

# Nutrient and Herbicide Movement in Streamflow from Two Midwestern Watersheds

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## Abstract

Watersheds in different geographic areas offer many opportunities to study how differences in climate, crops, soils, and landscapes affect the off-site movement of runoff, sediment, nutrients, herbicides, and other environmental contaminants. The objective of this research was to compare differences in nitrate-nitrogen ( $\text{NO}_3\text{-N}$ ) and atrazine concentrations and discharges in streamflow from two watersheds in the Midwest for a 10-year period, 1992 through 2001. One watershed was the 7,280-ha Goodwater Creek watershed located in north-central Missouri, the other, the 5,130-ha Walnut Creek watershed in central Iowa. The Goodwater Creek watershed is located in the Central Claypan Major Land Resource Area (MLRA 113). Soils within this watershed are poorly drained because of a subsurface horizon 150 to 300 mm deep that has a clay content greater than 50%. The Walnut Creek watershed is located in the Central Iowa and Minnesota Till Prairies Major Land Resource Area (MLRA 103). Many of the soils within this watershed are tile drained to increase productivity. Over 80% of the area within each watershed is cropped, but the fraction of corn cropping is higher in the Walnut Creek watershed. The drainage outlet of each watershed is instrumented with a concrete v-notch weir, water stage recorder, and refrigerated automatic pumping sampler. During low stages of streamflow, grab samples of baseflow were collected at the weir for chemical analyses. Mean annual precipitation values (1992-2001) for the Goodwater and Walnut Creek watersheds were 997 and 785 mm, with mean annual streamflow discharges of 392 and 223 mm,

respectively. Mean annual  $\text{NO}_3\text{-N}$  discharges from the Goodwater and Walnut Creek watersheds were 6.9 and 20.4  $\text{kg ha}^{-1}$ . Flow-weighted  $\text{NO}_3\text{-N}$  concentrations (10 years) from the Goodwater and Walnut Creek watersheds were 1.8 and 9.2  $\text{mg L}^{-1}$ , with flow-weighted annual concentrations ranging from 1.2 to 2.7  $\text{mg L}^{-1}$  for Goodwater Creek and 6.3 to 13.1  $\text{mg L}^{-1}$  for Walnut Creek. The highest  $\text{NO}_3\text{-N}$  concentrations from both watersheds occurred during the April through June seasonal period, with 10-year flow-weighted concentrations of 2.1 and 11.2  $\text{mg L}^{-1}$  for the Goodwater and Walnut Creek watersheds. Mean annual atrazine discharges from the Goodwater and Walnut Creek watersheds were 18.1 and 1.7  $\text{g ha}^{-1}$ . Flow-weighted atrazine concentrations from the Goodwater and Walnut Creek watersheds for the 10-year period were 4.6 and 0.8  $\text{ug L}^{-1}$ , with flow-weighted annual concentrations ranging from 0.8 to 19.3  $\text{ug L}^{-1}$  for Goodwater Creek and 0.1 to 1.9  $\text{ug L}^{-1}$  for Walnut Creek. The highest atrazine concentrations occurred during the April through June seasonal period, with 10-year flow-weighted concentrations of 9.3 and 1.3  $\text{ug L}^{-1}$  for the Goodwater and Walnut Creek watersheds. Our results show that water quality problems associated with crop production are dependent on how water moves within and through the watershed topography because of soil and anthropogenic factors. In the Goodwater Creek watershed, streamflow is comprised of about 90% surface runoff and 10% ground water recharge, and in such a hydrologic environment, atrazine is much more susceptible to movement. The soils within the Walnut Creek watershed are more permeable and the pot-hole topography limits the amount of natural surface runoff. About 74% of the streamflow discharge from Walnut Creek over the 10-year period was tile drainage.  $\text{NO}_3\text{-N}$ , being mobile in the soil, readily entered the tile drain system and moved rapidly from upland areas of the watershed to Walnut Creek.

**Keywords:** atrazine,  $\text{NO}_3\text{-N}$ , water quality

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## Introduction

The Clean Water Act of 1972 has improved the quality of our nation's water resources primarily by targeting and solving point-source pollution problems associated with discharge of contaminated industrial effluent. However, pollution from nonpoint sources is currently perceived as one of the nation's most serious water quality problems. The U.S. Environmental Protection Agency (EPA) has estimated that 70 percent of impaired rivers and streams and 49 percent of impaired lake areas are impacted adversely by agricultural activities (U.S. EPA 1998).

The most important nonpoint-source water quality problem in the Midwest is stream water contamination resulting from agricultural practices. This research focuses on contamination associated with nutrients and pesticides, specifically  $\text{NO}_3\text{-N}$  and atrazine. Discharges of  $\text{NO}_3\text{-N}$  from the Mississippi River Basin have been linked to the increased spread and severity of hypoxia within the Gulf of Mexico (Rabalais et al. 1996, CAST 1999). About 55% of the nitrogen released from the Basin has been attributed to nitrogen fertilizer used to supplement natural soil fertility in crop production. The leaching of  $\text{NO}_3\text{-N}$  and the interception and release from tile-drained fields have been identified as important causal factors (Tomer et al. 2003).

Atrazine has been used by farmers for over 40 years as a low-cost, broad spectrum, and season-long herbicide. In recent years, it has been linked to hormonal disruptions, both in humans and animals, and an increased risk of cancer. Currently, atrazine is applied to about two-thirds of the corn and sorghum acreage in the U.S. Atrazine from farm fields and watersheds has been found to be the major contaminant of stream water throughout the Midwestern U.S., being detected in 90% or more of the stream water samples. (Thurman et al. 1992, Lerch et al. 1998, Blanchard and Lerch 2000). Concentrations often exceed the EPA maximum contaminant level (MCL) of  $3 \text{ ug L}^{-1}$  in the post-plant period, following atrazine application. Because seasonal rainfall amounts and distribution cannot be accurately predicted, herbicide losses in runoff are largely unpredictable. To reduce atrazine losses in surface runoff, research has focused on approaches to reduce application rates, particularly on soils with high runoff potential (Donald et al. 2001).

Watersheds can vary greatly in their hydrologic and water quality responses to management inputs, even for similar cropping systems, because of differences in climate, soils, management inputs, and landscape topography. Research results from multiple watersheds located in different areas of the U.S. are needed to help assess regional and national impacts of agricultural practices on water quality.

The objective of this research was to compare differences in  $\text{NO}_3\text{-N}$  and atrazine concentrations and discharges in streamflow from two watersheds in the Midwest. The study spans a 10-year period, 1992 through 2001, and represents normal variations in precipitation characteristics; such as amount, intensity, and timing relative to cultural operations and chemical applications.

## Methods

### Goodwater Creek watershed

This 7,260-ha watershed is within the Central Claypan Soils Major Land Resource Area (MLRA 113), an area of about 4 M ha. About 90% of the watershed is cropped following the ranking of soybeans >> wheat > corn > sorghum > hay. Typical crop rotations are corn/soybeans, corn/soybeans/wheat, soybean/soybeans/wheat, and sorghum/soybean/wheat.

The topography is characterized by broad, nearly flat divides, gentle side slopes, and broad alluvial valleys often dissected with small streams. The soils generally have a silt-loam surface texture underlain by an argillic horizon 150 to 300 mm below the soil surface. The clay content of the argillic horizon is generally > 50% and is comprised primarily of montmorillonite. Principle soils are the Udollic Ochraqualfs, Albaquic Hapludalfs, and Vertic Ochraqualfs. Many soils that occupy moderately to severely eroded side slope positions have a silty clay texture due to the incorporation of the claypan into the surface horizon by plowing and disking operations.

The long-term mean annual precipitation is 929 mm. Spring rainfall often occurs as intense, short duration thunderstorms on recently tilled and planted soils. Fall rainfall often occurs as low intensity, long duration events associated with slow moving cold fronts. Water content of the soil root zone decreases during the summer because high evapotranspiration

from rapidly growing and maturing crops exceeds rainfall.

### Walnut Creek watershed

This 5,130-ha watershed is within the Central Iowa and Minnesota Till Prairies Major Land Resource Area (MLRA 103), an area of about 7.2 M ha. About 92% of the watershed is in crop production, primarily a corn-soybean rotation. About 15% of the corn acreage is in continuous cropping. Topography is undulating with poorly developed surface drainage. Low relief swells and swales create closed drainage depressional areas called potholes. The western portion of the watershed has an extensive tile drainage network that connects the potholes throughout the landscape. Many potholes have risers above the soil surface to capture surface runoff. Tile drainage feeds into a network of large subsurface drains maintained by county drainage districts. Almost 75% of the watershed is tile drained, and it is this underground delivery system of drainage water to Walnut Creek that is its major defining feature (Jaynes et al., 1999). There is more natural surface drainage in the eastern portion of the watershed near the outlet.

Principle soils within the watershed are Typic Hapludolls, Typic Haplaquolls, and Aquic Hapludolls. These upland soils generally have a loam texture and moderate permeability. Soils in, and adjacent to, the pot holes typically have mucky silt loam and silty clay loam textures and are poorly to very poorly drained.

The long-term mean annual precipitation is 818 mm. Rainfall during the spring and summer often occurs as brief, but intense, thunderstorms.

### Instrumentation and laboratory procedures

Similar procedures were used for field data and sample collection as well as laboratory preparation and analyses of streamflow samples. Streamflow was measured continuously at the outlet of both watersheds using a data logger to measure stream height (stage). Measured and/or theoretical relationships between discharge rate and stage were used to compute streamflow discharge. When stage height reached a predetermined level, the pumping sampler at each location was activated. Stringent quality assurance/quality control procedures were used in the field collection, transport, storage, processing, and analyses of all samples. NO<sub>3</sub>-N

concentrations were determined using similar autoanalyzers that reduce nitrate to nitrite with concentrations determined colorimetrically. For atrazine, samples were passed through a solid phase extraction cartridge and then analyzed using gas chromatography with N-P or mass spectral (MS) detection. To compute discharges, sample concentrations were matched with the representative flow volume and multiplied. The products of these computations were then summed over time.

## Results

### Precipitation and streamflow

Mean annual precipitation values for the Goodwater Creek and Walnut Creek watersheds were 997 and 785 mm. For the Goodwater Creek watershed, precipitation for the 10-year period was 7% higher than the 60-year long term value of 929 mm; while for Walnut Creek, the 10-year mean annual was 4% lower than the 30+ long-term value of 818 mm.

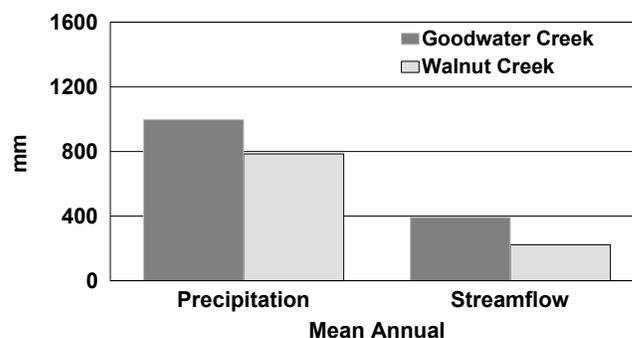


Figure 13. Mean annual precipitation and stream flow.

The 10-year mean annual streamflow values from Goodwater Creek and Walnut Creek were 392 and 223 mm, respectively (Figure 1).

Figure 2 shows the annual values of precipitation and streamflow during the 10-year period. Annual precipitation for Goodwater Creek ranged from 775 mm in 1992 to 1373 mm in 1993, while annual precipitation for Walnut Creek ranged from 497 mm in 2000 to 1288 mm in 1993. Highest streamflow from both watersheds occurred in 1993, with values of 785 and 865 mm from Goodwater Creek and Walnut Creek. Lowest streamflow from both watersheds occurred in 2000, with 50 mm of streamflow from Goodwater Creek and 7 mm from Walnut Creek.

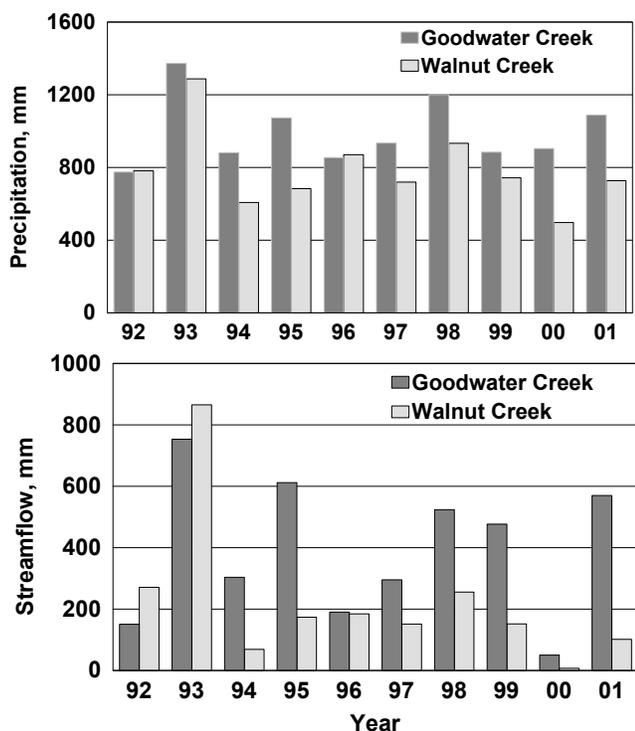


Figure 14. Annual precipitation and streamflow discharges.

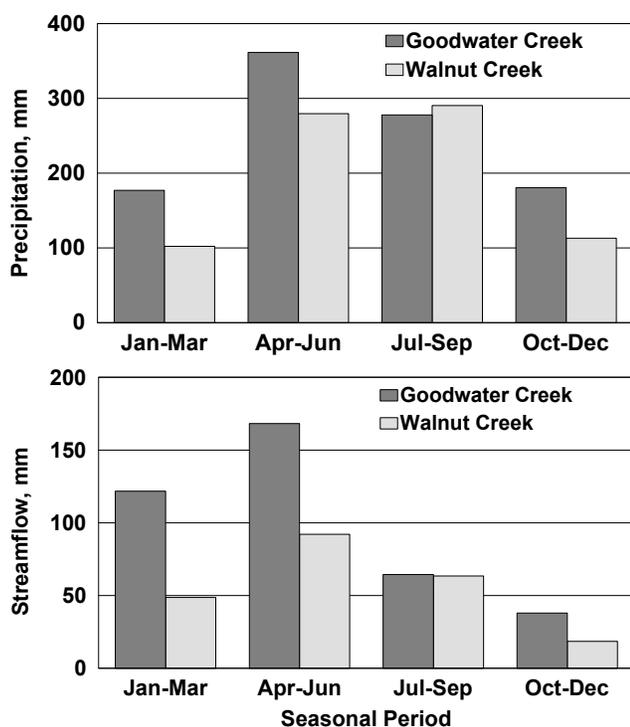


Figure 15. Seasonal precipitation and streamflow discharges.

For Goodwater Creek, 18, 36, 28, and 18% of the precipitation occurred for the Jan-Mar, Apr-Jun, Jul-Sep, and Oct-Dec seasonal periods (Figure 3). Respective values for Walnut Creek were 13, 36, 37, and 14%. For Goodwater Creek, 31, 43, 16, and 10% of the streamflow occurred for the Jan-Mar, Apr-Jun, Jul-Sep, and Oct-Dec seasonal periods. Respective values for Walnut Creek were 22, 41, 29, and 8%. On both an absolute and relative basis, the period of highest streamflow was the Apr-Jun period coinciding with the period of N fertilizer and atrazine application for row-crops in both watersheds.

### Nitrate-nitrogen

Mean annual  $\text{NO}_3\text{-N}$  discharges from the Goodwater and Walnut Creek watersheds for the 10-year period were 6.9 and 20.4  $\text{kg ha}^{-1}$ . Annual  $\text{NO}_3\text{-N}$  discharge from Goodwater Creek ranged from 0.75  $\text{kg ha}^{-1}$  in 1992 to 11.8  $\text{kg ha}^{-1}$  in 1993, while annual discharges from Walnut Creek ranged from 0.76  $\text{kg ha}^{-1}$  in 2000 to 61.5  $\text{kg ha}^{-1}$  in 1993 (Figure 4).

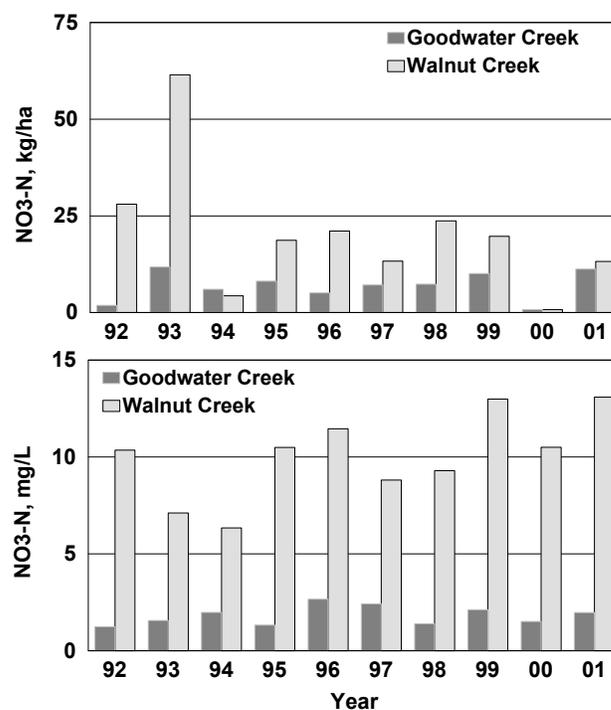


Figure 16. Annual discharges and concentrations of  $\text{NO}_3\text{-N}$ .

Flow-weighted  $\text{NO}_3\text{-N}$  concentrations from the Goodwater and Walnut Creek watersheds for the 10-year period were 1.8 and 9.2  $\text{mg L}^{-1}$ . Figure 4 shows the year-to-year values of flow-weighted  $\text{NO}_3\text{-N}$  concentrations. Flow-weighted  $\text{NO}_3\text{-N}$  concentrations for Goodwater Creek ranged from 1.2  $\text{mg L}^{-1}$  in 1992 to 2.7  $\text{mg L}^{-1}$  in 1996, while flow-weighted

concentrations for Walnut Creek ranged from 6.3 mg L<sup>-1</sup> in 1994 to 13.1 mg L<sup>-1</sup> in 2001. Flow-weighted concentrations for 6 of the 10 years from Walnut Creek exceeded the 10 mg L<sup>-1</sup> MCL established by the EPA for drinking water.

Seasonal NO<sub>3</sub>-N concentrations for the two watersheds are shown in Figure 5. For Goodwater Creek, seasonal flow-weighted concentrations for the Jan-Mar, Apr-Jun, Jul-Sep, and Oct-Dec periods were 1.6, 2.1, 1.5, and 1.2 mg L<sup>-1</sup>, while respective values for the Walnut Creek watershed were 7.2, 11.2, 7.6, and 9.7 mg L<sup>-1</sup>.

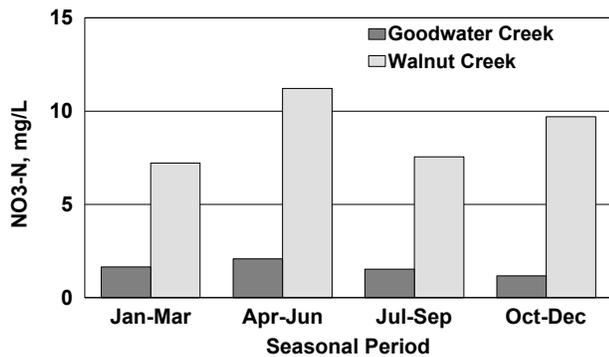


Figure 17. Seasonal NO<sub>3</sub>-N concentrations.

### Atrazine

Mean annual atrazine discharges from the Goodwater and Walnut Creek watersheds for the 10-year period were 18.1 and 1.8 g ha<sup>-1</sup>. Annual atrazine discharge from Goodwater Creek ranged from 1.3 g ha<sup>-1</sup> in 1992 to 36.7 g ha<sup>-1</sup> in 1996, while annual discharges from Walnut Creek ranged from 0.10 g ha<sup>-1</sup> in 2000 to 7.5 g ha<sup>-1</sup> in 1993 (Figure 6).

Flow-weighted atrazine concentrations from the Goodwater and Walnut Creek watersheds for the 10-year period were 4.6 and 0.78 ug L<sup>-1</sup>. Flow-weighted atrazine concentrations from Goodwater Creek ranged from 0.84 ug L<sup>-1</sup> in 1992 to 19.3 ug L<sup>-1</sup> in 1996, while flow-weighted concentrations from Walnut Creek ranged from 0.08 ug L<sup>-1</sup> in 1997 to 1.9 ug L<sup>-1</sup> in 2001 (Figure 6). Flow-weighted concentrations from Goodwater Creek exceeded the 3 ug L<sup>-1</sup> MCL established by the EPA for 7 of the 10 years.

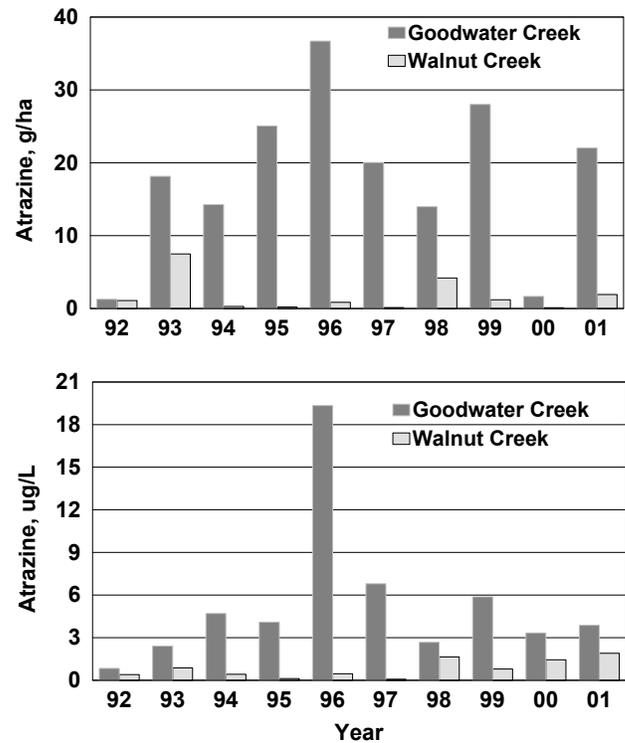


Figure 6. Annual discharges and concentrations of atrazine.

The importance of rainfall timing relative to atrazine application is shown by examining the 1996 data. Annual streamflow from the Goodwater Creek watershed was 190 mm (Figure 2), with 119 mm occurring in May. Atrazine discharge in May was 32.5 g ha<sup>-1</sup>, representing 88% of the 36.5 g ha<sup>-1</sup> annual loss.

Seasonal atrazine concentrations for the two watersheds are shown in Figure 7. For Goodwater Creek, seasonal flow-weighted concentrations for the Jan-Mar, Apr-Jun, Jul-Sep, and Oct-Dec periods were 0.70, 9.3, 2.3, and 0.53 ug L<sup>-1</sup>, while respective values for the Walnut Creek watershed were 0.10, 1.3, 0.81, and 0.07 ug L<sup>-1</sup>.

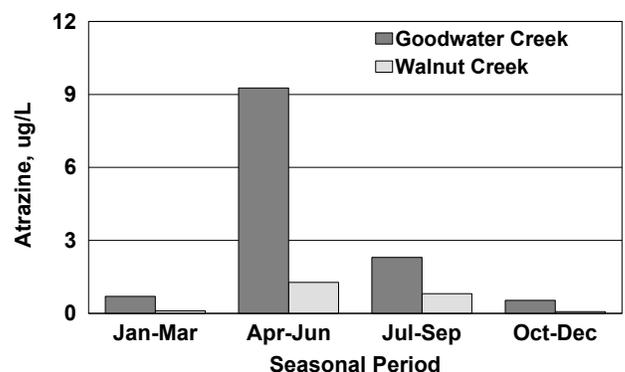


Figure 7. Seasonal atrazine concentrations.

## Conclusions

NO<sub>3</sub>-N and atrazine concentrations and discharges were measured over a 10-year period (1992-2001) from two Midwestern agricultural watersheds to better understand the influence of climate, soils, and topography on the transport of these chemicals through and out of the watersheds. One watershed was the 7,260-ha Goodwater Creek watershed located in north-central Missouri, the other was the 5,230-ha Walnut Creek watershed located in central Iowa. Our results showed that the primary water quality problem for each watershed was different. Annual flow-weighted NO<sub>3</sub>-N concentrations from the Walnut Creek watershed exceeded the 10 mg L<sup>-1</sup> maximum contaminant level (MCL) for drinking water 6 of 10 years. In contrast, the highest annual flow-weighted NO<sub>3</sub>-N concentration from the Goodwater Creek watershed was 2.7 mg L<sup>-1</sup>. Annual flow-weighted atrazine concentrations from the Goodwater Creek watershed exceeded the 3 ug L<sup>-1</sup> MCL for drinking water 7 of the 10 years. Atrazine concentrations and discharges from the Goodwater Creek watershed were highly seasonal, with 43% of the mean annual stream flow and 86% of the atrazine discharge occurring during the April through June seasonal period. The highest annual flow-weighted atrazine concentration from the Walnut Creek watershed was 1.9 ug L<sup>-1</sup>. One of the major differences between the watersheds is how water moves from the landscape into the Creek system. In the Walnut Creek watershed, about 74% of the streamflow is associated with tile drainage through an extensive network of field and county tile drains. NO<sub>3</sub>-N is mobile in the soil and can readily move through the soil and into the tile drainage system. In the Goodwater Creek watershed, about 90% of the streamflow is associated with surface runoff from a well-dissected landscape. Data will continue to be collected from these watersheds to better understand how improved nitrogen and atrazine best management practices at the field scale and other management practices at the watershed scale are improving streamflow water quality for optimum downstream water quality benefits and ecosystem protection.

## Acknowledgments

The authors appreciate the reviews of John Sadler and Fessehaie Ghidye.

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