

SEASONAL CHANGES IN STREAM WATER QUALITY ALONG AN AGRICULTURAL/URBAN LAND-USE GRADIENT

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ABSTRACT. We investigated downstream changes in dissolved oxygen (DO), pH, nitrate, total nitrogen (TN), total phosphorus (TP), Atrazine®, *E. coli*, and total suspended sediments (TSS) levels in two second-order watersheds with various amounts of riparian buffer coverage, and with more than 80% agriculture and 3% residential land-use in the headwaters and 60-65% agriculture and 10% residential land-use lower in the watersheds. DO, pH, nitrate, TP, *E. coli* and TSS showed little variation in the downstream direction along this land-use gradient or as a function of riparian buffer coverage. However, a decrease in Atrazine and TN concentrations was associated with the increased percentage of land used for housing in the downstream direction from less than 3% to approximately 10% urban land-use. Benchmark analysis indicated overall poor water quality in both watersheds with respect to nitrate, *E. coli*, TN and TP. This study provides a baseline of water quality data for future studies assessing the impact of changing land-use and riparian zones on water quality at the watershed scale in till landscapes of the midwestern U.S., where rapid population growth leads to the conversion of agricultural lands into residential areas.

Keywords: Water quality, watershed, land-use, benchmark analysis, riparian zones

Understanding the impact of changing land-use on water quality in glacial till landscapes of the midwestern U.S. is critical for proper management of water resources at the watershed scale. Land-use has been shown to affect nutrients, suspended sediment concentrations and overall stream water quality (Cooke & Prepas 1998; Sharpley et al. 1992; Kuhnle et al. 2000; Vanni et al. 2001). For instance, there is a significant positive correlation between N exports at the watershed scale and the percentage of watershed in crop (Hill 1978; Cooke & Prepas 1998). Urbanization generally results in higher runoff coefficients and higher losses of sediment and associated contaminants (McMahon & Harned 1998; Almendinger 2003).

Coulter et al. (2004) also reported that soluble reactive phosphorus (SRP) losses were greater in agricultural watersheds than in urban watersheds but that total phosphorus (TP) losses were similar in both settings, suggesting that the relative amount of TP and SRP varies as a function of land-use. McKergrow et al. (2003) studied the impact of a 1.7 km stretch of riparian zone on sediment exports in a catchment in Australia and showed that riparian zones led to a 90% reduction in sediment exports at the watershed scale. Data therefore suggest that land-use (agricultural vs. urban) and the occurrence of buffer zones along streams have an effect on water quality. There is nevertheless a lack of data on the impact of subtle land-use changes (< 20% change) on water quality. Understanding the impact of subtle land-use changes on water quality is nevertheless important in order to predict how water quality will evolve in the future as more land is converted from agricultural to residential (urban) land-use.

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Studies in till landscapes of the midwestern U.S. are especially important since nutrient exports from midwestern states like Indiana, Ohio and Illinois have been linked to pollution in the Gulf of Mexico where an anoxic zone develops every summer (Goolsby 2000; Royer et al. 2006). Land-use is also quickly changing in many watersheds of the midwestern U.S. that are traditionally dominated by agriculture. For instance, Coulter et al. (2004) indicated that in Fayette County, in the Inner Bluegrass region of Kentucky, population grew 15.6% between 1990 and 2000 and that many rural lands that were once managed for agriculture now support urban land-uses. Similarly, in the Tipton Till Plain region of central Indiana, Tedesco et al. (2003) estimated that the population in the Eagle Creek watershed, northwest of Indianapolis, has tripled in the last 40 years. The authors also project that population will continue to grow in this watershed in the years to come leading to the conversion of many agricultural lands into residential areas. Assessing water quality in these changing watersheds is critical in order to comprehend the impact of changing land-use on water quality and gather baseline information on water quality in these watersheds as these changes are taking place.

Nutrient concentration in streams is often reported as an indicator of water quality as excess nutrient in streams has been linked to eutrophication (Cooke & Prepas 1998; Martin et al. 1999). Many studies have also focused on pesticide mobility in soil (Benoit et al. 1998), including Atrazine® losses from artificially-drained landscapes of the American midwest as Atrazine is widely used in this area of the country (Kladivko et al. 1999). Many studies also looked at suspended sediment concentration in streams (Rostad et al. 1993; Kronvang et al. 1997) as high levels of suspended sediments have been shown to increase turbidity and limit the amount of light available to aquatic plants (U.S. EPA 2006a). The impact of buffer zones and various land-uses on bacteria concentrations such as total coliform and/or *E. coli* (*Escherichia coli*) concentration (as an indicator of fecal contamination) in streams have also received significant attention in the past few decades (Young et al. 1980; Schmitt et al. 1999; Dosskey 2002; Tate et al. 2006). Other indicators of stream health reported in the literature include pH and

dissolved oxygen concentration (DO). DO levels less than 4 mg/l have been reported to negatively impact aquatic life productivity and fish health in particular (IAC 2006). High levels of DO (> 125% DO saturation) have also been used as an indicator of poor stream health as they typically result from excessive algal growth in nutrient rich streams (Bright & Cutler 2000).

In this study, we used dissolved oxygen concentration (DO), pH, nitrate (N-NO₃⁻), total nitrogen (TN), total phosphorus (TP), *E. coli*, Atrazine and total suspended sediment (TSS) concentrations measured over a two-year period between April 2004 and April 2006 to assess water quality in two second-order watersheds with various amounts of riparian zone coverage and with more than 80% agriculture and 3% residential land-use in the headwaters and 60–65% agriculture and 10% residential land-use lower in the watersheds. Variations in DO, pH, NO₃⁻, TN, TP, *E. coli*, Atrazine and TSS as a function of land-use were analyzed, and the frequency at which water quality thresholds or water quality criteria identified from the literature for each of these parameters were exceeded or not met are discussed as a function of land-use (agricultural/urban), discharge (event flow vs. base-flow), seasons (winter/spring vs. summer/fall), and the occurrence of riparian buffers.

METHODS

Site description.—The two experimental watersheds used for this study are located in Eagle Creek Watershed (ECW) in the Tipton Till Plain near Indianapolis, Indiana (Fig. 1). Indiana has a humid temperate continental climate. The average annual temperature for central Indiana is 11.7°C with an average January temperature for Eagle Creek watershed of -3.0°C and an average July temperature of 23.7°C. The long term average annual precipitation (1971–2000) in the watershed is 105 cm (NOAA 2005). Highest stream discharge is observed in March while the lowest discharge occurs in September (Clark 1980). Topography in the area is nearly flat with slope angles mainly between 1–2% despite steeper areas with 2–6% slopes (Waldrip & Roberts 1972). Sediments are mainly composed of till, outwash and patchy thin loess. These unconsolidated glacial deposits may be several hundred feet thick in the watershed and are dominated by till. Soil profiles in Central

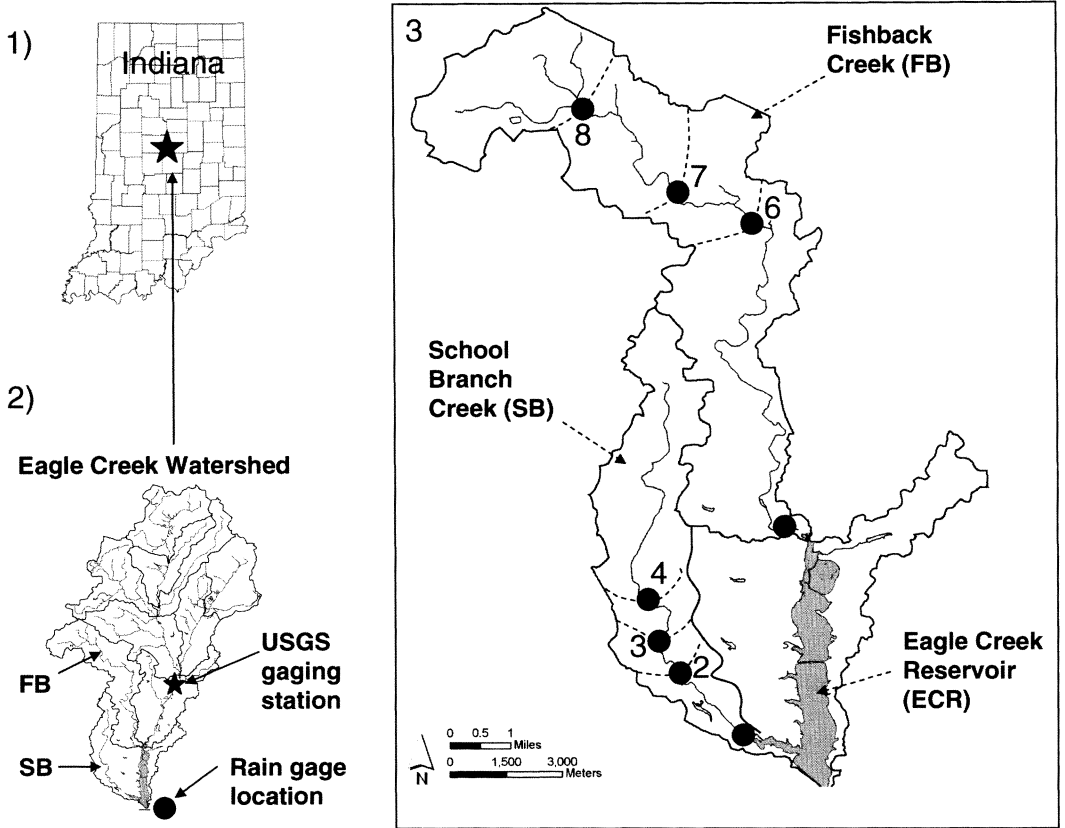


Figure 1.—Experimental site location. 1) State of Indiana; 2) Eagle Creek Watershed (ECW), and Fishback Creek (FB) and School Branch (SB) watershed locations in ECW; 3) Stream monitoring stations in FB and SB watersheds (FB6, FB7, FB8, SB2, SB3, SB4). Unlabelled black dots indicate the outlets of FB and SB watersheds.

Indiana and in Eagle Creek Watershed in particular are characterized by a 30 cm thick A horizon and an E horizon unless the soil has been ploughed extensively and generally belong to the Crosby-Treaty-Miami association. The B horizon is typically higher in clay than overlying and underlying horizons (Hall 1999). Most of central Indiana soils are poorly-drained and require artificial drainage in the nearly-flat till plain.

The two second order watersheds used in this study are Fishback Creek (58 km²) and School Branch (23 km²). These two watersheds feed directly into Eagle Creek Reservoir and are part of the larger Eagle Creek watershed (Fig. 1). Land-use is similar in both watersheds with 60–66% of land used for row-crop agriculture (mainly corn-soy rotation) and 9–10% of land used for medium density residential development (urban) (Table 1). The re-

maining 30% of each watershed mainly comprise forested or herbaceous areas. However, Fishback Creek has a steeper topography than School Branch (1.3% vs. 0.9%) and a higher percentage of stream bordered by riparian buffer at least 8 m wide (approximately 25 feet) (66% stream length for Fishback Creek, 33% stream length for School Branch). In addition, a significant land-use gradient is observed in both watersheds (Table 1). Six stream monitoring stations were established in these two watersheds to capture changes in water quality as land-use changes (Fig. 1). Stream monitoring stations FB8 and FB7 are located in the upper reaches of Fishback Creek and were chosen to capture the water quality signature of the section of the watershed with more than 80% agricultural land-use and little to no riparian buffer at least 8 m wide (approx. 25 feet). Monitoring station FB6 was chosen

Table 1.—Land-use information for Fishback Creek and School Branch watersheds and between each stream monitoring station. Total area and area between stream monitoring stations (km²), land-use (%), percent of stream length bordered with riparian buffer at least 8 m wide, and mean slope are also indicated. (* Legend: Agr. = agriculture, Urb. = urban, For. = forested, Herb = herbaceous, BZ = buffer zone).

	Area (Km2)	Agr.* (%)	Urb. (%)	For. (%)	Herb. (%)	BZ (% stream length)	Mean Slope (%)
Fishback Creek	57.84	59.6	9.42	15.2	14.48	65.7	1.3
upstream from FB8	13.29	82.19	4.31	5.86	8.41	0.00	0.47
FB8 to FB7	10.20	84.76	3.31	3.51	8.93	18.68	0.56
FB7 to FB6	7.88	66.68	4.81	16.50	10.76	100.00	1.14
FB6 to outlet	26.47	39.36	16.08	22.12	21.44	88.80	1.91
School Branch	23.2	65.9	10.5	9.7	13.90	33.5	0.9
Upstream from SB4	13.67	86.95	3.44	3.23	6.21	4.51	0.39
SB4 to SB3	1.22	84.67	0.41	3.73	10.32	23.38	0.56
SB3 to SB2	3.09	53.04	26.48	2.61	2.61	7.41	0.62
SB2 to outlet	5.22	34.22	20.92	18.94	21.93	97.36	1.48

because 100% of the stream is buffered with at least 8 m wide riparian zones between FB6 and FB7, so the effect of buffer zones on water quality could be studied. In School Branch, stream monitoring station SB4 was established to capture the water quality signature of the upper reaches of the watershed with little to no buffer and mainly agricultural land-use. Stream monitoring station SB2 was installed to capture changes in water quality as urbanization increases from less than 4% upstream from SB3 to 26% between SB3 and SB2 (10% total).

Methodology.—Watershed boundaries were established using ArcGIS surface hydrology tools and 30 m USGS digital elevation model (DEM) data. NRCS 1 m imagery was used to determine land-use in each of the watersheds studied. The NRCS imagery was also used to delineate portions of Fishback Creek and School Branch Creek with more than 8 m (approximately 25 feet) of riparian buffer. Stream discharge was estimated at the outlet of each watershed based on daily discharge measurements made at the USGS Zionsville stream gage station (Station #3353200) (Fig. 1) following the general equation:

$$Q_{\text{station}} = [A_{\text{station}}/A_{\text{zionsville}}] Q_{\text{zionsville}} \quad (1)$$

where Q_{station} is the discharge for each stream monitoring station (m³ per s), $Q_{\text{zionsville}}$ is the discharge measured at the USGS Zionsville stream gauging station (m³ per sec), $A_{\text{zionsville}}$ is the area upstream from Zionsville monitoring station (km²) and A_{station} the area upstream from each station (km²) (USGS 2005). This equation was used because discharge typically

scales linearly or nearly-linearly with contributing area (Dunne & Leopold, 1978; Pazzaglia et al. 1998). Instantaneous discharge was also measured in the field in 2004 to check for the accuracy of estimated discharge using a Doppler velocity meter (SONTEK Flow Tracker). Daily precipitation was measured at Eagle Creek Airpark (Fig. 1) and high flow defined as the 75th percentile for discharge (Q_{75}), i.e., the discharge exceeded 25% of the time based on long-term discharge measurements obtained at the USGS stream gauging station.

Water samples were collected monthly to bimonthly between April 2004 and April 2005 (8 sampling dates) and on a biweekly to monthly basis between April 2005 and April 2006 (27 sampling dates). A total of 13 sampling dates correspond to high flow conditions ($Q > Q_{75}$). Field blanks and triplicate analysis of selected samples were performed for quality control/quality assurance and samples were kept on ice after sampling until return to the laboratory. *E. coli* concentration was measured within a few hours of collection and samples for total phosphorus (TP) and total Kjeldahl nitrogen (TKN) analyses were collected in pre-acidified containers to maintain the pH < 2 until analysis. All other samples were filtered using disposable GF/F filters within 36 h of sampling and frozen until analysis. Dissolved oxygen concentration and pH were measured in the field using a multi-parameter probe (YSI, 600XLM-SV). Nitrate, nitrite and ammonium were measured using standard colorimetric methods (Clesceri et al. 1998) using a photometric analyzer (Aquachem 20 –

Table 2.—Dissolved oxygen (DO), pH, nitrate (N-NO₃⁻), total nitrogen (TN), total phosphorus (TP), *E. coli*, Atrazine and total suspended sediment (TSS) thresholds used to assess stream health and water quality. When two thresholds are identified for one parameter, the one in *italic* indicates the one used primarily in this study. * EPA Standard for Atrazine is based on an annual average.

Parameter	Threshold	Remarks	Reference
Dissolved oxygen	<i>Min: 4 mg/l</i> If > 125% saturation	For aquatic life protection Indicate excessive algal activity due to nutrient enrichment	IAC 2006 Bright & Cutler 2000
pH	Min: 6 and Max: 9	For aquatic life protection	IAC, 2006
Nitrate	Max: 10 mg N/l	Human Toxicity	EPA Drinking Water Standard
Total nitrogen	Max: 2.75 mg/l	National Average for US watersheds with 50–75% agriculture	Omernik 1977
Total phosphorus	Max: 0.125 mg/l	National Average for US watersheds with 50–75% agriculture	Omernik 1977
<i>E. coli</i>	Max: 235 CFU/100ml	Max for full body contact	IAC 2006
Atrazine	Max: 3 µg/l*	Human Toxicity	EPA Drinking water standard
Total suspended sediment	Max: 40 mg/l	For aquatic life protection	New Jersey Department of Environmental Protection 2003

EST Analytical). TKN was measured using the standard Kjeldahl Method (EPA method 351.4) and total nitrogen (TN) calculated as the sum of TKN, nitrate and nitrite concentrations in each sample. TP was determined using EPA standard method 4500 PE consisting of a strong acid and persulfate digestion analyzed colorimetrically using the ascorbic acid-molybdate blue method. *E. coli* concentration (most probable number (MPN) of colony forming unit (CFU) per 100 ml) was measured using the *E. coli* test using EC-MUG Medium and read using a fluorometer (long-wavelength UV) (standard method SM9221-F). The most probable number of colony forming units was used as an estimate of CFU. *E. coli* concentration is therefore reported as CFU/100 ml hereafter. Atrazine levels were determined by immunoassay using the Beacon Analytical Immunoassay. Total suspended sediment concentrations (TSS) were determined by weighing oven dried (65°C) sediment collected on pre-washed GF/F Whatman Fiber Glass filters (0.7 µm pore size). In order to characterize the impact of changing land-use (agriculture > medium density housing (urban) and no buffer to buffer) on water quality, an analysis of the probability that water quality thresholds or criteria identified in Table 2 are exceeded or not met was conducted for the entire study period, the summer/fall period, and event flow conditions. Seasons are

based on the calendar year. The summer/fall period therefore starts on June 21 and terminates on December 20.

RESULTS

Hydrological functioning.—Figure 2 shows daily precipitation in mm per day from April 2004 until April 2006 as well as daily discharge (m³ per sec) at the outlet of Fishback Creek watershed (School Branch data are not shown) and the distribution of sampling points for all stations for both watersheds over the duration of the study. Total precipitation from 1 April 2004 until 31 March 2005 (Year 1) was 987 mm and 1000 mm from 1 April 2005 until 31 March 2006 (Year 2). When compared to monthly normals (1971–2000), monthly precipitation amounts varied on average by 45% of normal values. However, over the entire duration of the study period, Year 1 and Year 2 were only 3.0% and 1.6% drier than the 30-year normal, respectively.

Because discharge estimates in School Branch and Fishback Creek are proportional to discharge at the USGS stream gauging station (equation 1), discharge data are not graphed for School Branch to avoid redundancy and to limit the number of figures. During Year 1 and Year 2, discharge varied from 0.007 m³ per sec (7 l/sec) to 19.8 m³ per sec in Fishback Creek (outlet) with an average discharge of 0.8 m³ per sec. Discharge in

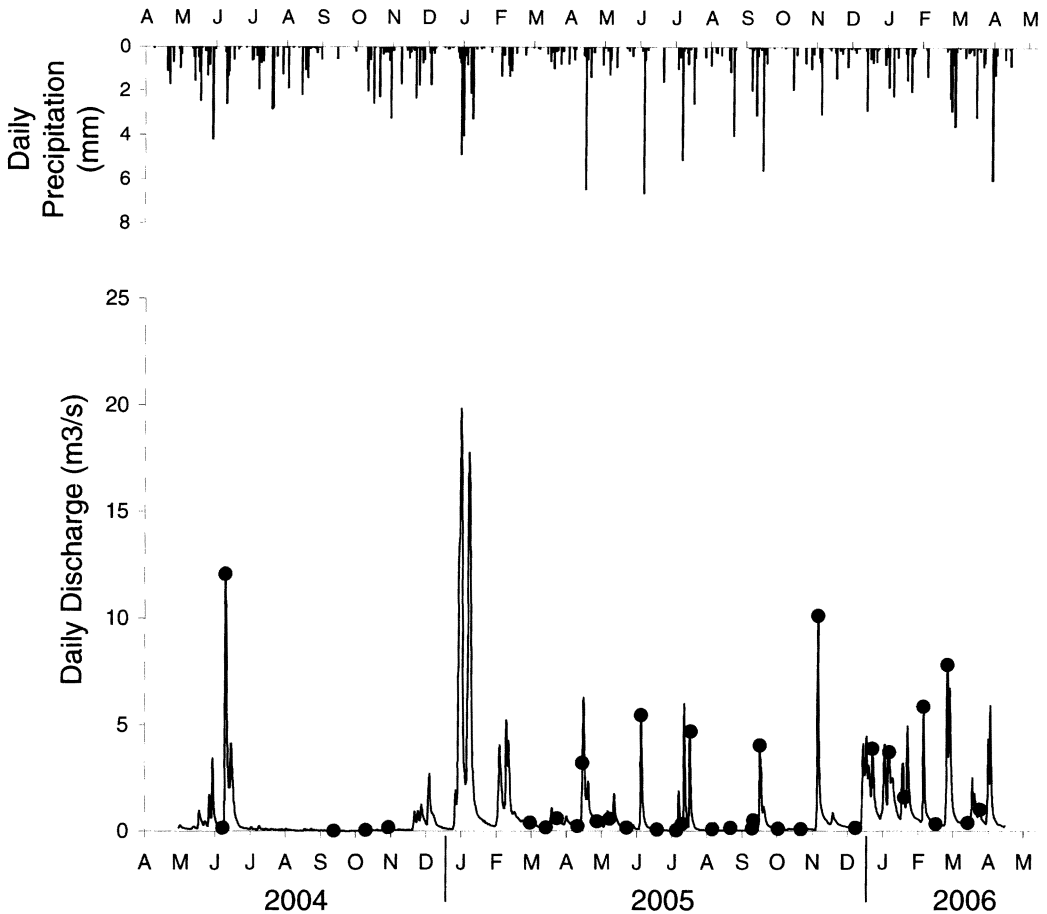


Figure 2.—Daily precipitation (mm), average daily discharge at the outlet of Fishback Creek (m^3 per s), and sampling dates (black dots) for all stream monitoring stations in Fishback Creek and School Branch watersheds between April 2004 and April 2006.

School Branch (outlet) varied from 0.002 m^3 per sec to 8.4 m^3 per sec (average = 0.3 m^3 per sec) (data not shown). Periods of low discharge in both watersheds corresponded to the June–November period, especially in Year 1 during which no major increase in discharge was observed (Fig. 2). Highest discharge occurred during the December–May period in both years.

In order to determine the proportion of annual streamflow occurring during high flow conditions ($Q > Q_{75}$), the discharge exceeded 25% of the time (75^{th} discharge percentile) was established for each station based on long term discharge data at the USGS Zionsville stream gauging station. Figure 3 shows the results for the outlet of Fishback Creek as an example. The 75^{th} percentile for discharge (Q_{75}) was 0.66 m^3 per sec for Fishback Creek (outlet)

(Fig. 3) and was 0.25 m^3 per sec at the outlet for School Branch (data not shown). Using Q_{75} and Fig. 3, which also shows cumulated daily discharge in descending order expressed as a function of the percent of the year, data indicated that 83.7% of total discharge (377 mm) during Year 1 and 78.8% of total discharge (325 mm) during Year 2 occurred during high flow ($Q > Q_{75}$) in Fishback Creek. Similar results were obtained for School Branch Creek as estimated discharge in School Branch is proportional to estimated discharge in Fishback Creek.

Water quality data.—Average, minimum and maximum values for DO, pH, nitrate, TN, TP, E. coli, Atrazine and TSS for each stream monitoring station are presented in Table 3. In Fishback Creek, DO, pH, nitrate, TN, TP and

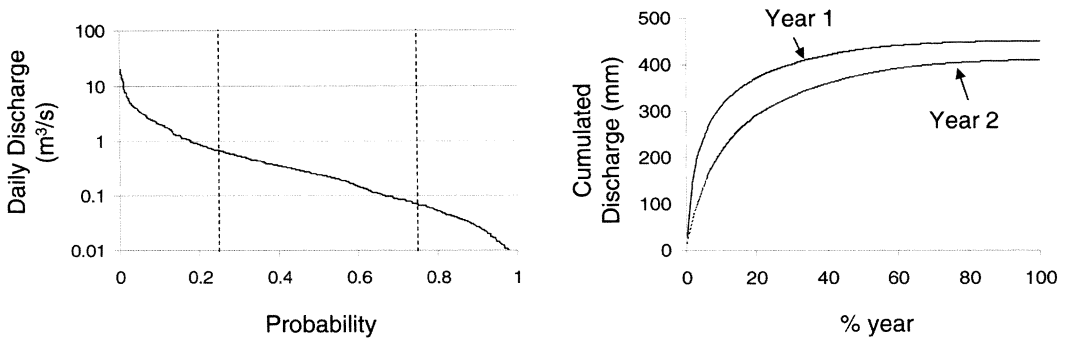


Figure 3.—Average daily discharge distribution curve (m^3 per s) at the outlet of Fishback Creek (left) and cumulated discharge (mm) at the outlet of Fishback Creek for year 1 (April 2004 – March 2005) and year 2 (April 2005 – March 2006) (right).

E. coli values showed little variation between stations FB8 and FB6 with average values of 9.7 mg/l for DO, 7.9 for pH, 5.6 mg/l for nitrate, 6.9 mg/l for TN, 0.2 mg/l for TP and 2763 CFU/100 ml for *E. coli*. However, Atrazine levels showed a consistent increase downstream between FB8 and FB6 with Atrazine levels increasing from 1.5 to 2.4 to 3.3. Contrary to what was found at Fishback Creek, Atrazine concentrations tended to decrease in the downstream direction in School Branch with average Atrazine levels for the study period of 2.3, 2.3 and 1.7 μl at SB4, SB3 and SB2, respectively. Average TSS concentrations were higher in Fishback Creek (34 mg/l) than in School Branch (22 mg/l). TSS levels showed a slight decrease (16%) between FB8 and FB6 with an average TSS concentration of 38 mg/l at FB8, and 32 mg/l and 33 mg/l at FB7 and FB6, respectively. Similarly, TSS concentrations dropped by 13% in School Branch between SB4 (24 mg/l) and SB3 and SB2 (21 mg/l).

Average *E. coli* levels in both Fishback Creek and School Branch varied between 1598 CFU/100 ml and 4374 CFU/100 ml. TP concentrations were slightly higher in Fishback Creek (0.21 mg/l) than School Branch (0.14 mg/l) but showed little variation among stations as a function of land-use. Indeed, TP concentrations were comparable at SB3 (0.14 mg/l) and SB2 (0.13 mg/l) even though land-use changed from < 3% urban upstream from SB3 to approximately 10% urban upstream from SB2. Contrary to Fishback Creek, where average TN values remained in the 6.9–7.0 mg/l range, TN concentrations dropped from 9.2–9.0 mg/l at SB4–SB3 to 7.5 mg/l at SB2 in School Branch.

In School Branch, nitrate concentrations were 25% higher at SB3 than at SB4 and SB2; however, in Fishback Creek, nitrate concentrations remained between 5.6–5.7 mg/l for all stations. As for Fishback Creek, pH (7.8–7.9) and DO (10.6–10.7 mg/l) values showed little variation between stations in School Branch.

Benchmark analysis.—Over the duration of the study, DO concentrations < 4 mg/l occurred relatively rarely at all stations (< 19% of the time); however, DO levels < 4 mg/l occurred more often in the upper reaches of the watershed (e.g., FB8, SB4) (13–19% of the time) than in the lower reaches (3–7% of the time) (Fig. 4). The pH levels remained between 6 and 9 pH units all year for all stations. Nitrate levels exceeded 10 mg/l, 20–30% of the time in School Branch and FB8 and approximately 14% of the time at FB7 and FB6. A concentration of 2.75 mg/l for TN is exceeded approximately 70% of the time for both watersheds. In Fishback Creek and SB4, TP exceeded 0.125 mg/l approximately 47% of the time; however, this threshold was exceeded only 41% and 35% of the time at SB3 and SB2, respectively. The *E. coli* standard for full body contact (235 CFU/100 ml) was exceeded between 53–70% of the year in both Fishback and School Branch. TSS concentration exceeded the 40 mg/l benchmark for non-trout surface water (New Jersey DEP 2003) more often in Fishback Creek (23–31%) than in School Branch (12–18%); however, the frequency at which this threshold was exceeded did not vary consistently in the downstream direction as a function of land-use (School Branch) or as a function of the occurrence of buffer zones (Fishback Creek).

Table 3.—Mean values for dissolved oxygen (DO) ($n = 29-32$), pH ($n = 32-34$), nitrate ($n = 33-35$), total phosphorus (TP) ($n = 29-32$), *E. coli* ($n = 26-29$), total nitrogen (TN) ($n = 33-35$), Atrazine ($n = 22-25$) and total suspended sediments (TSS) ($n = 32-35$) for stream monitoring stations FB8-6 and SB4-2. Minimum and maximum values for each parameter are indicated in parenthesis.

	FB8	FB7	FB6	SB4	SB3	SB2
DO (mg/l)	8.9 (1.2;16.8)	9.9 (1.6;17.7)	10.2 (1.6;17.9)	10.6 (0.8;20.7)	10.6 (1.7;22.8)	10.6 (1.6;18.4)
pH	7.8 (6.8;8.4)	7.8 (7.1;8.3)	8.0 (7.4;12.0)	7.8 (6.5;8.5)	7.9 (6.9;8.7)	7.8 (7.3;8.6)
N-NO3 (mg/l)	5.7 (0.2;14.6)	5.6 (0;16.8)	5.6 (0;20.5)	6.1 (0;16.8)	7.6 (0;34.7)	6.1 (0;25.9)
TN (mg/l)	7.0 (0.8; 17.7)	6.9 (0.5;20.7)	6.9 (0.7;25.0)	9.2 (0.6;36.4)	9.0 (0.4;35.7)	7.5 (0.5;29.7)
TP (mg/l)	0.23 (0.03;0.88)	0.20 (0.02;0.84)	0.21 (0.03;0.85)	0.16 (0.02;0.64)	0.14 (0.02;0.38)	0.13 (0.02;0.68)
<i>E. coli</i> (CFU/100 ml)	1598 (0;10140)	4374 (0;43520)	2315 (0;22240)	2002 (0;14136)	3202 (0;32550)	1851 (0;17329)
Atrazine (μ g/l)	1.5 (0.05;25.0)	2.4 (0.06;28.0)	3.3 (0.07;33.0)	2.3 (0.16;16.0)	2.3 (0.1;16.0)	1.7 (0.04;16.0)
TSS (mg/l)	38 (5.4;226)	32 (1.9;195)	33 (1.2;282)	24 (1.7;90)	21 (2.5;77.5)	21 (1.6;99.6)

The probabilities that these same thresholds or criteria are exceeded or not met during the low flow period each year (summer/fall) are shown in Fig. 5. The proportion of summer/fall samples not meeting the water quality criteria identified in Table 2 was comparable to the rest of the year for DO and pH. However, during summer/fall months, water quality thresholds were exceeded less often for nitrate, TN, and Atrazine than during the entire year. For instance, nitrate concentrations never exceeded 10 mg/l during the summer/fall period, even during summer precipitation events. Although Atrazine concentrations sometime exceeded the drinking water limit of 3 μ g/l, this happened less often in the summer/fall period (0–9% in FB and 0% in SB) than during a 12-month period (4–12% in FB and 9–17% in SB). Data also indicated that although there was very little variation (approximately 10%) between stations (except at SB2) regarding TN when looking at 12-month averages, there was a large decrease (approx. 40%) in the probability of TN being greater than 2.75 mg/l in the downstream direction in both watersheds in the summer/fall period with this threshold being exceeded 56%, 44% and 31% of the time at FB8, FB7, and FB6, and 50%, 29% and 31% at SB4, SB3 and SB2, respectively.

Contrary to other variables, high values for *E. coli* and TP occurred more often in the summer/fall period than during the rest of the year. *E. coli* levels above 235 CFU/100 ml occurred 80% of the time of the summer/fall period in Fishback Creek, and 68% of the time in School Branch, as opposed to only 60% and 59% of the time in Fishback Creek and School Branch over a 12-month period, respectively. During summer/fall, FB7 experienced large increases in percent exceedence for the *E. coli* standard (93%) but average counts increased only slightly (Table 2). Similarly, for TP, a concentration of 0.125 mg/l was exceeded 53% of the time in the summer/fall period in both watersheds (44% of the time for the whole year). There was nevertheless one exception to this pattern as TP did not exceed the 0.125 mg/l threshold more often in summer/fall (33.3%) than during the rest of the year (35.5%) at SB2.

Figure 6 indicates the probability of each variable exceeding thresholds identified in Table 2 during high flow conditions ($Q > Q_{75}$). DO and pH levels did not exceed water quality criteria more often during events than

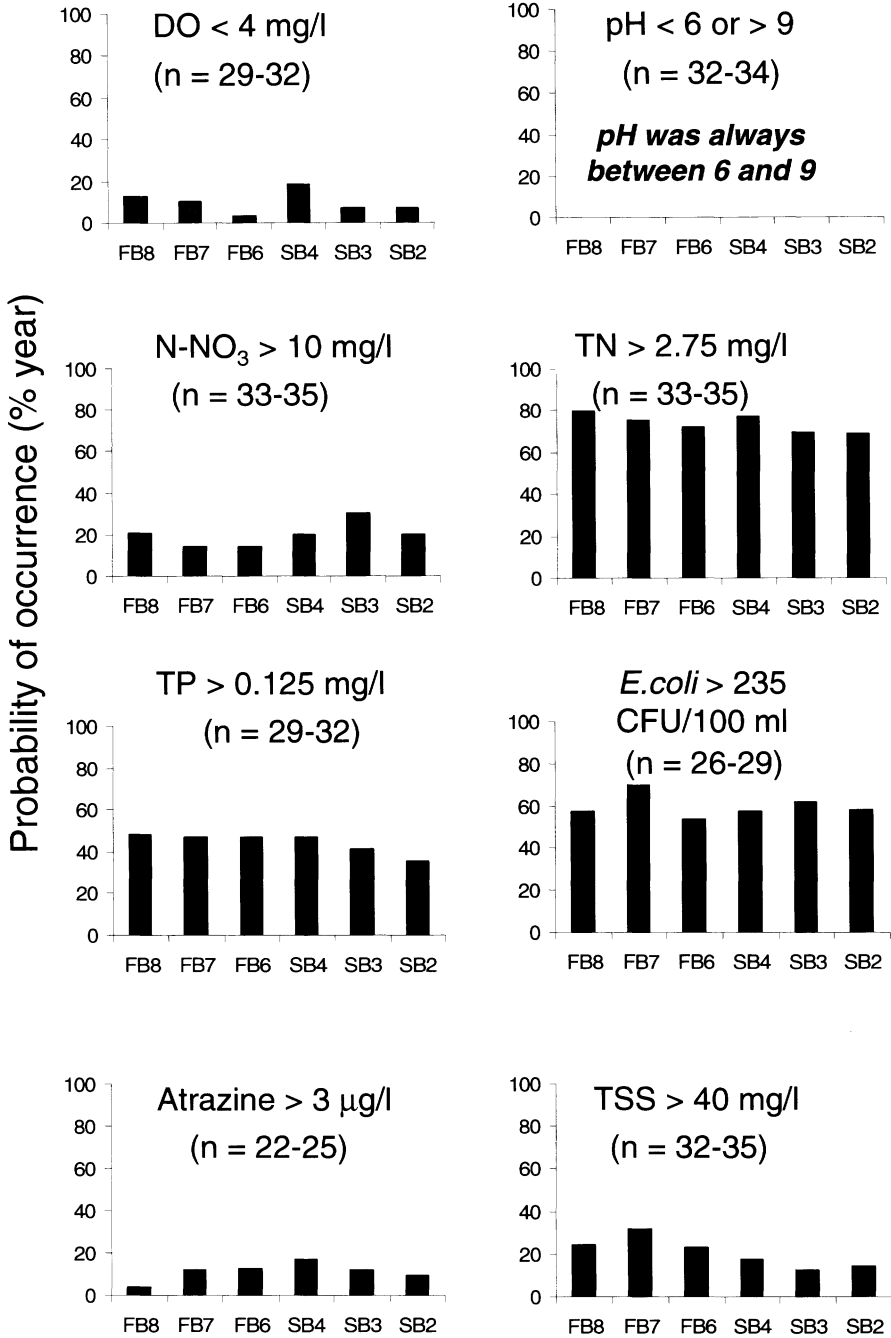


Figure 4.—Water quality benchmark analysis. Bar graphs indicate the probability that the water quality thresholds or criteria identified in Table 1 are exceeded or not met during a 12-month period between April 2004 and April 2006 for each stream monitoring station in Fishback Creek (FB8, FB7, FB6) and School Branch (SB4, SB3, SB2). (DO = dissolved oxygen concentration, N-NO₃ = nitrate, TN = total nitrogen, TP = total phosphorus, TSS = total suspended sediments).

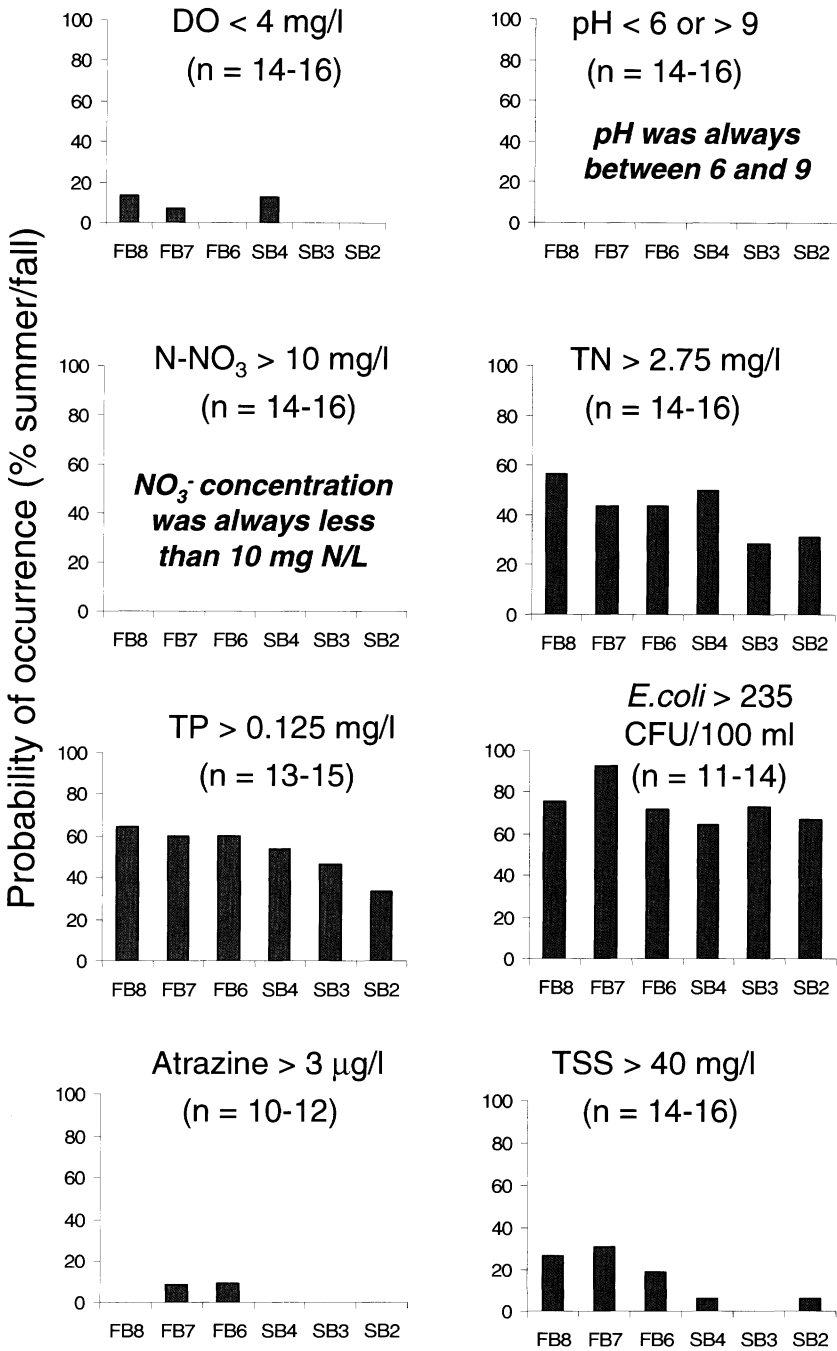


Figure 5.—Water quality benchmark analysis. Bar graphs indicate the probability that the water quality thresholds or criteria identified in Table 1 are exceeded or not met during the Summer/Fall period (June 21 to December 20) between April 2004 and April 2006 for each stream monitoring station in Fishback Creek (FB8, FB7, FB6) and School Branch (SB4, SB3, SB2). (DO = dissolved oxygen concentration, N-NO₃ = nitrate, TN = total nitrogen, TP = total phosphorus, TSS = total suspended sediments).

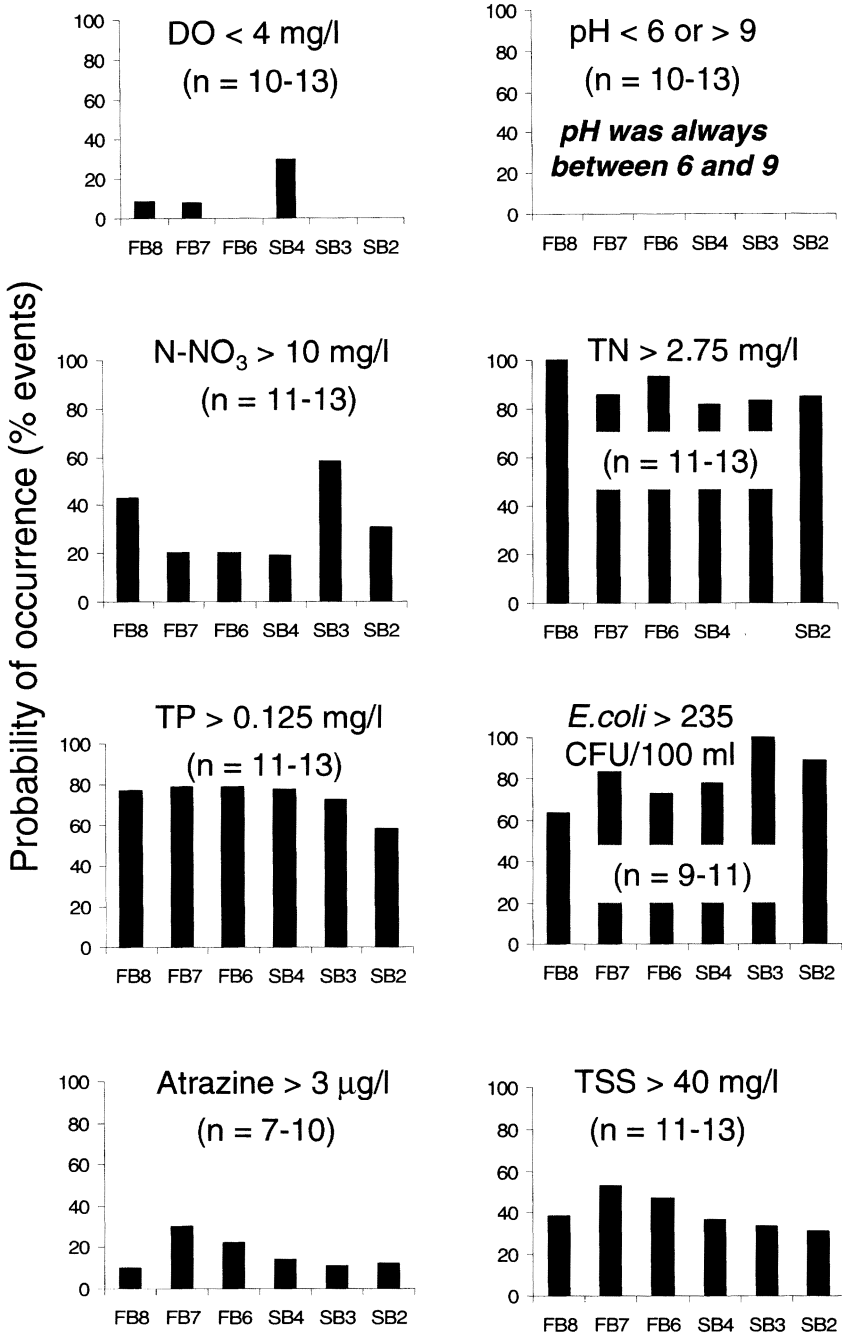


Figure 6.—Water quality benchmark analysis. Bar graphs indicate the probability that the water quality thresholds or criteria identified in Table 1 are exceeded or not met during high flow ($Q > Q_{75}$) between April 2004 and April 2006 for each stream monitoring station in Fishback Creek (FB8, FB7, FB6) and School Branch (SB4, SB3, SB2). (DO = dissolved oxygen concentration, N-NO₃ = nitrate, TN = total nitrogen, TP = total phosphorus, TSS = total suspended sediments).

during a 12-month period. TSS values were higher in the winter/spring period (36 mg/l) than during the summer/fall period (20 mg/l) (data not shown) and exceeded the 40 mg/l benchmark more often during events (31–53% of the time) than during a 12-month period (12–32% of the time). In Fishback Creek, Atrazine levels exceeded 3 $\mu\text{g/l}$ an average of 21% of the time during events as opposed to only 10% of the time over a 12-month period. In School Branch, the probability of Atrazine levels being $> 3 \mu\text{g/l}$ was the same during high flow conditions as during a 12-month period (13%).

For nitrate, TN, and TP, the probability of these variables exceeding thresholds identified in Table 2 was higher during high flow conditions than during either the summer/fall period or the entire year. Nitrate concentrations were $> 10 \text{ mg/l}$ for 20–43% of the time during high flow in Fishback Creek, and for 19–58% of the time in School Branch. TN levels of 2.75 mg/l were exceeded between 86–100% of the time in Fishback Creek and 82–85% of the time in School Branch during events. Similarly, the probability of TP concentrations exceeding the 0.125 mg/l benchmark during high flow periods was 73–79% in Fishback Creek, SB4 and SB3 and 58% at SB2.

The probability of *E. coli* levels exceeding the 235 CFU/100 ml maximum concentration for full body contact was higher during the summer/fall period (80% in Fishback Creek and 68% in School Branch) and high flow periods (73% in Fishback Creek and 89% in School Branch) than during a 12-month period (60% in Fishback Creek, 59% in School Branch).

DISCUSSION

Changes in water quality along the agricultural/urban land-use gradient.—Land-use analysis indicated that there was a change in land-use from more than 80% agriculture and 3% residential land-use in the headwaters to 60–65% agriculture and 10% residential land-use lower in the watersheds, as well as an increase in buffer zone coverage in the downstream direction in Fishback Creek.

Changes in land-use and in the percent of the stream where at least 8 m wide riparian buffers are present seemed to have little impact on dissolved oxygen concentration (DO) and pH as little variations in pH or DO were observed

between stations. DO values around 8–10 mg/l indicate a relatively well-oxygenated system most of the year. There are nevertheless times when streams were depleted in oxygen (DO $< 4 \text{ mg/l}$) or where DO level exceeded 125% DO saturation (data not shown) which indicates excessive algal growth due to nutrient enrichment (Bright & Cutler 2000).

Similarly, when viewed over a 12-month period, nitrate did not seem to be affected by changes in land-use or buffer coverage as no large variations ($> 25\%$) in nitrate concentrations were observed in a downstream direction in either watershed. Nitrate likely bypassed most riparian zones in drainage pipes in these watersheds where artificial drainage is common. The fact that nitrate concentration does not decrease between SB4 and SB2 as land-use changes from $< 4\%$ urban to approximately 9–10% urban (locally 27%) suggests that despite an increase in urbanization, 10% urban land-use is not enough to strongly affect nitrate concentration at the watershed scale over a 12-month period. TP concentrations did not seem to be affected by the presence of riparian buffer (FB8-FB6) or land-use as TP did not vary by more than 0.01 mg/l between SB3 and SB2, as residential land-use increased (Table 1). The 12% drop (0.16 to 0.14 mg/l) in TP concentration between SB4 and SB3 did not correspond to any change in land-use or buffer coverage and was likely due to differences in phosphorus application or leaching rates between stations. This result is consistent with results reported by Coulter et al. (2004) in two watersheds of the Inner Blue Grass region of Kentucky where no significant changes in TP concentrations were observed across an agricultural to urban land-use gradient. Overall, TP concentrations were higher in Fishback Creek than School Branch; however, both watersheds had similar land-uses (Table 1). Differences in TP concentrations were therefore likely due to higher P inputs in Fishback Creek.

Annual averages for TN values between 7 and 10 mg/l were high compared to other catchments in the United States with 50–70% agricultural land-use (see Table 2) (Omernik 1977), suggesting that agricultural land-use in the watersheds studied generated above average nitrogen losses over a 12-month period. School Branch watershed (66% agricultural) had higher annual TN concentrations than Fishback Creek (60% agricultural) despite similar per-

centage of agricultural land-use. Buffer coverage was higher in Fishback Creek than in School Branch (66% vs. 33%); however nitrate and TN concentrations did not decrease in Fishback Creek as buffer coverage increased. This suggests that, in addition to having little impact on nitrate concentrations in the stream, buffer zones also had little effect on stream TN concentrations. This result was not unexpected as nitrate, which constitutes most of TN, may bypass riparian zones via subsurface drainage. TN values were nevertheless typically lower at SB2 (7.5 mg/l) than at SB3 and SB4 (9.0–9.2 mg/l), suggesting that the change in land-use from less than 4% urban to 10% urban (locally 27% urban) likely contributed to lower in-stream TN concentrations. These results were consistent with those reported by Coulter et al. (2004) who reported lower total nitrogen concentration in streams as urbanization increased.

Over a 12-month period, instantaneous *E. coli* concentrations varied by several orders of magnitude in both streams (Table 3); however, average *E. coli* levels remained in the 1500–4500 CFU/100 ml at all locations. Atrazine concentrations increased downstream from 1.5 to 3.3 µg/l in Fishback Creek and drop from 2.3 to 1.7 µg/l in School Branch. Although the decrease in Atrazine concentration in School Branch can be easily explained by the increase in urbanization in the lower reaches of School Branch, the increase in Atrazine level in Fishback Creek did not correspond to either an increase in agricultural land-use or a decrease in the percentage of the stream where riparian zones are present. The reason for observed increases in Atrazine levels in Fishback Creek between FB8 and FB6 during events and winter/spring was not determined, but these increases were likely due to inflow from agricultural ditches that are concentrated in this area. Despite better buffer coverage in Fishback Creek than School Branch (66% vs. 33%), TSS concentrations were typically 36% lower in School Branch than Fishback Creek. This suggested that the presence of riparian buffer in the two watersheds studied had little impact on TSS concentration in these streams. However, other research suggests that buffer zones are typically very efficient at intercepting TSS in overland flow, with overall efficiencies varying between 60% and 98% depending on the study (Schmitt et al. 1999; Clausen et al.

2000; Abu-Zreig 2004). Our results therefore suggest that most of the suspended sediment in the stream may be due to stream bank erosion and stream incision rather than sediment losses from agricultural fields via overland flow. High sediment losses due to stream bank erosion have been reported in incised agricultural streams in northwest Mississippi (Shields et al. 1995), and other studies have shown that in-stream sediment losses could contribute significantly to overall sediment budgets at the watershed scale (Sekely et al. 2002; Jackson et al. 2005). This suggests that stream rehabilitation may be more effective than buffer restoration to minimize sediment losses in these watersheds. Overall, data suggest that the changes in land-use and buffer zone coverage in the watersheds studied have little impact on DO, pH, nitrate, TSS, *E. coli*, and TP. However, higher urbanization in the lower reaches of School Branch affects average Atrazine and TN concentrations.

Timing of contaminant exports.—Although the analysis of average annual values for the variables investigated in this study in relation to changes in land-use can bring insight; a more detailed analysis looking at contaminant exports as a function of season or discharge is critical to achieve a thorough understanding of nutrient/contaminant dynamics in the watersheds studied. In addition, although different thresholds could be used to assess water quality, an analysis of the frequency at which certain water quality thresholds were exceeded can bring additional insights into the severity of water quality concerns. The analysis of stream discharge dynamics during the year indicated that discharge varied over three orders of magnitude between baseflow and high flow and that 78% to 84% of annual discharge occurred during only 23 to 28% of the time, i.e., at high flow. This illustrates the importance of understanding the timing of contaminant export during the year and how water quality parameters vary as a function of discharge. The importance of understanding nutrient dynamics during high flow periods is also illustrated by a recent study (Royer et al. 2006) showing that nearly all nutrient exports in three watersheds in Illinois occurred at high flow. Seasonal trends in water quality, including during low flow periods, are nevertheless also critical to understand when it comes to characterizing the impact of changing land-

use on in-stream water quality. Indeed, the summer/fall period corresponds to the period of the year when water resources are the most limited and when most water quality problems related to excess nutrients or bacteria in streams are observed.

E. coli levels of 235 CFU/100 ml (maximum concentration for full body contact; Table 2) were exceeded more than 50% of the time throughout the watershed, suggesting a significant impairment of the streams studied with respect to *E. coli* contamination. *E. coli* bacteria are typically associated with mammalian intestinal tracts, which suggests that some contamination from defective septic systems or runoff from livestock operations may occur in the watersheds. When looking at the distribution of *E. coli* levels throughout the year, the 235 CFU/100 ml threshold was exceeded more often in the summer and during events than during the rest of the year. This is consistent with the fact that *E. coli* colonies are more likely to thrive in the stream at higher temperature during the summer when flow is low, as well as likely to be transported to the stream with overland flow during precipitation events (Collins 2004).

Contrary to *E. coli*, nitrate levels > 10 mg/l were never observed during the summer/fall period, including during summer/fall events. Nitrate losses in these two watersheds were therefore highly seasonal. Nitrate concentrations > 10 mg/l also occurred 1.5 to 2 times more often during events (high flow) than during the rest of the year. These results are consistent with previous data reported by Royer et al. (2006) indicating that most nitrate losses in artificially-drained landscapes of the midwestern U.S. occur during winter-spring months and during events. In Fishback Creek, benchmark analysis indicated that nitrate concentrations > 10 mg/l occurred more often in the upper reaches of the watershed during events where no buffer is present than in the lower reaches of the watershed where up to 100% buffer coverage is observed. However, in School Branch, higher nitrate concentration occurred more often at SB3 (24% buffer) than SB4 (5% buffer). High nitrate concentrations therefore did not appear to be clearly linked to the percentage of stream with riparian buffer. As discussed earlier, this is not an unexpected result as most nitrate bypasses the riparian zone in these artificially drained watersheds. Differences in nitrate con-

centration between stations are therefore more likely to be related to differences in drain density than the presence of riparian buffer.

Atrazine concentrations > 3 μ g/l are also seasonal and rarely occurred in summer. In Fishback Creek, the probability of Atrazine exceeding 3 μ g/l was twice as high during high flow as it was the rest of the year. In School Branch, the probability of Atrazine concentration being > 3 μ g/l during events was the same as for the rest of the year (12.6%). However, for both watersheds, Atrazine concentrations were much higher in the spring than during the rest of the year. This is illustrated by higher Atrazine concentrations in the streams in spring with average Atrazine levels of 5.5 μ g/l in Fishback Creek (annual average = 2.4 μ g/l) and 5.6 μ g/l in School Branch (annual average = 2.3 μ g/l) for the months of April, May and June. This is consistent with previous research on Atrazine delivery to streams. For instance, in a study of the transport of pesticides (including Atrazine) in artificially drained soil, Kladvik et al. (1999) indicate that 55–90% of pesticide losses occurred during the first storm event after application in the spring. Overall, data therefore suggest that nitrate concentrations in streams (and to some extent *E. coli* levels) are seasonal and that the timing of the first precipitation event after Atrazine application in the spring is a key factor in controlling Atrazine losses at the watershed scale.

The other set of criteria used to assess the impact of changing land-use on water quality focused on variables that are indicative of some level of anthropogenic impact or poor stream health (Table 2). High TSS concentrations increase turbidity and decrease the amount of light available for stream organisms, change benthic habitat (U.S. EPA 2006a), and many contaminants are also exported in association with suspended sediments (Rostad et al. 1993; Kronvang et al. 1997; McDowell & Wilcock 2004). The 40 mg/l TSS threshold was exceeded approximately 26% of the time in Fishback Creek and 15% of the time in School Branch suggesting that contamination by suspended sediments occurred in both watersheds but was more acute in Fishback Creek. This was consistent with higher average TSS concentration in Fishback Creek than School Branch despite better buffer coverage in Fishback Creek than School Branch.

DO concentrations below 4 mg/l occurred occasionally (3–19% of the time) during the

year. There was nevertheless no consistent seasonal pattern in the occurrence of low DO concentration; however, low DO concentrations typically occur more often at FB8, FB7 and SB4. One possibility is that lower discharge in the upper reaches of the watershed favors algal growth, which could lead to a higher BOD (Biological Oxygen Demand) during periods of algal decay.

The thresholds used in this study for TN (2.75 mg/l) and TP (0.125 mg/l) are the average values for TN and TP concentrations in streams in US watersheds with 50–75% agricultural land-use (Omernik 1977). Exceeding these thresholds does not necessarily indicate poor water quality but rather indicates how high TN and TP concentrations are in the two watersheds studied compared to other US watersheds with similar land-use. TN values > 2.75 mg/l occurred between 69–79% of the time in Fishback Creek and School Branch, especially during high flow conditions; however, as for nitrate, TN was less likely to exceed the 2.75 mg/l mark in the summer (29–56% of the time) than during a 12-month period or high flow conditions. For TP, concentrations above 0.125 mg/l were more common during events (58–79% of the time) than during a 12-month period (35–48% of the time) or the summer/fall period (33–64% of the time). This is consistent with higher TP losses during events when in stream sediment losses and overland flow are likely to occur. The percent of stream buffered does not seem to affect TN or TP values. Over a 12-month period, TN was equally likely to exceed 2.75 mg/l at all stations regardless of land-use or presence of buffer (Fig. 4). However, TP was less likely to exceed 0.125 mg/l at SB2 than at any other stations. This suggests that although average TP concentration were comparable at SB2 (0.13 mg/l) (10% urban) and SB3 (0.14 mg/l) (< 4% urban), medium density housing likely did not contribute as much to high TP concentration in streams as agricultural land-use.

Overall, this study provides a baseline of water quality data for future studies assessing the impact of riparian buffers and changing land-use on water quality in till landscapes of the midwestern U.S. as well as an assessment of the frequency at which water quality impairment occurs in these two watersheds. Data also indicate that small changes in land-use (3–10% urban) can have an impact on water quality

and suggest that more studies investigating the impact of subtle land-use changes on water quality should be conducted to predict water quality changes in watersheds where rapid population growth leads to the conversion of agricultural lands into residential areas.

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