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HERBICIDE TRANSPORT IN GOODWATER CREEK EXPERIMENTAL WATERSHED: I. LONG-TERM RESEARCH ON ATRAZINE[1]

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ABSTRACT: Atrazine continues to be the herbicide of greatest concern relative to contamination of surface waters in the United States (U.S.). The objectives of this study were to analyze trends in atrazine concentration and load in Goodwater Creek Experimental Watershed (GCEW) from 1992 to 2006, and to conduct a retrospective assessment of the potential aquatic ecosystem impacts caused by atrazine contamination. Located within the Central Claypan Region of northeastern Missouri, GCEW encompasses 72.5 km^2 of predominantly agricultural land uses, with an average of 21% of the watershed in corn and sorghum. Flow-weighted runoff and weekly base-flow grab samples were collected at the outlet to GCEW and analyzed for atrazine. Cumulative frequency diagrams and linear regression analyses generally showed no significant time trends for atrazine concentration or load. Relative annual loads varied from 0.56 to 14% of the applied atrazine, with a median of 5.9%. A cumulative vulnerability index, which takes into account the interactions between herbicide application, surface runoff events, and atrazine dissipation kinetics, explained 63% of the variation in annual atrazine loads. Based on criteria established by the U.S. Environmental Protection Agency, atrazine reached concentrations considered harmful to aquatic ecosystems in 10 of 15 years. Because of its vulnerability, atrazine registrants will be required to work with farmers in GCEW to implement practices that reduce atrazine transport.

(KEY TERMS: atrazine transport; correlation analysis; critical transport period; monitoring; cumulative frequency distributions; regression analysis; watershed regression for pesticides model; watershed; cumulative vulnerability index.)

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INTRODUCTION

Atrazine [6-chloro-N^2-ethyl-N^4-(1-methylethyl)-1,3,5-triazine-2,4-diamine] remains the most commonly used herbicide in the United States (U.S.), with over 26,000 mg used for corn (*Zea mays*) production in 2005 (USDA-NASS, 1992-2006). Because of its widespread use and frequent detections in surface waters (Blanchard and Lerch, 2000; Lerch and Blanchard, 2003; Scribner *et al.*, 2005), atrazine transport to streams in the Midwestern U.S. has been studied extensively over the last 15 years (e.g., Thurman *et al.*, 1992; Lerch *et al.*, 1995, 1998; Donald *et al.*,

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1998; Blanchard and Lerch, 2000; Lerch and Blanchard, 2003; Battaglin *et al.*, 2005; Scribner *et al.*, 2005; Gilliom *et al.*, 2006). These studies reported that atrazine was frequently detected and occasionally occurred at concentrations that may be harmful to humans and aquatic ecosystems in streams throughout the Midwest (Solomon *et al.*, 1996; USEPA, 1996). In addition, these studies demonstrated that a critical transport period exists during the second quarter of the year because of the coincidence of herbicide application and intense rainfall events that transport atrazine, via surface runoff, from treated fields to streams. Because of this timing, atrazine concentrations are highest immediately following application and decline exponentially with time (Leonard, 1990; Ng and Clegg, 1997; Ghidey *et al.*, 2005).

At the watershed scale (e.g., >20,000 ha), median relative atrazine loads (i.e., load expressed as a percent of applied mass) have been reported to be in the range of 0.47 to 3.9% of the applied herbicide (Capel *et al.*, 2001; Lerch and Blanchard, 2003). Of course, individual watersheds can have relative loads much lower or higher than the range of reported median values. For example, Capel and Larson (2001) reported that relative atrazine loads for 35 watersheds across the U.S. ranged from 0.03 to 6.8% of applied. Lerch and Blanchard (2003) reported that relative atrazine loads for 20 watersheds within the northern Missouri/southern Iowa region ranged from 0.28 to 13% of applied. These relative loads did not include atrazine metabolites, and therefore, they represent conservative estimates of the total atrazine transport (i.e., parent plus metabolites) in surface runoff.

In recent years, there has been considerable focus on identifying the characteristics or factors that contribute to a watershed's vulnerability to herbicide transport (Battaglin and Goolsby, 1999; Blanchard and Lerch, 2000; Homes *et al.*, 2001; Larson and Gilliom, 2001; Lerch and Blanchard, 2003; Larson *et al.*, 2004). There is a general consensus from these studies that four main factors control watershed vulnerability to herbicide transport: (1) chemistry of the contaminant; (2) the hydrology and soils of the watershed; (3) land use in the watershed (which includes herbicide use and crop management); and (4) climate (particularly precipitation). However, there is disagreement in the literature about the relative importance of these factors depending upon the scale at which the studies were conducted. For example, at plot to field scales, the timing of runoff-generating precipitation events relative to herbicide application is the critical factor affecting annual variation in atrazine concentrations and loads (Wauchope, 1978; Glotfelty *et al.*, 1984; Capel *et al.*, 2001; Shipitalo and Owens, 2003; Ghidey *et al.*, 2005). As scale increases to include multiple large watersheds, the variation in soil properties, particularly their impact on runoff potential, between watersheds emerges as the predominant factor affecting transport (Blanchard and Lerch, 2000; Homes *et al.*, 2001; Lerch and Blanchard, 2003). At the national scale, the Watershed Regression for Pesticides (WARP) models developed by the U.S. Geological Survey (Larson and Gilliom, 2001) showed that herbicide use intensity explained more of the variability in herbicide concentrations in streams than parameters for soils, climate, hydrology, and watershed area (Larson *et al.*, 2004). The WARP models predict herbicide concentration at specified percentiles. This allows for creation of a predicted cumulative frequency distribution (CFD) for a given watershed. Furthermore, WARP was developed based on data from 112 watersheds located throughout the continental U.S., with atrazine use intensity that varied from 0 to 57.2 kg/km^2 (Larson *et al.*, 2004). Thus, the CFD based on the WARP models provides a comparison of the predicted *vs.* observed atrazine contamination for a specified watershed against a national-scale database of watersheds.

Concerns associated with atrazine contamination of streams include human health and aquatic ecosystem impacts. Human health concerns associated with herbicide contamination of drinking water and their possible toxic effects have been regulated for many years in the U.S. by establishment of acceptable concentrations for human consumption (USEPA, 1996). For atrazine, the maximum contaminant level for finished drinking water is 3 μg/l based on the running average of four quarterly samples. Recently, the United States Environmental Protection Agency (USEPA) has been requiring that registrants assess the possible aquatic ecological effects of herbicides (USEPA, 2003; Hackett *et al.*, 2005). The USEPA atrazine interim re-registration eligibility decision (IRED) states that the level of concern for aquatic ecosystems is approximately 10 to 20 μg/l for exposure periods of two weeks to three months (USEPA, 2003). The level of concern was based on the USEPA's review of 25 micro- and mesocosm studies that focused on the toxic effects of atrazine on phytoplankton, periphyton, and macrophytes. Atrazine concentrations during the second quarter of the year typically fall within the range of 0.05 to 200 μg/l for streams in agricultural watersheds (Blanchard and Lerch, 2000; Lerch and Blanchard, 2003; Scribner *et al.*, 2005). This range includes the IRED level of concern, indicating that potentially toxic atrazine concentrations may occur annually in streams of agricultural watersheds.

Studies of long-term trends in herbicide contamination of streams have mainly investigated changes in concentration over broad geographic areas (e.g., the Corn Belt) and under spring runoff conditions (Battaglin and Goolsby, 1999; Scribner *et al.*, 2000, 2005). These studies reported that, in general, changes in median concentrations were associated with changes in herbicide use. However, median atrazine concentrations decreased from 1989 to 1998 despite similar use over this time (Battaglin and Goolsby, 1999; Scribner *et al.*, 2000, 2005). Battaglin and Goolsby (1999) speculated that the observed decreases in atrazine concentration may have been due to changes in herbicide management and better utilization of herbicide best management practices (BMPs). While these geographically broad studies highlight overall trends in herbicide contamination of streams, they do not involve intensive sampling throughout the year to provide detailed annual variation in concentrations and loads over an extended time period for the same location. Furthermore, much more detailed information with respect to changes in land and herbicide use, stream discharge, and precipitation may be acquired for smaller watershed areas than can be acquired at broader, regional scales.

This article summarizes the results of a 15-year study of atrazine transport conducted in the Goodwater Creek Experimental Watershed (GCEW) in northeastern Missouri. The two primary objectives of this study were to analyze trends in atrazine concentration and load in GCEW from 1992 to 2006, and to conduct a retrospective assessment of the potential aquatic ecosystem impacts caused by atrazine contamination of this watershed using criteria established in the 2003 IRED. A secondary objective was to assess the key factors controlling annual variation in atrazine transport at the watershed scale via the development of an annual index of herbicide loss vulnerability that accounts for the complex interactions of application timing, atrazine dissipation kinetics in soil, and the extreme temporal variability of surface runoff.

MATERIALS AND METHODS

Watershed Description

The GCEW is located in northeast Missouri within the Salt River Basin (Figure 1). The watershed encompasses 77 km^2, of which 72.5 km^2 is instrumented, with a stream network comprised of first- through third-order streams. Topography is characterized by broad gently sloping divides, with roughly 37-m elevation change from divide to outlet, which is at 235 m MSL. The GCEW is a subwatershed of Young's Creek (172 km^2), which is one of two major subwatersheds within Long Branch Creek (466 km^2). Long Branch Creek drains directly into Mark Twain Lake, the major public water supply in the region.

The watershed lies within the Central Claypan Region (Major Land Resource Area 113) (USDA-NRCS, 2006). The major soil series include Adco silt loam (0-2% slopes; fine, smectitic, mesic Vertic Alba-

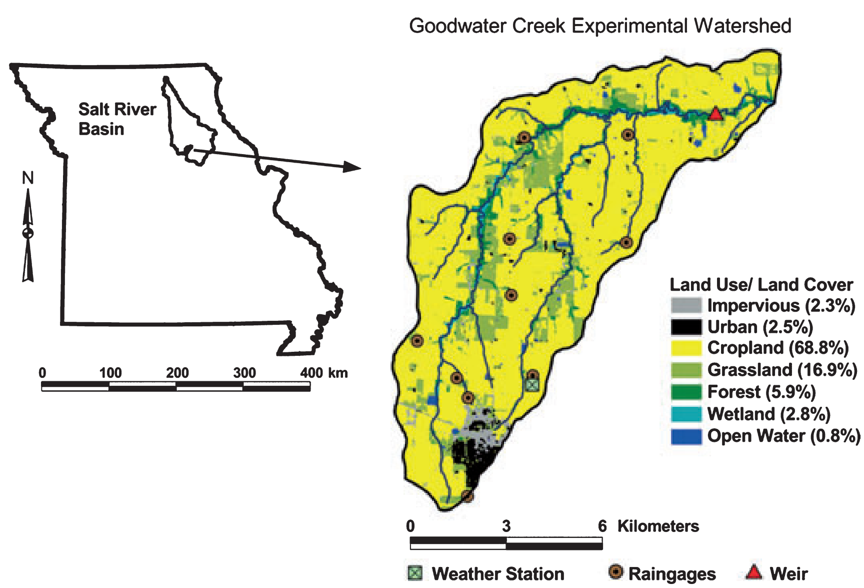

FIGURE 1. Monitoring Infrastructure and Land Use/Land Cover in Goodwater Creek Experimental Watershed. Land-use/land-cover data obtained from 30-m resolution Landsat imagery from 2000 to 2004.

qualfs), Mexico silt loam (1-3% slopes, eroded; fine, smectitic, mesic Vertic Epiaqualfs), and Putnam silt loam (0-1% slopes; fine, smectitic, mesic Vertic Albaqualfs). These soils are characterized by a naturally formed claypan argillic horizon (B_t) with an abrupt and large increase in clay content compared to the overlying horizons (Soil Science Society of America, 2008). The claypan represents the key hydrologic feature of the watershed resulting in high runoff potential soils that are predominantly classified as hydrologic soil groups C and D.

The watershed is dominated by agricultural land uses (Figure 1); row crops and grasslands cover 85.7% of the watershed. Other land cover includes farm ponds and small lakes, impervious surfaces, urban areas in and around Centralia, Missouri, on the southern watershed divide, and stream channels with narrow forested and wetland riparian corridors. Crops include soybean (*Glycine max*), corn (*Zea mays*), wheat (*Triticum aestivum*), and grain sorghum (*Sorghum bicolor*). The predominant crop production system is a corn-soybean rotation with some form of minimum tillage used for corn and no-till for soybeans.

Land and Herbicide Use Estimates

General land-use information for the major land-cover classes (forest, urban, impervious, cropland, grasslands, wetlands, and open water) was obtained from 30-m resolution Landsat imagery data collected from 2000 to 2004 (http://www.msdis.missouri.edu/data/lulc/lulc05.htm, *accessed* August, 2008). Crop-specific data for GCEW were obtained for 1992 and 1993 by Heidenreich (1996) from county-level USDA-Farm Service Agency (FSA) records. These records covered about 68% of the ~5,300 ha known to be cropland within the watershed (Figure 1). The unassigned cropland for these two years was assumed to have the same distribution as the USDA-FSA crop specific data. The relevant crops for the herbicide data presented in this and the companion article (Lerch *et al.*, this issue) were corn, soybean, and sorghum; thus, estimates of crop-specific land use focused only on these three crops. In 2006, a windshield survey was conducted, augmented with aerial photography, to determine the planted areas of corn, soybean, and sorghum. From 1994 to 2005, the relative annual change in these three crops was estimated using Audrain County planted area data (USDA-NASS, 1994-2005) since the majority of the watershed lies within this county. The Audrain County data were combined with an annual adjustment factor that forced the data to converge toward the known 2006 data. For example, if Audrain County data showed a 10% increase in planted corn area for a given year, the same percent increase was applied to GCEW. Applying these changes over years caused some slight divergence from the observed 2006 land-use data; thus, the annual adjustment was applied retroactively to force convergence with the observed data.

Herbicide use estimates were obtained from 1992 to 2006 from the USDA-NASS (1992-2006) annual crop reports. The USDA-NASS use estimates included the fraction of a crop treated with a given herbicide and the average application rate. A farmer survey conducted in 2006 confirmed that the USDA-NASS estimates were generally applicable to GCEW (Lerch *et al.*, this issue). Corn planting progress estimates for the northeastern Missouri crop reporting district, which includes GCEW, were also obtained from USDA-NASS (1996, 2000, 2003) and used as a surrogate for herbicide application timing. These data were scaled as percent of expected planting, which sometimes is not realized because of within-season weather conditions. Relative annual herbicide loads at the watershed scale (i.e., loss as a percent of applied) were based on the monitored watershed area (see below and Lerch *et al.*, this issue).

Watershed Instrumentation

The key instrumentation for the 15-year period of record reported here (1992-2006) includes a broad-crested 5:1 V-notch weir, rain gauges, and a weather station (Figure 1). The V-notch weir was installed near the watershed outlet (latitude 92°03′W; longitude, 39°18′N). The initial rating curves were developed between 1971 and 1986, with on-going refinement of the rating curve for high discharge events. A Salt River basin-scale water balance assessment indicated that the GCEW discharge data were overestimated by an average of 10% during the study period due to errors at the high end of the rating curve. This resulted in overestimation of atrazine loads (see below) by an average of 8%. Electronic head measurements were recorded at five-minute intervals, and all discharge data were aggregated to average daily discharge. A network of nine weighing, recording rain gauges was installed across the watershed in 1971. In 1997, load cells were installed under the buckets of all rain gauges to automate the measurement at two-minute intervals. An automated weather station, that also includes a rain gauge, was installed in 1991 (Figure 1). Additional details of the watershed infrastructure, data management, and quality assurance were reported by Sadler *et al.* (2006).

Water Quality Monitoring and Herbicide Analysis

All water samples were collected at the V-notch weir (described above). Grab samples were collected weekly under base-flow conditions. Under runoff conditions, flow-weighted samples were collected using an automated sampler that was programmed to collect samples for events of up to 150 mm of runoff. A maximum of eight separate samples were collected per runoff event, with each individual sample representing a composite of up to nine 100-ml sips collected at a discharge interval of 2.1 mm. The automated sampler was programmed to sample runoff events at a minimum discharge of 234 m^3/h. Samples were transferred to the laboratory on ice within 48 hours of collection, and stored in a cold room at 2-4°C.

In the laboratory, samples were filtered through 0.45-μm nylon filters within 48 hours of receipt, and herbicides were extracted with C_{18} solid-phase extraction cartridges using 200-ml samples spiked with terbutylazine [6-chloro-N^2-ethyl-N^4-(1,1-dimethylethyl)-1,3,5-triazine-2,4-diamine] to a concentration of 50 μg/l. From 1992 to 1997, samples were concentrated 200-fold and atrazine concentrations were determined by gas chromatography (GC) with N-P detection (Donald *et al.*, 1998; Lerch and Blanchard, 2003). The limit of detection was 0.04 μg/l. From 1998 to 2006, samples were concentrated 600-fold and atrazine concentrations were determined by GC-mass spectrometry (GC/MS) using a Saturn 2000 ion-trap MS detector (Varian Inc., Harbor City, CA, USA). The limit of detection was 0.003 μg/l. Details of the GC/N-P and GC/MS methods were detailed by Lerch and Blanchard (2003).

Computations and Statistics

Cumulative frequency distributions were developed on a daily basis for flow-weighted atrazine concentrations, atrazine load, and stream discharge to facilitate interpretation of temporal trends in the data (Oosterbaan, 1994). To compute daily flow-weighted concentrations, raw concentration values from grab and automated samples were interpolated linearly to estimate concentrations on un-sampled days. As the goal was to sample all runoff events, the only instances for which interpolations were conducted between two grab samples with an un-sampled runoff event between them was in the case of equipment failure or the inability to replace sample bottles from an event before a subsequent event occurred. A grab sample was obtained during most events to prevent the possibility of an un-sampled runoff event caused by such circumstances.

For days with multiple samples collected during runoff events, the concentration and corresponding discharge were used to compute the load for each sample; the masses were then summed for all samples to obtain the total load and divided by the total discharge to obtain flow-weighted concentration. For days with a single measured or interpolated concentration, loads were computed by multiplying the concentration by the daily discharge. All CFDs were developed by sorting the data in ascending order and computing the percentiles for each day. Percentiles were determined for all data (15 years) and for five 3-year periods (1992-1994, 1995-1997, 1998-2000, 2001-2003, and 2004-2006), and plotted as cumulative frequency *vs.* the log of stream discharge, atrazine concentration, or atrazine load.

Linear regression analysis was performed to discern temporal trends in selected percentile concentrations, annual load, and use on an annual basis, with time, in years, as the independent variable. 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. In addition, autocorrelation among years was assessed for 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 WARP models for 5th, 10th, 15th, 25th, median, 75th, 85th, 90th, 95th, and maximum concentrations were used to generate estimates of atrazine concentrations for comparison against the observed GCEW data (Larson *et al.*, 2004; Stone *et al.*, 2008). The WARP input data for GCEW were as follows: 15-year average use intensity, 30 kg/km^2; rainfall erosivity factor, 179; area-weighted soil erodibility factor, 0.413; Dunne overland flow, 1.33; and watershed area, 72.5 km^2. The input data for the area-weighted soil erodibility factor and Dunne overland flow were obtained from the USGS (Wesley Stone, personal communication, 2009).

To assess the possible ecological impacts of atrazine contamination in streams, running average herbicide concentrations were computed for 14-, 30-, 60-, and 90-day intervals for the entire period of record using Proc Expand (SAS Institute Inc., Cary, NC). These time intervals were chosen based on the USEPA atrazine IRED (USEPA, 2003). The exceedance criteria established by the IRED were 38, 27, 18, and 12 μg/l for the 14-, 30-, 60-, and 90-day running averages, respectively (USEPA, 2003). Daily flow-weighted herbicide concentrations were used for the running average calculations.

Creating a Cumulative Vulnerability Index for Predicting Herbicide Loss

A cumulative vulnerability index (CVI) was developed in an effort to predict annual atrazine loads. The index accounts for the interactions of atrazine application, atrazine dissipation kinetics, and the extreme temporal variability of surface runoff. The index was based on two equations, one for computing daily weights (Equation 1) and the other for computing the CVI for a given year (Equation 2). Equation (1) accounts for timing after application without involving quantitative discharge data by reducing the hydrograph to a series of binary event indicators,

$$\mathrm{DW}_i = \sum_{i=1}^{\mathrm{LA}} \mathrm{Ev}_i * \mathrm{e}^{(-kt)}, \tag{1}$$

where DW_i is the daily weight; Ev_i is the daily value of the event indicators, set equal to 0 if the daily discharge was <10 mm/day and equal to 1 if daily discharge was >10 mm/day; k is the first-order rate constant for atrazine dissipation kinetics, set equal to 0.0625/day based on field data from Ghidey *et al.* (2005); t is time, in days; and LA is the length of time over which the daily weights were computed, chosen to be 100 days. This corresponded to a minimum weight of 0.000335 using $k = 0.0625$/day. The application of a single value for k was based on the assumption that the atrazine dissipation rate was uniform in space and constant in time. Equation (2) computes the annual index weight for any particular year as given by,

$$\mathrm{CVI} = \sum_{j=1}^{\mathrm{LS}} \mathrm{DW}_j * \mathrm{DP}_j, \tag{2}$$

where CVI is the cumulative vulnerability index, DW_j is the daily weight computed from Equation (1), DP_j is the daily planting progress fraction, and LS is the length of the planting season for a given year. Daily planting progress was used as a surrogate for herbicide application timing, and these data were obtained from weekly planting progress data for the northeastern crop reporting district (USDA-NASS, 1992-2006a). In these data, the first reported planting progress value is the first nonzero value observed. Thus, a zero is prepended one week ahead of the first nonzero value, and all values are scaled to the maximum planting progress, making a range of weekly values from 0 to 1. This series of weekly values was then expanded to daily values by linear interpolation, and the daily planting values (DP_j) were found by difference from the prior day. The first day, last day, and length of the planting season were also obtained here. The time series of planting progress and runoff events started the first day of planting and was extended 100 days beyond the last day of planting. The CVI was determined for each of the 15 years of the study and then correlated to atrazine load to determine if the CVI explained a significant amount of the variation in annual atrazine load.

RESULTS AND DISCUSSION

Precipitation and Stream Discharge

Annual precipitation is reported as the deviation from the 37-year average annual precipitation of 915 mm for GCEW (Figure 2). Relative precipitation varied from 18.2% below to 49.5% above the annual average, with the two most extreme years occurring in 1992 and 1993. Eight years had above-average precipitation, and seven years had below-average precipitation. The magnitude of deviation from the annual average was greater overall for the wetter than normal years, with six of eight years >15% above normal precipitation.

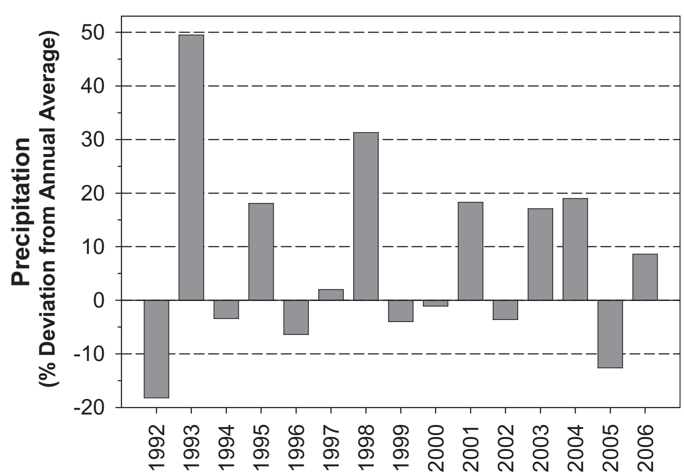

FIGURE 2. Relative Annual Precipitation in Goodwater Creek Experimental Watershed From 1992 to 2006.

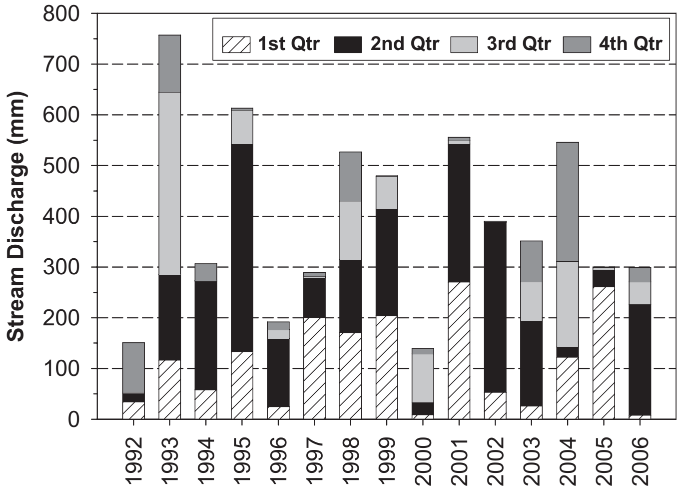

FIGURE 3. Annual and Quarterly Stream Discharge in Goodwater Creek Experimental Watershed From 1992 to 2006.

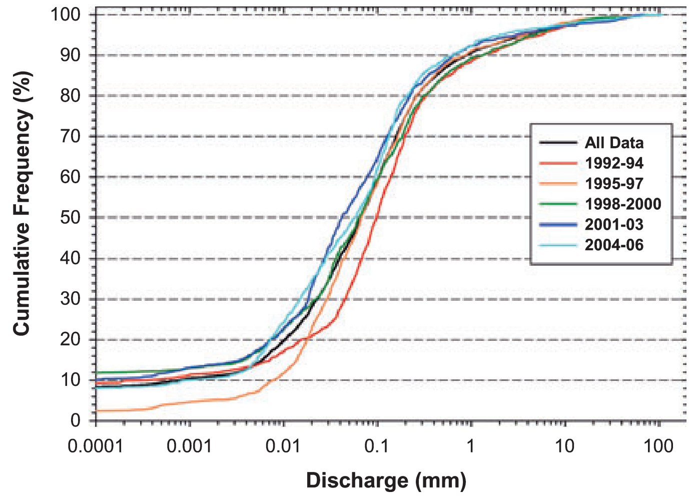

FIGURE 4. Cumulative Frequency Diagram of Daily Average Stream Discharge in Goodwater Creek Experimental Watershed.

Stream discharge varied from a low of 140 mm in 2000 to a high of 757 mm in 1993 (Figure 3). Discharge as a percent of precipitation averaged 39% over the 15-year period and ranged from 15% in 2000 to 57% in 1995. Second quarter discharge is potentially most important to herbicide transport as this period coincides with herbicide application and, as discussed above, is when the majority of the herbicide transport occurs. Those years in which >40% of annual discharge occurred during the second quarter included 1994-1996, 1999, 2001-2003, and 2006. In four years (1994, 1996, 2002, and 2006), ~70% of annual discharge occurred in the second quarter. For daily discharge, the low end of the distribution (<0.001 mm) showed that all three-year periods, except 1995-1997, had similar cumulative frequencies (8-13%) and an average of 30-40 days per year in which there was no discharge (Figure 4). In 1995-1997, there was an average of only nine days per year with no discharge. There was an increased frequency of discharge (i.e., lower cumulative frequency) in the 0.005-0.2 mm range during 1992-1994 and 1995-1997 compared to later periods. At the upper end of the distribution, the frequency of higher daily discharges (>1.0 mm) showed differences among the three-year periods, but no consistent time trend was apparent. The average number of days per year exceeding 1.0 mm of discharge was in the order: 1992-1994 (42 days) > 1998-2000 (39 days) > 1995-1997 (33 days) > 2001-2003 and 2004-2006 (28 days). Over the course of the study, overall changes among the major land-cover classes were minimal, but significant changes in the area planted to specific row crops did occur (Figure 5). Compared to variations in annual precipitation, the changes in row crop areas would be expected to have a negligible effect on stream discharge. These results indicated that higher base flow and/or more frequent small runoff events occurred during the first six years of the study, but the frequency of large runoff events showed no consistent time trend over the period of record.

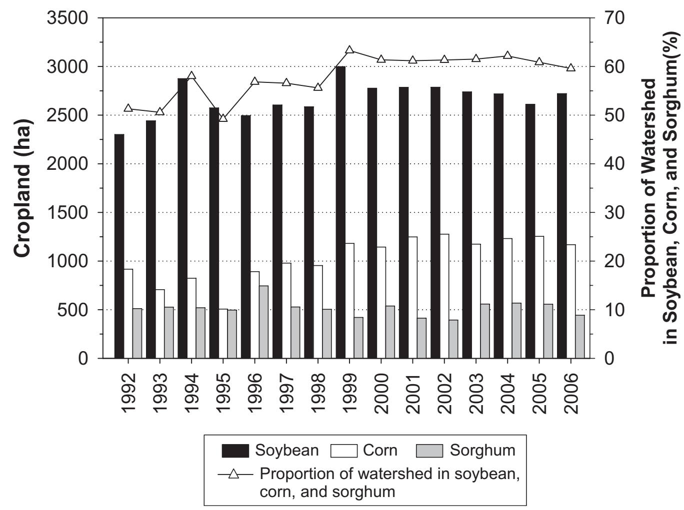

FIGURE 5. Planted Areas for Corn, Sorghum, and Soybean in Goodwater Creek Experimental Watershed, and the Combined Relative Proportion of the Watershed Planted to These Three Crops From 1992 to 2006.

Land and Herbicide Use

From 1992 to 2006, cropland areas within the watershed were in the order of soybean > corn > sorghum (Figure 5). Cropland planted to soybean ranged from 2,301 ha in 1992 to 2,998 ha in 1999, accounting

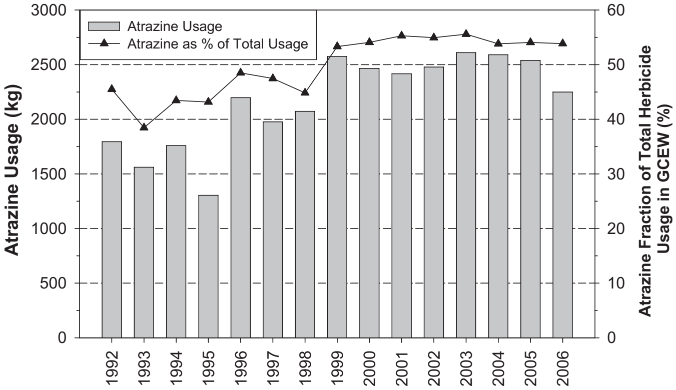

FIGURE 6. Estimated Atrazine Usage and Atrazine Usage as a Percent of the Total Soil-Applied Herbicide Usage in Goodwater Creek Experimental Watershed From 1992 to 2006.

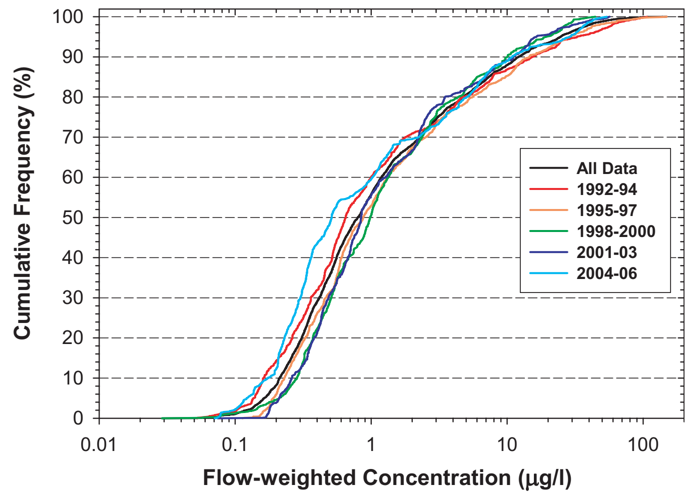

FIGURE 7. Cumulative Frequency Diagram of Daily Flow-Weighted Atrazine Concentrations in Goodwater Creek Experimental Watershed.

for 32-41% of the watershed. From 2000 to 2006, planted soybean area remained steady at about 2,700 ha. Cropland planted to corn ranged from 507 ha in 1995 to 1,277 ha in 2002. From 1992 to 1998, planted corn area was <1,000 ha, but in 1999 it increased to 1,182 ha and remained near 1,200 ha through 2006. Given the recent increase in demand for corn because of ethanol production, it was anticipated that planted corn area would increase in 2005 and 2006 compared to previous years. However, in 2005, planted corn area was very similar to previous years (i.e., 1999-2004), and it actually declined slightly in 2006. The area planted to corn ranged from 7 to 18% of the watershed, with an average of 14%. In most years, cropland planted to sorghum was about 500 ha, but it ranged from 394 ha in 2002 to 745 ha in 1996. The average planted sorghum area represented about 7% of the watershed area. Collectively, these three crops accounted for 49-63% of the watershed area (Figure 5).

Of the five herbicides included in this article and the companion article (Lerch *et al.*, this issue), atrazine was the most heavily used in every year, and it accounted for an increasing percentage of the total usage with time (Figure 6). From 1992 to 1998, atrazine usage was in the range of 1,300 to about 2,000 kg/year, and it accounted for 39-49% of the total herbicide usage in the watershed. From 1999 to 2006, atrazine usage was about 2,500 kg/year, except 2006 in which usage dropped to 2,250 kg, and it accounted for 53-56% of the soil-applied herbicide use in the watershed. From 1992 to 2006, atrazine use increased 25%. Despite significant decreases in the use of some soil-applied herbicides, the introduction of low application rate contact herbicides, and increased use of herbicide-resistant crop varieties, overall soil-applied herbicide use in the watershed increased with time from about 4,000 kg/year in the first three years of the study to about 4,600 kg/year from 1998 to 2005. In 2006, total use dropped to about 4,200 kg, a decline primarily attributed to decreased atrazine use (Figure 6). Discussion of the specific changes in use of the other four herbicides is presented in Lerch *et al.* (2010).

Atrazine Concentration and Load Trends

The CFD for daily flow-weighted atrazine concentrations showed little difference between three-year periods and no temporal trends in concentration were apparent (Figure 7). With respect to cumulative frequency, the largest spread in the data occurred at 50% (i.e., the median flow-weighted concentration). The lowest median concentration was 0.51 µg/l for 2004-2006, and the highest median concentration was 0.98 µg/l for 1998-2000. Furthermore, the median concentrations of all three-year periods were within 0.30 µg/l of the median for all data (0.80 µg/l). At the upper end of the concentration distribution, cumulative frequencies of the three-year periods differed by only about 5% for concentrations >2 µg/l.

For individual years, median flow-weighted atrazine concentrations varied from 0.35 µg/l in 1993 to 2.0 µg/l in 1999 (Table 1). Minimum concentrations were always above the detection limit, indicating that atrazine was always detectable in the >1,200 samples collected from Goodwater Creek over the course of the study. Maximum concentrations ranged from 23.6 µg/l in 2003 to 149 µg/l in 1996. These maximum concentrations exceeded the USEPA level of concern in every year of the study, but the duration

TABLE 1. Atrazine Flow-Weighted Concentrations (μg/l) for Selected Percentiles.

Year	Minimum	10th	25th	Median	75th	90th	Maximum
All data	0.029	0.212	0.350	0.797	3.09	12.2	149
1992	0.263	0.409	0.572	1.01	2.84	47.1	106
1993	0.130	0.163	0.246	0.354	1.03	18.1	59.5
1994	0.053	0.120	0.218	0.889	4.25	8.04	24.3
1995	0.162	0.253	0.399	0.599	1.38	5.71	66.8
1996	0.116	0.222	0.307	1.37	7.26	19.9	149
1997	0.113	0.197	0.569	1.16	3.09	19.2	99.3
1998	0.029	0.219	0.414	1.02	1.79	10.0	44.5
1999	0.074	0.285	0.493	2.01	8.10	13.5	26.5
2000	0.249	0.318	0.412	0.844	2.71	4.99	30.9
2001	0.170	0.261	0.365	0.725	2.10	11.0	56.7
2002	0.161	0.221	0.660	1.32	3.48	14.7	42.0
2003	0.074	0.341	0.434	0.748	2.46	6.96	23.6
2004	0.074	0.121	0.240	0.465	3.12	9.21	52.9
2005	0.070	0.142	0.292	0.931	3.29	11.8	44.8
2006	0.137	0.207	0.302	0.456	3.57	11.3	54.0
Median	0.116	0.221	0.399	0.889	3.09	11.3	52.9

TABLE 2. Linear Regression Analysis to Assess Trends in Atrazine Concentration and Load From 1992 to 2006.

Dependent Variable	r^2	p-Value	Slope
Minimum[1]	0.06	0.39	−0.004
10th percentile[1]	0.03	0.51	−0.003
25th percentile[1]	0.01	0.76	−0.003
Median concentration[1]	0.01	0.67	−0.011
75th percentile[1]	<0.01	0.89	0.018
90th percentile[1]	**0.26**	**0.09**	**−1.30**
Maximum concentration[1]	0.17	0.13	−3.23
Absolute load[1]	0.02	0.65	−2.48
Relative load[1]	0.11	0.22	−0.329

Notes: Regular type indicates no statistical significance for linear regression or autocorrelation. Bold type indicates significant autocorrelation, with the parameters derived from autoregression. r^2, coefficient of determination; p-value, probability of observing a more extreme value for the F-statistic; slope units = μg/l/year.
[1]Independent variable is time, in years.

in which atrazine concentrations remained above the level of concern varied considerably over the years (see below). In addition, the 90th percentile concentrations were 10 μg/l or greater in 10 of 15 years. Hence, the level of concern was exceeded for about 37 days per year in those years with a 90th percentile concentration >10 μg/l. Regression analyses showed no trends over years for any of the percentile concentrations, with the exception of the 90th percentile which showed a significant decrease (Table 2).

Although these concentrations were within the range reported for other agricultural watersheds (Blanchard and Lerch, 2000; Lerch and Blanchard, 2003; Battaglin *et al.*, 2005; Scribner *et al.*, 2005), these studies mainly focused on specific periods of the year, rather than year-round monitoring, so they were not directly comparable to the GCEW data. The prediction of specific percentile concentrations using the WARP model, which was based on year-round data, provided better insight as to how atrazine concentrations in GCEW compared against other watersheds across the nation. As the WARP model was regression based, it represents an estimation of the mean atrazine concentrations (for specific percentiles) from a spatially broad input dataset. The comparison of interest here was to assess whether or not the temporal variability encompassed within the GCEW dataset would fall within the spatially broad dataset used to develop WARP. Results of the WARP predictions showed that it underestimated concentration compared to those observed in GCEW for all percentiles (Figure 8). Estimates for the 10th and 25th percentiles were within a factor of two of that observed in GCEW, but the error increased considerably with increasing percentiles. In addition, all of the WARP estimates were below the 95% confidence interval for the observed median concentration at each percentile. This comparison indicated that atrazine concentrations in GCEW were greater than the average concentrations of the 112 watersheds in the National Water-Quality Assessment Program (NAWQA) and the National Stream Quality Accounting Network (NASQAN) used to develop WARP (Larson *et al.*, 2004). This was especially true at the upper end of the concentration distribution, indicating that GCEW likely had greater atrazine concentrations than most other agricultural watersheds of the U.S. A review of the available NAWQA and NASQAN atrazine data

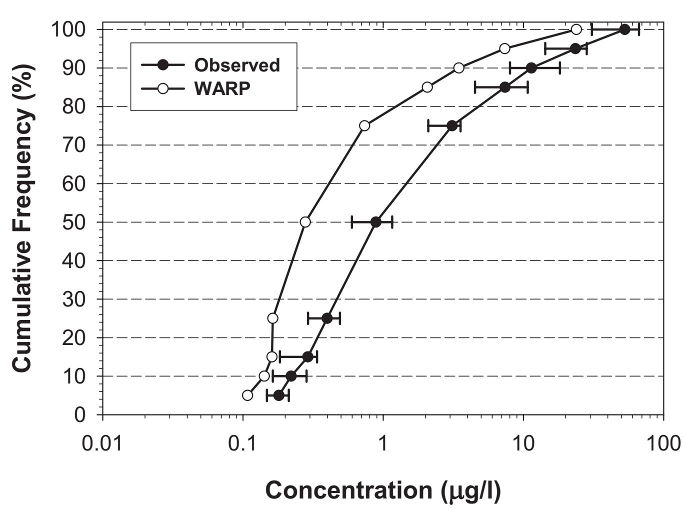

FIGURE 8. Cumulative Frequency Distributions Comparing Atrazine Concentrations Predicted by the Watershed Regression for Pesticides (WARP) Model Against the Observed Atrazine Concentrations for Goodwater Creek Experimental Watershed. Error bars for the observed median concentrations represent distribution-free 95% confidence intervals.

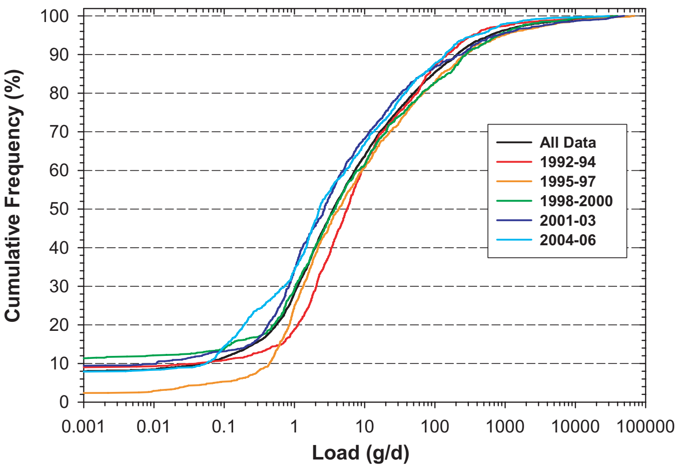

FIGURE 9. Cumulative Frequency Diagram of Daily Atrazine Load in Goodwater Creek Experimental Watershed.

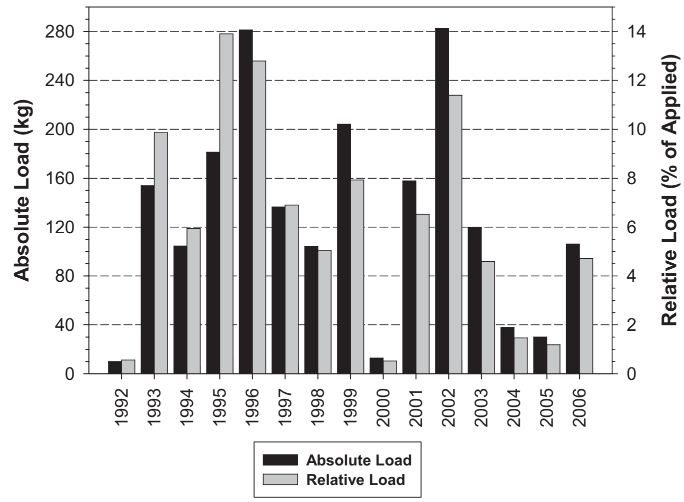

FIGURE 10. Absolute and Relative Annual Atrazine Loads in Goodwater Creek Experimental Watershed From 1992 to 2006.

(http://infotrek.er.usgs.gov/nawqa_queries/swmaster/) confirmed these conclusions. Two factors contributed to the underestimation of atrazine concentrations by WARP. First, three of the five WARP input parameters for GCEW were near the extremes of the input data used to develop WARP. These were the rainfall erosivity factor (75th percentile), atrazine use intensity (83rd percentile), and area-weighted soil erodibility factor (97th percentile). Collectively, the WARP input data for GCEW were more extreme than 104 of the 112 watersheds used to develop WARP (Larson *et al.*, 2004). Second, the sampling protocols for GCEW involved more frequent sampling, including all runoff events. The less intensive monitoring at the NAWQA and NASQAN sites would result in un-sampled runoff events, leading to lower estimations of atrazine concentrations for these sites.

Trends in daily atrazine load were confined to the lower end of the distribution (i.e., ≤10 g/day) (Figure 9). For example, median daily load decreased with time from 5.7 g/day in 1992-1994 to 2.3 g/day in 2004-2006 (Figure 9). The two earliest three-year periods (1992-1994 and 1995-1997) also had lower cumulative frequencies than later years over the range of 0.1-10 g/day (Figure 9). At daily loads of 10-300 g/day, the cumulative frequencies among three-year periods differed by 7% or less, and the differences continue to decrease as daily load increased above 300 g/day. Thus, for the higher end of the daily load distribution, there were no consistent time trends. Given the lack of trends for atrazine concentration, the trends observed for load were mainly attributed to stream discharge, and the pattern of the CFDs for discharge (Figure 4) and daily load (Figure 9) were very similar. Therefore, the consistently higher base-flow conditions observed for 1992-1994 and 1995-1997 resulted in a greater frequency of daily atrazine loads in the range of 0.1-10 g/day.

Annual atrazine load for the GCEW, on an absolute basis, ranged from 10.0 kg in 1992 to 282 kg in 2002, with a median of 120 kg (Figure 10). Relative atrazine loads, expressed as percent of applied, ranged from 0.56% in 1992 to 14% in 1995, with a median of 5.9% (Figure 10). These relative loads were within the range reported in other studies (Capel and Larson, 2001; Capel *et al.*, 2001; Lerch and Blanchard, 2003), but the median relative load for GCEW was even higher than the median relative load of 3.9% for 20 northern Missouri and southern Iowa streams (Lerch and Blanchard, 2003). The northern Missouri/southern Iowa region was shown by Lerch and Blanchard (2003) to be among the most vulnerable areas in the Midwest to herbicide transport. Moreover, vulnerability to herbicide transport was shown to correlate strongly with the proportion of the watershed area having high runoff potential soils. GCEW is located within the study area reported by Lerch and Blanchard (2003), and the watershed is dominated by high runoff potential soils, resulting in exceptionally high vulnerability to atrazine transport.

As expected, there was a strong correlation between relative and absolute load ($r = 0.91$; $p < 0.001$) over time, and linear regression analyses showed that both absolute and relative annual loads had negative slopes, but neither of the trends were significant (Table 2). Given the lack of a significant time trend in annual loads, atrazine use was also considered to help explain the observed variation in annual loads. However, annual atrazine use was not significantly correlated to absolute ($r = -0.06$; $p = 0.83$) or relative ($r = -0.41$; $p = 0.12$) annual loads, and the negative correlation coefficients indicate that annual use was an especially poor predictor of variation in annual loads for GCEW. This finding was also consistent with that of Richards *et al.* (1996) and Lerch and Blanchard (2003) in which land use (and therefore, herbicide use) was shown to be a less important factor to herbicide transport than soil properties and watershed hydrology. Second quarter stream discharge (Figure 3) was the only factor significantly correlated to absolute ($r = 0.69$; $p \leq 0.01$) or relative ($r = 0.77$; $p < 0.01$) annual loads. This finding is consistent with those of other studies that have documented the strong seasonal dependence of atrazine transport (Thurman *et al.*, 1992; Lerch *et al.*, 1995, 1998; Donald *et al.*, 1998; Blanchard and Lerch, 2000).

Annual Variation in Atrazine Transport

The significant relationship between load and second quarter discharge indicated that the dominant factor controlling annual variation in atrazine transport was weather; specifically, the timing of runoff-generating precipitation events relative to the extent of atrazine application in the watershed. Using crop district corn planting progress as a surrogate for atrazine application timing and extent across GCEW combined with the daily average stream discharge, a series of graphs was developed to show the dependence of atrazine transport on the timing of runoff events (Figure 11). The three years were chosen to represent a range in annual atrazine loads and stream discharge conditions (Figures 3 and 10), including the median load (2003), highest load (1996), and second lowest load (2000). For each year, the critical transport period was defined as a flexible window that begins with the initiation of spraying activities and ends 37 days after spraying ceased. The 37-day interval represents the point at which predicted atrazine concentrations fall to 10% of the maximum edge-of-field concentration when atrazine is incorporated or to 0.1% of maximum edge-of-field concentration for unincorporated atrazine, using the equations, $[C] = 355e^{-(0.0625*t)}$ or $[C] = 5{,}379e^{-(0.1774*t)}$, where C is the concentration (μg/l) and t is time (days) (Ghidey *et al.*, 2005).

In 1996, only 192 mm of stream discharge occurred for the year, but the majority of the year's discharge occurred during the second quarter (133 mm) (Figure 3), resulting in an extremely high atrazine load (Figure 10). The four runoff events that occurred during the critical transport period in 1996 accounted for 95% of the annual atrazine load and 67% of the annual stream discharge (Figure 11). Thus, 1996 represented a near worst-case scenario in which a significant portion of the corn area in the watershed was

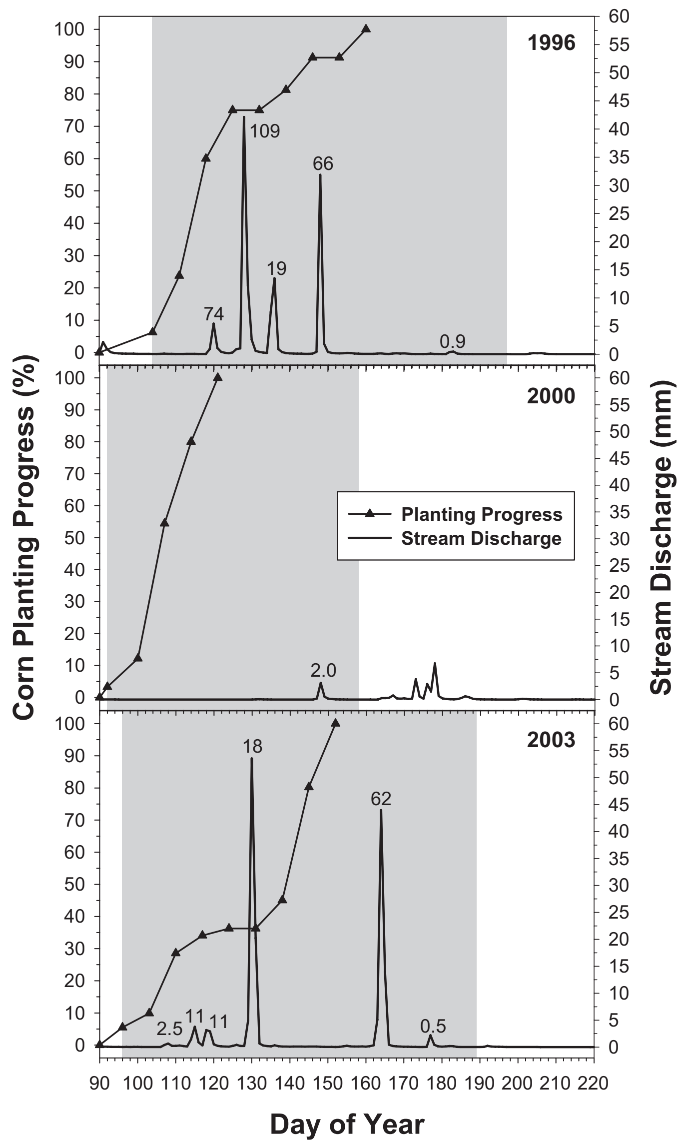

FIGURE 11. Relationship of Corn Planting Progress, Runoff Event Timing, and Runoff Event Magnitude for 1996, 2000, and 2003. Numbers adjacent to the runoff event hydrographs represent the atrazine load, in kg, transported by each event during the critical transport period (shown in gray).

sprayed (60% by day 118) immediately followed by a series of runoff events. The opposite scenario occurred in 2000 when spraying was completed by day 121 followed by only one small runoff event 26 days after spraying was completed (Figure 11). This event transported 2.0 kg of atrazine, and it accounted for only 16% of the annual load and 3.1% of the annual discharge. Three small runoff events just outside the critical transport period, from days 163 to 183 (Figure 11), accounted for an additional 2.8 kg of atrazine transported. Even if these additional events were included, the four events would have accounted for only 38% of the annual load and

17% of the annual discharge. Thus, the combination of a small magnitude runoff event during the critical transport period, a considerable time lag between application and the runoff event, and low annual stream discharge (140 mm) resulted in very little atrazine transport in 2000 (Figure 10). The interaction between the extent of spraying activities and the timing of runoff events in 2003 represented a typical scenario for atrazine transport in GCEW. There were six runoff events during the critical transport period, accounting for 87% of the annual load and 46% of the annual stream discharge (Figure 11). Four of the six runoff events occurred when only 36% or less of the corn area had been treated, and these events transported a total of 42.5 kg of atrazine. Following the fourth event, dry soil conditions permitted the remainder of the corn area to be treated, and this period of spraying activity was then followed 10 days later by the fifth and largest event, in terms of atrazine load, with 62.0 kg transported.

The mass of atrazine transported by runoff events occurring within the critical transport period demonstrated the interaction between the timing of a runoff event relative to spraying activities (Figure 11). Historical dependence of both concentration and load on the time to the first runoff event after application suggests that the hydrograph could be reduced to a sequence of binary event indicators, thus accounting for timing after application without involving quantitative flow. The CVI was developed to account for the complex interactions between herbicide application and the occurrence of surface runoff events, as well as the dissipation kinetics of atrazine. Regression analysis of the CVI *vs.* annual atrazine load (Figure 12) showed that the CVI explained 63% of the variation in atrazine loads ($r^2 = 0.63$; $p \leq 0.01$), demonstrating that it successfully captured the relevant variables that contribute to annual variation in atrazine transport at the watershed scale. Furthermore, when load data for 2007 and 2008 were predicted using the developed vulnerability index, the predictions were within 21 and 1.9% of their observed loads, respectively (Figure 12). Inclusion of these two years in the regression analysis further improved the relationship between the CVI and annual loads ($r^2 = 0.68$; $p < 0.01$).

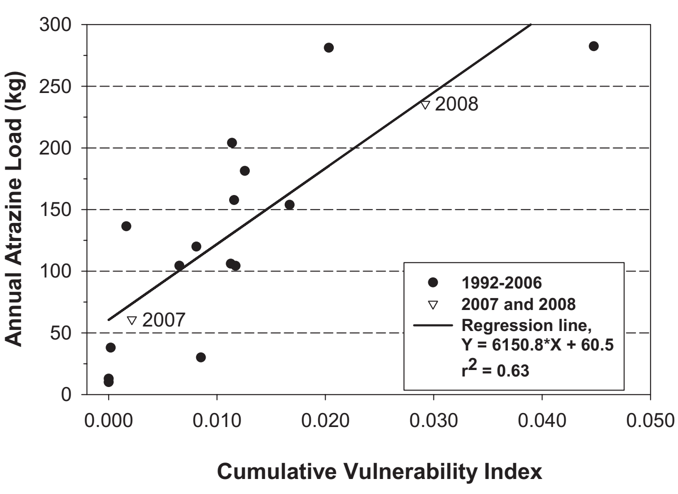

FIGURE 12. Annual Index of Atrazine Loss Vulnerability Correlated to Annual Atrazine Loads.

Retrospective Assessment of Potential Aquatic Ecosystem Impact

With the establishment of specific concentration criteria related to possible impacts of atrazine on aquatic ecosystems (USEPA, 2003), a retrospective assessment of the 15-year dataset was performed (Table 3). The four running average criteria (Table 3) were established under the IRED as screening concentrations that, when exceeded, require the application of the Comprehensive Aquatic Systems Model (CASM) (DeAngelis *et al.*, 1989; Bartell *et al.*, 1999) to assess the possible effects on aquatic communities. The running average criteria and CASM were developed to establish regulatory criteria for a monitoring project designed to assess the ecological significance of atrazine in 40 midwestern streams located in agricultural watersheds with high atrazine use intensity (USEPA, 2003, 2007). One site included in this monitoring project was GCEW, which was sampled from

TABLE 3. Days per Year in Which the Running Average Atrazine Concentration Exceeded the Screening Criteria Established by the USEPA Interim Re-registration Eligibility Decision (IRED)[1].

Year	14-Day	30-Day	60-Day	90-Day
1992	35 (86.4)	44 (71.1)	68 (47.1)	105 (32.3)
1993	0	6 (29.2)	34 (23.3)	66 (16.9)
1994	0	0	0	0
1995	8 (44.9)	5 (27.6)	0	0
1996	14 (62.1)	25 (38.7)	44 (26.4)	93 (23.4)
1997	18 (65.3)	30 (47.1)	56 (30.5)	89 (22.3)
1998	0	0	0	0
1999	0	0	0	0
2000	0	0	0	0
2001	5 (43.0)	2 (27.3)	0	24 (12.9)
2002	0	0	0	16 (13.1)
2003	0	0	0	0
2004	0	9 (29.4)	7 (18.4)	40 (13.2)
2005	0	0	0	59 (13.5)
2006	2 (38.3)	15 (34.5)	35 (19.5)	69 (14.8)

Note: Numbers in parentheses indicate the maximum running average for the year, in μg/l.
[1]Running average concentration screening criteria established by the IRED: 14-day = 38 μg/l; 30-day = 27 μg/l; 60-day = 18 μg/l; 90-day = 12 μg/l.

2004 to 2006 at the Agricultural Research Service (ARS) site described in this article.

In 10 of 15 years, at least one of the running average criteria was exceeded in GCEW, and in 8 of those years, multiple running averages were exceeded (Table 3). Four years exceeded all four running averages for multiple days (1992, 1996, 1997, and 2006). The 14- and 60-day criteria were exceeded least frequently (6 of 15 years), and the 90-day criterion was exceeded most frequently (9 of 15 years). Exceedance of any criteria for only one day is sufficient to invoke the application of CASM to assess possible ecological impacts (USEPA, 2003). The years with three or more criteria exceeded were quite dissimilar in terms of second quarter discharge (Figure 3) or annual atrazine loads (Figure 10). However, these years did share common patterns with respect to their flow-weighted concentrations, with >30 consecutive days per year exceeding 10 μg/l and peak concentrations >50 μg/l for at least one day per year. For example, in 1992 flow-weighted atrazine concentrations reached a peak of 106 μg/l, and atrazine concentrations exceeded 10 μg/l for 53 days. In the five years with no exceedance (1994, 1998, 1999, 2000, and 2003), high concentrations occurred in two or more discontinuous periods over shorter time intervals (<20 days), and peak concentrations were generally <40 μg/l and always <50 μg/l. There was only one period of consecutive years, from 1998 to 2000, without an exceedance of the screening criteria. Thus, short-term monitoring in relatively small watersheds like GCEW may result in underestimation of the potential ecological impact of atrazine. Because of the annual variation in conditions that cause high atrazine concentrations, these long-term monitoring results provided a more accurate characterization of the frequency with which atrazine impacted the aquatic ecosystem in GCEW.

Comparison of maximum running averages between the USEPA and the ARS monitoring at GCEW showed that the ARS results were consistently higher from 2004 to 2006 (Table 4). However, results in 2004 and 2006 showed much closer agreement than in 2005, when the ARS results were 1.5-1.8 times greater than the USEPA results. The differences in the two datasets reflected the different sampling protocols of the projects. The IRED sampling protocol required collection of grab samples every four days, regardless of flow conditions. It also called for the use of stair-step interpolation to estimate concentrations for un-sampled days (USEPA, 2007). As detailed above, the ARS data represented all runoff events combined with weekly base-flow samples and linear interpolation to estimate concentration on un-sampled days. As runoff events typically last less than four days in GCEW, the USEPA sampling protocol assuredly resulted in un-sampled peak concentrations. Apparently, the much lower running averages for the USEPA data in 2005 (Table 4) resulted from a greater proportion of un-sampled runoff events containing high atrazine concentrations than occurred in 2004 or 2006.

TABLE 4. Comparison of Maximum Running Average Atrazine Concentrations (μg/l) Between ARS[1] and USEPA[2] for Goodwater Creek Experimental Watershed.

Year	Agency	14-Day	30-Day	60-Day	90-Day
2004	ARS	33.0	29.4	18.4	13.2
	USEPA	33.0	25.9	16.8	12.3
2005	ARS	33.7	24.7	16.7	13.5
	USEPA	18.7	14.6	11.5	9.1
2006	ARS	38.3	34.5	19.5	14.8
	USEPA	34.7	27.4	15.4	11.3

[1]USDA-Agricultural Research Service monitoring project detailed in this report.
[2]USEPA (2007) monitoring project to assess the ecological significance of atrazine concentrations in streams.

SUMMARY AND CONCLUSIONS

This 15-year study of atrazine transport in GCEW facilitated the assessment of trends in atrazine concentration and load, as well as a retrospective assessment of potential aquatic ecological effects from atrazine exposure. Because of the long-term nature of this study, atrazine transport was studied under a broad range of precipitation and stream discharge conditions, as well as varying land and atrazine use. Relative annual atrazine loads varied from 0.56 to 14% of applied, with a median of 5.9%. This median relative load is among the highest reported in the literature. Comparisons between atrazine concentrations predicted by WARP with observed concentrations showed that WARP predictions were always less than the lower 95% confidence interval for percentiles ranging from 5 to 100%. The high median relative loads and the results of the WARP comparisons demonstrated the extreme vulnerability of this claypan watershed to herbicide transport.

Atrazine reached concentrations that may be harmful to aquatic ecosystems in 10 of 15 years, and in those years, running average concentrations typically exceeded the screening criteria established by the USEPA for days to weeks each year. Recent USEPA data showed that the ecological level of concern for atrazine was exceeded frequently enough that atrazine registrants are now required to work with farmers in GCEW to implement practices which will reduce atrazine transport. The results presented here show that these conditions have persisted for most of the last 15 years. The implications of this study relative to herbicide management and the extent of BMP implementation within the watershed are discussed in the companion study (Lerch *et al.*, this issue).

On the basis of CFDs and linear regression analyses, the results showed no significant time trends for atrazine concentration. This was the case over a broad range of concentrations, spanning four orders of magnitude. Atrazine load showed no trends existed with respect to the frequency of daily loads >10 g/day. Furthermore, the observed trends in daily load were mainly a function of trends in stream discharge. The small increase in atrazine use over the course of this study was too small to affect trends in atrazine concentration or load. A newly developed CVI based on crop planting progress (surrogate for spraying progress), atrazine soil dissipation kinetics, and the occurrence of runoff events was shown to correlate highly to annual atrazine loads. Thus, these three parameters appear to be the key factors controlling annual variation in atrazine transport at the scale of this watershed.

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DISCLAIMER

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