyl)-1,3,5-triazine], deisopropylatrazine [2,4-diamino-6-chloro-N-ethyl-1,3,5-triazine], and metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide] were also monitored at least weekly from 1993 to 1994 at three V-notch weirs through which 16.7, 43.4, and 100% of the watershed drained. Atrazine, deethylatrazine, and metolachlor were detected year round at concentrations above 0.1 µg/L. Atrazine concentrations observed at weirs were occasionally >100 µg/L and were similar to edge-of-field concentrations observed elsewhere shortly after spraying in May to June, probably because the watershed's poorly drained, silt loam soils contain a restrictive claypan horizon that limits infiltration and encourages surface runoff.

THE impact of herbicide and fertilizer use in agriculture on water quality is a growing public concern. Some people believe that herbicide contamination of surface water threatens both drinking water and the environment. The presence or absence of herbicides in surface water is one measure of water quality. Although contaminated water may contain herbicides, the water is not necessarily unfit for its intended use (i.e., polluted).

Surface water contamination by herbicides [atrazine, alachlor [2-chloro-2',6'-diethyl-N-(methoxymethyl)acetanilide], cyanazine [2-[[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropionitrile], and metolachlor] is widespread in the Midwest (Baker, 1985; Goolsby and Battaglin, 1993; Pereira et al., 1990) because these herbicides are widely used for weed control in field corn (*Zea mays* L.) and grain sorghum (milo) [*Sorghum vulgare* (L.) Moench] (Anonymous, 1994a,b; 1995a). Alachlor and metolachlor are also widely used on soybean [*Glycine max* (L.) Merr.]. Herbicide-contaminated runoff water from farmland can enter streams that feed lakes and reservoirs which are used for drinking water (Goolsby et al., 1993b). Because surface and groundwater are interconnected, herbicides in surface water may also contaminate groundwater (McMahon

et al., 1994; Squillace et al., 1993; Wang and Squillace, 1994).

Most surveys of herbicide-contaminated surface water report either edge-of-field concentrations (Logan et al., 1994; Ng et al., 1995; Wauchope, 1978) or concentrations at the regional scale (Baker, 1985; Goolsby and Battaglin, 1993; Leonard et al., 1979; Pereira et al., 1990). There are few published studies on herbicide concentrations and concentration variability in surface water at the small watershed scale.

Published water quality data are also limited for watersheds with soils having claypan layers that are usually thought to restrict water drainage and infiltration of herbicides through the soil profile (Baker and Lafen, 1983; Frank and Sirons, 1979; Leonard, 1990; Willis and McDowell, 1982). The long-term average stream flow exiting Goodwater Creek Watershed was estimated to consist of 85% surface runoff and 15% base flow (groundwater recharge to the stream) (Alberts et al., 1995). At one site in the Goodwater Creek Watershed, vertical water and nitrate (NO₃) movement were not restricted by the 61-cm thick claypan 41 to 43 cm below the surface at a summit with an Albaquic Hapludalf of the Adco series (Blevins et al., 1996). In this latter study, runoff and infiltration represented 22 and 78% of total precipitation (= 2357 mm) received from 12 July 1991 to 30 Sept. 1993. Most recharge occurred over winter when rainfall exceeded evapotranspiration (Blevins et al., 1996). Horizontal interflow was slow at the site. Nevertheless, herbicides in groundwater were unlikely to significantly contribute to observed stream concentrations because herbicide detections in groundwater were infrequent and usually well below 0.2 µg/L in glacial aquifer groundwater throughout the Goodwater Creek Watershed (Blanchard et al., 1995).

One objective of this assessment and monitoring research was to measure spatial and temporal variability in herbicide concentrations at the scale of an individual watershed for a watershed with claypan soils. A second objective was to monitor temporal changes in herbicide concentrations leaving this watershed over 2 yr.

MATERIALS AND METHODS

Site

Goodwater Creek Watershed, the study site, drains a 7250 ha agricultural watershed in north-central Missouri (Ward et al., 1994). This watershed in Boone and Audrain Counties feeds Youngs Creek, the southern fork of the Salt River and, finally, Mark Twain Reservoir, a major public water supply and recreation area. The watershed's topography is gently rolling with slopes of 1 to 3% (Ward et al., 1994). Soils in Goodwater Creek Watershed that formed in Wisconsin loess

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are classified as Udollic Ochraqualls of the Mexico series, Albaquic Hapludals of the Adco series, and Vertic Ochraqualls of the Leonard series (Anonymous, 1995c; Ward et al., 1994). These claypan soils contain an argillic horizon (claypan layer) about 0.15 to 0.3 m below the soil surface that drains slowly and restricts the rate of water infiltration (Blevins et al., 1996).

Mean annual precipitation for Centralia, MO, which is located in the southern boundary of the watershed, was 952 mm over the preceding 17 yr (Anonymous, 1995c). May to June rains during seedbed preparation and planting are short, but intense. Mean maximum and minimum daily temperatures are 17.1 and 6.3°C. The soil surface and soil in the crop rooting zone dries (Anonymous, 1992, 1993b, 1994c, 1995b) and often cracks during summer.

Sampling and Sample Bottles

Streams in Goodwater Creek Watershed were sampled for 2 yr at all intersections of roads and streams. Eighteen grab samples across the watershed were taken 10 times for 2 yr. Each year, one sample was taken before herbicide spraying, followed by three samples from May to July; one additional sample was taken much later when stream flow was sufficient for sampling at all sampling sites (August 1993 or November 1994). The dates of sampling during the 2-yr period were 9 Feb., 29 June, 1 July, 20 July, and 17 August of 1993 and 8 March, 24 May, 14 June, 27 June, and 30 Nov. of 1994. Two samples were taken close together in time in 1993 (29 June and 1 July) because a major precipitation event occurred between them. Grab samples were taken in the middle of the stream by bottle submersion 5 to 7 cm below the surface if there was sufficient flow. Collection throughout the watershed was completed in <3 h and the same sequence of sites was sampled each time.

In addition, from 1992 to 1996 weekly grab samples were taken at flow measurement weirs located at the upstream, midstream, and outlet of Goodwater Creek. Water draining from 16.7, 43.4, and 100% of the watershed area was sampled at these upstream, midstream, and outlet weirs, respectively. Grab samples (about 800 mL) were collected directly into amber glass bottles having Teflon-lined caps. Samples were stored at about 4°C in darkness after collection and during transport to the laboratory. Samples were refrigerated at about 4°C in the laboratory within 10 h of collection.

In addition to weekly grab samples, automated pumping samplers (Isco 3700 Portable Sampler, Isco Inc., 531 Westgate Boulevard, Lincoln, NE 68528) at each weir were used to take additional flow-weighted water samples during storm events. Thresholds for storm sampling are flow rates of 0.035, 0.030, and 0.32 m³ s⁻¹ for the upstream, midstream, and outlet sites, respectively. The samplers are programmed to fill all of the bottles when 5 cm of runoff have passed the gaging sites, and to fill the bottles with 72 sample increments. Thus, a sample increment is taken each time 0.069 cm of runoff has passed the weir. The size of the sample increment varies with bottle size and bottle rack in the particular sampler. Samples were taken at one fixed point in the stream cross section. Water flow (stage) was measured continuously using bubbler water level sensors associated with the automated samplers.

Amber collection bottles were reused after cleaning. Bottles were cleaned in soapy water and were rinsed sequentially in deionized water, methanol, and acetone before being heated at 300°C for at least 8 h to completely remove residual organic compounds (Adams, 1990). Quality assurance laboratory blanks and field blanks confirmed that there was no spurious contamination of sample bottles during the study period.

Chemicals and Reagents

American Chemical Society reagent- or chromatographic-grade chemicals were used. Herbicide analytical standards were obtained from Crescent Chemical Co.¹ and had purities of 99% for alachlor, atrazine, metribuzin [4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-triazine-5(4H)-one], metolachlor, and terbutylazine (4-tertbutylamino-2-chloro-6-ethylamino-*s*-triazine), and 97% for deethylatrazine and deisopropylatrazine. Ethyl acetate, methanol (Taylor Chemical Co., St. Louis, MO 63144), and water were HPLC-grade. Deionized reagent grade I water was prepared using a Labconco water purification system. Stock solutions prepared in methanol were refrigerated in volumetric flasks with tight-fitting stoppers before use. New analytical standards were used each year, and new herbicide stock solutions were prepared every 6 mo.

Extraction

Refrigerated water samples were usually allowed to stand overnight to let sediment settle before being filtered through 0.45 µm nylon filters. Herbicides dissolved in filtered water samples (100 mL) were extracted on C₁₈-solid phase extraction (SPE) columns. Most herbicides with water solubilities and partitioning coefficients like atrazine ($K_{oc} = 481$ at 25°C) remain dissolved in water, rather than being adsorbed on sediment (Baker and Lafen, 1983; Fawcett et al., 1994; Felsot et al., 1990; Wauchope, 1978). One milliliter of terbutylazine at a concentration of 100 µg/L in methanol was added to each surface water sample after filtration but before SPE extraction (Nash, 1990). The surrogate terbutylazine was used to estimate herbicide recovery. C₁₈-SPE cartridges (Bond Elute LRC from Varian Associates, Harbor City, CA) containing 0.5 g of octadecyl-bonded silica were preconditioned immediately before use by sequentially eluting with 8 mL of ethylacetate, 8 mL of methanol, and 16 mL of HPLC-grade water. Water subsamples (100 mL) were passed through moist, conditioned C₁₈-SPE cartridges under a vacuum at a flow rate of 7 to 10 mL/min. Then, SPE cartridges were dried by passing air through them under a vacuum at 25 to 40 cm Hg for periods from 1 to 2 h. Herbicides were eluted from dried SPE cartridges with 2.4 mL of ethyl acetate and the final volume was brought up to 2 mL.

The limits of detection (= 3 × background noise) for surface water samples were 0.04 µg/L for atrazine, 0.05 µg/L for both deisopropylatrazine and deethylatrazine, 0.10 µg/L for metribuzin, 0.23 µg/L for alachlor, and 0.29 µg/L for metolachlor, respectively. Maximum holding times were 2 d for samples before filtration, 5 d from filtration to SPE, and 42 d from collection to gas chromatography (GC).

Gas Chromatography

All analytes were separated and quantified by GC using a modified version of the method of Thurman et al. (1990). Gas chromatography was carried out on a Varian 3400 instrument (Varian Analytical Instruments, Sunnyvale, CA) equipped with a N-P thermionic specific detector and a Varian 8200 autoanalyzer. The gas chromatograph was interfaced via a 406 analog interface to an IBM AT that was operated under Beckman System Gold software ver. 7.11. The megabore column used was made from approximately 30 m by 0.53 mm i.d. fused silica coated with a 1.5 µm thick film of Restek

¹ Names are necessary to report factually on available data; however, the USDA neither guarantees nor warrants the standard of the product, and the use of the name by USDA implies no approval of the product to the exclusion of others that may also be suitable.

XTI-5 (crossbond 5% diphenyl-95% dimethyl polysiloxane) (Restek Corp., Bellefonte, PA). The helium carrier gas flow was 5.5 to 7 mL/min. Injector and detector temperatures were held at 250 and 305°C, respectively. Oven temperature was programmed starting from 75°C followed by an increase at a rate of 20°C/min to 145°C, followed by a rate of 3°C/min to 187°C, followed by a rate of 5°C/min to 215°C, followed by a rate of 25°C/min before being held at a final temperature of 280°C for 1 min. The total run time was about 30 min. The detector make-up N₂, air, and hydrogen gas flow rates were 25, 170, and 4 mL/min, respectively. The TDS bead current ranged from 2.4 to 3.8 amps with a bead bias of -4.0 volts. Injection volumes were 4 µL. The linear range of the gas chromatograph calibration curve for atrazine was 0.2 to 200 µg/L. Samples with herbicide concentrations (chiefly atrazine) greater than the linear range were diluted before reanalysis. The detector specifically responded to N- and P-containing compounds, and herbicides were routinely identified by comparing their retention times with analytical standards and knowledge of what pesticides were applied to Goodwater

Creek Watershed. In addition, all herbicides in selected water samples were confirmed using high pressure liquid chromatography-mass spectrometry-mass spectrometry (HPLC-MS-MS) by an external contract laboratory² ($n = 29$). In addition, from 1992 to 1995 our analysis of quarterly unknown standard reference materials and field splits that were gathered from Goodwater Creek were confirmed by an external quality assurance lab³ ($n = 142$) which used GC/MS for identification and quantitation, validating our laboratory's identification and quantitation of analytes.

A quality control program was instituted in which field blanks, duplicates, and spikes were gathered whenever water samples were gathered. Spiked surface water samples received

²Details of methodology available from Dr. Y-X. Li, Analytical Bio-Chemistry Laboratories, Inc., 7200 E. ABC Lane, Columbia MO 65202.

³Laboratory procedures of the external quality assurance lab are available, Huntingdon Engineering & Environmental, Inc., 662 Cromwell Ave., St. Paul, MN 55114-1776.

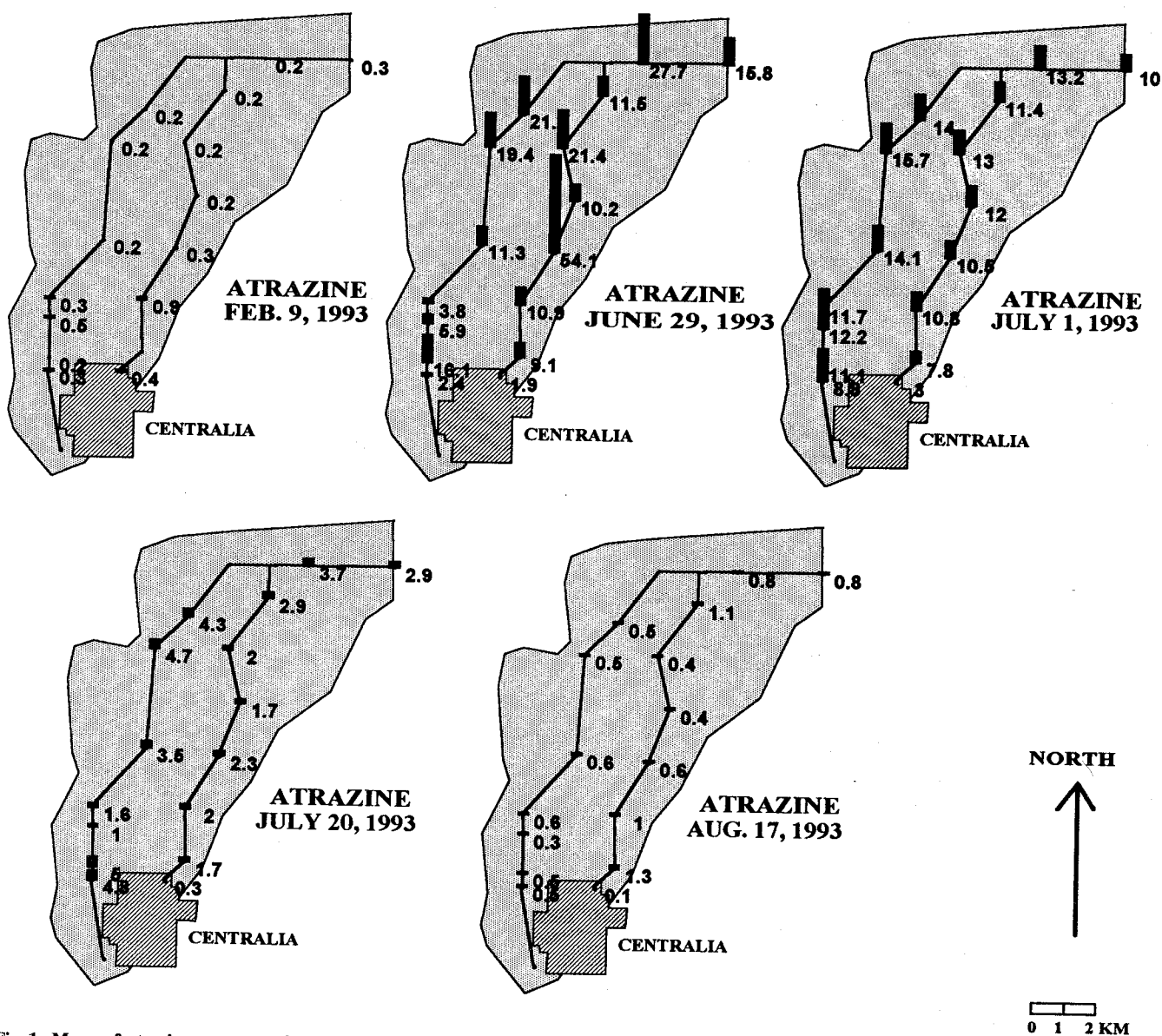


Fig. 1. Maps of atrazine concentration (µg/L) in stream water draining Goodwater Creek watershed toward the northeast throughout 1993. Atrazine concentrations (µg/L) are presented as bar graphs at each sampling site along the branched Goodwater Creek.

1 μg deisopropylatrazine, deethylatrazine, atrazine, and metribuzin, as well as 2 μg alachlor and metolachlor per 800 mL water sample. Herbicide recoveries for spiked field samples averaged 98.5% for alachlor, 93.9% for atrazine, 91.6% for deethylatrazine, 63.4% for deisopropylatrazine, 97.2% for metolachlor, and 91.6% for metribuzin for 1993 to 1996. The average relative percent differences for field duplicates were 3.5% for alachlor, 2.6% for atrazine, 2.1% for deethylatrazine, 2.8% for deisopropylatrazine, 0.3% for metribuzin, and 0.8% for metolachlor. Quality control charts of duplicate samples showed that duplicate precision was <20% at concentrations above the limit of quantitation.

Statistical Analysis and Data Presentation

Maps of herbicide concentration at sampling sites throughout the watershed were prepared using MapViewer (Ver. 2. Golden Software, Inc. 809 14th St., Golden, CO 80401-1866). Censored box plots of herbicide concentrations for the 7250-ha watershed were prepared vs. sampling time (sample size $n = 16-18$) (Helsel and Hirsch, 1992, p. 451-455). The boxplots were censored by the analytical limit of detection. Censored box plots included the 25th and 75th quartiles and the whiskers included the 90th and 10th quartiles. Outliers were represented as dots. For boxplot calculations, herbicide concentrations below the limit of detection were set equal to zero (Helsel

and Hirsch, 1992, p. 451-455). Herbicide limits of detection are presented in each boxplot.

One-dimensional geostatistical analysis was performed for herbicide concentration vs. distance along the branches of Goodwater Creek. Herbicide concentration ($\mu\text{g/L}$) was the regionalized variable and distance (m) between stream sampling sites was the lag variable for the stream branches in Goodwater Creek Watershed ($n = 10$ or 11 for distance). U.S. Geological Survey maps covering Goodwater Creek Watershed on a scale of 1:24 000 were digitized and the distances along streams between road intersections were determined using Arc/Info (Version 7.0.1, Environmental Systems Research Institute, Redlands, CA 92373). Semivariogram functions were graphed using GS+ software (GS+ ver. 2. software. Gamma Design Software, P.O. Box 201, 457 East Bridge St., Plainwell, MI 49080) and the steps involved in data processing were summarized (Donald, 1994). Isotropic semivariance [$\gamma(h)$] of each regionalized variable was related to the sampling "lag" distance h intervals between pairs of samples taken at increasing distances from each other (Phillips et al., 1992; Warrick et al., 1986). These graphs helped establish if a regionalized variable exhibited spatial dependence and at what lag distance h values became independent of distance (Nielsen and Alemi, 1989; Perrier and Wilding, 1986; Trangmar et al., 1985; Warrick et al., 1986; Webster, 1985). The fit of semivariogram functions to linear, linear/sill, spherical, exponential, and

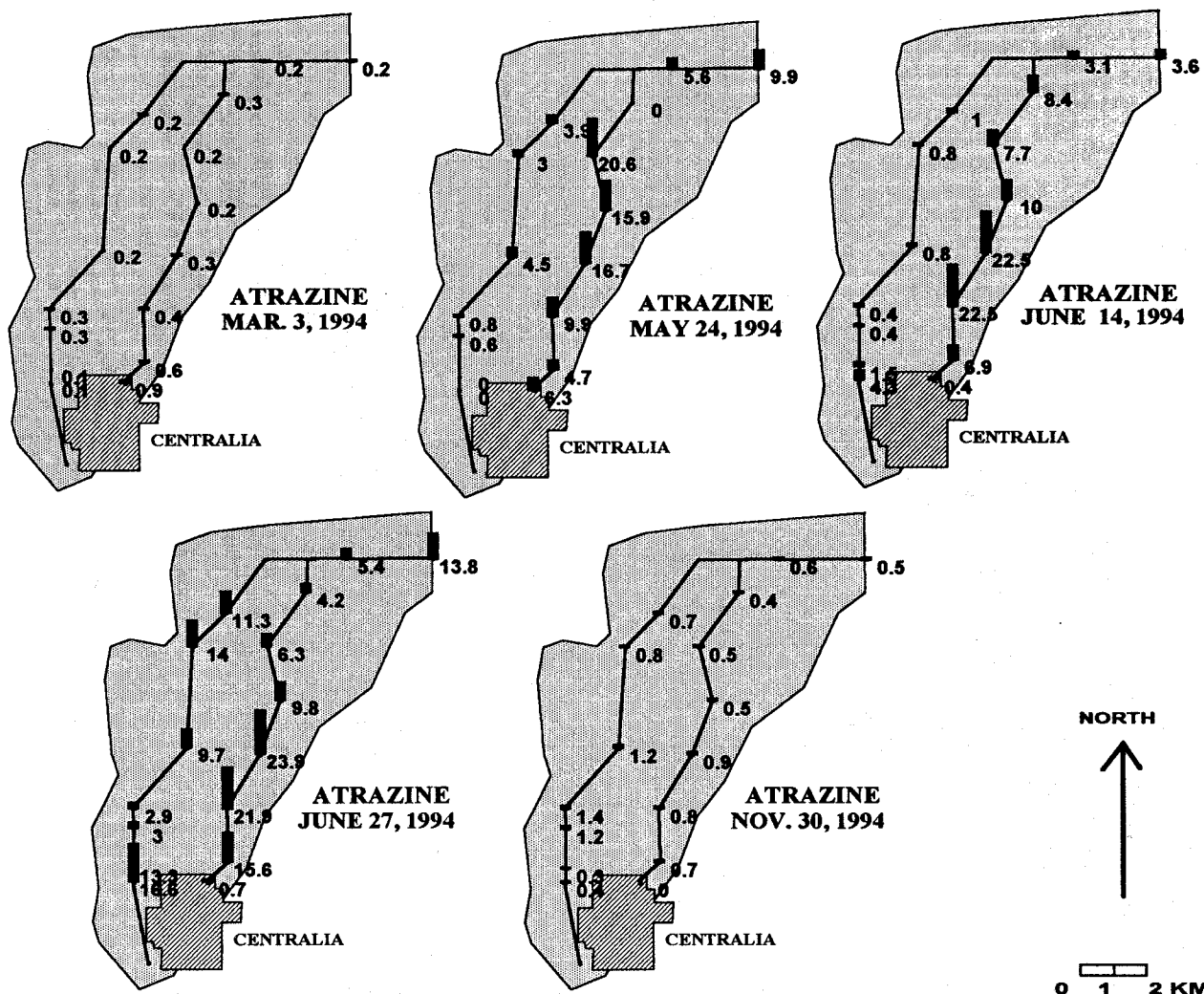


Fig. 2. Maps of atrazine concentration ($\mu\text{g/L}$) in stream water draining Goodwater Creek watershed toward the northeast throughout 1994. Atrazine concentrations ($\mu\text{g/L}$) are presented as bar graphs at each sampling site along branched Goodwater Creek.

Gaussian models with and without a nugget variance (C_0) was examined for each regionalized variable. The best semivariogram model had the lowest residual sum of squares and largest coefficient of determination (r^2). Kriging provides unbiased estimates of regionalized variables in unsampled locations that depend only on semivariogram properties based on data. Kriging also calculates the standard deviation associated with these interpolated estimates.

Estimates of Herbicide Applied to the Watershed

Specific herbicide use data for Goodwater Creek Watershed were unavailable. Herbicide use within the watershed was assumed to be identical to state survey statistics (Anonymous, 1993a; 1994a,b). Cropping survey data were gathered within Goodwater Creek Watershed (Heidenreich and Vance, 1994). The amount of either atrazine (applied to corn + sorghum) or metolachlor (applied to corn + sorghum + soybean) applied to the portion of Goodwater Creek Watershed above each weir for each year was calculated from the following formula:

$$M = A \times f_c \times f_h \times r_h \times f_w \quad [1]$$

where

- M = mass of herbicide applied to the portion of the watershed above each weir for each year, kg/yr
 A = total watershed area, ha
 f_c = fraction of the watershed in each crop (either corn + sorghum or soybean) each year from local surveys of Goodwater Creek Watershed
 f_h = fraction of each crop treated with herbicide each year from state herbicide use statistics
 r_h = average rate of herbicide applied to each crop in Missouri from state herbicide use statistics
 f_w = fraction of the watershed draining through weirs located upstream, midstream, and at the outlet of the watershed.

Local surveys of farmers showed that about 40% of Goodwater Creek Watershed was planted to soybean and 20% was planted to corn + sorghum in both study years (Heidenreich

and Vance, 1994). Corn and sorghum were assumed to be treated alike with atrazine and metolachlor. In state-wide surveys, 83 and 84% of Missouri corn hectares were treated with atrazine in 1993 and 1994, respectively (Anonymous, 1994a, 1995a). Twenty-five and 37% of the Missouri corn hectares and 6 and 6% of the Missouri soybean hectares were treated with metolachlor in 1993 and 1994, respectively. In state-wide surveys, average atrazine rates were 1.46 and 1.53 kg/ha in 1993 and 1994, respectively (Anonymous, 1994a, 1995a). The average metolachlor rate was 1.96 kg/ha for both Missouri corn and soybean in 1993. The average metolachlor rates were 2.15 and 2.26 kg/ha for Missouri corn and soybean, respectively, in 1994. Upstream, midstream, and outlet weirs drained 0.167, 0.434, and 1.0 of the total area of the 7250 ha Goodwater Creek Watershed.

Estimate of the Herbicide Loss from Upstream, Midstream, and Outlet Weirs

Samples were taken manually for determining herbicide concentration at each weir at least weekly and automated pumping samplers collected flow-weighted samples during surface runoff events, as described previously. Herbicide losses were determined by integrating concentrations with water flux over representative time intervals for samples collected manually and actual sample-time intervals for samples collected automatically. For example, when no surface runoff events occurred and streamflow was uniform between successive weekly samplings, the concentration for the sample collected 7 d was assumed to represent the flow until the next week. When surface runoff events occurred and automated samples were collected, the start and stop times for filling each sample bottle were determined and integrated with the actual flow over all sample-time intervals.

Estimate of Annual Herbicide Concentration

Annual average herbicide concentration was calculated for atrazine and metolachlor as

$$\text{Avg} = \sum_n H/n \quad [2]$$

Table 1. Semivariogram functions for various regionalized variables describing herbicide concentration ($\mu\text{g/L}$) as a function of sample distance (m) along the left fork of Goodwater Creek.

Regionalized variable	Sampling date	Best semivariogram function	Nugget variance, C_0	Sill (structure + nugget variance), $C + C_0$	Model range, A_0	r^2
Atrazine concentration, $\mu\text{g/L}$	9 Feb. 1993	NS†	—	—	—	—
	29 June 1993	Linear	13.80	>116.89	>14 014.8	0.36
	1 July 1993	Spherical	0.470	8.210	13 910.0	0.18
	20 July 1993, 17 Aug. 1993, 8 Mar. 1994	NS	—	—	—	—
	24 May 1994	Linear	0.010	>7.745	10 797.6	0.68
Deisopropylatrazine concentration, $\mu\text{g/L}$	14 June 1994, 27 June 1994, 30 Nov. 1994	NS	—	—	—	—
	9 Feb. 1993, 20 July 1993	Not sampled	Not sampled	Not sampled	Not sampled	Not sampled
	17 Aug. 1993	Linear	0.0540	>0.2640	>14 014.0	0.25
	8 Mar. 1994	NS	—	—	—	—
	24 May 1994	Linear	0.0001	>0.1252	>10 797.6	0.77
Deethylatrazine concentration, $\mu\text{g/L}$	14 June 1994, 27 June 1994, 30 Nov. 1995	NS	—	—	—	—
	9 Feb. 1993 and 29 June 1993	NS	—	—	—	—
	7 Jan. 1993	Linear	0.470	>4.740	>14 014.8	0.29
	20 July 1993 and 17 Aug. 1993	NS	—	—	—	—
	8 Mar. 1994	Linear	0.0002	>0.0009	>14 014.8	0.14
Metolachlor concentration, $\mu\text{g/L}$	24 May 1994	Linear	0	>0.0268	>10 797.6	0.62
	14 June 1994, 27 June 1994, 30 Nov. 1994	NS	—	—	—	—
	9 Feb. 1993	—	—	—	—	—
	29 June 1993	Linear	0.100	>42.214	>14 014.8	0.44
	1 July 1993	Linear	0.710	>4.214	>14 014.8	0.13
Metolachlor concentration, $\mu\text{g/L}$	20 July 1993	Spherical	0.0001	0.1441	12 360.0	0.37
	17 Aug. 1993 and 8 Mar. 1994	NS	—	—	—	—
	24 May 1994	Linear	0.001	>0.960	>10 797.6	0.68
	14 June 1994	Linear	0.0023	>0.0909	>14 014.8	0.18
	27 June 1994 and 30 Nov. 1994	NS	—	—	—	—

† NS = nonsignificant.

where

Avg. = annual average herbicide concentration, ($\mu\text{g/L}$)
 H = herbicide concentration ($\mu\text{g/L}$) on Julian day \times
 n = total number of sampling days in 1993 or 1994.

RESULTS AND DISCUSSION

Spatial Variability of Herbicide Contamination

Maps of atrazine concentration across Goodwater Creek Watershed directly demonstrated widespread, seasonal, nonpoint-source contamination of surface water in two successive years (Fig. 1 and 2). Throughout the year, deethylatrazine and deisopropylatrazine, two atrazine degradates, and metolachlor exhibited similar spatial distribution across the watershed compared to atrazine (maps not presented).

Geostatistical analysis was conducted for herbicide concentrations vs. distance along each branch of Goodwater Creek (Table 1). Only data for the left branch are presented for brevity. Herbicide semivariograms showed that stream herbicide concentrations depended on sampling distance only when Goodwater Creek concentrations were high following corn and sorghum planting and herbicide treatment. Generally, semivariance increased linearly, but had a high nugget variance (Table 1). Coefficients of determination (r^2) for all semivariograms were <0.77 . Geostatistical analysis suggests that all herbicide concentrations were related to each other along the entire stream length, but less strongly for samples that were taken farther apart.

In addition to changing along the length of Goodwater Creek, herbicide concentrations also differed between the two branches of Goodwater Creek when observed concentrations were high (Fig. 1 and 2). For example, atrazine and metolachlor concentrations were greater in the right than the left branch of Goodwater Creek in 1994 (24 May and 14 June), but not in 1993 ($P \leq 0.05$ for Mann Whitney U Test at each date). Observed differences along each branch and between branches likely reflect differences in the timing of field spraying along and between each stream branch. Unfortunately, maps of corn or sorghum distribution were incomplete (Heidenreich and Vance, 1994) and field-by-field herbicide use information was unavailable for the watershed.

Box plots document the variability in herbicide concentration across the entire Goodwater Creek Watershed over time ($n = 16-18$) (Fig. 3). Box plots showed that herbicide concentrations in surface water were generally nonhomogeneous and skewed (not normally distributed), with numerous outliers for most dates throughout the entire sampling period. As expected, variability increased as concentration increased, and variability was greatest in May and June. Herbicide concentrations later decreased and became less variable. Box plots showed that greatest observed atrazine concentrations were often 10-fold greater than deethylatrazine or deisopropylatrazine, the major chlorinated degradates of atrazine (Fig. 3). Whereas box plots averaged watershed-wide herbicide concentration data (Fig.

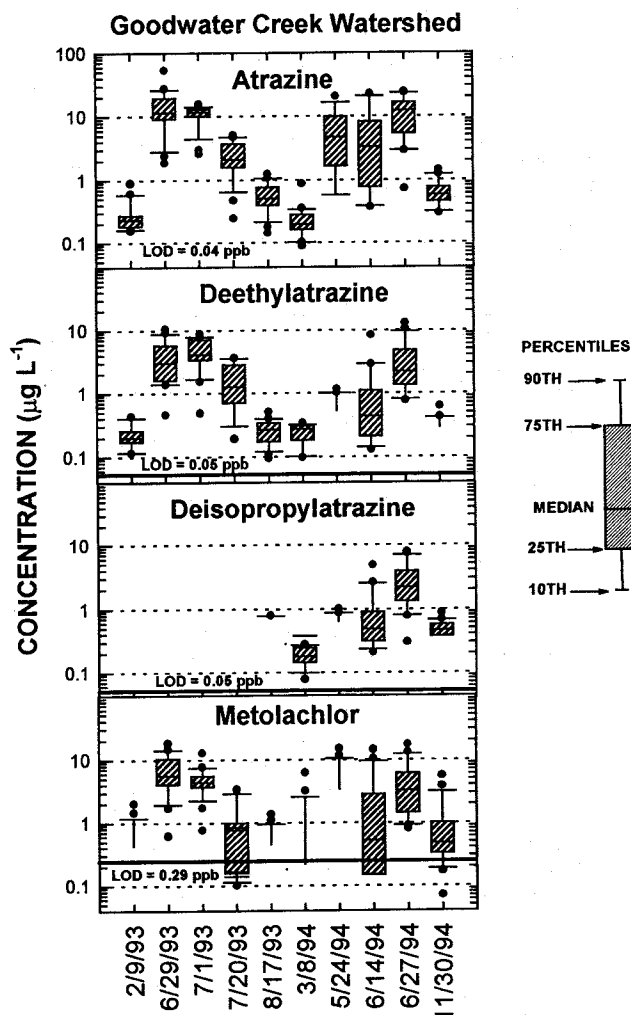


Fig. 3. Box plots for atrazine, deethylatrazine, deisopropylatrazine (sampling started 17 Aug. 1993), and metolachlor concentration are presented vs. sampling time averaged across the Goodwater Creek Watershed ($n = 16-18$). The sampling dates correspond to those in Fig. 1 and 2. Solid circles correspond to outliers.

3), maps retained spatial information concerning differences in atrazine concentration among subregions within the watershed (Fig. 1 and 2).

Temporal Variability of Herbicide Contamination

Herbicide concentrations in discharge from Goodwater Creek cycled seasonally both years and peaked in May (Fig. 4 and 5), as observed elsewhere (Battaglin et al., 1993; Frank and Sirons, 1979; Spalding and Snow, 1989). Observed maximum atrazine concentrations at the watershed outlet were 62.4 and 22.9 $\mu\text{g/L}$ in 1993 and 1994, respectively, whereas observed maximum metolachlor concentrations were 39.5 and 8.2 $\mu\text{g/L}$ in 1993 and 1994, respectively.

Peak herbicide concentrations in surface water leaving Goodwater Creek Watershed (Fig. 4 and 5) more closely resembled concentrations from runoff research plots (Leonard, 1988; Logan et al., 1994; Thurman et al., 1994; Wauchope, 1978) than from surveys of large

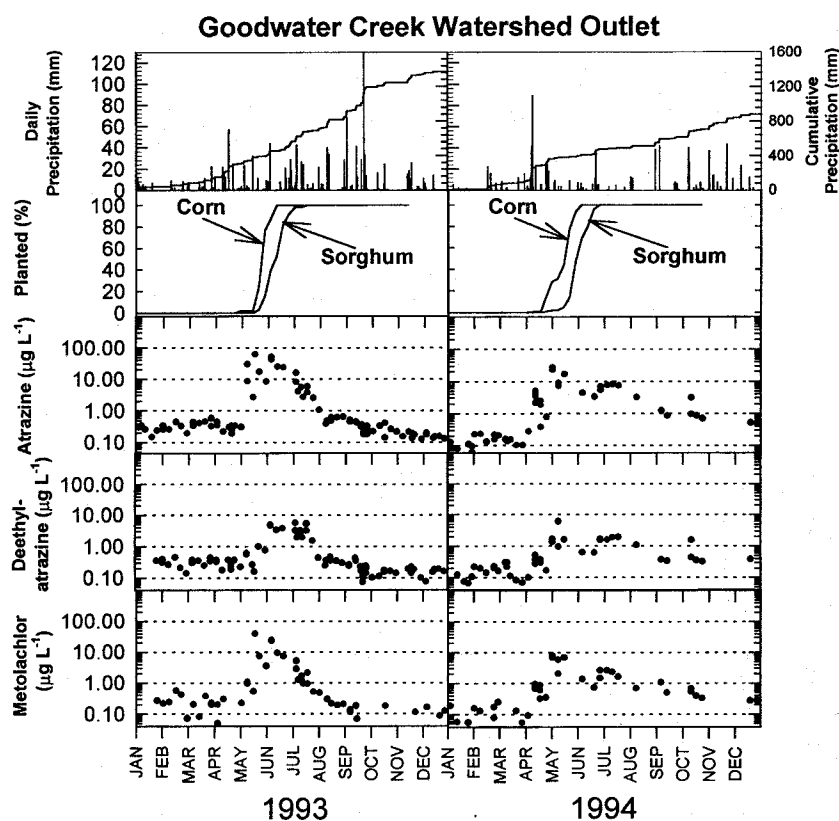


Fig. 4. Concentrations of atrazine, deethylatrazine, and metolachlor ($\mu\text{g/L}$) in stream water measured weekly and during storm events at the outlet of Goodwater Creek Watershed, daily precipitation, and percent of corn and sorghum plantings are presented vs. time.

river systems (Goolsby and Battaglin, 1993). In Ohio corn and soybean, low and peak concentrations in runoff at field edges ranged between 0.1 to 0.3 and 52.3 to 59.2 $\mu\text{g/L}$ for atrazine and between 0.1 to 0.3 and 84 to 164 $\mu\text{g/L}$ for metolachlor (Logan et al., 1994). In another study on a Brookston clay loam in Ontario, atrazine and alachlor levels were observed as high as 686 and 274 $\mu\text{g/L}$, respectively (Gaynor et al., 1992). Elsewhere, herbicide concentrations (atrazine and metolachlor) in tributaries were more than 10-fold greater than in rivers (Baker and Mickelson, 1994; Goolsby and Battaglin, 1993; Lemieux et al., 1995; Richards and Baker, 1993). Atrazine and metolachlor concentrations were similar between years for each herbicide in the Mississippi River from 1991 to 1993, despite flooding in 1993 (Goolsby et al., 1993a).

Peak atrazine concentrations at the watershed outlet (62.4 and 22.9 $\mu\text{g/L}$ in 1993 and 1994, respectively) were greater than for deethylatrazine (5.6 and 6.2 $\mu\text{g/L}$ in 1993 and 1994, respectively) (Fig. 4) verifying box plot of survey data for the entire watershed (Fig. 3). Because deethylatrazine is a degradate of atrazine, it is found in water at lower concentrations than atrazine. Seasonal peaks for deethylatrazine (Fig. 4) and deisopropylatrazine (data not shown) lagged slightly after the peak for atrazine (Fig. 4), as expected for precursor-product relationships. These observations bolster the assertion that herbicide contamination was due to nonpoint source contamination (Leonard, 1988, 1990). Deethylatrazine and deisopropylatrazine are similar to one an-

other in water solubility, and both are much more water soluble than atrazine, which is, in turn, more water soluble than metolachlor (Keller and Weber, 1995).

Peak herbicide concentrations exiting Goodwater Creek Watershed were slightly greater in 1993 than in 1994 (Fig. 4). Apparently, herbicide concentrations were not greatly diluted even though rainfall was greater in 1993 than in 1994 (1339.5 vs. 856.9 mm, respectively, compared with the 30-yr average, 953.3 mm). High rainfall in 1993 during the months immediately following herbicide treatment may have flushed atrazine from the watershed more quickly than in 1994 (Fig. 4 and 5), limiting the period over which differences in herbicide concentration could be observed between stream branches (Fig. 1 and 2).

Atrazine, deethylatrazine, and metolachlor were present year round when Goodwater Creek was flowing and had similar seasonal cycles in 1993 and 1994 (Fig. 4), as observed elsewhere (Baker, 1987; Goolsby and Battaglin, 1993). Others also observed that herbicide concentrations in surface water cycled and then leveled off, but were present year round for atrazine (Filcher et al., 1995; Hall et al., 1993; Lemieux et al., 1995; Raju et al., 1993; Schottler et al., 1994), deethylatrazine (Schottler et al., 1994), and metolachlor (Raju et al., 1993; Richards and Baker, 1993). In contrast, metolachlor was not found year-round in other research (Fischer et al., 1995; Hall et al., 1993).

After peaking following spraying, herbicide concentrations decreased more quickly and leveled off earlier

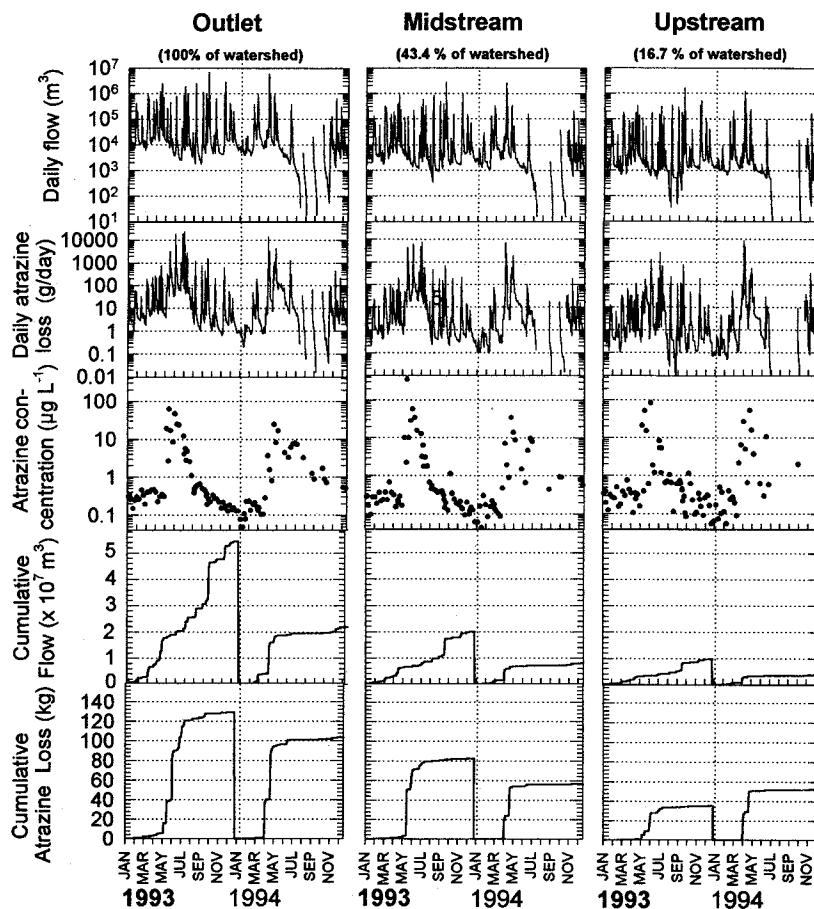


Fig. 5. Atrazine concentrations in stream water, daily and cumulative atrazine loss, and daily and cumulative water flow at three locations in Goodwater Creek Watershed are presented vs. time. The upstream, midstream, and outlet sampling sites drained 16.7, 43.4, and 100% of the watershed area, respectively.

in 1993 than in 1994 (Fig. 4 and 5). More rainfall for washing herbicides from the soil surface was available earlier in 1993 than 1994. In 1993, rainfall was above normal in April, July, August, and September, whereas in 1994, it was below normal in May, July, August, and September. From July to September of 1994, rainfall was more limited (Fig. 4) and resultant stream flow was intermittent (Fig. 5). In wet years, high herbicide concentrations in surface water reportedly either coincide with or lag slightly after both herbicide application and periods of high surface water flow (Gomme et al., 1991; Spalding and Snow, 1989; Weber et al., 1980).

Seasonal changes in atrazine concentrations generally varied concurrently at upstream, midstream, and outlet weirs which sampled from 16.7, 43.4, and 100% of the land area of Goodwater Creek Watershed (Fig. 5). Atrazine concentrations at the upstream weir were more variable over time than at the midstream and outlet weirs when concentrations were below $1 \mu\text{g/L}$ (Fig. 5). Goolsby et al. (1993a) suggested that large rivers may integrate events from many smaller tributaries, resulting in slower, less variable, concentration changes over time with lower peak concentrations in large rivers. Apparently, such integration also occurs at the smaller scale of the Goodwater Creek Watershed.

Using all data for each year (weekly samples and

storm runoff samples), the yearly average atrazine concentrations from the outlet of Goodwater Creek were 3.88 and $2.60 \mu\text{g/L}$ in 1993 and 1994, respectively. The U.S. Environmental Protection Agency's maximum contaminant level for atrazine in drinking water is $3 \mu\text{g/L}$, calculated as the yearly average of samples taken quarterly (USEPA, 1995). If Goodwater Creek water was ever used for drinking water, federal drinking water regulations would require treatment during some years.

Herbicide in discharge at each weir was expressed as a percentage of the herbicide applied to Goodwater Creek Watershed (i.e., relative herbicide loss) (Table 2 and bottom panel in Fig. 5). The amount of herbicide applied to the watershed is an estimate based on local and state survey statistics. The amount of herbicide leaving the watershed or the weirs is a chemical measurement based on periodic sampling. The relative herbicide loss from the watershed as a percent of the amount of herbicide applied to the watershed is only as accurate as the least accurate estimate (i.e., the amount of herbicide applied to the watershed). Relative herbicide loss at the outlet was lower in 1994 than 1993, probably because of dry conditions and reduced stream flow. Others observed that relative herbicide losses were lower in dry than wet years (Baker and Mickelson, 1994). In edge-of-field runoff studies, relative herbicide losses increased as

Table 2. Estimated amount of atrazine and metolachlor loss from Goodwater Creek watershed as a percentage of the amount estimated to be applied.

Herbicide	Herbicide loss from weirs					
	1993			1994		
	Outlet	Midstream	Upstream	Outlet	Midstream	Upstream
	%					
Atrazine	7.3	10.7	11.9	5.6	7.1	16.9
Atrazine + dea†	9.3	13.4	17.0	-	-	-
Atrazine + dea + dia	-	-	-	7.3	8.7	18.6
Metolachlor	4.6	7.4	6.8	2.0	2.1	3.7

† (dea = deethylatrazine and dia = deisopropylatrazine).

rainfall volume and intensity increased (Williams and Nicks, 1988; Dillaha et al., 1988; Wauchope, 1978). If significant rainfall followed soon after herbicide application, relative herbicide losses in runoff were greater than if rainfall lagged after application (Gaynor et al., 1992; Leonard et al., 1979; Southwick et al., 1990; Wauchope, 1978, 1987; Weber et al., 1980; Willis and McDowell, 1982). Others also found that herbicide losses were greater during wet than dry years (Baker and Mickelson, 1994).

SUMMARY

Results of this research should apply to areas with similar claypan soils. Claypan soils like those of Goodwater Creek Watershed cover about 4 M ha and stretch from northeastern Oklahoma to southern Indiana (Anonymous, 1995c). Similar soils with compacted layers that restrict rates of water drainage and herbicide infiltration may experience greater herbicide loss in runoff than soils which drain freely (Baker and Laflen, 1983; Fawcett et al., 1994). Maximum herbicide and degradate concentrations leaving Goodwater Creek Watershed (Fig. 1-5) were greater than reported for 11 watersheds having either clay, loam, or sandy soils (Frank and Sirons, 1979). Elsewhere, more runoff and atrazine were also lost to surface water from clay soils or soils with compacted subsurface layers (Baker and Laflen, 1983) than from finer textured or sandy soils (Baker and Laflen, 1983; Frank and Sirons, 1979; Willis and McDowell, 1982).

Generally, maximum observed atrazine concentrations in discharge from Goodwater Creek Watershed (Fig. 4) were greater than observed elsewhere in watersheds containing sandy or lighter textured soils without claypans (Fawcett et al., 1994; Frank and Sirons, 1979). This was surprising because only about 20% of Goodwater Creek Watershed was planted to corn and sorghum, which are usually sprayed with atrazine. Goodwater Creek Watershed contains extensive riparian zones, grassed waterways, grassed strips bordering streams and gullies, and filter strips bordering fields for erosion control and soil conservation. Concentrated runoff in gullies short circuiting these vegetated landscape features likely reduces their effectiveness for attenuating herbicide movement to streams (Paul Blanchard, 1996, personal communication). Runoff from fields

into drainage ditches bordering roads crisscrossing the watershed also runs directly into Goodwater Creek.

Channelized runoff does not infiltrate uniformly, especially from commercial-scale fields (Dillaha et al., 1988). One way to reduce herbicide loss in runoff would be to retard field-to-stream delivery of contaminated runoff water, encouraging infiltration of both runoff and herbicides (Felsot et al., 1990; Nelson and Jones, 1994). However, currently installed grassed waterways and riparian vegetation need to be redesigned to increase their effectiveness for reducing loss of water-soluble herbicide in runoff. This might entail increasing the surface roughness factor (e.g., microtopography factor).

This monitoring research suggests that alternative weed management strategies are needed which reduce herbicide use and new techniques are needed for managing runoff from agricultural fields with claypan soils. Reducing runoff leaving fields and lowering herbicide concentrations in runoff are complementary ways to minimize herbicide loss (Baker and Johnson, 1989; Felsot et al., 1990). Either approach by itself would likely be insufficient to minimize surface water contamination by herbicides. Using both preventative and remedial strategies holds more promise for reducing herbicides in runoff from treated fields, than using only vegetation along runoff pathways to retard runoff loss of herbicides.

ACKNOWLEDGMENTS

We thank Dr. Robert Lerch, Joe Absheer, and Jenny Fuseselman for their assistance and Chris Barnett and Steve Vance of UMC's Center for Agricultural, Resource and Environmental Systems (CARES) for geographic information systems analysis.

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